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CONTROLLED ALTERNATING COPOLYMERISATION OF MALEIC ANHYDRIDE AND ELECTRON DONATING MONOMERS

BY

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A DOCTORAL THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHILOSOPHY OF LOUGHBOROUGH UNIVERSITY.

AUGUST 2002

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To Mum, Dad and Adam
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ABSTRACT

Maleic anhydride (MA) is a strong electron acceptor and so homopolymerises with difficulty. Copolymerisations with electron donor monomers are however facile. Free-radical and controlled radical polymerisation (CRP) techniques have been used to probe the structure and mechanism of MA alternating copolymers.

Conventional free-radical polymerisation was used to synthesise poly (octadecene -alt- MA) (PODMA). Molar masses ranging from 4,000 g mol\(^{-1}\) to 61,000 g mol\(^{-1}\) were successfully prepared by variation of polymerisation conditions. Molar mass characterisation was by size exclusion chromatography (SEC) and dilute solution viscometry. Calculation of monomer reactivity ratios revealed PODMA to have a strictly alternating structure. NMR analysis indicated that PODMA had 100% trans stereochemistry and the initiation and termination mechanisms were elucidated. The optimised copolymerisation was scaled up from gram to kilo scale, providing an important precursor for high performance crankcase oil dispersants.

MA has proved to be a challenging monomer for CRP. Reverse addition fragmentation transfer (RAFT) copolymerisation was used to copolymerise MA with styrene (St) monomers. Kinetic studies indicated controlled copolymerisation and living characteristics were observed such as predetermined molar mass, narrow molar mass distribution and chain extension to form novel block copolymers. The RAFT mechanism and its effectiveness in producing controlled copolymers incorporating MA are discussed.
CONTENTS

1 Introduction.............................................................................................................. 1
  1.1 USE OF MA IN CRANKCASE DISPERSANTS...................................................... 2
  1.2 MA COPOLYMERS AS DISPERSANT CROSSLINKING AGENTS ....................... 4
  1.3 CONTROLLED RADICAL POLYMERISATION TECHNIQUES ......................... 5
  1.4 MAIN AIMS OF THIS RESEARCH...................................................................... 7

2 Background and theory .......................................................................................... 8
  2.1 RADICAL POLYMERISATION ........................................................................... 8
    2.1.1 INITIATION................................................................................................. 8
    2.1.2 PROPAGATION............................................................................................ 10
    2.1.3 TERMINATION............................................................................................ 11
    2.1.4 STEADY STATE KINETICS.......................................................................... 11
    2.1.5 KINETIC CHAIN LENGTH.......................................................................... 15
    2.1.6 MOLAR MASS DEFINITION........................................................................ 16
    2.1.7 HIGH CONVERSION POLYMERISATIONS AND THE GEL EFFECT............ 17
    2.1.8 CHAIN TRANSFER......................................................................................... 18
      2.1.8.1 CHAIN TRANSFER TO MONOMER, POLYMER, INITIATOR AND SOLVENT 21
      2.1.8.2 CHAIN TRANSFER TO MODIFIER............................................................... 22
  2.2 COPOLYMERISATION........................................................................................ 23
    2.2.1 KINETICS OF COPOLYMERISATION.......................................................... 23
    2.2.2 ESTIMATION OF MONOMER REACTIVITY RATIOS.................................... 25
      2.2.2.1 FINEMAN-ROSS METHOD....................................................................... 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.2.2 Kelen-Tüdös method</td>
<td>27</td>
</tr>
<tr>
<td>2.2.3 Monomer reactivity ratios and alternating copolymerisation</td>
<td>27</td>
</tr>
<tr>
<td>2.2.3.1 Resonance stabilisation</td>
<td>28</td>
</tr>
<tr>
<td>2.3.2.2 Polarity</td>
<td>28</td>
</tr>
<tr>
<td>2.3.2.3 The Q-e scheme</td>
<td>29</td>
</tr>
<tr>
<td>2.3.2.4 Charge transfer complexes</td>
<td>31</td>
</tr>
<tr>
<td>2.3 Alternating copolymerisation with MA</td>
<td>33</td>
</tr>
<tr>
<td>2.3.1 St and substituted St–MA copolymers</td>
<td>34</td>
</tr>
<tr>
<td>2.3.2 Olefin–MA copolymers</td>
<td>40</td>
</tr>
<tr>
<td>2.4 Controlled radical polymerisation</td>
<td>46</td>
</tr>
<tr>
<td>2.4.1 ATRP</td>
<td>47</td>
</tr>
<tr>
<td>2.4.1.1 Fundamentals of ATRP</td>
<td>47</td>
</tr>
<tr>
<td>2.4.1.2 Acidic monomers</td>
<td>48</td>
</tr>
<tr>
<td>2.4.2 RAFT</td>
<td>50</td>
</tr>
<tr>
<td>2.5 Solution viscometry</td>
<td>57</td>
</tr>
<tr>
<td>2.5.1 Intrinsic viscosity</td>
<td>57</td>
</tr>
<tr>
<td>2.6 Size exclusion chromatography</td>
<td>60</td>
</tr>
<tr>
<td>2.6.1 SEC standard calibration</td>
<td>60</td>
</tr>
<tr>
<td>2.6.2 SEC universal calibration</td>
<td>62</td>
</tr>
<tr>
<td>2.6.3 SEC detectors</td>
<td>63</td>
</tr>
<tr>
<td>2.6.3.1 Refractive index (RI) detectors</td>
<td>63</td>
</tr>
<tr>
<td>2.6.3.2 Ultra-violet (UV) detectors</td>
<td>63</td>
</tr>
</tbody>
</table>
2.7 Computational Chemistry ................................................. 65

3 Experimental ........................................................................ 68

3.1 List of Chemicals and Abbreviations ............................................. 68

3.2 Monomer Destabilisation .............................................................. 71

3.3 Free Radical Polymerisation ......................................................... 72

3.3.1 Small scale PODMA Synthesis .................................................. 72

3.3.2 Large scale PODMA Synthesis .................................................. 72

3.3.3 Bulk PODMA Synthesis ............................................................. 73

3.3.4 Pilot plant PODMA Synthesis .................................................... 73

3.4 Atom Transfer Radical Polymerisation (ATRP) ......................... 75

3.5 Reversible Addition Fragmentation Transfer Polymerisation (RAFT) ............................................................................. 76

3.5.1 Synthesis of benzyl dithiobenzoate (BDTB) ............................ 76

3.5.2 RAFT Kinetic Copolymerisations ................................................ 76

3.5.3 RAFT Monomer Reactivity Ratios in Copolymerisations .......... 77

3.5.4 RAFT Copolymerisation to form StMA-block-pMeSt ............... 77

3.5.5 RAFT Copolymerisation to form PODMA ................................. 77

3.6 Characterisation Techniques ....................................................... 79

3.6.1 Fourier Transform Infrared Spectroscopy (FTIR) ...................... 79

3.6.1.1 Qualitative FTIR Spectroscopy ............................................... 79

3.6.1.2 Quantitative FTIR Spectroscopy ............................................. 79

3.6.2 $^1$H and $^{13}$C Nuclear Magnetic Resonance Spectroscopy .......... 82

3.6.3 Size Exclusion Chromatography (SEC) .................................. 82

3.6.3.1 Acetic Acid Stabilised SEC .................................................. 82

3.6.3.2 Dual detector SEC using RI and UV detectors ...................... 82

3.6.3.3 Molar mass determination, calibration and purity ............... 83
4 Results and discussion ............................................. 89

4.1 Molar mass and conversion control in small scale PODMA synthesis ............................................. 89

4.1.1 Temperature ................................................................. 89

4.1.2 Initiator concentration .................................................. 90

4.1.3 Dependence of overall rate on AIBN concentration ....... 93

4.1.4 PODMA conversion ...................................................... 100

4.1.4.1 Dependence on temperature ........................................ 100

4.1.4.2 Dependence on initiator concentration .................... 100

4.1.4.3 Aliquot initiator addition ........................................... 102

4.1.5 Bulk PODMA synthesis ................................................. 102

4.1.6 Summary ...................................................................... 103

4.2 SEC analysis and molar mass calculation ..................... 105

4.2.1 Modification of the mobile phase ................................. 105

4.2.2 Molar mass determination ........................................... 106

4.2.3 Summary ..................................................................... 112

4.3 Structural properties of PODMA ................................. 116

4.3.1 FTIR analysis of PODMA .............................................. 116

4.3.2 Estimation of reactivity ratios ...................................... 116

4.3.2.1 Fineman-Ross method ............................................ 117

4.3.2.2 Keelen-Tüdös method ............................................ 119

4.3.3 $^1$H NMR analysis of PODMA .................................... 126

4.3.4 PODMA backbone structure ...................................... 128
4.3.4.1 $^{13}$C NMR ANALYSIS OF PODMA .......................................................... 128
4.3.4.2 MOLECULAR MODELLING OF PODMA ............................................. 128
4.3.5 END GROUP STRUCTURE AND INITIATION MECHANISM .................. 133
4.3.6 SUMMARY ......................................................................................... 139

4.4 OPTIMISATION AND SCALE UP OF PODMA SYNTHESIS ............. 141
4.4.1 HIGH CONVERSION OF OD VIA THE ENE REACTION .................. 141
4.4.2 LARGE SCALE PODMA SYNTHESIS .................................................. 142
4.4.3 QUANTITATIVE SEC DECONVOLUTION FOR PODMA ............... 146
4.4.4 PILOT PLANT PODMA SYNTHESIS .................................................. 150
4.4.5 SUMMARY ......................................................................................... 151

4.5 ATOM TRANSFER RADICAL POLYMERISATION ATRP ............ 153
4.5 SUMMARY ............................................................................................ 162

4.6 RAFT COPOLYMERISATION TO FORM COPOLYMERS OF MA AND ST MONOMERS ......................................................... 164
4.6.1 EVALUATION OF THE LIVING CHARACTERISTICS OF COPOLYMERS OF MA AND ST MONOMERS PRODUCED BY RAFT ............... 177
   4.6.1.1 LINEAR INCREASE IN MOLAR MASS WITH INCREASING CONVERSION 177
   4.6.1.2 COPOLYMERISATION KINETICS IN RAFT COPOLYMERISATION OF MA WITH ST MONOMERS ............................................. 180
   4.6.1.3 NARROW MOLAR MASS DISTRIBUTION (MMD) IN RAFT COPOLYMERISATION OF MA AND ST MONOMERS .......................... 182
   4.6.1.4 BLOCK COPOLYMERISATION OF StMA AND pMeStMA BY RAFT POLYMERISATION ......................................................... 183
   4.6.1.5 SUMMARY .............................................................................. 188

4.6.2 COMPOSITION ANALYSIS AND ESTIMATION OF REACTIVITY RATIOS FOR COPOLYMERS OF MA AND ST MONOMERS PRODUCED BY RAFT POLYMERISATION .................................................. 190
4.7 RAFT COPOLYMERISATION TO FORM COPOLYMERS OF \(\alpha\text{MeSt}\) AND MA (\(\alpha\text{MeStMA}\)) ...................................................... 207

4.7.1 COMPOSITION ANALYSIS AND ESTIMATION OF REACTIVITY RATIOS FOR \(\alpha\text{MeStMA}\) ..................................................................................... 217

4.8 IMPROVING CONTROL IN StMA PRODUCED BY RAFT COPOLYMERISATION .................................................................................. 221

4.9 RAFT COPOLYMERISATION TO FORM PODMA .......................... 233

5 Conclusion .................................................................................. 236

6 Further work .............................................................................. 239

7 References .................................................................................. 236

APPENDIX 1
APPENDIX 2
1 INTRODUCTION

An alternating copolymer is formed when two monomers add consecutively to form a polymer chain with a regular -(ABABABAB)- structure irrespective of monomer feed ratio. The study of copolymerisation was initiated during the 1930's when polymer science was in its infancy; however, the area has continued to grow as copolymers are of significant interest to both academics and industrialists. Alternating copolymers once thought of as chemical curiosities have proved to be much more important by virtue of the consistent structures that are formed. The majority of studies concerning alternating copolymerisation have focused on radically initiated systems. The addition of Lewis acids can promote alternation in otherwise statistical systems and this observation has expanded alternating copolymer studies greatly. The alternating copolymerisation of olefins and diolefins can be carried out using transition metal coordination catalysts, the first example of which was discovered by Natta et al. Alternating copolymers can also be formed by two monomers interacting to form a zwitterion intermediate. These intermediates are responsible for initiation and propagation and so the technique is sometimes referred to as 'spontaneous alternating copolymerisation via zwitterionic intermediates'.

Maleic anhydride (MA) is a strongly electron accepting monomer and reaction to form alternating copolymers is often facile when the comonomer is electron donating. MA is very reluctant to homopolymerise, this being a common feature of 1,2 disubstituted ethylenes. Alternating copolymers of styrene (St) and MA have received intense study and many of the mechanistic explanations for alternation have stemmed from this research activity. St is by no means the only comonomer studied and mechanisms postulated such as charge transfer complexation can be applied to other systems. There are over 6000 patents regarding MA alternating copolymers, which give an indication of its importance in polymer science. Alternating copolymers of MA find
application as dispersants, thickeners, detergents, oil additives and in many other areas. Trivedi and Culbertson have extensively reviewed MA copolymers.

**1.1 USE OF MA IN CRANKCASE DISPERSANTS**

Modern automotive engines offer a hostile environment to the oil used to lubricate and cool them. In order to enhance the performance of the oil, and to increase the drain interval time many additives are incorporated. Figure 1 presents the component breakdown for the fully formulated engine oil and its performance pack. The performance package makes up approximately 20% of the total oil formulation, the remaining components being base oils and viscosity modifiers. The performance package consists of many additives such as detergents, antiwear agents and dispersants. One of the biggest components of the performance package is the dispersant, making up approximately 40-50 wt %.

![Pie chart showing engine oil composition](chart.png)

- **Base oils 70-95%**
- **Performance package 5-20%**
- **Viscosity modifier 0-20%**
- **Pour point depressant 0-1%**

---

*Chapter 1: Introduction*
The function of an engine oil dispersant is to suspend and disperse insoluble particulates that form as the engine oil decomposes due to hydrocarbon oxidation. Decomposition in spark ignition passenger car engines forms sludge while decomposition in diesel engines results in soot formation. Dispersants are surfactant molecules that contain a hydrophobic tail and a hydrophilic head group. Sludge particles are acidic in nature and the polar head groups attach to the surface. The hydrocarbon tail is maintained in the oil phase and the sludge particle is dispersed.

Traditional crankcase dispersants have focused on the use of polyisobutylene (PIB). PIB with alkene functionality as the end group provides the hydrophobic tail. PIB is succinated with MA via a Diels Alder or Ene reaction to generate PIB-succinic anhydride (PIBSA). This is further converted to the finished dispersant by imidation with an amine to give the polar hydrophilic head group. Figure 2 presents a typical crankcase dispersant molecule. The performance characteristics of the dispersant can be tuned by varying the molecular weight of the PIB chain, the amount of succination (mono or di succination leading to one or two head groups) and the size and type of amine used.

![Typical PIB based dispersant molecule](image)
Chapter 1: Introduction

A major drawback of PIB based dispersants are their poor viscosity characteristics. The viscosity characteristics of an engine oil are critical to its performance. Ideally, engine oils would exhibit non-Newtonian viscosity. Newtonian liquids have a high viscosity at low temperatures, which decreases with increasing temperature. This behaviour, characteristic of base oils, results in difficulty in turning the engine over in cold conditions combined with poor lubrication under a high temperature/high shear environment. To counter these problems high molar mass polymers known as viscosity modifiers are added to the oil. Olefin copolymers and poly(methacrylate)s are commonly used. The presence of viscosity modifiers not only adds cost to the total formulation but also contributes towards sludge formation, brought about by chain scission. This increases the demand on the dispersant and may lead to higher concentrations being required. In order to be competitive therefore, future dispersants need to provide improved dispersancy and better viscosity properties.

1.2 MA COPOLYMER AS DISPER SANT CROSSLINKING AGENTS

Improvement of the viscosity characteristics of the finished dispersant can be achieved by using alternating MA copolymers as crosslinking agents. Condensation of a MA alternating copolymer and PIBSA with a polyamine leads to a complex mixture of dispersant molecules. An idealised structure of such a dispersant is shown in Figure 3. MA copolymers with long alkyl chain olefins as comonomers have demonstrated improved high and low temperature viscosity characteristics combined with superior dispersancy over conventional PIB based dispersants. In order to maintain oil solubility an alkyl chain length in excess of C\textsubscript{16} (hexadecene) for the comonomer is required, though C\textsubscript{18} (octadecene) is preferable.
In Figure 3, poly(octadecene-maleic anhydride) copolymer (PODMA) is a commercially available alternating copolymer. PODMA can be purchased in two molar mass grades\(^8\). Previous work\(^9\,10\) has shown that molar mass is a critical parameter in dispersant performance with high molar mass material offering substantial improvement over the low molar mass analogue. The use of MA copolymers as a component of automotive crankcase dispersants is an established concept; however, research should be directed towards further understanding the synthesis and structure of such copolymers.

1.3 CONTROLLED RADICAL POLYMERISATION TECHNIQUES

Radical polymerisation and copolymerisation are industrially the most common methods for producing polymeric materials. Radical polymerisation is more desirable than ionic methods due to the large variety of monomers that can be polymerised and reaction conditions that only require the absence of oxygen with reaction temperatures usually in the convenient 0–100°C range. The major drawbacks of radical polymerisation are the difficulty in controlling molar mass and polymer structure. High molar mass polymers with broad molar mass distributions (MMD) are characteristic of conventional free radical polymerisation.

Ionic polymerisation allows the preparation of well-defined polymers with controlled end group functionalities and the preparation of interesting architectures such as block and graft copolymers. Ionic polymerisation however necessitates stringent reaction conditions such as the complete exclusion of moisture and low reaction temperatures. In addition only a limited number of monomers can be used.
Recently, new methods to synthesize well-defined polymers and copolymers have been developed. This field is known as controlled radical polymerisation (CRP). Several systems have been applied to control molar mass and end functionality. These methods include the initiation transfer termination (INIFERTER) process using alkyl iodides\textsuperscript{11}, nitroxide mediated polymerisation\textsuperscript{12}, atom transfer polymerisation\textsuperscript{13} (ATRP), other transition metal systems using cobalt\textsuperscript{14} and nickel\textsuperscript{15} and reversible addition fragmentation chain transfer polymerisation\textsuperscript{16} (RAFT). CRP allows most of the benefits associated with living ionic polymerisation to be realised using reaction conditions normally only suitable for conventional radical polymerisation.

MA though versatile in many conventional copolymerisations has proved to be problematic when many of the CRP techniques are applied. This has served to further stimulate interest in developing CRP methodology to allow the synthesis of MA copolymers of well-defined molar mass and structure.
1.4 Main aims of this research

1) Synthesis of PODMA by conventional radical copolymerisation, to varying molar masses with an emphasis on high molar mass material by investigation of experimental techniques and conditions.

2) Investigation of the structure and mechanism of the PODMA reaction and other α-olefin-MA copolymers. Of particular importance are accurate molar mass analysis, structure and sequence distribution and stereochemical conformation.

3) Development of CRP methods with regard to preparing and characterising MA alternating copolymers. Strong electron donor comonomers are investigated to demonstrate CRP techniques and provide a range of MA alternating copolymers.
2 BACKGROUND AND THEORY

2.1 RADICAL POLYMERISATION

The concept and practice of free radical polymerisation dates back to the 1930’s. It is a diverse process and can be carried out in both homogeneous conditions (bulk or solution polymerisation) and in heterogeneous conditions (emulsion, suspension, precipitation and dispersion polymerisation)\textsuperscript{17,18}.

A radical is an atomic or molecular species whose normal bonding has been disrupted such that an unpaired electron remains associated with the new structure. Radicals can be generated from the decomposition of molecules known as initiators that have a strained bond with a low bond dissociation energy (BDE). This allows them to undergo homolytic fission when subjected to heat or electromagnetic radiation to form free radicals. Polymerisation of a vinyl monomer involves radical attack of the initiator fragment at the unsaturated bond of the monomer to produce the chain carrier that bears the initiator fragment at one end and a radical at the other. The chain carrier can then propagate subsequent monomer units retaining the terminal radical with each addition. Propagation ceases when the chain carrying the radical is terminated. Termination may occur via an abstraction mechanism or by combination of two active radicals. Other mechanisms that may interfere with the polymerisation include inhibition and retardation.

2.1.1 INITIATION

Common free radical initiators are peroxides such as benzyol peroxide (BPO) and azonitriles such as azobisisobutyronitrile (AIBN). Both molecules can be activated by heat and will generate useful concentrations of radicals at convenient reaction temperatures of 60-100°C. AIBN decomposes to form 2 radical species with the loss of
Chapter 2: Background and theory

nitrogen. Initiators containing azonitrile groups are useful for kinetic studies as their decomposition normally follows 1st order kinetics that are unaffected by the solvent environment. BPO decomposes to form two benzoyloxy radical species. Work by Bevington et al\textsuperscript{19} showed that further decomposition leads to 2 phenyl radicals with the evolution of CO\textsubscript{2}. Scheme 1 shows the decomposition of AIBN and BPO.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.4\textwidth]{initiator_decomposition.png}};
\end{tikzpicture}
\end{center}

\textit{Scheme 1 Initiator decomposition}

The radical formed from the initiator attacks the monomer to form the monomer radical, known as the chain carrier. This is the slowest part of the polymerisation reaction and so is the rate-determining step.

St and St derivatives are capable of being polymerised thermally in the absence of a free radical initiator as shown in Scheme 2. The favoured mechanism for initiation was proposed by Mayo\textsuperscript{20} and confirmed by others\textsuperscript{21, 22} to proceed via a Diels Alder reaction of two St molecules followed by homolysis with another St molecule to provide an aromatised trimer radical 1 and a radical derived from St 2, both of which are capable of initiating polymerisation.
Chapter 2: Background and theory

Scheme 2 Mayo mechanism for the thermal autopolymerisation of St

Hawker et al.\textsuperscript{2} have confirmed the presence of 1 and 2 by trapping the radicals with the stable free radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). The unimolecular initiators were then used to prepare polystyrene (PS) and a range of para substituted polystyrenes via nitroxide mediated controlled radical polymerisation.

2.1.2 PROPAGATION

A monomer unit is added in each propagation step, retaining the active centre. Generally, the propagation is linear and the average lifetime of a chain is very short.

\[
\begin{align*}
I & \quad \text{ + M} \quad \text{ + M} \\
\text{I--M} & \quad \text{I--M-M} \\
\end{align*}
\]

\textit{Equation 1}

where \(I\) and \(M\) represent the initiator fragment and monomer respectively. The propagation process can be represented by the general step:

\[
\begin{align*}
\text{I--M} & \quad \text{+ M} \\
\text{I--M-M} & \quad \text{I--(M)\text{--M}^\text{\textbullet}} \\
\end{align*}
\]

\textit{Equation 2}
2.1.3 **TERMINATION**

The most important termination reaction is the bimolecular interaction between two chain ends. There are two routes, the combination of two radicals or the abstraction of a small molecule. These mechanisms are termed combination and disproportionation respectively. Which process is active in a system depends on the monomer and the reaction conditions. In some cases both mechanisms operate. In St polymerisation, termination is via combination while in MMA polymerisation, disproportionation dominates at high temperatures and both processes operate at lower temperatures (Figure 4).

![Figure 4 Combination and disproportionation in St and MMA polymerisations respectively](image)

Distinction between the two mechanisms can be made by measuring the number of initiator fragments per chain. Two fragments indicate recombination while only one shows that disproportionation is the dominant termination mechanism.

2.1.4 **STEADY STATE KINETICS**

The three basic steps in radical addition polymerisation can be equated to the kinetics of a simple chain reaction. Neglecting the presence of inhibition and chain transfer, initiation, propagation and termination can be represented by the following equations with their respective rate constants.
Chapter 2: Background and theory

Initiation

\[ I \overset{k_i}{\rightarrow} 2R^* \]  
Equation 3

\[ R^* + M \overset{k_i}{\rightarrow} M^* \]  
Equation 4

Propagation

\[ M^*_x + M \overset{k_p}{\rightarrow} M^*_{x+1} \]  
Equation 5

Termination

Combination

\[ M^*_x + M^*_y \overset{k_{nc}}{\rightarrow} M_{x+y} \]  
Equation 6

Disproportionation

\[ M^*_x + M^*_y \overset{k_{ud}}{\rightarrow} M_x + M_y \]  
Equation 7

Derivation of these kinetic expressions requires four simplifying assumptions to be made.

1) The length of the propagating chain is large, so the total rate of monomer disappearance may be equated only to the rate of consumption due to propagation events alone.

2) The rate constants of propagation and termination are independent of chain length and the radical activity is only determined by the molecular structure near the radical.

3) A stationary state in radical concentration is quickly established that allows the rate of change of any radical intermediate to be equated to zero.
4) Termination due to primary radicals is negligible. This assumption is valid for most systems under conditions of long chain length since the primary radical concentration is small compared to the total radical concentration.

The rates of the three component reactions can be expressed in terms of the concentrations of species and their respective rate constants. The rate of initiation, $R_i$, can be defined as:

$$R_i = \left( \frac{d[M^*]}{dt} \right)_i = 2fk_d[I]$$

Equation 8

where $f$ represents the initiator efficiency (the fraction of produced radicals that successfully initiate the propagation of chains), $[M^*]$ the monomer radical concentration and $[I]$ the initiator concentration. In most cases, the initiator efficiency is not 100% due to primary recombination. This is usually affected by the polymerisation solvent; for example, BPO has $f = 0.3$ in tetrachloroethylene but $f = 0.85$ in ethyl acetate$^{18}$. The rate of termination, $R_t$, is defined as:

$$R_t = -\left( \frac{d[M^*]}{dt} \right)_i = 2k_t[M^*]^2$$

Equation 9

The rate constant $k_t$ is actually $(k_{ic} + k_{id})$ where $k_{ic}$ and $k_{id}$ represent the two mechanisms, combination and disproportionation respectively. For most cases $[M^*]$ becomes essentially constant early in the reaction as radicals are formed and destroyed at similar rates. This allows the steady-state condition $R_i = R_t$ to be applied and an expression for $[M^*]$ can be obtained (Equation 10):
Chapter 2: Background and theory

\[ [M^*] = \left( \frac{f k_d [I]}{k_i} \right)^{1/2} \]

Equation 10

The rate of propagation, \( R_p \), represents the rate of conversion of monomer to polymer and is essentially the same as the rate of disappearance of the monomer as the number of monomer molecules used in chain activation to form the chain carrier is small compared to the number used in propagation if polymer is obtained. The rate of bimolecular propagation is assumed to be the same for each addition so \( R_p \) can be defined as:

\[ R_p = -\left( \frac{d[M]}{dt} \right) = k_p [M] [M^*] \]

Equation 11

Substitution for \([M^*]\) allows the overall rate of polymerisation to be obtained:

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

Equation 12

This expression shows that the rate should be proportional to the square root of the initiator concentration and proportional to the first power of the monomer concentration at low conversions, providing the initiator efficiency, \( f \), is high and independent of monomer concentration.

The pseudo 1\textsuperscript{st} order kinetics of propagation in a polymerisation can be tested by integration of Equation 11 to provide Equation 13. Providing initiation is rapid a plot of \( \ln [M]_0/[M] \) against time should be linear.
Chapter 2: Background and theory

\[ \frac{\ln \left[ \frac{[M]_0}{[M]} \right]}{k_{obs} t} \]

*Equation 13*

2.1.5 KINETIC CHAIN LENGTH

The kinetic chain length, \( v \), is the average number of monomer units reacting with an active centre in its lifetime and can be expressed by:

\[ v = \frac{k_p [M]}{2k_t [M^*]} \]

*Equation 14*

The radical concentration can be eliminated by substitution of Equation 11 into Equation 14 giving the expression:

\[ v = \frac{k_p^2 [M]^2}{2k_t R_p} \]

*Equation 15*

For radically initiated polymerisation substitution of Equation 12 with Equation 15 leads to:

\[ v = \frac{k_p [M]}{2(fk_d k_i)^{1/2} [I]^{1/2}} \]

*Equation 16*

The kinetic chain length should be related to the degree of polymerisation, DP. DP is the number of monomer units making up a polymer chain and is calculated by dividing the molar mass of the polymer chain by the molar mass of the monomer unit. For termination by combination \( DP = 2v \) and for disproportionation \( DP = v \). Termination
can occur at any stage of chain growth and radicals can grow for different periods of

time. This results in a polymer that has a distribution of molecular sizes and therefore

DP is an average quantity.

2.1.6 Molar mass definition

Small molecules have a discrete molar mass. Polymers however are composed of a number of chains of differing molar mass that result in a characteristic MMD. The shape and breadth of the MMD is dependent upon the mechanism, reaction conditions, and kinetics. Figure 5 presents the molar mass distribution for a typical synthetic polymer. As a consequence of these distributions average molar masses are used. An average based on the number of molecules present is called a number average molar mass, \( M_n \) (Equation 17) which is the sum of all the masses of the molecules present in a polymeric sample divided by the number of molecules present.

\[
M_n = \frac{\sum N_i M_i}{\sum N_i}
\]

*Equation 17*

where \( N_i \) is the number of species \( i \) with mass \( M_i \). \( M_n \) is sensitive to low molar mass species. The presence of oligomers in a polymer for example will have a marked effect on \( M_n \) due to the high number concentration of molecules per unit mass.

The weight average molar mass, \( M_w \) is based on the average mass of the molecules. \( M_w \) is the sum of the mass multiplied by the molar mass of all the molecules divided by the total mass of the mixture (Equation 18).

\[
M_w = \frac{\sum N_i M^2_i}{\sum N_i M_i}
\]

*Equation 18*

\( M_w \) is always higher than \( M_n \) as heavier molecules contribute more to \( M_w \) than \( M_n \).
Chapter 2: Background and theory

Figure 5 Distribution of molar masses in a typical synthetic polymer

The ratio $M_w/M_n$ gives a representation of the MMD of a polymer sample known as the polydispersity index (PDI). Most polymers or copolymers prepared by conventional free radical techniques have a PDI between 1.5 and 2.0 while ionic living polymerisation delivers polymers with PDI<1.2. If the PDI is unity then the polymer is monodisperse. Other parameters used to describe molar mass include the viscosity average molar mass $M_v$ and the peak molar mass $M_p$.

2.1.7 HIGH CONVERSION POLYMERISATIONS AND THE GEL EFFECT

In many polymerisations a marked increase in rate is observed at higher conversions instead of the gradual decrease expected with the consumption of monomer and initiator. This effect is most dramatic when polymerisations are carried out in bulk or in concentrated solutions. This auto-acceleration is a direct result of an increase in viscosity of the medium that leads to the loss of steady-state kinetics. It is reasonable to presume that the rate of initiation will not increase with conversion, therefore auto-acceleration either stems from an increase in the rate of propagation $k_p$, or a decrease in the rate of termination $k_t$ or both. The increase in viscosity of the reaction medium leads to propagation and termination becoming diffusion controlled. Termination is a rapid process ($k_r\sim10^{811}$ mol dm$^{-3}$ s$^{-1}$) compared to propagation ($k_p\sim10^{321}$ mol dm$^{-3}$ s$^{-1}$) and requires the successful collision of two radical ends attached to long, highly entangled polymer chains. As termination becomes diffusion controlled $k_t$ drops and the overall radical concentration increases. As chain propagation is slower, the smaller monomer
molecules can diffuse through the entangled chains more effectively increasing the number of exothermic propagation steps, which results in an increase in polymerisation rate, \( R_p \) and molar mass. The first indications that restricted diffusion was important in termination came from the studies of Norrish and Smith\textsuperscript{24} and later Tromsdorff \textit{et al.}\textsuperscript{25}. Rotating sector experiments carried out by Matheson \textit{et al.}\textsuperscript{26} indicated that for MMA at 35% conversion \( k_t \) had decreased to 1% of its initial value while \( k_p \) remained essentially constant. Figure 6 represents typical bulk and dilute polymerisations.

![Figure 6 Schematic representation of polymerisation rate versus conversion for bulk polymerisation. (--- gel effect, - - - absence of gel effect)](image)

The polymerisation rate rises initially to a steady state as the radical concentration becomes constant. At higher conversions the gel effect begins to control the rate, leading to \textit{auto-acceleration}. Providing the polymerisation temperature is below the glass transition temperature, \( T_g \), of the polymer, then the mixture becomes glassy and the rate falls, as monomer can no longer diffuse to the active centres.

\textbf{2.1.8 CHAIN TRANSFER}

In many radical polymerisations the kinetic chain length is shorter than expected. Usually, DP will lie between the limits of \( v \) (disproportionation) and \( 2v \) (combination) but not always. This is due to chain transfer where the activity of a growing radical is transferred by abstraction of an atom from an inactive molecule XP yielding an inactive
chain and a new species that may be capable of initiating further chain growth as shown in Equation 19 and Equation 20.

\[ M_x^* + XP \rightarrow XM_x + P^* \]

*Equation 19*

\[ P^* + M \rightarrow PM^* \text{ etc...} \]

*Equation 20*

where XP is the chain transfer species and P* is the new radical formed as a consequence of the transfer reaction. Chain transfer reactions have significant effects on molar mass. The degree of polymerisation can be re-written in terms of the rate of growth divided by all the reactions that lead to dead polymer (Equation 21)

\[ DP = \frac{R_p}{fk_d[I] + k_{tr,M}[M][M^*] + k_{tr,S}[S][M^*] + k_{tr,I}[I][M^*] + k_{tr,X}[X][M^*]} \]

*Equation 21*

where the terms in the denominator represent termination by combination and transfer to monomer M, solvent S, initiator I and modifier X, respectively. When a species is added deliberately that is known to chain transfer, it is known as a chain transfer agent (CTA).

If termination is via disproportionation, then the first term becomes \(2fk_d[I]\). The kinetic parameter that describes the magnitude of the chain transfer reaction is the chain transfer constant C. Chain transfer constants for monomer, solvent, initiator and CTA can be defined as:

\[ C_m = \frac{k_{tr,M}}{k_p} \]

*Equation 22*
Chapter 2: Background and theory

\[ C_S = \frac{k_{r,S}}{k_p} \]

*Equation 23*

\[ C_I = \frac{k_{r,I}}{k_p} \]

*Equation 24*

\[ C_{CTA} = \frac{k_{r,CTA}}{k_p} \]

*Equation 25*

Then by assuming termination is by combination:

\[
\frac{1}{DP} = \frac{k_t}{k_p^2} \frac{R_p}{M^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_t}{k_p^2} \frac{R_p^2}{f[M]^3} + C_{CTA} \frac{[CTA]}{[M]} 
\]

*Equation 26*

Equation 26, known as the Mayo\textsuperscript{27} equation, assumes that the new radical formed is approximately as reactive as the initial chain radical and that the chain transfer radical plays no part in termination. This is a valid assumption when low concentrations of radicals resulting from transfer are present compared to propagation radicals. Deviations from the kinetic scheme may be found when there is significant transfer to initiator or polymer.

Chain transfer constants are important when attempting to predict the effect of an added CTA on a polymerisation. A CTA with a value near unity is consumed at the same rate as the monomer, so [CTA]/[M] is constant throughout the polymerisation. This makes them an ideal choice for controlling molar mass and producing macromonomers. If a CTA has a very low transfer constant, the newly formed radical may react very slowly retarding the polymerisation, or not at all therefore inhibiting polymerisation. A CTA of C > 5 is consumed quickly in the polymerisation. Recently, transfer agents with very high transfer constants (C > 1000) have been used in CRP (Section 2.4).
2.1.8.1 Chain Transfer to Monomer, Polymer, Initiator and Solvent

Chain transfer to monomer involves hydrogen abstraction and is in competition with propagation (Figure 7 1 vs. 2).

\[ \text{RH} + \text{CH}_2=\text{CX} \rightarrow \text{RCH}_2=\text{CHX} \cdot \]

\[ \text{R}^+ + \text{CH}_2=\text{CHX} \rightarrow \text{RCH}_2=\text{CHX}^+ \]

*Figure 7 Chain transfer to monomer*

In many chain transfer reactions, propagation can be continued but if the new radical generated is stabilised and cannot continue propagation then the process is called *degradative chain transfer*. This is particularly common with allylic type monomers where abstraction of the \( \alpha \)-hydrogen leads to a resonance stabilised allylic radical (Figure 8). Allyl esters, propylene and other \( \alpha \)-olefins such as decene are all known to undergo degradative chain transfer\(^{28,29,30}\).

*Figure 8 Allylic resonance of 1 pentene*

The Mayo equation (Equation 26) can be simplified for chain transfer to monomer (Equation 27).

\[
\frac{1}{DP} = \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_m
\]

*Equation 27*

Chain transfer to polymer leads to chain branching. An increase in \( M_w \) is observed with slight broadening of the MMD. Transfer to initiator can result in complications that are dependent on the transfer mechanism. A chain transfer reaction can destroy the activity of an initiator. Peroxide initiators are more susceptible to chain
transfer than azo initiators. Chain transfer reactions to solvent molecules are dependent on solvent concentration, the strength of the bond involved in the abstraction step and the stability of the solvent radical formed.

2.1.8.2 CHAIN TRANSFER TO MODIFIER

Specific compounds contain functional groups that are more susceptible to transfer reactions due to the weakness of the bond involved in the abstraction. Sulfur and sulfur based compounds are effective chain transfer agents and alkyl thiols are commonly used. Modifiers with chain transfer constants close to unity are effective in controlling molar masses of polymers. Rizzardo et al.\textsuperscript{31} showed that certain allylic compounds, vinyl ethers and thianoesters were effective chain transfer agents that operated via an addition-fragmentation mechanism. It was this work that lead to the development of RAFT polymerisation. The chain transfer activities of numerous compounds have been reported\textsuperscript{32}.

If a CTA is added to the polymerisation, then chain transfer involving the CTA usually dominates over transfer reactions to other species. The Mayo equation (Equation 26) can therefore be simplified assuming all other transfer reactions are negligible (Equation 28).

\[ \frac{1}{DP} = \frac{k_i}{k_p^2} \frac{R_p}{[M]^2} + C_x \frac{[X]}{[M]} \]

\textit{Equation 28}
2.2 COPOLYMERISATION

Copolymerisation, the incorporation of two monomers into a macromolecular chain, provides a powerful tool for controlling polymer structures and properties. Often a synergistic effect is observed for the copolymer when compared to a mixture of the two homopolymers. Copolymers form a variety of structures, which include alternating copolymers (units alternate regularly along the chain), statistical copolymers (units arranged statistically along the chain) and block copolymers (monomer units of one type successively along the chain). The type of copolymer formed is dependent upon the reactivity of the comonomers toward each other.

2.2.1 KINETICS OF COPOLYMERISATION

The first attempt to elucidate the copolymerisation mechanism was made by Dostal\textsuperscript{33} in 1936. He stated that the free radical addition of monomer depends only on the nature of the radical ended chain. To this end four possible propagation steps were proposed each with a characteristic rate constant $k$.

\begin{align*}
&M_1^\ast + M_1 \rightarrow M_1^\ast \quad k_{11}[M_1^\ast][M_1] \quad \text{Equation 29} \\
&M_1^\ast + M_2 \rightarrow M_2^\ast \quad k_{12}[M_1^\ast][M_2] \quad \text{Equation 30} \\
&M_2^\ast + M_1 \rightarrow M_1^\ast \quad k_{21}[M_2^\ast][M_1] \quad \text{Equation 31} \\
&M_2^\ast + M_2 \rightarrow M_2^\ast \quad k_{22}[M_2^\ast][M_2] \quad \text{Equation 32}
\end{align*}

where $k_{11}$ and $k_{22}$ are the rate constants for self propagation and $k_{12}$ and $k_{21}$ are the rate constants for cross propagation. Mayo and Lewis\textsuperscript{34} and Alfrey and Goldfinger\textsuperscript{35}
developed the kinetic expressions by applying steady state conditions, that is the concentration $M_1^*$ and $M_2^*$ remain constant so that the conversion of $M_1^*$ to $M_2^*$ must equal the conversion of $M_2^*$ to $M_1^*$ (Equation 33).

$$k_{12}[M_1^*][M_2] = k_{21}[M_2^*][M_1]$$

*Equation 33*

The rates of disappearance of $[M_1]$ and $[M_2]$ alone are given by:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]$$

*Equation 34*

$$-\frac{d[M_2]}{dt} = k_{22}[M_2^*][M_2] + k_{12}[M_1^*][M_2]$$

*Equation 35*

where $[m_1]$ and $[m_2]$ are the concentrations of the monomer units in the copolymer. To simplify calculations, the ratio of the rate constants for the two monomers adding to the same radical chain end can be utilised. These are defined as $r_1$ (Equation 36) and $r_2$ (Equation 37).

$$r_1 = \frac{k_{11}}{k_{12}}$$

*Equation 36*

$$r_2 = \frac{k_{22}}{k_{21}}$$

*Equation 37*

These terms are known as the monomer reactivity ratios for monomers $M_1$ and $M_2$ respectively. The copolymer equation can be obtained by considering Equation 33 and dividing Equation 34 by Equation 35. Substitution of the monomer reactivity ratios for the rate constants leads to Equation 38.
Chapter 2: Background and theory

\[
\frac{d[m_1]}{d[m_2]} = \left[ M_1 \right] r_1[M_1] + \left[ M_2 \right] \]

\[
\frac{d[m_2]}{d[m_2]} = \left[ M_2 \right] r_2[M_2] + \left[ M_1 \right] 
\]

Equation 38

The copolymer equation is applicable for all chain reaction copolymerisations regardless of chain carrier mechanism and is independent of the mode of termination. The values of the monomer reactivity ratios can give an indication of the copolymer structure.

\( r_1 < 1 \) \hspace{1cm} M_1^* \text{ prefers to add } M_2.

\( r_1 = 1 \) \hspace{1cm} M_1^* \text{ has an equal probability of adding } M_1 \text{ or } M_2.

\( r_1 > 1 \) \hspace{1cm} M_1^* \text{ prefers to add } M_1.

\( r_1 = r_2 = 0 \) \hspace{1cm} Tendency towards alternating copolymer.

\( 0 < r_1, r_2 < 1 \) \hspace{1cm} Tendency towards alternating copolymer (more common than above).

\( r_1 = r_2 = 1 \) \hspace{1cm} Tendency towards ideal copolymer formation

\( r_1 < 1 \text{ and } r_2 > 1 \) \hspace{1cm} Tendency towards composition drift, and rich in \( M_2 \) monomer units, the more reactive \( M_2 \) will be depleted until only \( M_1 \) remains.

\( r_1 r_2 >> 1 \) \hspace{1cm} Tendency to obtain block copolymer.

2.2.2 Estimation of Monomer Reactivity Ratios

The most common methods for estimation of monomer reactivity ratios involve the use of linear least squares regression. These techniques involve transforming the instantaneous copolymer equation (Equation 38) into a form that is linear in the parameters \( r_1 \) and \( r_2 \) so that the reactivity ratios can be estimated by a linear least squares fit. Copolymers are prepared with a range of monomer feed compositions. The
resulting copolymer composition is elucidated by experiment and the feed and composition data used to determine \( r_1 \) and \( r_2 \).

2.2.2.1 FINEMAN-ROSS METHOD

Fineman and Ross developed the first analysis of reactivity ratios\(^{36} \). By defining:

\[
y = \frac{d[m_1]}{d[m_2]}
\]

Equation 39

and

\[
x = \frac{[M_1]}{[M_2]}
\]

Equation 40

then Equation 38 can be rearranged to:

\[
G = r_1 F - r_2
\]

Equation 41

and/or

\[
\frac{G}{F} = -r_2 \frac{1}{F} + r_1
\]

Equation 42

where the transformed variables are:

\[
G = \frac{x(y-1)}{y} \quad \text{and} \quad F = \frac{x^2}{y}
\]

Graphically plotting Equation 41 gives \( r_1 \) as the slope and \( -r_2 \) as the intercept, while plotting Equation 42 delivers \( -r_2 \) as the slope and \( r_1 \) as the intercept.
2.2.2.2 **KELEN-TÜDŐS METHOD**

The Kelen-Tüdős\(^7\) method is an extension of the Fineman-Ross method that removes some of the weaknesses of the above. It was pointed out by Tidwell and Mortimer\(^8\) that the Fineman-Ross equations unequally weighted the data, such that results obtained at the extremes of the feed ratios had the most pronounced effect on the slopes of the plots. The spreading of data using the Kelen-Tüdős method avoids this source of error. The following linear equation was proposed:

\[
\frac{G}{(\alpha + F)} = r_1 \frac{F}{(\alpha + F)} - \frac{r_2}{\alpha} \left[ 1 - \frac{F}{(\alpha + F)} \right]
\]

*Equation 43*

where \(\alpha = \sqrt{F_{\text{min}} \cdot F_{\text{max}}}\) and \(F_{\text{min}}\) and \(F_{\text{max}}\) are the maximum and minimum values of \(F\) calculated from experiment. When the values of the reactivity ratios are expected to be similar, then a value of \(\alpha = 1\) can be used as an arbitrary constant. By defining:

\[
\sigma = \frac{G}{(\alpha + F)} \quad \text{and} \quad \xi = \frac{F}{(\alpha + F)}
\]

Equation 43 can be rewritten to provide Equation 44

\[
\sigma = r_1 \xi - \frac{r_2}{\alpha} (1 - \xi)
\]

*Equation 44*

A plot of \(\sigma\) against \(\xi\) to obtain a straight line is extrapolated to \(\xi = 0\) giving \((-r_2/\alpha)\), and extrapolated to \(\xi = 1\) delivering \(r_1\) (both as intercepts).

2.2.3 **MONOMER REACTIVITY RATIOS AND ALTERNATING COPOLYMERISATION**

The reactivity of the monomers is determined by the substituents on the double bond. The electronic effect of a second substituent on the same carbon is usually additive. Examination of many systems has revealed that cross propagation is favoured
when the comonomers have steric or electronic differences. Steric hindrance affects monomer reactivity; 1,1-substituted species react more easily than 1,2-substituted. However, the two main factors that influence monomer reactivity are resonance stabilisation and polarity.

2.2.3.1 RESONANCE STABILISATION

Following on from their work on the copolymer equation, Mayo et al studied a number of systems, finding that when using St as a constant monomer differing reactivity was shown towards different monomers\textsuperscript{39, 40}. When the St–MMA system was studied, it was suggested that resonance stabilisation brought about by the transfer of one electron, transforming the MMA radical to the more stable enolate ion (Figure 9).

$$\text{Figure 9 Resonance stabilisation of St} \text{ and MMA}$$

This stabilisation was thought to encourage alternation. A similar stabilisation was considered for St and MA (Figure 10).

$$\text{Figure 10 Resonance stabilisation for StMA}$$

2.3.2.2 POLARITY

Resonance stabilisation was not satisfactory in describing the tendency for some comonomers to alternate. A difference in polarity of the two comonomers has been accepted as a large contributing factor in the way in which pairs of monomers behave in a copolymerisation. Differences in reactivity of comonomers has been investigated by
Lewis et al.\textsuperscript{39}; they concluded that some of these effects may be due to dipole interactions. This was further developed by Price\textsuperscript{41}, who found that most efficient copolymerisation occurs between pairs of monomers where one has an electron poor double bond and the other has an electron rich double bond. He assumed that the polarity evident in the monomer was also reflected in the radical derived from it. Acrylonitrile can be expressed as a partially polarised structure.

\[
\begin{array}{c}
\text{HC} & \equiv & \text{C} & \equiv & \text{N} \\
\text{H} & & & & \\
\end{array}
\]

St has an opposing polarity.

\[
\begin{array}{c}
\text{+} & \text{C} & \equiv & \text{CH}_2 \\
\text{H} & & & \\
\end{array}
\]

The attraction of the differing polarities accounted for the facile copolymerisation and tendency to alternation in some systems.

2.3.2.3 THE Q-E SCHEME

Alfrey and Price\textsuperscript{42} attempted to combine the effect of resonance stabilisation and polarity in a semi-quantitative manner, pointing out that it would be useful to describe each individual monomer by characteristic constants. Previous theory using reactivity ratios meant that in order to investigate a copolymerisation, each pair of monomers had to be individually studied. Alfrey and Price suggested that if a limited number of polymerisations could be carried out on reference monomers and values computed characteristic of that monomer, then the behaviour of the monomer in unstudied systems could be predicted. The expression for the Q-e scheme is based on the cross propagation reaction (Equation 45)

\[
k_{12} = P_1 Q_2 \exp(-e_1 e_2)
\]

\textit{Equation 45}
where \( P \) characterises the radical state, \( Q \) the monomer reactivity or resonance stabilisation and \( e_1 \) and \( e_2 \) describe the polarisation of the radical and reacting monomer respectively. It is useful to state the reactivity ratios in terms of the \( Q-e \) equation (Equation 46 and Equation 47).

\[
\begin{align*}
r_1 &= \left( \frac{k_{11}}{k_{12}} \right) = \left( \frac{Q_1}{Q_2} \right) \exp\{-e_1(e_1 - e_2)\} \\
r_2 &= \left( \frac{k_{22}}{k_{21}} \right) = \left( \frac{Q_2}{Q_1} \right) \exp\{-e_2(e_2 - e_1)\}
\end{align*}
\]

Equation 46

Equation 47

As stated previously, the alternating tendency can be expressed as the product of \( r_1 \) and \( r_2 \) (Equation 48).

\[
r_1r_2 = \exp[-(e_1 - e_2)^2]
\]

Equation 48

Furukawa et al\(^{43}\) further developed the scheme while Fordyce et al\(^{44}\) extended it to three monomers. Further theoretical treatments of the \( Q-e \) scheme have been presented based on a molecular orbital basis. The original expression has been criticised \(^{45,46}\), but while not rigorous it is still a useful tool in copolymerisation, provided that it is regarded as a semi-empirical analysis. The \( Q \) and \( e \) values that have been recorded experimentally\(^{32}\) are shown below for MA and various electron-donating monomers (Table I).
Table 1 $Q$ and $e$ values for MA and electron donating comonomers

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$Q$ Value</th>
<th>$e$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>0.860</td>
<td>3.690</td>
</tr>
<tr>
<td>St</td>
<td>1.000</td>
<td>-0.800</td>
</tr>
<tr>
<td>Para methyl styrene</td>
<td>1.100</td>
<td>-0.630</td>
</tr>
<tr>
<td>$(p\text{MeSt})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Para chloro styrene</td>
<td>1.330</td>
<td>-0.640</td>
</tr>
<tr>
<td>$(p\text{ClSt})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Para methoxy styrene</td>
<td>1.530</td>
<td>-1.400</td>
</tr>
<tr>
<td>$(p\text{MeOSt})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ methyl styrene</td>
<td>0.980</td>
<td>-1.270</td>
</tr>
<tr>
<td>$(\alpha\text{MeSt})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.016</td>
<td>0.050</td>
</tr>
<tr>
<td>Propylene</td>
<td>0.009</td>
<td>-1.690</td>
</tr>
<tr>
<td>But-1-ene</td>
<td>0.007</td>
<td>-0.060</td>
</tr>
<tr>
<td>Hex-1-ene</td>
<td>0.035</td>
<td>0.92</td>
</tr>
</tbody>
</table>

2.3.2.4 CHARGE TRANSFER COMPLEXES

Early studies of alternating copolymers indicated that a common characteristic of such systems was the tendency to form an electron donor –acceptor charge transfer complex (CTC). The complexes exist in equilibrium with the unassociated species (Equation 49), the electron acceptor (A) and donor (D). The equilibrium constant, $K$, can be written (Equation 50)

$$A + D \rightleftharpoons CTC$$

*Equation 49*

$$K = \frac{[CTC]}{[A][D]} = \frac{[CTC]}{([A]_0 - [CTC])([D]_0 - [CTC])}$$

*Equation 50*

where $[A]_0$ and $[D]_0$ are the initial concentrations in the mixture. The formation of a CTC often brings about a colour change in the solution and a new absorption band in the
UV spectrum. The magnitude of the equilibrium constant can therefore be determined by measuring the new absorbance as a function of monomer concentration. More recently $^1$H NMR spectroscopy has been used to determine the K value of a CTC\textsuperscript{47,48}. In solution, there is rapid exchange between protons in the complexed and uncomplexed state and the chemical shift observed for one of the monomers is a weighted average of complexed and uncomplexed protons. Measurement of the shift of a chosen proton peak as a function of monomer concentration allows K to be evaluated. MA systems are amenable to the $^1$H NMR method as MA has only one proton peak at 7.02 ppm that is simple to assign and follow.

The value of K has been shown to have a dependence on both solvent and temperature. In some cases, spectroscopic evaluation of K results in negative values when the CTC formed is weak. The electron donating or accepting capability of the reaction solvent greatly affects K. CTC formation depends on the dielectric constant of the solvent with greater values of K being observed in non-polar solvents. Polar solvents may compete with acceptor monomers forming a solvent – monomer CTC that is stronger than the copolymerising CTC. Temperature also has a pronounced effect on the formation of a CTC. Higher temperatures usually lead to the dissociation of a CTC as its formation is an exothermic process. Seymour \textit{et al} studied the temperature effect of CTC formation with the MA – vinyl acetate system\textsuperscript{49}. The absorbance of the characteristic UV band at 230 nm was measured at several temperatures and the data extrapolated to zero absorbance where no CTC should exist. The temperature at which no CTC should form was determined to be 90°C. Copolymerisations carried out above that temperature were found to have statistical compositions while alternating copolymers were formed below 90°C.
### 2.3 Alternating Copolymerisation with MA

Even though MA does not polymerise easily, it will enter into copolymerisations with electron donor molecules with relative ease. Generally, the stronger the electron donor the more facile the reaction will be; for example, spontaneous copolymerisation without initiator has been observed for some vinyl ether monomers such as 1,2-dimethoxyethylene and \( p \)-dioxene\(^5\). Trivedi and Culbertson\(^7\) have carried out an excellent survey of donor molecules and a list is shown below that is by no means exhaustive (Table 2).

<table>
<thead>
<tr>
<th>Monomer Type</th>
<th>Examples</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl monomers</td>
<td>Allyl alcohol</td>
<td><img src="image" alt="Allyl alcohol structure" /></td>
</tr>
<tr>
<td></td>
<td>Allyl benzene</td>
<td><img src="image" alt="Allyl benzene structure" /></td>
</tr>
<tr>
<td>Vinyl ethers</td>
<td>1,2-dimethoxyethylene</td>
<td><img src="image" alt="1,2-dimethoxyethylene structure" /></td>
</tr>
<tr>
<td></td>
<td>Tert-butyl vinyl ether</td>
<td><img src="image" alt="Tert-butyl vinyl ether structure" /></td>
</tr>
<tr>
<td>Cyclic ethers</td>
<td>Furan</td>
<td><img src="image" alt="Furan structure" /></td>
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<tr>
<td>Divinyl monomers</td>
<td>Divinylether</td>
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<td>Vinyl heterocycles</td>
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<td>Butenes</td>
<td><img src="image" alt="Butenes structure" /></td>
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2.3.1 ST AND SUBSTITUTED ST – MA COPOLYMERS

St with its electron donating capacity has received considerable study as a comonomer for MA. Alternating copolymers have been prepared using common free radical initiators such as BPO at 70-80°C. Alfrey and Lavin found that copolymers having a value of $M_n$ of 1,300 g mol$^{-1}$ to 10,000 g mol$^{-1}$ were formed under these conditions, though in general temperatures of 40-100°C can be used to form alternating products.

The powerful alternating tendency of these two comonomers has been explained using two different mechanistic rationales. The first maintains that a high degree of alternation is a natural consequence of the reactivities of the monomers and the radicals
derived from them, i.e. that there is a marked preference for cross propagation. It is possible that this alternating tendency is enhanced by polar interactions in the transition state, where the acceptor, MA, is donated charge from the electron rich St. This is not present when a St-terminated radical adds St monomer and so the energy of activation for cross-propagation is lower than homo-propagation. The second proposal is that a CTC is formed between the two comonomers which may have a higher reactivity toward the growing radical than the free monomers and therefore this adds to the growing chain as a unit (Figure 11).

Figure 11 StMA CTC

Both mechanisms have merit. Barb\textsuperscript{52} examined this system and concluded that the alternation was due to a penultimate effect. The penultimate unit in the growing radical was thought to influence the terminal unit altering its reactivity to an incoming radical. Thus, a penultimate MA unit with a St radical will be more reactive to MA monomer than St monomer.

Tsuchida and Tomono\textsuperscript{53} carried out a detailed mechanistic study. At room temperature, they confirmed the presence of a CTC. This was observed from a UV absorption band at 282 nm that is not characteristic of either MA or St\textsuperscript{54}. The equilibrium constant was determined to be 0.31 mol dm\textsuperscript{-3} by \textsuperscript{1}H NMR spectroscopy. The initiation mechanism was studied using \textsuperscript{14}C labelled AIBN and the end groups of the copolymers determined. The results showed that initiation was only due to AIBN and not complex initiation or hydrogen abstraction. However, a low number of initiator fragments present in the copolymers suggested significant chain transfer to MA monomer or its CTC. The FTIR spectrum showed a band due to unsaturation at 1630 cm\textsuperscript{-1} that can be assigned to MA units in the chain. When the reaction was carried out in
trichloromethane, no chlorine was incorporated into the structure, so chain transfer to the solvent was considered to be insignificant. The copolymerisation behaved in a manner consistent with normal free radical copolymerisations such that the molar mass was constant throughout and $R_p$ was proportional to the square root of the initiator concentration. Strong donor and acceptor molecules such as naphthalene and dimethyl aniline, when added to the system, acted as chain transfer agents. It was concluded that the alternating mechanism probably included both a CTC and free MA. The presence of MA at the growing chain ends provided evidence for this. The amount of termination by disproportionation compared to recombination could not be determined due to the large amount of chain transfer to the complex or monomers.

Later, Dodgson and Ebdon also carried out an extensive investigation of the system, producing copolymers in bulk and in a number of solvents. The penultimate model as suggested by Barb was tested with reactions in methyl ethyl ketone (MEK) and gave only moderate agreement with the penultimate theory. The CTC theory was also tested. In order to take a complex into account, eight propagation steps must be considered. The experimental data provided a better fit to the CTC model indicating that free monomer and CTC mechanisms may participate. However, two experimental observations led the authors to conclude that a CTC was unlikely to play a role. If a CTC mechanism was operating, then the dilution of the total monomer concentration should affect the copolymerisation kinetics as the CTC has less influence. This was found not to be the case and the composition remained constant. More importantly, if a CTC aids in the propagating mechanism, then the addition of a Lewis acid should strengthen the complex and increase the alternation. The opposite was found to be true; the addition of ZnCl₂ increased the concentration of St in the product.

Pittman et al. investigated this copolymerisation in solvents at various temperatures. They confirmed the formation of a complex but noted that above 125°C the UV adsorption band disappeared, suggesting that above that temperature any CTC that has been formed is unstable. Experiments were carried out in strong $\pi$ donor solvents such as 1,3-dimethoxy benzene and in a non-polar non-donor solvent decalin. It was found that in the donor solvents alternating copolymers were prepared up to 145°C, 25°C above the dissociation temperature of the complex. The donor solvents
were thought to stabilise the polar transition state relative to the non-polar transition state. Such stabilisation would not occur in decalin and at high temperatures the structures are indeed more statistical. At lower temperatures, the copolymers in decalin are alternating and therefore can be explained by incorporation of a CTC into the growing chain. However O'Driscoll\textsuperscript{57} pointed out that monomer reactivity ratios are temperature dependent when they are either very small or very large. The tendency towards statistical copolymers is enhanced with increasing temperature and therefore the decalin result may be explained by conventional cross-propagation reactions.

\( \alpha \)-methyl styrene (\( \alpha \text{MeSt} \)) is a stronger electron donor than St and also forms alternating copolymers with MA. \( \alpha \text{MeSt} \) is sterically hindered and the monomer has a ceiling temperature of 334 K\textsuperscript{18} above which homopolymerisation is thermodynamically unfeasible (\( \Delta G_p = 0 \)). Under normal free radical conditions therefore, \( \alpha \text{MeSt} \) cannot be polymerised but it does form alternating copolymers with MA. Shirota \textit{et al.}\textsuperscript{8} developed a generalised kinetic model for alternating copolymerisation by considering the cross propagation reactions of both the free monomers and the CTC unit, if present. The Shirota model was applied to \( \alpha \text{MeSt} \) by Javni \textit{et al.}\textsuperscript{8}. The CTC equilibrium constant K was determined by \(^1\text{H} \) NMR spectroscopy in CDCl\textsubscript{3} to be 0.07 mol dm\textsuperscript{-3}. Relative rates of propagation due to free monomers and the CTC in copolymerisation in benzene and MEK were calculated. CTC participation in benzene was claimed to dominate over free monomer while in MEK the opposite was observed, though monomer concentration plays a significant role with free monomer becoming less significant at high concentrations. The difference in mechanism was attributed to solvent competition effects with MEK being a stronger donating solvent than benzene.

Fujimori \textit{et al.}\textsuperscript{9} reported the copolymerisation of \( p \text{MeOSt} \) with MA. The K value for the CTC was determined by UV spectroscopy to be 0.125 mol dm\textsuperscript{-3}. The copolymers were revealed to have high \textit{cis/trans} ratios and this high degree of stereoregularity was attributed to a significant contribution of the CTC to the copolymerisation. The authors pointed out however that free monomer addition couldn't be excluded from the overall mechanism.
Ebdon et al. reviewed the involvement of monomer-monomer complexes in the free radical polymerisation of StMA\textsuperscript{60}. Acknowledgment was made to the existence of complexes between St and MA though the authors point out that the high degree of alternation in a copolymerisation can only be accepted as evidence of CTC participation if it can be shown that high rates of cross propagation involving free monomers provide an insufficient explanation. The composition of copolymers prepared in MEK were consistent when the total monomer concentration was reduced from 8 to 0.5 mol dm\textsuperscript{-3} and reactivity ratios extrapolated to infinite dilution in dioxane showed that a high degree of alternation persists even when the CTC concentration is zero (\(r_{\text{MA}} = 0.018, r_{\text{SI}} = 0.074\)). Ratzsh and Steinert\textsuperscript{61} measured the relative reactivities of MA and St towards the cyclohexyl radical (a donor radical) and found that MA is 850 times more reactive than St. The method employed cyclohexylmercury acetate in the presence of reducing media (NaBH\textsubscript{4}). The radicals generated are the start radicals for the monomers present and are transformed into the hydrogenated species by NaBH\textsubscript{4}. The experimental conditions were controlled to prevent propagation and the starting species were identified by gas chromatography. A monomer ratio of St:MA of 80:1 was used, and in this mixture all the MA was expected to be complexed with St. The results indicated that no StMA units were detected and addition was only via free monomers. Bevington and Johnson\textsuperscript{62} showed that towards the benzoyloxy radical (an acceptor radical) St was 50 times more reactive than MA. Using Ratzsch and Bevington’s data leads to reactivity ratios of \(r_{\text{MA}} = 1/50 = 0.02\) and \(r_{\text{SI}} = 1/850 = 0.0012\) and therefore a high degree of alternation would be expected. Non-stationary state studies also support the above. Values for the rate constants \(k_p\) and \(k_t\) obtained were \(k_p = 5500\) mol dm\textsuperscript{-3} s\textsuperscript{-1} and \(k_t = 6.5\times10^{-7}\) mol dm\textsuperscript{-3} s\textsuperscript{-1}. Assuming that \(k_p\) is an average mainly of \(k_{\text{MAs}}\) and \(k_{\text{StMA}}\), that \(k_{\text{MAs}} \approx k_{\text{StMA}}\) and incorporating \(k_{\text{StSI}}\) as 190 mol dm\textsuperscript{-3} s\textsuperscript{-1} led to

\[
r_{\text{SI}} = k_{\text{StSI}}/k_{\text{StMA}} = 190/2750 \approx 0.06
\]

Thus the evidence indicates that there is a high probability that most, if not all alternation in StMA copolymers arises from enhanced cross-propagation involving free rather than complexed monomers.

In a further review Rätzsch\textsuperscript{63} focused on reaction mechanism and structural determination. The author criticised the theory of the sole addition of a CTC to a
growing radical chain end and developed an alternative mechanism. Three arguments were proposed which are in contrast to CTC theory.

1) The maximum enthalpy of CTC formation is near 20 kJ mol\(^{-1}\). During monomer addition, a minimum of 50 kJ mol\(^{-1}\) is liberated and therefore 100 kJ mol\(^{-1}\) if two units add simultaneously. The CTC might therefore be expected to be dissociated when one of the units adds to the propagating radical.

2) A dynamic and kinetic argument must consider the lifetime of the CTC. Few rate constants for the formation and dissociation of CTC’s are available. However, Brevard and Lehn\(^{64}\) reported the rate of formation and dissociation to be 2 or 3 orders of magnitude higher than would be expected for a propagation reaction. Any CTC therefore may not stay intact while adding to a propagating radical.

3) Olefin radical reactivity must also be taken into account. Olefin addition rate is determined by electrostatic interactions (indicated by the \(e\) value) and steric influences (\(Q\) value). A stronger interaction would be expected between an electrophilic radical chain and a free electron rich olefin than the same olefin bound within a CTC. The same would be true of a nucleophilic radical and an electron poor monomer. A greater steric hindrance would also be expected from the CTC.

Rätzsch concluded that in a monomer mixture a number of species are present as reactant, and that free comonomer addition is preferred because of electrostatic interactions between the growing radical and the monomer based on the points above. This is supported by often-low CTC concentrations, though it is noted that CTC participation cannot be excluded at higher concentrations. Rätzsch proposed an advanced theoretical mechanism of complex dissociation. During the addition of a CTC, complex dissociation occurs eliminating the second monomer. The eliminated comonomer is in close proximity to the radical chain end and can be quickly added after the energy of the radical chain end is reduced by molecular impacts (Figure 12).
Chapter 2: Background and theory

This mechanism combines elements of the free monomer and CTC theories and may describe a range of olefins including St and substituted St monomers accounting for the CTC arguments presented above.

Despite much effort, a general mechanism has not been elucidated for the copolymerisation of St monomers and MA. The most recent work supports the addition of free monomers through polar transition states, with a small contribution from a charge transfer complex, especially at low temperatures.

2.3.2 OLEFIN – MA COPOLYMERS

Ethylene was the first olefin to be copolymerised with MA. This was achieved by Hamford in 1945\textsuperscript{65}. Copolymerisation can be carried out with a free radical initiator such as AIBN or with $\gamma$ radiation\textsuperscript{66} at temperatures from 30-65°C. Equimolar products were formed irrespective of monomer feed ratios. No homopolymerisation was observed so it was concluded that an alternating copolymer had been formed. The polymerisation rate and molar mass were found to be proportional to the concentration of ethylene and independent of the concentration of MA, when the monomer feeds were not equal. From this result, it was presumed that the rate determining propagation step was the addition of ethylene to the growing chain end. The temperature dependence of both AIBN initiation and $\gamma$ ray irradiation was investigated. The AIBN initiated products showed a significant increase in rate with increasing temperature. High molar mass products can be formed in aromatic solvents using BPO under high pressure. Low molar mass versions are easily prepared at atmospheric pressure with the use of an appropriate CTA. Koenig\textsuperscript{67} carried out a detailed structural analysis of ethylene-alt-MA
copolymers. High resolution $^{13}$C NMR was used to elucidate the structure and mechanism of the system. The mode of initiation using BPO was found to be via a $\alpha$-phenyl ethyl radical. It is unclear as to the origin of the $\alpha$-phenyl ethyl radical as the author did not postulate on its formation mechanism, though benzoyloxy decarboxylation to form the phenyl radical followed by hydrogen abstraction from the copolymerisation solvent, ethyl benzene, would deliver the reported $\alpha$-phenyl ethyl radical. However, whether rates of decomposition and radical stabilities are conducive to this mechanism is unclear. The mode of initiation was explained by comparison of low molar mass copolymers with various model compounds that were found in the literature or prepared. Use of a low molar mass copolymer allows the end groups to be distinguished by $^{13}$C NMR. Copolymer termination was also investigated. Disproportionation was not a viable pathway due to a lack of unsaturation in the copolymers. Combination was also found to be insignificant as only one initiator molecule was found per chain. Chain transfer was concluded to be the main polymer formation route, with a succinic group at the end of the chain. The microstructure of the repeat units could also be distinguished by a $^{13}$C NMR experiment. Both the carboxyl and the backbone carbons of the succinic unit showed two peaks rather than one. These were attributed to the cis/trans stereochemistry that is possible due to the fixed position of the succinic moiety (Figure 13).

![Figure 13 Cis and trans stereochemistry of ethylene-MA copolymers](image)

By using long pulse delays in the NMR acquisition, the two peaks were integrated indicating a 14:86 cis/trans ratio.
Ratzsh et al\textsuperscript{68} confirmed the structural findings but commented that a higher cis configuration is observed when fumaric acid is used instead of MA when preparing the copolymers. When the analysis was extended to propene-MA copolymers, a small increase in cis structure was found (20:80 cis:trans) at 80°C. When the temperature was raised to 150°C, 33% cis configuration was observed.

Jenner and Kellou\textsuperscript{69} investigated high-pressure copolymerisations of MA with highly substituted ethylenes such as 2-methyl-2-butene. The lower reactivity of the double bond and the increased steric hindrance means that under normal conditions these comonomers do not easily form products. Increasing the pressure dramatically increased the copolymerisation rates, this change being most pronounced for the most bulky monomers. The pressure effect on composition was not as marked but monomer reactivity ratios were found to slightly decrease with pressure. The $e$ value of the comonomer is also slightly reduced. Frank\textsuperscript{70} has studied propylene as a comonomer for MA. A high molar mass product was prepared using BPO (2 wt \%) at 70°C. Using increased pressure, an essentially quantitative yield can be attained in 3 hours. Molar masses were found to increase with increasing pressure, but decrease with increasing temperature and initiator concentration as is consistent with free radical copolymerisations.

Butene with its greater number of isomers has stimulated much interest in its alternating copolymerisation with MA. Otsu\textsuperscript{71} found that the molar mass for the butene series of copolymers varied: isobutene $\gg$ n-butene $\geq$ cis butene $\geq$ trans butene. Otsu also pointed out that the reactivity of butene isomers towards hydrogen abstraction was in the opposite order. It was concluded that degradative chain transfer to the butene monomer was an important factor in the copolymerisation behaviour.

Bacskai et al have investigated the stereochemistry of isobutene-MA copolymers\textsuperscript{72}. \textsuperscript{1}H NMR spectroscopy indicated that the methyl resonance is composed of four peaks of approximately equal intensity (Figure 14).
Figure 14 $^1$H NMR spectra for isobutene/MA copolymers

The multiplicity of the methyl resonance is not caused by spin-spin splitting; each peak represents a chemical shift that is characteristic of methyl groups attached to a quaternary carbon, as was expected from the repeating structure. The splitting remained after hydrolysis with deuterated sodium hydroxide (NaOD). The fact that the methyl groups were in non-equivalent magnetic environments can be related to the cis/trans stereochemical conformation of the copolymer. The spectra indicated that two isomers were present in equal amounts, which disagrees with the findings of Koenig and Ratzsh for propene-alt-MA copolymer where the trans conformer was found to dominate. Bortel and Stysto\textsuperscript{73} considered both isobutene and 1-butene as comonomers for MA. $^{13}$C and $^1$H NMR data indicated identical structures for both butene isomers that were in contrast to the predicted result (Figure 15).
The spectra indicated that only structure A was present. The lack of a methyl triplet in the $^1\text{H}$ NMR spectrum and no spin-spin splitting due to the butane side chain protons supported the formation of A alone. A vibration at 1230 cm$^{-1}$ in the FTIR spectrum indicates geminal dimethyl groups, which suggests a quaternary carbon in the backbone chain. Copolymer structure A is only possible by a mechanism that involves a rearrangement of the butene unit from a higher energy secondary radical to the lower energy tertiary radical (Scheme 3).

Copolymerisation of a C$_4$-C$_6$ hydrocarbon mixture with MA was carried out by Lappalainen and Koskimies$^{74}$. The mixture contained 35 components of which eight
were found to copolymerise with MA. The conjugated dienes in the mixture were found to react more efficiently with MA than the mono-olefins. Various conditions were investigated with reaction in dioxane at 80°C being favoured. Molar masses in all the experiments were low (Mn = 1,500 – 3,000 g mol\(^{-1}\)). Structural analysis by \(^1\)H NMR was complex but a few copolymer structures were determined after comparison with authentic copolymers produced with single olefins.

Longer alkyl chain olefins show a reduced reactivity in forming copolymers with MA. Extensive studies have, however, been carried out as the longer alkyl chain offers increased solubility in non-polar hydrocarbons and aromatic solvents. A number of patents encompassing olefins from 4-30 carbon atoms allude to the industrial interest of these copolymers. PODMA has been produced by a solution copolymerisation in propylene dichloride at reflux temperature. Isolation of the product was by repeated precipitation into \(n\)-propanol. The white precipitate was then filtered and dried. Other solvents and conditions were proposed. Davis et al synthesised PODMA and its derivatives for use in Langmuir-Blodgett films. The yields of the copolymers were 20-50%. Analysis indicated alternating products with a \(cis/trans\) ratio of 15% \(cis\) to 85% \(trans\), this data being consistent with ethylene and propylene-MA copolymers.

Further patents describe the functionalisation of PODMA. Amides can be easily formed by reaction with primary or secondary amines. Half esters can be formed by addition of an alcohol.

The mechanism of alternation between \(\alpha\)-olefins and MA has received little attention. \(\alpha\)-Olefins produce very weak or non-existent CTC’s that can be inferred from weak olefin electron donation. Alternating copolymerisation is therefore likely to follow the free monomer mechanism with cross propagation kinetics and steric hindrance playing a vital role as is demonstrated by the decrease in reactivity of longer alkyl chain olefins. Indeed, measurements of K for CTC’s formed between isobutene and propene with MA were found to be 0.04 mol l\(^{-1}\) and 0.03 mol l\(^{-1}\) respectively. Whether these results are valid within experimental error is questionable, but the low K value points to little or no CTC participation with regard to \(\alpha\)-olefin – MA copolymerisation.
2.4 CONTROLLED RADICAL POLYMERISATION

Anionic and cationic living polymerisation can be distinguished from conventional polymerisation by a number of experimental criteria proposed by Quirk and Lee and outlined below.\(^\text{82}\)

1) Polymerisation proceeds until all of the monomer has been consumed. Addition of further monomer results in continued polymerisation.
2) The number average molar mass, \(M_n\), is a linear function of conversion.
3) The number of polymer molecules (and therefore active centres) is constant.
4) The molar mass can be controlled by the stoichiometry of the reaction.
5) Polymers of narrow MMD are produced.
6) Block copolymers can be prepared by sequential monomer addition.
7) The kinetics of propagation should follow pseudo 1\(^{\text{st}}\) order kinetics.

CRP techniques do however differ from living polymerisation, in its strictest definition, due to reversible termination (ATRP) and efficient chain transfer (RAFT). The key to successful CRP techniques is to suppress radical-radical termination. Radicals terminate at rates approaching the diffusion control limit (\(\sim 10^{8}\) mol dm\(^{-3}\) s\(^{-1}\)), which is considerably faster than the propagation rate (\(\sim 10^{3}\) mol dm\(^{-3}\) s\(^{-1}\)). These are the kinetic reasons why conventional radical polymerisations result in ill-defined polymers. The preparation of polymers by a CRP technique therefore requires a low stationary concentration of growing radicals that are in a fast dynamic equilibrium with the deactivated dormant species. Radical-radical termination is 2\(^{\text{nd}}\) order and propagation is 1\(^{\text{st}}\) order with respect to growing radicals, therefore at low radical concentrations the proportion of termination events versus propagation events are reduced. A fast exchange between growing radicals and dormant species ensures that there is always a low concentration of growing radicals.

Provided bimolecular termination to produce dead polymer is minimised, the living character of CRP polymerisations can be evaluated by experimentally testing such polymerisations against the criteria outlined above.
2.4.1 ATRP

ATRP was first developed in 1995 by Matyjaszewski and Wang as a development of atom transfer radical addition (ATRA), which is a well-known method for carbon–carbon bond formation in organic synthesis\textsuperscript{83,13}. ATRP has been effective in polymerising a number of monomers such as St\textsuperscript{84}, acrylates\textsuperscript{85} and methacrylates\textsuperscript{86}. Due to the mechanism, the polydispersities of the polymers are generally low ($M_w/M_n < 1.3$) and precisely controlled structures can be synthesised. Moreover, the end groups of the polymers are well defined as they are derived from the initiator. Careful selection of the initiator can allow end group functionality to be incorporated easily. Over the last 7 years, the field of ATRP has rapidly grown. Matyjaszewski et al have reviewed recent developments in this area.\textsuperscript{87}

2.4.1.1 FUNDAMENTALS OF ATRP

The control within CRP systems is governed by two principles. Initiation should be fast in order to rapidly provide a constant concentration of growing polymer chains. Secondly, the majority of the growing chains are dormant species that still have the ability of further growth due to a dynamic equilibrium that is established between the dormant species and the growing radicals. By keeping the concentration of active species low throughout the polymerisation, termination is suppressed. ATRP fulfils these principles by use of a transition metal catalyst (usually copper halide) in combination with a suitable ligand. The catalyst complex establishes the reversible equilibrium that can be altered by adjustment of the ligand. The ligand also provides solubility of the catalyst in the reaction medium. The proposed mechanism for ATRP is outlined below (Scheme 4).

\begin{center}
\begin{tikzpicture}

\node (Pm-X) at (0,0) {$P_m\cdot X$};
\node (Mt/L) at (1,0) {$M_t^n/L$};
\node (Pm) at (2,0) {$P_m^*$};
\node (X-Mt/L) at (3,0) {$X\cdot M_t^{n+1}/L$};
\node (monomer) at (0,1) {monomer};

\draw[->, thick] (Pm-X) -- node[above] {$k_a$} (Pm);
\draw[->, thick] (Pm) -- node[above] {$k_t$} (X-Mt/L);
\draw[->, thick] (Mt/L) -- node[below] {$k_d$} (Pm);
\draw[->, thick, dashed] (Pm) to [bend left=30] (Pm);
\draw[->, thick] (Pm) -- node[below] {$P_{m+t}$} (X-Mt/L);
\end{tikzpicture}
\end{center}

Scheme 4 ATRP mechanism
where $P_m$-$X$ represents the halide capped polymer chain, $M_i^{n/L}$ represents the transition metal-ligand complex, $P^*_m$ represents the formed polymer chain radical and $X$-$M_i^{n+1/L}$ represents the formed transition metal-ligand-halide complex of higher oxidation state. $k_a$, $k_d$ and $k_t$ represent the rates of activation, deactivation and termination respectively. $P_{m+1}$ represents polymer formed by bimolecular termination.

In homogeneous systems, the rate of ATRP polymerisations has been shown to be first order with respect to monomer and initiator. Initiation is via an activated alkyl halide $R-X$. After initiation, the initiator fragment $R$ is present at one chain end while the halogen at the other provides the capping unit that allows insertion of further monomer. Once the monomer has been consumed, the capped halogen group can be converted to a number of functionalities via standard organic procedures if required. The produced polymer can be reacted to produce block copolymers by addition of further monomer.

2.4.1.2 ACIDIC MONOMERS

Though ATRP has become a useful CRP method that is tolerant to a number of functionalities, acidic monomers are very difficult to polymerise directly. This is due to interactions of carboxylic acid functionalities with the catalyst. It was postulated that carboxylic acids react with Cu$^{II}$ species by displacing the halogen atom, resulting in the formation of metal carboxylates that inhibit polymerisation. Additionally, since many of the ligands used in ATRP are nitrogen based, protonation of the nitrogen may occur disrupting its coordination to the Cu centre (Figure 16).

![Figure 16 A: Ligand copper complex, B: Protonated ligand](image)
In order to prepare acidic polymers protecting group chemistry has to be used. Tertiary butyl acrylate was effectively polymerised using ATRP to produce well-defined polymers of molar mass up to $M_n = 50,000 \text{ g mol}^{-1}$ and PDI as low as $(M_w/M_n < 1.1)$. The esters were deprotected by hydrolysis to yield well-defined poly (acrylic acid).\footnote{88} Other protecting groups have been used to produce acidic polymers (Figure 17). The groups must remain stable under the polymerisation conditions and be easily converted to the corresponding acid at completion. Benzyl methacrylate was polymerised and the benzyl group removed by mild hydrogenation to furnish the acid\footnote{89}. MA also poses problems with regard to polymerisation and copolymerisation with the ATRP system. Attempts to copolymerise MA with St have failed\footnote{90}. MA functionality is similar to carboxylic acids and if hydrolysed a dicarboxylic acid is produced. Protecting group chemistry is not helpful as MA would need to be ring-opened and then the ester or acid groups protected. This increases the steric hindrance on the double bond lowering the reactivity of the monomer and making copolymerisation difficult. Monomers that have low reactivity, or are non-polymerisable by ATRP can be incorporated at the ends of growing radical chains.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{Protecting group chemistry for poly (methacrylic acid)}
\end{figure}
Addition of MA to already growing PS and subsequent deactivation lead to succinic anhydride terminated PS, which found application as a blend compatibiliser for nylon and PS.\textsuperscript{91}

2.4.2 RAFT

Rizzardo and co-workers developed RAFT polymerisation in 1998\textsuperscript{16, 92} and recently reviewed the current understanding of the mechanism\textsuperscript{93}. The discovery followed on from previous work utilising CTA chemistry with highly efficient transfer agents that were found to not only control molar mass but also bring about a reduction in MMD of the produced polymers. The distinguishing feature of RAFT polymerisation compared to other types of CRP is its applicability to a wide range of monomers\textsuperscript{16} containing for example acid (acrylic acid), acid salts (styrenesulfonic acid), hydroxy (hydroxyethyl methacrylate) or tertiary amino (dimethylaminoethyl methacrylate) that have proved to be difficult with other CRP methods. The process is similarly tolerant of the functionality in the RAFT reagent and the initiator that allows the synthesis of a wide range of polymers with end or side chain functionality in one step without the need for protecting group chemistry.

RAFT polymerisation involves the use of CTA's of the general structure (1), known collectively as RAFT reagents (Figure 18).

\begin{center}
\begin{tabular}{l}
R = CH\textsubscript{2}Ph & Z = Ph \\
R = CH(CH\textsubscript{3})Ph & Z = CH\textsubscript{3} \\
R = C(CH\textsubscript{3})\textsubscript{2}Ph & Z = OPh \\
R = C(CH\textsubscript{3})\textsubscript{2}CN & Z = OEt
\end{tabular}
\end{center}

\textit{Figure 18 RAFT reagents}

The mechanism of RAFT polymerisation involves a reversible addition-fragmentation sequence in which transfer of the S=C(Z)S- moiety between active and dormant chain
ends ensures that living character is maintained throughout the polymerisation (Scheme 5). Providing that the RAFT reagent is consumed quickly and that each chain contains one RAFT reagent derived end group, then the theoretical molar mass at any conversion can be calculated using Equation 51.

\[ M_n(\text{calc}) = xM_o \frac{[M]}{[\text{RAFT}]} \]

*Equation 51*

where [M] is the total monomer concentration, [RAFT] is the RAFT reagent concentration, \( x \) is the fractional conversion and \( M_o \) is the molar mass of the monomer or the average molar mass of the comonomers. Evidence for the mechanism is provided by identification of the S=C(Z)S- end group by UV/Vis and \(^1\text{H} \) NMR spectra. Chain transfer in RAFT polymerisation involves addition and fragmentation steps. The formation of the RAFT intermediates has been confirmed by ESR spectroscopy\(^{94} \). As in conventional chain transfer, \( C \) is given by the ratio of the rate constant for chain transfer to that of propagation (Equation 25). Values of \( C \) of various thiocarbonylthio RAFT reagents have been found to vary from 0.01 to >1000 depending on the groups \( Z \) and \( R \).\(^{95} \) The choice therefore of \( Z \) and \( R \) in reagent 1 is crucial to the success of the RAFT process. To ensure a high transfer constant, \( Z \) should activate the C=S double bond toward radical addition. Suitable groups are alkyl and aryl. The \( R \) group should be a good homolytic leaving group and should be efficient in reinitiating polymerisation. The effect of the \( Z \) group was tested by measuring the transfer constants of a series of benzyl dithiocarbonylthio compounds in a number of St polymerisations\(^{93} \). The relative rates of consumption of the RAFT reagent and the monomer were followed. As the leaving group \( R \) and the propagating species were common, differences in \( C \) can be attributed to differences in the C=S bond.
Chapter 2: Background and theory

Initiation

\[ \begin{align*}
  \text{monomer (M)} & \rightarrow Pn^- \\
\end{align*} \]

Chain transfer

\[ \begin{align*}
  Pn^- + S-S-R & \overset{k_{\text{add}}}{\rightarrow} Pn-S-S-R \\
  & \overset{k_{\text{add}}}{\rightarrow} Pn^- + S-R \\
\end{align*} \]

Reinitiation

\[ \begin{align*}
  \text{monomer (M)} & \rightarrow Pn^- \\
\end{align*} \]

Chain equilibration

\[ \begin{align*}
  Pm^- + S-S-Pn & \overset{k_{\text{add}}}{\rightarrow} Pm-S-S-Pn \\
  & \overset{k_{\text{add}}}{\rightarrow} Pm^- + S-Pn \\
\end{align*} \]

Termination

\[ \begin{align*}
  Pn^- + Pm^- & \rightarrow \text{Dead polymer} \\
\end{align*} \]

Scheme 5 RAFT polymerisation mechanism

The transfer constants were found to decrease in the series where Z is aryl > alkyl ≈ alkylthio > pyrrole > arylox > amido > alkylox > dialkylamino. The lower activity of xanthates and dithiocarbonate derivatives can be understood in terms of the stabilisation brought about by their zwitterionic canonical forms which serve to reduce the C=S double bond character (Scheme 6). In a similar experiment the effect of the R group was evaluated by determination of the transfer constants of a series of dithiobenzoate derivatives in a MMA polymerisation. The C value should reflect the leaving group ability. Benzyl dithiobenzoate had a much lower transfer constant than the hindered 2,4,4-trimethylpent-2-yl dithiobenzoate indicating that steric crowding increases the ease of partition. Cyanoisopropyl dithiobenzoate has a high chain transfer constant suggesting that polar effects are also important.
RAFT polymerisation, like all CRP techniques, involves free radical intermediates and so some bimolecular radical-radical termination cannot be avoided and an amount of dead polymer must be formed. This is derived from chains initiated by initiator-derived radicals. In order to form polymers of narrow MMD with the highest degree of control it is desirable to minimise the initiator concentration, or more accurately the number of initiator derived chains. Thermal polymerisation of St using cumyl dithiobenzoate as the RAFT reagent at concentrations ranging from $1 \times 10^{-4}$ M to $3 \times 10^{-3}$ M resulted in a reduction of molar mass and a narrowing of the MMD with increasing RAFT reagent concentration. SEC chromatograms of products prepared with low RAFT reagent concentrations showed a high molar mass shoulder of approximately double the peak molar mass ($M_p$) suggesting bimolecular termination by recombination. The fraction of dead chains formed can be estimated by comparing the number of moles of polymer formed, calculated by Equation 52, based on the complete consumption of RAFT reagent to the moles of RAFT reagent employed.

$$[\text{Polymer}] = \frac{[M]_f - [M]_o}{DP}$$

Equation 52

where $[M]_f - [M]_o$ is the monomer consumed. A further guide is to compare the molar mass of a polymer formed under identical conditions in the absence of the RAFT reagent. Assuming similar conversions a ten-fold lower molar mass for the polymer formed with the RAFT reagent will usually ensure that the fraction of dead chains is lower than 10%.

Though many RAFT reagents behave as ideal CTAs with the rates of polymerisation comparable to conventional polymerisation, it has been observed that some retardation may occur in some circumstances. Use of high concentrations (0.018 M) of cumyl dithiobenzoate in the thermal polymerisation of St resulted in an induction
period lasting approximately 1 hour during which the RAFT reagent was consumed slowly\textsuperscript{93}. The molar mass was significantly higher than the theoretical values based on complete consumption of the RAFT reagent. Once the initial RAFT reagent is converted to the polymeric species the rate of polymerisation increased. As the cumyl radical is anticipated to be a good leaving group, the problem is attributed to the slow reinitiation of St by the cumyl radical. Use of cyanoisopropyl dithiobenzoate with the more reactive cyanoisopropyl radical resulted in improved control throughout the polymerisation. Ambient temperature RAFT polymerisation has been carried out in order to develop a RAFT reagent that can be used at room temperature\textsuperscript{96}. Use of 1-phenylethyl dithiobenzoate 2 in Figure 19 strongly retarded the polymerisation of alkyl acrylates at ambient temperature. A variation was made to the Z group by changing from a phenyl to a benzyl group. The radical in the RAFT intermediate is changed from being in a disulfur benzylic position to a less stable disulfur alkyl position. This should increase the rate of fragmentation resulting in a faster establishment of the RAFT equilibrium. Use of 1-phenylethyl phenylthioacetate 3 at 25°C for the polymerisation of methyl acrylate resulted in living behaviour with a narrow MMD and no retardation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{ambient_temp_rafter.png}
\caption{Ambient temperature RAFT reagents}
\end{figure}

RAFT polymerisation under very high pressure (>5 kbar) has recently been carried out\textsuperscript{97}. Sterically hindered monomers such as \(\alpha\) methyl styrene (\(\alpha\)-MeSt) and methyl ethacrylate have low ceiling temperatures and are difficult to homopolymerise under conventional free radical conditions, though \(\alpha\)-substituted methacrylates can be polymerised under high pressure\textsuperscript{98}. The RAFT technique was used to polymerise methyl ethacrylate (\(T_c = 82^\circ\text{C}\)) at 65°C and 5 kbar using cyanoisopropyl dithiobenzoate. A
linear relationship between conversion and molar mass was observed confirming living character. A short inhibition period was reported, which was attributed to steric crowding. MMD's were low \((M_w/M_n < 1.2)\) throughout the polymerisation. Poly(methyl ethacrylate-block-St) was prepared by reinitiation of poly(methyl ethacrylate) by AIBN in the presence of St at ambient pressure and 60°C. The polymerisation proceeded smoothly and the block copolymer was analysed by SEC and \(^1\)H NMR.

Due to the tolerance of acidic and protic monomers, RAFT polymerisation is amenable to MA copolymerisation. Klumperman \textit{et al} \(^{90}\) predicted that StMA should proceed in a controlled fashion based on the penultimate unit model for free monomer cross propagation. SEC analysis revealed controlled growth with molar mass increasing with conversion. Unfortunately, there is no comparison of experimental molar mass with theoretical molar mass throughout the copolymerisation and so no conclusion can be drawn on the effectiveness of the RAFT reagent during the early stages of the reaction. The final product had a narrow MMD \((M_w/M_n = 1.06)\) and the final molar mass was close to the expected theoretical value. The same authors also prepared a macromolecular RAFT reagent by use of a hydroxyl-terminated ethylene-co-butylene copolymer that was esterified with an acid functional dithioester to yield a polyolefinic RAFT reagent (Scheme 7).

\[\text{Scheme 7 Esterification to form macromolecular RAFT reagent}\]
Chapter 2: Background and theory

St was polymerised with the macromolecular RAFT reagent and living characteristics were exhibited with the linear evolution of molar mass with conversion and low MMD throughout the polymerisation. It was noted that a small number of chains derived from the azo initiator were present and these were clearly seen in the SEC chromatograms of the low molar mass samples. Reducing the initiator concentration lowered the number of termination events compared to propagation and narrower MMDs were obtained. The same macromolecular RAFT reagent was used to prepare poly [(ethylene-co-butylene)-b-(StMA)] polymers. The final product had a molar mass close to its predicted value and a narrow MMD of \(M_w/M_n = 1.12\).

StMA has been prepared using benzyl dithiobenzoate (BDTB) at 80°C in dioxane with AIBN as the free radical initiator\(^9\). Alternating copolymers were formed with values of \(M_w/M_n\) in the range 1.19 to 1.24. The experimental molar masses determined by SEC were lower than the theoretical values suggesting an induction period though the data is not extensive. Use of a 9:1 St:MA molar feed ratio allowed poly [(StMA)-b-(St)] to be prepared in one step as the rate of copolymerisation of StMA is much faster than St homopolymerisation.
2.5 SOLUTION VISCOMETRY

The solution viscosity of a dilute polymer solution is much higher than the solvent in which it has been dissolved due to the large size difference between the polymer and solvent molecules. Measurement of the viscosities of polymer solutions can deliver useful information regarding molar mass, MMD, branching and chain dimensions. Viscosities of polymer solutions are relatively easy to measure and the apparatus is cheap and readily available.

2.5.1 INTRINSIC VISCOSITY

Capillary viscometry is generally used for intrinsic viscosity measurements. The ratio of the flow time of a polymer solution \( t \) to that of the pure solvent \( t_0 \) is equal to the ratio of their viscosities \( \eta / \eta_0 \) provided that the densities are equal. This is a fair assumption for dilute solutions. The relative viscosity \( \eta_r \) can therefore be measured (Equation 53).

\[
\eta_r = \frac{t}{t_0} = \frac{\eta}{\eta_0}
\]

*Equation 53*

As \( \eta_r \) has a limiting value of unity it is more useful to define the specific viscosity \( \eta_{sp} \) (Equation 54).

\[
\eta_{sp} = \frac{t - t_0}{t_0} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1
\]

*Equation 54*

Even in dilute solutions, chain entanglement is likely to occur. In order to measure the influence of an isolated polymer chain, the reduced viscosity is defined as \( \eta_{sp}/C \) and extrapolation of \( \eta_{sp}/C \) to infinite dilution (zero concentration) delivers the intrinsic viscosity \([\eta]\). The general relationship between \( \eta_{sp}/C \) and \([\eta]\) can be expressed in the form of a polynomial (Equation 55):
Chapter 2: Background and theory

\[
\frac{\eta_{sp}}{C} = [\eta] + k_1[\eta]^2 C + k_2[\eta]^3 C^2 + k_3[\eta]^4 C^3 + \ldots
\]

Equation 55

where \(k_1, k_2, k_3, \text{etc.}\) are dimensionless constants.

Huggins\textsuperscript{102} simplified Equation 55 by assuming that the higher terms in \(C\) are negligible (Equation 56). This is a reasonable assumption when dealing with straight chain homopolymers but problems can arise when the equation is applied to copolymers or branched structures. The higher polynomial terms in \(C\) can become important when dealing with block copolymers that may have different solubility characteristics associated with the arrangement of monomer units. The regular structure of alternating copolymers allows the chain to behave in a manner similar to that of a homopolymer as the solubility characteristics are expected to be consistent throughout the copolymer chain.

\[
\frac{\eta_{sp}}{C} = [\eta]_H + k_H[\eta]_H^2 C
\]

Equation 56

\([\eta]_H\) is the intrinsic viscosity determined by a plot of \((\eta_{sp}/C)\) against \(C\) and \(k_H\) is the Huggins slope constant that can also be determined from the plot. Values of \(k_H\) lie between 0.3 and 0.9, though for flexible chains in good solvents \(k_H\) should lie between 0.3 and 0.5\textsuperscript{101}.

Intrinsic viscosity is related to molar mass by the Mark-Houwink (MH) equation (Equation 57).

\[
[\eta] = K M_v^a
\]

Equation 57

where \(K\) and \(a\) are the MH constants for a given solvent, polymer and temperature system. The viscosity average molar mass \(M_v\) is defined by Equation 58:
Equation 58

\[ M_v = \left[ \frac{\sum_{i=1}^{\infty} N_i M_i^{1+a}}{\sum_{i=1}^{\infty} N_i M_i} \right]^{\frac{1}{a}} \]

The values of \( K \) and \( a \) are determined by experiment. A series of monodisperse standards of known molar mass are analysed and their intrinsic viscosities determined. A plot of \( \log [\eta] \) vs. \( \log M \) allows the two constants to be evaluated from the gradient and intercept. These plots are generally linear over a wide range of molar mass allowing a number of samples to be analysed and a value of \( M_v \) to be calculated. The value of \( a \) is mainly effected by the solvent; when dealing with linear polymers, the better the solvent quality, the higher the \( a \) value. Under good solvent conditions (where a polymer attains its unperturbed dimensions) it is found that \( a \) takes a value of 0.5 for all polymers. It has also been experimentally demonstrated for several polymers that \( a \) falls to 0.5 for short chains in good solvents\(^{103,104,105}\).
2.6 SIZE EXCLUSION CHROMATOGRAPHY

Size exclusion chromatography (SEC) or gel permeation chromatography (GPC) as it is often referred to, is a separation technique based on the size and shape of the molecules and not any physical or chemical interaction. From this technique, it is possible to obtain MMD's for a polymer or copolymer from which individual average molar masses ($M_n$, $M_w$ etc.) can be calculated.

The equipment required involves a suitable solvent, high-pressure HPLC pump, injector, columns and a detector. Computers with the appropriate software are often used to analyse the results from the detector.

The columns are filled with a semi rigid, or rigid, porous gel, normally prepared from cross-linked PS. The polymer sample is dissolved in the elution solvent and injected onto the column, after which separation is achieved selectively according to size. As the solvated polymer flows past the beads, it is possible for the molecules to enter the pores, the larger the molecule the more difficult the permeation. It follows then that the larger molecules are eluted at early retention times as they flow between the beads while smaller molecules are eluted at later retention times as they are more effectively retained in the column. A SEC chromatogram is obtained from the detector and represents a distribution of molecular size.

2.6.1 SEC STANDARD CALIBRATION

In order to establish the MMD of a polymer sample, a calibration plot is prepared, to which the unknown is compared. Commercially available standards of known molar mass and narrow MMD are used to construct a calibration plot of log $M$ vs. retention time (Figure 20). Retention volumes $V_0$ and $V_0 + V_i$ represent the separation limits for a given column. If the polymer undergoing analysis is the same as the calibrant then the y-axis of log solute size is replaced with log molar mass.
Elution of an unknown sample at a given retention time allows the molar mass to be determined via the calibration plot. Commercial standards are available for common polymers such as PS, polyethylene oxide and PMMA. Use of these standards can lead to errors as not all polymers or copolymers behave in solution in the same way as the standard. Factors such as chain stiffness and branching may have an effect. If the molecules are too large to enter the pores in the column, total exclusion occurs and the separation is not effective. Conversely if the molecules are too small then total permeation occurs and no difference in size can be distinguished. Inside these boundaries selective permeation results in successful sample elution. Choice of column therefore is vital so that all the analysis is maintained in the selective permeation region of the calibration graph.
Chapter 2: Background and theory

2.6.2 SEC UNIVERSAL CALIBRATION

Universal calibration is a technique that permits the measurement of molar mass for polymers for which standards are unavailable.

Providing that there is no secondary interaction between the column and the eluting polymer, separation is due to the hydrodynamic volume of the molecules in solution. The relationship between hydrodynamic volume and molar mass for flexible coils at infinite dilution is proportional to \([\eta]M\) where \([\eta]\) is the intrinsic viscosity of the polymer in the carrier solvent used and at the temperature of measurement. A universal calibration can therefore be obtained by plotting \([\eta]M\) against retention time. Knowledge of the MH constants \(K\) and \(a\) are required to correct between the differing sizes and expansions of the polymer standard and the unknown. If the universal calibration is valid at a given retention time then:

\[
\log[\eta]_s M_s = \log[\eta]_u M_u
\]

Equation 59

and

\[
\log K_s M_s^{(a_s+1)} = \log K_u M_u^{(a_u+1)}
\]

Equation 60

where \(s\) and \(u\) denote the polymer standard and the unknown respectively. The molar mass \(M_u\) can be calculated from:

\[
\log M_u = \frac{1}{1+a_u} \times \log \left[ \frac{K_s}{K_u} \right] + \frac{1+a_s}{1+a_u} \times \log M_s
\]

Equation 61

A calibration curve constructed for PS standards can therefore be used to determine molar masses for other polymers provided the MH constants are known. This can be avoided if a 'Viscotec' detector is used at the end of the column. This combined differential refractometer and viscometer system measures both the concentration and
the specific viscosity $\eta_{sp}$ for the fraction. By assuming $\eta_{sp}/C \approx [\eta]$ for dilute solutions the molar mass can be obtained from the MH relationship. For short chain polymers, the sensitivities of viscometry and other online detectors such as a light scattering detector are much reduced due to the low concentration of sample eluted. The accuracy of data for $M_n$ and $M_w$ by SEC with multi-detectors therefore may be questionable. In the case of polymers and copolymers with small values of DP, independent measurement of viscosity that allows the use of more concentrated solutions will invariably result in more accurate values of $\eta_{sp}/C$.

2.6.3 SEC DETECTORS

The detectors employed need to continuously monitor the column eluent. The output is then converted to a signal that is related to the concentration or molar mass of the polymer.

2.6.3.1 REFRACTIVE INDEX (RI) DETECTORS

RI detectors are the most common concentration detectors for SEC. A polymer in solution will have a different refractive index to the pure solvent and provided the difference is sufficiently large, it can be measured. The main problems experienced with RI detectors are their low sensitivity (very low concentrations of species cannot be measured) and their temperature stability. Statistical copolymers can also cause problems due to the refractive index differing across the MMD. Alternating copolymers with their regular structure however are expected to behave in a similar manner to linear homopolymers.

2.6.3.2 ULTRA-VIOLET (UV) DETECTORS

UV detectors are sample specific, as an active chromophore at the wavelength of detection is required to yield a response. Variable wavelength detectors offer improved versatility. UV detectors are very sensitive, only requiring a few nanograms per millilitre for adequate detection and are stable to environmental conditions. Though the number of polymers available for detection is limited, UV detectors are extremely useful
in block or graft copolymer analysis when a second graft or block contains a UV active chromophore.
2.7 **COMPUTATIONAL CHEMISTRY**

Computational chemistry has grown in to a mainstream chemistry discipline as a consequence of falling costs of computer hard and software coupled with increased power. Though top end molecular modelling requires the use of super computers in excess of £1 million, molecular modelling of small molecules can be performed and the results visualised on personal computers. Molecular modelling falls into three categories, molecular mechanics, semi empirical methods and *ab initio* methods. These categories are arranged in terms of the increasing detailed information that they provide, and increasing computational resource required.

Molecular mechanics\(^{107}\) is the least computationally intensive method. The theoretical basis of molecular mechanics considers nuclear motion while fixing the electron distribution associated with each atom. A model was therefore developed where the molecule is represented as a collection of spheres joined by springs. This allows the motion of these atoms to then be described by the laws of classical physics and potential energy functions can be used. The total potential energy, \(E\), of a molecule can be described by the following summation of interactions (Equation 62):

\[
E = \text{Stretching energy} + \text{Bending energy} + \text{Torsion energy} + \text{Non bonded interaction energy}
\]

*Equation 62*

From these terms a force field is generated. The most common force fields are those developed by Aligner\(^{107}\). Molecular mechanics involves finding the lowest potential energy of the molecule. Energy minimisation optimises the position of atoms subject to the restraining forces generated by the molecular force field. This task is complicated by local energy troughs that may not be the global minimum energy. One of the most difficult problems in computational chemistry is finding the global minimum and being sure it is the lowest energy state. Molecular mechanics is best suited to large systems consisting of many thousands of atoms and systems that do not involve any breaking or forming of bonds. It is therefore ideally suited to the investigation of conformation and stereochemistry of polymer chains.
Semi empirical and *Ab initio* methods are based on quantum mechanics. Both methods rely on the following principles

1) Nuclei and electrons are distinguished from each other.
2) Electron-electron and electron-nuclear interactions are explicit.
3) Interactions are governed by nuclear and electron charges (potential energy) and electron motions.
4) Interactions determine the spatial distribution of nuclei and electrons and their energies.
5) Quantum mechanical methods are concerned with approximate solutions to Schrödinger's wave equation (Equation 63)

\[
H\Psi = E\Psi
\]

*Equation 63*

Where the Hamiltonian operator, \( H \), contains information describing the electrons and nuclei in a system. The electronic wave function, \( \Psi \), describes the state of the electrons in terms of their motion and position. \( E \) is the energy associated with the particular state of the electron.

The Schrödinger wave equation can only be solved for the simplest 1 electron-1 nucleus system, however these solutions yield the basis for all quantum mechanics. The probability function describing the allowable states of an electron can be derived from the Schrödinger wave equation and the solutions to this function allow the atomic orbitals to be derived. In order to make use of quantum mechanics in computational chemistry approximations to the Hamiltonian have to be made. The first approximation is the Born-Oppenheimer approximation that the velocity of an electron is much faster than a nucleus and therefore the nucleus can be considered motionless. The second approximation is that each electron is in its own orbital and is unimpeded by its neighbours. The electronic Hamiltonian can therefore be represented as the sum of 1 electron Hamiltonians. This is the Fock approximation. *Ab initio* computations use the complete form of the Fock operator to construct the wave equation. This is highly computationally intensive and can only be used for small systems (10’s of atoms). Semi empirical calculations use simplified Fock operators that only consider valence electrons.
and a core consisting of the nucleus and the inner shell electrons. All the other elements from the Fock operator are replaced by empirical or calculated parameters. Semi empirical calculations can therefore provide useful data regarding charge and electron distribution for systems incorporating 100’s of atoms and are of greater use for polymer systems than \textit{ab initio} methods. A common semi empirical programme is MOPAC\textsuperscript{108} that incorporates a number of approximate Hamiltonians.
3 EXPERIMENTAL

3.1 LIST OF CHEMICALS AND ABBREVIATIONS

Acetic acid supplied by Fisher Chemicals (>99%)

Acetone supplied by Carless solvents (SLR grade)

Anisole supplied by Aldrich Chemical Company Ltd. (99%)

\(\alpha,\alpha^{\prime}\)-Azobis(isobutyronitrile) \((AIBN)\) supplied by Fluka, recrystallised from methanol and stored at 0°C at all times.

Benzyl bromide \((BzBr)\) supplied by Aldrich Chemical Company Ltd. (>99%).

Benzyl chloride \((BzCl)\) supplied by Aldrich Chemical Company Ltd. (>99%).

Benzyl magnesium chloride supplied by Aldrich Chemical Company Ltd (2 M solution in THF).

Benzoyl peroxide \((BPO)\) supplied by Aldrich Chemical Company Ltd (70% in water).

Bipyridene \((BPY)\) supplied by Aldrich Chemical Company Ltd (99%).

Butan-2-one \((MEK)\) supplied by Aldrich Chemical Company Ltd. (>99%).

Carbon disulfide supplied by Aldrich Chemical Company Ltd. (>99% anhydrous).

Chloroform \((CHCl_3)\) supplied by Fisher Chemicals (>99%).
**Chapter 3: Experimental**

*Chloroform-d (CDCl₃)* supplied by Cambridge Isotope Laboratories Inc. (99%) with 1% v/v tetra methyl silane (TMS) added as internal reference.

*p-chloro styrene (pClSt)* supplied by Aldrich Chemical Company Ltd. (97%), inhibited with 500 ppm 4-tert-butylcatechol.

*Copper chloride (CuCl)* supplied by Aldrich Chemical Company Ltd. (97%).

*Copper bromide (CuBr)* supplied by Aldrich Chemical Company Ltd. (98%).

*N-cyclohexyl maleimide (NCHM)* supplied by Aldrich Chemical Company Ltd. (97%).

*Diethyl ether (Et₂)* supplied by Fischer Chemicals (>99%).

*Dimethyl sulfoxide (DMSO)* supplied by Acros Organics (99.7%).

*Dimethyl sulfoxide d₆ (d₆-DMSO)* supplied by Aldrich Chemical Company Ltd. (98.5%) with 1% v/v tetra methyl silane (TMS) added as internal reference.

*1,4 Dioxane* supplied by Aldrich Chemical Company Ltd. (>99%).

*Di-tertiary butyl peroxide (DTBP)* supplied by Aldrich Chemical Company Ltd. (99%).

*Group 3 (refined mineral diluent oil) (GP3 oil)* supplied by Lubrizol Ltd.

*Inhibitor remover column (IRC) packing* supplied by Aldrich Chemical Company Ltd., for removal of 4-tert-butylcatechol and 3,5-di-tert-butylcatechol.

*Magnesium sulphate (MgSO₄)* supplied by Fisher Chemicals (>99%).

*Maleic anhydride (MA)* supplied by Aldrich Chemical Company Ltd. (>99%) recrystalised from toluene, dried and stored in a desiccator at all times.
Chapter 3: Experimental

*Methanol (MeOH)* supplied by Carless solvents (SLR grade).

**p-methoxy styrene (pMeOSt)** supplied by Aldrich Chemical Company Ltd. (97%).

**α-methyl styrene (αMeSt)** supplied by Aldrich Chemical Company Ltd. (99%) 15 ppm 4-tert-butylcatechol inhibitor added, destabilised using IRC before use.

**p-methyl styrene (pMeSt)** supplied by Aldrich Chemical Company Ltd. (96%) 3,5-di-tert-butylcatechol inhibitor added, destabilised using IRC and vacuum distilled over MgSO₄ at room temperature before use.

**Octadecene (OD)** supplied by Aldrich Chemical Company Ltd. (90%) with <2% of 2-ethyl-1-hexadecene, 2-butyl-1-tetradecene, 2-hexyl-1-dodecene, 2-octyl-1-decene and n-octadecane contained in the high boiling point fraction.

**Octadecenyl succinic anhydride (ODSA)** supplied by Lubrizol Ltd.

**Octene** supplied by Lancaster (>98%).

**1-phenyl ethyl bromide (1PEBr)** supplied by Aldrich Chemical Company Ltd. (99%).

**N-phenyl maleimide (NPM)** supplied by Aldrich Chemical Company Ltd. (97%).

**Phenyl magnesium bromide (PhMgBr)** supplied by Aldrich Chemical Company Ltd. (3 M solution in Et₂O).

**Poly(isobutylene) succinic anhydride (PIBSA)** commercial material supplied by Lubrizol Ltd.

**Poly(octadecene-maleic anhydride) PODMA**

1) Supplied by Aldrich Chemical Company Ltd. \((M_n = 30,000 \text{ g mol}^{-1})\).

2) Supplied by S.C. Johnson Ltd. \((M_n = 5,000 \text{ g mol}^{-1})\).
**Chapter 3: Experimental**

*Polystyrene (PS) standards* from Polymer Laboratories Ltd. for SEC calibration. A set of 10 ($M_p$ 580 g mol$^{-1}$ - 325,000 g mol$^{-1}$) used as supplied.

*Styrene (St)* supplied by Aldrich Chemical Company Ltd. (99%) 10-15 ppm 4-tert-butylcatechol inhibitor added, destabilised using IRC and vacuum distilled over MgSO$_4$ at room temperature before use.

*Tetrahydrofuran (THF)* supplied by Fisher Chemical. Unstabilised GPC grade.

*Toluene* Supplied by Carless solvents (SLR grade)

*Xylene* supplied by Aldrich Chemical Company Ltd. (mixed isomers with ethyl benzene).

All chemicals were used as received unless otherwise stated.

3.2 **MONOMER DESTABILISATION**

Destabilisation was carried out using the IRC method. A 30 cm glass column was filled with inhibitor remover to a depth of 10 cm with a small quantity of glass wool to prevent the particulate remover escaping. The monomer was loaded on to the column and allowed to pass through under gravity before being collected and stored at 253K. St and pMeSt were further distilled over MgSO$_4$ under reduced pressure at 293K before use.
3.3 FREE RADICAL POLYMERISATION

3.3.1 SMALL SCALE PODMA SYNTHESIS

**Method 1**

Freshly recrystallised MA dissolved in the appropriate solvent was added to a 100 mL round-bottom flask. A reflux condenser was fitted with a nitrogen bubbler, and a nitrogen inlet septum and magnetic flea were added. Initiator and octadecene (or octene) were further added, and the solution stirred and purged with nitrogen for 15 minutes before the solution was heated to the desired temperature. After the designated reaction time, the solution was cooled.

**Method 2**

Method 2 used glass schlenk tubes in order to carry out parallel copolymerisations. The same conditions were used as in method 1, except oxygen was removed by two freeze, pump, and thaw cycles.

The product was isolated by precipitation into a five-fold excess of cold (5°C) MeOH and the solid was recovered by suction filtration. The crude polymer was then redissolved in hot solvent and reprecipitated via dropwise addition in cold (5°C) MeOH. This was repeated 3 times before the product was dried under vacuum at 80°C for 24 hours to yield an off-white powder. Conversion was determined gravimetrically and confirmed by SEC if required. Structural characterisation was by FTIR, \(^1\)H NMR and \(^{13}\)C NMR spectroscopy. Molar mass characterisation was by SEC.

3.3.2 LARGE SCALE PODMA SYNTHESIS

MA, octadecene, xylene and initiator were charged to a 1 L flange flask. The flask was equipped with a lid and clip, overhead stirrer and paddle, condenser, nitrogen inlet and euotherm temperature controller. The mixture was stirred for 15 minutes with a fast nitrogen flow to remove oxygen before the rate was slowed and the heating mantle
Chapter 3: Experimental

temperature was increased to 100°C. After the designated reaction time, the mixture was further heated to 200°C for 1 hour.

The unreacted starting materials were removed by vacuum stripping at 200°C for 1 hour. The molten product was poured onto a tin tray, allowed to cool and ground to a powder. Conversion was determined gravimetrically and confirmed by SEC if required. Molar mass characterisation was by SEC.

3.3.3 BULK PODMA SYNTHESIS

Both small and large-scale systems were used to prepare PODMA in bulk. The procedure was the same as Section 3.3.1 and 3.3.2 except in the absence of a solvent.

3.3.4 PILOT PLANT PODMA SYNTHESIS

OD (9980 g 39.6 mol) was charged to the reactor. A small vacuum was applied to the reactor to reduce MA fumes before MA (4320 g 44.05 mol) was added and the reactor lid closed and secured. Xylene (7130 g 67.26 mol) was pumped in to the reactor and the mixture was stirred at 200 rpm. The reactor was blanketed with nitrogen and the condenser was switched on. The first aliquot of BPO solution (500 mL of 0.1 M solution) was pumped into the reactor and the temperature slowly increased to 100°C. A further 5 aliquots of BPO solution were added at 60 min intervals and the reaction allowed to proceed for 6 hours. A 500 g sample was removed for characterisation. GP3 diluent oil (6930 g) was pumped into the reactor and the temperature increased to 140°C in order to remove xylene by distillation. After approximately 6000 mL of xylene had been removed, a further portion of GP3 diluent oil (6930 g) was added to prevent viscosity build up of the copolymer. The remaining xylene was removed by stripping under vacuum. After complete removal of the solvent, the temperature was increased to 200°C for 60 min. Residual MA was removed by vacuum stripping at 200°C before the reactor was cooled to <100°C, and the product drained into two 25 L cans. On cooling, the product solidified.
Chapter 3: Experimental

The sample removed for characterisation was isolated from reactants as in Section 3.3.2. Conversion was determined gravimetrically and by quantitative SEC (Section 3.6.3.4) if necessary. Molar mass characterisation was by SEC.
3.4 ATOM TRANSFER RADICAL POLYMERISATION (ATRP)

ATRP was used to polymerise and copolymerise St, St-co-NCHM, St-co-NPM and attempts were made to copolymerise StMA.

Monomer (52.5 mmol), 1-phenyl ethyl bromide (0.307 g, 1.66 mmol), CuBr (0.238 g, 1.66 mmol), BPY (0.779 g, 4.98 mmol) and anisole (15 mL) were added to a 25 mL 2-necked round-bottomed flask. A reflux condenser was fitted with nitrogen bubbler, and a nitrogen inlet septum and magnetic flea were added. The flask was purged with nitrogen for 15 min before the temperature was increased to 110°C for 5 hours. After this time, the flask was cooled.

The contents of the flask were precipitated into MeOH and the solid collected by suction filtration. The crude polymer was then redisolved in THF and reprecipitated in MeOH. This was repeated 3 times before the product was dried under vacuum at 50°C for 24 hours. Structural characterisation was by \(^1\)H NMR. Molar mass characterisation was by SEC.
3.5 REVERSIBLE ADDITION FRAGMENTATION TRANSFER POLYMERISATION (RAFT)

3.5.1 SYNTHESIS OF BENZYL DITHIOBENZOATE (BDTB)

Carbon disulfide (3.44 g, 45 mmol) and dry THF were added to a pre-dried 250 mL 3 necked round-bottomed flask equipped with reflux condenser, addition funnel, stirrer flea and calcium chloride drying tube. PhMgBr (14 mL, 3 M Et₂O solution) was injected slowly via dry syringe at 25°C. The solution was heated to 40°C and BzBr (7.69 g, 40 mmol) was added via dropping funnel. The solution was heated to 50°C overnight. Ice water (100 mL) was added and the organic products extracted with Et₂O (200 mL). The aqueous phase was re-extracted with ether, and the combined ethereal phases washed with distilled water and dried over MgSO₄. The solvent was removed by rotary evaporation to furnish the title compound as a red oil; (9.76 g >99% yield). ¹H NMR: (CDCl₃) (ppm): 4.61 (s, 2H); 7.23-7.43 (m, 8H) and 8.02 (m, 2H).

3.5.2 RAFT KINETIC COPOLYMERISATIONS

RAFT copolymerisation was used to prepare copolymers of MA with a number of St monomers, namely St, pMeSt, pClSt, pMeOSt and αMeSt. The copolymerisations were carried out in schlenk tubes equipped with glass tap and glass stopper, secured by keck clip. A stock solution was prepared and divided such that each tube contained MA (1.47 g, 15 mmol), St monomer (15 mmol), AIBN (0.0135 g, 0.08 mmol), BDTB (0.0405 g, 0.16 mmol) and dioxane (10 mL). The tubes were evacuated by freezing the contents and pumping to constant pressure. The freeze, pump, thaw cycle was repeated twice before the tubes were immersed in an oil bath held at 60°C for a designated reaction time.
Chapter 3: Experimental

The vessels were cooled and the vacuum released before the product was precipitated into MeOH and the solid collected by suction filtration. The product was dried under vacuum at 80°C for 24 hours to yield a pale pink powder.

3.5.3 RAFT MONOMER REACTIVITY RATIOS IN COPOLYMERISATIONS

Preparation of copolymers for monomer reactivity ratio analysis utilised the same procedure as outlined above (Section 3.5.2). The MA concentration was varied from 0.5 M to 2.5 M with a total monomer concentration of 3.0 M.

3.5.4 RAFT COPOLYMERISATION TO FORM STMA-BLOCK-PMEST

MA (0.74 g, 7.5 mmol), St (0.78 g, 7.5 mmol), AIBN (0.007 g, 0.04 mmol), BDTB (0.02 g, 0.08 mmol) and dioxane (10 mL) were added to 2 schlenk tubes containing magnetic stirrer bars and equipped with glass taps and rubber septums. The tubes were evacuated by freezing the contents and pumping to constant pressure. The freeze, pump, thaw cycle was repeated twice before the tubes were immersed in an oil bath held at 60°C for 15 hours. The first tube was terminated by freezing the contents and opening the tap to air. A separate solution containing pMeSt (1.71 g, 15 mmol) in dioxane (10 mL) was added to the second tube by degassed syringe, and the contents were maintained at 60°C for a further 15 hours.

The contents of both tubes were precipitated into MeOH and the solid collected by suction filtration. The products were dried under vacuum at 80°C for 24 hours to yield pale pink powders. Structural characterisation was by FTIR and 1H NMR. Molar mass characterisation was by SEC.

3.5.5 RAFT COPOLYMERISATION TO FORM PODMA

MA (1.47 g, 15 mmol), OD (3.78 g, 15 mmol), AIBN (0.135 g, 0.15 mmol), BDTB (concentration varied) and xylene (10 mL) were added to a schlenk tube. The tube was sealed and evacuated by 2 freeze, pump, thaw cycles before being immersed in
an oil bath held at 100°C for 20 hours. The tube was cooled and the vacuum released. The product was isolated by precipitation into MeOH as per Section 3.3.1. Structural characterisation was by FTIR and $^1$H NMR. Molar mass characterisation was by SEC.
3.6 CHARACTERISATION TECHNIQUES

3.6.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY FTIR

A Nicolet 20 DXC-FTIR spectrometer was used for all the copolymer analysis. Research carried out by the Gulf Chevron Company\textsuperscript{109} had indicated an effective method for investigating both the structure and composition of MA containing copolymers. Qualitative analysis was carried out to give an indication of structure, while quantitative analysis allowed the composition to be determined.

3.6.1.1 QUALITATIVE FTIR SPECTROSCOPY

The copolymer samples were prepared as a 10 g L\textsuperscript{-1} solution in chloroform. When a sample was not soluble in chloroform, DMSO was used to solubilise the product.

Background spectra were run using the solvent in a solution cell made of two sodium chloride discs. Water vapour spectra were also run and both subtracted from the sample spectra. The number of scans for each sample was typically 50 over a wavenumber range of 650 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1}. Spectra were processed using an IBM compatible computer operating with Omnic software.

3.6.1.2 QUANTITATIVE FTIR SPECTROSCOPY

By analysing a particular group in a compound, it is possible to determine the concentration of that group from a suitable calibration curve. The absorption by IR radiation is proportional to the concentration of the group under study. The Beer-Lambert law provides the relationship

\[ A = \varepsilon bc \]

\textit{Equation 64}
where \( A \) is the absorbance, \( \varepsilon \) is the extinction coefficient, \( b \) is the path length and \( c \) is the concentration.

The carbonyl group of the backbone succinic anhydride units was the group of interest in the analysis. By measuring the carbonyl concentration, the amount of anhydride in the sample can be determined and so from the mass of sample, its composition. In order to determine the carbonyl concentration of PODMA, ODSA was chosen as the anhydride model as it was structurally similar to the repeat unit that was expected to be found in the copolymer. Succinic anhydride was used as the calibrant for the remaining copolymers. A series of increasingly concentrated standards was prepared for the anhydride model and the integrated absorbance measured between 1890 cm\(^{-1}\) and 1660 cm\(^{-1}\). These results were then plotted as absorbance against concentration of calibrant (Figure 21).

A copolymer sample of known concentration was then prepared in the same manner as the above qualitative analysis. The anhydride peak area was measured and the concentration of carbonyl groups determined from the calibration graph. As the molar mass of the carbonyl containing units is known, the mass of carbonyl containing groups, and therefore the mass of succinic anhydride in the copolymer can be calculated. It is then a case of subtraction to determine the mass of the comonomer units and so the molar composition of the copolymer.
Chapter 3: Experimental

Figure 21 FTIR Succinic anhydride calibration
3.6.2 \(^1\text{H}\) AND \(^{13}\text{C}\) NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

A Brucker 250 MHz spectrometer was used for \(^1\text{H}\) NMR analysis while a Brucker 400 MHz spectrometer was used for \(^{13}\text{C}\) NMR analysis that required improved resolution. In some cases \(^1\text{H}\) NMR analysis was carried out on the 400 MHz instrument to improve resolution. Samples were dissolved in CDCl\(_3\) (20 mg mL\(^{-1}\)) or d\(_6\) DMSO. All NMR solvents had TMS already added as an internal reference. Samples for \(^1\text{H}\) NMR determination were typically scanned 64 times between \(\delta\) values of 0 to 10 ppm. Samples for \(^{13}\text{C}\) NMR were typically scanned 3500 times between \(\delta\) values of 0 to 250 ppm. \(^1\text{H}\) NMR was used both qualitatively and quantitatively for structural analysis. \(^{13}\text{C}\) NMR was only used in a qualitative manner.

3.6.3 SIZE EXCLUSION CHROMATOGRAPHY (SEC)

SEC was performed on copolymers using two sets of apparatus. Both techniques utilised the same mixed gel columns but varied in mobile phase, analysis temperature, detection and data analysing techniques.

3.6.3.1 ACETIC ACID STABILISED SEC

The molar mass, PDI and purity of all MA copolymers were determined on a GPC-110 instrument supplied by Polymer Laboratories Ltd. The system was equipped with a double HPLC pump, pumping at a rate of 1.0 mL min\(^{-1}\), automatic six-point injection valve with 50 \(\mu\)L injection loop and an internal thermostated RI detector. A set of 2 Polymer Laboratories Ltd. columns (PLgel 5 \(\mu\)m MIXED-D 300 x 7.5 mm) was used. The eluent was a mixed (v/v) system of THF:acetic acid (9:1) and the analysis was carried out at 40°C to ensure a flat baseline. Dry toluene was used as an internal standard.

3.6.3.2 DUAL DETECTOR SEC USING RI AND UV DETECTORS
Chapter 3: Experimental

Copolymers prepared with UV active functionality were analysed by dual detection SEC. The set up is outlined below.

- Knauer HPLC pump 64, pumping at a rate of 1.0 mL min⁻¹.
- Rheodyne 7125 six-port injection valve with 50 μl injection loop.
- Knauer RI detector.
- Pye-Unicam GC-UV, UV detector set at 330 nm to correspond with $e_{\text{max}}$ for the S=C-S chromophore present in RAFT copolymer samples.
- 2 x (PLgel 5 μm MIXED-D 300 x 7.5 mm) SEC columns supplied by Polymer Laboratories Ltd.
- GPC grade THF.
- Dry toluene as internal standard.

The equipment was connected with the minimum quantity of narrow bore stainless steel tubing, with particular attention paid to the inter-detector tubing, which leads to inter-detector delay. The apparatus was operated at room temperature.

Both sets of equipment for SEC used the same data recording technique. The output from the detector(s) was transferred to a data capture unit (DCU) which in turn fed the data into an IBM personal computer operating PL caliber software that converted the DCU signal to a chromatogram. After complete elution, the chromatogram could be analysed using the software to produce molar mass data, by comparison of retention times to the previously recorded calibration plot. The chromatogram was converted to Microsoft Excel format via an ASCI file that allowed improved manipulation and presentation capability.

3.6.3.3 Molar Mass Determination, Calibration and Purity

The columns were calibrated with a series of monodisperse PS standards supplied by Polymer Laboratories Ltd. The PS standards were injected as solutions (2 mg mL⁻¹) with 10 μL of dry toluene as reference on to the columns. The results were plotted as $\log M_p$ against retention time for the standard peak to be eluted. A typical calibration plot is shown in (Figure 22).
Chapter 3: Experimental

Copolymers for analysis were prepared by dissolving the samples (2 mg mL\(^{-1}\)) in the appropriate mobile phase and allowing complete dissolution by standing for >2 hours. The solutions were filtered with Whatman microfibre glass filter paper and 10 μL of dry toluene was added as reference. The baseline was set to zero and the solutions were injected onto the columns. After complete elution, the baseline was manually set to the peak profile of the copolymer, and the software calculated average molar masses. The values for \(M_n\), \(M_w\), \(M_p\) and the PDI (\(M_w/M_n\)) were calculated.

The purity of the copolymer samples can be analysed in a qualitative manner by examination of the chromatogram. For low molar mass copolymers any peaks below a retention time corresponding to a molar mass <500 would indicate the presence of impurity. Peaks in this region result from an inefficient purification procedure and can be due to monomer, solvent or other small molecular species. The removal of OD in the purification of PODMA is particularly difficult, which not only leads to errors in conversion data, but also on a large scale the incorporation of unsaturated monomers leads to detrimental performance of the final crankcase dispersant in engine oils.

3.6.3.4 QUANTITATIVE SEC

When a concentration detector such as a RI detector is used, the area under a chromatogram peak is proportional to the concentration of the species being detected. If a copolymer has impurities present that are well resolved and separated from the main copolymer peak, then the concentration of these species can be determined provided a calibration is constructed with the authentic material. PODMA prepared on a large scale (Section 3.3.2) was expected to contain residual OD and ODSA.
Figure 22 SEC calibration of PS standards
Chapter 3: Experimental

A series of standards of OD (0.27-4.33 mg mL\(^{-1}\)) and ODSA (0.24-3.78 mg mL\(^{-1}\)) were prepared by dissolution in the mobile phase. Toluene was not added as the low molar mass reference was expected to interfere with the low molar mass standards. The solutions were then injected onto the columns. After elution the area of the standard peak was measured and a plot of peak area against concentration was plotted as shown in Figure 23. Copolymer samples were prepared such that an accurately known mass of sample was injected onto the columns. After elution the areas of the peaks due to ODSA and OD were measured separately, and the mass determined from the calibration. This approach allowed the mass of the impurities in the sample to be calculated, and thus the mass of copolymer by difference (Equation 65). In copolymerisations where impurities and side products were detected, this method provides a more accurate determination of conversion.

\[
Mass_{\text{copolymer}} = Mass_{\text{total}} - (Mass_{\text{OD}} + Mass_{\text{ODSA}})
\]

\textit{Equation 65}
Figure 23 OD (•) and ODSA (■) Quantitative SEC calibration
3.6.4 SOLUTION VISCOMETRY

Intrinsic viscosity measurements were carried out using an Ubbelohde capillary viscometer (Schott-Gerate 531-01) having an internal diameter of 0.53 mm and a length of 100 mm. The flow times were automatically recorded by a viscometer timer (Schotte Gerate AVS 310). PODMA solutions were made by dissolving either 0.05 g of low molar mass PODMA or 0.1 g of high molar mass PODMA in 15 mL of a mixed (v/v) system of THF:acetic acid (9:1). PS standard solutions were prepared in the same manner. The solutions were left for complete dissolution (>2 hours). The solutions were then filtered using Whatman microfibre filter papers directly into the viscometer reservoir. The viscometer was placed in a water bath set at 40°C for 15 min to allow the viscometer and its contents to reach thermal equilibrium. The flow times for both pure solvent and the PODMA samples were recorded. The measurements were repeated 3 times for each sample and the average of these times used in the intrinsic viscosity plot. The relative viscosity at four other concentrations was measured by diluting the PODMA solution in the reservoir by further addition of solvent. The range of relative viscosities ($\eta_r$) for each experiment was between 1.2-2.0. The data were plotted using the Huggins equation with the intrinsic viscosity [$\eta$] (dL g$^{-1}$) determined by extrapolation to infinite dilution.

3.6.5 MOLECULAR MODELLING

Molecular modelling was carried out using CS-Chem3D Pro and CS-Chem3D Ultra from Cambridgesoft. Molecules were generated in CSChemDraw and imported into Chem3D. Molecular mechanics computations were calculated using Alligner’s MM2 force field to find the local energy minimum of the molecule. Property calculations and further energy refinements were carried out using CS MOPAC with the PM3 Hamiltonian. Molecular models were visualised in Chem3D Pro and Web Lab Viewer Lite.
4 RESULTS AND DISCUSSION

4.1 MOLAR MASS AND CONVERSION CONTROL IN SMALL SCALE PODMA SYNTHESIS

The molar mass of PODMA is critical to performance when the copolymer is used as a component in crosslinked crankcase dispersants\textsuperscript{9,10}. Higher molar mass material has resulted in improved viscosity characteristics, with \( M_n = 10,000 \text{ g mol}^{-1} \) the lower limiting molar mass for the desired improvement to be realised. Consideration of the rate equation for the kinetics of chain reaction polymerisation (Equation 12) indicates a number of reaction variables that are expected to have an effect on the DP and therefore the molar mass of PODMA. With the aim of synthesising PODMA to \( M_n > 10,000 \text{ g mol}^{-1} \) reaction variables such as temperature, initiator concentration and monomer concentration were investigated.

4.1.1 TEMPERATURE

A series of PODMA copolymers was prepared as described in Section 3.3.1. The monomer concentration (MA + OD) was 10.6 mol dm\(^{-3}\) in dioxane. AIBN was used as the initiator at a concentration of 0.86 mol % with respect to (wrt) MA. Copolymerisations were carried out over a period of 24 hours in order to ensure adequate conversion and a high consumption of initiator. The temperature was varied from 65°C to 100°C and the results, including molar masses determined by SEC with a PS calibration, are shown in Table 3.
Table 3 Temperature dependence of molar mass data for PODMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature °C</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD30</td>
<td>65</td>
<td>0.13</td>
<td>7,900</td>
<td>20,000</td>
<td>2.52</td>
</tr>
<tr>
<td>MCD28</td>
<td>75</td>
<td>0.17</td>
<td>9,300</td>
<td>24,200</td>
<td>2.59</td>
</tr>
<tr>
<td>MCD27</td>
<td>87</td>
<td>0.18</td>
<td>6,100</td>
<td>12,300</td>
<td>2.03</td>
</tr>
<tr>
<td>MCD29</td>
<td>100</td>
<td>0.21</td>
<td>6,400</td>
<td>9,500</td>
<td>1.50</td>
</tr>
</tbody>
</table>

The copolymerisations carried out at 65°C and 75°C were turbid and phase separation was observed early in the reaction. To improve homogeneity the stirring speed was increased; however, these copolymerisations yielded products of broad PDI and bimodal SEC peaks. The calculation of $M_n$ for bimodal distributions cannot be considered an accurate representation of molar mass and values of $M_n$ for samples MCD30 and MCD28 are unreliable. Copolymerisation at 100°C resulted in a homogeneous solution with a narrower PDI and unimodal distribution. The value of $M_n$ for PODMA was observed to decrease with increasing temperature though the variation in molar mass is quite small. The molar mass of PODMA is depressed by the higher temperature reactions; however, conditions in which complete comonomer solubility is attained are favoured. Variation of the copolymerisation temperature did not bring about the successful preparation of PODMA with a molar mass $M_n \geq 10,000$.

4.1.2 INITIATOR CONCENTRATION

Steady state kinetics explains that in the absence of competing reactions the overall rate of polymerisation is proportional to $[1]^{1/2}$ and the kinetic chain length is inversely proportional to the radical concentration, as described by Equation 12 and Equation 16 respectively. Hence, at low radical concentrations the chain length is expected to be greater than at high radical concentrations. PODMA was prepared using AIBN at 100°C in dioxane with a total monomer concentration of 10 mol dm$^{-3}$ over a period of 24 hours. The data, including molar masses calculated relative to PS, are collected in Table 4 and presented graphically in Figure 24.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>[AIBN] (mol % wrt MA)</th>
<th>[AIBN] (mol dm⁻³)</th>
<th>Log Fractional conversion</th>
<th>Mₙ (g mol⁻¹)</th>
<th>Mₘ (g mol⁻¹)</th>
<th>PDI (Mₘ/Mₙ)</th>
<th>DP</th>
<th>1/DP</th>
<th>Log 1/DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD48</td>
<td>2.0</td>
<td>0.0092</td>
<td>-2.04</td>
<td>4,200</td>
<td>6,100</td>
<td>1.50</td>
<td>12</td>
<td>0.084</td>
<td>-1.08</td>
</tr>
<tr>
<td>MCD37</td>
<td>0.86</td>
<td>0.0046</td>
<td>-2.34</td>
<td>8,300</td>
<td>14,300</td>
<td>1.72</td>
<td>24</td>
<td>0.042</td>
<td>-1.37</td>
</tr>
<tr>
<td>MCD61</td>
<td>0.5</td>
<td>0.0027</td>
<td>-2.57</td>
<td>11,600</td>
<td>24,800</td>
<td>2.14</td>
<td>33</td>
<td>0.030</td>
<td>-1.52</td>
</tr>
</tbody>
</table>

Table 4 Molar mass dependence on [AIBN] for PODMA at 100°C
Chapter 4: Results and discussion

Figure 24 Molar mass dependence on [AIBN] for PODMA at 100 °C

Figure 25 Double logarithmic plot to evaluate DP on [AIBN] for PODMA at 100 °C
Chapter 4: Results and discussion

The molar mass increased with decreasing initiator concentration. Consideration of Equation 16 reveals that the kinetic chain length, $v$, should be proportional to the square root of the initiator concentration as a consequence of bimolecular termination depending solely on $[M^*]$. This relationship was tested by plotting Log 1/DP vs Log [AIBN] (Figure 25) from the data collected in Table 4. The linearised data from the double logarithmic plot resulted in a gradient of 0.84 rather than the expected 0.5. It is understood that two radical initiating species, $[I^+]$ are derived from each AIBN molecule; however, plotting the [AIBN] or the $[I^+]$ results in identical gradients. Walling et al.\textsuperscript{10} reported that for the homopolymerisation of allyl acetate degradative chain transfer accounted for the finding that $R_p$ was proportional to $[I]$. Therefore, a relationship in which molar mass and initiator concentration are inversely, directly proportional appears more likely for PODMA. The finding that molar mass and [AIBN] are proportional limits the control that can be achieved by varying the initiator concentration alone and alludes to the possibility of chain formation events other than disproportionation or combination. Though use of AIBN at low concentrations increased the molar mass to the required $M_n$, further investigation was required in order to evaluate the rates of copolymerisation and account for the low molar mass products obtained.

4.1.3 Dependence of overall rate on AIBN concentration

PODMA was prepared using AIBN at 100°C in glass schlenk tubes with toluene as solvent. The initiator concentration was varied, and for each AIBN concentration copolymerisations were carried out in parallel for different time periods such that a range of conversions was obtained. The data are collected in Table 5 and the conversion versus time plot is presented in Figure 26. In order to evaluate the kinetics of copolymerisation the conversion data was analysed by use of Equation 13, allowing Ln $[M]/[M]_t$ versus time to be plotted in Figure 27. The data however still showed marked curvature indicating that the system does not obey first order kinetics in the monomers. The rates of copolymerisation therefore were calculated by taking the gradient of a line, tangent to the conversion curve at low conversion, and with the intercept at the origin. Given the difficulty in producing a linear relationship this was considered to be the most accurate way of determining the copolymerisation rate. The rate data are collected in Table 6 along with average molar mass data for each system.
Chapter 4: Results and discussion

Figure 26 Time conversion plots for PODMA (◊ 1 mol% AIBN wrt MA, □ 2 mol% AIBN wrt MA, ▲ 3 mol% AIBN wrt MA) at 100°C.

Figure 27 Pseudo 1st order kinetic plots for PODMA (◊ 1 mol% AIBN wrt MA, □ 2 mol% AIBN wrt MA, ▲ 3 mol% AIBN wrt MA) at 100°C.
### Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initiator conc (mol % wrt MA)</th>
<th>Time (s)</th>
<th>Fractional conversion</th>
<th>[M] (mol dm(^{-3}))</th>
<th>[PODMA](_t) (mol dm(^{-3}))</th>
<th>Ln [M]_o/[M]_t</th>
<th>M(_n) (g mol(^{-1}))</th>
<th>DP</th>
<th>1/DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD345</td>
<td>1</td>
<td>3060</td>
<td>0.07</td>
<td>4</td>
<td>0.30</td>
<td>0.007</td>
<td>6,700</td>
<td>38</td>
<td>0.026</td>
</tr>
<tr>
<td>MCD346</td>
<td>1</td>
<td>5760</td>
<td>0.11</td>
<td>4</td>
<td>0.43</td>
<td>0.113</td>
<td>7,000</td>
<td>40</td>
<td>0.025</td>
</tr>
<tr>
<td>MCD347</td>
<td>1</td>
<td>9000</td>
<td>0.17</td>
<td>4</td>
<td>0.67</td>
<td>0.182</td>
<td>8,000</td>
<td>46</td>
<td>0.022</td>
</tr>
<tr>
<td>MCD348</td>
<td>1</td>
<td>13260</td>
<td>0.20</td>
<td>4</td>
<td>0.79</td>
<td>0.221</td>
<td>6,900</td>
<td>40</td>
<td>0.025</td>
</tr>
<tr>
<td>MCD349</td>
<td>2</td>
<td>1860</td>
<td>0.17</td>
<td>4</td>
<td>0.68</td>
<td>0.185</td>
<td>6,000</td>
<td>34</td>
<td>0.029</td>
</tr>
<tr>
<td>MCD350</td>
<td>2</td>
<td>4960</td>
<td>0.27</td>
<td>4</td>
<td>1.07</td>
<td>0.311</td>
<td>6,400</td>
<td>37</td>
<td>0.027</td>
</tr>
<tr>
<td>MCD351</td>
<td>2</td>
<td>9900</td>
<td>0.33</td>
<td>4</td>
<td>1.32</td>
<td>0.402</td>
<td>6,700</td>
<td>38</td>
<td>0.026</td>
</tr>
<tr>
<td>MCD352</td>
<td>2</td>
<td>14400</td>
<td>0.35</td>
<td>4</td>
<td>1.42</td>
<td>0.437</td>
<td>6,600</td>
<td>38</td>
<td>0.026</td>
</tr>
<tr>
<td>MCD353</td>
<td>3</td>
<td>1260</td>
<td>0.06</td>
<td>4</td>
<td>0.24</td>
<td>0.062</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD354</td>
<td>3</td>
<td>3000</td>
<td>0.40</td>
<td>4</td>
<td>1.60</td>
<td>0.511</td>
<td>5,600</td>
<td>32</td>
<td>0.031</td>
</tr>
<tr>
<td>MCD355</td>
<td>3</td>
<td>5100</td>
<td>0.52</td>
<td>4</td>
<td>2.08</td>
<td>0.734</td>
<td>6,000</td>
<td>34</td>
<td>0.029</td>
</tr>
<tr>
<td>MCD356</td>
<td>3</td>
<td>9300</td>
<td>0.54</td>
<td>4</td>
<td>2.16</td>
<td>0.777</td>
<td>6,400</td>
<td>37</td>
<td>0.027</td>
</tr>
</tbody>
</table>

*Table 5 Dependence of conversion and molar mass on AIBN concentration for PODMA*
Chapter 4: Results and discussion

The mean values for $M_n$, DP and $1/\text{DP}$ were calculated from the individual results presented in Table 5. The formation of dead chains early in the reaction is characteristic of radical polymerisation due to rapid initiation, propagation, and termination events. It follows therefore that the molar mass of the polymer or copolymer produced should stay constant throughout the reaction provided there is no influence from the gel effect (Section 2.1.7). To this end it is reasonable to take mean molar mass values for the following calculations. Molar masses below 10,000 g mol$^{-1}$ were obtained and therefore can be considered accurate when SEC measurements are carried out with a PS calibration (Section 4.2.4). The degree of chain transfer to monomer, $C_m$ can be evaluated by use of the Mayo equation (Equation 27), provided there is no significant chain transfer from initiator, solvent or modifier. A plot of $\text{IIDP}$ versus $R_p/[M^2]$ allows $C_m$ to be evaluated from the intercept. The dependence of molar mass on initiator concentration was small and therefore a relatively flat linear relationship was observed in Figure 28. A value of $C_m = 0.025$ was obtained for PODMA. This is significantly higher than for St ($C_m = 3.8-7.5 \times 10^{-5}$)$^{111}$ and MMA ($C_m = 1.0-8.5 \times 10^{-5}$)$^{111}$ which are considered to have small $C_m$ constants. The $C_m$ value for PODMA is however significantly lower than that determined for poly MA ($C_m = 0.075$)$^{112}$ and for polydecene ($C_m = 0.125$)$^{30}$. The PODMA experiments were carried out in toluene in order to avoid influence from the gel effect. It is accepted that chain transfer to toluene is possible, via hydrogen abstraction from the methyl group. However the reported $C_s$ values for toluene are ($C_s = 5.3 \pm 8.0 \times 10^{-5}$)$^{32}$, which are significantly less than the value calculated for PODMA. It is also pertinent to note that the benzylic radical formed by hydrogen abstraction from toluene is capable of

<table>
<thead>
<tr>
<th>Initiator concentration (mol% wrt MA)</th>
<th>Rate of copolymerisation $R_p$ (mol dm$^{-3}$ s$^{-1}$)</th>
<th>Mean $M_n$ (g mol$^{-1}$)</th>
<th>Mean DP</th>
<th>$1/\text{Mean DP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.0 \times 10^{-5}$</td>
<td>7,100</td>
<td>41</td>
<td>0.025</td>
</tr>
<tr>
<td>2</td>
<td>$4.0 \times 10^{-4}$</td>
<td>6,400</td>
<td>37</td>
<td>0.027</td>
</tr>
<tr>
<td>3</td>
<td>$1.3 \times 10^{-3}$</td>
<td>6,000</td>
<td>34</td>
<td>0.029</td>
</tr>
</tbody>
</table>

Table 6 Rate of copolymerisation and molar mass data for PODMA

The formation of dead chains early in the reaction is characteristic of radical polymerisation due to rapid initiation, propagation, and termination events. It follows therefore that the molar mass of the polymer or copolymer produced should stay constant throughout the reaction provided there is no influence from the gel effect (Section 2.1.7). To this end it is reasonable to take mean molar mass values for the following calculations. Molar masses below 10,000 g mol$^{-1}$ were obtained and therefore can be considered accurate when SEC measurements are carried out with a PS calibration (Section 4.2.4). The degree of chain transfer to monomer, $C_m$ can be evaluated by use of the Mayo equation (Equation 27), provided there is no significant chain transfer from initiator, solvent or modifier. A plot of $1/\text{DP}$ versus $R_p/[M^2]$ allows $C_m$ to be evaluated from the intercept. The dependence of molar mass on initiator concentration was small and therefore a relatively flat linear relationship was observed in Figure 28. A value of $C_m = 0.025$ was obtained for PODMA. This is significantly higher than for St ($C_m = 3.8-7.5 \times 10^{-5}$)$^{111}$ and MMA ($C_m = 1.0-8.5 \times 10^{-5}$)$^{111}$ which are considered to have small $C_m$ constants. The $C_m$ value for PODMA is however significantly lower than that determined for poly MA ($C_m = 0.075$)$^{112}$ and for polydecene ($C_m = 0.125$)$^{30}$. The PODMA experiments were carried out in toluene in order to avoid influence from the gel effect. It is accepted that chain transfer to toluene is possible, via hydrogen abstraction from the methyl group. However the reported $C_s$ values for toluene are ($C_s = 5.3 \pm 8.0 \times 10^{-5}$)$^{32}$, which are significantly less than the value calculated for PODMA. It is also pertinent to note that the benzylic radical formed by hydrogen abstraction from toluene is capable of
reinitiation*. $^1$H NMR analysis indicates that no aromatic end groups are present when AIBN was used as radical initiator.

![Mayo plot for the determination of $C_m$ for PODMA](figure)

*The benzylic radical derived from toluene can initiate polymerisation of MA containing copolymers as demonstrated by the use of BDTB in section 4.6, which expels the benzylic radical as part of the RAFT mechanism.
Chapter 4: Results and discussion

the finding that only one initiator derived end group per chain is present (Section 4.3.5). If chain transfer were not degradative, then less than one initiator derived end group would be observed. The degradative nature of the chain transfer can be further supported by considering radical reactivities from a bond dissociation energy (BDE) perspective. The lower the BDE the more stable a derived radical is. The values for BDE of the ethyl and allyl radicals are 98 kcal mol\(^{-1}\), and 77 kcal mol\(^{-1}\) respectively\(^{110}\).

In order for the allylic stabilised radical to add to the vinyl bond of OD, forming a less stable alkyl radical, an increase in BDE of approximately 21 kcal mol\(^{-1}\) is required. The formation of products that are more reactive than the starting species is thermodynamically unfavourable and therefore is not observed. The BDE of the radical derived from MA is not reported though radical grafting of MA onto unsaturated carbon chains suggests that under appropriate conditions the addition is possible.

The chain transfer mechanism for PODMA therefore involves hydrogen abstraction from OD forming a dead PODMA chain and an allylic stabilised radical, which is unable to reinitiate copolymerisation. The mechanism is presented graphically in Scheme 8.
Chapter 4: Results and discussion

Scheme 8 Chain transfer to OD for PODMA at 100°C
4.1.4 PODMA CONVERSION

Molar mass though critical to performance must be coupled with high conversion in order to provide a viable industrial procedure that may be scaled up to offer an efficient route to a high performance crankcase dispersant. As well as copolymerisation kinetics offering an explanation for DP, the dependence of conversion on the above reaction variables can also be considered.

4.1.4.1 DEPENDENCE ON TEMPERATURE

As previously stated, copolymerisations carried out at temperatures below 80°C in dioxane are heterogeneous and consequently there is a reduction in contact between the comonomers. Lower temperatures also result in a lower concentration of initiating radicals, which while aiding in increasing molar mass will reduce conversion, or at least slow the copolymerisation. These points considered, Figure 29 shows that using AIBN (0.86 mol% wrt MA) a maximum fractional conversion of <0.25 is obtained at 100°C after 24 hours with the expected decrease in conversion with decreasing temperature for copolymerisation carried out for the same time.

4.1.4.2 DEPENDENCE ON INITIATOR CONCENTRATION

Similar to the above concept, a trend in the opposite direction to the one desired for molar mass increase is anticipated for the conversion dependence on initiator concentration. That is, the low initiator concentrations utilised in order to slow the copolymerisation rate and increase DP are also likely to result in low conversions. While this is beneficial for careful kinetic evaluation of the system, it does not fulfil the need for development of an industrially applicable procedure. Figure 30 illustrates that increasing initiator concentration results in greater conversion. Copolymerisations were carried out over 24 hours to ensure the complete consumption of AIBN.
Chapter 4: Results and discussion

Figure 29 Dependence of conversion for PODMA on temperature over 24 hours

Figure 30 Dependence of conversion for PODMA on [AIBN] at 100°C over 24 hours
4.1.4.3 ALIQUOT INITIATOR ADDITION

In order to satisfy the conflicting requirements of high molar mass with maximum possible conversion, a method involving the addition of a series of aliquots containing low concentrations of initiator was developed. The aim was to perform the copolymerisation as a number of mini-copolymerisations, each delivering the required molar mass, but also building up conversion to a degree that was acceptable for scale up and process development. It should be noted that previous work regarding the kinetics of copolymerisation is not valid here, though the information gained was used in a qualitative manner in deciding the concentration and interval time of each aliquot. Copolymerisations were carried out using aliquots of AIBN (0.86 mol % wrt. MA) dissolved in the minimum amount of dioxane, which was used as the copolymerisation solvent at 100°C. Using copolymerisation rate data from Section 4.1.3, the aliquots were injected every 60 minutes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>No aliquots</th>
<th>Fractional conversion</th>
<th>Molar mass (g mol⁻¹)</th>
<th>PDI (Mₘ/M₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M₀</td>
<td>Mₘ</td>
</tr>
<tr>
<td>MCD37</td>
<td>1</td>
<td>0.305</td>
<td>8,300</td>
<td>14,300</td>
</tr>
<tr>
<td>MCD45</td>
<td>2</td>
<td>0.408</td>
<td>7,700</td>
<td>12,100</td>
</tr>
<tr>
<td>MCD46</td>
<td>4</td>
<td>0.644</td>
<td>7,300</td>
<td>12,600</td>
</tr>
</tbody>
</table>

*Table 7 PODMA synthesis with aliquot AIBN addition at 100°C*

Table 7 presents the aliquot addition data. It can be clearly seen that the addition of further initiator increases the conversion by maintaining a steady production of radicals throughout the copolymerisation. The increase in overall radical concentration however did slightly depress the molar mass below the expected value.

4.1.5 BULK PODMA SYNTHESIS

PODMA was synthesised in bulk with AIBN (0.86 mol% wrt. MA) at 100°C. Small scale PODMA synthesis in bulk is problematic due to the insolubility of the
comonomers. The copolymerisation at low conversions, therefore, is heterogeneous with significant sublimation of MA. As the reaction proceeds, and providing the MA is not charred, the formation of PODMA solvates the comonomers and a homogeneous system is observed. Table 8 presents the results for bulk copolymerisation of PODMA compared to solution copolymerisations carried out in dioxane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[M] (mol dm⁻³)</th>
<th>Molar Mass (g mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mₙ</td>
</tr>
<tr>
<td>MCD62</td>
<td>Bulk</td>
<td>14,300</td>
</tr>
<tr>
<td>MCD37</td>
<td>10</td>
<td>8,300</td>
</tr>
<tr>
<td>MCD63</td>
<td>2.5</td>
<td>4,600</td>
</tr>
</tbody>
</table>

*Table 8 Molar mass results for bulk and solution PODMA synthesis at 100 °C*

It is clear that synthesis in the bulk, though problematic, yields high molar mass material. The dramatic increase in molar mass at high monomer concentrations can be attributed to the *Norrish* or *Gel effect* (Section 2.1.7). This is caused by the loss of steady state kinetics as the viscosity of the medium increases. At higher conversions, achieved with the aliquot initiator technique described in Section 4.1.4.3, the bulk synthesis of PODMA became highly viscous and difficulty in stirring was experienced. This increase in viscosity leads to the different steps in the copolymerisation becoming diffusion controlled. Termination reactions generally have the lowest activation energy and become diffusion controlled first. The increase in viscosity of the PODMA medium leads to a reduction in termination rate and an increase in kinetic chain length, and, therefore molar mass.

4.1.6 SUMMARY

Investigation of reaction variables has provided evidence for the difficulty in preparing PODMA of high molar mass. Deviation from conventional pseudo 1st order kinetics limited the effect of initiator concentration in controlling the DP and therefore the molar mass. Mₙ ~ 10,000 g mol⁻¹ for PODMA was prepared by use of low initiator
concentrations coupled with an aliquot addition technique to increase conversion. The formation of low molar mass products can be attributed to degradative chain transfer to the comonomers, with OD responsible due to hydrogen abstraction. The allylic stabilised radical is of insufficient energy to reinitiate copolymerisation. Bulk copolymerisation has resulted in PODMA of high molar mass. This is a consequence of the gel effect and though not as kinetically predictable as solution copolymeriations does provide a simple route to PODMA of high molar mass provided suitable care is taken to avoid runaway reactions due to trapped radicals.
Chapter 4: Results and discussion

4.2 SEC ANALYSIS AND MOLAR MASS CALCULATION\textsuperscript{113}

4.2.1 Modification of the Mobile Phase

Initial work investigating PODMA copolymers used THF as the mobile phase. The use of THF for the separation of PODMA, however, does not provide good chromatographic resolution. Over a period of time, the chromatogram is shifted to longer elution times and the PDI of the sample increases. Tacx et al\textsuperscript{114} reported similar observations during the analysis of StMA copolymers. Both light scattering and viscometry indicated no enhancement of molar mass or intrinsic viscosity and so intermolecular aggregation was not considered to be a reasonable explanation for this behaviour. It was suggested that a mixed exclusion/adsorption mechanism contributes to adsorption of StMA onto the column packing, and our similar observations using THF as the SEC eluent for PODMA confirm this behaviour. As PS does not exhibit such anomalies, it is assumed that the polar anhydride rings are responsible. Copolymers containing anhydride groups may also contain a number of dicarboxylic acid groups due to ring opening hydrolysis. This reaction is facilitated by THF that may contain low levels of water. It was reported\textsuperscript{114} that StMA copolymer containing 27wt % MA had a 7wt % maleic acid content. Adsorption of MA copolymers is only likely if the column packing contains polar active sites that may consist of oxidised packing material or incorporation of polar surfactant molecules used in the polymerisation process to obtain the column packing material\textsuperscript{115}. X-ray photon electron spectroscopy showed that the column packing used for StMA copolymer analysis had significant amounts of oxygen present indicating copolymer adsorption. The adsorption of StMA copolymer and PODMA can be suppressed by the addition of an acid. The addition of acetic acid to THF stabilises the anhydride ring and competes for the adsorption sites present on the column packing. For StMA copolymers of low anhydride content, THF/acetic acid (95:5 v/v) was sufficient to correct for adsorption\textsuperscript{114}. Figure 31 shows molar mass data from SEC for the same set of PODMA samples analysed at Lubrizol, operating with THF/acetic acid (95:5 v/v) and at Loughborough using an increased acid concentration of THF/acetic acid (90:10 v/v). It is clear that a higher acid concentration is required for PODMA that contains 50 mol% anhydride. The addition of acetic acid to THF was found to affect the intrinsic viscosity of a PS standard of $M_n = 151,700$ g mol\textsuperscript{-1}. A lower
value of 0.55 dL g\(^{-1}\) was measured compared to 0.57 dL g\(^{-1}\) in THF alone. The MH constant, \(a\), however did not show a marked difference when acetic acid was added indicating that PS solubility was little affected by the change in solvent. Similar behaviour was expected from PODMA. Use of the modified mobile phase allows a size exclusion mechanism to operate without any interference.

![Molar mass of PODMA from SEC analysis](image)

**Figure 31 Molar mass of PODMA from SEC analysis** (\(\bullet\) 5 \% v/v acetic acid) (\(\bigtriangledown\) 10 \% acetic acid)

### 4.2.2 Molar mass determination

SEC is a relative technique and thus far all PODMA SEC results have been quoted relative to PS standards. Due to the long alkyl side chains from the octadecene functionality of PODMA, the copolymer dimensions may be significantly different from those of PS. PODMA may behave more like a comb graft copolymer than a conventional linear polymer in solution, and would be expected to occupy a smaller hydrodynamic volume than linear PS of equal molar mass. To this end molar masses for PODMA from SEC calibrated with PS were found to be erroneous and a more accurate SEC method was sought.
Chapter 4: Results and discussion

Under circumstances where the MH constants are known for the copolymer and the standard universal calibration approach can be employed (Equation 59). Utilisation of this method allows the calculation of molar masses involving a SEC chromatogram and a calibration plot of \( \log M_{\text{PODMA}} \) versus retention time. The only reported MH constants for PODMA\textsuperscript{116} were obtained by fractionation of a polydisperse sample and measurement of \([\eta]\) by viscometry and \(M_w\) by light scattering in ethyl acetate at 25°C. The viscosities were described by the MH relationship below (Equation 66):

\[
[\eta] = 5.5 \times 10^{-4} M_w^{0.48}
\]

*Equation 66*

As \([\eta]\) is dependent on solvent and temperature, the MH constants are not applicable to the modified mobile phase system used in the SEC analysis. In the absence of MH constants, variations on the universal calibration have been developed that use a trial and error, iterative approach\textsuperscript{117, 118}. Initially, a universal calibration for the standards is constructed. The SEC retention time and \([\eta]\) for the unknown are then measured independently.

In order to construct a universal calibration curve for PS, the MH constants for PS under the experimental conditions need to be utilised. Values of \([\eta]\) were determined by experiment for a number of PS standards using the Huggins equation (Equation 56) and a double logarithmic plot was employed to evaluate these constants (Figure 32). The following MH relationship was derived (Equation 67).
A series of PODMA samples with apparent molar masses $M_n$ (app) in the range 4,000 to 24,000 g mol$^{-1}$ (determined by PS calibration) was selected for analysis. The chromatograms are presented in Figure 34. Intrinsic viscosities $[\eta]$ were determined for the same PODMA samples by use of the Huggins equation (Equation 56) and extrapolation to infinite dilution (Figure 33). The experimental intrinsic viscosities $[\eta]_{\text{exp}}$ and the apparent molar mass $M_n$ (app) are presented in Table 9. A plot of $[\eta]_{\text{exp}}$ against retention time for PODMA was constructed and a best fit function applied to the data. This is presented along with the chromatogram for MCD44 in Figure 35. This initial plot together with SEC chromatograms for PODMA samples permitted the calculation of $[\eta]_{\text{calc}}$ for all PODMA samples by use of Equation 68.

$$[\eta]_{\text{PS}} = 1.52 \times 10^{-4} M^{0.71}$$

*Equation 67*
\[ [\eta]_{\text{calc}} = \frac{\sum W_{\text{PODMA}} [\eta]_{\text{PODMA}}}{\sum N_{\text{PODMA}}} \]

Equation 68

It follows from earlier calibration studies\textsuperscript{119} that the molar mass value corresponding to the peak position of a chromatogram should be close to the viscosity-average molar mass \( M_v \). The iteration method requires matching \([\eta]_{\text{exp}}\) and \([\eta]_{\text{calc}}\) for all PODMA samples by trial-and-error placements of the plot of \( \log [\eta] \) versus retention time. The values of \([\eta]_{\text{calc}}\) are compared with \([\eta]_{\text{exp}}\) in Table 9. The iteration method involves extrapolation of the plot beyond experimental data points as illustrated for the tails of the chromatogram for sample MCD44 in Figure 35. However, only for the sample of lowest molar mass is there a problem in matching \([\eta]_{\text{calc}}\) and \([\eta]_{\text{exp}}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured intrinsic viscosity ([\eta]_{\text{exp}})</th>
<th>Calculated intrinsic viscosity ([\eta]_{\text{calc}})</th>
<th>Apparent ( M_n ) (app) (g mol(^{-1}))</th>
<th>True ( M_n ) (true) (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C. Johnson</td>
<td>0.057</td>
<td>0.066</td>
<td>4,000</td>
<td>3,900</td>
</tr>
<tr>
<td>MCD27</td>
<td>0.066</td>
<td>0.067</td>
<td>6,200</td>
<td>15,600</td>
</tr>
<tr>
<td>MCD44</td>
<td>0.074</td>
<td>0.073</td>
<td>12,700</td>
<td>29,700</td>
</tr>
<tr>
<td>Aldrich</td>
<td>0.098</td>
<td>0.099</td>
<td>14,400</td>
<td>37,100</td>
</tr>
<tr>
<td>MCD66</td>
<td>0.128</td>
<td>0.128</td>
<td>23,400</td>
<td>56,300</td>
</tr>
</tbody>
</table>

Table 9 Intrinsic viscosity results and molar mass data for PODMA using PS (\( M_n \) (app)) and PODMA (\( M_n \) (true)) calibrations.
Figure 33 Huggins plots for PODMA in THF:acetic acid (90:10 v/v) at 40 °C. (●) S. C. Johnson, (■) MCD27, (▲) MCD44, (♦) Aldrich and (■) MCD66.
Chapter 4: Results and discussion

Figure 34 SEC chromatograms for PODMA used in universal calibration determination
The determination of Equation 67 enables a universal calibration to be constructed with Equation 59 from which a calibration for $M_{\text{PODMA}}$ can be calculated since the dependence of $[\eta]_{\text{PODMA}}$ on elution time is available from Figure 35.

The resulting calibration for PODMA is displayed in Figure 36, demonstrating linearity in the region of high $M_{\text{PODMA}}$ with a similar slope to the calibration for PS, indicating that the MH exponents for the two polymers in THF/acetich acid (90:10 v/v) are quite similar. The downturn in the plot for PODMA at low $M_{\text{PODMA}}$ is consistent with the observation that the MH exponent should fall to 0.5 for short chains in good solvents, which has been demonstrated experimentally for several polymers\textsuperscript{103,104,105} and is in agreement with Stockmayer et al who also note a low a value for PODMA\textsuperscript{116}.

The molar mass calibration for PODMA allows the true $M_n$ values to be calculated from SEC retention times and compared to $M_n$ (app). Table 9 presents $M_n$ (true) and $M_n$ (app) molar mass data for PODMA. For PODMA samples of high molar mass ($>10,000$ g mol\textsuperscript{-1}), values of $M_n$ (true) in Table 9 obtained with the constructed calibration are approximately twice $M_n$ (app). For the lowest molar mass PODMA sample ($<10,000$ g mol\textsuperscript{-1}), which is positioned in the downturn of the calibration (at higher elution times) similar values of $M_n$ (true) and $M_n$ (app) are obtained. This finding illustrates that for low molar mass PODMA a PS calibration is an appropriate and convenient analytical method. However, at higher molar masses significant deviation from a PS calibration was observed and for accurate molar mass data, the adjusted PODMA calibration should be used.

4.2.3 SUMMARY

The determination of accurate molar mass values for PODMA has been achieved by a combined analysis technique involving SEC and dilute solution viscometry. The mobile phase for SEC was modified to inhibit adsorption of the acidic anhydride or dicarboxylic acid groups to the column packing and allow a size exclusion mechanism to operate. The use of dilute solution viscometry permitted the differences in hydrodynamic volume of PS and PODMA to be realised and an approach based on the universal calibration method resulted in a molar mass calibration based on PODMA.
Use of this calibration allows accurate molar mass data to be calculated for PODMA directly from SEC retention times.
Figure 35 SEC calibration curve for PODMA samples based on intrinsic viscosity, and chromatogram for sample MCD44.
Figure 36 SEC calibration curves for PODMA. (■) PS calibration; (▲) calibration based on SEC/\left[\eta\right] analysis for PODMA.
4.3 STRUCTURAL PROPERTIES OF PODMA

4.3.1 FTIR ANALYSIS OF PODMA

A FTIR spectrum of the PODMA copolymer MCD7 is shown in Figure 37. The CH stretching absorption at 2927 cm\(^{-1}\) and 2854 cm\(^{-1}\) is characteristic of alkane residues due to OD. The stretching absorption at 1781 cm\(^{-1}\), and the weaker absorption at 1857 cm\(^{-1}\) of the carbonyl groups, are indicative of anhydrides. This unique structural feature is due to the symmetric and asymmetric stretching possible when the carbonyl groups vibrate in, or out of phase with each other\(^{120}\). The two strong bands at 1463 cm\(^{-1}\) and 1231 cm\(^{-1}\) are due to C-O stretching. The weak absorption at 1721 cm\(^{-1}\) falls in the ester region. Half esters can be formed by reaction with MeOH used in the PODMA purification procedure. The band may also be attributed to the partial hydrolysis of the copolymer. A strong band at 929 cm\(^{-1}\) due to carboxylic acid formation supports both arguments. Reconversion to succinic anhydride was accomplished by stirring in acetic acid over-night and filtering, or drying at >80°C under vacuum for 24 hours. Composition analysis was carried out as detailed in Section 3.6.1.2 by integration of the carbonyl region of the spectrum from 1667 cm\(^{-1}\) to 1897 cm\(^{-1}\).

4.3.2 ESTIMATION OF REACTIVITY RATIOS

PODMA was prepared varying the initial mole fraction of the comonomers as described in Section 3.3.1. The final composition of PODMA was determined by FTIR and the results for the series of PODMA copolymers are illustrated in Table 10. Conversions were varied from 1% to 65% using both single shot and aliquot initiator addition techniques. The greater conversions allowed the effect of composition drift to be tested. If an alternating copolymer is formed and neither comonomer can be homopolymerised, then the composition is expected to be independent of the feed composition and conversion. Statistical copolymers on the other hand will be subject to composition drift and conversions should be kept below 5%. All the copolymers were prepared with \(M_n<10,000\) g mol\(^{-1}\) and were measured by SEC using a PS calibration. Figure 38 plots PODMA composition against the comonomer feed composition. Copolymers approaching equimolar composition are found across the range of feed ratios.
investigated. The reactivity ratios were estimated using the Fineman-Ross, and Kelen-Tŭdős methods of linear regression. These methods are outlined in Section 2.2.2.

4.3.2.1 FINEMAN-ROSS METHOD

The experimental data obtained for PODMA copolymers (Table 10) were utilised to obtain the monomer reactivity ratios for MA and OD at 100°C. The results are plotted graphically in Figure 39 and the results from the calculations included in Table 12. A plot of $G$ versus $F$ produced a straight line with slope $r_1$ and intercept $-r_2$. In addition $G/F$ versus $1/F$ produced a straight line with slope $-r_2$ and the intercept $r_1$. The values for $r_1$ and $r_2$ for PODMA are collected in Table 11.
Chapter 4: Results and discussion

Figure 37 FTIR absorbance spectrum of PODMA copolymer (sample MCD7).
Chapter 4: Results and discussion

4.3.2.2 KELEN-TŰDŐS METHOD

The experimental data were also analysed using the Kelen-Tüdős method to obtain the monomer reactivity ratios for MA and OD. A value of \( \alpha = 1 \) was used (Section 2.2.2.2). The results are plotted graphically in Figure 40 and the data used for the calculation are collected in Table 12. A plot of \( \sigma \) against \( \xi \) produced a straight line, which was extrapolated to \( \xi = 0 \) to give \(-r_2/\alpha\) and \(\xi = 1\) to deliver \(r_1\) (both as intercepts).

The data for both methods for the estimation of monomer reactivity ratios show significant scatter and therefore the \(R^2\) values for the plots are not as high as hoped. This is partially due to the very small changes in composition measured for PODMA leading to shallow gradients and intercepts in the region of the origin. The monomer reactivity ratios for PODMA are shown below (Table 11).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feed mol fraction</th>
<th>PODMA mol fraction</th>
<th>Fractional conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MA</td>
<td>OD</td>
<td>MA</td>
</tr>
<tr>
<td>MCD27</td>
<td>0.75</td>
<td>0.25</td>
<td>0.46</td>
</tr>
<tr>
<td>MCD30</td>
<td>0.75</td>
<td>0.25</td>
<td>0.46</td>
</tr>
<tr>
<td>MCD9</td>
<td>0.75</td>
<td>0.25</td>
<td>0.49</td>
</tr>
<tr>
<td>MCD8</td>
<td>0.68</td>
<td>0.32</td>
<td>0.48</td>
</tr>
<tr>
<td>MCD42</td>
<td>0.53</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>MCD45</td>
<td>0.53</td>
<td>0.47</td>
<td>0.49</td>
</tr>
<tr>
<td>MCD46</td>
<td>0.53</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>MCD21</td>
<td>0.5</td>
<td>0.5</td>
<td>0.48</td>
</tr>
<tr>
<td>MCD69</td>
<td>0.5</td>
<td>0.5</td>
<td>0.42</td>
</tr>
<tr>
<td>MCD70</td>
<td>0.4</td>
<td>0.6</td>
<td>0.42</td>
</tr>
<tr>
<td>MCD7</td>
<td>0.32</td>
<td>0.68</td>
<td>0.43</td>
</tr>
</tbody>
</table>

*Table 10 Monomer feed mole fractions and copolymer mole fractions for PODMA composition.*
### Table 11: Monomer reactivity ratios for PODMA

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{MA}$</th>
<th>$r_{OD}$</th>
<th>$r_{MA}r_{OD}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman and Ross 1</td>
<td>-0.040</td>
<td>0.080</td>
<td>-0.0030</td>
</tr>
<tr>
<td>Fineman and Ross 2</td>
<td>0.001</td>
<td>0.155</td>
<td>0.0002</td>
</tr>
<tr>
<td>Kelen and Tüdös</td>
<td>-0.020</td>
<td>-0.120</td>
<td>0.0020</td>
</tr>
</tbody>
</table>
Figure 38 Copolymer composition and monomer feed plot for PODMA.
Figure 39 Fineman-Ross plot for the estimation of $r_1$ and $r_2$ for PODMA.
Chapter 4: Results and discussion

Figure 40 Kelen-Tüdös plot for the estimation of $r_1$ and $r_2$ for PODMA.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>M₁ MA</th>
<th>M₂ OD</th>
<th>m₁ MA</th>
<th>m₂ OD</th>
<th>x</th>
<th>y</th>
<th>F</th>
<th>G</th>
<th>G/F</th>
<th>1/F</th>
<th>σ</th>
<th>ξ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD27</td>
<td>0.75</td>
<td>0.25</td>
<td>0.46</td>
<td>0.54</td>
<td>3.03</td>
<td>0.84</td>
<td>10.98</td>
<td>-0.60</td>
<td>0.09</td>
<td>-0.05</td>
<td>-0.05</td>
<td>0.92</td>
</tr>
<tr>
<td>MCD30</td>
<td>0.75</td>
<td>0.25</td>
<td>0.46</td>
<td>0.54</td>
<td>3.03</td>
<td>0.87</td>
<td>10.58</td>
<td>-0.47</td>
<td>0.09</td>
<td>-0.04</td>
<td>-0.04</td>
<td>0.91</td>
</tr>
<tr>
<td>MCD9</td>
<td>0.75</td>
<td>0.25</td>
<td>0.49</td>
<td>0.51</td>
<td>3.00</td>
<td>0.95</td>
<td>9.44</td>
<td>-0.15</td>
<td>0.11</td>
<td>-0.02</td>
<td>-0.01</td>
<td>0.90</td>
</tr>
<tr>
<td>MCD8</td>
<td>0.68</td>
<td>0.32</td>
<td>0.48</td>
<td>0.52</td>
<td>2.08</td>
<td>0.93</td>
<td>4.68</td>
<td>-0.16</td>
<td>0.21</td>
<td>-0.03</td>
<td>-0.03</td>
<td>0.82</td>
</tr>
<tr>
<td>MCD42</td>
<td>0.53</td>
<td>0.47</td>
<td>0.50</td>
<td>0.50</td>
<td>1.13</td>
<td>0.98</td>
<td>1.29</td>
<td>-0.02</td>
<td>0.77</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.59</td>
</tr>
<tr>
<td>MCD45</td>
<td>0.53</td>
<td>0.47</td>
<td>0.49</td>
<td>0.51</td>
<td>1.13</td>
<td>0.95</td>
<td>1.34</td>
<td>-0.06</td>
<td>0.75</td>
<td>-0.04</td>
<td>-0.03</td>
<td>0.57</td>
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<tr>
<td>MCD46</td>
<td>0.53</td>
<td>0.47</td>
<td>0.50</td>
<td>0.50</td>
<td>1.13</td>
<td>0.99</td>
<td>1.29</td>
<td>-0.02</td>
<td>0.78</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.56</td>
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<tr>
<td>MCD21</td>
<td>0.5</td>
<td>0.5</td>
<td>0.48</td>
<td>0.52</td>
<td>1.00</td>
<td>0.93</td>
<td>1.08</td>
<td>-0.08</td>
<td>0.93</td>
<td>-0.07</td>
<td>-0.04</td>
<td>0.52</td>
</tr>
<tr>
<td>MCD69</td>
<td>0.5</td>
<td>0.5</td>
<td>0.42</td>
<td>0.58</td>
<td>1.00</td>
<td>0.73</td>
<td>1.36</td>
<td>-0.36</td>
<td>0.73</td>
<td>-0.27</td>
<td>-0.15</td>
<td>0.70</td>
</tr>
<tr>
<td>MCD70</td>
<td>0.4</td>
<td>0.6</td>
<td>0.42</td>
<td>0.58</td>
<td>0.67</td>
<td>0.73</td>
<td>0.61</td>
<td>-0.25</td>
<td>1.64</td>
<td>-0.40</td>
<td>-0.15</td>
<td>0.38</td>
</tr>
<tr>
<td>MCD7</td>
<td>0.32</td>
<td>0.68</td>
<td>0.43</td>
<td>0.57</td>
<td>0.48</td>
<td>0.77</td>
<td>0.30</td>
<td>-0.15</td>
<td>3.32</td>
<td>-0.49</td>
<td>-0.11</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 12 Copolymer data and results from calculations using the Fineman-Ross and Kelen-Tüdős methods to determine $r_1$ and $r_2$ for PODMA.
Chapter 4: Results and discussion

The monomer reactivity ratios obtained for MA \((r_{MA})\) indicated that MA would not add its own radical and prefers to cross-propagate and add OD monomer. Similarly, the values obtained for OD \((r_{OD})\) also show that the radical would rather cross-propagate and add MA monomer than add its own monomer. The results show that the synthesis of PODMA under the conditions stated leads to the formation of an alternating copolymer. Values of \(r_{MA}r_{OD} \approx 0\) support this finding. It was noted however that the values for \(r_{OD}\) were slightly higher than those for MA. Though this may indicate a small amount of self-addition, a more likely explanation stems from the difficulty in purification of PODMA. Analysis by \(^1\)H NMR and SEC indicates that a small amount of OD remains entrained in the copolymer in some cases (see Figure 41 D and E). Composition analysis by FTIR relies on accurate masses of copolymer. Artificially low masses of PODMA due to the presence of trace OD skews the composition analysis towards low values of MA in the copolymer. This error manifests itself in a slightly inflated \(r_{OD}\) value. In order to test this hypothesis, homopolymersations of MA and OD were attempted under identical reaction conditions to those used to form PODMA. Neither monomer polymerised, confirming that self-addition is not a viable propagation step in the synthesis of PODMA. Therefore, a strictly alternating copolymer is formed. This finding is further supported by literature values of \(r_{MA}=0.0\), \(r_{ethylene}=0.04\) for MA-alt-ethylene\(^{32}\) and \(r_{MA}=0.065\), \(r_{isobutylene}=0.012\) for MA-alt-isobutylene\(^{32}\).

Knowledge of \(r_{MA}r_{OD}\) permits the calculation of the \(Q\) and \(e\) values from Equation 46 and Equation 48 as the \(Q\) and \(e\) values for MA are known (Table 1). The \(Q\) and \(e\) values for OD are shown in Table 13 and are similar to the reported constants for other \(\alpha\)-olefins (Table 1).

<table>
<thead>
<tr>
<th>Monomer</th>
<th>(r_{MA}r_{OD})</th>
<th>(Q)</th>
<th>(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>0.00128</td>
<td>0.860</td>
<td>3.690</td>
</tr>
<tr>
<td>OD</td>
<td>0.002</td>
<td>-0.734</td>
<td></td>
</tr>
</tbody>
</table>

*Table 13 Calculated \(Q\) and \(e\) values for OD*

The participation of a CTC in the alternating copolymerisation to form PODMA is considered highly unlikely, which is supported by the low CTC equilibrium constants.
Chapter 4: Results and discussion

reported for MA and propylene and MA and isobutylene (Section 2.3.2). The Q-e values for PODMA support a free monomer mechanism in which differences in monomer polarity allow an alternating copolymer to be prepared from monomers that do not homopolymerise under the reaction conditions used here (Section 3.3.1).

4.3.3 $^1$H NMR ANALYSIS OF PODMA

$^1$H NMR was accomplished for PODMA as was described in Section 3.6.2 and a spectrum is shown in Figure 41. The spectrum is similar to those reported in the literature for MA -co- α-olefins of shorter chain length$^{67, 71, 73}$. The triplet due to the CH$_3$ (A 0.9 ppm) of the octadecene unit is easily distinguished as is the broad singlet peak due to the CH$_2$ (B 1-1.5 ppm) groups that make up the octadecene chain and backbone of the copolymer. The $^1$H NMR does show the anhydride protons (C 2.5-3.6 ppm) but the peak is very broad. This makes the method unreliable for composition determination, as the integral of the anhydride protons would have to be compared to the triplet of the methyl protons on the octadecene chain. FTIR is the preferred method for composition determination.

---

$^\dagger$ Errors were not reported for this work, though the use of UV or $^1$H NMR spectroscopy for the determination of equilibrium constants for CTC's results in data scatter.
Figure 41 $^1$H NMR spectrum for PODMA (sample MCD66).
4.3.4 PODMA BACKBONE STRUCTURE

4.3.4.1 $^{13}$C NMR ANALYSIS OF PODMA

$^{13}$C NMR was used to investigate the backbone structure of PODMA. Initially, copolymers of ethylene and MA were analysed by $^{13}$C NMR and DEPT. Carbonyl carbons are often weak due to their long relaxation time in comparison to other carbons. This effect is intensified when polymers are analysed due to restricted movement brought about by chain entanglement. However, when long pulse delay times (several seconds) were used the pertinent carbons due to ethylene, succinic anhydride and carbonyl were visible. Analysis of PODMA was more difficult. Initially, even high concentrations of copolymer coupled with long pulse delay times revealed only a weak peak for the carbonyl carbons and the CH carbons of the succinic anhydride moiety were unresolved. In order to investigate the stereochemistry of PODMA, knowledge regarding the succinic anhydride backbone carbons was required. PODMA was prepared using MA doped with $^{13}$C MA (95:5 wt/wt) to increase the concentration of $^{13}$C carbon on the backbone. Figure 42 shows the $^{13}$C NMR spectrum for PODMA, with the DEPT analysis inserted. The spectra revealed two broad peaks due to the succinic carbons. (45 ppm and 49 ppm). These peaks were broad singlets and represent only the trans stereochemical environment. There were no signals due to the corresponding cis environment†. The lack of the cis isomer is in contrast to similar MA copolymers with shorter α olefin comonomers that do contain a small amount of the cis isomer$^{68}$.

4.3.4.2 MOLECULAR MODELLING OF PODMA

In order to support the spectroscopic evidence of a 100% trans copolymer, molecular models were constructed for both the hypothetical cis and trans isomers. The structures were generated by CS-ChemOffice using Allinger's MM2 force-field followed by MOPAC refinement using the AM1 Hamiltonian, as described in Section 3.6.5. The resulting models are visualised in WebLab Viewer (Figure 43 and Figure 44). It is clear that the trans stereochemical environment is more sterically favoured over the cis. The cis configuration forces the long alkane side chains close together, while the trans

† cis succinic carbons observed for copolymers of propene and MA at 40.5ppm$^{68}$

128
structure provides a more ordered domain for the alkane branches. The steric factors are, therefore, considered to be the most important parameters in the formation of a 100% trans PODMA copolymer.
Figure 42 $^{13}$C NMR and DEPT spectra of $^{13}$C labelled PODMA (sample MCD73).
Figure 43 Trans molecular models for PODMA.
Figure 44 Cis molecular models for PODMA.
4.3.5 END GROUP STRUCTURE AND INITIATION MECHANISM

The structure of the end groups of polymer chains can provide important information regarding the reaction mechanism. The structure of the end groups can be determined by use of $^1$H NMR spectra, this task being simplified when an initiator with easily identifiable groups in the $^1$H NMR spectrum, such as BPO, is used. Modern predictive chemical software, such as Chem Draw $^1$H NMR now allows the $^1$H NMR spectra of the conceivable end group structures to be viewed without the need to synthesise the model compounds. This approach has been used to generate the appropriate end group spectra, an example of which is presented in Figure 47. The predicted spectra were then compared to the experimentally obtained $^1$H NMR spectra for the copolymer.

PODMA and octene-MA copolymers were prepared with BPO as the radical initiator. The shorter $\alpha$ olefin was used as it was considered that an improvement in the resolution of the spectra might be realised; however, C$_8$ was the shortest $\alpha$ olefin that still allowed reaction temperatures of 100°C to be used.

BPO is known to undergo a two-stage decomposition process (Section 2.1.1). Initially the peroxide bond is broken to form the benzoyloxy radical. This can further decarboxylate to form the phenyl radical and evolve CO$_2$. The two possible radical species can attack either MA monomer or $\alpha$ olefin monomer to initiate copolymerisation. Figure 46 shows the four possible initiation mechanisms with the corresponding end group structures. The $^1$H NMR spectrum of octene-alt-MA is illustrated in Figure 45. The shift at 7.9 ppm represents the aromatic protons adjacent to the benzoyloxy group. Comparison of the integral of those protons with the remaining aromatic protons between 7.1 ppm and 7.6 ppm indicates that the benzoyloxy radical is responsible for the majority of initiation with little or no contribution from the phenyl radical. The addition of the initiating radical is thought to be extremely rapid, and this efficient reaction may dominate over the formation of the phenyl radical. The two broad shifts between 4.1 ppm and 4.5 ppm appear to show a preference for the addition of the benzoyloxy radical to the $\alpha$ olefin. A smaller proportion of the end groups are due to the addition of the benzoyloxy radical to MA evidenced by two broad shifts at 5.4 ppm and 5.6 ppm. The chemical shifts assigned to the end group functionality in the copolymer
do not exactly match the predicted values. The restricted movement of the copolymer chains compared to the small molecules on which the predictions are based is responsible. Peak broadening and changes in chemical shift lead to error in end group determination and this is appreciated, though not calculated, in the results presented. The end group structures can be quantified by comparison of the integrals of the aromatic protons with the protons due to the primary monomer unit in the chain. The results for a selection of octene-alt MA copolymers and PODMA are collected in Table 14.
Chapter 4: Results and discussion

Figure 45 $^1$H NMR for Octene-alt-MA illustrating benzoyloxy end groups
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Olefin</th>
<th>Mₙ (g mol⁻¹) PS equivalents</th>
<th>Total end groups per chain</th>
<th>Mₙ (g mol⁻¹) calculated relative to 1 end group per chain</th>
<th>Benzoyloxy Olefin %</th>
<th>Benzoyloxy MA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD75</td>
<td>Octene</td>
<td>7,600</td>
<td>1.1</td>
<td>6,800</td>
<td>69</td>
<td>31</td>
</tr>
<tr>
<td>MCD76</td>
<td>Octene</td>
<td>5,900</td>
<td>1.4</td>
<td>4,200</td>
<td>64</td>
<td>36</td>
</tr>
<tr>
<td>MCD77</td>
<td>Octene</td>
<td>3,500</td>
<td>1.6</td>
<td>2,200</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>MCD79</td>
<td>Octadecene</td>
<td>30,000§</td>
<td>0.45</td>
<td>67,300</td>
<td>64</td>
<td>36</td>
</tr>
<tr>
<td>MCD80</td>
<td>Octadecene</td>
<td>4,100</td>
<td>0.99</td>
<td>4,100</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 14 End group and initiation data for octene MA copolymers and PODMA.

Approximately 33% of the initiation is brought about by benzoyloxy radical addition to MA while the dominant initiation mechanism involves the attack of the benzoyloxy radical on the α olefin. The benzoyloxy radical is an acceptor radical and therefore preferential attack of OD would be expected. This is supported by the finding of Bevington and Johnson that St is 50 times more reactive towards the benzoyloxy radical than MA. As OD is a weaker donor monomer compared to St the observation that OD is 2 times more reactive towards the benzoyloxy radical is reasonable.

---

§ Mₙ(app) = 30,000 g mol⁻¹, Mₙ(true) = 60,000 g mol⁻¹ by PODMA SEC calibration
Figure 46 Initiation structure models for octene MA copolymers with predicted $^1$H NMR shifts.
Figure 47 Predicted $^1$H NMR spectrum for benzoyloxy addition to MA.
The total end groups per chain were calculated by comparing the integrals due to the aromatic protons of the benzoyloxy radical with the CH₃ protons of the olefin. Samples MCD75 and MCD80 have one end group per chain. This suggests termination by disproportionation; however, the ¹H NMR spectra of the pure copolymers did not indicate any unsaturation at the chain ends. Sample MCD79 has an apparent reduction in end group concentration. This result is not accurate due to the high molar mass of the sample. An apparent \( M_n \) of 30,000 g mol\(^{-1}\) falls outside the region where a PS calibration is valid (Section 4.2.2) and the true \( M_n \) is double the value reported above. Use of the correct DP results in one end group per chain for PODMA of high molar mass as well as low molar mass. Samples MCD76 and MCD77 both indicate more than one end group per chain. Both samples were prepared with initiator concentrations of 8 mol\% wrt. MA added at the start of the reaction. The copolymers also show a lack of unsaturated chain ends suggesting that chain transfer still operates. The high initiator concentration leading to bimolecular combination would account for the increase in end group concentration. Recalculation of copolymer molar masses based on one initiator end group was carried out. The molar masses are similar to the values obtained by SEC** and confirm the validity of the method. Quantification of the termination mechanism is difficult due to the error of the total end group calculations as a consequence of broad, weak, NMR peaks. However, the results support the finding in Section 4.1.3 that significant chain transfer to the monomer accounts for majority of chain formation events, especially in PODMA and as chain transfer to OD is degradative, the allylic stabilised radical is unable to reinitiate copolymerisation. When higher initiator concentrations were used, a contribution from bimolecular combination was observed.

4.3.6 SUMMARY

Structural elucidation of PODMA and related copolymers was achieved by combining spectroscopic techniques with modern computational chemistry methods. PODMA comprises a sequence of strictly alternating MAOD units exclusively in the trans conformation. When BPO is used, the initiation route is via a benzoyloxy radical.

** The calculated molar mass of sample MCD79 corresponds to the molar mass obtained by SEC when the calibration based on PODMA is used.
Chapter 4: Results and discussion

with preferential attack of the \( \alpha \) olefin monomer. High molar mass PODMA is not formed due to degradative chain transfer accounting for the majority of chain formation events that results in PODMA comprising one initiator derived end group and one saturated end group.
4.4 OPTIMISATION AND SCALE UP OF PODMA SYNTHESIS

4.4.1 HIGH CONVERSION OF OD VIA THE ENE REACTION

The ene reaction was recognised by Alder et al.\textsuperscript{121} and the reaction is often known as the \textit{Alder ene} reaction due to his discovery. The ene reaction involves the reaction of an olefin with an allylic hydrogen atom (ene) with another olefin (enophile). A new bond is formed between the two unsaturated carbons and the allylic hydrogen is transferred to the enophile through a cyclic transition state. The mechanism of the ene reaction has been debated but a cyclic mechanism involving a four centre concerted process\textsuperscript{122} as shown in Scheme 9 has gained most favour over a radical mechanism.

\[
\text{[Diagram showing the ene reaction]} 
\]

\textit{Scheme 9 Thermal ene reaction to form ODSA.}

The entropy of activation for $\alpha$-olefins with MA of $-126.9$ J/deg mol has been calculated\textsuperscript{123}. This very low entropy is an indication of an organised transition state and the value is similar to the concerted Diels Alder reaction again lending weight to the concerted mechanism.

The thermal ene reaction requires temperatures as high as $200^\circ$C when no catalyst is used. In order to increase the consumption of OD in PODMA synthesis, the ene reaction can be carried out post-polymerisation. There are three benefits from this procedure. Firstly, the reaction mixture at $100^\circ$C has increased viscosity due to the formation of PODMA, especially in the bulk. The increase in temperature allows the reaction to be maintained in the molten state. Secondly, the reduction in viscosity and increase in temperature facilitates the consumption of any unreacted initiator species that may have been trapped in the matrix. Lastly and most importantly, the ene reaction will force the conversion of remaining comonomers to ODSA. The presence of OD in a
finished dispersant is particularly unfavourable due to its decomposition under a high temperature, high shear environment. This contributes to sludge formation and therefore requires a higher concentration of dispersant to be employed.

4.4.2 LARGE SCALE PODMA SYNTHESIS

Scale up synthesis of PODMA was carried out as described in Section 3.3.2. In order to further optimise the synthesis for industrial use, a number of variables were investigated. These included a new C$_{16}$/C$_{18}$ olefin supplied by BP, the initiator aliquot concentration and the aliquot addition time. An approach using matrix statistics was employed. The matrix used for PODMA synthesis with AIBN as initiator is shown in Figure 48.

![Figure 48 AIBN matrix for PODMA synthesis.](image)

The results for the AIBN matrix are collected in Table 15. The molar masses of PODMA were similar to those gained in previous small-scale copolymerisations (Table 4 and Table 8). Reducing the initiator aliquot interval from 60 min to 30 min lowered the molar mass, a likely consequence of an increase in total initiator concentration. PODMA synthesis with the BP C$_{16}$/C$_{18}$ olefin resulted in similar molar mass
characteristics; however, the conversions were lower. Reducing the initiator concentration from 0.5 mol% wrt MA to 0.1mol% wrt MA did not result in the expected molar mass increase but did reduce the conversion. The matrix of reactions allowed optimum conditions for the preparation of PODMA to be established. These were found to be Aldrich C$_{18}$ octadecene, with 6 aliquots of AIBN of concentration 0.5 mol% wrt MA at 60 min intervals.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>α olefin</th>
<th>AIBN aliquot concentration (mol % MA)</th>
<th>Aliquot addition interval (mins)</th>
<th>Fractional conversion</th>
<th>SEC molar mass</th>
<th>PDI (M_w (app) / M_n (app))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M_n(app)</td>
<td>M_n(true)</td>
</tr>
<tr>
<td>MCD132</td>
<td>Aldrich C_{18}</td>
<td>0.5 x 6</td>
<td>60</td>
<td>0.98</td>
<td>15,200</td>
<td>38,900</td>
</tr>
<tr>
<td>MCD135</td>
<td>BP C_{16}/C_{18}</td>
<td>0.5 x 6</td>
<td>60</td>
<td>0.74</td>
<td>15,400</td>
<td>39,400</td>
</tr>
<tr>
<td>MCD133</td>
<td>Aldrich C_{18}</td>
<td>0.5 x 6</td>
<td>30</td>
<td>0.93</td>
<td>10,100</td>
<td>-</td>
</tr>
<tr>
<td>MCD134</td>
<td>BP C_{16}/C_{18}</td>
<td>0.5 x 6</td>
<td>30</td>
<td>0.53</td>
<td>18,000</td>
<td>46,200</td>
</tr>
<tr>
<td>MCD139</td>
<td>Aldrich C_{18}</td>
<td>0.1 x 6</td>
<td>60</td>
<td>0.84</td>
<td>18,000</td>
<td>46,200</td>
</tr>
<tr>
<td>MCD137</td>
<td>BP C_{16}/C_{18}</td>
<td>0.1 x 6</td>
<td>60</td>
<td>0.74</td>
<td>11,700</td>
<td>29,800</td>
</tr>
</tbody>
</table>

Table 15 Matrix results for PODMA synthesis with AIBN as initiator.
### Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>α olefin</th>
<th>BPO aliquot concentration (mol % MA)</th>
<th>Aliquot addition interval (mins)</th>
<th>Fractional conversion</th>
<th>SEC molar mass</th>
<th>PDI (M&lt;sub&gt;w&lt;/sub&gt; (app) / M&lt;sub&gt;n&lt;/sub&gt; (app))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M&lt;sub&gt;n&lt;/sub&gt;(app)</td>
<td>M&lt;sub&gt;n&lt;/sub&gt;(true)</td>
</tr>
<tr>
<td>MCD141</td>
<td>Aldrich C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>0.5 x 2</td>
<td>60</td>
<td>0.96</td>
<td>10,300</td>
<td>-</td>
</tr>
<tr>
<td>MCD143</td>
<td>Aldrich C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>0.1 x 5</td>
<td>60</td>
<td>0.93</td>
<td>16,300</td>
<td>41,800</td>
</tr>
<tr>
<td>MCD145</td>
<td>Aldrich C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>-</td>
<td>-</td>
<td>0.91</td>
<td>12,800</td>
<td>32,700</td>
</tr>
<tr>
<td>MCD147</td>
<td>Aldrich C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>0.1 x 5</td>
<td>60</td>
<td>0.97</td>
<td>13,900</td>
<td>35,500</td>
</tr>
<tr>
<td>MCD152</td>
<td>Chevron Phillips C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>0.1 x 5</td>
<td>60</td>
<td>0.93</td>
<td>11,500</td>
<td>29,300</td>
</tr>
<tr>
<td>MCD153</td>
<td>Chevron Phillips C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>0.1 x 5</td>
<td>60</td>
<td>0.99</td>
<td>20,400</td>
<td>52,500</td>
</tr>
<tr>
<td>MCD154</td>
<td>Chevron Phillips C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>0.1 x 5</td>
<td>60</td>
<td>0.91</td>
<td>13,200</td>
<td>33,700</td>
</tr>
</tbody>
</table>

*Table 16 Results for PODMA synthesis with BPO as initiator.*
Chapter 4: Results and discussion

The use of AIBN as an initiator for large-scale concentrated polymerisations is unfavourable due to production plant safety issues; however, peroxide initiators are considered acceptable. BPO with its similar half-life to AIBN was chosen as the replacement. In addition, the \( \alpha \) olefin was again changed to an OD supplied by Chevron/Phillips. This was the proposed material for further scale-up as a large batch had been obtained. Further preparations of PODMA were carried out, initially using the established optimised conditions and the results are collected in Table 16. The reaction for MCD141 was violent and 'ran away' with an exotherm of >50°C. Only two aliquots of BPO were added and the reaction was stopped. Subsequently, the concentrations of each aliquot were reduced from 0.5mol% wrt MA to 0.1mol% wrt MA. Molar masses (\( M_a \) (app)) ranged from 10,000 g mol\(^{-1}\) to 20,000 g mol\(^{-1}\), which provided some manoeuvrability with regard to reaction conditions in order to provide a final 'pilot plant friendly' procedure. The fractional conversions were >0.9, which is acceptable for scale up. MCD153 was carried out with an increase in reaction volume from 1 litre to 3 litres. An uncontroIlable 40°C exotherm was observed. A change in reaction characteristics on scale up is often due to the reduced surface area to volume ratio of the reactants compared to the vessel. Heat dissipation is less efficient and exotherms and hotspots are common. Bulk reactions have been used successfully to provide high molar mass PODMA by virtue of the gel effect. Bulk reactions, however, are not amenable to large-scale preparations of PODMA. Xylene has previously been used as a suitable polymerisation solvent. The use of a solvent would impact negatively on molar mass so dilution was kept to a minimum of 33wt%. Reactions on both the 1-litre and 3-litre scale proceeded smoothly with limited exotherms indicating that heat dissipation had been improved. As predicted a reduction in molar mass was observed (\( M_a \) (app) = 13,200 g mol\(^{-1}\) for MCD154).

4.4.3 QUANTITATIVE SEC DECONVOLUTION FOR PODMA

SEC analysis of PODMA produced on a large scale provided data on both molar mass and product purity. PODMA prepared at Hazelwood was not purified in the rigorous manner of the material synthesised on a small scale at Loughborough. The quantity of copolymer produced made repeated precipitations unreasonable. Residual MA was removed from the reaction by vacuum stripping but removal of OD was very
difficult. In addition, ODSA was present as a low molar mass side product due to the thermal ene reaction carried out post copolymerisation. Examination of SEC chromatograms for PODMA revealed that OD and ODSA were visible and well resolved (Figure 49). Spiking PODMA with authentic OD and ODSA confirmed that the observed peaks were due to the low molar mass species.

Calibrations of peak area against known concentrations of impurity were constructed as described in Section 3.6.3.4. Use of Equation 65 allowed the PODMA crude mixture to be deconvoluted into the mass composition of copolymer, OD and ODSA. The results collected in Table 17 indicate the presence of ODSA in all the reactions where the ene step was carried out. The range of ODSA concentrations varied from 1.5-10 wt%. MCD153 and MCD154 were not subjected to the thermal ene reaction and the results for ODSA composition reflect this. MCD158.2 was prepared using xylene as a solvent so the ene reaction could not be carried out due to the high temperatures required for succination. A sample of MCD158.2 was however stripped of xylene and subjected to the ene reaction in the bulk. An increase in ODSA content from 0.5 wt% (sample MCD153) to 2.5 wt% (sample MCD158.2) provides evidence for the conversion of some remaining OD to ODSA. All the samples prepared still contain significant quantities of OD, illustrating the problem of achieving complete conversion in the synthesis of PODMA.
Figure 49 SEC chromatogram for large scale PODMA showing ODSA side product and OD impurity (sample MCD145).
## Chapter 4: Results and Discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass PODMA (g)</th>
<th>Concentration (g L(^{-1}))</th>
<th>Mass injected (g 10(^{-4}))</th>
<th>Peak area OD</th>
<th>Mass OD (g 10(^{-5}))</th>
<th>Mass % OD</th>
<th>Peak area ODSA</th>
<th>Mass ODSA (g 10(^{-5}))</th>
<th>Mass % ODSA</th>
<th>Mass % PODMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD131</td>
<td>0.0268</td>
<td>5.36</td>
<td>2.68</td>
<td>18640</td>
<td>4.30</td>
<td>16.1</td>
<td>4782</td>
<td>0.78</td>
<td>2.9</td>
<td>81.0</td>
</tr>
<tr>
<td>MCD134</td>
<td>0.0221</td>
<td>4.42</td>
<td>2.21</td>
<td>14950</td>
<td>3.45</td>
<td>15.6</td>
<td>5561</td>
<td>0.91</td>
<td>4.1</td>
<td>80.3</td>
</tr>
<tr>
<td>MCD135</td>
<td>0.0267</td>
<td>5.34</td>
<td>2.67</td>
<td>8002</td>
<td>1.85</td>
<td>6.9</td>
<td>8045</td>
<td>1.31</td>
<td>4.9</td>
<td>88.2</td>
</tr>
<tr>
<td>MCD143</td>
<td>0.0215</td>
<td>4.30</td>
<td>2.15</td>
<td>9756</td>
<td>2.25</td>
<td>10.5</td>
<td>1696</td>
<td>0.28</td>
<td>1.3</td>
<td>88.2</td>
</tr>
<tr>
<td>MCD145</td>
<td>0.0190</td>
<td>3.80</td>
<td>1.90</td>
<td>12783</td>
<td>2.95</td>
<td>15.5</td>
<td>10697</td>
<td>1.74</td>
<td>9.2</td>
<td>75.3</td>
</tr>
<tr>
<td>MCD153</td>
<td>0.0171</td>
<td>3.42</td>
<td>1.71</td>
<td>11052</td>
<td>2.55</td>
<td>14.9</td>
<td>482</td>
<td>0.08</td>
<td>0.5</td>
<td>84.6</td>
</tr>
<tr>
<td>MCD154</td>
<td>0.0197</td>
<td>3.94</td>
<td>1.97</td>
<td>14326</td>
<td>3.31</td>
<td>16.8</td>
<td>192</td>
<td>0.03</td>
<td>0.2</td>
<td>83.1</td>
</tr>
<tr>
<td>MCD158.2</td>
<td>0.0192</td>
<td>3.84</td>
<td>1.92</td>
<td>14872</td>
<td>3.43</td>
<td>17.9</td>
<td>2984</td>
<td>0.49</td>
<td>2.5</td>
<td>79.6</td>
</tr>
</tbody>
</table>

*Table 17 SEC deconvolution data for PODMA.*
4.4.4 PILOT PLANT PODMA SYNTHESIS

PODMA was prepared using the Hazelwood pilot plant test rig. The pilot plant is built in such a way that reactions carried out on a lab scale can be scaled up without the need to modify reaction procedures. To this end, the reactor is a batch type reactor with the option of material addition through 2 pumps, operating at different rates. Stirring is achieved with an overhead mechanical stirrer. Both vacuum, for distillation and stripping, and nitrogen for deoxygenation can be applied to the reactor. Product is drained from the reactor base via a base valve, which allows viscous material to be drained while hot to containers for storage.

The preparation of PODMA was carried out as described in the Section 3.3.4. The results for the preparation are collected in Table 18 and compared to the commercially available sample of high molar mass supplied by Aldrich.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fractional conversion</th>
<th>PODMA (wt %)</th>
<th>OD (%</th>
<th>ODSA (wt %)</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$(app))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrich</td>
<td>-</td>
<td>94.9</td>
<td>3.9</td>
<td>1.2</td>
<td>15,500</td>
<td>28,800</td>
<td>1.90</td>
</tr>
<tr>
<td>MCD166</td>
<td>0.97</td>
<td>95.9</td>
<td>4.1</td>
<td>0.1</td>
<td>10,500</td>
<td>22,100</td>
<td>2.10</td>
</tr>
<tr>
<td>Pilot plant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 18 Pilot plant data for PODMA.

The reaction was carried out over two days. On addition of the first aliquot of BPO, an exotherm of 15°C was observed once the reactor had reached 100°C. This exotherm persisted for 30 minutes before the temperature slowly dropped to 105°C. Each subsequent addition of BPO caused smaller exotherms of 2-6°C. The final addition of BPO resulted in only a 1°C exotherm, which indicated that the reaction had proceeded to a high conversion with the consumption of the majority of monomers. A sample was taken from the reactor before the addition of the diluent oil. This sample
was reacted in the lab in an analogous manner to the pilot plant to provide a pure PODMA sample, free from oil in order to carry out molar mass and structural analysis.

The molar mass was lower than predicted. This was due to carrying out the reaction in xylene. It has already been shown that monomer concentration has the greatest effect on molar mass (Section 4.1.5). The reaction exhibited an exotherm of 15°C, so although reducing the volume of the solvent would lead to higher molecular weights the risk of a runaway reaction would be increased. The conversion of comonomers to the product was very high, indicating that the reaction was efficient when scaled up. The deconvolution of the final product by SEC also showed that the majority of the starting materials were converted to PODMA with a small amount of ODSA being formed during the ene phase. A small amount of OD remained in the product. The composition of the pilot plant reaction was compared to the high molar mass commercial product. Both samples indicated almost identical compositions.

The pilot plant sample, free from oil, was analysed by $^1$H NMR and FTIR and identical spectra to previous small-scale samples were obtained that were correct for a 1:1 alternating copolymer (Figure 37 and Figure 41).

4.4.5 SUMMARY

The preparation of PODMA has been successfully converted from a small-scale academic procedure to an industrially viable synthesis. Important information concerning chain reaction kinetics gained from small-scale copolymerisations (Section 4.1) has allowed the choice of suitable reaction conditions for industrial scale up. Further optimisation was carried out by investigating a number of OD monomers along with subtle changes to reaction conditions, including the post succination of OD to form ODSA, such that PODMA was prepared to high conversion with a desirable molar mass. SEC analysis was further developed to provide a method for deconvolution of the mixed products obtained, in order to accurately determine PODMA purity. Thus SEC can be used to determine true molar mass and product purity in one analysis. PODMA prepared by pilot plant reaction was of lower molar mass compared to the commercial
sample available from Aldrich; however, the purity and structural features were identical.
Chapter 4: Results and discussion

4.5 ATOM TRANSFER RADICAL POLYMERISATION ATRP

ATRP, developed by Matyaszewski et al\(^87\), is a CRP method that allows the synthesis of functional polymers and copolymers by use of alkyl halide initiators with a transition metal halide complexed with a nitrogen containing ligand. It was reported that MA cannot be copolymerised by ATRP\(^87\); however attempts to produce MA containing copolymers via ATRP were made.

Initial work focused on method evaluation. St was polymerised using the CuBr/BPY catalyst system. Various aromatic halide initiators were used including \(\alpha,\alpha\)
dibromo xylene, which acts as a difunctional initiator. The results for ATRP of St are collected in Table 19. Reaction conditions are also provided.

PS of low molar mass was prepared with the three investigated initiators producing polymer of low PDI. Polymerisation temperature was important with greater control and narrower MMD's gained at 110°C compared to 130°C, this being supported by lower PDI values. Reducing the temperature did however decrease the degree of polymerisation and thus lower molar mass PS was produced. Sample MCD90 illustrated the evolution of molar mass with increasing conversion though a linear plot of the data does not pass through the origin. This indicated poor control during the early stages of polymerisation, an effect that is attributed to initiator efficiency.

The ATRP methodology was extended to copolymerisation. Previous workers have successfully copolymerised St and N substituted maleimides\(^124,125\). This work was repeated and extended to include homopolymerisation of the maleimide derivatives, copolymerisation with octene and an attempt to prepare StMA. The results for the ATRP reactions are collected in Table 20. Each reaction used the same catalytic system as the above PS synthesis with 1PEBr used as initiator and anisole as solvent at 110°C.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Initiator</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD89</td>
<td>Anisole</td>
<td>100</td>
<td>1PEBr</td>
<td>0.12</td>
<td>1,800</td>
<td>2,600</td>
<td>1.45</td>
</tr>
<tr>
<td>MCD90.1</td>
<td>Anisole</td>
<td>130</td>
<td>1PEBr</td>
<td>0.22</td>
<td>1,850</td>
<td>2,620</td>
<td>1.40</td>
</tr>
<tr>
<td>MCD90.2</td>
<td>Anisole</td>
<td>130</td>
<td>1PEBr</td>
<td>0.43</td>
<td>2,850</td>
<td>3,740</td>
<td>1.30</td>
</tr>
<tr>
<td>MCD90.3</td>
<td>Anisole</td>
<td>130</td>
<td>1PEBr</td>
<td>0.58</td>
<td>3,280</td>
<td>4,300</td>
<td>1.30</td>
</tr>
<tr>
<td>MCD90.4</td>
<td>Anisole</td>
<td>130</td>
<td>1PEBr</td>
<td>0.59</td>
<td>3,210</td>
<td>4,330</td>
<td>1.35</td>
</tr>
<tr>
<td>MCD94.3</td>
<td>Anisole</td>
<td>110</td>
<td>1PEBr</td>
<td>0.04</td>
<td>1,020</td>
<td>1,100</td>
<td>1.08</td>
</tr>
<tr>
<td>MCD94.4</td>
<td>Anisole</td>
<td>110</td>
<td>1PEBr</td>
<td>0.13</td>
<td>1,280</td>
<td>1,400</td>
<td>1.10</td>
</tr>
<tr>
<td>MCD95</td>
<td>Anisole</td>
<td>130</td>
<td>1PEBr</td>
<td>0.57</td>
<td>2,490</td>
<td>2,790</td>
<td>1.12</td>
</tr>
<tr>
<td>MCD96</td>
<td>Anisole</td>
<td>110</td>
<td>α, α dibromo xylene</td>
<td>0.99</td>
<td>3,070</td>
<td>3,480</td>
<td>1.13</td>
</tr>
<tr>
<td>MCD97</td>
<td>Bulk</td>
<td>110</td>
<td>α, α dibromo xylene</td>
<td>0.65</td>
<td>3,110</td>
<td>3,490</td>
<td>1.12</td>
</tr>
<tr>
<td>MCD119</td>
<td>Toluene</td>
<td>110</td>
<td>Benzyl bromide</td>
<td>0.18</td>
<td>2,240</td>
<td>2,960</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table 19 St polymerisation by ATRP (Initiator:CuBr:BPY = 1:1:3, St = 3.5 mol dm$^{-3}$, initiator = 0.1 mol dm$^{-3}$).
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer 1</th>
<th>Monomer 2</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD99</td>
<td>NCMI</td>
<td>St</td>
<td>0.58</td>
<td>3,930</td>
<td>4,620</td>
<td>1.18</td>
</tr>
<tr>
<td>MCD100</td>
<td>NPhMI</td>
<td>St</td>
<td>0.97</td>
<td>4,560</td>
<td>6,040</td>
<td>1.33</td>
</tr>
<tr>
<td>MCD101</td>
<td>MI</td>
<td>St</td>
<td>Fail</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD102</td>
<td>MA</td>
<td>St</td>
<td>Fail</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD104</td>
<td>NPhMI</td>
<td>-</td>
<td>Fail</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD94.3</td>
<td>MI</td>
<td>-</td>
<td>Fail</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD94.4</td>
<td>NPhMI</td>
<td>Octene</td>
<td>Trace</td>
<td>1,840</td>
<td>2,610</td>
<td>1.42</td>
</tr>
<tr>
<td>MCD108*</td>
<td>NPhMI</td>
<td>Octene</td>
<td>Trace</td>
<td>1,970</td>
<td>2,812</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Table 20 ATRP copolymerisation data at 110 °C ($M_1:M_2 = 50:50$).

*Reaction at 100 °C
Chapter 4: Results and discussion

Copolymerisation of NCMI and NPhMI with St resulted in low molar mass products with low PDI. Copolymerisation of MI with St was not successful. The imide is not substituted and may compete with the ligand for complexation with the copper catalyst. Use of a polydentate ligand with a stronger affinity to form a complex with the copper catalyst may improve the copolymerisation.

Copolymerisation of MA with St was also unsuccessful. A black insoluble solid was quickly formed in the copolymerisation. Though no further analysis of this solid was carried out, it was anticipated that the precipitate may be a copper carboxylate as noted in Section 2.4.1.2. It is apparent that the presence of MA completely destroys the catalytic system as no PS was formed in the reaction.

Copolymerisation of NCMI and NPhMI with octene resulted in very low conversions. The products were brown in colour and may have contained copper as impurity. SEC analysis revealed that the copolymers were of low molar mass with PDI approaching 1.5 that indicates the copolymerisations were poorly controlled. Further structural evaluation was not carried out on these copolymers.

Homopolymerisation of NPhMI and MI by ATRP were fruitless. It has been noted that ATRP has been problematic for monomers that do not form radicals stabilised by inductive or resonance effects. This may be due to a low equilibrium constant in these systems.

The difficulties in using acidic monomers including MA have been discussed in Section 2.4.1.2. A further investigation was carried out into the use of MA containing backbones with ATRP initiators incorporated to test the remote influence of MA on graft ATRP. It was hoped that this approach would allow MA copolymers including PODMA to be further functionalised. For comparison, maleimide and St backbones were also prepared. Chloromethyl styrene (CMS) is a bifunctional monomer. The St functionality allows it to be easily polymerised or copolymerised while the benzyl chloride functionality can be used as an ATRP initiator. Copolymers and terpolymers containing low concentrations of CMS were prepared by conventional radical polymerisation in
The backbone consisting of St and CMS units (sample MCD172) was effective in ATRP graft copolymerisation of MMA. The molar mass of the copolymer increased from \( (M_n = 5,900 \text{ g mol}^{-1}) \) to \( (M_n = 16,900 \text{ g mol}^{-1}) \) demonstrating that further polymerisation had taken place, which was also supported by the increase in mass balance. Figure 50 presents \(^1\text{H}\) NMR spectra for both the backbone and graft copolymers. The presence of the CMS functional groups (A 2H, \( \text{CH}_2\text{Cl} \), broad 4.5 ppm) is clear for the backbone polymer. The peak is however absent in the graft copolymer indicating total consumption of the ATRP initiator. Peaks due to PMMA are however observed (B 3H, \( \text{OCH}_3 \), broad, 3.6 ppm), (3H \( \text{CH}_3 \), broad, 0.9 ppm) and (2H, \( \text{CH}_2 \), broad 1.1 ppm). Thermal polymerisation of MMA at 110°C, without benzyl chloride, but otherwise under ATRP conditions did not result in polymer formation. This finding provides further evidence for the successful grafting of MMA onto MCD172 via an ATRP mechanism. Grafting onto backbones containing substituted maleimide moieties was partially successful, although conversions were low. \(^1\text{H}\) NMR spectroscopy did indicate the presence of PMMA attached to the backbone as shown in Figure 51.

ATRP grafting onto backbones containing succinic anhydride units (MCD176, StMA) and (MCD179, PODMA) failed. Black insoluble material was formed early in the reaction, analogous to copolymerisation with MA, and only starting material was collected. The fact that graft ATRP was unsuccessful with saturated succinic anhydride present does shed further light on the failure of the technique. Protonation of the ligand from the copolymer is unlikely, as the abstraction of hydrogen from the backbone would require more energy than the breaking of the benzyl chloride bond. The reason for failure then most probably lies with copper carboxylate formation due to reaction with MA.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Monomer 1 (mol fraction)</th>
<th>Monomer 2 (mol fraction)</th>
<th>CMS (mol fraction)</th>
<th>Fractional conversion</th>
<th>$M_n$ (app) (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD172</td>
<td>St (0.9)</td>
<td>-</td>
<td>0.1</td>
<td>0.20</td>
<td>5,900</td>
<td>9,100</td>
<td>1.60</td>
</tr>
<tr>
<td>MCD176</td>
<td>St (0.45)</td>
<td>MA (0.5)</td>
<td>0.05</td>
<td>0.93</td>
<td>22,800</td>
<td>84,200</td>
<td>3.70</td>
</tr>
<tr>
<td>MCD179</td>
<td>OD (0.5)</td>
<td>MA (0.45)</td>
<td>0.05</td>
<td>0.67</td>
<td>10,400</td>
<td>20,000</td>
<td>1.92</td>
</tr>
<tr>
<td>MCD181</td>
<td>OD (0.5)</td>
<td>NPhMI (0.49)</td>
<td>0.01</td>
<td>0.62</td>
<td>5,800</td>
<td>13,700</td>
<td>2.38</td>
</tr>
<tr>
<td>MCD182</td>
<td>OD (0.5)</td>
<td>NCMI (0.49)</td>
<td>0.01</td>
<td>0.68</td>
<td>4,700</td>
<td>11,600</td>
<td>2.45</td>
</tr>
<tr>
<td>MCD183</td>
<td>St (0.5)</td>
<td>NPhMI (0.45)</td>
<td>0.05</td>
<td>0.95</td>
<td>38,800</td>
<td>128,400</td>
<td>3.31</td>
</tr>
<tr>
<td>MCD184</td>
<td>OD (0.5)</td>
<td>NPhMI (0.45)</td>
<td>0.05</td>
<td>0.56</td>
<td>8,300</td>
<td>23,500</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Table 21 Polymerisation with CMS; SEC and conversion data (Temp = 100 °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Backbone</th>
<th>CMS concentration (mol dm$^{-3}$)</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD177</td>
<td>MCD172</td>
<td>0.19</td>
<td>0.28</td>
<td>16,900</td>
<td>46,000</td>
<td>2.72</td>
</tr>
<tr>
<td>MCD178</td>
<td>MCD176</td>
<td>0.05</td>
<td>Fail</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD180</td>
<td>MCD179</td>
<td>0.05</td>
<td>Fail</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MCD185</td>
<td>MCD183</td>
<td>0.02</td>
<td>Trace</td>
<td>11,000</td>
<td>20,600</td>
<td>1.88</td>
</tr>
<tr>
<td>MCD186</td>
<td>MCD184</td>
<td>0.01</td>
<td>Trace</td>
<td>8,400</td>
<td>22,900</td>
<td>2.72</td>
</tr>
</tbody>
</table>

Table 22 Graft ATRP of MMA onto CMS containing backbones (Temp = 130 °C).
Figure 50 $^1$H NMR spectra for poly(Si-co-CMS) (MCD172 top) and poly(Si-co-CMS -graft-MMA) (MCD177 bottom)
Chapter 4: Results and discussion

Figure 51H NMR spectra for poly(St-co-NPMI-co-CMS) (MCD183 top) and poly(St-co-NPMI-co-CMS- graft-MMA) (MCD185 bottom)
In order to further investigate the reason behind the failure of MA to be copolymerised by ATRP, attempts to complex MA with CuCl were carried out. An excess of MA (0.176g, 2 mmol 4 equivalents) was mixed with CuCl (0.044g, 0.5 mmol, 1 equivalent) in a range of solvents including anisole (sample MCD365), toluene (sample MCD367), acetonitrile (sample MCD360) and methanol (sample MCD364). In each case the mixtures were heated to reflux or complete dissolution. On heating samples MCD365 and MCD360 a blue insoluble precipitate was formed that dropped out of solution. On heating MCD364 the heterogeneous green mixture formed a clear blue solution. This was allowed to cool slowly to 22°C overnight after which blue crystals were recovered. Single crystal x-ray crystallography was used to determine the crystal structure of the complex, which is presented in Figure 52. Comprehensive structural information regarding the crystal structure can be found in Appendix 2. The elevated temperatures required for dissolution of the starting materials resulted in the esterification of MA to form the methanol half ester (Scheme 10).

![Scheme 10 Methanol half esterification of MA.](image)

The carboxylic acid functionality of the half ester was responsible for the bonding to two copper atoms, which have been oxidised from Cu (I) to Cu (II). Each copper has square pyramidal geometry with longer axial bonds to two methanol molecules. Two free molecules of methanol were also present and these are responsible for the hydrogen bonding between complexes, leading to a honeycomb 2 dimensional structure. Though it is appreciated that ATRP to produce MA containing copolymers was carried out in organic solvents such as anisole, in which ring opening of MA is not facilitated. This structure does however support the finding that carboxylic acids can complex with copper\(^87\) and due to the excess of monomer compared to nitrogen containing ligand this reaction may be kinetically favourable providing that the bond strength of the complexed monomer and ligand are similar. The complex structure and extended arrays due to hydrogen bonding show that the copper catalyst has been deactivated toward the redox switching necessary for ATRP to be successful. It was
postulated that the 2 lone pairs associated with the anhydride oxygen of MA would also facilitate complexation of MA with CuCl. Reaction in anisole and acetonitrile resulted in a colour change from green to blue indicating a reaction. The precipitate was however insoluble in a variety of organic solvents and a single crystal was not obtained.

4.5 SUMMARY

The work presented verifies ATRP as a useful technique for formation of polymers and copolymers of narrow MMD. The difficulty of the technique with regard to MA has been confirmed, and this difficulty is not confined to polymerisation with MA as the monomer. In fact the presence of the anhydride functional group in the monomer or copolymer deactivates the catalytic system. In order to prepare MA copolymers of well-defined structure and narrow MMD, an alternative CRP method was required.
Figure 52 4:2 MA methanol half ester copper carboxylate complex.
4.6 RAFT COPOLYMERISATION TO FORM COPOLYMERS OF MA AND ST MONOMERS

RAFT polymerisation has proven to be a useful CRP technique for many monomers including acidic derivatives. The RAFT reagent used for initial copolymerisation of MA and St monomers was BDTB. BDTB was prepared by a Grignard reaction as outlined in Section 3.5.1. The mechanism is shown below.

St monomers were copolymerised with MA using BDTB as the RAFT mediator as detailed in Section 3.5.2. AIBN was used as the radical initiator at a concentration of 0.012 mol % wrt MA. BDTB was used at a concentration of 0.024 mol % wrt MA. A series of copolymerisations were performed in parallel for different periods of time in order to achieve differing conversions. The results for StMA, pMeStMA, pClStMA and pMeOStMA are collected in Table 23/Table 26. The molar mass-conversion plots, kinetic plots and SEC chromatograms follow each set of results.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (mins)</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>$M_n$ (SEC) (g mol$^{-1}$)</th>
<th>PDI ($M_n/M_w$ (SEC))</th>
<th>$M_n$ (Calc) (g mol$^{-1}$)</th>
<th>$[M]_0$ (mol dm$^{-3}$)</th>
<th>$[M]_f$ (mol dm$^{-3}$)</th>
<th>Ln ([M]$_0$/[M]$_f$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD236</td>
<td>60</td>
<td>0.67</td>
<td>0.22</td>
<td>11,100</td>
<td>1.30</td>
<td>4,000</td>
<td>3.0</td>
<td>2.35</td>
<td>0.25</td>
</tr>
<tr>
<td>MCD237</td>
<td>120</td>
<td>1.36</td>
<td>0.44</td>
<td>19,300</td>
<td>1.20</td>
<td>8,100</td>
<td>3.0</td>
<td>1.68</td>
<td>0.58</td>
</tr>
<tr>
<td>MCD238</td>
<td>240</td>
<td>2.16</td>
<td>0.70</td>
<td>27,400</td>
<td>1.19</td>
<td>12,900</td>
<td>3.0</td>
<td>0.90</td>
<td>1.21</td>
</tr>
<tr>
<td>MCD240</td>
<td>1040</td>
<td>2.99</td>
<td>0.97</td>
<td>33,500</td>
<td>1.27</td>
<td>17,800</td>
<td>3.0</td>
<td>0.09</td>
<td>3.49</td>
</tr>
</tbody>
</table>

Table 23 RAFT copolymerisation results for StMA at 60°C ($M_1:M_2 = 50:50$).

$M_n$ (Calc) from Equation 51
Figure 53 Molar mass and PDI data for SiMA ($M_1:M_2 = 50:50$) ($\bullet M_n$ (SEC), \textcolor{red}{PDI}, \textcolor{blue}{--- $M_n$ (Calc), \textcolor{green}{$M_n$(SEC)}-$M_n$(SEC intercept)).

Figure 54 RAFT copolymerisation kinetics for SiMA at 60°C ($M_1:M_2 = 50:50$) (Fractional conversion $\bullet$, $\ln[M_f]/[M]$, \textcolor{red}{}).
Figure 55 SEC chromatograms for StMA produced by RAFT copolymerisation in dioxane at 60 °C ($M_1:M_2 = 50:50$).
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time  (mins)</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>$M_n$ (SEC) (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$ (SEC))</th>
<th>$M_n$ (Calc) (g mol$^{-1}$)</th>
<th>$[M]_0$ (mol dm$^{-3}$)</th>
<th>$[M]_1$ (mol dm$^{-3}$)</th>
<th>Ln ($[M]_0/[M]_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD302</td>
<td>60</td>
<td>0.23</td>
<td>0.07</td>
<td>6,800</td>
<td>1.35</td>
<td>1,400</td>
<td>3.0</td>
<td>2.79</td>
<td>0.07</td>
</tr>
<tr>
<td>MCD303</td>
<td>120</td>
<td>1.04</td>
<td>0.32</td>
<td>12,700</td>
<td>1.30</td>
<td>6,400</td>
<td>3.0</td>
<td>2.04</td>
<td>0.39</td>
</tr>
<tr>
<td>MCD304</td>
<td>180</td>
<td>1.59</td>
<td>0.49</td>
<td>16,400</td>
<td>1.27</td>
<td>9,700</td>
<td>3.0</td>
<td>1.53</td>
<td>0.67</td>
</tr>
<tr>
<td>MCD306</td>
<td>439</td>
<td>2.60</td>
<td>0.80</td>
<td>21,800</td>
<td>1.25</td>
<td>15,900</td>
<td>3.0</td>
<td>0.59</td>
<td>1.62</td>
</tr>
<tr>
<td>MCD307</td>
<td>1218</td>
<td>2.94</td>
<td>0.91</td>
<td>26,000</td>
<td>1.26</td>
<td>18,000</td>
<td>3.0</td>
<td>0.28</td>
<td>2.38</td>
</tr>
</tbody>
</table>

Table 24 RAFT copolymerisation results for pMeStMA in dioxane at 60°C ($M_1:M_2 = 50:50$.)

$M_n$ (Calc) from Equation 51
Chapter 4: Results and discussion

Figure 56 Molar mass and PDI data for pMeSiMA ($M_1:M_2 = 50:50$) (○ $M_n$ (SEC), ■ PDI, --- $M_n$ (Calc) Δ $M_n$(SEC) - $M_n$(SEC intercept).

Figure 57 RAFT copolymerisation kinetics for pMeSiMA in dioxane at 60 °C ($M_1:M_2 = 50:50$) (Fractional conversion ○, $\ln[M_f]/[M_i]$ ■).
Chapter 4: Results and discussion

Figure 58 SEC chromatograms for pMeStMA produced by RAFT copolymerisation in dioxane at 60 °C ($M_1:M_2 = 50:50$).
## Chapter 4: Results and discussion

### Table 25 RAFT copolymerisation results for pClStMA in dioxane at 60 °C (M₁:M₂ = 50:50).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (mins)</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>Mₙ (SEC) (g mol⁻¹)</th>
<th>PDI (Mₙ/Mₚ (SEC))</th>
<th>Mₙ (Calc) (g mol⁻¹)</th>
<th>[M]₀ (mol dm⁻³)</th>
<th>[M]₁ (mol dm⁻³)</th>
<th>Ln ([M]₀/[M]₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD269</td>
<td>300</td>
<td>0.37</td>
<td>0.21</td>
<td>7,100</td>
<td>1.28</td>
<td>4,500</td>
<td>3.0</td>
<td>2.37</td>
<td>0.23</td>
</tr>
<tr>
<td>MCD279</td>
<td>279</td>
<td>0.97</td>
<td>0.27</td>
<td>8,300</td>
<td>1.26</td>
<td>5,900</td>
<td>3.0</td>
<td>2.18</td>
<td>0.31</td>
</tr>
<tr>
<td>MCD270</td>
<td>621</td>
<td>0.80</td>
<td>0.45</td>
<td>14,200</td>
<td>1.22</td>
<td>9,600</td>
<td>3.0</td>
<td>1.66</td>
<td>0.59</td>
</tr>
<tr>
<td>MCD266</td>
<td>1110</td>
<td>2.63</td>
<td>0.74</td>
<td>18,400</td>
<td>1.21</td>
<td>15,900</td>
<td>3.0</td>
<td>0.79</td>
<td>1.33</td>
</tr>
</tbody>
</table>

*Mₙ (Calc) from Equation 51*
**Chapter 4: Results and discussion**

![Figure 59 Molar mass and PDI data for pCISiMA (M1:M2 = 50:50) (●Mn (SEC), ▼PDI, --- Mn (Calc), □Mn(SEC)-Mn(SEC intercept)).

![Figure 60 RAFT copolymerisation kinetics for pCISiMA in dioxane at 60°C (M1:M2 = 50:50) (Fractional conversion ●, Ln[M]/[M1], ▼).](image-url)
Chapter 4: Results and discussion

Figure 61 SEC chromatograms for pClStMA produced by RAFT copolymerisation in dioxane at 60 °C (M1:M2 = 50:50).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (mins)</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>$M_n$ (SEC) (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$ (SEC))</th>
<th>$M_n$ (Calc) (g mol$^{-1}$)</th>
<th>$[M]_0$ (mol dm$^{-3}$)</th>
<th>$[M]_1$ (mol dm$^{-3}$)</th>
<th>Ln ($[M]_0/[M]_1$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD317</td>
<td>60</td>
<td>0.19</td>
<td>0.11</td>
<td>8,200</td>
<td>1.68</td>
<td>2,300</td>
<td>3.0</td>
<td>2.67</td>
<td>0.12</td>
</tr>
<tr>
<td>MCD319</td>
<td>90</td>
<td>0.44</td>
<td>0.25</td>
<td>10,600</td>
<td>1.60</td>
<td>5,300</td>
<td>3.0</td>
<td>2.24</td>
<td>0.29</td>
</tr>
<tr>
<td>MCD318</td>
<td>120</td>
<td>0.62</td>
<td>0.36</td>
<td>13,000</td>
<td>1.60</td>
<td>7,400</td>
<td>3.0</td>
<td>1.93</td>
<td>0.44</td>
</tr>
<tr>
<td>MCD320</td>
<td>120</td>
<td>0.70</td>
<td>0.40</td>
<td>15,100</td>
<td>1.43</td>
<td>8,400</td>
<td>3.0</td>
<td>1.79</td>
<td>0.51</td>
</tr>
<tr>
<td>MCD321</td>
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<td>1.02</td>
<td>0.59</td>
<td>19,000</td>
<td>1.47</td>
<td>14,900</td>
<td>3.0</td>
<td>1.24</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 26 RAFT copolymerisation results for pMeOSiMA in dioxane at 60 °C ($M_1:M_2 = 50:50$).

$M_n$ (Calc) from Equation 51
Figure 62 Molar mass and PDI data for pMeOSTMA ($M_1:M_2 = 50:50$) ($\bullet M_n$ (SEC), $\blacksquare$ PDI, --- $M_n$ (Calc), $\square M_n$(SEC)-$M_n$(SEC intercept)).

Figure 63 RAFT copolymerisation kinetics for pMeOSTMA in dioxane at 60 °C ($M_1:M_2 = 50:50$) (Fractional conversion $\bullet$, $\ln[M_f]/[M_i]$, $\blacksquare$).
Chapter 4: Results and discussion

Figure 64 SEC chromatograms for pMeOSTMA produced by RAFT copolymerisation in dioxane at 60°C (M1:M2 = 50:50.)
4.6.1 Evaluation of the Living Characteristics of Copolymers of MA and St Monomers Produced by RAFT

The success of a CRP technique depends on the satisfaction of a number of polymerisation criteria proposed by Quirk and Lee\textsuperscript{82}, and outlined in Section 2.4. Most of the criteria are common to living polymerisation. The term ‘living polymerisation’ has been used to describe a chain polymerisation in which chain breaking reactions are absent\textsuperscript{126}. As will be described, transfer and termination reactions are evident in ATRP and RAFT even though these methods can deliver well defined polymers. These systems should be termed CRP although the living character of these systems can be evaluated. A living polymerisation should proceed until all the monomer or monomers have been consumed. This is true of RAFT and can be confirmed by considering the quantitative copolymerisation of StMA (sample MCD240) and pMeStMA (sample MCD307). Further evaluation of this criterion can be found in Section 4.6.1.4.

4.6.1.1 Linear Increase in Molar Mass with Increasing Conversion

The criterion that molar mass increases lineally with conversion has been used extensively for CRP systems to determine their living character in the first instance. Molar masses measured by SEC were found to increase with increasing conversion for StMA (Figure 53), pMeStMA (Figure 56), pClStMA (Figure 59) and pMeOStMA (Figure 62). Linear regression of these data results in straight lines and therefore may indicate a degree of living character brought about by BDTB mediation. However, further examination of the molar mass conversion plots and comparison to the theoretical molar masses calculated by Equation 51 reveals that for all the systems studied the molar masses measured by SEC are greater than those predicted for the total consumption of BDTB. Reasons for the difference in molar mass may include error in molar mass measurement by SEC due to differences in hydrodynamic volume between PS and the copolymers subject to analysis, or loss of copolymerisation control due to inefficient fragmentation and transfer of BDTB.

Errors in molar mass measurement can be evaluated by considering StMA. Knowledge of the MH constants for both PS\textsuperscript{32} and StMA\textsuperscript{127} in THF allows the SEC
calibration for PS to be adjusted to a calibration valid for StMA. This new calibration can then be used to assess the difference in molar mass between the experimental and predicted values. The universal calibration (Equation 59) and the MH equation (Equation 57) can be rearranged to obtain Equation 69, which is a version of Equation 61.

$$\log M(\text{pStMA}) = \frac{1 + a(\text{PS})}{1 + a(p\text{StMA})} \log M(\text{PS}) + \frac{1}{1 + a(p\text{StMA})} \log \frac{K(\text{PS})}{K(p\text{StMA})}$$

Equation 69

The calibrations for both PS and StMA are presented in Figure 65. The difference in gradient is due to the $a$ value in the MH equation. Use of the adjusted calibration allowed the correct molar mass for StMA to be calculated. Table 27 compares the molar mass data from both the PS calibration and StMA calibration to the theoretical molar mass. For sample MCD236 there is a reduction in molar mass when the corrected StMA calibration is used. The linear calibration plots converge at approximately $M_n = 20,000$ g mol$^{-1}$ and so sample MCD237 has a similar molar mass irrespective of the calibration used. The reduction in molar mass for low molar mass samples brought about by using the correct calibration is not significant enough to account for the differences between the experimental and theoretical molar masses of StMA produced by RAFT polymerisation. It should be borne in mind that the above analysis used MH constants for PS and StMA dissolved in THF. The SEC analysis was carried out in THF/acetic acid (90:10 v/v); however, previous analysis for PODMA (Section 4.2.2) indicated that use of THF/acetic acid for PS only had a small effect on the MH constants $K = 1.16 \times 10^{-4}$ dL g$^{-1}$ (THF), $K = 1.52 \times 10^{-4}$ dL g$^{-1}$ (THF/acetic acid), $a = 0.72$ (THF), $a = 0.71$ (THF/acetic acid). The use therefore of MH constants based on THF rather than THF/acetic acid was not considered to invalidate the above conclusion that hydrodynamic volume differences do not account for the observed differences in molar mass in Table 23.
Examination of the molar mass conversion plots for StMA (Figure 53), pMeStMA (Figure 56), pClStMA (Figure 59) and pMeOStMA (Figure 62) all reveal positive intercepts on the molar mass axis by linear extrapolation to zero conversion. pMeStMA (Figure 56) exhibits an intercept of approximately 5000 g mol⁻¹. Providing the SEC analysis is reliable, this value may approximate to the molar mass of instantly formed copolymer by conventional radical copolymerisation, as initiation, propagation and termination all occur in a short period of time. Subtraction of the intercept molar mass from the experimental molar mass, results in data that corresponds to the theoretical molar mass values. Similar observations can be made with StMA, pClStMA and pMeOStMA. This qualitative analysis leads to the proposal that early in the copolymerisation RAFT mediation and conventional copolymerisation are in competition. Efforts to suppress conventional copolymerisation are presented in Section 4.8. It is interesting to note that while linear molar mass conversion plots are widely used to prove living behaviour this criterion should not be relied upon. It was pointed
out by Quirk and Lee\(^8\) that this is not a rigorous test for living polymerisation. If termination is occurring, then the number of chains will still be a constant throughout the polymerisation. This was illustrated by the living polymerisation of St initiated by sec-butyllithium, which was deliberately terminated to varying degrees throughout the polymerisation. A linear relationship between \(M_n\) and conversion was obtained even when 15\% of the polymer chains had been terminated. This type of plot therefore is not sensitive to termination reactions, and as most CRP techniques involve a small contribution from radical-radical termination, linear molar mass conversion plots should be used in combination with a range of other criteria such as narrow MMD or the evaluation of end groups to establish the living character of a CRP technique.

4.6.1.2 COPOLYMERISATION KINETICS IN RAFT COPOLYMERISATION OF MA WITH ST MONOMERS

The kinetic plots for StMA (Figure 54), \(p\text{MeStMA}\) (Figure 57), \(p\text{ClStMA}\) (Figure 60) and \(p\text{MeOStMA}\) (Figure 63) result in straight lines in the semilogarithmic axis. This indicates that the number of active centres is constant. The 1\(^{st}\) order kinetics in the monomers is brought about by fast initiation. A constant number of active centres are also possible for a conventional radical system in the steady state as radicals are generated and destroyed at similar rates; therefore, these radicals are short lived. Though this criterion alone is not indicative of living polymerisation, it adds further support to the living character of RAFT copolymerisation of MA and St monomers. The kinetic plot for StMA results in a linear regression that has an intercept close to the origin. Examination of the conversion data and copolymerisation kinetics for \(p\text{MeStMA}\) reveals an induction period of approximately 60 min where no copolymerisation takes place. A similar observation was found for \(p\text{MeOStMA}\). Incomplete removal of inhibitor by the IRC method may be responsible and distillation of the monomers in a manner similar to St could eliminate this artefact.

The initial rate of copolymerisation \(R_p\) for each system, was calculated by converting fractional conversion to values for concentration of copolymer produced and then taking the gradient of a limiting tangent to the data points at low conversion. The rates are collected in Table 28 below.
Chapter 4: Results and discussion

Table 28 Copolymerisation rates for MA and St monomers produced by RAFT copolymerisation.

<table>
<thead>
<tr>
<th>Comonomer</th>
<th>Initial rate of polymerisation $R_p$ (mol dm$^{-3}$ s$^{-1}$)</th>
<th>Differences in $e$ value MA – St comonomer$^{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>St</td>
<td>$1.8 \times 10^{-4}$</td>
<td>4.49</td>
</tr>
<tr>
<td>$p$MeSt</td>
<td>$1.2 \times 10^{-4}$</td>
<td>4.32</td>
</tr>
<tr>
<td>$p$ClSt</td>
<td>$1.2 \times 10^{-5}$</td>
<td>4.33</td>
</tr>
<tr>
<td>$p$MeOSSt</td>
<td>$2.4 \times 10^{-4}$</td>
<td>5.36</td>
</tr>
</tbody>
</table>

The value of $R_p$ for $p$MeStMA is slightly slower than the rate obtained for StMA. The methyl group does not provide a large electronic effect to the monomer so the small increase in steric hindrance brought about by the methyl group may account for the small difference. The value of $R_p$ for $p$ClStMA was significantly lower than StMA. The electron withdrawing chlorine has a marked effect on the copolymerisation kinetics, which may be supplemented by the steric hindrance brought about by the large chlorine atom. In contrast the electron donation of the $p$MeO group brought about an increase in the rate of copolymerisation of $p$MeOSStMA when compared to StMA. The differences in rate can be qualitatively evaluated by considering the differences in Q-$e$ values of the St comonomers (Table 1 Section 2.3.2.3). The rate of cross-propagation ($k_{12}$) is dependent upon the differences in polarity of the comonomers, described by the $e$ value. The greater the difference in the $e$ value the greater the rate of cross-propagation. It follows therefore that provided the products are strictly alternating (Section 4.6.2) then the rate of cross-propagation approximates to the rate of copolymerisation. The difference in $e$ value between MA and $p$ClSt is smaller than between MA and St, while a greater difference is found between MA and $p$MeOSSt when compared to StMA. The Q-$e$ analysis serves to confirm that the experimental results show differences in rate that depends upon the electronic character of the comonomers.
4.6.1.3 NARROW MOLAR MASS DISTRIBUTION (MMD) IN RAFT COPOLYMERISATION OF MA AND ST MONOMERS

The essential requirements for the formation of a polymer or copolymer with a Poisson distribution is that monomers add exclusively to active centres, all the active centres are equally susceptible to reaction with monomer, initiation is very fast and that propagation is irreversible. If all these conditions are met, then a near monodisperse MMD of $M_w/M_n < 1.1$ will be achieved and the system must behave as a living one. It is also noted that a living system does not require a narrow MMD. Polymers of broad MMD can be obtained if one of the above conditions is not met but the system does not undergo chain termination or chain transfer. For RAFT to be an effective CRP technique for MA copolymerisations, initiation and the addition-fragmentation equilibrium must be rapid in order to produce copolymers of narrow MMD.

SEC chromatograms for StMA indicate relatively narrow MMD’s as illustrated by PDI values of 1.19-1.30. The chromatogram for sample MCD236 in Table 23 (Figure 55) has the greatest PDI, due to peak tailing, which may indicate the slow consumption of BDTB and subsequent establishment of the RAFT equilibrium. The chromatogram for sample MCD240 (Figure 55) exhibits a high molar mass shoulder. This suggests bimolecular combination or diffusion control brought about by the onset of the gel effect. The conversion is nearly quantitative and the solution was observed to increase in viscosity at 60°C. Similar results are obtained for $p$MeStMA in Table 24 (Figure 58). The MMD narrowed with increasing conversion, a common characteristic of polymerisation in which initiation is slow, or in the case of a RAFT polymerisation the establishment of the addition-fragmentation equilibrium is slow. The slower rate of copolymerisation of $p$ClStMA resulted in slightly narrower MMD’s (Table 25) compared to StMA and $p$MeStMA while $p$MeOSTMA exhibited broader MMD’s (Table 26) indicating a loss of control. The rate of propagation compared to the fragmentation efficiency of the RAFT reagent affects the MMD of the produced copolymers and has an influence on the control that can be gained when a consistent initiator/RAFT system is used. Slow copolymerisation rates therefore result in greater control as the addition-fragmentation of the thiocarbonyl RAFT reagent (BDTB) is more kinetically favourable. PDI values $M_w/M_n < 1.15$ were not produced with any of the systems investigated. As
noted above, for a narrow MMD the active centres have to be equally reactive with monomer. In the case of the RAFT technique this relates to the susceptibility of the RAFT reagent, BDTB, to react with radical ended chains derived from the St monomer or MA monomer. The thiocarbonyl sulfur atom is nucleophilic and so reaction with the electrophilic MA radical would be more viable than reaction with the nucleophilic St radical. This explanation may help to account for the increase in MMD of MA copolymers produced by RAFT compared to say, PS, produced under similar conditions\(^92\).

4.6.1.4 BLOCK COPOLYMERISATION OF STMA AND pMeStMA BY RAFT POLYMERISATION

An important criterion of ionic living polymerisation is the capacity to add further monomer, either to extend the kinetic chain length of a homopolymer, or to add a different monomer to form a block copolymer. This architectural control is a useful attribute of ionic living polymerisation\(^126, 129\). If RAFT polymerisation is to be considered as an effective CRP technique, it should also fit this criterion. To test this, a three-component system consisting of an alternating A block of StMA with a B block of pMeSt was prepared (Scheme 12). pMeSt was chosen for the B block as the methyl group is easily identifiable by \(^1\)H NMR spectroscopy.

![Scheme 12 RAFT block copolymerisation to form StMA-b-pMeSt.](image)

StMA-b-pMeSt was prepared as described in Section 3.5.4. AIBN was used as the radical initiator at a concentration of 0.012 mol % wrt MA. BDTB was used at a concentration of 0.024 mol % wrt MA. On addition of pMeSt no further initiator or RAFT mediator was added. It is understood that the overall AIBN and BDTB concentrations are therefore different with regard to total monomer concentration for the
Chapter 4: Results and discussion

Initial StMA copolymer and StMA-b-pMeSt copolymer. This approach does, however, give the most reliable information regarding attachment of the second block. Approaches examined by others\textsuperscript{128} include the isolation of the A block before reinitiation with further addition of initiator, the A block acting as a macromolecular RAFT reagent. The results for the formation of StMA-b-pMeSt are collected in Table 29 and the SEC chromatograms comparing the A block comprising StMA with StMA-b-pMeSt are presented in Figure 66.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Product</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD327</td>
<td>StMA</td>
<td>1.25</td>
<td>0.83</td>
<td>20,900</td>
<td>25,600</td>
<td>1.23</td>
</tr>
<tr>
<td>MCD329</td>
<td>StMA-b-pMeSt</td>
<td>1.74</td>
<td>0.54 (0.29)*</td>
<td>24,400</td>
<td>33,600</td>
<td>1.38</td>
</tr>
</tbody>
</table>

*Conversion of pMeSt

Table 29 Molar mass and conversion data for StMA-b-pMeSt produced by RAFT copolymerisation in dioxane at 60°C.

The RAFT alternating copolymerisation of StMA (MCD327) was allowed to proceed to high conversion before the addition of the B block. The conversion of pMeSt was lower than the A block and this may be due to the introduction of impurity on addition of pMeSt. A gravimetric increase was however observed, indicating further polymerisation had taken place. Analysis by SEC resulted in an increase in molar mass that signifies the attachment of the B block. A broadening of the MMD indicated by an increase in PDI was also observed. Examination of the SEC chromatogram for StMA-b-pMeSt reveals tailing of the peak at low molar mass and a shoulder at high molar mass.
Chapter 4: Results and discussion

Figure 66 SEC chromatograms for StMA (■) and StMA-b-pMeSt (▲).
Figure 67 Dual detection SEC chromatogram for StMA-b-pMeSt (RI detector ♦ UV detector ---).
Figure 67 shows the chromatograms obtained for StMA-b-pMeSt using the dual detector method (Section 3.6.3.2). The interdetector delay was accounted for. The shoulder observed at high molar mass with the RI detector is absent in the chromatogram obtained with the UV detector. As the UV detector is specific to the thiocarbonyl-ended chains, the high molar mass shoulder that contributed to the broadening of the MMD is due to conventional radical polymerisation of pMeSt. The concentration of material making up the high molar mass shoulder is however small compared to the differences observed in the chromatogram profiles at low molar mass. The low molar mass shoulder observed with the RI detector is accentuated with the more sensitive UV detector. Four smaller peaks combine to further broaden the MMD; however, the low molar mass species contain the thiocarbonyl group. It is possible that the pMeSt block does not grow in a controlled fashion. Although the chains may not be growing at the same rate, it should be noted that BDTB is still mediating the polymerisation and an increase in $M_n$ was observed. In order to fully evaluate the structure of the obtained block copolymer on line spectroscopic analysis would be of great benefit. However, in order to confirm the presence of the pMeSt block, $^1$H NMR spectroscopy for both StMA and StMA-b-pMeSt and the appearance of a broad peak at $\sim 1.0$ ppm was indicative of the methyl group associated with the pMeSt block.

4.6.1.5 SUMMARY

RAFT polymerisation using BDTB as mediator has been used to successfully copolymerise MA with a number of St monomers. Para substituted St monomers are tolerant to the RAFT technique and well defined copolymers with narrow MMD’s were produced. The caveat to this success was the deviation of experimental molar masses from the theoretical values. This was attributed to the slow consumption of BDTB due to inefficient fragmentation, allowing conventional radical copolymerisation to occur early in the reaction, producing high molar mass copolymer that broadens the MMD and shifts the average molar masses to higher values. The establishment of the RAFT equilibrium, therefore, was considered to be the governing factor for the inflated experimental molar mass values. Attempts to improve the RAFT systems are investigated in Section 4.8.
RAFT polymerisation has proved to be a useful CRP technique. Care however should be taken not to confuse CRP with living polymerisation. A CRP technique has been defined as “a synthetic method to make polymers with pre-determined molecular weights, low polydispersity, controlled functionality and architecture”\textsuperscript{129}. Thus, transfer and termination can occur in a CRP (the success of RAFT depends upon transfer) but termination is sufficiently reduced by the appropriate choice of reaction conditions. Although CRP may exhibit many of the advantageous aspects of living polymerisation it should not be named as such.
4.6.2 Composition analysis and estimation of reactivity ratios for copolymers of MA and St monomers produced by RAFT polymerisation

RAFT copolymerisation to form copolymers of MA and St monomers was carried out with varying monomer feed ratios to low conversions as described in Section 3.5.3. The conversion and molar mass data for StMA, pMeStMA, pClStMA and pMeOStMA are presented in Tables 30-33. The composition of the resulting copolymers was elucidated by FTIR spectroscopy as described in Section 3.6.1.2. The composition and feed ratios are plotted in Figures 68 - 71. Monomer reactivity ratios were calculated using the Fineman - Ross, and Kelen - Tüdös methods as described in Section 2.2. A value of $\alpha = 1$ was used for the Kelen- Tüdös calculations. The results are collected in Tables 34 - 41.


<table>
<thead>
<tr>
<th>Sample</th>
<th>MA (mol)</th>
<th>St (mol)</th>
<th>Fractional conversion</th>
<th>( M_a ) (g mol(^{-1}))</th>
<th>( M_w ) (g mol(^{-1}))</th>
<th>PDI (( M_w/M_a ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD295</td>
<td>0.025</td>
<td>0.005</td>
<td>0.28</td>
<td>10,300</td>
<td>12,200</td>
<td>1.19</td>
</tr>
<tr>
<td>MCD294</td>
<td>0.020</td>
<td>0.010</td>
<td>0.12</td>
<td>11,900</td>
<td>14,400</td>
<td>1.21</td>
</tr>
<tr>
<td>MCD236</td>
<td>0.015</td>
<td>0.015</td>
<td>0.22</td>
<td>11,100</td>
<td>14,400</td>
<td>1.30</td>
</tr>
<tr>
<td>MCD296</td>
<td>0.010</td>
<td>0.020</td>
<td>0.18</td>
<td>6,100</td>
<td>7,700</td>
<td>1.25</td>
</tr>
<tr>
<td>MCD297</td>
<td>0.005</td>
<td>0.025</td>
<td>0.07</td>
<td>5,100</td>
<td>6,200</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 30 Monomer feed, conversion and molar mass data for StMA produced by RAFT polymerisation in dioxane at 60 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MA (mol)</th>
<th>pMeSt (mol)</th>
<th>Fractional conversion</th>
<th>( M_a ) (g mol(^{-1}))</th>
<th>( M_w ) (g mol(^{-1}))</th>
<th>PDI (( M_w/M_a ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD309</td>
<td>0.025</td>
<td>0.005</td>
<td>0.33</td>
<td>9,300</td>
<td>11,900</td>
<td>1.28</td>
</tr>
<tr>
<td>MCD308</td>
<td>0.020</td>
<td>0.010</td>
<td>0.44</td>
<td>13,200</td>
<td>17,400</td>
<td>1.32</td>
</tr>
<tr>
<td>MCD304</td>
<td>0.015</td>
<td>0.015</td>
<td>0.49</td>
<td>16,400</td>
<td>20,800</td>
<td>1.27</td>
</tr>
<tr>
<td>MCD310</td>
<td>0.010</td>
<td>0.020</td>
<td>0.48</td>
<td>14,600</td>
<td>20,100</td>
<td>1.36</td>
</tr>
<tr>
<td>MCD311</td>
<td>0.005</td>
<td>0.025</td>
<td>0.31</td>
<td>13,900</td>
<td>19,100</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table 31 Monomer feed, conversion and molar mass data for pMeStMA produced by RAFT polymerisation in dioxane at 60 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MA (mol)</th>
<th>pClSt (mol)</th>
<th>Fractional conversion</th>
<th>( M_a ) (g mol(^{-1}))</th>
<th>( M_w ) (g mol(^{-1}))</th>
<th>PDI (( M_w/M_a ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD299</td>
<td>0.025</td>
<td>0.005</td>
<td>0.11</td>
<td>4,600</td>
<td>5,700</td>
<td>1.24</td>
</tr>
<tr>
<td>MCD298</td>
<td>0.020</td>
<td>0.010</td>
<td>0.19</td>
<td>6,700</td>
<td>8,400</td>
<td>1.24</td>
</tr>
<tr>
<td>MCD279</td>
<td>0.015</td>
<td>0.015</td>
<td>0.27</td>
<td>8,300</td>
<td>10,500</td>
<td>1.26</td>
</tr>
<tr>
<td>MCD300</td>
<td>0.010</td>
<td>0.020</td>
<td>0.03</td>
<td>4,700</td>
<td>5,700</td>
<td>1.20</td>
</tr>
<tr>
<td>MCD301</td>
<td>0.005</td>
<td>0.025</td>
<td>0.02</td>
<td>4,400</td>
<td>5,100</td>
<td>1.17</td>
</tr>
</tbody>
</table>

Table 32 Monomer feed, conversion and molar mass data for pClStMA produced by RAFT polymerisation in dioxane at 60 °C.
# Chapter 4: Results and Discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>MA (mol)</th>
<th>pMeOSt (mol)</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol(^{-1}))</th>
<th>$M_w$ (g mol(^{-1}))</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD324</td>
<td>0.025</td>
<td>0.005</td>
<td>0.33</td>
<td>10,800</td>
<td>16,700</td>
<td>1.54</td>
</tr>
<tr>
<td>MCD323</td>
<td>0.020</td>
<td>0.010</td>
<td>0.58</td>
<td>16,600</td>
<td>24,500</td>
<td>1.48</td>
</tr>
<tr>
<td>MCD318</td>
<td>0.015</td>
<td>0.015</td>
<td>0.36</td>
<td>12,900</td>
<td>20,600</td>
<td>1.60</td>
</tr>
<tr>
<td>MCD325</td>
<td>0.010</td>
<td>0.020</td>
<td>0.46</td>
<td>20,800</td>
<td>32,500</td>
<td>1.56</td>
</tr>
<tr>
<td>MCD326</td>
<td>0.005</td>
<td>0.025</td>
<td>0.28</td>
<td>10,000</td>
<td>15,200</td>
<td>1.52</td>
</tr>
</tbody>
</table>

Table 33 Monomer feed, conversion and molar mass data for pMeOStMA produced by RAFT polymerisation in dioxane at 60°C.
Chapter 4: Results and discussion

Figure 68 Monomer feed and copolymer composition plot for StMA produced by RAFT copolymerisation in dioxane at 60 °C.
Figure 69 Monomer feed and copolymer composition plot for pMeStMA produced by RAFT copolymerisation in dioxane at 60 °C.
Chapter 4: Results and discussion

Figure 70 Monomer feed and copolymer composition plot for pClStMA produced by RAFT copolymerisation in dioxane at 60°C.
Chapter 4: Results and discussion

Figure 71 Monomer feed and copolymer composition plot for pMeOStMA produced by RAFT copolymerisation in dioxane at 60 °C.
Chapter 4: Results and Discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>M₁ MA</th>
<th>M₂ St</th>
<th>m₁ MA</th>
<th>m₂ St</th>
<th>x</th>
<th>y</th>
<th>F</th>
<th>G</th>
<th>G/F</th>
<th>1/F</th>
<th>σ</th>
<th>ξ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD294</td>
<td>0.17</td>
<td>0.83</td>
<td>0.49</td>
<td>0.51</td>
<td>0.20</td>
<td>1.81</td>
<td>0.02</td>
<td>0.09</td>
<td>45.33</td>
<td>4.07</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>MCD295</td>
<td>0.33</td>
<td>0.67</td>
<td>0.59</td>
<td>0.41</td>
<td>0.50</td>
<td>1.04</td>
<td>0.24</td>
<td>0.02</td>
<td>4.18</td>
<td>0.09</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>MCD296</td>
<td>0.50</td>
<td>0.50</td>
<td>0.51</td>
<td>0.49</td>
<td>1.00</td>
<td>1.40</td>
<td>0.72</td>
<td>0.28</td>
<td>1.40</td>
<td>0.34</td>
<td>0.17</td>
<td>0.42</td>
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<tr>
<td>MCD297</td>
<td>0.67</td>
<td>0.33</td>
<td>0.64</td>
<td>0.36</td>
<td>2.00</td>
<td>0.96</td>
<td>4.18</td>
<td>-0.09</td>
<td>0.24</td>
<td>-0.02</td>
<td>-0.02</td>
<td>0.81</td>
</tr>
<tr>
<td>MCD236</td>
<td>0.83</td>
<td>0.17</td>
<td>0.58</td>
<td>0.42</td>
<td>5.00</td>
<td>1.49</td>
<td>16.77</td>
<td>1.65</td>
<td>0.06</td>
<td>0.10</td>
<td>0.09</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table 34 Copolymer data and results from calculations using the Fineman-Ross, and Kelen-Tüdös methods to determine r₁ and r₂ for StMA.

<table>
<thead>
<tr>
<th>Method</th>
<th>r₇MA</th>
<th>r₇St</th>
<th>r₇MAR₇St</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman and Ross 1</td>
<td>0.093</td>
<td>0.018</td>
<td>0.002</td>
</tr>
<tr>
<td>Fineman and Ross 2</td>
<td>0.015</td>
<td>-0.09</td>
<td>-0.001</td>
</tr>
<tr>
<td>Kelen and Tüdös</td>
<td>0.054</td>
<td>0.082</td>
<td>0.005</td>
</tr>
<tr>
<td>Literature²²</td>
<td>0.001</td>
<td>0.040</td>
<td>4.0 x 10⁻³</td>
</tr>
</tbody>
</table>

Table 35 Monomer reactivity ratios for StMA.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>M₁ MA</th>
<th>M₂ pMeSt</th>
<th>m₁ MA</th>
<th>m₂ pMeSt</th>
<th>x</th>
<th>y</th>
<th>F</th>
<th>G</th>
<th>G/F</th>
<th>1/F</th>
<th>σ</th>
<th>ξ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD311</td>
<td>0.17</td>
<td>0.83</td>
<td>0.41</td>
<td>0.59</td>
<td>0.20</td>
<td>0.69</td>
<td>0.06</td>
<td>-0.09</td>
<td>17.14</td>
<td>-1.57</td>
<td>-0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>MCD310</td>
<td>0.33</td>
<td>0.67</td>
<td>0.52</td>
<td>0.48</td>
<td>0.50</td>
<td>1.11</td>
<td>0.22</td>
<td>0.05</td>
<td>4.46</td>
<td>0.23</td>
<td>0.04</td>
<td>0.18</td>
</tr>
<tr>
<td>MCD304</td>
<td>0.50</td>
<td>0.50</td>
<td>0.54</td>
<td>0.46</td>
<td>1.00</td>
<td>1.20</td>
<td>0.84</td>
<td>0.16</td>
<td>1.20</td>
<td>0.20</td>
<td>0.09</td>
<td>0.46</td>
</tr>
<tr>
<td>MCD308</td>
<td>0.67</td>
<td>0.33</td>
<td>0.47</td>
<td>0.53</td>
<td>2.00</td>
<td>0.87</td>
<td>4.59</td>
<td>-0.29</td>
<td>0.22</td>
<td>-0.06</td>
<td>-0.05</td>
<td>0.82</td>
</tr>
<tr>
<td>MCD309</td>
<td>0.83</td>
<td>0.17</td>
<td>0.47</td>
<td>0.53</td>
<td>5.00</td>
<td>0.87</td>
<td>28.70</td>
<td>-0.74</td>
<td>0.03</td>
<td>-0.03</td>
<td>-0.02</td>
<td>0.97</td>
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</table>

Table 36 Copolymer data and results from calculations using the Fineman-Ross, and Kelen-Tüdös methods to determine r₁ and r₂ for pMeStMA.

<table>
<thead>
<tr>
<th>Method</th>
<th>r_{MA}</th>
<th>r_{pMeSt}</th>
<th>r_{MA}r_{pMeSt}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman and Ross 1</td>
<td>-0.027</td>
<td>-8.0x10⁻⁴</td>
<td>2.0x10⁻⁵</td>
</tr>
<tr>
<td>Fineman and Ross 2</td>
<td>0.194</td>
<td>0.096</td>
<td>0.0186</td>
</tr>
<tr>
<td>Kelen and Tüdös</td>
<td>-0.013</td>
<td>-6.0x10⁻⁴</td>
<td>7.7x10⁻⁶</td>
</tr>
</tbody>
</table>

Table 37 Monomer reactivity ratios for pMeStMA.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>M₁ MA</th>
<th>M₂ pClSt</th>
<th>m₁ MA</th>
<th>m₂ pClSt</th>
<th>x</th>
<th>y</th>
<th>F</th>
<th>G</th>
<th>G/F</th>
<th>1/F</th>
<th>σ</th>
<th>ξ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD301</td>
<td>0.17</td>
<td>0.83</td>
<td>0.41</td>
<td>0.59</td>
<td>0.20</td>
<td>0.74</td>
<td>0.05</td>
<td>-0.07</td>
<td>18.54</td>
<td>-1.29</td>
<td>-0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>MCD300</td>
<td>0.33</td>
<td>0.67</td>
<td>0.52</td>
<td>0.48</td>
<td>0.50</td>
<td>0.88</td>
<td>0.28</td>
<td>-0.07</td>
<td>3.52</td>
<td>-0.24</td>
<td>-0.05</td>
<td>0.22</td>
</tr>
<tr>
<td>MCD279</td>
<td>0.50</td>
<td>0.50</td>
<td>0.54</td>
<td>0.46</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.005</td>
<td>1.00</td>
<td>0.005</td>
<td>0.002</td>
<td>0.50</td>
</tr>
<tr>
<td>MCD298</td>
<td>0.67</td>
<td>0.33</td>
<td>0.47</td>
<td>0.53</td>
<td>2.00</td>
<td>0.97</td>
<td>4.13</td>
<td>-0.07</td>
<td>0.24</td>
<td>-0.02</td>
<td>-0.01</td>
<td>0.80</td>
</tr>
<tr>
<td>MCD299</td>
<td>0.83</td>
<td>0.17</td>
<td>0.47</td>
<td>0.53</td>
<td>5.00</td>
<td>1.07</td>
<td>23.44</td>
<td>0.31</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 38 Copolymer data and results from calculations using the Fineman-Ross, and Kelen-Tüdős methods to determine r₁ and r₂ for pClStMA.

<table>
<thead>
<tr>
<th>Method</th>
<th>r₁ MA</th>
<th>r₂ pClSt</th>
<th>r₁ MA r₂ pClSt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman and Ross 1</td>
<td>0.016</td>
<td>0.069</td>
<td>0.001</td>
</tr>
<tr>
<td>Fineman and Ross 2</td>
<td>0.026</td>
<td>0.071</td>
<td>0.002</td>
</tr>
<tr>
<td>Kelen and Tüdős</td>
<td>0.017</td>
<td>-0.064</td>
<td>-0.001</td>
</tr>
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</table>

Table 39 Monomer reactivity ratios for pClStMA.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>M1 MA</th>
<th>M2 pMeOS t</th>
<th>m1 MA</th>
<th>m2 pMeOS t</th>
<th>x</th>
<th>y</th>
<th>F</th>
<th>G</th>
<th>G/F</th>
<th>I/F</th>
<th>σ</th>
<th>ξ</th>
</tr>
</thead>
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<td>MCD326</td>
<td>0.17</td>
<td>0.83</td>
<td>0.48</td>
<td>0.52</td>
<td>0.20</td>
<td>0.94</td>
<td>0.04</td>
<td>-0.01</td>
<td>23.49</td>
<td>-0.30</td>
<td>-0.01</td>
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<td>MCD325</td>
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<td>0.67</td>
<td>0.51</td>
<td>0.49</td>
<td>0.50</td>
<td>1.03</td>
<td>0.24</td>
<td>0.02</td>
<td>4.14</td>
<td>0.07</td>
<td>0.01</td>
<td>0.19</td>
</tr>
<tr>
<td>MCD318</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>1.00</td>
<td>1.02</td>
<td>0.98</td>
<td>0.02</td>
<td>1.01</td>
<td>0.02</td>
<td>0.007</td>
<td>0.50</td>
</tr>
<tr>
<td>MCD323</td>
<td>0.67</td>
<td>0.33</td>
<td>0.47</td>
<td>0.53</td>
<td>2.00</td>
<td>0.87</td>
<td>4.57</td>
<td>-0.29</td>
<td>0.22</td>
<td>-0.06</td>
<td>-0.05</td>
<td>0.82</td>
</tr>
<tr>
<td>MCD324</td>
<td>0.83</td>
<td>0.17</td>
<td>0.48</td>
<td>0.52</td>
<td>5.00</td>
<td>0.93</td>
<td>26.81</td>
<td>-0.36</td>
<td>0.04</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 40 Copolymer data and results from calculations using the Fineman-Ross, and Kelen-Tüdös methods to determine $r_1$ and $r_2$ for pMeOStMA.

<table>
<thead>
<tr>
<th>Method</th>
<th>$r_{MA}$</th>
<th>$r_{pMeOS t}$</th>
<th>$r_{MA}r_{pMeOS t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman and Ross 1</td>
<td>-0.013</td>
<td>0.041</td>
<td>-5.3×10^{-4}</td>
</tr>
<tr>
<td>Fineman and Ross 2</td>
<td>0.015</td>
<td>0.013</td>
<td>1.8×10^{-5}</td>
</tr>
<tr>
<td>Kelen and Tüdös</td>
<td>-0.028</td>
<td>0.006</td>
<td>-1.6×10^{-4}</td>
</tr>
</tbody>
</table>

Table 41 Monomer reactivity ratios for pMeOStMA.
Monomer reactivity ratios calculated for StMA, pMeStMA, pClStMA and pMeOStMA all result in values that approach zero within experimental error. These results confirm that alternating copolymers are formed, which are in line with reported results for the conventional free radical copolymerisation of StMA\textsuperscript{56,133}, pMeStMA\textsuperscript{32}, pClStMA\textsuperscript{32} and pMeOStMA\textsuperscript{59}. It is noted that negative values of monomer reactivity ratios were calculated in some cases. As reactivity ratios are ratios of rate constants, negative values are not valid. The consistent composition of the copolymers leads to linear plots with shallow gradients due to indifferent data points. Zero falls within experimental error for these results and therefore values of zero can be assumed.

It is interesting to note that for StMA, pMeStMA and pClStMA, copolymers of greatest molar mass were formed at equimolar feed ratios, as illustrated by Figure 72. Observations indicating maximum copolymerisation rates at equimolar feed ratios have been reported for StMA\textsuperscript{53}, αMeStMA\textsuperscript{48} and olefin-co-MA copolymers\textsuperscript{71}. CTC formation at, and approaching equimolar feed ratios was postulated to account for the behaviour. These observations appear to be contradictory. Equation 15 teaches that for conventional radical polymerisation, $R_p$ is inversely proportional to the kinetic chain length $v$, and therefore DP. Polymers of lower molar mass are produced at higher $R_p$. Combination of Equation 70 with Equation 71 to produce Equation 72 for living polymerisation also reveals an inversely proportional relationship between DP and $R_p$.

\[ R_p = k_p [M][C^*] \]

\[ DP = \frac{[M]}{[C^*]} \]

\[ DP = \frac{k_p[M]^2}{R_p} \]

\textit{Equation 70}

\textit{Equation 71}

\textit{Equation 72}

where $C^*$ represents the active propagating species.
Chapter 4: Results and discussion

Consideration of the maximum available monomer concentration, \([M]_{av}\), rather than the total monomer concentration allows an explanation for the maximum DP at equimolar feed ratios to be postulated. The determination of strictly alternating structures for the copolymers produced stipulates that only at equimolar feed ratios can the total monomer concentration be involved in copolymerisation. At all other feed ratios \([M]_{av}\) is double the concentration of the starved comonomer. As the RAFT reagent concentration is constant to the overall \(\text{[M]}\), it is variable to \([M]_{av}\). It is this variation that accounts for the observed relationship between molar mass and monomer feed ratio. This is exemplified in Figure 73 that presents theoretical molar mass results based on \([M]_{av}\) for StMA, \(p\text{MeStMA}\) and \(p\text{ClStMA}\). Table 42 presents the data used for the \(p\text{MeStMA}\) plot.

![Figure 72 Molar mass dependence on MA feed for StMA, pMeStMA, and pClStMA](image-url)
Figure 73 Theoretical Molar mass dependence on MA feed for StMA, pMeStMA, and pCISStMA.

Table 42 Theoretical Molar mass dependence on MA feed for pMeStMA based on $[M]_{av}$.

$pMeOSStMA$ did not exhibit a maximum molar mass at equimolar feed ratios, which may be due to reduced mediation by BDTB. MMD’s >1.5 for $pMeOSStMA$ indicate a loss of control and therefore the above molar mass analysis for $pMeOSStMA$ is invalid. Similar observations are reported for $aMeStMA$ (Section 4.7).

†† The fractional conversion was calculated based on conversion of available monomer and therefore differs from the values collected in Table 31 that are based on the total monomer present.
$R_p$ for each monomer feed ratio was not measured and so the observation that for some conventional radical systems a maximum rate is observed at equimolar feed ratios cannot be confirmed here. The presence of a CTC was however examined. The formation of a CTC is unlikely for olefin-co-MA copolymers as the complex would be very weak (see Section 2.3.2, page 45). The presence of a CTC was not established for PODMA. $^1$H NMR experiments to establish the existence of a CTC for MA copolymerised with St monomers were attempted. A shift in the peak due to MA was observed indicating the possibility of a CTC for StMA. However, the results were not reproducible and a reliable result for the CTC equilibrium constant was not obtained. A stronger CTC would be anticipated for pMeOSTMA as a consequence of the increased electron donating capacity of the monomer. On addition of pMeOS to MA, an intense yellow colour was observed. The formation of a CTC can bring about a colour change, and although this was not observed with the other St monomers, this was considered indicative of a possible stronger CTC. The investigation of the existence of a CTC was carried out using UV spectroscopy and $^1$H NMR spectroscopy. Scanning UV spectroscopy did not reveal a unique absorbance that could be assigned to the CTC. The absorbance due to the aromatic chromophore was intense and may have hidden any CTC absorbance. $^1$H NMR experiments to establish the existence of a CTC were also attempted. A shift in the peak due to MA was observed indicating the possibility of a CTC. However, the results again were not reproducible and as for StMA, a reliable result for the CTC equilibrium constant was not obtained.

$Q-e$ values were not determined for the RAFT systems. The literature $Q-e$ values reported for conventional radical copolymerisation in Section 2.3.2.3 (Table 1) were considered valid for the RAFT system as during each activation-deactivation cycle a number of monomer units were expected to be added as the rate of propagation for StMA copolymers is very fast (see Section 4.8). When the chains are active therefore, the monomer characteristics in RAFT copolymerisation were expected to be the same as those in conventional radical polymerisations. Calculation of $Q-e$ values depends on the accuracy of the $r_1r_2$ value. As this value and the value for $r_1$ tend to zero Equation 48 delivers unreliable values for $e_2$. For a strictly alternating copolymer of $r_1r_2=0$ Equation 48 delivers an ‘unreal’ number. A more accurate method for determining the $Q-e$ values for St monomers in RAFT copolymerisation would be to carry out a statistical
copolymers with, for example methyl acrylate, which would deliver useful values of $r_1/r_2$. This approach however cannot be applied to MA as it is difficult to homopolymerise and therefore produce statistical copolymers. Consideration of the Q-e values presented in Table 1, Section 2.3.2.3, provides semi-empirical information regarding the reactivity of St monomers towards MA. The electron withdrawing $p$ClSt has the highest e value of the St monomers investigated. This correlates well to the observed rate of polymerisation, which is slowest for $p$ClStMA. In contrast $p$MeOSt has the lowest e value and therefore the greatest difference in polarity compared to MA. The fastest rate of polymerisation was observed for $p$MeOStMA.

The Q-e approach supports the free monomer theory for alternation. The differences in polarity of the monomers accounts for the increased rate of cross-propagation compared to homo-propagation. CTC formation may contribute to the copolymerisation; however, the lack of sound spectroscopic evidence leads to the conclusion that the alternating structures and differences in $R_P$ are mainly due to polar and kinetic effects brought about by differences in donor strength of the electron donor monomers.
4.7 RAFT COPOLYMERISATION TO FORM COPOLYMERS OF $\alpha$MeSt AND MA ($\alpha$MeStMA)

$\alpha$MeSt was chosen to test the effect of a sterically hindered St on RAFT copolymerisation with MA. $\alpha$MeSt has a ceiling temperature, $T_c$, of 61°C, above which it cannot be polymerised. At $T_c$, the rates of propagation and depropagation are equal and the overall Gibbs free energy of the system is zero. The high steric strain that exists in poly($\alpha$MeSt) caused by the interaction of the phenyl rings and $\alpha$-methyl groups accounts for the low $T_c$ and a low enthalpy of polymerisation, $\Delta H_p$, of 34.1 kJ mol$^{-1}$. $\alpha$MeSt will undergo facile copolymerisation with electron accepting monomers such as MA and the electron donating $\alpha$-methyl group results in $\alpha$MeSt being a stronger electron donor than St.

$\alpha$MeStMA was prepared using BDTB as detailed in Section 3.5.2. AIBN was used as the radical initiator at a concentration of 0.012 mol % wrt MA. BDTB was used at a concentration of 0.024 mol % wrt MA. A series of copolymerisations was performed in parallel for different periods of time in order to achieve differing conversions. The results are collected in Table 43. Figure 74 illustrates the relationship of molar mass versus fractional conversion for $\alpha$MeStMA. Molar mass does not vary with conversion and copolymer of high molar mass is formed early in the reaction. This characteristic is consistent with conventional free radical polymerisation. Initiation, propagation and termination are rapid and dead polymer chains are formed early in the reaction. Longer reaction times serve only to increase conversion to polymer and have no effect on molar mass. PDI values of 1.7-1.9 for $M_w/M_n$ indicate MMD’s expected for conventional radical polymerisation with termination by combination ($M_w/M_n = 1.5$) or disproportionation ($M_w/M_n = 2.0$).
Chapter 4: Results and discussion

| Sample   | Time (mins) | Yield (g) | Fractional conversion | $M_n$ (SEC) (g mol\(^{-1}\)) | PDI ($M_w/M_n$ (SEC)) | $M_n$ (Calc) (g mol\(^{-1}\)) | $[M]_0$ (mol dm\(^{-3}\)) | $[M]_t$ (mol dm\(^{-3}\)) | Ln ($[M]_0/[M]_t$) |
|----------|-------------|-----------|-----------------------|----------------------------|----------------------|----------------------------|----------------|----------------|----------------|----------------|
| MCD249   | 60          | 0.24      | 0.07                  | 17,400                     | 1.77                 | 1,400                      | 3.0            | 2.78           | 0.08           |
| MCD250   | 128         | 0.37      | 0.11                  | 14,000                     | 1.86                 | 2,200                      | 3.0            | 2.66           | 0.12           |
| MCD251   | 249         | 0.46      | 0.14                  | 13,000                     | 1.84                 | 2,700                      | 3.0            | 2.58           | 0.15           |
| MCD252   | 491         | 0.62      | 0.19                  | 18,700                     | 1.71                 | 3,700                      | 3.0            | 2.44           | 0.21           |
| MCD253   | 1303        | 1.49      | 0.45                  | 16,800                     | 1.76                 | 8,900                      | 3.0            | 1.64           | 0.60           |
| MCD254   | 5565        | 3.06      | 0.93                  | 16,300                     | 1.88                 | 18,200                     | 3.0            | 0.21           | 2.64           |

Table 43 RAFT copolymerisation results for $\alpha$MeStMA in dioxane at 60 °C ($M_1:M_2 = 50:50$).

$M_n$ (Calc) from Equation 51
Figure 74 Molar mass and PDI data for pMeOSiMA (\(M_n\) (SEC), \(PDI\), \(M_n\) (Calc)).

Figure 75 presents the time conversion plot for \(\alpha\)MeStMA with StMA provided as a comparison. The rate of copolymerisation for \(\alpha\)MeStMA is significantly slower than StMA, and as \(\alpha\)MeSt is a stronger donor monomer this effect must only be due to steric hindrance of the \(\alpha\)-methyl group. The copolymerisation proceeds with 1st order kinetics indicating that the rate of copolymerisation is proportional to the comonomer concentration.

RAFT copolymerisation mediated by BDTB is not successful for the copolymerisation of \(\alpha\)MeStMA. The isolated products were white rather than the pink colour observed with previous successful RAFT copolymerisations. This observation along with the data for the molar mass conversion experiment suggests that mediation by BDTB was ineffective. Dual detection SEC using a RI detector and a UV detector set at 330 nm was used to examine the presence of thiocarbonyl-ended chains.
Figure 75 RAFT copolymerisation kinetics for αMeStMA in dioxane at 60°C (♦αMeStMA conversion, □StMA conversion and ▲Ln[M]₀/[M], for αMeStMA).

Figure 76 presents SEC chromatograms for a PS standard, StMA prepared by RAFT copolymerisation and αMeStMA also prepared by RAFT copolymerisation. Examination of the chromatogram for PS reveals a strong peak due to the RI detector and only a very weak peak from the UV detector set at 330 nm. The S=С-S chromophore absorbs at 330 nm and a lack of absorbance for PS, produced by ionic polymerisation, confirms that the UV detector is selective for chains ended with a thiocarbonyl fragment. Equal concentrations of StMA and αMeStMA copolymers of similar molar mass were analysed. Similar responses were detected by RI for both copolymers. However, a significantly greater UV absorbance for StMA copolymer was detected compared to αMeStMA copolymer. UV detectors for SEC are more sensitive than RI detectors as is illustrated by the difference in peak intensities for StMA. End group detection at 330 nm provides conformation that there is a significant reduction in concentration of thiocarbonyl ended chains when RAFT copolymerisation is used to prepare αMeStMA copolymers compared to non-sterically hindered StMA copolymers.
Chapter 4: Results and discussion

Figure 76 Dual detection SEC for (from left to right) PS Standard, StMA and αMeStMA (RI detector, UV detector at 330nm).
Investigation of electronic and steric influences on the reactivity of αMeStMA towards MA and BDTB were carried out with the aid of molecular modelling. Charge distribution in the monomers provides semi empirical information regarding reactive sites. St, αMeSt, MA and BDTB were modelled using Chem Office Ultra as described in Section 3.6.5. Figure 77 shows the charge distribution calculated as partial charges. The models are rendered with blue and red representing negative and positive charges respectively. The intensity of the rendering indicates the magnitude of the charge. The partial charge data for the reactive sites is collected in Table 44.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>Partial charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>St</td>
<td>C₈</td>
<td>-0.29</td>
</tr>
<tr>
<td>αMeSt</td>
<td>C₈</td>
<td>-0.48</td>
</tr>
<tr>
<td>MA</td>
<td>C₁ and C₂</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

*Table 44 Monomer partial charges calculated from Chem Office Ultra using MOPAC computation.*
Chapter 4: Results and discussion

Figure 77 Molecular models from left to right St, αMeSt and MA, rendered by partial charge (Blue = negative, red = positive).
Chapter 4: Results and discussion

The partial charge provides an approximation to the polarity of the monomer and therefore the difference in partial charge between MA and St was not as great as expected for two monomers that form alternating copolymers so readily. In considering the molecular models for the monomers an assumption is made that the radical derived from the monomer in question will have a similar polarity. This is a similar assumption that was made for the Q-e scheme and may be incorrect; therefore this data should also be considered from a semi empirical viewpoint. The partial charge centred over the reactive site in \( \alpha \text{MeSt} \) is significantly more negative than the equivalent site in St due to the electron donating methyl group directly substituted at C7. This increase in electron donation enhances cross propagation with MA. Consideration of the charge distribution in BDTB indicates that the thiocarbonyl sulfur is highly nucleophilic. Reaction with MA radicals therefore is anticipated to be facile, while mediation when the chain carrier is a St radical may depend upon the polarity of that radical. The increased electrophilic character of the \( \alpha \text{MeSt} \) radical may result in preferential cross propagation with MA compared to BDTB mediation. It has been noted that the rate of addition of a PS radical species to a dithiobenzoate ester was about seven orders of magnitude larger than the rate of fragmentation of the intermediate radical\(^{130} \). This suggests that the fragmentation step in the RAFT equilibrium effects control more than the addition step. Figure 78 presents the addition-fragmentation mechanism for the \( \alpha \text{MeSt} \) radical adding to BDTB. The radical intermediate may fragment in favour of the radical leaving group by cleaving the S-CH\(_2\) bond or in favour of \( \alpha \text{MeSt} \) reforming the propagating centre and the RAFT reagent. In the case of \( \alpha \text{MeStMA} \), fragmentation to form the \( \alpha \text{MeSt} \) radical is likely to be favoured as the tertiary radical formed is more stable than the primary radical formed from the leaving group. Additionally, the primary radical leaving groups have smaller steric size than the \( \alpha \text{MeSt} \) radical, which in the intermediate adduct favours cleavage of the \( \alpha \text{MeSt}-\text{sulfur} \) bond versus the leaving group-sulfur bond. When the fragmentation step favours the propagating centre rather than the leaving group a new chain cannot be initiated and further monomer is added to the active chain. This results in conventional radical characteristics with significant termination and a low concentration of thio carbonyl ended chains. Similar observations have been reported for PMMA, which also contains a tertiary radical propagating centre\(^{130} \). When the RAFT reagent contained a leaving group which yields a primary radical, fragmentation to reform the PMMA radical was favoured resulting in uncontrolled polymerisation. Use
of a RAFT reagent with a tertiary leaving group such as the cumyl or cyano isopropyl radical pushed the fragrance equilibrium towards the fragmentation of the leaving group allowing a new chain to be initiated. The initial consumption of the RAFT reagent is therefore considered more important than the equilibrium between the macro RAFT reagent formed by the capped polymer chain. In this second equilibrium the intermediate radical will have identical leaving groups (assuming only one of the monomers in a copolymerisation dominates the mechanism) and so fragmentation to one species over another is not favoured.

A recent study employing electron spin resonance (ESR) spectroscopy indicated that the intermediate radical formed during the RAFT copolymerisation of StMA was derived from a MA ended propagating radical[131]. This result infers that MA is the only governing species in controlling the copolymerisation. This is questionable as the results presented here indicate significant differences in control when the St comonomer is altered and the MA monomer is held constant. Investigation of the location of the RAFT agent by NMR would therefore be a useful exercise and would aid in the understanding of the RAFT copolymerisation mechanism.

Failure of RAFT copolymerisation for αMeStMA may be attributed to inefficient fragmentation of BDTB to release the tolyl radical leaving group. Steric hindrance caused by the α-methyl substituent and enhanced cross propagation with MA due to the increased electron donating capacity of the monomer contribute to the conventional radical characteristics observed.
Figure 78 Addition-fragmentation mechanism for αMeStMA mediated by BDTB.
4.7.1 COMPOSITION ANALYSIS AND ESTIMATION OF Reactivity RATIOs FOR αMeStMA

RAFT copolymerisation to form αMeStMA was carried out with varying monomer feed ratios as described in Section 3.5.3. The conversion and molar mass data are presented in Table 45. The composition of the resulting copolymers was elucidated by FTIR spectroscopy as described in Section 3.6.1.2. The composition and feed ratios are plotted in Figure 79 indicating a constant copolymer composition across a range of monomer feed ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MA (mol)</th>
<th>αMeSt (mol)</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI ($M_w/M_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD287</td>
<td>0.025</td>
<td>0.005</td>
<td>0.11</td>
<td>12,200</td>
<td>20,300</td>
<td>1.67</td>
</tr>
<tr>
<td>MCD286</td>
<td>0.020</td>
<td>0.010</td>
<td>0.22</td>
<td>6,000</td>
<td>10,700</td>
<td>1.78</td>
</tr>
<tr>
<td>MCD254</td>
<td>0.015</td>
<td>0.015</td>
<td>0.93</td>
<td>16,300</td>
<td>30,600</td>
<td>1.88</td>
</tr>
<tr>
<td>MCD284</td>
<td>0.010</td>
<td>0.020</td>
<td>0.51</td>
<td>17,900</td>
<td>30,500</td>
<td>1.70</td>
</tr>
<tr>
<td>MCD285</td>
<td>0.005</td>
<td>0.025</td>
<td>0.32</td>
<td>10,400</td>
<td>18,400</td>
<td>1.78</td>
</tr>
</tbody>
</table>

*Table 45 Monomer feed, conversion and molar mass data for αMeStMA produced by RAFT polymerisation in dioxane at 60 °C.*
Figure 79 Monomer feed and copolymer composition plot for αMeSIMA produce by RAFT copolymerisation in dioxane at 60 °C.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>M_1 MA</th>
<th>M_2 αMeSt</th>
<th>m_1 MA</th>
<th>m_2 αMeSt</th>
<th>x</th>
<th>y</th>
<th>F</th>
<th>G</th>
<th>G/F</th>
<th>1/F</th>
<th>σ</th>
<th>ξ</th>
</tr>
</thead>
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<tr>
<td>MCD285</td>
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<td>0.83</td>
<td>0.47</td>
<td>0.53</td>
<td>0.20</td>
<td>0.90</td>
<td>0.04</td>
<td>-0.02</td>
<td>22.51</td>
<td>-0.50</td>
<td>-0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>MCD284</td>
<td>0.33</td>
<td>0.67</td>
<td>0.46</td>
<td>0.54</td>
<td>0.50</td>
<td>0.86</td>
<td>0.29</td>
<td>-0.08</td>
<td>3.43</td>
<td>-0.29</td>
<td>-0.06</td>
<td>0.23</td>
</tr>
<tr>
<td>MCD254</td>
<td>0.50</td>
<td>0.50</td>
<td>0.46</td>
<td>0.54</td>
<td>1.00</td>
<td>0.86</td>
<td>1.17</td>
<td>-0.17</td>
<td>0.86</td>
<td>-0.15</td>
<td>-0.08</td>
<td>0.54</td>
</tr>
<tr>
<td>MCD286</td>
<td>0.67</td>
<td>0.33</td>
<td>0.48</td>
<td>0.52</td>
<td>2.00</td>
<td>0.91</td>
<td>4.41</td>
<td>-0.21</td>
<td>0.23</td>
<td>-0.05</td>
<td>-0.04</td>
<td>0.82</td>
</tr>
<tr>
<td>MCD287</td>
<td>0.83</td>
<td>0.17</td>
<td>0.44</td>
<td>0.56</td>
<td>5.00</td>
<td>0.80</td>
<td>31.37</td>
<td>-1.27</td>
<td>0.03</td>
<td>-0.04</td>
<td>-0.04</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 46 Copolymer data and results from calculations using the Fineman - Ross, and Kelen - Túdós methods to determine r_1 and r_2 for αMeStMA.

<table>
<thead>
<tr>
<th>Method</th>
<th>r_{MA}</th>
<th>r_{αMeSt}</th>
<th>r_{MA}r_{αMeSt}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman and Ross 1</td>
<td>-0.039</td>
<td>0.063</td>
<td>-0.002</td>
</tr>
<tr>
<td>Fineman and Ross 2</td>
<td>-0.104</td>
<td>0.018</td>
<td>-0.002</td>
</tr>
<tr>
<td>Kelen and Túdós</td>
<td>-0.050</td>
<td>-0.047</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table 47 Monomer reactivity ratios for αMeStMA.
Chapter 4: Results and discussion

Monomer reactivity ratios were calculated using the Fineman-Ross, and Kelen-Túdós methods as described in Section 2.2. The results are collected in Table 46 and Table 47. Values approaching zero indicate that alternating copolymers are formed.

In contrast to previous St monomers (Section 4.6.2), evaluation of the molar mass data did not reveal a relationship between molar mass and monomer feed ratio. This finding supports the argument that the molar mass dependence in Section 4.6.2 is related to available monomer for mediation by BDTB. This therefore is not applicable for a system that is not controlled by the RAFT reagent.

On addition of αMeSt to MA, no colour change was observed. It has been proposed that a CTC is responsible for the alternation in αMeStMA and a CTC equilibrium constant of 0.07 mol dm\(^{-3}\) has been calculated by \(^1\)H NMR spectroscopy\(^{48}\). The calculated equilibrium constant is an order of magnitude lower than those calculated for StMA\(^{53, 132, 133}\). The alternation can also be explained in terms of polar and steric effects. The increased electron donor capacity of αMeSt compared to St increases the kinetic feasibility for cross propagation. If electronic and polar effects are not responsible for alternation in αMeStMA and a CTC plays a major role, then the equilibrium constant should be greater than that of the StMA monomer pair. CTC formation cannot therefore dominate the alternation mechanism, though it is accepted that it may play a small part, with differences in polarity of the double bond having the greatest effect on the formation of an alternating product. Further support for this proposal can be found by considering the Q and \(\varepsilon\) values calculated above that indicate a substantial difference in polarity between MA and αMeSt. Steric factors may also be important; the separation of 2 αMeSt units by a MA unit reduces the steric hindrance brought about by interaction of the α-methyl groups with neighbouring phenyl rings, which lead to the low ceiling temperature. The formation of an alternating copolymer is therefore kinetically and thermodynamically favourable.
4.8 IMPROVING CONTROL IN StMA PRODUCED BY RAFT COPOLYMERISATION

The success of a CRP technique depends on suppressing conventional radical polymerisation in favour of the controlled addition of monomer units with limited influence from bimolecular termination. In terms of RAFT polymerisation, this can be achieved by reduction of the number of chains derived from initiator fragments compared to the number of chains capped by the RAFT mediator. Strategies include optimisation of the concentration of RAFT mediator compared to initiator, and development of improved RAFT mediators which may incorporate functionality that provides a less stable disulfur radical to increase the rate of fragmentation, and a more reactive reinitiating group. The approach presented here involves maintaining the BDTB RAFT mediator, but adjusting its concentration in an attempt to increase the ratio of controlled to uncontrolled chains. StMA was prepared in a manner analogous to that presented in Section 4.6 except the concentration of BDTB was increased from 0.024 mol% wrt MA to 0.06 mol% wrt MA. The initial molar ratio of AIBN:BDTB of 1:2 was therefore increased to 1:5. It was appreciated that increasing the concentration of BDTB would decrease the theoretical molar mass of StMA provided BDTB is completely consumed and there is one thiocarbonyl fragment per chain. The results for StMA are collected in Table 48 and are presented graphically in Figure 80 and Figure 81. The results indicate that increasing the BDTB concentration relative to the AIBN concentration has not had the desired effect, i.e. to match the experimental molar mass to the theoretical values. A linear increase in molar mass with increasing conversion along with PDI values <1.33 confirm however that BDTB is still exhibiting control over the copolymerisation. As predicted, a reduction in molar mass was observed due to the increased concentration of BDTB leading to an increase in the number of moles of StMA but a decrease in chain length.

In a further attempt to reduce the number of initiator-derived radicals that are not capped by the thiocarbonyl fragment, a number of thermal copolymerisations were carried out in the absence of a radical initiator. The generally preferred mechanism for the thermal polymerisation of St was elucidated by Mayo and confirmed by others (see Section 2.1.1). It was therefore predicted that StMA could be produced in the
absence of initiator (Scheme 13). Table 49, Figure 80 and Figure 82 present the results for StMA produced by thermal initiation at 100°C. Sample MCD375 was prepared without BDTB to validate the method, when StMA of high molar mass and broad MMD was isolated. The molar mass data must be considered qualitatively as the chromatogram for this copolymer fell outside the exclusion limits of the SEC columns used in the analysis. Sample MCD377 was prepared with BDTB (0.024 mol% wrt MA) as per Section 4.6. StMA of narrow MMD was produced and the molar mass measured by SEC was closer to the theoretical value though it was again higher than predicted.
Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (mins)</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>Mₙ (SEC) (g mol⁻¹)</th>
<th>PDI (Mₚ/Mₙ (SEC))</th>
<th>Mₙ (Calc) (g mol⁻¹)</th>
<th>[M]₀ (mol dm⁻³)</th>
<th>[M]₁ (mol dm⁻³)</th>
<th>Ln ([M]₀/[M]₁)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD378</td>
<td>510</td>
<td>1.03</td>
<td>0.67</td>
<td>6,600</td>
<td>1.27</td>
<td>4,900</td>
<td>3.0</td>
<td>0.99</td>
<td>1.11</td>
</tr>
<tr>
<td>MCD379</td>
<td>830</td>
<td>1.14</td>
<td>0.74</td>
<td>7,500</td>
<td>1.20</td>
<td>5,400</td>
<td>3.0</td>
<td>0.78</td>
<td>1.35</td>
</tr>
<tr>
<td>MCD372</td>
<td>1330</td>
<td>1.28</td>
<td>0.83</td>
<td>10,900</td>
<td>1.19</td>
<td>6,100</td>
<td>3.0</td>
<td>0.51</td>
<td>1.78</td>
</tr>
<tr>
<td>MCD373</td>
<td>2964</td>
<td>1.44</td>
<td>0.94</td>
<td>11,400</td>
<td>1.27</td>
<td>6,800</td>
<td>3.0</td>
<td>0.19</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Table 48 RAFT copolymerisation results for StMA in dioxane at 60°C (BDTB:AIBN = 5:1) (M₁:M₂ = 50:50).

Mₙ (Calc) from Equation 51
Table 49 Thermal RAFT copolymerisation results for StMA at 100 °C (M₁:M₂ = 50:50).

$M_n$ (Calc) from Equation 51

---

StMA prepared in the absence of BDTB

StMA prepared with 0.024 mol% BDTB wrt MA
Chapter 4: Results and discussion

Figure 80 Molar mass and PDI data for StMA produced by RAFT copolymerisation (▲ Thermal copolymerisation with 0.06 mol% BDTB wrt MA, ▲ AIBN:BDTB = 1:5, ▲ PDI for thermal copolymerisation, ▲ for AIBN:BDTB = 1:5).
Figure 81 SEC chromatograms for StMA produced by RAFT copolymerisation in dioxane at 60 °C (AIBN:BDTB = 1:5).
Chapter 4: Results and discussion

Figure 82 SEC chromatograms for StMA produced by RAFT copolymerisation at 100°C (BDTB = 0.06 mol% wrt MA).
Chapter 4: Results and discussion

StMA was prepared using the thermal method with BDTB (0.06 mol % wrt MA) in order to combine the positive effects of reduced initiating radical concentration and increased BDTB concentration. Narrow MMD's and a linear relationship between molar mass and conversion were again obtained demonstrating the controlling effect of BDTB. As with the previous RAFT copolymerisations to produce StMA, the experimental molar masses were greater than the theoretical values calculated for the total consumption of BDTB. Statistical analysis was carried out on the molar mass data obtained for StMA prepared under differing conditions and is presented in Table 50. The differences in molar mass between the SEC and theoretical values were calculated as a percentage difference for each series of copolymerisations and the mean of the differences calculated. It is clear that the system with the greatest radical initiator to RAFT reagent ratio results in molar mass values that are over double the theoretical value. Suppressing the contribution from the initiator-derived radicals by increased BDTB concentration, reduction of initiator concentration, or both, results in an improvement in matching the theoretical values. However, it was not possible to be within 150% of the theoretical value. The variance and standard deviation calculations are based on the mean of the difference between SEC and theoretical molar mass and

Scheme 13 Thermal initiation of St and subsequent reaction to form StMA.
Chapter 4: Results and discussion

cover the range of molar masses prepared for each system***. The results show that suppressing the contribution from initiator derived radicals provides data with a narrower distribution indicating consistent differences in theoretical and experimental molar mass throughout the conversion range.

<table>
<thead>
<tr>
<th></th>
<th>BDTD:AIBN = 2:1</th>
<th>BDTB:AIBN = 5:1</th>
<th>Thermal BDT = 0.024 mol% wrt MA</th>
<th>Thermal BDTB = 0.06 mol% wrt MA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean SEC molar mass % of theory</td>
<td>229</td>
<td>155</td>
<td>163</td>
<td>163</td>
</tr>
<tr>
<td>Variance</td>
<td>1486</td>
<td>471</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>39</td>
<td>22</td>
<td>-</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 50 Statistical analysis for StMA produced by RAFT copolymerisation.

Attempts to improve the control that can be gained using BDTB as RAFT mediator for the preparation of StMA have had limited success. Improved control was achieved by increasing the BDTB concentration relative to the free-radical initiator concentration. Linear increases in molar mass with increasing conversion coupled with narrow MMD’s provide evidence for the mediating effect of BDTB. However, the system cannot be considered fully controlled, as molar masses measured by SEC did not match the theoretical values. It is generally accepted that termination reactions lead to an increase in observed molar mass relative to the calculated one for anionic and cationic polymerisations126, 129. It is therefore reasonable to propose that conventional radical copolymerisation with its accompanied termination reactions is in competition with BDTB mediated copolymerisation. A likely explanation for this behaviour is the slow establishment of the RAFT equilibrium brought about by the slow fragmentation of BDTB. Before considering improvements to the RAFT reagent it is useful to consider the fragmentation or transfer kinetics from available literature data. The fragmentation

*** For example StMA of $M_a$ (SEC) = 19,300 g mol$^{-1}$ and $M_a$ (Calc) = 8,100 g mol$^{-1}$ : (19,300/8,100) $\times$ 100 = 238%. The calculation was repeated for a range of molar masses ($M_a$ (SEC) $11,100 - 33,500$ g mol$^{-1}$) delivering a range of % differences. The statistical analysis was then based on these % differences allowing a range of molar mass data to be analysed in the same manner.
constant (or chain transfer constant) \( (C_{ex}) \) has been estimated for the polystyryl dithiobenzooate system \((-\text{St-SCSPh})\) to be approx \( C_{ex} = k_{ex}/k_p \approx 6,000 \). The propagation rate constant measured from steady state methods\(^{60}\) was \( k_p \approx 190 \text{ mol dm}^{-3} \text{ s}^{-1} \). Using this data the exchange rate constant \( k_{ex} = 1.15 \times 10^6 \text{ mol dm}^{-3} \text{ s}^{-1} \). Klumperman \textit{et al} reported fresh evidence that StMA obeys the penultimate model and the majority of propagating radicals carry a terminal St unit\(^{134}\). Therefore the exchange rate constant for St, \( k_{ex} \) can be combined with the reported cross-propagation rate for MA adding to a St chain end\(^{62}\) \( k_{StMA} = 4.08 \times 10^3 \text{ mol dm}^{-3} \text{ s}^{-1} \). An approximate transfer constant of \( C_{ex(StMA)} \approx 300 \) can therefore be calculated. This approximate value is 20 times smaller than that for St when an identical RAFT reagent is used. This analysis based solely on differences in propagation rates, leads to a reduction in the transfer efficiency of the RAFT reagent and may explain in a semi empirical manner the reduction in control between St and StMA.

Improvements of RAFT reagents to increase the speed of fragmentation have been reported\(^{93}\) (Section 2.4.2). Increasing the fragmentation speed can be achieved by creating a less stable disulfur radical. BDTB forms a disulfur benzylic radical that can be stabilised by resonance (Figure 83). The radical leaving group is of vital importance to the success of the RAFT mechanism as was illustrated with the \( \alpha\text{MeStMA} \) system. Use of a tertiary radical leaving group would shift the fragmentation equilibrium towards favouring the leaving group rather than the propagating chain. The expelled radical should however be capable of reinitiating polymerisation and the captodative cyano isopropyl radical with its low BDE of 86 kcal mol\(^{-1}\) would be an ideal choice. Further development of the RAFT reagent therefore, may be necessary to further improve the CRP of MA and St monomers.
Chapter 4: Results and discussion

Immediately prior to the submission of this thesis Charlene Wager working for Dr Stephan Le Bon’s group at Warwick University kindly supplied the RAFT reagent 2 cyanoprop-2-yl dithiobenzoate (Figure 84). Very preliminary experiments were carried out to test this RAFT reagent with StMA. Table 51 provides the resulting copolymerisation data and indicates that the RAFT reagent with the tertiary cyanoisopropyl leaving group provides improved control for the copolymerisation of StMA. This is evidenced by narrow MMD represented by PDI values of $M_w/M_n = 1.10$ and a significantly closer correlation to the calculated molar mass than was observed with BDTB. These early results provide some support to the hypothesis that the use of a RAFT reagent with a tertiary leaving group will increase the rate of fragmentation allowing the RAFT equilibrium to be established early in the reaction. It should be noted that these results are by no means conclusive and further work is required.

Figure 83 Resonance stabilisation of disulfur carbon radicals.

Figure 84 2 cyanoprop-2-yl dithiobenzoate RAFT reagent
### Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_n$ (Calc) (g mol$^{-1}$)</th>
<th>PDI (M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt; SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD396</td>
<td>1.27</td>
<td>0.42</td>
<td>5,700</td>
<td>6,300</td>
<td>1.10</td>
</tr>
<tr>
<td>MCD397</td>
<td>2.96</td>
<td>0.98</td>
<td>12,900</td>
<td>14,600</td>
<td>1.10</td>
</tr>
</tbody>
</table>

*Table 51 RAFT copolymerisation results for StMA with 2 cyanoprop-2-yl dithiobenzoate (RAFT:AIBN = 5:1) in dioxane at 60 °C ([St]/[MA] = 50:50).*
Chapter 4: Results and discussion

4.9 RAFT COPOLYMERISATION TO FORM PODMA

Given the proceeding work concerning the conventional radical copolymerisation to form PODMA and the RAFT copolymerisation to form controlled copolymers of MA and St monomers attempts were made to combine the previous efforts in order to produce PODMA via CRP. PODMA of predetermined molar mass and narrow MMD would be of great benefit industrially as well as being academically interesting. Structure activity relationships between molar mass and crankcase dispersant performance, among other variables could be investigated with greater accuracy.

Table 52 presents the data for the preparation of PODMA using BDTB as the RAFT mediator at 100°C. Low molar mass products were obtained in low yield after 24 hours. PDI < 1.5 was obtained for PODMA however the molar masses calculated based on the total consumption of BDTB do not match the molar masses obtained by SEC. The molar mass for sample MCD217 was calculated by $^1$H NMR spectroscopy. Integration of the resonances due to the aromatic protons of the BDTB mediator were compared to the methyl triplet of the OD comonomer. The molar mass calculated by $^1$H NMR delivers values higher than the values obtained by SEC. Comparison of PODMA produced by conventional radical copolymerisation (samples MCD29, Table 3, MCD37, Table 4) and CRP (Table 52) indicate that the molar masses obtained by RAFT are approximately half those obtained by conventional radical copolymerisation. This qualitative analysis combined with the identification of thiocarbonyl end groups by $^1$H NMR suggests that a limited amount of control can be gained by using BDTB in the formation of PODMA. To claim that the copolymerisation adheres to the criteria laid out in Section 4.6.1 would be premature based on the results presented here and further work to test the copolymerisation of MA with $\alpha$ olefins is required before any sound conclusion can be drawn on the mechanism. Predictions can however be made when previous findings concerning degradative chain transfer are considered (Section 4.1.3). For CRP to be successful initiation must be fast and a constant concentration of chain carrying radicals maintained throughout the reaction. Termination therefore should be minimised. Degradative chain transfer acts as a chain formation step and the resulting allylic stabilised radical does not reinitiate polymerisation. Therefore the concentration
of growing centres will not be constant and the success of RAFT for the CRP of PODMA is questionable.
### Chapter 4: Results and discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>[AIBN] mol % wrt MA</th>
<th>[BDTB] mol % wrt MA</th>
<th>Yield (g)</th>
<th>Fractional conversion</th>
<th>$M_n$ (SEC) g mol$^{-1}$</th>
<th>$M_n$ (calc) g mol$^{-1}$</th>
<th>$M_n$ ($^1$H NMR) g mol$^{-1}$</th>
<th>$M_w$ g mol$^{-1}$</th>
<th>PDI ($M_n/M_w$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCD206</td>
<td>1</td>
<td>2</td>
<td>0.24</td>
<td>0.06</td>
<td>3,600</td>
<td>1,100</td>
<td>-</td>
<td>5,400</td>
<td>1.49</td>
</tr>
<tr>
<td>MCD207</td>
<td>1</td>
<td>1</td>
<td>0.58</td>
<td>0.13</td>
<td>3,600</td>
<td>4,600</td>
<td>-</td>
<td>5,000</td>
<td>1.39</td>
</tr>
<tr>
<td>MCD217</td>
<td>1</td>
<td>1</td>
<td>0.67</td>
<td>0.15</td>
<td>4,500</td>
<td>5,300</td>
<td>6,300</td>
<td>6,500</td>
<td>1.45</td>
</tr>
</tbody>
</table>

Table 52 RAFT copolymerisation data for PODMA at 100 °C.
5 Conclusion

MA copolymers have been prepared and characterised by conventional radical copolymerisation and by CRP.

Variation of the copolymerisation conditions has allowed PODMA of molar mass 4,000 g mol\(^{-1}\) to 60,000 g mol\(^{-1}\) to be prepared. The highest molar mass material was prepared by bulk copolymerisation. The gel effect and a loss in steady state kinetics resulted in high molar mass material. Degradative chain transfer to monomer accounted for the slow rates of copolymerisation and low molar mass when PODMA was prepared to low conversions. Chain transfer to OD was the main chain formation route and the allylic stabilised radical formed was not reactive enough to reinitiate polymerisation. The chain transfer constant was calculated at \(C_m = 0.025\) for PODMA.

A method was successfully developed for the accurate determination of molar mass for PODMA. This was achieved by a combined analysis technique involving SEC and dilute solution viscometry. The mobile phase was modified with acetic acid to inhibit adsorption. The use of dilute solution viscometry allowed the differences in hydrodynamic volume between PS and PODMA to be realised and an approach based on the universal calibration method allowed accurate molar masses for PODMA to be calculated directly from SEC measurements. For high molar mass PODMA samples the true molar mass was found to be approximately twice the value obtained from a PS calibration.

The main chain composition, stereochemistry and the end group structures were elucidated by FTIR and NMR spectroscopy. FTIR was used to obtain the copolymer composition from which the monomer reactivity ratios were calculated, confirming that PODMA has a strictly alternating structure. \(^{13}\)C NMR spectroscopy indicated that the backbone consisted of ODMA units in a 100% trans conformation, which was supported by molecular modelling. Identification of the end groups was accomplished by \(^1\)H NMR
spectroscopy. When BPO was used as the radical initiator, all the initiation was by the benzoyloxy radical with preferential attack of the OD monomer. Only one end group per chain was found and the absence of unsaturated chain ends supported the previous finding that the main chain formation route was degradative chain transfer to the OD monomer.

Preparation of PODMA on a large industrial scale was achieved by transferring a small scale academic procedure to an industrially viable synthesis. Optimisation of reaction conditions was carried out and PODMA of molar mass 11,000 g mol\(^{-1}\) was prepared on the pilot plant. The material was structurally consistent with the previous material produced on a small scale and is showing promise as a component in a high performance crankcase dispersant.

ATRP was attempted for a number of copolymerisations involving MA. The failure of the technique was attributed to copper carboxylate formation leading to catalyst deactivation. The failure of the catalyst was not restricted to the use of MA as monomer, grafting of MMA onto a backbone containing succinic anhydride units also was unsuccessful.

RAFT copolymerisation of MA with a number of St monomers was carried out using BDTB\(^{135}\). StMA, pMeStMA and pClStMA exhibited a number of living characteristics such as the incremental increase in molar mass with increasing conversion, narrow MMD, a constant concentration of growing centres and chain extension to form block copolymers. pMeOStMA had a wider MMD which was attributed to a faster propagation rate. The experimental molar mass from SEC data did not match the calculated molar mass for the complete consumption of the RAFT reagent and competition between the RAFT mechanism and uncontrolled propagation brought about by inefficient fragmentation was though to be responsible. aMeStMA was not mediated by BDTB and did not copolymerise by the RAFT mechanism. Decreasing the concentration of initiator derived radicals for the StMA system by increasing the RAFT reagent concentration or using the thermal initiation route brought about small improvements in the control that could be gained by using BDTB as the RAFT mediator. Monomer reactivity ratios of zero were calculated for all the investigated comonomer
pairs indicating that alternating copolymers were formed. The existence of a CTC could not be confirmed for any of the systems investigated and the proposed mechanism for alternation favours a free monomer model with differences in monomer polarity accounting for the observed alternation.

The preparation of PODMA by RAFT copolymerisation resulted in low molar mass products with values of PDI >1.3. The lack of control was attributed to the high degree of degradative chain transfer acting as a chain formation step. As the formed radical could not reinitiate copolymerisation the number of termination events could not be suppressed, a requirement that is essential in forming polymers and copolymers of narrow MMD.
Chapter 6: Further work

6 FURTHER WORK

1) Prepare a number of RAFT reagents with different radical leaving groups, R, such as the cyano isopropyl radical, cumyl radical and a leaving group derived from MA.

2) Prepare a series of RAFT reagents with less stable Z groups such that the less stable disulfur alkyl radical intermediate is formed rather than the disulfur benzylic radical intermediate. It is anticipated that this may increase the rate of fragmentation.

3) Test the developed RAFT reagents in the StMA system in an attempt to improve control by increasing the rate of addition and fragmentation.

4) Evaluate the RAFT mechanism with regard to alternating MA copolymers. Establish by NMR the location of the transfer agent and its preferred chain end, MA or St monomer.

5) Test a range of RAFT reagents with αMeStMA in order to improve the control with this system.

6) Preparation of block copolymers by the macromonomer approach and compare the control gained with the sequential addition method.

7) Preparation of interesting MA copolymer architectures such as stars, grafts, arms and block involving multifunctional RAFT reagents.
Chapter 7: References

7 REFERENCES

8 Chevron/Gulf PA-18 Technical data sheet.
Chapter 7: References

Chapter 7: References

75 Gulf Research. U.S. Pat 3,461,108.
76 Gulf Research. U.S. Pat 3,560,455.

241
Chapter 7: References

113 Davies, M. C., Dawkins, J. V. Hourston, D. J. and Meehan, E., Polymer, 43 (15) 4311 (2002).
Chapter 7: References

126 Hsieh, H. L. and Quirk, R. P., Anionic Polymerization, Marcel Dekker, New York, 1996
129 Matyjaszewski, K. Cationic Polymerizations, Marcel Dekker, New York, 1996
APPENDIX 1

PUBLICATIONS, POSTERS AND CONFERENCES ATTENDED
CONFERENCES

March 2000  RSC Annual meeting and Macro Group young researchers meeting, Attended  Manchester University

September 2000  Controlled Radical Polymerisation meeting, Attended  Cambridge University

March 2001  Additives 2001, Poster presented  Keble College, Oxford University

March 2001  Macro Group young researchers meeting, Poster presented  Strathclyde University, Glasgow

May 2001  Lubrizol technical symposium, Poster presented  Lubrizol UK, Hazelwood, Derby

December 2001  Macro Group polymer synthesis 1 day meeting, Attended  SCI headquarters

May 2002  Lubrizol technical symposium, Poster presented  Lubrizol UK, Hazelwood, Derby

July 2002  Macro Group International Conference on Polymer Synthesis, Lecture and Poster presented  Warwick University

August 2002  ACS Fall Meeting, Symposium on Controlled Radical polymerisation, ACS Preprint and Poster presented  Boston, USA
Molar mass determination of poly(octadecene-alt-maleic anhydride) copolymers by size exclusion chromatography and dilute solution viscometry

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Abstract

The number average molar mass $M_n$ of poly(octadecene-alt-maleic anhydride) (PODMA) copolymers calculated from data obtained by size exclusion chromatography (SEC) using a polystyrene (PS) calibration was found to be inaccurate. The use of SEC combined with dilute solution viscometry enabled a method to be developed using an iterative approach, which does not require knowledge of the Mark–Houwink constants for PODMA samples. A new calibration curve was constructed as a plot of molar mass $M_n$ for PODMA. True number-average molar masses $M_n$ (true) calculated using the new calibration are approximately twice the apparent molar mass $M_n$ (app) based on a PS calibration for higher molar mass samples (>10 000 g mol$^{-1}$).

Keywords: Maleic anhydride; α-Olefin; Alternating copolymers

1. Introduction

The combination of on-line molar mass $M$ sensitive detectors such as light scattering (LS) and viscometry with a concentration detector such as a refractometer for separations of polymers by size exclusion chromatography (SEC) provides considerable potential for characterisation of molar mass distributions and for number and weight average molar masses, $M_n$ and $M_w$, respectively [1]. In order to achieve reliability of results, practical procedures must be directed to optimising signal-to-noise output from detectors and to defining concentrations of polymer solutions consistent with detector response and with chromatographic conditions. For short chain polymers, the sensitivities of LS and viscometry detectors are much reduced, and so the accuracy of data for $M_n$ and $M_w$ by SEC with multi-detectors may be questionable [2]. For a polymer for which standards or reference materials are unavailable, one of several procedures based on the universal calibration approach can be considered [3], although a range of secondary problems, which might invalidate this approach, will have to be assessed. The universal calibration approach at a given elution time is defined by Eq. (1)

$$\log[\eta]_d \times M_d = \log[\eta]_u \times M_u$$

where $[\eta]$ is the intrinsic viscosity of a sample in the SEC eluent and $d$ and $u$ denote standards and unknown, respectively. Utilisation of this method allows the calculation of molar masses involving a SEC chromatogram and a calibration plot of log $M_u$ versus elution time.

Copolymers of long alkyl chain α-olefins and maleic anhydride have short chain lengths [4], and studies of copolymerisations and properties require knowledge of $M_n$. A trial-and-error method originally proposed by Weiss and Cohn-Ginsberg [5], and developed by others [3], permits the determination of a Mark–Houwink (MH) equation between $[\eta]_u$ and $M_u$ for a polymer from a universal calibration established with polystyrene (PS) standards. This method utilises values of $[\eta]$ for at least two polydispersed samples of that polymer measured off-line to the SEC instrument, in conjunction with SEC chromatograms for the same samples. A variation of this method in order to find a calibration curve for $M_u$ for alternating copolymers of octadecene and maleic anhydride (PODMA) is presented here, without the need for constants in the MH equation.
2. Experimental

2.1. Synthesis of PODMA

Commercial samples (MCD1 and MCD2) were supplied by Aldrich and SC Johnson, respectively. The following procedure was typical of that used for copolymerisations (MCD27, 44 and 66). The monomer and initiator concentrations were varied so as to produce samples of differing molar masses.

Maleic anhydride (4.90 g, 50 mmol, Aldrich, freshly recrystallised from toluene) was dissolved in dioxane (10 ml, Aldrich). Octadecene (12.63 g, 50 mmol, Aldrich) was added and the mixture decanted into a three-necked flask. Azo bis-iso-butyronitrile (0.0821 g, 0.5 mmol, Fluka, freshly recrystallised from methanol) was added. The vessel was evacuated by nitrogen sparge for 15 min before the nitrogen flow rate was reduced and the system was heated to 100 °C. Typically, the reaction ran for 12 h after which the solution was added dropwise to cold methanol (10 volumes). The PODMA sample was collected, reprecipitated from tetrahydrofuran (THF) into cold methanol (10 volumes) and dried under vacuum for 24 h at 60 °C. The copolymers were free-flowing pale yellow powders. Analysis was carried out by 1H NMR (CDCl3) and FTIR (CHCl3) spectroscopies to elucidate the structure and composition.

All the copolymers were free-flowing pale yellow powders. Analytical methods developed by Fineman and Ross [6], and Kelen and Tudos [7] were used to calculate the values of the monomer reactivity ratios \( r_1 \) and \( r_2 \). The product \( r_1 r_2 \) was zero providing evidence for the strictly alternating structure of PODMA.

2.2. Size exclusion chromatography

SEC was performed on a Polymer Laboratories instrument (PL-GPC 110) equipped with a refractive index detector. A set of two Polymer Laboratories columns (PLgel 5μM MIXED-D 300×7.5 mm) was used. The eluent was a mixed system (v/v) of THF (90%, Aldrich)/acetic acid (10%, Aldrich) and was used at a flow rate of 1.0 ml min\(^{-1}\). The analysis was carried out at 40 °C. Calibration was carried out using 10 different PS standards with narrow distributions and molar masses ranging from 580 to 325 000 g mol\(^{-1}\). The data were processed using a RM 575 computer operating Caliber GPC software from Polymer Laboratories.

2.3. Dilute solution viscometry

Intrinsic viscosity measurements were carried out using an Ubbelohde capillary viscometer having an internal diameter of 0.53 mm and a length of 10 cm. The flow times were automatically recorded by a viscometer timer (Schotte Gerate AVS 310). The solvent and temperature were the same as those used for the SEC analysis. Corrections for kinetic energy could be ignored as the flow times were relatively long (t0 ~ 100 s). The samples were dissolved in 15 ml of solvent, filtered and then added to the viscometer reservoir. Dilutions were carried out by adding fresh solvent to the viscometer and allowing 10 min for the solution to reach thermal equilibrium. The range of relative viscosities \( \eta_r \) for each experiment was between 1.2 and 2.0. The data were plotted using the Huggins equation with the intrinsic viscosity \( [\eta] \) (dl g\(^{-1}\)) determined by extrapolation to infinite dilution.

3. Results and discussion

THF is the solvent of choice for a number of polymer separations by SEC [2]. The use of THF for the separation of PODMA; however, does not provide good chromatographic resolution. Over a period of time, the chromatogram is shifted to longer elution times and the polydispersity of the sample is broadened. Tacx et al. [8] reported similar observations during the analysis of styrene-maleic anhydride (SMA) copolymers. Both LS and viscometry indicated no enhancement of molar mass or intrinsic viscosity and so intermolecular aggregation was not considered to be a reasonable explanation for this behaviour. It is suggested that a mixed exclusion/adsorption mechanism contributes to adsorption of SMA and PODMA onto the column packing. As PS does not exhibit such anomalies, it is assumed that the polar anhydride rings are responsible. Copolymers containing anhydride groups may also contain a number of dicarboxylic acid groups due to ring opening hydrolysis. This reaction is facilitated by THF that may contain low levels of water. The adsorption of SMA and PODMA can be suppressed by the addition of an acid. The addition of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Measured intrinsic viscosity ([\eta]_{exp})</th>
<th>Calculated intrinsic viscosity ([\eta]_{calc})</th>
<th>Apparent number average molar mass, (M_a) (app)</th>
<th>True number average molar mass, (M_a) (true)</th>
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</thead>
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<tr>
<td>MCD2</td>
<td>0.0874</td>
<td>0.066</td>
<td>4000</td>
<td>3900</td>
</tr>
<tr>
<td>MCD27</td>
<td>0.0664</td>
<td>0.0672</td>
<td>6200</td>
<td>15 600</td>
</tr>
<tr>
<td>MCD44</td>
<td>0.0737</td>
<td>0.0734</td>
<td>12 700</td>
<td>29 700</td>
</tr>
<tr>
<td>MCD1</td>
<td>0.0976</td>
<td>0.0998</td>
<td>14 400</td>
<td>37 100</td>
</tr>
<tr>
<td>MCD66</td>
<td>0.1278</td>
<td>0.1284</td>
<td>23 400</td>
<td>56 300</td>
</tr>
</tbody>
</table>
acetic acid to THF (10:90) stabilizes the anhydride ring and competes for the adsorption sites present on the column packing. Use of the modified mobile phase allows a size exclusion mechanism to operate without any interference.

In order to construct a universal calibration curve for PS, the MH constants for PS under the experimental conditions need to be utilized. Because of the modified mobile phase, MH constants were not available and so were determined by experiment. Values of $[\eta]$ for a number of PS standards were measured and a double logarithmic plot used to evaluate these constants. The following MH relationship was derived (Eq. (2)):

$$[\eta]_{ps} = 1.52 \times 10^{-4} M^{0.71}$$

(2)

Our proposed variation of the method of Weiss and Cohn-Ginsberg [5] starts with a plot of $\log [\eta]$ versus peak elution time for PODMA samples with apparent molar masses in the range 4–24 kg mol$^{-1}$. These apparent number average molar masses $M_a$ (app) which were determined by a PS calibration are given in Table 1. Values of $[\eta]_{exp}$ determined experimentally by solution viscometry are also given in Table 1. This initial plot together with SEC chromatograms for PODMA samples permitted the calculation of $[\eta]_{calc}$ for all PODMA samples. The PODMA samples characterised by SEC have polydispersities in the range 1.6–2.0, which are typical of conventional radical polymerisation and for which exponential molar mass distributions are generated [9]. It follows from earlier calibration studies [10] that the value of $M$ corresponding to the peak position of a chromatogram should be close to the viscosity–average molar mass $M_v$. The iteration method requires matching $[\eta]_{exp}$ and $[\eta]_{calc}$ for all PODMA samples by a series of calculations involving SEC chromatograms and trial-and-error placements of the plot of $\log [\eta]$ versus elution time. The resulting quadratic function is shown in Fig. 1 and values of $[\eta]_{calc}$ are compared with $[\eta]_{exp}$ in Table 1. The iteration method involves extrapolation of the plot beyond experimental data points as illustrated for the tails of the chromatogram for sample MCD44 in Fig. 1. However, only for the sample of lowest $M$, there is a problem in matching $[\eta]_{calc}$ and $[\eta]_{exp}$.

A major aim was to establish a SEC calibration $M_a$ for PODMA samples in THF/acetic acid (90:10) at 40 °C. The derivation of Eq. (2) enables a universal calibration to be determined with Eq. (1) from which a calibration for $M_a$ can be calculated since the dependence of $[\eta]_m$ on elution time is available from Fig. 1. The resulting calibration for PODMA is displayed in Fig. 2, demonstrating linearity in the region of high $M$ with a similar slope to the calibration for PS, indicating that the MH exponents for the two polymers in THF/acetic acid (90:10) are quite similar. The downturn in the plot for PODMA at low $M$ is consistent with the observation that the MH exponent should fall to 0.5 for short chains in good solvents, which has been demonstrated experimentally for several polymers [11–13]. Our method avoids the stipulation by Weiss and Cohn-Ginsberg [5] who determined fixed results for MH constants.

The described method allows the calculation of the true number average molar mass $M_a$ (true) for PODMA based on the $M_a$ calibration displayed in Fig. 2. For PODMA samples of high molar mass ($>10,000$ g mol$^{-1}$), values of $M_a$ in Table 1 obtained with the constructed calibration are approximately twice the apparent molar mass results based on a PS calibration. For the lowest molar mass PODMA sample (<10,000 g mol$^{-1}$) which is positioned in the downturn of the calibration (at higher elution times), similar values of $M_a$ (true) and $M_a$ (app) are obtained.

4. Conclusions

An iterative method for the calculation of average molar masses of PODMA has been demonstrated. The technique utilizes SEC elution times in conjunction with dilute solution viscometry, measured off-line to the SEC instrument. This method does not require knowledge of the MH constants for the unknown copolymer. The values of $M_a$ (true) of the PODMA samples were calculated and in all but the lowest molar mass sample, the $M_a$ (true) was at least twice the $M_a$ (app). The lowest molar mass PODMA sample had an $M_a$ (true) that was very similar to $M_a$ (app).
Acknowledgements

The authors wish to thank Douglas Barr and David Moreton from Lubrizol for helpful discussions and are indebted to the Lubrizol Corporation for a research grant and to Polymer Laboratories Ltd for the generous supply of PS standards.

References

CONTROLLED RADICAL COPOLYMERIZATION OF MALEIC ANHYDRIDE AND SUBSTITUTED STYRENES BY REVERSIBLE ADDITION-FragmentATION CHAIN TRANSFER (RAFT) POLYMERIZATION

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Introduction

Controlled radical polymerization (CRP) techniques have rapidly developed over the last decade. CRP is particularly appealing as it not only involves controlled polymer systems with a narrow molar mass distribution (MMD) and e-determined molar masses, but also can be performed using normal free radical procedures without the need for the stringent conditions required in living polymerization. CRP now encompasses nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and the more recently developed reversible addition-fragmentation chain transfer (RAFT) polymerization. With regard to maleic anhydride (MA), the RAFT process involves free radical polymerization in the presence of a dithiothreitol reagent. The synthesis of this highly efficient chain transfer agent ensures effective transitions between growing free radical chains and dormant end-capped chains. Providing exchange reaction is fast compared to propagation, the application of a thioketone compound will result in a pseudo living system. This work aimed to further investigate the RAFT copolymerization of MA with various styrene comonomers. The effect of differing functional groups substituted on the aromatic ring and the use of the sterically hindered monomer t-methyl styrene allowed the application of the RAFT method to be evaluated.

Experimental

Materials

All materials were purchased from the Sigma Aldrich Corporation and used as received unless otherwise stated. 2,2'-Azobisobutyronitrile (AIBN) (Fluka) (98%) was recrystallized from methanol. Maleic anhydride (95%) was recrystallized from toluene. Styrene (95%), α-methyl styrene (99%) and p-methyl styrene (96%) were passed through a silica gel column. The molar mass of the monomers was determined by a gel permeation chromatography (GPC) method. The number average M(n), weight average Mw, and the dispersity D MMD were higher than 1.0. Synthesis of benzyl dimethoxyazide (BDDT). The title compound was prepared using the procedure of Rickards et al. with the following modifications. Dry triethylamine (TEA) (30 mL) and carbon disulfide (3.44 g, 0.045 mol) were mixed at 25°C. Phenyl magnesium bromide (14 mL, 3M ether solution) was added dropwise over 30 min. The dark red solution was heated to 40°C and benzyl bromide (7.69 g, 0.04 mol) was added dropwise over 30 min. The solution was heated at 50°C for 12 hours.

Copolymerization

All copolymers were prepared in glass schlenk tubes equipped with taps and magnetic stirring bars. Solutions were degassed by repeated freeze pump thaw cycles. For kinetic experiments a stock solution was prepared and divided equally such that each tube contained MA (0.015 mol), a styrene monomer (0.015 mol), AIBN (0.0832 mmol), BDDT (0.167 mol) and dioxane (10 mL). The tubes were immersed in a pre-heated oil bath at 60°C and allowed to react for a designated time. For reactivity ratio experiments a series of MA concentrations (5 mmol to 25 mmol) (total monomer 30 mmol) was prepared under the same conditions as above. The reactions were terminated by rapid cooling and the products isolated by precipitation into methanol and dried under vacuum at 80°C for 12 hours. Conversions were determined gravimetrically.

Instrumentation

Size exclusion chromatography (SEC) was performed on a Polymer Laboratories instrument (PL-GPC 110) equipped with a reflective index detector. A set of 2 Polymer Laboratories columns (PL-gel 5mm MIXED-D 300 x 7.5 mm) was used. The eluent was a mixed system (v/v) of THF (90%) and acetic acid (10%) and was used at a flow rate of 1.0 mL min⁻¹. The analysis was carried out at 40°C. Calibration was carried out using 10 different polystyrene (PS) standards with narrow distributions and molar masses ranging from 280 to 325,000 g mol⁻¹. The data was processed using a RM575 computer operating Caliber GPC software from Polymer laboratories. Experimental values of molar masses, number average M(n), (SEC) and weight average Mw, (SEC) were computed, and the ratio Mw/M(n),(SEC) represents the width of the MMD.

Dual detection SEC was carried out using a Knauer HPLC pump 64 with a six port injection valve coupled to a Knauer refractive index detector and a Pyro Unique QC-1V, UV detector. The same column type as stated above was used with THF as the eluent at a flow rate of 1.0 mL min⁻¹ at 20°C. Fourier transform infrared (FTIR) spectroscopy was carried out on a Nicolet 20 DNIC-FTIR spectrometer. Samples were prepared (10% w/v) in a mixed system (v/v) of chloroform (50%) and dimethyl sulfoxide (DMSO) (50%). A calibration curve was constructed with maleic anhydride as the calibrant. The number of scans was typically 50 over a wavenumber range of 650 cm⁻¹ to 4000 cm⁻¹. Spectra were processed using an IBM compatible computer operating Omni software.

Results and Discussion

RAFT copolymerization characteristics. Living polymerization can be distinguished from conventional polymerization by a number of specific characteristics, namely incremental increase in Mw with increasing conversion, narrow MMD and a constant concentration of active centres. For a CRP method to be successful it must show these characteristics. Styrene-co-maleic anhydride copolymer (SMA) was prepared using the RAFT system. Figure 1 shows that SMA has living character by virtue of the incremental increase in Mw, (SEC) with increasing conversion, along with narrow MMD's throughout the reaction. The following formula allows the theoretical number average molar mass M1 (calc) to be calculated.

\[ M_1 (calc) = x M_n (RAFT) \]

where [M] is the total monomer concentration, [RAFT] is the DBDT concentration, x is the fractional conversion and M1 is the average molar mass of the copolymer.

Figure 1. Evolution of M1 (SEC) (A), MMD (a) with conversion during copolymerization of SMA at 60°C. M1 (calc) (—). The values of M1 (SEC) are higher than M1 (calc). This was initially thought to be due to the use of PS standards in the SEC analysis, which will have different hydrodynamic volumes to the analysed copolymers. Use of the Mark Houwink constants for both St and SMA allows the PSD calibration to be converted to a calibration valid for SMA. The adjusted calibration predicted lower M1 values than M1 (SEC), though the compensation for hydrodynamic volume was not sufficient to account for the difference between M1 (SEC) and M1 (calc). Figure 2 presents the kinetics of copolymerization for SMA. The straight line in the semi-logarithmic plot of ln([M]/[M]) indicates that there is a constant concentration of growing radicals throughout the copolymerization.

Copolymers of p-chlorostyrene-co-MA (pClStSMA), p-bromostyrene-co-MA (pBrStSMA) and p-methyl/styrene-co-MA (pMeStSMA) were all prepared using BDDT. The M1 (SEC) versus conversion data are presented in Figure 3. All three investigated comonomers result in linear increases in M1 (SEC), with values of M1 (SEC) in the range 1.1 to 1.4. A common factor in all the presented copolymerizations is that the linear plots of M1 (SEC) do not intersect the molar mass axis at the origin.
RAFT technique. The high concentration of thiobenzoate groups in pMeStMA, observed throughout the copolymerization with aMeStMA, can be attributed to differences in electronic functionality substituted at the para position. The hydrodynamic volume reasons stated above do not provide a reasonable explanation for this observation. A competition between a conventional radical polymerization mechanism and the RAFT mechanism is more likely. If AIBN initiation at 60°C is rapid in comparison to the establishment of the addition-fragmentation equilibrium, then initially conventional copolymerization may take place. This theory is supported by the light reduction in $M_n/M_g$ (SEC) at higher conversions. In addition, the difference $M_g$ (SEC) - $M_g$ (calc) is consistent throughout the copolymerization and indicates that a constant molar mass is produced between $M_n$ (SEC) and $M_g$ (calc). Variations of the RAFT reagent that provide a less stable macro-radical intermediate have been found to increase the rate of fragmentation. This results in the faster establishment of the RAFT equilibrium, which would be anticipated to suppress conventional copolymerization. The fact that all the copolymers examined resulted in controlled copolymerization demonstrates that the RAFT method is not sensitive to different electronic functionality substituted at the para position in a styrene monomer.

$\alpha$-methylstyrene-co-MA copolymer (aMeStMA) was prepared using the RAFT technique. Figure 4 presents the relationship between conversion, $M_n$ (SEC) and MMD. It can be clearly seen that a constant molar mass is produced throughout the copolymerization with $M_g/M_n$ (SEC) varying between 1.6 and 1.8.

Dual detection SEC with the use of a UV/Vis detector set 330 nm, where only the end groups absorb, is presented in Figure 5. Higher concentrations of end groups are observed for copolymers of SIMA, pCISMA, pMeSIMA and pMeOStMA of known concentrations and similar $M_n$ (SEC) compared to aMeSIMA. The low concentration of thioesterate groups in aMeSIMA indicates that chain transfer of the RAFT reagent is inefficient and propagation dominates leading to conventional copolymerization characteristics.

Alternating Copolymerization. The structural composition of all the prepared copolymers was determined by FTIR. The anhydride group present in all the materials is easily identifiable. Absorbance measurements of a known mass of copolymer allow the molar quantity of anhydride to be calculated and therefore the composition of the chain elucidated by difference. The normal linear methods developed by Fineman and Ross and Kelin and Tudos were then used to calculate the reactivity ratios for the prepared copolymers and compared to conventional systems.

Monomer reactivity ratios for all the systems studied are very close to zero within experimental error indicating that the copolymer chains possess a strictly alternating structure. Composition analysis along with reactivity ratio calculations revealed all the copolymers to have an alternating structure, the reactivity ratios being consistent with both conventional and RAFT copolymerization methods.

Conclusions

CRP has been carried out using the RAFT method to copolymerize MA with a number of styrene comonomers. Copolymers with ST and para-substituted styrenes were found to have living characteristics though there were differences between $M_n$ (SEC) and $M_g$ (calc). aMeSIMA copolymers did not form via the RAFT mechanism, which was confirmed by the low concentration of the thiolesterate end group and the uncontrolled molar mass coupled with broad MMD. Composition analysis along with reactivity ratio calculations revealed all the copolymers to have an alternating structure, the reactivity ratios being consistent with both conventional and RAFT copolymerization methods.

Acknowledgements. The authors of this paper would like to thank the Lubrizol Corporation for funding this research.

References

APPENDIX 2

X-RAY CRYSTALLOGRAPHY STRUCTURAL AND DATA COLLECTION INFORMATION
Table 1. Crystal data and structure refinement for jvd1.

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<thead>
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<th>Identification code</th>
<th>jvd1</th>
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<tr>
<td>Chemical formula</td>
<td>C_{12}H_{18}CuO_{10}</td>
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<td>Formula weight</td>
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<td>Temperature</td>
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<td>Radiation, wavelength</td>
<td>MoKα, 0.71073 Å</td>
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<tr>
<td>Unit cell parameters</td>
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<tr>
<td></td>
<td>b = 15.8056(7) Å, β = 90.033(2)°</td>
</tr>
<tr>
<td></td>
<td>c = 12.0948(6) Å, γ = 90°</td>
</tr>
<tr>
<td>Cell volume</td>
<td>1628.85(13) Å³</td>
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<tr>
<td>Z</td>
<td>4</td>
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<td>Calculated density</td>
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<td>F(000)</td>
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<tr>
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<td>Reflections for cell refinement</td>
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<td>Refinement method</td>
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<td>Weighting parameters a, b</td>
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<tr>
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<td>Final R indices [F²&gt;2σ]</td>
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<td>Goodness-of-fit on F²</td>
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<td>Largest and mean shift/su</td>
<td>0.034 and 0.000</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.379 and -0.355 e Å⁻³</td>
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Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for jvd1. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

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<th>x</th>
<th>y</th>
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<td>0.44990(2)</td>
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<td>0.17399(9)</td>
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Table 3. Bond lengths [Å] and angles [°] for jvd1.

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<th>Angles</th>
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<td>Cu(1)–O(2)</td>
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<tr>
<td>Cu(1)–O(9)</td>
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<tr>
<td>O(1)–C(1)</td>
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<tr>
<td>O(2)–C(1)</td>
<td>1.251(2)</td>
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<tr>
<td>C(2)–C(3)</td>
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<tr>
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<tr>
<td>O(4)–C(5)</td>
<td>1.451(2)</td>
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<tr>
<td>O(6)–C(6)</td>
<td>1.255(2)</td>
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<tr>
<td>C(6)–C(7)</td>
<td>1.501(2)</td>
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<td>O(7)–C(8)</td>
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<tr>
<td>C(9)–O(8)</td>
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</tr>
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<td>124.91(11)</td>
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<tr>
<td>C(3)–C(2)–C(1)</td>
<td>125.39(16)</td>
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<td>123.95(18)</td>
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<td>C(6)–O(5)–Cu(1)</td>
<td>121.28(11)</td>
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<td>127.14(16)</td>
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</table>

Symmetry operations for equivalent atoms

\(-x+1, -y, -z\)
Table 4. Anisotropic displacement parameters (Å²) for jvd1. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + \ldots + 2hka*b*U_{13}]

<table>
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<tr>
<th></th>
<th>U_{11}</th>
<th>U_{22}</th>
<th>U_{33}</th>
<th>U_{23}</th>
<th>U_{13}</th>
<th>U_{12}</th>
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<td>-0.00106(7)</td>
<td>0.00111(7)</td>
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<td>0.0187(6)</td>
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<td>0.0008(4)</td>
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<tr>
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<td>0.0209(6)</td>
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<td>-0.0034(6)</td>
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<tr>
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<td>0.0196(8)</td>
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<td>-0.0013(7)</td>
<td>-0.0003(7)</td>
</tr>
<tr>
<td>C(3)</td>
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<td>0.0265(9)</td>
<td>0.0195(8)</td>
<td>0.0023(7)</td>
<td>-0.0048(7)</td>
<td>-0.0005(7)</td>
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<tr>
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<td>0.0241(9)</td>
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<td>-0.0053(7)</td>
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<tr>
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<td>-0.0005(5)</td>
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<td>0.0415(8)</td>
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<tr>
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<td>0.0275(12)</td>
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Table 5. Hydrogen coordinates and isotropic displacement parameters (Å²) for jvd1.

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<th>x</th>
<th>y</th>
<th>z</th>
<th>U</th>
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<td>H(5B)</td>
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<tr>
<td>H(5C)</td>
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<tr>
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<td>0.041</td>
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Table 6. Hydrogen bonds for jvd1 [Å and º].

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<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
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</thead>
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<tr>
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<tr>
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<td>2.10(3)</td>
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<td>168(3)</td>
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</tbody>
</table>

Symmetry operations for equivalent atoms
" = -x+1,y+1/2,-z+1/2
c:\pel_data\spectra\katy\jvd1.sp - Blue/green xtais from CuCl + 4 maleic anhydride in MeOH