NEUTRON STUDY OF STRUCTURED POLYMERS AT INTERFACES

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NEUTRON STUDY OF STRUCTURED POLYMERS AT INTERFACES

A Dissertation
Presented to the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Thusitha N. B. Etampawala
December 2013

Accepted by:
Dr. Dvora Perahia, Committee Chair
Dr. Christopher J. Cornelius
Dr. Stephen Creager
Dr. Steven J. Stuart
ABSTRACT

This work focuses on interfacial structure and dynamics of structured polymers in thin films and in solutions using neutron techniques accompanied by atomic force microscopy. We probed polymers with a common theme that were highly segregated either because of presence of ionic groups or topological constraints. In these polymers the interfacial regions often define their function in different applications such as clean energy, printing adhesions and drug delivery systems.

Thin film studies include systems of polystyrene/sulfonated polystyrene, a rigid sulfonated polyphenylene and polystyrene three-arm stars/linear polystyrene. The first two systems include ionic components and the last exhibits topological constraints. Polystyrene is often used as a model polymer because of the ease of exercising synthetic control over its molecular weight.

Interdiffusion at the polymer-polymer interface was followed as well as diffusion of guest molecules. We found that the interfacial diffusion at the interfaces of ionic-nonionic polymers is strongly impacted by the presence of ions. The presence of ionic groups results in surface aggregation which in turn impacts the interfacial diffusion. The rigidity of the polymer also plays an important role as it results in significant interstitial spaces that dominate diffusion. The interfaces formed by these polymers are often inhomogeneous and contain both ionic and nonionic species that impact the onset of dynamics.

In parallel, we studied the interfacial segregation of three-arm star polymers in a matrix of polystyrene. The contact point between the three-arms forms topological
constraints that impact the segregation. The interfacial compositions were found to be balanced between entropic forces that drove polymer chain ends to the interfaces and the effects of topological constraints that hindered the motion of polymers.

Interfacial segregation effects are seen not only in thin films but also strongly affect the assembly of polymers in solution. Here we studied a penta-block copolymer that consists of an ionic center block in hydrophobic solution. We found that very stable aggregates are formed where these shapes and stability are attributed to the ionic block.

Finally the synthesis of structured alternating copolymers and their optical characteristics are introduced.
DEDICATION

This dissertation is dedicated to my wife, Madhubashini Medagoda, my mother, late father, my sister and my parents-in-law for their love and support given me throughout my life. Without them, I will be unable to make this achievement.
ACKNOWLEDGMENTS

First and foremost, I would like to express my sincere gratitude to my doctoral research advisors, Dr. Dvora Perahia for her guidance, encouragement and invaluable support given throughout my Ph.D. study. I would like to thank Dr. Christopher J. Cornelius (currently at Chemical & Biomolecular Engineering Department at University of Nebraska-Lincoln), Dr. Rhett Smith and Ms. Brynna Laughlin for their valuable guidance throughout the synthesis of some of the polymer materials used in this study. I am grateful to my dissertation committee, Dr. Christopher J. Cornelius, Dr. Steven J. Stuart and Dr. Stephen Creager for their suggestions and evaluation of my dissertation. Their advice and support have always been appreciated.

I would like to thank some neutron beam line scientists including Dr. Jaroslaw Majewski (SPEAR at LANSCE, LANL), Dr. Rex Hjelm (LQD at LANSCE, LANL), Dr. Jim Browning, Dr. John F. Ankner and Ms. Candice Hilbert (LR at SNS, ORNL), Dr. William T. Heller and Dr. Christopher B. Stanley (EQ-SANS at SNS, ORNL), Dr. Lilin He (GP-SANS at HFIR, ORNL), for their priceless technical help and advices on the neutron scattering and reflectivity experiments. I would like to thank Dr. Don Vanderveer for his help on X-ray diffraction experiments. Special thank goes to my colleagues in our “polymer physics” research group at Clemson University particularly Dilru R. Ratnaweera, Naresh C. Osti, Umesh M. Shrestha, Sidath I. Wijesinghe, Dipak Aryal and Sabina Maskey for their support given me to success the neutron related experiments. Without them, I will be unable to make this work happen.
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TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>Ionomers</td>
<td>1</td>
</tr>
<tr>
<td>Motivation and objectives</td>
<td>1</td>
</tr>
<tr>
<td>Morphological models of ionomers</td>
<td>5</td>
</tr>
<tr>
<td>Ionomers in solution</td>
<td>7</td>
</tr>
<tr>
<td>Ionomers in thin film</td>
<td>9</td>
</tr>
<tr>
<td>Polymers with topological constraints</td>
<td>10</td>
</tr>
<tr>
<td>Motivation and objectives</td>
<td>10</td>
</tr>
<tr>
<td>Outline and contribution</td>
<td>11</td>
</tr>
<tr>
<td>References</td>
<td>13</td>
</tr>
<tr>
<td>II. EXPERIMENTAL METHODS</td>
<td>18</td>
</tr>
<tr>
<td>Small angle scattering</td>
<td>18</td>
</tr>
<tr>
<td>Small angle neutron scattering</td>
<td>23</td>
</tr>
<tr>
<td>Non-polarized specular neutron reflectivity</td>
<td>25</td>
</tr>
<tr>
<td>References</td>
<td>30</td>
</tr>
<tr>
<td>III. INSIGHT INTO THE STABILITY OF POLYMER THIN FILM:</td>
<td>33</td>
</tr>
<tr>
<td>EFFECTS OF THREE-ARM POLYSTYRENE STARS IN LINEAR POLYSTYRENE THIN FILMS AGAINST THERMAL ANNEALING</td>
<td>33</td>
</tr>
<tr>
<td>Abstract</td>
<td>33</td>
</tr>
<tr>
<td>Introduction</td>
<td>34</td>
</tr>
</tbody>
</table>
# Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>36</td>
</tr>
<tr>
<td>Samples</td>
<td>36</td>
</tr>
<tr>
<td>Thin films preparations</td>
<td>38</td>
</tr>
<tr>
<td>Silicon wafer treatment</td>
<td>38</td>
</tr>
<tr>
<td>Neutron reflectivity experiment</td>
<td>38</td>
</tr>
<tr>
<td>Analysis of the density profiles</td>
<td>40</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>42</td>
</tr>
<tr>
<td>Summary</td>
<td>56</td>
</tr>
<tr>
<td>Supporting information</td>
<td>57</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>58</td>
</tr>
<tr>
<td>References</td>
<td>58</td>
</tr>
</tbody>
</table>

## IV. NEUTRON REFLECTIVITY STUDY OF THE INTERFACIAL REGIONS BETWEEN IONOMERS AND VAN DER WAALS POLYMERS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>63</td>
</tr>
<tr>
<td>Introduction</td>
<td>64</td>
</tr>
<tr>
<td>Experimental</td>
<td>67</td>
</tr>
<tr>
<td>Materials</td>
<td>67</td>
</tr>
<tr>
<td>Preparation of polymer solutions</td>
<td>68</td>
</tr>
<tr>
<td>Preparation of composite layers</td>
<td>68</td>
</tr>
<tr>
<td>Silicon wafer treatment</td>
<td>69</td>
</tr>
<tr>
<td>Neutron reflectivity experiment</td>
<td>70</td>
</tr>
<tr>
<td>Data analysis</td>
<td>71</td>
</tr>
<tr>
<td>Calculation of interfacial widths</td>
<td>71</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>72</td>
</tr>
<tr>
<td>Summary</td>
<td>82</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>83</td>
</tr>
<tr>
<td>References</td>
<td>83</td>
</tr>
</tbody>
</table>

## V. IN SITU NEUTRON REFLECTIVITY STUDY OF ALCOHOLS AT THE INTERFACE WITH THIN IONOMER FILMS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>88</td>
</tr>
<tr>
<td>Introduction</td>
<td>88</td>
</tr>
<tr>
<td>Experimental</td>
<td>93</td>
</tr>
<tr>
<td>Thin film preparation</td>
<td>93</td>
</tr>
<tr>
<td>Silicon wafer oxidation</td>
<td>94</td>
</tr>
<tr>
<td>Neutron reflectivity experiment</td>
<td>94</td>
</tr>
<tr>
<td>Neutron data analysis</td>
<td>95</td>
</tr>
<tr>
<td>Density profiles</td>
<td>95</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer profile analysis</td>
<td>96</td>
</tr>
<tr>
<td>Calculations of solvent uptake</td>
<td>97</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>97</td>
</tr>
<tr>
<td>Summary</td>
<td>122</td>
</tr>
<tr>
<td>Supporting information</td>
<td>123</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>125</td>
</tr>
<tr>
<td>References</td>
<td>126</td>
</tr>
<tr>
<td>VI. ASSOCIATION OF A MULTIFUNCTIONAL BLOCK</td>
<td></td>
</tr>
<tr>
<td>COPOLYMER IN A SELECTIVE SOLVENT</td>
<td>132</td>
</tr>
<tr>
<td>Abstract</td>
<td>132</td>
</tr>
<tr>
<td>Introduction</td>
<td>132</td>
</tr>
<tr>
<td>Experimental</td>
<td>137</td>
</tr>
<tr>
<td>Materials</td>
<td>137</td>
</tr>
<tr>
<td>SANS experiment</td>
<td>137</td>
</tr>
<tr>
<td>SANS data analysis</td>
<td>138</td>
</tr>
<tr>
<td>Micellar form factor</td>
<td>139</td>
</tr>
<tr>
<td>Results and discussion</td>
<td>141</td>
</tr>
<tr>
<td>Summary</td>
<td>155</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>156</td>
</tr>
<tr>
<td>References</td>
<td>156</td>
</tr>
<tr>
<td>VII. SYNTHESIS AND CHARACTERIZATION OF CARBOXYLATE</td>
<td></td>
</tr>
<tr>
<td>SUBSTITUTED IONIC POLYPHENYNYLINES</td>
<td>162</td>
</tr>
<tr>
<td>Abstract</td>
<td>162</td>
</tr>
<tr>
<td>Introduction</td>
<td>162</td>
</tr>
<tr>
<td>Synthesis of PPE</td>
<td>164</td>
</tr>
<tr>
<td>Hexyloxy Group Substituted Ionic PPE</td>
<td>164</td>
</tr>
<tr>
<td>Dooctyloxy Group Substituted Ionic PPE</td>
<td>171</td>
</tr>
<tr>
<td>Characterization of PPE</td>
<td>175</td>
</tr>
<tr>
<td>Summary</td>
<td>177</td>
</tr>
<tr>
<td>Acknowledgement</td>
<td>177</td>
</tr>
<tr>
<td>References</td>
<td>177</td>
</tr>
<tr>
<td>VII. SUMMARY</td>
<td>179</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>2.1</td>
<td>Specifications of SPEAR at Los Alamos National Laboratory.</td>
</tr>
<tr>
<td>2.2</td>
<td>Specifications of LR at SNS, Oak Ridge National Laboratory.</td>
</tr>
<tr>
<td>3.1</td>
<td>Characteristics of the PS samples used in reflectivity measurements.</td>
</tr>
<tr>
<td>3.2</td>
<td>Segregation diffusivities at the polymer/substrate and the polymer/air</td>
</tr>
<tr>
<td></td>
<td>interfaces of indicated HPS additives in 15k linear DPS matrix at 120 °C.</td>
</tr>
<tr>
<td>4.1</td>
<td>Characteristics of the polystyrene samples used in reflectivity measurements</td>
</tr>
<tr>
<td>4.2</td>
<td>Thickness of the layers determined from ellipsometry prior to make</td>
</tr>
<tr>
<td></td>
<td>composites.</td>
</tr>
<tr>
<td>4.3</td>
<td>Thickness of the composite layers determined from neutron reflectometry and</td>
</tr>
<tr>
<td></td>
<td>from scattering length density profiles. The subscript represents the</td>
</tr>
<tr>
<td></td>
<td>corresponding method used to determined thickness.</td>
</tr>
<tr>
<td>4.4</td>
<td>Diffusivities of the composites annealed at 120 °C.</td>
</tr>
<tr>
<td>5.1</td>
<td>Diffusivities of methanol at room temperature in sPP thin films having</td>
</tr>
<tr>
<td></td>
<td>variable sulfonation levels.</td>
</tr>
<tr>
<td>5.2</td>
<td>Diffusivities of hexanol at room temperature at the indicated polymer</td>
</tr>
<tr>
<td></td>
<td>sulfonation levels.</td>
</tr>
<tr>
<td>5.3</td>
<td>Diffusivities of different alcohols (methanol, hexanol and octanol) within</td>
</tr>
<tr>
<td></td>
<td>sPP thin films with 27.0 mol% sulfonation at room temperature.</td>
</tr>
<tr>
<td>5.4</td>
<td>Diffusivities of octanol at room temperature in sPP thin films having</td>
</tr>
<tr>
<td></td>
<td>different sulfonation levels.</td>
</tr>
<tr>
<td>7.1</td>
<td>Photophysical properties of A-D in THF at 25 °C.</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A cartoon of multiplet structure in a melt of polymers. Strongly interacting ion pairs are shown explicitly. Multiplets are circled and shaded. Light green corresponds to the polymer chains, red correspond to counter ions and green circles correspond to anions.</td>
<td>6</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic of the conformation of ionomer solution as a function of type of solvent. A - mutually good solvent, B - polar solvent and C - non-polar solvent.</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>An illustration of scattering by different electromagnetic radiation and interaction with matter.</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>An illustration of a scattering of incoming beam by a sample.</td>
<td>20</td>
</tr>
<tr>
<td>2.3</td>
<td>A vector diagram that shows relationship between wave-vectors and momentum transfers for elastic scattering.</td>
<td>20</td>
</tr>
<tr>
<td>2.4</td>
<td>A schematic of a basic scattering configuration, ( \theta ) is the scattering angle and ( \Omega ) is the solid angle.</td>
<td>22</td>
</tr>
<tr>
<td>2.5</td>
<td>Geometry of reflection and refraction: where ( k_i ) is the incident wave vector, ( k_f ) is the final wave vector, ( q_z ) is the Z component of the wave vector ( ( q_z = \bar{k}_f - \bar{k}_i ) ), ( \theta_0 ) is the incident angle, ( \theta ) is the reflected angle, ( \theta_1 ) is the refracted angle, ( n_0 ) and ( n_1 ) is the neutron refractive index of medium 0 and 1 respectively.</td>
<td>25</td>
</tr>
<tr>
<td>2.6</td>
<td>Calculated neutron reflectivity profiles for the Fresnel reflectivity of a bare silicon oxide surface with no roughness (( \sigma )) and a thin polymer film with a thickness of 40 nm and ( \sigma ) of 1 nm on a silicon oxide substrate.</td>
<td>28</td>
</tr>
<tr>
<td>3.1</td>
<td>The chemical structure of three-arm PS. ( n = 181 ) and 1056.</td>
<td>37</td>
</tr>
<tr>
<td>3.2</td>
<td>Illustration of the definitions of the polymer/substrate interface, the center of the film, and the polymer/air interface used to integrate the area under the curve. The profile of the thin film before annealing is shown by the brown solid line, and the profile after annealing is shown by the blue solid line.</td>
<td>41</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Neutron reflectivity profiles in terms of $Rq^4$ vs. $q$ as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, c) 15k DPS/13k linear HPS. The zoomed-in regions of the first fringes of (a) and (c) are shown in (b) and (d), respectively. The symbols correspond to the experimental reflectivity data, and the solid lines are the best fits. The error bars of the reflectivity data are smaller than the symbols and thus are not displayed. .................................................................43</td>
</tr>
<tr>
<td>3.4</td>
<td>The height of the first fringe in terms of $Rq^4$ determined from Figures 3a–d. The matrix of all the films was 15k DPS, and the molecular weights of the additives are indicated in the figure. The solid lines are the fits to an exponential function and the quality of the fits are given in $R^2$ which is in the range of (a) 0.94–0.97 and (b) 0.97–0.98. .............44</td>
</tr>
<tr>
<td>3.5</td>
<td>Reflectivity in terms of $Rq^4$ vs. $q$ for a thin film of 15k linear DPS and 110k three-arm HPS in the ratio of 95:5 wt% spin coated on silicon oxide wafer before annealing. The dashed lines illustrate the simulated reflectivity patterns for the total segregation of the three-arm to the polymer/air interface (green) and polymer/substrate interface (orange). The black solid line represent the best fit for the reflectivity data. ............46</td>
</tr>
<tr>
<td>3.6</td>
<td>Evolution of volume fraction profiles in terms of additive volume fraction ($\Phi$) vs. distance from solid substrate (d) as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS. ........48</td>
</tr>
<tr>
<td>3.7</td>
<td>Area change, $\Delta A =</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>Log-log plot of area change, ΔA, as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS. The solid lines are the best linear fits with $R^2 = 0.99$ and the dashed lines are the extrapolation of the linear fits. ........................................... 52</td>
</tr>
<tr>
<td>3.9</td>
<td>Normalized area change of the polymer/substrate (open symbol) and the polymer/air (solid symbol) interfaces with respect to additive volume fraction at the center of the film as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS. The dotted lines are the guide to the eye. ................................................................. 54</td>
</tr>
<tr>
<td>3.10</td>
<td>Neutron reflectivity profiles in terms of $Rq^4$ vs. $q$ as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/110k three-arm HPS, c) 15k DPS/160k linear HPS. The zoomed-in regions of the first fringe of plots (a) and (c) are shown in (b) and (d) respectively. The symbols correspond to the experimental reflectivity data, and the solid lines are the best fits. The error bars of the reflectivity data are smaller than the symbols and thus are not displayed. ................................................................. 57</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic representation of the definitions of interfacial widths ($\sigma_i$) and the initial roughness ($\sigma_0$). ................................................................. 72</td>
</tr>
<tr>
<td>4.2</td>
<td>NR profiles and the corresponding fits at the indicated annealing times and sulfonation levels. Left column corresponds to low molecular weight DPS and right column corresponds to high molecular weight DPS. Symbols are the experimental reflectivities and solid lines are the best fits. The profiles are vertically shifted for clarity. ......................................... 75</td>
</tr>
<tr>
<td>4.3</td>
<td>Polymer profiles of in terms of scattering length density ($b/V$) as a function of distance from the composite interface as a function of annealing times for indicated composites. Left column corresponds to low molecular weights and right column corresponds to high molecular weights. For clarity of the interface region the x-axis varies. ... 77</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>Log-log plots of interfacial width, $\Delta \sigma_t$ and annealing time for indicated samples as a function of sulfonation level as indicated. The symbol corresponds to the experimental data and the dash lines are best linear fits. 80</td>
</tr>
<tr>
<td>4.5</td>
<td>Interfacial widths as a function of $t^{1/2}$ and sulfonation level of HPS for indicated samples. The symbol corresponds to the experimental data and the dash lines are guide to the eye. 81</td>
</tr>
<tr>
<td>5.1</td>
<td>Chemical formula of randomly sulfonated polyphenylene ionomer. 92</td>
</tr>
<tr>
<td>5.2</td>
<td>Definition of the center of film and polymer/air interface that is used to determine the composition with solvent exposure. $h_1=h_1'$, $h_2=h_2'$ and $h_3=h_3'$. 96</td>
</tr>
<tr>
<td>5.3</td>
<td>NR profiles in terms of $R_{q4}$ vs. $q$ for sPP thin films exposed to saturated methanol vapor for a) 13.5 mol% sulfonation, b) 27.0 mol% sulfonation and c) 33.3 mol% sulfonation of sPP. The insets zoom in on the range around $q_c$ as a function of solvent exposure time. The symbols correspond to the experimental reflectivity data and the solid lines are the best fits. The $t$ corresponds to the exposure time. Measurements were taken until no further significant changes were observed. 100</td>
</tr>
<tr>
<td>5.4</td>
<td>Normalized time dependence of $a-\Delta q$, $b-\Delta q$ and $c-R_{q4}$. The solid lines are the fits to an exponential function where $R^2$ is in the range of 0.95 to 0.99. The dash line at the onset of figure “a” is an extrapolation. 103</td>
</tr>
<tr>
<td>5.5</td>
<td>Film profiles in terms of $b/V$ vs distance from solid substrate exposed to saturated methanol vapor for a) 13.5 mol% sulfonation, b) 27.0 mol% sulfonation, and c) 33.3 mol% sulfonation ionomer thin films. The profiles have been shifted along time-axis for clarity. 105</td>
</tr>
<tr>
<td>5.6</td>
<td>Methanol volume fraction at the polymer/vapor interface and at the center of film as a function of solvent exposure time for a) 13.5 mol% sulfonation, b) 27 mol% sulfonation, and c) 33.3 mol% sulfonation sPP thin films. The solid lines are the fits to an exponential function with $R^2$ is in the range of 0.96 to 0.99. The dash lines at the onsets are the extrapolations. 107</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7</td>
<td>Methanol uptake as a function of normalized $t^{1/2}$ with respect to the film thickness of dry sample for three different sulfonation levels, 13.5 mol%, 27.0 mol% and 33.3 mol% of sPP thin films. The solid lines are the fits to an exponential function with $R^2$ is in the range of 0.97 to 0.99. The dash lines at the onsets are the extrapolations.</td>
<td>109</td>
</tr>
<tr>
<td>5.8</td>
<td>Film profiles in terms of b/V vs. distance from solid substrate exposed to saturated Hexanol vapor for a) 13.5 mol% sulfonation, b) 27.0 mol% sulfonation, and c) 33.3 mol% sulfonation ionomer thin films. The profiles have been shifted along time-axis for clarity.</td>
<td>113</td>
</tr>
<tr>
<td>5.9</td>
<td>Hexanol volume fractions as a function of solvent exposure time for a) 13.5 mol% sulfonation, b) 27 mol% sulfonation, and c) 33.3 mol% sulfonation sPP thin films. The solid lines are the fits to an exponential function with $R^2$ is in the range of 0.98 to 0.99.</td>
<td>115</td>
</tr>
<tr>
<td>5.10</td>
<td>Hexanol uptake as a function of normalized $t^{1/2}$ with respect to the film thickness of dry sample for three different sulfonation levels, 13.5 mol%, 27.0 mol% and 33.3 mol% of sPP thin films. The solid lines are the fits to an exponential function with $R^2$ is 0.99. The dash lines at the onsets are the extrapolations.</td>
<td>116</td>
</tr>
<tr>
<td>5.11</td>
<td>Uptake of methanol, hexanol and octanol by the 27 mol% sulfonation thin films as a function of $t^{1/2}$ normalized to the thickness of the films. (a) Total uptake, (b) alcohols fractions at the centers of films, and (c) alcohols fractions at the polymer–vapor interface. The solid lines are the fits to an exponential function where $R^2$ is 0.99. The dashed lines at the onsets are the extrapolations. The tangent dashed line in (a) shows the crossover point from fast to slow alcohols uptake.</td>
<td>119</td>
</tr>
<tr>
<td>5.12</td>
<td>NR profiles in terms of log R vs. q for Hexanol diffusion into sulfonated polyphenylene thin films of a)13.5 mol% sulfonation, b)27 mol% sulfonation and c)33.3 mol% sulfonation levels. Symbols in NR profiles are experimental reflectivity and solid lines are the best fits. Reflectivity profiles have been shifted along Y-axis for clarity. The error bars in the NR profiles denote the standard deviation for each measurement.</td>
<td>123</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.13</td>
<td>NR profiles in terms of log R vs q for Octanol diffusion into sulfonated polyphenylene thin films of A) 27 mol% and B) 33.3 mol% sulfonation levels. Symbols in NR profiles are experimental reflectivity and solid lines are the calculated models. The error bars in the NR profiles denote the standard deviation for each measurement. ........................................ 123</td>
</tr>
<tr>
<td>5.14</td>
<td>Film profiles in terms of b/V vs. distance from solid substrate exposed to saturated Octanol vapor for a) 27.0 mol% sulfonation and b) 33.3 mol% sulfonation sPPs. ................................................................. 124</td>
</tr>
<tr>
<td>5.15</td>
<td>Octanol volume fractions as a function of solvent exposure time in terms of normalized t½ with respect to the film thickness of dry thin films for (a) 27.0 mol% sulfonation and (b) 33.3 mol% sulfonation. The symbols correspond to the experimental data and the solid lines are guides to the eye. ........................................................................ 124</td>
</tr>
<tr>
<td>5.16</td>
<td>Octanol uptake by sPPs having different sulfonation levels as a function of normalized t½ with respect to the film thickness of dry thin films. The symbols correspond to the experimental data and the dash lines are the best fits to an exponential function. The solid lines are the fits to an exponential function where R² is 0.99. ........................................ 125</td>
</tr>
<tr>
<td>6.1</td>
<td>Chemical structure of randomly sulfonated block copolymer, poly[t-butyl styrene- b-isoprene-b-sulfonated styrene-b-isoprene -b-t-butyl styrene], (tBPS-PI-PS/sPS-PI-tBPS). The weight distribution = 15-10-28-10-15 kg/mol. The sulfonated polystyrene block is randomly sulfonated to approximately 42 mol% n, m, x and p, are approximately 94,142, 0.42 and 203 respectively. .............................. 136</td>
</tr>
<tr>
<td>6.2</td>
<td>SANS profiles in terms of (a) log I vs. log q, (b) q^2I(q) vs. q for the penta-block copolymer solution having concentration from 0.01 wt% to 6 wt% (orange – 0.01 wt%, blue -0.025 wt%, pink – 0.05wt%, cyan – 0.1 wt%, green – 0.5wt%, red – 1 wt%, violet – 2 wt%, yellow green – 4wt% and navy blue - 6 wt%) at 25 ºC. The symbols represent the experimental data and the solid lines represent the best fits to the models described in text. .............................................. 142</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3</td>
<td>Radius of gyration extracted from Guinier analysis for the penta-block copolymer as a function of polymer concentration at 25 °C. The error bars in the profiles denote the standard deviation for each of the fits.</td>
<td>144</td>
</tr>
<tr>
<td>6.4</td>
<td>Calculated parameters from ellipsoidal core-shell model for the penta-block copolymer solutions as a function of polymer concentration at 25 °C. (a) Radius of core, (b) ( R_g ) of corona, (c) aggregation number and (d) solvent fraction in the core.</td>
<td>147</td>
</tr>
<tr>
<td>6.5</td>
<td>A snapshot of molecular dynamic simulations of penta-block with a total molecular weight of 50 kg/chain and the ratio of tBPS:Pi:PS/sPS:Pi:tBPS of 10:20:40:20:10 and sulfonation fraction of 0.3 at 300 K in 1:1 mixture of cyclohexane and heptane, all modeled by OPLS potentials. Simulations were run using LAMPS classical MD code with a time step of 1 fs.</td>
<td>149</td>
</tr>
<tr>
<td>6.6</td>
<td>SANS profiles of the penta-block copolymer as a function of temperature and polymer concentration, (a) 0.025 wt%, (b) 0.05 wt% (c) 0.1 wt% and (d) 2 wt%. The symbols represent the experimental data and the solid lines represent the best fits.</td>
<td>151</td>
</tr>
<tr>
<td>6.7</td>
<td>Calculated parameters from the model of ellipsoidal core-shell form factor for the penta-block copolymer as a function of temperature (25 °C - solid squares, 50 °C - open circles and 75 °C - solid triangles) and polymer concentration for (a) major radius of core, (b) ( R_g ) of corona, (c) aggregation number and (d) solvent fraction in the core. Insets represent the changes at lower concentrations.</td>
<td>152</td>
</tr>
<tr>
<td>6.8</td>
<td>Enthalpy of micellization process determined from the Arrhenius relation of the change of aggregation number.</td>
<td>154</td>
</tr>
<tr>
<td>7.1</td>
<td>Molecular structure of poly(phenylene ethynylene) substituted with sodium acetyloxy group and (A) Hexyloxy and (B) Doocyloxy grafted polymers.</td>
<td>163</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>7.2</td>
<td>Schematic route for synthesis of monomer 5: (i) Bromohexane, K₂CO₃, acetonitrile, reflux 47 hours; (ii) Br₂, dichloromethane, stir at RT for 24 hours; (iii) Pd(PPh₃)₄, CuI, trisilyl acetylene, triethylamine, toluene, stir at 90 °C for 60 hours; (iv) Methanol/THF, 5N NaOH, stir at RT for 2 hours. ..............................................................164</td>
<td></td>
</tr>
<tr>
<td>7.3</td>
<td>Schematic route for synthesis of monomer 9. (v) Bromomethane, K₂CO₃, acetonitrile, reflux for 47 hours; (vi) ICl, methanol, reflux at 70 °C for 5 hours; (vii) BBr₃, dichloromethane, reflux for 20 hours; (viii) K₂CO₃, ethylbromoacetate, acetonitrile reflux for 24 hours. ............167</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>Schematic synthesis route of polymer 12 (Hexyloxy grafted ionin PPE): (ix) Pd(PPh₃)₂Cl₂, CuI, triethylamine, dichloromethane, reflux for 72 hours; (x) NaOH/methanol, reflux for 24 hours; (xi) Acetone/methanolic HCl, stir at RT for 1 hour. .................................................169</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>Synthesis of monomer 16: (xii) Bromooctadecane, K₂CO₃, acetonitrile, reflux for 47 hours; (xiii) Br₂, dichloromethane, stir at RT for 24 hours; (xiv) Pd(PPh₃)₄, CuI, trisilyl acetylene, triethylamine, toluene, stir at 90 °C for 48 hours; (xv) Methanol/THF, 5N NaOH, stir at RT for 2 hours. ...........................................................................171</td>
<td></td>
</tr>
<tr>
<td>7.6</td>
<td>Schematic route for synthesis of polymer 19 (doocyloxy grafted ionic PPE): (xvi) Pd(PPh₃)₂Cl₂, CuI, triethylamine, dichloromethane, reflux for 72 hours, (xvii) NaOH/methanol, reflux for 24 hours; (xviii) Acetone/methanolic HCl, stir at RT for 1 hour. .................................173</td>
<td></td>
</tr>
<tr>
<td>7.7</td>
<td>Absorption (A) and fluorescence (B) spectra for compound A–D in THF. ........................................................................................................175</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER ONE
INTRODUCTION

The goal of my PhD research is to enhance the fundamental understanding of the interrelationship of structure, dynamics and function of ion-containing polymers and complex structured polymers including semi-rigid ionomers, conjugated polymers and block co-polymers in solution and thin films. The polymers for specific projects were chosen to represent the different constraints. The behavior of polymers constrained by ionic groups will be first described followed by impact of topological constraints exerted either by nano particles or branch of the polymers.

Ionomers

Motivations and Objectives

Polymers that consists of ionic groups are of great scientific interest because of their extensive practical importance for current and potential technological applications such as ion-selective coatings\(^1\), electro-dialysis\(^2\), actuators\(^3\), bio-medical applications\(^4\), and energy-related devices\(^5\) such as hydrogen fuel cells and batteries. Ions containing soft matter in solution, thin films, and bulk have been tailored for a vast variety of applications due to their unique chemical and physical properties including hydrophobicity and electrical conductivity while maintaining structure integrity. Almost all these applications desire electro-chemical stability, durability, and structural integrity, which are not fulfilled simply by inorganic ionic materials. For example, thin polymeric films lie at interfaces in areas as diverse as selective transport layers in batteries and fuel cells and biocompatible multilayers in artificial skin and muscles. These polymeric thin
layers must remain stable at the interface where thermal, mechanical, and electrical changes are often present. Instabilities leading to rupture or de-functionalize these polymeric films often dominate with amount of ion content, types of counter ions, guest molecules in the polymer matrix and polymer backbone or side chains.

Over the past years, the fundamental understanding of segregation of ionomers, interfacial effects, solvent-ionomer interactions, surface and interfacial dynamics of polymer have been studied intensively on flexible ionomers. However, less attention has been paid on the effects of polymer rigidity and interfacial composition on its physical and mechanical characteristics. Degree of flexibility of ionomer backbones is extremely significant since it allows the formation of distinctive domains that can rearrange upon perturbations such as interaction with small guest molecules or thermal annealing. The flexibility of ionic polymers depends on both Kuhn length and Bjerrum length. The Kuhn length is the size of the smallest rigid segment and the Bjerrum length is the minimum distance at which the un-screened Coulomb interaction energy of a pair of monovalent ions is comparable in magnitude to the thermal energy. Further, the Bjerrum length is strongly affected by the degree of ionization. In rigid ionomers, the backbone is almost arrested at large Kuhn lengths, which in turn limits the rearrangements of the polymer in presence of external perturbations. Thus, our effort is to expand our fundamental understanding of the structure, dynamics and function of different ion containing polymers and complex polymers. To accomplish our goals, this research will address the following effects.
1. Effects of ionic groups on interdiffusion of polymer chains across the polymer-ionomer interface.

2. Effects of degree of sulfonation and ionomer concentration on surface segregation of a semi rigid ionomer.

3. Effects of size of guest molecules on interfacial diffusion within thin, semi rigid ionomer films

4. Effects of solvent quality on the aggregation of structured multi-functional block-co-polymer in solution

The investigations of these effects will allow expanding the fundamental understanding of interrelationship of structure, dynamics and function of different types of ions containing soft matter, which will allow one to tailor the characteristics of ion containing polymers depending on the applications. For an example, one can synthesize polymer materials or polymer coatings that will allow diffusing only humidity while blocking other gas molecules.

Ionomers are essentially polymers that consist of electrically neutral repeating units and monomer units that have ionic groups than can dissociate into anion and counter cation, an ion associated with the ionic group of the polymer and is responsible for charge neutrality, depending on the dielectric nature of the medium: If the dielectric constant is low, ionic groups do not dissociate into ions and the polymer is dominated by the ionomer behavior. If the dielectric constant is high, ionic groups are dissociated into charges of opposite signs and the polymers have polyelectrolyte behavior.
Among many, one of the first used ionomer in industrial applications, sulfonated polystyrene, (sPS) is date back to 1950’s. The sPS was introduced to a polymer electrolyte membrane fuel cell by General Electric Company, USA\textsuperscript{8}. However, due to many mechanical and chemical drawbacks of sPS, developments of new ionomers were distinguished. DuPont\textsuperscript{TM} introduced a perfluorinated sulfonic acid membrane in 1960’s which is benchmarked the starting point of advanced materials used in current energy related applications\textsuperscript{9,10}. However, even today, no one managed to synthesize a durable ionomer with desired chemical and thermo-mechanical properties for energy related applications to provide clean, efficient and emission-free energy generation to meet the ever-growing energy need. This encourages scientists to develop new ionomers and investigate the structure-property relationships to understand the chemical, physical and mechanical limits.

Structural complexity of ionomers is achieved by several ways. Among them, introducing different monomer units, heteroatoms, or by introducing different polymer blocks are well known. Further modifications to an ionomer can be achieved by varying distribution of ionic groups; type of anion and counter ion. Current available synthetic polymers consist of a variety of monomers with relatively few pendent anionic groups such as carboxylic acid, acrylic acid, methacrylic acid, phosphoric acid, and sulfonic acid are available.

The incompatibilities between the components of an ionomer including hydrophilic-hydrophobic, polar-nonpolar, and rigid-flexible leads the phase separation lowering the total free energy of the system. The morphologies of phase separated
ionomers in solution, thin films, and bulk have been studied extensively. However, none of morphologies can be used to explain all the behaviors\textsuperscript{11,12}.

**Morphological Models of Ionomers**

Significance of technological development of ionomers ended up with large number of morphological models\textsuperscript{13-22}. These models are able to explain the two-phase morphology of the ionomers and experimental results of different ionomers up to certain extent. In 1990, Eisenberg along with Hird and Moore suggested a model\textsuperscript{23} of clustering in random ionomers which was an advanced version of Eisenberg’s original model\textsuperscript{14}. This model is basically the one that is currently universally accepted. The formations of multiplets were the essentials for this model too. A cartoon of a multiplet structure in an ionomer melt is presented in Figure 1.1. They considered that the strength of the electrostatic interactions between the ion pairs is the most important parameter that affects the multiplet formation which was determined by the sizes of the ions and the partial covalent character of the ionic bond. If the elastic forces are greater than the electrostatic interactions between ion pairs, no multiplets will form. The ion content of the polymer matrix determines the closeness of the ion pairs. At low ion content, ion pairs are far apart to experience enough electrostatic attraction to form aggregates. Further, small ions prefer to aggregate rather than bigger ions. The polymers with low dielectric constant and low T\textsubscript{g} tends to favor ionic aggregation while high dielectric constant and high T\textsubscript{g} inhibit the multiplet formation\textsuperscript{23}. Since each ion pair is effectively bind to the polymer chains, the mobility of the polymer chains in immediate vicinity to the multiplets are arrested compared to that of the polymer chains in bulk. By today, this
new approach is widely used and it is successfully used to describe “ionic” peak in the scattering data, and most of the other experimental observations including mechanical properties of most of ionomers.

Figure 1.1 A cartoon of multiplet structure in a melt of polymers. Strongly interacting ion pairs are shown explicitly. Multiplets are circled and shaded. Light green corresponds to the polymer chains, red circles correspond to counter ions and green circles correspond to anions\textsuperscript{24}.

Other than the models that were discussed, a number of attempts were made to describe the behavior and properties of different ionomers including flexible per fluorosulfonated\textsuperscript{25, 26}, ionic block co-polymers\textsuperscript{27}, semicrystalline ionomers\textsuperscript{13}. However, the detail descriptions of such models are out of the scope of this thesis.

The models that are discussed earlier are suitable to describe the structure and properties of ionomers in bulk. However, in many of the applications, ionomers are often
supported on some substrate. If an ionomer is placed on a solid substrate, one has to consider the interaction between substrate and ionomer in addition to the above mentioned interactions and interfacial effects due to the confinement of ionomer chains in order to determine the mechanical and physical nature. Likewise, when an ionomer is exposed to solvent, ionic clusters may allow the solvent to infuse into the center of clusters depending on the hydrophobic-hydrophilic nature of solvent. Thus, the behavior of ionomer in solution is determined by the interaction between ionic groups, polymer backbone and surrounded solvent molecules\textsuperscript{28,10}.

**Ionomers in Solution.** As presented in Figure 1.2, conformations of ionomers in solution mainly depend on the balance between polymer-polymer and polymer-solvent interactions. The structure of flexible and semi flexible polymers in solution is well described by Flory-Huggins theory\textsuperscript{29}. The presence of ionic groups or highly rigid segments results in higher inter-molecular interactions that often leads to aggregation and the system can no longer be described by Flory-Huggins theory. There are numerous models that account the behavior of ionomers and polyelectrolytes. Among many models of ion-containing polymers in solution, Odijk\textsuperscript{30}, Skolnick and Fixman\textsuperscript{31} were among the first who suggested a model that consider the effects of the dielectric constant of the solvents. They correlated the dielectric constant of the medium to the persistence length (the size of the smallest rigid segment that has correlations from one end to the other) of the polymer chain. They consider an ionomer solution in a theta solvent, where solvent-solvent interactions are assumed to be same as the solvent-polymer interactions. The persistence length, $l_0$, was defined as the distance between ionic groups separated by
distance $A$. Further, they only consider the electrostatic interactions. For strongly charged chains with $A < l_0$, the counter ion condensation into ionic aggregates can take place. In the limit of $l_0 \ll A$, which is characteristic of a weakly charged chain, this model is equivalent to the Gaussian polymer chains in solution in which the average size of the polymer chain scales with $N^{1/2}$ where $N$ is the degree of polymerization.

In general, as shown in Figure 1.2-a, ionomer chains are stretched out if the solvent is mutually good for both non-polar polymer segments and polar ionic groups. If the dielectric constant of the solvent is high (polar solvents), the ionomer chains tend to collapse as shown in Figure 1.2-b so that ionic group exposed to solvent molecules. If the dielectric constant of the solvent is low (non-polar solvents), polymer chains expose to solvent and ionic groups collapse to form ionic clusters as shown in Figure 1.2-c. In addition to the interactions between polymer-polymer and polymer-solvent, molecular weight, chain rigidity, type of pendent anion, type of counter ion, distribution of ionic groups along the polymer chain, and ionic strength determines the conformation of ionomers in solution.
Tailoring multiple functions into one macromolecule such as in ionic block-co-polymers has been one of the most promising solutions to overcome drawbacks of current materials as for ionic transport. In presence of each blocks, interfacial effects between all blocks and each one of them with the solvent comes into play. The introduction of the specific interactions into multi-component polymers by introducing different functional blocks has been proven an efficient way of tailoring miscibility and forming polymer complexes while maintaining the inherent features of ionomers.

**Ionomers in Thin Films.** The melting point of ionic polymers is too high for effective melt extrusion. Therefore, they are often processed via extrusions of ionomer solutions. In this case solution structure often controls the film morphology. In labs polymer thin films are prepared from dilute polymer solution either by spin casting or dip coating or drop casting on a solid substrates. Nano-scale surface morphologies are spontaneously formed in both dip coating and drop casting process depending on numerous factors such as polymer-substrate interaction (adhesion), polymer-polymer interactions, solvent-substrate interactions and solvent evaporation rate. In spin casting, shear forces due to spinning of sample are involved in addition to the above-mentioned interactions. The properties of thin films such as glass transition temperature, density, surface ordering are deviated from bulks due to the confinement of polymer chains which in turn limits the number of possible configurations. Further, film thickness has
contributions to difference of the properties of a material in thin films. For film thickness comparable to the molecular size, intermolecular interactions are dominated\textsuperscript{34}. These interfacial behaviors can be harnessed to form films with desired properties.

**Polymers with Topological Constraints**

**Motivations and Objectives**

The stability of the interfaces of polymer thin films cast on solid substrates plays a key role in applications that require a stable, continuous film. However, in presence of external perturbations the stability of thin films remained a challenge. One of the promising ways to enhance the stability is to incorporate a small quantity of inorganic or organic additives with different topologies such as nanoparticles or another polymer molecule into the matrix polymer. These additives are often segregated to interfaces with external perturbations such as thermal annealing. The degree of segregation within the film and the affinity of the additives to specific interface depend on numerous factors, including interaction between polymer segments\textsuperscript{35, 36} and the size,\textsuperscript{37} shape,\textsuperscript{38, 39} and tacticity\textsuperscript{40} of the additives. Overall both enthalpy and entropy contribute to the interfacial composition\textsuperscript{41-43}. Thus, our effort is to expand our fundamental understanding of the structure and dynamics of polymers that has constraints. To accomplish our goal, this research will address the effects of topology on distribution of polymer additives within polymer thin films. Specifically we studied the effects of the molecular weight of three-arm PS additives on segregation. We will compare the distributions of the three-arm star polymers normal to the interface with the distribution of linear analogs that had comparable molecular weights to the star arms.
Outline and Contribution

This dissertation includes several approaches to enhance the fundamental understanding of the interrelationship of structure, dynamics and function of polymers that contains highly interacting blocks or topological constraints in solution and thin films. The thesis is organized in the following way.

Chapter 2 will review the fundamentals of experimental techniques. Our investigations by their nature need techniques such as surface probing, interfacial probing and solution characterization over multiple length scales. The basics of techniques used to probe the surface and interfacial dynamics including Small Angle Neutron Scattering (SANS) and Non-polarized specular neutron reflectivity (NR) will be briefly reviewed.

Chapter 3 discusses fundamental understandings of the interdiffusion of polymer chains across the polymer-polymer interface in presence of ionic groups. The study was carried out as a function of ionic content and number of entanglements of the polymer. We found that in contrast to non-ionic analogs, polymer chains inter diffuse slowly in presence of ionic groups.

Chapter 4 discusses stability of polymer thin films induced by presence of polymer additives with different topologies. The thin films prepared from the blend of linear and three-arm polystyrene as a function of molecular weight of the arms were investigated using neutron reflectometry. The role of three arm polymer additives in suppressing the de-wetting was illustrated. We observed a clear migration of the three-arm star polymer segments to both interfaces. Segregation of star polymers is compared
to the segregation of linear analogs with molecular weights comparable to those of the star polymer arms.

Chapter 5 discusses the study of supramolecular aggregation of sulfonated polyphenylene ionomer on silicon oxide surfaces. We studied interfacial structures of a rigid ionomer, sulfonated polyphenylene, as a function of ionic content and concentration of the polymer solution used to prepare the thin films. AFM and NR were employed as techniques to obtain the sizes and shapes of ionic aggregates. Molecular arrangement of polyphenylene ionomer thin films was studied by WAXS.

Chapter 6 will be dedicated to describing the complex structures of ionomers in presence of guest molecules. Particularly, we studied alcohols diffusion into sulfonated polyphenylene thin films as a function of solvent exposure time, ionomer content and size of alcohol molecules using neutron reflectometry. We found that the mass uptake was initially linear with $t^{\frac{1}{2}}$ and transitions to a slower stage at prolonged exposure times. Interfacial effects dominate the onset of diffusion resulting in significant delay in diffusion in comparison with the bulk polymer. Surprisingly, these interfacial effects hardly depend on the hydrophobicity of the alcohols.

Chapter 7 discusses the self-aggregation of a complex, structured block copolymer in mutually good solvent. Multifunctional polymers have been in the core of current and immersing technologies in which their capacity to transport ions and solvents is a key to their function. The structures of a multifunctional polymer, an ionic penta block-co-polymer, in solutions determine its function and stability. First, pentablock ionomer in mutually good mix solvent as a function of concentration was studied. Then,
the temperature effects were investigated. We found that the size of the micelle, the thickness of the corona and the aggregation number increased with increasing the solution concentration and temperature, while the solvent fraction in the core decreased. The dilute solutions promptly responded to thermal fluctuations. However, the temperature effects disappeared with increasing the solution concentration.

Chapter 8 discusses the synthesis and characterization of carboxylate substituted ionic polyphenylene. Alternating carboxylate substituted and either hexloxy or dooctyloxy chains grafted polymers were synthesized. Further they functionalized with different counter ions, H⁺ and Na⁺ and a neutral ethyl groups. The characterization of optical properties showed that in C-18 substituted PPEs blue shift of λ_max is observed when neutral form of PPE convent into acid form. However, in C-6 substituted PPE red shift is observed when neutral form converted into acid form.

Chapter 9 presents the research summary, overall conclusion and a discussion of suggested future work.

Reference:


CHAPTER TWO

EXPERIMENTAL METHODS

The techniques used to probe the interfacial structure and dynamics including small angle neutron scattering (SANS), and non-polarized specular neutron reflectivity (NR) will be briefly reviewed in this chapter\textsuperscript{1,2}. Additional complimentary techniques such as atomic force microscopy\textsuperscript{3}, nuclear magnetic resonance\textsuperscript{4} (NMR), differential scanning calorimetry\textsuperscript{5} (DSC), ellipsometry\textsuperscript{6}, Fourier-transform infra-red spectroscopy\textsuperscript{7} (FT-IR) were used as needed.

Small Angle Scattering

Small angle scattering is an elastic scattering technique that probes structures of about 10-1000 Å. It provides size and shape of objects called form factor as well as long range correlation called structure factor.

In general, scattering of a beam of radiation depends on the charge and the spin of the incident beam and their interaction with the sample\textsuperscript{1}. In X-ray scattering, incoming radiation interacts with electrons of the matter while in neutron scattering they interact with the neutron. In this research we mostly used neutron scattering which has the advantage of making the same material look different for incoming neutron radiation by isotope labeling. As shown in Figure 2.1, Roger Pynn has shown that the schematic of scattering by different electromagnetic radiation together with specific interaction with matter\textsuperscript{8}. 
Figure 2.1 An illustration of scattering by different electromagnetic radiation and interaction with matter.

A basic scattering process is schematically shown in Figure 2.2 where, $k_i$ and $\omega_i$ are the initial incident wave-vector and angular frequency respectively. $k_f$ and $\omega_f$ are the final scattered wave-vector and angular frequency of the scattered particle respectively. The definitions of $k$ and momentum transfer vector, $q$, are given in following Equations 2.1 and Equation 2.2.

$$|k| = \frac{2\pi}{\lambda}$$  \hspace{1cm} (2.1)

$$q = k_i - k_f$$  \hspace{1cm} (2.2)
In an elastic scattering, neither energy nor momentum is exchanged. That means the change of energy is zero and hence as shown in Equation 2.3 the modulus of wave vector and the wavelength is unchanged upon scattering.

\[ |k_i| = |k_f| = \frac{2\pi}{\lambda} \]  

(2.3)

The vector diagram for a typical elastic scattering process is shown in Figure 2.5.

Figure 2.2 An illustration of a scattering of incoming beam by a sample.

Figure 2.3 A vector diagram that shows relationship between wave-vectors and momentum transfers for elastic scattering.²
As illustrated in the Figure 2.3, incoming radiation with momentum $k_i$ is deflected with momentum $k_f$ through an angle of $2\theta$; the factor of two is used for convenience of presentation. The triangle representing in Figure 2.3 is isosceles triangle with the two equal sides being of length $2\pi/\lambda$, which leads to the equation 2.4 and 2.5 where $q = |q|$. 

$$\frac{q}{2} = |k_i| \sin \theta$$  \hspace{1cm} (2.4) 

$$q = \frac{4\pi \sin \theta}{\lambda}$$  \hspace{1cm} (2.5)

Equation 2.6 relates the momentum transfer to the wavelength of incident radiation and scattering angle. The magnitude of momentum transfer and the distance between diffraction planes is obtained by combining Equation 2.5 with Bragg’s law$^1$; $n\lambda = 2d \sin \theta$, where $\theta$ is the scattering angle, $d$ is the distance between the diffraction planes and $n$ is the diffraction order which is an integer. 

$$q = \frac{2\pi n}{d}$$  \hspace{1cm} (2.6)

According to Equation 2.6, large-scale structures are observed at small $q$ values and small-scale structures are observed at large $q$ values. Since $q$ depends on both scattering angle and wavelength, small angle scattering techniques can probe the samples by varying either wavelength or scattering angle or both$^1$.

The quantity that is measured in a scattering experiment is the fraction of incident radiation that are scattered from the sample and going into a unit solid angle ($d\Omega$) per unit time$^2$, which is known as the differential scattering cross-section. A schematic of a basic scattering configuration is given in Figure 2.4.
The differential scattering cross-section, which is proportional to the intensity of scattered radiation is given in Equation 2.7,

$$\frac{d\sigma}{d\Omega}(q) = \frac{1}{N} \left| \sum_{j=1}^{N} b_{j} e^{i q r_{j}} \right|^{2}$$ (2.7)

where \( r \) describes the position of nuclei with scattering length \( b \) and \( N \) is the number of scattering atoms. Therefore, the summation over the individual atoms can be replaced by integration over the volume of the sample as shown in Equation 2.8. Further, the differential scattering cross-section is the square of the modulus of the Fourier transformation of the scattering length density.

$$\frac{d\sigma}{d\Omega}(q) = \frac{1}{N} \left| \int dr \rho(r) e^{iqr} \right|^{2} = \frac{1}{N} I(q)$$ (2.8)

where \( \rho(r) \) is the local scattering length density.

Particularly in the research reported in this thesis involves the Small Angle Neutron Scattering (SANS) technique in which neutron beam is used as incident radiation and it is briefly reviewed in the following.
**Small Angle Neutron Scattering.** SANS involves scattering of incident neutron beam from the sample and measuring the scattered neutron intensity as a function of either scattering angle or wavelength of neutron beam. Neutrons have high penetration power to hydrocarbon media because of their small neutron scattering cross sections\(^1\). Incident neutrons can interact with scattering objects in two ways\(^2\); inter nuclear interaction in which incident neutron interact with the neutron in the nucleus of the scattering objects and magnetic interaction of the unpaired electron of the atoms in scattering objects and the \(\frac{1}{2}\) spin of the neutron. Magnetic interactions are avoided in our measurements by using un-polarized incident neutron beam\(^2\). The ability of neutron to interact with atoms is expressed by scattering length density of the nucleus. It is calculated as shown by Equation 2.9, the normalized sum of scattering length of all the elements in the scattering object.

\[
b = \frac{\rho N_A}{M_w} \sum_i b_i \tag{2.9}
\]

Where \(\rho\) is the density of scattering object, \(N_A\) is the Avogadro’s number, \(M_w\) is the molecular weight of the scattering objects and \(b_i\) is the scattering length of each element in the scattering object. This offers neutron related techniques an advantage in studying soft matter that consists of light elements. The scattering contrast (\(\Delta b\)) of deuterium (\(b = 6.671 \times 10^{-6} \text{ Å}^{-1}\)) and hydrogen (\(b = -3.7390 \times 10^{-6} \text{ Å}^{-1}\)) is sufficiently large to give rise to scattering from structures that cannot be resolved by X-rays due to the lack of contrast\(^1\).

The intensity of scattered waves consists of coherent and incoherent component\(^1\). The coherent scattering component contains the spatial arrangement of scattering objects
while the incoherent component contains the information of dynamics of the scattered objects. In SANS, the incoherent component is subtracted as background. Therefore, differential scattering cross section for SANS data can be given by the Equation 2.10.

\[
\frac{d\sigma}{d\Omega} = I(q) = \frac{N}{V} (\Delta b_v)^2 V_{obj} F(q) S(q) + B_{inc}
\]

(2.10)

Where, \(N\) is the number of scattering objects, \(V\) is the volume of the sample, \(\Delta b_v\) is the scattering contrast that equals to the scattering length density difference of scattered objects and their surrounding medium, \(V_{obj}\) is the volume of one scattering object, \(F(q)\) is the form factor that explains the shape of scattering object, \(S(q)\) is the correlation of scattered objects that equals to one for diluted systems and \(B_{inc}\) is the incoherent scattering component.

All the SANS measurements of this research were performed at EQ-SANS at SNS and GP-SANS at HFIR, Oak Ridge National Laboratory. SANS detectors measures the superposition of scattering intensities of different origins such as background noise, scattering from sample holder and scattering of the sample. To determine the differential cross-section of the sample, all the differential contribution to the total scattering intensities have to be considered and determined separately by individual measurements. In general, the scattering contribution of the isolated sample cannot be measured directly.

The standard data reduction procedures were used to eliminate the background. Finally, the SANS data were analyzed using the SASfit version 0.93.5 developed by Joachim Kohlbrecher and Ingo Bressler in Paul Scherrer Institute. The quality of fitting was
determined by the $\chi^2$ value. The specific form factors used to resolve the structures are given under the specific chapters.

**Non-Polarized Specular Neutron Reflectometry**

Specular neutron reflectometry has been a key tool to investigate polymer surfaces and buried interfaces normal to the surface\(^1\). Resolution of 5-10 Å coupled with selective isotope labeling is appropriate to probe the guest molecules within a polymer matrix. Density profiles that describe the distribution of the components in a system perpendicular to the substrate interface were determined by simulating the experimental data. Those density profiles were utilized to infer the interrelation of structures and associations. The following section will include a brief review of neutron reflectometry.

When incoming neutron beams strike an interface between two materials with different neutron refractive indices as illustrated in Figure 2.5, part of the beam is reflected at the interface and the rest is transmitted through the system\(^2\). The angles between the incident, reflected and refracted beams are related by law of reflection, $\cos \theta_0 = \cos \theta$, and Snell’s law, $n_0 \cos \theta_0 = n_1 \cos \theta_1$, where the $\theta_0$ is the incident angle, $\theta$ is the reflected angle and the $\theta_1$ is the refraction angle.
Figure 2.5 Geometry of reflection and refraction: where \( k_i \) is the incident wave vector, \( k_f \) is the final wave vector, \( q_z \) is the Z component of the wave vector (\( q_z = k_f - k_i \)), \( \theta_0 \) is the incident angle, \( \theta \) is the reflected angle, \( \theta_1 \) is the refracted angle, \( n_0 \) and \( n_1 \) are the neutron refractive index of medium 0 and 1 respectively.

In most cases, medium 0 is air, and hence \( n_0 \) is equal to 1. Since \( n_1 \) is less than one in general, the refraction angle \( \theta_1 \) is smaller than the incident angle, \( \theta_0 \). As a result, at incident angle below a certain critical angle, \( \theta_c \), the radiation is totally reflected. In order to have the information about the buried interfaces, beam should be reflected from inner interfaces. For that, the reflection of neutron beam is measured from starting a small angle to some incident angle larger than \( \theta_c \).

The neutron refractive index, \( n \), is given by Equation 2.11. The real component, \( \delta \), controls the transmission and reflection while imaginary component, \( \beta \), is related to magnetic interaction and absorption.

\[
n = 1 - \delta + i\beta \tag{2.11}
\]

Where, \( \delta = \frac{\lambda^2 \rho}{2\pi} \) and \( \beta = \frac{\lambda \rho_{abs}}{4\pi} \). Where \( \lambda \) is the neutron wavelength, \( \rho \) is the scattering length density of the specimen and \( \rho_{abs} \) is the absorption cross section density. The \( \delta \) is of the order of \( 10^{-6} \) for most polymeric materials\(^1\). A special case to be noted is that the neutron scattering length density of hydrogen is negative and hence a substance with a high concentration of hydrogen can exhibit a neutron refractive index slightly larger than 1, as
in the case of saturated hydrocarbon and water. Neutrons absorption cross section density for non-magnetic materials is sufficiently small so that $\beta$ can be neglected in most cases without introducing significant error. For example, $\beta$ for most polymer materials is about $10^{-8}$ to $10^{-9}$. The scattering length does not vary in a systematic manner with atomic number. In fact, one of the largest differences in scattering length is that between two isotopes, hydrogen ($b = -3.7390 \times 10^{-6} \text{ Å}^{-1}$) and deuterium ($b = 6.671 \times 10^{-6} \text{ Å}^{-1}$). This provides a unique means of labeling polymers with minimal perturbation to the chemistry of the material.

In general, the reflectivity, $R$, is defined as the ratio of the reflection neutron intensity to the incident neutron intensity. For an incident angle, $\theta_0$, larger than $\theta_c$, $R$ is less than 1 and generally $R$ decreases as the angle $\theta_0$ increases which is calculated by Fresnel law assuming ideal situation as shown in Equation 2.1.

\[
R = \frac{|\overline{k}_{zo} - \overline{k}_{z1}|^2}{|\overline{k}_{zo} + \overline{k}_{z1}|} \tag{2.12}
\]

Where, $\overline{k}_{zo}$ and $\overline{k}_{z1}$ are the Z component or the component perpendicular to surface, of the incident wave vector and refracted wave vector respectively. Wave-vector in general is defined as in Equation 2.13.

\[
\overline{k} = \frac{2\pi}{\lambda} \sin \theta \tag{2.13}
\]

Therefore, $R$ is a function of both $\theta$ and $\lambda$. Consequently, the reflectivity profiles can be obtained varying either $\theta$ or $\lambda$ as in a conventional spectrometer.
For a single and ideal interface with no roughness, the reflected intensity relative to the incoming intensity is given in Equation 2.13 which is also known as the Fresnel reflectivity. For angles larger than $\theta_c$, the Fresnel reflectivity decreases as $q^{-4}$. In presence of diffuse interface causes the scattering intensity to fall off faster than $q^{-4}$. Actual sample as well as roughness will result in faster decay as shown in Figure 2.6. Fringes are observed in presence of sample on silicon oxide. The fringes are developed due to the interference of reflected beam coming from different interfaces of the sample.

Figure 2.6 Calculated neutron reflectivity profiles for the Fresnel reflectivity of a bare silicon oxide surface with no roughness ($\sigma$) and a thin polymer film with a thickness of 40 nm and $\sigma$ of 1 nm on a silicon oxide substrate.
In reality, it is hard to get ideal interface with zero roughness. Hence, one can account the interface roughness in the simplest way\(^1\) by a Gaussian distribution with variance, \(\sigma\). This causes deviation from Fresnel reflectivity and these deviations can be interpreted, as shown in Equation 2.14, in terms of the scattering length density variation normal to the surface.

\[
R = \frac{16\pi^2}{q^4} (\Delta\rho_z)^2 \exp\left(-\sigma^2 q^2\right)
\]  
(2.14)

Where, \(q\) is the scattering vector normal to the surface, \(\Delta\rho_z\) is the scattering length density variation normal to the surface and \(\sigma\) is the width of the diffuse interface. According to Equation 2.14, the larger the difference in scattering length density, \(\Delta\rho_z\), the stronger the intensity of fringes are. Further, this equation shows that the reflectivity of a diffuse interface falls below that for a sharp interface.

The thickness, surface roughness and scattering length density of thin films were determined by modeling the reflectivity profiles. MOTOFIT, a fitting analysis package, running in IGOR Pro 6.21 platform was used to fit the reflectivity data\(^1\). A multilayer recursive Parratt-formalism was used to analyze data\(^2\), by simulating reflectivity profiles and adjusting the parameters using genetic optimization to obtain the best least square fit. The quality of a fit was determined \(\chi^2\) where acceptable values were: \(\chi^2 \leq 1.5\). The initial guesses of scattering length density values for the samples are calculated using densities.

All the neutron reflectivity measurements of this research were performed at the time-of-flight reflectometry (SPEAR) at Los Alamos National Laboratory and liquid
reflectometry (LR) at SNS, Oak Ridge National Laboratory. Instrument specifications for SPEAR and LR are given in the Table 2.1 and Table 2.2 respectively.

<table>
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<th>Moderator-to-sample distance</th>
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<td>Wavelength frames</td>
<td>4.5 Å &lt; λ &lt; 16 Å or 16 Å &lt; λ &lt; 32 Å</td>
</tr>
<tr>
<td>Q range (liquid/gas interface)</td>
<td>0.006 Å⁻¹ &lt; Q &lt; 0.15 Å⁻¹</td>
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<tr>
<td>Minimum reflectivity</td>
<td>~10e⁻⁷</td>
</tr>
</tbody>
</table>

Table 2.1 Specifications of SPEAR at Los Alamos National Laboratory¹³,¹⁴.

<table>
<thead>
<tr>
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<tr>
<td>Sample-to-detector distance</td>
<td>1.5 m</td>
</tr>
<tr>
<td>Wavelength frames</td>
<td>4.5 Å &lt; λ &lt; 17.5 Å</td>
</tr>
<tr>
<td>Q range (air/liquid or air/solid interface)</td>
<td>0 Å⁻¹ &lt; Q &lt; 0.3 Å⁻¹</td>
</tr>
<tr>
<td>Minimum reflectivity</td>
<td>~10e⁻⁷</td>
</tr>
</tbody>
</table>

Table 2.2 Specifications of LR at SNS, Oak Ridge National Laboratory¹⁵.

References


13. *Surface Profile Analysis Reflectometer (SPEAR) LANSCE Lujan Center*,

15. *LR: the Liquids Reflectometer at SNS - ORNL Neutron Sciences*,
http://neutrons.ornl.gov/lr/.
CHAPTER THREE

INSIGHT INTO STABILITY OF POLYMER THIN FILMS: EFFECTS OF THREE-ARM POLYSTYRENE STARS IN LINEAR POLYSTYRENE THIN FILMS AGAINST THERMAL ANNEALING

Abstract

While polymeric coatings are ubiquitous, their long-term stability remains a challenge. Small changes in composition through the incorporation of additives are sufficient to influence the properties of thin films. In this work, we reported a neutron reflectometry (NR) study that follows the distribution of three-arm polystyrenes in linear polystyrene thin films. The segregation of the additive polymers due to the branching normal to the substrate interface was measured for blends of linear and three-arm star polymers as a function of annealing time. The three-arm star polymer enhanced film stability and delayed dewetting. The results showed a clear migration of the three-arm polymers to both the air and solid interface. As expected, as the molecular weights of the star arms increased, they migrated slower to the interfaces. In comparison with the segregation of linear analogs with molecular weights comparable to those of the star polymer arms, the degree of segregation of three-arm additives was higher. Quantitatively, a \( t^{1/2} \) kinetics was observed at short annealing times which crossed over to a slow segregation process for prolonged annealing times. These results were compared with studies of nanoparticles as well as multi-arm stars segregations in polymer thin films.
Introduction

The stability of the interfaces of polymer thin films cast on solid substrates plays a key role in applications that require a stable, continuous film. Examples range from protective layers and thin films with selective transport such as in batteries\textsuperscript{1} and fuel cells\textsuperscript{2} to formation of biocompatible, multilayer films for artificial skin\textsuperscript{3-5}. These applications require the interfacial layer to remain stable through exposure to an environment in which the thermal, mechanical, and electrical characteristics often change. However, with decreasing film thickness instabilities often dominate, leading to rupture and dewetting of the layers\textsuperscript{6}. Enhancing the stability of polymer thin films without changing their chemical and physical properties motivates the development of new strategies, despite the wide use of macromolecules as additives on thin films\textsuperscript{7-10}.

One of the promising ways to enhance the stability is to incorporate a small quantity of inorganic or organic additives such as nanoparticles or another polymer molecule into the matrix polymer. These additives are often segregated to interfaces with external perturbations such as thermal annealing. The degree of segregation within the film and the affinity of the additives to specific interface depend on numerous factors, including interaction between polymer segments\textsuperscript{11, 12}, size\textsuperscript{13}, shape,\textsuperscript{14, 15} and tacticity\textsuperscript{16} of the additives. Overall both enthalpy and entropy contribute to the interfacial composition\textsuperscript{17-19}. Among many studies, Jones et al.\textsuperscript{20} were first to observe interfacial enrichment of one component within thin films of a binary linear–linear polymer blend of protonated polystyrene (HPS) and deuterated polystyrene (DPS) using neutron reflectometry, dynamic secondary ion mass spectrometry and forward recoil
spectrometry. This enrichment decays into the bulk with a decay length of a few hundred Angstroms. These results were successfully explained with mean-field theory. With increasing complexity of the polymer topology, interfacial behavior is further modified.

Further studies were carried out on more structured additives. Mackay et al.\textsuperscript{8} studied the dewetting of linear–dendrimer blends of polystyrene (PS) and poly(benzyl ether) thin films. They found that dendrimers with the lowest generation (n = 3) effectively inhibit dewetting. These dendrimers are approximated as soft spheres. In comparison, Krishnan et al.\textsuperscript{10, 21, 22} studied the segregation of spherical PS nanoparticles with varying dimension in thin films of linear PS. They showed that homogeneously distributed nanoparticles migrate to the solid substrate upon annealing. Further, they observed that dewetting was further suppressed as more particles migrated to the interface. Foster et al.\textsuperscript{23} expanded the understanding of additive behavior to incorporate the polymer topology via investigation of the effects of branching in a ~157 kg/mol PS star polymers in an ~230 kg/mol linear PS matrix using dynamic secondary ion mass spectrometry and neutron reflectometry. They observed that the star polymer migrates preferentially to the air interface with annealing. Forster et al.\textsuperscript{9} also studied the architectural effects of branch points and chain ends on the bulk thermodynamic interaction parameter in binary blends of branched polymers with 6, 9, and 13 branch ends with their linear analogues using small-angle neutron scattering. They found that the value of the bulk thermodynamic interaction parameter increases as the number of branch points increased. They correlated the impact of branch points and chain ends. Most of
these studies have shown that film thickness plays a critical role in stability of thin films\textsuperscript{6, 8, 24, 25}.

As described above branching has a strong impact on dewetting. Here we investigate the simplest system where one branch point is introduced and changed the molecular weight of the arms and segregation was followed by NR. One branch point yields three-arm PS star polymers. In contrast to the other studies, we followed distribution of one branch point polymer in non-entangled polymer thin films, thus avoiding matrix entanglements that would constrain the additive motion. We compared the distributions of the three-arm star polymers normal to the interface with the distribution of linear analogs that had comparable molecular weights to the star arms.

In order to elucidate nano-scale changes and distribution of star polymers in buried interfaces of PS thin films, specular neutron reflectometry was utilized. Specular neutron reflectometry has been a key tool in investigating polymer surfaces and interfaces normal to the surface\textsuperscript{26-28}. The NR resolution of 5–10 Å coupled with selective isotope labeling is appropriate to follow the changes in the order of one nanometer at the interfaces. The density profiles perpendicular to the substrate surface infer the composition of thin film as a function of distance from the solid substrate.

**Experimental**

**Samples.** Linear DPS was used as the polymer matrix, while three-arm HPS and linear HPS were used as the additives. Linear DPS was purchased from Pressure Chemicals Co. USA. Three-arm HPS and linear HPS were purchased from Polymer Source Inc. USA. All polymer samples were used as received. The chemical structure of
the three-arm HPS is given in Figure 3.1, and the molecular characteristics of the polymers used in this work are presented in Table 3.1.

![Chemical structure of three-arm PS](image)

Figure 3.1. The chemical structure of three-arm PS. \( n = 181 \) and 1056.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_n ) (kg mol(^{-1}))</th>
<th>( M_w/M_n \pm 0.01 )</th>
<th>( T_g \pm 0.5 ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPS-15k</td>
<td>15.0</td>
<td>1.04</td>
<td>98.5</td>
</tr>
<tr>
<td>HPS-13k</td>
<td>12.7</td>
<td>1.06</td>
<td>98.0</td>
</tr>
<tr>
<td>HPS-160k</td>
<td>160.4</td>
<td>1.06</td>
<td>106.6</td>
</tr>
<tr>
<td>3-arm HPS-19k</td>
<td>18.9*</td>
<td>1.09</td>
<td>104.4</td>
</tr>
<tr>
<td>3-arm HPS-110k</td>
<td>109.9*</td>
<td>1.07</td>
<td>108.5</td>
</tr>
</tbody>
</table>

*per arm

Table 3.1. Characteristics of the PS samples used in reflectivity measurements.
Two sets of samples were prepared: 95:5 wt%, linear/three-arm PS blends and 95:5 wt% linear/linear PS blends. For all the samples, 15k linear DPS was used as the matrix. For the first set, we used 19k three-arm star HPS and 13k linear HPS analogs as the additives. For the second set, 15k DPS was blended separately with 110k three-arm HPS and 160k linear HPS.

**Thin Film Preparation.** The polymer solutions were prepared by dissolving 1 wt% of the blends in toluene. The solutions were sonicated for 30 minutes before spin coating. The thin films were prepared by spin coating the 1 wt% solutions on surface-oxidized silicon wafers at 1800 rpm for 2 minutes followed by overnight vacuum dried at 28 psi and at 50 °C.

**Silicon Wafer Treatment.** One-side-polished, 50mm-wide and 5mm-thick silicon oxide wafers were used as substrates to spin coat the PS blend solutions. The silicon oxide wafers were purchased from Virginia Semiconductor Inc. USA. The silicon oxide wafers were oxidized by Piranha etching, a solution of 7:3 v/v concentrated sulfuric acid and hydrogen peroxide, at 80 °C for 2 hours. The surface-oxidized wafers were then rinsed thoroughly with deionized water and blown dry with nitrogen. Concentrated H$_2$SO$_4$ and H$_2$O$_2$ were used as received from Aldrich Chemicals Co. USA.

**Neutron Reflectivity Experiment.** Specular neutron reflectivity measurements were carried out on the liquid reflectometry at the Spallation Neutron Source in Oak Ridge National Laboratory$^{29,30}$. The instrument is operated in time-of-flight mode using an unpolarized pulsed neutron beam with neutron wavelengths ranging from 2.5–17.5 Å. In this study, $q$ values ranging from approximately 0.006–0.17 Å$^{-1}$ were probed. The $q$ is
momentum transfer vector and is given by \( q = 4\pi \sin \theta / \lambda \), where \( \lambda \) is the neutron wavelength and \( \theta \) is the incident angle normal to the sample surface. The background was subtracted from raw data, and reflected intensities were normalized with respect to incident beam intensity to get the reflectivity profiles. The error bars on the reflectivity profiles correspond to the statistical errors of the measurements.

The reflectivity profiles of all the as-cast films were measured. The as-cast thin films are referred to the thin films that were allowed to dry overnight in a vacuum oven at 50 °C before annealing them above the \( T_g \) of PS. The samples were then annealed for a given time at 120 °C in a vacuum oven. The samples were quenched immediately after being removed from the vacuum oven by placing them on an aluminum plate connected to a \( \text{N}_2 \) inlet. We assumed the rapid quenching process would freeze the dynamics of the polymer chains within short-length scales compared to the length scales of the film thickness. Repeating the above quenching process, we followed the events at the interfaces for 320 minutes of annealing.

The reflectivity data were modeled to determine the distribution of protonated additives in a DPS matrix. Scattering length density (SLD) of linear DPS (6.0 x 10\(^{-6}\) Å\(^{-2}\)) and linear HPS (1.42 x 10\(^{-6}\) Å\(^{-2}\)) were calculated by the bulk density of DPS (1.13 gcm\(^{-3}\)) and HPS (1.05 gcm\(^{-3}\)) as well as their molecular formulas. The density of three-arm PS has not been reported. Therefore, to calculate the SLD of three-arm HPS (1.21 x 10\(^{-6}\) Å\(^{-2}\)), we assumed the density of linear HPS. MOTOFIT, a fitting analysis package running on the IGOR Pro 6.21 platform was used to simulate the reflectivity data\(^{31}\). A multilayer recursive Parratt formalism was used by MOTOFIT to analyze the data by simulating the
reflectivity profiles using genetic optimization to obtain the best least square fit\textsuperscript{31, 32}. The quality of a fit was determined by the $\chi^2$ and for all the fittings we obtained $\chi^2 \leq 1.5$. The profiles of SLD as a function of the distance from the solid substrate were generated using a multilayer model where each layer was described as a box with a given thickness and SLD. The roughness between two adjacent layers was described by an error function centered at the interface.

**Analyses of the density profiles.** The SLD profiles were further analyzed to quantify the volume fraction of additives at a given distance from the substrate interface as a function of annealing time. The amount of polymer additives at a given depth were quantified by transforming the SLD profiles to additive volume fraction ($\Phi_A$) profiles using the relationship given in Equation 3.1. Volume fraction was expressed in terms of the observed scattering length density, SLD\text{obs}, and that of the matrix, SLD\text{DPS}, and the additive, SLD\text{A}.

$$\Phi_A(d) = \frac{\text{SLD}(\text{obs})(d) - \text{SLD}(\text{DPS})}{\text{SLD}(A) - \text{SLD}(\text{DPS})}$$ (3.1)

These profiles were then used to determine the segregation of additives to the interfaces with annealing. The polymer/substrate and the polymer/air interfaces were defined in order to determine the segregation of additives to a particular interface by dividing the volume fraction profiles into three regions: the polymer/substrate interface, the center of the film, and the polymer/air interface, as presented in Figure 3.2. The polymer/substrate interface, the center of film, and the polymer/air interface were defined as the distance from A to B, B to C, and C to D, respectively.
Figure 3.2. Illustration of the definitions of the polymer/substrate interface, the center of the film, and the polymer/air interface used to integrate the area under the curve. The profile of the thin film before annealing is shown by the brown solid line, and the profile after annealing is shown by the blue solid line.

The area under the profile is used to determine the degree of segregation with annealing time. Finally, the mutual diffusivity constant, $D_m$, for both interfaces was determined by following the relationship shown by Equation 3.2, as used by Arlen et al.\textsuperscript{33}

$$\frac{\Delta A}{\phi_{(A)}} = (D_m t)^{1/2} \quad (3.2)$$

The slope of the linear region at the onset of the annealing process of the plot of normalized area change with respect to the additive volume fraction at bulk versus the square root of annealing time gave the diffusivity constant.
Results and Discussion

Thin films of 300–600 Å of 95:5 wt% linear PS/three-arm PS were studied. We probed the distribution of a protonated three-arm PS in a linear DPS matrix. The results were compared with those of the linear analogs. The study focused on a matrix of 15 kg/mol PS which is below the entanglement molecular weight for PS (~18 kg/mol). The molecular weights of the arms of the star PS were 19 kg/mol and 110 kg/mol.

The neutron reflectivity profile in terms of $Rq^4$ vs. $q$ as a function of annealing time for the blends of 19 kg/mol three-arm star PS and 13 kg/mol linear PS in a 15 kg/mol DPS matrix are presented in Figure 3.3. The data for the blend of 110 kg/mol three-arm star PS and 160 kg/mol linear PS in a 15 kg/mol DPS matrix are given in the supporting information. $R$ corresponds to the reflectivity as a function of the momentum transfer vector, $q$. The data representation in terms of $Rq^4$ as a function of $q$ compensates for the sharp decrease of $R$ as $q^4$ of the ideal Fresnel reflectivity and better resolves the features of the reflectivity profiles.

All reflectivity profiles were first characterized by three features: the position of critical angle, the distance between consecutive minima, and the oscillation intensity. The well-defined critical edge at the critical momentum transfer vector, $q_c$, corresponded to the angle below which total reflection took place. The position of the critical angle of the as-cast sample hardly changed with annealing. While qualitatively, $q_c$ appeared almost unchanged, the differences between consecutive minima that corresponded to film thickness changed about 3%–5% with annealing. These changes corresponded to stress release from spin coating that took place upon annealing. Interestingly, the intensities
of the reflectivity fringes changed as a result of the migration. The evolution of the intensities of the first fringe was prominent, as shown in Figures 3b and d. The changes of fringe intensities were more pronounced in the presence of three-arm PS than they were in the presence of linear PS analogs.

Figure 3.3. Neutron reflectivity profiles in terms of $Rq^4$ vs. $q$ as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, c) 15k DPS/13k linear HPS. The zoomed-in regions of the first fringes of
(a) and (c) are shown in (b) and (d), respectively. The symbols correspond to the experimental reflectivity data, and the solid lines are the best fits. The error bars of the reflectivity data are smaller than the symbols and thus are not displayed.

The intensities of the first fringe in all patterns significantly decreased with annealing time, as observed in Figure 3.4, for up to 60 minutes of annealing. Beyond 60 minutes the intensities of the first fringe for the three-arm PS further decreased but significantly slower. For the linear PS blends, hardly any changes were observed. The intensities of fringes were proportional to the SLD contrast; i.e. with increase of contrast the intensity of the fringes increase. This was a clear mark of the migration of the three-arm PS additives in the DPS polymer matrix.

Figure 3.4. The height of the first fringe in terms of $Rq^4$ determined from Figures 3a–d. The matrix of all the films was 15k DPS, and the molecular weights of the additives are
indicated in the figure. The solid lines are the fits to an exponential function and the quality of the fits are given in $R^2$ which is in the range of (a) $0.94–0.97$ and (b) $0.97–0.98$.

The reflectometry profiles were analyzed in terms of arbitrary multi-layer models\textsuperscript{32} with varying film thickness, SLD, and roughness. This simple approach put constraints and allowed the system to evolve as the minority component migrates. The evolutions of these parameters with annealing time along with the SLD profiles were extracted to determine the distribution of additives. The number of layers chosen was the minimum needed to allow the data to evolve while minimizing the number of free parameters. Figure 3.5 presents the reflectometry patterns of 15k/110k thin films before annealing together with calculated reflectometry profiles using 11-layer models for the two extreme cases; one in which the three-arm PS was fully segregated to the air interface and the other in which it was fully segregated to the solid interface as well as one in which it was distributed homogeneously. Comparison of the experimentally and calculated profiles showed that the three-arm PS was homogeneously distributed before the films were annealed.
Figure 3.5. Reflectivity in terms of $Rq^4$ vs. $q$ for a thin film of 15k linear DPS and 110k three-arm HPS in the ratio of 95:5 wt% spin coated on silicon oxide wafer before annealing. The dashed lines illustrate the simulated reflectivity patterns for the total segregation of the three-arm to the polymer/air interface (green) and polymer/substrate interface (orange). The black solid line represents the best fit for the reflectivity data.

The polymer profiles were derived from the analysis in terms of SLDs ($b/V$) as a function of distance from the silicon oxide substrate. They were then translated to additive volume fraction ($\Phi_A$) profiles, as presented in Figures 3.6 a–d. Volume fraction is expressed in terms of the observed SLD, SLD$_{obs}$, and that of the matrix, SLD$_{DPS}$, and the additive, SLD$_A$ as shown in Equation 3.1. The values of SLD determined from the fitting of thin films before annealing were comparable to the theoretical SLD values calculated for the blend of DPS and HPS. The slight deviations of SLD prior to annealing were attributed to the presence of residual solvents.$^{37}$ The profiles of all the thin films
before annealing were characterized by homogeneous distribution of HPS additives within the DPS matrix with roughness of less than 1.5 nm at the polymer/air interface. Qualitatively, in all the profiles, the volume fraction of additives at both the polymer/substrate and polymer/air interfaces dropped after annealing compare to the profiles of the thin films before annealing. These reductions were attributed to segregation of the protonated species to the interfaces. The volume fraction of additives at the center of the film decreased with annealing due to the depletion of additives from the center of the film. These changes were more pronounced in the thin films with low molecular weight additives than in presence of the high molecular weight analogs. Further, the changes in volume fractions of additives at both interfaces were more noticeable in the films containing three-arm polymer additives than in those containing linear analogs.
Figure 3.6. Evolution of volume fraction profiles in terms of additive volume fraction ($\Phi$) vs. distance from solid substrate (d) as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS.

Regardless of the molecular weight of the additives, the trends of changes were similar. Qualitatively, the main difference was that the degree of segregation of the additives was higher for those with low molecular weights than for those with high molecular weights. Similar behaviors of surface enrichments have been observed in
different polymer blends. These results agree with previous observations. For example, Jones and Kramer$^{38}$ who studied the distribution of linear DPS and HPS in binary PS blends and described the kinetics of the segregation of DPS to the surface by mean field theory. A similar analysis was carried out by Arlen et al.$^{33}$ for a series of styrene/methyl methacrylate alternating copolymers dispersed in a matrix of deuterated poly(methyl methacrylate). According to these studies, polymer segments segregated to the interfaces with initial time dependence of square root of time, $t^{1/2}$. The enrichment saturated after prolonged exposure.

In the current study, the volume fraction of the migrated additive to the interfacial regions at a given time, $\Delta A(t)$, were determined using the equation presented by Arlen et al.$^{33}$

$$\Delta A(t) = \int_{i}^{j} [\Phi(t,z) - \Phi(0,z)]dz$$  \hspace{1cm} (3.3)

where $\Phi(t,z)$ is the segregated additive volume fraction as a function of distance normal to the substrate interface, $z$, defined by position $i$ and $j$ at a given time, $t$, and $\Phi(0)$ is the volume fraction of the additive within the positions of $i$ and $j$ at a given interface of the profiles of thin films before annealing. According to Equation 3.3, the area change, $A_t - A_0$, at a given interface corresponds to the total migration of additives to that interface within time, $t$, where $A_t$ and $A_0$ are the area under the volume fraction profiles of each interface at a given annealing time, $t$, and before annealing the sample, respectively. The absolute area changes, $|A_t - A_0|$, at the polymer/substrate interface, the center of the film, and the polymer/air interface as a function of annealing time at 120 °C are presented in Figures 3.7 a–d.
Figure 3.7. Area change, $\Delta A = |A_t - A_0|$, at the polymer/substrate interface, the center of the film, and the polymer/air interface as a function of annealing time for the blends of a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS. The solid lines are the fits to an exponential function where $R^2$ is in the range of 0.98 to 0.99.

The area change in presence of three-arm additives is higher than that in presence of linear analogs with comparable molecular weights. These changes are attributed to the entropy difference of three-arm vs. linear polymers. Since a three-arm molecule has three
chain ends, the entropy gain due to annealing is higher for the three-arm additives than it is for their linear analogs. Consequently, more three-arm additives segregate to the interfaces. Even though, qualitatively, almost symmetric segregation is observed in the volume fraction profiles, the quantitative area analysis, as shown in Figure 3.7 a–d, shows that the segregation of additives is asymmetric. The area analysis reveals that the three-arm polymers are preferentially segregated to the air interface; in contract, their linear analogs show hardly any preferential segregation to either interface, although the segregation is slightly asymmetric at prolonged exposure times. Qualitatively, for all the samples, fast area changes at the onset of the annealing process and slow area changes at prolonged annealing times are observed. However, the crossover is more noticeable in segregation of low molecular weight PS additives. The fast area changes at the onset of annealing reflects the segregation of additives to interfaces, while the leveling-off at extended annealing times represents the saturation of additives at the interfaces. The segregation of PS additives shows a power law behavior, in which the area change scales as approximately $t^{1/2}$. The data are only fitted up to the starting point of plateau values of $\Delta A$, which is about $3 \times 10^3$ to $4 \times 10^3$ seconds. The corresponding time coefficients, $a$, are indicated in the figures, which are comparable to the values observed by Arlen et al.$^{33}$ for the surface segregation of a series of styrene/methyl methacrylate alternating copolymers dispersed in a matrix of deuterated poly(methyl methacrylate).
Figure 3.8. Log-log plot of area change, ΔA, as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS. The solid lines are the best linear fits with $R^2 = 0.99$ and the dashed lines are the extrapolation of the linear fits.

To elucidate the effects of molecular weight of the three-arm and linear PS additives on interfacial segregation, we compared the interfacial behavior and
diffusivities for the additives with different molecular weights. This diffusive process requires the movement of one polymer to the surface and the coordinated diffusion of the other polymer away from the surface. Therefore, the diffusivities that are determined in this process are called mutual diffusivities. As shown in Equation 3.2, the mutual diffusivities at a given interface were determined from the plots of linear regions of normalized area change of the given interface with respect to additive volume fraction at the center of the film vs. time. The plots for different systems that we studied are shown in Figure 3.9. In presence of three-arm PS additives, the degree of segregation of three-arm PS additives to the substrate interface is high compared to their segregation to the air interface. However, in presence of linear PS additives, less segregation was observed at the substrate interface compared to the air interface. Further, the relative total segregation decreased as the size of the polymer additives increased, regardless of their architecture. The corresponding diffusivities of the polymer additives to both interfaces are given in Table 3.2.
Figure 3.9. Normalized area change of the polymer/substrate (open symbol) and the polymer/air (solid symbol) interfaces with respect to additive volume fraction at the center of the film as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/19k three-arm HPS, b) 15k DPS/13k linear HPS, c) 15k DPS/110k three-arm HPS, and d) 15k DPS/160k linear HPS. The dotted lines are the guide to the eye.
We found that the diffusivities of linear and three-arm PS additives in a 15k DPS matrix are on the order of $10^{-17}$ cm$^2$s$^{-1}$, which is comparable to values determined by the number of researchers using polymers of various sizes and various annealing temperatures. For example, Reiter et al.$^{39}$ and Bucknell et al.$^{40}$ found that mutual diffusivities are in the order of $10^{-17}$ cm$^2$s$^{-1}$ for linear HPS and DPS having molecular weights of 660k and 752k at 140 °C and for end-functionalized DPS brush in a miscible poly(vinyl methyl ether) (PVME) polymer at 133 °C respectively. However, Wool et al.$^{41}$ and Karim et al.$^{42}$ found that faster diffusivities, in order of $10^{-16}$ cm$^2$s$^{-1}$, than those we observed for linear HPS and DPS having molecular weights of 111k and 93k at 125 °C and 233k and 203k at 155 °C respectively.

<table>
<thead>
<tr>
<th>Additive</th>
<th>$D_{(poly/sub)} \times 10^{-17}$ cm$^2$s$^{-1}$</th>
<th>$D_{(poly/air)} \times 10^{-17}$ cm$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>19k three-arm HPS</td>
<td>9.05</td>
<td>6.13</td>
</tr>
<tr>
<td>110 three-arm HPS</td>
<td>3.98</td>
<td>3.43</td>
</tr>
<tr>
<td>13k linear HPS</td>
<td>4.35</td>
<td>5.86</td>
</tr>
<tr>
<td>160k linear HPS</td>
<td>2.92</td>
<td>3.14</td>
</tr>
</tbody>
</table>

Table 3.2. Segregation diffusivities at the polymer/substrate and the polymer/air interfaces of indicated HPS additives in 15k linear DPS matrix at 120 °C.
Summary

This study presents for the first time, an investigation of effects of molecular weight of three-arm PS additive on segregation in thin PS films using NR. We investigated the simplest system where one branch point is introduced to the additives and changed the molecular weight of the arms from almost non-entangled to highly entangled molecular weights and incorporated them with non-entangled linear PS matrix thus avoiding matrix entanglements that would constrain the additive motion. We compared the distributions of the three-arm star polymers normal to the interface with those of the linear analogs that had comparable molecular weights to the star arms. We found that a homogeneous distribution of additives in as-cast thin films. With annealing, both three-arm PS and linear PS analogs segregated to both substrate and air interfaces. While both polymer additives segregated, a significant difference was observed even in the presence of one polymer junction. The enrichment of interfaces with three-arm additives was asymmetric while almost symmetric segregation was observed in presence of linear PS analogs. Qualitatively, the segregation trend is similar for high and low molecular weight additives. However, with increasing the molecular weight of additives, the degree of segregation was decreased. Quantitatively, segregation of additives followed $t^{1/2}$ kinetics at short annealing times and crossed over to slow segregation process at prolonged annealing times. We suggest that the segregation of polymer additives to interfaces occurs due to the balance of enthalpic and entropic effects. The migration of additives to the interfaces enhances the effective surface area and hence lowers the interfacial surface tensions and alters the intermolecular interaction free energy. We
attribute these changes of intermolecular interaction free energy to enhancing the wettability of solid substrates which, in turn, slows down the dewetting of thin films.

**Supporting Information**

Figure 3.10. Neutron reflectivity profiles in terms of $Rq^4$ vs. $q$ as a function of annealing time at 120 °C for blends of PS additives in 15k linear DPS matrix; a) 15k DPS/110k three-arm HPS, c) 15k DPS/160k linear HPS. The zoomed-in regions of the first fringe of plots (a) and (c) are shown in (b) and (d) respectively. The symbols correspond to the

57
experimental reflectivity data, and the solid lines are the best fits. The error bars of the reflectivity data are smaller than the symbols and thus are not displayed.

**Acknowledgment**

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**References**


CHAPTER FOUR

NEUTRON REFLECTIVITY STUDY OF THE INTERFACIAL REGION BETWEEN IONOMERS AND VAN DER WAALS POLYMERS

Abstract

Interdiffusion of polymers across interfaces controls many current and potential applications from alternative energy devices to selective drug delivery systems. The interdiffusion is determined by numerous factors including the chemical and phase structure of polymer coupled with interfacial effects. The interfacial structure is particularly important since in numerous applications the polymer molecules resided at an interface with other polymers. The current work reveals the effects of ionic groups on interdiffusion of a model system that consist of polystyrene and polystyrene sulfonate as resolved from neutron reflectometry measurements. Similar to previous studies we found that at the onset of diffusion the polymer chains interdiffuse at the interface between non-ionic polystyrenes with $t^{1/2}$ dependence independent of molecular weights and transforms to $t^{1/4}$ as time progresses. In contrast, in presence of ionic groups dynamics at the interface is hindered significantly. For low sulfonation levels the initial rates scale with approximately $t^{1/2}$, but transitions to a much slower exponent. The fast regime is attributed predominantly to chain end crossing the interface where at later stage effects of confinement either by entanglements of ionic groups becomes dominant. At higher sulfonation levels, the spatial dynamics is very limited.
**Introduction**

Interdiffusion of polymer chains across interfaces plays a critical role in applications that require controlled motion of polymer chains in thin films. Examples include polymer coatings in dielectric actuators\(^1\), microelectronics\(^2\), composite lamination\(^3\), self-healing\(^4\), and fracture-strength development\(^5\). The interfacial region is often a key to the use of polymers. In lamination for example, the most desired characteristics are mechanically stable interfaces, where for coating of optical devices, the interfacial regions must be smooth to maintain transparency. Similar challenges exist when response to external perturbation and in polymeric self-healing processes. Interfacial behavior of polymers is controlled by a set of coupled factors that affect the miscibility of two polymers. Among them, are the difference in molecular weight\(^6\), chemical compatibility\(^7\), tacticity\(^8\) and isotope labeling\(^9\). These factors were elegantly studied experimentally\(^10-15\) and theoretically\(^6,16\) over the past few decades. One important interface is that formed between ionic and non-ionic polymers. In contrast to interface between Van der Waals polymers, the interfacial regions of ionic polymers are often structured\(^17\). This chapter presents a first insight into dynamics at the interfaces between polystyrene (PS) and its sulfonated analog, polystyrene sulfonated (sPS). The presence of ionic groups results in diverse polymer morphologies where the shape and the stability of the assemblies depend on the relative ionic strengths of the polymers, the interactions between the ionic as well as the interaction between the ionic groups with the matrix. We found that both ionic clusters and entanglements slow down interdiffusion. Surprisingly
though the ionic clustrs are slow to rearrange and therefore slow down significantly the dynamics at the interface.

The diffusion of simple liquids into polymers follows Fickian diffusion in which the liquid propagated within the polymer matrix with $t^{1/2}$ dynamics\textsuperscript{18}. The dynamics of polymer melts are an intricate process in which dynamics depend on the interaction of the polymers and topological constraints\textsuperscript{19, 20}. Flexible and semi flexible polymers in the low interaction regime, (i.e. $\chi N \leq 10$) often follow a Fickian process with $t^{1/2}$ average displacements of chains segment. In this range the dynamics are explained by the Rouse model\textsuperscript{19}. However above the entanglement length, the diffusion slows down and dynamics in melts are described by the Reptation model\textsuperscript{20, 21}. In this model, the motion of the polymer chains is confined to a hypothetical tube formed by the neighboring chains in the matrix\textsuperscript{20, 21}. In presence of ionic groups, additional constraints imposed by ionic clusters where the degree of association and the ability of the clusters to rearrange impact the dynamics.

Furthermore, in thin films of thicknesses within the several radii of gyration of the polymers, interfacial forces become significant. Specifically interfacial forces between substrate-polymer and polymer-polymer would determine the arrangement of polymer segments in thin films. Along the same lines, entropy often drives chain ends to the interface, impacting both the structure and the dynamics. With decreasing film thicknesses, thermal fluctuations are reduced as well. For example, Lin \textit{et al.}\textsuperscript{22} using neutron reflectometry have shown reduced mobility of deuterated and hydrogenated poly(methyl methacrylate) near a solid interface. Along the same lines, Stamm \textit{et al.}\textsuperscript{23}
showed that conformation of polymers consists of alternating layers of hydrogenated and deuterated polystyrene and the interfacial effects have to be accounted on the interdiffusion of polymers in thin films. Similar observations were made by Brulet et al.\textsuperscript{24} and Russell et al.\textsuperscript{25} in which they found that polymer chains retain their unperturbed Gaussian conformations parallel to the surface, where as normal to the interface confinement effects perturbed. In addition to the chain confinement effects that impact the dynamics across an interface, small changes, erasing from chemical diversity becomes significant. Doyle et al.\textsuperscript{26} have shown that protonated PS (HPS) and deuterated PS (DPS) are not fully miscible with a slightly positive $\chi$ at room temperature, which turned negative with increasing temperature.

There is very little known on the effects of ionic groups\textsuperscript{17}. Herein the interdiffusion of PS and sPS are studied in comparison with that of HPS, DPS using neutron reflectometry. This technique probes buried interfaces in sub nm-scale, using the inherent contrast of neutrons between protonated and deuterated polymers. Resolution of 5-10 Å coupled with selective isotope labeling is able to follow the changes of the order of 1 nm at normal to the interface, which is approximately one order of magnitude less compare to the radius of gyration of the PS studied. We found that at early stage of annealing, a fast interfacial broadening which crossovers to a slow process at prolong annealing times. The widths of the interface between two polymers capture the degree of spatial interpenetration and are correlated to their mean square displacement. The evolution of the interfacial widths with time captures the diffusion process. At the both interfaces, ionic PS/PS and that between non-ionic PS/PS, an early fast diffusion stage is
observed. In contrast to van der Waals polymers the presence of ions and constraints the extent of interdiffusion is significantly hindered.

**Experimental**

**Materials.** Highly monodispersed linear HPS and DPS (The molecular characteristics are presented in Table 4.1) were used to prepare thin films. Linear DPS were purchased from Pressure Chemicals Co. USA, and linear HPS were purchased from Polymer Source Inc. USA. All non-sulfonated PS samples were used as received. The sPS was prepared by dissolving the HPS in dichloromethane followed by addition of freshly prepared acetyl sulfate at 50 ºC as discussed elsewhere\(^\text{27}\). This reaction produce randomly substituted \(-\text{SO}_3\text{H}\) groups primarily at the *para*-position of the phenyl group along the polymer chain\(^\text{27}\). The sulfonation levels were determined by titration of sPS in a mixture of 9:1 toluene and methanol with 0.01 M sodium hydroxide dissolved in methanol. The sulfonation levels are presented as the mol\%, which is defined as the number of \(-\text{SO}_3\text{H}\) groups-substituted styrene repeat units per 100 of styrene units. The glass transition temperature was determined by differential scanning calorimetric measurements on PerkinElmer DSC-4000, calibrated with Indium standards. The heating rate was 10 °C/min. Multiple scans were used.
Table 4.1. Characteristics of the polystyrene samples used in reflectivity measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kgmol$^{-1}$)</th>
<th>$M_w/M_n \pm 0.01$</th>
<th>$T_g \pm 0.5^\circ C$</th>
<th>Sulfonation Level (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPS-160k</td>
<td>160.3</td>
<td>1.06</td>
<td>107.2</td>
<td>0.0</td>
</tr>
<tr>
<td>DPS-15k</td>
<td>15.0</td>
<td>1.04</td>
<td>98.5</td>
<td>0.0</td>
</tr>
<tr>
<td>DPS-132k</td>
<td>132.0</td>
<td>1.06</td>
<td>106.5</td>
<td>0.0</td>
</tr>
<tr>
<td>sPS160k-2 mol% sulfo</td>
<td>162.8</td>
<td>1.06</td>
<td>110.8</td>
<td>2.1</td>
</tr>
<tr>
<td>sPS160k-8 mol% sulfo</td>
<td>170.2</td>
<td>1.06</td>
<td>113.2</td>
<td>7.9</td>
</tr>
</tbody>
</table>

**Preparation of Polymer Solutions.** Polymer solutions of HPS and DPS were prepared by dissolving 1 wt% of the polymers in toluene. The 1 wt% of sPS solution was prepared by dissolving sPS in mixture of 9:1 toluene and methanol. The solutions were filtered using 2.0 μm Millipore filters prior to spin coating.

**Preparation of Composite Layers.** A series of two layers were prepared. A DPS layer was cast on silicon oxide surface and either HPS or sPS layer was transferred on top. The composite layer preparation is detailed elsewhere$^{28}$ and only briefly reviewed. First, a 1 wt% DPS solution was cast on silicon oxide wafers at 1800 rpm for 2 minutes. The samples were vacuum dried for 16 hours at 28 psi and at 55 °C to remove residual solvent. Then, the HPS and the sPS films were spin cast on silicon oxide wafers and subsequently floated off onto deionized water. The HPS and sPS films were then transferred on top of the DPS films. These DPS/HPS and DPS/sPS composite films were allowed to dry at room temperature under vacuum at 28 psi for about 60 hours to remove residual solvent. The film thicknesses of each layer were measured by ellipsometry.
Thicknesses reported are the average of measurements made from at least five spots on the dry thin films. The dimension of the each layers and the composite films are given in Table 4.2.

<table>
<thead>
<tr>
<th>Composite Layers Top/Bottom</th>
<th>Layer Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HPS layer</td>
</tr>
<tr>
<td>HPS160k/DPS15k</td>
<td>69.1 ± 0.2</td>
</tr>
<tr>
<td>HPS160k/DPS132k</td>
<td>55.3 ± 0.2</td>
</tr>
<tr>
<td>HPS160k-2 mol% Sulfo/DPS15k</td>
<td>50.9 ± 0.2</td>
</tr>
<tr>
<td>HPS160k-2 mol% Sulfo/DPS132k</td>
<td>57.4 ± 0.2</td>
</tr>
<tr>
<td>HPS160k-8 mol% Sulfo/DPS15k</td>
<td>26.6 ± 0.3</td>
</tr>
<tr>
<td>HPS160k-8 mol% Sulfo/DPS132k</td>
<td>23.6 ± 0.1</td>
</tr>
</tbody>
</table>

Table 4.2. Thicknesses of the layers determined from ellipsometry prior to make composites.

**Silicon Wafer Treatment.** One-side-polished, 50mm-wide and 5mm-thick silicon oxide wafers were used as substrates. The silicon oxide wafers were purchased from Virginia Semiconductor Inc. USA. The substrates were oxidized by Piranha etching, a solution of 7:3 v/v concentrated sulfuric acid and hydrogen peroxide, at 80 °C for 2 hours. The surface-oxidized wafers were then rinsed thoroughly with deionized water and
blown dry with nitrogen. Concentrated H$_2$SO$_4$ and H$_2$O$_2$ were used as received from Aldrich Chemicals Co. USA.

**Neutron Reflectivity Experiment.** Specular neutron reflectivity measurements were carried out on the Surface Profile Analysis Reflectometer$^{29}$ (SPEAR) at the Lujan Neutron Scattering Center at Los Alamos National Laboratory, USA and the Liquid Reflectometer$^{30,31}$ (LR) at the Spallation Neutron Source, Oak Ridge National Laboratory, USA. Both spectrometers operated in the time-of-flight mode with a non-polarized pulsed neutron beam with a range of neutron wavelengths from 4.5 to 16 Å and from 2.5 to 17.5 Å respectively. Measurements were carried out over a momentum transfer vector, q range from 0.008 Å$^{-1}$ to 0.2 Å$^{-1}$ on SPEAR and from 0.006 Å$^{-1}$ to 0.18 Å$^{-1}$ on LR. The momentum transfer vector is given by $q = 4\pi \sin \theta / \lambda$, where $\lambda$ is the neutron wavelength, and $\theta$ is the incident angle normal to the sample surface. The background was subtracted from the raw data and reflected intensities were normalized with respect to Fresnel reflectivity of a silicon wafer. The error bars on the reflectivity profiles correspond to the statistical errors of the measurements.

Interdiffusion studies were carried out on the composite samples described in Table 4.2 as a function of annealing time at 120 °C. The reflectivity profiles of “as-prepared” composite films were measured as a base line. The reflectivity profiles of “as-prepared” are defined as the reflectivity patterns acquired immediately after drying the composite in a vacuum oven. For time dependent interdiffusion measurements, samples were annealed for varying times under vacuum at temperatures above the $T_g$ (120 °C).
The samples were then quenched to room temperature which is significantly below $T_g$ of the system.

**Data Analysis.** Scattering length density (SLD) of each polymer was calculated using their corresponding bulk densities. MOTOFIT, a fitting analysis package running on the IGOR Pro 6.21 platform was used to analyze the reflectivity data\(^{32}\). A multilayer recursive Parratt formalism was used to analyze the data by simulating the reflectivity profiles using genetic optimization to obtain the best least square fit\(^{33}\). The quality of a fit was determined by the $\chi^2$ where the acceptable $\chi^2 < 2.0$. The profiles of SLD as a function of the distance from the solid substrate were generated using a multilayer model where each layer was described as a box with a given thickness and SLD. The roughness between two adjacent layers was described by the Gaussian function.

**Calculations of Interfacial Widths.** The SLD profiles obtained from the data analysis in terms of scattering length density as a function of distance from the solid substrate were shifted such that the polymer/polymer interface is located at the origin. The interfacial widths were extracted as shown in Figure 4.1. The interfaces of composites layers prior to annealing are not smooth, the experimentally determined interfacial widths $\sigma_t$ were corrected to the initial roughness $\sigma_0$, as shown in Equation 4.1.

$$\Delta \sigma = \sqrt{\sigma_t^2 - \sigma_0^2} \quad (4.1)$$
Figure 4.1. Schematic representation of the definitions of the interfacial widths ($\sigma_i$) and the initial roughness ($\sigma_0$).

**Results and Discussion**

Using neutron reflectometry we have studied the dynamics at the interface between ionic polystyrene and polystyrene, in comparison to that of two polystyrene films. Two factors were probed: the effects of molecular weights and those of degree of sulfonation with the rationale that both entanglements and ionic clusters would constrain the dynamics. The neutron reflectivity profiles together with the corresponding fits as a function of annealing time are presented in Figure 4.2. For each sulfonation level 0, 2 and 8 mol %, the study probed the interface with low, 15 kg/mol, and high, 132 kg/mol, molecular weight polystyrene.
The reflectivity patterns are characterized by the position of critical edge, \( q_c \), the distance between consecutive minima, \( \Delta q \), and often the intensity of fringes. A clear critical edge was observed for all as-prepared samples. We found that \( q_c \) hardly changes with annealing time. This is a strong indication that the air and solid interfaces remain unperturbed as the samples are annealed. The sample thicknesses were extracted from \( 2\pi/\Delta q \), where \( \Delta q \) is the distance between two successive minima. Note that the thicknesses are sensitive to reflection of substrate/DPS and DPS/HPS interfaces. The thicknesses calculated from \( \Delta q \) are in agreement with those measured by ellipsometry and are shown in Table 4.3. With annealing the reflectometry patterns become more complex and structured.

<table>
<thead>
<tr>
<th>Composite Layers Top/Bottom</th>
<th>Layer Thickness (nm)</th>
<th>Composite(_{NR})</th>
<th>Composite(_{SLD})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPS160k/DPS15k</td>
<td>38.7</td>
<td>107.4</td>
<td></td>
</tr>
<tr>
<td>HPS160k/DPS132k</td>
<td>41.4</td>
<td>95.3</td>
<td></td>
</tr>
<tr>
<td>HPS160k-2 mol% Sulfo/DPS15k</td>
<td>44.2</td>
<td>93.1</td>
<td></td>
</tr>
<tr>
<td>HPS160k-2 mol% Sulfo/DPS132k</td>
<td>38.1</td>
<td>96.2</td>
<td></td>
</tr>
<tr>
<td>HPS160k-8 mol% Sulfo/DPS15k</td>
<td>51.1</td>
<td>73.7</td>
<td></td>
</tr>
<tr>
<td>HPS160k-8 mol% Sulfo/DPS132k</td>
<td>47.0</td>
<td>67.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3. Thicknesses of the composite layers determined from neutron reflectometry and from scattering length density profiles. The subscript represents the corresponding method used to determine the thickness.

The reflectometry profiles were analyzed in terms of a two layer model, a HPS layer on top of a DPS layer. The SLD of the each layers were not allowed to vary while allowing the film thickness and the interfacial roughness to change. The values of SLD determined from the fitting of non-annealed samples are comparable to that of the SLD values calculated using molecular parameters and the density of bulk PS. We attribute slight deviation of SLD differences from theoretical values either to trapped solvent during the sample preparation or to different interfacial densities due to confinement of polymer chains on thin films. The total film thicknesses are hardly changed as annealing progressed. However the roughness at polymer/polymer interface evolves with annealing time as a result of interdiffusion of polymer chains across the polymer/polymer interface. The roughness is described by a Gaussian function $G(z)$, given in Equation 4.2.
Figure 4.2. NR profiles and the corresponding fits at the indicated annealing times and sulfonation levels. Left column corresponds to low molecular weight DPS and right column corresponds to high molecular weight DPS. Symbols are the experimental reflectivities and solid lines are the best fits. The profiles are vertically shifted for clarity.
\[ G(z) = \frac{\Delta(b/V)}{(2 \pi)^{1/2} z_0} \exp \left( -\frac{z^2}{2z_0^2} \right) \]  

(4.2)

where, \( \Delta(b/V) \) is the scattering length density difference between the two layers across the interface, \( Z_0 \) is standard deviation of the Gaussian function that reflects the interfacial width and \( Z \) is the depth of the film. The evolution of interfacial widths with annealing time is used to extract the interdiffusion of HPS and DPS. The polymer profiles in terms of scattering length densities \( (b/V) \) as a function of distance \( (Z) \) from the polymer/polymer interface derived from the best fits are shown in Figure 4.3. All non-annealed profiles are characterized by an inherited interfacial roughness approximately 10 to 15 Å. The roughness may originated from trapped solvent introduced during the sample preparation or partially crystalized polymer domains\(^{36} \).
Figure 4.3. Polymer profiles in terms of scattering length density (b/V) as a function of distance from the composite interface as a function of annealing times for indicated
composites. Left column corresponds to low molecular weights and right column corresponds to high molecular weights. For clarity of the interface region the x-axis varies.

The interfacial width increases with annealing. However in presence of ionic groups the degree of interfacial broadening is significantly lower. For nonionic PS the degree of migration of the polymers across interfaces is primarily determined by the molecular weight. The symmetry is impacted by the choice of a Gaussian function to characterize the roughness between the polymer/polymer interfaces. Although the dynamics of individual polymers cannot be extracted from the interfacial broadness, the characteristics of the mutual diffusion of both polymers across the interface were resolved.

As expected, in absence of sulfonation Figure 4.3 a and b, show that the interfacial width increases significantly faster for polystyrene below the entanglement length than that for high molecular weight analog, above the entanglement length. For both polymers however the initial broadening is rather fast followed by slow changes. Similar observation of fast dynamics in low molecular weight PS than that of high molecular weight PS was observed by Karim et al.\textsuperscript{36, 37} for series of HPS/DPS melt having molecular weights above 200 kg/mol.

Introducing even small number of ionic groups onto the PS backbone significantly reduces the degree of inter-penetration. The evolution of interfaces in presence of 2and 8 mol% sulfonation on HPS is shown in Figure 4.3 c-d and e-f
respectively. While the interdiffusion is significantly hampered, the origin of the effects of ionic groups is not obvious. The ionic groups may simply enhance $T_g$, of the PS or when clustering they add further constraints for rearrangements. Our $T_g$ measurements at thin films show that $T_g$ is only slightly enhanced. Therefore we attributed the limited interdiffusion to the constraints exerted by ionic groups.

The evolution of interfacial widths with annealing times were quantified and compared with Rouse and Reptation characteristics. The $\Delta \sigma(t)$ with annealing time are presented in Figure 4.5. We assume that the mean square displacements of the polymer across the interfaces are reflected in the interfacial broadening, $\Delta \sigma(t)$. The broadening strongly depends on the sulfonation level. In absence of sulfonation interfacial widths increase rather fast at early stages of annealing and then crossed over to slow changes after approximately 20-30 minutes.

In analogous with diffusion of solvents in bulk polymers, the diffusion process or mass transport, is characterized by $t^\alpha$ where $t$ is time and $\alpha$ is a scaling exponent. The $\alpha = \frac{1}{2}$ is characterized for a diffusive process38. As $\Delta \sigma(t)$ is a result of chain diffusion it follows a similar scaling behavior. The scaling exponents for each of the composites are extracted from a log-log plot of the data shown in Figure 4.4. At zero degree sulfonation both the short 15k DPS and the 132 k DPS exhibit a $t^{\frac{1}{2}}$ behavior with extended time. It transitions to 0.28 for 15k DPS and 0.25 to 132k DPS.
Figure 4.4. Log-log plots of interfacial width, $\Delta \sigma(t)$, and annealing time for indicated samples as a function of sulfonation level as indicated. The symbol corresponds to the experimental data and the solid lines are the best linear fits.

These findings are agreement with recent results of Pierce et al. who determined that the chain ends are the first to cross an interface. At this stage the entanglements do not affect the interdiffusion. As sulfonation is slightly increase to 2 mol% the initial stage scaling remains close to 0.5 however the scaling exponent at later times decreases significantly. These low values of 0.13 for 15kg/mol and 0.11 for 132kg/mol DPS are a result of the additional constraints by the ionic groups. Increasing the sulfonation level to 8 mol% $\Delta \sigma(t)$ becomes order of magnitude smaller and $\alpha$ at onset decrease.

In order to compare the mutual inter-diffusivities of HPS and sPS with DPS, we have plotted the interfacial widths with $t^{15}$. Figure 4.5 are the changes of interfacial widths with time. Mutual diffusion coefficients were determined using $(\Delta \sigma)^2 = 2D\tau^{37}$. 
The results are given in Table 4.4. As expected interdiffusion of low molecular weight HPS/DPS is higher than that of high molecular weight HPS/DPS regardless of the sulfonation level. However, in presence of sulfonation groups, diffusion constant becomes one to two orders of magnitude slower. This large impact must be correlated with a significant constraint. As the glass transition temperature is only slightly affected in these ionic constraints, it becomes apparent that the ionic groups pin down the polymer.

Figure 4.5. Interfacial widths as a function of $t^{1/2}$ and sulfonation level of HPS for indicated samples. The symbol corresponds to the experimental data and the dash lines are guide to the eye.

The order of magnitude we observed for the interdiffusion of HPS/DPS composites on silicon oxide substrates is comparable with the previously observed values of the interdiffusion of polymers across interfaces using neutron reflectometry$^{37,39}$. 

81
However, it is significantly slow compared to the bulk diffusivities\textsuperscript{40, 41}. The mutual diffusion constants in presence of ionic groups are significantly small. To the best of our knowledge no mutual diffusion constant are available for the interdiffusion of polystyrene sulfonate at interfaces to compare.

<table>
<thead>
<tr>
<th>HPS\textsubscript{(sulfo)} (mol%)</th>
<th>$D_{(15k\ DPS/160k\ HPS)} \times 10^{-17}$ (cm$^2$s$^{-1}$)</th>
<th>$D_{(132k\ DPS/160k\ HPS)} \times 10^{-17}$ (cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>28.37</td>
<td>13.15</td>
</tr>
<tr>
<td>2</td>
<td>3.51</td>
<td>3.19</td>
</tr>
<tr>
<td>8</td>
<td>0.10</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 4.4. Diffusivities of the composites annealed at 120 °C.

**Summary**

The effects of constrains imposed by ionic groups on the evolution of interfacial broadening at polymer/polymer interface of ionic and nonionic PS bilayers at temperature above the $T_g$ of the PS were presented for the first time. The polymer composites of thin PS and sulfonated PS with different sulfonation levels were annealed at 120 °C and the reflectivity patterns of quenched samples were measured as a function of annealing time. In order to quantify the process, interfacial widths were extracted and interpreted in terms of the diffusion of the polymers. At early stage of the annealing a fast interfacial broadening was observed which transit into a slow process at prolong annealing times. The transition time increased with increasing the sulfonation level. At early stages of annealing, the interfacial broadening was linearly changed with $t^{1/2}$ and deviated at
extended annealing times. Surprisingly, even in presence of small amount of ionic groups hindered the motion of polymer chains across the interface.

Acknowledgment

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Reference


27. H. S. Makowski, R. D. Lundberg and G. S. Singhal, *US patent*, 1975, **3870841**.


CHAPTER FIVE
IN SITU NEUTRON REFLECTIVITY STUDY OF ALCOHOLS AT THE INTERFACE WITH THIN STRUCTURED IONOMER FILMS

Abstract

Selective transport of solvents within ionic polymers as determined by their chemical and phase structure controls their diverse current and potential application. Using in situ neutron reflectometry we elucidate the transport of alcohols across an interface of thin films which consist of a new class of highly rigid ionic polymers. The films were exposed to alcohols with varying chain lengths and the reflectometry patterns were recorded as a function of time. At early exposure the solvent was distributed homogeneously, while at later stages alcohols-rich polymer layer was developed at the polymer–vapor interface. The mass uptake was initially linear with $t^{1/2}$ and transitions to a slower stage at prolonged exposure times. Interfacial effects dominate the onset of diffusion resulting in significant slower diffusion in comparison with the bulk polymer. Surprisingly, these interfacial effects hardly depend on the hydrophobicity of the alcohols.

Introduction

The dynamics of guest molecules in ion-containing polymers (ionomers) play a key role in applications that require controlled ion transport across interfaces. Examples include hydrogen and alkaline fuel cells\(^1\), separation membranes\(^2\), controlled drug release media\(^3\), sensors\(^4\), and electro-chemical switches\(^5,6\). While ionic polymers are widely
used, one critical issue remains: under the conditions in which transport is optimized, both chemical and mechanical stability are often compromised. For example, maximizing ionic transport in hydrogen fuel cells requires high hydration levels, which in turn result in structural changes that lead eventually to failure. A similar issue is manifested in selective transport of solvent molecules in dialysis membranes, for example, where chemical resistance to transport of liquids while blocking specific substances is a key to their function. Depending on the interfacial composition and morphology, the processes that take place at the interfaces may further facilitate or inhibit transport. The current study probes the diffusion of alcohols across a structured interface of the films that consists of rigid polyphenylene ionic polymers. The polymer forms a structured interface with hydrophilic and hydrophobic groups co-residing at the interface. In contrast to flexible and semi-flexible polymers rearrangements and segregations are limited by the rigidity of the polymer. Changing the hydrophobicity of solvents affects a mean to probe diffusion across structured interfaces.

The significance of small molecule transport in ionomers has generated a wealth of studies\textsuperscript{7-14}. Controlled transport of guest molecules within ionomers is an intricate process that depends on the nature of both the ionomer matrices and the guest molecules in addition to temperature and external driving forces\textsuperscript{15-21}. These studies have shown that interfaces are critical in facilitating transport. Most of the studies have focused on the dynamics of guest molecules and ions in Nafion\textsuperscript{TM}1,6,7,10,12-15,22-26, a semi-flexible fluorinated co-polymer, predominantly due to the chemical stability that originates from its fluorinated nature. Several groups have demonstrated the significance of diffusion at
structured polymer interfaces. For example, Zawodzinski et al. found a delay in water penetration into Nafion™ membranes. They attributed this lag to surface rearrangements that took place upon contact with water and preceded penetration of the solvent. Moore et al. investigated the transport of water molecules within perfluorosulfonate ionomers. They observed that the uniaxial deformations strongly influenced the ordering of the ionic domain, which in turn affected the water transport and distribution across the interfaces. The significance of interfacial regions was also demonstrated by Monroe et al., who showed that water transport at the water vapor–Nafion™ interface depended on the membrane thickness. Similar results were also observed by Benziger et al. Recently, Eastman et al. probed Nafion™ thin films with thicknesses of approximately 20–220 nm using neutron and X-ray scattering techniques. They determined water content, extent of swelling, and the effective diffusion coefficient of water as a function of film thickness while varying the relative humidity. They demonstrated that in a film approximately 60 nm thick, those properties had clear transitions, which were attributed to confinement of the ionomer film. Researchers found that these interfacial effects arose due to the confinement of ionic domains between polymer interfaces, which were mainly governed by the flexibility of the polymer. Most studies have been carried out on ionic polymers that readily rearranged as the surfaces were exposed to vapors.

The degree of flexibility of the ionomer backbones is extremely significant since it allows the formation of distinctive domains that can rearrange upon interaction with small guest molecules. The flexibility of ionic polymers depends on the Kuhn length, the size of the smallest rigid segment, coupled with the Bjerrum length, the minimum
distance at which the unscreened Coulomb interaction energy of a pair of monovalent ions is comparable in magnitude to the thermal energy, where the Bjerrum length is strongly affected by the degree of ionization. In rigid ionomers, the backbone is almost arrested at large Kuhn lengths, which limits the rearrangements of the polymer in the presence of guest molecules. The rigidity of an ionomer affects its structure and dynamics, and, therefore, the diffusivity of guest molecules.

Only limited knowledge is currently available on the interfacial interaction of rigid ionic polymers. He et al. \^{11} studied the interaction of water with a rigid ionomer, sulfonated polyphenylene (sPP), the structure of which is shown in Figure 5.1. They observed that the interfacial region consisted of both hydrophilic and hydrophobic groups. Similar to previous studies of flexible polymers, the film absorbed water and swelled. However, a non-homogeneous distribution of the solvent was observed. The current study uses neutron reflectometry to probe the interfacial behavior of the films exposed to alcohols with different chain lengths. Varying the length of the alcohols chain modifies the hydrophobicity of the guest molecules and therefore affects their interaction with the polymers.
Specular neutron reflectometry has been a key tool in investigating polymer surfaces and interfaces\textsuperscript{32-34}. A resolution of 5–10 Å coupled with selective isotope labeling offers a means to follow the changes on the order of 1 nm at interfaces. The density profiles perpendicular to the substrate surface infer the composition of the thin film as a function of distance from the solid substrate.

The sPP ionomer consists of a polyphenylene backbone decorated with randomly sulfonated pendent phenyl groups. This polymer was developed as an ion transport material with potential electrochemical applications to achieve structural integrity while controlling transport\textsuperscript{35-37}. The degree of phase separation between ion-rich regions and hydrophobic polymer regions depends on the number of sulfonated pendent phenyl groups per polymer chain. Ultimately, phase separation determines the diffusion pathways and controls the rate of solvent penetration. To distinguish the interfacial
behavior from bulk behavior, this study was performed on thin films with thicknesses of less than 35 nm. These thicknesses were within the several radii of gyration of the ionomer. Therefore, substrate–polymer and polymer–polymer interfacial forces would affect the structure and dynamics of the polymer.

Measurements of the diffusion and distribution of alcohol molecules within the sulfonated polyphenylene thin films have shown that, after exposure to alcohols vapor, the interfaces were not uniform. In contrast to the distribution of water molecules within sPP thin films observed by He et al.\textsuperscript{11}, a lesser amount of alcohols accumulated at the substrate–polymer interface than accumulated at the polymer–vapor interface. When exposed to alcohols, the sPP thin films absorbed the vapor and distributed the alcohol molecules homogeneously at the center of the film. However, as time elapsed, a non-uniform distribution of alcohol molecules with high concentration at the polymer–vapor interface was observed. Similar to the diffusion of water molecules in sPP thin films, the mass uptake changed linearly with $t^{\frac{1}{2}}$ at the early stage of exposure to alcohols, but it crossed over to an anomalous process with prolonged exposure.

**Experimental**

**Thin Film Preparation.** Ionomer solutions of sPP with different sulfonation levels, 13.5 mol\%, 27.0 mol\%, and 33.3 mol\%, were prepared by dissolving 1 wt\% of ionomer in N,N-dimethylformamide (Sigma-Aldrich Chemicals Co., LLC, USA). The solutions were vigorously mixed and filtered using 2-\textmu m Millipore\textsuperscript{TM} filters before spin coating. Thin ionomer films with thicknesses less than 35 nm were prepared by spin coating the 1 wt% solution on surface-oxidized silicon wafers at 1650 rpm for 2 minutes.
**Silicon Wafer Oxidation.** One-side-polished, 75 mm-wide and 5 mm-thick silicon oxide wafers, purchased from Virginia Semiconductor Inc., USA were used as the substrate. The silicon wafers were oxidized in a 70:30 by volume solution of concentrated sulfuric acid and hydrogen peroxide (Piranha solution) at 80 °C for 2 hours. The wafers were then rinsed thoroughly with deionized water and dried with nitrogen. H$_2$SO$_4$ and H$_2$O$_2$ were used as received (Sigma-Aldrich Chemicals Co., LLC, USA).

**Neutron Reflectivity Experiment.** Specular neutron reflectivity measurements were carried out using the surface profile analysis reflectometer (SPEAR) at the Lujan Neutron Scattering Center at Los Alamos National Laboratory, Los Alamos, New Mexico. SPEAR is a time-of-flight reflectometer with an unpolarized pulsed neutron beam with a range of neutron wavelengths from 4.5 to 16 Å. Measurements were carried out over a momentum transfer vector ($q$), which covered the total $q$ range from 0.008 Å$^{-1}$ to 0.25 Å$^{-1}$. The momentum transfer vector is given by $q = 4\pi \sin \theta / \lambda$, where $\lambda$ is the neutron wavelength and $\theta$ is the incident angle normal to the sample surface. When thin films exposed to vapors, the measured $q$ range was decreased to 0.07 Å$^{-1}$ in order to capture short time intervals. The background was subtracted from raw data and reflected intensities were normalized to the incident beam intensity to obtain the reflectivity profiles. The error bars on the reflectivity profiles correspond to the statistical errors of the measurements.

Diffusion studies were carried out as a function of sulfonation level (13.5 mol%, 27.0 mol%, and 33.3 mol% sulfonation) of sPP thin films with deuterated methanol (99.8% D), n-hexanol (98% D), and n-octanol (98% D) purchased from Cambridge
Isotope Laboratories, USA. Each sample was encapsulated in a sealed aluminum container. The reflectivity profile of as-cast thin films was measured covering the momentum transfer vector from approximately 0.008 Å\(^{-1}\) to approximately 0.25 Å\(^{-1}\). Hereafter, the as-cast films are referred to as “dry films.” The reflectivity patterns acquired immediately after drying the samples in vacuum oven before exposure to alcohols served as the baseline for following changes. A saturated vapor environment was achieved by placing the deuterated solvents in a groove around the silicon wafer in the sealed aluminum container. In this closed vessel, the liquid and vapor reached equilibrium. Therefore, the chemical potential of the vapor was equal to that of the liquid. The reflectivity patterns were recorded every 2 minutes for the first 20 minutes, followed by intervals of 10 minutes up to 2 hours after the vapor was put in contact with the film. Samples were then allowed to equilibrate for an additional 8 hours, and the reflectivity profiles were obtained, which were defined as “saturated”.

**Neutron Data Analysis**

**Density Profiles.** The thickness, surface roughness, and scattering length density of the thin films were determined by modeling the reflectivity profiles. MOTOFIT, a fitting analysis package running on IGOR Pro 6.21 platform, was used to fit the reflectivity data\(^{39}\). A multilayer, recursive Parratt formalism was used to analyze the data\(^{40}\) by simulating reflectivity profiles and adjusting the parameters using genetic optimization to obtain the best least square fit. The quality of a fit was determined by \(\chi^2\) where acceptable values were \(\chi^2 \leq 1.5\). The scattering length density values for the ionomers and alcohols were bound by the calculated values using densities. The
roughness between two adjacent layers was described by an error function centered at the interface.

**Polymer Profile Analysis.** The polymer profiles obtained from the data-fitting in terms of scattering length density as a function of distance from the solid substrate were further analyzed to extract the changes that took place at both interfaces of the films as a function of time. The films were divided into the center of the film and the interfaces, as shown in Figure 5.2. The center of the film was defined as the thickness of the film between points A and B, while the polymer–air interface was defined as the thickness between points B and C.

Figure 5.2 Definition of the center of film and polymer–air interface that is used to determine the composition with solvent exposure. $h_1 = h'_1$, $h_2 = h'_2$, and $h_3 = h'_3$. 
Calculations of Solvent Uptake. The solvent volume fraction at each interface, $\phi_{\text{sol}}$, was calculated using $SLD_{\text{tot}} = \phi_{\text{sol}}SLD_{\text{sol}} + (1 - \phi_{\text{sol}})SLD_{\text{poly}}$. The $SLD_{\text{tot}}$ is the average scattering length density of the corresponding interface determined according to our definition from the polymer profiles. The $SLD_{\text{sol}}$ and the $SLD_{\text{poly}}$ are the scattering length densities of the solvent and the polymer, respectively, calculated using the corresponding molecular formula and their densities. The average volume fraction of solvent at the center of film and at the polymer–vapor interface was determined as a function of time. The time was normalized to the thickness of the dry films to account for variations in film thickness.

The area changes corresponded to the total uptake of solvent. The data are presented as a fraction of the total uptake of each film: $(A_t - A_0)/(A_\infty - A_0)$, where $A_t$, $A_0$, and $A_\infty$ are the areas under the polymer profile at a given time $t$, before and after exposure to a solvent for an extended time, respectively. $A_\infty$ for all the calculations were taken as 120 minutes, after which no further changes were observed in film thickness and the normalized area changes became asymptotic. Therefore, at a given time the normalized area change represented the fraction of solvent uptake. This normalization process has been used in several studies\textsuperscript{11,34,41}.

Results and Discussion

Thin films of sulfonated polyphenylene with 13.5, 27.0, and 33.3 mol\% sulfonation were exposed to deuterated methanol, n-hexanol, and n-octanol saturated vapors. The reflectivity profiles of sPP were measured to $q$ of approximately 0.25 Å$^{-1}$ prior to exposure. The films were then exposed to vapors, and neutron reflectivity
profiles were recorded. To capture early stages of the process, the profiles were recorded over a smaller $q$ range to average over intervals as short as possible until hardly any changes were observed. At this stage, the entire $q$ range was recorded again. Below, the results for the films exposed to methanol are first discussed followed by the results for the films exposed to hexanol. Finally, the data for the three alcohols are compared.

Representative neutron reflectivity profiles of thin films as a function of exposure time to methanol are presented in Figure 5.3. The data are presented in terms of $R(q)q^4$ as a function of $q$, which compensates for the sharp decrease of $R(q)$ as $q^{-4}$ of the ideal Fresnel reflectivity and better resolves the features of the reflectivity profiles, where $R(q)$ corresponds to the reflectivity as a function of the momentum transfer vector. The fringes of the reflectivity patterns originated from the interference of the reflected beam coming from all interfaces where the substrate–polymer and polymer–vapor interfaces dominated. The evolution of the reflectivity patterns with exposure time was characterized by three features: the position and shape of the critical edge, the distance between consecutive minima, and the oscillation intensity. The patterns of the dry films were characterized by a well-defined critical edge at the critical momentum transfer vector, $q_c$, which corresponded to the angle below which total reflection took place. The clear critical edge for the films was a consequence of a well-defined interface with sufficient contrast of scattering length densities. The sharp critical angles observed for the dry thin films broadened and shifted to higher $q$ value with exposure to vapors, as shown in the insets in Figure 5.3 a–c. This shift was a result of the absorption of methanol, which changed the interfacial composition and, hence, the critical edge.
Figure 5.3 NR profiles in terms of $Rq^4$ vs. $q$ for sPP thin films with (a) 13.5 mol%, (b) 27.0 mol%, and (c) 33.3 mol% sulfonation exposed to saturated methanol vapor. The insets zoom in on the range around $q_c$ as a function of solvent exposure time. The symbols correspond to the experimental reflectivity data, and the solid lines are the best fits. The $t$ corresponds to the exposure time. Measurements were taken until no further significant changes were observed.

The position of the critical edge, the fringe spacing, and the fringe heights are presented in Figure 5.4 a-c, respectively. The data are normalized to dry film thickness in order to compare films with thickness variations. This experiment captures changes after about 7 minutes of exposure. The data show that methanol had been incorporated into the films by that time. The momentum vector, $q$, corresponding to the critical angle was correlated to the scattering length density, SLD, and given by $q_c = (16\pi\text{SLD})^{1/2}$. As
methanol penetrated into the thin films, the composition changed, and the total scattering length density of the reflecting vapor interface increased. The position of the critical edge shifted to higher $q$ with vapor exposure time. With an increase in the sulfonation level, the position of the critical edge moved to higher $q$ quicker than that of the thin films with lower sulfonation levels. This suggested that more alcohol molecules will be absorbed onto thin films as the sulfonation level increases.

The penetration of a solvent into polymers has been described as a power law expression with time, $t^\alpha$, where $t$ is the solvent exposure time and $\alpha$ is the scaling exponent related to the solvent uptake mechanism. For the diffusive process, $\alpha = \frac{1}{2}$. The diffusive process has often been characterized by a Gaussian diffusion front. The other extreme is $\alpha = 1$, in which the process is characterized by a flat progressing front. When $\alpha$ deviates from either $\frac{1}{2}$ or 1, the solvent diffusion process is constrained and is often impacted by rearrangements of the polymer chains.

Therefore, the changes that take place in the reflectivity patterns that correspond to solvent uptake are presented as a function of $t^{1/2}$. The average thickness of the dry films was approximately 20 nm, as determined initially by $d \sim 2\pi/\Delta q$, where $\Delta q$ is the distance between two successive minima. As the thin films were exposed to saturated alcohol vapors, the position of the first-fringe minimum shifted to a lower $q$, resulting in a decrease of $\Delta q$ between successive minima. This indicated the increase of thin film thickness perpendicular to the substrate interface. At early stages of vapor exposure, $\Delta q$ decreased due to the absorption of methanol. However, as time propagated, a cross over to slower regime was observed. The intensity of reflectivity fringes is proportional to the
scattering length density contrast. With absorption of alcohols the intensity of fringes increased as seen in $R_q^4$ vs. $q$ plots. These increases are proportional to the amounts of alcohols absorption.

The slow changes of $q_c$, $\Delta q$, and $R_q^4$ height at prolonged exposure times to methanol offer a clear mark of the formation of a thin, solvent-rich polymer layer at the polymer–vapor interface. The development of such a wetting layer is consistent with the observation of He et al.\textsuperscript{11} that detected the formation of a thin D$_2$O rich layer after sPP exposure to water vapor. The surface of polymer thin films consists of both hydrophobic and hydrophilic components. Therefore, alcohols that also consist of hydrophilic and hydrophobic segments easily penetrate the interfacial regions. The polymer interface has both a hydrophobic and hydrophilic nature due to the rigidity of the polymer backbone. The compounded nature of the surface reduces the barrier to methanol penetration.
Figure 5.4 Normalized time dependence of (a) $q_c$, (b) $\Delta q$ and (c) $R_q^4$. The solid lines are the fits to an exponential function where $R^2$ is in the range of 0.95 to 0.99. The dashed line at the onset of (a) is an extrapolation.

While diffusion into polymer matrices has been thoroughly investigated, there are hardly any theoretical predictions of solvent penetration into complex polymeric interfaces that consist of hydrophilic and hydrophobic domains. Therefore, we analyzed...
the reflectometry profiles in terms of multilayers with varying thickness, SLDs, and roughness. These parameters were allowed to evolve with time to reflect the changes due to the solvent penetration. The number of layers chosen allowed the data to evolve while minimizing the number of free parameters. A five-layered model, including one layer at the polymer–vapor interface, one layer at the polymer–substrate interface, and three layers between them, was used to describe the distribution of alcohol molecules within thin films.

The polymer profiles derived from the analysis in terms of scattering length densities as a function of distance (d) from the solid substrate are presented in Figure 5.5 a–c. All the profiles derived for the dry films show a homogeneous distribution of sPP ionomers across the film with roughness of less than approximately 2 nm at the polymer–air interface. The values of SLD calculated from the fitting of dry films are around 1.98x10^{-6} \text{Å}^{-2}, the SLD value calculated using the polymer density of 1.36 \text{gcm}^{-3} (average experimental value). With increasing sulfonation level the SLD value decreased. We attributed this difference to the absorption of minute amounts of water from the air, which reduced the effective SLD of the polymer, or to different interfacial densities than that of the bulk due to hydrophobic–hydrophilic segregation as sulfonation increased.
Figure 5.5 Film profiles in terms of b/V vs. distance from solid substrate exposed to saturated methanol vapor for ionomer thin films with (a) 13.5 mol%, (b) 27.0 mol%, and (c) 33.3 mol% sulfonation. The profiles have been shifted along the time-axis for clarity.

All films swell with exposure to methanol, where with increasing sulfonation more solvent penetrates into the center of the polymer layer. The alcohol’s distribution is not homogeneous. Therefore, the composition changes that took place both at the center of film and at the polymer–vapor interface, as presented in Figure 6.6 a–c, was extracted. At the early stage of alcohols exposure, the methanol volume fraction at both the polymer–vapor interfaces and the center of the films increased rapidly with the \( t^{1/2} \). The rate of uptake slowed down with longer exposure time. Further, the methanol fraction at both interfaces at a given exposure time increased with increasing the sulfonation level of sPP. The fraction of methanol at the polymer–vapor interface was always higher than that of the center of the films. For a simple Fickian diffusion, one would expect a linear uptake with time. As shown by the dashed lines in Figure 5.6 a, there was a barrier to the absorption of methanol at the onset of diffusion for the thin film with the lowest sulfonation level. A closer look at the shorter time scales reveals that the volume fraction diverted from linearity (i.e., extrapolation of the linear measured region did not intersect zero). This time lag indicated a barrier to penetration. The presence of vapors unlocked the interface and allowed interfacial rearrangements that lead to penetration of the alcohols.
Figure 5.6 Methanol volume fractions at the polymer–vapor interface and at the centers of films as a function of solvent exposure time for sPP thin films with (a) 13.5 mol%, (b) 27 mol%, and (c) 33.3 mol% sulfonation. The solid lines are the fits to an exponential function where $R^2$ is in the range of 0.96 to 0.99. The dashed lines at the onsets are the extrapolations.

To compare the diffusivities of methanol as a function of the sulfonation level of sPP, the area change in the polymer profiles was determined as a function of time. The normalized area changes with respect to the maximum area change as a function of $t^{1/2}$ are presented in Figure 5.7. A fast absorption of methanol followed by a slow uptake was observed, regardless of the sulfonation level. In contrast to the uptake of water, the penetration of methanol was rather faster. Although uptake at high sulfonation level at extended time slowed down at prolonged exposure times, it did not fully level off. At higher exposure times, the film began to dissolve. These slow and fast uptake regions can be attributed to different processes. At the onset of diffusion, a considerable amount of methanol was absorbed into interstitial ionomer spaces, whereas at later times, structural rearrangements took place. The amount of interstitial spaces increased as the incompatibility of the polymer’s hydrophilic and hydrophobic segments increased. Further, as seen in the solvent fraction analyses, the total uptake of methanol within the sPP thin films increased as the sulfonation level increased.
Figure 5.7 Methanol uptake as a function of normalized $t^{1/2}$ with respect to the film thickness of dry samples for three different sulfonation levels (a) 13.5 mol%, (b) 27.0 mol% and (c) 33.3 mol% of sPP thin films. The solid lines are the fits to an exponential function where $R^2$ is in the range of 0.97 to 0.99. The dashed lines at the onsets are the extrapolations.

The diffusivity at the early stage of methanol exposure was determined from the linear range at the onset of diffusion, as shown in Figure 5.7, using

$$(A_t - A_0)/(A_\infty - A_0) = \left(\frac{4Dt}{d^2\pi}\right)^{1/2}$$

where $D$ is the diffusivity of the solvent, $t$ is the solvent exposure time, and $d$ is the film thickness of the dry samples. This model assumes that the area changes in scattering length density profiles with solvent exposure are proportional to the mass of solvent uptake by the thin films. In practice, all the molecules penetrated through the faces of the films, with a negligible amount penetrating through
the edges. Table 5.1 presents the diffusivities of methanol for sPP thin films with different sulfonation levels. The diffusivities varied in the order of $10^{-14}$ to $10^{-15}$ cm$^2$ s$^{-1}$ and increased with an increase in the sulfonation of sPP for the thin films with surface areas of 19.6 cm$^2$.

<table>
<thead>
<tr>
<th>Sul level (mol%)</th>
<th>$D_{(MeOH)} \times 10^{-15}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>7.45</td>
</tr>
<tr>
<td>27.0</td>
<td>19.13</td>
</tr>
<tr>
<td>33.3</td>
<td>23.15</td>
</tr>
</tbody>
</table>

Sul level (mol%) = Sulfonation level in mole percent, $D_{(MeOH)}$ = Diffusivity of methanol

Table 5.1 Diffusivities of methanol at room temperature in sPP thin films having variable sulfonation levels.

The low values of the diffusivity are consistent with previously observed diffusion into structured interfaces, where interfacial interactions significantly slowed the penetration of solvents. In comparison to water diffusion into sPP, methanol diffusivity was an order of magnitude faster. We attributed these higher values to the fact that methanol is a relatively small molecule that consists of small segments of both hydrophilic and hydrophobic groups. As a result, methanol interacted favorably with both components of the polymer.

In order to understand the impact of the structured nature of the interface that consists of both hydrophobic and hydrophilic regions, we probed the diffusion of longer...
alcohols, n-hexanol and n-octanol, into sPP thin films, following the same procedure and analysis as presented for methanol. Prior studies of penetration of alcohols into polymeric matrices have shown that interactions between guest molecules and polymer matrices have a significance influence on the distribution and diffusion of guest molecules \(^{18,43-48}\).

For example, Gall et al.\(^ {44}\) studied the diffusion of a series of 1-iodo-n-alkane vapors in polystyrene using Rutherford back-scattering. They observed that the diffusion coefficient decreased exponentially as the chain length of the alkanes increased. Koszinowski showed\(^ {48}\) that linear alcohols and comparable linear alkanes diffused within low density polyethylene film by a permeation. He observed that the alcohols approach alkane behavior with an increase in the number of carbon atoms due to the shielding of polar hydroxyl groups. Bernardo et al.\(^ {46,47}\) have described the sorption kinetics of a series of linear alcohols from methanol to 1-hexadecanol by a gravimetric technique within amorphous polystyrene films over a broad range of temperatures. They accounted the mass uptake using a Fickian model and explained the diffusivity as being based on the variation of the polymer–solvent chemical affinity that varied with the size of the alkyl chain. These efforts concluded that no simple and general correlation is currently available to describe the distribution of guest molecules within polymeric materials.

Qualitatively, the patterns in presence of long chain alcohols were similar to those observed in presence of methanol. Figure 5.8 a–c presents the polymer profiles as a function of time for three different sulfonation levels. The reflectivity patterns are given as supportive information. Similar to the results for methanol, both the film thickness and the SLD of hexanol-exposed films increased relative to those of dry films. Moreover, a
hexanol-rich polymer layer at the polymer–vapor interface was observed. However, this hexanol-rich layer that developed at polymer–vapor interfaces with prolonged hexanol exposure was more pronounced in 13.5 mol% and 27.0 mol% samples compared to that of the 33.3 mol% thin films in which the surface excess layer was hardly observed. This is rather surprising, since hexanol has a longer hydrophobic tail and one would expect a more even distribution in films with lower sulfonation levels. Comparing the results of these sulfonation levels shows that with increasing sulfonation the distribution is more homogeneous. The origin of the surface excess is not fully understood.
Figure 5.8 Film profiles in terms of b/V vs. distance from solid substrate exposed to saturated hexanol vapor for ionomer thin films with (a) 13.5 mol%, (b) 27.0 mol%, and (c) 33.3 mol% sulfonation. The profiles have been shifted along the time-axis for clarity.

The average volume fraction of hexanol at the centers of the films and at the polymer–vapor interface as a function of time is shown in Figure 5.9 a–c as a function of $t^{1/2}$ normalized to the film thickness of the dry samples. The absorption of hexanol followed a trend similar to that of methanol. The hexanol fraction at both interfaces increased linearly with $t^{1/2}$ at the early stage of exposure and transitioned to significantly slower rates as exposure was prolonged. Similar to methanol diffusion, two regions, fast and slow, were observed and the fast region was linear with time. In contrast to the methanol-exposed films, no time lag at the onset of diffusion was observed. The volume fraction of hexanol increases exponentially with $t^{1/2}$. At lower sulfonation levels the fraction of the solution was higher at the air interface in comparison to the center of
films. However, in 33.3 mol% sPP thin films, the hexanol resided predominantly in the centers.

With increasing sulfonation level, the hydrophilic groups along the bundle of the polymers propagated across the film, making hydrophilic pathways. Consequently, the alcohol resides across the entire film. With increasing the length of alkyl group hydrophobicity is enhanced. Subsequently, less hexanol penetrated into the ionomer matrix at a given time compared to thin films with higher sulfonation levels. At higher sulfonation levels, the hydrophilic pathways allowed the penetration of the hexanol, despite the long hydrophobic tail.
Figure 5.9 Hexanol volume fraction as a function of solvent exposure time for sPP thin films with (a) 13.5 mol%, (b) 27 mol%, and (c) 33.3 mol% sulfonation. The solid lines are the fits to an exponential function with $R^2$ in the range of 0.98 to 0.99.
The normalized area changes as a function of $t^{1/2}$ are presented in Figure 5.10. The absorption of hexanol with $t^{1/2}$ linearly changed. Similar to methanol penetration at short times, the diffusion of hexanol exhibited a fast stage at the onset of exposure that transitioned to a significantly slower one at about 20 minute of exposure. In comparison with methanol, the crossover was more defined at 27.0 and 33.3 mol% sulfonation, whereas in low sulfonation levels, a crossover was observed at about 40 minutes, although it was less pronounced. The transition time increased with decreasing the sulfonation level, which in turn indicated the slow absorption process of hexanol into the interstitial spaces. Overall, the absorption of hexanol was slower than that of methanol.

![Figure 5.10 Hexanol uptake as a function of normalized $t^{1/2}$ with respect to the film thickness of dry sample for three different sulfonation levels (13.5 mol%, 27.0 mol%, and 33.3 mol%) of sPP thin films. The solid lines are the fits to an exponential function where $R^2$ is 0.99. The dashed lines at the onsets are the extrapolations.](image)
Table 5.2 shows diffusivities of hexanol in sPP thin films with different sulfonation levels. The diffusivities varied in the order of $10^{-15}$ to $10^{-16}$ as a function of sulfonation content. These values of the diffusivity were consistent with previously observed diffusivities of methanol into sPP thin films. However, the range was one order of magnitude less than that of methanol diffusivities. Further, these values increased with increasing sulfonation, similar to methanol diffusivities.

<table>
<thead>
<tr>
<th>Sul level (mol%)</th>
<th>$D_{(\text{Hexanol})} \times 10^{-15}$ (cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5</td>
<td>0.45</td>
</tr>
<tr>
<td>27.0</td>
<td>3.39</td>
</tr>
<tr>
<td>33.3</td>
<td>5.15</td>
</tr>
</tbody>
</table>

Sul level (mol%) = Sulfonation level in mole percent, $D_{(\text{HeOH})} = $ Diffusivity of hexanol

Table 5.2 Diffusivities of hexanol at room temperature at the indicated polymer sulfonation levels.

Similar experiments were carried out for octanol diffusion into sPP thin films. In this case, we chose sPPs with higher sulfonation levels, 27.0 mol% and 33.3 mol%, and repeated the same procedure as with methanol and hexanol. Qualitatively, the reflectometry patterns in presence of octanol vapors are similar to those observed in presence of the smaller alcohols. The reflectivity patterns and their analysis are given as supportive information. To elucidate the effects of alcohols hydrophobicity, we compared the interfacial behavior and diffusivities for the three alcohols. The total
amounts of solvent as well as the solvent fraction at both interfaces as a function of $t^{1/2}$ for the three alcohols are given in Figure 5.11. The comparison was carried out for films with 27.0 mol% sulfonation. Films with this level of sulfonation of the polymer capture the behavior of all films that retain their integrity (i.e., do not dissolve or dewet) throughout the experiment.
Figure 5.11 Uptake of methanol, hexanol and octanol by the 27 mol% sulfonation thin films as a function of $t^{1/2}$ normalized to the thickness of the films. (a) Total uptake, (b) alcohols fractions at the centers of films, and (c) alcohols fractions at the polymer–vapor interface. The solid lines are the fits to an exponential function where $R^2$ is 0.99. The dashed lines at the onsets are the extrapolations. The tangent dashed line in (a) shows the crossover point from fast to slow alcohols uptake.

The solvent uptake in the entire film decreased with increased size of the alcohol molecules, as observed in Figure 5.11 a. For all three alcohols, two distinctive linear regions of diffusion were observed: a fast uptake followed by a slower propagation. The time corresponding to the crossover of solvent uptake from fast to slow increased as the size of the alcohol molecules increased. As shown by a crossover tangent in Figure 5.11 a, in the presence of methanol crossover occurs at about 15 minutes after exposure, whereas in the presence of hexanol and octanol, it takes place around 20 and 25 minutes,
respectively. The fast absorption at the onset of exposure corresponds to the migration of the alcohols into interstitial spaces, and it involves hardly any swelling. The slow stage corresponds to the onset of rearrangement of the polymer films. Further, smaller alcohols absorbed faster into interstitial spaces. Once the interstitial spaces were filled, the polymer network swelled. The rate of rearrangement of the polymer network in the later stage is surprisingly faster for longer-chain alcohols. We attributed the faster rearrangements to the conjunction of favorable interactions of the hydrophilic segments of the polymer and the hydroxyl region of the alcohols with significant enhancement of penetration due to favorable hydrophobic interactions of the alcohols chains with the hydrophobic region of the polymer network.

The diffusivities as a function of the size of alcohols determined as the sulfonation level was kept constant are given in Table 5.3. Diffusivities decreased one order of magnitude by increasing the number of carbons in the alcohols from one to six. Methanol is a relatively small molecule that consists of small segments of both hydrophilic and hydrophobic groups, which allow fast diffusion into interstitial space. With the increase in the size of the alkyl chain, the drag of the hydrophobic tail slowed the initial diffusion.

Overall, alcohols were not homogeneously distributed within the films; there was a rich layer at the polymer–vapor interface and uniform distribution at the centers of the films. At the centers of the films, alcohols uptake increased with a decrease in the length of the alcohol molecules. The absorption of methanol in the center and at the interface was the largest. Because of its small size and the similar dimensions of its hydrophilic
and hydrophobic groups, methanol has a relatively lower penetration barrier. Hexanol and octanol are relatively similar. However, in our study, hexanol penetrated a bit more into the films’ centers, where octanol remained at the interface. We attributed this to the hydrophobicity of the alcohol molecules, where octanol is slightly more hydrophobic than is hexanol.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>(D_{\text{alcohol}} \times 10^{-15} \text{ (cm}^2\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>19.13</td>
</tr>
<tr>
<td>Hexanol</td>
<td>3.39</td>
</tr>
<tr>
<td>Octanol</td>
<td>2.06</td>
</tr>
</tbody>
</table>

\(D_{\text{alcohol}} = \text{Diffusivity of alcohols}\)

Table 5.3 Diffusivities of different alcohols (methanol, hexanol, and octanol) within sPP thin films with 27.0 mol% sulfonation at room temperature.

The diffusivities of alcohols in sPP thin films as determined in our experiments were comparable to the \(D_2O\) diffusivities within sPP thin films reported by He et al.\(^{11}\) and those of water diffusion in other ionomer thin films:\(^{13,33,34}\). However, these diffusivities of small molecules in thin films were several orders of magnitude lower than those in freestanding membranes of the perfluoro sulfonated ionomer, Nafion\textsuperscript{TM}. The diffusivity of water and methanol in Nafion\textsuperscript{TM} freestanding membranes as determined from NMR and sorption techniques:\(^{10,49-52}\) was on the order of \(10^{-5}\) to \(10^{-8}\) cm\(^2\)s\(^{-1}\). These differences were attributed to interfacial effects that form a barrier. Interfacial rearrangements took
place as the alcohol molecules diffused into the membranes, and the ionomer’s network became more dynamic, which in turn allowed further permeation of alcohols.

**Summary**

The study probed for the first time the impact of solvent hydrophobicity on diffusion across a structured ionic polymer interface. Films of polyphenylene ionomer with different sulfonation levels were exposed to alcohol vapors, and the reflectivity patterns were followed as a function of time. All films were swollen in presence of the alcohols. At an early stage of alcohols exposure, the mass uptake by sPP scaled linearly with $t^{1/2}$ and deviated at extended exposure times. A non-uniform distribution of alcohols with an alcohol-rich polymer layer at the polymer–vapor interface was observed. The alcohols diffusivity within sPP thin films was significantly slower than that within membranes. This difference was attributed to interfacial effects. In comparison to water diffusivity within sPP thin films, methanol diffused faster and alcohols with long chains diffused slower. Hydrophobicity of the alcohols had only limited effects on the diffusion across the interface. In view of the rigidity of the polymer, surface rearrangements in presence of the solvent may take extended time and therefore the diffusion within the time frame of several hours was impacted predominantly by interstitial spaces where both hydrophobic and hydrophilic parts of the solvents are in contact with similar groups of the polymer.
Figure 5.12 NR profiles in terms of log R vs. q for Hexanol diffusion into sulfonated polyphenylene thin films of a) 13.5 mol% sulfonation, b) 27 mol% sulfonation and c) 33.3 mol% sulfonation levels. Symbols in NR profiles are experimental reflectivity and solid lines are the best fits. Reflectivity profiles have been shifted along Y-axis for clarity. The error bars in the NR profiles denote the standard deviation for each measurement.

Figure 5.13 NR profiles in terms of log R vs. q for Octanol diffusion into sulfonated polyphenylene thin films of A) 27 mol% and B) 33.3 mol% sulfonation levels. Symbols in NR profiles are experimental reflectivity and solid lines are the calculated models. The error bars in the NR profiles denote the standard deviation for each measurement.
Figure 5.14 Film profiles in terms of b/V vs. distance from solid substrate exposed to saturated Octanol vapor for a) 27.0 mol% sulfonation and b) 33.3 mol% sulfonation sPPs.

Figure 5.15 Octanol volume fractions as a function of solvent exposure time in terms of normalized $t^{1/2}$ with respect to the film thickness of dry thin films for a) 27.0 mol% sulfonation and b) 33.3 mol% sulfonation. The symbols correspond to the experimental data and the solid lines are guides to the eye.
Figure 5.16 Octanol uptakes by sPPs having different sulfonation levels as a function of normalized $t^{1/2}$ with respect to the film thickness of dry thin films. The symbols correspond to the experimental data and the dash lines are the best fits to an exponential function. The solid lines are the fits to an exponential function where $R^2$ is 0.99.

Table 5.4 Diffusivities of octanol at room temperature in sPP thin films having different sulfonation levels.

<table>
<thead>
<tr>
<th>Sulfonation level (mol%)</th>
<th>$D_{(Octanol)} \times 10^{-15}$ (cm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.0</td>
<td>2.06</td>
</tr>
<tr>
<td>33.3</td>
<td>2.34</td>
</tr>
</tbody>
</table>

Acknowledgement

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References


CHAPTER SIX
ASSOCIATION OF A MULTIFUNCTIONAL BLOCK COPOLYMER IN A SELECTIVE SOLVENT

Abstract

The self-assembly of a multi block copolymer in solutions and thin films is controlled by a delicate balance between inherent phase segregation due to incompatibility of the blocks and the interactions of the individual blocks with the interfaces. The current study elucidates the association of ABCBA penta-block copolymers in a mutually good mixture of solution using small angle neutron scattering (SANS). The penta-block comprises of centered randomly sulfonated polystyrene block to which rubbery polyisoprene is connected, terminated by blocks of polystyrene decorated with tertiary butyl group. We found that the penta-block forms ellipsoidal core-shell micelles in solutions with the sulfonated polystyrene in the core and Gaussian decaying density of swollen polyisoprene and tertiary butyl polystyrene in the corona. The size of the micelle, the thickness of the corona and the aggregation number increased with increasing the solution concentration and temperature, while the solvent fraction in the core decreased. The dilute solutions promptly responded to thermal fluctuations. However, the temperature effects disappeared with increasing the solution concentration.

Introduction

Di block copolymers in selective solvents form rich phase diagrams that include miceller phases, gels as well as ordered complex fluids. A diverse miceller structures are
observes where the shape and the stability of the assemblies depend on the relative dimensions of the block, their interactions, as well as the interaction of each block with the solvent\textsuperscript{1-4}. These structured solutions often serve as precursors for casting membranes, where the morphology of the micelles impacts the film structure and properties. Enhancing the complexity of the co-polymer by tailoring polymers with multiple blocks, each of specific role, has been one of the most promising pathways to multi-functional materials. Most experimental and theoretical studies however, provided insight into assembly of di and tri-block co-polymers in the low segregation regime\textsuperscript{5-12}. The effects of complexity presented in assemblies of multiple blocks containing highly interacting blocks on their structure and dynamics remains to be resolved.

One important example is block co-polymers in which one of the blocks facilitates transport and others provide mechanical stability. These co-polymers are of a particular interest in applications such as fuel cells, organic photovoltaic devices, battery separators, electro-dialysis as well protective breathable cloth\textsuperscript{13-15}. Despite immense efforts\textsuperscript{1-12}, under the conditions that transport is optimized, the mechanical and chemical stability are compromised. Structured polymers exhibit a potential to form mechanically stable multi-functional materials capable of transporting substances. An in-depth understanding of the association of structured polymer in solution and the propagation of solution structures into thin films is warranted in order to design membranes with well-defined properties. Here we present an insight into the shape and stability of assemblies formed by a penta-block co polymer that consist of a highly interacting ionic segment obtained from small angle neutron scattering (SANS). Taking advantage the inherent
contrast of hydrogen and deuterium to neutrons as well as the cross section of the sulfonated groups, we reveal a unique detailed internal structure of aggregates. We found that the complexity of the polymer and the incompatibility of the blocks results in divergence of the micelles from sphericity and their internal structures are more structured than a core-shell.

Among the most extensively studied structured polymers are di-block copolymers with flexible blocks in the low interaction regime$^{5-12}$. When dissolved in selective solvents, they form core-shell structures with different geometries such as spherical, elliptic, and cylindrical where the less soluble blocks are surrounded by a corona formed by the soluble blocks. The dimensions, geometries, and stability of block copolymer micelles are mainly determined by the overall free energy$^{16, 17}$ with the basic driving force of the self-assembly process is the minimization of the free energy of the system. Most of these studies were carried out in the low segregation limit. However, with increasing incompatibility of the block copolymers, interfacial tension between the core and the corona blocks increases and becomes a significant contribution$^{18, 19}$. Over all, the delicate balance between entropy loss upon confinement and the tendency to minimize unfavorable interactions control the stability of the micelles.

The realization of the technological potential of structured polymers, the complexity the structure has increased, and co-polymers incorporating an ionic block have been investigated. Among the many examples have been studies by Geise et al.$^{15, 20, 21}$ who showed that sulfonation of random co polymer such as poly(styrene-b-hydrogenated butadiene-b-styrene) end block leads to uncontrolled swelling of both polar
solvents resulting in poor mechanical stability when hydrated. Eisenberg et al.\textsuperscript{22} have realized that di-block-copolymer topology, where only one of the blocks swells provides a mechanically stable manifold. They showed that polystyrene-b-poly(cesium acrylate) and polystyrene-b-poly(cesium methacrylate) form spherical micro-domains surrounded by non-ionic polystyrene corona, in presence of toluene, a solvent selective for the polystyrene blocks. Increasing the topological complexity by tailoring multiple blocks with significantly different chemistries provides pathways to form stable multifunctional polymers.

One example for a topology controlled polymer is a penta-block co-polymer of the form ABCBA. This structured polymer was designed by Kraton LLC, with the rational of tailoring an ion transport-facilitating block surrounded by aliphatic chains for flexibility and a sturdy end block for stability. Specifically this block copolymer shown in Figure 6.1, consists of a randomly and selectively sulfonated polystyrene midblock bound on both side to rubbery aliphatic polyisoprene blocks to allow control over mobility and rearrangements of the polymer, and the chain terminated on both sides by a tert-butyl polystyrene block, a group that contributes to mechanical stability\textsuperscript{15}. Recently Winey and co workers\textsuperscript{14, 23-25} reported based on X-ray scattering studies and transmission electron microscopy that this penta-block copolymer forms spherical micelles with a core of sulfonated polystyrene block and a corona of solvated polyisoprene and t-butyl polystyrene blocks regardless of its sulfonation level. These studies focused on relatively high concentrations, approximately 11wt\%, and provided a first glimpse into the
morphologies of micelles formed by a structured ionic polymer. Further, Freeman et al. 15,26 followed transport of guest molecules across these membranes.

The symmetry of the micelles and the structural details of the segregation of the blocks within the assembly determine the association of the polymer into films in solution cast process. Building on the knowledge acquired by Winey and co-workers, using neutron scattering we probed the assembly process of the micelles and their stability in a mixed solvent of heptane and cyclohexane in the dilute limit. The in situ temperature and concentration studies revealed extremely stable assemblies whose symmetry is impacted by the assembly of the ionic groups.

Figure 6.1 Chemical structure of randomly sulfonated block copolymer, poly[t-butyl styrene-b- isoprene-b-sulfonated styrene-b-isoprene-b-t-butyl styrene], (tBPS-PI-PS/sPS-PI-tBPS). The weight distribution = 15-10-28-10-15 kg/mol. The sulfonated polystyrene block is randomly sulfonated to approximately 42 mol%. n, m, x and p, are approximately 94,142, 0.42 and 203 respectively.
The paper is organized as follows: following an experimental section, the self-assembly of the sulfonated penta-block copolymer solutions as a function of polymer concentration is presented followed by a temperature study. The methodology section includes experimental details as well as form factors used.

**Experimental**

**Materials.** The penta-block copolymer was kindly provided by Kraton Polymers LLC. The polymer was synthesized via anionic polymerization and the middle styrene block was selectively sulfonated\(^2\). This study focuses on MD 9150 with molecular weight of the unsulfonated tBPS-PI-PS/sPS-PI-tBPS are 15-10-28-10-15 kg/mol with a 42 mol% of randomly sulfonation middle styrene block. The stock solution of MD 9150 was diluted, adding 1:1 volume ratio of deuterated cyclohexane and dueterated n-heptane purchased from Cambridge Isotope Laboratories Inc., USA to form solutions with concentrations ranging from 0.025 wt% to 6.0 wt%.

**Small Angle Neutron Scattering**

**SANS Experiment.** SANS measurements were carried out on two instruments including Extended Q – Small Angle Neutron Scattering (EQ-SANS) at the Spallation Neutron Source (SNS) and on General Purpose Small Angle Neutron Scattering (GP-SANS) High Flux Isotope Reactor (HFIR) both at Oak Ridge National Laboratory. The data were collected over a broad momentum transfer vector range. The momentum transfer q vector is given by \(q = 4\pi \sin(\theta)/\lambda\), where \(\theta\) is the angle of incidence and \(\lambda\) is the neutron wave length. Measurements of penta-block copolymer solutions ranging from 0.5 wt% to 6 wt% were carried out on EQ-SANS over two \(q\) ranges, 0.0028 \(\text{Å}^{-1}\) to
0.07 Å⁻¹ and 0.0078 Å⁻¹ to 0.4 Å⁻¹, keeping detector-to-sample distance constant, at 4 m. Dilute solution from 0.025wt% to 0.1wt% were studied on GP-SANS with two different configurations were used covering a q range from ca. 0.003 Å⁻¹ to 0.06 Å⁻¹ and ca. 0.028 Å⁻¹ to 0.38 Å⁻¹ with keeping the wave length constant at 4.72 Å and varying the normal detector-to-sample distances of 18.5 m and 2 m respectively. Measurements were performed on the penta-block copolymer solutions, empty cell and the solvents of d₁₂-cyclohexane and d₁₆-heptane in each configuration. The scattering of solvents and empty Banjo cell were subtracted from the data. Data were recorded on 2-dimentional detectors. Finally, the two dimensional data were azimuthally averaged into one dimensional scattering patterns.

**SANS Data Analysis.** The SANS data were analyzed using the SASfit²⁸ version 0.93.5 developed by Joachim Kohlbrecher and Ingo Bressler in Paul Scherrer Institute. Neutron scattering length densities (SLD); 0.71 x 10⁻⁶ Å⁻² for t-butyl styrene, -0.30 x 10⁻⁶ Å⁻² for isoprene, 1.69 x 10⁻⁶ Å⁻² for sulfonated styrene blocks and 6.35 x 10⁻⁶ Å⁻² for 1:1 volume ratio of d₁₂-cyclohexane and d₁₆-heptane, were determined using their chemical formula and their bulk densities (tBPS = 1.08gcm⁻³, PI = 0.87gcm⁻³, PS/sPS = 1.47 gcm⁻³, d₁₂-cyclohexane = 0.78 gcm⁻³ and d₁₆-heptane = 0.68 gcm⁻³). These values were used as the starting SLDs in the fitting routine.

The average dimensions of the scattering objects were initially estimated by calculating the radius of gyration from the Guinier approximation for spherical particles given in Equation 6.1.
\[ I(q) \approx SLD^2V^2 \exp \left( -\frac{1}{3} q^2 R_g^2 \right) \]  

\[ \text{(6.1)} \]

\( I(q) \) is the measured intensity, \( SLD \) is the contrast term determined from the scattering length densities of the components, \( V \) is the volume of the particle, \( q \) is the momentum transfer vector and \( R_g \) is the radius of gyration of the scattering object. The Guinier approximation is valid for dilute and homogeneous solutions, where particles in the system scatter independently and are randomly orientated\(^{29}\).

**Micellar form factor.** Previous studies reported a spherical core shell micelles. While spherical core-shell model as well as an onion-model did match some of the low \( q \) data, they do not capture the scattering function across the broad \( q \) measured. To capture the behavior of the micelles across a broad \( q \) range, an ellipsoidal core-shell with Gaussian decaying chains was used to analyze the scattering data. This form factor was previously derived by Pederson\(^{30-33}\) and is briefly reviewed herein. Four different contributions including self-correlation terms of core and corona together with the cross terms between the core-c Corona and the corona-corona chains are encapsulated in this form factor, \( F_{\text{Micelle}} \) given in Equation 6.2.

\[ F_{\text{Micelle}} = N \beta_{\text{Core}}^2 F_{\text{Core}}(q) + N \beta_{\text{Brush}}^2 F_{\text{Brush}}(q) + 2N^2 \beta_{\text{Core}} \beta_{\text{Brush}} S_{\text{Core-Brush}}(q) + \]

\[ N(N-1) \beta_{\text{Brush}}^2 S_{\text{Brush-Brush}}(q) \]  

\[ \text{(6.2)} \]

\( N \) is the number of chains associated to form a micelle, \( \beta_{\text{Core}} \) and \( \beta_{\text{Brush}} \) are the total excess scattering length densities of the core and the shell. The brush refers to the polymer
chains in corona. Self-correlation term of core and corona is given in $F_{\text{Core}}$ and $F_{\text{Brush}}$ respectively. The $F_{\text{Core}}$ describes the interaction of chains in the core and defined it as a homogeneous core in the center and decaying core-chain density at the core-corona interface. $F_{\text{Brush}}$ describes as Gaussian chains and it obeys the Debye function. The cross terms between the core-corona and the corona-corona chains are given in $S_{\text{Core-Brush}}$ and $S_{\text{Brush-Brush}}$ respectively. The $S_{\text{Core-Brush}}$ consists of roughness of the interfaces between the two while $S_{\text{Brush-Brush}}$ reflects the interactions among the corona chains themselves. Mathematical description of $F_{\text{Core}}$, $F_{\text{Brush}}$ $S_{\text{Core-Brush}}$ and $S_{\text{Brush-Brush}}$ are given in the following equations 6.3, 6.4, 6.5 and 6.6\textsuperscript{30-34}.

$$F_{\text{Core}}(q, R_{\text{Core}}, \varepsilon) = \int_0^{\pi/2} \Phi^2[q \varphi (R_{\text{Core}}, \varepsilon, \alpha)] \sin \alpha \, d\alpha$$  \hspace{1cm} (6.3)

$$F_{\text{Brush}}(q, R_g) = \frac{2(e^{-x} + x - 1)}{x^2}, x = (qR_g)^2$$  \hspace{1cm} (6.4)

$$S_{\text{Core-Brush}}(q, R_{\text{Core}}, R_g, \varepsilon, \omega) = \Upsilon(qR_g) \int_0^{\pi/2} \Phi[q \varphi (R_{\text{Core}}, \varepsilon, \alpha)] \omega \sin \alpha \, d\alpha$$  \hspace{1cm} (6.5)

$$S_{\text{Brush-Brush}}(q, R_{\text{Core}}, R_g, \varepsilon, \sigma) = \Psi^2(qR_g) \int_0^{\pi/2} \sigma^2 \sin \alpha \, d\alpha$$  \hspace{1cm} (6.6)

$\sigma$ is the interface thickness, $\Phi(qR_{\text{Core}}) = 3[\sin(qR_{\text{Core}}) - qR_{\text{Core}} \cos(qR_{\text{Core}})]/(qR_{\text{Core}})^3$ is the form factor amplitude of solid sphere and $\Upsilon(qR_g) = [1 - \exp(-q^2R_g^2)]/q^2R_g^2$ is the form factor amplitude of the brush. $\omega = \sin(q[R_{\text{Core}} + \varepsilon]^2)/(qR_{\text{Core}})^2$.
A sharp interface between core and corona is represented by $d = 1$ while penetration of corona into core is represented by $0 < d < 1$. The orientation-dependent radius of the ellipsoid is given by $r(R_{core}, \varepsilon, \alpha) = R_{core}(\sin^2 \alpha + \varepsilon^2 \cos^2 \alpha)^{1/2}$. Where, $\alpha$ is the angle of the long axis of ellipsoid with respect to $q$.

Scattering length densities of 1:1 volume ratio of $d_{16}$-heptane and $d_{12}$-cyclohexane, each polymer blocks, sPS, PI and tBPS, were used as initial input parameters with initial $R_g$ of the micelles estimated from the Guinier analysis. The initial $R_g$ estimates of the corona were obtained from calculating $R_g$ of the PI and tBPS blocks determined using $\langle R_g^2 \rangle = b^2 N / 6$ where $b$ is the Kuhn length and $N$ is the number of Kuhn segments. The dimensions of the core, corona, aggregation numbers, and eccentricity of the ellipsoidal micelles as well as the volume fraction of solvent in the miceller core were allowed to vary. Best fits were obtained by minimizing the $\chi^2$. Fits were acceptable with $\chi^2$ less than 2.0. It is noted that the attempts to analyze the data with form factors of the spherical core-shell micelle and the core with two shells were not successful.

Results and Discussion

The penta-block copolymers solutions were investigated as a function of concentration and temperature. The evolution of the micelle structures with concentration will be first discussed followed by temperature effects.

The structure of the aggregates was studies as a function of concentration. The scattering patterns at 25 °C are presented in Figure 6.2 a and b. The patterns appear rather similar at concentrations above 0.025 wt%. Further structural features are observed in a
Kratky plot, presented in Figure 6.2.b. At 0.01 wt%, the scattering intensity decreases significantly and the high q-range is no longer detectable. This concentration will be separately discussed following the analysis of the miceller structure.

The intensity of the scattering patterns at intermediate q regime drops as $I \propto q^{-\alpha}$. Where, $I$ is the intensity and $q$ is the momentum transfer vector. In scattering of isolated objects in the middle q range, the exponent $\alpha$ is characteristics of the shapes of the scattering objects. As shown in Figure 6.2 a, the intermediate q regime $\alpha$ is approximately 3.8 at low concentrations which decreased to approximately 3.2 at highest concentration. The scattering of a spherical object is characterized by $\alpha = 4$. In a lower q range the scattering function is dominated by internal structure of the micelle. This initial scaling analysis show that the overall symmetry of the micelle diverges from fully spherical. The divergence from sphericity could either result from kinetically trapped ionic clusters in a mixture of heptane and cyclohexane which are not polar solvents.
Figure 6.2 SANS profiles in terms of (a) log I vs. log q, (b) $q^2I(q)$ vs. q for the penta-block copolymer solution having concentration from 0.01 wt% to 6 wt% (orange – 0.01 wt%, blue -0.025 wt%, pink – 0.05wt%, cyan – 0.1 wt%, green – 0.5wt%, red – 1 wt%, violet – 2 wt%, yellow green – 4wt% and navy blue - 6 wt%) at 25 ºC. The symbols represent the experimental data and the solid lines represent the best fits to the models described in text.

A cross over from the intermediate q region is observed at approximately 0.04 Å⁻¹. At low concentrations, the slopes crossed over to approximately 2.0. With increasing the concentration the slopes cross over to approximately 1.5. These cross over regions are essentially a crossover from q range that captures the dimensions of the entire to that of internal features, as will be further discussed together with the full analysis of the scattering patterns.

The data are plotted as generalized Kratky plot, $q^2I(q)$ vs. q in Figure 6.2 b. This presentation offers a clearer view of the scattering features at different q values and offers a more accurate insight into the shape and internal structure of the scattering object. At low q region a clear peak, accompanies by a shoulder are observed. Their intensities grow with increasing concentration, where some overlap of the curves is observed at lower concentrations and increases at higher concentrations. This behavior is consistent with an assembly process in which miceller size grows with increasing concentration up to a dimension in which the energetic of the system balanced. Further increase in concentration results in formation of more micelles. This behavior is reflected in the values of radius of gyration of the micelles, extracted from the Guinier analysis as
presented in Figure 6.3. Above 0.01 wt% \( R_g \) increases linearly with concentration and then levels off. \( R_g \) values determined from the Guinier analysis are used as initial values for full form factor analysis.

A close look at the higher q regime, presented in Figure 6.2 b, provides further insight into the internal structure of the micelles. At the cross over dimensions of approximately 0.04 Å\(^{-1}\) all curves exhibit a minimum beyond which q and increases monotonically, however no plateau is observed, supporting the divergence from sphericity. The features at low q are the results of well-defined aggregated, where the monotonic increase of the \( q^2 I(q) \) values at higher q is are consistent with Gaussian distribution the corona segments that swells with the solvent\(^{35}\).
Figure 6.3 Radius of gyration extracted from Guinier analysis for the penta-block copolymer as a function of polymer concentration at 25 °C. The error bars in the profiles denote the standard deviation for each of the fits.

A form factor of an ellipsoidal core-shell with Gaussian decaying chains at the corona captured well the features of the scattering patterns. This model has successfully captured the characteristics of asymmetric and highly interacting di-block copolymer micelles in solutions$^{30-33, 36}$. Pedersen et al.$^{36}$ for example describe the micellar structure of asymmetric polystyrene-polyisoprene di-block copolymer in a slightly selective solvent for polystyrene, di-n-butyl phthalate, and Ratnaweera et.al$^{6}$ determined the shape of a di-block copolymer, poly(trifluoromethyl) methylsiloxane-b-polystyrene, in toluene, a selective solvent for polystyrene.

The best fits are shown as solid lines in Figure 6.2. As discussed above, the association of the pentablock into micelles is driven by mutually exclusive interactions between the blocks and the affinities of the blocks to the solvent. With the solvent being hydrophobic the ionic block segregates into the center of the micelles and the rest of the blocks appear Gaussian. This results show that the shape of the ionic domain dominated the overall shape of the micelle. Our molecular dynamic simulations$^{37}$ have shown that the ionic segment of the penta-block assumes a slightly elongated shape. These results are consistent with previous finding that of have shown elongated ionic domains in ionic homopolymers and random co-polymers such as Nafion®$^{38, 39}$. In this study, the presence of multiple highly incompatibility of blocks along with the mutual compatibilities of
solvent results in breaking of a fully spherical symmetry, resulting in elongation captures by an elliptical core-shell model.

The dimensions of the aggregates including those of the miceller core, and corona together with the volume fraction of solvent in the core as well as the aggregation number were extracted from fits to a form factor of ellipsoidal core-shell with Gaussian decaying chains at corona, are presented in Figure 6.4 a-d. With increasing concentrations, both the core and the corona size increased rapidly up to about 2 wt% and then levels off as shown in Figure 6.4 a and b.

The long and the short dimensions of the core retain relatively similar eccentricities with increasing concentrations providing a first insight into the growth pathways of the micelle. At the initials stage of association the number of polymer molecules increases and consequently, the size of the self-assembled structures increased. In this regime, the overall dimension of the micelle is determined by an internal balance of interfacial energies between the ionic domain and the area per chain in the corona. Above the concentration an optimal structure in which the area per corona chain is optimized, no further changes in the dimensions of the micelle take place and with increasing concentration the number of micelles increases.
Figure 6.4 Calculated parameters from ellipsoidal core-shell model for the penta-block copolymer solutions as a function of polymer concentration at 25 ºC. (a) Radius of core, (b) $R_g$ of corona, (c) aggregation number and (d) solvent fraction in the core.

Even though the core size increases with increasing the concentration, the volume fractions of the trapped solvent, $\Phi$, in the miceller core decreases. The $\Phi$ varies from approximately 0.68 to 0.26 as presented in Figure 6.4 d. With increasing concentration, the hydrophilic nature of the core enhances as a result of aggregation of more sulfonated
PS groups. This results in repulsion of hydrophobic solvent molecules out of the micelle core. Similar observations were made by Eisenberg et al.\textsuperscript{22, 40, 41} for highly incompatible block copolymers. They observed the system tends to maximize their size and move the solvents out from the core due to the presence of incompatible blocks to minimize the surface energies. Further, the entropy cost for the expansion of core and corona chains at equilibrium is balanced by surface energy gained by an increase in size.

At low concentrations concentration, the data can no longer be described by an elliptical micelle form factor. The data were therefore analyzed in terms of a form factor of an ellipsoid coupled with that of a Gaussian chain. The fit is shown in Figure 6.2-a the dimensions obtained are approximately 40 Å for the radius of major core, 0.78 for the eccentricity of the ellipsoid and 176 Å for the $R_g$ of the whole object. At these lower concentrations the penta-block consists of an ionic collapsed segment with an ellipsoid shape surrounded by the flexible PI and tBPS highly swollen chains. The ionic cluster holds a significant amount of solvent, though it retained a collapsed configuration. Molecular dynamics simulations of a single molecule in heptane and cyclohexane reveal a similar configuration as shown in Figure 6.5. Details of the simulations are provided elsewhere\textsuperscript{37}. The corresponding calculated $S(q)$ is shown as well.
Figure 6.5 A snapshot of molecular dynamic simulations of penta-block with a total molecular weight of 50 kg/chain and the ratio of tBPS:PI:PS/sPS:PI:tBPS of 10:20:40:20:10 and sulfonation fraction of 0.3 at 300 K in 1:1 mixture of cyclohexane and heptane, all modeled by OPLS potentials. Simulations were run using LAMPS classical MD code\textsuperscript{42-44} with a time step of 1 fs.

Note that the scattering function of experimental low concentration solution is scattering from an ensemble and is impacted by its variability. These results however clearly demonstrate that in this hydrophobic solvent, the ionic block remains collapsed.

The stability of the micelles of penta-block copolymer and the impact of temperature of their structure was studied at the low concentration regime 0.025 to 2 wt%. The samples were heated up to 75 °C (limited by the boiling temperature of the solvents). The scattering profiles are presented in Figure 6.6 a-d. In this temperature
range, the micelles remain stable. Only small changes are observed in the low q region for all concentrations. The slopes of the scattering patterns, at intermediate q range slightly decrease i.e. the micelles become less spherical with increasing temperature. At high q however, the slope changes significantly at low concentrations and is less pronounced as the concentration increases. At the high q range, changes in internal structure of the micelles are reflected, where changes are observed predominantly at the low concentration regime. At the lowest concentration, a slope of approximately 1.99 is observed. This is consistent with conformation of a Gaussian chain. Upon heating the chains stretch out into the solvent. As the corona becomes more miscible in the solvent, there is no clear distinction between the solvent and the corona and $S(q)$ is dominated by the scattering from the ionic core. With increasing concentration, the corona becomes more defined and the impact of temperature less pronounced.

All the profiles were analyzed in terms of the form factor of ellipsoidal core-shell micelles with Gaussian decaying chains at the corona. The best fits are given in solid lines in Figure 6.6 a-d. The eccentricities of the micelles are hardly affected by temperature. The overall shape of the scattering profile did not alter significantly with increasing temperature which attributed that the micelles did not dissociate in this temperature range. The experiment was carried out up to 75 °C because of the volatility of the mix solvents.
Figure 6.6 SANS profiles of the penta-block copolymer as a function of temperature and polymer concentration, (a) 0.025 wt%, (b) 0.05 wt% (c) 0.1 wt% and (d) 2 wt%. The symbols represent the experimental data and the solid lines represent the best fits.

The dimensions of the aggregates including those of the micellar core, and corona together with the volume fraction of solvent in the core as well as the aggregation number were extracted from the full data analysis as a function of concentration and temperature. The parameters as a function of concentration are presented in Figure 6.7 a-d. The insets represent the changes of corresponding parameter at low concentrations.
Figure 6.7 Calculated parameters from the model of ellipsoidal core-shell form factor for the penta-block copolymer as a function of temperature (25 °C - solid squares, 50 °C – open circles and 75 °C - solid triangles) and polymer concentration for (a) major radius of core, (b) $R_g$ of corona, (c) aggregation number and (d) solvent fraction in the core. Insets represent the changes at lower concentrations.

The size of the micelles increases with increasing the temperature regardless of the concentration of the penta-block copolymer solution as shown in Figure 6.7 a and b, where the degree of changes of core size is higher than that of the corona. Fairly large
micelles with more trapped solvents were observed even at 0.025 wt% in comparison with higher concentrations. At the highest temperature, the core size changes only slightly compare to the changes at room temperature. This supports our assertion that the ionic segment dominates the structure and provides stability where extensions of the PI and tBPS blocks do not result in pulling out molecules from the micelle.

Number of polymer chains associate for the miceller assembly or the aggregation number increases with increasing concentration and temperature as shown in Figure 6.7c, which is in agreement with the increase in core size. The increase of aggregation number with increasing the temperature is rather slow in higher concentration solutions in comparison to the lower concentration solutions. We calculated the enthalpy of, $\Delta H$, of association of chains to micelles at room temperature using the changes of aggregation number as a function of the concentration using the $N_{agg} = A e^{-\Delta H / RT}$. Where $N_{agg}$ is the aggregation number, $A$ is the pre-exponential factor, $R$ is the universal gas constant and $T$ is the temperature. The values of the enthalpy of association are on Figure 6.8. The enthalpy of association is positive and decreased with increasing the concentrations. The positive values of $\Delta H$ of micellization show that this process is endothermic. As concentration increases, the solvent fraction in the core decreases at all the temperatures as shown in Figure 6.7-d. With association of more ionic groups at the core, the poor solvent is repelled. With increasing temperature the system becomes more dynamic allowing further segregation between incompatible components. Hence the solvent is expelled from the core.
The ΔH of micellization of the penta-block co-polymer in a mixture of none-polar solvents are higher than that observed for well-known polar block copolymer, pluronic [poly(ethylene oxide) poly(propylene oxide) poly(ethylene oxide)], micellization in selective solvents. Lien Trong et al.\textsuperscript{45} investigated the enthalpy of micellization of pluronic, triblock copolymer in aqueous solution is approximately 25 J/g of polymer using differential scanning calorimetry. It was shown that micellization is endothermic. They attributed the endothermic process is mainly due to the micelle formation whereas at high concentrations a small contribution is also coming from the ordering of micelles.

![Graph showing enthalpy change vs concentration](image)

**Figure 6.8** Enthalpy of micellization process determined from the Arrhenius relation of the change of aggregation number.
Summary

Self-assembly of tBPS-PI-PS/sPS-PI-tBPS penta-block copolymer in heptane and cyclohexane mixture have been investigated as a function of concentration and temperature by SANS. In solution, the penta-block copolymer self-assembles into ellipsoidal micelles with a sulfonated polystyrene center surrounded by solvated polyisoprene and tertiary butyl polystyrene. The radius of the micelle, the thickness of the corona and the aggregation number increased rapidly and levels off with increasing concentrations, while the solvent fraction in the core decreased with increasing the polymer concentration. The increase of micellar size with increasing the solution concentration attributed to the enhance incompatibilities between ionic sPS and non-ionic PI and tBPS blocks. The size of the micelle and the aggregation number increased slightly with increasing temperature, while solvent fraction at the core decreased. The thermal responsiveness of the micellar solutions decreased with increasing the polymer concentrations. We attributed the changes of the sizes of the blocks in core and corona with increasing both solution concentration and temperature to minimization of the surface energy. In dilute solutions single structured molecules are solvated with a swollen ionic core surrounded by a Gaussian chain.

These findings provide first insight into the assembly process of a multifunctional polymer that contains an ionic block. We found that in selective solvent for the none-ionic blocks, the ionic block dominated the assembly process and the shape of the micelles. This in turn will impact the formation of membranes from solution casting process.
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References


CHAPTER SEVEN
SYNTHESIS AND CHARACTERIZATION OF CARBOXYLATE SUBSTITUTED
IONIC POLYPHENYLENE ETHYNYLENE

Abstract

Poly(phenylene ethynylene)s substituted with ethyl acetyloxy and either hexloxy or dooctyloxy where the ionic substituent with either H⁺ or Na⁺ and alkylloxy chains alternating copolymers were synthesized. Optical properties were determined using UV/Vis and fluorescence spectroscopy. In C-18 substituted PPEs blue shift of λ_max was observed when neutral form of PPE convert into acid form. However, in C-6 substituted PPEs red shift of λ_max was observed when neutral form converted into acid form. In contrast, red shift was observed in fluorescence spectra when PPEs are converted into their acid counterparts regardless of the size of the side chains. These shifts represent different conformational changes. Moreover, all the chromosphere solutions showed approximately similar fluorescence quantum yields.

Introduction

Poly(phenylene ethynylene)s (PPE), π-conjugated polymers, are chemically stable and fluorescence emissive compounds which form linear rigid rods to spherical nano particles in solution and display a supramolecular arrangements on the thin films⁰. Among them, poly-dots have been incorporated successfully into living cells while their fluorescence remains sufficiently strong to be superior to quantum dots². Their conformation when confined to nano dimensions and their surface structure are a key to their stability and optical activity¹². Though poly-dots have shown an enormous
potential, their configuration, the dynamics and the forces that hold them together remains an open question. In order to address these questions, our research group studies the behavior of PPEs by molecular dynamics simulation as well as by neutron scattering techniques. Controlling the structure of poly-dots require the ability to manipulate chemical structure of the polymer. Here we report the synthesis of two different ionic PPEs, shown in Figure 7.1, having poly(phenylene ethynylene)s substituted with ethyl acetyloxy and either hexloxy or dooctyloxy where the ionic substituent with either H\(^+\) or Na\(^+\) counter ions and alkyloxy chains. Solubility in polar solvent is introduced into PPEs by the addition of ionic groups while grafted alkoxy groups introduce the various functionalities to the polymer.

![Molecular structure of poly(phenylene ethynylene) substituted with sodium acetyloxy group and (A) Hexyloxy and (B) Dooctyloxy grafted polymers](image)

Figure 7.1 Molecular structure of poly(phenylene ethynylene) substituted with sodium acetyloxy group and (A) Hexyloxy and (B) Dooctyloxy grafted polymers
Synthesis of PPE

The synthesis routes are summarized in Figure 7.2 to 7.6. All reagents and solvents for extraction and chromatography were used as received from Acros, Aldrich Chemicals Co., TCI America, and Alfa Aesar. The solvents for the reactions were further purified by passing through Aluminum columns under N$_2$ atmosphere employing an MBRAUN solvent purification system. Compound 2-5$^{3,4}$ and Compound 6-9$^5$ were synthesized improving previously reported pathways. All the air sensitive reactions were performed in the MBRAUN dry box or using standard Schlenk techniques under N$_2$ atmosphere. Proton and carbon-13 NMR spectra were acquired on Bruker Avance 300 spectrometer operating at 300 MHz. All spectra were acquired at 25 ºC using either trimethylsilane or residual solvent peak as a reference. The yields are reported either in gram or percent yield as appropriated.

Synthesis of Hexyloxy Group Substituted Ionic PPE.

Figure 7.2 Schematic route for synthesis of monomer 5: (i) Bromohexane, K$_2$CO$_3$, acetonitrile, reflux 47 hours; (ii) Br$_2$, dichloromethane, stir at RT for 24 hours; (iii) Pd(PPh$_3$)$_4$, CuI, trisilyl acetylene, triethylamine, toluene, stir at 90 ºC for 60 hours; (iv) Methanol/THF, 5N NaOH, stir at RT for 2 hours.
Synthesis of 1,4-bis(hexyloxy)benzene (2). Hydroquinone (40.0 g, 0.363 mol) was added to a suspension of K$_2$CO$_3$ (150.6 g, 1.089 mol) in 500 ml of acetonitrile under N$_2$. Bromohexane (179.9 g, 1.089 mol) was added dropwise using a syringe to the stirred mixture. The resulting mixture was reflux at 30 ºC for 47 hrs. After refluxing, 300 ml of hot toluene was added to the reaction mixture. Solid residues were decanted off and the filtered solution was rotary evaporated under reduced pressure. The resulted oily crude was dissolved in 10 ml of dichloromethane. This solution was added dropwise to the 1000 ml of methanol in a cold water bath. The white solid (71.2 % yield) was collected. 1H NMR (CDCl$_3$): δ 6.82 (s, 4H), 3.9 (t, 4H), 1.80-1.70 (m, 4H), 1.46-1.30 (m, 12H), 0.90 (t, 6H).

Synthesis of 1,4-bis(hexyloxy)-2,5-dibromobenzene (3). 1,4-dihexyloxybenzene (33.3 g, 0.120 mol) was dissolved in 250 ml of dichloromethane and allowed to cool to 0 ºC in a cold water bath under N$_2$ atmosphere. Br$_2$ (42.2 g, 1.089 mol) was added dropwise while maintaining the 0 ºC. The reaction mixture was stirred at room temperature for 24 hours. After overnight stirring, excess Br$_2$ was quenched with 300 ml of saturated Na$_2$S$_2$O$_3$. The organic layer was washed with water (3 x 300 ml), saturated NaCl and water respectively. The off-white solid (92.5% yield) was collected by rotary evaporating the dichloromethane under reduce pressure. 1H NMR (CDCl$_3$): δ 7.17 (s, 2H), 3.92 (t, 4H), 1.84-1.75 (m, 4H), 1.55-1.34 (m, 12H), 0.91 (t, 6H).
Synthesis of 1,4-bis[(trimethylsilyl)ethynyl]-2,5-bishexyloxybenzene (4). 1,4-
bishexyloxy-2,5-dibromobenzene (15.0 g, 34.4 mmol), trimethylsilylacetylene (13.5 g, 
137.6 mmol), Pd(PPh₃)₄, (4.77 g, 4.13 mmol), CuI (0.786 g, 4.13 mmol), 
diisopropylamine (55 ml) and toluene (100 ml) were charged into a 250 ml pressure flask 
under the glove box. The mixture was stirred for 60 hours at 90 °C. After allowing the 
reaction mixture to cool down to room temperature diethylether (200 ml) was added. 
Then, this solution was passed through silica gel. The filtrate was washed with saturated 
NaHCO₃ (2x500 ml), H₂O (500 ml) and 5-10 mol% HCl (300 ml). Finally, organic layer 
was collected and rotor evaporated. In order to remove the phosphonium salts, the solid 
compound was re-dissolved in Hexane (100 ml) and passed through silica gel. The 
solution was rotor evaporated to get brownish orange solid. This solid was recrystallized 
in ethanol to yield Compound 4, as a pale yellow powder. (79.5% yield) 1H NMR 
(CDCl₃): δ 6.88 (s, 2H), 3.93 (t, 4H), 1.81-1.76 (m, 4H), 1.53-1.33 (m, 12H), 0.88 (t, 6H), 
0.25 (s, 18H).

Synthesis of 1,4-bis(ethynyl)-2,5-bishexyloxybenzene (5). 1,4-
bis[(trimethylsilyl)ethynyl]-2,5-bishexyloxybenzene (2.85 g, 6.05 mmol), 
tetrahydrofuran (150 ml), methanol (60 ml) and 20% NaOH (30 ml) were charged into a 
500 ml three neck round bottom flask under N₂ and stirred at room temperature for 2 
hours. After stirring dimethylether (45 ml) was added to the reaction mixture. The 
organic layer was collected and washed with H₂O. Diethylether was rotor evaporated to 
get the crude. The crude was purified by stirring it in methanol (30 ml) and filtered to
yield Compound 5, as an off-white powder (82.5% yield). 1H NMR (CDCl₃): 7.447 (2H, s), 3.93 (t, 4H), 2.840 (s, 2H), 1.53-1.33 (m, 12H), 1.81-1.76 (m, 4H), 0.865 (t, 6H).

![Chemical structure image]

Figure 7.3. Schematic route for the synthesis of monomer 9. (v) Bromomethane, K₂CO₃, acetonitrile, reflux for 47 hours; (vi) ICl, methanol, reflux at 70 ºC for 5 hours; (vii) BBr₃, dichloromethane, reflux for 20 hours; (viii) K₂CO₃, ethylbromoacetate, acetonitrile reflux for 24 hours.

**Synthesis of 1,4-bismethoxybenzene (6).** Hydroquinone (40.0 g, 0.363 mol) was added to a suspension of K₂CO₃ (150.6 g, 1.09 mol) in acetonitrile (500 ml) in 1 L three neck round bottom flask under N₂. Bromomethane (103.4 g, 1.09 mol) was syringed dropwise to the stirred mixture. The resulting mixture was reflux for 40 hours at 30 ºC. After 40 hours, hot toluene (300 ml) was added to the reaction mixture. Solid residues were decanted off. The decanted solution was rotor evaporated under reduced pressure. Dichloromethane (10 ml) was added to the resulted oily crude. The above solution was added dropwise to the methanol (1000 ml) in a cold water bath. The solid product was collected by vacuum filtration as white crystals (71.2% yield). 1H NMR (CDCl₃): δ 6.89 (q, 4H), 3.75 (s, 6H).
Synthesis of 1,4-bismethoxy-2,5-diodobenzene (7). Methanol (120 ml) was allowed to cool to 0 °C in a 250 ml three-neck round bottom flask under N₂. Iodine monochloride (50.6 g, 0.312 mol) was slowly added into cold methanol. 1,4-bismethoxybenzene (10.0 g, 72 mmol) was added small portion at a time to the above solution. The reaction mixture was refluxed at 70 °C for 5 hours. After refluxing, the mixture was allowed to cool and filtered to get the brownish orange solid (67.9% yield). 1H NMR (CDCl₃): δ 6.78 (d, 2H), 3.72 (s, 6H).

Synthesis of 2,5-diiodohydroquinone (8). 1,4-bismethoxy-2,5-diodobenzene (4.0 g, 10.3 mmol) and dichloromethane (65 ml) was mixed in 250 ml three-neck round bottom flask under N₂ and allowed to cool in a dry ice bath. Boron tribromide (61.8 ml, 61.5 mmol) was slowly syringed into the above cooled mixture. The mixture was stirred and allowed to warm to room temperature. Then it was refluxed for 20 hours. After allowing the mixture to cool down the refluxed mixture, reaction mixture was poured into ice water (700 ml). Concentrated HCl (7 ml) was added dropwise into ice-cold solution. This solution was extracted into ethylacetate (200 ml). The organic layer was rotor evaporated to get the brown solid (72.7% yield). 1H NMR (CD₃OD): δ 6.78 (d, 2H).

Synthesis of 2,5-diiodo-1,4-ethylacetyloxybenzene Compound 9. 1,4-diiodo-2,5-dihydroquinone (3.0 g, 8.29 mmol), potassium carbonate (11.5 g, 82.9 mmol), ethyl bromoacetate (5.54 g, 33.2 mmol) and acetonitrile (45 ml) were placed in a 100 ml round bottom flask and refluxed for 24 hours under N2. The mixture was allowed to cool to room
temperature, the solution was filtered, and rotor evaporated to yield crude, brown crystalline powder. The crude solid was crystallized from a mixture of ethyl acetate (250 ml) and hexane (150 ml) to yield Compound 9, as an off-white solid (56.2% yield). 1H NMR (CDCl₃): δ 7.019 (2H, d), 4.479 (4H, s), 4.333 (4H, s), 1.177 (6H, t).

Figure 7.4 Schematic synthesis route of polymer 12 (Hexyloxy grafted ionin PPE): (ix) Pd(PPh₃)₂Cl₂, CuI, triethylamine, dichloromethane, reflux for 72 hours; (x) NaOH/methanol, reflux for 24 hours; (xi) Acetone/methanolic HCl, stir at RT for 1 hour.

**Synthesis of Polymer 10.** Monomer 5 (0.946 g, 2.88 mmol), monomer 9 (1.4 g, 2.62 mol), (Ph₂P)₂PdCl₂ (9.12 mg, 0.013 mmol), CuI (2.47 mg, 0.013 mmol), diisopropylamine (6.5 ml) and dichloromethane (27 ml) was placed in a 50 ml pressure
vessel under the glove box. This mixture was heated at 50 ºC for 64 hours. The mixture was allowed to cool after heating and added to diethylether (600 ml) to form precipitate. The precipitate was filtered to yield Polymer 10, as an orange solid (84.4% yield). 1H NMR (CDCl₃): δ 6.31-7.368 (aromatic 4H), 4.46 (s, 4H), 4.37 (q, 4H), 4.10 (t,4H), 1.27 (t, 6H), 1.28-1.89(m, 20H), 0.866 (t, 6H)

**Synthesis of Polymer 11.** Polymer 10 (1.7 g) and methanol (100 ml) was charged into a 500 ml round bottom flask. A solution of NaOH (5.1 g) in methanol (150 ml) was added to the above round bottom flask. The mixture was refluxed for 20 hours. The mixture was allowed to cool overnight in refrigerator. The orange precipitate was collected (1.6 g).

**Synthesis of Polymer 12.** Polymer 11 (1.5 g) was dissolved in acetone (150 ml) and 10% v/v methanolic HCl (38 ml) was slowly added in to the solution. The mixture was stirred at room temperature for 1 hour. After stirring, the solution was rotor evaporated. The resulted brown precipitate was washed with excess water to yield brown precipitate (1.2 g) 1H NMR (d-THF): δ 6.31-7.368 (aromatic 4H), 4.46 (s, 4H), 4.37 (q, 4H), 1.28-1.89(m, 20H), 0.866 (t, 6H)
Figure 7.5 Synthesis of monomer 16: (xii) Bromooctadecane, K₂CO₃, acetonitrile, reflux for 47 hours; (xiii) Br₂, dichloromethane, stir at RT for 24 hours; (xiv) Pd(PPh₃)₄, CuI, trisilyl acetylene, triethylamine, toluene, stir at 90 ºC for 48 hours; (xv) Methanol/THF, 5N NaOH, stir at RT for 2 hours.

**Synthesis of 1,4-bisdoctyloxybenzene (13).** The synthesis of Compound 13, was done according the previously reported procedures with some modifications. Potassium Hydroxide (24 g, 428 mmol) and dimethylsulfoxide (120 ml) was degassed in a 250 ml three neck round bottom flask for 1 hour. Hydroquinone (5 g, 45.4 mmol) and 1-bromooctadecane (53.9 g, 160 mmol) were mixed together and then added to above degassed solution small portion at a time while vigorous stirring. The reaction mixture was stirred at room temperature for 4 hours under N₂. After 4 hours, the mixture was poured into ice water (200 ml). The off white precipitate was collected and recrystallized from a 1:1 mixture of acetone (200 ml) and toluene (200 ml). The solid crystals were further purified by dissolving in diethylether (200 ml) and washed with 5M NaOH.
solution. The organic layer was rotor evaporated to yield white crystals (56.2% yield). 1H NMR (CDCl₃): δ 6.853 (4H, q), 4.026 (t, 4H), 1.27-1.83 (m, 64H), 0.865 (t, 6H).

**Synthesis of 1,4-bishexyloxy-2,5-dibromobenzene (14).** 1,4-didooctyloxybenzene (5.5 g, 8.96 mmol) was dissolved in dichloromethane (100 ml) and cooled to 0°C in an ice-water bath under N₂ atmosphere. Br₂ (3.15 g, 19.7 mmol) was added dropwise while maintaining the temperature at 0 ºC. The reaction mixture was stirred 20 hours at room temperature. After overnight stirring, excess Br₂ was quenched with saturated Na₂S₂O₃ (200 ml). The organic layer was washed with water (3 x 200 ml), saturated NaCl (200 ml) and water (200 ml) respectively. An off-white product was collected by rotor evaporating the dichloromethane under reduce pressure (83.9% yield). 1H NMR (CDCl₃): δ 6.983 (d, 2H), 4.048 (t, 4H), 1.23-1.84 (m, 32H), 0.865 (t, 6H).

**Synthesis of 1,4-bis[(trymethylsilyl)ethynyl]-2,5-bisdoctyloxybenzene (15).** 1,4-bisdoctyloxy-2,5-dibromobenzene (5.5 g, 7.12 mmol), trimethylsilylacetylene (2.8 g, 28.5 mmol), Pd(PPh₃)₄ (0.98 g, 0.85 mmol), CuI (0.16 g, 0.85 mmol), diisopropylamine (20 ml) and toluene (35 ml) were charged into a 100 ml pressure flask under a glove box. The mixture was stirred for 48 hours at 90 ºC. After allowing the reaction mixture to cool down to room temperature diethylether (150 ml) was added. Then this solution was passed through silica gel. The filtrate was washed with saturated NaHCO₃ (2x300 ml), H₂O (300 ml) and 5-10 mol% HCl (300 ml). Finally, organic layer was collected and rotor evaporated. In order to remove the phosphonium salts, the solid compound was re-dissolved in pentane (100 ml) and passed through silica gel. The filtrate was rotor evaporated to get brownish orange solid. This solid was re-crystallized
in ethanol to yield Compound 15, as pale yellow crystals (74.9% yield). 1H NMR (CDCl₃): δ 6.88 (s, 2H), 3.93 (t, 4H), 1.20-1.79 (m, 32H), 0.87 (t, 6H), 0.25 (s, 18H).

**Synthesis of 1,4-bis(ethynyl)-2,5-bisdoctyloxybenzene (16).** 1,4-bis[(trymethylsilyl)ethynyl]-2,5-bis0ctyloxybenzene (2.0 g, 2.48 mmol), tetrahydrofuran (170 ml), methanol (70 ml) and 20 wt% NaOH (35 ml) were charged into a 500 ml round bottom flask under N₂ and stirred at room temperature for 3 hours. After stirring dimethylether (50 ml) was added to the reaction mixture. The organic layer was collected and washed with H₂O. The solution was rotor evaporated to get the crude. The crude was purified by stirring it in methanol (30 ml) and filtered to yield Compound 16, as an off-white powder (89.5% yield). 1H NMR (CDCl₃): 6.98 (2H, s), 3.97 (t, 4H), 3.33 (s, 2H), 1.81-1.25 (m, 32H), 0.879 (t, 6H),

Figure 7.6. Schematic route for synthesis of polymer 19 (dooctyloxy grafted ionic PPE): (xvi) Pd(PPh₃)₂Cl₂, CuI, triethylamine, dichloromethane, reflux for 72 hours, (xvii)
Synthesis of Polymer 17. Monomer 16 (1.45 g, 2.19 mmol), Monomer 9 (1.06 g, 1.99 mmol), (Ph₂P)₂PdCl₂ (6.98 mg, 9.95 μmol), CuI (1.89 mg, 9.95 μmol), diisopropylamine (8 ml) and dichloromethane (30 ml) was placed in a 50 ml pressure vessel under the glove box. This mixture was heated at 50 °C for 30 hours. After 30 hours, the solution was allowed cool and diethylether (300 ml) was added and it was washed with H₂O (200 ml). The resulted ether layer was rotor evaporated. The resulted slurry was dissolved in minimum amount of dichloromethane (3 ml). This solution was added to methanol (200 ml) drop wise to yield polymer 17 as an orange solid (2.08 g). 1H NMR (CDCl₃): δ 6.31-7.368 (aromatic 4H), 4.46 (s, 4H), 4.37 (q, 4H), 1.27 (t, 6H), 1.28-1.89 (m, 32H), 0.866 (t, 6H)

Synthesis of Polymer 18. Polymer 17 (0.9 g) and methanol (50 ml) was charged into a 250 ml round bottom flask. A solution of NaOH (2.7 g) in methanol (50 ml) was added to the above round bottom flask. The mixture was refluxed for 22 hours. After refluxing, the mixture was kept in refrigerator and orange precipitate was collected (0.8 g).

Synthesis of Polymer 19. Polymer 18 (0.5 g) was dissolved in acetone (50 ml) and 10% v/v methanolic HCl (13 ml) was slowly added in to the solution. The mixture was stirred at room temperature for 1 hour. After stirring, the solution was rotor evaporated. The resulted solid was washed with excess water to yield orange precipitate.
Characterization of PPE

UV absorption and fluorescence emission behavior of neutral and acid form of PPEs in THF were measured as a function of concentration at room temperature. The absorption and the emission spectra of 20 ppm solution are shown in Figure 7.7. Absorption and emission intensity of C-18 substituted PPEs is higher than that of C-6 substituted PPEs. Further, the neutral PPEs have higher intensities that that of acid form of the corresponding PPEs.

Figure 7.7 Absorption (A) and fluorescence (B) spectra for compound A–D in THF

The critical micelle concentration (CMC), absorption wavelength, absorptivity, emission wavelength and the quantum yield of PPE’s in THF at room temperature were
measured. These photophysical values are given in Table 7.1. In C-18 substituted PPEs blue shift of $\lambda_{\text{max}}$ is observed when neutral form of PPE convent into acid form. However, in C-6 substituted PPE red shift is observed when neutral form converted into acid form. In fluorescence spectra, red shift is observed when PPE is converted into its acid form regardless of the size of the side chain. These shifts represent different conformational changes. Further, these chromosphere solutions show a very similar fluorescence quantum yields. Based on the preliminary optical properties of PPEs we can see that the size of the alkyl side chain has influenced for the structural arrangement of carboxylate substituted PPEs in solution. This might be due to the different inter-chain interactions and conformational effects. At this point we cannot further elucidate the behavior PPEs.

In order to better describe the structure and dynamic behavior of these PPEs, a detail characterization is necessary. The structural behavior will be characterized using SANS and dynamic behavior will be characterized using QENS.

<table>
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<th>Chromophore</th>
<th>CMC (ppm)</th>
<th>Absorption</th>
<th>Fluorescence</th>
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<td></td>
<td></td>
<td>$\lambda_{\text{abs}}$ (nm)</td>
<td>$\varepsilon$ (ppm$^{-1}$cm$^{-1}$)</td>
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<td>PPE C-18/-C$_2$H$_5$</td>
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<tr>
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<tr>
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</tbody>
</table>

Table 7.1 Photophysical properties of A-D in THF at 25 °C.
Summary

We synthesized a series of poly(phenylene ethynylene)s substituted with ethyl acetyloxy and either hexloxy or dooctyloxy where the ionic substituent with either H⁺ or Na⁺ and alkyloxy chains alternating copolymers. The optical properties were characterized using UV/Vis and fluorescence spectroscopy. We found that the λ.max of UV/Vis and fluorescence spectra changed depending of the size of the alkoxy group. We attribute these changes to the different conformation of poly(phenylene ethynylene) in solution.

Acknowledgement

I would like to thank Rhett Smith and Brynna Laughlin from Clemson University for their valuable guidance throughout the synthesis of the polymers.

References


CHAPTER EIGHT

SUMMARY

The main goals of this study were to resolve structure and dynamics at interfaces of structured polymers in solution and in thin films. We found that the interfacial behavior of the polymers varied as a function of the degree of constraint where ionic clusters, rigidity of polymer and topological features play a role. Herein we summarize the results obtained for the different polymers.

1. Segregation of three-arm star polymers within linear polymer matrix

We studied the distribution of three-arm PS in linear PS matrices as a function of annealing time and molecular weight of star-arms using neutron reflectometry and compared the results with the segregation of linear PS in linear PS matrices. We found that the additives distributed homogeneously in as-cast samples and segregated to interfaces with annealing. While both polymer additives segregated, a significant difference was observed even in the presence of one polymer junction. The enrichment of interfaces with three-arm additives was asymmetric while almost symmetric segregation was observed in presence of linear PS analogs. Quantitatively, segregation of additives followed $t^{1/2}$ kinetics at short annealing times and crossed over to slow segregation process at prolonged annealing times. We attributed these changes to balance of enthalpic and entropic effects.
2. **Interdiffusion of polymers across macromolecular interfaces**

We studied the interdiffusion of ionic polystyrenes across polystyrene interfaces using neutron reflectometry and compared the results with those obtained for non-ionic PS films, HPD/DPS. This study has shown that in the presence of the entanglements and ionic clusters slows down the dynamics. The widths of the interface between two polymers capture the degree of spatial interpenetration and were correlated to their mean square displacement. The evolution of the interfacial widths with time captured the diffusion process. At early stage of the annealing a fast interfacial broadening was observed which transit into a slow process at prolong annealing times. The transition time increased with increasing the sulfonation level. At early stages of annealing, the interfacial broadening was linearly changed with $t^{1/2}$ and deviated at extended annealing times. Surprisingly, even in presence of small amount of ionic groups hindered the motion of polymer chains across the interface.

3. **Diffusion of guest molecules within ultra-thin rigid ionomer films.**

In this study the impacts of solvent hydrophobicity on diffusion across a structured ionic polymer interface were investigated. Films of polyphenylene ionomer with different sulfonation levels were exposed to alcohol vapors, and the reflectivity patterns were followed as a function of time. All films were swollen in presence of the alcohols. At an early stage of alcohols exposure, the mass uptake by sPP scaled linearly with $t^{1/2}$ and deviated at extended exposure times. Further,
we found that hydrophobicity of the alcohols had only limited effects on the diffusion across the interface.

4. **Association of a multifunctional, structured block copolymer in solution**

   We investigated the interfacial segregation of ABCBA type penta-block ionic copolymer in mixture of cyclohexane and heptane as a function of polymer concentration and temperature using small angle neutron scattering. The polymer consists of incompatible blocks, a randomly sulfonated polystyrene center block, polyisoprene middle blocks and tertiary butyl polystyrene terminal blocks. In general we found that very stable ellipsoidal micelles were formed with sulfonated polystyrene in the core and solvated polyisoprene and tertiary butyl polystyrene in the corona. With increasing concentration and temperature, the size of the micelle increased while the trapped solvent fraction at the core decreased.

5. **Synthesis and characterization of carboxylate substituted ionic polyphenylenes**

   We synthesized poly(phenylene ethynylene) substituted with ethyl acetyloxy and either hexloxy or dooctyloxy where the ionic substituent with either $\text{H}^+$ or $\text{Na}^+$ and alkylxy chains alternating copolymers. Optical properties were determined using UV/Vis and fluorescence spectroscopy. We found that $\lambda_{\text{max}}$ absorption and emission spectra change with changing the size of the alkyl group.
We attributed these shifts to different conformational changes. Further, all the chromospheres in THF show approximately similar fluorescence quantum yields.