ACRYLIC WATER SOLUBLE POLYMERS

By

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ABSTRACT

The mechanism of the free radical polymerization of acrylic water soluble monomers has been elucidated. Donor-acceptor interactions between initiator and monomer form a weak charge transfer complex which acts as a secondary source of initiation. This accounts for the unusually high rate dependence on monomer concentration observed for nonionic, anionic and cationic monomers. In polymerizations where the initiator and monomer are segregated, as for example in inverse-microsuspension, monomer enhanced decomposition is absent. Three other reactions dominate: unimolecular chain termination with interfacial emulsifier, heterophase diffusion of primary and oligoradicals and long chain branching with unsaturated carbons on the terminal oleate groups.

A new light scattering procedure has been developed based on the theoretical prediction of the second virial coefficient. The method eliminates greater than fifty percent of the variance in estimation of molecular weight, concomitant with a fivefold reduction in measurement time, and can be applied to any linear polymer, including polyelectrolytes.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>iv</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xxiii</td>
</tr>
<tr>
<td><strong>INTRODUCTION</strong></td>
<td></td>
</tr>
<tr>
<td><strong>CHAPTER 1: CHARACTERIZATION OF WATER SOLUBLE POLYMERS</strong></td>
<td></td>
</tr>
<tr>
<td>1. Introduction to Light Scattering</td>
<td>5</td>
</tr>
<tr>
<td>1.1 Light Scattering Theory</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Derivation of the Rayleigh Factor</td>
<td>6</td>
</tr>
<tr>
<td>1.3 Derivation of the Light Scattering Equation</td>
<td>10</td>
</tr>
<tr>
<td>1.4 Extension to Solutes with Heterogeneous Molecular Weights</td>
<td>14</td>
</tr>
<tr>
<td>1.5 Experimental Determination of the Rayleigh Factor</td>
<td>15</td>
</tr>
<tr>
<td>2. One Point Method to Calculate Molecular Weight from Low Angle Laser</td>
<td>19</td>
</tr>
<tr>
<td>Light Scattering Data</td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Experimental</td>
<td>19</td>
</tr>
<tr>
<td>2.3 Theory: Second Virial Coefficient</td>
<td>20</td>
</tr>
<tr>
<td>2.3.1 Relationship of $\beta$ to the Mark-Houwink-Sakurada Constant</td>
<td>22</td>
</tr>
<tr>
<td>2.3.2 Effect of Polydispersity on the Second Virial Coefficient</td>
<td>28</td>
</tr>
<tr>
<td>2.3.3 Modelling of the Second Virial Coefficient</td>
<td>32</td>
</tr>
<tr>
<td>2.4 Results and Discussion</td>
<td>32</td>
</tr>
<tr>
<td>2.4.1 New 1-point LALLS Method</td>
<td>32</td>
</tr>
<tr>
<td>2.4.2 Method of Calculation for the new LALLS procedure</td>
<td>39</td>
</tr>
<tr>
<td>3. Molecular Weight Characterization of Polyacrylamide-co-sodium acrylate</td>
<td>45</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>45</td>
</tr>
<tr>
<td>3.2 Experimental Methods and Procedures</td>
<td>49</td>
</tr>
<tr>
<td>3.2.1 Polymer Preparation</td>
<td>49</td>
</tr>
<tr>
<td>3.2.2 Polymer Fractionation</td>
<td>51</td>
</tr>
<tr>
<td>3.2.3 Polymer Hydrolysis</td>
<td>51</td>
</tr>
<tr>
<td>3.2.4 Copolymer Characterization</td>
<td>55</td>
</tr>
<tr>
<td>3.2.5 Light Scattering of Polyelectrolytes</td>
<td>56</td>
</tr>
<tr>
<td>3.2.6 Dialysis</td>
<td>57</td>
</tr>
<tr>
<td>3.2.7 Determination of the Refractive Index Increment at Constant Chemical Potential</td>
<td>58</td>
</tr>
<tr>
<td>3.3 Results and Discussion</td>
<td>62</td>
</tr>
<tr>
<td>3.3.1 Evaluation of the Molecular Weight Method for Polyacrylamide-co-sodium acrylate</td>
<td>62</td>
</tr>
<tr>
<td>References</td>
<td>65</td>
</tr>
</tbody>
</table>
# Table of Contents (continued)

## CHAPTER 2: POLYMERIZATION OF ACRYLAMIDE BY INVERSE-MICROSUSPENSION

1. Introduction 70  
   1.1 Steric Stabilization 71  
   1.2 A Comparison of Water-in-Oil Polymerization Processes 73  
   1.3 Summary of Recent Kinetic Research 75

2. Experimental 78

3. Results and Discussion 82  
   3.1 Mechanism 90  
   3.2 Kinetic Model 92  
      3.2.1 Initiation 92  
      3.2.2 Rate of Polymerization 94  
      3.2.3 Molecular Weights 97  
      3.2.4 Emulsifier Concentration in the Boundary Layer 99  
      3.2.5 Particle Sizes 101  
      3.2.6 Summary of Kinetic Model 103  
   3.3 Parameter Estimation 103  
   3.4 Evaluating the Kinetic Model against Experimental Data 109

References 134

## CHAPTER 3: POLYMERIZATION OF QUATERNARY AMMONIUM CATIONIC MONOMERS

1. Introduction 138  
   1.1 Solution Behaviour of Cationic Polymers 142  
   1.2 Kinetics 145  
   1.3 Experimental Plan 146

2. Experimental Methods and Procedures 150  
   2.1 Monomer Purification 150  
   2.2 Determination of Monomer and Polymer Composition 153  
      2.2.1 Description of the HPLC Method for Residual Monomer Concentration 155  
   2.3 Polymerization Procedure 159  
      2.3.1 Reagent Preparation 159  
      2.3.2 Description of Reactor 161  
      2.3.3 Reactor Operation 161  
      2.3.4 Reactor Cleaning 166  
   2.4 Polymerization Conditions 166  
   2.5 Estimation of Reactivity Ratios 168  
   2.6 Monomer Partitioning Measurements 170  
   2.7 Particle Size Measurements 170

(ix)
Table of Contents (continued)

CHAPTER 3 (continued)

3. Results and Discussion
   3.1 Homopolymerization of Cationic Monomers 176
   3.2 Copolymerization of Acrylamide and Cationic Monomers in Solution: Estimation of Reactivity Ratios 180
      3.2.1 The Error-in-Variables Method 180
      3.2.2 Reactivity Ratios in Solution Polymerization 182
   3.3 Monomer Partitioning between Aqueous and Organic Phases 192
   3.4 Copolymerization of Acrylamide and Cationic Monomers in Inverse-microsuspension 196
      3.4.1 Mechanism 196
      3.4.2 Derivation of the Kinetic Model 202
         3.4.2.1 Balance on Macroradicals 202
         3.4.2.2 Monomer Consumption Rate 206
         3.4.2.3 Balance on Initiator 206
         3.4.2.4 The Efficiency of Initiation of Primary Radicals 207
         3.4.2.5 Equations for Conversion and Composition 207
   3.5 Parameter Estimation 208
   3.6 Evaluation of the Kinetic Model against Experimental Data 211
   3.7 Simulations 221

References 224

CHAPTER 4: POLYMERIZATION OF ACRYLAMIDE AT HIGH MONomer CONCENTRATIONS

1. Introduction 229
   1.1 Review of Polymerization 230
      1.1.1 Effect of Solvents 233
      1.1.2 Inhibition 233
   1.2 Review of Kinetics 234
      1.2.1 Evaluation of the Cage-Effect and Complex Theories 238
   1.3 Elucidation of an Initiation Mechanism 244
      1.3.1 Historically used Mechanism 246
      1.3.2 Proposed Mechanism 249
      1.3.3 Proposed Experimental Investigation 255

2. Experimental Methods and Procedures 256
   2.1 Residual Monomer Concentration 256
   2.2 Molecular Weight Determination 257
   2.3 Experimental Procedures 258
      2.3.1 Method of Polymerization 258
   2.4 Experimental Conditions 260
### Table of Contents (continued)

### CHAPTER 4 (continued)

3. Results and Discussion
   3.1 Rate Order with Respect to Monomer Concentration 262
   3.2 Limiting Conversion 262
   3.3 Parameter Estimation 264
   3.4 Comparison of Kinetic Model to Experimental Data 268
   3.5 Generalization of the Initiation Mechanism to Other Water Soluble Monomers
      3.5.1 Generalization to Cationic Monomers 281

References 285

### CONCLUSIONS 291

### RECOMMENDATIONS 293

### APPENDIX A: PREPARATION AND CHARACTERIZATION OF SUPERABSORBENT POLY(SODIUM ACRYLATES) 294

### APPENDIX B: THEORETICAL PREDICTION OF THE SECOND VIRIAL COEFFICIENT 314

### APPENDIX C: CATEGORIZING EMULSIONS 340

### APPENDIX D: DERIVATION OF THE MOLECULAR WEIGHT EQUATIONS BY THE METHOD OF MOMENTS 347

### APPENDIX E: OXYGEN PARTITIONING 357

### APPENDIX F: HPLC VARIANCE STUDY 369

### APPENDIX G: PROPERTIES OF REAGENTS USED IN SYNTHESIS 374

### APPENDIX H: INVESTIGATION OF THE VARIANCE IN MOLECULAR WEIGHT BY LOW ANGLE LASER LIGHT SCATTERING 376
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1:</td>
<td>Interrelationships between the objectives of this thesis.</td>
<td>4</td>
</tr>
<tr>
<td>Figure 1.1:</td>
<td>Depiction of light scattering from a single particle.</td>
<td>7</td>
</tr>
<tr>
<td>Figure 1.2:</td>
<td>Optical system of a KMX-16 Low Angle Laser Light Scattering Photometer.</td>
<td>13</td>
</tr>
<tr>
<td>Figure 1.3:</td>
<td>Relationship between the second virial coefficient and molecular weight for polyacrylamide in 0.02 M Na₂SO₄.</td>
<td>23</td>
</tr>
<tr>
<td>Figure 1.4:</td>
<td>Relationship between the second virial coefficient and molecular weight for polyethyleneoxide in methanol.</td>
<td>24</td>
</tr>
<tr>
<td>Figure 1.5:</td>
<td>Relationship between the second virial coefficient and molecular weight for polymethylmethacrylate in acetone.</td>
<td>25</td>
</tr>
<tr>
<td>Figure 1.6:</td>
<td>Relationship between the second virial coefficient and molecular weight for polystyrene in toluene.</td>
<td>26</td>
</tr>
<tr>
<td>Figure 1.7:</td>
<td>Kc/R₀ versus concentration for a molecular weight sample of polyacrylamide measured on three occasions.</td>
<td>27</td>
</tr>
<tr>
<td>Figure 1.8:</td>
<td>Relationship between the second virial coefficient and molecular weight for high molecular weight polyacrylamides in 0.02 M Na₂SO₄.</td>
<td>29</td>
</tr>
<tr>
<td>Figure 1.9:</td>
<td>Standard deviation of Kc/R₀ as a function of concentration for a polyacrylamide measured on several occasions.</td>
<td>35</td>
</tr>
<tr>
<td>Figure 1.10:</td>
<td>Variation in the photomultiplier signal of the scattered light for several concentrations.</td>
<td>36</td>
</tr>
<tr>
<td>Figure 1.11:</td>
<td>Kc/R₀ versus concentration for a polyacrylamide sample measured on three occasions.</td>
<td>37</td>
</tr>
<tr>
<td>Figure 1.12:</td>
<td>Ninety five percent confidence intervals of Kc/R₀ as a function of concentration.</td>
<td>38</td>
</tr>
<tr>
<td>Figure 1.13:</td>
<td>Confidence region for weight average molecular weight predicted from the new LALLS procedure.</td>
<td>40</td>
</tr>
<tr>
<td>Figure 1.14:</td>
<td>Optimal concentration range for LALLS of polyacrylamide as a function of molecular weight.</td>
<td>42</td>
</tr>
</tbody>
</table>
## List of Figures (continued)

| Figure 1.15: | Kinetics of alkaline hydrolysis of polyacrylamide. | Page 46 |
| Figure 1.16: | $^{13}$C NMR spectra of polyacrylamide. | Page 50 |
| Figure 1.17: | SEC chromatograms showing the reduction in polydispersity upon fractionation. | Page 53 |
| Figure 1.18: | Refractive index increment of polyacrylamide-co-sodium acrylate as a function of dialysis time. | Page 59 |
| Figure 1.19: | Refractive index increment at constant chemical potential as a function of the acrylate level in a polyacrylamide-co-sodium acrylate. | Page 61 |
| Figure 1.20: | Light scattering plots showing the equivalence of molecular weight determined for polyelectrolytes and the nonionic polymer from which they were derived. | Page 63 |
| Figure 2.1: | Experimental conversion-time data showing an induction period of 13 minutes. The reaction conditions were: $T=47\, ^\circ\text{C}$, $[\text{Acrylamide}] = 5.75\, \text{mol/L}_\text{w}$, $[\text{Sorbitanmonoooleate}] = 0.103\, \text{mol/L}_\text{o}$, $[\text{AIBN}] = 4.02\, \text{mmol/L}_\text{o}$, $\Phi_{w/o} = 1:1$, $N = 1000\, \text{RPM}$. | Page 80 |
| Figure 2.2: | Rate of polymerization versus the first and half powers of initiator (AIBN) concentration. Experimental conditions were: $T=47\, ^\circ\text{C}$, $[\text{Acrylamide}] = 5.75\, \text{mol/L}_\text{w}$, $[\text{Sorbitanmonoooleate}] = 0.103\, \text{mol/L}_\text{o}$, $\Phi_{w/o} = 1:1$, $N = 1000\, \text{RPM}$. | Page 84 |
| Figure 2.3: | Weight average molecular weight as a function of measurement temperature. | Page 87 |
| Figure 2.4: | Proposed reaction mechanism of interfacial emulsifier (sorbitanmonoooleate) with macroradicals. | Page 88 |
| Figure 2.5: | Conversion-time data and model predictions for polymerizations with AIBN initiators at the following conditions: $T=47\, ^\circ\text{C}$, $[\text{Acrylamide}] = 5.75\, \text{mol/L}_\text{w}$, $[\text{Sorbitanmonoooleate}] = 0.103\, \text{mol/L}_\text{o}$, $\Phi_{w/o} = 1:1$, $N = 1000\, \text{RPM}$. | Page 110 |
| Figure 2.6: | Conversion-time data and model predictions for ADVN initiators. The reaction conditions were: $T=47\, ^\circ\text{C}$, $[\text{Acrylamide}] = 5.75\, \text{mol/L}_\text{w}$, $[\text{Sorbitanmonoooleate}] = 0.103\, \text{mol/L}_\text{o}$, $\Phi_{w/o} = 1:1$, $N = 1000\, \text{RPM}$. | Page 111 |
List of Figures (continued)

Figure 2.7: Final weight average molecular weight data and model predictions for AIBN polymerizations. Experimental conditions were: $T = 47 \, ^\circ\text{C}$, [Acrylamide] = 5.75 mol/L$_w$, [Sorbitanmonooleate] = 0.103 mol/L$_o$, $\Phi_{w/o} = 1:1$, $N = 1000$ RPM. 112

Figure 2.8: Experimental weight average molecular weight data and model predictions for a reaction under the following conditions: $T = 47 \, ^\circ\text{C}$, [Acrylamide] = 5.75 mol/L$_w$, [Sorbitanmonooleate] = 0.103 mol/L$_o$, [AIBN] = 4.02 mmol/L$_o$, $\Phi_{w/o} = 1:1$, $N = 1000$ RPM. 113

Figure 2.9: Rate of initiation of primary and emulsifier radicals as a function of conversion. 115

Figure 2.10: Number and weight average molecular weights for polymerizations with sorbitanmonooleate and sorbitanmonostearate. 115

Figure 2.11: Efficiency of initiation of emulsifier radicals as a function of conversion at several temperatures. 116

Figure 2.12: Conversion-time data and model predictions for polymerizations at various temperatures under the following conditions: [Acrylamide] = 5.75 mol/L$_w$, [Sorbitanmonooleate] = 0.103 mol/L$_o$, [AIBN] = 4.02 mmol/L$_o$, $\Phi_{w/o} = 1:1$, $N = 1000$ RPM. 117

Figure 2.13: Final weight average molecular weight data and model predictions as a function of temperature. Experimental conditions were: [Acrylamide] = 5.75 mol/L$_w$, [Sorbitanmonooleate] = 0.103 mol/L$_o$, [AIBN] = 4.02 mmol/L$_o$, $\Phi_{w/o} = 1:1$, $N = 1000$ RPM. 118

Figure 2.14: Volume-to-Surface average particle diameter as a function of reaction temperature. Experimental conditions were: [Acrylamide] = 5.75 mol/L$_w$, [Sorbitanmonooleate] = 0.103 mol/L$_o$, [AIBN] = 4.02 mmol/L$_o$, $\Phi_{w/o} = 1:1$, $N = 1000$ RPM. 120

Figure 2.15: Experimentally measured number of particles per litre of continuous phase and model predictions at several reaction temperatures. Polymerization conditions were: [Acrylamide] = 5.75 mol/L$_w$, [Sorbitanmonooleate] = 0.103 mol/L$_o$, [AIBN] = 4.02 mmol/L$_o$, $\Phi_{w/o} = 1:1$, $N = 1000$ RPM. 121
List of Figures (continued)  

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.16:</td>
<td>Efficiency of initiation of primary radicals as a function of interfacial area.</td>
<td>122</td>
</tr>
<tr>
<td>Figure 2.17:</td>
<td>Average number of radicals per particle as a function of conversion for several reaction temperatures.</td>
<td>122</td>
</tr>
<tr>
<td>Figure 2.18:</td>
<td>Extent of diffusion controlled termination for inverse-microsuspension and solution polymerizations of acrylamide at 47 °C.</td>
<td>123</td>
</tr>
<tr>
<td>Figure 2.19:</td>
<td>Volume-to-surface average particle size data and model predictions as a function of bulk emulsifier concentration. Other reaction conditions were: T = 47 °C, [Acrylamide] = 5.75 mol/Lw, [AIBN] = 4.02 mmol/Lo, ( \Phi_{w/o} = 1:1 ), N = 1000 RPM.</td>
<td>124</td>
</tr>
<tr>
<td>Figure 2.20:</td>
<td>Conversion-time data and model predictions for polymerizations with sorbitanmonooleate at various concentrations. Experimental conditions were: T = 47 °C, [Acrylamide] = 5.75 mol/Lw, [AIBN] = 4.02 mmol/Lo, ( \Phi_{w/o} = 1:1 ), N = 1000 RPM.</td>
<td>125</td>
</tr>
<tr>
<td>Figure 2.21:</td>
<td>Final weight average molecular weight data and model predictions for polymerization with various concentrations of sorbitanmonooleate. Experimental conditions were: T = 47 °C, [Acrylamide] = 5.75 mol/Lw, [AIBN] = 4.02 mmol/Lo, ( \Phi_{w/o} = 1:1 ), N = 1000 RPM.</td>
<td>127</td>
</tr>
<tr>
<td>Figure 2.22:</td>
<td>Conversion-time data and model predictions for polymerizations with sorbitanmonooleate and sorbitanmonostearate. The reaction conditions were: T = 47 °C, [Acrylamide] = 5.75 mol/Lw, [Emulsifier] = 0.103 mol/Lo, [AIBN] = 4.02 mmol/Lo, ( \Phi_{w/o} = 1:1 ), N = 1000 RPM.</td>
<td>128</td>
</tr>
<tr>
<td>Figure 2.23:</td>
<td>Experimentally measured volume-to-surface average particle diameter and model predictions as a function of the rate of agitation. Other reaction conditions were: T = 47 °C, [Acrylamide] = 5.75 mol/Lw, [Sorbitanmonooleate] = 0.103 mol/Lo, [AIBN] = 4.02 mmol/Lo, ( \Phi_{w/o} = 1:1 ).</td>
<td>129</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.24</td>
<td>Conversion-time data and model predictions as a function of the rate of agitation. Experimental conditions were: ( T = 47 , ^{\circ}\text{C} ), ( [\text{Acrylamide}] = 5.75 , \text{mol/L_w} ), ( [\text{Sorbitanmonoooleate}] = 0.103 , \text{mol/L_o} ), ( [\text{AIBN}] = 4.02 , \text{mmol/L_o} ), ( \Phi_{w/o} = 1:1 ).</td>
<td>130</td>
</tr>
<tr>
<td>2.25</td>
<td>Conversion-time data and model predictions for polymerizations with various monomer concentrations. Other reaction conditions were: ( T = 47 , ^{\circ}\text{C} ), ( [\text{Sorbitanmonoooleate}] = 0.103 , \text{mol/L_o} ), ( [\text{AIBN}] = 4.02 , \text{mmol/L_o} ), ( \Phi_{w/o} = 1:1 ), ( N = 1000 , \text{RPM} ).</td>
<td>132</td>
</tr>
<tr>
<td>3.1</td>
<td>Polymerization reactions of diallylamines.</td>
<td>141</td>
</tr>
<tr>
<td>3.2</td>
<td>Structure of some common quaternary ammonium cationic monomers.</td>
<td>143</td>
</tr>
<tr>
<td>3.3</td>
<td>Cyclization of DMAEM in the presence of added electrolyte.</td>
<td>144</td>
</tr>
<tr>
<td>3.4</td>
<td>Interrelationships of research objectives (Polymerization of cationic monomers).</td>
<td>149</td>
</tr>
<tr>
<td>3.5</td>
<td>HPLC chromatograms of DMAEM monomer at various stages of purification.</td>
<td>151,2</td>
</tr>
<tr>
<td>3.6</td>
<td>Photograph of the HPLC system used in this investigation.</td>
<td>156</td>
</tr>
<tr>
<td>3.7</td>
<td>Example of a HPLC chromatogram for the system acrylamide-dimethylaminoethy methacrylate.</td>
<td>158</td>
</tr>
<tr>
<td>3.8</td>
<td>HPLC calibration curve for acrylamide.</td>
<td>160</td>
</tr>
<tr>
<td>3.9</td>
<td>Photograph of the reactor used for polymerizations.</td>
<td>162</td>
</tr>
<tr>
<td>3.10</td>
<td>Temperature profile for the copolymerization of acrylamide with DMAEM at 60 (^{\circ}\text{C} ). Experimental conditions: ( [\text{Monomer}] = 6.09 , \text{mol/L_w} ), ( [\text{AIBN}] = 3.329 \cdot 10^{-3} , \text{mol/L_o} ), ( f_{10} = 0.875 ), ( \Phi_{w/o} = 0.74 ).</td>
<td>163</td>
</tr>
<tr>
<td>3.11</td>
<td>Variation in power input to the cooling jacket as a function of reaction time for a copolymerization of acrylamide and DMAEM at 40 (^{\circ}\text{C} ). Experimental conditions: ( [\text{Monomer}] = 6.13 , \text{mol/L_w} ), ( [\text{AIBN}] = 14.83 \cdot 10^{-3} , \text{mol/L_o} ), ( f_{10} = 0.877 ), ( \Phi_{w/o} = 0.74 ).</td>
<td>165</td>
</tr>
</tbody>
</table>
List of Figures (continued)

Figure 3.12: Dependence of conversion on dimensionless time for the system AAM/DMAEA. The monomer feed ratio was 1.7:1 and the residence time 30 minutes. 169

Figure 3.13: Photomicrographs of an AAM-DMAEA copolymer. 172-5

Figure 3.14: Kinetics of the inverse-microsuspension homopolymerization of DMAEM at 60 °C. Conversion data measured by HPLC, and model prediction. Experimental conditions: [Monomer] = 0.637 mol/Lw, [AIBN] = 3.327\times10^{-3} mol/Lw, Φw/o = 0.74. 177

Figure 3.15: Kinetics of the aqueous solution polymerization of DMAEA at 60 °C. Conversion data measured by HPLC, and model prediction. Experimental conditions: [Monomer] = 0.350 mol/Lw, [K_2S_2O_8] = 0.127\times10^{-3} mol/Lw. 179

Figure 3.16: Joint confidence regions for the reactivity ratios in the system AAM/DMAEM at 60 °C with K_2S_2O_8 and ACV as the initiators. 185

Figure 3.17: Joint confidence region for the reactivity ratios in the system AAM/DMAEA at 60 °C with ACV as the initiator. 186

Figure 3.18: Joint confidence region for the reactivity ratios in the system AAM/DADMAC at 50 °C with ACV as the initiator. 187

Figure 3.19: Copolymer composition diagram for the system AAM/DMAEM, with ACV as the initiator at 45 and 60 °C, and with K_2S_2O_8 as an initiator at 60 °C. 188

Figure 3.20: Copolymer composition diagram for the system AAM/DMAEA with ACV as the initiator, at 45 and 60 °C. 189

Figure 3.21: Copolymer composition diagram for the system AAM/DADMAC at 50 °C. 190

Figure 3.22: Comparison of the joint confidence regions obtained by HPLC and colloid titration for AAM/DADMAC at 50 °C. 193

Figure 3.23: $^{13}$C NMR spectra of an AAM/DADMAC copolymer with peak assignments. 194
List of Figures (continued)

Figure 3.24: Conversion-time data and kinetic model predictions for an AAM/DMAEM copolymerization at 60 °C. Experimental conditions: [Monomer] = 6.09 mol/L, [AIBN] = 3.329·10⁻³ mol/L, f₁₀ = 0.875, Φ₃⁷/o = 0.74. 212

Figure 3.25: Conversion-time data and kinetic model predictions for an AAM/DMAEM copolymerization at 50 °C. Experimental conditions: [Monomer] = 6.11 mol/L, [AIBN] = 7.373·10⁻³ mol/L, f₁₀ = 0.875, Φ₃⁷/o = 0.74. 213

Figure 3.26: Conversion-time data and kinetic model predictions for an AAM/DMAEM copolymerization at 40 °C. Experimental conditions: [Monomer] = 6.13 mol/L, [AIBN] = 14.83·10⁻³ mol/L, f₁₀ = 0.877, Φ₃⁷/o = 0.74. 214

Figure 3.27: Conversion-time data and kinetic model predictions for an AAM/DMAEA copolymerization at 60 °C. Experimental conditions: [Monomer] = 6.05 mol/L, [AIBN] = 3.337·10⁻³ mol/L, f₁₀ = 0.840, Φ₃⁷/o = 0.74. 215

Figure 3.28: Drift in monomer composition with conversion for an AAM/DMAEM inverse-microsuspension copolymerization at 50 °C. Experimental data measured by HPLC, and predicted composition based on the reactivity ratios measured in solution polymerization with 95% confidence limits. 217

Figure 3.29: Drift in monomer composition with conversion for an AAM/DMAEA inverse-microsuspension copolymerization at 40 °C. Experimental data measured by HPLC, and predicted composition based on the reactivity ratios measured in solution polymerization with 95% confidence limits. 218

Figure 3.30: Trend in particle size with conversion for a copolymerization of acrylamide and DMAEA at 60 °C under the following conditions: [Monomer] = 6.05 mol/L, [AIBN] = 3.337·10⁻³ mol/L, f₁₀ = 0.840, Φ₃⁷/o = 0.74. 219

Figure 3.31: Particle size distribution of an AAM/DMAEA latex measured by photomicroscopy and dynamic light scattering. 220

Figure 3.32: Composition drift for copolymerizations of AAM and DMAEM at 60 °C. 222
List of Figures (continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 3.33:</td>
<td>Initial rate of polymerization as a function of comonomer composition. Simulations were performed for an AAM/DMAEM copolymerization at 60 °C. The monomer concentration was 0.5 mol/L.</td>
<td>223</td>
</tr>
<tr>
<td>Figure 4.1:</td>
<td>Variation in conductivity with time for a solution of acrylamide (4.6 mol/L) and potassium persulfate (0.075 mol/L).</td>
<td>242</td>
</tr>
<tr>
<td>Figure 4.2:</td>
<td>Charge-transfer mechanism for the polymerization of acrylamide with potassium persulfate.</td>
<td>243</td>
</tr>
<tr>
<td>Figure 4.3:</td>
<td>Conversion-time data for acrylamide polymerizations in solution and inverse-microsuspension under identical experimental conditions: [Monomer] = 3.40 mol/L&lt;sub&gt;w&lt;/sub&gt;, [K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;] = 0.52·10&lt;sup&gt;-3&lt;/sup&gt; mol/L&lt;sub&gt;w&lt;/sub&gt;, Temperature = 60 °C. For inverse-microsuspension: [Sorbitanmonooleate] = 0.168 mol/L&lt;sub&gt;ω&lt;/sub&gt;, Φ&lt;sub&gt;ω/0&lt;/sub&gt; = 1.42.</td>
<td>259</td>
</tr>
<tr>
<td>Figure 4.4:</td>
<td>Conversion-time data for the polymerization of acrylamide. The experimental conditions were: Temperature 50 °C, [Monomer] = 5.37 mol/L&lt;sub&gt;w&lt;/sub&gt;, [K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;] = 2.442·10&lt;sup&gt;-3&lt;/sup&gt; mol/L&lt;sub&gt;w&lt;/sub&gt;. An increase in temperature to 60 °C after the limiting conversion was reached did not result in additional monomer consumption.</td>
<td>265</td>
</tr>
<tr>
<td>Figure 4.5:</td>
<td>(a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 50 °C. [Monomer] = 3.35 mol/L&lt;sub&gt;w&lt;/sub&gt;, [K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;] = 0.252·10&lt;sup&gt;-3&lt;/sup&gt; mol/L&lt;sub&gt;w&lt;/sub&gt;. (b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.</td>
<td>269</td>
</tr>
<tr>
<td>Figure 4.6:</td>
<td>(a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 50 °C. [Monomer] = 4.03 mol/L&lt;sub&gt;w&lt;/sub&gt;, [K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;] = 0.228·10&lt;sup&gt;-3&lt;/sup&gt; mol/L&lt;sub&gt;w&lt;/sub&gt;. (b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.</td>
<td>270</td>
</tr>
<tr>
<td>Figure 4.7:</td>
<td>(a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 50 °C. [Monomer] = 4.69 mol/L&lt;sub&gt;w&lt;/sub&gt;, [K&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;] = 0.251·10&lt;sup&gt;-3&lt;/sup&gt; mol/L&lt;sub&gt;w&lt;/sub&gt;. (b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.</td>
<td>271</td>
</tr>
</tbody>
</table>
List of Figures (continued)

Figure 4.8: (a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 50 °C.

[Monomer] = 5.37 mol/Lw, [K₂S₂O₈] = 0.248·10⁻³ mol/Lw.

(b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.

Figure 4.9: (a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 50 °C.

[Monomer] = 6.04 mol/Lw, [K₂S₂O₈] = 0.250·10⁻³ mol/Lw.

(b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.

Figure 4.10: (a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 50 °C.

[Monomer] = 6.41 mol/Lw, [K₂S₂O₈] = 0.238·10⁻³ mol/Lw.

(b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.

Figure 4.11: (a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 60 °C.

[Monomer] = 6.70 mol/Lw, [K₂S₂O₈] = 0.0609·10⁻³ mol/Lw.

(b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.

Figure 4.12: (a) Conversion-time data and kinetic model predictions for an acrylamide polymerization at 40°C.

[Monomer] = 6.70 mol/Lw, [K₂S₂O₈] = 1.573·10⁻³ mol/Lw.

(b) Weight average molecular weight-conversion data and kinetic model predictions for the same experiment.

Figure 4.13: Fraction of polymer chains initiated by monomer-enhanced decomposition of potassium persulfate as a function of conversion. Simulations were performed at 40 °C and 60 °C with [K₂S₂O₈] = 6.09·10⁻⁵ mol/Lw,

[Acrylamide] = 7.04 mol/Lw and Φₚ = 0.74.

Figure 4.14: Concentration of potassium persulfate scaled with respect to its initial level as a function of conversion. Simulations were performed at 60 °C with [K₂S₂O₈] = 2.4·10⁻⁴ mol/Lw and initial acrylamide concentrations of 1,5,10,25 and 50 wt.% based on the aqueous phase.

(xx)
List of Figures (continued)

| Figure A.1: | CP-MAS $^{13}$C NMR spectra of (a) linear poly(sodium acrylate) and of two crosslinked poly(sodium acrylate) samples containing (b) 0.0494 and (c) 0.1348 mol fraction $N,N'$-methylenebisacrylamide. | 300 |
| Figure A.2: | Relative intensity of the CP-MAS $^{13}$C NMR peak at 180 ppm plotted as a function of the mol fraction of crosslinking monomer. | 304 |
| Figure A.3: | $^{13}$C NMR spectra of (a) a D$_2$O solution of linear poly(sodium acrylate) and of two crosslinked poly(sodium acrylate) samples swollen in D$_2$O, the latter containing (b) 0.0494 and (c) 0.1348 mol fraction of $N,N'$-methylenebisacrylamide in the dry state. | 306 |
| Figure A.4: | Linewidths (Hz) of the CH and CH$_2$ $^{13}$C resonances of crosslinked poly(sodium acrylate) samples in D$_2$O versus the mol fraction of crosslinking monomer. | 308 |
| Figure B.1: | An illustration of intermolecular excluded volume. | 315 |
| Figure B.2: | Cluster diagram for double and triple intermolecular contacts. | 319 |
| Figure B.3: | Schematic representation of single and double intramolecular contacts. | 322 |
| Figure B.4: | Theoretical values of $\sigma_R^{\theta}$ as a function of the excluded volume parameter. | 326 |
| Figure B.5: | Theoretical values of $\sigma_0(Z)$ as a function of the excluded volume parameter. | 331 |
| Figure B.6: | Cluster diagrams illustrating two intermolecular contacts in the presence of a single intramolecular contact. | 333 |
| Figure B.7: | Comparison of theoretical and experimental values of the interpenetration function as a function of $\sigma_0^{\theta}$. | 336 |
| Figure B.8: | Comparison of experimental and theoretical second virial coefficients. | 336 |
| Figure C.1: | Illustration of the types of macroemulsions. | 341 |
| Figure C.2: | Hypothetical phase diagram showing micro- and macroemulsion domains. | 343 |
### List of Figures (continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.3</td>
<td>Minimum weight percentage of emulsifier (sorbitan sesquioleate-poly oxyethylene sorbitol hexaoleate) required to achieve microemulsification as a function of HLB.</td>
<td>344</td>
</tr>
<tr>
<td>C.4</td>
<td>Effect of the organic phase on the minimum level of emulsifier (sorbitan sesquioleate-poly oxyethylene sorbitol hexaoleate) needed to achieve microemulsification.</td>
<td>345</td>
</tr>
<tr>
<td>E.1</td>
<td>Apparatus used for oxygen partitioning measurements.</td>
<td>358</td>
</tr>
<tr>
<td>E.2</td>
<td>Schematic of a syringe passing through a thin section of a rubber stopper.</td>
<td>360</td>
</tr>
<tr>
<td>E.3</td>
<td>Measurements of the oxygen partition coefficient at various water-to-oil phase ratios.</td>
<td>366</td>
</tr>
<tr>
<td>E.4</td>
<td>Change in the oxygen content of the aqueous phase with time. (a) Temperature 50 °C, ( \Phi_{w/o} = 12.63 ); (b) Temperature 30.2 °C, ( \Phi_{w/o} = 16.94 ).</td>
<td>367</td>
</tr>
<tr>
<td>F.1</td>
<td>Histogram of the HPLC measurements of a 50.0 ppm DMAEM standard.</td>
<td>371</td>
</tr>
<tr>
<td>H.1</td>
<td>Histogram showing the distribution of ( (G_0/G_o)_c ) for replicate Low Angle Laser Light Scattering measurements of a single polyacrylamide sample.</td>
<td>378</td>
</tr>
<tr>
<td>H.2</td>
<td>Dot diagram of the distribution of ( (G_0/G_o)_c ) for five independently prepared samples of the same polyacrylamide measured by Low Angle Laser Light Scattering.</td>
<td>378</td>
</tr>
</tbody>
</table>
**LIST OF TABLES**

| Table 1.1 | Values of the parameters $a$ and $\beta$ in the expression $A_2 = aM_w^\beta$ for several polymer-solvent systems. | 21 |
| Table 1.2 | Relationship between the Mark-Houwink-Sakurada exponent, $a$, and the exponent $\beta$ in the equation $A_2 = aM_w^\beta$. | 30 |
| Table 1.3 | Effect of polydispersity on the Second Virial Coefficient for Polyacrylamide. | 33 |
| Table 1.4 | Optimal Concentration for the measurement of weight average molecular weight of polyacrylamide by LALLS. | 41 |
| Table 1.5 | A comparison of the accuracy in the prediction of weight average molecular weight by the conventional and new LALLS procedure. | 43 |
| Table 1.6 | Summary of hydrolysis kinetics. | 48 |
| Table 1.7 | Fractionation Conditions | 52 |
| Table 1.8 | Weight average molecular weight and second virial coefficients for polyacrylamide fractions. | 54 |
| Table 1.9 | Refractive index increments at constant chemical potential for various compositions of polyacrylamide-co- sodium acrylate. | 60 |
| Table 1.10 | A comparison of the polyelectrolyte and nonionic molecular weight characterization procedures. | 64 |
| Table 2.1 | A comparison of heterophase polymerizations. | 74 |
| Table 2.2 | Summary of kinetics of acrylamide polymerization in heterophase processes. | 76 |
| Table 2.3 | Weight average molecular weights of polyacrylamides produced in solution with and without sorbitan monooleate. | 85 |
| Table 2.4 | Summary of kinetic model equations (Inverse- microsuspension of acrylamide). | 104,5 |
| Table 2.5 | Summary of parameter values (Kinetic model for the inverse-microsuspension of acrylamide). | 107,8 |
List of Tables (continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 3.1</td>
<td>Uses of cationic polyelectrolytes.</td>
<td>139</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Purification of dimethylaminoethyl methacrylate.</td>
<td>154</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Experimental conditions for polymerizations with cationic monomers.</td>
<td>167</td>
</tr>
<tr>
<td>Table 3.4</td>
<td>Residual monomer concentrations and mol fraction of AAM in the polymer for the copolymerization of AAM and DMAEM with KPS and ( \Lambda CV ) at 60 °C in solution at various feed ratios.</td>
<td>183</td>
</tr>
<tr>
<td>Table 3.5</td>
<td>Reactivity ratios of the polymerization of acrylamide with different cationic monomers at various conditions.</td>
<td>184</td>
</tr>
<tr>
<td>Table 3.6</td>
<td>Comparison of the reactivity ratios determined by different authors for the copolymerization of acrylamide with diallyldimethylammonium chloride.</td>
<td>191</td>
</tr>
<tr>
<td>Table 3.7</td>
<td>Monomer partitioning between aqueous and organic phases.</td>
<td>195</td>
</tr>
<tr>
<td>Table 3.8</td>
<td>Summary of kinetic constants for the copolymerization of acrylamide and quaternary ammonium monomers.</td>
<td>210</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Acrylamide polymerizations with redox couples.</td>
<td>232</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Kinetic investigations of acrylamide polymerizations in aqueous media.</td>
<td>235,6</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Equivalence of two kinetic processes which provide 5/4th power rate dependencies.</td>
<td>254</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Polymerization conditions (Acrylamide polymerization at high monomer concentrations).</td>
<td>261</td>
</tr>
<tr>
<td>Table 4.5</td>
<td>Limiting conversion versus monomer and initiator concentration (Acrylamide polymerization at high monomer concentrations).</td>
<td>263</td>
</tr>
<tr>
<td>Table 4.6</td>
<td>Parameter estimates (Acrylamide polymerization at high monomer concentrations)</td>
<td>267</td>
</tr>
<tr>
<td>Table 4.7</td>
<td>Rate equations for several acrylic water soluble monomers.</td>
<td>283</td>
</tr>
<tr>
<td>Table A.1</td>
<td>Experimental conditions for the synthesis of superabsorbent poly(sodium acrylate).</td>
<td>296</td>
</tr>
<tr>
<td>Table A.2</td>
<td>(^{13})C chemical shifts (relative to TMS) for crosslinked and linear poly(sodium acrylates) in solid state and in D_2O.</td>
<td>301</td>
</tr>
</tbody>
</table>
List of Tables (continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table A.3</td>
<td>Solid-state intensities and hydrogel linewidths of crosslinked poly(sodium acrylates).</td>
<td>303</td>
</tr>
<tr>
<td>Table A.4</td>
<td>Model parameters for the prediction of crosslinking density from measurements of methine and methylene linewidths of D₂O swollen poly(sodium acrylate) hydrogels.</td>
<td>310</td>
</tr>
<tr>
<td>Table B.1</td>
<td>History of the development of dilute solution theory.</td>
<td>321</td>
</tr>
<tr>
<td>Table B.2</td>
<td>Summary of models for excluded volume.</td>
<td>324</td>
</tr>
<tr>
<td>Table B.3</td>
<td>Comparison of approximate and exact theories of the expansion factor at low values of Z.</td>
<td>325</td>
</tr>
<tr>
<td>Table B.4</td>
<td>Comparison of the first two contact terms for various intermolecular theories.</td>
<td>330</td>
</tr>
<tr>
<td>Table B.5</td>
<td>Self consistent theories for the second virial coefficient of real polymer chains.</td>
<td>334</td>
</tr>
<tr>
<td>Table E.1</td>
<td>Solubility of Oxygen in Decane.</td>
<td>362</td>
</tr>
<tr>
<td>Table E.2</td>
<td>Experimental Conditions (Partitioning of oxygen between aqueous and organic phases).</td>
<td>363</td>
</tr>
<tr>
<td>Table E.3</td>
<td>Summary of partition coefficients (oxygen) at each temperature.</td>
<td>365</td>
</tr>
<tr>
<td>Table F.1</td>
<td>Estimation of instrument variance from ten injections of a 50.0 ppm standard DMAEM sample.</td>
<td>370</td>
</tr>
<tr>
<td>Table F.2</td>
<td>Estimation of the total sample preparation and measurement variances for a sample withdrawn from a DMAEM homopolymerization.</td>
<td>373</td>
</tr>
<tr>
<td>Table H.1</td>
<td>Photomultiplier signal for several samples of the same polymer (polyacrylamide).</td>
<td>377</td>
</tr>
</tbody>
</table>
INTRODUCTION

Water soluble polymers are distinguished by strong hydrogen bonding interactions. They occur naturally as polypeptides, polysaccharides and proteins, including DNA which encodes our genetic heritage through a binary base pair sequence. They are also commonly synthesized by the free radical polymerization of ethynically unsaturated monomers.

Acrylic water soluble polymers gain their utility from their large molecular size, ionic substitution and charge density distribution. As such they are used primarily for water modification purposes. For example linear polyacrylamides exhibit an expanded configuration in aqueous solution and thereby decrease the hydrolytic resistance. Quaternary ammonium copolymers are used to flocculate anionic contaminants and are applied as clarifiers for water treatment, and as retention aids in paper suspensions. Hydrolyzed polyacrylamides are employed in microemulsion form as pushing fluids for enhanced oil recovery. Crosslinked sodium acrylates are superabsorbent and are used for water retention, both agriculturally and in diapers. In general the application of acrylic water soluble polymers involves either environmental maintenance and development or resource recovery, treatment and processing. These have a unique significance in Canada, where the extensive natural resources serve as a primary base for economic activity, and environmental conscientiousness is embedded in the collective social character.

Improving the quality of water soluble polymers requires developing the mechanism of free radical reactions in aqueous media and improving polyelectrolyte characterization methods. As a basis for this investigation acrylamide and its ionic acrylic derivatives have been selected since their high propagation velocities enable the production of charged supermolecular structures.

The first chapter of the thesis addresses polymer characterization in aqueous media. A new general light scattering method will be developed and shown to reduce the variance in
measurements of weight average molecular weight twofold. The characterization of poly-electrolytes will also be investigated. The reliable estimation of molecular parameters for charged macromolecules will be shown to depend on the establishment and measurement of equilibrium electrochemical potential of counterions between the polymer chain and bulk fluid.

The second chapter of the thesis investigates the inverse-microsuspension polymerization of acrylamide. A mechanism will be developed which contains three new elementary reactions: unimolecular termination with interfacial emulsifier, long chain branch formation through propagation with terminally unsaturated macroradicals and polymer chains, and heterophase mass transfer of primary and oligoradicals. The corresponding kinetic model will be shown to be consistent with data generated herein and by external sources. Further, it will provide inferences as to the selection of the stabilization mixture for optimization of polymer molecular weight.

The third chapter of the thesis investigates the copolymerization of acrylamide with quaternary ammonium cationic monomers. An improved high performance liquid chromatography method for residual monomer concentration will be coupled with the error-in-variables method to estimate reactivity ratios. This combination will be shown to be more reliable than any previously employed for cationic-acrylamide polymers. Experiments will be designed to isolate kinetic and mass transport effects so that unambiguous parameter estimates can be obtained and used to extend the inverse-microsuspension kinetic model to copolymerizations with quaternary ammonium monomers.

The fourth chapter seeks to mechanismically explain the high order rate dependencies on monomer concentration observed for polymerizations of acrylamide and other nonionic and ionogenic acrylic water soluble monomers. Experiments were performed between 25 and 50 weight percent monomer, to supplement the available data at low and
moderate concentrations. It will be inferred that hydrogen bonding leads to a charge transfer interaction between initiator and monomer. This weakly bonded complex will be shown to be equivalently represented as a diffuse monomer swollen cage. This analogy will enable the unification of the cage and complex theories which independently cannot correctly describe the polymerization mechanism. The mechanism will also be improved by incorporating the relative efficiencies of thermal and monomer-enhanced decomposition. This will be shown to predict rate, molecular weight and initiator consumption data well. The localization of monomer and initiator will be shown to be the cause of kinetic differences between solution and heterophase polymerizations.

Appendix A discusses the synthesis and characterization of superabsorbent polymers. $^{13}$C NMR techniques in the swollen and solid states, will be used to probe the microstructure. A method based on the methine and methylene line widths will be developed for estimating the fraction of divinyl monomer in the sample.

The relationship between each of the objectives in the thesis is shown in Figure 1.

The study of acrylic water soluble polymers involves the maintenance and modification of our water resources. It is therefore related to both the primary forces that motivate any artistic or scientific endeavour: satisfaction of the demand of the human species and the sustenance of life.
Figure 1: Interrelationships between the objectives of this thesis.
CHAPTER 1
CHARACTERIZATION OF WATER SOLUBLE POLYMERS

1. INTRODUCTION TO LIGHT SCATTERING

The scattering of light in liquid media was first observed on colloidal gold dispersions by Richter in 1802. Tyndall (1869) later investigated the interaction of light with vapors and found that by polarizing the incident beam, the light was visible exclusively in one plane.\(^1\) Rayleigh (1871) interpreted this phenomenon as evidence of diffraction and developed light scattering theory from electromagnetic principles. Debye (1944, 1946, 1947) was the first to apply this to the characterization of polymer solutions. He showed that the molecular weight and second virial coefficient, a measure of the interaction between solute molecules, could be estimated simultaneously.

In 1948, Zimm introduced the well known double extrapolation procedure to zero concentration and zero angle. With the advent of laser light scattering photometers (Kaye, 1973), scattering could be viewed only a few degrees off the path of the incident beam. This eliminated the need for angular extrapolation. Later in this chapter it will be shown that by theoretically predicting the second virial coefficient the necessity of multiple dilutions can also be eliminated.

1.1 Light Scattering Theory

When an incident light beam falls upon matter it induces oscillating electrical dipoles in the particles. These dipoles act as secondary sources of radiation, and it is this

\(^1\) The "Tyndall Effect", was used to account for the bluish appearance of the sky.
phenomenon that has historically been referred to as Rayleigh Scattering. When light is passed through an ideal gas, there is no phase relationship with the secondary radiation and the total scattering intensity is the sum of the contribution from each molecule. In the case of a solution, there is excess scattering from the solute particles over the solvent alone. At infinite dilution, the problem reduces to the scattering of an ideal gas. However, at a finite concentration, there is destructive interference between radiation emitted from different particles. When the solute molecules are large, such as for polymers, the intramolecular interference is present even at infinite dilution.

The evaluation of the intensity of scattered light can be approached in two ways. The fluctuation theory developed by Smoluchowski (1908, 1912) and Einstein (1910) treats the scattering as statistical fluctuations in density or concentration, caused by Brownian motion. These induce fluctuations in the dielectric constant and refractive index. Alternatively, molecular distribution functions can be used to describe the distribution of scattering particles in the system (Mayer-Montroll, 1941; McMillan-Mayer, 1945). In this chapter we will develop the former, which is strictly valid at low angles only and for particles small relative to the wavelength of light. For a discussion of the distribution function approach the reader is referred to excellent works by Kurata (1982) or Yamakawa (1971).

We will first discuss the radiation caused by a single particle and then generalize the analysis to multicomponent systems and solutions.

1.2 Derivation of the Rayleigh Factor

An incident light beam, plane polarized, with electric field \( E_0 \) oscillates as follows:

\[
E_0 = E_0^0 \exp(i\omega t)
\]

where \( E_0^0 \) is the amplitude, \( \omega \) the angular frequency and time \( t \). This is depicted in Figure 1.1. 

The induced dipole, \( p \), of a particle located at the origin is:
Figure 1.1: Depiction of light scattering for a particle located at the origin. Incident light with an intensity ($I_0$) is scattered at an angle ($\theta$) with a reduced intensity ($I_\theta$). At a distance $r$ from the particle an induced dipole ($p$) radiates perpendicular electric ($\mathbf{E}$) and magnetic ($\mathbf{H}$) fields.
\[ p = \alpha E_0 \]

where \( \alpha \) is the polarizability of the particle.

At a distance \( r \) from the particle, the dipole radiates electromagnetic waves and an electric field. These are perpendicular with velocities \((c/n)\) given by:

\[
E = -\left(\frac{\omega}{c}\right)^2 \frac{r \times (r \times \{p\})}{r^3}
\]

\[
H = n \left(\frac{\omega}{c}\right)^2 \frac{r \times \{p\}}{r^2}
\]

where \( c \) is the velocity of light in a vacuum and \( n \) is the refractive index of the medium. The curly brackets indicate that \( p \) is to be evaluated at the reduced time \((t-r)(c/n))\). Now we locate the particle at the origin, and specify the incident light to be parallel to the z-axis, with the associated dielectric field, \( E_0 \), parallel to the x-axis. The scattered electric field must lie in a plane perpendicular to \( r \), and the scattered magnetic field will be perpendicular to both \( E \) and \( r \). The magnitude of \( E \) and \( H \) are given by Yamakawa (1971):

\[
E = p_o \left(\frac{\omega}{c}\right)^2 \frac{\sin \theta}{r} \cos \left[ \omega \left( t - \frac{r}{(c/n)} \right) \right]
\]

\[
H = n E
\]

If light is used which has not been plane polarized both x and y components of \( E_o \) must be considered:

\[
E^0_x = E^0_{ox} \exp(i(\omega t + \delta_x))
\]

\[
E^0_y = E^0_{oy} \exp(i(\omega t + \delta_y))
\]

Where \( \delta_x \) and \( \delta_y \) are the phase shifts. The corresponding induced moments are:

\[
p_x = e_x p_o \exp(i(\omega t + \delta_x))
\]

\[
p_y = e_y p_o \exp(i(\omega t + \delta_y))
\]
Where $e_x$ and $e_y$ are the unit vectors. Now, if we define $E_1$ and $H_1$ as the electric and magnetic fields at $r$ caused by $p_x$, and $E_2$ and $H_2$ are the corresponding fields due to $p_y$, the total fields can be expressed as:

$$E = E_1 + E_2$$

$$H = H_1 + H_2$$

Where $E_{1,2}$ and $H_{1,2}$ can be defined analogous to the case where polarized light was used, with $\{p_x\}$ or $\{p_y\}$ in place of $\{p\}$.

The intensity of light is defined as the average energy which crosses a unit perpendicular area in a given time. The energy flow across an area $dA$ is given by $SdA$ where $S$ is the Poynting vector defined as:

$$S = \frac{c}{4\pi}(E \times H)$$

$S$ has the intensity

$$S = \frac{nc}{4\pi}E^2 = \frac{nc}{8\pi}I$$

We can define the intensity $I$ as, $I = 2E^2 = 2(E_x^2 + E_y^2)$, where the bars designate time averages.

This can be evaluated by substituting equation (1.1) into the above equation:

$$\frac{I}{I_0} = p_0^2 \left( \frac{\omega}{c} \right)^4 \frac{\sin^2 \theta_x}{r^2}$$

and with the incident intensity given by $I_0 = p_0^2/\alpha^2$, the ratio of scattered to incident intensities can be expressed as:

$$\frac{I}{I_0} = \frac{16 \pi^4 a^2}{\lambda^4 r^2 \sin^2 \theta_x}$$

Where the wavelength of light is defined as:

$$\lambda = \frac{2 nc}{\omega}$$

When unpolarized light is used the intensity ratio is given by Yamakawa (1971):
\[
\frac{I}{I_o} = \frac{8 \pi^4 a^2}{\lambda^4 r^2} (1 + \cos^2 \theta)
\]

If the system contains \( N \) independent particles in a volume \( V \), the total intensity ratio is:

\[
\frac{I}{I_o} = \frac{8 \pi^4 a^2 N}{\lambda^4 r^2} (1 + \cos^2 \theta)
\]

Normalizing this expression with respect to volume, angle and the geometric terms we can define an intrinsic physical property that is independent of the measurement conditions. The Rayleigh ratio can be defined as:

\[
R_\theta = \frac{r^2 I}{V I_o (1 + \cos^2 \theta)} = \frac{r^2 I_\theta}{V I_o}
\]

\[ (1.2) \]

\[
R_\theta = \frac{8 \pi^4 a^2}{\lambda^4} \rho
\]

\[ (1.3) \]

Where \( \rho = N/V \).

For solutions, the \( R_\theta \) in equation (1.2) is the excess scattering over that of the solvent. Similarly \( a \) is the excess polarizability which can be determined from the dielectric constants of the solvent and solute:

\[
a = \frac{1}{4\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right) = \frac{M}{2\pi N_A} n^0 \left( \frac{\partial n}{\partial \varepsilon} \right)_0
\]

Where \( \varepsilon = \varepsilon^2 \), \( \rho = N_A c/M \), with \( N_A \) being Avogadro's number, \( M \) the molecular weight of the solute and \( c \) the mass concentration.

1.3 Derivation of the Light Scattering Equation

If we consider an infinitesimal volume \( (V) \) of a solution, there will be fluctuations in the concentration in such volumes due to Brownian motion. This density fluctuation will induce fluctuations in the dielectric constant about its mean \( \langle \varepsilon \rangle \). Therefore in a volume \( V \), a
particle will experience an "excess dielectric constant" \( \Delta \varepsilon = \varepsilon - \langle \varepsilon \rangle \). This is equivalent to expressing an excess polarizability:

\[
\Delta \alpha = \alpha - \langle \alpha \rangle = \frac{V}{4\pi} \Delta \varepsilon = \frac{V}{2\pi} \Delta n
\]

Therefore, for solutions we must redefine the Rayleigh factor as:

\[
R_0 = \frac{2\pi^2 n^2 V}{\lambda^4} \langle (\Delta n)^2 \rangle
\]

(1.4)

where \( \rho \) in equation (1.3) has been replaced by \( V^{-1} \) in equation (1.4). To evaluate the Rayleigh factor we must find an expression for the fluctuation in refractive index. This is given by Kurata (1982):

\[
\Delta n = \left( \frac{\partial n}{\partial V} \right)_{T,N} \Delta V + \sum_{i=1}^{h} \left( \frac{\partial n}{\partial N_i} \right)_{T,V,N_k} \Delta n_i
\]

Where \( h \) is the number of components in the system.

From thermodynamics the following identities are known:

\[
\left( \frac{\partial n}{\partial V} \right)_{T,N} = \left( \frac{\partial n}{\partial \rho} \right)_{T,m} \left( \frac{\partial \rho}{\partial V} \right)_{T,N} = -\frac{1}{\kappa V} \left( \frac{\partial n}{\partial \rho} \right)_{T,m}
\]

\[
\left( \frac{\partial n}{\partial N_i} \right)_{T,V,N_k} = \left( \frac{\partial n}{\partial \rho} \right)_{T,m} \left( \frac{\partial \rho}{\partial N_i} \right)_{T,V,N_k} + \left( \frac{\partial n}{\partial N_i} \right)_{T,N_k}
\]

\[
= \frac{V_i}{\kappa V} \left( \frac{\partial n}{\partial \rho} \right)_{T,m} + \frac{M_i}{N_0} \left( \frac{\partial n}{\partial m_i} \right)_{T,p,m_k}
\]

Where \( \kappa \) is the isothermal compressibility and \( m \) is the concentration. The solution is simplified by introducing a reduced volume and reduced number of molecules:

\[
\xi = -\frac{\Delta V}{\langle V \rangle} + \sum_{i=1}^{h} \frac{V_i \Delta n_i}{\langle V \rangle}
\]

\[
X_i = \frac{\Delta N_i}{\langle N_i \rangle} = \frac{\Delta m_i}{\langle m_i \rangle} \quad (i = 1, 2, \ldots h)
\]
The fluctuation in refractive index can then be re-expressed in terms of the reduced variables (Yamakawa, 1971; Kurata, 1982):

\[
<\langle \Delta n \rangle^2> = \frac{<\xi^2>}{k^2} \left( \frac{\partial n}{\partial \rho} \right)_{T, \rho} + \sum_i \sum_j m_i m_j <x_i x_j> \left( \frac{\partial n}{\partial m_i} \right)_{T, \rho, m_k} \left( \frac{\partial n}{\partial m_j} \right)_{T, \rho, m_k}
\]

This expression shows that fluctuations in the refractive index increment are expressed in terms of fluctuations in composition and density about the averages \(<x_i x_j>\) and \(<\xi^2>\) respectively. Kurata has shown that for a two component system (o = solvent, 1 = solute), at constant pressure, the above equation reduces to:

\[
<\langle \Delta n \rangle^2> = \frac{M_1 k T}{N_A C_o} \left( \frac{\partial n}{\partial m_1} \right)_{T, \rho}^2
\]

Where \(\mu\) is the chemical potential.

Therefore the Rayleigh factor can be expressed as:

\[
R_0 = \frac{2n^2 M_1 k T}{N_A \lambda^2 C_o} \left( \frac{\partial n}{\partial m_1} \right)_{T, \rho}^2
\]

From the Gibbs-Duhem equation:

\[
\left( \frac{\partial \mu_1}{\partial m_1} \right)_{T, \rho} = -\frac{N_o}{N_1} \left( \frac{\partial \mu_o}{\partial m_1} \right)_{T, \rho}
\]

(1.6)

where

\[
\left( \frac{\partial \mu_o}{\partial m_1} \right) = \frac{c_o V_o N_o}{V} \left( \frac{\partial \mu_o}{\partial c} \right)
\]

(1.7)

and \(V_o\) is the molar volume.

From thermodynamics:

\[
\mu - \mu_o^0 = RT \ln \chi_o
\]
Where \( x_1 = 1 - x_0 \) for a two component system. Now, we perform a virial expansion on the logarithm to yield:

\[
\mu - \mu^0 = RT \left( \frac{V_o C_1}{M_1} + \frac{1}{2} \left( \frac{V_o C_1}{M_1} \right)^2 + \frac{1}{3} \left( \frac{V_o C_1}{M_1} \right)^3 + \ldots \right)
\]

where \( V_o/2M_1^2 \) is the second virial coefficient,

\( V_o/3M_1^3 \) is the third virial coefficient, etc.

Therefore:

\[
\frac{\partial \mu_o}{\partial c} = - V_o RT \left( \frac{1}{M_1} + 2A_2c + 3A_3c^2 + \ldots \right) \tag{1.8}
\]

Combining equations (1.5)-(1.8):

\[
R_0 = \frac{2\pi^2 n_o^2}{N_A \lambda^4} \left( \frac{\partial n}{\partial c} \right)^2 \frac{M_1 k N_1}{RV} \left( \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \right)
\]

Where \( N_A = R/k \) and \( c = M_1 N_1 / N_A V \).

For natural light the Rayleigh ratio at an observation angle \( \theta \) must be corrected by a factor \( (1 + \cos^2 \theta) \) to account for light depolarization.

If we group optical constants into a single parameter \( K \), given by:

\[
K = \frac{2\pi^2 n_o^2}{N_A \lambda^4} \left( \frac{\partial n}{\partial c} \right)^2 (1 + \cos^2 \theta)
\]

we can express the Rayleigh factor as:

\[
\frac{Kc}{R_0} = \frac{1}{M} + 2A_2c + 3A_3c^2 + \ldots \tag{1.9}
\]

Where the subscript 1 has been dropped from the molar mass of the solute. Equation (1.9) allows us to calculate the molar mass of a solute from measurements of the Rayleigh factor at several concentrations.
1.4 Extension to Solvents with Heterogeneous Molecular Weights

For a solution containing species of different molecular weights, the Rayleigh factor is made up of the sum of contributions of all chains of length \(i (i = 1 \rightarrow \infty)\). This can be expressed as \(Yamakawa, 1971\):

\[
R_\theta = \frac{2nm^2}{N_A \lambda C_0} \left( \frac{d\eta}{dM} \right)^2 \left( \sum_i M_i m_i - \sum_i \sum_j M_i M_j B_{2ij} m_i m_j \right)
\]  

(1.10)

Where \(m_i\) is the mass of polymer of length \(i\) and \(B_{2ij}\) is the second virial coefficient for interactions between two chains of length \(i\) and \(j\).

Simplifying equation (1.10) we obtain:

\[
\frac{R_\theta}{K} = \overline{M_w} c - 2 \sum_i \sum_j M_i M_j \left[ \frac{\overline{\nu}}{2} B_{2ij} + \frac{\nu}{2} \left( \frac{1}{M_i} + \frac{1}{M_j} \right) \right] \overline{w_i w_j} c^2 + \ldots
\]

Where \(w_i\) is the weight fraction of polymer of length \(i\), \(\overline{\nu}, \nu\) are the partial specific volumes of the solvent and solute and \(\overline{M_w}\) is the weight average molecular weight.

This reduces to the familiar form:

\[
\frac{Kc}{R_\theta} = \frac{1}{\overline{M_w}} + 2 A_2 c + \ldots
\]

(1.11)

\(A_2\) is the average second virial coefficient defined by:

\[
A_2 = \frac{1}{\overline{M_w}} \sum_i \sum_j M_i M_j A_{ij} \overline{w_i w_j}
\]

(1.12)

where

\[
A_{ij} = \frac{\overline{\nu}}{2} B_{2ij} + \frac{\nu}{2} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)
\]

(1.13)

From equation (1.12) it is obvious that for polydisperse molecular weight distributions the light scattering and osmotic virial coefficients will differ.

There are several aspects of light scattering which have not been addressed in this chapter. These include inter and intra particle interference, optical anisotropies, scattering in
mixed solvents and the estimation of the radius of gyration. Huglin (1972) may be cited as an authoritative, although somewhat dated, reference on these subjects. This chapter has also neglected Mie's theory (1910) which has utility for the study of large particles where significant differences can exist in the refractive index of the particles and the solvent.

1.5 Experimental Determination of the Rayleigh Factor

In the previous section it was shown that the Rayleigh factor is defined as:

\[ R_\theta = \frac{l_\theta r^2}{l_o V} \]

This equation is not directly applicable since photomultiplier detectors do not measure the light intensity. Rather they detect the total radiant power falling on the photocathode. A more useful form of the Rayleigh factor can be obtained if we define the following physical quantities: the radiant power (P) and the radiant intensity (J).

\[ P = lA \]
\[ J = P/\sigma \]

Where A is the illuminated area and \( \sigma \) is the solid angle over which J is viewed a distance r from the scattering volume. This is defined by:

\[ \sigma = A_0 r^2 \]

With these definitions the Rayleigh factor can be expressed as:

\[ R_\theta = \frac{P_\theta}{P_o \sigma \ell} \]

Where \( \ell = V/A_o \) is the length of the scattering volume parallel to the incident beam.

A diagram of the optical system of the KMX-6 Low Angle Laser Light Scattering Photometer (Chromatix) is shown in Figure 1.2. A detailed description of the apparatus is given by Kaye (1971, 1973, 1973, 1974) and in the reference (Chromatix Application Note LS-1, 1976).
Figure 1.2: Optical system of a KMX-16 Low Angle Laser Light Scattering Photometer. The upper diagram is for the measurement of scattered light and the lower for the incident beam.

Experimentally, the Rayleigh factor is determined by measuring the photomultiplier signal of the incident \( G_0 \) and transmitted beams \( G_\theta \). Assuming the detector behaves linearly, these photomultiplier signals can be expressed as:

\[
G_0 = S_a P_0 D_0 T_0
\]

\[
G_\theta = S_a P_\theta T_0
\]

Where \( S_a \) is the anode sensitivity, \( D_0 \) is the transmittance of the four attenuators (A1-A4) and \( T_0 \) is the transmittance of the optical system excluding the attenuators. If the radiant flux does not vary between the measurement of the incident and scattered beams, the Rayleigh factor can be expressed in its usual form:

\[
R_\theta = \frac{G_\theta D_0}{G_0 \sigma \ell}
\]

The solid angle in solution, \( \sigma' \), is defined as (Kaye, 1973):

\[
\sigma' = 2\pi S_p (\cos \theta_i' - \cos \theta_i'')
\]

Where \( \theta_i' \) and \( \theta_i'' \) are the minimum and maximum scattering angles and \( S_p \) is a factor which accounts for beam blockage by the annulus and attenuator supports. The scattering angles are functions of the inner and outer radii of the annulus, the width of the relay lens, and the refractive index of the sample. \( \sigma' \) is therefore a geometric parameter of the instrument which varies only with the refractive index.

The equivalent sample path length \( (\ell') \) is related to the depth of focus of the optical system and must be experimentally determined. Kaye provides values for \( \sigma' \), \( \ell' \) and \( \sigma'\ell' \) for various field stops and annulus'. These values must be determined for each instrument. Therefore, given the optical and physical configuration of the LALLSP, represented by the solid angle and the effective scattering length, the Rayleigh factor is determined from a ratio of the electrical signals developed by the photomultiplier detector. The measurement of \( R_\theta \) using low angle photometers is consistent with accepted literature values for several common
solvents measured with wide angle instruments. Under good optical conditions, a measurement variance of less than one percent has been reported (Kaye, 1973).
2. **ONE POINT METHOD TO CALCULATE MOLECULAR WEIGHT FROM LOW ANGLE LASER LIGHT SCATTERING DATA**

2.1 **Introduction**

Low Angle Laser Light Scattering Photometry is a relatively slow procedure for the determination of weight average molecular weight. In a typical day of operation it is possible to measure a maximum of three to four samples. Furthermore, the accuracy of the LALLS procedure is limited to about ±10%, requiring duplication in order to obtain confident estimates. Therefore, a procedure is needed from which we can improve the accuracy in the estimation of the weight average molecular weight, so that duplicate measurements are either expedient or unnecessary. This will be done by statistically scrutinizing the conventional LALLS procedure with the aim of isolating and reducing some of the variance that exists in the measurement of molecular weight.

2.2 **Experimental**

Polyacrylamide was synthesized in this laboratory by two methods. The low molecular weight polymer (<1 million) was synthesized by free radical aqueous solution polymerization using ethanol mercaptan (BDH) as a chain transfer agent. High molecular weight polymer was obtained by inverse-microsuspension polymerization using sorbitan monooleate as a stabilizer and Isopar K as the continuous phase. The aqueous phase consisted of monomer solutions, ranging from 30 to 50% by weight, in distilled deionized water. In all experiments a water soluble initiator, potassium persulphate, was used. Versenex 80 was used to remove the metal ions from the acrylamide monomer. Polymerizations were performed at 40, 50 and 60°C, in a 1-gallon batch reactor. Further details on the experimental procedure will be discussed in Chapter 4.
Molecular weights were measured using a Chromatix KMX-6 LALLS photometer, with a cell length of 15 mm and a field stop of 0.2. This corresponded to an average scattering angle of 4.8°.

A 0.45 μm cellulose-acetate-nitrate filter (Millipore) was used for polymer solutions. A 0.22 μm filter of the same type was used to clarify the solvent. Distilled deionized water with 0.02M Na₂SO₄ (BDH, analytical grade) was used as a solvent.

The refractive index increment of the solvent was determined using a Chromatix KMX-16 laser differential refractometer at 25°C and a wavelength of 632.8 nm. The dn/dc was found to be 0.1869.

The polymer concentrations used in LALLS were determined using a linear calibration between the differential refractive index (Δn) and concentration. This calibration was established using a polymer dried at 60°C for 48 hours whose concentration was corrected for water content by the Karl Fischer titration procedure.

All polymers were unfractionated with polydispersities between 2.0 and 2.5, as determined by aqueous size exclusion chromatography.

The acrylamide polymers were analyzed for possible acrylic acid groups by the ¹³C NMR, Infrared spectroscopy, elemental analysis and titration (Gunari, 1981). In all measurements no hydrolysis was detected and this confirmed the polymer was indeed a homopolymer of acrylamide.

2.3 Theory: Second Virial Coefficient

The second virial coefficient is experimentally observable through osmotic pressure or light scattering studies. Several investigators (Fox, 1949; Grimley, 1952; Ishihara, 1957; Casassa, 1958) have found that \( A_2 \) depends on the molecular weight of the polymer. The relationship is usually expressed by the following empirical form for linear polymers:

\[
A_2 = \alpha M^\beta
\]  

(1.14)

where \( \alpha \) and \( \beta \) are constants independent of the molecular weight and \( M \) is the molecular weight of the polymer which is assumed to be monodisperse. Table 1.1 gives values of \( \alpha \) and \( \beta \) for several polymer-solvent combinations.
Table 1.1

Values of the parameters $\alpha$ and $\beta$ in the expression $A_2 = \alpha M_w^\beta$ for several polymer-solvent systems.

<table>
<thead>
<tr>
<th>Polymer-Solvent combination</th>
<th>$\alpha \times 10^3$</th>
<th>$\beta$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylamide in 0.02M Na$_2$SO$_4$</td>
<td>8.18</td>
<td>-0.211</td>
<td>This work</td>
</tr>
<tr>
<td>Polyethylene oxide in Methanol</td>
<td>37.9</td>
<td>-0.320</td>
<td>This work</td>
</tr>
<tr>
<td>Polymethylmethacrylate in THF</td>
<td>6.62</td>
<td>-0.242</td>
<td>This work</td>
</tr>
<tr>
<td>Polymethylmethacrylate in Acetone</td>
<td>3.51</td>
<td>-0.221</td>
<td>This work</td>
</tr>
<tr>
<td>Polymethylmethacrylate in Dioxan</td>
<td>-</td>
<td>-0.32</td>
<td>This work</td>
</tr>
<tr>
<td>Polymethylmethacrylate in Butyl Acetate</td>
<td>-</td>
<td>-0.34</td>
<td>This work</td>
</tr>
<tr>
<td>Polystyrene-Toluene</td>
<td>12.41</td>
<td>-0.269</td>
<td>This work</td>
</tr>
<tr>
<td>Polystyrene-Toluene</td>
<td>-</td>
<td>-0.22</td>
<td>Casassa and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Markovitz (1958)</td>
</tr>
<tr>
<td>Polystyrene-Butanone</td>
<td>2.73</td>
<td>-0.247</td>
<td>This work</td>
</tr>
<tr>
<td>Polystyrene-Butanone</td>
<td>-</td>
<td>-0.264</td>
<td>Ishihara and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Koyama (1957)</td>
</tr>
<tr>
<td>Polystyrene-Dichloroethane</td>
<td>-</td>
<td>-0.296</td>
<td>Ishihara and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Koyama (1957)</td>
</tr>
</tbody>
</table>
Figures 1.3 to 1.6 show this relationship for polyacr/laude, polyethyleneoxide, polymethyl methacrylate and polystyrene. The linear dependence between $A_2$ and $M_w$ on a log-log scale is verified for a variety of polymer compositions in several solvents, indicating the universality of the relationship between the second virial coefficient and molecular weight for linear polymers. However, the scattering in these plots indicates that the accuracy in experimentally determining $A_2$ is poor. This is particularly true for polyacrylamide (Francois, 1979; Munk, 1980; Klein, 1980; Ali, 1985) because of the larger errors involved in LALLS measurements in aqueous solutions (Tabor, 1972; Kulicke, 1980; Molyneux, 1983; Hunt, 1986; Holzworth, 1986; McCarthy, 1987).

These inaccuracies in the measurement of the second virial coefficient lead to large errors in the estimates of molecular weights. In Figure 1.7 the fluctuation in the calculated molecular weights of a polymer measured on three occasions is seen to be almost exclusively caused by variations in the slope. Therefore, to improve the accuracy of LALLS a new method is needed from which estimates of the weight average molecular weight can be obtained without relying on the experimental determination of the second virial coefficient.

2.3.1 Relationship of $\beta$ to the Mark-Houwink-Sakurada exponent

Flory and Orofino (1957) have shown that for high molecular weight polymers in good solvents the second virial coefficient can be expressed as:

$$\frac{A_2 M}{[\eta]} = \text{constant}^2$$  \hspace{1cm} (1.15)

where $M$ is the molecular weight and $[\eta]$ is the intrinsic viscosity, given by

$$[\eta] = KM^a$$  \hspace{1cm} (1.16)

Combining equations (1.15) and (1.16) yields after rearrangement:

$$A_2 = K' M^{a-1}$$  \hspace{1cm} (1.17)

---

2 Flory and Orofino found this dimensionless constant to be 150, but other authors (Casassa, 1953; Shulz, 1954; Chinai, 1956; Flory, 1957) have found values ranging from 110 to 160, where $[\eta]$ has the units decilitres/gram.
Figure 1.3  Relationship between the second virial coefficient and molecular weight for polyacrylamide in 0.02 M Na₂SO₄. (▲): This work, (■): Stanislawczyk (1985), (△): Kulicke, et al. (1982), (●): Kim (1983), (○): Klein et al. (1980).
Figure 1.4  Relationship between the second virial coefficient and molecular weight for polyethyleneoxide in methanol. (•): Elias et al. (1966), (○): Allen et al. (1967), (△): Moldovan et al. (1970), (■): Ritscher et al. (1959).
Figure I.5  Relationship Between the second virial coefficient and molecular weight for polymethylmethacrylate in acetone. (●): Bischoff et al. (1952), (○): Schulz and Craubner (1959), (∆): Cantow et al. (1966).
Figure 1.6  Relationship between the second virial coefficient and molecular weight for polystyrene in toluene. (•): Schulz, Baumann et al. (1966), (▲): Outer et al. (1950), (●): Schulz and Heilfritz (1953), (○): Fukada et al. (1974), (△): Zhang et al. (1985).
Figure 1.7  Kc/R_g versus concentration for a high molecular weight sample of polyacrylamide measured on three occasions.
Equation (1.17) suggests that the second virial coefficient is dependent on the molecular weight and this dependence is related to the exponential term of the Mark-Houwink-Sakurada equation \( \beta = a - 1 \). Hence, from viscosity data we have an apriori estimate of the strength of the relationship between the second virial coefficient and molecular weight.

For a poor solvent, \( a = 0.5 \) and \( A_2 = K' M^{-0.5} \). For very good solvents \( a \to 1 \) and \( A_2 = K' \), independent of molecular weight. Therefore, as the solvent power rises, the influence of molecular weight on the second virial coefficient is reduced, and in extremely good solvents, the second virial coefficient is independent of molecular weight. This has been verified experimentally by several investigators (Sotobayashi, 1962; Kurata, 1963, 1964; Imai, 1969) and is shown for polyacrylamide of very high molecular weights in Figure 1.8.

For polyacrylamide, the Mark-Houwink-Sakurada equation at 25°C in water is (Molyneux, 1983):

\[
[\eta] = 5.6 \times 10^{-3} M^{0.8}
\]

This suggests \( \beta = -0.2 \), which agrees with the experimental value of \( \beta = 0.211 \), determined later herein.

Table 1.2 summarizes the values of \( a \) and \( \beta \) for various polymer-solvent systems.

2.3.2 **Effect of polydispersity on the second virial coefficient**

We have shown in equation (1.14) that for a monodisperse polymer, with molecular weight \( M \), the second virial coefficient is given by:

\[
A_2 = a M^\beta
\]

where \( a \) and \( \beta \) are characteristics of the polymer-solvent pair at a given temperature and are independent of molecular weight.

For polydisperse molecular weights, the average second virial coefficient \( \langle A_2 \rangle \) can be expressed as

\[
\langle A_2 \rangle = \frac{\int_0^\infty \int_0^\infty A_2(m, n) m f(m) n f(n) \, dm \, dn}{\int_0^\infty \int_0^\infty m f(m) n f(n) \, dm \, dn}
\]

(1.18)
Figure 1.8  Relationship between the second virial coefficient and molecular weight for high molecular weight polyacrylamides in 0.02 M Na₂SO₄. Symbols are the same as in Figure 1.1
Table 1.2

Relationship between the Mark-Houwink-Sakurada exponent, $a$, and the exponent $\beta$ in the equation $A_2 = \alpha M_w^\beta$.

<table>
<thead>
<tr>
<th>Polymer-Solvent combination</th>
<th>Temperature ($^\circ$C)</th>
<th>$a$</th>
<th>$a - 1$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylamide in 0.02M Na$_2$SO$_4$</td>
<td>25</td>
<td>0.80</td>
<td>-0.20</td>
<td>-0.211</td>
</tr>
<tr>
<td>Polystyrene-Toluene</td>
<td>25</td>
<td>0.79</td>
<td>-0.21</td>
<td>-0.22</td>
</tr>
<tr>
<td>Polystyrene-Butanone</td>
<td>25</td>
<td>0.58$\to$0.635</td>
<td>-0.365$\to$-0.42</td>
<td>-0.264$\to$-0.247</td>
</tr>
<tr>
<td>Polystyrene in Dichloroethane</td>
<td>25</td>
<td>0.66$\to$0.74</td>
<td>-0.26$\to$-0.34</td>
<td>-0.296</td>
</tr>
<tr>
<td>Polyethylene oxide in Methanol</td>
<td>25</td>
<td>0.72</td>
<td>-0.28</td>
<td>-0.320</td>
</tr>
<tr>
<td>Polymethyl methacrylate in Acetone</td>
<td>25</td>
<td>0.69$\to$0.73</td>
<td>-0.27$\to$-0.31</td>
<td>-0.221</td>
</tr>
</tbody>
</table>
where $\Lambda_2(m,n)$ is the interaction between two polymer chains of length $m$ and $n$.

$$\Lambda_2(m, n) mn = \frac{a}{8} [m^{(2+\beta)} + n^{(2+\beta)}]^3$$  \hspace{1cm} (1.19)

Other forms of $\Lambda_2(m,n)$ are possible\(^3\), but equation (1.19) is preferred because it assumes the interactions between chain elements are similar to those between two hard spheres. This is a basic assumption of excluded volume treatments of dilute polymer solutions (Flory, 1957), where a molecule is represented as an impenetrable sphere with a volume proportional to the cube of the radius of gyration.

Now, we adopt the approach of Casassa (1962) and assume the molecular weight distribution is adequately described by the Schulz distribution:

$$f(m) = \frac{y^{z+1} m^z e^{-ym}}{\Gamma(z+1)}$$  \hspace{1cm} (1.20)

$$y = \frac{z+1}{M_w}$$

where $f(m) \, dm$ is the weight fraction of solute with molecular weight $m$ and $\Gamma(z)$ is the gamma function. The parameter $z$ corresponds to the polydispersity, where $z = \infty$ is a monodisperse sample and $z = 1$ corresponds to the most probable distribution and a polydispersity of 2.

Equations (1.19) and (1.20) are inserted into equation (1.18) and integrated to yield:

$$\overline{A_2} = \Phi \, A_{2,ww}$$  \hspace{1cm} (1.21)

where $A_{2,ww}$ is the second virial coefficient of a monodisperse polymer with a molecular weight equal to $M_w$ of the polydisperse sample, and is given by:

$$A_{2,ww} = a \, M_w^\beta$$  \hspace{1cm} (1.22)

$\Phi$ is a constant which is dependent on the polydispersity and the parameter $\beta$, and is given by:

$$\Phi = \frac{(z+1)^{-\beta}}{4(\Gamma(z+2))^2} \cdot \left[ \frac{\Gamma(z+3+\beta) \Gamma(z+1)}{\Gamma(z+3+2\beta)} \right] \cdot 3! \left[ \frac{(3z + 17 + 2\beta)}{3} \right]$$  \hspace{1cm} (1.23)

Combining equations (1.21) and (1.22)

$$\overline{A_2} = \Phi(a \, M_w^\beta)$$  \hspace{1cm} (1.24)

\(^3\) Other authors (Blum and Morales, 1950) have expressed $A_2(m,n)$ as the simple geometric mean of virial coefficients of monodisperse polymers of length $m$ and $n$, respectively.
Equation (1.24) shows that $\beta$, the dependence of the second virial coefficient on molecular weight, is independent of the polydispersity and that the second virial coefficients of polymers with different polydispersities can be compared provided they are corrected by a factor $\Phi$. The effect of polydispersity on the value of $\Phi$ is shown in Table 1.3.

For polyacrylamide, with a molecular weight distribution taken as the most probable, equation (1.24) reduces to:

$$\overline{A}_2 = 1.07 \alpha \overline{M}_w^\beta$$

(1.25)

In other words, the second virial coefficient of a polyacrylamide with a polydispersity of 2.0 is 7% larger than the second virial coefficient that would occur if the polymer were monodisperse with a molecular weight equal to $M_w$ of the polydisperse sample.

All second virial coefficients measured in this study were corrected for polydispersity using the above procedure.

2.3.3 Modelling the second virial coefficient

Many theories exist for modelling the second virial coefficient and its dependence on molecular weight. The Kurata-Yamakawa-Tanaka theory is generally accepted as the best in predicting second virial coefficients from measurements of molecular weight and the mean-square radius of gyration. However, Kok and Rudin (1981, 1984) have developed a method to predict $A_2$ from intrinsic viscosities, and it appears to be marginally better than the K-Y-T theory for the polymers studied.

A complete discussion of this topic is given in Appendix B.

2.4 Results and Discussion

2.4.1 New One-point LALLS method

In conventional low angle laser light scattering a series of polymers are prepared at different concentrations and the Rayleigh factor is measured. A plot of $Kc/R_g$ versus $c$ is constructed and the weight-average molecular weight is obtained by linear extrapolation to zero concentration; the slope of the line is twice the second virial coefficient. This procedure, although statistically poor because
Table 1.3

**Effect of the polydispersity on the Second Virial Coefficient for polyacrylamide.**

<table>
<thead>
<tr>
<th>Polydispersity</th>
<th>$A_2/A_{2,ww}$ (with $\beta = -0.211$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.2</td>
<td>1.028</td>
</tr>
<tr>
<td>1.5</td>
<td>1.054</td>
</tr>
<tr>
<td>2.0</td>
<td>1.071</td>
</tr>
<tr>
<td>2.5</td>
<td>1.094</td>
</tr>
<tr>
<td>3.0</td>
<td>1.104</td>
</tr>
<tr>
<td>5.0</td>
<td>1.123</td>
</tr>
<tr>
<td>100.0</td>
<td>1.149</td>
</tr>
</tbody>
</table>
concentration appears on both axis, is nonetheless valid provided the variance of all the measurements is the same. However, as Figure 1.9 shows, the variance is indeed not constant and passes through a minima as a function of concentration. This is the result of two effects:

1) At very low concentrations the photomultiplier signal and the Rayleigh factor are small. The variation in this signal with time is, however, a constant which is independent of concentration (Figure 1.10). Therefore the instrument is less sensitive at low concentrations due to a lower signal to noise ratio. This leads to irreproducible estimates of molecular weight when measured at low concentrations, as is shown in Figure 1.7.

2) At high concentrations the filtering of the polymer before it enters the light scattering cell is difficult, due to polymer retention on the membrane. This problem can only be circumvented by using a larger pore size filter. This however, introduces impurities into the cell which causes large variations in the photomultiplier signal. The baseline often becomes obscured and the measurement is unreliable. An example of this phenomena is observed in Figure 1.11.

Figure 1.12 shows the experimentally determined 95% confidence region for a polyacrylamide sample. The degree of uncertainty is largest at low concentrations, which is the very region we are extrapolating to in order to obtain the molecular weight. These large variances in $Kc/R_0$ lead to poor estimates of the slope and the second virial coefficient. These inaccuracies are translated into a poor estimate of molecular weight when extrapolating to zero concentration.

To improve the estimate of molecular weight, we could perform weighted least squares analysis, where each value of $Kc/R_0$ is weighted by the reciprocal of its variance. However, this procedure would require several measurements of $Kc/R_0$ at each concentration, and from a practical point of view, this is not feasible.

The weighted least squares procedure can be simplified by setting the weighting of all points to zero except the one for which we have the most confidence. That is, we measure only at a single concentration at which the variance in $Kc/R_0$ is smallest. If we take the example shown in Figure 1.9 this would be at a concentration of $2.0E-4$ g/mL. The molecular weight is then obtained by extrapolating to zero concentration using values of $A_2$ from previous light scattering measurements, such
Figure 1.9  Standard deviation of $Kc/R_0$ as a function of concentration for a polyacrylamide measured on several occasions.
Figure 1.10 Variation in the photomultiplier signal of the scattered light ($C_0$) for several concentrations.
Figure 1.11  \( K_e/R_0 \) versus concentration for a polyacrylamide sample measured on three occasions.
Figure 1.12  Ninety five percent confidence intervals of $Kc/R_0$ as a function of concentration.
as in Figures 1.3–1.6. This gives us more confidence in the estimate of weight-average molecular weight than if we calculated the slope from a few dilutions. Figure 1.13 shows that by using a historical value of $A_2$ the confidence interval of the estimate of the weight average molecular weight is reduced significantly over the conventional procedure.

2.4.2 Method of calculation for the new LALLS procedure

We recall that the molecular weight is related to the Rayleigh factor by:

$$\frac{K_c}{R_0} = \frac{1}{M_w} + 2A_2c$$  \hspace{2em} (1.11)

where

$$A_2 = \alpha M^\beta$$  \hspace{2em} (1.26)

Combining equations (1.11) and (1.26) we obtain:

$$\frac{K_c}{R_0} = \frac{1}{M_w} + 2\alpha M_w^{\beta}c$$  \hspace{2em} (1.27)

For polyacrylamide, these parameters and their 95% confidence intervals are:

$$\alpha = 0.00818 \pm 0.00380$$

$$\beta = -0.211 \pm 0.037$$

Substituting these values into equation (1.27) yields:

$$\left(\frac{K_c}{R_0}\right)_0 = \frac{1}{M_w} + (1.636 \times 10^{-2} M_w^{-0.211}) C_0$$  \hspace{2em} (1.28)

From equation (1.28) we can predict the weight-average molecular weight from a single measurement at a concentration ($C_0$) where the variance is smallest; ($K_c/R_0)_0$. These concentrations have been determined for polyacrylamide and are shown in Table 1.4 and Figure 1.14. These represent optimal values for measurement in the sense that they produce the lowest confidence intervals in the estimate of weight-average molecular weight. Table 1.5 shows the molecular weights predicted by the conventional method and by equation (1.28). The new method gives a reproducibility of $\pm 4.7\%$ which is less than half the error of the conventional procedure ($\pm 11.2\%$).
Figure 1.13  Confidence region for weight average molecular weight predicted from the new LALLS procedure.
Table 1.4

Optimal concentration for the measurement of weight average molecular weight of polyacrylamide by LALLS.

<table>
<thead>
<tr>
<th>$\bar{M}_w$ \ (× 10^3)</th>
<th>Optimal Concentration \ (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10→30</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>30→70</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>70→400</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>400→650</td>
<td>$9 \times 10^{-4}$</td>
</tr>
<tr>
<td>650→1,000</td>
<td>$4 \times 10^{-4}$</td>
</tr>
<tr>
<td>&gt; 1,000</td>
<td>$2 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Figure 1.14  Optimal concentration range for polyacrylamide as a function of molecular weight.
Table 1.5

A comparison of the accuracy in the prediction of weight average molecular weight by the conventional and the new LALLS procedure.

<table>
<thead>
<tr>
<th>( M_w ) (conventional method)</th>
<th>Average deviation (%)</th>
<th>( M_w ) (new method)</th>
<th>Average deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11,200</td>
<td>1.3</td>
<td>11,400</td>
<td>0.9</td>
</tr>
<tr>
<td>11,500</td>
<td></td>
<td>11,200</td>
<td></td>
</tr>
<tr>
<td>21,300</td>
<td></td>
<td>23,200</td>
<td></td>
</tr>
<tr>
<td>21,900</td>
<td></td>
<td>23,500</td>
<td></td>
</tr>
<tr>
<td>22,600</td>
<td>2.0</td>
<td>22,800</td>
<td>1.1</td>
</tr>
<tr>
<td>57,000</td>
<td></td>
<td>60,900</td>
<td></td>
</tr>
<tr>
<td>61,500</td>
<td></td>
<td>63,000</td>
<td></td>
</tr>
<tr>
<td>72,500</td>
<td>9.3</td>
<td>73,700</td>
<td>7.9</td>
</tr>
<tr>
<td>79,000</td>
<td></td>
<td>84,000</td>
<td></td>
</tr>
<tr>
<td>80,000</td>
<td>0.8</td>
<td>82,000</td>
<td>2.5</td>
</tr>
<tr>
<td>81,000</td>
<td></td>
<td>78,400</td>
<td></td>
</tr>
<tr>
<td>253,000</td>
<td></td>
<td>284,000</td>
<td></td>
</tr>
<tr>
<td>290,000</td>
<td>9.8</td>
<td>248,000</td>
<td>6.8</td>
</tr>
<tr>
<td>344,000</td>
<td></td>
<td>422,000</td>
<td></td>
</tr>
<tr>
<td>393,000</td>
<td></td>
<td>407,000</td>
<td></td>
</tr>
<tr>
<td>420,000</td>
<td></td>
<td>405,000</td>
<td></td>
</tr>
<tr>
<td>698,000</td>
<td>25.3</td>
<td>414,000</td>
<td>0.9</td>
</tr>
<tr>
<td>576,000</td>
<td></td>
<td>495,000</td>
<td></td>
</tr>
<tr>
<td>617,000</td>
<td></td>
<td>512,000</td>
<td></td>
</tr>
<tr>
<td>800,000</td>
<td>13.6</td>
<td>470,000</td>
<td>3.0</td>
</tr>
<tr>
<td>540,000</td>
<td></td>
<td>519,000</td>
<td></td>
</tr>
<tr>
<td>754,000</td>
<td></td>
<td>672,000</td>
<td></td>
</tr>
<tr>
<td>865,000</td>
<td></td>
<td>665,000</td>
<td></td>
</tr>
<tr>
<td>890,000</td>
<td>15.1</td>
<td>640,000</td>
<td>8.4</td>
</tr>
<tr>
<td>1,062,000</td>
<td></td>
<td>990,000</td>
<td></td>
</tr>
<tr>
<td>1,136,000</td>
<td></td>
<td>944,000</td>
<td></td>
</tr>
<tr>
<td>1,145,000</td>
<td>3.1</td>
<td>900,000</td>
<td>3.2</td>
</tr>
<tr>
<td>1,500,000</td>
<td></td>
<td>1,500,000</td>
<td></td>
</tr>
<tr>
<td>2,400,000</td>
<td></td>
<td>1,600,000</td>
<td></td>
</tr>
<tr>
<td>2,900,000</td>
<td>22.5</td>
<td>2,000,000</td>
<td>11.8</td>
</tr>
<tr>
<td>Overall Average deviation</td>
<td>11.2%</td>
<td></td>
<td>4.7%</td>
</tr>
</tbody>
</table>
This 1-point method can be applied to any linear polymer for which the relationship between the second virial coefficient and molecular weight is known or can be elucidated from the literature\(^4\). For polymers other than acrylamide, the parameters in equation (1.27) will be different, but the computational procedure remains unchanged.

The one-point method also has utility for the estimation of molecular weight distributions by SEC/LALLS. For these measurements an apriori estimate of the second virial coefficient is required (Barth, 1980). The current practice is to arbitrarily specify a mean \( A_2 \) for all polymer molecules, independent of chain length. However, even in the limit of perfect column resolution, this provides an inaccurate distribution by overpredicting the polydispersity. The true distribution can only be obtained by using a single point method to interpret the photomultiplier signal from the light scattering detector.

\(^4\) For branched polymers, the procedure cannot be used since \( A_2 \) does not vary linearly on a log-log scale with the weight average molecular weight. Therefore, Equation (4) is invalid for non-linear polymers.
3. MOLECULAR WEIGHT CHARACTERIZATION OF POLYACRYLAMIDE-CO-SODIUM ACRYLATE

3.1 Introduction

Copolymers of acrylamide and sodium acrylate are used in aqueous solutions as drug reduction agents, flocculants and thickeners. They are also employed in tertiary oil recovery as thixotropic aqueous polymer emulsions. These solutions are pseudoplastics and exhibit typical polyelectrolyte behaviour with respect to salinity. The polymers can be prepared by direct copolymerization or derivatization from polyacrylamides. When the ionogenic monomer is introduced through a free radical addition mechanism, long acrylate and amide sequences form, with the microstructure conforming to Bernouillian statistics (Troung, 1986; Canda, 1986). By comparison, polymers produced through alkaline saponification of the amide side chain are atactic (Troung 1986 II). This provides a relatively uniform charge density distribution which maximizes the viscosity increase for a given molecular weight and improves the polymer's performance (Ellwanger, 1980). The hydrolysis substitution reaction is however limited to approximately sixty five percent conversion (Figure 1.15).\textsuperscript{5} This has been explained (Nagase and Sakaguchi, 1985) by a neighbouring group catalysis model. Upon attack by a hydroxyl ion the NH\textsubscript{2} group is pushed aside and simultaneously attracted by the adjacent amide. Although this reaction is usually interpreted by second order retardation kinetics, a more valid approach is to treat an acrylamide diad as the reactive species. Troung (1986) has shown that near the limits of hydrolysis the acrylamide diad and triad concentrations become negligible. These are replaced by an

\textsuperscript{5} Kurenkov (1984, 1984, 1984, 1986) has found the limiting extent of hydrolysis decreased as the polymer synthesis temperature of monomer concentration was increased. Preliminary investigations in this work have supported these results, concluding that the limiting degree of hydrolysis decreases slightly as molecular weight rises.
Figure 1.15: Kinetics of the Alkaline hydrolysis of polyacrylamide. The experimental conditions were: $T=22^\circ C$, $[\text{NaOH}]=1.0 \text{ mol/L}$, $[P] = 0.05 \text{ g/mL}$, $\bar{M}_w = 8.0 \times 10^4$. Compositions were determined from the ratio $N/(C+N)$ from elemental analysis.
abundance of AMA triads which, under the proposed mechanism, would be unreactive. The intramolecular catalysis or "joint-site" mechanism seems plausible, since for an atactic polymer the concentration of MM diads reaches zero at two-thirds acrylamide content, in excellent agreement with experimental findings.

Complete hydroxy substitution can be obtained in acidic media at high temperatures. However, intramolecular imidization (Moens and Smets, 1957), degradation (Kulicke and Horl, 1985) and a Bernouillian sequence length distribution (Halverson, 1985) limit the polymers' utility.

The modelling of the hydrolysis kinetics over the complete range of pH has recently been attempted by Kheradmon et al. (1988). The model seems to have good predictive power and is consistent with experimental data. Table 1.6 summarizes these and previous results.

Typical of polyelectrolytes, the solution behaviour of polyacrylamide-co-sodium acrylate has several peculiarities. For example the intrinsic viscosity, radius of gyration, and second virial coefficient all show maximums at 60-70 percent acrylate levels (Kulicke, 1985; Candau, 1986). This is due to a combination of electrostatic repulsion and intermolecular hydrogen bonding. The latter diminishing as the amide groups are hydrolyzed. The viscosity also reaches a limit at a degree of neutralization of approximately sixty percent. Above this level counterion shielding has been postulated to reduce the electrostatic repulsion (Muller, 1979 I).

The purpose of this research is to develop a valid characterization method for weight average weights of copolymers of acrylamide and sodium acrylate. Initially a series of polyacrylamides will be synthesized and fractionated to yield narrow molecular weight

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6 This work has been confirmed by observing downward shifts in the wave number of the $\delta(NH_2)$ absorption (Kulicke, 1985).
Table 1.6
Summary of hydrolysis kinetics.

<table>
<thead>
<tr>
<th>pH</th>
<th>Description of kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5</td>
<td>Intramolecular catalysis results in an acceleration in rate due to neighbouring undissociated carboxyl groups.</td>
</tr>
</tbody>
</table>
| 8-13| Retardation caused by the occurrence of amide diads which cooperate to hydrolyze a single amide†.  
     | Retardation is not caused by Coulombic repulsion.                                        |
| 4-7 | Combination of acceleration and retardation.                                             |
| >13 | Neighbouring group effect no longer occurs. Catalysis is by hydroxy ions.                |

† Nagase and Sakaguchi (1965) hydrolyzed model amides (acrylamide, propionamide, succinamide and adipamide) and found that retardation did not occur in the monofunctional compounds. For diamides or polyfunctional amides the kinetic trends are equivalent. Therefore retardation only occurs when neighbouring amides are hydrolyzed.
distributions. These will first be measured in their nonionic form where light scattering is more reliable and accurate than for ion containing polymers. These will then be hydrolyzed to various degrees and analyzed in their ionic form. The measured weight average chain length will be used to evaluate the absolute accuracy of the polyelectrolyte characterization method. Such an error estimate is impossible without an apriori knowledge of the polymer's molecular weight. Therefore, polyelectrolyte methods development must be proceeded by derivatization from nonionic species. Nagai and Osishi (1987) have reached the same conclusion studying cationic polyelectrolytes.

3.2 Experimental Methods and Procedures

3.2.1 Polymer preparation

Polyacrylamides were synthesized by aqueous free radical polymerizations using potassium persulfate (BDH, 99% purity) as an initiator and ethanol mercaptan (BDH) as a chain transfer agent. The polymers were heterodisperse in molecular weight, with polydispersities between 2.0 and 2.5 as measured by Size Exclusion Chromatography (SEC). SEC chromatograms were measured with a Varian 5000 liquid chromatograph, using Toya Soda columns (TSK 3000,5000,6000 PW) and an aqueous mobil phase (0.02 M Na₂SO₄ (BDH), 0.1 wt% Sodium Azide (Aldrich) and 0.01wt% Tergitol NPX (Union Carbide Corp.)). The spectrum were recorded on a Varian CDS 401 Data Station.

The synthesis conditions did not lead to preliminary hydrolysis as is shown by the ¹³C NMR spectra in Figure 1.16. The spectra was recorded for a 10 wt% D₂O solution at 125.76 MHz and 70.9°C in the Fourier transform mode with inverse gate decoupling. The pulse width was 6.8 ms with an acquisition time of 0.557s.
Figure 1.16: $^{13}$C NMR spectra of a polyacrylamide with molecular weight $8.2 \times 10^4$ g/mol. A single peak is observed in the carbonyl region ($\approx 180$ ppm) indicating the absence of hydrolysis during synthesis.
3.2.2 Fractionation

Polymer fractionation can be performed by a variety of techniques based on differential solubility, sedimentation, diffusion and chromatographic exclusion. For the large scale fractionation of high molecular weight polyacrylamide fractional precipitation is preferred, since it provides good separation efficiency and high yields, without requiring excessively dilute solutions. Previous investigations on polyacrylamide fractionation have used several nonsolvents including methanol (Shulz, 1954; Baysal, 1963 I,II), isopropanol (Venkataro, 1970) acetone, dioxane and THF (Ramazanov, 1984). Wu (1988,1989) found acetone to have the highest solvent power by the solvent-precipitation-fractionation (SPF) method. She also observed the narrowest polydispersity for fractions separated with mixtures of water and acetone as a nonsolvent. However, at high molecular weights, methanol performed better, providing a more uniform polymer distribution between the lean and rich phases. A summary of the fractionation conditions and procedures used in this research is given in Table 1.7. This method is the first large scale procedure to be applied to polyacrylamide, although large scale apparatus have been used before (Kamide, 1981). Figure 1.17 illustrates the magnitude in the reduction in polydisperisty due to fractionation.

Excellent reviews of the theory of polymer fractionation are given by Tung (1977), Kamide (1973) and Koningsveld and Staverman (1968).

Weight average molecular weights and second virial coefficients were measured for each fraction in 0.02 M Na₂SO₄. The conventional LALLS dilution technique, described earlier in this chapter, was utilized. The results are given in Table 1.8.

3.2.3 Polymer hydrolysis

The fractionated polyacrylamides were hydrolyzed in an aqueous solution containing 4 wt% polymer. The reaction was performed in a three neck 250 mL round bottom
Table 1.7
Fractionation Conditions.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Distilled deionized water.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-solvent</td>
<td>Acetone, Methanol (BDH, Reagent grade)</td>
</tr>
<tr>
<td>Temperature</td>
<td>23 ± 2°C</td>
</tr>
<tr>
<td>Polymer concentration</td>
<td>1-8 wt% of initial solution†</td>
</tr>
<tr>
<td>Reservoir</td>
<td>Polyethylene: 20L, 50L</td>
</tr>
<tr>
<td>Agitation</td>
<td>1/8 HP heavy duty lab stirrer with torque limiting controller (Series II, G.K. Heller Corp. Floral Pk. N.Y.)</td>
</tr>
<tr>
<td>Non-solvent addition</td>
<td>Dropwise</td>
</tr>
<tr>
<td>Length of non-solvent addition</td>
<td>2-48 h††</td>
</tr>
<tr>
<td>Settling time</td>
<td>2 - 7 days</td>
</tr>
<tr>
<td>Method of phase separation</td>
<td>Supernatant layer was siphoned off and refractionated</td>
</tr>
</tbody>
</table>

† Polymer concentration was reduced for higher molecular weight samples to maintain low viscosities and high fractionation efficiencies.

†† Larger amounts of non-solvent were needed to separate lower molecular weight polymers and refractionated samples.
Figure 1.17: Unnormalized SEC chromatograms showing the reduction in polydispersity upon fractionation.
Dashed line: original polymer
Solid lines: Fractions 1 – 4.
Table 1.8

Weight average molecular weight and second virial coefficients for polyacrylamide fractions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\bar{M}_w \times 10^{-3}$ (g/mol)</th>
<th>$A_2 \times 10^4$ (mL mol/g$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA-1R</td>
<td>1,240</td>
<td>5.718</td>
</tr>
<tr>
<td>S2</td>
<td>1,220</td>
<td>5.600</td>
</tr>
<tr>
<td>LFA2-1</td>
<td>1,140</td>
<td>5.930</td>
</tr>
<tr>
<td>S7</td>
<td>984</td>
<td>4.048</td>
</tr>
<tr>
<td>LFA4-1</td>
<td>466</td>
<td>7.695</td>
</tr>
<tr>
<td>S8</td>
<td>286</td>
<td>8.194</td>
</tr>
<tr>
<td>LFA2-2</td>
<td>233</td>
<td>8.605</td>
</tr>
<tr>
<td>LFB1-1D</td>
<td>119</td>
<td>12.060</td>
</tr>
<tr>
<td>AL-1</td>
<td>72.6</td>
<td>14.126</td>
</tr>
<tr>
<td>LFB1-2</td>
<td>64.4</td>
<td>20.833(?)</td>
</tr>
<tr>
<td>LFA4-2</td>
<td>48.2</td>
<td>7.528(?)</td>
</tr>
<tr>
<td>LFB1-1U</td>
<td>40.0</td>
<td>16.508</td>
</tr>
<tr>
<td>LFB1-3</td>
<td>26.9</td>
<td>17.195</td>
</tr>
<tr>
<td>LFB1-4</td>
<td>13.0</td>
<td>12.102</td>
</tr>
</tbody>
</table>
Pyrex flask. The centre opening was tightly fit with a glass agitator equipped with two, one-inch teflon blades. The agitator was connected to an external motor (type RZRI-66, Caframo, Wiarton, Ont.). The two side necks housed a thermometer and were available for sample withdrawals respectively. The flask was immersed in a constant temperature bath, operating at 30 ± 0.5 °C. Distilled deionized water with 0.5 M NaOH (BDH) was used as the reaction medium. Experiments were carried out for six hours in duration, with aliquots withdrawn periodically at approximately fifteen minute intervals.

Hydrolysis was performed on five nonionic fractions with nominal molecular weights of 30,000, 120,000, 200,000, 400,000 and 1,000,000 daltons. At each molecular weight a range of polymer compositions from zero to thirty percent sodium acrylate was obtained. These polymers were precipitated in methanol; an ideal solvent since it solubilizes the unreacted sodium hydroxide, and dried in vacuo to constant weight. The samples were subsequently stored in a sealed glass desiccator over silica gel.

3.2.4 **Copolymer characterization**

The composition of copolymers of acrylamide with sodium acrylate can be measured using a variety of chromatographic, spectrometric, elemental or titrative techniques. Early investigations into these copolymers measured the extent of hydrolysis by potentiometric (Nagase, 1965; Muller, 1979, 1979, 1980; Gunari and Gundiah, 1981; Schwartz, 1981; Kurenkov, 1985) or conductiometric titrations (Moens and Smets, 1957). Elemental analysis (C-H-N) is also common (Klein and Heitzmann, 1978; Kulicke and Kniewske, 1981). However, it is sensitive to trace residuals of water which are difficult to completely remove. $^{13}$C NMR techniques have been reported (Candau, 1986; Troung, 1986 I,II) and give excellent results for low to moderate molecular weight polymers, but require extensive data acquisition for chain lengths above approximately one thousand. Infrared methods have been developed
(Shaglayeva, 1978; Kulicke and Siesler, 1982; Kulicke and Horl, 1985) and while they provide quick estimates of the composition, their reliability and reproducibility are poor (Hansen, 1987). Recently Maurer and Klemann (1987) have used ion chromatography and found it provided excellent agreement with atomic absorption spectroscopy (for Na$^+$. Indeed, the elemental analysis of Na$^+$ directly is insensitive to residual water, but Wu (1989) has found it to underpredict the degree of ionization, likely because of incomplete neutralization. Elemental sodium methods are also susceptible to contamination by sodium ions, either from insufficient washing of NaOH or residual on the glassware. Therefore, although elemental methods have the best reproducibility, their absolute accuracy is insufficient.

In this work both potentiometric and conductimetric electrodes were placed in the titration reservoir. This was equipped with a flow through jacket to control temperature, and sealed such that an inert nitrogen atmosphere could be maintained over the sample. Entrance holes for the probes and titrant were included. Homogenized aqueous solutions of polyacrylamide-co-sodium acrylate were titrated with 1.0 M HCl (BDH; reagent grade), and backtitrated with 0.1 M NaOH (BDH; reagent grade). The potentiometric and conductimetric calculation gave compositions within one percent of each other. Duplicate titrations were performed on a representative number on samples to estimate the reproducibility. Further details of these experimental techniques are given by Gunari (1981) and Wu (1989).

3.2.5 Light scattering of polyelectrolytes

When performing light scattering on polyelectrolyte samples, the effect of ionogenic monomers is manifested in an apparent second virial coefficient and refractive index increment. Nonetheless, the light scattering equation derived in section 1.1.2,3 for nonionic polymers can be generalized for polyelectrolytes (Alexandrowicz, 1959) provided the following criterion are met:
1) The local fluctuations in concentration, density and refractive index are electrically neutral (Richards, 1980)

2) The refractive index increment is obtained at constant electro-chemical potential of the counterions in the solution and the environment of the polymer coil (Nagasawa, 1972).

The second criterion is satisfied by dialyzing the polymer and aqueous salt solutions against each other. At 'Donnan Equilibrium', the sodium concentration will be the same at all locations in the solution. Therefore, to correctly measure the molecular weights of polyelectrolytes we must first determine $\delta n/\delta c)_\mu$ as a function of copolymer composition.

3.2.6 Dialysis

A cellulose dialysis membrane (Spectra/Por 6) with a molecular weight cutoff of 1000 was purchased from Spectrum Medical Industries, Inc. (Los Angeles Ca.). A small pore size was selected to prevent oligomers from diffusing into the dialysate. Prior to use the membranes were conditioned in the dialyzing buffer (0.2 M Na$_2$SO$_4$) for one hour, and rinsed with distilled deionized water.

Polymer solutions were prepared at a concentration suitable for light scattering (Table 1.4). One hundred mL of these solutions were pipetted into the membrane which was sealed at one end with a dialysis tubing enclosure. After the second end of the membrane was secured, it was submersed in three litres of saline solution. This was housed in a four litre polyethylene container, isolated from the atmosphere.

After a predetermined time the vessel was opened and the membrane removed. Several concentrations of the polymer were prepared by diluting the dialyzed solution with the dialysate. The samples were immediately analyzed by light scattering or differential refractometry.
3.2.7 Determination of the refractive index increment at constant chemical potential

In order to determine the time required for donnan equilibrium of the sodium ion in this particular solvent/membrane combination, several parallel experiments were performed. A polyaacrylamide-co-sodium acrylate with thirty percent ionic content and a nominal molecular weight of 400,000 daltons was selected as a representative sample. A 0.15 wt% polymer solution was prepared and was separated into six samples, which were dialyzed for 0, 24, 48, 72, 96 and 120 hours respectively. After these periods the solutions were diluted and their refractive index increments determined against the dialysate. A Chromatix KMX-16 laser differential refractometer was used for $\delta n/\delta c$ measurements. A plot on the trend in the refractive index increment with dialysis time is shown in Figure 1.18. Clearly equilibrium is reached after 72 hours, although for subsequent measurements a dialysis time of 120 hours was used. The refractive index increment at constant chemical potential was determined as a function of the extent of hydrolysis (Table 1.9 and Figure 1.19). The observed decrease in $\delta n/\delta c_{\mu}$ with acrylate content, a manifestation of the negative selective sorption of sodium sulphate, has been reported previously (Klein and Conrad, 1978; Schwartz, 1981; and Kulicke and Horl, 1985). Only Kulanari and Gundiah (1984) have found a contradictory dependency. None of these authors have used the same solvent as in this work and therefore direct comparison of the magnitude of $\delta n/\delta c$ is not possible. Nonetheless, the validity of these measurements will be confirmed in the next section.

The equation

$$\left(\frac{\delta n}{\delta c}\right)_{\mu} = 0.1869 \text{ (% hydrolysis)}^{-0.076}$$

has been fit from this data so that the refractive index may be computed at any specific copolymer composition between zero and thirty three percent sodium acrylate.
Figure 1.18: Refractive index increment ($\delta n/\delta c$) as a function of dialysis time. Chemical potential equilibrium of the sodium counterion, between the polymer coil and bulk solution, is reached after 72 hours ($t_e$). The corresponding refractive index increment at constant chemical potential, $\delta n/\delta c)_\mu$ is 0.1464.
Table 1.9
Refractive index increments at constant chemical potential for various compositions of polyacrylamide-co-sodium acrylate.

<table>
<thead>
<tr>
<th>Acrylate content in copolymer (mol %)</th>
<th>$\frac{\partial n}{\partial c}_\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.1869</td>
</tr>
<tr>
<td>6.4</td>
<td>0.1624</td>
</tr>
<tr>
<td>9.6</td>
<td>0.1551</td>
</tr>
<tr>
<td>15.0</td>
<td>0.1503</td>
</tr>
<tr>
<td>33.0</td>
<td>0.1464</td>
</tr>
</tbody>
</table>
Figure 1.19: Refractive index increment at constant chemical potential as a function of the acrylate level in a polyacrylamide-co-sodium acrylate. Solid line is the regressed equation, dashed lines are the 95% confidence limits.
3.3 Results and Discussion

3.3.1 Evaluation of the molecular weight method for polyacrylamide-co-sodium acrylate

Light scattering measurements were made for each of the five narrow polymer standards. A typical result, showing the Rayleigh factor as a function of composition, is given in Figure 1.20. From these linear plots the weight average molecular weights ($\bar{M}_w$) were regressed. These were normalized with respect to composition, with the corresponding chain lengths summarized in Table 1.10. The polyelectrolyte chain lengths deviate on average by 7.68% from the original polyacrylamide homopolymer. Such an agreement is well within the random errors of aqueous light scattering ($\pm 11.2\%$). We can conclude therefore that the measured molecular sizes of the ionic and nonionic polymers agree. Therefore, the polyelectrolyte method, and the specific refractive index increments at constant chemical potential are accurate and reliable. Furthermore, it is sufficient to correct the optical constant for $\delta n/\delta c|_\mu$, in order to obtain accurate molecular weights of polyelectrolytes. It is worthwhile to note that without the correct refractive index increment, the estimation of the molecular weight of a thirty percent hydrolyzed polyacrylamide is 62% underpredicted.

Table 1.10 also lists the second virial coefficients of the copolymers. Although the variance in $A_2$ is large, as usual, the general trend of increasing virial coefficients with ionic charge is evident. This is consistent with theoretical models which predict a second order dependence between $A_2$ and the macroion charge (Richards, 1980).
Figure 1.20: Light scattering plots showing the equivalence of molecular weight determination for polyelectrolytes and the nonionic polymer from which they were derived. (O): Polyacrylamide, (□): HPAM with 9.53% hydrolysis, (Δ): HPAM with 33.7% hydrolysis.
### Table 1.10

A comparison of the polyelectrolyte and nonionic molecular weight characterization procedures.

| Molecular weight of polyacrylamide measured by the nonionic method | Molecular weight measured on polyacrylamide-co-sodium acrylate by the polyelectrolyte method | Percent Deviation from Nonionic
<table>
<thead>
<tr>
<th>(nonionic polyacrylamide)</th>
<th>$\bar{\tau}_w$ (10% hydrolysis)</th>
<th>$\bar{\tau}_w$ (30% hydrolysis)</th>
<th>(10% hydrolysis) (30% hydrolysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{\tau}_w$</td>
<td>$\bar{\tau}_w$</td>
<td></td>
</tr>
<tr>
<td>379</td>
<td>482</td>
<td>402</td>
<td>21.4</td>
</tr>
<tr>
<td>1,676</td>
<td>1,633</td>
<td>1,702</td>
<td>2.6</td>
</tr>
<tr>
<td>3,282</td>
<td>3,413</td>
<td>3,439</td>
<td>3.8</td>
</tr>
<tr>
<td>6,563</td>
<td>6,412</td>
<td>5,959</td>
<td>2.4</td>
</tr>
<tr>
<td>13,859</td>
<td>13,845</td>
<td>10,446</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Average deviation 7.68%

<table>
<thead>
<tr>
<th>$A_2^\dagger \left(\frac{\text{mL mol}}{g^2}\right) \times 10^4$</th>
<th>$A_2^\dagger \left(\frac{\text{mL mol}}{g^2}\right) \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(nonionic polyacrylamide)</td>
<td>(10% hydrolysis)</td>
</tr>
<tr>
<td>4.05</td>
<td>6.29</td>
</tr>
<tr>
<td>7.70</td>
<td>5.88</td>
</tr>
<tr>
<td>8.61</td>
<td>7.89</td>
</tr>
<tr>
<td>12.66</td>
<td>10.89</td>
</tr>
<tr>
<td>17.20</td>
<td>9.47</td>
</tr>
</tbody>
</table>

$^\dagger$ Listed in order of decreasing molecular weight
REFERENCES


80. Rayleigh, Lord, Phil. Mag., 41, 447 (1871).
82. Richter, J.B., Ueber fie neurn Gegenstande der Chemie, 11, 81 (1802).
98. Tyndall, J., Phil.Mag., 37, 384 (1869).
CHAPTER 2
POLYMERIZATION OF ACRYLAMIDE BY
INVERSE-MICROSUSPENSION

1. INTRODUCTION

In recent years the consumption of high molecular weight synthetic water soluble polymers has grown to over 250 thousand tonnes per annum. The largest portion of this market is occupied by polyacrylamide and its acrylic derivatives. Polyacrylamide homopolymers are used in water modification, as viscosity enhancers, drag reduction and gelling agents, drilling fluids, and in microemulsion form in enhanced oil recovery. Copolymers with acrylic acid, methacrylic acid and quaternary ammonium cationics are also common and will be discussed separately in Chapters 3 and 4. Acrylic water soluble polymers are available as solutions, powders or water-in-oil emulsions. They are utilized in dilute aqueous form prepared by direct dilution, homogenization and inversion respectively.

The production of supermolecular polymers in aqueous solutions is not viable on large scales due to extreme viscosities, which restrict monomer loadings and limit heat transfer. The dried polymer also experiences gel blocking when added to water. To overcome these difficulties Vanderhoff (1962) developed a heterophase polymerization procedure where the aqueous monomer solution was dispersed in a continuous organic medium. Dispersed phase ratios of greater than sixty percent provided efficient reactor utilization, and high molecular weights. Vanderhoff’s process required a low HLB stabilizer and continuous, vigorous agitation to maintain emulsification. Over the past two decades several variations have evolved employing novel surfactant and hydrocarbon recipes. With few exceptions these
utilize steric stabilizers since electrostatic repulsive forces are ineffective in organic media due to the low dielectric constant and the diffuse nature of the electrical double layer.

Heterophase polymerizations can be initiated in either the continuous or dispersed phases. The selection is governed by thermal stability and final polymer characteristics and performance. Oil soluble initiators are preferred for water-in-oil processes since they produce longer linear chain dimensions and can solubilize oxygen in larger proportions; oxygen pulses (Vallino, 1973; Louie, 1985 I,II) limit the risk of temperature acceleration by scavenging primary radicals and reducing the efficiency of initiation (Wu, 1960).

Inverse-emulsion polymerizations are usually carried out in batch processes due to a limited product demand and extensive coagulum buildup (Pellon, 1974). The latter is a consequence of the macromolecular size and the high enthalpy of polymerization (which causes large thermal gradients between the suspension and the cooling equipment).

1.1 Steric Stabilization

Ford and Furmidge (1966) have determined that the formation of water-in-oil emulsions requires a strong, condensed interface. This supplements Albers and Overbeek's observation (1959) that interfacial ions reduce stability. These authors have also shown that the presence of hydrogen bonding between neighbouring adsorbed species improves the rigidity of the boundary. Consequently, most suitable emulsifiers are nonionic, with the exception of amine salts of long chain acids, where both anionic and cationic groups are adsorbed, with the interface remaining electrically neutral. The efficiency of nonionogenic emulsifiers for inverse-emulsion type polymerizations is evidenced by their high solubilizing power for water soluble monomers at low surfactant concentrations. Candau (1986) has found that emulsification is more readily obtained if the solubility parameters and molar volumes of the oil are matched with the hydrophobic moiety of the emulsifier. Stability can also be
improved by adding a cosurfactant such as a medium length alcohol (Birdi, 1982; Li, 1983; Venable, 1984; Schauer, 1987; Delgado, 1987), or by mixing high and low HLB surfactants. In the latter case the low HLB emulsifier functions as a cosurfactant, providing a more densely packed interfacial boundary (Holtzscherer, 1987).

The selection of an emulsifier for a water-in-oil polymerization is influenced by the continuous phase. Aliphatic oils generally require a less hydrophobic emulsifier than aromatics, and produce better emulsification at lower surfactant levels (Ford and Furmidge, 1966). The cost, required dosage and toxicity are also factors. Natural surfactants are generally preferred for polymers used in water treatment because they are non-toxic (Allen, 1984). Typical surfactants include fatty acid esters of sorbitan, Aerosol OT, polyoxyethylene fatty acid esters and Tergitols. Stabilization has also been reported with di- and triblock polymers (Hseigh, 1986) and with aminated inorganics such as bentonites (Zwergie, 1980).

The selection of suitable emulsifiers for polymerizable emulsions is also delineated by factors other than stability. For example, small molecule cosurfactants cannot be employed in excess because of the high lability of hydroxy groups (Stoffer and Bone, 1980; Leong, 1981 I,II) which tend to reduce molecular weights. The presence of monomer must also be considered. Holtzscherer (1988) has calculated that 28 wt% of an oleate interface is composed of monomeric acrylamide.\footnote{This interfacial behaviour was not expected a priori since acrylamide does not have a significant surface activity.} Furthermore, salting-out electrolytes also affect stability (Boghina, 1985) by consuming molecules that would otherwise hydrate the hydrophilic head of the emulsifier.
1.2 A Comparison of Water-in-Oil Polymerization Processes

The nomenclature of a specific water-in-oil polymerization is derived from either a physical or kinetic analogy to a process with an aqueous continuous phase. If the former is used, these processes can be categorized into three groups. "Inverse Emulsion" is analogous to emulsion polymerization from a colloidal perspective, with nucleation proceeding by a micellar mechanism. Systems where inverse-micelles are absent physically resemble suspensions, and are termed "Inverse-Suspension" or "Inverse-Microsuspension"; the prefix micro added when the latex size is nominally one micrometer. "Inverse-Microemulsion" polymerization is based on an entirely different premise and employs very high surfactant concentrations to form a thermodynamically stable, clear, monophasic system prior to polymerization. Particle sizes are quite small (500-1000Å), and the dispersed phase ratio tends to be lower than for inverse-emulsion or inverse-suspensions. These processes are compared with conventional heterophase processes in Table 2.1. They are discussed in further detail in Appendix C.

Unfortunately the distinction between these processes is often ambiguous. Inverse-macroemulsion is frequently used as a generic name for all water-in-oil polymerizations, with the prefix macro usually omitted for brevity. For example Dimonie (1982) has noted the absence of inverse-micelles and correctly described his polymerization as an inverse-suspension. Pichot (1985), based on the same observations, refers to the process as an inverse-emulsion. The description of these polymerizations has also proliferated due to a tendency to select the nomenclature prior to completing the kinetic or latex characterization. Therefore, Reichert uses "Dispersion" to describe a process where there is no evidence of homogeneous nucleation. Reverse-Micelle (Fouassier, 1986) has also been used, although it is better described as an inverse-emulsion.

The majority of literature in this area can be categorized as inverse-microsuspension. This description is preferred by this author since it simultaneously
<table>
<thead>
<tr>
<th>Polymerization Procedure</th>
<th>Physical Description</th>
<th>Particle Size</th>
<th>Locus of Initiation</th>
<th>Kinetics</th>
<th>Morphology</th>
</tr>
</thead>
</table>
| Inverse-Emulsion         | Water droplets dispersed in organic media, stabilized by a surfactant(s). Inverse-micelles are present. | $d_p \sim 0.1 \mu m$  
$\bar{d}_m \sim 50-100\AA$ | Micellar | Resemble Emulsion | Particles grow with reaction |
| Inverse-Suspension/Inverse-Microsuspension | Water droplets dispersed in organic media, stabilized by a surfactant(s). No inverse-micelles. | $d_p \sim 100/1 \mu m$ | Monomer droplets | Resemble solution with mass transfer of radicals and the absence of initiator-monomer interactions. | Particle size invariant to conversion level |
| Inverse-Microemulsion    | Thermodynamically stable, monophasic. Inverse-micelles exist. Particle size distribution can be monodisperse. | $d_p \sim 0.02-0.1 \mu m$  
$\bar{d}_m \sim 30\AA$ | Monomer swollen micro-emulsion droplets | Same dominant features as inverse-microsuspension. Each particle contains one collapsed macroradical. | Particles grow with reaction |
| Emulsion                 | Monomer droplets in aqueous media. Micelles exist. Electrostatic Stabilization. | $d_p \sim 0.1 \mu m$  
$\bar{d}_m \sim 50-100\AA$  
$d_{monomer} \sim 1-10\mu m$ drop | Micellar, homogeneous nucleation | Smith-Brant case I, II, III. Polymerization in monomer droplets negligible. | Particles grow with reaction |
| MiniEmulsion             | Same as emulsion, with a cosurfactant. | $d_p \sim 0.05-0.15\mu m$  
$\bar{d}_m \sim 50-100\AA$ | Monomer droplets | Area of Monomer is large enough that it can compete with micelles for radical capture. | Particles grow with reaction |
| Dispersion               | Initially a solution of monomer and solvent. Growing polymer precipitates into particles. Particle size distribution can be monodisperse. | $d_p \sim 1-10\mu m$ | Homogeneous nucleation | Solution polymerization in solvent and monomer swollen polymer particles. | Particles grow with reaction |
| Suspension               | Large oil droplets in water. Stabilizer employed. No Micelles. | $d_p \sim 100\mu m$ | Monomer droplets | Resemble solution. Special kinetics for suspension polymerization of gaseous monomers. | Particle size invariant to conversion level |
identifies particle characteristics, kinetics and the physical state of the reaction medium. Its acceptance, however, is still at present limited, with inverse-emulsion more commonly referenced due to historic precedence (Vanderhoff 1962, 1984).

The kinetics of water-in-oil polymerizations are also distinguished by the solubility of the initiator. When water soluble initiators are employed, all the reactive species are contained in the aqueous phase. Consequently, each latex particle behaves like a micro-batch reactor, with interphase transport negligible. Additionally, the proximity of the monomer to undecomposed initiator can lead to secondary radical formation reactions. This will be the topic of discussion in Chapter 4. The present chapter will be limited to a discussion of inverse-microsuspension polymerization with oil soluble initiators.

1.3 Summary of Recent Kinetic Research

The kinetics of the polymerization of acrylamide by the three heterophase processes discussed in the preceding section are summarized in Table 2.2. Research prior to 1984 yielded no conclusive evidence towards the elucidation of the reaction mechanism. However, recent publications by three independent laboratories (Kurenkov, 1984; Baade, 1986; Carver, 1989) have identified a common rate behaviour

$$R_p \propto M^{1.0} I^{1.0} E^\gamma$$

(2.1)

where \( \gamma \) depends on the specific emulsifier pair.2

The first order dependence on initiator is evidence of a unimolecular termination reaction. This was first postulated by Kurenkov (1984), however he was unable to identify specific reactions. Mechanistic contributions have also been made by Dimonie (1982), Pichot

2 Recent evidence (Baade, 1985) has also shown that the kinetics differ in paraffinic and aromatic media.
Table 2.2
Summary of kinetics of Acrylamide polymerization in heterophase processes

<table>
<thead>
<tr>
<th>Reference</th>
<th>System</th>
<th>$R_p$</th>
<th>$M^*$</th>
<th>$I^*$</th>
<th>$E_c$</th>
<th>Initiator</th>
<th>Emulsifier</th>
<th>Organic Phase</th>
<th>Monomer Concentration (mM/L_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haude, 1984</td>
<td>Inverse-microsuspension</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.2</td>
<td>AIBN, ADVN</td>
<td>SMO</td>
<td>Isopar-M 452</td>
<td>4.5-7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>0.5</td>
<td>0.45</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>Toluene 10</td>
<td>&quot;</td>
</tr>
<tr>
<td>Kurenkov, 1984</td>
<td>Inverse-emulsion</td>
<td>1.25</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
<td>AIBN</td>
<td>OP-10</td>
<td>Toluene 7</td>
<td>1.2-2.1</td>
</tr>
<tr>
<td>Candau, 1985, 1989</td>
<td>Inverse-microemulsion</td>
<td>1.1</td>
<td>1.0</td>
<td></td>
<td>0.55</td>
<td>AIBN</td>
<td>AOT</td>
<td>Toluene 7</td>
<td>3.0-6.7</td>
</tr>
<tr>
<td>Vanderhoff, 1984</td>
<td>Inverse-emulsion</td>
<td>1.0</td>
<td>2.0</td>
<td>1.0</td>
<td></td>
<td>BPO</td>
<td>Tetronic 1102</td>
<td>Xylene 4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Kurenkov, 1982</td>
<td>Inverse-emulsion</td>
<td>1.3</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
<td>AIBN</td>
<td>Sodium, potassium salts of p-styrene sulphonic acid</td>
<td>Toluene 0.92-2.54</td>
<td>0.9-2.54</td>
</tr>
<tr>
<td>Leong, 1981</td>
<td>Inverse-Microemulsion</td>
<td>1.9</td>
<td>0.5</td>
<td></td>
<td>1.0</td>
<td>AIBN</td>
<td>Polystyrene-polyethylene oxide block copolymer</td>
<td>Toluene 3.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

AIBN: Azobisisobutyronitrile  
SMO: Sorbitan monooleate  
ADVN: Azobisisobutyronitrile  
OP-10: A mixture of mono and dialkylphenols (10% oxyethylation)  
BPO: Benzoyl peroxide  
AOT: Aerosol OT
(1986,1987) and Vanderhoff (1984 I,II). However, a reliable reaction scheme was until recently unavailable (Hunkeler 1985,1987,1988, 1989).

In 1986 Baade published the most exhaustive experimental study to date. In it he systematically varied the monomer, initiator and emulsifier concentrations as well as the temperature and rate of agitation. Experiments were performed with two oil soluble azo-initiators and three emulsifiers. The availability of this data has confirmed Hunkeler's reaction mechanism and allowed the estimation of several kinetic parameters, as will be detailed later in this chapter. It has also clarified much of the disparity in the kinetic data that preceded it.

The specific system selected by Baade, and used in this work, is an inverse-microsuspension polymerization in paraffinic media with fatty acid esters of sorbitan as emulsifiers. A single surfactant system was used for kinetic studies to avoid confounding of the rate effects. Sorbitan monooleate and monostearate were selected because they provided good stability at moderate concentrations and are common to commercial recipes (Bikales,1973; Durand 1985,1986).

The purpose of the research in this chapter is to elucidate a set of elementary reactions for the polymerization of acrylamide in inverse-microsuspension. Each step in the mechanism will be verified experimentally against Baade's data, and the resulting kinetic model will be used to predict rate, molecular weight and particle characteristics.
2. EXPERIMENTAL

High temperature light scattering studies were performed on a Chromatix KMX-6 LALLS photometer with a cell length of 15mm and a Field Stop of 0.2. This corresponded to an average scattering angle of 4.8°. A 0.45 micrometer cellulose-acetate-nitrate filter (Millipore) was used for polymer solutions. A 0.22 micrometer filter of the same type was used to clarify the solvent. Distilled deionized water with 0.02 M Na₂SO₄ (analytical grade) was used as a solvent. Temperature control was excellent and was always within 0.1°C. Further details were provided in Chapter 1.

Details of the monomer and oxygen partitioning experiments between Isopar and water are described in Chapter 3. For acrylamide with 4 weight percent sorbitan monooleate the ratio of organic to aqueous monomer is 0.017:1. This agrees quite well with acrylamide partitioning measurements between toluene and water (0.02:1, Pichot, 1985).

A brief synopsis of Baade's (1986) experimental and analytical methods is provided below:

Aqueous solutions of acrylamide were dispersed in isoparaffinic hydrocarbons, with various emulsifiers based on sorbitan esters, by stirring with a propeller type agitator to form a water-in-oil emulsion. After purging with nitrogen the polymerization was initiated by injecting an oil soluble azo initiator into the system. The polymerization was run in a batch mode at constant temperature.

The chemicals used were acrylamide monomer (American Cyanamid, Naico) polymerization grade, Isopar M (Esso Chemie), a narrow cut isoparaffinic mixture with a boiling range of 204-247°C as the continuous phase, sorbitan monooleate (SMO) and sorbitan monostearate (SMS) (Atlas Chemie), 99% purity, as emulsifiers, ethyldiaminetetraacetetic acid (EDTA, Merck) as chelating agent to remove metal ion inhibitors, bortrioxide (Merck) as a
buffering agent and the initiators azobisisobutyronitrile (AIBN, Bayer AG) and azobisdimethylvaleronitrile (ADVN, Wako).

The polymerization procedure was as follows: oil with the dissolved emulsifier was added to the water phase and stirred at 1000 RPM to produce a dispersion. During this time the system was purged with rarefied nitrogen (99.99%) to remove residual oxygen. Then approximately 5 mL of the initiator solution was injected through a silicone cap to start the polymerization. All polymerizations were isothermal with temperature control within one degree Celsius. The reactor was a 1.3 L batch reactor (ratio of height to diameter 3:1) with two baffles and a propeller stirrer of one quarter diameter (15 cm) of the vessel, arranged symmetrically about the center.

All polymerizations were carried out with equiphase ratios of water to oil. This corresponded to 570 g of aqueous phase and 430 g of organic phase.

Trace levels of oxygen, that could not be removed by purging, inhibit the reaction by consuming initiator radicals. Initially the high propensity for this reaction stops the polymerization completely. As the oxygen level depletes, propagation becomes more favorable and the polymerization commences. The rate slowly increases until all residual oxygen is consumed at which point it reaches a maximum. In order to use the kinetic data the effect of oxygen is removed by performing a first order correction to the S-shaped conversion-time data as is shown in Figure 2.1.

In general the conversion was determined by dilatometry, where an 8.6% decrease in volume was observed for polymerizations with equiphase ratio of oil to water. This was monitored by the oil level of a burette placed above the completely filled reactor. These results agreed well with gravimetric and densitometric measurements.

The molecular weights were determined by viscometric measurements in 0.1 M aqueous Na₂SO₄ solutions using the Mark-Houwink parameters of Klein (1980).
Figure 2.1: Experimental conversion-time data showing an induction time ($T_i$) of 13 minutes. The reaction conditions were: $T = 47^\circ C$, $[M] = 5.75 \text{ mol/L}_w$, $[E] = 0.103 \text{ mol/L}_w$, $[\text{AIBN}] = 4.02 \text{ mmol/L}_o$, $\phi_{w/o} = 1:1$, $N = 1000 \text{ RPM}$.
The number of particles and the particle size distribution were determined by scanning electron microscopy, and dynamic light scattering. Baade (1986) provides a complete description of the polymerization and analytical procedures.
3. RESULTS AND DISCUSSION

Experiments have indicated that the rate of polymerization can be expressed as follows:

\[ R_p \propto \frac{[I]^{1.0}[M]^{1.0}}{[E]^a} \]

where \( a \) is a constant equal to 0.2 for acrylamide polymerizations.

The first order monomer dependence is normal in free radical polymerizations and has been reported for heterophase acrylamide polymerizations previously (Table 2.2). However, the inverse dependence on emulsifier concentration is contrary to what would be expected if the emulsifier's sole function was stabilization. In such cases, increasing the level of emulsifier would lower the surface tension and produce a larger number of smaller particles. Since the total interfacial area would be larger, the capture efficiency of primary radicals would rise and the rate would increase. Since this investigation and others (Candau, 1985; Glukhikh, 1987) have observed inverse relationships between bulk emulsifier level and rate there must be additional effects to consider. It is believed that sorbitan monostearate, which saturates the interface at relatively low levels, with the remainder residing in the continuous phase, reacts with primary radicals through the double bond in the oleic acid backbone. Therefore, the addition of higher levels of SMO increases the radical scavenging efficiency and reduces the rate. To test this hypothesis a series of experiments were performed with sorbitan-monostearate, a chemically identical emulsifier with no unsaturation. All conditions of the experiments were the same as those with SMO: temperature 47\(^\circ\)C, acrylamide concentration 5.75 mol/L of oil, emulsifier concentration 0.103 mol/L of oil, rate of agitation 1000 RPM, AIBN concentration 4.02 mmol/L of oil, phase ratio of oil to water 1:1. In polymerizations with SMS the rate was significantly faster, confirming that the presence of double bonds in the emulsifier influences the kinetics, likely by consuming primary radicals in the oil phase. This
mechanism is supported by recent experimental evidence which found the efficiency of initiation in water-in-oil polymerizations to be hindered by radical consumption in the continuous phase (Fouassier, 1986) and the interfacial layer (Valentin, 1979; Candau, 1986).

The observed order of the rate with respect to the initiator level is also peculiar. Figure 2.2 shows the rate plotted against [I] and [I]^{1/2}. Clearly the traditional one-half order dependence is not observed. This indicates the presence of a unimolecular termination reaction which competes with the bimolecular step and is more favorable at lower macro-radical levels. In general, unimolecular termination involves the reaction of a polymeric radical with a small molecule, such as solvent, initiator or emulsifier. Since the solvent used for inverse-microsuspension is water, and AIBN has not been observed to have any significant transfer activity (Leong, 1981) the emulsifier seems the most probable candidate. This has been confirmed by previous investigations of inverse-microsuspensions with water soluble initiators (Dimonie, 1982; Hunkeler, 1985), where transfer to the stearic and oleic acid portions of the emulsifier has been found to be rate controlling, and for inverse-emulsion polymerization with oil soluble initiators (Lambla, 1976; Pichot, 1985; Kim, 1988; Carver, 1989). Additionally, Sjoblom (1987) has determined that acrylamide radicals are very efficient at abstracting hydrogens from compounds which are interfacially active.

To confirm the transfer activity of sorbitanmonooleate a series of solution polymerizations were performed both with and without emulsifier. The conditions and final weight average molecular weights are reported in Table 2.3. On average polymerizations with emulsifier gave molecular weights 19% larger. This increase is presumed to be due to one of two factors:

1) The reaction of macroradicals with emulsifier followed by agglomeration of the hydrophobic ends of the polymer molecules to yield an apparent molecular weight that was higher than actual, or
Figure 2.2: Rate of polymerization ($R_p$) versus the first and half powers of initiator (AIBN) concentration. Experimental conditions were: $T = 47^\circ C$, $[M] = 5.75$ mol/L$_w$, $[E] = 0.103$ mol/L$_o$, $\phi_{w/o} = 1:1$, $N = 1000$ RPM.
Table 2.3: Weight average molecular weights of polyacrylamides produced in solution* with and without sorbitan monooleate.

<table>
<thead>
<tr>
<th>Without sorbitan monooleate $\overline{M}_w$ (g/mol) $\times 10^{-6}$</th>
<th>With sorbitan monooleate$^\dagger$ $\overline{M}_w$ (g/mol) $\times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>3.3</td>
</tr>
<tr>
<td>2.7</td>
<td>3.5</td>
</tr>
<tr>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Average 2.80</td>
<td>Average 3.37</td>
</tr>
</tbody>
</table>

* Reaction conditions were: Temperature 50°C, Acrylamide concentration 1.41 mol/L, Initiator ($K_2S_2O_8$) concentration $5 \times 10^{-3}$ mol/L

$^\dagger$ Emulsifier concentration 0.091 mol/L
2) Extraction of a hydrogen from the hydrophilic portion of the emulsifier to form a dead polymer molecule and an emulsifier radical. When this polymerizes it would generate a macroradical with a terminal double bond which could later react to form a branched polymer. 

To distinguish between branching and agglomeration, high temperature light scattering has been recommended (Stacey, 1956). This has been found to be an ideal method of identifying agglomeration since as the temperature rises the additional energy is able to break loose flocks but is insufficient to cleave bonds. Figure 2.3 shows no trend in the measured weight average molecular weight between 25 and 80°C. Therefore, the rise in molecular weight observed in solution polymerizations with sorbitanmonooleate is most likely due to branching. The proposed mechanism for this is shown in Figure 2.4. This mechanism has been further verified by comparing inverse-microsuspension polymerizations with sorbitanmonooleate and sorbitanmonostearate under the same conditions. SMS polymerizations gave molecular weights 30% lower ($3.5 \times 10^6$ vs $5 \times 10^6$), primarily due to the absence of unsaturation which eliminates long chain branching. Goddard (1986) has concurred with these observations, noting that the polyacrylamide does not form multimolecular associates.

Experiments have also indicated that the rate of polymerization is dependent on the level of agitation. This must be due to a mass transfer limitation of one of the reacting species: initiator, primary radicals or oligoradicals. The diffusion of undecomposed azo-initiators is improbable given Graillot's observation (1986) that organically soluble radical

---

3 Transfer to monomer also generates terminal double bonds which have been found unreactive, since branching has not been detected in solution polymerizations of acrylamide (Collinson, 1957; Dainton, 1957; Suen, 1960; Currie, 1965; Riggs, 1967; Friend, 1968; Ishigie, 1971, 1973; Cavell, 1972; Misra, 1974; Trubitsyna, 1978; Pohl, 1980; Kim, 1984).

4 Vanderhoff (1984) has found that undecomposed benzoyl peroxide diffuses between toluene and water.
Figure 2.3: Weight average molecular weight ($\bar{M}_w$) as a function of measurement temperature. The polymer was prepared in aqueous solution in the presence of sorbitanmonoleate. The experimental conditions are listed in Table 2.3.
Figure 2.4: The proposed reaction mechanism of interfacial emulsifier (SMO) with macroradicals.
scavengers lower the initiation rate. Additionally, the solubility of AIBN in water (0.016 wt%) is approximately one order of magnitude smaller than would be required to generate the rapid kinetics that have been observed. Given the significant solubility of acrylamide in paraffins, it therefore appears that primary and oligoradicals are the dominant transferring species. This suggests that the initiation mechanism involves decomposition and propagation in the continuous phase. When the critical chain length for solubility is exceeded the radicals then precipitate through the interfacial boundary, into the aqueous phase.

The postulate of initiation in the monomer droplets has been substantiated by Glukhikh (1987), Vanderhoff (1984 I, II), Candau (1985 III), Baade (1986) and Hunkeler (Chapter 4). All have reported constant particle morphologies throughout the polymerization and have failed to detect inverse-micelles. Candau (1986) has also determined that inter-particle monomer transport is negligible in paraffinic media. Further support of the segregated reactor hypothesis is given by Glukhikh who reported identical kinetics in solution and inverse-microsuspension.

The observed increase in rate with power input to the reactor is therefore caused by the formation of smaller particles, which increase the total interfacial area and increases the radical capture efficiency.

Based on these observations a general mechanism for homopolymerizations will be presented in the next section. This will be evaluated against experimental conversion, molecular weight and particle size data for acrylamide polymerizations. Once verified, we will be able to use the resulting kinetic model to improve polymerization procedures. This includes isolating the conditions under which the highest molecular weight polymer is obtained.
3.1 Mechanism

Reactions in the oil phase:

1. \[ \text{I} \xrightarrow{k_d} 2R_{\text{in},0} \]

2. \[ R_{\text{in},0} + E_0 \xrightarrow{k_1} \text{inert products} \]

3. \[ R_{\text{in},0} + HC \xrightarrow{k_4} \text{inert products} \]

4. \[ R_{\text{in},0} + M_0 \xrightarrow{k_p} R_{1,0} \]

5. \[ R_{r,0} + M_0 \xrightarrow{k_p} R_{r+1,0} \]

where \( R_{\text{in},0} \), HC, \( E_0 \), \( M_0 \) and \( R_{r,0} \) are the symbols for primary radicals, hydrocarbon, emulsifier, monomer and macroradicals in the oil phase.

Transfer between phases:

6. \[ R_{\text{in},0} \xrightarrow{k_r} R_{\text{in},w} \]

7. \[ R_{r,0} \xrightarrow{k_{r,r}} R_{r,w} \]

8. \[ M_0 \xrightarrow{\phi_m} M_w \]

where the subscript \( w \) denotes a water phase concentration. \( k_{r,r} \) is the mass transfer constant of an oligoradical of length \( r \), which will tend to \( k_r \) at small chain lengths.

Water phase reactions:

9. \[ R_{\text{in},w} + M_w \xrightarrow{k_p} R_{1,w} \]

10. \[ R_{r,w} + M_w \xrightarrow{k_p} R_{r+1,w} \]
11. $^{*}R_{r,w}^{*} + M_{w} \xrightarrow{k_{p}} {^{*}R}_{r+1,w}^{*}$

12. $R_{r,w}^{*} + \Gamma_{E} \xrightarrow{k_{fe}} P_{r} + E^{*}$

13. $^{*}R_{r,w}^{*} + \Gamma_{E} \xrightarrow{k_{fe}} {^{*}P}_{r} + E^{*}$

14. $E^{*} + M_{w} \xrightarrow{k_{p}} {^{*}R}_{1,w}^{*}$

15. $E^{*} + HC_{imp} \xrightarrow{k_{5}}$ inert products

16. $R_{r,w}^{*} + M_{w} \xrightarrow{k_{fm}} P_{r} + {^{*}R}_{1,w}^{*}$

17. $^{*}R_{r,w}^{*} + M_{w} \xrightarrow{k_{fm}} {^{*}P}_{r} + {^{*}R}_{1,w}^{*}$

18. $R_{r,w}^{*} + R_{s,w}^{*} \xrightarrow{k_{td}} P_{r} + P_{s}$

19. $^{*}R_{r,w}^{*} + R_{s,w}^{*} \xrightarrow{k_{td}} {^{*}P}_{r} + P_{s}$

20. $^{*}R_{r,w}^{*} + ^{*}R_{s,w}^{*} \xrightarrow{k_{td}} {^{*}P}_{r} + {^{*}P}_{s}$

21. $P_{r,w} + R_{s,w}^{*} \xrightarrow{k^{*}} R_{r+s,w}^{*}$

22. $P_{r,w} + ^{*}R_{s,w}^{*} \xrightarrow{k^{*}} R_{r+s,w}^{*}$

where $^{*}R^{*}$ is a radical which contains a terminal emulsifier double bond, $\Gamma_{E}$ is the surface concentration of emulsifier, $E^{*}$ is the symbol for emulsifier radicals and $HC_{imp}$ represents hydrocarbon phase impurities or radicals.

The mechanism can be generally described as a free radical heterophase polymerization in which mass transfer of primary and oligoradicals between the organic and aqueous phases is important. Termination occurs by both unimolecular (steps 12 and 13) and bimolecular (steps 18 to 20) reactions, the latter being exclusively disproportionation. Uni-
molecular termination produces emulsifier radicals that contain double bonds. These radicals can either propagate with monomer (step 14) or terminate with oil phase impurities (step 15). When propagation occurs, macroradicals are produced which can react to form a branched polymer (steps 21 and 22). The remaining steps in the mechanism are initiation, propagation, transfer and termination reactions which are common to any free radical process. Initiation is assumed to occur by primary radicals in the oil phase reacting with slightly soluble acrylamide to form oligoradicals which quickly reach their solubility limit and diffuse into the water phase. Primary radicals may also diffuse into the monomer droplets unreacted and propagate.

3.2 KINETIC MODEL

3.2.1 Initiation

Applying the stationary state hypothesis to primary radicals in the oil and water phases we obtain:

\[
\frac{d[R_{in,0}^*]}{dt} = 0 = 2k_d[I] - k_p[R_{in,0}^*][M_0] - k_4[R_{in,0}^*][HC]
\]

\[
- k_{11}R_{in,0}^*[E_0] - \frac{k_r}{V_0} \left\{ \frac{[R_{in,0}^*]}{\Phi_r} - [R_{in,w}^*] \right\}
\]

(2.1)

\[
\frac{d[R_{in,w}^*]}{dt} = 0 = \frac{k_r}{V_w} \left\{ \frac{[R_{in,0}^*]}{\Phi_r} - [R_{in,w}^*] \right\} - k_p[R_{in,w}^*][M_w]
\]

(2.2)

where \( V_0 \) and \( V_w \) are the volume of the oil and water phases and \( \Phi_r \) is the partition coefficient of primary radicals between oil and water.

From partitioning measurements, we can express the concentration of monomer in the oil phase as:

\[ [M_0] = \Phi_m [M_w] \]
Adding (2.1) and $V_w/V_0$ (2.2) and rearranging, one obtains:

$$[R^*_{in,w}] = \frac{2k_d[I] - k_p[M_w][R^*_{in,w}]}{k_p\phi_m[M_w] + k_{q[HCl]} + k_{1[E_0]}} \frac{V_w}{V_0}$$  

(2.3)

Substituting (2.3) into (2.2) and solving for $[R^*_{in,w}]$ yields:

$$[R^*_{in,w}] = 2k_d[I] \frac{Y}{\delta}$$  

(2.4)

where

$$Y = \frac{k_r}{V_w\phi_r} \left( \frac{1}{k_p[M_w]+\frac{k_r}{V_w}} \right) \left( \frac{1}{k_p\phi_m[M_w] + k_{q[HCl]} + k_{1[E_0]}} \right)$$  

(2.5)

$$\delta = 1 + \frac{k_r}{V_w\phi_r} \left( \frac{1}{k_p[M_w]+\frac{k_r}{V_w}} \right) \left( \frac{k_p[M_w]\frac{V_w}{V_0}}{k_p[M_w] + k_{q[HCl]} + k_{1[E_0]}} \right)$$  

(2.6)

Now, if we assume that the main source of initiation is the diffusion of primary radicals into polymer particles, we can define the rate of initiation as:

$$R_1 = k_p[M_w][R^*_{in,w}]$$

$$= 2k_d[I] \left( \frac{k_p[M_w]}{\delta} \frac{Y}{\delta} \right)$$  

(2.7)

We may also say that

$$R_1 = 2fk_d[I]$$  

(2.8)

Comparing these two definitions of the rate of initiation, we have an expression for $f$, the efficiency of initiation:

$$f = \frac{k_p[M_w][Y]}{\delta}$$

which can be simplified to yield:
\[ f = \frac{1}{1 + \frac{k_r}{k_p[M_w]V_w}\left(1 + \frac{k_r}{k_p[M_w]V_w}\right)\left(k_p[M_w] + k_4[HC] + k_1[E_o]\right)} \cdot \frac{V_0}{V_w} \]

\( k_p[M] \) is large, and \( k_r \) is of the order 100^-3, therefore,
\[ 1 + \frac{k_r}{k_p[M_w]V_w} = 1 \]

Defining the overall mass transfer constant \( (k_r) \) as:
\[ k_r = k_r^* \cdot A_{\text{rest}} \]

and
\[ A_{\text{rest}} = a_{\text{sp}} \cdot V_0 \]

where \( A_{\text{rest}} \) is the total interfacial area and \( a_{\text{sp}} \) is the specific interfacial area per litre of oil.

The expression for \( f \) can now be reduced to:
\[ f = \frac{1}{1 + \frac{\phi_r}{k_r^*}\left(\frac{k_p[M_w]}{a_{\text{sp}}} + \frac{k_4[HC]}{a_{\text{sp}}} + \frac{k_1[E_o]}{a_{\text{sp}}}\right)} \cdot \frac{V_0}{V_w} \quad (2.9) \]

This can be further simplified for conditions where \( f \) is not observed to be a function of conversion to yield:
\[ f = \frac{1}{1 + \frac{\phi_r}{k_r^*}\left(\frac{k_4[HC]}{a_{\text{sp}}} + \frac{k_1[E_o]}{a_{\text{sp}}}\right)} \cdot \frac{V_0}{V_w} \quad (2.10) \]

3.2.2 Rate of polymerization

We can now apply the stationary state hypothesis to macroradicals with no active terminal carbon-carbon double bonds \([R^*] \), macroradicals which contain a terminal emulsifier double bond \([^*R^*] \), and emulsifier radicals \([E^*] \):
\[ \frac{d[R^*]}{dt} = R_1 - k_{td}[R^*]([R^*] + [R^\ddagger]) - k_{fe}[R^*]\Gamma_E + k_{fm}[M_w][R^*] \quad (2.11) \]

\[ \frac{d[R^\ddagger]}{dt} = 0 = k_p[E^*][M_w] - k_{td}[R^\ddagger][R^*] - k_{fe}[R^\ddagger]\Gamma_E - k_{fm}[M_w][R^\ddagger] \quad (2.12) \]

\[ \frac{d[E^*]}{dt} = 0 = k_{fe}([R^*] + [R^\ddagger]\Gamma_E - k_p[E^*][M_w] - k_s[H]_{imp}[E^*] \quad (2.13) \]

where

\[ [R^*] = \sum_{r=1}^{\infty} [R^*_r] \]

and

\[ [R^\ddagger] = \sum_{r=1}^{\infty} [R^\ddagger_r] \]

The total macroradical concentration \([R^*]_T\) is given by:

\[ [R^*]_T = [R^*] + [R^\ddagger] \]

Adding equations (2.11) and (2.12):

\[ R_1 - k_p[E^*][M_w] - k_{td}[R^*]^2 - k_{fe}[R^\ddagger]\Gamma_E = 0 \quad (2.14) \]

where the rate of initiation of emulsifier radicals is:

\[ R_{I,e} = k_p[M_w][E^*] \quad (2.15) \]

Rearranging equation (2.14) and combining with (2.15) yields:

\[ R_{I,e} = \frac{k_{fe}[R^*]\Gamma_E}{1 + \frac{k_s[H]_{imp}}{k_p[M_w]}} \]

The rate of initiation of emulsifier radicals can also be expressed as:

\[ R_{I,e} = \int_e \frac{k_{fe}[R^*]\Gamma_E}{1 + \frac{k_s[H]_{imp}}{k_p[M_w]}} \quad (2.16) \]

Therefore, we can define the efficiency of initiation of emulsifier radicals \(\epsilon_e\) as:

\[ \epsilon_e = \frac{1}{\frac{k_s[H]_{imp}}{k_p[M_w]}} \quad (2.17) \]
Substituting equations (2.16) and (2.17) into (2.14), we obtain a quadratic expression for the total macroradical concentration:
\[ 2f k_d [I] - k_{ud} [R_{T1}^e]^2 - (1 - \Gamma_0) k_{fe} [R_{T1}^e] \Gamma_0 = 0 \]  
(2.18)

Now, we apply the long chain approximation, which assumes that monomer is consumed entirely in propagation in the aqueous phase and that the monomer consumed in the following steps is negligible:

i) Transfer to monomer,

ii) Reaction between emulsifier radical and monomer,

iii) Propagation in the oil phase to form oligoradicals.

Therefore, the rate of polymerization is:
\[ R_p = k_p [M_w] [R_{T1}^e] \]

We can now examine two extreme cases.

Case 1: (Unimolecular termination dominates)
\[ k_{fe} [R_{T1}^e] \Gamma_0 > > k_{ud} [R_{T1}^e]^2 \]

and
\[ R_p = \frac{2f k_d k_p [I] [M]}{(1 - \Gamma_0) k_{fe} \Gamma_0} \]

This suggests that the rate of polymerization is proportional to the initiator concentration, which is what we and others have observed for inverse-microsuspension polymerization of acrylamide.

We also see that the rate is inversely proportional to the surface emulsifier level.

Experimentally, we have observed a dependence that is 0.2 order with respect to the bulk emulsifier level. The difference between these two orders is due to the difference between bulk and interfacial concentrations. This will be discussed further in the next section.
Case 2: (Bimolecular termination dominates)

\[
k_f [R^*_t] [I]_E < \frac{k_{td} [R^*_t]^2}{k_{td} [I]^2}
\]

\[
R_p = \left( \frac{2f k_d [I]}{k_{td}} \right)^{1/2} \cdot k_p [M]
\]

which is the classical free radical polymerization equation.

In inverse-microsuspension, the contribution of unimolecular termination decreases as the reaction proceeds, and a transition from Case 1 to Case 2 occurs.

At high conversions, termination and the reaction with terminal double bonds will be diffusion controlled. This has been modelled using the following empirical equations:

\[
k_{td} = k_{td}^* c_x p (A \text{ wp})
\]

\[
k^* = k^* / \exp (A \text{ wp})
\]

where \( A = a_0 + a_1 T \)

where \( T \) is the temperature in Kelvin and

wp is the weight fraction of polymer in the aqueous phase

The magnitude of the diffusion limitation of these two reactions is assumed to be the same, as a first approximation.

3.2.3. Molecular weights

Using the method of moments (Appendix D) the following equations have been derived for the number and weight average molecular weight (\( \overline{M}_N \) and \( \overline{M}_w \)):

\[
\overline{M}_N = \frac{M_m Q_{1T}}{Q_{0T}}
\]

\[
\overline{M}_w = \frac{M_m Q_{2T}}{Q_{1T}}
\]

where \( M_m \) is the molecular weight of the monomer.
$Q_i$ is the $i$th moment of the distribution of polymer molecules without terminal double bonds

$Q_i$ is the $i$th moment of the distribution of polymer molecules which contain terminal double bonds

$Q_{iT}$ is the $i$th moment of the total dead polymer distribution ($Q_{iT} = Q_i + \tilde{Q}_i$).

These moments may be found by solving the following equations:

\[
\frac{dQ_0}{dt} = Y_0 X
\]

\[
\frac{dQ_0}{dt} = \tilde{Y}_0 X - k^*Q_0 Y_{0T}
\]

\[
\frac{dQ_1}{dt} = Y_1 X
\]

\[
\frac{dQ_1}{dt} = \tilde{Y}_1 X - k^*Q_1 Y_{0T}
\]

\[
\frac{dQ_2}{dt} = Y_2 X
\]

\[
\frac{dQ_2}{dt} = \tilde{Y}_2 X - k^*Q_2 Y_{0T}
\]

where $X = k_{fe} \Gamma_E + k_{fm} M + k_{id} Y_{0T}$

$\tilde{Y}_i$, $Y_i$ are the moments of the macroradical distribution for molecules with and without terminal double bonds respectively.

$Y_{iT}$ is the $i$th moment of the total macroradical distribution ($Y_{iT} = Y_i + \tilde{Y}_i$)

The zeroth, first and second moments of the macroradical distribution are given by:
\[ Y_0 : \quad 0 = R_1 - k_{1E} \Gamma_E Y_0 + k_{fm} M Y_0 - k_{ud} Y_0(Y_{OT}) \]

\[ Y'_{0} : \quad 0 = R'_1 - k_{1E} \Gamma_E Y'_{0} - k_{fm} M Y'_{0} - k_{ud} Y'_{0}(Y_{OT}) \]

\[ Y_{OT} : \quad 0 = R_1 + R'_1 - k_{1E} \Gamma_E Y_{OT} - k_{td} (Y_{OT})^2 \]

\[ Y_1 = \frac{R_1 + k_{fm} M Y_{OT} + k_p M Y_0 + k^* Y_0 Q_1}{X} \]

\[ Y'_1 = \frac{R'_1 + k_p M Y'_0 + k^* Y'_0 Q_1}{X} \]

\[ Y_{1T} = \frac{R_1 + R'_1 + k_p M Y_{OT} + k^* Y_{OT} Q_1 + k_{fm} M Y_{OT}}{X} \]

\[ Y_2 = \frac{R_1 + 2k_p M Y_1 + k_{fm} M Y_{OT} + k^* (Y_0 Q_2 + 2 Y_1 Q_1)}{X} \]

\[ Y'_2 = \frac{R'_1 + 2k_p M Y'_1 + k^* (Y'_0 Q_2 + 2 Y'_1 Q_1)}{X} \]

\[ Y_{2T} = \frac{R_1 + R'_1 + 2k_p M Y_{1T} + k_{fm} M Y_{OT} + k^* (Y_{OT} Q_2 + 2 Y_{1T} Q_1)}{X} \]

3.2.4 Emulsifier concentration in the boundary layer

The distribution of emulsifier between the continuous phase and the surface of the particles\(^5\) has been modelled with a Langmuir adsorption isotherm. The fraction coverage of the surface of the polymer particles (6) is given by:

\[
\theta = \frac{\nu}{\nu_m} = \frac{K[E_0]}{1 + K[E_0]} \tag{2.19}
\]

\(^5\) The solubility of emulsifier in the aqueous phase is essentially zero.
where $v$ is the volume of emulsifier adsorbed and $v_m$ is the maximum volume adsorbed if the monolayer is completely full. $K$ is the equilibrium adsorption constant.\(^6\)

The surface concentration of emulsifier can be expressed as:

$$\Gamma_{E,bl} = \frac{v \rho_E}{MW_E A_T}$$  \hspace{1cm} (2.20)

where $\rho_E$ and $MW_E$ are the density and molecular weight of the emulsifier and $A_T$ is the total interfacial area.

The moles of emulsifier in the oil phase ($N_{E,0}$) can be calculated from the difference between total ($N_E$) and interfacial emulsifier ($N_{E,bl} = \Gamma_{E,bl} \cdot A_T$).

$$N_{E,0} = N_E - \frac{v \rho_E}{MW_E}$$

From this, the emulsifier concentration in the organic phase is given by:

$$[E_0] = \frac{N_E MW_E - v \rho_E}{V_0 MW_E} $$  \hspace{1cm} (2.21)

To solve equations (2.19) to (2.21) requires an expression for the volume of a complete monolayer ($V_m$). This can be obtained through a balance on the total area occupied by the emulsifier ($A_E$). $A_E$ can be defined as the fraction of the total area occupied ($\theta A_T$) and equivalently by the number of emulsifier molecules at the interface, multiplied by the area occupied by each molecule ($A_p$).

$$A_E = \theta A_T = \left( \frac{v \rho_E N_A}{MW_E} \right) A_p$$

Rearranging this expression in terms of $v_m$ yields

$$v_m = \frac{MW_E A_T}{\rho_E N_A A_p}$$  \hspace{1cm} (2.22)

\[^6\] In order to obtain steric stabilization in inverse-microsuspensions, the surface must be rigid and almost completely covered. Therefore, the equilibrium constant will be quite large.
where the area occupied by a single molecule of sorbitan monooleate has been determined to be 69Å² using a Wilhelmy balance.

Equations (2.19) to (2.22) represent a set of equations that can be used to calculate the surface and continuous phase concentrations of emulsifier, as well as the fractional coverage of the polymer particles.

3.2.5 Particle size

Predicting the drop size in mechanically agitated systems requires understanding the breakup and coalescence mechanisms. Drop breakup occurs when the kinetic energy of droplet oscillations, caused by turbulence, exceeds the surface energy of the droplet. By balancing these two factors Sprow (1967) has shown that the volume-to-surface average diameter ($d_{32}$) can be expressed as:

$$
\frac{d_{32}}{D} = C W_e^{-\frac{1}{5}}
$$

(2.23)

where $D$ is the impeller diameter and $C$ is a constant. The Weber number is defined as:

$$
W_e = \frac{\rho N^2 D^3}{\sigma}
$$

where $N$ is the rate of agitation (RPS), $\rho$ is the density of the continuous phase, and $\sigma$ is the surface tension.

The turbulence will also cause droplets to collide with each other. If these droplets remain in contact long enough for the intervening film of liquid to drain, coalescence will occur. In heterogeneous polymerizations, this is prevented through the addition of electrostatic or steric stabilizers.

---

7 For Isopar-M, the density (g/cm³) is: $\rho = 0.995 - 7.047 \times 10^{-4} (T)$, where the temperature is in Kelvin.
In polymeric reactions, where dispersed phase volume fractions of 50% or more are common, the effect of holdup must also be considered. Larger holdups, which dampen the turbulence intensity, will result in larger drop sizes. This is usually expressed by the empirical equation:

\[ d_{32} = d_{32}^0 (1 + C_2 \phi) \]  

(2.24)

where \( d_{32}^0 \) is the volume-to-surface diameter at low holdups (\( \phi = V_w/(V_w + V_d) \)). Combining equations (2.23) and (2.24) yields

\[ \frac{d_{32}}{D} = C_1 (1 + C_2 \phi) W_e^{-3/5} \]  

(2.25)

Several combinations of \( C_1 \) and \( C_2 \), exist in the literature (Vermeulen, 1955; Calderbank, 1958; Brown, 1970; Mynek, 1972; Caulalagou, 1976; Lee and Tasakorn, 1979). For suspension polymerization, the Lee and Tasakorn equation has been recommended, where \( C_1 = 0.063 \) and \( C_2 = 1.81 \). This was developed for high holdups, in a sterically stabilized system which is very similar to inverse-microsuspensions, and is used in this paper.

From experiments, in this Chapter the surface tension has been correlated with the emulsifier concentration, rate of agitation and temperature as:

\[ \sigma = a[E]^{-0.233} N^{1.44} \]

where \( a = 5.67 \times 10^{-6} - 1.71 \times 10^{-8} \) T

This equation will be restricted to systems with the same reactor configuration as was used in this work. For other systems, similar correlations can be established. In the absence of surface tension measurements, the experimental value of \( d_{32} \) can be used directly in the rate expression.

The number of particles \( (N_p) \) can be computed from the volume average diameter \( (d_v) \) as follows:

\[ N_p = \frac{\text{volume of the dispersed phase}}{\text{volume of one particle}} = \frac{V_w}{\frac{\pi}{6} d_v^3} \]
where the volume average diameter is related to the surface-to-volume diameter as (Woods, 1986):

\[ d_v = \frac{a_s}{(6a_v)^{2/3} n^{1/3}} d_{32} \]

For a monodisperse system of spherical particles, the proportionality constant between \( d_v \) and \( d_{32} \) is 1.0. In the system studied in this work, the proportionality constant was found to be 1.363, the larger value being due to the breadth of the particle size distribution.

3.2.6 Summary of kinetic model

Table 2.4 summarizes the equations needed to model rate, molecular weight, particle size and particle number for inverse-microsuspension homopolymerizations. These can be solved analytically with the exception of the differential equations for monomer consumption and the moments of the molecular weight distribution which must be solved numerically. In the simulations done in this chapter a variable order Runge-Kutta procedure was used.

3.3 Parameter Estimation

When the model is applied to the polymerization of a specific monomer several rate, mass transfer and partition coefficients are needed. In the absence of available literature values these must be estimated from experimental data. In this work parameters were determined by non-linear weighted least squares regression using Marquardt's procedure to minimize the sum of squares of the residuals. The total residual was comprised of two independent measurements, conversion and weight average molecular weight which were weighted by the reciprocal of their variances as follows:

\[
\text{Min} \sum_{i=1}^{n} \left\{ \left| \left( \frac{X_{i,p} - X_{i,d}}{\sigma_{X_i}^2} \right) \right|^2 + \left| \left( \frac{\text{MW}_{i,p} - \text{MW}_{i,d}}{\sigma_{\text{MW},i}^2} \right) \right|^2 \right\}
\]
Table 2.4: Summary of kinetic model equations.

Rate:

Rate of Polymerization: \[ R_p = k_p [M]_w [R^*_T] \]

Total macroradical concentration
\[ 0 = 2f k_{d}[I] - k_{ao} [R^*_T]^2 - (1 - f_e) k_e [R^*_T] \]

Efficiency of initiation of primary radicals
\[ f = \frac{1}{1 + \left( \frac{k_1 \phi_r}{k_r^*} \right) \left[ E \right]_0 + \left( \frac{k_4 \phi_r}{k_r^*} \right) \frac{[HC]}{a_{sp}}} \frac{V_0}{V_w} \]

Efficiency of initiation of emulsifier radicals
\[ f_e = \frac{1}{1 + \frac{k_5 [HC]_{imp}}{k_p [M]_w}} \]

Molecular Weights:

Number average molecular weight
\[ \bar{M}_n = M_m \frac{Q_{1T}}{Q_{0T}} \]

Weight average molecular weight
\[ \bar{M}_w = M_m \frac{Q_{2T}}{Q_{1T}} \]

where \( Q_{0T}, Q_{1T}, \) and \( Q_{2T} \) are the zeroth, first and second moments of the dead polymer distribution.

Emulsifier Distribution

Surface emulsifier concentration:
\[ \Gamma_{E, bi} = \frac{\nu \cdot \rho_E}{M W_E \cdot A_T} \]

Continuous phase emulsifier concentration
\[ [E]_0 = \frac{N_E M W_E - \nu \cdot \rho_E}{V_0 M W_E} \]

Fractional coverage of interface
\[ \theta = \frac{\nu}{\nu_m} = \frac{K[E]_0}{1 + K[E]_0} \]
Table 2.4: (continued)

Volume of a complete monolayer:

\[ v_m = \frac{M W_E \cdot A_T}{p_E N_A A_p} \]

Particle Characteristics:

Average surface-volume diameter

\[ \frac{d_{32}}{D} = 0.063(1 + 1.81 \phi)W_e^{-0.5} \]

Number of particles

\[ N_p = \frac{V_w}{n \frac{d_{32}^3}{6}} \]

Volume average diameter

\[ d_v = \frac{a_s}{(6a_v)^{2/3} \pi^{1/3} d_{32}} \]
where $n$ is the number of observations, $X_{i,p}$ and $X_{i,d}$ are the predicted and measured conversion, $MW_{i,p}$ and $MW_{i,d}$ are the model and experimental weight average molecular weights and $\sigma^2_{X,i}$ and $\sigma^2_{MW,i}$ are the variance of the $i$-th conversion and molecular weight measurements.

Table 2.5 lists the parameters used for simulations of acrylamide homopolymerizations.

The important conclusions from the parameter estimation are summarized below:

1) The transfer to monomer constant is roughly twice as large as has been reported for solution polymerizations (Dainton, 1957; Ishigie, 1973; Kim, 1984). The difference is likely due to the presence of interfacial acrylamide in inverse-microsuspension (Holtzscheer, 1987, 1988). This monomer would reside with the amide group in the aqueous phase and the vinyl group oriented toward or in the emulsifier boundary layer. In such a configuration the labile hydrogens will be more accessible than the double bond, which will increase the likelihood of transfer relative to propagation.

2) The transfer to emulsifier and surface emulsifier equilibrium constant were determined individually at 47°C. However, the temperature dependencies could not be estimated independently and therefore transfer to emulsifier and the interfacial emulsifier concentration were fit as a single parameter $r$. The activation energy is positive, which is typical in physical adsorption and also indicates that the contribution of transfer to emulsifier to the grouped activation energy is small. This is consistent with other termination reactions, which have very low temperature dependencies.

To determine the individual values of $k_{fe}$ and $\Gamma_E$ requires knowledge of the emulsifier partitioning between the continuous phase and the interface at different temperatures.
Table 2.5: Summary of parameter values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{d1}$, AIBN</td>
<td>$9.48 \times 10^{16} \exp \left( \frac{-30,800}{RT} \right)$</td>
<td>min$^{-1}$</td>
<td>Wako Pure Chemical Industries, 1983</td>
</tr>
<tr>
<td>$k_{d1}$, ADVN</td>
<td>$4.316 \times 10^{16} \exp \left( \frac{-29,000}{RT} \right)$</td>
<td>min$^{-1}$</td>
<td>Overberger, 1949</td>
</tr>
<tr>
<td>$k_p$</td>
<td>$9.9 \times 10^{7} \exp \left( \frac{-2.743}{RT} \right)$</td>
<td>L/mol/min</td>
<td>Currie, 1953; Dainton, 1957; Ishige, 1973</td>
</tr>
<tr>
<td>$k_{td}^{12}$</td>
<td>$9.192 \times 10^{4} \exp \left( \frac{-741}{RT} \right)$</td>
<td>L/mol/min</td>
<td>Currie, 1953; Dainton, 1957; Ishige, 1973</td>
</tr>
<tr>
<td>$k_{fm}$</td>
<td>$5.73 \times 10^{8} \exp \left( \frac{10,438}{RT} \right)$</td>
<td>L/mol/min</td>
<td>This work</td>
</tr>
<tr>
<td>$k_{g[HC_{impl}]}$</td>
<td>$0.147 \exp \left( \frac{1380.5}{T} \right)$</td>
<td>min$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>$A$</td>
<td>$16.08 - 2 \times 10^{-2} T$</td>
<td>dimensionless</td>
<td>This work</td>
</tr>
<tr>
<td>$k_{fe} \cdot \Gamma_{E_{smo}}$</td>
<td>$1.51 \times 10^{-7} \exp \left( \frac{1.415}{T} \right)$</td>
<td>min$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>$k_{fe} \cdot \Gamma_{E_{sms}}$</td>
<td>$1.05 \times 10^{-7} \exp \left( \frac{1.415}{T} \right)$</td>
<td>min$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>$k_{smo}^{-}$</td>
<td>$1.74 k_p$</td>
<td>L/mol/min</td>
<td>This work</td>
</tr>
<tr>
<td>$k_{sms}^{-}$</td>
<td>$0 \cdot 0$</td>
<td>L/mol/min</td>
<td>This work</td>
</tr>
<tr>
<td>$\frac{k_{1} \Phi_{r}}{k_{r}^{AIBN}}$</td>
<td>$1.05 \times 10^{3}$</td>
<td>m$^{2}$/mol</td>
<td>This work</td>
</tr>
<tr>
<td>$\frac{k_{1} \Phi_{r}}{k_{r}^{ADVN}}$</td>
<td>$1.22 \times 10^{3}$</td>
<td>m$^{2}$/mol</td>
<td>This work</td>
</tr>
</tbody>
</table>
Table 2.5: (continued)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{k_4 \Phi_r}{k_r^*} )_{\text{AlBN,smo}}</td>
<td>4.14 \times 10^4</td>
<td>m^2 mol</td>
<td>This work</td>
</tr>
<tr>
<td>( \frac{k_4 \Phi_r}{k_r^*} )_{\text{ADVN,smo}}</td>
<td>4.81 \times 10^4</td>
<td>m^2 mol</td>
<td>This work</td>
</tr>
<tr>
<td>( \frac{k_4 \Phi_r}{k_r^*} )_{\text{ams}}</td>
<td>0.0</td>
<td>m^2 mol</td>
<td>This work</td>
</tr>
</tbody>
</table>

* At 47°C, \( \Gamma_E = 2.40 \times 10^{-6} \text{ mol/m}^2 \) and \( k_{f_0} = 5.20/d_{32} \)

† At 47°C, \( \Gamma_E = 2.40 \times 10^{-6} \text{ mol/m}^2 \) and \( k_{f_0} = 3.64/d_{32} \)
3) The individual values of the parameters $k_1$, $k_4$, $\phi_r$ and $k^*_r$ cannot be determined without further experimentation into the partitioning and mass transfer of primary radicals between the oil and water phases. For the purpose of modelling the parameters were fit as two grouped rate constants:

\[
\left( \frac{k_1 \phi_r}{k^*_r} \right) \quad \text{and} \quad \left( \frac{k_4 \phi_r}{k^*_r} \right)
\]

as they appear in the expression for rate of polymerization.

4) The rate constant for propagation with terminal emulsifier double bonds was determined to be roughly twice the propagation rate constant. This is reasonable since both reactions involve a macroradical and an unsaturated carbon, and should be similar in magnitude.

3.4 Evaluating the Kinetic Model Against Experimental Data

The kinetic model is compared with experimental conversion, molecular weight, particle size and number data for various levels of initiator, monomer, emulsifier, temperature, rate of agitation and types of initiator and emulsifier. In all cases the model is represented by a solid line and the data by symbols.

The kinetic model can predict the conversion-time behaviour very well over a broad range of initiator levels for two initiators (AIBN: Figure 2.5; ADVN: Figure 2.6). The model also gives good estimates of the terminal weight average molecular weight at different AIBN concentrations (Figure 2.7) and the trend in molecular weight with conversion (Figure 2.8). The increase in molecular weight at low conversions is caused by unimolecular termination with emulsifier which produces dead polymer and an emulsifier radical. This radical propagates, to produce polymer which contains a terminal double bond, and later reacts to form a long chain branch. The molecular weight levels off at high conversions due to the
Figure 2.5: Conversion-time data and model predictions (——) for polymerizations with AIBN initiators at the following conditions: $T = 47^\circ C$, $[M] = 5.75 \text{ mol/L}$, $[E] = 0.103 \text{ mol/L}_0$, $\phi_{w0} = 1:1$, $N = 1000 \text{ RPM}$, $[\text{AIBN}] = 1.92 \text{ mmol/L}_0$ ($\blacktriangle$), 4.02 mmol/L$_0$ ($\blacksquare$), 6.03 mmol/L$_0$ ($\bullet$), and 7.92 mmol/L$_0$ ($\times$).
Figure 2.6: Conversion-time data and model predictions (---) for ADVN initiators. The reaction conditions were: T = 47°C, [M] = 5.75 mol/L, [E] = 0.103 mol/L, \( \Phi_{w_0} \) = 1:1, N = 1000 RPM, [ADVN] = 0.65 mmol/L (x), and 1.33 mmol/L (▲).
Figure 2.7: Final weight average molecular weight ($\overline{MW}_w$) data (●) and model predictions (—) for AIBN polymerizations. Other reaction conditions were the same as in Figure 2.5.
Figure 2.8: Experimental weight average molecular weight ($\bar{M}_w$) data (○) and model predictions (—) for a reaction under the following conditions: $T=47^\circ\text{C}$, $[M]=5.75 \text{ mol/L}_w$, $[E]=0.103 \text{ mol/L}_0$, $[\text{AIBN}]=4.02 \text{ mmol/L}_0$, $\Phi_{w/o}=1:1$, $N=1000 \text{ RPM}$.
reduced reactivity of the terminal double bonds with macroradicals, which corresponds to a
decrease in the formation rate of branched polymers.

The calculated rates of initiation from primary and emulsifier radicals are shown in
Figure 2.9. The initiation by emulsifier radicals contributes significantly to the overall rate at
the outset of the polymerization and then decreases to zero. This decline is caused by com-
petition for the emulsifier radicals between monomer and organic phase impurities and
radicals. As the reaction proceeds the emulsifier radical is in an environment with a lower
monomer level and has a greater probability of diffusing into the oil phase and terminating.

Figure 2.10 shows the trend in number and weight average molecular weight for
two chemically similar emulsifiers, sorbitanmonooleate and sorbitanmonostearate, distin-
guished only by the absence of unsaturation in the stearic chain of SMS. When SMS is used
molecular weights are fairly constant with conversion confirming the linearity of the resulting
polymer.

Increasing the initiator concentration causes a higher fraction of macroradicals to
be terminated by a bimolecular process and reduces the fraction of polymer molecules with
terminal double bonds. The terminal double bond density is also reduced at higher
temperatures, which favour propagation over termination of emulsifier radicals with oil phase
impurities. This increases the efficiency of initiation of emulsifier radicals (Figure 2.11).

Particle size and number were found to be invariant to initiator concentration.

Thermal effects

The model gives good predictions of the conversion of monomer to polymer
(Figure 2.12) and final weight average molecular weight (Figure 2.13) at temperatures
between 42 and 57°C. Kinetically, the thermal effects are dominated by two factors: the large
activation energy of the decomposition of initiator and the surface tension. At high
Figure 2.9: Rate of initiation \( (R_t) \) of primary (—) and emulsifier (— — —) radicals as a function of conversion. Conditions of the simulation were the same as in Figure 2.8.

Figure 2.10: Number and weight average molecular weights for polymerizations with sorbitanmonooleate (—) and sorbitanmonostearate (— — —). Conditions of the simulations were the same as in Figure 2.8.
Figure 2.11: Efficiency of initiation of emulsifier radicals \( f_e \) as a function of conversion at several temperatures: 40°C (---), 50°C (-- -- --), and 60°C (--- ---). The remaining experimental conditions of the simulations were: [M] = 5.75 mol/L_w, [E] = 0.103 mol/L_o, [AIBN] = 4.02 mmol/L_o, \( \phi_{w/o} = 1:1 \), N = 1000 RPM.
Figure 2.12: Conversion-time data and model predictions (---) for polymerizations under the following conditions: [M] = 5.75 mol/Lw, [E] = 0.103 mol/Lw, [AIBN] = 4.02 mmol/L0, ϕw₀ = 1:1, N = 1000 RPM, T = 42.5°C (●), 47°C (Δ), and 54°C (x).
Figure 2.13: Final weight average molecular weight (MW) data (O) and model predictions (—) as a function of temperature. Other reaction conditions were the same as in Figure 2.12.
temperatures the surface tension is reduced which generates smaller particles in a larger number (Figures 2.14 and 2.15). Smaller particles generate a larger total interfacial area, which increases the capture of primary and oligo radicals generated in the oil phase and increases the efficiency of initiation (Figure 2.16). The smaller particles also have a higher surface to volume ratio which improves the accessibility of macroradicals to the interfacial emulsifier and increases the transfer to emulsifier.

The efficiencies for azo radical capture, predicted by this model, are consistent with Lambla’s (1976) experimental measurements for AIBN radicals transferring between toluene and water (f ≈ 0.05).

Figure 2.17 shows the average number of radicals per particle (\( \bar{n} \)) as a function of conversion at several temperatures. For typical temperatures of 40 to 50°C, \( \bar{n} \) is quite large. At higher temperatures the average number of radicals per particle is significantly reduced because of the large increase in the number of particles per unit volume.

The rise in \( \bar{n} \) with conversion is evidence of diffusion controlled termination, which causes the total macroradical concentration to rise. The extent of diffusion controlled termination in inverse-microsuspension is similar in magnitude to solution acrylamide polymerizations as is shown in Figure 2.18.

**Effect of emulsifier type and concentration**

Increasing the bulk level of emulsifier will cause both the interfacial and organic phase concentrations to rise. The first effect lowers the surface tension which produces smaller particles (Figure 2.19) and a slightly faster rate. However, these surface effects are small relative to the decrease in rate caused by the consumption of primary and oligo radicals due to the additional soluble emulsifier (Figure 2.20). This coupled with the very strong transfer to monomer reaction imply that molecular weights should be fairly insensitive to the level of
Figure 2.14: Volume-to-Surface average particle diameter ($d_{32}$, micrometers) as a function of reaction temperature. Other experimental conditions were the same as in Figure 2.12.
Figure 2.15: Experimentally measured number of particles per litre of continuous phase (Np) and model predictions (---) at several reaction temperatures. Other experimental conditions were the same as in Figure 2.12.
Figure 2.16: Efficiency of initiation of primary radicals ($f$) as a function of interfacial area. Other conditions of the simulations were: $T = 47^\circ C$, $[M] = 5.75 \text{ mol/L}_w$, $[AIBN] = 4.02 \text{ mmol/L}_o$, $\phi_{w/o} = 1:1$.

Figure 2.17: Average number of radicals per particle ($\bar{n}$) as a function of conversion for several reaction temperatures: $45^\circ C$ (---), $50^\circ C$ (−−−−), $53^\circ C$ (−−−), $55^\circ C$ (−−−−), and $60^\circ C$ (· · · ·). Other conditions of the simulations were: $[M] = 5.75 \text{ mol/L}_w$, $[E] = 0.103 \text{ mol/L}_o$, $[AIBN] = 4.02 \text{ mmol/L}_o$, $\phi_{w/o} = 1:1$, $N = 1000 \text{ RPM}$. 
Figure 2.18: Extent of diffusion controlled termination for inverse-microsuspension (----) and solution (------) polymerizations of acrylamide at 47°C. The gel effect was modelled using the empirical equation $k_d/k_d^0 = \exp(A w_p)$, where $w_p$ is the weight fraction of polymer in the aqueous phase and $A$ is a constant determined from experimental data.
Figure 2.19: Volume-to-surface average particle size ($d_{32}$) data and model predictions (—) as a function of bulk emulsifier concentration. Other reaction conditions were: $T = 47^\circ C$, $[M] = 5.75 \text{ mol/L}_w$, $[\text{AIBN}] = 4.02 \text{ mmol/L}_o$, $\phi_{w/o} = 1:1$, $N = 1000 \text{ RPM}$. 
Figure 2.20: Conversion-time data and model predictions (---) for polymerizations with sorbitanmonooleate at various concentrations: 0.103 mol/L₀ (△), and 0.211 mol/L₀ (×). Other conditions were the same as Figure 2.19.
emulsifier. This is verified experimentally (Figure 2.21) over a broad range of SMO concentrations. At present there is insufficient evidence to ascertain whether the deviation between predicted and measured molecular weight at the highest emulsifier level, is due to a modeling deficiency or an experimental anomaly.

The effect of different emulsifiers on rate has been discussed in the last section. Figure 2.22 shows good agreement between the model and experimental data for both SMO and SMS.

The model can be applied to other types of emulsifiers or mixtures with cosurfactants, provided the transfer activity and the influence on interfacial tension are known.

**Effect of phase ratio on rate**

The reciprocal relationship between the rate of polymerization and the phase ratio of water to oil (equation 2.10) is surprising since it would be expected that as the volume of the continuous phase is reduced the consumption of primary radicals by reactions with emulsifier and hydrocarbons decreases. However, this effect is negligible compared to the reduction in turbulent intensity caused by the higher holdups. This produces larger particles and smaller interfacial areas which reduce the radical capture efficiency and the rate.

**Effect of the rate of agitation**

The role of agitation is to maintain a stable emulsion throughout the polymerization. As the power input from the impeller increases, the droplets, which are produced by mechanical agitation and not homogeneous nucleation or micellar growth, become smaller (Figure 2.23). This increases the interfacial area and the rate (Figure 2.24).
Figure 2.21:  Final weight average molecular weight (MWw) data (O) and model predictions (——) for polymerizations with various concentrations of sorbitanmonooleate. Other conditions were the same as in Figure 2.19.
Figure 2.22: Conversion-time data and model predictions (——) for polymerizations with sorbitanmonoleate (Δ) and sorbitanmonostearate (X). The reaction conditions were: \( T = 47^\circ{}C, \) \([M] = 5.75 \text{ mol/L}_w, \) \([\text{AIBN}] = 4.02 \text{ mmol/L}_0, \) \([E] = 0.103 \text{ mol/L}_0, \) \( \Phi_m = 1:1, \) \( N = 1000 \text{ RPM}. \)
Figure 2.23: Experimentally measured volume-to-surface average particle diameter ($d_{32}$) and model predictions (——) as a function of the rate of agitation. Other reaction conditions were: $T = 47^\circ C$, $[M] = 5.75 \text{ mol/L}_w$, $[E] = 0.103 \text{ mol/L}_o$, $[AIBN] = 4.02 \text{ mmol/L}_0$, $\phi_{w/o} = 1:1$. 
Figure 2.24: Conversion-time data and model predictions (—) as a function of the rate of agitation: 1000 RPM (△), and 1270 RPM (x). Other experimental conditions were the same as Figure 2.23.
At very low rates of agitation (≤500 RPM) the power input is insufficient to maintain emulsification and the kinetic model cannot be applied. This is also true at low emulsifier levels (≤0.04-0.06 mol/L₀).

The model gives good agreement with experimental data at various monomer concentrations up to fifty percent by weight (Figure 2.25).

Production of super high molecular weight polymers

Under normal polymerization conditions high molecular products are obtained by lowering the temperature and initiator concentration. In inverse-microsuspension molecular weights can also be raised by increasing the level of double bonds in the polymer backbone. This can be accomplished by proper selection of the emulsifier where suitable emulsifiers would contain an extractable hydrogen in the hydrophilic end, and an accessible reactive carbon-carbon double bond. The presence of multiple double bonds may improve the branching probability and further increase molecular weights. In addition suitable emulsifiers will also have to form a rigid interface that offers good stability for long periods, and lower the surface tension with moderate dosages.

In cosurfactant systems where several interfacial components are present, some species can be used to confer stability and others to provide sources of unsaturation.

Extension of the mechanism to include copolymerizations and the role of oxygen

The fundamental features of the mechanism are unchanged for homo and copolymerizations as will be seen in Chapter 3. Additional reactions are however required to account for the difference in reactivity between the two types of monomers and macroradicals. If electrolytes are used, the influence of pH and salt level on the rate constants and dissociation equilibrium must also be known.
Figure 2.25: Conversion-time data and model (---) for various monomer concentrations: 4.23 mol/L (x) and 7.04 mol/L (Δ). Other reaction conditions were: T = 47°C, [E] = 0.103 mol/L, [AIBN] = 4.02 mmol/L, ϕ<sub>φ</sub> = 1:1, N = 1000 RPM.
The addition of oxygen to control the polymerization rate is common industrially. Upon addition to an inverse-microsuspension the oxygen diffuses into the oil and aqueous phases and consumes primary radicals. This can be modelled by adding the following steps to the kinetic mechanism:

\[
\begin{align*}
\phi_{O_2}^{-1} & : \\
O_{2(g)} & \equiv \ O_{2(0)} \\
\ & \\
& \\
\phi_{O_2}^{-2} & : \\
O_{2(0)} & \equiv \ O_{2(W)} \\
\ & \\
& \\
k_2 & : \\
O_{2,0} + R_{in,0} & \rightarrow \text{Inert products} \\
\ & \\
& \\
k_3 & : \\
O_{2,W} + R_{in,W} & \rightarrow \text{Inert products}
\end{align*}
\]

where \( \phi_{O_2}^{-1} \) and \( \phi_{O_2}^{-2} \) are the partition coefficients of oxygen between the gas and oil and oil and water phases respectively. The subscripts \( g \), \( o \) and \( w \) designate gas, organic and water phase concentrations. Knowledge of these partition coefficients and rate constants allows us to quantify the effect of an air pulse on rate. These experiments are discussed in Appendix E.

The presence of excess oxygen may also reduce the molecular weight of the polymer by reacting with macroradicals. These polyoxyradicals have been postulated to propagate with monomer (George, 1978; Ghosh, 1978), generating a backbone which contains a weak O-O bond. This would be susceptible to scission at the elevated temperatures used at the end of commercial polymerizations.
REFERENCES


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71. 'Azo Polymerization Initiators', Wako Pure Chemical Industries Ltd., 1983.


CHAPTER 3
POLYMERIZATION OF QUATERNARY AMMONIUM CATIONIC MONOMERS

1. INTRODUCTION TO CATIONIC POLYMERS

Over the past two decades the consumption of cationic water soluble polymers has increased rapidly. Cationic homopolymers and copolymers with acrylamide are now applied for fines retention in paper making, as flocculants and biocides in water treatment, as stabilizers for emulsion polymerization, in cosmetics and pharmaceuticals, and in general wherever aqueous solid-liquid separations are required (Table 3.1).

Cationic polymers can be categorized by the chemical nature of the charged substituent. Ammoniums (primary, secondary, tertiary and quaternary) have had the most significant commercial impact since they can be synthesized to a variety of chain architectures and sizes. By comparison, polyphosphoniums are limited to oligomeric molecular weights (Hoffmann, 1861; Rabinowitz, 1961; Tsetlin, 1961; Pellon, 1964) and sulphonium monomers are generally unstable and less readily available than quaternary ammonium compounds (Bell, 1966; Lacombe, 1966).

Ammonium containing polymers were first synthesized by Marvel in 1930. However, it was not until 1949 that quaternized macromolecules were produced (Butler and Bunch). In that investigation tri and tetra allyl ammonium salts were polymerized to form highly crosslinked ion-exchange resins. In 1951, Butler and Ingle reported the formation of a water soluble polymer from diallyl quaternary bromides. Later Butler (1966) showed that

---


2 The apparent unreactivity of monoallyl compounds is due to a strong depopagation reaction.
<table>
<thead>
<tr>
<th>Application</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purify potable water, sewage</td>
<td>Klonina, 1984</td>
</tr>
<tr>
<td>Antibacterial and antifungicide agent</td>
<td>Panarin, 1985</td>
</tr>
<tr>
<td>Neutralize detergents</td>
<td>Suen and Schiller, 1965</td>
</tr>
<tr>
<td>Clarify coal tailings, metal plating wastes</td>
<td>Easterly, 1984</td>
</tr>
<tr>
<td>Floatation aids</td>
<td>Burkhardt, 1986</td>
</tr>
<tr>
<td>Dehydrating agents in sludge digestion</td>
<td>Meltzer, 1979</td>
</tr>
<tr>
<td>Paper sizing agents</td>
<td>Schuller, 1959</td>
</tr>
<tr>
<td>Drainage and Retention aids</td>
<td>Tanaka, 1986</td>
</tr>
<tr>
<td>De-emulsifier for dispersed oils</td>
<td>Ottenbrite, 1980</td>
</tr>
<tr>
<td>Fluorescent whiteners</td>
<td>Ottenbrite, 1980</td>
</tr>
<tr>
<td>Stabilizers for polymerization</td>
<td>Orlov, 1986; Hammid, 1987; Nagai, 1987</td>
</tr>
<tr>
<td>Associative thickeners</td>
<td>McCormick, 1988</td>
</tr>
<tr>
<td>Dispersants</td>
<td>Flesher, 1986</td>
</tr>
<tr>
<td>Antistatic agents</td>
<td>Yocum and Nyquist, 1974</td>
</tr>
<tr>
<td>Dye retention additives</td>
<td>Yocum and Nyquist, 1974</td>
</tr>
<tr>
<td>Cosmetics: hairdressing, shampoo</td>
<td>Coyner, 1962; Long, 1967</td>
</tr>
<tr>
<td>Pressure sensitive adhesives</td>
<td>Meltzer, 1979</td>
</tr>
<tr>
<td>Sequestering agents</td>
<td>Butler, 1980</td>
</tr>
<tr>
<td>Permeselective membranes</td>
<td>Butler, 1980</td>
</tr>
<tr>
<td>Inks, grease thickening, soil conditioning</td>
<td>Hoover, 1970</td>
</tr>
</tbody>
</table>
the chloride ion form of diallylammonium monomers provided more useful products due to their higher molecular weights. The solubility of diallyl monomers was surprising, since at the time it was believed that all dienes yielded crosslinked gels (Staudinger, 1934). To account for this phenomena Butler and Angelo (1957) proposed an alternating inter-intramolecular chain propagation. "Cyclopolymerization" occurs because the ring formation is kinetically more favorable than a second intermolecular linkage. Wandrey (1981) has determined that ring closure accounts for up to 99.9% of addition reactions, with the remaining forming pendant double bonds (Figure 3.1). Butler and Angelo's mechanism included a radical attack on the α-carbon followed by cyclization to the c-carbon of the residual double bond (Figure 3.1).

Over the past thirty years research in cyclopolymerization has grown rapidly. Almost all nonconjugated dienes are now believed to undergo cyclic formation in competition with, and often in preference to crosslinking. Suitable monomers can be initiated by a number of mechanisms including free radical, anionic and cationic processes (Butler, 1982).

The elucidation of the mechanism of ring closure has propelled cyclopolymerization from the status as a novel polymerization technique to the forefront of theoretical free radical chemistry. Originally a six member ring structure was postulated, since it can be obtained via a secondary radical intermediate which is thermodynamically more favorable than the reaction pathway required for five-member rings (Figure 3.1). However, Brace (1970, 1971) investigated the free radical addition of perfluoro allyl radicals to N-substituted diallylamines and observed exclusively five-membered ring formation. 13C Nuclear magnetic resonance studies of diallyldimethylammonium chloride and bromide have also failed to detect six-member rings (Lancaster, 1979; Ottenbrite and Shillady, 1979). Electron Spin Resonance (ESR) investigations have supported these findings (Solomon, 1976).

Ottenbrite and Shillady have applied molecular orbital theory to show that the approach of a radical to a β-carbon is less hindered, implying monocyclic reactions
Figure 3.1: Polymerization reactions of diallylamine.
are kinetically controlled, and for diallylammoniums, produce pyrrolidinium rings in preference to piperdininium rings. In general, five-member ring formation is energetically more favorable unless the β-carbon contains large substituents, which interfere with its approach to the radical (Solomon and Hawthorne, 1976).

Polydiallyldimethylammonium chloride (PDADMAC) was the first synthetic flocculant approved for potable water clarification by the United States Public Health Service, and has historically been the most widely produced polyelectrolyte. Other commercially important cationic polymers are derived from dimethylaminoethyl methacrylate (DMAEM), first synthesized by Winberg in 1956, dimethylaminoethyl acrylate (DMAEA) and acrylamido-methylpropanedimethylammonium chloride (AMPDAC). The structure of these monomers is shown in Figure 3.2. These cationic monomers are often copolymerized with acrylamide to produce supermolecular polyelectrolyte structures. The resulting flocculants are nontoxic and more efficient than either of the respective nonionic and cationic homopolymers (Nicke, 1985). They also offer advantages over inorganic flocculants such as alum, including smaller dosage requirements, less floc generation and a reduction of the ash produced during incineration. As such synthetic polyelectrolytes have occupied a growing portion of the water treatment market over the past two decades.

1.1 Solution Behaviour of Cationic Polymers

The intrinsic viscosity of dilute solutions of quaternary ammonium polymers has been found to be inversely related to the salinity of the medium (Linow, 1982). This "polyelectrolyte effect" is eliminated at inorganic salt levels above approximately one molar (Stickler, 1984; Mabire, 1984; Flandor, 1986) due to the formation of a loose intermolecular cyclic structure (Figure 3.3) which shields the cation and reduces Coulombic repulsion (Pradny

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Figure 3.2: Structure of some common quaternary ammonium cationic monomers. DADMAC: diallyldimethylammonium chloride; DMAEA: dimethylaminoethyl acrylate; DMAEM: dimethylaminoethyl methacrylate; AMPDAC: acrylamidomethylpropanedimethylammonium chloride.
Figure 3.3: Cyclization of DMAEM in the presence of added electrolyte.
1985, 1987). By comparison fully ionized polymers possess a flexible coil structure (McCormick, 1986 II). McCormick (1986 I) has also determined that aqueous solutions of cationic polymers have stable viscosities over long periods. Aging phenomena has however been observed for copolymers with acrylamide. This has been interpreted as evidence that the quaternary ammonium and amide monomers do not cross-propagate, and alternatively produce a tenacious mixture of homopolymers during synthesis. Although this has not been refuted by measurements of the chain microstructure, Huang (1988) has found different physical properties for copolymers and mixtures of homopolymers.

Measurements of molecular sizes and configurations in aqueous solutions have been reported only for DADMAC (Wandrey, 1982; Stickler, 1984; Burkhardt, 1987) and DMAEA (Mabire, 1984).

1.2 Kinetics

Kinetic investigations of the polymerization of quaternary ammonium monomers are limited to observations on dimethylamines and diallylammoniums. For DMAEM, Longi (1964), Egoyan (1979, 1979, 1982), Martynenko (1979) and Fujimori (1984) have conducted polymerizations in solvents with various polarity and found conformation to the classical free radical polymerization mechanism. However, investigations with DADMAC (Boothe, 1970; Hahn, 1984; Jaeger, 1984; Martynenko, 1985; Topchiev, 1985) have revealed two kinetic anomalies: a linear dependence of the propagation rate constant on monomer concentration (Wandrey, 1981 I, II) and the formation of a molecular complex with anionic peroxide initiators (Hahn, 1983 I, II). The former is caused by an increase in the electrolyte level of the mixture with added monomer, which suppresses Coulombic interactions and increases the reactivity of charged monomers and macroradicals. The latter is due to the ionogenic nature of the monomer and initiator and will be discussed in further detail in Chapter 4.
Investigations of the copolymerization kinetics are also limited even though acrylamide and quaternary ammoniums were first reacted by Schuller in 1959. Wandrey and Jaeger (1985) have found that the reactivity ratios for DADMAC/AAM depend on the monomer concentration and composition. This was attributed to electrostatic and penultimate influences on propagation. Singh (1986) has observed a linear dependence for the reactivity ratio of DADMAC with simple electrolyte concentration. Recently Tanaka (1986) published an extensive kinetic study of several cationic comonomers with acrylamide, including all three monomers used in this investigation. The agreement between these and previously published reactivity ratios (Jaeger, 1984; Wandrey, 1985; Huang, 1986) is poor. This is due to the low reproducibility of measurements of monomer concentration by colloid titration and the application of non-statistical parameter estimation methods, which fail to identify the magnitude of the measurement errors. An analysis of the variance of colloid titration relative to other analytical methods for copolymer characterization will be presented in section 3.2.

The reactivity of quaternary ammonium monomers has been determined to be insensitive to the pH of the reaction mixture (Tanaka, 1986) and the size of the substituents on the ammonium groups (Yocum, 1973). However, functional groups closer to the reactive centre can have an appreciable influence on the rate and molecular size, with monomers with ester linkages polymerizing faster than their amino counterparts (Boussouira, 1987).

1.3 Experimental Plan

The generalization of the inverse-microsuspension mechanism to copolymers and electrolytes requires several physical and kinetic parameters. These include propagation, termination and cross-termination constants for the cationic monomers, reactivity ratios for quaternary ammonium monomers with acrylamide, mass transfer and partition coefficients for monomers and radicals, and an estimate of the magnitude of diffusion controlled
termination. With the exception of the reactivity ratios, for which there is no consensus as to the numerical value, these parameters have not been determined. The following four phase experimental program is proposed such that independent parameter estimates can be elucidated from kinetic, latex characterization and partitioning measurements.

A preliminary set of homopolymerizations of DMAEA and DMAEM will be conducted to determine the Arrhenius dependence of the rate parameter $k_p/k_c^{1/2}$. Experiments will be performed isothermally between 40 and 60°C in solution and inverse-microsuspension, and combined with available literature data at other temperatures.

The second phase of the research will estimate the reactivity ratios of acrylamide with three cationic comonomers: DMAEM, DMAEA and DADMAC. Experiments will be carried out in dilute aqueous solutions (0.5 mol/L) to avoid the influence of diffusion controlled termination. Polymerizations will be performed over a range of temperatures and monomer feed compositions with two water soluble initiators: azocyanovaleric acid and potassium persulfate. Parallel experiments with two initiators are planned to elucidate the effect of primary radical structure and charge on the reactivity of quaternary ammonium monomers.

A third set of experiments will spectrometrically measure the partitioning of acrylamide, DMAEM and DMAEA between water and Isopar-K. Experiments will be performed over a range of phase ratios and emulsifier concentrations (sorbitanmonooleate), in order to mimic the conditions that exist during inverse-microsuspension polymerizations.

The final stage of this research, and the primary task of this chapter, will investigate the copolymerization of acrylamide with quaternary ammonium monomers in inverse-microsuspension. Experiments will be performed with DMAEM and DMAEA, at fifty weight

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4 The heterophase kinetics of acrylamide/DADMAC polymerizations have been investigated by Singh (1986) in a system very similar to inverse-microsuspensions.
percent total monomer concentration. An oil soluble azo initiator (azobisisobutyronitrile) will be used with reactions performed isothermally over the temperature range 40 to 60°C.

The interrelationships between the research objectives and the four experimental programs are shown in Figure 3.4.
Figure 3.4: Interrelationships of research objectives (Polymerization of cationic monomers).
2. EXPERIMENTAL METHODS AND PROCEDURES

2.1 Monomer Purification

Quaternary ammonium monomers are hygroscopic and tend to spontaneously polymerize at normal storage temperatures. They are therefore unavailable as recrystallized solid reagents, and are usually provided as concentrated aqueous solutions inhibited with 1000 ppm of hydroquinone monomethylether (CPS Chemical Co.). DMAEM, the fastest reacting ammonium cationic, is further stabilized with 10 ppm of cupric ions, to chelate the monomer. The hydroquinone monomethylether (MeHQ) can be extracted from the aqueous solution using ether (Singh, 1986), benzene, acetone or activated charcoal. Alternatively, purified quaternary ammonium can be prepared indirectly from the tertiary amine by bubbling methyl chloride through a solution of monomer in acetone. The quaternized fraction of the monomer precipitates, leaving the inhibitor and the unreacted amine in the solvent. In this work, extraction is preferred over derivatization due to the toxicity and flammability of methyl chloride (Ahlstrom, 1979).

Figure 3.5a identifies the MeHQ peaks in dimethylaminoethyl methacrylate monomer. Single and multiple extractions with benzene have a minimal effect on the inhibitor removal (Figure 3.5b), and introduced benzene into the monomer solution which would certainly affect the initiation efficiency. Activated charcoal also removed a relatively small fraction of the MeHQ (Figure 3.5c). However, acetone eliminates a significant portion after three extractions (Figure 3.5d). Further, it causes the quaternary ammonium to precipitate out as a crystalline solid containing less than 0.5 ppm of hydroquinone monomethylether following the fifth extraction (Figure 3.5e). This novel procedure purifies the raffinate by extracting both MeHQ and water in the acetone. With each stage the concentration of quaternary ammonium increases until a sufficient portion of the moisture is removed.

---

Five extractions were required to precipitate DMAEM and six for DMAEA.
Figure 3.5: HPLC chromatograms of DMAEM.
(a) 0.5 wt.% unpurified DMAEM solution. The large peak at 3.56 minutes is monomer. The peak at 1.96 minutes is the hydroquinone monomethylether inhibitor.
(b) A reduced hydroquinone monomethylether peak is observed following extraction with benzene. Note the benzene impurity in monomer at 2.19 minutes.
(c) A reduced hydroquinone monomethylether peak after extraction with 1 gram of activated charcoal (in 50 mL of 75 wt.% DMAEM) for 24 hours.
(d) A large reduction in hydroquinone monomethylether peak is observed after the third extraction with acetone, without contamination to the residual monomer.

(e) Complete elimination of hydroquinone monomethylether from the monomer following extraction and precipitation with acetone.
that the monomer can crystallize (Table 3.2). The solids were subsequently filtered, washed with acetone, dried in vacuo to constant weight and stored in desiccators over silica gel.

Solid acrylamide monomer (Cyanamid B.V., The Netherlands) was recrystallized in 500g batches from two litres of chloroform (Caledon, Reagent Grade), washed with benzene (BDH, Reagent Grade), dried in vacuo to constant weight and stored over silica gel in desiccators.

The concentration of cupric ion in the monomer was measured by optical emission spectroscopy on a Jarrett Ash Division ICAP 9000. Copper nitrate (Fisher) was used to calibrate the instrument.

2.2 Determination of Monomer and Polymer Composition

The copolymer composition of cationic polyelectrolytes is usually determined by colloid titration (Metcalf, 1966; Kokufuta, 1979; Tanaka, 1986) although recently conductimetric (Wandrey, 1985) and silver nitrate titrations (Singh, 1986) have also been employed. Colloid titrations were developed by Terayama (1949) based on observations of stoichiometric complexes formed between high molecular weight polyanions and polycations. The formation of these symplexes has recently been verified by measuring the chemical shift displacement in $^{13}$C NMR (Kolz, 1986). Colloid titration is volumetric incorporating a metachromatic end point detection (Terayama, 1952), which provides a steeper gradient than potentiometric detection. To titrate positively charged macromolecules potassium polyvinylalcohol sulphate (PVS K) is usually used as a negative colloid, with toluidine blue (a cationic dye) as the indicator (Senyuu, 1953; Schempp, 1981). A distinct colour change from blue to reddish-purple, and the precipitation of the polyelectrolyte, are observed at the end point. However, these titrations are affected by trace levels of multivalent salts and, despite claims to the contrary, have very slow symplex formation. Furthermore, they are not stoichiometric
Table 3.2: Purification of Dimethylaminoethylmethacrylate

<table>
<thead>
<tr>
<th>Extraction</th>
<th>Volume of Aqueous Phase</th>
<th>Appearance of Aqueous Phase (Raffinate)</th>
<th>Appearance of Supernatant Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>500</td>
<td>Clear</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>800</td>
<td>Clear</td>
<td>Slightly turbid</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>Clear</td>
<td>Slightly turbid</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>Clear</td>
<td>Slightly turbid</td>
</tr>
<tr>
<td>4</td>
<td>550</td>
<td>Clear</td>
<td>Slightly turbid</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>Very turbid, followed by precipitation of the quaternary ammonium monomer</td>
<td>Clear</td>
</tr>
</tbody>
</table>
for chain lengths below about three hundred (Ueno and Kina, 1985). Other means of end-point
detection such as ion-selective electrodes (Ishibashi, 1975), conductivity (Toei and Kohara,
1976) and turbidimetry (Toei and Sawada, 1977) have been used, but offer similar accuracy to
colourimetry.

For titrations in this chapter PVSK was standardized against a 1/400 N cetylpyridi-
nium chloride monohydrate solution. One mL of a copolymer solution containing 200-600 ppm
of copolymer and one drop of toluidine blue (Nalco Chemical Co.) were placed in a beaker on a
magnetic stirrer. A PVSK solution (Nalco) was added titrimetrically until the endpoint was
reached. Each titration was repeated four times. In this thesis colloid titrations have only
been used as a comparison with the chromatographic method discussed in the next section.

2.2.1 Description of the HPLC Method for Residual Monomer Concentration

A recent review of the statistical estimation of reactivity ratios (Hamielec, 1989)
concludes that chromatographic techniques, specifically gas and liquid chromatography,
provide the most accurate measurements of residual monomer concentration. While Gas and
Liquid chromatography methods have been employed for acrylamide detection for several
no procedures have been reported for quaternary ammonium monomers.

In the present study a CN column (9% groups bonded to a μ-porasil (silica) sub-
strate, Waters Assoc.) with a 8 mm I.D. and 4 μm particles was used as the stationary phase.
The column was housed in a radial compression system (RCM-100, Waters) and was operated
at a nominal pressure of 180 kg/cm². The HPLC system (Figure 3.6) consisted of a degasser
(ERC-3110, Erma Optical Works) a Waters U6K injector, a stainless steel filter and a CN
 precolumn (Waters). An ultra violet detector (Beckman 160) with a zinc lamp operating at a
Figure 3.6: Photograph of the HPLC system used in this investigation.
wavelength of 214 nm was used to measure the monomer absorption. A Spectra-Physics SP4200 integrator was used to compute peak areas.

The mobil phase was a mixture of 50 vol% acetonitrile (Caledon, Distilled in Glass, UV Grade) and 50 vol% double distilled deionized water, containing 0.005 mol/L dibutylamine phosphate. The flow rate was 2.0 mL/min. The peak separation was optimized by varying the acetonitrile-water ratio.

Figure 3.7 shows an example chromatogram for acrylamide-dimethylaminoethyl methacrylate. The quaternary ammonium is retained longer in the column because of adsorption onto the polar groups of the packing. The signals can be reproduced within 1 ppm. An analysis of the variance in the determination of residual monomer concentration by this HPLC apparatus/procedure is given in Appendix F.

Residual monomer concentrations were determined on polymer samples treated as follows: A 2 mL portion of the reactor sample was centrifuged for 16 h in a Adams Analytical Centrifuge to separate the organic and aqueous phases. The supernatant layer phase was syringed off and a sample of the remaining polymer-monomer-water mixture (nominally 0.01 g) was removed, weighed to five decimal places, and immersed in 20.00 mL of double distilled deionized water. This was subsequently sealed in a 20 mL vial and agitated vigorously with a magnetic stirrer until dissolved. This required up to seven days. Homogenized samples were filtered through a 0.45 μm cellulose-acetate-nitrate filter (Millipore) and diluted, if necessary, to obtain a monomer concentration below 100 ppm. One hundred μL of each sample was injected into the HPLC using a 100 μL glass syringe (Scientific Glass Engineering, Ltd.). Four replications were performed. Residual monomer concentrations were determined from a regressed calibration curve derived from standard samples from 0.006 to 100 ppm, prepared with recrystallized and vacuum dried monomer. An example calibration curve for acrylamide is

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6 At 0 ppm, a negative peak due to the solvent (water) front was observed.
Figure 3.7: Example of a HPLC chromatogram for the system acrylamide (AAM)/dimethylaminoethyl methacrylate (DMAEM). The peaks correspond to a concentration of 47.5 ppm of AAM and 90.1 ppm of DMAEM respectively.
shown in Figure 3.8. The calibration curve was reconstructed each day of operation. All samples from a given experiment were analyzed within a ten hour period. To monitor changes in absorption the system was recalibrated at the conclusion of each analysis. The absorption concentration dependence followed Beer's law up to 100 ppm for acrylamide and 500 ppm for the cationic monomers.

The precolumn and prefILTER were replaced for each experiment, and every 200 injections. Prefilters were cleaned for two hours in 6 N nitric acid in an ultrasonic bath (Bronson, B-52) and stored in distilled deionized water.

2.3 Polymerization Procedure

2.3.1 Reagent Preparation

Purified monomers were removed from their storage desiccators and dissolved at the appropriate concentration in distilled deionized water. Mild heating was required to overcome the negative enthalpy of dilution.7 A thermometer was immersed in the solution and the temperature was maintained below 20°C during this procedure. When dissolved, the monomer solution was covered and purged with rarefied nitrogen (UHP Grade, 99.999% purity, Canadian Liquid Air) for 15-30 minutes. Purging was stopped when the residual oxygen level dropped below 1.5 ppm, as measured with a dissolved oxygen probe (Yellow Springs Instrument Co., Model 54). A presample of this solution was taken to measure the initial monomer composition. The organic phase was prepared by weighing the appropriate amounts of Isopar-K8 (Esso Chemicals) and sorbitanmonooleate (Alkaril Chemicals, Ltd.). The

---

7 The dilution of acrylamide in water is endothermic (−2.9 kcal/mol) due to the formation of hydrogen bonded molecular dimers in the solid state (Grunov, 1980) which require excess energy to dissociate.

8 This reagent was used as received.
Figure 3.8: HPLC calibration curve for acrylamide. The following calibration equation was regressed: \[ \text{ppm} = -0.503 + 5.51 \cdot 10^{-6} \cdot \text{(Area)} \]. The correlation coefficient was 0.999998.
emulsifier dissolved readily in the isoparaffinic solvent and the mixture was purged with nitrogen for 10-20 minutes.

The initiator solution was prepared by dissolving azobisisobutyronitrile (AIBN: Kodak), once recrystallized from methanol (BDH, reagent grade), in 15 g of acetone (BDH, reagent grade). Labelled, cleaned glass sample bottles and a stock 1 wt% hydroquinone (Aldrich) solution were prepared prior to the reaction.

2.3.2 Description of Reactor

A well cleaned one-gallon stainless steel batch reactor (Chemineer) was used for the polymerizations (Figure 3.9). A PID controller varied steam to chilled water feed ratio entering the cooling jacket. Temperature control was excellent for all polymerizations with deviations always below 1°C, excluding an initial perturbation when the initiator was added (Figure 3.10).

2.3.3 Reactor Operation

The temperature was adjusted to 30°C and the reactor charged with the degassed organic phase. The aqueous phase was subsequently added and the system pre-emulsified. The reactor was then sealed and agitation (323 ± 1 RPM) was commenced. Nitrogen sparging at a very slow rate (< 20 mL/s) was continued for the duration of the polymerization. The temperature was ramped slowly (3°C/min) until the set point was reached. After thermal instabilities were reduced to below ±1°C for a period of no less than five minutes, a presample was taken and the initiator solution was added. A 20 mL glass syringe (Multifit) was used to inject the initiator solution through a resealable hole in the top of the reactor. The agitation was stopped for approximately twenty seconds during the initiator addition. The mid-time of the addition was noted and taken as the commencement of the polymerization.
Figure 3.9: Photograph of the reactor used for polymerizations.
Figure 3.10: Temperature profile for the copolymerization of acrylamide with DMAEM at 60°C showing an early perturbation after the initiator was added. Experimental conditions: [Monomer] = 6.09 mol/Lw, [AIBN] = 3.329 \cdot 10^{-3} \text{ mol/Lw}, f_{10} = 0.875, \Phi_w = 0.74.
Samples were withdrawn periodically at time intervals of at least five minutes in order to obtain twenty well spaced conversion-time data for each experiment. The sampling procedure was as follows: A sampling valve at the bottom of the reactor was opened and approximately five mL of sample was drained to waste. A 20 mL glass sample bottle containing 0.1 mL of a 1 wt% hydroquinone solution was placed below the valve and filled. This provided an aqueous phase concentration of hydroquinone of 100 ppm, sufficient to scavenge any unreacted radicals and cease the polymerization. The sample was vigorously shaken and immersed in an ice bath. The exact time (hours:minutes:seconds) of the sample withdrawal was then recorded. At the conclusion of the experiment the samples were refrigerated at 10°C prior to centrifugation. A sampling frequency of once per five minutes was the maximum attainable with a single operator.

The course of the polymerization was monitored on-line by recording the power input to the reactor as is shown in Figure 3.11. The steam input, shown as a percentage of the maximum, initially decreases due to the negative enthalpy of polymerization. It then slowly rises and levels off as the rate declines.

After a sufficient time (four to six hours) the reaction was stopped by draining the contents into a collection vessel. One litre of each reaction mixture was retained.

For homopolymerizations in inverse-microsuspension the same procedure was employed. In solution polymerizations the aqueous phase treatment was identical. However, the reaction was initiated with a water soluble initiator (potassium persulfate, Fisher "certified", min. assay 99.5%). This was recrystallized from double distilled deionized water. The preparation of samples for HPLC from solution polymerization consisted exclusively of dilution and filtration.

9 Replicate polymerizations with recrystallized potassium persulfate from another supplier (BDH, Reagent grade, minimum assay 99.0%) gave indistinguishable kinetics, as determined in a preliminary experimental sequence.
Figure 3.11: Variation in power input to the cooling jacket as a function of reaction time for a copolymerization of acrylamide and DMAEM at 40°C. Experimental conditions: [Monomer] = 6.14 mol/L, [AIBN] = 14.83 \times 10^{-3} \text{ mol/L}, f_{10} = 0.877, \Phi_{w/0} = 0.74.
2.3.4 Reactor Cleaning

The reactor was cleaned immediately after use by stripping the coagulum from the baffles, agitator and walls of the vessel with high pressure steam. The reactor was then filled with distilled deionized water and heated to 95°C for thirty minutes. It was subsequently cooled and rinsed by hand. This was repeated two to three times until all observable traces of polymer were removed. The vessel was then rinsed four times with distilled deionized water and then sealed from the atmosphere with a protective cover. All polymerizations were performed on successive days. Under no circumstances were polymerizations of other monomers permitted in this reactor between individual runs of an experimental sequence.

2.4 Polymerization Conditions

Inverse-microsuspension copolymerization of acrylamide with dimethylaminoethyl acrylate or dimethylaminoethyl methacrylate were performed isothermally over the temperature range of 40-60°C. A low dispersed phase ratio (0.74:1) was used to reduce the heat generation rate and improve the thermal stability. The cationic monomer fraction was kept low (25 wt%) to duplicate commercial recipes. An oil soluble azo initiator (azobisisobutyronitrile, Kodak) was used with Isopar-K, a narrow cut isoparaffinic mixture, as a dispersion medium. Sorbitanmonooleate, common to several industrial heterophase polymerizations of water soluble monomers (Srinivasan (Nalco), 1982; Easterly (Dow), 1984; Becher (Allied), 1988) was employed as the stabilizer. The specific reaction conditions for each experiment are listed in Table 3.3. Included are the conditions for the homopolymerization of DMAEM and DMAEA by inverse-microsuspension and solution respectively.

The specifications for the monomers, emulsifiers and hydrocarbons used throughout this thesis are provided in Appendix G.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Initiator</th>
<th>Cationic Monomer Concentration (mol/L; 10^3)</th>
<th>Total Monomer Concentration (mol/L; 10^3)</th>
<th>Mass of Oil (Isopar-K) (g)</th>
<th>Mass of Aqueous Phase (SMO, g)</th>
<th>Mass of Emulsifier (g)</th>
<th>ϕ_{em}</th>
</tr>
</thead>
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<tr>
<td>60</td>
<td>AIBN</td>
<td>3.327</td>
<td>0.637</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>0.74</td>
</tr>
<tr>
<td>60</td>
<td>K_2S_2O_8</td>
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<td>0.350</td>
<td>0.0</td>
<td>0.0</td>
<td>2000.0</td>
<td>0.74</td>
</tr>
<tr>
<td>60</td>
<td>AIBN</td>
<td>3.329</td>
<td>0.350</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>0.74</td>
</tr>
<tr>
<td>60</td>
<td>DMAEMA</td>
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<td>0.875</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>0.74</td>
</tr>
<tr>
<td>50</td>
<td>AIBN</td>
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<td>0.350</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>0.74</td>
</tr>
<tr>
<td>40</td>
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<td>0.350</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>0.74</td>
</tr>
<tr>
<td>40</td>
<td>AIBN</td>
<td>3.329</td>
<td>0.350</td>
<td>0.0</td>
<td>0.0</td>
<td>1000.0</td>
<td>0.74</td>
</tr>
</tbody>
</table>

*For copolymerizations with acrylamide. Potassium Persulfate (mol/L; 10^3)*
2.5 Estimation of Reactivity Ratios

Acrylamide was copolymerized with dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate and diallyldimethylammonium chloride. Syntheses were performed at a total monomer concentration of 0.5 mol/L to avoid the influence of diffusion controlled termination. The nonionic to cationic monomer feed ratio was varied between 0.3 and 0.7. Two water soluble initiators were employed: azocyanovaleric acid (ACV, Wako Chemical Co.) and potassium persulfate (KPS, BDH Chemicals). The polymerization temperatures were 45 and 60°C for reactions with dimethylamines and 50°C for DADMAC. The initial pH of the dilute monomer solution was 5.2 and did not appreciably change throughout the reaction.

The polymerizations were carried out in aqueous solution using a 0.5 L continuous stirred tank reactor. At steady state this provided copolymers of constant composition and enabled the estimation of reactivity ratios using the instantaneous copolymer composition equation. Steady state operation was obtained in approximately four mean residence times as is shown in Figure 3.12. After this time 20 mL samples were withdrawn from the reactor effluent and mixed with 200 μL of a 1 wt% hydroquinone to scavenge unreacted radicals. These were then stored in an ice bath for the duration of the reaction and subsequently refrigerated at 10°C prior to analysis by HPLC (see section 2.2.1). Samples were withdrawn every fifteen minutes in order to provide replicate measurements of the residual monomer concentration and estimate the measurement variance.

$^{13}$C NMR spectra were recorded for an 8.06 wt% D$_2$O solution at 62.89 MHz and ambient temperature on a Bruker WM 250 spectrometer operating at 5.87 T in the pulsed Fourier Transform mode with inverse gated decoupling. The $^{13}$C pulse width and acquisition time were 50.5 ms and 0.442 s respectively. Each spectrum contained 16 K data points over a frequency of 18,518 Hz, with approximately 2000 acquisitions.
Figure 3.12: Dependence of conversion of dimensionless time ($\tau$) for the system AAM/DMAEA. The monomer feed ratio was 1.7:1 and the residence time ($\theta$) 30 minutes.
2.6 Monomer Partitioning Measurements

Ultraviolet spectrometry was used to measure the partitioning of acrylamide, dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate between aqueous monomer solutions and hydrocarbons. Experiments were performed at monomer concentrations of 0.5 and 1.4 mol/L, prepared with double distilled deionized water. Isopar-K and sorbitanmonooleate constituted the oil phase. For each monomer a series of samples with organic to aqueous phase ratios of 1:1, 2:1 and 4:1 were prepared with oil phases containing one, four and eight weight percent emulsifier. Samples were agitated vigorously for a period of approximately six hours to ensure equilibrium partitioning was obtained. The phases were then separated by a two stage centrifugation procedure. The Isopar-K was separated from the aqueous phase by centrifuging for ten minutes in a Sorvall RCSB Superspeed Centrifuge operated at 11000 g. This was subsequently centrifuged in an Eppendorf Model 5415 Centrifuge operated at 14000 g to separate the emulsifier. This was continued until the aqueous phase was clear.

The partition coefficient was calculated by measuring the initial and equilibrium monomer concentration in the aqueous phase. An Ultra Violet spectrophotometer with variable wavelength detector (Gilford Response) was used. The measurement wavelengths were: 200 nm for DMAEA, 212 nm for AAM and 220 nm for DMAEM. These corresponded to the maximum UV absorption for each monomer. The absorbency was translated to a mass concentration by calibrating with standards between 1 and 100 ppm.

2.7 Particle Size Measurement

Particle sizes were determined by dynamic light scattering (Nicomp 370, Pacific Scientific) and optical photomicrography. In the former a helium-neon laser operating at 633
nm was used to measure the mean diffusion coefficient of the particles. Diameters are then inferred using the Stokes-Einstein relationship. Measurements were performed at 23°C with disposable glass stationary cells. Autocorrelation functions were accumulated for periods ranging from twenty five minutes to three and a half hours. All samples were measured at least twice. Solutions with a nominal concentration of 1 wt% were prepared by diluting inverse-microsuspension samples with Isopar-K. This concentration has been found to be ideal for the characterization of inverse-lattices (Candau, 1987). Photomicrographs were taken with Kodak TMAX-3200 and Tri X-400 Black and White film at 250X magnification. A Lietz Labor/UX microscope equipped with NPL objectives was used. Figure 3.13 shows sample photographs taken under normal, uneven and dark field illumination. Particle size distributions were determined from photomicrographs by measuring at least four hundred images.
Figure 3.13:
Optical Photomicrographs of an AAM/DMAEA copolymer produced at 60°C under the following experimental conditions: [Monomer1] = 6.05 mol/L, [AIBN] = 3.337 × 10^{-3} mol/L, f_0 = 0.843, ϕ = 0.74.
(b) Photomicrograph taken with uneven illumination to provide relief to the particle images.
(c) Photomicrograph taken with a darkfield substage condenser, providing the appearance of a three dimensional image.
Photomicrograph taken with a darkfield substage condenser. The white particle outlines allow for unambiguous particle diameter measurements.
3. RESULTS AND DISCUSSION

3.1 Homopolymerization of Cationic Monomers

Figure 3.14 shows the experimental conversion-time data for the inverse-microsuspension polymerization of dimethylaminoethyl methacrylate at 60°C. The monomer and initiator concentrations were 0.637 mol/L and 3.327 \times 10^{-3} \text{ mol/L} respectively. Under such conditions primary radical generation is principally due to the thermal bond rupture of the azo group, which results in a predominance of bimolecular macroradical termination. The inverse-microsuspension model therefore reduces to the classical free radical rate expression:

\[
R_p = (2f k_d [I])^{1/2} \frac{k_p}{k_t^{1/2}} [M]
\]

With the heterophase initiation efficiency defined as:

\[
f = \frac{1}{1 + \frac{k_r^*}{k_r} \left( \frac{k_4 [HC]}{a_{sp}} + \frac{k_1 [E_o]}{a_{sp}} \right)} \cdot \frac{V_o}{V_w}
\]

For the reaction conditions listed above, with a concentration of sorbitanmonooleate of 0.388 mol/L, and a measured average particle diameter of 7 \mu m, the calculated heterophase efficiency is 0.03. Using this value the kinetic parameter \( k_p/k_t^{1/2} \) and its 95% confidence intervals have been estimated from the conversion data:

\[
\left( \frac{k_p}{k_t^{1/2}} \right)_{\text{DMAEM,60°C}} = 32.73 \pm 2.17 \frac{L^{1/2}}{\text{mol}^{1/2} \text{min}^{1/2}}
\]

Previous experimental values for the activation energy of DMAEM polymerizations are summarized in the following Table:
Figure 3.14: Kinetics of the inverse-microsuspension homopolymerization of DMAEM at 60°C. (*) Conversion data measured by HPLC, (———): Model prediction. Experimental conditions: \([\text{Monomer}] = 0.637 \text{ mol/L}_w, \ [\text{AIBN}] = 3.327 \times 10^{-3} \text{ mol/L}_w, \Phi_{w0} = 0.74.\)
\[ \frac{k_p}{k_t^{1/2}} \text{ (DMAEM)} = 1.68 \cdot 10^{13} \exp\left( \frac{-17,850}{RT} \right) \frac{L^{1/2}}{\text{mol}^{1/2} \text{min}^{1/2}} \]

Although these magnitudes are quite large, \( E_a \) is typically of the order 5 kcal/mol, they appear reliable in light of the very low rates found in this research for polymerizations at 40°C (\( R_p = 0 \) over 5 hours).

Using the median activation energy from the table the following Arrhenius expression for \( \frac{k_p}{k_t^{1/2}} \) is obtained:

Figure 3.15 shows the conversion-time data for the potassium persulfate initiated polymerization of dimethylaminoethyl acrylate in aqueous solution. The corresponding monomer and initiator levels were 0.350 mol/L and 1.27 \( \cdot \) 10\(^{-4} \) mol/L respectively. The classical free radical polymerization expression can again be applied to these kinetics provided an estimate of the initiator decomposition rate (\( k_d = 2.12 \cdot 10^{18} \exp(-33320/RT) \), Koltzoff, 1951; Shawki, 1978) and the efficiency of initiation are available. For reactions with highly purified reagents in contaminant free media Riggs (1967), Singh (1979) and Kim (1984) have indicated that \( f \) deviates insignificantly from unity. Using an arbitrary value of \( f = 1.0 \) the rate parameter \( \frac{k_p}{k_t^{1/2}} \) can be estimated:

\[ \frac{k_p}{k_t^{1/2}} \text{ (DMAEA, 60°C)} = 25.29 \pm 1.99 \frac{L^{1/2}}{\text{mol}^{1/2} \text{min}^{1/2}} \]
Figure 3.15: Kinetics of the aqueous solution polymerization of DMAEA at 60°C. (•): Conversion data measured by HPLC, (———): Model prediction. Experimental conditions: $[\text{Monomer}] = 0.350 \text{ mol/L}_w$, $[\text{K}_2\text{S}_2\text{O}_8] = 0.127 \cdot 10^{-3}$ mol/L$_w$. 
The ninety five percent confidence limits are narrow, as was also found for DMAEM. This reflects the accuracy of the HPLC method for residual monomer concentration determination. Furthermore, the magnitude was near\(^{10}\) to what was estimated for DMAEM, as was expected based on prior research. This is significant since \(k_P/k_{t^{1/2}}\) was determined for DMAEM in inverse-microsuspension and for DMAEA in solution. This suggests that the calculated value for the heterophase initiator efficiency, and indeed the entire heterophase initiation efficiency model (Chapter 2, section 3.2.1) is reliable and consistent with independent experimental observation.

Using Luskin's value of the activation energy for DMAEA polymerizations the Arrhenius expression for \(k_P/k_{t^{1/2}}\) is:

\[
\frac{k_P}{k_{t^{1/2}}}_{\text{DMAEA}} = 7.61 \cdot 10^{13} \left(\frac{-19,020}{RT}\right) \frac{L^{1/2}}{\text{mol}^{1/2} \text{min}^{1/2}}
\]

3.2 Copolymerization of Acrylamide and Cationic Monomers in Solution:

Estimation of Reactivity Ratios

3.2.1 The Error-in-Variables Method

The error-in-variables method was used for the estimation of the reactivity ratios. This method was developed by Reilly et al. (1974,1981), and was first applied for the determination of reactivity ratios by O'Driscoll and Reilly (1980,1985). In this chapter, a modified version by MacGregor and Sutton (1977) adapted by Cloor (1987) for a continuous stirred tank reactor was used. The error-in-variables method shows two important advantages compared to the other common methods for the determination of copolymer reactivity ratios such as Fineman-Ross (1950) or Kelen-Tudos (1975). First, it accounts for the errors in

\(^{10}\) With the efficiency of initiation arbitrarily set at 0.77, a very plausible value for potassium persulfate, \(k_P/k_{t^{1/2}}\), is identical for DMAEA and DMAEM.
both dependent and independent variables; the other estimation methods assume the measured values of monomer concentration and copolymer composition have no variance. Secondly, it computes the joint confidence region for the reactivity ratios, the area of which is proportional to the total estimation error.

The use of a continuous stirred tank reactor permits one to apply the instantaneous copolymer equation for reactivity ratios estimation.

\[ F_1 = \frac{r_1 f_1^2 + f_1(1 - f_1)}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \]  \hspace{1cm} (3.1)

with

\[ f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad \text{and} \quad F_1 = \frac{m_1}{m_1 + m_2} \]

where \( r_1 \) and \( r_2 \) are the reactivity ratios, \( M_1 \) and \( M_2 \) the monomer concentrations at the outlet of the reactor and \( m_1 \) and \( m_2 \) the monomer bound in the copolymer. In this chapter the index 1 refers always to the AAM and the index 2 to the cationic monomer. Equation 3.1 may be written as

\[ \text{Residual} (R) = \frac{r_1 f_1^2 + f_1(1 - f_1)}{(r_1 + r_2 - 2)f_1^2 + 2(1 - r_2)f_1 + r_2} \cdot F_1 \]  \hspace{1cm} (3.2)

and the residual for each observation of a series can be determined. Afterwards \( r_1 \) and \( r_2 \) are estimated in a nonlinear regression where the sum of the squared residuals weighted in relation to the variance is minimized using Marquardt’s procedure. The variance of the residuals can be determined by summing the products of the partial differential of the residuals for each variable and the variances of the variables.

\[ V_R = \left( \frac{\partial R}{\partial [M_1]} \right)^2 V_{M_1} + \left( \frac{\partial R}{\partial [M_2]} \right)^2 V_{M_2} + \left( \frac{\partial R}{\partial F_1} \right)^2 V_{F_1} \]  \hspace{1cm} (3.3)
V represents the variance and R the residual of equation (3.2). The confidence region can be determined by plotting the sum of squares contour for several $r_1$ and $r_2$ values which satisfy the instantaneous copolymer equation for the variables given.

3.2.2 Reactivity Ratios in Solution Polymerization

Table 3.4 lists the monomer concentrations and their variances experimentally determined by HPLC as well as the mol fractions of AAM in the copolymer and its variances for the copolymerization of AAM with DMAEM at 60°C using ACV and KPS as initiators. From these data, the reactivity ratios and their confidence regions were calculated. The same calculations were performed for the copolymerization of DMAEA and DADMAC with the results listed in Table 3.5. Figures 3.16 to 3.18 show the 95% confidence regions of these reactivity ratios. The 95% confidence regions for the copolymerization of AAM and DMAEM with ACV and KPS overlap extensively and the reactivity ratios determined with the two initiators are not significantly different. A slight difference can be explained by the fact that KPS is charged and, therefore, interactions with the cationic monomer are possible. The temperature variation causes also only slight changes in the reactivity ratios, as is to be expected. Figures 3.19 to 3.21 show plots of the instantaneous copolymer composition equation for the reactivity ratios determined for these three systems. An azeotropics point is only observed for the system AAM/DMAEA.

For the system AAM/DADMAC, good agreement with the results of Jaeger and Wandrey was found (Table 3.6). According to the results obtained by these authors at various monomer concentrations and those obtained for a monomer concentration of 0.5 mol/L in this work, the reactivity ratios of both monomers decrease slightly with decreasing monomer concentration.
Table 3.4: Residual monomer concentrations and mol fraction of AAM in the polymer for the copolymerization of AAM and DMAEM with KPS and ACV at 60°C in solution at various feed ratios.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Sample Number</th>
<th>[M₁] (AAM) mol/L</th>
<th>V₁</th>
<th>[M₂] (DMAEM) mol/L</th>
<th>V₂</th>
<th>F₁</th>
<th>V₁F₁</th>
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</thead>
<tbody>
<tr>
<td>ACV</td>
<td>I-Mono</td>
<td>0.384</td>
<td>0.0010</td>
<td>0.116</td>
<td>0.00001</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>I-7</td>
<td>0.236</td>
<td>0.0005</td>
<td>0.054</td>
<td>0.00002</td>
<td>0.703</td>
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</tr>
<tr>
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<td>I-9</td>
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<td>0.00001</td>
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<td>0.00001</td>
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</tr>
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<td>KPS</td>
<td>II-Mono</td>
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<td>0.0010</td>
<td>0.116</td>
<td>0.00001</td>
<td>–</td>
<td>–</td>
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<td>0.147</td>
<td>0.00002</td>
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<td>0.0010</td>
</tr>
<tr>
<td></td>
<td>IV-9</td>
<td>0.106</td>
<td>0.0006</td>
<td>0.146</td>
<td>0.00001</td>
<td>0.242</td>
<td>0.0012</td>
</tr>
<tr>
<td></td>
<td>IV-11</td>
<td>0.106</td>
<td>0.0005</td>
<td>0.146</td>
<td>0.00002</td>
<td>0.242</td>
<td>0.0010</td>
</tr>
<tr>
<td></td>
<td>IV-12</td>
<td>0.107</td>
<td>0.0004</td>
<td>0.149</td>
<td>0.00002</td>
<td>0.243</td>
<td>0.0010</td>
</tr>
<tr>
<td>KPS</td>
<td>V-Mono</td>
<td>0.266</td>
<td>0.0005</td>
<td>0.232</td>
<td>0.00005</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>V-9</td>
<td>0.177</td>
<td>0.0007</td>
<td>0.107</td>
<td>0.00002</td>
<td>0.420</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>V-11</td>
<td>0.202</td>
<td>0.0005</td>
<td>0.123</td>
<td>0.00001</td>
<td>0.376</td>
<td>0.0010</td>
</tr>
<tr>
<td></td>
<td>V-12</td>
<td>0.193</td>
<td>0.0005</td>
<td>0.115</td>
<td>0.00002</td>
<td>0.392</td>
<td>0.0010</td>
</tr>
<tr>
<td></td>
<td>V-13</td>
<td>0.173</td>
<td>0.0004</td>
<td>0.105</td>
<td>0.00003</td>
<td>0.429</td>
<td>0.0010</td>
</tr>
<tr>
<td>ACV</td>
<td>VI-Mono</td>
<td>0.182</td>
<td>0.0007</td>
<td>0.318</td>
<td>0.00002</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>VI-7</td>
<td>0.127</td>
<td>0.0004</td>
<td>0.164</td>
<td>0.00001</td>
<td>0.262</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>VI-8</td>
<td>0.122</td>
<td>0.0003</td>
<td>0.159</td>
<td>0.00002</td>
<td>0.275</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>VI-10</td>
<td>0.130</td>
<td>0.0003</td>
<td>0.172</td>
<td>0.00001</td>
<td>0.262</td>
<td>0.0014</td>
</tr>
<tr>
<td></td>
<td>VI-11</td>
<td>0.135</td>
<td>0.0003</td>
<td>0.178</td>
<td>0.00001</td>
<td>0.250</td>
<td>0.0014</td>
</tr>
</tbody>
</table>

ACV = azocyanovarlic acid, KPS = potassium persulfate
Table 3.5: Reactivity ratios of the polymerization of acrylamide with different cationic monomers at various conditions.

<table>
<thead>
<tr>
<th>Monomer System</th>
<th>$r_1$ (AAM)</th>
<th>$r_2$ (Cationic)</th>
<th>Initiator</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAM/DMAEM†</td>
<td>0.49 ± 0.15</td>
<td>2.46 ± 0.40</td>
<td>ACV</td>
<td>60</td>
</tr>
<tr>
<td>AAM/DMAEM</td>
<td>0.61 ± 0.07</td>
<td>2.52 ± 0.19</td>
<td>KPS</td>
<td>60</td>
</tr>
<tr>
<td>AAM/DMAEM†</td>
<td>0.43 ± 0.18</td>
<td>2.39 ± 0.38</td>
<td>ACV</td>
<td>45</td>
</tr>
<tr>
<td>AAM/DMAEA††</td>
<td>0.29 ± 0.07</td>
<td>0.34 ± 0.09</td>
<td>ACV</td>
<td>60</td>
</tr>
<tr>
<td>AAM/DMAEA††</td>
<td>0.33 ± 0.09</td>
<td>0.40 ± 0.11</td>
<td>ACV</td>
<td>45</td>
</tr>
<tr>
<td>AAM/DADMAC</td>
<td>6.4 ± 0.4</td>
<td>0.06 ± 0.03</td>
<td>ACV</td>
<td>50</td>
</tr>
</tbody>
</table>

ACV = azocyanoverlicacid,  KPS = potassium persulfate.

†  $r_1 = 7.823 \exp(-923/T)$,  $r_2 = 4.538 \exp(-204/T)$

†† $r_1 = 1.871 \times 10^{-2} \exp(913/T)$,  $r_2 = 1.083 \times 10^{-2} \exp(1148/T)$
Figure 3.16: Joint confidence regions for the reactivity ratios in the system AAM/DMAEM at 60°C. (______): With K$_2$S$_2$O$_3$ as initiator, (-----): With ACV as the initiator.
Figure 3.17: Joint confidence region for the reactivity ratios in the system AAM/DMAEA at 60°C with ACV as the initiator.
Figure 3.18: Joint confidence region for the reactivity ratios in the system AAM/DADMAC at 50°C with ACV as the initiator.
Figure 3.19: Copolymer composition diagram for the system AAM/DMAEM. 
(________): 60°C with ACV as the initiator, (____ . ____): 60°C with 
$\text{K}_2\text{S}_2\text{O}_8$ as the initiator, (-----): 45°C with ACV as the initiator.
Figure 3.20: Copolymer composition diagram for the system AAM/DMAEA with ACV as the initiator. (———): 60°C, (-----): 45°C. Azeotropic composition: 0.481.
Figure 3.21: Copolymer composition diagram for the system AAM/DADMAC at 50°C.
Table 3.6: Comparison of the reactivity ratios determined by different authors for the copolymerization of acrylamide with diallyldimethylammonium chloride.

<table>
<thead>
<tr>
<th>$r_1$</th>
<th>$r_2$</th>
<th>Monomer Concentration [mol/L]</th>
<th>Temperature (°C)</th>
<th>Range of Feed Ratios ($r_1$)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4 ± 0.4</td>
<td>0.06 ± 0.03</td>
<td>0.5</td>
<td>50</td>
<td>0.3→0.7</td>
<td>This work</td>
</tr>
<tr>
<td>6.7</td>
<td>0.58</td>
<td>1.5</td>
<td>20</td>
<td>0.1→0.9</td>
<td>Tanaka (1986)</td>
</tr>
<tr>
<td>6.62*</td>
<td>0.074*</td>
<td>3.0</td>
<td>35</td>
<td>0.11→0.89</td>
<td>Jaeger &amp; Wandrey (1985)</td>
</tr>
<tr>
<td>7.14*</td>
<td>0.22*</td>
<td>4.0</td>
<td>35</td>
<td>0.2→0.72</td>
<td>Jaeger &amp; Wandrey (1985)</td>
</tr>
<tr>
<td>7.54+</td>
<td>0.049+</td>
<td>5.75</td>
<td>47</td>
<td>0.2→0.3</td>
<td>Huang et al. (1986)</td>
</tr>
</tbody>
</table>

* These are average values, since $r_1$ and $r_2$ were observed to depend on the feed ratio.

+ Determined in inverse emulsion polymerization.
The accuracy of the reactivity ratios determined by HPLC and colloid titration are compared in Figure 3.22. The errors involved in colloid titration are several orders of magnitude larger than for HPLC. Furthermore, the individual 95% confidence intervals from colloid titration surround the origin, which implies that inferences based on such data are arbitrary and insignificant. Therefore, reactivity ratios which have been estimated from colloid titration must be regarded with extreme skepticism. The reactivity ratios estimated by EVM-HPLC are recommended.

$^{13}$C-NMR measurements confirmed that five member rings were formed in the copolymerization of DADMAC and AAM. A typical NMR spectra is shown in Figure 3.23. The assignments agree with those made by Lancaster for DADMAC homopolymers (1976). It is also shown that the compositions obtained by HPLC and NMR agreed reasonably well. However, the time required for an NMR analysis is about 20 hours and it is obviously not suitable for routine measurement of a series of samples. One HPLC measurement takes, by comparison, only about three or four minutes. The determination of the sequence length distribution may be possible by $^{13}$C-NMR as has already been described for other systems in the literature, Brar (1986). Further investigations are necessary to confirm this for these cationic copolymers.

3.3 Monomer Partitioning Between Aqueous and Organic Phases

The partition coefficient of acrylamide between double distilled deionized water and Isopar-K, with 1 wt% sorbitanmonooleate, was experimentally determined to be 0.0153. This is in excellent agreement with Glukhikh's (1987) result ($n=0.02$) measured with Toluene as an organic phase. Furthermore, since the partitioning of the quaternary ammonium monomers was also found to be significantly greater than zero (Table 3.7), the mechanism for initiation in inverse-microsuspension, developed in Chapter 2 (section 3.2.1) can be
Figure 3.22: Comparison of the joint confidence regions obtained by HPLC (______) and colloid titration (-----) for AAM/DADMAC at 50°C.
$^{13}$C NMR spectra of an AAM/DADMAC copolymer with peak assignments.

$F_1 = 0.680$ by HPLC and 0.639 by NMR.
Table 3.7: Monomer Partitioning between Aqueous and Organic Phases

<table>
<thead>
<tr>
<th>Composition of the Organic Phase (wt% sorbitanmonoooleate)</th>
<th>n_o/w ++</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acrylamide</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0153</td>
</tr>
<tr>
<td>4.0</td>
<td>0.0170</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0201</td>
</tr>
</tbody>
</table>

+ The aqueous phase consisted of 1.4 mol/L of monomer in double distilled deionized water. Isopar-K and sorbitanmonoooleate comprised the organic phase.

++ (mol/L)_o / (mol/L)_w
generalized to include copolymerizations of acrylamide with these cationic monomers. This will be the topic of discussion in the section 3.4.

The partitioning measurements also demonstrate that sorbitan emulsifiers promote the solubility of acrylamide and dimethylamines in aliphatic media. This was originally postulated by McKechnie (1982) and provides experimental verification of Candau's (1988) inference that the interfacial region in inverse-microemulsion polymerization contains appreciable levels of unreacted monomer. The monomer-emulsifier interaction also provides a credible explanation for the interfacial propagation reaction proposed by Hunkeler (Chapter 2, section 3.1).

3.4 Copolymerization of Acrylamide and Cationic Monomers in Inverse-Microsuspension

3.4.1 Mechanism

The mechanism derived in the second chapter can easily be extended to copolymerizations by considering the unique reactivities of two monomers and two types of macroradicals; the latter distinguished by the composition of the terminal chain unit. For the notation used in this thesis: subscript 1 denotes acrylamide and 2 the cationic comonomer.

Oil Phase Reactions

Initiation

1. \[ I \rightarrow 2 R_{in,0} \]
Reactions of primary radicals

2. \[ R_{in,0}^* + HC \rightarrow \text{Inert products} \quad k_1 \]

3. \[ R_{in,0}^* + E \rightarrow \text{Inert products} \quad k_2 \]

4. \[ R_{in,0}^* + M_{1,0} \rightarrow R_{i,1,0}^* \quad k_{p1} \]

5. \[ R_{in,0}^* + M_{2,0} \rightarrow R_{i,2,0}^* \quad k_{p2} \]

Where \( R_{i,j}^* \) is a radical of length \( i \) with an end unit of type \( j (j = 1,2) \). The subscript \( o \) denotes an oil phase concentration. \( R_{in}^* \) designates a primary radical.

Propagation

6. \[ R_{r,1,0}^* + M_{1,0} \rightarrow R_{r+1,1,0}^* \quad k_{p11} \]

7. \[ R_{r,1,0}^* + M_{2,0} \rightarrow R_{r+1,2,0}^* \quad k_{p12} \]

8. \[ R_{r,2,0}^* + M_{1,0} \rightarrow R_{r+1,1,0}^* \quad k_{p21} \]

9. \[ R_{r,2,0}^* + M_{2,0} \rightarrow R_{r+1,2,0}^* \quad k_{p22} \]

Where \( I \) and \( M \) denote the initiator and monomer respectively.

Transfer between Phases

10. \[ \phi_{m1} M_{1,0} = M_{1,w} \]
11. \[ M_{2,o} \rightleftharpoons M_{2,w} \]

12. \[ R^*_{in,o} \rightarrow R^*_{in,w} \]

13. \[ R^*_{r,1,o} \rightarrow R^*_{r,1,w} \]

14. \[ R^*_{r,2,o} \rightarrow R^*_{r,2,w} \]

Where the subscript \( w \) denotes a water phase concentration and \( k_{r,ij} \) is the mass transfer constant between the organic and aqueous phases for a macroradical of length \( i \) with terminal monomer group \( j \).

Aqueous Phase Reactions

Reactions of Primary Radicals

15. \[ R^*_{in,w} + M_{1,w} \rightarrow R^*_{1,1,w} \]

16. \[ R^*_{in,w} + M_{2,w} \rightarrow R^*_{1,2,w} \]

Propagation

17. \[ R^*_{r,1,w} + M_{1,w} \rightarrow R^*_{r+1,1,w} \]

18. \[ R^*_{r,1,w} + M_{2,w} \rightarrow R^*_{r+1,2,w} \]

19. \[ R^*_{r,2,w} + M_{1,w} \rightarrow R^*_{r+1,1,w} \]
20. \[ R_{r,2,w}^* + M_{2,w} \xrightarrow{k_{p22}} R_{r+1,2,w}^* \]

21. \[ "R_{r,1,w}^* + M_{1,w} \xrightarrow{k_{p11}} "R_{r+1,1,w}^* \]

22. \[ "R_{r,1,w}^* + M_{2,w} \xrightarrow{k_{p12}} "R_{r+1,2,w}^* \]

23. \[ "R_{r,2,w}^* + M_{1,w} \xrightarrow{k_{p21}} "R_{r+1,1,w}^* \]

24. \[ "R_{r,2,w}^* + M_{2,w} \xrightarrow{k_{p22}} "R_{r+1,2,w}^* \]

Where "\( R^* \) denotes a macroradical with a terminally unsaturated hydrocarbon.

**Unimolecular Termination with Interfacial Emulsifier**

25. \[ R_{r,1,w}^* + \Gamma_E \xrightarrow{k_{IE}} P_r + E^* \]

26. \[ "R_{r,1,w}^* + \Gamma_E \xrightarrow{k_{IE}} "P_r + E^* \]

27. \[ R_{r,2,w}^* + \Gamma_E \xrightarrow{k_{IE2}} P_r + E^* \]

28. \[ "R_{r,2,w}^* + \Gamma_E \xrightarrow{k_{IE2}} "P_r + E^* \]

Where \( \Gamma_E \) denotes interfacial emulsifier. Steps 26 and 28 are negligible since at any instant in the reaction \[ "R^* \ll [R^*] \].

**Reactions of Emulsifier Radicals**

29. \[ E^* + M_{1,w} \xrightarrow{k_{p1}} "R_{l,1,w}^* \]
30.  
\[ \text{E}^* + M_{a,w} \xrightarrow{k_p} \text{"R}_{1,2,w} \]  

31.  
\[ \text{E}^* + \text{HC}_{\text{imp}} \xrightarrow{k_5} \text{Inert Products} \]  

Where HC_{imp} designates hydrocarbon phase impurities or radical scavengers.

**Transfer to Monomer**

32.  
\[ \text{R}^*_{r,1,w} + M_{1,w} \xrightarrow{k_{fm11}} \text{P} + \text{R}^*_{1,1,w} \]  

33.  
\[ \text{"R}^*_{r,1,w} + M_{1,w} \xrightarrow{k_{fm11}} \text{"P} + \text{R}^*_{1,1,w} \]  

34.  
\[ \text{R}^*_{r,1,w} + M_{2,w} \xrightarrow{k_{fm12}} \text{P} + \text{R}^*_{1,2,w} \]  

35.  
\[ \text{"R}^*_{r,1,w} + M_{2,w} \xrightarrow{k_{fm12}} \text{"P} + \text{R}^*_{1,2,w} \]  

36.  
\[ \text{R}^*_{r,2,w} + M_{1,w} \xrightarrow{k_{fm21}} \text{P} + \text{R}^*_{1,1,w} \]  

37.  
\[ \text{"R}^*_{r,2,w} + M_{1,w} \xrightarrow{k_{fm21}} \text{"P} + \text{R}^*_{1,1,w} \]  

38.  
\[ \text{R}^*_{r,2,w} + M_{2,w} \xrightarrow{k_{fm22}} \text{P} + \text{R}^*_{1,2,w} \]  

39.  
\[ \text{"R}^*_{r,2,w} + M_{2,w} \xrightarrow{k_{fm22}} \text{"P} + \text{R}^*_{1,2,w} \]  

**Transfer to Terminal Double Bonds**

40.  
\[ \text{"P} + \text{R}^*_{a,1,w} \xrightarrow{k_1} \text{R}^*_{r+s,1,w} \]
41. 
\[ \text{"P}_r^* + \text{"R}_{s,1,w}^* \rightarrow + \text{"R}_{r+s,1,w}^* \]
\[ k_1^* \]

42. 
\[ \text{"P}_r + \text{"R}_{s,2,w}^* \rightarrow + \text{"R}_{r+s,2,w}^* \]
\[ k_2^* \]

43. 
\[ \text{"P}_r + \text{"R}_{s,2,w}^* \rightarrow + \text{"R}_{r+s,2,w}^* \]
\[ k_2^* \]

By analogy to the mechanism for unimolecular termination, reactions 41 and 43 are negligible compared with steps 40 and 42 since \([\text{"R}^*] < < [\text{R}^*] \).

**Termination by Disproportionation**

44. 
\[ \text{"R}_{r,1,w}^* + \text{"R}_{s,1,w}^* \rightarrow \text{P}_r + \text{P}_s \]
\[ k_{t11} \]

45. 
\[ \text{R}_{r,1,w}^* + \text{"R}_{s,1,w}^* \rightarrow \text{P}_r + \text{"P}_s \]
\[ k_{t11} \]

46. 
\[ \text{"R}_{r,1,w}^* + \text{"R}_{s,1,w}^* \rightarrow \text{"P}_r + \text{"P}_s \]
\[ k_{t11} \]

47. 
\[ \text{R}_{r,1,w}^* + \text{"R}_{s,2,w}^* \rightarrow \text{P}_r + \text{P}_s \]
\[ k_{t12} \]

48. 
\[ \text{R}_{r,1,w}^* + \text{"R}_{s,2,w}^* \rightarrow \text{P}_r + \text{"P}_s \]
\[ k_{t12} \]

49. 
\[ \text{"R}_{r,1,w}^* + \text{"R}_{s,2,w}^* \rightarrow \text{"P}_r + \text{P}_s \]
\[ k_{t12} \]

50. 
\[ \text{"R}_{r,1,w}^* + \text{"R}_{s,2,w}^* \rightarrow \text{"P}_r + \text{"P}_s \]
\[ k_{t12} \]

51. 
\[ \text{R}_{r,2,w}^* + \text{"R}_{s,2,w}^* \rightarrow \text{P}_r + \text{P}_s \]
\[ k_{t22} \]
52. 
\[ R_{r,2,w}^* + R_{s,2,w}^* \xrightarrow{k_{122}} P_r + P_s \]

53. 
\[ R_{r,2,w}^* \xrightarrow{k_{122}} P_r + P_s \]

3.4.2 Derivation of the Kinetic Model

The derivation of the kinetic equations from the mechanism is analogous to the procedure outlined in Chapter 2 for homopolymers, and will only be highlighted in the following discussion.

3.4.2.1 Balance on Macroradicals

\( R^*_r \) and \( R^*_s \) are defined as macroradical chains with \( r \) monomer segment units. The superscript " distinguishes chains with terminal double bonds.

The total macroradical concentration can be expressed as:

\[ [R^*_r] = [R^*_r] + ["R^*_r] \]

where

\[ [R^*_r] = \sum_{r=1}^{\infty} [R^*_r] \] and \[ ["R^*_r] = \sum_{r=1}^{\infty} ["R^*_r] \]

We may also distinguish between macroradicals with terminal monomer groups of type 1 \( (R^*_1) \) and type 2 \( (R^*_2) \). Therefore:

\[ [R^*_r] = [R^*_1] + [R^*_2] \]

\[ ["R^*_r] = ["R^*_1] + ["R^*_2] \]

We can also define:

\[ [R^*_{1T}] = [R^*_1] + ["R^*_1] \]

\[ [R^*_{2T}] = [R^*_2] + ["R^*_2] \]
Where the subscript "w" has been deleted from macroradical concentrations for brevity. For the remainder of the discussion it is, however, implied that all macromolecular species are expressed in aqueous phase units.

The balance for macroradicals with terminal acrylamide units and no terminal double bonds\(^\text{11}\) is:

\[
\frac{d [R_1^*]}{dt} = k_{p1} [R_{in,w}^*][M_{1,w}] + k_{p21} [R_2^*][M_{1,w}] - k_{p12} [R_1^*][M_{2,w}]
- k_{re} [R_1^*] E + k_{fm21} [R_2^*][M_{1,w}] - k_{fm12} [R_1^*][M_{2,w}]
- k_{t11} [R_1^*] (R_{1T}^*) - k_{t12} [R_1^*] (R_{2T}^*) = 0
\]  
(3.4)

The balance for macroradicals with terminal acrylamide units and a terminally unsaturated hydrocarbon is:

\[
\frac{d ["R_1^*]}{dt} = k_{p1} [E^*][M_{1,w}] + k_{p21} ["R_2^*][M_{1,w}] - k_{p12} ["R_1^*][M_{2,w}]
- k_{re} ["R_1^*] E - k_{fm12} ["R_1^*][M_{2,w}]
- k_{t11} ["R_1^*] ("R_{1T}^*) - k_{t12} ["R_1^*] ("R_{2T}^*) = 0
\]  
(3.5)

Summing equations 3.4 and 3.5 we obtain a balance for all types of macroradicals with terminal acrylamide groups. Analogous balances for macroradicals with terminal quaternary an monium monomer units, with and without terminal double bonds are:

\[
\frac{d [R_2^*]}{dt} = k_{p2} [R_{in,w}^*][M_{2,w}] + k_{p12} [R_1^*][M_{2,w}] - k_{p21} [R_2^*][M_{1,w}]
- k_{re2} [R_2^*] E + k_{fm12} [R_1^*][M_{2,w}] - k_{fm21} [R_2^*][M_{1,w}]
- k_{t22} [R_2^*] (R_{2T}^*) - k_{t12} [R_2^*] (R_{1T}^*) = 0
\]  
(3.6)

\(^\text{11}\) It will be assumed that primary radicals are the dominant transferring species between phases. The partitioning of macroradicals with length greater than 1 is therefore, as a first approximation, completely in the aqueous phase.
\[
\frac{d[^{\infty}R^e_2]}{dt} = k_p [E^e_1][M_{j,w}] + k_{p21}[^{\infty}R^e_2][M_{2,w}] - k_{p21}[^{\infty}R^e_2][M_{1,w}]
\]

\[\quad - k_{\text{fE2}}[^{\infty}R^e_2][R^e_T] - k_{\text{f22}}[^{\infty}R^e_2][R^e_{1T}] = 0\]  

(3.7)

By summing equations 3.6 and 3.7 the total balance for macroradicals with terminal cationic monomer groups can be derived. Alternatively, we can calculate the overall macroradical concentration by summing equations 3.4 to 3.7.\(^{12}\)

\[
\frac{d[R^e]}{dt} = R_1 + R_1' - \Gamma_e \left( k_{\text{fE}} [R^e_{1T}] + k_{\text{fE2}} [R^e_{2T}] \right)
\]

\[\quad - k_{t11} [R^e_{1T}]^2 - 2 k_{t12} [R^e_{1T}][R^e_{2T}] - k_{t22} [R^e_{2T}] = 0\]  

(3.8)

Where \(R_1\) and \(R_1'\) are the rates of initiation from primary and emulsifier radicals. These can respectively be expressed as:

\[R_1 = [R^e_{1n,w}] (k_{p1} [M_{1,w}] + k_{p2} [M_{2,w}])\]

\[R_1' = [E^e_1] (k_{p1} [M_{1,w}] + k_{p2} [M_{2,w}])\]

Invoking the long chain approximation, the concentration of macroradicals with terminal acrylamide and quaternary ammonium groups can be related:

\[k_{p21} [M_{1,w}] [R^e_{2T}] = k_{p12} [M_{2,w}] [R^e_{1T}] \pm 1\]

\[\quad = k_{p12} [M_{2,w}] [R^e_{1T}]\]

Therefore

\[ [R^e_{2T}] = \frac{k_{p12} [M_{2,w}]}{k_{p21} [M_{1,w}]} [R^e_{1T}] \]  

(3.9)

and

\(^{12}\) Transfer to monomer from macroradicals containing unsaturated hydrocarbons has been neglected since \(k_{\text{fml}}[^{\infty}R^e] < k_p[R^e_{in}]\)
\[ [R_{1}^{e}] = [R_{1}^{e}]_0 \left(1 + \frac{k_{p12}}{k_{p21}} \frac{[M_{2,w}]}{[M_{1,w}]}\right) \]  

Substituting equation 3.9 into 3.8 and simplifying:

\[ [R_{1}] + [R_{1}^{e}] - \langle k_{fE,group} \rangle [R_{1}^{e}] \Gamma_E - \langle k_{td,group} \rangle [R_{1}^{e}]^2 = 0 \]  

(3.11)

Where \( k_{fE,group} \) and \( k_{td,group} \) are grouped pseudo-rate constants for transfer to emulsifier and disproportionation termination. These are expressed as:

\[ k_{fE,group} = k_{fE} + k_{fE2} \left( \frac{k_{p12}}{k_{p21}} \frac{[M_{2,w}]}{[M_{1,w}]} \right) \]  

(3.11a)

\[ k_{td,group} = k_{t11} + 2k_{t12} \left( \frac{k_{p12}}{k_{p21}} \frac{[M_{2,w}]}{[M_{1,w}]} \right) + k_{t22} \left( \frac{k_{p12}}{k_{p21}} \frac{[M_{2,w}]}{[M_{1,w}]} \right)^2 \]  

(3.11b)

Where

\[ k_{t12} = 2(k_{t11} \cdot k_{t22})^{1/2} \]  

(3.11c)

The balance on emulsifier radicals is given by:

\[ \frac{d[E^e]}{dt} = (k_{fE,group}) [R_{1}^{e}] \Gamma_E - k_{p1} [E^e] [M_{1,w}] - k_{p2} [E^e] [M_{2,w}] \]

\[ - k_{5} [E^e] [HC_{imp}] = 0 \]  

(3.12)

Rearranging equation 3.12 in terms of \( R_1^{e} \):

\[ R_1^{e} = \frac{\langle k_{fE,group} \rangle [R_{1}^{e}] \Gamma_E}{k_{5} [HC_{imp}] \left(1 + \frac{k_{p11}}{k_{p12}} \frac{[M_{1,w}]}{[M_{2,w}]} + k_{p22} \frac{[M_{1,w}]}{[M_{2,w}]} \right)} \]  

(3.13)

Combining equations 3.11 and 3.12 yields:

\[ 2 \Gamma_d + k_{fE,group} \left(1 - f_e \right)[R_{1}^{e}] \Gamma_E - k_{td,group} [R_{1}^{e}]^2 = 0 \]  

(3.14)

Where

\[ f_e = \frac{1}{k_{5} [HC_{imp}] \left(1 + \frac{k_{p11}}{k_{p22}} \frac{[M_{1,w}]}{[M_{2,w}]} + k_{p22} \frac{[M_{1,w}]}{[M_{2,w}]} \right)} \]
This is analogous to the expression for the efficiency of initiation by emulsifier radicals derived in Chapter 2.

Equation 3.14 is a quadratic which can be solved for \([R^*_{1T}]\). The concentrations \([R^*_{2T}]\) and \([R^*_{1T}]\) can then be computed from equations 3.9 and 3.10 respectively.

3.4.2.2 Monomer Consumption Rate

The rate of consumption of acrylamide and the quaternary ammonium monomer can be expressed as:

\[
- \frac{d [M_{1,w}]}{dt} = k_{p11} [M_{1,w}] [R^*_{1T}] + k_{p21} [M_{1,w}] [R^*_{2T}]
\]

\[
- \frac{d [M_{2,w}]}{dt} = k_{p22} [M_{2,w}] [R^*_{2T}] + k_{p12} [M_{2,w}] [R^*_{1T}]
\]

or in a more convenient form:

\[
\frac{d [M_{1,w}]}{dt} = -k_{p11} [R^*_{1T}] \left( [M_{1,w}] + \frac{[M_{2,w}]}{r_1} \right) \tag{3.15}
\]

\[
\frac{d [M_{2,w}]}{dt} = -k_{p12} [R^*_{1T}] \left( [M_{2,w}] + r_2 \frac{[M_{2,w}]^2}{[M_{1,w}]} \right) \tag{3.16}
\]

From equations 3.15 and 3.16 it is clear that the relative consumption rate the monomers \((d[M_1]/d[M_2])\), and the copolymer composition, is determined exclusively from the reactivity ratios and the monomer concentrations and is independent of all other experimental conditions.

3.4.2.3 Balance on Initiator

\[
\frac{d[I]}{dt} = -k_d [I] \tag{3.17}
\]
3.4.2.4 The Efficiency of Initiation of Primary Radicals

By an identical procedure to that described in Chapter 2 (Section 3.2), the efficiency of initiation can be shown to be expressed by:

\[ f = \frac{1}{1 + \frac{\phi_r}{k_r^*} \left( \frac{k_1[HCl]}{a_{sp}} + \frac{k_4[E_0]}{a_{sp}} + \frac{k_{p1}[M_{1,w}]}{a_{sp}} + \frac{k_{p2}[M_{2,w}]}{a_{sp}} \right) \cdot \frac{v_o}{v_w}} \]

For the special case where the efficiency does not depend on monomer concentration this can be simplified to yield:

\[ f = \frac{1}{1 + \frac{\phi_r}{k_r^*} \left( \frac{k_1[HCl]}{a_{sp}} + \frac{k_4[E_0]}{a_{sp}} \right) \cdot \frac{v_o}{v_w}} \tag{3.18} \]

Where \( k_r \) is the mass transfer constant for primary radicals, defined as:

\[ k_r = k_r^* a_{sp} \cdot \frac{v_o}{v_w} \]

and \( a_{sp} \) is the specific interfacial area per litre of oil:

\[ a_{sp} = \frac{a_T}{v_w} \]

\( a_T \) is the total interfacial area in m².

3.4.2.5 Equations for Conversion and Composition

The molar (\( X \)) and mass (\( X_m \)) conversions are respectively given by:

\[ X = 1 - \frac{[M_{1,w}] + [M_{2,w}]}{[M_{1,w}]^0 + [M_{2,w}]^0} \] \tag{3.19}

\[ X_m = 1 - \frac{M_{w1}[M_{1,w}] + M_{w2}[M_{2,w}]}{M_{w1}[M_{1,w}]^0 + M_{w2}[M_{2,w}]^0} \] \tag{3.20}

Where \( M_{w1} \) and \( M_{w2} \) are the molar masses of acrylamide and the quaternary ammonium cationic monomer. The superscript "⁰" denotes an initial concentration.
The monomer and cumulative polymer compositions are given by:

\[
f_1 = \frac{[M_{1,w}]}{[M_{1,w}] + [M_{2,w}]} \tag{3.21}
\]

\[
\bar{F}_1 = 1 - \frac{[M_{1,w}]^0 - [M_{1,w}]}{[M_{1,w}]^0 + [M_{2,w}]^0 - [M_{1,w}] - [M_{2,w}]} \tag{3.22}
\]

Therefore equations 3.11a-c and 3.14-22 constitute the kinetic model for inverse-microsuspension copolymerization. The coupled differential equations will be solved by a sixth order Runge-Kutta procedure.

### 3.5 Parameter Estimation

From the kinetic model of section 3.4 there are five unknown parameters: \(k_{p22}, k_{t22}, k_{fe2}, k_r^*\) and \(A\), the gel effect parameter defined in:

\[
k_{td} = \frac{k_t^0}{\exp (A \cdot wp)}
\]

Where \(wp\) is the weight fraction of polymer in the aqueous phase.

Of these parameters only four are independent since the propagation and termination kinetic constants are coupled through the ratio \(k_{p22}/k_{t22}^{1/2}\). Furthermore, unimolecular termination with emulsifier is likely controlled by the diffusion of the macroradical to the interface. In this case the chemical composition of the reactive endgroup is inconsequential and transfer to emulsifier occurs at approximately equal rates for macroradicals with terminal acrylamide and cationic groups. It is therefore a valid approximation to write \(k_{fe2} = k_{fe}\).

The remaining three parameters can be estimated independently from the rate and particle size data. The propagation rate constant \((k_{p22})\) will influence the initial rate of polymerization, the gel effect parameter \((A)\) will be of primary consequence at high conversions.
and the mass transfer constant \((k_T^*)\) will be inferred from measurements of the total interfacial area of the latex.

These will be estimated from the conversion and average particle diameter data using weighted non-linear least squares algorithm based on Marquardt's procedure. All experiments for a given monomer pair will be fit in a single estimation routine so that the activation energies of these parameters can be estimated directly. This is preferable to estimating unique parameters for each experiment, since the latter procedure is susceptible to over fitting inaccurate data, and therefore is incapable of isolating inconsistent results.

The results of the parameter estimation are given in Table 3.8. For copolymerizations with either dimethylamine, the gel effect parameter was not significantly greater than zero \((A < 10^{-4})\) and was therefore eliminated. The efficiency of initiation for DMAEM copolymerizations was 0.52 compared with 0.21 for DMAEA. This is consistent with the monomer partitioning experiments in section 3.3, which determined that the solubility of DMAEM in the continuous phase is 67% larger than DMAEA, at high emulsifier levels. Propagation in the continuous phase will therefore be favored for DMAEM relative to DMAEA, which will reduce the fraction of radicals scavenged by hydrocarbon phase impurities and increase the efficiency of initiation. This is strong evidence that the proposed oligoradical nucleation mechanism is correct.

For these copolymers the efficiency of initiation was found invariant to temperature, as was also observed in Chapter 2 for acrylamide homopolymers.

The quoted propagation constants for the cationic monomers are approximate and rigorously should be determined by a non-stationary method such as the rotating sector, or by direct measurement of the radical concentration by Electron Spin Resonance. Furthermore, the values determined herein are only valid in inverse-microsuspension, since (Hunkeler, 1989) has shown that propagation reactions between two charged species, in a heterophase
Table 3.8: Summary of kinetic constants for the copolymerization of acrylamide and quaternary ammonium monomers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1) AAM-DMAEM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r_1 )</td>
<td>7.823 ((-923/T))</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( r_2 )</td>
<td>4.538 exp ((-204/T))</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( k_p/k_t^{1/2})</td>
<td>(1.68 \cdot 10^{13}) exp ((-17,850/RT))</td>
<td>(L^{1/2}/(mol^{1/2} min^{1/2}))</td>
</tr>
<tr>
<td>( k_p/k_t )</td>
<td>(1.31 \cdot 10^{9} ) exp ((-17,850/RT))</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( A )</td>
<td>0.0</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( k_1 \phi_r/k_r^* )</td>
<td>(2.24 \cdot 10^{3})</td>
<td>(m^2/mol)</td>
</tr>
<tr>
<td>( k_4 \phi_r/k_r^* )</td>
<td>(5.66 \cdot 10^{1})</td>
<td>(m^2/mol)</td>
</tr>
<tr>
<td>( k_1/k_4 )</td>
<td>39.5</td>
<td>Dimensionless</td>
</tr>
<tr>
<td><strong>2) AAM-DMAEA</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( r_1 )</td>
<td>(1.871 \cdot 10^{-2}) exp ((913/T))</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( r_2 )</td>
<td>(1.083 \cdot 10^{-2}) exp ((1148/T))</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( k_p/k_t^{1/2})</td>
<td>(7.61 \cdot 10^{13}) exp ((-19,020/RT))</td>
<td>(L^{1/2}/(mol^{1/2} \cdot \text{min}^{1/2}))</td>
</tr>
<tr>
<td>( k_p/k_t )</td>
<td>(5.093 \cdot 10^{9} ) exp ((-19,020/RT))</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( A )</td>
<td>0.0</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>( k_1 \phi_r/k_r^* )</td>
<td>(7.785 \cdot 10^{3})</td>
<td>(m^2/mol)</td>
</tr>
<tr>
<td>( k_4 \phi_r/k_r^* )</td>
<td>(1.970 \cdot 10^{2})</td>
<td>(m^2/mol)</td>
</tr>
<tr>
<td>( k_1/k_4 )</td>
<td>39.5</td>
<td>Dimensionless</td>
</tr>
</tbody>
</table>

*  \( E_T = E_p \cdot E_t = E_p \) given the large magnitude of \( E_p \) and the general tendency for low activation energies for macroradical termination reactions.
environment, are reduced by the presence of oil dissolved in the aqueous phase. The magnitudes of the propagation rates are: $k_{p22,\text{DMAEM}} > k_{p22,\text{DMAEA}} > > k_{p22,\text{AAM}}$. This seems reasonable given the greater tendency for quaternary ammonium monomers to spontaneously polymerize.

### 3.6 Evaluation of the Kinetic Model Against Experimental Data

Figures 3.24 to 3.27 show experimental conversion-time data and model predictions for copolymerizations of acrylamide with DMAEM at 60, 50 and 40°C, and with DMAEA at 60°C. The kinetic model predicts the polymerization rate well over the range of conditions investigated. The inverse-microsuspension mechanism is therefore not refuted by this data. Furthermore, the magnitude of the parameter estimates are in agreement with expectation with the exception of the disproportionation termination rate constant which was found to be unaffected by diffusion limitations. This is likely the result of two effects: lower molecular weights in cationic copolymerizations relative to acrylamide homopolymers and electrostatic interactions. Both of these reduce the density of chain entanglements and the gel effect.\(^{13}\) The latter phenomena can be rationalized as follows: Charged macroradicals tend to have less configurational entropy than nonionic polymers because of the Coulombic interactions which reduce the number of sites on a hypothetical lattice for charged groups to locate. Therefore, chains grow in a more extended form with the radical avoiding the polymer-rich and charge-rich segments of its own and neighbouring chains. Hence, growing chain ends tend to propagate away from the centre of mass and into the solution where termination reactions would not likely be as hindered.

\(^{13}\) In acrylamide homo- and copolymerizations, the predominant diffusion limitation is the result of chain entanglements between the high molecular weight macromolecules. Free volume influences are negligible due to the high fraction of solvent in the reaction mixture.
Figure 3.24: Conversion-time data (■) and kinetic model predictions (-----) for an AAM/DMAEM copolymerization at 60°C. Experimental conditions: [Monomer] = 6.09 mol/L_w, [AIBN] = 3.329 \times 10^{-5} \text{ mol/L}_o, f_{10} = 0.875, \phi_{w/o} = 0.74.
Figure 3.25: Conversion-time data (■) and kinetic model predictions (---) for an AAM/MA SEM copolymerization at 50°C. Experimental conditions:

- [AIBN] = 7.373 \times 10^{-3} \text{ mol/L}_o,
- f_{10} = 0.875,
- \Phi_{w_0} = 0.74.
Figure 3.26: Conversion-time data (■) and kinetic model predictions (——) for an AAM/DMAEM copolymerization at 40°C. Experimental conditions: [Monomer] = 6.13 mol/L_w, [AIBN] = 14.83 · 10^{-3} mol/L_o, f_{10} = 0.877, ϕ_{w/o} = 0.74.
Figure 3.27: Conversion-time data (■) and kinetic model predictions (——) for an AAM/DMAEA copolymerization at 60°C. Experimental conditions: [Monomer] = 6.05 mol/L_w, [AIBN] = 3.337 x 10^{-3} mol/L_o, f_{10} = 0.840, 
Φ_{w0} = 0.74.
Composition Drift

Figures 3.28 and 3.29 illustrate the magnitude of the composition drift with conversion for copolymerizations of acrylamide with DMAEM (50°C) and DMAEA (40°C) respectively. The data are compared to the predicted copolymer composition using the reactivity ratios determined from solution polymerizations in section 3.2. The majority of the data lie within the 95% confidence region. Therefore, the hypothesis that the reactivity ratios in solution and inverse-microsuspension are equivalent is not rejected, at the ninety five percent confidence level.

The severity of the compositional inhomogeneity, even at very low conversions, renders molecular weight measurement methods invalid on these samples. Without such data we cannot verify the absence of diffusion limitations on bimolecular termination.

Particle Size

The particle sizes were found to be invariant with conversion (Figure 3.30). This confirms the model assumption of nucleation in monomer droplets, and is consistent with the trend for acrylamide homopolymerizations in Chapter 2. Measurements made by dynamic light scattering and photomicrography gave very similar results, as is shown for an inverse-microsuspension latex in Figure 3.31. The size distribution was quite broad for all samples as is to be expected for particles produced through a breakup-coalescence mechanism.

The volume-average particle size was nominally $7 \pm 1.5 \mu m$ for all polymerizations. The absence of a thermal dependence is attributed to pre-emulsification and slow agitation speeds. At 323 RPM, the power input is insufficient to induce significant droplet breakup, and the particle sizes remain as formed by the initial mixing operation.
Figure 3.28: Drift in monomer composition with conversion for an AAM/DMAEM inverse-microsuspension copolymerization at 50°C. (O): Experimental data measured by HPLC, (-----): Predicted composition based on the reactivity ratios measured in solution polymerization, (---------): 95% confidence limits based on the reactivity ratios measured in solution polymerization.
Figure 3.29: Drift in monomer composition with conversion for an AAM/DMAEA inverse-microsuspension copolymerization at 40°C. (O): Experimental data measured by HPLC, (---): Predicted composition based on the reactivity ratios measured in solution polymerization, (-----): 95% confidence limits based on the reactivity ratios measured in solution polymerization.
Figure 3.30: Trend in particle size ($d_p$) with conversion for a polymerization of DMAEA at 60°C under the following conditions: $[\text{Monomer}] = 6.05$ mol/L$_w$, $[\text{AIBN}] = 3.337 \cdot 10^{-3}$ mol/L$_w$, $f_{10} = 0.840$, $\Phi_{w0} = 0.74$. 

219
Figure 3.31: Frequency versus diameter (μm) for a particle size distribution of a latex determined by measuring the images from a photomicrograph (Figure 3.13a). The dashed vertical lines represent the number ($d_n$) and intensity ($d_i$) average particle diameter determined by dynamic light scattering. The sample was withdrawn from a DMAEA polymerization at 60°C. Additional experimental conditions were: [Monomer] = 6.05 mol/L, [AIBN] = 3.337 · 10^{-3} mol/L, $f_{i0} = 0.840, \Phi_{w/o} = 0.74$. 
3.7 Simulations

Figures 3.32 and 3.33 simulate the composition drift and initial reaction rate for copolymerizations of acrylamide with DMAEA and DMAEM respectively. The slower reactivity of the quaternary ammoniums, relative to the nonionic monomer, results in compositional heterogeneities (Figure 3.33). These are most acute over the commercial range of copolymer compositions ($F_1 \approx 0.9-0.95$) (Figure 3.32), and yield a blocky distribution of charge groups along the polymer backbone. This can only be circumvented by eliminating monomer composition drift throughout the polymerization. Continuous processes, semi-batch feed strategies and the utilization of more than one cationic monomer, each with a unique reactivity (Becker, 1985), have all been used successfully to this end.
Figure 3.32: Composition drift for copolymerizations of AAM (1) and DMAEA (2) at 60°C.
Figure 3.33: Initial rate of polymerization as a function of comonomer composition. Simulations were performed for an AAM/DMAEM copolymerization at 60°C. The monomer concentration was 0.5 mol/L. Other conditions were identical to those reported in Table 3.4 for these comonomers at the same temperature.
REFERENCES

43. Hoffmann, A.W., Justus Liebigs Annalen der Chemie, 145 (Supplement 1), 275 (1861).


CHAPTER 4
POLYMERIZATION OF ACRYLAMIDE AT HIGH MONOMER
CONCENTRATIONS

1. INTRODUCTION

Polyacrylamide homopolymers derive their utility from their long chain lengths and expanded configuration in aqueous solutions. As such they are used primarily for water modification purposes. For example, drag reduction agents function by transferring energy from the eddies to provide a laminar flow regime and decrease the hydrolytic resistance. Polyacrylamides are also applied as thickening agents (Seymour, 1965), cutting fluids (Gramain, 1981), soil stabilizers (Mowry, 1953) and to a lesser extent in gel electrophoresis (Bikales, 1973), soaps (Pye, 1963) and textile applications (Cyanamid, 1969). They are also used in emulsion or microemulsion form as cleaners and in enhanced oil recovery (Melter, 1979). Recently, hydrophobic modifications have expanded the market for polyacrylamides. For commercial applications polyacrylamide quality is derived from its moisture insensitivity, oxidative stability (Stackman, 1987) and rapid dissolution in water.

The amide substituent groups are capable of undergoing most of the reactions characteristic of their small molecule counterpart. By comparison the polymer backbone is relatively inert, although it is susceptible to attack from strong oxidizing agents, such as persulfates and peroxides (MacWilliams, 1974). Polymer degradation can occur through excessive high speed agitation (Nagashiro, 1975) or attack from hydroxy radicals (Grollman, 1982). The latter results in chain scission only in the presence of dissolved oxygen (Ramsden, 1986). Ferric ions and EDTA, often part of redox initiation systems and residual to the
product, can also enhance degradation (Ramsden, 1987). This effect is most severe at elevated temperatures (Klein, 1981).

Polyacrylamide prepared with free radical initiators is atactic in nature with the sequence length distribution conforming to Bernoullian statistics (Lancaster, 1982), as is generally observed for the addition polymerization of vinyl monomers. Isotactic polyacrylamide has, however, been prepared indirectly (Alaya, 1985) by reacting polyphenolacrylate and ammonia in dimethyl sulfoxide.

Aqueous solutions of high molecular weight polyacrylamides ($\geq$ one million daltons) experience a decrease in intrinsic viscosity with standing time. This "aging" phenomena has been interpreted as evidence of an intermolecular hydrogen bond rearrangement to a less extended structure (Kulicke, 1982). The flocculation efficiency is however unaffected by the decrease in molecular size (Hunt, 1986; Henderson, 1987).

1.1 Review of Polymerization

Acrylamide is most often polymerized by a radical addition mechanism in aqueous solution. These reactions proceed at moderate temperatures (40-60°C) in order to generate a high molecular weight linear product. At more extreme temperatures (140-160°C) or in strongly acidic media, crosslinking occurs via an intra-intermolecular imidization process (Minsk, 1974; Guerrero, 1985). The onset of polymer degradation occurs at 180°C (Molyneux, 1983). Low temperatures can also be employed, in conjunction with redox couples, which are operative down to 0°C.

The enhanced decomposition of initiators by reducing agents or "activators" was inadvertently discovered by Bacon (ICI, 1946) while testing inhibitors for persulfate initiated polymerization of acrylonitrile. This new initiation process was termed "Reduction Activation", although it is presently referred to as Reduction Oxidation. Since this discovery
there have been several investigations of acrylamide polymerization with redox pairs (Table 4.1). Other initiation methods such as irradiation by $^{60}$Co γ-rays (Collinson, 1957, 1960; Gromov, 1967), electrolytic initiation (Ogumi, 1974; Samal, 1988) and photosensitized polymerization (Dainton, 1957; Venkatarao, 1970; Rodriguez, 1985; Iwai, 1985; Fouassier, 1987) have been studied. Acrylamide can also be polymerized through an anionic mechanism to yield poly-β-alanine (Nylon 3) (Ogata, 1960), and in the solid state (Fadner and Morawetz, 1960). The latter were the first investigators to utilize ESR to measure radical concentrations in the acrylamide-polyacrylamide lattice.

Dainton and co-workers (1957 I, II, III, IV) were the first to perform a detailed kinetic investigation on acrylamide polymerization. They applied the rotating sector method to measure propagation and termination rate constants, and found the former to be much larger than for any other commercial monomer. They postulated that termination was principally due to combination, although subsequent investigations have determined that disproportionation is predominant (Suen and Rossler, 1960).

Cavell (1962) was the first to employ azo initiators, and determined that molecular weight was controlled by transfer to monomer. Currie (1965) determined the effect of pH on propagation and termination and found both to decrease by an order of magnitude as pH rose from 1 to 13. However, the rate parameter $k_p/k_t^{1/2}$ did not significantly vary over the entire pH range. This was later confirmed by Gromov (1967). Ishige and Hamielec (1974) were the first to investigate the kinetics at moderate monomer concentrations. They concluded that diffusion limitations on termination reactions existed for polymer concentrations beyond approximately 7 wt.%. Later Kim and Hamielec (1984) would quantify this, and suggest the primary cause of the gel effect was entanglement between the polymer chains.
Table 4.1: Acrylamide Polymerizations with Redox Couples

<table>
<thead>
<tr>
<th>Redox System</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium persulfate/Sodium thiosulfate</td>
<td>Morgan, 1946</td>
</tr>
<tr>
<td>Ammonium persulfate/Sodium metabisulfite</td>
<td>Rodriguez, 1961</td>
</tr>
<tr>
<td>Ammonium persulfate/Sodium metabisulfite/EDTA</td>
<td>Hoover, 1966</td>
</tr>
<tr>
<td>Ammonium persulfate/Sodium bisulfite/Cu++</td>
<td>Hoover, 1967</td>
</tr>
<tr>
<td>Sodium chlorate/Sodium sulfite</td>
<td>Suen, 1958</td>
</tr>
<tr>
<td>Potassium persulfate/Sodium metabisulfite</td>
<td>Jursich, 1969</td>
</tr>
<tr>
<td>Potassium persulfate/Sodium metabisulfite/Fe++</td>
<td>Kurekovic, 1987</td>
</tr>
<tr>
<td>Potassium persulfate/Sodium thiosulfate</td>
<td>Sackis, 1967</td>
</tr>
<tr>
<td>Ceric ammonium sulfate/mercaptoethanol</td>
<td>Riggs and Rodriguez, 1967</td>
</tr>
<tr>
<td>Cerium (IV)/2-chloroethanol</td>
<td>Pohl and Rodriguez, 1980</td>
</tr>
<tr>
<td>Peroxydiphosphate/sodium thiosulfate</td>
<td>Hussain and Gupta, 1977</td>
</tr>
<tr>
<td>Permangante/Glycolic acid</td>
<td>Gupta, 1987</td>
</tr>
<tr>
<td></td>
<td>Lenka, 1984</td>
</tr>
<tr>
<td></td>
<td>Behari, 1986</td>
</tr>
</tbody>
</table>
1.1.1  Effect of Solvents

The effect of organic additives such as methanol (Misra and Rebello, 1974; Pantar, 1986), ethanol (Saini, 1971; Behari, 1986), dimethyldiformamide (Chapiro, 1971; Iwai, 1985) and dimethyl sulfoxide (Zhiravleva, 1986) reduce the rate of polymerization and the molecular weight. At high levels organic solvents also cause the polymer to precipitate (Gromov, 1967). Chapiro (1975) conducted an extensive investigation of the solvent effects on acrylamide polymerization and reported:

\[ R_{p, \text{water}} > R_{p, \text{acetic acid}} > R_{p, \text{methanol}} > R_{p, \text{DMF}} \approx R_{p, \text{dioxane}} \approx R_{p, \text{toluene}} > R_{p, \text{acetonitrile}} \]

These strong effects are due to the polarity and hydrogen bonding affinity of acrylamide. Gromov (1980) studied acrylamide polymerization in water, DMSO and THF and concluded that as the polarity of the solvent rises its ability to donate protons to the carbonyl rises. This results in a positive charge on the amide and an increased electron localization on the α-carbon. Bune et al. (1986) have confirmed, by proton and $^{13}$C NMR, that hydrogen bonding occurs predominantly through the carbonyl group ($\delta_{\text{C=O}}$ shifts to weaker field positions while $\delta_{\text{NH}_2}$ is essentially unchanged). They also correlated the electron accepting ability of the carbonyl with an increased electron density on the conjugated double bond. Furthermore, they observed that the downfield displacement of the olefinic carbons, upon increasing solvent polarity, was proportional to the rate of polymerization (or $k_p/k_{1/2}$) in that solvent.

The rate is also affected by the dielectric constant of the medium, which influences the stability of the growing macroradical.

1.1.2  Inhibition

Free radical polymerization of acrylamide is very sensitive to residual oxygen, which efficiently scavenges primary radicals even at concentrations as low as 1 ppm. Ghosh and George (1978) have quantified the effect of oxygen on the polymerization of acrylamide in
water and ethanol. They have concluded that O₂ also reacts with macroradicals, and the poly-
peroxides produced terminate through a unimolecular reaction. Kishore (1986) has postulated
that polyperoxide radicals can also participate in monomer addition reactions. This would
produce backbone O-O bonds which would be susceptible to scission at elevated temperatures,
although this has not been directly observed. Recently, Vaskova (1988) has shown that 4-
hydroxy-2,2,6,6-tetramethyl piperdin-1-oxy1 functions strictly as an inhibitor, rendering
\( k_p/k_c^{1/2} \) unchanged.

1.2 Review of Kinetics

In 1967, Riggs and Rodriguez observed an unusual rate dependence for aqueous
acrylamide polymerizations initiated with potassium persulfate:

\[ R_p = k[M]^{1.25}[I]^{0.5} \]

Over the past two decades, twenty two investigations have confirmed a monomer dependency
exceeding first order while maintaining that termination occurs predominantly through a
bimolecular macroradical reaction (Table 4.2). Riggs and Rodriguez (1967, II) interpreted the
high rate order as evidence of monomeric influences on the rate of initiation. This had pre-
viously been postulated by Jenkins (1958) to account for similar observations made while
polymerizing styrene in toluene with benzoyl peroxide as an initiator. Morgan (1946) had
taken the inference a step further, suggesting his sesquimolecular order was attributable to
secondary initiation caused by the monomer-enhanced decomposition of peroxide. The
credibility of this hypothesis has been substantiated through experimental work performed by
Dainton and co-workers (1957). They observed the rate dependence to revert to unity in the
absence of chemical initiators.¹

¹ Polymerizations were initiated with 60Co-γ rays, which generated H and OH radicals,
but left propagation, termination and transfer reactions unchanged.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>&quot;a&quot; in $R_p=Ma$</th>
<th>Initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Morgan</td>
<td>1946</td>
<td>1.50</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>Riggs and Rodriguez</td>
<td>1967</td>
<td>1.25</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>Gromov</td>
<td>1967</td>
<td>1.60</td>
<td>ammonium persulfate</td>
</tr>
<tr>
<td>Friend and Alexander</td>
<td>1968</td>
<td>1.25</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>Gecky</td>
<td>1971</td>
<td>1.50</td>
<td>potassium persulfate/ascorbic acid</td>
</tr>
<tr>
<td>Ishigie and Hamielec</td>
<td>1973</td>
<td>1.24</td>
<td>4,4'-azobis-4-cyanovaleric acid</td>
</tr>
<tr>
<td>Hussain and Gupta</td>
<td>1977</td>
<td>1.50</td>
<td>Ce(IV)-mercaptoethanol</td>
</tr>
<tr>
<td>Trubitsyna</td>
<td>1977</td>
<td>1.50</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>Osmanov</td>
<td>1978</td>
<td>1.20 in H$_2$O</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.30 in H$_2$O/</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>DMSO (1:1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.50 in DMSO</td>
<td></td>
</tr>
<tr>
<td>Trubitsyna</td>
<td>1978</td>
<td>1.60</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>Kurenkov</td>
<td>1978</td>
<td>1.70</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>Singh, Manickam</td>
<td>1979</td>
<td>1.50</td>
<td>potassium persulfate</td>
</tr>
<tr>
<td>and Venkataramo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Osmanov</td>
<td>1979,</td>
<td>1.70 in LiBr sol.</td>
<td>UV irradiation</td>
</tr>
<tr>
<td></td>
<td>1980</td>
<td>1.90 in LiCl sol.</td>
<td>with AlBN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.60 in CaCl$_2$ sol.</td>
<td>photosensitizer</td>
</tr>
<tr>
<td>Pohl and Rodriguez</td>
<td>1980</td>
<td>1.53</td>
<td>potassium persulfate/sodium bisulfite</td>
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<tr>
<td>Kurenkov</td>
<td>1981</td>
<td>1.30</td>
<td>ammonium persulfate</td>
</tr>
<tr>
<td>Lenka</td>
<td>1984</td>
<td>1.12</td>
<td>peroxodiphosphate/sodium thiosulfate</td>
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<tr>
<td>Khokhrin</td>
<td>1985</td>
<td>1.47</td>
<td>alkylbenzene sulfonato-bis acetylacetonate</td>
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Table 4.2 Continued...

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>&quot;a&quot; in $R_p=Ma$</th>
<th>Initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurenkov</td>
<td>1986</td>
<td>1.10</td>
<td>potassium persulfate/sodium bisulfite</td>
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<tr>
<td>Baade</td>
<td>1986</td>
<td>1.10</td>
<td>2,2'-azobis[N-2-hydroxyethyl butramidine]</td>
</tr>
<tr>
<td>Fouassier</td>
<td>1987</td>
<td>1.50 1.60</td>
<td>benzophenone/triethylamine/benzophenone</td>
</tr>
<tr>
<td>Kurenkov</td>
<td>1987</td>
<td>1.37</td>
<td>potassium persulfate/sodium bisulfite</td>
</tr>
<tr>
<td>Chen and Kuo</td>
<td>1988</td>
<td>1.38</td>
<td>Co(III)/triethylene tetramine</td>
</tr>
<tr>
<td>Raf‘ee Fanood</td>
<td>1988-I</td>
<td>1.16</td>
<td>4,4'-azobis-4-cyanovaleric acid</td>
</tr>
</tbody>
</table>
To account for high rate orders with respect to monomer three mechanisms have been proposed: the cage-effect theory (Matheson, 1946), the complex theory (Gee and Rideal, 1936, 1939) and the solvent-transfer theory (Burnett, 1955; Allen, 1955). The latter assumes that the solvent acts as a unimolecular terminating agent. A necessary consequence is that the corresponding transfer radical is unreactive. The solvent-transfer mechanism is not applicable in aqueous media where the hydroxy radical is very unstable and is capable of initiating olefinic monomers (Noyes, 1955). Chambers (1966) quantified the initiation by hydroxy radicals and found the rate constant for the reaction with acrylamide to be $1.1 \times 10^{11}$ L/mol·min, far in excess of that for sulfite radicals formed via persulfate decomposition.

The complex theory assumes a reversible association complex is formed between the monomer and initiator. This decomposes to produce a primary radical and a macroradical of length $1$:

1. \[
\frac{K_c}{I + M} \rightleftharpoons I - M
\]

2. \[
I - M \rightarrow R_1^* + R_m^*
\]

Matheson's alternative explanation for the initiation mechanism assumes that as two fragments of a dissociated molecule are produced they are contained in a "cage" of solvent molecules. This radical pair may combine several times before diffusing out of the cage. This hypothesis is based on Eyring's (1940) observation for benzene at room temperature, where a molecule made $10^{10}$ movements in its equilibrium position per second but underwent $10^{13-14}$ collisions in the same period. The persulfate initiated polymerization of acrylamide the cage-effect theory can be written as:

1. \[
\frac{k_1}{k_1} \rightleftharpoons (R_m^* \cdot R_m^*)
\]
Although based on very different premises both these mechanisms reduce to an identical rate equation:

\[ R_p = \frac{k_p}{k_t^{1/2}} [1]^{1/2} [M]^{2/3} (2k_t)^{1/2} \left( \frac{K}{1 + K[M]} \right)^{1/2} \]

where \( k_t \) is the complex/initiator decomposition constant for the complex and cage theories respectively, and \( K \) is the complex association constant \( (K_c) \) or the ratio \( k_{M1}/k_r \), which represents the relative rate a caged radical undergoes propagation and recombination.

These predict an increase in the rate order from 1.0 to 1.5 as the conversion increases. While either mechanism can satisfactorily predict the conversion time development for acrylamide polymerizations (Ishige, 1974), there has been no direct verification that the order is changing with monomer concentration. Furthermore, since both theories reduce to the same rate equation, kinetics cannot be used to discriminate between the mechanisms.

### 1.2.1 Evaluation of the Cage-Effect and Complex Theories

Flory (1953) has shown that for typical values of radical diffusivities \( (10^{-5} \text{ cm}^2/\text{s}) \) the monomer cannot appreciably influence the events in the cage. That is, the enhanced decomposition of caged radicals is insignificant relative to diffusion out of the cage, unless, as Jenkins showed (1958), the cage has enormous dimensions \( (10^4 \text{ Å radius}) \), which seems improbable. The theory does however predict low efficiencies of initiation (Baer, 1972) and
these have been reported for aqueous acrylamide polymerizations (Hussain and Gupta, 1977: \( f = 0.024 \)).

Noyes (1955) invoked the concept of a hierarchical cage structure and defined the following:

**Primary recombination:** Between two molecular fragments that are separated by less than one molecular diameter.

**Secondary recombination:** Between two fragments of the same molecule that have diffused greater than one molecular diameter apart.

**Tertiary recombination:** Between two fragments from different initiator molecules.

Primary and secondary recombination occur in \( \approx 10^{-13} \) and \( 10^{-9} \) seconds respectively. Since the time between diffusive displacements is approximately \( 10^{-11} \) seconds, monomer-enhanced decomposition cannot compete with primary recombination. However, if the scavenger (monomer) concentration is high, Noyes calculated that the fraction of radicals reacting with scavenger that would otherwise have undergone secondary recombination is, to the first approximation, proportional to \([M]^{1/2}\). That is:

\[
R_i \propto [M]^{1/2}
\]

which accounts for the observed rate behavior for acrylamide polymerizations.

Noyes' theoretical calculation is equivalent to the kinetic approach if we assume the existence of two cage entities: "compact", where the radicals are separated by less than one molecular diameter and "diffuse" where they have diffused further apart. It is assumed that only the latter are susceptible to monomer attack. These calculations suggest that although monomer-cage interactions are insignificant for cages with short lifetimes, for the fraction of cages where radicals are significantly separated, the enhanced decomposition reactions are competitive. Furthermore, the long cage lifetimes necessary for enhanced decomposition
suggest that if the cage theory is true, Flory and Jenkins have overestimated the macroradical diffusion coefficient.

**Complex Theory**

The complex theory has been historically criticized and rejected because experimental data indicate that the association constant rises with temperature. This is inconsistent with energetic predictions which indicate the complex is less favorable at higher temperatures. Further indirect evidence against amide-persulfate complexability was presented by Riggs and Rodriguez (1967) who showed the overall activation energy for aqueous acrylamide polymerization (16, 900 cal/mol) was almost exclusively composed of the contribution from the thermal decomposition of potassium persulfate \( E_{d2d} = 16, 800 \text{ cal/mol} \).\(^2\) However, more recent experiments (Trubitsyna, 1978 II) indicate that the overall activation energy is appreciably lowered; to below 10 kcal/mol in the presence of monomer. In the same investigation ultraviolet spectrometry was used to identify new complexes produced when acrylonitrile and N-vinyl pyrrolidone; two nitrogen containing monomers were mixed with potassium persulfate. Furthermore, the optical intensity of the new bands reached a maximum at a time coincident with the induction period of the reaction. The authors concluded a donor-acceptor complex was produced between the nitrogen containing monomer and the persulfate (Trubitsyna, 1966).\(^3\) Further evidence to this end came from polymerizations with monomers that are stronger proton donors than acrylonitrile and N-vinyl pyrrolidone: styrene, methyl methacrylate, isoprene and methyl acrylate. When these are added to persulfate no

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\(^2\) Complex formulation should lower the activation energy.

\(^3\) These authors also attributed the colour change, noticeable immediately after mixing nitrogen containing monomers and persulfates, to the formation of a molecular complex.
polymerization occurs although iodometrically the concentration of potassium persulfate decreases by 70% in the first hour. These monomers are preferentially forming a complex with potassium persulfate and blocking out the nitrogen containing monomers. This is significant in three respects: it shows that the new bands in the UV spectrum cannot be attributable to non-monomeric species, such as oxygen, secondly it demonstrates that proton donation from the monomer to the persulfate is a prerequisite for enhanced decomposition. It also implies that the complex is initiating polymerization, since potassium persulfate alone at 20°C is incapable of initiating the reaction.

Other peroxide initiators (benzoyl peroxide: Trubitsyna, 1965) have also been shown to decompose at faster rates in the presence of nitrogen containing additives. In this case the enhanced decomposition was also accompanied by a decrease in the overall activation energy. This was observed by the same authors several years later for reactions between benzoyl peroxide and aminated polystyrene (Trubitsyna, 1971), indicating that the donor-acceptor interactions are not dependent on molecular architecture.

In 1978, Trubitsyna used conductivity to monitor the charged particles produced from the interaction of acrylamide and potassium persulfate. The observed change in conductivity with time is shown in Figure 4.1.
These conductivity experiments were performed below 20°C, where the thermal decomposition of potassium persulfate is negligible, indicating a secondary decomposition reaction was occurring. Furthermore, the onset of charged particle generation (80 minutes) corresponded to the induction period of the reaction and the onset of radical generation, as determined by ESR. Based on these observations Trubitsyna (1978) proposed the following electron donor mechanism, with concurrent radical and charge generation:
Morsi (1976) observed that diphenyl amine enhanced the decomposition of benzoyl peroxide. He also attributed this to a donor-acceptor interaction between the amine and the peroxide, and suggested the interaction was caused by a modification of the peroxides dihedral angle. Further evidence that acrylamide complexes with potassium persulfate comes from Bekturov (1987) who found SO$_4^{2-}$ salted out polyvinyl pyrrolidone, but could not precipitate polyacrylamide, presumably because it was neutralized by a reaction with the amide side chains. The reaction of amides with persulfate is not surprising in light of NMR evidence (Zhuravleva, 1986) which shows that the carbonyl groups are hydrogen bonded to water but the amides are relatively free. Coleman (1987) has confirmed that the carbonyl and amide
substituents behave complementarily, in that the binding of one functional group is concurrent with the reactivity of the second.

Based on the literature review the following conclusions can be made:

1) Highly electronegative monomers can form "associates" with persulfates which lead to donor-acceptor interactions between the monomer and the peroxide. These enhance the decomposition of, for example, potassium persulfate, at low temperatures, reducing the activation energy and extending the useful range of the initiator.

2) The electrical environment of the monomer is the primary factor in its interaction with peroxide.

3) The enhanced decomposition of complexed persulfate is caused by hindered recombination and not a greater frequency of fragment dissociations. When the initiator is bound to the monomer the dissociated radical pair cannot regenerate potassium persulfate by recombination. Either radicals or an inert recombination product of the form \( \cdot \text{OSO}_3 \text{M}_2 \text{SO} \cdot \) are produced. Therefore, in the presence of donor-acceptor interactions each radical separation or "transient dissociation" results in the consumption of one initiator molecule. In the absence of bound monomer, an initiator transiently decomposes and recombines \( 10^{2-3} \) times for each "permanent decomposition".

1.3 Elucidation of an Initiation Mechanism

Both the cage and complex theories are inapplicable in their present forms as they require a unit efficiency for monomer-enhanced initiation. Additional reactions must therefore be included to account for cage or complex destruction, either of which can potentially generate non-reactive products.

Complex/Cage Equivalence

Prior to monomer enhanced decomposition an intermediate "associate" must be formed. This allows the electron donating group to attack the peroxide for a sufficient period

---

4 Manickam (1979) has developed a mechanism where monomer enhanced decomposition is included outside the framework of cage or complex theories, but this also assumes a 100% efficiency for enhanced decomposition.
to be competitive with the rapid radical fragmentation and recombination reactions. This monomer-initiator associate can result from either the diffusive displacement of a monomer to the volume element of the peroxide (cage approach) or the formation of a molecular complex. Both of these phenomena can be represented by a general reaction that is non-specific to the forces drawing the monomer and initiator into close proximity:

\[
[\text{R}_{\text{in}}^\bullet \cdot \text{R}_{\text{in}}] + M \rightarrow \left\{ \frac{\text{R}_{\text{in}}^\bullet + \text{R}_{\text{in}}^\bullet}{M} \right\}
\]

That is, the "associate" is a broadly defined concept encompassing both covalent and weak-bonding interactions. However, since experimental measurements (Trubitsyna, 1978) have found the associate to be irreversibly formed, uncharacteristic of covalently bonded molecules, the weak-bonding interaction must be responsible for monomer-initiator association. This "associate" can therefore be represented as a "weak complex", formed presumably due to hydrogen bonding, or equivalently, as a "diffuse monomer swollen cage", the difference being entirely semantic since in both models the monomer is physically contained within the three dimensional volume element of a diffuse radical pair. In other words, the complex and cage treatments are non-discriminating models of the same physical phenomena as far as amidopersulfate interactions are concerned.

The ambiguity in defining cage or complex structures allows us to combine the positive features of both mechanisms. Specifically, Noyes' hierarchical cage structure will be used as a precursor to charge transfer interactions. This allows the implementation of an electron donating mechanism without the inconsistency of association phenomena increasing with temperature. This will be presented in a subsequent section following a discussion of the existing mechanism.

---

5 This modification must also be applied to Manickam's mechanism to successfully apply it.
1.3.1 Historically used Mechanism

Based on experimental observations the following mechanism has been proposed (Trubitsyna, 1978):

1. \[ S_2O_8^{2-} \xrightarrow{k_d} 2 SO_4^{2-} \]

2. \[ S_2O_8^{2-} + M \rightarrow I - M \quad \text{(Complex formation)} \]

where \( M \) designates acrylamide monomer.

3. \[ I - M \xrightarrow{k_b} CH_2C\equiv CONH_2 + SO_4^{2-} \]

4. \[ I - M \xrightarrow{k_c} Q \quad \text{(Inert products)} \]

Bunn (1946) has shown that sulfate radicals can also react with water to produce hydroxy radicals, which are capable of initiation (Chambers, 1966):

5. \[ SO_4^{2-} + H_2O \xrightarrow{k_H} HSO_4^{-} + OH \]

6. \[ SO_4^{2-} + M \xrightarrow{k_{i1}} R_1^* \]

7. \[ OH + M \xrightarrow{k_{i2}} R_1^* \]

where \( R_1^* \) denotes a macroradical of length 1.

---

6 I have added this step to avoid the improbable situation of a unit efficiency for monomer-enhanced decomposition.
We must also include the propagation, termination and transfer reactions that have previously been identified for aqueous acrylamide polymerizations with water soluble initiators.

8. \[ R_r^* + M \rightarrow R_{r+1} \]

9. \[ R_r^* + M \rightarrow P_r + R_1^* \]

10. \[ R_r^* + R_s^* \rightarrow P_r + P_s \]

Where \( R_r^* \) is a macroradical of length \( r \) and \( P_r \) is a dead polymer chain of length \( r \).

Defining

\[ [R^*] = \sum_{r=1}^{\infty} [R_r^*] \]

we can construct the balances on the reactive species:

\[ \frac{d[S_2O_8^{2-}]}{dt} = -k_d[S_2O_8^{2-}] - k_a[S_2O_8^{2-}][M] \] \[ (4.1) \]

\[ \frac{d[SO_4^{2-}]}{dt} = 2k_c[S_2O_8^{2-}] + k_b[I-M] - k_{i1}[SO_4^{2-}][M] - k_{i2}[SO_4^{2-}][H_2O] = 0 \] \[ (4.2) \]

\[ \frac{d[OH]^*}{dt} = k_{i1}[SO_4^{2-}][H_2O] - k_{i2}[OH]^*[M] = 0 \] \[ (4.3) \]

\[ \frac{d[I-M]}{dt} = k_a[I][M] - (k_b + k_c)[I-M] = 0 \] \[ (4.4) \]

\[ \frac{d[R^*]}{dt} = k_{i1}[SO_4^{2-}][M] + k_{i2}[OH]^*[M] + k_b[I-M] - k_{td}[R^*]^2 = 0 \] \[ (4.5) \]
Assuming \( k_p \) is independent of chain length \( (k_{11} = k_{i2} = k_p) \), equations (4.2–4.4) can be substituted into (4.5) to yield:

\[
    k_{td}[R^*]^2 = 2f_c k_d [S_2O_8^{2-}] + \frac{2 k_a [S_2O_8^{2-}][M]}{k_c + \frac{1}{k_b}}
\]

The macroradical concentration may be written as:

\[
    [R^*] = \left( \frac{2f_c k_d [S_2O_8^{2-}]}{k_{td}} + \frac{2f_c k_a [S_2O_8^{2-}][M]}{k_{td}} \right)^{1/2}
\]

Where the complex/cage efficiency is defined as:

\[
    f_c = \frac{1}{k_c + \frac{1}{k_b}}
\]

Where the first term represents chains initiated by thermal decomposition of the persulfate and the second monomer-enhanced decomposition.

The rate of polymerization \( (R_p) \) may be expressed as:

\[
    R_p = k_f [M] \left( \frac{2f_c k_d [S_2O_8^{2-}]}{k_{td}} + \frac{2f_c k_a [S_2O_8^{2-}]}{k_{td}} \right)^{1/2}
\]

This can be used to describe the kinetics for acrylamide polymerizations. However, if applied, two parameter inconsistencies occur: The complex decomposition efficiency is very low \( (f_c = 0.06–0.4) \) suggesting a cage process is responsible for the kinetics, and the association constant \( (k_a) \) increases with temperature.

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7 See section 3 of this chapter of the thesis.
1.3.2 Proposed Mechanism

The apparent increase in $k_a$ with temperature and the low efficiency can be rationalized by considering the charge transfer reaction to be preceded by the generation of diffuse cage radical fragments which have large enough molecular separations to prevent recombination and provide access to proton donating monomers. The mechanism can therefore be expressed as a hybrid of the cage and complex theories as follows:

Initiator reactions

1. $\begin{align*}
S_2O_8^{2-} & \underset{k_1}{\overset{k_2}{\rightleftharpoons}} (SO_4^{2-} - O_4S) \\
\end{align*}$

2. $\begin{align*}
(SO_4^{2-} - O_4S) & \rightarrow (SO_4^{2-} - O_4S) \\
\end{align*}$

3. $\begin{align*}
(SO_4^{2-} - O_4S) & \rightarrow 2SO_4^{2-} \\
\end{align*}$

4. $\begin{align*}
(SO_4^{2-} - O_4S) & \rightarrow S_2O_8^{2-} \\
\end{align*}$

Solid parenthesis indicate a "compact cage" and braced parenthesis signify a "diffuse cage".

Swollen cage formation and decomposition

5. $\begin{align*}
(SO_4^{2-} - O_4S) + M & \overset{k_4}{\rightarrow} \begin{bmatrix} SO_4^{2-} - O_4S \end{bmatrix} \\
\end{align*}$

6. $\begin{align*}
\left[ \begin{array}{c}
SO_4^{2-} - O_4S \\
M
\end{array} \right] & \overset{k_b}{\rightarrow} SO_4^{2-} + HSO_4^- + CH_2C(O)NH_2 \\
\end{align*}$
7. \[
\begin{pmatrix}
\text{SO}_4^{\cdot-} & \cdot^\cdot \text{O}_4 \text{S} \\
M & \\
\end{pmatrix}
\xrightarrow{k_c}
\text{Q} \quad \text{(Inert products)}
\]

Chain Initiation

8. \[
k_{i1}
\text{SO}_4^{\cdot-} + M \rightarrow R_1^\cdot
\]

9. \[
k_{i11}
\text{SO}_4^{\cdot-} + \text{H}_2\text{O} \rightarrow \text{HSO}_4^{\cdot-} + \cdot^\cdot \text{OH}
\]

10. \[
k_{i12}
\cdot^\cdot \text{OH} + M \rightarrow R_1^\cdot
\]

Propagation

11. \[
k_p
R_r^\cdot + M \rightarrow R_{r+1}^\cdot
\]

Transfer to Monomer

12. \[
k_{im}
R_r^\cdot + M \rightarrow P_r + R_1^\cdot
\]

Termination

13. \[
k_{td}
R_r^\cdot + R_s^\cdot \rightarrow P_r + P_s
\]

At any time t, the persulfate is comprised of undissociated initiator \((\text{S}_2\text{O}_8^{2-})\), "compact caged fragments" \((\text{SO}_4^{\cdot+} \cdot^\cdot \text{O}_4 \text{S})\), and "diffuse cage fragments" \((\text{SO}_4^{\cdot+} \cdot^\cdot \text{O}_4 \text{S})\). The total persulfate in the system \((\text{SO}_4)\) is:
\[ I_t = [S_2O_8^{2-}] + (SO_4^{2-} - \cdot O_4S) + \{SO_4^{2-} - \cdot O_4S\} \]

Where
\[ [S_2O_8^{2-}] = \Phi_0 I_t \]
\[ (SO_4^{2-} - \cdot O_4S) = \Phi_1 I_t \]
\[ \{SO_4^{2-} - \cdot O_4S\} = \Phi_2 I_t \]

and \( \Phi_0 + \Phi_1 + \Phi_2 = 1.0 \)

The balances on all reactive species follow:

\[ \frac{d[S_2O_8^{2-}]}{dt} = -k_1[S_2O_8^{2-}] + k_1(SO_4^{2-} - \cdot O_4S) + k_1\{SO_4^{2-} - \cdot O_4S\} \] (4.7)

\[ \frac{d(SO_4^{2-} - \cdot O_4S)}{dt} = k_1[S_2O_8^{2-}] - (k_1 + k_2)(SO_4^{2-} - \cdot O_4S) \] (4.8)

\[ \frac{d(SO_4^{2-} - \cdot O_4S)}{dt} = k_2(SO_4^{2-} - \cdot O_4S) - k_3\{SO_4^{2-} - \cdot O_4S\} \]

\[ -k_1(SO_4^{2-} - \cdot O_4S) - k_4\{SO_4^{2-} - \cdot O_4S\}[M] \] (4.9)

\[ \frac{d\left[ \frac{SO_4^{2-} - \cdot O_4S}{M} \right]}{dt} = k_4(SO_4^{2-} - \cdot O_4S)[M] - (k_b + k_c)\left[ \frac{SO_4^{2-} - \cdot O_4S}{M} \right] = 0 \] (4.10)

\[ \frac{d(SO_4^{2-})}{dt} = 2k_d(SO_4^{2-} - \cdot O_4S) + k_b\left[ \frac{SO_4^{2-} - \cdot O_4S}{M} \right] - k_{12}[SO_4^{2-}][H_2O] - k_{11}[SO_4^{2-}][M] = 0 \] (4.11)
\[
\frac{\text{d}[^\circ \text{OH}]}{\text{d}t} = k_{i1}[\text{SO}_4^{\circ-}][\text{H}_2\text{O}] - k_{i2}[^\circ \text{OH}][\text{M}] \approx 0
\]

(4.12)

\[
\frac{\text{d}[R^\circ]}{\text{d}t} = k_{i1}[\text{SO}_4^{\circ-}][\text{M}] + k_{i2}[^\circ \text{OH}][\text{M}] + k_b \left[ \begin{array}{c} \text{SO}_4^{\circ-} \\ \text{M} \end{array} \right] - k_{ud}[R^\circ]^2 \approx 0
\]

(4.13)

From equation (4.10):

\[
\left[ \begin{array}{c} \text{SO}_4^{\circ-} \\ \text{M} \end{array} \right] = \left( \frac{k_u}{k_u + k_c} \right) [\text{SO}_4^{\circ-}][\text{M}]
\]

(4.10')

Substituting (4.10'), (4.11) and (4.12) into (4.13) yields:

\[
[R^\circ] = \left( \frac{2f k_d [\text{SO}_4^{\circ-}][S_2\text{O}_8^{2-}]}{k_{td}} + \frac{2f k_u [\text{SO}_4^{\circ-}][S_2\text{O}_8^{2-}][\text{M}]}{k_{td}} \right)^{1/2}
\]

Where

\[
[S_2\text{O}_8^{2-}] = \phi_d [S_2\text{O}_8^{2-}]
\]

and

\[
f_c = \frac{1}{1 + \frac{k_c}{k_b}}
\]

Where \(f_c\) can be defined equivalently as a cage-destruction of complex-decomposition efficiency.

The long chain approximation subsequently yields:

\[
R_p = k_p [\text{M}] \left( \frac{2f \phi_d k_d [S_2\text{O}_8^{2-}]}{k_{td}} + \frac{2f \phi_d k_u [S_2\text{O}_8^{2-}][\text{M}]}{k_{td}} \right)^{1/2}
\]

(4.14)

Discussion of the derived rate equation

The decomposition constant \((k_d)\) has been determined from measurements of the concentration of undecomposed initiator (Kolthoff and Miller, 1951):

\[
\frac{\text{d}[S_2\text{O}_8^{2-}]}{\text{d}t} = -k_d[S_2\text{O}_8^{2-}]
\]

(4.15)
However, since only diffuse cage fragments can dissociate to produce unpaired free radicals, equation (4.15) can more appropriately be written as:

$$\frac{d[S_2O_8^{2-}]}{dt} = k_d^* [SO_4^{*-}O_4^*]$$  \hspace{1cm} (4.16)

Expressing the concentration of these diffuse cages as a fraction of the overall initiator level, equations (4.15) and (4.16) can be combined to yield:

$$\frac{d[S_2O_8^{2-}]}{dt} = \Phi_2 k_d^* [S_2O_8^{2-}]$$

Which provides the identity $k_d = \Phi_2 k_d^*$. By an analogous procedure it can be shown $k_u = \Phi_3 k_u^*$. Where $k_u$ is the apparent (overall) association constant and $k_u^*$ is the actual (specific) association constant.

In the hybrid cage/complex theory, the apparent association constant is experimentally observed to rise with temperature. This can be attributed to either an increase in the specific association parameter, which is entropically unfavorable, or an increase in the fraction of persulfate present as diffuse cages. The latter appears to be the correct explanation, since supplying additional energy to the system would increase the frequency of equilibrium displacements while reducing the probability of radical recombination. This important conclusion enables us to include donor-acceptor interactions between monomer and initiator without the thermodynamic inconsistencies of prior charge transfer mechanisms. The mechanism derived herein will be used for the remainder of the chapter for evaluation against experimental data.

The rate equation (4.14) is unique in a second regard. It suggests that the 1.25 order for acrylamide polymerization with persulfate is comprised of two initiation reactions: thermal decomposition, providing first order kinetics, and monomer-enhanced decomposition which has a sesquimolecular rate order. Table 4.3 shows that the rate data generated from equation (4.14), with arbitrary parameter values, are virtually indistinguishable from kinetics
Table 4.3: Equivalence of two kinetic processes which provide 5/4th power rate dependencies

<table>
<thead>
<tr>
<th>Monomer Concentration [M]</th>
<th>( R_p = k_1^\dagger [M]^{1.25} )</th>
<th>( R_p = k_1^\dagger ([M]+[M]^{1.5})/2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2.0</td>
<td>2.38</td>
<td>2.41</td>
</tr>
<tr>
<td>3.0</td>
<td>3.95</td>
<td>4.10</td>
</tr>
<tr>
<td>4.0</td>
<td>5.66</td>
<td>6.00</td>
</tr>
<tr>
<td>5.0</td>
<td>7.48</td>
<td>8.09</td>
</tr>
<tr>
<td>6.0</td>
<td>9.39</td>
<td>10.34</td>
</tr>
<tr>
<td>7.0</td>
<td>11.39</td>
<td>12.76</td>
</tr>
</tbody>
</table>

\( k_1^\dagger \) is assigned an arbitrary value of 1.0
generated by a rate equation with a single $5/4$th order term. This implies we cannot make inferences as to whether the observed order is caused by single or multiple initiation reactions. Furthermore, kinetics exclusively cannot disprove the hybrid mechanism, or distinguish complex and cage theories.

1.3.3 Proposed Experimental Investigation

Based on the literature review and mechanistic and kinetic derivations we can propose the following problem to be addressed in an experimental investigation:

Are the kinetics of the persulfate initiated polymerization of acrylamide in aqueous media sensitive to the monomer concentration or does a universal mechanism apply?
2. EXPERIMENTAL METHODS AND PROCEDURES

2.1 Residual Monomer Concentration

The usual chemical methods for amide concentration determination are not applicable for polyacrylamides due to its limited solubility in organic solvents (Husser, 1977). Therefore, conversions are usually inferred from measurements of monomer concentration. Residual monomer levels have historically been determined by bromate-bromide or coulometric titrations (Suen, 1960). Chromatography (SEC: Ishige, 1974; Kim, 1984, LC: Husser, 1977) and UV absorption spectroscopy (Chatterjee, 1971) have also been used. Spectrophotometric methods (NMR, IR) have also been employed however they are limited to relatively high levels of residual acrylamide.

Croll (1971) has shown that Gas Chromatography is more sensitive to trace monomer levels than titrations, which fail below 0.1 wt.%. Croll (1972) and Hashimoto (1976) have developed a GC procedure suitable for the quantification of environmental samples, with a sensitivity below 0.1 ppb. The technique requires bromination of the unsaturated carbons followed by detection of the resulting α, β-dibromopropionamide.

For analysis of polymerized samples a liquid chromatography method has been described (Chapter 3), which is applicable below 1 ppm with a 95% confidence limit of ± 0.25%. This is a significant improvement in the accuracy for rapid LC measurement of acrylamide, which was previously limited to ± 2.7% (Ludwig, 1978). The improved accuracy is likely due to measurement (UV) at a wavelength (215 nm) closer to the peak absorption wavelength of acrylamide (201 nm). Previous investigations have detected acrylamide at 225 nm (Husser, 1977) and 240 nm (Ludwig, 1978), where the signal strength is more than an order of magnitude weaker.
Researchers have also determined residual monomer levels by indirect inferences from gravimetric or dilatometric observations (Morgan, 1946; Dainton, 1957; Riggs and Rodriguez, 1967; Gromov, 1967; Baer, 1972; George, 1978; Trubitsyna, 1978).

2.2 Molecular Weight Determination

Polyacrylamide molecular weight averages are usually determined indirectly from intrinsic viscosity measurements (Cavell, 1962; Rodriguez, 1967; Shawki, 1978; Baade, 1986; Kurekov, 1987; Rafiee Fanood, 1988 I, II). However, molecular weight estimates from this procedure are ambiguous because of uncertainty in the Mark-Houwink-Sakurada parameters, and the specificity of the correlation to the breadth of the molecular weight distribution. These produce estimates as divergent as ±50%. By comparison light scattering offers reproducibilities below ±10%, and the single point method of Chapter 1 reduces this error twofold.

Molecular weight distributions have been measured by size exclusion chromatography (Klein, 1981). However, non-steric separation mechanisms are operative in aqueous solvents. The method is further limited to molecular weights below 10^7 g/mol, even for optimal mobile and stationary phase combinations. This is often insufficient for characterizing polymeric flocculants. Recently, SEC/LALLS have been coupled with reasonable success. However, the technique is limited by the column resolution, and often results in underprediction of the polydispersity (Oono and Kaye, 1974). Holzworth (1986) has coupled Band Sedimentation/LALLS with very good results. Band Sedimentation avoids some of the disadvantages of SEC, for example adsorption, while preclarifying the solvent before it passes through the light scattering detector. The procedure, which separates molecules based on their sedimentation velocity, has an upper limit of 10^8 g/mol. Furthermore, it has been shown to deviate by <5% from static light scattering measurements on DNA samples of 30 and 60
million daltons. Viscosity has also been coupled with SEC (Styring, 1987) and with LALLS/DRI/SEC (Tinland, 1988), although it has not been used for polyacrylamide.

The molecular weight distribution of polyacrylamide has also been measured by electron microscopy in a solvent-nonsolvent mixture (Quale, 1967; Ishige, 1974) and by turbidimetric titration (Omorodion, 1976; Ramazanov, 1984).

2.3 Experimental Procedures

Residual acrylamide concentration was determined by the HPLC procedure outlined in Chapter 3. The monomer purification, dissolution and reactor procedures are also the same as for inverse-microsuspension copolymerization, with two exceptions. Potassium persulfate (Fisher Certified, assay 99.5%), recrystallized from distilled deionized water, was used as an initiator and sorbitanmonostearate (Alkaril Chemicals) was used as the steric stabilizer.

The weight average molecular weight was measured using Low Angle Laser Light Scattering by the procedure outlined in Chapter 1. Appendix H discusses the sources and magnitude of the variance in measuring the Rayleigh factor by aqueous LALLS.

2.3.1 Method of Polymerization

Polymerization at high monomer concentrations in solutions require chain transfer additives to lower molecular weight, reduce viscosity and provide more efficient heat transfer. However, for this experimental set, chain transfer agents are undesirable since they can affect the initiation mechanism through redox coupling with persulfate. Therefore, inverse-microsuspension polymerization was used. A prior investigation has demonstrated that inverse-microsuspension and solution polymerization are kinetically equivalent if a water soluble initiator is employed (Figure 4.3). In such instances, each isolated monomer droplet
Figure 4.3: Conversion-time data for acrylamide polymerizations in solution (■) and inverse-microsuspension (□) under identical experimental conditions: 

\[ [\text{Monomer}] = 3.40 \text{ mol/L}_w, \quad [\text{K}_2\text{S}_2\text{O}_8] = 0.52 \cdot 10^{-3} \text{ mol/L}_w, \]

Temperature = 60°C. For inverse-microsuspension:

\[ [\text{Sorbitanmonooleate}] = 0.168 \text{ mol/L}_0, \quad \Phi_{w/o} = 1.42. \]

Solution polymerization data are from Kim (1984).
contains all reactive species and behaves like a microbatch reactor. Furthermore, the large particle diameter (≈ 10 μm) in this work minimizes interfacial effects.

2.4 Experimental Conditions

Polymerizations were performed isothermally at 40, 50 and 60°C at monomer concentrations between 25 and 50 wt% of the aqueous phase. The latter corresponding to the solubility limit of acrylamide in water. Table 4.4 summarizes the experimental conditions for all polymerizations.

For all experiments reactor control was excellent, with thermal deviations never exceeding 1°C.
<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>[Acrylamide] (mol/L)</th>
<th>[K$_2$S$_2$O$_8$] (mmol/L)</th>
<th>Mass of Aqueous Phase (g)</th>
<th>Mass of Isopar-K (g)</th>
<th>Mass of SMS (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.35</td>
<td>0.252</td>
<td>1000.0</td>
<td>1000.0</td>
<td>100.0</td>
</tr>
<tr>
<td>50</td>
<td>4.03</td>
<td>0.228</td>
<td>1000.0</td>
<td>1000.3</td>
<td>100.0</td>
</tr>
<tr>
<td>50</td>
<td>4.69</td>
<td>0.251</td>
<td>1000.0</td>
<td>999.9</td>
<td>100.0</td>
</tr>
<tr>
<td>50</td>
<td>5.37</td>
<td>0.248</td>
<td>1000.0</td>
<td>1000.0</td>
<td>100.0</td>
</tr>
<tr>
<td>50</td>
<td>6.04</td>
<td>0.250</td>
<td>1000.0</td>
<td>1002.1</td>
<td>99.9</td>
</tr>
<tr>
<td>50</td>
<td>6.41</td>
<td>0.238</td>
<td>1000.0</td>
<td>1000.3</td>
<td>100.0</td>
</tr>
<tr>
<td>40</td>
<td>6.70</td>
<td>1.573</td>
<td>1000.0</td>
<td>1000.2</td>
<td>100.0</td>
</tr>
<tr>
<td>60</td>
<td>6.70</td>
<td>0.0609</td>
<td>1000.0</td>
<td>1000.6</td>
<td>100.0</td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

3.1 Rate Order with Respect to Monomer Concentration

The measured residual monomer concentrations were used to calculate the initial rates of polymerization. A series of six experiments were performed at 50°C with monomer concentrations between 25 and 50 wt.% of the aqueous phase, varied in 5% increments. From these data the following rate equation was estimated:

\[ R_p \propto M^{1.34 \pm 0.12} \]

The 95% confidence limits were determined from a non-linear least squares estimation routine based on Marquardt’s algorithm. The 95% confidence interval surrounds 1.25 and therefore we reject the hypothesis that at high monomer concentration the rate order deviates from the $5/4$th power. This has mechanistic implications as it suggests the variable order rate models, the unmodified cage-effect and complex theories, are not applicable to aqueous persulfate initiated polymerization of acrylamide. The reliability of the 1.34 order is accentuated by Kurenkov’s recent (1987) result: $R_p \propto M^{1.37}$ for monomer levels between 0.86 and 4.93 mol/L, which has been published after this work began.

3.2 Limiting Conversion

During these polymerizations, limiting conversions were observed for several reactions at high monomer or low initiator levels\(^8\) (Table 4.5). This is generally attributed to either a depletion of the initiator or isolation of the macroradicals. These phenomena can be distinguished by raising the temperature after the limiting conversion is reached. If residual initiator is present but is physically hindered from reaching the acrylamide monomer, increasing the thermal energy to the system will increase the diffusion of small molecules and

---

\(^8\) The usual reciprocal relationship between the limiting conversion and the rate of polymerization (Joshi, 1987) is also observed in this investigation.
Table 4.5: Limiting Conversion versus Monomer and Initiator Concentration

<table>
<thead>
<tr>
<th>Limiting Conversion ($X_i$)</th>
<th>Acrylamide Concentration (mol/L)</th>
<th>Potassium persulfate/Concentration (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.92</td>
<td>6.41</td>
<td>0.238</td>
</tr>
<tr>
<td>0.95</td>
<td>6.04</td>
<td>0.250</td>
</tr>
<tr>
<td>0.96</td>
<td>5.37</td>
<td>0.248</td>
</tr>
<tr>
<td>0.996</td>
<td>4.69</td>
<td>0.251</td>
</tr>
<tr>
<td>0.996</td>
<td>4.03</td>
<td>0.228</td>
</tr>
<tr>
<td>0.997</td>
<td>3.35</td>
<td>0.252</td>
</tr>
<tr>
<td>0.76</td>
<td>6.70</td>
<td>0.0609</td>
</tr>
<tr>
<td>0.999</td>
<td>6.70</td>
<td>1.573</td>
</tr>
</tbody>
</table>
increase the rate. Figure 4.4 shows such an experiment for this system. The temperature rise did not increase the conversion, indicating the initiator concentration had previously been exhausted. Therefore, the limiting conversions offer additional evidence of a second initiator decomposition reaction. Furthermore, the simultaneous occurrence of limiting conversions in polymerizations with high rate orders with respect to monomer concentration, which has historically been attributed to enhanced decomposition, suggest the following:

The unique kinetics for potassium persulfate initiated polymerization of acrylamide in aqueous media are due to the experimentally verifiable enhancement in the decomposition of peroxides by the proton donating monomer via a charge transfer complex interaction. Furthermore, the incorporation of this single modification to the mechanism is sufficient to explain all the unique phenomena for aqueous free radical polymerization of acrylamide and other acrylic water soluble monomers.

3.3 Parameter Estimation

The conversion-time data were used to estimate two grouped parameters: $\Phi_2 k_n^*$ and $f_c = 1/(1 + k_c/k_b)$, which are unique to the hybrid mechanism. Additionally, measurements of weight average molecular weight were used to estimate the transfer to interfacial emulsifier parameter. The differential equations were solved with a variable order Runge-Kutta procedure with a step size of one minute.

At each temperature parameter estimates were obtained from a non-linear least squares regression routine based on Marquardt's procedure. These estimates were obtained utilizing residual monomer concentration and molecular weight data for all polymerizations at a given temperature. This is preferable to the common practice of estimating parameters

---

9 Molecular weight development in inverse-microsuspension polymerization is detailed in Appendix D.
Figure 4.4: Conversion-time data (*) for an acrylamide polymerization. The experimental conditions were: [Monomer]: $5.37 \text{ mol/L}_w$, $[K_2S_2O_8] = 2.44 \times 10^{-3} \text{ mol/L}_w$, Temperature $= 50^\circ C$. A limiting conversion of 0.97 is observed. Increasing the temperature to 60°C (arrow) did not lead to consumption of additional monomer.
from individual experiments, which is unable to identify inter-experimental data inconsistencies. This parameter overfitting leads to unreliable estimates which cannot be generalized to other reaction conditions.

Table 4.6 shows the values of parameters determined in this investigation. The activation energy for transfer to emulsifier was found to be $-141 \text{ J/mol}$, typical of a termination reaction. It was not however, significantly smaller than zero at the 95% confidence level, and we can conclude that unimolecular termination with interfacial emulsifier is thermally invariant over the range investigated. The magnitude of $k_{fe}$ is slightly larger than was found for inverse-microsuspension polymerization in Chapter 2, but is likely more reliable since it is based on absolute molecular weight measurements; intrinsic viscosity correlations were used in Chapter 2.

The complex/cage efficiency is observed to decrease with temperature, implying the monomer-swollen-cage preferentially forms inert species rather than active radicals. This is consistent with limiting conversion data which indicate that initiator deactivation is more favourable at higher temperatures.

The apparent association parameter ($k_a = \phi_2 k_a^*$) is found to increase with temperature according to an Arrhenius dependence. This has been reported previously for acrylamide polymerizations initiated by potassium persulfate (Riggs and Rodriguez, 1967). As was discussed in section 1.3.2, this is the manifestation of two independent phenomena: a decrease in the specific association constant ($k_a^*$) which is entropically less favourable at elevated temperatures, and an increase in the fraction of potassium persulfate present as diffuse cages ($\phi_2$). The latter, which is the only form of potassium persulfate capable of participating in monomer-enhanced decomposition reactions, are more abundant at high temperatures due to a greater frequency of radical diffusive displacements and a lower rate of radical fragment recombination.
Table 4.6: Parameter Estimates

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_c$</td>
<td>40°C: 1.0</td>
<td>dimensionless</td>
</tr>
<tr>
<td></td>
<td>50°C: 0.372</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60°C: 0.065</td>
<td></td>
</tr>
<tr>
<td>$\left(\phi_2 k_a^*\right)$†</td>
<td>40°C: $3.17 \cdot 10^{-5}$</td>
<td>L/mol·min</td>
</tr>
<tr>
<td></td>
<td>50°C: $1.06 \cdot 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60°C: $1.93 \cdot 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$k_{fe}$</td>
<td>$2.433 \cdot 10^{-9}$</td>
<td>dm²/mol·min</td>
</tr>
<tr>
<td>$A_0$††</td>
<td>8.01</td>
<td>dimensionless</td>
</tr>
<tr>
<td>$A_1$††</td>
<td>$2.0 \cdot 10^{-2}$</td>
<td>K⁻¹ (Kim and Hamielec, 1984)</td>
</tr>
</tbody>
</table>

† $k_a = (\phi_2 k_a^*) = 8.77 \cdot 10^{41} \exp(-66,500/RT)$

†† $A$ is a gel effect parameter in the expression:

\[
\frac{k_0}{k_{td}} = \exp(A \cdot wp)
\]

where $A = A_0 - A_1 T$
All other rate parameters \((k_p, k_{td}, k_{fm}, k_d)\) were obtained from the literature and have been summarized in Chapter 2 during the discussion of the modelling of the inverse-microsuspension polymerization of acrylamide.

3.4 Comparison of Kinetic Model to Experimental Data

Figures 4.5 to 4.12 show conversion-time and weight average molecular weight-conversion data and model predictions for all experimental conditions. The hybrid mechanism is capable of predicting the initial polymerization rate and weight average molecular weight well over a range of temperatures, monomer concentrations and rates of initiation. The molecular weight behavior with conversion is typical of acrylamide polymerizations where transfer to monomer dominates. A slight decrease in molecular weight with conversion, and the increase with the initial monomer concentration, is evidence that a fraction of the chains are terminated through a bimolecular process. The limiting conversion is predicted well at low initiator levels and moderate monomer concentrations, however, is slightly overpredicted when it occurs at very high conversions (>90%). This is due to the authors personal preference to obtain accurate reliable kinetic parameter estimates, at the expense of fitting limiting conversion data. Consequently initial rate data were given a greater weighting in the analysis to compensate for the larger number of residual monomer measurements at high conversions.

Figure 4.13 illustrates the relative magnitudes of thermal and monomer-enhanced decomposition of potassium persulfate. At the onset of polymerization the majority of chains are initiated through a donor-acceptor interaction between the acrylamide and persulfate. This effect is most extreme at elevated temperatures. As the conversion rises both the monomer and initiator have depleted (Figure 4.14) and thermal bond rupture of the peroxide becomes the predominant initiation reaction. Figure 4.14 also shows that the rate of consumption of initiator is strongly dependent on the initial monomer concentration. Furthermore, for
Figure 4.5:  
(a) Conversion-time data (*) and kinetic model predictions (---) for an acrylamide polymerization at 50°C. [Monomer] = 3.35 mol/L, \([K_2S_2O_8] = 0.252 \cdot 10^{-3} \text{ mol/L} \).

(b) Weight average molecular weight-conversion data (*) and kinetic model predictions (---) for the same experiment.
Figure 4.6: (a) Conversion-time data (○) and kinetic model predictions (---) for an acrylamide polymerization at 50°C. [Monomer] = 4.03 mol/L, [K2S2O8] = 0.228 \cdot 10^{-3} \text{ mol/L}.

(b) Weight average molecular weight-conversion data (○) and kinetic model predictions (---) for the same experiment.
Figure 4.7: 

(a) Conversion-time data (■) and kinetic model predictions (———) for an acrylamide polymerization at 50°C. [Monomer] = 4.69 mol/L_w, [K_2S_2O_8] = 0.251 × 10^{-3} mol/L_w.

(b) Weight average molecular weight-conversion data (■) and kinetic model predictions (———) for the same experiment.
Figure 4.8: (a) Conversion-time data (■) and kinetic model predictions (———) for an acrylamide polymerization at 50°C. [Monomer] = 5.37 mol/L_w, [K_2S_2O_8] = 0.248 \cdot 10^{-3} \text{ mol}/L_w.

(b) Weight average molecular weight-conversion data (■) and kinetic model predictions (———) for the same experiment.
Figure 4.9:  
(a) Conversion-time data (*) and kinetic model predictions (—) for an acrylamide polymerization at 50°C. [Monomer] = 6.04 mol/L, 
$$[K_2S_2O_8] = 0.250 \cdot 10^{-3} \text{ mol/L}$$.
(b) Weight average molecular weight-conversion data (*) and kinetic model predictions (—) for the same experiment.
Figure 4.10:  
(a) Conversion-time data (■) and kinetic model predictions (-----) for an acrylamide polymerization at 50°C. [Monomer] = 6.41 mol/L, [K₂S₂O₈] = 0.238 - 10⁻³ mol/L.  
(b) Weight average molecular weight-conversion data (■) and kinetic model predictions (-----) for the same experiment.
Figure 4.11:  
(a) Conversion-time data (■) and kinetic model predictions (———) for an acrylamide polymerization at 60°C. [Monomer] = 6.70 mol/L, [K₂S₂O₈] = 0.0609·10⁻³ mol/L.  
(b) Weight average molecular weight-conversion data (■) and kinetic model predictions (———) for the same experiment.
Figure 4.12:  
(a) Conversion-time data (●) and kinetic model predictions (———) for an acrylamide polymerization at 40°C. [Monomer] = 6.70 mol/L, [K₂S₂O₈] = 1.573 · 10⁻³ mol/L.  
(b) Weight average molecular weight-conversion data (●) and kinetic model predictions (———) for the same experiment.
Figure 4.13: Fraction of polymer chains initiated by monomer-enhanced decomposition of potassium persulfate (KPS) as a function of conversion. Simulations were performed at 40°C (-----) and 60°C (- - - -) with $\frac{1}{n}$ $K_2S_2O8 = 6.088 \times 10^{-5}$ mol/L, water = 0.74.
Figure 4.14: Concentration of potassium persulfate scaled with respect to its initial level ($I/I_0$) as a function of conversion. Simulations were performed at 60°C with $[\text{K}_2\text{S}_2\text{O}_8]=2.4 \cdot 10^{-4} \text{ mol/}L$ and initial acrylamide concentrations of 1, 5, 10, 25 and 50 wt.% based on the aqueous phase.
the conditions of the simulation, the potassium persulfate is exhausted before the reaction is completed for initial acrylamide concentrations exceeding 25 wt.%. For example, at 50 wt.% monomer, the radical generation ceases at 78% conversion, in agreement with experimental observations ($X_L = 0.76$).

3.5 Generalization of the Initiation Mechanism to Other Water Soluble Monomers

The charge transfer complexes that form between persulfate and nitrogen containing monomers require free electrons on the donor (monomer) and a polar medium. For acrylamide polymerizations in dimethyl sulfoxide-water mixtures the rate order with respect to monomer increases as the fraction of DMSO in the solvent mixture rises (Osmanov, 1978 I, II). This is caused by the aprotic nature of dimethyl sulfoxide and its inability to hydrogen bond to the acrylamide carbonyl group. This less solvated monomer is therefore more readily complexed with the peroxyde, and undergoes enhanced decomposition at an accelerated rate. The rate therefore approaches sesquimolecular order, the limit if monomer and initiator form 1:1 complexes, as the fraction of DMSO rises, in agreement with experimental observations.

This effect is also observed in other monomers with electronegative atoms, for example in acrylic acid(oxygen)-persulfate systems (Manickam, 1979). The polarity and hydrogen bonding affinity of the hydroxy group exceed that of the corresponding amide, and the rate order again approaches the sesquimolecular limit. Indeed, the monomer's ability to form hydrogen bonds, through the side chain functional group, appears to be one of the contributing factors for the formation of monomer-initiator complexes.

For N, N, dimethyl acrylamide, which cannot hydrogen bond to either the peroxyde or persulfate oxygens, due perhaps to steric interference of the bulky methyl substituents, a unimolecular rate order with respect to monomer is observed (Saini, 1971; Jacob, 1972). This
confirms Trubitsyna's postulate (1978) that the amide is responsible for the electron rearrangement leading to the monomer-initiator association. Haas (1970) has observed that other amide containing monomers, for example acrylylglycinamide, enhance the decomposition of potassium persulfate, and have the same rate order with respect to monomer concentration as acrylamide. If methacrylamide replaces acrylamide as the monomer in a persulfate reaction a greater than first order dependence is again observed \( (R_p \propto M^{1.13}; \text{Gupta, } 1987) \). The reduced order from the \( 5/4 \)th power may be an experimental anomaly, as methacrylamide has not been extensively investigated. However, it is more likely that the \( \alpha \)-methyl substitution is affecting the electron rearrangement\(^\text{11}\) necessary to produce a monomer-initiator complex (Manickam, 1980).

The mechanism, therefore, in its present form can explain the rate behavior for several water soluble monomers (acrylamide, acrylic acid, \( N \), \( N \)-dimethyl acrylamide, methacrylamide). The stronger the monomer polarity, or its proton donating ability, the greater the proportion of initiator that decomposes through a monomer-enhanced mechanism. Contrarily, steric interferences reduce the ability of charge transfer complexes to form, and increase the proportion of sulfate radicals produced via thermal decomposition of the peroxide.

The sum of a first and sesquimolecular order initiation mechanism is therefore flexible enough to describe a broad array of kinetic observations for ionogenic and nonionic monomers.

\(^{10}\) Ergozhin (1987) investigated the kinetics of a series of \( N \)-substituted amides and observed the rate order with respect to monomer concentration to decrease as the accessibility to the vinyl group was hindered.

\(^{11}\) Methacrylamide radicals are present in a resonance stabilized structure where the \( \beta \)-carbon can more easily stabilize a radical than the \( \alpha \)-methyl substituted carbon (Burfield, 1976).
3.5.1 Generalization to Cationic Monomers

Friend and Alexander (1968) were the first to observe an interaction between persulfate and quaternary ammonium compounds. Trubitsyna (1977, 1978) and Kurenkov (1980) latter observed complexes and enhanced decomposition of persulfate due to cationic ammonium additives. Further, the magnitude of the enhanced decomposition was significantly greater than was observed for acrylamide. It has been shown (Friend and Alexander, 1968) that charge transfer interactions are responsible for the formation of a 1:2 stoichiometric complex of the following type:

\[
\begin{array}{cccccc}
\text{O} & \text{O} \\
\text{\|} & \text{\|} \\
R_4N^+ & \text{\|} & \text{\|} & \text{\|} & \text{\|} & \text{\|} \\
\text{O} & \text{O} \\
\end{array}
\]

These decompose to produce two macroradicals of length 1.\textsuperscript{12} Such a mechanism reduces to a second order rate dependence on monomer concentration, in agreement with experimental observations for diallyldimethylammonium chloride polymerization (Jaeger, 1984). Jaeger also showed that the rate order was reduced by 1 when a non-complexing initiator (azobispentanoic acid) was used in place of potassium persulfate. Therefore, the high rate

\textsuperscript{12} When 1:1 complexes are produced, one primary radical is liberated.
orders observed for polymerization of acrylic water soluble monomers in aqueous media initiated by persulfate are almost certainly due to the unique donor-acceptor interaction of the monomer-initiator pair. The strength in this interaction determines the deviation in order from unity. Table 4.7 summarizes the observed kinetic relationships for several nonionic, anionic and cationic acrylic water soluble monomers. A correlation between the rate order with respect to monomer and the strength of the monomer-initiator complex is again observable.

Based on the preceding literature survey we can propose the following general initiation mechanism for acrylic water soluble monomers with persulfate:

1. \( S_2O_8^{2-} \rightarrow (SO_4^{*-} - O_4S) \)

2. \( (SO_4^{*-} - O_4S) \rightarrow \{SO_4^{*-} - O_4S\} \)

3. \( \{SO_4^{*-} - O_4S\} \rightarrow S_2O_8^{2-} \)

4. \( \{SO_4^{*-} - O_4S\} \rightarrow 2SO_4^{*-} \)

5. \( SO_4^{*-} + H_2O \rightarrow HSO_4^{*-} + OH\)

6. \( SO_4^{*-} + M \rightarrow R_1^* \)

7. \( OH^* + M \rightarrow R_1^* \)

8. \( \{SO_4^{*-} - O_4S\} + xM \rightarrow \left\lfloor \begin{array}{c} SO_4^{*-} - O_4S \\ xM \end{array} \right\rfloor \)

9. \( \left\lfloor \begin{array}{c} SO_4^{*-} - O_4S \\ xM \end{array} \right\rfloor \rightarrow (2-x)R_{1n}^* + xR_1^* \)
Table 4.7: Rate Equations for Several Acrylic Water Soluble Monomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>&quot;a&quot; in $R_p$ &amp; $M_a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N,dimethylacrylamide</td>
<td>1.0</td>
<td>Kurenkov, 1980</td>
</tr>
<tr>
<td>Methacrylamide</td>
<td>1.13</td>
<td>Gupta, 1987</td>
</tr>
<tr>
<td>Acryl/iglycinamide</td>
<td>1.22</td>
<td>Haas, 1970</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>1.25</td>
<td>Riggs and Rodriguez, 1967</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>1.50</td>
<td>Manickam, 1979</td>
</tr>
<tr>
<td>Diallyl dimethyl ammonium chloride</td>
<td>2.0+</td>
<td>Jaeger, 1984 Hahn, 1983 I,II</td>
</tr>
</tbody>
</table>

* A third order dependence has been reported. However, the monomeric salt influences propagation between charged radicals and monomer molecules. This results in a first order relationship between the propagation rate constant and the monomer concentration.
10. \[
\left[ \begin{array}{c}
\text{SO}_4^2- \\
x \cdot \text{M}
\end{array} , \begin{array}{c}
\cdot \text{O}_4^4 \\
\text{M}
\end{array} \right] \rightarrow Q \quad \text{(Inert products)}
\]

Where \( x \) is the stoichiometric ratio of monomer in the initiator complex. That is:

For anionic and nonionic monomers, \( x = 1 \) and \( R_p \propto k \cdot M + k' \cdot M^{3/2} \)

For cationic monomers, \( x = 2 \) and \( R_p \propto k \cdot M + k'' \cdot M^2 \)

An oppositely charged monomer-initiator pair is therefore able to form higher stoichiometric complexes than if the initiator and monomer are of the same charge, or if one or both of the species are uncharged. This accounts for the higher order in rate with respect to monomer concentration for aqueous polymerizations of cationic monomers with persulfate.
REFERENCES


102) Quayle, D.V., Polymer, 8, 217 (1967).


CONCLUSIONS

1. A new single-point method has been developed for the estimation of weight average molecular weights from Low Angle Laser Light Scattering data. The procedure improves the accuracy of molecular weight measurement to ±5%, compared with ±10% for the conventional technique, concomitant with a fivefold reduction in measurement time. The method is general and can be applied to any linear polymer.

2. The variance in the measurement of the Rayleigh factor is sensitive to the polymer concentration. Therefore, the accuracy of molecular weight estimates can be improved by identifying, a priori, the minimum variance concentration for a range of molecular sizes.

3. For accurate molecular weight measurements of polyelectrolytes it is necessary and sufficient to obtain equilibrium electrochemical potential of the counterion in the domain of the polymer coil and the bulk solution. Once this is achieved light scattering theory derived for nonionic scattering bodies can be applied to ionic systems, provided the specific refractive index increment is measured for a dialysed polymer solution against the dialysate.

4. A mechanism has been developed for the inverse-microsuspension polymerization of acrylic water soluble monomers. It includes three previously unidentified reactions: monomolecular termination of macroradicals with interfacial emulsifier, secondary initiation from emulsifier radicals to generate terminally unsaturated polymer molecules, and the heterophase mass transfer of primary and oligoradicals. The identification of the unimolecular terminating agent provides a means of improving polymer quality through the appropriate selection of the interfacial recipe.
5. A kinetic model has been developed based on the preceding mechanism to describe the inverse-microsuspension polymerization of acrylamide and its copolymerization with cationic monomers. The model provides predictions of the reaction rate, molecular weight and particle characteristics, all of which have been previously unquantifiable, over a range of experimental conditions. It has been verified against data generated herein and by independent laboratories.

6. The five-fourths rate dependence on monomer concentration is invariant to the initial acrylamide level up to its solubility limit in water.

7. The enhanced decomposition of alkali persulfates and other peroxide initiators exists in polar media containing acrylic water soluble monomers with electronegative substituents. This occurs via a donor-acceptor charge transfer mechanism and is responsible for initiator depletion, manifested as limiting conversions, and high rate orders with respect to monomer concentration.

8. The "diffuse monomer swollen cage" and "weak complex" are equivalent representations of the same physical phenomena as far as amide-persulfate interactions are concerned. This cage-complex equivalence allows us to combine both mechanisms to quantitatively describe monomer-enhanced decomposition without the thermodynamic inconsistencies that have plagued previous models. As such, a general mechanism has been developed for the aqueous copolymerization of acrylic water soluble monomers with persulfate. This can predict the observed rate dependencies on monomer concentration for nonionic, anionic and cationic monomers, a hitherto unresolved issue.
RECOMMENDATIONS

1. The single point light scattering method should be generalized to polyelectrolytes and polymers of various molecular architecture.

2. Polyelectrolyte characterization methods should be developed for cationic and ampholytic polymers.

3. The effect of Coulombic interactions on the propagation and termination reactions in the addition polymerization of ionogenic monomers should be investigated.

4. Direct verification of amide-persulfate interactions should be performed spectrometrically using model compounds.

5. Investigations are required on the effect of denaturing agents and simple electrolytes on the monomer enhanced decomposition of peroxides.

6. The role of molecular oxygen in the free radical polymerization mechanism should be identified.

7. The feasibility of the preparation of monodisperse water soluble latices by dispersion polymerization should be investigated.

8. The universality of monomolecular termination in heterophase polymerizations should be investigated for a variety of monomers and emulsifiers.

9. An attempt should be made to generalize both the physical (colloidal) and chemical (kinetic) behaviour of heterophase water-in-oil and oil-in-water polymerizations. This includes developing a useful criteria to distinguish and group processes, and the establishment of a systematic nomenclature.
APPENDIX A
PREPARATION AND CHARACTERIZATION OF SUPERABSORBENT
POLY(SODIUM ACRYLATE)

1. INTRODUCTION

Crosslinked poly(sodium acrylates) are commercially important superabsorbent polymers. They have penetrated a significant portion of the health-care product market (Masuda, 1983) and are candidates for a wide range of other applications including packaging, public works, and forestry. Their potential large-scale use for the drying of organic solvents, moisture retention in agriculture and as water-sealing agents in the construction industry have also been investigated. In these applications the degree of crosslinking plays an important role, since it is the primary factor governing the polymer’s absorbency (Buchanan, 1986). At the present there has not been any $^{13}$C NMR investigations on crosslinked poly(sodium acrylate), although there has been considerable NMR work on the corresponding linear polymer (Hiraoka, 1981; Truong, 1986, Candau, 1986 I, II) and on related polymers such as poly(acrylic acid) (Schaefer, 1971; Fyfe, 1986) and polyacrylamide (Cais, 1978; Muller, 1979; Gupta, 1981; Lancaster, 1982; Inoue, 1983; Zurimendi, 1984; Guerrero, 1985; Halverson, 1985).

Recently, a combination of cross-polarization (CP) and magic-angle spinning (MAS) (Andrew, 1971; Pines, 1973) with high-power proton decoupling has provided a great deal of $^{13}$C NMR information about various solid crosslinked polymers such as epoxy (Garroway, 1982), phenolic resins (Fyfe, 1983; Hatfield, 1987) and polyimides (Maciel, 1982). $^{13}$C NMR spectra can be obtained on high-resolution instruments without recourse to the CP-MAS technique by using crosslinked polymers that have been highly swollen in good solvents (Yokota, 1978; Mannatt, 1980; Ford, 1981, 1983). This technique has the advantage that the
measurements are made on samples in the same physical state in which the superabsorbent polymers are utilized.

In this appendix the $^{13}$C NMR spectra of a series of divinyl-crosslinked poly(sodium acrylates) with various degrees of crosslinking are reported. Measurements on dry polymers as well as on samples in the hydrogel state are discussed. These spectra show systematic changes with crosslinking monomer content, which provide a method for estimating the concentration of divinyl crosslinks in these materials.

2. EXPERIMENTAL

2.1 Polymerization of Poly(sodium acrylate)

Lightly crosslinked poly(sodium acrylate) was prepared by copolymerizing acrylic acid (Glacial: Rohm and Haas) and N, N'-methylenebisacrylamide (Aldrich, Electrophoresis Grade, >99% purity) by free radical polymerization at 60°C using potassium persulfate (BDH, Analytical Grade, minimum assay 99%) as an initiator. Table A.1 lists the experimental conditions. The experimental procedure can be summarized as follows: The crosslinking agent was dissolved in the acrylic acid and then diluted with double distilled deionized water. This was added to a Pyrex glass ampoule (10 mm I.D., 12 mm O.D., and 40 mm long) which had been soaked for 24 hours in a cleaning solution prepared by mixing Chromerge (Caledon Laboratories) containing chromium trioxide and concentrated sulfuric acid. Before use the ampoule was rinsed with distilled deionized water and dried at 60°C for four hours. A 50 wt.% aqueous solution of sodium hydroxide (BDH, Analytical Grade) was added dropwise while maintaining the temperature of the ampoule contents below 30°C\(^1\) to avoid prepolymerization. This resulted in a degree of neutralization of 99%. The ampoules were agitated moderately

---
\(^1\) The ampoule was held in an ice bath.
Table A.1: Experimental Conditions

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Overall Concentration</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic Acid</td>
<td>4.7 mol/L</td>
<td>6.0g in 3.7g of distilled deionized water.</td>
</tr>
<tr>
<td>N,N'-methylene bisacrylamide</td>
<td>0.1 → 25 wt.% of total monomer</td>
<td>Dissolve in acrylic acid.</td>
</tr>
<tr>
<td>Potassium persulfate</td>
<td>5.0 · 10⁻⁴ mol/L</td>
<td>2.4 · 10⁻³g in 1.0g of distilled deionized water.</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>4.7 mol/L</td>
<td>3.35g of NaOH in 3.35g of distilled deionized water.</td>
</tr>
</tbody>
</table>
during this step to improve the rate of dissolution of the sodium hydroxide. The initiator solution was then added to the ampoule, which was subsequently mixed well and attached to the vacuum apparatus. The ampoules were immersed in liquid nitrogen and evacuated to $10^{-4}$ mmHg using rotary (Edwards, 2 stage) and diffusion (Edwards EO 40/53) pumps. The liquid nitrogen was then removed and the neck of the ampoule sealed with a methane-oxygen flame. Repeated freeze and thaw cycles were not used since significant polymerization has been observed during this procedure (Hruska, 1984). The ampoules were immersed in an oil bath and polymerized at $60 \pm 0.1^\circ C$ for 24 hours. This provided conversions in excess of 0.99 as determined by gravimetry.

For the sake of comparison, a linear poly(sodium acrylate) sample was also synthesized in the above manner.

2.2 Separation of Polymer

After the reaction was completed the ampoule was broken and immersed in an equimolar mixture of acetone and methanol. The recovered polymer was dried in a vacuum oven at $40^\circ C$ for one day. The sample was then swollen with distilled deionized water, reprecipitated and dried under vacuum. The latter procedure was repeated twice. The resulting polymer was then crushed with a mortar and pestle while freezing with liquid nitrogen. This provided particle sizes in the submillimeter range. The powder was then passed through a 100 μm nylon sieve.

All polymers were divided into a control sample and an extracted sample. The latter had the linear polymer chains removed by Soxhlet extraction; a 0.1 g sample was extracted for 24 hours. In all cases the sol fraction was below 0.2 wt.%. 
2.3  $^{13}$C Nuclear Magnetic Resonance Spectroscopy

The spectra of the crosslinked polymers were recorded in the dry condition by using CP-MAS and in the gel state under normal high-resolution conditions. Gel samples were prepared by slowly adding 5 mL D$_2$O to 0.5 grams of dry polymer powder, while the mixture was stirred magnetically. The gels were measured approximately 24 hours after preparation to allow sufficient time to attain complete swelling. The linear poly(sodium acrylate) sample was measured as a dry powder by using CP-MAS and in 9.96 wt.% solution in D$_2$O.

The CP-MAS spectra were obtained at 25.14 MHz and ambient temperature on a Bruker MSL 100 spectrometer operating at 2.349 T with high-power proton decoupling. The samples were spun at about 4.0 kHz in a dual-bearing magic-angle spinning probe. The optimum conditions for data collection of CP-MAS spectra for quantitative purposes were found to be 1 ms contact time and 1 s delay between pulse sequences, and all data were collected using these parameters. The $^{13}$C and $^1$H 90° pulses were 4 ms. An acquisition time of 72.7 ms was employed. Resolution enhancement was achieved with the 'Gaussian multiplication' feature included in the Bruker MSL software. Each CP-MAS spectrum contained 8000 data points over a 7042 Hz range with 40 000 to 60 000 acquisitions.

Gel- and solution-state $^{13}$C spectra were recorded at 62.89 MHz and ambient temperature on a Bruker WM 250 spectrometer operating at 5.87 T in the pulsed Fourier transform mode with broad-band proton decoupling. The $^2$H resonance of the diluent was employed for frequency lock. Sample spinning rates were about 20 Hz. Sample height was at least 40 mm. The $^{13}$C pulsewidth and acquisition times were 7 ms (20° pulse) and 0.442 s, respectively. Each gel- or solution-state spectrum contained 16 000 data points over a frequency range of 18 518 Hz with 120 000 to 160 000 acquisitions.

All of the $^{13}$C chemical shifts are reported relative to tetramethylsilane (TMS). Spin-lattice relaxation times were determined for a representative crosslinked poly(sodium
acrylate) gel and for a comparable linear polymer solution by the inversion recovery method (Craik, 1984).

3. RESULTS AND DISCUSSION

3.1 Cross Polarization/Magic-Angle Spinning Spectra

The solid-state $^{13}$C NMR spectra of two crosslinked poly(sodium acrylates) is shown in Figure A.1, together with the solid-state spectrum of a linear polymer synthesized under identical conditions. The corresponding assignments are summarized in Table A.2. The carboxylate, methine and methylene resonances occur at approximately the same chemical shifts in all three spectra. These peaks have been assigned on the basis of recent solution $^{13}$C NMR work involving poly(sodium acrylate) (Halverson, 1985, Truong, 1986), and poly(ammonium acrylate) (Zurimendi, 1984). Despite the CP-MAS technique employed, the methine and methylene peaks tend to overlap and could not be resolved completely. A similar limitation was reported for the overlapping backbone $^{13}$C peaks of linear poly(acrylic acid) in a recent solid state study (Fyfe, 1986). In addition, a weak, somewhat broad, peak appears in the spectra of the crosslinked polymers shown in Figures A1.b and A1.c. This peak is absent from the spectrum of linear poly(sodium acrylate) (Figure A1.a). Although it overlaps with the stronger carboxylate peak, its intensity clearly increases as the crosslinking monomer content increases. Furthermore, its position falls within the range common to amides of carboxylic acids (Wehrli, 1976) and nearly coincides with the chemical shift reported for the carbonyl carbon in polyacrylamide (Inoue, 1983; Zurimendi, 1984; Guerrero, 1985). For comparison with the above results, the solid-state $^{13}$C spectrum of N,N'-methylenebisacrylamide was also recorded, with the chemical shifts reported in Table A.2. It displays two peaks in the carbonyl region, to high field of 180 ppm, namely at 175 and 168 ppm. The peak at 180 ppm in the spectra of crosslinked poly(sodium acrylates), therefore, cannot be attributed to unreacted
Figure A.1: CP-MAS $^{13}C$ NMR spectra of (a) linear poly(sodium acrylate) and of two crosslinked poly(sodium acrylate) samples containing (b) 0.0494 and (c) 0.1348 mol fraction $N,N'$-methylenebisacrylamide.
Table A.2: $^{13}$C Chemical Shifts (relative to TMS) for Crosslinked and Linear Poly(Sodium Acrylates) in Solid State and in D$_2$O

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-CO$_2^-$</td>
</tr>
<tr>
<td>Linear poly(sodium acrylate), solid state$^a$</td>
<td>185</td>
</tr>
<tr>
<td>Crosslinked poly(sodium acrylate), solid state$^a$</td>
<td>185</td>
</tr>
<tr>
<td>$N,N'$-methylenebisacrylamide$^b$</td>
<td>e</td>
</tr>
<tr>
<td>Linear poly(sodium acrylate), solution$^c$</td>
<td>184.5</td>
</tr>
<tr>
<td>Crosslinked poly(sodium acrylate), solution$^d$</td>
<td>185</td>
</tr>
</tbody>
</table>

$^a$ Recorded on dry samples by using CP-MAS and high-power proton decoupling
$^b$ $N,N'$-methylenebisacrylamide, CP-MAS, olefinic carbon peaks appear at 135, 132 and 130 ppm
$^c$ 9.96 wt% in D$_2$O, broad-band proton decoupling
$^d$ 0.5g polymer and 5ml D$_2$O, broad-band proton decoupling
$^e$ Absent
$^f$ Doublet of approximately equal peak intensities
$^g$ 48.8(rr), 46.6(mr), 45.8(mr), 44.7(mm)
$^h$ 38.5, 36.4, 35.5
$^i$ Could not be resolved from CO$^-$ peak
divinyl monomer. The change in chemical shift relative to the monomer is, however, consistent with the change of the neighboring unsaturated carbons to alkyl carbons. Such a change is generally assumed to occur during vinyl-divinyl copolymerization (Dusek, 1969; Binisch, 1971; Macosko, 1976). Thus, because of its chemical shift and its absence from the spectra of linear poly(sodium acrylate) and the crosslinking monomer, we have attributed the 180 ppm peak to the carbonyl carbons of the N, N'-methylenbisacrylamide units in the crosslinked polymer.

If our assignments in the carbonyl region are correct, the intensity of the 180 ppm peak provides a measure of the number of crosslinking N, N'-methylenbisacrylamide repeat units. It would be reasonable to compare the intensity of this peak to that of the other copolymer carbonyl peak at 185 ppm if they have approximately the same NOE (nuclear Overhauser effect) factors. This supposition is supported by the observation that analogous peaks in polyacrylamide (Halverson, 1985) have similar NOE values. Accordingly, the relative intensity of the 180 ppm peak was determined by dividing its area by the sum of both (180 and 185 ppm) carbonyl peak areas.

These intensities are presented in Table A.3 and are plotted against the mol fraction of the crosslinking monomer in Figure A.2. This mol fraction (x) corresponds to that of the reaction mixture. It is not expected to differ largely from the N, N'-methylenbisacrylamide repeat-unit mol fraction of the crosslinked polymer since conversions exceeded 99%. In turn, we have designated the final mol fraction on N, N'-methylenbisacrylamide repeat units as (ax), while anticipating the proportionality factor (a) to be close to unity. Since each N, N'-methylenbisacrylamide repeat unit contains two carbonyl groups, the intensities of the 180 and 185 ppm peaks may be assumed to be proportional to 2ax and (1−ax) respectively. This assumption yields a simple approximate relationship between crosslinking monomer content and the relative intensity of the 180 ppm peak.
Table A.3: Solid-State Intensities and Hydrogel Linewidths of Crosslinked Poly(Sodium Acrylates)

<table>
<thead>
<tr>
<th>Mol fraction of divinyl monomer(^a)</th>
<th>Relative intensity at 180 ppm (CP-MAS)(^b)</th>
<th>Linewidth (Hz) for hydrogels(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(-\text{CH}^-)</td>
</tr>
<tr>
<td>0(^d)</td>
<td>0</td>
<td>10.55(^e,f)</td>
</tr>
<tr>
<td>0.0071</td>
<td>i</td>
<td>78.96</td>
</tr>
<tr>
<td>0.0191</td>
<td>i</td>
<td>131.39</td>
</tr>
<tr>
<td>0.0290</td>
<td>i</td>
<td>178.26</td>
</tr>
<tr>
<td>0.0311</td>
<td>i</td>
<td>176.87</td>
</tr>
<tr>
<td>0.0339</td>
<td>i</td>
<td>195.40</td>
</tr>
<tr>
<td>0.0391</td>
<td>i</td>
<td>196.36</td>
</tr>
<tr>
<td>0.0494</td>
<td>0.1001</td>
<td>207.52(^i)</td>
</tr>
<tr>
<td>0.0599</td>
<td>0.182</td>
<td>i</td>
</tr>
<tr>
<td>0.0762</td>
<td>0.1416</td>
<td>236.24</td>
</tr>
<tr>
<td>0.1046</td>
<td>0.1922</td>
<td>239.31</td>
</tr>
<tr>
<td>0.1348</td>
<td>0.2662</td>
<td>233.48</td>
</tr>
</tbody>
</table>

\(^a\) N,N'-Methylenebisacrylamide  
\(^b\) Area of the 180ppm peak divided by the sum of the areas of this peak and of the 185ppm peak  
\(^c\) Measured on gels containing 0.5g polymer and 5ml D\(_2\)O  
\(^d\) Linear poly(sodium acrylate)  
\(^e\) Measured at 44.7ppm for 9.96 wt% solution in D\(_2\)O  
\(^f\) \(T_1 = 174 \pm 28\) ms  
\(^g\) Measured at 38.5ppm for 9.96 wt% solution D\(_2\)O  
\(^h\) \(T_1 = 51 \pm 12\) ms  
\(^i\) This peak could not be resolved  
\(^j\) \(T_1 = 179 \pm 16\) ms  
\(^k\) \(T_1 = 96 \pm 9\) ms
Figure A.2: Relative intensity of the CP-MAS $^{13}$C NMR peak at 180 ppm (r) plotted as a function of the mol fraction of crosslinking monomer (x). Non-linear least squares analysis yielded 0.935 as the best fit value of the parameter a.
This relationship is compared to $^{13}$C intensity data in Figure A.2. Least-squares analysis of these data supports this model. This analysis also results in a proportionality factor near unity ($a=0.935$), with 99% confidence limits of [0.825, 1.045]. This is not significantly different from unity and indicates that the divinyl monomer was essentially completely reacted into the polymer backbone.

3.2 Hydrogel and Solution Spectra

The CP-MAS approach is somewhat limited in the present case by the overlap of the two carbonyl peaks (Figures A1.b, c) which restrict its application to samples with a fairly high degree of crosslinking. To complement the CP-MAS results, we have also measured the same superabsorbent polymers as highly swollen hydrogels. The $^{13}$C NMR spectra of two of these hydrogels are presented in Figure A.3 together with the solution spectrum of a linear poly(sodium acrylate) synthesized under identical conditions. Assignments for these spectra are proposed in Table A.2 on the basis of recent work on the linear polymer (Halverson, 1985; Truong, 1986; Candau, 1986). As reported, the carbonyl region of linear poly(sodium acrylate) appears to be relatively insensitive to tacticity. In contrast, the methine and methylene resonances tend to split according to odd and even monomer sequence lengths respectively (Koenig, 1980). This splitting was discussed in terms of triad resolution for the methine region by Truong (1986). Their spectra and assignments agree with ours, with the exception of a methine peak at 48.8 ppm, which was not reported by Truong. Nevertheless, Truong predicted a methine peak to appear somewhat downfield from 47 ppm, which would correspond to a syndiotactic triad sequence (rr). This sequence may be attributed to the 48.8 ppm peak in our linear poly(sodium acrylate) spectrum (Figure A.3a). This assignment seems plausible partly because it also fits the sequence distribution pattern for the polyacrylamide methine region by
Figure A.3: $^{13}$C NMR spectra of (a) a D$_2$O solution of linear poly(sodium acrylate) and of two crosslinked poly(sodium acrylate) samples swollen in D$_2$O, the latter containing (b) 0.0494 and (c) 0.1348 mol fraction of N, N'-methylenebisacrylamide in the dry state.
Lancaster and O'Connor (1982), namely, that the lowest and highest field peaks correspond to syndiotactic and isotactic sequences, respectively, at the triad level. In the same manner and in accord with Truong (1986), we have attributed the highest field methine peak to an isotactic sequence and the central two, somewhat overlapping, methine peaks to heterotactic sequences.²

Comparison of Figures A.1b, c with Figure A.3b, c reveals good agreement between CP-MAS and hydrogel spectra apart from the relatively weak CP-MAS peak at 180 ppm. In the gel measurements, this peak could not be resolved from the very broad CO₂⁻ peak centered around 185 ppm. If, in Figure 3, spectra 3b and 3c are compared to spectrum 3a, the strong line broadening in the spectra of crosslinked poly(sodium acrylate) becomes obvious. Furthermore, the linewidths appear to increase with increasing crosslinking density (i.e from 3b to 3c). A similar effect was reported for crosslinked polystyrene gels that contained chloroform as a diluent (Ford, 1981, 1983).

We have investigated the possibility that the line broadening described above might act as an empirical measure of the extent of crosslinking. For this purpose, the ¹³C NMR spectra of a series of hydrogels with different crosslinking levels were measured. Since the linewidths of some other gel spectra had been found to depend on diluent concentration (Yokota, 1978), we have maintained a constant D₂O content in our hydrogel samples. The methine and methylene linewidths of these swollen polymers are listed in Table A.3 and plotted against the crosslinking monomer content in Figure A.4. The extent of methine peak broadening remains considerably below that of the methylene peak broadening in the entire composition range examined. Both of these peaks reveal the same trend, namely, that they

² The absence of the 48.8 ppm peak from a previous poly(sodium acrylate) spectrum (Truong, 1986) probably stems from the somewhat different synthetic approach taken in that investigation.
Figure A.4: Linewidths (Hz) of the CH (●) and CH$_2$ (Δ) $^{13}$C resonances (w) of crosslinked poly(sodium acrylate) samples in D$_2$O versus the mol fraction of crosslinking monomer (x).
broaden sharply up to about 0.02 mol fraction crosslinking monomer then level off until they reach a maximum at approximately 0.08 mol fraction crosslinking monomer content. The solid line in Figure A.4 represents a regressed equation fit to the data.

\[ L_w = \theta_1 (1 - e^{-\frac{\theta_2}{x}}) + \theta_0 \]

Where \( L_w \) is the linewidth (Hz), \( \theta_0 \) is the line broadening for a linear polymer, and \( \theta_1 \) and \( \theta_2 \) are empirical parameters. Table A.4 lists the magnitude of \( \theta_{0.2} \) and the corresponding 95% confidence intervals for both methine and methylene peaks. The confidence intervals are large, reflecting the limited amount of data at low levels of divinyl monomer. Nonetheless, the empirical equations for line broadening can be used to estimate the extent of crosslinking. For example, a polymer with 0.1 wt.% N, N'-methylenebisacrylamide and a measured line width of 34 Hz would have 95% confidence limits of \([0.073\%, \ 0.162\%]\) as determined by this method.

The origin of this line broadening is not unambiguous. It may be due in part to an increasing diversity of environments, and hence of chemical shifts, with increasing crosslinking. Alternatively, more restricted mobility in the crosslinked polymer may result in shorter relaxation times and hence broader lines. It is also possible that the broadening is greater for some carbons than for others, depending on their position in the chain relative to the crosslinks, and that the apparent limiting linewidth reflects the inability to measure a very broad component at high crosslinking. We would suggest, though, that measurement of the linewidth could provide an empirical measure of the extent of crosslinking at low levels of divinyl monomer, particularly if more data is generated at low crosslinking densities. Thus the gel measurements complement the CP-MAS measurements to the extent that the latter only provide useful information on the extent of crosslinking at high crosslinking densities. Data shown in Table A.3 indicate that there is relatively little change of \( T_1 \) with crosslinking.

There have been varied reports on this topic in the literature (Schaefer, 1973; Komoroski,
Table A.4: Parameter Estimates for Methine and Methylene Line Broadening

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Magnitude</th>
<th>Units</th>
<th>95% confidence limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Methine peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_0 )</td>
<td>10.55</td>
<td>Hz</td>
<td>- +</td>
</tr>
<tr>
<td>( \theta_1 )</td>
<td>222.1</td>
<td>Hz</td>
<td>[207.1, 237.2]</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>53.4</td>
<td>Dimensionless</td>
<td>[41.0, 65.7]</td>
</tr>
<tr>
<td>2) Methylene peak</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \theta_0 )</td>
<td>17.71</td>
<td>Hz</td>
<td>- +</td>
</tr>
<tr>
<td>( \theta_1 )</td>
<td>338.2</td>
<td>Hz</td>
<td>[306.8, 369.6]</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>47.8</td>
<td>Dimensionless</td>
<td>[33.7, 61.8]</td>
</tr>
</tbody>
</table>

* Measured from the linewidths of a linear polysodium acrylate.
1976; Rowland, 1978; Barrett, 1979; Charlesby, 1977, 1979, 1980; Munie, 1980; McCormick, 1987). This observation would favor a chemical shift explanation for the line broadening.
REFERENCES


APPENDIX B:

THEORETICAL PREDICTION OF THE SECOND VIRIAL COEFFICIENT

1. INTRODUCTION

The modelling of the second virial coefficient and the growth of dilute polymer solution theories was the focus of intense investigation for a period of about twenty years beginning in the early 1950's. The principal investigators were Flory, Zimm, Stockmayer and Yamakawa, although many others made important experimental or theoretical contributions. The first work on dilute solution theory was carried out by Flory and various coworkers, most notably Orofino, Krigbaum and Fox.

In 1950 Flory and Krigbaum applied the excluded volume concept to polymer solutions (Figure B.1). By analogy to Van der Waals theory for gases, where the excluded volume causes an increase in gas pressure, they showed that in polymer solutions, intermolecular interactions between chain segments increased the configurational entropy. This led to an increase in the osmotic pressure. They also demonstrated that the theta temperature represented the absence of excluded volume effects, just as repulsive and attractive forces perfectly compensate at the Boyle temperature for gases. It is these excluded volume effects which cause the configuration of flexible polymer chains to deviate from the statistics of random flights.

The parallel to Van der Waals gases was extended further by showing that the second virial coefficient was a function of the intermolecular excluded volume (u) (Flory and Krigbaum, 1950).

\[ A_2 = \frac{N_A u}{2 M^2} \]

or
Figure B.1: An illustration of intermolecular excluded volume. The volume $\frac{4}{3}\pi (2r)^3$ is excluded to the molecule on the right (Carpenter, 1970).
\[ A_2 = \frac{-2}{N_A V_o} \psi (1 - \frac{\theta}{T}) h(Z) \]

where \( \psi \) is the partial specific volume of the polymer

\( V_o \) is the molar volume of the solvent

\( M \) is the molecular weight of the polymer

\( N_A \) is Avogadro's number

\( \psi \) is the interpenetration function, an empirical parameter which characterizes the enthalpy of dilution of a polymer in a given solvent

\( \theta \) is the Theta temperature

\( h(Z) \) is a function accounting for intermolecular interactions.

For this derivation Flory and Krigbaum assumed a Gaussian segment density distribution\(^1\) within the volume element of interest.

The second virial coefficient accounts for interactions of short segments of two polymer chains that are in close contact. Although the influence of the solvent molecules is not explicitly accounted for, their presence affects the solute-solute interaction potential.

Because of the difficulties in extending the Flory-Huggins theory to dilute solutions, a second group of investigators used an approach based on the statistical mechanical methods for real gases. In 1953 Zimm, Fixman and Stockmayer applied the molecular distribution functions developed by McMillan, Mayer and Montroll (1941,1945) to compute the distribution functions of two macromolecules in contact with each other. Under their approach \( A_2 \) is represented as:

\[ A_2 = \frac{N_A n^2 \beta h(Z)}{2 M^2} \]

---

\(^1\) Flory (1945) had previously assumed a uniform segment density distribution, but this predicted \( A_2 \)'s which were independent of molecular weight, in disagreement with experimental findings.
where \( n \) is the number of chain bonds per theoretical chain \( \langle \beta = \vec{R}_i^2/b^2 \rangle \)

\( \beta \) is the binary cluster integral or excluded volume

\( b \) is the random flight bond length

\( Z \) is the "excluded volume parameter" defined as

\[
Z = \left( \frac{3}{2n \langle R^2 \rangle_o} \right)^{3/2} \beta n^2
\]

From such a theory the molecular dimensions can be predicted with the knowledge of three parameters, \( n, b \) and \( \beta \). Since these parameters never occur separately, but only in two combinations, \( n^2b^2 \) and \( n^2\beta \), solution theories based on this approach have been historically referred to as two parameter theories.\(^2\) \( b^2 \) is a short range parameter that depends on interactions of segments near one and other, through potential energies of internal rotation. The excluded volume or cluster integral (\( \beta \)) is an intramolecular interaction between unbounded segments. It causes deviations in macroscopic properties of polymer solutions over what would be predicted from random flights. These are often expressed in terms of an expansion function, \( \alpha \):

\[
\alpha^2_R = \frac{\langle R^2 \rangle}{\langle R^2 \rangle_o}
\]

Provided that clusters of three or more segments can be ignored, which seems quite certain for dilute solutions, the cluster integral is a function of a single variable, \( Z \).\(^3\)

---

\(^2\) The dependence of \( A_2 \) on only two parameters is a consequence of the superposition approximation, in which inter-segmental interactions are taken to be pairwise and additive. If this assumption were invalid then a single parameter (\( Z \)) would be unable to correlate \( A_2 \) as a function of molecular weight and temperature. Berry (1966) had demonstrated the validity of the superposition principal.

\(^3\)
For these reasons expansion coefficients are modelled as a function of $Z$ exclusively. A more detailed discussion of intramolecular interactions will be presented later in this appendix.

The function $h(Z)$ accounts for intermolecular interactions between pairs, triplets, quadruplets etc. of segments of two polymer chains in very close contact. These "short range" interactions are expressed as

$$h(Z) = 1 - Z n^{-5/2} \sum_{i_1,j_2,i_2} C_1^{-3} + Z^2 n^{-3} \sum_{i_1,j_2,i_2,i_3,j_3} C_2^{-3} \ldots$$

The constants in this expression are called the first, second, third etc. contact terms. Where the $i$th contact term represents $i$ intermolecular contacts between two chains. A visual representation of these contacts is given in Figure B.2. This function for $h(Z)$ is a very slowly converging series and in generally truncated after three or fewer terms. The intermolecular and intramolecular interactions are seen to be coupled through the excluded volume parameter, and therefore rigorous modelling of $A_2$ must simultaneously consider both these interactions. Unfortunately, early research in dilute solution theory saw inter- and intramolecular theories pursued separately. For this reason they will be discussed independently in the next section.

---

Expansion factors can also be defined based on the radius of gyration of intrinsic viscosity:

$$a_S^2 = \frac{<S^2>}{<S^2>_{o}}$$

$$a_\eta^2 = \frac{|\eta|^2}{|\eta|_o^2}$$

Subscripts $o$ or $\theta$ represent the unperturbed or theta state.
Figure B.2: Cluster diagram for double and triple intermolecular contacts. (Kurata, 1958; Yamakawa, 1971).
In 1955, Stockmayer showed that Flory's lattice theory and the distribution function approach, although very different conceptually, were actually based on the same premises. He also proved that their equations for the second virial coefficient were equivalent. For the remainder of the chapter the notation of Zimm et al. (Distribution function approach) will be used. A further history of the developments in dilute solution theory is given in Table B1.

2. **MODELLING EXCLUDED VOLUME**

Two segments of a chain, separated by a large number of bonds, can find themselves in neighbouring volume elements because of the random nature of the chain orientation. Van der Waals forces of repulsion will tend to exclude one segment from the vicinity of the other. These intramolecular interactions are referred to as excluded volume effects. Fox and Flory (1951) were the first to model excluded volume, and they found that chain expansion could be expressed as:

\[
\alpha^5 - \alpha^3 = 2 C_m \psi \left(1 - \frac{6}{T}\right) M^{1/2} = 2.60Z
\]

where

\[
C_m = \left(\frac{2}{25^2 n^{3/2}}\right) \left(\frac{\nu}{N_A V_o}\right) \left(\frac{<R^2>_o}{M}\right)^{-3/2}
\]

This can be rewritten as a series expansion of \(\alpha^2\):

\[
a_R^2 - 1 = C_1 Z - C_2 Z^2 + C_3 Z^3 - \ldots
\]

where \(C_1, C_2, C_3, \ldots\) are the first, second, third etc. intramolecular contact terms. \(C_1\) represents i intramolecular contacts of a single chain (Figure B3). Theories that evaluate \(C\) up to \(k\) terms are referred to as \(k^{th}\) order perturbation theories. Early theories of the expansion factor sought to evaluate the individual contact terms. Several investigators (Teromoto, 1951; Grimley, 1953; Zimm, Stockmayer and Fixman, 1953; Saito, 1954) found \(C_1 = 4/3\). In 1955
Table B.1

History of the development of dilute solution theory

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1946</td>
<td>Zimm</td>
<td>Applied statistical mechanical methods to dilute polymer solutions</td>
</tr>
<tr>
<td>1949</td>
<td>Flory</td>
<td>Introduced excluded volume and the fifth power relationship for the expansion factor</td>
</tr>
<tr>
<td>1950</td>
<td>Flory-Krigbaum</td>
<td>Modified theory of $A_2$ to account for molecular weight dependence</td>
</tr>
<tr>
<td>1951, 49</td>
<td>Fox-Flory</td>
<td>Treatment of viscosities</td>
</tr>
<tr>
<td>1955</td>
<td>Stockmayer</td>
<td>Demonstrated equivalence of lattice and distribution function theories</td>
</tr>
<tr>
<td>1957</td>
<td>Orofino-Flory</td>
<td>First closed expression for $h(Z)$</td>
</tr>
<tr>
<td>1960</td>
<td>Stockmayer</td>
<td>Modified Flory-Krigbaum-Orofino theory</td>
</tr>
<tr>
<td>1962</td>
<td>Casassa</td>
<td>Modelled the effect of heterogeneity in molecular weight on the second virial coefficient</td>
</tr>
<tr>
<td>1964</td>
<td>Kurata-Yamakawa</td>
<td>Hierarchical approach for modelling the expansion factor. Showed need for self consistency in inter-and intramolecular theories</td>
</tr>
<tr>
<td>1966</td>
<td>Berry</td>
<td>Experiments supported the idea of a two parameter model</td>
</tr>
<tr>
<td>1967</td>
<td>Yamakawa-Tanaka</td>
<td>Closed expression for $a$</td>
</tr>
<tr>
<td>1968</td>
<td>Yamakawa</td>
<td>Derived hierarchical theory for second virial coefficient</td>
</tr>
<tr>
<td>1982-5</td>
<td>Oono; Douglas-Freed</td>
<td>Renormalization Group Methods applied to polymer solution theory</td>
</tr>
</tbody>
</table>
Figure B.3: Schematic representation of single and double intramolecular contacts (Yamakawa, 1971).
Fixman, using a cluster expansion method found $C_2 = 2.075$. Later Yamakawa and Tanaka (1967) used a numerical calculation, which is necessary for third and higher order perturbation theories, to find $C_3 = 6.459$. The corresponding expression for $a_s^2$ is:

$$a_s^2 - 1 = 1.275Z - 2.082Z^2 + \ldots$$

The first contact term was evaluated by Zimm, Stockmayer and Fixman (1953) and the second by Yamakawa, Aoki and Tanaka (1966). These equations for $a_R^2$ and $a_s^2$ are exact solutions. However, because the series is very slowly converging, they are valid only at low values of $Z$. Evaluating a higher order perturbation theory would be difficult, if not unsolvable. Therefore the focus of research shifted to developing an approximate closed expression for the expansion factor. All such theories predict that $a$ will increase with $Z$ without limit and have the asymptotic form:

$$\lim_{Z \to \infty} a^\gamma = \text{constant} \cdot Z$$

There are four types of theories:

$$\nu = 1 \text{ James (1953)}$$

3 Fixman (1955); Kurata, Stockmayer and Roig (1960); Ptitsyn (1961)

4 Bueche (1953)

5 Flory (1949)

Yamakawa and Tanaka (1967) later showed that $\nu$ lies between the limits of 3 and 6.67. Table B2 summarized the expressions for the expansion factor. Table B3 lists the first three contact terms for each model and Figure B4 compares them to the exact solution at low values of $Z$. The Bueche-James, Fixman and Kurata theories have second and third contact terms that are far too low, and must be eliminated from consideration. The remainder of the theories all appear to conform to the exact behaviour of $a$ at low $Z$ within reasonable bounds. In evaluating the approximate expressions for the expansion factor Yamakawa (1971) concluded that the Ptitsyn and modified Flory theories represent the upper and lower limits respectively,
<table>
<thead>
<tr>
<th>Model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_R^4 - a_R^2 = \frac{48}{69} Z \left( 1 + \frac{2}{3a_R^2} + \frac{1}{4a_R^4} \right)$</td>
<td>Bueche (1953)</td>
</tr>
<tr>
<td>$a_R^2 = 1 + \frac{4}{3} a_R Z$</td>
<td>Bueche, James (1953)</td>
</tr>
<tr>
<td>$a_R^2 = 1 + 2Z$</td>
<td>Fixman (1962)</td>
</tr>
<tr>
<td>$a_S^3 = 1 + 1.914Z$</td>
<td></td>
</tr>
<tr>
<td>$a_R^5 - a_R^3 = 4/3Z$</td>
<td>Flory, modified: Stockmayer (1955)</td>
</tr>
<tr>
<td>$a_S^5 - a_S^3 = 134/105Z$</td>
<td></td>
</tr>
<tr>
<td>$a_S^5 - a_S^3 = 0.648Z \left( 1 + 0.969 \left( \frac{1+10Z}{a_S^3} \right)^{-23} \right)$</td>
<td>Flory, Fisk (1966)</td>
</tr>
<tr>
<td>$a_S^2 = 1 + 0.4649 \text{(CZ)} - 0.2458 \text{(CZ)}^2$</td>
<td>Fujita, Norrisuge (1970)</td>
</tr>
<tr>
<td>$C = 2.745$</td>
<td></td>
</tr>
<tr>
<td>$a_R^5 - 0.4931 a_R^3 - 0.2499 a_R^{-1.332} \sin(1.073 \ell \ln a_R) - 0.5069 a_R^{-1.332} \cos(1.073 \ell \ln a_R) = 2.63Z$</td>
<td>Fujita, Okita, Norrisuge (1967)</td>
</tr>
<tr>
<td>$\frac{1}{5} (a_R^5 - 1) + \frac{1}{3} (a_R^3 - 1) = 4/3Z$</td>
<td>Kurata (1968)</td>
</tr>
<tr>
<td>$a_R^3 - a_R = 2.053Z \left( 1 + \frac{1}{3a_R^2} \right)^{-32}$</td>
<td>Kurata, Stockmayer, Roig (1960)</td>
</tr>
<tr>
<td>$4.67 a_R^2 = 3.67 + (1 + 9.34Z)^{23}$</td>
<td>Ptitsyn (1961)</td>
</tr>
<tr>
<td>$5.12 a_S^2 = 4.12 \left( 1 + 9.79Z \right)^{22}$</td>
<td></td>
</tr>
<tr>
<td>$a_R^2 = 0.572 + 0.428 (1 + 6.23Z)^{1/2}$</td>
<td>Yamakawa, Tanaka (1967)</td>
</tr>
<tr>
<td>$a_S^2 = 0.541 + 0.459 (1 + 6.04Z)^{1/2}$</td>
<td></td>
</tr>
</tbody>
</table>
### Table B.3

Comparison of approximate and exact theories of the expansion factor at low values of Z

<table>
<thead>
<tr>
<th>Theory</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact</td>
<td>1.33</td>
<td>2.08</td>
<td>6.46</td>
</tr>
<tr>
<td>Bueche-James (1953)</td>
<td>1.33</td>
<td>-0.89</td>
<td>0.30</td>
</tr>
<tr>
<td>Fixman (1962)</td>
<td>1.33</td>
<td>0.44</td>
<td>0.40</td>
</tr>
<tr>
<td>modified Flory (Stockmayer, 1955)</td>
<td>1.33</td>
<td>2.67</td>
<td>9.78</td>
</tr>
<tr>
<td>Fujita-Okita-Norrisuge (1967)</td>
<td>1.33</td>
<td>1.50</td>
<td>2.96</td>
</tr>
<tr>
<td>Kurata (1968)</td>
<td>1.33</td>
<td>0.89</td>
<td>1.09</td>
</tr>
<tr>
<td>Ptitsyn (1961)</td>
<td>1.33</td>
<td>2.08</td>
<td>3.61</td>
</tr>
<tr>
<td>Yamakawa-Tanaka (1967)</td>
<td>1.33</td>
<td>2.08</td>
<td>6.46</td>
</tr>
</tbody>
</table>
Figure B.4: Theoretical values of $\sigma R^3$ calculated from various theories. (Yamakawa, 1971).
BJ: Bueche-James
F1: Fixman
K: Kurata
P: Pitsyn
F0: Original Flory theory
Fm: Modified Flory theory
FON: Fujita-Okita-Norrisuge
YT: Yamakawa-Tanaka
B: Bueche
over the ordinary range of interest. These theories will be coupled with their corresponding intermolecular interaction theories and evaluated against experimental data at the end of the appendix.

3. MODELLING OF THE SECOND VIRIAL COEFFICIENT IN THE ABSENCE OF INTRAMOLECULAR INTERACTIONS

3.1 Intermolecular Interactions

As was noted in the preceding section the intermolecular interactions can be represented by the function \( h_0(Z) \), which is expressed as an infinite series. The double contact term has been evaluated by Zimm (1946) and Fixman (1953), with the triple contact term provided by Albrecht (1957) and Tagami and Casassa (1969). The exact form of the second order perturbation theory of the second virial coefficient is:

\[
h_0(Z) = 1 - 2.865Z + 9.202Z^2 - \ldots
\]

The subscript "o" indicates that these intermolecular interactions have been computed in the absence of intramolecular forces. This solution would require on the order of \( 10^2 \) contact terms to be valid over a useful range of \( Z \). In its present form it is limited to \( |Z| \leq 0.15 \). Because \( h_0 \) is a function of \( Z \) only, the second virial coefficient may be expressed in terms of two parameters, \( n^b \) and \( n^2 \beta \) in analogy to models for the excluded volume effect.

In order to evaluate the short range interactions at large values of \( Z \) three approximate closed expressions were developed. The smoothed-density model developed by Flory and Krigbaum (1950) and Grimley (1952) and improved by Isihara and Koyama (1956) assumes a distribution for the average segment density about its centre of mass, and computes intermolecular interaction parameters as a function of separation.\(^4\) The results can be expressed as:

---

\(^4\) These forces can be thought of as intermolecular excluded volume effects.
\[ h_o(Z) = \sum_{k=1}^{\infty} \frac{(-3^{3/2}Z)^{k-1}}{k! k^{3/2}} \]

Orofino and Flory (1957) later converted this into an approximate closed form:

\[ h_o(Z) = \frac{1}{2.30 Z} \ln (1 + 2.30Z) \]

Stockmayer (1960) later suggested altering the value of the numerical constant 2.30 to make the model consistent with first order perturbation theory. The result

\[ h_o(Z) = \frac{1}{5.73 Z} \ln (1 + 5.73Z) \]

is now referred to as the modified-Flory-Krigbaum-Orofino theory.

Fixman (1953), Casassa (1957) and Markovitz (1958) modified the smooth density model by selecting an arbitrary intermolecular contact as a reference for the segment distribution instead of the centre of mass. This overcame the inherent problem of the FKO,m theory, its inability to correctly estimate the double contact term. The FCM model has the form:

\[ h_o(Z) = \frac{1 - \exp(-5.73Z)}{5.73Z} \]

The form of this function was arbitrarily selected to provide a closed expression for \( h_o(Z) \). It does however yield a function that is accurate to within two percent of the corresponding series formulation of \( h_o(Z) \) over the range of \( Z \) investigated.

Using an analogy to models for the expansion factor where the \( i \)th contact terms were evaluated by an \( i \)th order differential equation (\( \alpha \) differentiated with respect to \( \beta \)), Yamakawa (1968) created a hierarchy of differential equations for the second virial coefficient. By truncating after the third term and assuming an asymptotic function of \( h(Z) \) at large \( Z \)

\[ \lim_{Z \to \infty} h(Z) = \beta_1 Z^{-1} + \beta_2 Z^{-2} \]

Yamakawa derived the equation
\[ h_0(Z) = \frac{1 - (1 + KZ)^{\frac{-3C_2}{3C_2 - 2C_1}}}{(2C_1 - K)Z} \]

where
\[ K = \frac{3C_2}{C_1} - 2C_1 \]

This equation is general and can transform into all the approximate equations for \( h_0(Z) \) by the appropriate choice of \( C_1 \) and \( C_2 \). Using the exact values for \( C_1 \) and \( C_2 \) Yamakawa defined
\[ h_0(Z) = \frac{1 - (1 + 3.903Z^{-0.4683})}{1.828Z} \]

which, of course, reduces to the exact second order perturbation model. A summary of all intermolecular models, in the second order form, is shown in Table B4 and Figure B5. All these theories except the original FKO are reasonable, give the correct initial slope and have the fully asymptotic behaviour:

\[ \lim_{Z \to \infty} h_0(Z) = \text{constant} \cdot Z^{-1} \]

In the next section the models for short and long range interactions will be combined to provide a comprehensive approach to dilute solution properties. The most suitable models will be selected by a comparison to experimental \( A_2, [\eta] \), and \( < R_G > \) data.

4. **MODELLING SECOND VIRIAL COEFFICIENTS IN THE PRESENCE OF INTRAMOLECULAR INTERACTIONS**

The presence of intramolecular Van der Waals forces influences the strength of the intermolecular excluded volume interactions. Although the single and double contact terms are unaffected, the third and higher order terms increase. Kurata (1964) and Casassa (1969) have used a second order perturbation theory to evaluate the third contact term. The resulting expression for \( h(Z) \) is:

\[ h(Z) = 1 - 2.365Z + 14.278Z^2 - \ldots \]
Table B.4
Comparison of the first two contact terms for various intermolecular theories

<table>
<thead>
<tr>
<th>Theory</th>
<th>$C_1$</th>
<th>$C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact Solution</td>
<td>2.865</td>
<td>9.202</td>
</tr>
<tr>
<td>Flory-Krigbaum (1950), Grimley (1962)</td>
<td>2.865</td>
<td>0.867</td>
</tr>
<tr>
<td>Original Flory-Krigbaum-Orofino (1957)</td>
<td>1.151</td>
<td>1.767</td>
</tr>
<tr>
<td>Modified Flory-Krigbaum-Orofino (Stockmayer, 1960)</td>
<td>2.865</td>
<td>10.944</td>
</tr>
<tr>
<td>Fixman (1955), Casassa-Markovitz (1958)</td>
<td>2.865</td>
<td>5.472</td>
</tr>
<tr>
<td>Isihara-Koyama (1956)</td>
<td>1.043</td>
<td>1.135</td>
</tr>
<tr>
<td>Kurata-Yamakawa (1968)</td>
<td>2.865</td>
<td>9.202</td>
</tr>
<tr>
<td>Kurata (1968)</td>
<td>2.865</td>
<td>6.124</td>
</tr>
<tr>
<td>Stockmayer (1960)</td>
<td>2.865</td>
<td>8.208</td>
</tr>
</tbody>
</table>
Figure B5: Theoretical values of $h_o(z)$ calculated from various theories (Yamakawa, 1971).

$FKO_o$: original Flory-Krigbaum-Orofino
$FKO_m$: modified Flory-Krigbaum-Orofino
$K$: Kurata
$KY$: Kurata-Yamakawa
$S$: Stockmayer
$FCM$: Fixman-Casassa-Markovitz
The absence of the subscript \( \sigma \) in \( h(Z) \) indicates that inter- and intramolecular interactions are coupled. Figure B6 illustrates some of the combinations of inter- and intramolecular interactions that can be postulated.

In order to couple the short and long range interactions the concept of an "effective bond length" is introduced. The intramolecular excluded volume effects, normally represented in terms of bulk properties such as viscosity or radii of gyration are reduced to the atomic level. Each covalent bond is hypothesized to be stretched by a factor \( \alpha^* \) due to intramolecular forces. Although \( \alpha^* \) in principal bears no relationship to \( \alpha \), Flory and Krigbaum (1950) have shown that the microscopic and bulk expansion factors are essentially equivalent. Since the parameter \( Z \) is a function of the bond length to the reciprocal third power, the effective excluded volume parameter \( \overline{Z} \) in the presence of intramolecular interactions, can be expressed as:

\[
\overline{Z} = \frac{Z}{a_3^3}
\]

or alternatively

\[
h(Z) = h_0(\overline{Z})
\]

We can therefore generalize the closed expressions for \( h_0(Z) \) to include the coupling of inter- and intramolecular forces by replacing the argument \( Z \) by \( \overline{Z} \). However, we must only integrate theories that are based on the same premises. For example, the original Flory-Krigbaum-Orofino theory for \( h_0 \) can be used with Flory's theory for \( a_3 \), as both are based on the smoothed Gaussian density model. We may also combine the modified FKO and Flory's \( c_3 \) theories. Similarly, the Kurata-Yamakawa theory for \( h_0 \) can be coupled with the Yamakawa-Tanaka theory for the expansion factor since both were derived by the hierarchy approach. These three theories are summarized in Table B.5.

The equation for the second virial coefficient is:
Figure B.6: Cluster diagrams illustrating two intermolecular contacts in the presence of a single intramolecular contact (Yamakawa, 1971).
Table B.5
Self consistent theories for the second virial coefficient of real polymer chains

<table>
<thead>
<tr>
<th>Theory</th>
<th>Interpenetration function ($\psi$)</th>
<th>Expansion factor ($a_s$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>original Flory – Krigbaum – Orofino (1957)</td>
<td>$\frac{\ln(1 + 2.30 \bar{Z})}{2.30}$</td>
<td>$a_5^s - a_3^s = 2.60Z$</td>
</tr>
<tr>
<td>modified Flory – Krigbaum – Orofino (Stockmayer, 1960)</td>
<td>$\frac{\ln(1 + 5.73 \bar{Z})}{5.73}$</td>
<td>$a_5^s - a_3^s = 1.1276Z$</td>
</tr>
<tr>
<td>Kurata – Yamakawa – Tanaka (1968)</td>
<td>$0.547 \left[1 - (1 + 3.903 \bar{Z})^{-0.4683}\right]$</td>
<td>$0.541 + 0.459(1 + 6.04Z)^{0.46}$</td>
</tr>
</tbody>
</table>
\[ A_2 = \left( \frac{N_A n^2 \beta}{2 M^2} \right) h(Z) \]

where

\[ Z = \frac{\beta n^2}{(4 n \langle S_2 \rangle_o)^{3/2}} \]

This can be rewritten for real solutions (inter- and intramolecular interactions occurring simultaneously) as:

\[ A_2 = \frac{4 n^{32} N_A \langle S^2 \rangle^{3/2} \psi}{M^2} \]

where

\[ \psi = \overline{Z} h_o(\overline{Z}) \]

Therefore, from measurements of molecular weight and the radius of gyration in the perturbed and unperturbed states, one can predict the second virial coefficient.

Yamakawa (1971) has evaluated the three self sufficient theories of \( A_2 \) and has found that both the KYT and FKO,m give satisfactory agreement to experimental data, Figure B.7. The KYT theory is marginally better predicting the trend in the interpenetration function, particularly in good solvents.

Kok and Rudin (1981) have found the KYT theory predicts experimental second virial coefficients within about \( \pm 21\% \). This is 2\% more accurate than the modified FKO and 10\% better than the original FKO theories. Kok and Rudin also developed a method where the expansion factor was calculated from intrinsic viscosity correlations in good and theta solvents. Using the Kurata-Yamakawa theory for the interpenetration function (\( \psi \)) they predicted \( A_2 \) in good agreement with experimental results (Figure B.8). Their approach gave marginal improvement over the KYT theory, although at this stage both should be considered acceptable. Recent refinements to the KYT or "bare perturbation" theory have also included the extension to three dimensional polymer chains (Muthukumar, 1984).
Figure B.7: Comparison of theoretical and experimental values of the interpenetration function ($\psi$) as a function of $\alpha_3^0$ (Yamakawa, 1971).
(1): original Flory-Krigbaum-Orofino
(2): modified Flory-Krigbaum-Orofino
(3): Kurata-Yamakawa-Tanaka

Figure B.8: Comparison of experimental and theoretical second virial coefficients. The predicted values are from Kok and Rudin's (1981) modification of the Kurata-Yamakawa-Tanaka model.
In the mid 1970's the asymptotic behaviour of the expansion factor was re-examined. Several researchers (Edwards, 1975; Oono, 1975, 1976; Gordon, 1976) concluded that the series expression for \( a_g(Z) \) was indeed not convergent. This evidence, and the search for a phenomenological theory for polymer solutions led to the development of the "Renormalized Perturbation Theory". This applies renormalization group methods to the evaluation of the distribution functions. By extending the perturbation theory to four dimensional space, the singularity in the Hamiltonian at \( Z = 0 \), present in the solutions to two parameter theories, can be avoided. Renormalized perturbation theories are applicable for a variety of chain architectures (linear, ring, star, comb) in both poor and good solvents. By comparison unrenormalized models are restricted to linear polymers in the vicinity of the theta point. However, the renormalization group theory cannot, at present, quantify the dilute solution behaviour at low values of the excluded volume parameter, for highly branched polymers or for the crossover region between poor and good solvents. It has therefore been slow to displace bare perturbation models, which are conceptually simpler and can describe the experimental observations for a variety of polymer-solvent combinations.
REFERENCES

APPENDIX C:
CATEGORIZING EMULSIONS

Dispersions of water, oil and emulsifiers can exist as either macro- or micro-emulsions. Macroemulsions are produced by agitation and require steric or electrostatic repulsive forces to maintain stabilization. They are turbid, thermodynamically unstable and can be formed with either aqueous or organic continuous phases. The structure is delineated by the relative interfacial tensions of the water-hydrophile and oil-lipophile. The free energy is minimized by reducing the area of the side of the film with the higher surface tension. Macroemulsions can be inverted by the addition of an "inverting surfactant" which functions by lowering the dispersed phase interfacial tension. For example a water-in-oil emulsion stabilized with a low HLB surfactant (sorbitanmonooleate, HLB 4.3) can be inverted with a dilute aqueous solution of ethoxylated octyl phenol (HLB 12-13) (Becker, 1982). Macroemulsions are used in liquid-liquid extraction, controlled release systems, in agriculture and medicine and in commercial products including paints and foams. Multiple emulsions (Figure C1) and reticulated particles (Vanderhoff, 1984) can also be produced.

Cosurfactants are often employed to enhance stabilization. Their utility can be appreciated by recalling the Gibbs Adsorption isotherm which states that any positively adsorbed species lowers the interfacial tension. An interface saturated with a single surfactant can therefore form a more condensed boundary layer by adding a small molecule cosurfactant to fill the voids and maximize the entropy of mixing.

Microemulsions are clear, monophase, stable dispersions of two immiscible liquids. They form small particles (≈10^2-10^3 Å) and exist only at high emulsifier levels. They can be easily inverted by direct dilution in excess quantities of the dispersed phase (Candau, 1987). They are commonly used in tertiary oil recovery, as cutting fluids and in waxes, polishes,
Figure C.1: Illustration of the types of macroemulsions: (a) oil-in-water, (b) water-in-oil, (c) water-oil-water, (d) oil-water-oil. From Shah (1985).
cosmetics and pharmaceuticals. Prince (1977) has constructed a hypothetical phase diagram showing the micro- and macroemulsion domains (Figure C2). Holtzschwerter (1988) has measured the minimum emulsifier concentration required for the formation of a microemulsion as a function of the HLB of the surfactant mixture (Figure C3). The optimum HLB appears to be approximately 8.65, higher than is generally reported for water-in-oil emulsions. This is caused by a stabilizing or cosurfactant effect of acrylamide, which constitutes one-fourth of the interfacial mass (Candau 1984, 1987). This decreases the overall HLB and enables the formation of microemulsions with more hydrophobic emulsifiers.1

Holtzschwerter has also developed a theoretical procedure whereby the oil phase can be optimally selected by matching its molar volume and solubility parameters to those of the lipophile. Stabilization is also improved by using mixtures of emulsifiers which contain the same hydrophilic head. As an example Figure C4 demonstrates that for their emulsifier system (sorbitan sesquioleate and polyoxyethylene sorbitol hexaoleate), Isopar-M is the most efficient hydrocarbon for the formation of a microemulsion. Isopars K and M have been used for the inverse-microsuspension polymerization experiments in chapters 3 and 4, and 2 respectively.

---

1 The effect of monomer on the size of the micro-and macro emulsion domains is dependent on the specific monomer-emulsifier-oil system. For heptane stabilized with AOT, the addition of acrylamide reduces the microemulsion domain (Candau, 1984)
Figure C.2: Hypothetical phase diagram showing micro- and macroemulsion domains. From Prince (1972).
Figure C.3: Minimum weight percentage of emulsifier (E: sorbitan sesquioleate-poly oxyethylene sorbitol hexaoleate) required to achieve microemulsification (+) as a function of HLB. From Holtzschener (1988).
Figure C.4: Effect of the organic phase on the minimum level of emulsifier (E: sorbitan sesquioleate-poly oxyethylene sorbitol hexaoleate) needed to achieve microemulsification. From Holtzscherer (1988). (†): Toluene, (Δ): Cyclohexane, (●): Isopar-M.
REFERENCES


APPENDIX D:
DERIVATION OF THE MOLECULAR WEIGHT EQUATIONS
BY THE METHOD OF MOMENTS

In this section, the \( i \)th moment of macroradicals \( (Y_i) \), and dead polymer \( (Q_i) \) will be defined as:

\[
Y_i = \sum_{r=1}^{\infty} r^i [R_r^*]
\]

\[
Q_i = \sum_{r=1}^{\infty} r^i [P_r]
\]

We will also define the moments for macroradicals and dead polymer which contain a terminal double bond, which was formed by transfer to emulsifier

\[
^*Y_i = \sum_{r=1}^{\infty} r^i [^*R_r^*]
\]

\[
^*Q_i = \sum_{r=1}^{\infty} r^i [^*P_r]
\]

The total macroradical \( (Y_{IT}) \) and dead polymer \( (Q_{IT}) \) moments are given by:

\[
Y_{IT} = Y_i + ^*Y_i
\]

\[
Q_{IT} = Q_i + ^*Q_i
\]

For brevity, the square brackets and the subscript \( w \) used to indicate water phase concentrations have been omitted.

I. Derivation of Live Polymer Balances

1. Derive the balance for the zeroth moment of macroradicals without terminal emulsifier double bonds.
For chain lengths \( r \geq 2 \):

\[
\frac{dR^*_r}{dt} = k_p M R^*_r R^*_{r-1} - k_{RE} R^*_r \Gamma_E - k_p M R^*_r - k_{td} R^*_r \sum_{s=1}^{\infty} (R^*_s + \Gamma^*_s) - k^* R^*_r \sum_{s=1}^{\infty} \Gamma^*_s + k^* \sum_{s=1}^{r-1} \sum_{s=1}^{\infty} \Gamma^*_{r-s} R^*_s - k_{fm} R^*_r M
\]

(D.1)

For macroradicals of length 1:

\[
\frac{dR^*_1}{dt} = R_1 - k_p M R^*_1 - k_{RE} \Gamma_E R^*_1 - k_{fm} M R^*_1 - k_{td} R^*_1 \sum_{r=1}^{\infty} (R^*_r + \Gamma^*_r) - k^* R^*_1 \sum_{s=1}^{\infty} \Gamma^*_s + k^* M \sum_{r=1}^{\infty} (R^*_r + \Gamma^*_r)
\]

(D.2)

Summing equation (D.1) from \( r = 2 \) to \( \infty \) and adding (D.2):

\[
\frac{d}{dt} \sum_{r=1}^{\infty} R^*_r = R_1 + k_p M \sum_{r=2}^{\infty} R^*_r R^*_{r-1} - k_p M \sum_{r=1}^{\infty} \sum_{r=1}^{\infty} R^*_r - k_{RE} \sum_{r=1}^{\infty} \sum_{r=1}^{\infty} R^*_r - k_{fm} M \sum_{r=1}^{\infty} \sum_{r=1}^{\infty} R^*_r

- k_{td} \sum_{r=1}^{\infty} R^*_r \sum_{s=1}^{\infty} (R^*_s + \Gamma^*_s) - k^* \sum_{r=1}^{\infty} R^*_r \sum_{s=1}^{r-1} \sum_{s=1}^{\infty} \Gamma^*_s

+ k^* \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} \sum_{s=1}^{\infty} \Gamma^*_{r-s} R^*_s + k_{fm} M \sum_{r=1}^{\infty} \sum_{r=1}^{\infty} (R^*_r + \Gamma^*_r)
\]

(D.3)

We know that

\[
\sum_{r=2}^{\infty} \sum_{s=1}^{r-1} \Gamma^*_{r-s} R^*_s = Y_0 Q_0
\]

and

\[
\sum_{r=2}^{\infty} R^*_r = Y_0 - R^*_1 = Y_0
\]

which reduces equation (D.3) to:

\[
\frac{dY_0}{dt} = R_1 - k_{RE} \Gamma_E Y_0 + k_{fm} M Y_0 - k_{td} Y_0 (Y_0 + \Gamma_0)
\]

(D.4)
2. Derive the balance for macroradicals with terminal emulsifier double bonds and the zeroth moment of the distribution.

For chain lengths \( r \geq 2 \):

\[
\frac{d \dot{R}_r^\bullet}{dt} = -k_p M \dot{R}_r^\bullet + k_p M \dot{R}_{r-1}^\bullet - k_{fm} M \dot{R}_r^\bullet - k_{td} R_r^\bullet \sum_{s=1}^{\infty} (R_s^\bullet + R_s^\bullet)
\]

\[-k_{fE} R_r^\bullet \Gamma_E - k^\bullet R_r^\bullet \sum_{s=1}^{\infty} \Gamma_s + k^\bullet \sum_{s=1}^{\infty} R_s^\bullet \Gamma_{r-s}. \quad (D.5)
\]

For macroradicals of length 1:

\[
\frac{d \dot{R}_1^\bullet}{dt} = k_p E^\bullet M - k_p M \dot{R}_1^\bullet - k_{fm} M \dot{R}_1^\bullet - k_{fE} \Gamma_E \dot{R}_1^\bullet
\]

\[-k_{td} R_1^\bullet \sum_{s=1}^{\infty} (R_s^\bullet + R_s^\bullet) - k^\bullet R_1^\bullet \sum_{s=1}^{\infty} \Gamma_s. \quad (D.6)
\]

Summing (D.5) from \( r = 2 \) to \( \infty \), adding (D.6), yields after rearrangement

\[
\frac{d \sum_{r=1}^{\infty} \dot{R}_r^\bullet}{dt} = k_p M E^\bullet - k_p M \sum_{r=1}^{\infty} \dot{R}_r^\bullet + k_p M \sum_{r=2}^{\infty} \dot{R}_r^\bullet - k_{fm} M \sum_{r=1}^{\infty} \dot{R}_r^\bullet
\]

\[-k_{fE} \Gamma_E \sum_{r=1}^{\infty} \dot{R}_r^\bullet - k_{td} \sum_{r=1}^{\infty} \dot{R}_r^\bullet \sum_{s=1}^{\infty} (R_s^\bullet + R_s^\bullet)
\]

\[-k^\bullet \sum_{r=1}^{\infty} \dot{R}_r^\bullet \sum_{s=1}^{r-1} \Gamma_s + k^\bullet \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} R_s^\bullet \Gamma_{r-s}. \quad (D.7)
\]

This simplifies to give:

\[
\frac{d \dot{Y}_0}{dt} = k_p E^\bullet M - k_{fm} M \dot{Y}_0 - k_{fE} \Gamma_E \dot{Y}_0 - k_{td} \dot{Y}_0 (Y_0 + \dot{Y}_0) \quad (D.8)
\]

The total macroradical concentration \( (Y_{0T}) \) is:

\[Y_{0T} = Y_0 + \dot{Y}_0\]

so that
\[
\frac{dY_{OT}}{dt} = \frac{dY_0}{dt} + \frac{dY_0}{dt}
\]

or

\[
\frac{dY_{OT}}{dt} = R_1 + R_1 - k_{RE} \Gamma_E Y_{OT} - k_{td} Y_{OT}^2
\]

(D.9)

where \( R_1 \) is the rate of initiation of emulsifier radicals which are produced by transfer to emulsifier, and is defined as:

\[
R_1 = k_p M \Gamma E
\]

\[
= \gamma_{e} k_{RE} \Gamma_E Y_{OT}
\]

where \( \gamma_{e} \) is the efficiency of initiation of emulsifier radicals.

Next, the first moment equations are derived.

3. Derive the first moment equation for macroradicals without terminal emulsifier double bonds.

Multiplying equation (D.1) by \( r \), summing from \( r = 2 \) to \( \infty \) and adding equation (D.2) yields:

\[
\frac{d}{dt} \sum_{r=1}^{\infty} r R_r^e = R_1 + k_p M \sum_{r=2}^{\infty} r R_{r-1}^e - k_p M \sum_{r=1}^{\infty} r R_r^e - k_{RE} \Gamma_E \sum_{r=1}^{\infty} r R_r^e - k_{fm} M \sum_{r=1}^{\infty} r R_r^e
\]

\[
- k_{td} \sum_{r=1}^{\infty} r R_r^e \sum_{s=1}^{\infty} (R_s^e + R_s^e) - k^* \sum_{r=1}^{\infty} r R_r^e \sum_{s=1}^{\infty} \tau P_s
\]

\[
+k^* \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} \tau P_{r-s} R_s^e + k_{fm} M \sum_{r=1}^{\infty} (R_r^e + R_r^e)
\]

(D.10)

Using the identities:
\[ \sum_{r=2}^{\infty} r R_{r-1}^* = Y_0 + Y_1 \]

and

\[ \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} r P_{r-s} R_s^* = Y_0 \gamma Q_1 + Y_1 \gamma Q_0 \]

equation (D.10) reduces to:

\[ \frac{dY_1}{dt} = R_1 - k_{RE} \gamma E Y_1 + k_{rm} M (Y_{0T} - Y_1) - k_{id} Y_1 (Y_0 + Y_1) \]

\[ + k^* (Y_0 \gamma Q_1) + k_p M Y_0 \] (D.11)

where

\[ Y_1 \gg Y_{0T} \]

4. Derive the first moment equation for macroradicals with terminal emulsifier double bonds.

Multiply equation (D.5) by r, sum from r = 2 to \( \infty \) and add equation (D.6):

\[ \frac{a}{\gamma \sum_{r=1}^{\infty} r R_r^*} = k_p M E^* - k_p M \sum_{r=1}^{\infty} r R_r^* + k_p M \sum_{r=2}^{\infty} r R_r^* - k_{RE} \gamma E \sum_{r=1}^{\infty} r R_r^* \]

\[ - k_{rm} M \sum_{r=1}^{\infty} r R_r^* - k_{RE} \gamma E \sum_{r=1}^{\infty} r R_r^* - k_{id} \sum_{r=2}^{\infty} \sum_{s=1}^{\infty} r R_r^* (R_s^* + P_s^*) \]

\[ - k^* \sum_{r=1}^{\infty} r R_r^* \sum_{s=1}^{\infty} P_s \] (D.12)

Using the same identities as for equation (D.10) and realizing

\[ \sum_{r=2}^{\infty} r R_{r-1}^* = Y_0 + Y_1 \]

we can reduce equation (D.12) to:

\[ \frac{dY_1}{dt} = R_1 - k_{rm} M Y_1 - k_{RE} \gamma E Y_1 - k_{id} \gamma Y_1 (Y_0 + Y_1) \]

\[ + k^* (Y_0 \gamma Q_1) + k_p M Y_0 \] (D.13)
The total first moment of the macroradical balance \( Y_{1T} \) is given by:

\[
Y_{1T} = Y_1 + \gamma Y_1 \quad \text{or} \quad \frac{dY_{1T}}{dt} = \frac{dY_1}{dt} + \frac{d\gamma Y_1}{dt}
\]

therefore,

\[
\frac{dY_{1T}}{dt} = R_i + R_i' - k_{IE} \Gamma_e Y_{1T} - k_{id} Y_{1T} Y_{0T} (Y_0 + \gamma Y_0) + k_p \gamma Q_1 Y_{0T} + k_{fm} M (Y_{0T} - Y_{1T}) + k_p M Y_{0T}
\]

(D.14)

where

\( Y_{1T} \gg Y_{0T} \)

Next, the second moment equations are derived.

5. Derive the second moment equation for macroradicals without terminal emulsifier double bonds.

Multiply equation (D.1) by \( r^2 \), sum from \( r = 2 \) to \( \infty \) and add equation (D.2):

\[
\frac{d \sum_{r=1}^{\infty} r^2 R_r^*}{dt} = R_i + k_p M \sum_{r=2}^{\infty} r^2 R_{r-1}^* - k_p M \sum_{r=1}^{\infty} r^2 R_r^* - k_{IE} \Gamma_e \sum_{r=1}^{\infty} r^2 R_r^*
\]

\[- k_{fm} M \sum_{r=1}^{\infty} r^2 R_r^* - k_{id} \sum_{r=1}^{\infty} r^2 R_r^* \sum_{s=1}^{\infty} (R_s^* + \gamma R_s^*)
\]

\[-k \sum_{r=1}^{\infty} r^2 R_r^* \sum_{s=1}^{\infty} P_{as} + k \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} r^2 P_{r-s} R_s^*
\]

\[+ k_{fm} M \sum_{r=1}^{\infty} (R_r^* + \gamma R_r^*) \quad \text{(D.15)}
\]

Using the identities
\[ \sum_{r=2}^{\infty} r^2 R_r^e = Y_2 + 2Y_1 + Y_0 \]

and
\[ \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} r^2 P_{r-s}^e R_s^e = Y_0 Q_2 + 2Y_1 Q_1 + Y_2 Q_0 \]

Equation (D.15) reduces to
\[ \frac{dY_2}{dt} = R_1 + k_p M(2Y_1 + Y_0) - k_{\text{re}} \Gamma E Y_2 + k_{\text{em}} M(Y_{0T} - Y_2) \]
\[ -k_{td} Y_2 Y_{0T} + k(Y_0 Q_2 + 2Y_1 Q_1) \]

where
\[ 2Y_1 > Y_0 \]
\[ Y_2 > Y_{0T} \]

6. Derive the second moment equation for macroradicals with terminal emulsifier double bonds.

Multiply equation (D.5) by \( r^2 \), sum from \( r = 2 \) to \( \infty \) and add equation (D.6)
\[ \frac{d}{dt} \sum_{r=1}^{\infty} r^2 R_r^e = k_p M E^e - k_p M \sum_{r=1}^{\infty} r^2 R_r^e + k_p M \sum_{r=2}^{\infty} r^2 R_r^e - k_{\text{em}} M \sum_{r=1}^{\infty} r^2 R_r^e \]
\[ -k_{\text{re}} \Gamma E \sum_{r=1}^{\infty} r^2 R_r^e - k_{td} \sum_{r=1}^{\infty} r^2 P_r^e \sum_{s=1}^{\infty} (R_s^e + R_r^e) \]
\[ -k^* \sum_{r=1}^{\infty} r^2 R_r^e \sum_{s=1}^{\infty} P_s^e + k^* \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} r^2 R_r^e P_{r-s} \]

Using the identities for equation (D.15), plus
\[ \sum_{r=2}^{\infty} \sum_{s=1}^{r-1} r^2 R_r^e P_{r-s} = Y_2 + 2Y_1 + Y_0 \]

one obtains, after rearrangement:
\[
\frac{d^\prime Y_2}{dt} = R_1 + k_p M (2^\prime Y_1 + Y_0) - k_{fr} M^\prime Y_2 - k_{IE} \Gamma_E \cdot Y_2
\]

\[ - k_{td}^\prime (Y_0 + Y') + k^\prime (Y_0 Q_1 + 2^\prime Y_1 Q_1) \]  

(D.18)

where

\[ 2^\prime Y_1 >> Y_0 \]

The total second moment radical balance \((Y_{2T})\) is:

\[ Y_{2T} = Y_2 + Y_2' \]

which can also be expressed as

\[
\frac{d Y_{2T}}{dt} = R_1 + R_1' + k_p M (2 Y_{1T} + Y_{OT}) - k_{fr} M (Y_{OT} - Y_{2T}) - k_{IE} \Gamma_E Y_{2T}
\]

\[ - k_{td} Y_{2T} Y_{OT} + k^\prime (Y_0 Q_2 + 2 Y_{1T} Q_1) \]  

(D.19)

where

\[ 2 Y_{1T} >> Y_{OT} \]

\[ Y_{2T} >> Y_{OT} \]

Next, we apply the stationary state hypothesis to \(Y_0\), \(Y_0\), \(Y_{OT}\), \(Y_1\), \(Y_{1T}\), \(Y_2\), \(Y_2\) and \(Y_{2T}\) to obtain:

\[ Y_0: \quad 0 = R_1 - k_{IE} \Gamma_E Y_0 + k_{fr} M Y_0 - k_{td} Y_0 (Y_{OT}) \]  

(D.20)

\[ Y_0': \quad 0 = R_1' - k_{IE} \Gamma_E Y_0 + k_{fr} M Y_0 - k_{td}^\prime Y_0 (Y_{OT}) \]  

(D.21)

\[ Y_{OT}: \quad 0 = R_1 + R_1' - k_{IE} \Gamma_E Y_{OT} - k_{td} Y_0 (Y_{OT}) \]  

(D.22)

\[ Y_1 = \frac{R_1 + k_{fr} M Y_{OT} + k_p M Y_0 + k^\prime Y_0 Q_1}{X} \]  

(D.23)

\[ Y_1' = \frac{R_1' + k_p M Y_{OT} + k^\prime Y_{OT} Q_1}{X} \]  

(D.24)

\[ Y_{1T} = \frac{R_1 + R_1' + k_p M Y_{OT} + k^\prime Y_{OT} Q_1 + k_{fr} M Y_{OT}}{X} \]  

(D.25)
\[ Y_2 = \frac{R_i + 2k_p M Y_1 + k_{fm} M Y_{0T} + k^* (Y_0^* Q_2 + 2Y_1^* Q_1)}{X} \]  
(D.26)

\[ Y_2^* = \frac{R'_i + 2k_p M^* Y_1 + k^* (Y_0^* Q_2 + 2Y_1^* Q_1)}{X} \]  
(D.27)

\[ Y_{2T} = \frac{R_i + R'_i + 2k_p M Y_{1T} + k_{fm} M Y_{0T} + k^* (Y_{0T}^* Q_2 + 2Y_{1T}^* Q_1)}{X} \]  
(D.28)

where

\[ X = k_{fe} \Gamma_E + k_{fm} M + k_{td} Y_{0T} \]

II. Calculate the Dead Polymer Balances

1. Derive the dead polymer balances for molecules which do not contain a terminal emulsifier double bond.

\[ \frac{dP_r}{dt} = k_{fm} M R_r^* + k_{td} R_r^* \sum_{s=1}^{\infty} (R_s^* + R_s^*) + k_{fe} \Gamma_E R_r^* \]  
(DII.1)

Summing equation (DII.1) from \( r = 1 \) to \( \infty \) yields the zeroth moment, after rearrangement:

\[ \frac{dQ_0}{dt} = Y_0 (k_{fm} M + k_{fe} \Gamma_E + k_{td} Y_{0T}) \]  
(DII.2)

Multiplying equation (DII.1) by \( r \) and \( r^2 \) and summing from \( r = 1 \) to \( \infty \) produces the first and second dead polymer moment equations; respectively

\[ \frac{dQ_1}{dt} = Y_1 (k_{fm} M + k_{fe} \Gamma_E + k_{td} Y_{0T}) \]  
(DII.3)

\[ \frac{dQ_2}{dt} = Y_2 (k_{fm} M + k_{fe} \Gamma_E + k_{td} Y_{0T}) \]  
(DII.4)

2. Derive the dead polymer balances for molecules that contain a terminal emulsifier double bond.
\[
\frac{d \star P}{dt} = k_{mM} \star R_r + k_{ud} \star R_r \sum_{s=1}^{\infty} (R_s^\star + R_s^\star) + k_{IE} \Gamma_E \star R_r
\]

\[
- k^\star \star P \sum_{s=1}^{\infty} (R_s^\star + R_s^\star)
\]  \hspace{1cm} \text{(DII.8)}

Summing equation (DII.8) from \( r = 1 \) to \( \infty \) and rearranging yields the zeroth moment

\[
\frac{d \star Q_0}{dt} = \star Y_0 (k_{mM} + k_{ud} \star Y_{0T} + k_{IE} \Gamma_E) - k^\star \star Q_0 \star Y_{0T}
\]  \hspace{1cm} \text{(DII.9)}

The total dead polymer concentration \((Q_{0T})\) as given by:

\[
Q_{0T} = Q_0 + \star Q_0 \quad \text{or} \quad \frac{dQ_{0T}}{dt} = \frac{dQ_0}{dt} + \frac{d \star Q_0}{dt}
\]

therefore

\[
\frac{dQ_{0T}}{dt} = \star Y_{0T} (k_{mM} + k_{ud} \star Y_{0T} + k_{IE} \Gamma_E) - k^\star \star Q_0 \star Y_{0T}
\]  \hspace{1cm} \text{(DII.10)}

Next, multiply equation (DII.8) by \( r \) and sum from \( r = 1 \) to \( \infty \).

\[
\frac{d \star Q_1}{dt} = \star Y_1 (k_{mM} + k_{ud} \star Y_{0T} + k_{IE} \Gamma_E) - k^\star \star Q_1 \star Y_{0T}
\]  \hspace{1cm} \text{(DII.11)}

The total first moment of the polymer concentration is:

\[
\frac{dQ_{1T}}{dt} = \star Y_{1T} (k_{mM} + k_{ud} \star Y_{0T} + k_{IE} \Gamma_E) - k^\star \star Q_1 \star Y_{0T}
\]  \hspace{1cm} \text{(DII.12)}

The second moments can be calculated by multiplying equation (DII.8) by \( r^2 \) and summing from \( r = 1 \) to \( \infty \).

\[
\frac{d \star Q_2}{dt} = \star Y_2 (k_{mM} + k_{ud} \star Y_{0T} + k_{IE} \Gamma_E) - k^\star \star Q_2 \star Y_{0T}
\]  \hspace{1cm} \text{(DII.13)}

and

\[
\frac{dQ_{2T}}{dt} = \star Y_{2T} (k_{mM} + k_{ud} \star Y_{0T} + k_{IE} \Gamma_E) - k^\star \star Q_2 \star Y_{0T}
\]  \hspace{1cm} \text{(DII.14)}
APPENDIX E:
OXYGEN PARTITIONING

In the kinetic modelling discussed in Chapters 2 and 3, oxygen can be added to control the reaction rate by scavenging primary radicals in the organic phase. At high levels, oxygen may also diffuse into the aqueous droplets and terminate macroradicals. Furthermore, George and Ghosh (1978 I, II) have postulated that peroxy radicals undergo copolymerization addition reactions with monomer. These polyperoxides may be susceptible to scission, particularly at the elevated temperatures used in the finishing stages of commercial inverse-microsuspension polymerizations (Becker, 1982). To quantify degradation preliminary partitioning experiments of oxygen between the aqueous and organic phases are required. The mass transfer constant will also be estimated, although based on estimates of the diffusion coefficient (Wilkie, 1949) the dynamics of small molecule transfer in this system are believed to be very fast.

Experimental Procedure

A glass apparatus has been constructed (Figure E1) so that two immiscible phases may be contacted in a sealed, inert atmosphere. The aqueous and organic phases were distilled deionized water and Isopar-K, respectively. A description of the apparatus and the experimental procedures follow.

A 1000 mL round bottom flask was immersed in a constant temperature bath 30 cm high by 28.75 cm in diameter. The liquid level was maintained even with the top of the submersed flask. The bath was insulated with 2.5 cm of fiberglass insulation containing a 6 cm diameter circular viewport. The contacting reservoir was sealed with a rubber stopper (No.8) and connected to two Erlenmeyer flasks which housed the aqueous and organic phases.
Apparatus for oxygen partitioning. Procedure: 1) Connect A to Nitrogen supply, open stopcock 1 and direct stopcock 2 toward the water reservoir. 
2) Connect E to oxygen supply. 
3) When the organic phase is saturated and the aqueous phase purged of oxygen, close stopcock 1 and open stopcock 2 to the round bottom flask. Connect B to C and push the aqueous phase into the round bottom flask with nitrogen pressure. 
4) Close stopcock 2. Withdraw a sample from the water phase to measure the initial dissolved oxygen concentration. 
5) Connect F to the oxygen supply and E to stopcock 3. Push the organic phase into the round bottom flask by elevating the reservoir. 
6) Seal stopcock 3 and begin the experiment.
A 125 mL flask, sealed with a No. 5 rubber stopper, was used to degas the aqueous phase. Rarefied nitrogen (Canadian Liquid Air, UHP grade) was bubbled through the water for a period sufficient to reduce the dissolved oxygen concentration to below 1 ppm. A 1000 mL flask, sealed with a No. 9 stopper, was used to saturate the organic phase with oxygen (Canadian Liquid Air). Saturation was complete after approximately fifteen minutes, although the bubbling was maintained for one hour.

When the two phases were ready they were added to the round bottom flask. The water was pushed through under nitrogen pressure and the organic phase was subsequently added slowly (gravity driven) so as to not disturb the interface. After contact began, 15 mL samples were withdrawn periodically for the first ten minutes and then less frequently over the next twelve hours. Samples were withdrawn by injecting a syringe through a thin section of the rubber stopper on the round bottom flask (Figure E2). This procedure enabled measurement of the oxygen content of the aqueous phase without contaminating the contact vessel to the atmosphere. The samples were immediately placed in a 20 mL beaker containing a one inch magnetic stirring bar. They were mildly agitated on a Fisher Thermix 120MR magnetic stirrer. The oxygen level in each sample was measured by two dissolved oxygen meters (Yellow Springs Instrument Co., Models 54, 57) operating in series. The time required for measurement was approximately two minutes. During this period atmospheric contamination did not significantly alter the oxygen level (deviation ≤0.1 ppm). Two probes were used in the event one failed during the experiment and to obtain better absolute estimates of the oxygen concentration. Each experiment required two operators; one for sample removal and one to perform the analytical measurements.

The temperature was controlled to within ±1°C using a Haake 210-240 V controller/circulator. The glassware was all pyrex. Glass tubing had the dimensions 7 mm I.D. and 11 mm O.D. Plastic tubing (11 mm I.D. and 13 mm O.D.) was sealed by melting and
Figure E.2: Syringe passing through a thin section of a drilled out rubber stopper.
clamping to the glass tubing ends. Two and three direction glass stopcocks (A.D. Wood Model HV and Pyrex No. 4 3-way) were used to control the flow of nitrogen and the aqueous phase. In systems with small water to oil ratios a 1000 mL Erlenmeyer was connected to the system to house the organic phase.

The partition coefficient was calculated from measured values of the initial and equilibrium oxygen concentrations in the aqueous phase and the oxygen solubility in decane\(^1\) (Table E1). The following formulas were used:

\[
\text{Total initial oxygen in the system} = [O_2]_{o,s} + [O_2]_{w^0}
\]

\[
\text{Equilibrium oil concentration} = \text{Total oxygen} - [O_2]_{w,\infty}
\]

\[
\text{Partition coefficient (n)} = [O_2]_{w,\infty} / [O_2]_{o,\infty}
\]

Where the subscripts \(o\) and \(w\) denote oil and water phases respectively with \(s\) and \(\infty\) signifying solubility and equilibrium concentrations. The superscript \(o\) designates an initial concentration.

**Experimental Conditions**

Twenty experiments were performed at two temperatures, a range of phase ratios and at different emulsifier concentrations. The latter was added to mimic the surface effects that exist in inverse-microsuspension polymerizations. Sorbitanmonoooleate was used as a single surfactant to be consistent with the kinetic studies in chapters 2 and 3. The conditions of each experiment are listed in Table E2.

---

\(^1\) Isopar-K is a narrow cut isoparaffinic mixture with properties (molar volume, density, viscosity) very close to decane.
Table E1: Solubility of Oxygen in Decane.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility of O₂† (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>351</td>
<td>Malkrenczy, 1976</td>
</tr>
<tr>
<td>30</td>
<td>312</td>
<td>&quot;</td>
</tr>
<tr>
<td>40</td>
<td>234</td>
<td>&quot;</td>
</tr>
<tr>
<td>50</td>
<td>156</td>
<td>&quot;</td>
</tr>
<tr>
<td>52</td>
<td>140</td>
<td>&quot;</td>
</tr>
<tr>
<td>54</td>
<td>125</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

† Solubilities were converted from ppm O₂ in decane to mg/L in Isopar using the density of Isopar-K.
Table E2: Experimental Conditions.

<table>
<thead>
<tr>
<th>( \phi_{w/o} ) (Phase Ratio)</th>
<th>Volume of Aqueous Phase (mL)</th>
<th>Volume of Organic Phase (mL)</th>
<th>Temperature (°C)</th>
<th>Mass of Emulsifier (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>505</td>
<td>228.0</td>
<td>49.7</td>
<td>0</td>
</tr>
<tr>
<td>0.81</td>
<td>403</td>
<td>500.0</td>
<td>49.7</td>
<td>0</td>
</tr>
<tr>
<td>7.70</td>
<td>630</td>
<td>82.0</td>
<td>49.1</td>
<td>0</td>
</tr>
<tr>
<td>11.8</td>
<td>655</td>
<td>55.5</td>
<td>54.0</td>
<td>0</td>
</tr>
<tr>
<td>12.25</td>
<td>845</td>
<td>69.0</td>
<td>53.4</td>
<td>0</td>
</tr>
<tr>
<td>12.63</td>
<td>826</td>
<td>65.4</td>
<td>50.0</td>
<td>0</td>
</tr>
<tr>
<td>6.11</td>
<td>477</td>
<td>78.0</td>
<td>52.0</td>
<td>0.072</td>
</tr>
<tr>
<td>11.46</td>
<td>596</td>
<td>51.8</td>
<td>51.8</td>
<td>0.070</td>
</tr>
<tr>
<td>18.90</td>
<td>537</td>
<td>28.4</td>
<td>52.7</td>
<td>0.071</td>
</tr>
<tr>
<td>21.10</td>
<td>608</td>
<td>28.7</td>
<td>49.3</td>
<td>0.072</td>
</tr>
<tr>
<td>9.47</td>
<td>530</td>
<td>53.9</td>
<td>30.2</td>
<td>0</td>
</tr>
<tr>
<td>9.65</td>
<td>483</td>
<td>50.0</td>
<td>30.2</td>
<td>0</td>
</tr>
<tr>
<td>16.94</td>
<td>527</td>
<td>31.1</td>
<td>30.2</td>
<td>0</td>
</tr>
<tr>
<td>30.97</td>
<td>564</td>
<td>18.2</td>
<td>30.3</td>
<td>0</td>
</tr>
<tr>
<td>3.21</td>
<td>436</td>
<td>136.0</td>
<td>30.3</td>
<td>0.121</td>
</tr>
<tr>
<td>3.51</td>
<td>480</td>
<td>137.0</td>
<td>30.3</td>
<td>0.121</td>
</tr>
<tr>
<td>7.17</td>
<td>488</td>
<td>68.0</td>
<td>30.3</td>
<td>0.121</td>
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<td>11.84</td>
<td>437</td>
<td>36.9</td>
<td>30.2</td>
<td>0.066</td>
</tr>
<tr>
<td>16.05</td>
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<td>33.2</td>
<td>30.3</td>
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</tr>
<tr>
<td>30.50</td>
<td>519</td>
<td>17.0</td>
<td>30.2</td>
<td>0.031</td>
</tr>
</tbody>
</table>
Results and Discussion

The partition coefficients of oxygen between water and Isopar-K at each temperature are summarized in Table E3. No trend was observed with the phase ratio of water to oil, as is to be expected. At 50°C n was determined to be $38.4 \times 10^{-4}$ based on the average of four measurements. These were all scattered with a low variance about the mean (Figure E3). The effect of added surfactant was to lower the equilibrium oxygen level in the water by adding to the interfacial mass transfer resistance. Lower temperatures also restricted oxygen partitioning due primarily to the enhanced solubility in the oil. This appears to dominate over the surface effects which result in a slightly less saturated boundary at lower temperatures. The variance in the individual partition coefficients at 30°C is excessive and these must be repeated to obtain reliable estimates. For modelling purposes the data at 50°C are sufficient. Future partitioning studies at 40, 60 and 70°C would generalize the model for the complete range of interest.

The mass transfer coefficients were estimated at each temperature from dynamic oxygen measurements. In most cases the transfer was too rapid to collect sufficient data. Figures E4 a, b represent the slowest mass transfer behaviour observed. These provided mass transfer parameters of 0.16 and 0.072 cm/s at 30 and 50°C respectively. These lower limits are already quite large and confirm the suspicion that interphase diffusion is rapid. The slight decrease in k with temperature is again consistent with interfacial rigidity caused by lower surface tensions.
Table E3: Summary of partition coefficients at each temperature.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\Phi_{w/o}$ (Phase ratio)</th>
<th>$[O_2]_{o, initial}$ (mg/L)</th>
<th>$[O_2]_{w, final}$ (mg/L)</th>
<th>$[O_2]_{o, final}$ (Mg/L)</th>
<th>$n \times 10^3$</th>
<th>$\bar{n} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50°C</td>
<td>0.45</td>
<td>156</td>
<td>5.5</td>
<td>143.8</td>
<td>38.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>156</td>
<td>5.8</td>
<td>151.3</td>
<td>38.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.7</td>
<td>156</td>
<td>4.7</td>
<td>119.9</td>
<td>39.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.63</td>
<td>156</td>
<td>3.8</td>
<td>108.0</td>
<td>35.2</td>
<td></td>
</tr>
<tr>
<td>50°C With Emulsifier</td>
<td>6.11</td>
<td>156</td>
<td>1.75</td>
<td>123.9</td>
<td>14.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.46</td>
<td>140</td>
<td>1.35</td>
<td>124.5</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.90</td>
<td>140</td>
<td>1.1</td>
<td>128.8</td>
<td>8.5</td>
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<tr>
<td></td>
<td>21.10</td>
<td>140</td>
<td>1.7</td>
<td>135.0</td>
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<td>11.5</td>
</tr>
<tr>
<td>30°C</td>
<td>9.47</td>
<td>312</td>
<td>1.5</td>
<td>297.3</td>
<td>5.0</td>
<td></td>
</tr>
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<td></td>
<td>9.65</td>
<td>312</td>
<td>2.2</td>
<td>290.7</td>
<td>7.6</td>
<td></td>
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<td></td>
<td>16.94</td>
<td>312</td>
<td>1.6</td>
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<td>0.9</td>
<td>284.1</td>
<td>3.2</td>
<td>5.4</td>
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<tr>
<td>30°C With Emulsifier</td>
<td>3.21</td>
<td>312</td>
<td>1.9</td>
<td>305.9</td>
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<td></td>
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<tr>
<td></td>
<td>3.51</td>
<td>312</td>
<td>0.6</td>
<td>309.9</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.17</td>
<td>312</td>
<td>2.1</td>
<td>296.9</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>11.84</td>
<td>312</td>
<td>1.14</td>
<td>298.5</td>
<td>3.8</td>
<td></td>
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<td></td>
<td>16.05</td>
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<td>0.7</td>
<td>300.8</td>
<td>2.3</td>
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<tr>
<td></td>
<td>30.50</td>
<td>312</td>
<td>0.5</td>
<td>296.7</td>
<td>1.6</td>
<td>3.8</td>
</tr>
</tbody>
</table>

$n, \bar{n}$ are partition coefficients $\left( \frac{\text{mol}_w L_o}{\text{mol}_o L_w} \right)$
Figure E.3: Measurements of the oxygen partition coefficient ($n$) at various water-to-oil phase ratios ($\Phi_{wo}$).
Figure E.4: Change in the oxygen content of the aqueous phase with time. (a) Temperature 50°C, $\Phi_{w/o} = 12.63$; (b) Temperature 30.2°C, $\Phi_{w/o} = 16.94$. 
REFERENCES


APPENDIX F:

HPLC VARIANCE STUDY

The total estimation error for residual monomer concentration measurement by high performance liquid chromatography (HPLC) is comprised of three contributions: instrument, sample preparation and sampling variances. The latter is due to inaccuracies in recording the exact time of sample withdrawal and non-representative sample selection due to reactor inhomogeneities. These should be negligible in inverse-microsuspension polymerization, where a low viscosity fluid is agitated continuously and vigorously to provide intimate mixing and a good distribution of reactants and products throughout the vessel. The well mixed hypothesis is verified by the excellent agreement observed in measurements of the initial monomer concentration directly from the degassed aqueous phase and from an emulsified sample withdrawn from the reactor. The total time for sampling was less than two seconds which is rapid enough to minimize, although not totally eliminate, the effect of time uncertainties.

The instrument and sample preparation measurement variances will be estimated by separate experiments. The HPLC error was determined as follows: A 50.0 ppm sample of recrystallized and vacuum dried dimethylaminomethyl methacrylate was prepared by dissolving a known weight in 20.0 mL of double distilled deionized water. The sample was injected into the HPLC ten times and the peak area measured. This was converted to ppm's from a calibration curve constructed from standards at 9.9, 19.8 and 99.0 ppm. The areas and concentrations are listed in Table F1. Figure F1 is a histogram of the results. The mean concentration estimated by HPLC was 50.18 ppm, with a ninety nine percent confidence limit of ±0.205 (0.4%). The measured concentration surrounds the actual value, and the variance is quite low.
Table F.1: Estimation of Instrument Variance from Ten Injections of a 50.0 ppm Standard DMAEM Sample

<table>
<thead>
<tr>
<th>Area (Arbitrary Units)</th>
<th>Concentration of DMAEM (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8,856,425</td>
<td>50.34</td>
</tr>
<tr>
<td>8,844,229</td>
<td>50.27</td>
</tr>
<tr>
<td>8,831,961</td>
<td>50.20</td>
</tr>
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<td>8,842,173</td>
<td>50.26</td>
</tr>
<tr>
<td>8,309,475</td>
<td>50.07</td>
</tr>
<tr>
<td>8,559,729</td>
<td>50.36</td>
</tr>
<tr>
<td>8,772,032</td>
<td>49.86</td>
</tr>
<tr>
<td>8,787,896</td>
<td>49.95</td>
</tr>
<tr>
<td>8,857,879</td>
<td>50.35</td>
</tr>
<tr>
<td>8,833,085</td>
<td>50.21</td>
</tr>
<tr>
<td>8,829,420</td>
<td>50.18</td>
</tr>
<tr>
<td>$\overline{x}$</td>
<td></td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>0.02996</td>
</tr>
<tr>
<td>95% C.I.</td>
<td>$\pm 0.124$</td>
</tr>
<tr>
<td>99% C.I.</td>
<td>$\pm 0.205$</td>
</tr>
</tbody>
</table>

Summary: $\overline{x} = 50.18 \pm 0.124 \pm 0.25\%$

99% Confidence limits [49.97, 50.39]
Figure F.1: Histogram of the HPLC measurements of a 50.0 ppm DMAEM standard.
The variance due to sample preparation was estimated by preparing five independent HPLC samples, from a single reactor sample. Each HPLC sample was measured five times. The data are listed in Table F.2. The results are given as ppm/weight to normalize the measured area with the initial mass of the polymer-monomer-water mixture. The results included a ninety five percent confidence interval of ± 1.4%. This is an estimate of the sum of sample preparation and HPLC variances. The dilution is clearly the predominant source of error, which is largely due to the difficulty in homogenizing the samples. Nonetheless the total error is reasonable, and the HPLC system is capable of providing reliable kinetic data, as is demonstrated in Chapters 3 and 4.
Table F.2: Estimation of Total Sample Preparation and Measurement Variances for a Sample Withdrawn from a DMAEM Homopolymerization

<table>
<thead>
<tr>
<th>Area (Arbitrary Units)</th>
<th>Concentration (ppm)</th>
<th>Weight of Initial Sample in 20.0 mL of Solvent$^+$</th>
<th>PPM Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,858,214</td>
<td>355.69</td>
<td>0.140</td>
<td>2540.6</td>
</tr>
<tr>
<td>8,158,392</td>
<td>294.12</td>
<td>0.113**</td>
<td>2615.9</td>
</tr>
<tr>
<td>8,351,889</td>
<td>361.13</td>
<td>0.117</td>
<td>2573.8</td>
</tr>
<tr>
<td>8,375,951</td>
<td>302.00</td>
<td>0.118</td>
<td>2559.4</td>
</tr>
<tr>
<td>9,797,210</td>
<td>353.48</td>
<td>0.139***</td>
<td>2549.4</td>
</tr>
<tr>
<td>$\bar{x}$</td>
<td></td>
<td></td>
<td>$2567.8$</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td></td>
<td></td>
<td>$873.3$</td>
</tr>
<tr>
<td>95% Confidence Interval</td>
<td></td>
<td></td>
<td>$\pm 36.68$</td>
</tr>
</tbody>
</table>

Summary: $\bar{x} = 2567.8 \pm 36.68$ $
\pm 1.4\%$

$^+$ Double distilled deionized water
** in 20.10 mL of solvent
*** in 20.05 mL of solvent
APPENDIX G:

PROPERTIES OF REAGENTS USED IN SYNTHESIS

**Acrylamide**

- **Boiling Point:** 125°C @ 25 mmHg
- **Melting Point:** 84.5°C
- **Solubility:** Water (215.5 g/100 mL), acetone, alcohol
- **Vapour Pressure:** 1.6 mmHg @ 84.5°C
- **Specific Gravity:** 1.05 @ 25°C, 1.122 @ 30°C
- **TLV:** 0.03 mg/m³ of air
- **Hazards:** Toxic. Can cause central nervous system paralysis if ingested. Irritant to skin and eyes. Polymerizes spontaneously at temperatures above 60°C ($\Delta H_p = 19.5$ kcal/mol).

**Dimethylaminoethyl methacrylate**

- **Boiling Point:** 182-190°C
- **Solubility:** Water
- **Vapour Pressure:** 24 mmHg @ 25°C
- **Specific Gravity:** 0.933 @ 25°C
- **Flash Point:** 73.9°C
- **Refractive Index:** 1.4376
- **pKₐ:** 5.6
- **Tₛ:** 18°C
- **Hazards:** Irritant to skin and eyes. Incompatible with metal salts, CO₂, oxidizing agents, rust. Store in the dark, below 75°C in contact with oxygen (to activate the hydroquinone monomethylene inhibitor).

**Dimethylaminoethyl acrylate**

- **Boiling Point:** 100°C (75% aqueous solution)
- **Solubility:** Water
- **Specific Gravity:** 1.1226
- **pKₐ:** 6.1
- **Hazards:** Irritant to skin and eyes. Incompatible with CO, CO₂, amines. Store in dark below 75°C. Usually inhibited with hydroquinone monomethylene (1000 ppm).

**Sorbitan monooleate**

- **Boiling Point:** >100°C
- **Solubility:** Some oils. Completely insoluble in water.
- **Specific Gravity:** ≈1.0
- **Vapour Pressure:** <0.1 mmHg @ 20°C
- **Flash Point:** >300°C
- **volatile volume %:** 1.5
- **Hazards:** Non irritating. Approved by FDA for a food additive.
Sorbitan monostearate

Boiling Point: >100°C
Solubility: Oils at elevated temperatures. Insoluble in water
Specific Gravity: ≈ 1.0
Flash Point: >300°C
Physical State: Waxy solid at room temperature
Hazards: Material is listed as "not a health hazard"

Isopar-K

Boiling Point: 180-220°C
Solubility: Alcohol
Specific Gravity: 0.86975 - 4.124 × 10^-4 · T (g/cm³)
Autoignition Temperature: >300°C
Specifications: A narrow cut isoparaffinic mixture with properties similar to decane. Contains <2% aromatics.
Hazards: Flammable (listed as a "moderate" fire risk). Skin irritant. Little tendency to migrate through polyethylene containers. Permitted by FDA for food applications.
APPENDIX H
INVESTIGATION OF THE VARIANCE IN MOLECULAR WEIGHT
MEASUREMENT BY LOW ANGLE LASER LIGHT SCATTERING

The light scattering procedures outlined in Chapter 1 were followed to prepare five samples of a polyacrylamide synthesized at 50°C with an initial monomer concentration of 4.69 mol/L. These samples (A-E) were dissolved in 0.02 M Na₂SO₄ at the optimal concentration corresponding to their molecular weight (2.5 · 10⁻⁴ g/mL). They were measured in duplicate with the exception of sample B which was measured six times. Table H.1 lists the photomultiplier signals for scattered and incident light, as well as their ratio, scaled with respect to concentration.¹ Figures H.1 and H.2 show the distribution in the measured ratio (G₀/Gₛ)/c. An average deviation of ±1.3% (95% confidence interval ±1.9%) was found for replicate measurements of sample B. The corresponding deviation and confidence interval for measurements of independently prepared samples were ±6.3% and ±9.7% respectively. Clearly the major contribution to molecular weight uncertainty comes from the sample preparation step. This is particularly acute in aqueous systems, as has been discussed in the literature (Tabor, 1972; Kaye, 1974; Hunt, 1986). The light scattering instrument error of ±1.3% is reasonable and corresponds to an error in R₀ of ±1.8 · 10⁻⁶ cm⁻¹. This is not unusual for an aqueous measurement considering the sensitivity of the instrument in the cleanest organic solvent is ±2 · 10⁻⁷ cm⁻¹ (Ouano and Kaye, 1974).

¹ \[ R₀ \propto \frac{G₀}{Gₛ} \cdot \frac{1}{C} \propto \frac{1}{M_w} \]
Table H.1: Photomultiplier Signals for Replicate Measurements of Independently Prepared Samples of an Acrylamide Homopolymer

<table>
<thead>
<tr>
<th>Sample</th>
<th>(G^+\theta)</th>
<th>(G^+_o)</th>
<th>(C) (g/dL)</th>
<th>((G_0/G_\theta \cdot C))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>630</td>
<td>169</td>
<td>0.0260</td>
<td>143.4</td>
</tr>
<tr>
<td></td>
<td>685</td>
<td>172</td>
<td>&quot;</td>
<td>138.6</td>
</tr>
<tr>
<td>B</td>
<td>670</td>
<td>171</td>
<td>0.0253</td>
<td>154.9</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>173</td>
<td>&quot;</td>
<td>148.5</td>
</tr>
<tr>
<td></td>
<td>670</td>
<td>172</td>
<td>&quot;</td>
<td>154.0</td>
</tr>
<tr>
<td></td>
<td>680</td>
<td>173</td>
<td>&quot;</td>
<td>155.4</td>
</tr>
<tr>
<td></td>
<td>675</td>
<td>173</td>
<td>&quot;</td>
<td>154.4</td>
</tr>
<tr>
<td></td>
<td>660</td>
<td>173</td>
<td>&quot;</td>
<td>150.8</td>
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<tr>
<td>C</td>
<td>690</td>
<td>171</td>
<td>0.0264</td>
<td>152.8</td>
</tr>
<tr>
<td></td>
<td>685</td>
<td>173</td>
<td>&quot;</td>
<td>150.0</td>
</tr>
<tr>
<td>D</td>
<td>590</td>
<td>172</td>
<td>0.0268</td>
<td>128.0</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>173</td>
<td>&quot;</td>
<td>127.3</td>
</tr>
<tr>
<td>E</td>
<td>575</td>
<td>173</td>
<td>0.02495</td>
<td>133.2</td>
</tr>
<tr>
<td></td>
<td>575</td>
<td>173</td>
<td>&quot;</td>
<td>133.2</td>
</tr>
</tbody>
</table>

+ The absolute values of \(G_\theta\) and \(G_\theta\) are arbitrary since \(G_\theta\) is adjusted by the user. The reduction in the light intensity after passing through a sample \((G_\theta)\) relative to the incident intensity \((G_\theta)\) is, however, a physical parameter related to molecular weight.
Figure H.1: Histogram showing the distribution of \( \frac{G_\theta}{G_\phi \cdot c} \) for replicate Low Angle Laser Light Scattering measurements of a single polyacrylamide sample.

Figure H.2: Dot diagram of the distribution of \( \frac{G_\theta}{G_\phi \cdot c} \) for five independently prepared samples of the same polyacrylamide measured by Low Angle Laser Light Scattering.
REFERENCES


