Ion-beam analysis – A novel study of diffusion in ionic polymers.

by

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A thesis submitted to the Faculty of Engineering at the University of Surrey for the degree of Doctor of Philosophy

Department of Materials Science and Engineering,
University of Surrey,
October 1990.
Für Omi
Waterloo! Waterloo! Waterloo!
morne plaine!

Comme une onde qui boue
dans une urne trop pleine.

- Victor Marie Comte Hugo.
Abstract

An ion-beam technique based on the nuclear reaction \( d(^3\text{He}, p)^4\text{He} \) has been applied to measurements of polymer interdiffusion. A diffused bilayer of deuterated polystyrene and unmodified polystyrene is analysed by a beam of \(^3\text{He} \) ions and a concentration-profile of deuterium is extracted by analysis of the energy-spectrum of the emitted energetic protons. This technique can be used to measure diffusion over several microns with a depth-resolution of 20 nm.

Reptation has been confirmed as the mechanism governing polymer self-diffusion over the molecular weight range 90,000 to 1,800,000. The \(^3\text{He}-d\) method has also been used to study mechanisms of diffusion in ionomers, a class of polymers containing pendant ionic groups. The effect of ionic concentration on diffusion shows that the critical concentration for the formation of diffusion-inhibiting ionic aggregates lies in the range 2.8 - 5 weight \% of ionic material. Ionomers with concentrations below this range diffuse by reptation at an effective temperature equal to the difference between the annealing temperature and the glass-transition temperature.
Acknowledgements

I should like to express my deepest gratitude to my supervisors; Dr. P.J.Mills, for supervising the early stages of the project and for a great number of illuminating conversations thereafter; Prof.J.E.Castle, for giving me the benefit of his experience in countless areas of materials science and for showing real interest at short notice; Dr.A.S.Clough, to whom special thanks are due for his vast contribution in terms of both time and willingness to help throughout my four years at Surrey.

My warmest thanks also go to Julie Scott Lynn for turning ramblings into English and for, once again, ensuring the fluent concatenation of this work. I also thank Dr.R.S.Payne for his assistance in getting me started and Andy MacInnes, Jonathan Wood and Jiping Liu for making life in the lab almost as much fun as life out of it.

Ich möchte mich auch recht herzlich bei meinen Eltern bedanken sowohl für ihre finanzielle Unterstützung wie auch für ihre Zuversichtlichkeit und für ihre Geduld.
List of Contents

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>1</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>11</td>
</tr>
<tr>
<td>List of Contents</td>
<td>iii</td>
</tr>
<tr>
<td>List of Illustrations</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>List of Plates</td>
<td>x</td>
</tr>
<tr>
<td>List of Abbreviations</td>
<td>xi</td>
</tr>
<tr>
<td>Chapter 1: Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Polymer systems</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1 Ionomers</td>
<td>3</td>
</tr>
<tr>
<td>1.1.2 Aims of this work</td>
<td>8</td>
</tr>
<tr>
<td>1.2 Review of techniques for studying polymer diffusion</td>
<td>8</td>
</tr>
<tr>
<td>1.2.1 Rutherford Backscattering</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2 Infra-red Microdensitometry</td>
<td>12</td>
</tr>
<tr>
<td>1.2.3 Fluorescence Recovery After Pattern Photobleaching</td>
<td>12</td>
</tr>
<tr>
<td>1.2.4 Forced Rayleigh Light Scattering</td>
<td>13</td>
</tr>
<tr>
<td>1.2.5 Radioactive Tracer</td>
<td>14</td>
</tr>
<tr>
<td>1.2.6 Secondary-Ion Mass Spectrometry</td>
<td>16</td>
</tr>
<tr>
<td>1.2.7 Elastic Recoil/Forward Scattering</td>
<td>18</td>
</tr>
<tr>
<td>1.2.8 The $^3$He-d Technique</td>
<td>19</td>
</tr>
<tr>
<td>1.3 Descriptions of diffusion</td>
<td>20</td>
</tr>
<tr>
<td>1.4 Outline of this work</td>
<td>24</td>
</tr>
<tr>
<td>Chapter 2: The technique of $^3$He-d Nuclear Reaction Analysis</td>
<td>26</td>
</tr>
<tr>
<td>2.1 Nuclear Reaction Analysis</td>
<td>27</td>
</tr>
<tr>
<td>2.2 Portrait of the d($^3$He,p)$^4$He reaction as a charged particle technique</td>
<td>29</td>
</tr>
</tbody>
</table>
2.2.1 The case for backward angles.

2.2.2 Interpreting the energy-scale

2.3 Measuring Diffusion Profiles

2.4 Measuring the Resolution

2.5 Refinements to the technique

2.6 Summary

Chapter 3: An assessment of ion beam damage

3.1 Measurement of damage

3.1.1 Disappearance of the carbon shake-up satellite

3.1.2 The effect of damage on subsequent diffusion

3.1.3 Measuring the extent of cross-linking

3.2 Summary

Chapter 4: Materials modification and sample preparation

4.1 Deuteration of Polystyrene

4.1.1 The deuteration reaction

4.1.2 NMR evaluation of deuteration.

4.1.3 Post-deuteration integrity

4.2 Sulphonation of Polystyrene

4.2.1 The Sulphonation Reaction

4.2.2 Evaluation of the sulphonation process

4.3 Sample preparation

4.4 The experimental chamber

Chapter 5: Results

5.1 Initial evidence of inter-chain links

5.2 Small molecule diffusion

- The effect of ionic concentration

5.3 Characterization results: Titration, $T_g$ and PIXE
5.3.1 Acid-base titration results
5.3.2 Glass-transition measurements
5.3.3 PIXE measurements
5.4 Diffusion experiments
  5.4.1 Diffusion baselines
  5.4.2 Mechanisms of diffusion
    - Effect of molecular weight
  5.4.3 Mechanisms of diffusion
    - Effect of ionic concentration
5.5 Summary

Chapter 6: Summary, conclusions and suggestions for future work.
  6.1 Summary
  6.2 Conclusions
  6.3 Suggestions for future work

Appendix A: TURBOBASIC™ routines written for this work
Appendix B: A solution of Fick's second law
Appendix C: List of Chemicals
References
List of Illustrations

<table>
<thead>
<tr>
<th>Figure 2.1</th>
<th>Reaction cross-section versus energy.</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.2</td>
<td>Proton and alpha energy-dependence on beam energy.</td>
<td>35</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Schematic diagram of d(^3He,p)^4He reaction.</td>
<td>38</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Schematic diagram of experimental arrangement.</td>
<td>40</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>Annealing bilayers to induce diffusion.</td>
<td>41</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>Range-energy curves for various particles in silicon.</td>
<td>44</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Ranges in detector material.</td>
<td>45</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>Spectra from thick and thin deuterated-PS layers.</td>
<td>49</td>
</tr>
<tr>
<td>Figure 2.9</td>
<td>Theoretical and experimental profiles.</td>
<td>50</td>
</tr>
<tr>
<td>Figure 2.10</td>
<td>Consequences of a glancing beam incidence.</td>
<td>55</td>
</tr>
<tr>
<td>Figure 2.11</td>
<td>Stopping-power curve for Helium-3 in polystyrene.</td>
<td>58</td>
</tr>
<tr>
<td>Figure 2.12</td>
<td>Typical multilayer sample spectrum. Beam energy 700 keV, normal beam incidence.</td>
<td>61</td>
</tr>
<tr>
<td>Figure 2.13</td>
<td>Depth-resolution against depth and beam energy.</td>
<td>64</td>
</tr>
<tr>
<td>Figure 2.14</td>
<td>Views of detector and slit collimator.</td>
<td>67</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>XPS spectra showing effect of ion beam analysis on aromatic ring shake-up satellite.</td>
<td>73</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>^3He-d Spectra from annealed samples with no previous analysis and one previous analysis.</td>
<td>76</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Results from hydrogen-loss experiment.</td>
<td>79</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Steps in the deuteration of polystyrene.</td>
<td>85</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Nomenclature of positions on styrene group.</td>
<td>88</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>Proton-NMR spectrum from normal</td>
<td></td>
</tr>
</tbody>
</table>
polystyrene (h-PS).

**Figure 4.4** Proton-NMR spectrum from deuterated polystyrene (d-PS).

**Figure 4.5** Molecular weight distributions of h-PS and d-PS by GPC.

**Figure 4.6** Schematic diagram of sulphonation apparatus.

**Figure 4.7** Steps in the sulphonation of polystyrene.

**Figure 4.8** Molecular weight distributions of h-PS and s-PS by GPC.

**Figure 4.9** EDAX spectrum of sodium sulphonate salt of polystyrene, showing sulphur, oxygen and sodium.

**Figure 4.10** Schematic of PIXE chamber.

**Figure 4.11** Schematic diagram of annealing system.

**Figure 4.12** Side-view of detector mounting and cooling system.

**Figure 5.1** RBS spectrum of polystyrene film exposed to IOH vapour.

**Figure 5.2** RBS spectra from ionomer films of differing ionic concentration after exposure to iodohexane vapour for 60 seconds.

**Figure 5.3** DSC trace of ionomer acid.

**Figure 5.4** Sulphur concentration calibration curve from PIXE.

**Figure 5.5** Diffusion baselines for extremes of molecular weight.

**Figure 5.6** Molecular weight dependence of 90k polystyrene with prediction from reptation model.

**Figure 5.7** Comparison between 90k data from this work and
prediction from WLF theory together with Green's data for other molecular weights.

Figure 5.8  Effect of ionic concentration on diffusion coefficient.

Figure 5.9 $^3$He–d spectra showing the effect of ionic concentration on polymer diffusion.

Figure 5.10 WFL plot of ionomers of 90k with best fit.
### List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Energy-dependence of angular contribution to resolution.</td>
<td>59</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Range of technique as a function of beam energy.</td>
<td>59</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Effect of beam energy and angle of incidence on measured experimental resolution.</td>
<td>62</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Proton-NMR evaluation of deuteration of polystyrene: degree of reduction of hydrogen signal after deuteration.</td>
<td>89</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Results of titration of sulphonic acid with NaOH.</td>
<td>126</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Glass-transition measurements of 90k ionomers used in diffusion experiments.</td>
<td>127</td>
</tr>
<tr>
<td>Table 5.3</td>
<td>PIXE results from ionomers used in diffusion experiments and from PES/PO blends used as standards.</td>
<td>130</td>
</tr>
<tr>
<td>Table 5.4</td>
<td>Summary of characterisation results.</td>
<td>133</td>
</tr>
<tr>
<td>Table 5.5</td>
<td>Diffusion baseline data for 90k and 1.8M.</td>
<td>137</td>
</tr>
<tr>
<td>Table 5.6</td>
<td>Effect of ionic concentration on diffusion over a range of temperatures.</td>
<td>143</td>
</tr>
</tbody>
</table>
List of Plates

Plate 1: Downstream view of experimental chamber showing load-lock and sorption pump.

Plate 2: Upstream view of experimental chamber with detection electronics.

Plate 3: View of experimental chamber with lid removed to show cold finger.

Plate 4: Close-up view of end of cold finger showing dove-tail.

Plate 5: Interior view of experimental chamber with detector and protection magnet.
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC</td>
<td>Analog-to-Digital Converter</td>
</tr>
<tr>
<td>C</td>
<td>concentration</td>
</tr>
<tr>
<td>$C_0$</td>
<td>initial concentration</td>
</tr>
<tr>
<td>d</td>
<td>deuterium</td>
</tr>
<tr>
<td>d-PS</td>
<td>deuterated polystyrene</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$D^*$</td>
<td>centre-of-mass diffusion coefficient</td>
</tr>
<tr>
<td>$D_s$</td>
<td>self-diffusion coefficient</td>
</tr>
<tr>
<td>$D_{CR}$</td>
<td>Constraint-release diffusion coefficient</td>
</tr>
<tr>
<td>$D_{RO}$</td>
<td>Rouse diffusion coefficient</td>
</tr>
<tr>
<td>$D_{SE}$</td>
<td>Stokes-Einstein diffusion coefficient</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2 dichloroethane</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>$E_{\alpha}$</td>
<td>Helium-4 energy</td>
</tr>
<tr>
<td>$E_{He}$</td>
<td>Helium-3 energy</td>
</tr>
<tr>
<td>$E_p$</td>
<td>proton energy</td>
</tr>
<tr>
<td>EDAX</td>
<td>Energy-Dispersive X-ray Analysis</td>
</tr>
<tr>
<td>ERDA</td>
<td>Elastic Recoil Detection Analysis</td>
</tr>
<tr>
<td>EtAlCl$_2$</td>
<td>Ethyl aluminium dichloride</td>
</tr>
<tr>
<td>f</td>
<td>frictional drag per unit velocity</td>
</tr>
<tr>
<td>FRAPP</td>
<td>Fluorescence Recovery After Pattern Photobleaching</td>
</tr>
<tr>
<td>FRLS</td>
<td>Forced Rayleigh Light Scattering</td>
</tr>
<tr>
<td>FRS</td>
<td>Forward Recoil Spectrometry</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>h</td>
<td>thickness of initial diffusing slab</td>
</tr>
<tr>
<td>h-PS</td>
<td>hydrogenous polystyrene</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>HE3CALC&lt;sup&gt;™&lt;/sup&gt;</td>
<td>Program to calculate collision kinematics</td>
</tr>
<tr>
<td>&lt;sup&gt;3&lt;/sup&gt;He</td>
<td>Helium ion, singly-charged, mass 3</td>
</tr>
<tr>
<td>&lt;sup&gt;4&lt;/sup&gt;He</td>
<td>Helium ion, doubly-charged, mass 4</td>
</tr>
<tr>
<td>IOH</td>
<td>Iodohexane</td>
</tr>
<tr>
<td>IRM</td>
<td>Infra-Red Microdensitometry</td>
</tr>
<tr>
<td>k&lt;sub&gt;B&lt;/sub&gt;</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>keV</td>
<td>kiloelectronvolt</td>
</tr>
<tr>
<td>L</td>
<td>tube length</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight</td>
</tr>
<tr>
<td>M&lt;sub&gt;c&lt;/sub&gt;</td>
<td>critical molecular weight for entanglements</td>
</tr>
<tr>
<td>M&lt;sub&gt;e&lt;/sub&gt;</td>
<td>molecular weight between entanglements</td>
</tr>
<tr>
<td>M&lt;sub&gt;o&lt;/sub&gt;</td>
<td>monomer molecular weight</td>
</tr>
<tr>
<td>MCA</td>
<td>Multi-Channel Analyser</td>
</tr>
<tr>
<td>MCB</td>
<td>Multi-Channel Buffer</td>
</tr>
<tr>
<td>MeV</td>
<td>megaelectronvolts</td>
</tr>
<tr>
<td>MHz</td>
<td>megahertz</td>
</tr>
<tr>
<td>MV</td>
<td>megavolts</td>
</tr>
<tr>
<td>NaOH</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>NEWONE21™</td>
<td>Program to extract diffusion coefficients from data</td>
</tr>
<tr>
<td>NIM</td>
<td>Nuclear Instruments and Methods</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>NRA</td>
<td>Nuclear Reaction Analysis</td>
</tr>
<tr>
<td>p</td>
<td>proton</td>
</tr>
<tr>
<td>P</td>
<td>matrix molecular weight</td>
</tr>
<tr>
<td>PES</td>
<td>poly(ethersulphone)</td>
</tr>
<tr>
<td>PIXE</td>
<td>Proton-Induced X-ray Emission</td>
</tr>
<tr>
<td>PO</td>
<td>phenoxy</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PTFE</td>
<td>poly(tetrafluoroethylene)</td>
</tr>
<tr>
<td>QELS</td>
<td>Quasi-Elastic Light Scattering</td>
</tr>
<tr>
<td>R</td>
<td>end-to-end distance</td>
</tr>
<tr>
<td>R_H</td>
<td>radius of diffusing coil</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford BackScattering</td>
</tr>
<tr>
<td>sPS</td>
<td>sulphonated polystyrene</td>
</tr>
<tr>
<td>SENMR</td>
<td>Spin-Echo Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>SO_3Na</td>
<td>sodium sulphonate</td>
</tr>
<tr>
<td>STOP™</td>
<td>program to calculate energy-loss with depth</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>t_R</td>
<td>characteristic reptation time</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>T_g</td>
<td>glass-transition temperature</td>
</tr>
<tr>
<td>TALYSTEP™</td>
<td>Stylus measurement of film thickness</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-Of-Flight</td>
</tr>
<tr>
<td>TURBOBASIC™</td>
<td>computer language used for customised programs</td>
</tr>
<tr>
<td>UCST</td>
<td>Upper Critical Solution Temperature</td>
</tr>
<tr>
<td>WLF</td>
<td>Williams-Landel-Ferry</td>
</tr>
<tr>
<td>x</td>
<td>depth normal to surface</td>
</tr>
<tr>
<td>x̅</td>
<td>average depth</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>Δ</td>
<td>Experimental resolution</td>
</tr>
<tr>
<td>Δ_{int}</td>
<td>intrinsic resolution of detector</td>
</tr>
<tr>
<td>Δ_{noise}</td>
<td>electronic noise contribution to resolution</td>
</tr>
<tr>
<td>Δ_θ</td>
<td>angle subtended by detector at sample</td>
</tr>
<tr>
<td>Δ(x)_θ</td>
<td>angular spread contribution to resolution</td>
</tr>
<tr>
<td>θ</td>
<td>detection angle</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>( \zeta_0 )</td>
<td>monomeric friction coefficient</td>
</tr>
<tr>
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<td>zero shear rate viscosity</td>
</tr>
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<td>( \sigma )</td>
<td>standard deviation</td>
</tr>
<tr>
<td>( \mu C )</td>
<td>microCoulombs</td>
</tr>
<tr>
<td>90k</td>
<td>90,000 molecular weight</td>
</tr>
<tr>
<td>1.8M</td>
<td>1,800,000 molecular weight</td>
</tr>
</tbody>
</table>
**Chapter 1: Introduction**

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Polymer systems</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1</td>
<td>Ionomers</td>
<td>3</td>
</tr>
<tr>
<td>1.1.2</td>
<td>Aims of this work</td>
<td>8</td>
</tr>
<tr>
<td>1.2</td>
<td>Review of techniques for studying polymer diffusion</td>
<td>8</td>
</tr>
<tr>
<td>1.2.1</td>
<td>Rutherford Backscattering</td>
<td>10</td>
</tr>
<tr>
<td>1.2.2</td>
<td>Infra-red Microdensitometry</td>
<td>12</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Fluorescence Recovery After Pattern Photobleaching</td>
<td>12</td>
</tr>
<tr>
<td>1.2.4</td>
<td>Forced Rayleigh Light Scattering</td>
<td>13</td>
</tr>
<tr>
<td>1.2.5</td>
<td>Radioactive Tracer</td>
<td>14</td>
</tr>
<tr>
<td>1.2.6</td>
<td>Secondary-Ion Mass Spectrometry</td>
<td>16</td>
</tr>
<tr>
<td>1.2.7</td>
<td>Elastic Recoil/Forward Scattering</td>
<td>18</td>
</tr>
<tr>
<td>1.2.8</td>
<td>The $^3$He-d Technique</td>
<td>19</td>
</tr>
<tr>
<td>1.3</td>
<td>Descriptions of diffusion</td>
<td>20</td>
</tr>
<tr>
<td>1.4</td>
<td>Outline of this work</td>
<td>24</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Polymer systems

Recent years have seen an explosive proliferation in the applications of polymers as engineering materials. The versatility of polymer materials has been the chief reason for their popularity amongst engineers, with the volume of polymers used in the Western economy outstripping that of metals. Polymers can be fashioned to be rigid or flexible, opaque or clear and electrically-insulating or conducting. They have useful ranges of deformability and durability in a variety of environments and temperatures.

At the core of designing a polymer for a specific application must lie a knowledge of how the structure of a polymer affects the properties such as those listed above. The last decade has witnessed remarkable advances in establishing molecule structure-property relationships in polymeric systems. This thesis is concerned with the current challenge of structure-processability relationships.

Polymers are long chain-like molecules formed by chemically linking together small molecules known as monomers. The final molecular architecture can be linear, branched, cyclic or star-shaped, depending on the chemistry of polymerisation. The chain can also have pendant side-groups. Above a critical molecular weight, the polymer chains can interpenetrate to form an entangled network, giving the polymer increased structural stability. The application of heat or of a shear force can
nevertheless induce irreversible flow of chains past each other. Such polymers are referred to as "thermoplastics".

Another class of polymer exists, known as "thermosets", in which the molecular architecture involves chemical links between polymer chains, resulting in a network. The inter-chain links of a thermoset present certain advantages to the engineer in the form of improved properties. Specifically, a thermoset will stand a greater range of temperature and load than a thermoplastic; in order to produce irreversible flow, the chemical links of a thermoset have to be broken. However, the extreme conditions required to produce this disruption cause the material to degrade rather than melt, such that an inherent complication in the use of thermosets is the fact that they cannot be recycled.

It would be highly desirable, therefore, to develop polymeric materials which at once exhibit the structural properties of thermosets whilst retaining the processability of thermoplastics. This thesis is concerned with elucidating the structure of an exciting new class of polymer - "ionomers" - which research to date has shown to be a strong candidate for this rôle. Ionomers contain inter-chain links that are electrostatic in nature and which emulate chemical cross-links but are thermally labile, allowing reprocessing of the polymer without degradation.

1.1.1 Ionomers

Ionomers are a class of polymer consisting of a carbon backbone with
pendant acid groups randomly distributed along the chain, these groups having been neutralised to form salts. They have found applications in areas as diverse as thermoplastic elastomers, permselective membranes and microencapsulation membranes. Ionomer synthesis can be achieved in two ways: Firstly, by copolymerisation of a low level of functionalised monomer and, secondly, by direct functionalisation of a preformed polymer. The resultant acid is then neutralised partially or fully with an appropriate base to form a salt which is the final form of the ionomer. The concentration of acid groups is usually no greater than 1 per 10 backbone carbon atoms. Such modified thermoplastics do indeed exhibit superior chemical resistance, modulus and creep resistance [Kinsey, 1969].

Despite a considerable research effort there is still a lack of general agreement about the structure of ionomers. The central question concerns the distribution of salt groups in the bulk and the nature of the inter-chain links. In an early theoretical paper, Eisenberg [1970] assumed the ion-pair, consisting of the anion attached to the polymer and the metal cation present after formation of the salt, to be the fundamental structural entity. A small number of these ion-pairs can associate by means of dipole-dipole interactions to form small aggregates or "multiplets", resulting in pockets of ion-rich material in the hydrocarbon medium. The maximum number of ion-pairs contained in such a "direct-contact" aggregate is a consequence of the backbone's willingness to be deformed to allow this microphase segregation to take place.

Multiplets are thought to associate into larger aggregates, termed "clusters", with interspersed hydrocarbon material. As with individual
multiplets, cluster aggregation is favoured by electrostatic interactions. Each multiplet is, however, surrounded by a hydrocarbon "shell" of material attached to the ion-pairs in that multiplet, imposing a lower limit on the distance of closest approach of two adjacent multiplets. Clusters are therefore thought to be more loosely associated than multiplets.

The structure, size and energy characteristics of aggregates have been investigated by groups using a variety of techniques:

Low angle X-ray scattering [Wilson, 1968] has identified the existence of scattering centres in ionomer salts that are not present in the acid form, suggesting the existence of an ion-rich phase in the hydrocarbon matrix.

Far-infra-red spectroscopy of polymer salts [Tsatsas, 1971 and Rouse, 1979] has observed three resonances associated with the presence of ionic aggregates. The first resonance appears as the acid is neutralised, which suggests that it corresponds to the primary ion-pair. This conclusion is supported by the observation that the resonance shifts with a change in the mass of the cation used to neutralise the acid. Two more resonances appear as ionic functionality is increased, supporting the concept that the formation of aggregates is dependent on the concentration of ion-pairs.

Raman spectroscopy studies [Neppel, 1981] on various ionomers confirm that ionomers based on low polarity hydrocarbon backbones can be
viewed as consisting of three phases: matrix, multiplets and clusters. Two resonance bands observed in a sodium salt of polystyrene which do not appear in normal polystyrene are attributed to vibrational modes associated with the ions present in ionomers. Clusters having larger masses than multiplets, ion-pairs in clusters are expected to vibrate at lower energies than ion-pairs in multiplets. As ion content in the ionomer is increased the lower-energy band, corresponding to clusters, increases in intensity while the other band remains unchanged. This suggests that there is an upper limit on the multiplet concentration, beyond which additional ion-pairs contribute to clusters.

Electron microscopy [Longworth, 1975] confirms that profound structural changes occur upon neutralisation of polymer acids. Surface replicas of an acid copolymer show clear evidence of a lamellar structure typical of a crystalline morphology. The corresponding ionomer shows no such structure, having only a random grainy appearance.

The quantitative aspects of ionic aggregate size are somewhat ambiguous. Various models have been proposed, ranging from a homogeneous aggregate to a phase-separated cluster but no single model gives an adequate description of the wide range of structures observed and this area is currently the subject of intensive research. What is certain is that whatever form aggregates adopt, inter-chain interactions will reduce the mobility of the polymer by the addition of constraints over and above those normally encountered in the melt. The ionic group concentration at
which cluster formation first occurs in sulphonate ionomers is still an unresolved question [Fitzgerald, 1988].

The rheological behaviour of ionomers offers convincing evidence that microphase separation has a significant impact on properties [Agarwal, 1980]. Work to date in this area has invariably involved dynamic mechanical measurements, requiring the imposition of stress on the material. This thesis describes the first attempt at measuring the structure and rheological properties of ionomers by measurement of the centre-of-mass diffusion coefficient of polymers in ionomer systems. The attraction of measuring the intrinsic rheological behaviour of ionomers under zero strain-rate lies in the fact that it does not require any deformation of the sample, allowing its structure to be probed without incurring the possibility of perturbation due to stress.

This is achieved by observing the effect of ionic concentration on the centre-of-mass diffusion of polymer molecules; the natural flow of molecules past each other is greatly influenced by any inter-chain attraction and measurements of this flow should provide a sensitive indication of the inception of different stages of aggregation.

An ionomer that has proved popular with researchers is sulphonated polystyrene, S-PS. The precursor polymer, polystyrene, has a high thermal stability [Wegner, 1970] and its size, architecture and tacticity can be controlled to a high degree. It is therefore possible to conduct precise structure–property experiments on polystyrene and its derivatives.
The synthesis of S-PS is relatively straightforward [Makowski, 1975]. A sulphonic acid group can be substituted for the para hydrogen on the styrene side-group by a one-step electrophilic substitution reaction. This is then neutralised with a base such as sodium hydroxide to produce a sulphonate salt.

1.1.2 Aims of this work

In summary, therefore, the objectives of this project were:

i) to determine the concentration of sulphonic groups necessary to form aggregates,
ii) to determine the thermal stability of aggregates,
iii) to study mechanisms of polymer diffusion in ionomers.

1.2 Review of techniques for studying polymer diffusion

Several techniques are currently being used to measure polymer diffusion, a brief but complete review of which has been published by Mills [1988].

A common approach is to "tag" one of the polymers, allow it to penetrate a second polymer and to monitor its progress by collecting a concentration depth-profile of the tag. In order to infer mechanisms of polymer diffusion it is necessary to measure self-diffusion coefficients. There is concern, however, that tagging might have a significant effect on
diffusion behaviour. Therefore a desirable feature of a technique would be that it use a tag that keeps modification to a minimum or, where possible, dispense with tagging altogether.

Two other criteria that affect the choice of technique are sensitivity and depth resolution. Sensitivity describes the level of signal returned for a given input of effort, giving an idea of necessary analysis times. An example from the field of ion beams would be how much charge needs to hit the target to provide a statistically significant number of counts at the detector. From this estimate of charge, beam current and analysis time can be juggled by the experimenter to either increase sample throughput or minimise beam damage to the sample. The sensitivity of a technique also determines the detection limit, the minimum concentration of a substance that the technique can identify.

Resolution is a measure of the degree to which the signal can be distinguished from other, unwanted signals. In most diffusion measurements, the progress of one material through another is monitored, in which case it is more normal to speak of a depth-resolution. How this may vary with depth will be discussed at a later stage, with reference to a specific technique. It is important to note here that that it is desirable to use a technique with a sharp resolution as this enables diffusion over short distances to be measured accurately. This applies to situations where diffusion is slow, such as in networks of very long molecules, and is also particularly useful when there is a suspicion that no diffusion has taken place.
A characteristic diffusion distance is

\[ \bar{x} = 2 \sqrt{Dt} \]

where \( D \) is typically \( 10^{-13} \) cm\(^2\)/sec. In this situation, diffusion over 1 \( \mu \)m would take 25000 seconds and over 100 \( \AA \) would take 2.5 seconds. The presence of any interchain bonding will oppose diffusion, increasing the diffusion time-scale and in order to keep experimental diffusion times viable depth-resolution must be at least an order of magnitude smaller than 1 \( \mu \)m.

1.2.1 Rutherford Backscattering

Rutherford Backscattering (RBS) involves bombarding a sample with an ion beam, usually \(^4\)He\(^+\), and measuring the kinetic energy of particles elastically scattered in a backward direction. A necessary condition for backscattering to occur is that the target atom be heavier than the beam ion, so hydrogen cannot be detected. The recoil energy is a fraction of the energy at collision, that fraction increasing with target mass.

The maximum probe depth of RBS as applied to polymers depends on the beam energy used but is typically of the order of 2 \( \mu \)m. This can be reduced quite substantially, however, by the presence of other heavy elements in the sample, as the signals from these may overlap and produce a confusing spectrum.
The resolution achieved by RBS is very good, around 30 nm, and sensitivity increases with mass so there is a trade-off between the concentration of tags and their impact on the physical situation; a heavy tag can be profiled to a large depth before its signal overlaps with that from carbon, whereas the use of a light tag minimises the effect of tagging on the behaviour of the polymer in the melt.

RBS can be applied in two ways: The first method has been mentioned above and basically exploits the presence of a heavy element in one of the diffusants. This method has been applied successfully to the diffusion of small molecules in polymers [Payne, 1988]. Tagging a polymer with a heavy element is, however, far from satisfactory. Firstly, it is a non-trivial problem from a chemical stand-point and, secondly, it is felt that this will modify the physical properties of the polymer significantly, yielding results which do not accurately reflect the self-diffusion process.

Instead, in the second method, a thin layer of a heavy element, typically gold [Green, 1984], is sandwiched between two polymer layers. As these interdiffuse, the molecules move past the gold "markers". Any imbalance in the mobilities of the two layers will result in a net displacement of the gold. This can be caused by using polymers of differing molecular weights, a shorter molecule will diffuse into a matrix of longer molecules faster than the reverse will occur. By measuring the depth of the gold after various annealing times, a figure for the self-diffusion coefficient, $D_s$, of the shorter polymer can be inferred. This method is comparable to the Kirkendall effect in metals and as such is most suited to an asymmetric diffusion couple, with one molecular weight much greater than the other.
and consequently, is of no use in measuring self-diffusion.

1.2.2 Infra-red Microdensitometry

Infra-Red Microdensitometry (IRM) requires the presence of some functional group in the polymer that absorbs strongly at an infra-red frequency against little absorption in the matrix [Klein, 1979]. The IR-sensitive molecule is present as a dispersion in the polymer matrix. A narrow slice of such a polymer is placed in contact with a slice impervious to infra-red. The diffusion broadening of the initial step-function is monitored by scanning the intensity transmitted by the area around the interface. This requires sectioning of the sample normal to the interface.

The limitation of the technique is the depth-resolution of 100 μm which, for realistic diffusion times, limits D to the range $2 \times 10^{-10} \text{cm}^2\text{s}^{-1}$ to $10^{-5} \text{cm}^2\text{s}^{-1}$ and rendering IRM unsuitable for the experiments proposed here. Similarly to the gold marker use of RBS, there are doubts as to how much the physical situation is altered by the presence of the additive, though IRM seems to be an ideal method for measuring the progress of a specific additive through a given polymer.

1.2.3 Fluorescence Recovery After Pattern Photobleaching

Fluorescence Redistribution after Pattern Photobleaching (FRAPP) makes use of fluorescent dyes which can be irreversibly bleached by intense light
[Wang, 1987]. A small area of sample is bleached by a strong laser beam and the subsequent fluorescence from the area monitored by a weak light beam. As fresh fluorescent molecules diffuse into the bleached area, the fluorescence recovers to its pre-bleaching value and the diffusion coefficient of the probe molecules is obtained from the recovery rate.

This technique has been applied to epoxy resins [Wang, 1987] to identify the onset of cure at different temperatures. It has also been used [Smith, 1982] to measure high polymer diffusion. The diffusion referred to is that of a solvent in a polymer film and it is measured in a similar fashion to that described above. As such, FRAPP is not suitable for self-diffusion measurements as it measures the movement of dye molecules in a surrounding polymer matrix, rather than observing polymer molecules in motion directly. FRAPP can be used for diffusion measurements when the fluorophore is attached to the polymer chain but this involves a substantial modification of the starting polymer and the observed diffusion cannot therefore be considered as self-diffusion.

1.2.4 Forced Rayleigh Light Scattering

Forced Rayleigh Light Scattering (FRLS) also relies on the use of dyes. Laser beams are used to produce a sinusoidal interference pattern in a system consisting of a polymer, a dye and a solvent. In the dark bands of the resultant grating, the dye molecules have been isomerized into a different form. The sample is then illuminated with a "read-out" laser to measure the diffracted intensity at a fixed angle. As the two isomers
interdiffuse, the diffracted intensity decays exponentially with time, from which a diffusion coefficient can be extracted.

Widmaier [1989] goes some way to improving the suitability of FRLS by labelling one half of a batch of polymer with a chromophore. In this way the need for free dye molecules is removed, simplifying the diffusion situation. The unlabelled half of the batch is used for characterization and diffusion measurements are performed as normal on the labelled, light-sensitive polymer.

Although with these changes FRLS is measuring diffusion directly, it is still measuring the diffusion of a modified polymer. It will never provide measurements of the intrinsic polymer. This, together with Widmaier's admission of the difficulty in preparing the materials, makes FRLS unsuitable for the work proposed here.

1.2.5 Radioactive Tracer

Kumagai [1979] used tritium-labelling to monitor diffusion in polystyrene. A thin layer of radioactively-labelled polymer was applied to the top surface of a thick film of unlabelled polymer. Interdiffusion was followed by the change in strength of the radioactive signal in the originally unlabelled domain. Diffusion coefficients were extracted by fitting theoretical functions to the observed decrease in count-rate.

Whilst the use of isotopic labelling ensures minimal modification of the
polymer's physical and chemical properties, the technique does not measure the detailed concentration-profile in the sample. As a result information is lost as, without measuring the complete concentration profile across the interface, one has very little way of knowing whether diffusion is proceeding normally or is being perturbed by something abnormal at the interface.

There are two techniques available that do not require the diffusing molecules to be labelled. These are spin-echo nuclear magnetic resonance (SENMR) [von Meerwall, 1983 and Fleischer, 1987] and quasi-elastic light-scattering (QELS) [Chu, 1974]. Both perform direct measurements on the degree of movement in a sample, relating response times to a diffusion coefficient. At best, used in pulsed mode, SENMR has a lower limit of $10^{-14} \text{ cm}^2 \text{s}^{-1}$ on measurements of the diffusion coefficient, D. Other techniques can improve on this by several orders of magnitude by using longer sample-treatment times. Whilst QELS in slow mode is reported to yield measurements down to $10^{-17} \text{ cm}^2 \text{s}^{-1}$, there is at present no accepted theory to support it and self-diffusion coefficients produced using QELS are inferred from results obtained for diffusion in solution, whereas one would like to observe melt diffusion directly.

There are also two techniques that use isotopic labelling of polymers as a means of distinguishing between the two halves of polymer bilayer. In both, some of the hydrogen has been replaced by deuterium. In this manner it is hoped that modification of the chemical and physical properties of the polymer is minimised.
1.2.6 Secondary-Ion Mass Spectrometry

Secondary-Ion Mass Spectroscopy (SIMS) has been used to perform a quantitative analysis of diffusion in a deuterated-protonated bilayer system [Whitlow, 1989]. Atoms or clusters of atoms are sputtered out of a sample surface by a beam of heavy, primary ions. A small number of these atoms undergo charge exchange with their local environment and, as secondary ions, are analysed by a mass spectrometer. Depth-profiling is performed by collecting consecutive mass spectra as the primary ion beam erodes the sample surface and spectra are originating from ever-increasing depths relative to the initial sample surface.

This technique achieves a depth-resolution of 10 - 15 nm and produces direct depth-profiles of hydrogen and deuterium, such that the interdiffusion of a deuterated and a hydrogenated polymer can be monitored. Whilst on this evidence SIMS seems an ideal technique for measuring polymer diffusion, there are certain complications associated with its use.

Obviously a major problem in working with polymeric systems is charge build-up. Positive ions are being injected into an insulating substrate. This can be overcome by flooding the irradiated area with low energy electrons and the largest area over which imaging can be achieved is then determined by the requirements for uniform charge neutralisation. Furthermore, the primary ion beam must be of low current density, typically 1 nA cm$^{-2}$, in order to eliminate sample damage and consequent
atomic mixing during spectral acquisition. Work by Briggs [1986] on the
ion-beam damage rates of polystyrene and poly(methyl methacrylate) has
shown that the threshold dose for damage is $2 \times 10^{13}$ ions cm$^{-2}$ but that
undamaged spectra can be obtained with doses well below this (5%).

This threshold, however, applies to static SIMS, wherein sputtering is
restricted to the top few atomic monolayers and materials can be
identified by their characteristic groups. Depth-profiling with SIMS
requires use of the dynamic mode and the correspondingly higher current
densities used to etch a sample effectively degrade molecular information
in the immediate sub-surface region. The loss of such information rules
out the use of dynamic SIMS in the extraction of concentration-profiles of
interdiffused dissimilar polymers unless an isotopic tag is used to
distinguish between polymers, as done by Whitlow (1989).

In situ depth measurements are very difficult as the sputtering rate
varies between targets. A depth scale is obtained by assuming the
sputtering rate to have been constant throughout a measurements and by
measuring the depth of the sputtered crater.

An intrinsic feature of SIMS is sample destruction. It is not possible to
analyse a bilayer before and after an anneal; such data must be inferred
from two similar samples. While progress is being made in other areas of
the technique, by using time-of-flight mass spectrometers to improve
sensitivity and pulsed beams to reduce the charging problem, the
destructive nature of SIMS cannot be avoided. This necessary interpolation
of data from different samples, together with the ambiguity of any
depth–scale used made SIMS an impractical candidate for this work.

1.2.7 Elastic Recoil/Forward Scattering

Elastic Recoil Detection Analysis (ERDA) was developed to study hydrogen in the near-surface region of solids [Turos, 1984]. A beam of $^4\text{He}^+$, incident on the sample at a glancing angle, scatters nuclei out of the material. A stopper foil over the detector removes elastically-scattered beam ions and any heavier nuclei that may have been ejected so that only protons are detected. From a knowledge of energy-loss characteristics of protons and $^4\text{He}^+$ in the sample material and from elastic collision kinematics, the variation of hydrogen concentration with depth can be extracted from the proton energy histogram.

This technique was extended to measurements of polymer diffusion by Mills [1984], the new method being christened Forward Recoil Spectrometry (FRS). By labelling one polymer with deuterium and diffusing it into a matrix of unlabelled, hydrogenous polymer a deuterium depth-profile can be generated by ERDA. This is directly analogous to a concentration-profile of the labelled polymer from which the extent of diffusion can be ascertained.

The limitations on the technique are chiefly due to the glancing incidence that is necessary to ensure the escape of scattered nuclei. Diffusion can be followed down to just under 1 μm in depth, before the D and H profiles begin to overlap on the energy spectrum. Resolution is impaired by straggling in the stopper foil, typically 80 nm. So, while there is more
confidence in FRS giving a truer picture of polymer self-diffusion, the profiling depth and subsequent orders of magnitude of $D_s$ that can be measured, together with the depth resolution, are clearly inferior to RBS which is still far from ideal for the experiments proposed here.

Recent improvements to ERDA have been implemented by Sokolov [1989]. By replacing the stopper foil with a time-of-flight (TOF) detector He and H recoils could be separated without incurring significant energy-straggling. The improved technique of ERDA-TOF can achieve depth resolutions of the order of 35 nm at the sample surface. While this performance compares well to that of RBS, the limited profiling-depth of ERDA-TOF restricts its usefulness to the study of polymer surfaces.

1.2.8 The $^3$He-d Technique

This technique was developed at Surrey as it is clear that it is the optimum technique for this project when applied to the specific question of measuring polymer self-diffusion.

The following chapter will show, that the $^3$He-d technique, hereafter referred to simply as $^3$He-d, is a non-destructive ion beam technique that can yield a depth-profile of a deuterium-labelled polymer up to 8 μm with a top resolution of 40 nm. It exploits the best feature of ERDA, namely requiring only isotopic labelling. $^3$He-d yields a concentration-profile of the polymer diffusing in the melt over a wide range of diffusion coefficients with the attractive feature that samples can be analysed
several times, enabling before and after anneal spectra to be collected from the sample.

Other advantages of this technique are the ease with which samples can be prepared and the speed of analysis. Samples consist of a bilayer of deuterated polymer on hydrogenous polymer. Polymer films are prepared by drying a polymer solution on a glass slide and floating the resultant film off on water. Analysis time depends on the beam current and deuterium concentration used but sample-friendly currents typically yield sufficient counts for statistically-reliable profiles in 30 minutes.

1.3 Descriptions of diffusion

In order to interpret data for the ionomer systems it is necessary to understand diffusion behaviour in the precursor polymer. Kramer [1985] has summarised current thought on the equations describing the processes by which a polymer molecule diffuses.

Interest in the mixing of two layers of chemically identical polymer was triggered by attempts at crack healing. It was found that the strength of a joint repaired by heating above the glass-transition temperature, \( T_g \), increased at a rate dependent on the molecular weight of the material and the temperature of annealing. This suggests that the healing process is governed by the diffusion kinetics of the material; only when there has been thorough mixing across the crack and the material is indistinguishable from the original polymer will the full strength be
reached.

The effect on the polymer of changing its chemistry or physical environment can be studied by measuring self-diffusion as this is sensitive to any modification that affects the polymer's ability to translate, rotate or vibrate on a molecular and segmental scale.

On a simple level, a polymer chain can be considered as a large molecule with its centre-of-mass motion affected by the ambient temperature and the frictional drag exerted by adjacent molecules. Beyond a certain length, however, a chain becomes entangled with others thus adding a further constraint to its motion and complicating the diffusion situation.

The critical length for entanglement to occur, expressed as a critical molecular weight \( M_c \), was found by measuring the zero shear rate viscosity at several values of the molecular weight, \( M \). At \( M_c \), there is an abrupt change in the index of the molecular weight dependence of the viscosity, implying a fundamental structural difference. This view is supported by modulus measurements, which show a rubbery plateau for \( M > M_c \).

**The Rouse model**

This model restricts itself to the effect of friction, using the Einstein relation

\[
D = \frac{k_B T}{f}
\]

defining the frictional drag per unit velocity as
where $M_0$ is the monomer molecular weight, $M$ is the chain molecular weight and $\zeta_0$ is the monomeric friction coefficient.

The Rouse diffusion coefficient is therefore

$$D_{RO} = \frac{k_B T M_0}{\zeta_0 M}$$

This model does not take into account the added effect of entanglements and can therefore only be applied to the $M < M_c$ regime.

The Reptation model

In this model the chain is considered to wander randomly along a virtual tube whose shape is defined by the constraints imposed by its entangled neighbours. The tube length, $L$, is proportional to $M$ but, due to conformational randomness, is less than the chain contour length. The matrix molecular weight, $P$, is irrelevant as the constraints are assumed to be fixed. Diffusion along the tube is governed by friction, hence $D_{RO}$ applies in the tube. After a characteristic time $t_R'$, the chain has escaped the initial tube.

$$t_R' \propto L^2 \propto M^3$$
The centre-of-mass of the chain has travelled a distance proportional to the root-mean-square end-to-end distance, \( <R^2>^{1/2} \), in this time and the centre-of-mass diffusion coefficient is therefore given by

\[
D^* \propto \frac{<R^2>}{t_R} \propto M^{-2}
\]

where \( <R^2> \) scales as \( M \).

The reptation model is a recent development proposed and pioneered by de Gennes [1971]. Self-diffusion measurements in polyethylene [Klein 1978] have showed good agreement with the model and, very recently, Kremer's [1990] computer simulations involving equations of motion for each monomer in each molecule have observed all the effects predicted by the reptation model, finding that polymers do "move in something like a constraining tube".

**The Constraint Release model**

In this model, which is an extension of the reptation model, the molecules imposing constraints on the "reptating" chain are allowed to move on a similar timescale. This will occur when \( M \approx P \), assuming that the matrix contains no chemical cross-links. The tube containing the M-chain diffuses by reptation, giving rise to the term "constraint release".

By considering constraint release as motion of the tube through a viscous matrix of P-chains, the friction coefficient varies with \( L \) and \( \eta_0 \), the zero shear rate viscosity at \( M = M_c \).
The Coil Diffusion model

At very high $M$, the specific shape the penetrant molecule will assume will be commensurate with its minimum free-energy conformation in a given molecular environment. The increasing significance of intratube hydrodynamic interactions will result in the chain diffusing as a coil of radius $R_H$. Its motion is described by the Stokes-Einstein equation

$$D_{SE} = \frac{k_B T}{(6\pi \eta_0 R_H)} \propto M^{-1/2} P^{-3}$$

As this effect is predicted to occur for $M > 3 \times 10^7$, it can be neglected when considering commercial polymers as these are typically orders of magnitude shorter.

1.4 Outline of this work

The presentation of the work carried out in the course of this project has been arranged into chapters as follows. In Chapter 2, $^3$He-d will be explained in detail and its performance compared to existing methods. Chapter 3 will treat the matter of ion beam damage to the sample. A discussion of the chemical reactions used to prepare and deuterium-label
ionomers of polystyrene in Chapter 4 will then be followed by an account of sample preparation. Chapter 5 will present the results from the diffusion experiments in conjunction with the rationale behind each experiment and their implications discussed in terms of the various diffusion models available.

Finally it is hoped that this work will provide polymer physicists with a powerful tool and promote the cause of ionomers as the next generation of polymer materials.
# Chapter 2: The Technique of $^3$He-d Nuclear Reaction Analysis

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Nuclear Reaction Analysis</td>
<td>27</td>
</tr>
<tr>
<td>2.2 Portrait of the d($^3$He,p)$^4$He reaction as a charged particle technique</td>
<td>29</td>
</tr>
<tr>
<td>2.2.1 The case for backward angles</td>
<td>31</td>
</tr>
<tr>
<td>2.2.2 Interpreting the energy-scale</td>
<td>36</td>
</tr>
<tr>
<td>2.3 Measuring Diffusion Profiles</td>
<td>39</td>
</tr>
<tr>
<td>2.4 Measuring the Resolution</td>
<td>52</td>
</tr>
<tr>
<td>2.5 Refinements to the technique</td>
<td>65</td>
</tr>
<tr>
<td>2.6 Summary</td>
<td>68</td>
</tr>
</tbody>
</table>
Chapter 2: The Technique of Nuclear Reaction Analysis

From the previous chapter we have identified our requirements from a technique; it must allow us to measure self-diffusion, by differentiating between two layers of the same polymer. It must do this without radical alteration of either polymer such that diffusion behaviour remains unaffected. Ideally, it would also yield a direct concentration-profile of the diffusing polymer such that a diffusion coefficient could be extracted, although this and non-destruction of the sample would be a bonus.

2.1 Nuclear Reaction Analysis

The name "Nuclear Reaction Analysis" (NRA) applies to a group of techniques, each of which has at its core the exploitation of a specific nuclear reaction. These techniques are ideally suited to measuring trace impurities in bulk samples, due to their isotopic specificity. The reaction can be initiated by neutrons, γ-rays or charged particles and measurements of the reaction products can be interpreted to yield concentration information.

In particular, charged-particle-induced nuclear reactions have many attractive features and these can be summarised as follows:

- There is no natural background.
- A high Q-value reaction can be triggered by low-energy particles, requiring little acceleration and reducing sample
heating. Furthermore, the high Q-value ensures energetic reaction products which can escape from substantial depths within the sample, thereby extending the probe depth of the technique.

- Reactions are confined to low-Z nuclei by Coulomb repulsion, allowing trace concentrations to be detected in heavy substrates.
- Reactions are very isotope-specific.
- Results are generally independent of the chemical or physical state of the nuclei as the reaction yield depends only on the nuclear cross-section.
- Measurements are non-destructive and quick.
- Depth distributions can be determined directly in the top few microns of a sample with a resolution of 0.1 μm or better.

Due to these beneficial features charged particles have seen widespread application in the field of materials analysis: Oxygen diffusion in metals has been studied by deuteron beams [Amsel, 1968] and in quartz by proton bombardment [Palmer, 1965]. Amsel [1971] have used charged particles to measure small quantities of $^{16}\text{O}$, $^{18}\text{O}$, $^{14}\text{N}$, and $^{19}\text{F}$ by bombarding with protons and deuterons and detecting alpha particles, protons and γ-rays. Ziegler [1978] have used a number of techniques to profile hydrogen in materials, one of which is based on the reaction of $^3\text{He}$ with a deuteron.
2.2 Portrait of the $d(^3\text{He},p)^4\text{He}$ reaction as a charged particle technique.

A reaction between $^3\text{He}$ and $^2\text{H}$ (deuterium) has been identified by Yarnell [1953] who bombarded gaseous $^3\text{He}$ with energetic deuterons. This $d(^3\text{He},p)^4\text{He}$ reaction has a strong resonance (0.9±0.1 barns), the cross-section maximum being at a deuteron energy of 430±30 keV. The energetic yield of the reaction is 18.352 MeV, with the result that both the emitted particles have energies greater than the incident particle.

Extensive work has been done using this reaction to study $^3\text{He}$ concentrations in metals and materials for fusion reactor walls [Pronko, 1974; Picraux, 1974; Langley, 1974] by energy-analysing the $^4\text{He}$ ions. Langley have shown that depth resolution is enhanced since both incident and emitted particles lose energy on their paths through the sample. This is enhanced for emission angles $\leq 75^0$, i.e. a forward scattering arrangement. At these angles, the emitted $^4\text{He}$ energy decreases as the incident particle energy decreases such that particles emitted from reactions occurring at a depth in the sample will have lower energies than those from events taking place at the sample surface. Forward scattering from a thick sample necessitates a glancing incidence arrangement which improves the depth resolution still further by stretching out the depth-scale vis-a-vis the energy scale.

The reaction has also been used in its reverse form to study deuterium concentrations in various materials [Moeller, 1978; Boergesen, 1978; Alstetter, 1978] by using a beam of $^3\text{He}$ ions. This $d(^3\text{He},p)^4\text{He}$ reaction
is identical to that discussed above when observed in the centre-of-mass frame.

There are two distinct methods of applying nuclear reactions with charged particles, depending on the width of the resonance in the particular nuclear reaction. In the case of a narrow resonance depth-profiles are obtained by total yield measurements. The incident particle energy is increased in steps to increase the depth within the sample at which the resonance occurs with the yield giving a measure of the concentration at that depth. For nuclear reactions involving wide resonances this method is impracticable. Instead, a depth-profile obtained using a wide resonance is evaluated directly from the energy spectrum of an emitted particle.

The d(\(^3\)He,p)\(^4\)He reaction falls into the latter category, ranging from 400 keV to upwards of 2.5 MeV with a maximum at 650 keV [Altstetter, 1978]. A sample containing a deuterium concentration profile and bombarded by a monoenergetic beam of \(^3\)He ions emits protons and alpha particles with a range of energies. The final energy of a reaction product varies with the depth at which the reaction occurred. This parameter uniquely defines other variables affecting the emitted energy, such as energy-loss of the incoming ion and of the exiting reaction product resulting from travel through the sample. Consequently, by measuring a particle’s energy and taking into account the experimental geometry, the depth of reaction can be determined within the experimental errors due to detector resolution and statistical effects such as energy straggling.

An energy-histogram is then accumulated to show the relative frequencies
of particle energies and this can then be interpreted as a first approximation to the concentration depth-profile of deuterium, provided the resolution is reasonable. This approach was first used with the alpha particles in a forward scattering arrangement [Langley, 1974; Boergesen, 1978], using oblique incidence and take-off angles for reasons of depth-resolution and maximisation of the emitted alpha particle's energy.

2.2.1 The case for backward angles.

Dieumegard [1979] advocated the detection of protons at backward angles as an improvement on alpha-detection at forward angles on the grounds of improved performance, the rationale for which is outlined below.

The reaction products are produced in the centre-of-mass frame with equal and oppositely-directed momenta. As such, the kinetic energy is shared unequally, according to the relation

\[
\frac{E_p}{E_\alpha} = \frac{m_\alpha}{m_p}
\]

arising from classical energy and momentum relations, where \(E_p\) and \(E_\alpha\) are the proton and alpha particle energies, respectively, and \(m_p\) and \(m_\alpha\) are their respective masses. From the Q-value of 18.352 MeV [Dieumegard, 1979], the respective kinetic energies of proton and alpha particle are 14.661 MeV and 3.691 MeV for an incident \(^3\)He energy of 0 MeV. As protons are more penetrating than alpha particles it is therefore immediately
clear that this proton will have a far greater range in matter than the alpha particle. Consequently, this makes a backscattering arrangement possible as the proton will be able to escape from greater depths in the sample than the alpha particle.

Detecting the alpha particle at backward angles produces an inferior depth-resolution; the alpha's emission energy to backward angles from the point of reaction increases as the beam energy falls. At a point within the sample, therefore, the alpha particle will be produced with a greater energy while having more material to traverse than an alpha particle produced at a point near the surface. These two effects of backward kinematics and energy-loss in matter will partially cancel out, resulting in a narrow alpha particle energy-spectrum. Conversely, in the forward direction, these effects combine to spread the same alpha-spectrum over a greater energy-range, giving a sharper resolution and explaining Langley's choice of method.

When detecting the protons, however, they have such a high kinetic energy that they lose virtually no energy in traversing a few microns of material. Their final energy at the point of detection is therefore only a function of the beam energy at the point of reaction and the angle of detection with respect to the beam direction. The depth information is carried predominantly by the energy-loss of the beam ion to the point of reaction. Resolution due to energy-loss and kinematics is similar at all angles.

For the largest probe-depth, which is achieved using a normal incidence,
the mechanics of sample analysis point strongly towards a backscattering configuration. The situation is similar to that of scattering and transmission electron microscopy; detection in the forward direction requires a thin sample to allow the signal to reach the detector, resulting in fragile samples.

A possible argument in favour of a forward scattering arrangement was that of reaction cross-section; a significantly larger cross-section for either configuration would ensure a higher count-rate at the detector, saving time and money. A comparison of the cross-sections was therefore performed to verify this. Yarnell [1953] has measured the cross-section of the d(³He,p)⁴He reaction at a laboratory angle of 86° for ³He-energies between 400 and 1300 keV, as shown in Figure 2.1. Whilst the angle used in the present work was the backward angle of 165°, Figure 2.1 shows that the cross-sections at the two angles differ only slightly. This suggests a quasi-isotropic emission of reaction products, which is explained by the large Q-value of the reaction. The products share circa 18 MeV while the beam energy is typically nearer 1 MeV. As such, the velocity of the centre-of-mass is a minor correction to the products' velocity vectors.

An experimental aspect that favours proton detection at backward angles is the angular dependence of a reaction product's energy. Langley [1974] demonstrates that dE/dθ is considerably smaller in the region of 170° than it is at around 60° to the beam direction. Figure 2.2 shows this to also be the case for protons. This is a strong argument in favour of using backward angles as the physical dimension of the detector will induce less of an energy-spread at the detector. A larger detector can therefore be
Figure 2.1: Reaction cross-sections versus energy taken from Yarnell, 1953 (top) and this work.
Figure 2.2: Proton and alpha energy-dependence on beam energy and angle of emission, taken from Langley, 1974 (left) and this work.
used, ensuring a higher count-rate, without the need to restrict the angular acceptance by means of a pinhole or slit.

Proton detection is less open to confusing events arising from other reactions, especially in mixed-element samples with significant concentrations of light elements. Interactions between $^3$He and the elements Li, Be and B can produce alpha-energies similar to those arising from deuterium reactions. Proton energies produced by these reactions do not overlap with those from deuterium, thereby ensuring spectra free from distortion by "false" counts.

The reaction is a broad resonance, peaking at 70 millibarns per steradian (mb/sr) at an energy of 650 keV \(^3\)He lab energy and at all times greater than 20 mb/sr for the range quoted. Some of the reactions mentioned above leading to "false" counts have cross-sections of the order of 1 mb/sr [Dieumegard, 1979] and can therefore be a confusing element. In deuterated materials containing light elements such as listed above, it is essential to proceed by detecting the protons.

In summary, the detection of backscattered protons has been shown to be the stronger candidate for the proposed work and the following section will show how the technique as a whole is applied to the task of measuring diffusion in polymers.

2.2.2 Interpreting the energy-scale
Viewed in the centre-of-mass frame, the reaction products are emitted with equal and oppositely-directed momenta. This frame has a velocity relative to the laboratory frame which is purely dependent on the energy of the beam ion, as the deuterium is taken to be at rest by comparison. The velocities of the reaction products seen in the lab frame are the resultant of the addition of their respective centre-of-mass velocities with the velocity of the centre-of-mass [Figure 2.3].

Two important features are worthy of note here to facilitate the interpretation of the technique. Firstly, the energy of a reaction product is a function of the $^3$He energy and the angle of emission. The proton has an energy significantly larger than that of the beam ion and is intrinsically more penetrating. It therefore loses very little energy over the range of sample material sufficient to stop the beam ion. This can be extended to say that the proton energy is purely dependent on the angle of emission and on the energy of the beam ion at the point of reaction.

Secondly, for products emitted in a backward direction, towards the beam source, the energy falls as the beam energy increases. As the beam ion's energy decreases, so does the velocity of the centre-of-mass in the laboratory frame. This velocity is always directed in the forward direction and as its magnitude falls, the backward component of the resultant increases. Consequently, reaction products emitted in a backward direction have a higher kinetic energy when the beam energy is lower.

So, due to the strong exothermic nature of the reaction between $^3$He and deuterium, protons arising from events within the sample and emitted in a
Figure 2.3: Schematic diagram of $^3\text{He}, p\rightarrow ^4\text{He}$ reaction.
backward direction are both produced and arrive at the detector with more kinetic energy than those produced at the sample surface.

2.3 Measuring Diffusion Profiles

Figure 2.4 shows the experimental arrangement used in the analysis chamber. A depth-profile of deuterium is obtained by probing the sample with a beam of $^3\text{He}^+$ ions obtained from a Van de Graaff generator. Analysis energies are typically in the range $0.7 - 2\ \text{MeV}$, the upper limit being imposed by the capabilities of the generator at Surrey. Below $0.7\ \text{MeV}$ the reaction cross-section falls off sharply, severely reducing the sensitivity. Energies in excess of $2\ \text{MeV}$ would not enhance the technique's performance. On the contrary, it will be shown below that depth-resolution grows worse above $1.5\ \text{MeV}$.

The sample consists of a deuterated polymer diffused into a hydrogenous polymer such that there is a deuterium concentration-profile normal to the sample surface [Figure 2.5]. A detailed account of sample preparation is presented in Chapter 4. A $^3\text{He}^+$ ion entering the sample can undergo a nuclear reaction with a deuterium atom, initially forming a compound excited state of $^5\text{Li}$ which then breaks up into an alpha particle and a proton.

A silicon surface barrier detector is placed at a backward angle to detect the protons and the alpha particles produced by reactions between beam ions and deuterium in the sample. The detector is essentially made up of
Figure 2.4: Schematic diagram of experimental arrangement.
Figure 2.5: Annealing bilayers to induce diffusion.
two layers of silicon, one p-type and the other n-type. A reverse bias voltage is then applied to this bilayer to create a "depletion region", a region void of charge carriers, around the junction between the two silicon types. All the bias voltage is dropped across the depletion region and this can lead to very localised, high electric fields which ensure the rapid separation of charge carriers and greatly reduces the chances of recombination and subsequent loss of signal. The depletion region is the sensitive volume of the detector and, for purposes of energy measurement, it is desirable to have an incident particle deposit all its energy in this region. This is achieved by the use of reverse biases of several hundred volts to maximise the sensitive volume.

When a particle enters matter, it loses energy by several processes, the most common of which is ionisation of the atoms in the stopping material. In the silicon surface barrier detector described above, this manifests itself as the creation of ion-hole pairs. In the normal state of silicon these carriers would eventually recombine but in the high-field depletion region they are pulled apart, rapidly swept away from the junction and to their respective ends of the silicon bilayer. This signal is expressed by the detector as a voltage pulse whose amplitude depends on the number of carriers created in the material by the passage of the incident particle.

There is a statistical fluctuation in the number of charge carriers produced by a particle of a given energy, independent of particle type [Knoll, 1979]. This results in a related spread in the pulse-heights produced by the detector. In the interests of resolution (which is discussed at length later), it is desirable that this spread be as narrow
as possible, so as to reduce the uncertainty in the energy of a given event. Following Poisson statistics, the uncertainty in counting N random events is simply $\sqrt{N}$. Expressed as a percentage, this uncertainty decreases with increasing N and a desirable feature of a detecting material is clearly that a large number of charge carriers be generated per event. Silicon is just such a material and has therefore seen widespread application in the detection of charged particles.

A further consideration which affects the choice and handling of a detector, is the ability of the detector to stop the incoming particle in the depletion region. Only in this manner can the full kinetic energy be measured. The particles produced in the $^3$He reaction with deuterium have very different ranges in matter. Figure 2.6 shows these differences [Skyrme, 1967]. It can be seen that a thin depletion region of around 100 $\mu$m might stop the alpha particles, registering the full energy of around 3 MeV, yet will only slow the protons, recording a fraction of their full energy of 14 MeV. Consequently, on an energy-frequency histogram, these signals could overlap and cause confusion.

In order to avoid this problem, a detector with a thick depletion region was employed [Figure 2.7]. The detector used for the work presented here was depleted to 1500 $\mu$m, whereas standard surface barrier detectors have 100 $\mu$m depletion regions. In this manner, the full kinetic energies of both particle types were collected and their respective counts were widely removed on the energy-spectrum.

The output pulse from the detector is read by a MultiChannel Analyser
Figure 2.6: Range–energy curves for various particles in silicon (Skyrme, 1967).
Figure 2.7: Ranges in detector material.
(MCA) after passing through two amplification stages and an Analog-to-Digital Converter (ADC). Each channel on the MCA corresponds to a narrow range of pulse-heights which, in turn, reflects a range of particle energies. The particle energy, for a fixed beam energy, is merely a function of the depth at which it was produced. As discussed earlier, the number of particles produced with that energy reflects the deuterium concentration at that depth. Consequently, while the MCA actually collects a frequency distribution of pulse-heights, its display can be interpreted as a plot of deuterium concentration against depth.

However, before the display can be interpreted, the channel axis must be converted to a depth-scale. The initial step in calibrating channel numbers is to convert channels to energies. The lowest-energy protons arise from events at the sample surface. From the inelastic kinematics governing this reaction and an accurate knowledge of the beam energy, this lowest proton energy, $E_{p}^{\text{low}}$, can be calculated. HE3CALC™ is a TURBOBASIC™ program written to perform such kinematic calculations on inelastic collisions and is presented in Appendix A. A different beam energy will give a different $E_{p}^{\text{low}}$, producing counts in different channels. Consequently, by collecting spectra at several beam energies, the channels corresponding to several specific energies can be obtained. If the pulse-amplification stages behave linearly, an energy-per-channel calibration figure is derived. The linearity of the system can be verified using a precision pulse generator.

The next step in converting channels to depth involves knowledge of the energy-loss characteristics of the beam ion in matter. Energy-losses of
various charged particles have been measured for a range of materials and energies. Energy-loss with depth, \( \frac{dE}{dx} \), is sometimes expressed in keV per \( \mu \text{m} \) and sometimes as a material-independent quantity, in keV per mg/cm\(^2\). By integrating \( \frac{dE}{dx} \) over a given depth, the total energy lost in traversing that depth of material is obtained and the energy-per-channel figure can then be used to identify the depths to which individual channels correspond. As each channel corresponds to a small change in energy, \( \frac{dE}{dx} \) is assumed to be constant over that change and the ensuing channel-to-depth conversion is a close approximation to the real situation.

Furthermore, before a spectrum can be said to show a true concentration-profile of deuterium with depth, the spectrum must also be normalised. This is done in order to remove the effects of beam attenuation and of cross-section variation from the data. As the beam travels through the sample, ions are removed from the flux by scattering and reacting. The effect of scattering is negligible; the ion loses energy primarily by interacting with atomic electrons, whose mass is very small in comparison. The interaction therefore has very little effect on the ion's trajectory. This is significant, as ions scattered at large angles to the beam would not provide "true" depth information. As the ion flux drops, so does the number of counts produced. This decrease is, however, an artefact of the technique and does not reflect the deuterium-concentration.

Figure 2.1 showed how strongly the reaction cross-section varies with energy. An incident beam of, for example, energy 1300 keV would lose
energy on traversing the sample, passing through the peak in the
cross-section. An evenly-deuterated sample would show more counts at the
depth where the beam energy was 650 keV than at the surface. This again
does not reflect the true physical situation. In order to counteract this,
an experimental spectrum is always divided by a spectrum obtained from an
evenly-deuterated sample at the same energy. This act of removing the
combined effects of attenuation and cross-section variation is known as
"normalisation".

Two such spectra are presented in Figure 2.8. The "thin" spectrum was
collected from an annealed bilayer similar to those used in diffusion
experiments. The "thick" spectrum was collected at the same energy from a
layer of deuterated polymer of a thickness significantly greater than the
range of the technique and shows the combined variation of cross-section
and beam attenuation that will be removed upon division of the "thin" by
the "thick".

Figure 2.9 shows a spectrum whose axes have been converted and whose
counts have been normalised. The profile shown is therefore a true
representation of the deuterium concentration-profile normal to the sample
surface.

The final step in extracting useful information from this technique is to
measure the diffusion coefficient of the labelled polymer represented by
the profile. This is achieved by fitting theoretical diffusion-profiles to
the data and taking the curve with the best fit, as represented by the
solid line in Figure 2.9. The value of D used to generate this curve is
Figure 2.8: Spectra from thick (top) and thin deuterated-PS layers.
Figure 2.9: Theoretical (—) and experimental (o) profiles.
then taken to correspond to the real situation.

Theoretical curves are a convolution of a diffusion-profile with a spreading function representing the experimental resolution. The diffusion-profile is produced by a solution of Fick's second law. In a rectilinear frame, this law takes the form

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

where $D$ is a constant, independent of concentration. $C$ is the concentration of the diffusing substance, $t$ is time and $x$ is the spatial coordinate, in this case the depth normal to the sample surface. A general solution to Fick's second law is

$$C(x,t) = \frac{C_0}{2} \left\{ \text{erf} \left[ \frac{(h-x)}{(4Dt)^{1/2}} \right] + \text{erf} \left[ \frac{(h+x)}{(4Dt)^{1/2}} \right] \right\}$$

where erf is the error function. A full derivation of this solution is presented in Appendix B. This solution gives the concentration of diffusant at a given point after a given time, from a starting slab of thickness $h$ diffusing into an infinitely-thick sample. The diffusing time of a sample is known so the variation of concentration with depth can be plotted.

At the sample surface there is an abrupt change in the deuterium concentration. This surface "edge" is seen on the experimental spectrum as a steep slope or curve, due to the spreading effect of the experimental resolution. This final difference between the real situation and the
experimental representation of that situation is taken into account by convoluting the sharp-edged theoretical profile with the previously-measured experimental resolution to produce the slope-edged experimental profile.

To summarise the steps, then; the effects of beam attenuation and cross-section variation are removed, to bring the spectrum closer to the real picture. The theoretically-generated profile, which corresponds to the real deuterium profile in the sample, is then brought to meet the spectrum by adding in the resolution.

Finally, the best theoretical fit is found by varying the diffusion coefficient and the area under the curve until the least-squares difference between theory and experiment is minimised. In this manner one obtains a value for \( D \), the diffusion coefficient of the diffusant.

2.4 Measuring the Resolution

The intrinsic resolution of a detector is a measure of its performance and therefore gives an indication of its suitability to a given application. In the case of polymer diffusion measurements by NRA, this resolution must be small compared to the typical diffusion distances measured to guarantee the accuracy of such measurements. The extraction of diffusion coefficients from spectra relies on the generation of theoretical diffusion-profiles by the convolution of a Fickian profile with the intrinsic detector resolution.
Resolution is measured by observing the experimental spread of a signal of known width. A deuterated film of known thickness, from stylus TALYSTEP™ measurements (discussed in detail in Chapter 4), is analysed by NRA. At the surface, several factors combine to make the film appear larger on the spectrum depth-scale than it really is. These factors are the intrinsic detector resolution, electronic noise and the energy-range seen by the detector due to its range of angular acceptance. The energy of a reaction product varies with angle of emission as well as depth. A detector with a small but finite window will accept events from a range of angles, with the consequence that an event from depth could have a similar energy to a surface event emitted at a slightly different angle. There is therefore a trade-off between acceptable angular spread and count-rate.

This angular spread contribution to the resolution can be calculated from a knowledge of the experimental geometry and several kinematic dependencies. The angular spread contribution to the depth resolution expressed in units of depth, \( \Delta(x)_\theta \), is given by

\[
\Delta(x)_\theta = \frac{dE_p}{d\theta} \times \Delta_\theta \times \frac{dE_{3He}}{dE_p} \times \frac{dx}{dE_{3He}} \tag{2.1}
\]

where \( E_p \) is the proton energy, \( E_{3He} \) is the \(^3\)He energy, \( x \) is the depth and \( \Delta_\theta \) is the angle subtended. \( \Delta(x)_\theta \) is therefore found by measuring \( \Delta_\theta \), calculating the range of proton energies accepted in that angle from one event and converting these energies to a depth.
To keep $\Delta(x)_0$ small, the various contributions should be minimised. As shown in Figure 2.2, $dE_p/d\theta$ is lowest for large angle. Figure 2.2 also shows how $dE_{He}/dE_p$ varies with beam energy and detection angle. It is smallest at large angle and low energy. Here the experimenter must balance the desire for good resolution with the energy necessary to probe the required depth. Once experimental arrangement and method have been chosen, this contribution remains constant.

Resolution can be optimised by minimising the lengths of signal-carrying cables, which will reduce the capacitance and hence the noise amplitude, and by cooling the detector and the preamplifier. Beyond the preamplifier, the signal-to-noise ratio has been established and there is no further advantage to be derived from cooling. These measures taken, there is a way to artificially enhance the depth-resolution; by tilting the sample relative to the beam, the depth-profile is then spread over a greater sampling depth, automatically spreading features out on the spectrum [Figure 2.10]. This is best suited to near-surface profiling as "real" depth is greatly reduced in doing this.

The spread due to electronic noise can be measured using a precision pulse generator. Highly similar pulses are fed into the amplification system and the resulting spread observed on the MCA. The signal should appear in one channel but the random addition of noise acts to produce a distribution of amplitudes, collected over a number of channels.

These contributions to the total experimental spreading can be removed arithmetically to give the intrinsic detector resolution.
Figure 2.10: Consequences of a glancing beam incidence.
\[ \Delta^2 = \Delta_{\text{int}}^2 + \Delta_\theta^2 + \Delta_{\text{noise}}^2 \]

These can be expressed in channels or converted to depth as done above for \( \Delta(x) \). The resolution is sharpest at the surface. As the beam ions move into the sample, they will have an increasingly broad spread of energies, due to the statistical nature of energy-loss in matter. This effect, known as "energy-straggling", serves to blunt the depth-resolution by introducing ambiguity into the energy-depth trade-off.

The magnitude of \( \Delta(x) \) depends on the experimental arrangement and on the beam energy used. With the collimator positioned at 100 mm from the sample and having a width of 1 mm, the slit subtended an angle of 0.573° at the sample. Table 2.1 shows how \( \Delta E_p(\theta) \), the difference in proton energy due to this subtended angle, varies with beam energy with the detector placed at an angle of 165° to the beam. The values were obtained by postulating a reaction taking place at the surface of the sample, defining the angle of emission as being either edge of the slit and using HE3CALC to work out the proton energy that satisfies these conditions.

\( \Delta E_p(\theta) \) was then converted from an energy-range to a depth-range by converting proton energy to \(^3\text{He}\) energy to depth, in keeping with Equation 2.1. Again using HE3CALC\(^m\), the energies of \(^3\text{He}\) ions needed to produce given proton energies were obtained. In this manner, \( \Delta E_{\text{He}}(\theta) \), the range of \(^3\text{He}\) energies corresponding to the detector’s angle of acceptance, was calculated. The sample depth to which this corresponded was derived from a knowledge of the energy-loss characteristics of \(^3\text{He}\) in polystyrene.
Figure 2.11 shows the variation of $\frac{dE}{dx}$ with $^3$He energy. $\frac{dE}{dx}$ is a smoothly varying function, peaking in the region of 500 keV. It is dependent on the nature of the ion, the ion's energy and the chemical composition of the stopping medium. Stopping-powers were obtained from the program STOP™ which, calculates an ion's energy-loss with depth taking into account the three factors listed above.

STOP™ was then used to determine the near-surface depth that would cause the ion to lose $\Delta E_{^3He}(\theta)$, the amount of energy corresponding to the angular spread. Table 2.1 shows the final results for the effect on resolution of the finite detector size expressed as a depth, $\Delta(x)_\theta$.

STOP™ was also used to produce the results in Table 2.2. These show the useful "window" of the technique for a range of beam energies. Below 400 keV, $E_{^3He}$ is almost insufficient to trigger the reaction and the reaction cross-section is therefore very small. The range of the technique is therefore the depth of material required to slow the beam ions to 400 keV. Comparing tables 2.1 and 2.2 reveals a trade-off between depth-resolution and probe-depth which suggests 700 – 1100 keV as the optimum energy-range for analysis. Higher energies only have an application when large profiling depths are essential.

Table 2.2 also presents the protons' energy-loss in traversing the useful window and illustrates that this is a negligible fraction of the total energy lost by the $^3$He.
Figure 2.11: Stopping-power curve for Helium-3 in polystyrene.
### Table 2.1: Energy-dependence of angular contribution to resolution.

<table>
<thead>
<tr>
<th>Beam Energy (keV)</th>
<th>$\Delta E_p(\theta)$ (keV)</th>
<th>$\Delta E_{He}$ (keV)</th>
<th>$\Delta(x)_\theta$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>9.9</td>
<td>8.8</td>
<td>36</td>
</tr>
<tr>
<td>1100</td>
<td>12.0</td>
<td>14.3</td>
<td>70</td>
</tr>
<tr>
<td>1500</td>
<td>13.7</td>
<td>20.4</td>
<td>117.5</td>
</tr>
<tr>
<td>2000</td>
<td>15.3</td>
<td>28.5</td>
<td>194.7</td>
</tr>
</tbody>
</table>

### Table 2.2: Range of technique as a function of beam energy.

<table>
<thead>
<tr>
<th>$E_{He}$ (keV)</th>
<th>Window (µm)</th>
<th>$\Delta E_p$ over window (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.041</td>
<td>0.16</td>
</tr>
<tr>
<td>700</td>
<td>1.22</td>
<td>4.82</td>
</tr>
<tr>
<td>1000</td>
<td>2.57</td>
<td>10.38</td>
</tr>
<tr>
<td>1100</td>
<td>3.064</td>
<td>12.42</td>
</tr>
<tr>
<td>1500</td>
<td>5.25</td>
<td>21.7</td>
</tr>
<tr>
<td>1700</td>
<td>6.49</td>
<td>27.1</td>
</tr>
<tr>
<td>2000</td>
<td>8.45</td>
<td>35.7</td>
</tr>
</tbody>
</table>

Table 2.2: Range of technique as a function of beam energy.

(The window is the depth to reduce beam to 400 keV.)
In order to find the optimum experimental arrangement, it was necessary to perform depth-resolution measurements under various conditions of beam energy of incident angle. The samples prepared for these measurements consisted of alternate layers of deuterated polystyrene (d-PS) and hydrogenous polystyrene (h-PS). The h-PS layers were invisible to the technique and the depth-resolution was measured by comparing the apparent d-PS layer thicknesses to their known value, determined prior to analysis by TALYSTEP™ stylus measurements.

Figure 2.12 shows a typical spectrum obtained during this exercise. Each peak corresponds to an 80 nm layer of d-PS. The intervening h-PS layers are 480 nm thick. The left-most peak represents the surface layer of d-PS and is clearly the sharpest of the three. As the depth is increased, the peaks become increasingly spread, thus becoming less resolved. This observation can be quantified by referring to the full-width-half-maximum (FWHM) of each peak. The resolution then is obtained by converting the FWHM from channels to a depth and removing the known thickness of the d-PS layer.

Taking Figure 2.12 as an example, the FWHM of the surface peak is 5.35 channels. The channel-to-energy conversion factor is 11.12 keV/channel, which is calculated from the surface channels of spectra collected at different beam energies. Thus the FWHM in terms of proton energies is 5.35 x 11.12 = 59.49 keV. This is converted to a depth using the same approach as that used for the angular spread calculation.

The results from several multilayer samples are presented in Table 2.3 and
Figure 2.12: Typical multilayer sample spectrum.
Beam energy 700 keV, normal beam incidence.
<table>
<thead>
<tr>
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</tbody>
</table>

Table 2.3: Effect of beam energy and angle of incidence on measured experimental resolution.
summarised in Figure 2.13. The final resolution figure presented was extracted by removing the effective width of a top-hat distribution from the measured d-PS layer thickness, as suggested by Dieumegard [1979]. A square distribution over the range \(-\phi_m < x < \phi_m\) has a standard deviation, \(\sigma_\phi\), defined by

\[
\sigma_\phi^2 = \frac{1}{2\phi_m} \int_{-\phi_m}^{+\phi_m} x^2 \, dx = \frac{1}{3} \phi_m^2
\]

with the effective width, \(W\), given by

\[
W = 2.35\sigma = 1.36\phi_m
\]

The resolution is then given by

\[
\Delta^2(\text{resolution}) = \Delta^2(\text{measured}) - \Delta^2(\text{effective})
\]

As the beam travels through the sample depth-resolution is degraded by energy-straggling. Some of the resolution measurements in Figure 2.13 bear this out whilst in others the resolution actually improves beyond a certain depth. This apparent anomaly is caused by the combined effect of reduced angular spread and slowing of the beam ion. While the former contribution is negligibly small the latter effect is clearly significant, owing to the fact, observed above, that depth-resolution is more sharp at low energies. From Figure 2.11, the stopping-power increases as the energy drops from 2 MeV to 500 keV. As a result, more energy is lost per \(\mu m\), therefore more channels are occupied by the information contained in a given \(\mu m\). By a similar logic to that used in the glancing incidence case,
Figure 2.13: Depth-resolution against depth and beam energy.
the features are more spread out on the energy-scale and are more easily resolved.

To summarise, therefore, the experimental resolution is seen to improve with decreasing beam energy, further underlining the trade-off between performance and required profiling-depth mentioned above. The use of a glancing incidence can be used to improve the resolution greatly, bringing it down to 20 nm. This compares favourably with the other techniques available for studying polymer diffusion but limits the technique to the top 500 nm of a sample.

### 2.5 Refinements to the technique

The generating and fitting of theoretical curves was carried out by a program written in TURBOASIC™ which is presented and annotated in Appendix A. The user enters the names of a diffused spectrum and a thick, fully-deuterated spectrum as shown in Figure 2.8. As the first spectrum is divided by the latter, there exists the danger that division will produce a large fluctuation in the numbers in channels with very few counts. For this reason, curve-fitting is restricted to the range from the surface edge to the half-height of the probe limit tail-off, where the thick spectrum has sufficient counts to ensure that division produces a continuous profile.

As discussed earlier in this chapter, the angle of detection is important for reasons of energy resolution. The smaller dE/dθ, the energy variation
with angle, the smaller the need for a narrow, angle-specific detector window. This means that a larger-area detector can be used at a more backward angle, thus giving a higher count-rate. Conversely, the same narrow detector can be used at the more backward angle, giving a better resolution by accepting a smaller energy-range as a consequence of the range of angles subtended at the sample.

The initial diffusion measurements were made using a detector with a circular end-window, limiting the angle of detection by means of a slitted brass collimator placed over the window [Figure 2.14]. The physical size of the detector placed a limit on the largest angle at which it could be placed in the chamber, being 165°. Beyond this, the detector was obstructing the beam. An improvement on this was to use an annular detector centred on the beam. This had the consequences that a larger surface area of detection was used and the angle of detection was now close to 175°.

The annular detector also had the ability to be cooled; encased in a ceramic bracket, as opposed to the usual practice of mounting in epoxy resin, it was designed to withstand temperatures as low as the boiling point of liquid nitrogen. Substantial cooling of the detector is aimed at reducing electronic noise; random pulses are caused by thermal energy fluctuations exciting valence electrons into the conduction band, registering as a signal. These random pulses can coincide with charged-particle events, changing the pulse amplitude and inducing a spreading of the pulse-height distribution. Lowering the temperature greatly reduces the thermal energy available and hence reduces the
Figure 2.14: Views of detector and slit collimator.
likelihood of a spurious jump across the band-gap.

The detector was cooled using a Peltier device [RS 618-724]. This takes advantage of the temperature characteristics of a p-n junction to work as a heat pump. Upon experiencing a current flow, one side of the device grows cold while the other grows warm. The warm side is then placed in contact with a large mass of high thermal conductivity, as a heat sink, whilst the detector is placed in contact with the cold side. A power input of 5 Watts was found to produce a detector temperature of $-30^\circ$ C or 242 Kelvin. This change of 50 Kelvin from the normal room-temperature detection showed a clear reduction in the noise level when monitored on an oscilloscope.

2.6 Summary

A technique has been developed to exploit the $d(^3\text{He},p)^4\text{He}$ reaction to profile deuterium-labelled polymer. This technique has been found to out-perform other established techniques in terms of the depth-resolution achieved and the probe-depth available. The large range enables fast diffusing species to be observed, such that experiments to be performed at higher temperatures than before. Furthermore, the technique produces a direct diffusion-profile of the labelled polymer.
## Chapter 3: An assessment of ion beam damage.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Measurement of damage</td>
<td>71</td>
</tr>
<tr>
<td>3.1.1 Disappearance of the carbon</td>
<td>72</td>
</tr>
<tr>
<td>shake-up satellite</td>
<td></td>
</tr>
<tr>
<td>3.1.2 The effect of damage on subsequent diffusion</td>
<td>74</td>
</tr>
<tr>
<td>3.1.3 Measuring the extent of cross-linking</td>
<td>77</td>
</tr>
<tr>
<td>3.2 Summary</td>
<td>80</td>
</tr>
</tbody>
</table>
The passage of energetic ions through matter is always accompanied by the transfer of energy to the material. This transfer can take several forms ranging from peripheral electrical interaction, leading to ionization or excitation, to direct atomic collision, in which atoms can be displaced from their molecular sites. Almost all the known forms of interaction have at some time been used as the basis for a particle detection system. Whilst some of these changes induced by interactions are transient, others result in permanent modifications to the material or "damage". In the course of any work involving such invasive methods the extent of damage must be assessed so that the reliability of the information obtained can be known.

Ion beam techniques are often referred to as being "non-destructive". This term refers more to the preservation of the information contained in a sample than to any invulnerability on the part of that sample. If a sample repeatedly yields a given result upon successive analyses, then the technique can be said to be non-destructive.

The thermally and electrically insulating nature of polymers poses additional problems for their analysis by ion beams. The polymer's inability to conduct away the heat generated by the beam leads to localised heating which can in turn cause diffusion in the sample, thus corrupting an existing concentration-profile. Excessive heating can cause chemical changes such as graphitisation to take place, resulting in a black spot at the point of beam incidence.
As a consequence of its electrically insulating nature, the polymer cannot conduct away the localised deposition of charge by the beam and subsequent arc discharges to the metal sample-holder can affect the beam's position and energy at the sample surface. It is also very difficult to make accurate measurements of beam current from an insulating sample.

In the case of electron-beam analysis, which is a low-momentum analogue of ion-beam analysis, samples must have a thin surface layer of carbon to earth the sample lest the charge build-up deflect the electron beam. In ion beam work, the beam energy is much higher than in the case of an electron beam and beam deflection is not a major problem. An arc discharge, however, can seriously damage the sample material as the electrical energy released during this process is sufficient to drive chemical reactions in the sample material. This can lead to molecular rearrangements, altering the nature of the material.

3.1 Measurement of damage

Damage to a polymer chain can express itself in one of two ways; the carbon–carbon bonds can be broken, leading to fragmentation and a drop in molecular weight, or links can be forged between carbons on adjacent polymer chains, known as "cross-linking". The effect of cross-linking is to raise the molecular weight. It is widely accepted that polymer diffusion coefficients vary inversely with molecular weight. Thus the effect of the two kinds of damage would be to accelerate or retard
diffusion, respectively, and the matter of ion-beam damage is therefore of great importance to diffusion measurements.

3.1.1 Disappearance of the carbon shake-up satellite

Storp [1985] has used X-ray Photoelectron Spectroscopy (XPS) to study the decomposition of organic compounds by ion bombardment. The aromatic ring in polystyrene gives rise to a "shake-up satellite" on the high-energy side of the Carbon-1s peak. Storp reports the disappearance of this satellite after a short period of bombardment with 5 keV Ar\(^+\) ions. As the aromatic ring is one of the most stable units in organic chemistry, Storp extrapolates this observation to assume that all organic compounds are easily destroyed by ion bombardment.

5 keV Ar\(^+\) ions have very different stopping powers to 1000 keV \(^3\)He\(^+\) ions, so Storp's findings cannot be assumed to hold for the \(^3\)He situation. In order to assess this situation independently, XPS spectra were taken from a polystyrene sample both before and after exposure to a 5 nA, 1.1 MeV \(^3\)He\(^+\) beam for 15 minutes, the typical analysis parameters used to extract diffusion-profiles. The results are shown in Figure 3.1, which shows the XPS spectra in the region of the carbon-1s peak. Most important is the complete disappearance of the shake-up satellite after exposure to the beam, apparently confirming the destructive nature of the beam technique as regards organic units.
Figure 3.1: XPS spectra showing effect of ion beam analysis on aromatic ring shake-up satellite.
The disappearance of the shake-up satellite could, however, be caused by the deposition of carbon on the sample surface during analysis. This explanation is supported by the fact that the vacuum used during $^3$He-d work is worse than that used in XPS work by several orders of magnitude. Consequently, it was difficult to infer the extent of damage from the disappearance of the shake-up satellite. The matter of whether ion beam analysis causes damage in the sample that is of any consequence in the measurement of diffusion-profiles therefore required further investigation.

3.1.2 The effect of damage on subsequent diffusion

Brown [1989] has examined the effect of ion beam fluences on several polymers, reporting that both cross-linking and gas release take place. The efficiency of cross-link formation is expressed as a G-value and was found to be the same for the three ions used, $\text{Ar}^+$, $\text{Ne}^+$ and $\text{He}^+$. It would, however, be scientifically unsound to extrapolate from Brown's dose-data to the $^3\text{He}^+$ ions used in the present work as the energies used in that work were in the range 100-400 keV whereas the energies used in $^3\text{He}$ work are in the range 700-2000 keV.

Brown [1989] also studied the effect of increasing ion fluence by measuring the change in the molecular weight distribution of a sample of polystyrene. Although the appearance of a low molecular weight tail testifies to the presence of some chain scission, the significantly greater height of the high molecular weight tail shows cross-linking to be
by far the more important process. Hence, in the context of a diffused sample containing a concentration gradient of material across its depth, this result suggests that damage during analysis will tend to lock the profile in place. Although the sample cannot be diffused further to provide further data points, the information contained within it will be preserved after analysis, enabling the same information to be read repeatedly and justifying the "non-destructive" label.

This conclusion was put to the test by repeatedly analysing a diffused sample. Each spectrum gave rise to the same diffusion coefficient, the visual differences between the spectra being due to the low counting statistics obtained.

An experiment of greater interest would be to observe the effect of analysis on the subsequent diffusion in a sample, to assess whether any cross-linking taking place was having a noticeable effect.

This experiment was performed by preparing two samples in identical fashion, analysing one and then annealing both. The spectra obtained from the samples after this treatment are shown in Figure 3.2. The extent of diffusion is virtually identical in the two samples, a fact confirmed by the close similarity of the diffusion coefficients produced by the curve-fits performed on these spectra. This suggests that the damage observed by Brown was more likely to affect molecular weight than that caused by a 1.1 MeV beam of $^3\text{He}^+$. When one considers that Brown was using similar total-energy doses of 0.1 MeV $^4\text{He}^+$ ions a possible explanation for this difference emerges; 0.1 MeV ions deposit their energy more surface-
Figure 3.2: $^3$He–d spectra from annealed samples with (top) no previous analysis and (bottom) one previous analysis.
locally than their 1.1 MeV counterparts and, as such, the chances of activating a cross-link are energetically favoured.

### 3.1.3 Measuring the extent of cross-linking

An experiment to provide an insight into the number of cross-links being formed involved measuring the hydrogen-loss during analysis by studying the $^3$He backscatter signal. As cross-links are formed by the transformation of two carbon-hydrogen bonds to a carbon-carbon bond, one molecule of $\text{H}_2$ is released. This will result in a change in the carbon backscatter signal, or "carbon edge", which can be used to calculate the increasing proportion of carbon in the sample. However, as a polymer reaches the point at which each molecule contains one cross-link it begins to gel. In a polymer with a molecular weight of 100,000 this corresponds to losing only one hydrogen in 8000. This minuscule change is not detectable over the small change in the height of the carbon-edge, in going from a polymer to a pure carbon sample, which is approximately 23%.

It might be possible, however, to measure whether a large number of cross-links was forming in the sample. This experiment was therefore performed by applying a very high beam current of 2 $\mu\text{A}$, which is three orders of magnitude above that usually employed for analysis. Subsequent spectra were collected and the heights of the carbon edges were normalised to the total charge deposited during each acquisition. Carbon edge-heights were measured by averaging the counts in ten channels, starting ten channels below the edge half-height. A typical backscatter spectrum is
The results, presented in Figure 3.3, show a gradual increase in the height of the carbon edge, indicating an increase in the fraction of carbon present in the sample and, consequently, in the number of cross-links. The scatter in the data and the difficulty inherent in measuring current from an insulating material make it difficult to draw any firm conclusion from this experiment. However, a least-squares fit to the data indicated an increase in the carbon-edge of 21.7% during the course of the experiment. Calculations based on stopping-power predict a change of 23% in the carbon-edge in the transformation of a (CH)\textsubscript{x} polymer to pure graphite. The hydrogen-loss data in Figure 3.3 were calculated using the first carbon edge from the first measurement as corresponding to pure polymer. Then, by combining the stopping powers of polymer and graphite in various ratios to obtain the measured percentage differences in the carbon-edge, the composition of the sample was inferred for several doses.

The charge or dose to completely graphitize a polystyrene sample was found to be 5.6 mC. In the course of a typical analysis, a sample would receive 5 µC. By interpolation in Figure 3.3, this was found to correspond to the loss of 68 hydrogen atoms in 100,000 atoms. As two hydrogen atoms are assumed to be lost for every cross-link formed, this implies a value of 34 cross-links in 100,000 atoms. As a monomer of polystyrene is C\textsubscript{8}H\textsubscript{8}, comprising 16 atoms and weighing 104 mass units, this corresponds to a cross-link density of 34 cross-links in 6250 monomers or one in 19,000 mass units.
Figure 3.3: Results from hydrogen-loss experiment showing (top) carbon edge increase with typical RBS carbon-edge (insert) and (bottom) hydrogen fall-off with dose.
As the calculated cross-link density is identical to the naturally occurring entanglement density according to Green [1986] of 19,000, one would expect to see an effect on the diffusion characteristics of the material after these cross-links have been introduced. In other words, if two identically-prepared samples were annealed after one had previously been analysed, the extent of diffusion should have been greater in the sample that had not been analysed. The similarity of the spectra in Figure 3.2 suggests that this is not the case, implying that the cross-link density is lower than that calculated. A possible explanation of this observation is that the assumption that hydrogen-loss always leads to cross-links is incorrect. The loss of hydrogen atoms from a given backbone site may instead bring about the formation of a carbon=carbon double bond. There is certainly sufficient energy available to drive this chemical change, as shown by the XPS work on the aromatic ring.

3.2 Summary

The work carried out in this section shows that, although the ion beam analysis does affect the sample, the effect is minimal and normal diffusion proceeds even after a sample has been analysed previously. Storp showed that cross-linking was much more likely than chain scission, such that extended analysis would tend to lock a concentration-profile in place rather than induce further diffusion to blur the information. As such, the technique can be said to be non-destructive in the sense defined at the beginning of the chapter. Additionally, good experimental practice can serve to reduce damage even further, by cooling the sample to reduce localised beam heating and by using sufficiently low beam currents for charge to leave the sample surface without arcing.
Chapter 4: Materials modification and sample preparation.

4.1 Deuteration of Polystyrene 82
   4.1.1 The deuteration reaction 83
   4.1.2 NMR evaluation of deuteration. 87
   4.1.3 Post-deuteration integrity 92

4.2 Sulphonation of Polystyrene 93
   4.2.1 The Sulphonation Reaction 96
   4.2.2 Evaluation of the sulphonation process 101

4.3 Sample preparation 108

4.4 The experimental chamber 114
Chapter 4: Materials modification and sample preparation.

In order to investigate the structure of ionomers of polystyrene by the $^3$He-d method presented in Chapter 2 it was first necessary to develop methods of deuterating and sulphonating polystyrene. The presence of deuterium in a polymer is required to allow the $^3$He-d method to provide measurements of the diffusion of that polymer. Sulphonation is the process of converting a polymer to an ionomer by the addition of sulphonate groups.

Once these processes were established, a system for the preparation of bilayer samples for diffusion was developed. These samples were then heated to induce diffusion, by being placed in a furnace at a known temperature, with the extent of subsequent diffusion being monitored by NRA.

4.1 Deuteration of Polystyrene

The aim in deuterating a polymer was to incorporate a significant amount of deuterium into each molecule, to allow detection by $^3$He-d, whilst preserving the nature of that molecule. It was important that the process of deuterium-labelling should affect neither the molecular weight nor the configuration of polymer chains as such changes would alter the chains' diffusion behaviour.

The use of deuterium as a label relies on the fact that deuterons behave
very similarly to protons in terms of their effect on the stochastic movements involved in diffusion or on the forces between molecules. There is thought to be some change in the intersegmental forces [Nicholson, 1989] present as a result of deuteration because some evidence exists of an Upper Critical Solution Temperature (UCST) of 120° C [Bates, 1986]. As long as diffusion takes place at temperatures well in excess of this value, however, the deuterated polystyrene will be totally compatible with the normal polystyrene matrix [Green, 1986].

The polystyrenes used were monodisperse, which means that they had a very narrow molecular weight distribution, so that each molecule would behave in a very similar fashion to any other. In this manner, the diffusion of a certain molecular weight of polystyrene at a given temperature could be measured by interdiffusing films of labelled and unlabelled polymer, provided molecular architecture is unaffected by the labelling process.

4.1.1 The deuteration reaction

Samples of polystyrene were labelled with deuterium by replacing some of the hydrogen atoms in the molecule with deuterium. It was felt that direct isotope exchange was most likely to preserve the nature of the molecule, as deuterium has physical and chemical properties very similar to those of hydrogen.

Garnett [1972] has described a method for deuteration using organoaluminium dihalide catalysts, whereby rapid exchange of hydrogen
atoms occurs between aromatic compounds. After dissolving organic substrates in benzene-$d_6$, which is fully-deuterated benzene, the exchange reaction was instigated by the addition of a small quantity of ethylaluminium dichloride ($\text{EtAlCl}_2$) as a catalyst with the presence of traces of water as a co-catalyst greatly enhancing the rate of reaction. The reaction was terminated by the addition of an excess of water.

The suggested mechanism of this reaction is one of electrophilic aromatic substitution [Figure 4.1]. It is thought [Garnett, 1971] that the catalyst acts as a proton-transfer agent, associating with the $\Pi$-electrons of the aromatic group and de-stabilizing the aromatic ring sufficiently to allow electrophilic attack, resulting in the formation of a reaction intermediate with a hydrogen atom and a deuterium atom attached to the same carbon atom on the ring. The catalyst then leaves the ring as two of the $\Pi$-electrons have been drawn to the site of attack and the electron-poor ring can no longer form a $\Pi$-complex with the catalyst. Following this development, the more stable delocalised $\Pi$-electron ring reforms by the ejection of the hydrogen atom of the attack site.

The preference of hydrogen-release to deuterium-release is much under discussion. One explanation is based on the relative energies of the C-H and C-D bonds; the greater mass of deuterium may produce a tighter bond with carbon than the lighter hydrogen, making hydrogen-release energetically more favourable than deuterium-release. Another explanation is based on the statistics dictated by the relative concentrations of hydrogen and deuterium in the reaction mixture; a vast excess of deuterium will ensure a greater likelihood of deuterium being found at exchange
Figure 4.1: Steps in the deuteration of polystyrene.
sites, once equilibrium has been reached.

The yield of this reaction has been assessed quantitatively by Willenberg [1976], who finds it to be highly selective for aromatic hydrogen atoms and nearly free from steric effects. Replacements of the order of 90% were measured in polystyrene by nuclear magnetic resonance (NMR), which suggests that the reaction in question will indeed produce labelled polymers which produce a strong signal when investigated by NRA. These measurements also revealed the replacement to have been restricted to the five aromatic positions. The ring-specificity of the labelling suggests that the reaction is not involving the backbone bonds and is therefore unlikely to result in significant molecular weight degradation. This is confirmed by molecular weight measurements [Willenberg, 1976] which show only small changes in the weight-average molecular weight of the polymer, $M_w$, and in the monodispersity of the sample.

All deuteration reactions for the present work were carried out under a dry nitrogen atmosphere in a dry-box in the Department of Chemistry, as the safe use of $(\text{EtAlCl}_2)$ requires a relative humidity of less than 25%. In a typical preparation, 1 gram of polymer was dissolved in 10 ml of benzene-$d_6$ to which 250 $\mu$l of $(\text{EtAlCl}_2)$ were then added and the mixture was stirred for 2 hours, during which time a change in colour from yellow to pink was observed. After termination by the addition of water, the polymer was precipitated in methanol and any catalytic residuals were removed by washing with methanolic hydrochloric acid.
4.1.2 NMR evaluation of deuteration.

An analysis of the extent of deuteration achieved was carried out to verify that labelling had been successful and had not affected the polymer's structure in any way.

The extent of deuteration was examined by proton NMR at 300 MHz. This technique measures the frequency and intensity of a magnetic resonance in the material under study. In the case of polystyrene, NMR was used to examine the resonances of C-H bonds. The frequency at which the bond resonates is influenced by its magnetic environment and the strength of the resonance gives an indication of the number of bonds of that type present in the sample. Bonds where hydrogen atoms have been replaced by deuterium, no longer contribute to the signal, as carbon-deuterium resonates at a different frequency, ca. 45 MHz.

On the styrene ring there are five hydrogen protons; one in the para-, two in the ortho- and two in the meta-positions respectively [Figure 4.2]. The dissociated II-electron ring current produces an oppositely-directed magnetic field to that of the protons and, as a result, these protons experience a lower magnetic field than the three in the CH and CH$_2$ groups on the polystyrene backbone. The C-H bonds in these positions therefore resonate at a different frequency to those in the backbone. Consequently one can discriminate between ring and backbone signals on an NMR spectrum to gauge any specificity of the deuteration process.

In order to assess the extent of deuteration, a deuterated polystyrene was
Figure 4.2: Nomenclature of positions on styrene group
compared to its protonated precursor [Figures 4.3 and 4.4]. The strengths of the resonances are obtained by integrating the peak areas on the NMR spectra. In addition to resolving ring and backbone resonances, it should be noted that the ortho signal was resolved from the meta and para signals. This is presumably caused by the ortho position's proximity to the region of high electron density at the C-C bond linking the ring to the backbone. The peak areas of the proton signals from the three resolvable groups of positions are presented in Table 4.1 together with the calculated percentages of hydrogen replacement by deuterium.

The ratio of the peak areas in the protonated sample is approximately 3:2:3, which corresponds to the numbers of protons in the respective positions. This confirms that the three regions observed are indeed caused by the meta and para positions, the ortho positions and the backbone positions, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative intensities of proton signals from positions on polymer</th>
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<tr>
<td></td>
<td>para &amp; meta</td>
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<tr>
<td>protonated</td>
<td>2250</td>
</tr>
<tr>
<td>deuterated</td>
<td>219</td>
</tr>
<tr>
<td>degree of replacement</td>
<td>90.0%</td>
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Table 4.1: Proton-NMR evaluation of deuteration of polystyrene: degree of reduction of hydrogen signal after deuteration.
Figure 4.3: Proton-NMR spectrum from normal polystyrene (h-PS).
Figure 4.4: Proton–NMR spectrum from deuterated polystyrene (d–PS).
It can be seen from these results that the deuteration process used is highly ring-specific. As there is little isotope-exchange occurring along the backbone of the polymer the likelihood of the backbone bonds being broken is very limited. This is most encouraging as it suggests that the deuterated polymer will contain the same number of monomers as its precursor and that, consequently, the labelling process will be no more than just that.

The near-total replacement at the meta and para positions guarantees rapid accumulation of NRA spectra. Diffusion experiments were designed such that the labelled penetrant concentration in depth would be of the order of 5%. In this manner, the labelled polymer was present as a tracer quantity whose diffusion behaviour was reflective of the bulk material without dictating it. It was therefore important to have a high replacement level in order to maximise the nuclear reaction rate for a given concentration of labelled polymer whilst simultaneously keeping beam-time per sample to a minimum, a desire partly motivated by financial considerations.

This assessment of the yield of the deuteration process was carried out for every batch of material that was deuterated. In all cases, the ring positions were deuterated in excess of 90% whilst the backbone carbons were relatively untouched.

4.1.3 Post-deuteration integrity

The effect of the deuteration reaction on the polymer chains in terms of
the extent of chain break-up, referred to as molecular weight degradation, was ascertained by gel permeation chromatography (GPC). This technique is used to measure the molecular weight distribution of a polymer by passing it through a column of gel. According to its molecular weight, the polymer is retarded differentially; material leaving the column after a given time will be of a higher molecular weight than material leaving the column at a later time.

GPC analyses were performed on a hydrogenated, monodisperse polystyrene with a molecular weight of 90,000 (90k h-PS), and on a deuterated sample of the same polymer (90k d-PS). The curves obtained for 90k h-PS and 90k d-PS [Figure 4.5] are very similar. There is some broadening on the low molecular weight side but this can be deemed to be negligible as significant degradation would give rise to a second peak or to a shoulder on the low side of the main peak, indicating a new molecular weight distribution. All deuterated polymers were checked in this way before being used in experiments. All the reagents used are listed in Appendix C.

4.2. Sulphonation of Polystyrene

There are several ways in which sulphonate groups can be introduced into a polymer. One method consists of copolymerizing a sulphonated monomer and a non-sulphonated monomer to produce a sulphonate-containing copolymer. Weiss [1980] has performed emulsion copolymerizations of a sulphonated monomer with butadiene and, more recently [1985], of a sodium styrene
Figure 4.5: Molecular weight distributions of h-PS and d-PS by GPC.
sulphonate monomer with styrene. The latter preparation is effectively a neutralized sulphonate ionomer of polystyrene. There is, however, doubt as to the randomness of the ionic content; copolymerizations of this kind frequently result in block copolymers, with a long section of ionic material followed by a long section of non-ionic material.

A second approach to sulphonation involves incorporation of sulphonate groups into an existing polymer chain. Makowski [1980] has polymerized a diene monomer, leaving one bond unsaturated as a site for electrophilic attack by a sulphonating agent. Chlodzinski [1971] has carried out sulphonations in a chloroform solution, using chlorosulphonic acid as a sulphonating agent. Both authors report cross-linking as a significant effect of these preparations.

Makowski [1980] has also used acetyl sulphate as a sulphonating agent in a chlorinated solvent medium, adding sulphonic acid groups to the aromatic group of polystyrene. These groups are then neutralized by means of a metal hydroxide or a metal acetate. The sulphonation process takes place in homogeneous solution, resulting in a purely random ionic functionality. Furthermore, there is no noticeable degradation of the polymer chains [Lundberg, 1978] during sulphonation.

Polymers prepared by the first and second methods have been compared and were found to have significant differences in their thermal characteristics [Weiss, 1985; Turner, 1985]. These are attributed to fundamental differences in structure, with the distribution of sulphonate groups being more random in the sulphonated polystyrene (S-PS) produced by
acetyl sulphate sulphonation [Fitzgerald, 1988].

4.2.1 The Sulphonation Reaction

For this work, the method using acetyl sulphate as a sulphonating agent was used as it was best suited to the starting materials, monodisperse fully-saturated polystyrenes. The generation of a truly random ionic functionality along the polymer backbone is necessary to avoid biasing the onset of ionic aggregation by having ionic material in artificially close proximity, as in the case of a block copolymer.

The reaction proceeds by a mechanism of electrophilic aromatic substitution, whereby the sulphonating agent attacks the para position on a styrene side-group. In this way, the backbone is not involved in the reaction and there is little chance of breaking the backbone or forming chemical crosslinks with adjacent backbones, altering the molecular weight. The attack is restricted to the para position by a combination of steric considerations and the size of the sulphonate group, thus ensuring a limit of one sulphonate group per styrene.

This method was therefore best suited to the starting materials used which took the form of monodisperse, fully-saturated atactic polystyrenes. The method follows the preparation procedure described by Makowski [1975], beginning with the formation of a sulphonic acid and its subsequent neutralization with sodium hydroxide to form the sodium sulphonate salt.
The recipe used is as follows: 1 gram of 90k polystyrene is dissolved in 40 ml of 1,2 dichloroethane (DCE) in a three-neck flask. The solution is heated to 50° C and stirred throughout with the temperature being monitored by means of a mercury thermometer introduced via a side-neck. A reflux condenser fitted to the top neck minimizes pressure buildup in the flask whilst retaining the reagents [Figure 4.6].

Once the solution has reached the desired temperature the sulphonating agent, acetyl sulphate, is added. Acetyl sulphate was prepared by mixing 8 ml of acetic anhydride with 40 ml of DCE, chilling the solution to 5° C and adding 3 ml of 98% sulphuric acid. The reaction rate has a first-order dependence on the concentration of sulphonating agent present and the final extent of sulphonation is therefore varied by using different amounts of the latter, typically in the range 0.1 - 5 ml. In order to keep the total reaction volume invariant from one preparation to the next, the required volume of sulphonating agent is always made up to the same volume with dichloroethane (DCE). In this way yields can be expected to be in the ratio of the amounts of sulphonating agent added.

The sulphonating agent dissociates to produce a sulphur trioxide group, \( \text{SO}_3^- \), which is electrophilic. Attracted by the high electron density of the styrene group, the \( \text{SO}_3^- \) group de-stabilizes the \( \Pi \)-electron system to form a stable reaction intermediate [Figure 4.7]. It does this by taking two \( \Pi \)-electrons to form a bond with one of the ring carbons. The four remaining \( \Pi \)-electrons form two double bonds between four of the ring carbons, leaving the fifth with a net positive charge. The formation of this reaction intermediate is the rate-limiting step of the overall
Figure 4.6: Schematic diagram of sulphonation apparatus.
Figure 4.7: Steps in the sulphonation of polystyrene.
substitution reaction as it is endothermic and requires the aromatic ring to lose its stabilization energy.

The following reaction step is highly exothermic, as it involves the ring regaining its stability, and is the energetic driving force for the overall substitution reaction. The hydrogen sharing a carbon atom with the sulphide group is released as a proton, yielding two electrons to balance the net positive ring carbon and regenerate the delocalised ring of π-electrons. The \( \text{SO}_3^- \) group balances its charge by covalently bonding a proton from the acidic and therefore proton-donating reaction environment. The styrene group has become a sulphonic acid styrene group.

The solution is stirred at 50° C for one hour whereupon the reaction is terminated by the addition of 20 ml of methanol. The polymer is then precipitated by pouring the solution into a large excess of methanol, causing the polymer to form a tight gum-like gel. This is dried at 50° C overnight under vacuum.

For comparison purposes, some of the sulphonated polymer is retained in this sulphonic acid form. The remainder is re-dissolved in DCE and neutralized to a phenolphthalein end-point with methanolic sodium hydroxide (NaOH) [Figure 4.7]. The resulting sodium sulphonate salt of polystyrene (S-PS) is then precipitated in the same manner as above, dried and stored. It was found to be necessary to use methanolic NaOH as its aqueous analogue induced premature precipitation of the polymer.

Ionomers with different sulphonate contents are prepared by varying the
amount of sulphonating agent added. All the reagents used are listed as a Chemicals section in Appendix C.

4.2.2 Evaluation of the sulphonation process

An analysis of the extent of sulphonation was carried out after each preparation to measure the ionic content of the polymer and to verify that sulphonation had not affected the polymer's structure in any way. Measurement of the extent of sulphonation was found to be a non-trivial matter; a variety of techniques was employed as some were found to be unable to measure the low concentrations of sulphur present.

The extent of molecular weight degradation caused by the sulphonation reaction was assessed by GPC in similar fashion to that used to check post-deuteration integrity. Figure 4.8 shows the comparison between a sulphonated polystyrene and its fully-hydrogenated precursor, in which the curves are nearly identical. It can therefore be concluded that the molecular weight distribution of the polymer was hardly affected by its being sulphonated.

NMR was used to examine the extent of replacement of the para proton by sulphonate groups. According to the same logic as that applied to deuteration, it was felt that substitution of the hydrogen atom in the position with a sulphonate group would remove that bond's contribution to the para peak on the NMR spectrum. No change was measured in the strength of the combined para- and meta-peak after sulphonation, suggesting that
Figure 4.8: Molecular weight distributions of h-PS and S-PS by GPC.
the concentration of sulphonate groups in the para position was very low.

Differential Scanning Calorimetry (DSC) gave the first indication that sulphonation of the polymer was in fact taking place. In this technique, a polymer sample is heated in tandem with a reference sample. The heat flow required to maintain the two samples at the same temperature is monitored as they undergo a user-specified heating program. Sudden changes in heat flow correspond to changes of state in the polymer sample and their intensity as well as the temperature at which they take place can be identified.

In the case of polystyrene, the glass-transition temperature, $T_g$ is a useful indicator of the state of the polymer. As its name suggests, $T_g$ is the temperature at which the polymer changes from the glassy state to one where it behaves more as a super-cooled liquid [Hall, 1981]. It can be defined as the point at which the thermal energy is sufficient to induce movement of "complete blocks or segments of the polymer chain as local entities" [Powell, 1983].

$T_g$ increases with the molecular weight of a polymer as a consequence of the reduction in chain mobility. In a polymer, the presence of cross-links acts to increase its molecular weight. The dipole-dipole interactions arising from the presence of ionic groups in the polymer are thought to act in a similar fashion to cross-links, such that an increase in $T_g$ after sulphonation would indicate successful sulphonation. During the course of the present work, early attempts at sulphonation using large quantities of sulphonating agent produced polymers with $T_g$ in the region of $125^\circ$ C,
whereas $T_g$ for polystyrene is typically in the range 90-105° C [Brandrup, 1975]. From this it was concluded that some form of intermolecular interaction, analogous to cross-links, was indeed taking place.

Wallace [1971] has studied the effect of sulphonate concentration on the $T_g$ of polystyrene, observing a linear dependence of $T_g$ on the weight percent of sulphonic acid monomer units. In the range 0 - 15% (monomeric ionic content), the $T_g$ increases from 102° to 130° C and this change is explained in terms of intermolecular forces of attraction. Wallace's data could be used to characterize sulphonate-containing polystyrenes. This work has been done for the sulphonic acids prepared during this work, together with $T_g$ measurements on the corresponding sulphonate salts. The results of this thermal characterization work are presented in the following chapter.

Subsequent work with Energy-Dispersive X-ray Analysis (EDAX) on an electron microscope confirmed the presence of sulphur in the material, although quantification of the sulphur concentration was not possible. Figure 4.9 shows an X-ray spectrum obtained by EDAX from a sodium sulphonate salt of polystyrene. The peaks due to oxygen, sodium and sulphur confirm the presence of these elements in the material. The material had previously undergone several dissolutions and precipitations in order to remove traces of reagents and had been dried for long periods to remove the solvent. It can therefore be concluded that the continued presence of these elements is due to their being bonded to the polymer.

In an effort to quantify the sulphur content, the stage of neutralizing
Figure 4.9: EDAX spectrum of sodium sulphonate salt of polystyrene, showing sulphur, oxygen and sodium.
the sulphanic acid to produce the sulphonate salt was performed as a meticulous titration. An accurate knowledge of the amount of base needed to neutralize the acid would in turn yield an estimate of the number of ionic groups present in the material. The results of this exercise are presented in Chapter 5.

The sulphur contents of modified polystyrenes were further verified by the use of a complementary ion-beam technique, Proton-Induced X-ray Emission (PIXE). Figure 4.10 shows the experimental arrangement used for PIXE. The proton beam was generated by the same Van de Graaff used to produce the $^3$He beam for the diffusion work.

Quantification of PIXE data is simplified by the negligible background and the corresponding virtual absence of noise. Any quantitative analysis must, however, take into account the combined effects of the stopping power of the sample material, absorption of induced X-rays and subsequent fluorescence. The stopping power dictates the depth-range of the sample over which X-rays will be produced; the smaller the range, the greater will be the likelihood of an X-ray escaping from the sample without interacting with any atoms in the sample. The probability of an X-ray being absorbed depends on the sample composition as do the energies of X-rays produced by fluorescence. In order to simplify the analysis, it would therefore be desirable to use samples of very similar compositions and stopping powers.

Quantifications of sulphur concentrations in s-PS were in fact performed by direct comparison with the X-ray yields from standard samples of known
Figure 4.10: Schematic of PIXE chamber.
composition. The standards consisted of known blends of poly(ethersulphone) (PES) with phenoxy (PO), ranging from 100% to 10% PES content. These materials have very similar densities and compositions to slightly sulphonated polystyrenes. The number of sulphur X-rays produced by a unit incident charge was compared to the known sulphur content of a sample. Sulphur concentrations in ionomers of unknown ionic content were then calculated by interpolation of their X-ray yield on the calibration curve produced by the PES/PO standards. The results obtained by both PIXE and titration are presented in the following chapter.

All sulphonated polystyrenes were analysed in this manner before being used in experiments.

The earliest sulphonate-salts that were made proved difficult to handle, precipitating out of solution partway through the sulphonation reaction time. As these preparations were subsequently hard to dissolve, for purposes of sample preparation, it was concluded that the extent of sulphonation was excessive and later preparations aimed at producing much lower concentrations of sulphonate groups. Although this entailed significant deviation from the quantities used by Makowski [1975], it should be noted that the present work aims at casting polymers from solution whereas Makowski was concerned with melt processing of his materials.

4.3 Sample preparation
Samples for diffusion experiments consist of two polymer layers on an aluminium token. The token's function is to provide mechanical support for the polymer layers. The first polymer layer on the token is cast from hydrogenated polystyrene (h-PS), which is invisible to NRA. The layer is produced by repeatedly dropping a solution of polymer in toluene. This layer of "bulk" material is built up until it is thicker than the range of the beam ion at the accelerator's maximum energy, so that there is no chance of ions recoiling from the aluminium into the sample as this would provide misleading counts. As the accelerator at Surrey has a maximum potential of 2 MV, it produces a maximum beam energy of 2 MeV for the singly-charged $^3$He$^+$ ion. It is known that $^3$He$^+$ ions with this energy have a range of approx. 8 μm in polystyrene [Skyrme, 1976] and the h-PS layer is therefore built up to a thickness of more than 10 μm.

In order to drive off all traces of solvent that might remain in the polymer, this layer is dried overnight in an oven at 50°C. The final step in the preparation of this h-PS layer consists of the layer being heated to 170°C, which is above the $T_g$ of polystyrene, in order to anneal out any residual stresses left in the material from the solution casting or the egress of solvent molecules.

The second layer, to be placed on top of the first, is made from deuterated polystyrene (d-PS). It is important to keep this layer thin compared to the window of the technique, so that diffusion of the d-PS into the h-PS material can be observed. For reasons outlined earlier in this chapter, it is also desirable to keep the level of d-PS in the bulk material at a tracer concentration. In order to ensure trace quantities of
d-PS in the bulk polymer during diffusion, this layer is kept very thin, typically 0.1 μm. This ensures the rapid establishment of a Fickian diffusion profile over the 2 μm window available using NRA.

A glass slide is dipped into a solution of d-PS in toluene and drawn out again, both by means of an electric motor, to ensure an equal velocity throughout the drawing process. The switching is done remotely, so as to minimize the vibration experienced by the slide, for fear of damaging the delicate film. The film is dried at room temperature, its thin nature ensuring rapid evolution of the solvent.

The speed of drawing is of paramount importance in guaranteeing the formation of an even film. At slow speeds the polymer remains close to the solvent environment long enough to allow it to flow and form a wedge on the slide, with material accumulating at the bottom of the slide. At high speeds, the polymer is removed from the solvent environment swiftly and dries before significant flow towards the bottom of the slide has taken place. The drawing speed also affects the film thickness with the film thickness increasing with the drawing speed. The solution concentration can, however, also be used to control the film thickness. The conditions used to repeatedly produce an even film of 0.1 μm thickness were therefore

$$\text{Drawing Speed} = 0.6 \pm 0.1 \text{ cm/s.} \quad \text{Solution concentration} = 0.1 \text{ gm/ml}$$

Once the film on the slide is dry, it is floated onto water by introducing the slide into a beaker of distilled water at a near-flat angle. The film
is then picked up on the h-PS layer and the sample is again dried at 50°C, to remove the water.

The thickness of a d-PS layer on the slide is measured by a TALYSTEP™, which consists of a sensitive stylus drawn across a previously-made scratch made in the polymer film. The drop in height as the stylus travels from the polymer to the exposed glass can be measured to an accuracy of 3%. The film thickness was measured at different heights on the slide and was found to be very uniform. This shows that the solvent evaporates very quickly such that the polymer cannot flow down the slide and one need not be concerned over which part of the floated film should be picked up.

Once the sample is completely dry it is annealed to induce inter-diffusion of the h-PS and d-PS layers. Annealing takes place inside an evacuated pyrex tube placed in a tubular furnace [Figure 4.11]. The furnace is allowed to settle to the selected temperature with the annealing tube in place and the sample, on the boat, at the end of the tube outside the furnace. Once the desired temperature is reached, the sample is slid swiftly down the tube to the hot end of the tube. The tube is connected to a vacuum pump throughout, as polymers can be degraded by oxygen when at elevated temperatures. The temperature at the end of the annealing tube is monitored throughout by a thermocouple attached to an aluminium token similar to the one supporting the diffusing polymer bilayer. This reference token is permanently located at the hot end of the tube.

A further precaution taken against the presence of oxygen in the tube is performed prior to introduction into the furnace as follows; the tube,
Figure 4.11: Schematic diagram of annealing system.
with sample and boat in place, is evacuated and then filled with pure argon. With the tube held vertically, the argon will sink preferentially, displacing the oxygen to the top, whereupon the tube is evacuated a second time and then constantly pumped out during the anneal.

Annealing times are dictated by the need to obtain a diffusion-profile in the depth-window accessible to the technique. An anneal that is too long will produce a flat profile, from which no information about the diffusion coefficient can be obtained, as the labelled material has been evenly distributed throughout the bulk material. An anneal that is too quick will not show any diffusion at all, resulting in a rectangular profile. Estimates of annealing times are based on an assumption of the order of magnitude of the diffusion coefficient and the use of the relation

$$\bar{x} = 2 \sqrt{Dt}$$

where $\bar{x}$ is a characteristic diffusion distance and $t$ is the time of anneal. This expression is derived from the solution to Fick's second law presented in Chapter 2. Estimates of the order of magnitude of $D$ are initially drawn from published values, notably from ERDA work by Green [1986]. Ionomer samples are annealed together with an ordinary polystyrene sample as a control for times designed to produce a diffusion profile of deuterated material over the first 2 $\mu$m of the sample, such that a beam energy of 1.1 MeV can be used, as this gives the best resolution. After several such experiments a library of $D$(PS) values for ranges of molecular weight and temperature is built up. These results are presented in the following chapter.
4.4 The experimental chamber

Important considerations in the design of the experimental chamber were as follows:

- The chamber had to achieve a vacuum compatible with that of the beam-line, so that the \(^{3}\text{He}^+\) ions could reach the chamber with minimal attenuation.
- A system for rapid sample change-over was necessary to make the best use of available beam-time, as well as ensuring that beam conditions were similar for consecutive samples. Such a system must therefore not overly degrade the chamber vacuum.
- Rotation of the sample to allow glancing incidences would give access to the best depth-resolution achievable by \(^{3}\text{He}-\text{d}\).
- The ability to cool the sample was required to reduce beam damage and to "freeze" the diffused molecules in place during analysis.
- The operator had to be able to observe the sample directly, to assure himself of the beam's position on the sample. striking the sample.

The analysis chamber used for the \(^{3}\text{He}\) work is located at the end of Line 2 of the Van de Graaff area of the D.R. Chick Ion Beam Facility at the University of Surrey. The stainless-steel chamber can be evacuated to a pressure of \(10^{-6}\) torr by means of an oil diffusion pump. There are several openings in the chamber wall which give access to the chamber. One of these allows the beam to enter the chamber. Two flanges with lead-glass
windows allow the operator to look into the chamber and observe the beam's shape and location on the sample. The beam can only be seen when it strikes a fluorescing material, resulting in a "beam-spot". Fortunately, polymeric materials fluoresce in the necessary manner and the operator can tell when the beam is on the target. The beam's shape is important for reasons of resolution; by the arguments presented in chapter 2, a narrow beam produces a better depth resolution than a broad beam.

The detector is mounted on an electrically-insulated stand, in order to prevent earth pickup. This precaution is taken in an effort to minimize the noise and thereby obtain good detector resolution. The stand is bolted onto a ring on the floor of the chamber which runs around the inner circumference and has bolting positions every five degrees. This allows the experimenter to place a detector at almost any angle, ranging from a very large backscatter angle to a glancing incidence.

The detector is cooled by means of a Peltier device clamped between the support column and the detector holder [Figure 4.12]. The two poly(tetrafluoroethylene) (PTFE) layers on either face of the Peltier device insulate the detector from the chamber. When the annular detector is being used, suggested as an improvement to the technique in chapter 2, a protection plate is bolted to the stand upstream of the detector. This plate has a hole concentric with the annulus but smaller than the hole in the detector. Its purpose is to prevent the beam from hitting the back of the detector, as this would damage the detector and impair the resolution.

The detector is biased at 600 Volts by a Northern Electric™ 4701 high
Figure 4.12: Side-view of detector mounting and cooling system.
voltage supply located in and powered by a Nuclear Instrument Module (NIM) bin. The signal from the detector travels out of the chamber by means of a "lead-through" in a PTFE flange. This flange material again ensures that the detector's casing is insulated from the chamber earth. The preamplifier, an ORTEC™ Model 142 AH, receives the signal just outside the PTFE flange, following which the signal travels to the main amplifier, an ORTEC™ Model 572, and then to the multi-channel analyser (MCA) in the control room. This arrangement ensures the minimum length of cable between the detector and the preamplifier and is essential to minimize electronic noise.

The MCA consists of an EG&G Maestro™ multi-channel buffer (MCB) card resident in an Amstrad 1512 PC. This buffer reads pulse-heights from the detector by means of an analog-to-digital (ADC) port before displaying a cumulative pulse-height frequency histogram on the screen. This histogram, or "spectrum", can be plotted and saved on disk for future use.

The sample is placed on the end of a finger protruding down from the chamber lid. The finger is hollow, so that liquid nitrogen can be poured in to cool it, and can be swivelled through a complete turn. The sample is clamped to a metal block which slides onto a dove-tail on the end of the finger. This block can be removed from the chamber by means of a retractable arm and a "load-lock" stage. The load-lock is an intermediate chamber designed to allow the repeated insertion and removal of the arm without degrading the chamber vacuum significantly. A sorption pump is used to achieve a pressure of $10^{-4}$ torr in the comparatively small volume of the load-lock such that the latter can then be opened to the chamber.
with negligible effect on the chamber vacuum. The arm ends in a thread which screws into a hole in the block. All this allows the experimenter to change samples without letting the whole chamber up to air, thus saving a great deal of time and expense.

The dove-tail arrangement ensures that the centre of the sample is in line with the axis of the swivel finger, when the block is in place. The finger can therefore be rotated without moving the sample out of the line of the beam. Furthermore, the arrangement is such that the block is in exactly the same position in relation to the finger before removal as after re-loading. In this manner, the sample will always be struck by the analysing beam.
Plate 2: Upstream view of experimental chamber with (left) detection electronics.
Plate 3: View of experimental chamber with lid removed to show cold finger.
Plate 4: Close-up view of end of cold finger showing dove-tail.
Plate 5: Interior view of experimental chamber with detector and protection magnet.
## Chapter 5: Results

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Initial evidence of inter-chain links</td>
<td>120</td>
</tr>
<tr>
<td>5.2 Small molecule diffusion</td>
<td></td>
</tr>
<tr>
<td>- The effect of ionic concentration</td>
<td>121</td>
</tr>
<tr>
<td>5.3 Characterization results: Titration, ( T_g ) and PIXE</td>
<td>125</td>
</tr>
<tr>
<td>5.3.1 Acid-base titration results</td>
<td>125</td>
</tr>
<tr>
<td>5.3.2 Glass-transition measurements</td>
<td>127</td>
</tr>
<tr>
<td>5.3.3 PIXE measurements</td>
<td>129</td>
</tr>
<tr>
<td>5.4 Diffusion experiments</td>
<td>133</td>
</tr>
<tr>
<td>5.4.1 Diffusion baselines</td>
<td>134</td>
</tr>
<tr>
<td>5.4.2 Mechanisms of diffusion</td>
<td></td>
</tr>
<tr>
<td>- Effect of molecular weight</td>
<td>137</td>
</tr>
<tr>
<td>5.4.3 Mechanisms of diffusion</td>
<td></td>
</tr>
<tr>
<td>- Effect of ionic concentration</td>
<td>142</td>
</tr>
<tr>
<td>5.5 Summary</td>
<td>148</td>
</tr>
</tbody>
</table>
Chapter 5: Results

This chapter is concerned with the results of various experiments carried out with ionomers. The first task involved characterising the various ionomers that had been made in terms of their ionic content. This was carried out by a combination of techniques with the aim of determining ionic content with good confidence, i.e. achieving agreement between different techniques, and of finding the method best suited to characterisation. The second task was the execution of diffusion experiments to investigate the aims presented in chapter 1, to wit the elucidation of the critical ionic concentration for aggregation, the thermal stability of aggregates and the mechanism governing polymer diffusion in ionomers. These experiments were conducted using the $^3$He-d technique developed during the course of this work.

5.1 Initial evidence of inter-chain links

The first evidence of a significant difference between an ionomer and ordinary polystyrene was observed during sample preparation. The higher ionomers were not soluble in toluene once they had been neutralised unless a small amount of methanol was present. This confirmed the thought that some parts of the chains were polar in nature.

It was also found that ionomer films obtained by drawing glass slides from such a solution would not re-dissolve in toluene, suggesting that solvent-resistant intermolecular links were formed as the film dried.
There was therefore no need to seek the energy of activation of aggregates; the chains needed only to be mobile, to be above $T_g$, in order to aggregate.

5.2 Small molecule diffusion – The effect of ionic concentration.

Early experiments in this work on ionomers involved measuring the diffusion of small molecules by Rutherford BackScattering (RBS). Thick layers of sulphonated polystyrenes were exposed to a vapour of short-chain alkanes containing an iodine tag. RBS was then used to extract iodine concentration-profiles normal to the exposed surface, thus showing the extent of penetration by small molecules as well as their relative amounts [Payne, 1988]. Whilst the presence of this tag may perturb the behaviour such that measurements are not truly representative of the movement of small molecules, the chief interest in this work lies in the extent to which an ionomer swells to accommodate the influx of small molecules and the rate at which this swelling takes place.

Polystyrene has been shown to exhibit non-Fickian, or Case-II, diffusion [Mills, 1985], wherein a diffusion-profile consists of two components; a Fickian precursor in the glassy core, followed by a sharp front behind which the polymer is swollen and rubbery and the penetrant concentration is nearly constant. At a later time, the front will have progressed to a greater depth, still preceded by a Fickian slope, and the concentration in the swelled region will have increased with the upper limit being the external penetrant activity. A further restriction can be imposed on the
swelling limit by the nature of polymer; if a polymer contains entanglements or cross-links, there comes a point at which these physically resist additional swelling. Therefore, by comparing the swelling rates of an ionomer and a normal polymer, the presence of such an effect would confirm the existence of inter-chain links.

The experimental method used was similar to that of Lasky [1988]. Samples were swiftly immersed in liquid nitrogen after exposure, in order to freeze the highly-mobile penetrant molecules in place. After rapid transfer from the liquid nitrogen bath to the experimental chamber, samples were maintained at a low temperature by filling the hollow cold-finger with liquid nitrogen.

Figure 5.1 shows an RBS spectrum obtained from a polystyrene film exposed to iodohexane (IOH) at room temperature for 20 seconds. The right-hand edge corresponds to the sample surface. The spectrum shows the Fickian precursor preceding a Case-II region of almost constant penetrant concentration. This flat region shows a gentle fall-off in concentration towards the surface which can be attributed to the increase in scattering cross-section with falling beam energy. This is an inherent feature of RBS. The small shoulder on the surface edge is caused by penetrant leaching out of the polymer during the various transfer stages, thus emphasising the need for rapid sample refrigeration after exposure.

An extension of this experiment can be seen in Figure 5.2, which shows a comparison between the rates of uptake of IOH by three ionomer films of differing ionic content. The ionic percentages quoted in Figure 5.2 were
Counts

Figure 5.1: RBS spectrum of polystyrene film exposed to IOH vapour.
### Ionic Content (by weight)

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**Figure 5.2:** RBS spectra from ionomer films of differing ionic concentration after exposure to iodohexane vapour for 60 seconds.
obtained by the characterisation methods presented in the following section. The films were exposed to IOH simultaneously for 60 seconds before being frozen and transferred as outlined above. The spectra show that increasing ionic concentration reduces the rate of penetrant uptake, specifically the front velocity. This shows that the polymer molecules resist the transition from the glassy to the rubbery state, implying that there is an additional binding energy that must be overcome before they will swell to accommodate the incoming small molecules.

5.3 Characterization results: Titration, T, and PIXE

5.3.1 Acid-base titration results

In order to measure the ionic concentration in a sample of sulphonated polystyrene, the volume of NaOH required to completely neutralise the poly (styrene sulphonic acid / styrene) copolymer resulting from the sulphonation reaction was measured by careful titration. The results of these titrations for the four ionomers used throughout the diffusion experiments are presented in Table 5.1.
<table>
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</tbody>
</table>

Table 5.1: Results of titration of sulphonic acid with NaOH.

The sulphonic acid weight percentages predicted by titration exhibit a degree of correlation with the amount of sulphonating agent used. However, these percentages are very high, being firmly in the polyelectrolyte rather than in the ionomer range. As the sulphonation sulphonation of Makowski [1980 Patent] was followed assiduously and the amounts of sulphonating agent used here were smaller, it seems extraordinary to obtain polymers modified to such a large extent. Therefore one must look to the method of titration for an explanation.

Standard acid-base titrations take place in an aqueous environment whereas the neutralisation of poly(styrene sulphonic acid) preparations was, of necessity, carried out in a mixture of dichloroethane and methanol. As each of these solvents is slightly acidic they may well have interacted with the NaOH, such that not only the dissolved acidic polymer but also the environment was being neutralised. This would explain the comparatively large quantities of NaOH required to completely neutralise the solution. Furthermore, acid-base titrations performed in a solvent environment exhibit a broad transition range [Charlot, 1969], resulting in a large uncertainty in measuring the point of neutrality.
These measurements have therefore served to confirm the presence of acid groups in the polymer after sulphonation whilst retaining some ambiguity as to the absolute concentrations involved.

5.3.2 Glass-transition measurements

The ionomer concentrations were characterised by measurements of the glass transition temperature, $T_g$, using the technique of differential scanning calorimetry (DSC) described in the previous chapter. Measurements were carried out on the sulphonic acids using a Mettler TC 10A instrument. The $T_g$ results are presented in Table 5.2 below together with their corresponding ionic concentrations obtained by interpolation from the data published by Wallace [1971], who observed a linear relationship between weight percent of styrene sulphononic acid and $T_g$ of the form

$$T_g = 102 + (183 \times \text{weight\%})$$

<table>
<thead>
<tr>
<th>Ionomer (ml sulph. agent)</th>
<th>$T_g$ after anneal$^a$ (\text{(degrees Celsius)})</th>
<th>Sulphonic acid weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>103.9 ± 0.5</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>0.1 acid</td>
<td>105.4 ± 0.5</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>0.3 acid</td>
<td>106.9 ± 0.5</td>
<td>2.7 ± 0.3</td>
</tr>
<tr>
<td>0.7 acid</td>
<td>110.0 ± 0.5</td>
<td>4.4 ± 0.3</td>
</tr>
</tbody>
</table>

Table 5.2: Glass-transition measurements of 90k ionomers used in diffusion experiments.
The samples used for $T_g$ measurements were annealed at $150^\circ$ C for 10 minutes, to remove any thermal ageing effects and traces of solvent, before being rapidly quenched. Figure 5.3 shows a typical DSC trace with the $T_g$ taken as the mid-point of the step change in the heat flow.

The sulphonic acids of polystyrene prepared for diffusion experiments were characterized by interpolating between their measured $T_g$ values and the corresponding weight percent of sulphonic acid contained in each using the linear relationship found by Wallace. All the preparations lie in the range 0-5 % ionic material by weight and are therefore truly ionomers.

An interesting feature exists in the form of the initial decrease in $T_g$ relative to unmodified polystyrene at low ionic contents. A probable explanation for this decrease is the effect on the free volume of adding a bulky group, such as $\text{SO}_3\text{Na}$, to the styrene side-group of the polymer. Polymers with side-branches have lower values of $T_g$ than their linear counterparts, due to their occupying more space and therefore requiring a lower temperature to achieve the close packing required to confine their segmental motions. Similarly, the addition of bulky sulphonate groups initially has the effect of maintaining a greater separation between adjacent molecules, with the consequence of a reduction in $T_g$. As the ionic content increases, however, the effect of intermolecular attractions becomes more significant than the effect on the free volume and the $T_g$ increases. Consequently, the value of $T_g$ of the unmodified polymer does not fit the linear relation describing the $T_g$ values of ionic polymers. It should be noted here that Wallace does not present a value of $T_g$ for his...
Figure 5.3: DSC trace of ionomer acid.
unmodified polymer.

5.3.3 PIXE measurements

Proton-induced X-ray emission (PIXE) was used to measure the sulphur content in ionomer salts as described in the previous chapter. The results of this work are presented in Table 5.3. The counts in the sulphur peak were normalised to the deposited charge to enable direct comparison between samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge(μC)</th>
<th>Sulphur peak area</th>
<th>Normalised counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Polystyrene)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 salt</td>
<td>1.67</td>
<td>256 ± 16</td>
<td>153 ± 10</td>
</tr>
<tr>
<td>0.3 &quot; &quot;</td>
<td>2.91</td>
<td>192 ± 14</td>
<td>66 ± 5</td>
</tr>
<tr>
<td>0.1 &quot; &quot;</td>
<td>5.73</td>
<td>212 ± 15</td>
<td>37 ± 3</td>
</tr>
<tr>
<td>(PES/PO)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(weight %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>2.88</td>
<td>11346 ± 106</td>
<td>3940 ± 37</td>
</tr>
<tr>
<td>90/10</td>
<td>2.86</td>
<td>9290 ± 96</td>
<td>3248 ± 34</td>
</tr>
<tr>
<td>70/30</td>
<td>2.87</td>
<td>8153 ± 90</td>
<td>2841 ± 31</td>
</tr>
<tr>
<td>30/70</td>
<td>2.86</td>
<td>3197 ± 57</td>
<td>1116 ± 20</td>
</tr>
<tr>
<td>10/90</td>
<td>2.86</td>
<td>1314 ± 36</td>
<td>460 ± 13</td>
</tr>
</tbody>
</table>

Table 5.3: PIXE results from ionomers used in diffusion experiments and from PES/PO blends used as standards.
The error in measuring the charge is less than 0.01 μC so the error in the normalised counts figure is dominated by the error in the peak area which, by Poisson statistics, is the square root of the counts.

A calibration curve between normalised sulphur counts and known sulphur content is obtained from the poly(ethersulphone)/phenoxy (PES/PO) standards (supplied by I.C.I. Wilton). This curve is displayed in Figure 5.4 together with the line resulting from a least-squares linear fit to the points. The sulphur concentrations, and thereby the overall ionic contents, of the ionomers were obtained by direct interpolation on the calibration curve.

The evident linear nature of the data enabled extrapolation to sulphur concentrations below the range covered by the standards to be performed with confidence. Furthermore, one would expect any deviation from a linear relationship between counts and sulphur concentration to occur at high sulphur concentrations, where the probability of reabsorption of sulphur X-rays may be significant. No such deviation is expected at low sulphur concentrations.

Once the sulphur concentration is known, it can be converted to either a weight or monomer percentage from a knowledge of the composition of the polymers making up the blend. In the case of the standard samples, these are a blend of PES (C₉O₃S₇H₈) and PO (C₁₉O₃H₂₀). The ionomers are a blend of PS (C₈H₈) and sPS (C₈H₇SO₃Na). An iterative calculation was used to find the PS/sPS blend that corresponded to the sulphur concentration measured in a given ionomer. The results are listed in Table 5.4 together
Figure 5.4: Sulphur concentration calibration curve from PIXE.
with the results from the $T_g$ measurements, both expressed in terms of monomer weight percent to facilitate comparison.

<table>
<thead>
<tr>
<th>Ionomer (ml. sulph. agent)</th>
<th>PIXE DATA</th>
<th>Tg DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulphur (ppt)</td>
<td>Ionic monomer weight %</td>
</tr>
<tr>
<td>1.0</td>
<td>.59 ± 0.07</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>0.7</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.3</td>
<td>.69 ± 0.04</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>.38 ± 0.02</td>
<td>1.2 ± 0.1</td>
</tr>
</tbody>
</table>

Table 5.4: Summary of characterization results.

The absence of a PIXE result for 0.7 salt is due to experimental difficulties experienced during analysis. Nevertheless, the close agreement of the results for the other preparations shows that the data from either PIXE or $T_g$ can be used reliably to determine ionic content.

In summary, the ionomers to be used in diffusion experiments have been characterised successfully by two sensitive techniques. The effect of ionic concentration on polymer diffusion can therefore be assessed quantitatively.

5.4 Diffusion experiments

Diffusion experiments are performed by annealing a dPS/hPS bilayer to
induce diffusion and subsequently assessing the extent of diffusion by extracting a concentration-profile of deuterium using the $^3\text{He}-d$ technique described in Chapter 2. A value for $D$, the diffusion coefficient, is obtained for each diffused bilayer, based on a knowledge of the annealing time. $D$ has been measured against changes in molecular weight, annealing temperature and ionic concentration in order to investigate the questions posed at the introduction to this work.

The range of annealing temperatures is dictated in each case by the corresponding annealing times: At high temperatures, only very short times are required lest excessive diffusion produce a flat, and therefore useless, profile. The lower limit on the temperature is set by the time available for the experiment. Consequently, realistic annealing times range from several minutes to several days.

A further consideration in determining annealing times is the depth-range of the $^3\text{He}-d$ technique. As concluded in Chapter 2, the optimum conditions for analysis use a beam energy of 1.1 MeV which provides a depth-"window" over approximately 2 $\mu$m. It is therefore desirable to obtain a diffusion-profile over this distance in order to take maximum advantage of the sharp resolution of the technique in these conditions.

5.4.1 Diffusion baselines

The self-diffusion coefficients of two molecular weights of polystyrene, 90,000 (90k) and 1,800,000 (1.8M), were measured over a range of
temperatures to establish baselines against which to compare subsequent experiments with ionomers. An ionomer diffusing noticeably more slowly than the unmodified polymer would indicate the presence of an interaction between polymer molecules over and above normal friction as described in Chapter 1.

All ionomers were made from 90k polystyrene and their diffusion is compared to that of unmodified 90k polystyrene as an upper limit. An ionomer diffusing at a similar rate to unmodified 90k polystyrene would therefore be adjudged to be experiencing no additional inter-chain interactions due to the presence of ionic material. Significant aggregation would, however, increase the effective molecular weight of the chains, such that ionomer diffusion would occur at a rate similar to a polymer of a higher molecular weight. The diffusion baseline of 1.8M unmodified polystyrene is therefore presented as a very low level of diffusion, the molecules being 200 times as long as those in the ionomers.

The results are presented in Table 5.5 and Figure 5.5. The solid lines in Figure 5.5 are extrapolations from the data based on linear fits to Arrhenius plots. This extrapolation is justified by the excellence of linear fits to the data.
Figure 5.5: Diffusion baselines for extremes of molecular weight.
<table>
<thead>
<tr>
<th>Temperature (Celsius)</th>
<th>Diffusion Coefficient ($D_s$) (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>$3.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>160</td>
<td>$5.5 \times 10^{-13}$</td>
</tr>
<tr>
<td>170</td>
<td>$9.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>175</td>
<td>$1.3 \times 10^{-12}$</td>
</tr>
<tr>
<td>184</td>
<td>$1.9 \times 10^{-12}$</td>
</tr>
<tr>
<td>188</td>
<td>$2.9 \times 10^{-12}$</td>
</tr>
<tr>
<td>194</td>
<td>$3.2 \times 10^{-12}$</td>
</tr>
<tr>
<td>200</td>
<td>$5.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>253</td>
<td>$5.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>279</td>
<td>$1.6 \times 10^{-10}$</td>
</tr>
<tr>
<td>322</td>
<td>$6.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>368</td>
<td>$2.6 \times 10^{-9}$</td>
</tr>
<tr>
<td>90k</td>
<td>* $7.9 \times 10^{-16}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $1.4 \times 10^{-15}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $2.4 \times 10^{-15}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $3.1 \times 10^{-15}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $4.8 \times 10^{-15}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $7.2 \times 10^{-15}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $8.0 \times 10^{-15}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $1.3 \times 10^{-14}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $1.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $3.9 \times 10^{-13}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $1.7 \times 10^{-12}$</td>
</tr>
<tr>
<td>1.8M</td>
<td>* $6.6 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

* denotes extrapolation

Table 5.5: Diffusion baseline data for 90k and 1.8M.

5.4.2 Mechanisms of diffusion - Effect of molecular weight

The molecular weight-dependence of self-diffusion in polystyrene was measured and compared to the models proposed in the introduction to this work. Samples consisted of dPS/hPS bilayers of identical molecular weights ranging from 90k to 1.8M annealed at 170° C. The results, presented in Figure 5.6, are compared to the curve predicted by the reptation model,

$$D^* = \frac{0.008}{M^2}$$
Figure 5.6: Molecular weight dependence of 90k polystyrene with prediction from reptation model.
where $D^*$ is the centre-of-mass diffusion coefficient. The value 0.008 has been measured by marker-marker displacement methods [Green, 1984] and is confirmed here; given an uncertainty of 10% in the measured values of $D$, the agreement with the model is very close. This strongly suggests that reptation is indeed the dominant diffusion mechanism in this range of molecular weight.

A theory for the temperature dependence of polystyrene diffusion coefficients has been developed [Green, 1986] based on the zero shear rate viscosity, $\eta_0$. In Figure 5.7, the diffusion data for unmodified 90k polystyrene are compared to the values predicted by the Williams–Landel–Ferry (WLF) equation used by Green

$$\log \left( \frac{D^*}{T} \right) = A - \frac{B}{T - T_0}$$  \hspace{1cm} (5.1)

where the empirical parameters $B = 710$ and $T_0 = 49^0 \text{C}$ are obtained from measurements of $\eta_0$ and $T$ is the temperature. The constant $A$ for a given molecular weight, $M$, is predicted by the reptation model based on the entanglement molecular weight, $M_e$, and the value of the average monomeric friction factor, $\xi_o$, measured at one temperature. The curves obtained from experiment and theory follow the same trend but are offset by a constant amount.

If reptation is the mechanism governing diffusion, then the relationship between the centre-of-mass diffusion coefficient and the
Figure 5.7: Comparison between 90k data from this work and prediction from WLF theory (left) together with Green's data for other molecular weights (right).
temperature, $T$, is given by the relation

$$\frac{D^*}{T} = G(M)\xi^{-1}(T) \quad (5.2)$$

where $G(M)$ [Green, 1984] is purely dependent on $M$ and is defined as

$$G(M) = \frac{4}{15} M e M_o k_B M^{-2} \quad (5.3)$$

where $M_o$ is the monomer molecular weight and $k_B$ is Boltzmann's constant.

A value for $A$ in equation 5.1 is obtained by combining equations 5.2 and 5.3 and this value is then used in equation 5.1 to predict $D^*$ at any temperature. The temperature-depending of $D$ is therefore independent of molecular weight.

Figure 5.7 shows Green's results from theory and experiment. While there is good agreement between measured values (symbols) and theory (solid lines) over the molecular weight range 55k - 430k, it should be noted that at the lower weights the values of $D^*$ predicted by the WLF equation are consistently lower. This observation tallies with the results for 90k unmodified polystyrene obtained during this work and can be explained by Green's failure to take into account the increasingly important contribution to the diffusion coefficient at low molecular weights of the mechanism of constraint release. In accordance with the models presented in Chapter I, as $M$ tends to $M_e$, 

141
\[ D^* = D_R \]

becomes

\[ D^* = D_R + D_{CR} \]

Nevertheless, the close agreement between theory and experiment demonstrate that, over the range of \( M \) studied in this work, the temperature–dependence of \( D^* \) is aptly described by the WLF equation. For a polymer of a known molecular weight one can therefore predict \( D^* \) for any value of \( T \).

In summary, the work in this section has confirmed reptation as the mechanism whereby polymers in the molecular weight range under study diffuse. The close agreement between experimental values of \( D^* \) with curves predicted by the WLF equation indicates that there is a relationship between diffusion and the zero shear rate viscosity and that the temperature–dependence of \( D^* \) is independent of the molecular weight of the polymer.

5.4.3 Mechanisms of diffusion - Effect of ionic concentration

The effect of ionic concentration on diffusion was studied in an effort to measure the critical concentration for aggregation. Diffusion samples consisted of a 0.1 \( \mu \text{m} \) film of deuterated 90k ionomer on a thick layer of hydrogenous 90k ionomer, with both layers containing a similar ionic concentration. Four ionomers with respective ionic weight percentages of 1.1, 2.2, 2.8 and 5 % were used. These samples were then annealed at
temperatures in excess of $T_\epsilon$ ranging from $150^\circ$ to $210^\circ$ C in order to investigate the effect of temperature on diffusion.

The results of these measurements are presented in Table 5.6 and Figure 5.8 together with the 90k baseline established earlier. As the ionic concentration increases, diffusion is reduced until, at the highest concentration used, diffusion is halted altogether. For this to happen, the polymer must have formed a network. This effect persists to high temperatures, showing that the inter-chain links have a high thermal stability. Figure 5.9 demonstrates this by comparing the diffusion-profiles of four ionomers annealed at $207^\circ$ C. The 1.1, 2.2 and 2.8% ionomers show Fickian profiles of varying slopes whereas the 5% ionomer shows no diffusion at all.

<table>
<thead>
<tr>
<th>Ionic content (weight %)</th>
<th>Diffusion coefficient $\times 10^{13}$ (cm$^2$/s) at annealing temperatures ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150</td>
</tr>
<tr>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>2.2</td>
<td>0.4</td>
</tr>
<tr>
<td>2.8</td>
<td>0.4</td>
</tr>
<tr>
<td>5.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 5.6: Effect of ionic concentration on diffusion over a range of temperatures.

The minimum concentration of ionic monomer for aggregation is therefore in
Figure 5.8: Effect of ionic concentration on diffusion coefficient.
Figure 5.9: $^3$He–d spectra showing the effect of ionic concentration on polymer diffusion.
the range 2.7 - 5 % by weight or 1.6 - 3 % by number. These results demonstrate the power of ionomers; at comparatively low ionic concentrations, with one monomer in fifty containing an ionic group, the structure of the material is significantly altered. As a polystyrene chain of 90k molecular weight contains approximately 900 monomers, a 2 % ionomer could form an average of 18 links with adjacent molecules. Figure 5.9 demonstrates that this relatively low concentration of active groups is nevertheless sufficient to produce a marked effect on the mobility of the chains.

The 90k polystyrene ionomer diffusion coefficients have also been plotted against $1/(T-T_g)$ in order to study the temperature dependence in more detail. Figure 5.10 shows how all the ionomer diffusion data now lie on the same WLF curve as the data from the unmodified 90k polystyrene. This indicates that, with the exception of the 5% ionomer, the ionomers diffuse in an identical manner to ordinary PS, albeit at a lower rate. By comparing $D$ to $1/(T-T_g)$, one shows that the ionomers have an effective annealing temperature lower than polystyrene by the difference in their $T_g$ values.

Polystyrene molecules diffuse by virtue of statistically-governed conformational changes based on the thermal energy available, which dictates the probability of individual chain segments altering their configuration. This temperature-dependence is described by the WLF curve, in which the diffusion coefficient is related to the temperature above $T_g$. The effect of adding ionic groups to the polymer is therefore equivalent to a time-temperature superposition; the higher the ionic
Figure 5.10: WLF plot of ionomers of 90k with best fit curve.
concentration, the higher $T$ and the lower the effective annealing temperature. The significance of this superposition between ionic concentration and effective annealing temperature lies in the fact that diffusion is still governed by the polystyrene segment-segment conformational transitions; there is no fundamental structural change associated with ionic groups. In the region of 5% ionic content, however, a significant change does take place and diffusion is halted, presumably by the formation of a network involving all the molecules.

5.5 Summary

The ionic contents of a range of ionomers have been established by the complementary techniques of PIXE and thermal analysis. Based on these measurements, the effect of ionic content on polymer diffusion has been examined using $^3$He-d. Over the range 0 - 2.8 weight % of ionomer, diffusion occurs by reptation, with higher ionic content having a retarding effect akin to a reduction in the annealing temperature. At 5 weight %, though, diffusion is halted. The critical concentration for aggregation is therefore felt to be in the range 2.8 - 5 weight %.
Chapter 6: Summary, conclusions and suggestions for future work.

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Summary</td>
<td>150</td>
</tr>
<tr>
<td>6.2 Conclusions</td>
<td>150</td>
</tr>
<tr>
<td>6.3 Suggestions for future work</td>
<td>153</td>
</tr>
</tbody>
</table>
Chapter 6: Summary, conclusions and suggestions for future work.

6.1 Summary

This thesis has concerned itself with the study of diffusion in ionic polymers. In the course of this investigation, a number of preliminary exercises were required. An assessment of existing techniques used to study polymer inter-diffusion revealed the absence of an ideally-suited method for the measurement of polymer self-diffusion. A large part of this work is therefore taken up with the implementation and assessment of an ion beam technique to perform these measurements. Following this there was a need to develop methods for the synthesis and characterization of ionic polymers as well as for their deuteration for the purposes of diffusion measurement. Only then was it possible to carry out diffusion experiments with the aim of answering the questions asked in the introduction to this work.

6.2 Conclusions

The $^3$He-d technique has been shown to outperform existing ion-beam techniques in terms of direct application to the question of measuring polymer interdiffusion and to effectively bridge the gap between those techniques measuring diffusion on a microscopic scale (nm) and those which measure diffusion on a macroscopic scale (mm). A strong feature of $^3$He-d is its ability to measure polymer self-diffusion by exploiting the minimal
labelling of hydrogen replacement by deuterium.

To achieve optimum performance, the protons produced by the $^3\text{He}$-d technique must be detected at a backward angle. This requires a detector with a depletion region of the order of 1500 μm in order to detect the full energy of the highly-energetic protons produced during analysis. A backward detection angle as close to 180° as possible has been shown to provide the optimum resolution. At a glancing beam incidence, the depth resolution of 20 nm achieved by $^3\text{He}$-d is a great improvement on the 800 nm resolution provided by ERDA.

Ion beams invariably cause some damage to samples and the effect of the $^3\text{He}$ beam on the polymer and on the diffusion-profile was investigated using a combination of techniques. Carbonisation of the polymer surface after analysis was apparent on every sample and XPS results suggested that the beam might be damaging the polymer's structure. However, these results were not conclusive and further investigation of the question of damage was required.

An estimate of the degree of cross-linking due to exposure to the beam was performed, with the result that a typical analysis induces, at most, a cross-link density equal to the existing entanglement density. As such, the effect on diffusion will not be great and will in any case tend to lock a diffusion-profile in place. Nonetheless, no effect on the polymer's subsequent diffusion behaviour was observed, with pre- and post-analysis samples being seen to diffuse to an equal extent.
Furthermore, an identical value for the diffusion coefficient was extracted from a single sample by subsequent analyses to confirm the preservation of the diffusion information in a sample under analysis. The $^3$He–d technique can therefore be described as being "non-destructive".

Various experimental refinements are suggested to minimise damage to the sample as a precautionary measure to which must be added a comment on the deuterium level in the polymer; the greater the concentration of deuterium in the penetrating polymer, the more rapidly a spectrum will be collected and the less beam charge will be needed with a consequent reduction in the beam damage. The deuterium content of a deuterated polymer was determined by measuring the reduction in the post-deuteration hydrogen signal from different bonds on a proton-NMR spectrum. Typically 90% of carbon-hydrogen bonds in the five positions around the styrene group became carbon-deuterium bonds whereas the degree of replacement along the backbone was of the order of 10%. This ring-specificity of the deuteration process suggested that the chain integrity would hardly be affected by deuteration. Gel permeation chromatography measurements of the molecular weight distribution before and after deuteration confirmed this by showing very little change.

The ionic polymers used for diffusion experiments were sulphonate ionomers of polystyrene. Their preparation required modification of an existing sulphonation procedure patented by Makowski [1975] as this methodology produced ionic concentrations vastly in excess of the 0–5% by weight typically associated with ionomers. Characterization of sulphonated polystyrenes was successfully carried out using measurements
of their glass-transition temperature and sulphur contents, by thermal analysis and proton-induced x-ray analysis, respectively.

Post-sulphonation chain integrity was studied by gel permeation chromatography and confirmed that sulphonation hardly affected the monodispersity of the polymer. Consequently, the molecular weight dependence of the diffusion coefficient was investigated with good precision and was found to agree with the reptation model proposed in the introduction over the molecular weight range 90k - 1.8M.

The effect of ionic content on diffusion was then studied, yielding the result that over the range 0 - 2.8 weight %, diffusion occurs in an identical manner to the diffusion of an unmodified polymer, by reptation, but in the range 2.8 - 5 weight % diffusion is halted. This can only be explained by the onset of gellation in the ionomer, attributed to the formation of ionic aggregates. Consequently, the critical concentration for aggregate formation is taken to be in the range 2.8 - 5 weight % of ionic monomer.

6.3 Suggestions for future work

Regarding the thermal characteristics of ionic aggregates, the 5.0 % ionomer showed no diffusion over the temperature range 150 - 210 °C. As samples were produced from room temperature solutions this suggests that aggregation occurs either in solution or as the polymer dries and the interchain distance is reduced. As such, it is difficult to identify an
energy of formation of ionic aggregates. Future work could examine diffusion of 5% ionomers over the temperature-range 100 - 150 °C in case they diffuse freely below a critical temperature at which aggregation is triggered. This work was not done here for reasons of time; at such low temperatures, annealing times would be of the order of weeks. A possible solution would be to use lower molecular weight ionomers while bearing in mind that the diffusion mechanism begins to resemble a combination of reptation and constraint release as one approaches the critical molecular weight for entanglements.

Perhaps of greater interest is the temperature of breakup of ionic aggregates. A study of this parameter would give an indication of the strength of aggregates as well as suggesting the ideal temperature for the melt processing of ionomer materials.

Future work should also focus on the critical concentration of ionic material for aggregate formation, to give some insight into their size and structure, both of which are matters currently experiencing heated debate.

The \(^3\)He-\(d\) technique is a valuable addition to the arsenal of the polymer physicist, enabling him to measure the self-diffusion of a single polymer whilst also being applicable to the mixing of dissimilar polymers as well as to the questions of water uptake and small molecule penetration, where these can be deuterated. To further improve both the resolution and the sensitivity, the use of a cooled annular detector centred on the incoming beam is strongly recommended.
Appendix A: TURBOBASIC™ routines written for this work.

A.1. NEWONE21.BAS

The program NEWONE21 performs the function of extracting a value for the diffusion coefficient from an experimental spectrum. Normalisation of the experimental spectrum by a spectrum from a thick, fully-deuterated sample is carried out by the program.

After inputting the time of anneal and the analysis parameters by which the spectrum was collected, the user is asked to make a guess at a first fit from a display of the normalized spectrum. The fitting routine uses this guess as a starting point to a least-squares fit to the normalized slope. From the initial thickness of the penetrating layer, the routine calculates the concentration at depth using the error-function solution to the second-order diffusion equation quoted in Chapter 2. By doing this for every channel in the range specified by the user, a theoretical diffusion-profile is built up. After convolution with the experimental resolution, the fit is compared to the experimental data.

The maximum height and slope of each fit is varied by changing the diffusion coefficient used in its generation. An array of theoretical profiles is generated in this manner and the corresponding least-squares fits to the data calculated. The final "best-fit" profile is then displayed along with the value of the diffusion coefficient used in its generation and the value of $\chi^2$. 

155
NEWONE21: a Program written by Tony Clough, Robin Payne and Peter Murphy to fit diffusion coefficients to spectra obtained by Helium-3,d reaction analysis.

rem dimension variables and arrays

dim ed(i5),s(i5),kk(2500),l(2500),res(100,100),x2(100)
dim y2(l100:1400)
dim da(l100:1400),x3(100),y3(l100:1400),sum(2000),de(l100:1400)
dim sumsq(30,200)
DIM DEE(1100:1400)
dim delda(l100:1400)
dim lda(100),dep(100)

rem HE-3 ENERGIES

j20=0
j10=2000
ED(1)=.15
ED(2)=.18
ED(3)=.21
ED(4)=.24
ED(5)=.27
ED(6)=.30
ED(7)=.375
ED(8)=.48
ED(9)=.60
ED(10)=.75
ED(11)=.96
ED(12)=1.2
ED(13)=1.5
ED(14)=1.8
ED(15)=2.1
rem STOPPING POWERS IN MEV-CM²/MG: ZIEGLER 1985

\[
\begin{align*}
S(1) &= 1.9064 \\
S(2) &= 2.01906 \\
S(3) &= 2.11197 \\
S(4) &= 2.188 \\
S(5) &= 2.2493 \\
S(6) &= 2.29747 \\
S(7) &= 2.37033 \\
S(8) &= 2.38766 \\
S(9) &= 2.33391 \\
S(10) &= 2.21513 \\
S(11) &= 2.02528 \\
S(12) &= 1.82445 \\
S(13) &= 1.61713 \\
S(14) &= 1.45303 \\
S(15) &= 1.32172 \\
\end{align*}
\]

\[
\begin{align*}
a_1 &= 0.254829592 \\
a_2 &= -0.284496736 \\
a_3 &= 1.421413741 \\
a_4 &= -1.453152027 \\
a_5 &= 1.061405429 \\
p &= 0.3275911 \\
\end{align*}
\]

rem user to input conditions

gosub 121
gosub 122
gosub 123
gosub 124
gosub 125
gosub 126
gosub 127
alpha=alph*3.14159/180
mp=938.28
m3=2808.413
md=1875.63
m4=3727.41

phi=ang*3.14159/180
q=m3+md-mp-m4
bb=-2*(m3*mp*e3b)^.5*cos(phi)
bbb=-2*(m3*m4*e3b)^.5*cos(phi)

aa=mp+m4
cc=m3*e3b-m4*e3b-m4*q
ccc=m3*e3b-mp*e3b-mp*q

rem PROTON ENERGY AT HALF-HEIGHT OF SPECTRUM LEADING EDGE

ep0=((bb+(bb^2-4*aa*cc)^.5)/(2*aa))^-2
ealpha=((bbb+(bbb^2-4*aa*ccc)^.5)/(2*aa))^-2

? " Input Diffused Filename: ";: line input namein1$

OPEN namein1$ AS #4 LEN=8605
FIELD #4,2 AS F$;2 AS M$;2 AS S$;2 AS E$;2 AS R1$;_
    2 AS R2$;2 AS L1$;2 AS L2$;8 AS D$;4 AS T$;_
    2 AS C$;2 AS N$;8192 AS I$;321 AS FF$;60 AS P$
GET #4
PRINT namein1$; " INFO.: ":PRINT P$
CLOSE #4

INPUT "ENTER 1st CHN.(5 CHNS BELOW HALF-HGHT OF LEADING EDGE):",J1
INPUT "ENTER THE LAST CHANNEL NO. TO BE ANALYSED ":",J2

open namein1$ as #4 len=16
field #4, 4 as a$, 4 as b$, 4 as c$, 4 as d$
tempsize= lof(4)/16
for i=3 to tempsize
    get 4,i
\[ m = (i-2) \times 4 \]
\[ kk(m-3) = cvl(a) \]
\[ kk(m-2) = cvl(b) \]
\[ kk(m-1) = cvl(c) \]
\[ kk(m) = cvl(d) \]

Next \(i\)

Close #4

\[ j0 = j1 + 5 \]
\[ jdif = J1 - J1N \]

For \(j = j1\) to \(j2\)

\[ jj = j - jdif \]

If \(l(jj) = 0\), THEN GOTO 20

\[ da(j) = kk(j)/l(jj) \]

If \(kk(j) = 0\) then \(da(j) = 1/l(jj):kk(j) = 1\)

\[ delda(j) = da(j) \times (1/kk(j) + 1/l(jj))^{0.5} \]

GOTO 22

20 PRINT "THE NORMALISATION CHANNEL " jj " WAS ZERO."

22 Next \(j\)

DEE(J0-1) = 0

DE(J0-1) = 0

If \(J2 > J20\) THEN GOTO 111

If \(J1 < J10\) THEN GOTO 111 ELSE GOTO 112

111 For \(j = J0\) to \((J2 - J1 + J0)\)

rem CALIBRATION OF CHANNELS IN TERMS OF PROTON ENERGIES

\[ ep = ep0 + (j-(j1+5)) \times ke/1000 \]

Let \(b = -(2 \times \text{sqr}(m3 \times mp \times ep) \times \cos(\phi))\)

Let \(a = m3 - m4\)

Let \(c = (mp + m4) \times ep - m4 \times q\)

Let \(ans1 = (-b + \text{sqr}(b^2 - 4 \times a \times c))/(2 \times a)\)

Let \(e3 = ans1^2\)

Let \(dele = e3b - e3\)

Let \(dx = 0.0000001\)
let $\text{dee}(j) = 0$

let $e = e_{3b} - \text{dee}(J-1)$

FOR $I=0$ TO $8000$

FOR $g=1$ TO $15$

$Z = E - \text{ED}(g)$

IF $Z<0.0$ THEN GOTO 60

IF $Z=0.0$ THEN GOTO 70

NEXT $g$

60

$E_1 = E - \text{ED}(g-1)$

$E_2 = \text{ED}(g) - \text{ED}(g-1)$

$E_3 = E_1 / E_2$

$S_1 = S(g) - S(g-1)$

$\text{DEDX} = S(g-1) + S_1 * E_3$

GOTO 80

70

$\text{DEDX} = S(g)$

rem dedx in Mev/mg/cm$^2$

80

let $\text{dee}(J) = \text{DEDX} * \text{DENS} * \text{DX} * 1000.0 + \text{DEE}(J)$

REM DE IN MEV

IF $(\text{DEE}(J)+\text{DEE}(J-1)) > \text{dele}$ THEN $\text{DEE}(J) = \text{DX} * 10000 + \text{DEE}(J-1)$: GOTO 10

let $e = e_{3b} - \text{DEE}(J) - \text{DEE}(J-1)$

NEXT $I$

10

$\text{dee}(J) = \text{DEE}(J) + \text{DEE}(J-1)$

REM DE(J)-DEPTH ALONG THE BEAM DIRECTION FOR ENERGY LOSS DELE IN MICRONS

PRINT $j, \text{DE}(J), e$

40

NEXT $j$

for $n=0$ to $n_{max}$

$\text{dep}(n) = \text{de}(j_0+2+n*5)^2$

next $n$

112

gosub 1000

gosub 4500

gosub 5000

gosub 6000
rem FIRST GUESS AT NORMALISATION, SLOPE

locate 1,1: input "Norm const(peak height/10) :", entry
cCO = entry
gosub 14000
locate 2,1: input "Spectrum slope(normally .05) :", entry
kO = entry
gosub 14000
locate 3,1: input "slope increment(normally .05) :", entry
dk = entry
gosub 14000
rem ..........redraw data
gosub 12000
locate 1,1: ?"first fit"
rem dc is increment during fit
dc=.01
cc=ccO
k=kO
rem ? k
z=1
for x=j1 to j2
xx=x-j1+1
res(xx,z) = 0
for mu = j0 to (j2-j1+j0)
xmun=(x-mu-n)^2
if xmun>50 then goto 156
xp=(h+de(mu)*sin(alpha))*(k^.5)
t=1/(1+p*xp)
erfp=1-(a1*t+a2*t^2+a3*t^3+a4*t^4+a5*t^5)*exp(-1*xp^2)
xp=0
xm=(de(mu)*sin(alpha)-h)*(k^0.5)
if xm<0 then xp=xm:xm=-xm
tl=1/(1+p*xm)
erfm=1-(a1*tl+a2*tl^2+a3*tl^3+a4*tl^4+a5*tl^5)*exp(-1*xm^2)
if xp<0 then erf=m=-erfm
amu=0.5*(erfp-erfm)
sig = 1.25+de(mu)^2/4
res(xx,z) = res(xx,z)+(amu/(sig*(2*3.14159)^.5))*exp(-xmun/(2*(sig)^2))

next mu
next x
gosub 1500
gosub 2000
gosub 3000
kop=k0
locate 1,1: input "All o.k.? (YES or NO):", entry$
d$ = entry$
gosub 14000
dd$ = lcase$(d$)
ddd$ = left$(dd$, 1)
if(dd$ = "y") then goto 100 else goto 134

REM  FIRST SHOT AT ESTIMATING "D" HOLDING MAXIMUM Y-VALUE CONSTANT

100
n=0
for z=1 to 100

cc=cc0
k=k0+dk*(z-1)
for x=j1 to j2
xx=x-j1+1
res(xx,z) = 0
for mu = j0 to (j2-j1+j0)
xmun=(x-mu-n)^2
if xmun>50 then goto 157
xp=(h+de(mu)*sin(alpha))*(k^.5)
t=1/(1+p*xp)
erfp=1-(a1*t+a2*t^2+a3*t^3+a4*t^4+a5*t^5)*exp(-1*xp^2)
xp=0
xm=(de(mu)*sin(alpha)-h)*(k^0.5)
if xm<0 then xp=xm: xm=-xm
tl=1/(1+p*xm)
erfm=1-(a1*tl+a2*tl^2+a3*tl^3+a4*tl^4+a5*tl^5)*exp(-1*xm^2)
if \( xp < 0 \) then \( \text{erfm} = -\text{erfm} \)

\[
\text{amu} = 0.5 \times (\text{erfp} - \text{erfm})
\]

\[
\text{sig} = 1.25 + \text{de}(\text{mu})^2 / 4
\]

\[
\text{res}(\text{xx}, \text{z}) = \text{res}(\text{xx}, \text{z}) + (\text{amu} / (\text{sig} \times (2 \times 3.14159)^{0.5})) \times \exp(-\text{xmun} / (2 \times (\text{sig} \times (2 \times 3.14159)^{0.5})))
\]

157

next \( \text{mu} \)
next \( \text{x} \)
gosub 1500
gosub 2000
gosub 3000
gosub 7000
if \( \text{z} = 1 \) then goto 21
if \( \text{sum}(\text{z}) > \text{sum}(\text{z} - 1) \) then \( \text{k} = \text{k} + (\text{z} - 1) \times \text{dk} \): goto 101

21

next \( \text{z} \)

rem GENERATING SUMSQ FOR RANGES OF MAGNITUDE cc AND "D"
rem get number of steps between slope limits for fitting

101

\[
\text{z1} = \text{int}(0.7 \times \text{k} / \text{dk})
\]

\[
\text{z2} = \text{int}(1.3 \times \text{k} / \text{dk})
\]

for \( y = 1 \) to 30

\[
\text{cc} = \text{cc} - (y - 1) \times \text{dc} \times \text{cc} 0
\]

if \( \text{cc} < \text{cc} 0 \) then goto 41

for \( \text{z} = \text{z1} \) to \( \text{z2} \)

\[
\text{k} = \text{dk} \times \text{z}
\]

for \( \text{x} = \text{j1} \) to \( \text{j2} \)

\[
\text{xx} = \text{x} - \text{j1} + 1
\]

\[
\text{res}(\text{xx}, \text{z}) = 0
\]

for \( \text{mu} = \text{j0} \) to \((\text{j2} - \text{j1} + \text{j0})\)

\[
\text{xmun} = (\text{x} - \text{mu} - \text{n})^2
\]

if \( \text{xmun} > 50 \) then goto 257

\[
\text{xp} = (\text{h} + \text{de}(\text{mu}) \times \sin(\text{alpha})) \times (\text{k}^{0.5})
\]

\[
\text{t} = 1 / (1 + \text{p} \times \text{xp})
\]
erfp = 1 - (a1*t + a2*t^2 + a3*t^3 + a4*t^4 + a5*t^5) * exp(-1*xp^2)

xp = 0

xm = (de(mu)*sin(alpha) - h)*(k^0.5)

if xm < 0 then xp = xm; xm = -xm

tl = 1/(1+p*xm)

erfm = 1 - (a1*tl + a2*tl^2 + a3*tl^3 + a4*tl^4 + a5*tl^5) * exp(-1*xm^2)

if xp < 0 then erfm = -erfm

amu = 0.5*(erfp - erfm)

sig = 1.25 + de(mu)^2/4

res(xx,z) = res(xx,z) + (amu/(sig*(2*3.14159)^0.5)) * exp(-xm^2/(2*(sig)^-2))

next mu
next x

gosub 1500

gosub 2000

gosub 7000

sumsq(y,z) = sum(z)

next z

goto 50

for z = z1 to z2

gosub 1500

gosub 2000

gosub 7000

sumsq(y,z) = sum(z)

next z

next y

rem FINDING MINIMUM SUMSQ

min = sumsq(1,z1)

YMIN = 1

ZMIN = Z1
for y = 1 to 30
    for z = z1 to z2
        if sumsq(y,z)<min then min=sumsq(y,z); ymin=y; zmin=z
    next z
next y
z=zmin

rem PRINTING BEST-FIT VALUE OF "D"

k=zmin*dk
cc=cc0-(ymin-1)*dc*cc0
gosub 1000
gosub 8000
gosub 9000
gosub 1500
gosub 10000
gosub 11000
SU1=0
FOR I= J1 TO J2
    SU1=SU1+Y3(I)-10
NEXT I
k=k*1e8
ddd=1/(4*ta*k)
print namein1$
locate 2,1: print ddd " cm2s-1. Chi^2 = " min
locate 1,1: input"Finished ? (Type YES or NO ) :",entry$
a$=entry$
rem gosub 14000
aa$=lcase$(a$)
aaa$=left$(aa$,1)
if(aaa$="y") then goto 119

SCREEN 0
J10=J1
J20=J2
? "Type any one difference from previous run"
?" 0-No difference"
1-Specimen density
2-Annealing time
3-Thickness of d-ps film
4-He3 beam energy
5-Angle of detector
6-Angle of sample
7-Normalisation filename

input entry
ss = entry

if ss=0 then goto 129
if (ss=1) then gosub 121
if (ss=2) then gosub 122
if (ss=3) then gosub 123
if (ss=4) then gosub 124
if (ss=5) then gosub 125
if (ss=6) then gosub 126
if (ss=7) then gosub 127
input "Are there more differences? (type YES or NO):", c$

cc$=lcase$(c$)
ccc$=left$(cc$, 1)
if (ccc$="y") then goto 97
goto 129

119

go to 14500
stop

END

REM border creation; window 600 by 200 - border 500 by 160

1000
SCREEN 1
CLS
WINDOW (0,0)-(600,200)
LINE (50,10)-(550,10)
REM to find the maximum y value

1500

FLAG = res(1,z)
FOR I=j1 TO j2
    ii=i-j1+1
    IF res(ii,z)>FLAG THEN FLAG=res(ii,z)
NEXT I
LET YMAX = FLAG
RETURN

if ymax = 0 then stop

REM to scale data to the border for plotting

2000

SCALEY = 160/YMAX
SCALEX = 500/(j2-j1+1)
FOR I=0 TO j2-j1
    LET X2(I) = 50 + SCALEX*I
NEXT I
FOR I=j1 TO j2
    ii=i-j1+1
    LET Y2(I) = 10 + SCALEY*cc*res(ii,z)
NEXT I
RETURN

REM plotting the data

3000

FOR I=j1 TO j2
    CIRCLE (X2(I-j1),Y2(I)),1.5
NEXT I
RETURN

REM to find the maximum y value

4500
FLAG = da(j0)
FOR I=j0 TO j0+10
   IF da(I)>FLAG THEN FLAG=da(I) : jmax=i
NEXT I
LET YMAX1 = FLAG
RETURN

REM to scale data to the border for plotting

5000
SCALEY1 = 160/YMAX1
SCALEX = 500/(j2-j1)
FOR I=0 TO j2-j1
   LET X3(I) = 50 + SCALEX*I
NEXT I
FOR I=j1 TO j2
   LET Y3(I) = 10 + SCALEY1*da(i)
   if (y3(i)>170) then y3(i)=170
NEXT I
RETURN

REM plotting the data

6000
FOR I=j1 TO j2
   CIRCLE (X3(I-j1),Y3(I)),3.0
NEXT I
FOR I=J1 TO J2 STEP int((j2-j1)/8 +0.5)
   LINE(X3(I-J1),8)-(X3(I-J1),12)
NEXT I
for i=1 to 9
   line(45,10+16*i)-(55,10+16*i)
next i 
RETURN

7000 
sum(z)=0 
for i =j0 to j2 
  sum(z)=(y2(i)−y3(i))^2/(scaley1^2*delda(i)^2) + sum(z) 
next i 
return 

REM to scale data to the border for plotting FINALLY 

8000 
SCALEX = 500/DE(J2) 
FOR I=0 TO J2−J0 
  LET X3(I) = 50 + SCALEX*DE(I+J0)*sin(alpha) 
NEXT I 
RETURN 

REM plotting the data FINALLY 

9000 
FOR I=J0 TO J2 
  CIRCLE (X3(I−J0),Y3(I)),3.0 
NEXT I 

defs=SCALEX*de(j2)/10 
for i= 1 to 10 
  LINE(50+defs*(i−1),8)−(50+defs*(i−1),12) 
NEXT I 
for i=1 to 9 
  line(45,10+16*i)−(55,10+16*i) 
next i 
RETURN 

REM to scale data to the border for plotting
10000
scaley=160/ymax
FOR I=0 TO j2-j0
    LET X2(I) = 50 + SCALEX*DE(I+J0)*SIN(ALPHA)
NEXT I
FOR I=j0 TO j2
    ii=i-j1+1
    LET Y2(I) = 10 + SCALEY*cc*res(ii,z)
NEXT I
RETURN

REM plotting the data

11000
FOR I=j0 TO j2
    CIRCLE (X2(I-j0),Y2(I)),1.5
NEXT I
RETURN

121
cls
    INPUT "ENTER THE SPECIMEN DENSITY (IN GRAMS PER CM3): ",DENS
RETURN

122
    input "time of anneal (in secs!! ) ",ta
RETURN

123
    input "enter thickness of d-PS film (um) :",h
RETURN

124
    input "he3 beam energy in MEV (e.g. 1.1) : ",e3b
RETURN
input "angle of detector in degrees (e.g.160) :", ang
RETURN

input "angle of sample to beam (normally 90 deg) in deg. :", alph
input "Condition still green ? (nay = 1)", resp
if resp = 1 then goto 2
RETURN

126

"Input Normalisation Filename: "; line input namein2$
OPEN namein2$ AS #4 LEN=8605
FIELD #4, 2 AS F$, 2 AS M$, 2 AS S$, 2 AS E$, 2 AS RI$, _
   2 AS R2$, 2 AS LI$, 2 AS L2$, 8 AS D$, 4 AS T$, _
   2 AS C$, 2 AS N$, 8192 AS I$, 321 AS FF$, 60 AS P$
GET #4
PRINT namein2$; " INFO.: "; PRINT P$
CLOSE #4
INPUT "ENTER 1st CHN.(PRECISELY 5 CHNS BELOW HALF-HGT OF LEADING EDGE) :", JIN
INPUT "ENTER PROTON ENERGY PER CHN. IN keV/CHN.(10 if not measured) :", ke
open namein2$ as #4 len=16
field #4, 4 as a$, 4 as b$, 4 as c$, 4 as d$
tempsize= lof(4)/16
for i= 3 to tempsize
   get 4,i
   m=(i-2)*4
   l(m-3) = cvl(a$)
   l(m-2) = cvl(b$)
   l(m-1) = cvl(c$)
   l(m) = cvl(d$)
next i
CLOSE #4
RETURN

12000
rem ........routine to draw display
cls
gosub 1000: gosub 4500: gosub 5000: gosub 6000
return

13000
rem ......pause routine
for t = 1 to 50
let tt = t
next t
return

14000
rem ........quit routine
if entry = 0 then goto 14500
if entry$ = "0" then goto 14500
let entry = 1
let entry$ = "1"
return

14500
rem ........add-on to quit routine
cis
locate 1,1: print "You wish to leave the program (1) "
locate 2,22: ? " or restart (2)"
locate 3,17: input " or continue (3) ?",ans
if ans = 2 then goto 1
if ans = 1 then goto 14510
if (aaa$="n") then goto 97
return

14510
cis
locate 10,30: ? "Goodbye."
end

'End of Program - Layout and comments by Peter Murphy

A.2. HE3CALC.BAS
The program HE3CALC calculates the laboratory energies of the reaction products of the d($^3$He,p)$^4$He reaction and was used to investigate the effects of detection angle and beam-energy on the depth resolution in Chapter 2. The user provides the angle and energy whereupon the routine transposes the question to the centre-of-mass. The energetic yield, or Q-value, of the reaction is used to determine the energies and trajectories of the products in the centre-of-mass frame. These quantities in the laboratory frame are calculated by vector addition using the beam energy to determine the velocity of the centre-of-mass relative to the laboratory. Finally, the angles and energies are displayed and are added to disk files to enable series of calculations to be performed.

' Program HE3CALC by Peter Murphy 1990

' This program allows user to calculate the energy of reaction products from helium3/deuterium reaction in the lab frame.

' User gives beam energy and lab angle of detection and program produces emitted energy.

OPEN "Eplab.prn" FOR OUTPUT AS #1
OPEN "Angle.prn" FOR OUTPUT AS #2
OPEN "E4lab.prn" FOR OUTPUT AS #3
OPEN "Thet4lab.prn" FOR OUTPUT AS #4
OPEN "Ebeam.prn" FOR OUTPUT AS #5

10

' Startup Display

cls
Locate 10,30
Print "&*&&&&&&&&&&&&&&&&&&&&&"
Locate 12,20

173
Print "Welcome to HE3CALC – the program that answers"
Locate 14,20
Print "your wildest dreams about reaction calculations."
Locate 16,30
Print "$$$$$$$$$$"

Locate 20,20

CALL Pause

cls

' end of Startup Display

' User Input Section

Locate 5,10: Print "Right, let’s do some work. I’m assuming we’re using"
Print "a Helium-3 beam on a deuterium nucleus. Let’s have some starting"
Print "values, please."

Locate 10,20: Input "What is the Helium-3 energy (in MeV) ?"; Ebeam
IF Ebeam = 0 THEN Call Reject

Locate 13,20: Input "And how about the lab angle (in deg) ?"; Angle
IF Angle = 180 THEN Call Awkward
pi = 3.14159
Thetalab = Angle * pi / 180

' end of User Input Section

massp = 938.28
massd = 1875.63
mass3 = 2808.413
mass4 = 3727.41

massd3 = massd + mass3
massp4 = massp + mass4

' Variable Generation

V3  = ( 2 * Ebeam / mass3 ) ^ 0.5
Vcm = V3 * ( mass3 / massd3 )
E3cm = 0.5 * mass3 * ( massd * V3 / massd3 ) ^ 2
Edcm = 0.5 * massd * ( mass3 * V3 / massd3 ) ^ 2

Q = massd3 - massp4

K = Q + E3cm + Edcm

' Energies in centre of mass frame

Epcm = K * ( mass4 / massp4 )
E4cm = K * ( massp / massp4 )

' Velocities in centre of mass frame

Vpcm = ( 2 * Epcm / massp ) ^ 0.5
V4cm = ( 2 * E4cm / mass4 ) ^ 0.5

Print "Vcm = "; Vcm; "Vpcm = "; Vpcm; "V4cm = "; V4cm
' Call Pause

' Calculation of c.o.f.m. angle from lab angle

' Thetacm = Invsin ( Vcm * sin(Thetalab) / Vpcm ) + Thetalab
' TURBOB doesn't have an Invsin function, so use
' Invsin subroutine to do calc.

Thetacm = Vcm * sin(Thetalab) / Vpcm
Print "Thetacml = "; Thetacm
' Call Pause
Thetacm = ATN(Thetacm/(1-Thetacm^2)^0.5)
Print "Thetacm2 = "; Thetacm
' Call Pause
Thetacm = Thetacm + Thetalab

175
Print "Thetacm3 = "; Thetacm
Call Pause

* Final lab velocities

Vpcos = ( Vpcm * cos( Thetacm ) + Vcm )^2
Vpsin = ( Vpcm * sin( Thetacm ) )^2
Vp = ( Vpcos + Vpsin )^0.5
Eplab = 0.5 * massp * Vp^2

Thet4cm = pi - Thetacm

* Print "proton c.m. angle = "; thetacm *180 / pi
Print "alpha c.of.m. angle = "; thet4cm * 180 / pi
Call Pause

* Cosine Rule to get V4, alpha velocity in lab.

shunt = V4cm^2 + Vcm^2 - (2 * Vcm * V4cm * cos( pi - Thet4cm ))
V4 = shunt^0.5
Print "V4 = "; V4
Call Pause

E4lab = 0.5 * mass4 * V4^2

* Sine Rule to get Thet4lab, alpha angle in lab.

Thet4lab = ( V4cm * sin( Thet4cm ) / V4 )

Print "V4cm = "; V4cm; "V4 = "; V4
Print "Thet4lab = "; Thet4lab
Call Pause

IF 0.999999 < Thet4lab < 1.00001 then FLOAT = 1
IF FLOAT = 1 THEN GOTO 40

Thet4lab = ATN(Thet4lab/(1-Thet4lab^2)^0.5)
40 if fLOAT = 1 THEN Thetlab = PI/2

' To determine Alpha lab-angle must go via tangent as
' this preserves sign.

V4cos = V4cm * cos(Thet4cm) + Vcm
V4sin = V4cm * sin(Thet4cm)
Thet4lab = ATN ( V4sin / V4cos )
Thet4lab = ( Thet4lab ^ 2 ) ^ 0.5
IF V4sin>0 AND V4cos<0 THEN Thet4lab = pi - Thet4lab
Thet4lab = Thet4lab*180/pi

'There is a problem with ATN only giving values between -45 and 45 degrees
'A way must found round this to get correct spread of Thet4lab

' Results Display

cls
Locate 10,10
Print "Angle = "; Angle ; "Energy = "; Ebeam
Print
Print "Proton energy = "; Eplab
Print "Alpha energy = "; E4lab
Print "Alpha angle = "; Thet4lab

'Data Tidying Routine before store

Eplab = INT(Eplab*1000)
E4lab = INT(E4lab*1000)

Print Ebeam; Eplab; Angle; E4lab; Thet4lab
' Call Pause
PRINT #1, Eplab
PRINT #2, Angle
PRINT #3, E4lab
PRINT #4, Thet4lab
PRINT #5, Ebeam
Print
Input "Another calculation perchance ? "; ans$
If ans$ = "Y" OR ans$ = "y" THEN GOTO 25

Print "Thank you for availing yourself of He3Calc."
Print " Have a nice day."
    CLOSE
End

SUB Pause

Print "Press any key to continue"
inChar$ = ""
DO WHILE LEN(inChar$) = 0
    inChar$ = INKEY$
LOOP

END SUB

SUB Reject

Print "Look, Pal. If the Helium is standing still, how do you" Print "expect it to reach the deuterium, eh? Try again."
Call Pause
Goto 25

END SUB

SUB Awkward

Print "Woah! The detector will be blocking the beam! Try again."
GOTO 35

END SUB
Appendix B: A solution of Fick's second law.

In one dimension Fick's second law can be written as

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

where \( C \) is the concentration of a diffusing substance, \( D \) is the diffusion coefficient, \( t \) is time and \( x \) is the depth in the direction of diffusion.

Assuming a constant value for \( D \), a general solution of this diffusion equation can be obtained:

\[ C = \frac{Ae^{-\frac{x^2}{4Dt}}}{t^{1/2}} \quad \text{(B.1)} \]

where \( A \) is an arbitrary constant. The total amount of diffusing substance, \( M \), is given by

\[ M = \int_{-\infty}^{+\infty} C \, dx \quad \text{(B.2)} \]

such that

\[ M = 2AD^{1/2} \int_{-\infty}^{+\infty} e^{-\phi^2} \, d\phi = 2A(\pi D)^{1/2} \quad \text{(B.3)} \]

for the substitution \( \phi^2 = \frac{x^2}{4Dt} \).

From equation B.3, equation B.1 becomes

\[ C = \frac{Me^{-\frac{x^2}{4Dt}}}{2(\pi Dt)^{1/2}} \quad \text{(B.4)} \]
If the diffusant initially occupies a finite region such that

\[
\begin{align*}
  x < 0 : & \quad C = C_o \\
  x > 0 : & \quad C = 0
\end{align*}
\]

\[ t = 0 \]

\[ x=0 \]

\[ \delta \phi \]

\[ \text{source} = C_o \delta \phi \]

Figure B.1: Initial penetrant distribution.

At a time \( t \), the concentration at point \( P \) due to the shaded element is

\[
C(P) = \frac{C_o \, d\phi \, e^{-\phi^2/4Dt}}{2(\pi Dt)^{1/2}}
\]

The concentration due to the total initial distribution is found by summing over all the elements \( \delta \phi \),

\[
C(x,t) = \frac{C_o \, d\phi}{2(\pi Dt)^{1/2}} \int_{-\infty}^{+\infty} e^{-\phi^2/4Dt} \, d\phi
\]

which, upon substituting \( n = \phi/2(Dt)^{1/2} \),

becomes

\[
C(x,t) = \frac{C_o}{\pi^{1/2}} \int_{\frac{x}{k}}^{+\infty} e^{-n^2} \, dn
\]

where \( k = 2(Dt)^{1/2} \).
In the case of limited initial penetrant distribution of the form

\[
\begin{align*}
 x < -h &: C = 0 \\
 -h < x < +h &: C = C_0 \\
 x > +h &: C = 0
\end{align*}
\]

t = 0

the limits of the integral B.6 become \( x-h \) and \( x+h \), giving

\[
C(x,t) = \frac{C_0}{2(\pi Dt)^{1/2}} \int_{x-h}^{x+h} e^{-\frac{\phi^2}{4Dt}} d\phi = \frac{C_0}{\pi^{1/2}} \int_{x-h}^{x+h} e^{-\frac{n^2}{k}} dn \tag{B.8}
\]

The error function is defined as

\[
erf(z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-n^2} dn \tag{B.9}
\]

and has the property

\[
erf(-z) = -\text{erf}(z) \tag{B.10}
\]

Equation B.8 can therefore be re-written

\[
C(x,t) = \frac{C_0}{\sqrt{\pi}} \left[ \int_{0}^{x+h} e^{-\frac{n^2}{k}} dn - \int_{0}^{x-h} e^{-\frac{n^2}{k}} dn \right] = \frac{1}{2} C_0 \left\{ \text{erf} \left( \frac{h-x}{2\sqrt{Dt}} \right) + \text{erf} \left( \frac{h+x}{2\sqrt{Dt}} \right) \right\} \tag{B.11}
\]
Appendix C: List of Chemicals

The monodisperse polystyrenes were purchased from the Pressure Chemical Company, Pittsburgh, PA., U.S.A. and were of seven molecular weights ranging from 90,000 to 1,800,000.

The solvents used were methanol, toluene and 1,2 dichloroethane (DCE). All three were general purpose reagents (GPR) obtained in 2.5 litre Winchesters from BDH Chemicals Ltd, Poole, England.

Acetic anhydride and 98% sulphuric acid (GPR) were purchased from BDH.

Analytical reagent standard sodium hydroxide pellets were purchased from May & Baker Ltd, Dagenham, England.

Benzene-d$_6$, benzene and ethyl aluminium dichloride (EAD) were obtained from the Aldrich Chemical Company Ltd, Gillingham, England. The EAD was a 1.0 M solution in hexane, stored under nitrogen.
References:


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scientists."", The Macmillan Press.


Mills P.J. (1988) Proc. 2nd Int. Conf. on Diffusion in Polymers, PRI, 9/1-5.


