An in-depth study for the acceleration RAFT polymerisation of vinyl acetate utilising microwave heating and supercritical carbon dioxide

Thesis submitted for the degree of Doctor of Philosophy

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September 2016

Declaration

Except where specific reference has been made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole, or in part, for any other degree or professional qualification.

Signed…… Date……..

Acknowledgements

Firstly, I would like to thank my supervisors, Professor Steve Howdle and Dr Derek Irvine, for their ongoing help and guidance whilst working on such an interesting project.

I am indebted to Synthomer, particularly Peter Shaw and Jon Batty, who provided me with the opportunity to work in such as interesting area, as well as giving me plenty of encouragement throughout my PhD.

I am grateful to Dr. Juliano Katrib, Dr Georgios Dimitrakis and Dr Vincenzo Taresco for all their help and advice with regard to my research.

Thank you to everyone down in the workshop who were also so helpful whenever a problem arose with my autoclave! I would also like to thank Clive Dixon in glass blowing and Mark Guyler who helped keep the lab running, particularly my shlenck line!

A big thank you to everyone both past and present in B10 who made working in the lab so enjoyable. A special mention to Silvio, Marina, Amy, Tom, George, Simon, Harry, Richard, Katie, Alba, Mohammad and Kevin. I would also like to mention Dr. James Jennings who really provoked my interest in research and Chris my summer student.

Finally I would like to thank my Mum, Dad and Brother David who have continued to show unwavering support and encouragement throughout my research. A big thank you to my wonderful fiancée Nicola, who has been my inspiration and has never stopped supporting me.

Abstract

The intention for this thesis was to observe whether the application of microwave heating, or using CO_2 as a reaction medium, could induce an acceleration for producing both homopolymers and block copolymers containing Poly(vinyl acetate) using RAFT polymerisation while maintaining the desired control.

Chapter 1 examines the various polymer synthesis techniques utilised throughout this thesis. This includes an introduction to controlled radical polymerisations such as RAFT, microwave heating and the use of supercritical carbon dioxide as an alternative reaction medium.

Chapter 2 details the various experimental reactors and characterisation methods used. The high pressure autoclaves used for solubility studies and producing polymers are examined, as well as the microwave reactor. Characterisation techniques used such as Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR) are also detailed

Chapter 3 examined the influence of applying conventional and microwave heating during the RAFT polymerisation of vinyl acetate. A series of experiments were designed to observe the effect of varying different reactant concentrations, as well as introducing a solvent into the reaction mixture. Each of these were examined to determine which induced an acceleration when using microwaves, while maintaining the desired control.

Chapter 4 investigated the RAFT polymerisation of vinyl acetate while using CO_2 as a viscosity modifier. Various reaction parameters such as monomer loading and RAFT : AIBN ratio were altered to examine the effect on the final polymer produced. Kinetic studies allowed the application of CO_2 to be compared with RAFT polymerisation with conventional and microwave heating from Chapter 3.

Chapter 5 studied the synthesis of block copolymers of PVAc and poly (vinyl pivalate) (PVPi). This involved the application of conventional and microwave heating for both the PVAc macro-RAFT agent and the 2nd PVPi block, to see the influence on the final block polymer properties, including the level of homopolymer impurity and final conversion. Additional reactions also looked at the use of CO_2 when producing the PVPi block.

Chapter 6 summarises the overall conclusions from the research presented in this thesis, and discusses possible future work.

Abbreviations

4VP – 4-vinylpyridine

AIBN - 2,2′-Azobis(2-methylpropionitrile)

ATRP – Atom Transfer Radical Polymerisation

BzMA – Benzyl Methacrylate

CRP – Controlled Radical Polymerisation

Đ – Dispersity

DCM – Dichloromethane

DMA – N,N-Dimethyl Acrylamide

DMAEMA – (2-Dimethylamino)ethyl methacrylate tert-butyl methacrylate

DMSO – Dimethyl Sulfoxide

D_p – Penetration Depth

DSC – Differential Scanning Calorimetry

ε' – Dielectric Constant

ε" – Dielectric Loss

EPDM – Ethylene Propylene Diene Monomer

FOMA – (1,1-dihydroperfluorooctyl) methacrylate

GPC – Gel Permeation Chromatography

IR – Infra-Red

ISM – Industrial, Scientific and Medical

HIP – High Injection Pressure

J_{crit} – Critical Chain Length

kp^{app} – Apparent Propagation Rate

LAM – Less Activated Monomer

MADIX – Macromolecular Design via the Interchange of Xanthates

MA – Methyl Acrylate

MAM – More Activated Monomer

NIPAM – N-Isopropyl Acrylamide

NMP – Nitroxide Mediated Polymerisation

NMR – Nuclear Magnetic Resonance

MMA – Methyl Methacrylate

M_n – Number Average Molecular Weight

$M_{n.th}$ – Theoretical Number Average Molecular Weight

M_w – Weight Average Molecular Weight

PDMS – Poly(Dimethyl Siloxane)

PEEK – Poly Ether Ether Ketone

P_n – Polymer Radical

PVAc – Poly (vinyl acetate)

R – Leaving Group from RAFT agent

$scCO_2$ – Supercritical Carbon Dioxide

SCF – Supercritical Carbon Dioxide

SG1 – N-tert-butyl-N-[1-diethylphosphono(2,2-dimethylpropyl)] nitroxide

$t_{1/2}$ – Half-life Time

TBA – Tertiary Butyl Alcohol

TEM – Transmission Electron Microscope

TEMPO – (2,2,6,6-Tetramethylpiperidin-1-yl)oxidanyl

T_g – Glass Transition Temperature

VPi – Vinyl Pivalate

V-70 – 2,2'-Azobis (4-Methoxy-2,4-Dimethylvaleronitrile)

Z – Stabilising Group from RAFT agent

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Chapter 1 - Introduction

1.1 Outline

This chapter focusses on introducing the major topics of this thesis. This includes a general introduction to polymer chemistry, with a particular focus on Reversible Addition Fragmentation chain Transfer (RAFT) polymerisation. There will also be an insight into the use of supercritical fluids and microwaves as alternatives to conventional methods, which have been proven to be applicable to a wide range of chemical processes, including polymerisations.

1.2 Polymers

Polymers are made from smaller units known as monomers, which add together to make a growing polymer chain, the more monomer units that add to this chain the longer the resultant polymer will be. A polymer made from only one type of monomer unit is known as a homopolymer.

If another monomer is introduced during the synthesis process a copolymer is produced, which can drastically affect the polymer's properties, such as its glass transition temperature (T_g). This is dependent not only on the type of monomer, but on the structure of the copolymer formed, which can vary as a result of differences in reactivity of the monomers and the ratio of monomer concentrations. Examples of the variety of possible copolymer structures are shown (Figure 1.1)

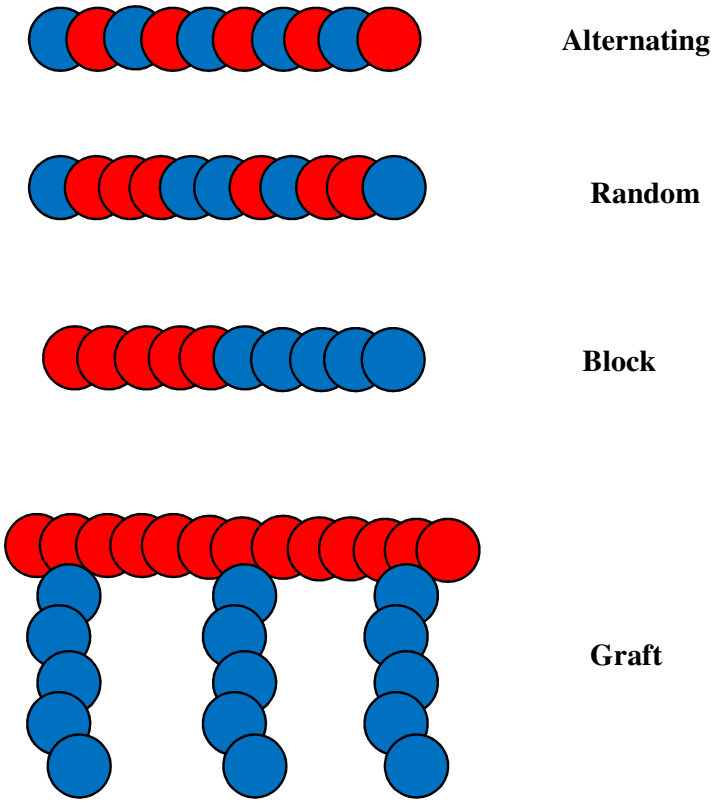


Figure 1.1 - Representations of some of the various possible copolymer structures

The varying possible structures and chain lengths for both homopolymers and copolymers leads to a wide variety of potential uses which can range from adhesives to paints, coatings and pipes.[1-4]

The methods for producing polymers can be separated into two broad categories, the first being step-growth polymerisation, which involves the forming of polymer molecules *via* the addition or condensation reaction of two monomer units.[5] A vital requirement for a successful step-growth polymerisation is that any monomer used must have a minimum of two functional groups present, which are located at either chain end, thus making the monomer bifunctional. These groups are then capable of combine together through a simple reaction step such as

polyesterification. Initially only dimer molecules are formed until high conversion levels are reached, at which point trimers, tetramers etc. are made, thus eventually facilitating the synthesis of high molecular weight chains.[6]

The other category for polymerisation is known as chain growth, where the process of polymer formation can be divided into three distinct stages; initiation, propagation and termination. The most common application of an initiator is to activate the π orbital in a double bond within the monomer molecule, making the bond susceptible to rearrangement. There are exceptions to this such as Ring Opening Polymerisation (ROP), where the action of an initiator relieves the ring strain in the cyclic monomer, thus driving the polymerisation process. A separate reagent is usually required to begin initiation, often in the form of free radicals, although there are alternatives such as using anionic/cationic initiators.[5] These "active species" are then able to grow and form long chains in the propagation step, which continues until termination prevents further polymer growth. The difference between these two methods of polymerisation can be demonstrated using the graph shown (Figure 1.2)

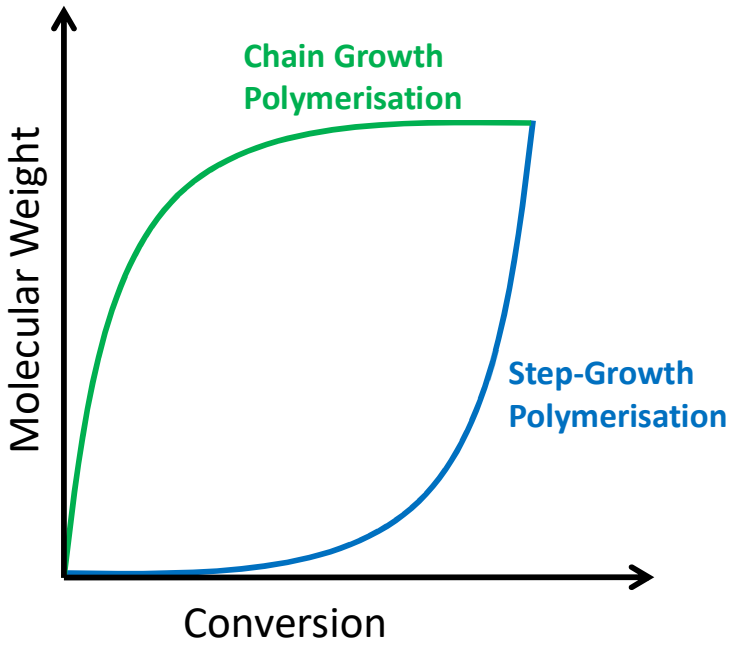


Figure 1.2 – Demonstrating the difference in mechanism between chain growth and step growth polymerisation

1.2.1 Free Radical Polymerisation

Free radical polymerisation is an example of chain growth, where the formation of radical species is used to start the polymerisation process. While it is possible for a monomer to self-polymerise, usually through the application of high temperatures,[5] it is much more common to use an external initiator radical source. These initiating radicals are produced by homolytic fission induced by an energy source such as light or ionising radiation,[5, 6] although the most frequently used method involves using thermal decomposition. An example of the formation of these radicals is given (Figure 1.3).

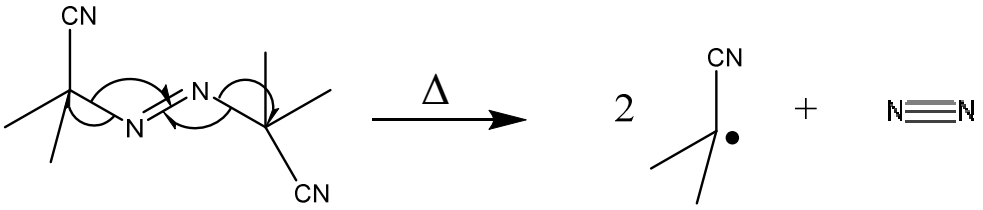


Figure 1.3 - Example of initiator decomposition using 2,2′-Azobis(2-methylpropionitrile) (AIBN)

When selecting a potential initiator, the bond dissociation energy is often one of the most important considerations, as this value must be within a particular range in order to initiate the polymerisation process effectively. Peroxides are a good example of initiators as the energy range required to break the O-O bond is 100-170 kJ.mol^{-1}.[5] The example of AIBN (Figure 1.3) is unusual in this regard, as the driving force to produce radicals is the formation of the highly stable nitrogen (~ 945 kJ.mol^{-1}) rather than dissociation energies for the C-N bond, which is high for any azo compound (~ 290 kJ.mol^{-1}).[7]

Another factor when choosing an initiator for free radical polymerisation is the half-life ($t_{1/2}$); the time taken for the initiator concentration to reach half its original value at a particular temperature.[8] A rise in temperature when using a thermal initiator increases the rate of radical production by reducing the half-life, which becomes relevant for experiments throughout this study.

The initiator efficiency is also an important aspect for the successful production of polymer chains.[9] When radicals are produced they are described as being in a 'solvent cage', which the radicals need to escape to initiate polymerisation,[5, 10] therefore high efficiencies result from a large proportion of radicals formed from the initiator reacting with a monomer molecule. This efficiency can be influenced by various factors such as solvents, viscosity and temperature. Furthermore, the initiator radicals must be sufficiently stable to initiate polymerisation before undergoing other processes such as self-termination.

The mechanism for a typical free radical initiation is shown (Figure 1.4), with the electron deficient initiator radical being attracted to the high electron density of the C=C bond in the monomer.

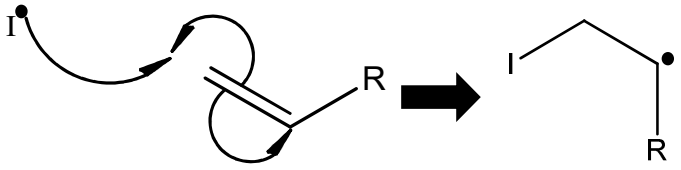


Figure 1.4 - Example of radical initiation of a monomer molecule

The next step in free radical polymerisation is propagation; the growth of the polymer radical chain by continuous addition of monomer units (Figure 1.5). As with initiation, the polymer radicals are highly reactive owing to the presence of an unpaired electron, therefore propagation is a rapid step in the polymerisation mechanism.

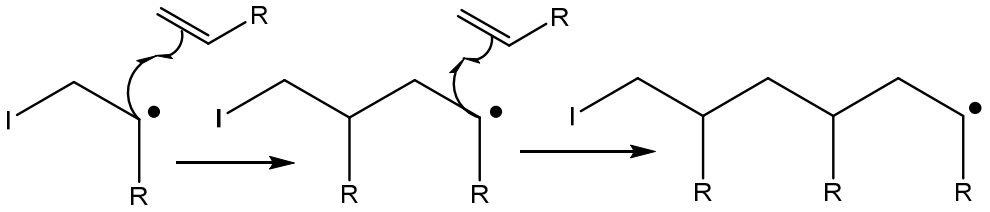


Figure 1.5 - Mechanism for a typical propagation, showing the continuing addition of monomer units to the polymer chain

The polymer radical could potentially attach to either end of the C=C bond in the monomer molecule. However the scenario shown (Figure 1.5) is the most predominant process for a vast majority of polymerisations owing to the presence of substituents, which help stabilise the radical species far more effectively than the hydrogens on the other carbon in the vinyl bond. This procedure for propagation, known as a head-to-tail arrangement, also avoids steric hindrance from the bulkier substituents, further enhancing the favourability of this particular polymer configuration.[5, 7]

A polymer radical attacking the least favoured carbon, i.e. the carbon with the non-hydrogen substituents, produces a head-to-head arrangement. An increased probability for this configuration can be induced by using monomer molecules with small substituent groups, thus minimising the influence of steric effects and resonance structures. The rapid nature of propagation with either arrangement results in high molecular weight polymer chains being produced even at low conversion levels.

The final stage for a free radical polymerisation is the termination of the polymer chains, which occurs either *via* combination or disproportionation of two polymer radicals as shown (Figure 1.6).[11]

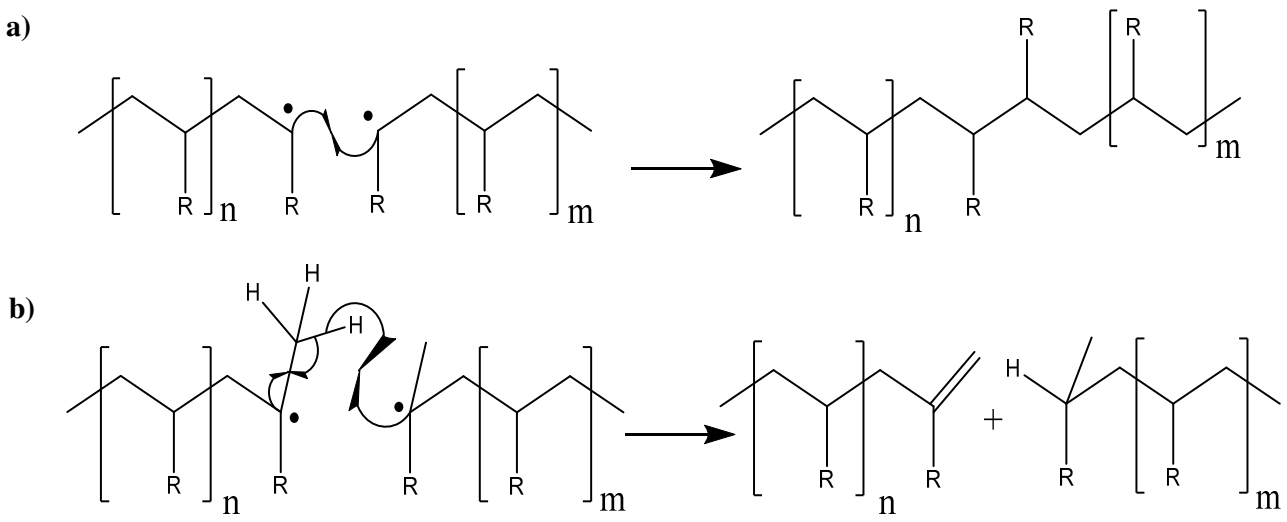


Figure 1.6 - Mechanisms for the two main methods of polymerisation termination. a) = combination termination and b) = disproportionation termination.

The first route to irreversible termination (Figure 1.6a) is *via* the combination of two polymer radicals, making a single saturated chain. Termination by disproportionation involves the rearrangement of the bonds in two polymer radicals, leaving one saturated and one unsaturated chain end (Figure 1.6b). Polymer radical chains have a short lifetime in the reaction as their highly reactive nature results in rapid termination, therefore potentially limiting the level of conversion that can be reached.[12] This produces a 'steady state approximation', where the rate of initiation is equivalent to the rate of termination, therefore the number of radicals present in the system is constant.

However as the viscosity of the polymer mixture rises, the level of termination is lowered as this process is controlled by diffusion, whereas initiation and propagation are unaffected.[13] Therefore the number of radicals in the reaction increases, inducing a chain reaction of further propagation as the viscosity continues to rise, which also consequently leads to an increase in temperature. Eventually termination is almost non-existent, therefore the rate of the chain

reaction is very rapid, which eventually causes the polymer mixture to gel. This runaway reaction is referred to as the Trommsdorff-Norrish Effect.[12]

A low radical concentration can reduce the degree of termination, making it possible to achieve higher molecular weights and conversions in a short time, however there is still a noticeable lack of control over the polymerisation reaction. This combination of rapidly producing high molecular weight species, fast rates of termination and broad dispersities makes it impossible to form block copolymers with standard free radical polymerisations.

1.2.2 Controlled Radical Polymerisation

An ideal solution to the limitations of standard free radical polymerisation would be to apply a 'living' polymerisation, where each chain grows at the same rate and there is no termination of the radical species. While entirely removing termination is extremely difficult, the demand for a higher degree of control over the polymerisation has led to the development of controlled radical polymerisations (CRP), with the introduction of a controlling agent that is capable of producing dormant polymer chains from the radical species in a reversible process (Figure 1.7).

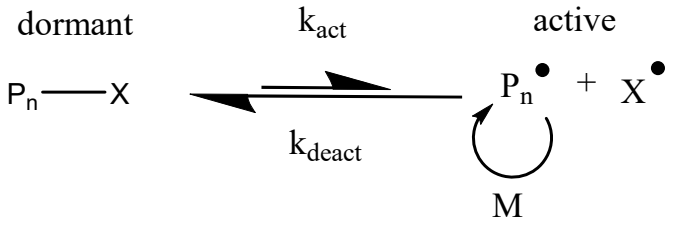


Figure 1.7 - General scheme for controlled radical polymerisations. P_n = polymer molecule, M = monomer unit and X = group capable of undergoing reversible termination without acting as initiator

In most CRP, all the chains are initiated very quickly, therefore in order to maintain a low radical concentration the equilibrium should favour the formation of the dormant polymer, therefore the rate of reaction is determined by the balance between the activation/deactivation rate constants of the control agent. This minimal radical concentration significantly reduces the level of termination but it is not entirely removed, hence why this is referred to as a controlled polymerisation instead of living. As most of the polymer chains are dormant, each chain grows at a similar rate, resulting in a linear relationship between the rising molecular weight and conversion values over time (Figure 1.8).

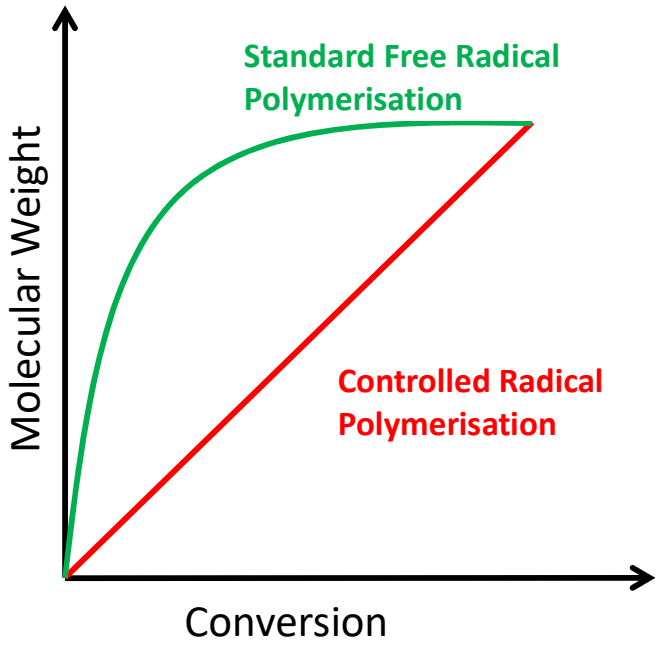


Figure 1.8 - Graph demonstrating the difference in the relationship between molecular weight and conversion for free radical and controlled radical polymerisation

Altering the concentration ratio of the control agent to the monomer facilitates the targeting of specific molecular weight values. A further consideration is the dispersity (Đ) of the final polymer produced, which represents the distribution of the different chain lengths. An ideal living polymerisation, where each grows at the same rate with no termination, would demonstrate a dispersity of 1. As there is a limited degree of termination with these CRP

techniques there is not perfect uniformity with regards to the chain length, however the dispersities produced remain relatively low, usually in a range between 1.2-1.4.[6, 7] The introduction of a controlling agent during polymer synthesis also provides end group functionality, enabling the production of particular molecular architectures and block copolymers through the addition of a second monomer or post-functionalisation.[14-16]

There are three main types of controlled radical polymerisations. ATRP and NMP will be given a brief overview, whereas RAFT/MADIX polymerisation is the basis for this thesis, so will be covered in greater detail.

1.2.2.1 **Atom Transfer Radical Polymerisation (ATRP)**

ATRP controls the polymerisation process through the use of a metal-ligand complex (Figure 1.9).

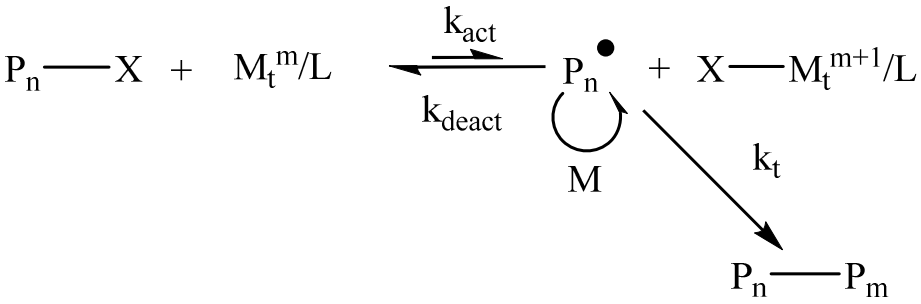


Figure 1.9 - General mechanism for ATRP where X = halide species, L = Ligand, M = Metal with charge represented by m

The polymer radical species in ATRP are generated by a reversible redox process,[17] catalysed by the presence of a transition metal complex.[18] Copper is frequently used as the metal centre, but research has confirmed the successful application of other transition metals such as iron

and osmium.[19] This metal complex is required to undergo a one electron oxidation process, whilst also abstracting the halide atom from the dormant polymer species. This abstraction allows propagation to occur *via* the addition of more monomer molecules to the polymer radical while generating the oxidised $X\text{-}M_t^{m+1}$ complex as a persistent radical, therefore maintaining a low concentration of radical species in order to reduce termination. As mentioned previously, the equilibrium between the dormant and radical species allows for controlled growth of the polymer chains, however it is essential that the forming of the dormant polymer species is the dominant process. This equilibrium can be influenced by various aspects, such as the selection for the ligand in the metal complex.[20]

The main issue with using ATRP is the high probability of the metal catalyst being present in the final polymer, as the process of removal can be both time consuming and expensive. Furthermore, when using copper there is gradual build-up of the Cu^{II} species which slows the polymerisation rate, therefore additional Cu^{I} is required for the reaction to continue.[21]

1.2.2.2 **Nitroxide Mediated Polymerisation (NMP)**

A nitroxide is used as the controlling agent in the case of NMP, where the formation of an alkyloxyamine species is the dominant process in the equilibrium (Figure 1.10).[22]

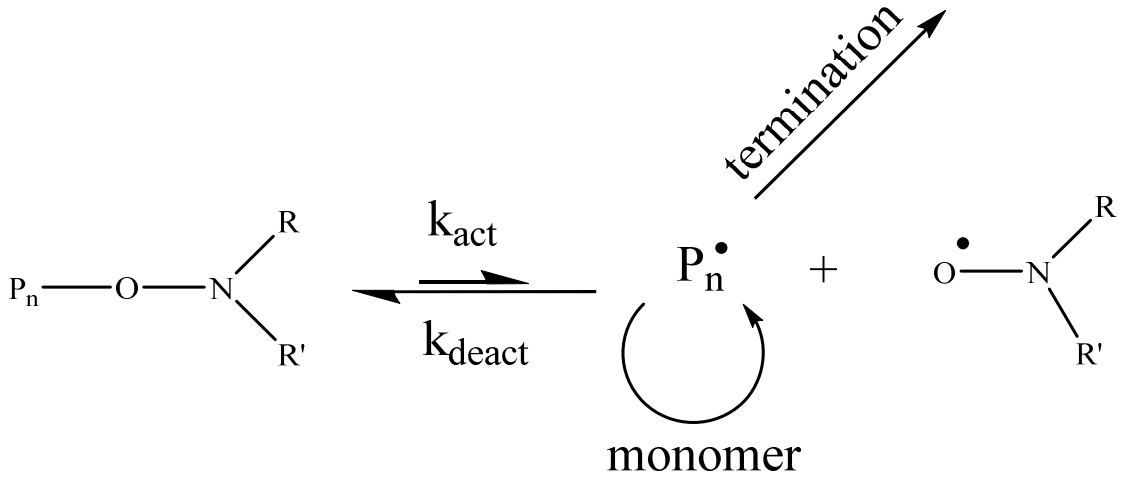


Figure 1.10 –Equilibrium system required for a successfully controlled nitroxide mediated polymerisation[23]

Propagation in NMP requires the re-generation of both radical species, which requires using a high temperature (~120 °C) to cleave the polymer-oxygen bond.[24] This equilibrium is advantageous as it is a purely thermal process, meaning that no catalyst is required as with ATRP. The equilibrium between the activation/deactivation rates and the persistent radical effect has a significant influence on the reaction kinetics for NMP.[25]

Various other factors can influence the rate of reaction during an NMP as well, such as steric hindrance around the polymer-oxygen bond, radical stability, polar groups on the nitroxide and hydrogen bonding.[26, 27] The main difficulties with using NMP are the slow polymerisation kinetics and the inability to control the growth of methacrylate monomers owing to the occurrence of side reactions.[28]

1.2.2.3 **Reversible Addition Fragmentation Chain Transfer (RAFT) / Macromolecular Design *via* the Interchange of Xanthates (MADIX)**

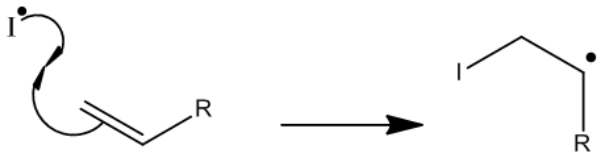
RAFT polymerisation is possibly the most versatile of the controlled polymerisation techniques as it has been proven to be applicable to a wide range of monomers,[29-31] used under a variety of reaction conditions,[32-34] and has been utilised in several applications such as light emitting films and producing pH responsive block copolymers.[35-37]

1.2.2.3.1 Mechanism of RAFT

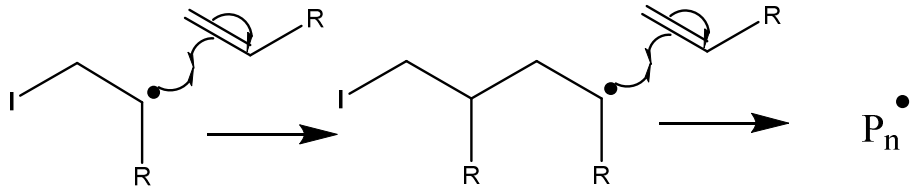
A RAFT polymerisation usually requires an external source to provide the initial source of radicals, as with a standard free radical polymerisation. However, the method by which control over the reaction is maintained is noticeably different from the other controlled polymerisations. NMP and ATRP use the persistent radical effect as the method to regulate the growth of the polymer chains,[38] involving the formation of another species (Figures 1.8 and 1.9) when generating the polymer radical, which is more stable and has a higher concentration compared to the propagating polymer. The increasing concentration of this persistent radical means it is more favourable to bond with the polymer radical rather than the polymer undergoing irreversible termination.

A RAFT polymerisation uses degenerative chain transfer reactions to control chain growth in order to produce polymers with low dispersities. A general mechanism for a typical RAFT polymerisation is shown below (Figure 1.11).

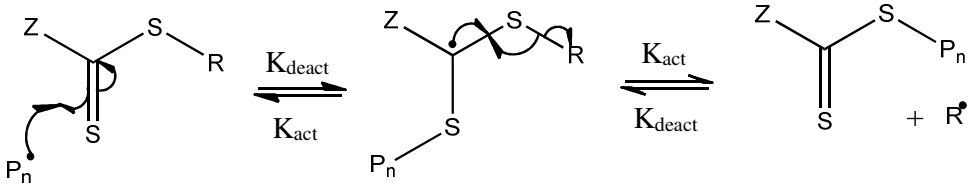
Initiation



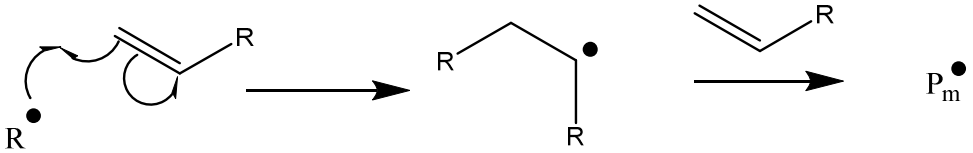
Propagation



Chain Transfer



Reinitiation



Chain Transfer

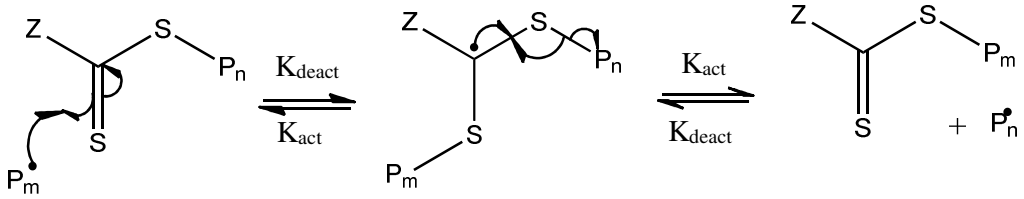


Figure 1.11 – Mechanism for RAFT Polymerisation

In the early stages of a RAFT polymerisation, the polymer radical ($P_n^{\bullet}$) undergoes addition with a RAFT agent to produce an intermediate radical. At this point the R group on the RAFT agent, which should be a better leaving group than the incoming polymer chain, leaves in the form of a radical species.[39] The polymer chain now has the RAFT end group functionality, and is therefore in a dormant state that can no longer propagate, while the R group radical that has been generated is able to initiate a new polymer chain (Figure 1.11).[40]

A rapid equilibrium is then reached between the active radical species and the dormant RAFT-capped chains, which provides an equal probability for all the chains to grow at the same rate, resulting in polymers being produced with narrow dispersities.[23] During these chain transfer equilibria, radicals are neither formed or destroyed,[41] therefore in theory the rates of polymerisation should be similar to those observed for a standard free radical reaction.

One of the most important aspects to a controlled polymerisation is the linear increase of molecular weight with conversion (Figure 1.8). Theoretically all the chains should be growing at the same rate, therefore the molecular weight can be calculated using the following equation, where the concentration of radicals present is assumed to be negligible.

$$M_{n,th} \approx \frac{[M]_0 - [M]_t}{[RAFT]_0} m_M + m_{RAFT}$$

Equation 1.1 – Theoretical molecular weight equation where $[M]_0$ = initial monomer concentration, $[M]_t$ = monomer concentration at time t, $[RAFT]_0$ = initial RAFT agent concentration, m_M = molecular weight of monomer, m_{RAFT} = molecular weight of RAFT agent

The conditions applied during a RAFT polymerisation have a significant influence on the level of control over the polymer chain growth, such as applying rapid initiation to ensure simultaneous growth of the polymer chains.[42] Additionally, the number of monomer units

added onto an active polymer radical during the equilibrium process must be kept low to maintain control over molecular weight. Low dispersities for the final polymer require a low initiator concentration in comparison to the RAFT agent to reduce the number of irreversibly terminated chains.

1.2.2.3.2 RAFT Agent Structure

The general requirements for the RAFT agent structure are shown (Figure 1.12)

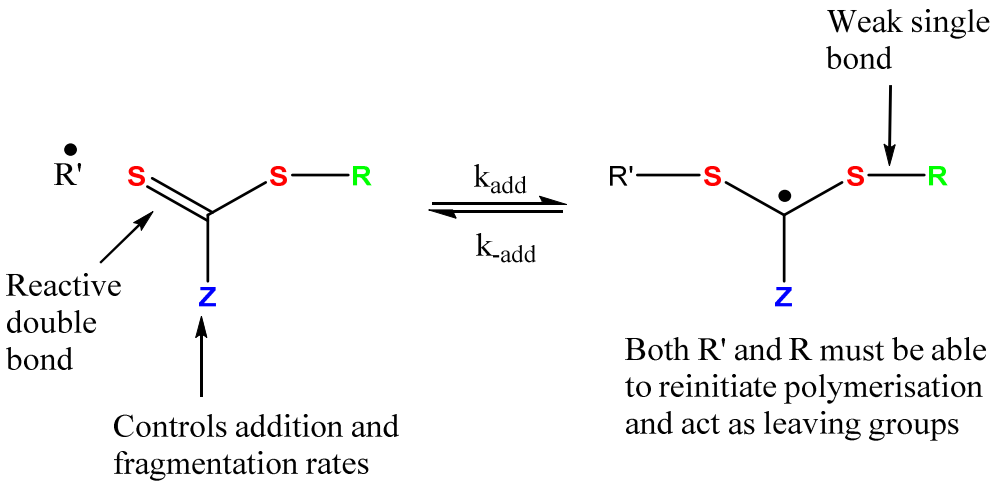


Figure 1.12 - Mechanism for RAFT agent intermediate radical

There are several important criteria for the RAFT agent that are required for a controlled polymerisation. The C=S bond must be reactive to ensure the approaching polymer radical can attack, while the intermediate radical that is then produced should favour rapid fragmentation to the polymer product, to avoid any potential side reactions.[43] Additionally, the R group radical should also be able to effectively re-initiate the polymerisation process.[44]

The Z group has a direct influence on the rate of addition and fragmentation of the RAFT agent. The various types of groups are shown (Figure 1.13).

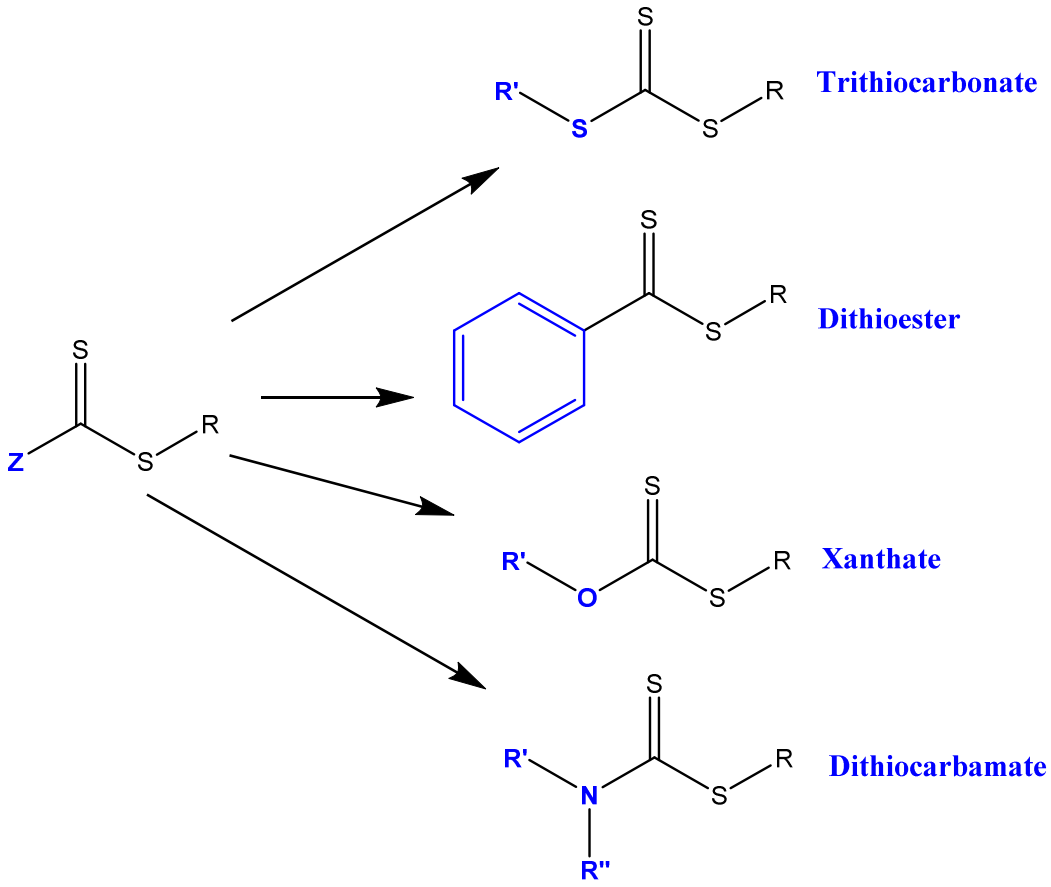


Figure 1.13 - The various classifications for RAFT agents based on the Z group present

The Z group is required to activate the C=S bond as much as possible to provide a high rate of addition by polymer radicals to compete with propagation, whilst also ensuring low stability of the intermediate radical to allow fragmentation to occur.[45] The ability of a particular Z group in a RAFT agent to produce a successfully controlled polymerisation is dependent on the compatibility with the selected monomer. An aryl, alkyl or S alkyl Z group (Figure 1.13) would enhance the addition rate for methacrylate or styrene based monomers, but using either an O-

alkyl or N-alkyl group would retard the polymerisation and produce broad dispersities as a result of resonance forms for the RAFT agent (Figure 1.14).[46]

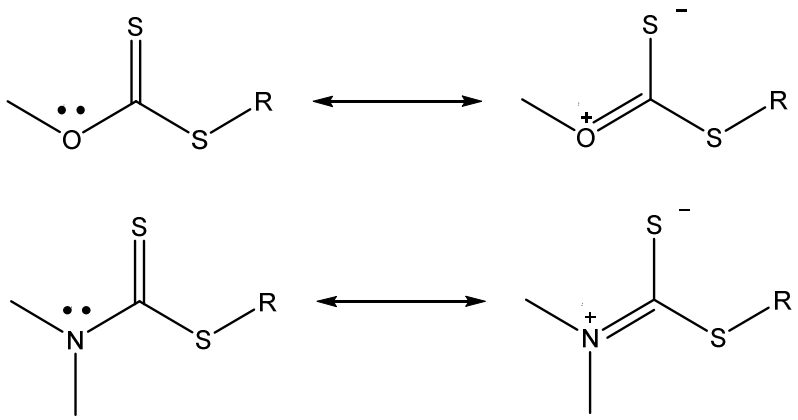


Figure 1.14 - Canonical form of O-alkyl and N-alkyl RAFT agents

The resonance forms raise the energy of the LUMO and HOMO, which reduce the double bond character of the C=S bond and subsequently lowers the rate of addition to the sulfur atom.[47] Therefore using a monomer such as methyl methacrylate (MMA) would result in poor control over polymer chain growth, however O-alkyl xanthates can work effectively with highly reactive radicals such as vinyl acetate.[48, 49] It is possible to alter the reactivity of xanthates and dithiocarbamates by using groups such as aromatic rings, which make the lone pair on the oxygen/nitrogen less available for producing these resonance structures, allowing radical addition to the C=S bond for other monomers.[47]

An appropriate choice of R group is also an important consideration for a controlled RAFT polymerisation, as this group must be a better homolytic leaving group than the incoming polymer radical.[32] Additionally, the resulting R• radical formed must be capable of re-initiating the polymerisation process efficiently. Balancing these factors can be complicated, as a better leaving group usually produces a stable radical and therefore results in slower re-initiation.[45]

To avoid side reactions, the R group should also preferably react with a monomer unit rather than with the RAFT agent.

The functionality of the R group is determined by various aspects such as the use of bulkier substituents, which have been shown to improve the leaving group ability and thus give better control in the early stages of the reaction.[50] Furthermore, a more effective R group can be formed through the use of highly electrophilic groups such as CN.[23] The use of substituents which help stabilise the resulting R• radical also shift the equilibrium towards the formation of dormant polymer chains.[45] As with the Z groups, the monomer used determines whether a particular R group is compatible for a particular RAFT polymerisation. A $C(CH_3)_2CO_2R'$ group would be suitable for styrene but would exhibit poor control over methacrylates, as it would not act as an effective leaving group.[49]

The choice of both Z and R groups is important to produce a successfully controlled polymerisation. However, examination of the RAFT polymerisation mechanism (Figure 1.11) determines that the Z group is present throughout the entire polymerisation process, whereas the R group is only influential during the initial stages of the reaction.

1.2.3 Controlled Polymerisation Kinetics

Several criteria have been listed as requirements to determine whether a polymerisation reaction can be classified as controlled, with one of the most important features with regard to work in this study being the conversion over time.[6, 7, 51] At any point during a controlled polymerisation the number of radicals present should be constant, but kept low to ensure the vast majority of polymer chains are in a dormant state. The radical concentration in a

conventional free radical polymerisation is also constant, however this as a result of new radicals being formed at the same rate at which irreversible termination occurs.[51]

Using the assumption that the polymer radical concentration is constant means the relationship of monomer consumption over time can be expressed with the following equations;

Equation 1.1 : $\frac{-d\,[M]}{dt} = k_p\,[P^*]\,[M]$

Equation 1.2 : $ln(\frac{[M]_0}{[M]_t}) = k_p\,[P^*]\,t = k_p^{app}\,t$

Where [M] = monomer concentration, t = time, k_p = propagation rate constant, [P*] = polymer radical concentration, $[M]_0$ = initial monomer concentration, $[M]_t$ = monomer concentration at time t, k_p^{app} = apparent propagation rate constant

A plot using Equation 1.2 can then be used to show the ideal behaviour for monomer over time (Figure 1.15)

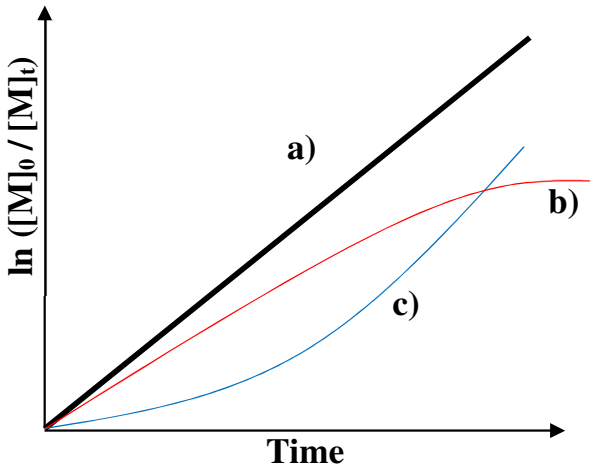


Figure 1.15 - Relationship between monomer consumption over time. a) ideal controlled polymerisation, b) high number of termination and / or side reactions and c) slow initiation

An ideal RAFT polymerisation demonstrates a linear rise in monomer consumption throughout the course of the reaction (Figure 1.15a), whereas the other reaction profiles illustrate possible scenarios where the reaction profile has deviated. A build-up of terminated chains (Figure 1.15b) eventually slows the rate at which monomer is consumed, resulting in a non-linear relationship. Similarly if a slow rate of initiation is used (Figure 1.15c), the initial rise in conversion is observed to be slow. In certain cases, it can take a noticeable length of time for polymer formation to begin, known as an induction period.

1.3 Polymerisation Methods

The purpose of this study was to investigate numerous methods to optimise the RAFT polymerisation of vinyl acetate, including the utilisation of various polymerisation methods to see whether it was possible to accelerate the usually slow rate of reaction while maintaining the desired level of control. Polymerisation processes can be divided into two separate

categories, homogeneous and heterogeneous. These characterisations are determined by whether the reaction mixture is either a single or multi-phase system.

1.3.1 Bulk Polymerisations

Bulk polymerisations are an example of a single phase system. This is the simplest method for carrying out a polymerisation reaction where the only necessary reactants are the monomer, initiator and potentially a RAFT agent, with the monomer also acting as the solvent for the reaction to ensure effective mixing. This minimal use of reactants for producing a polymer reduces the possibility of contamination, but also leads to a variety of potential problems. The main issue arises when viscosity increases, resulting from the monomer being continuously consumed during the reaction, which requires the use of substantial stirring equipment to ensure continued effective mixing.

A bulk free radical polymerisation usually follows three stages.[52] At the start there is little conversion as the radical concentration is very low, therefore propagation and termination rates are independent of the level of conversion. Eventually the reaction will reach its gel point, where the viscosity rises as a result of monomer consumption over time. This creates a situation where the polymer radical chains can continue to propagate as this is a chemically controlled process, whereas termination is controlled by diffusion and is therefore vastly reduced in a viscous mixture, leading to a lack of control of the polymerisation.

This loss of control can potentially lead to an auto acceleration where continuing propagation with little/no termination leads to continually increasing viscosity, which is referred to as the Trommsdorff-Norrish effect.[53, 54] A high viscosity reaction also leads to increasing temperature

and an uneven distribution of heat in the reaction mixture, causing a faster rate of initiator decomposition and therefore producing more radicals. The final stage after the Trommsdorff effect occurs when the polymer enters a glassy state, at which point the diffusion of monomer is reduced, causing the rate of polymerisation to rapidly drop.[52] Few industrial processes use bulk polymerisation owing to the inherent problems associated with it.

The bulk polymerisation of vinyl acetate has been studied to determine the variation of branching that occurs from chain transfer to the polymer through the use of NMR spectroscopy.[55] Initiator concentration was found to have no effect on the degree of branching owing to the high reactivity of the PVAc radical. The various factors that influence the polymerisation process in a bulk system means it is only possible to control the rate of propagation and produce narrow dispersities at low conversion levels.[56-58]

The highly reactive nature of the PVAc radical makes it unsuitable for bulk polymerisations, which is highlighted by an investigation designed to determine the rate of propagation for MMA and vinyl acetate.[59] Aspects such as lowering the initiator concentration, which had a noticeable effect on the polymerisation of MMA, were shown to have little effect on vinyl acetate. This is a result of the rapid increase in the polymer chain length, therefore taking the multiple measurements required to determine the propagation rate during a reaction proved to be very difficult. The only effective way to obtain enough data was through the use of a solvent to lower the rate of polymerisation.

1.3.2 Solution Polymerisations

The use of a solvent overcomes some of the problems found when reacting in bulk as it removes the issues regarding viscosity at higher conversion levels, meaning there are fewer difficulties regarding effective mixing, as well as ensuring effective heat transfer to the whole reaction mixture. The presence of a solvent also aides in maintaining a single phase reaction mixture. However the selection of solvent is crucial to avoid potential side reactions such as chain transfer.[60-62]

Several papers have investigated the effect of solution polymerisations with vinyl acetate which highlighted how influential the selection of the solvent can be..[59, 63, 64] The lower viscosity of the reaction mixture is not affected by the consumption of monomer as in a bulk reaction, meaning diffusion controlled processes such as termination are favoured, which lowers the polymerisation rate and produces lower molecular weight polymer chains.[65]

One investigation for the polymerisation of vinyl acetate was examined with tertiary butyl alcohol (TBA) and dimethyl sulfoxide (DMSO), where it was observed that the use of TBA produced higher molecular weight chains and lowered the extent to which branching occurred.[66] However the use of DMSO led to a faster polymerisation rate owing to a certain degree of precipitation which lowered the rate of termination.

Another comparative study studied the influence of using toluene and ethyl acetate in the solution polymerisation of vinyl acetate,[67] which determined that the monomer concentration when using either solvent had a significant impact on the polymerisation rate. The solvent was expected to exert a degree of influence on the radicals, however the radical to solvent ratio was unchanged. Therefore it was possible that a secondary effect was occurring, where the kinetic

termination rate for vinyl acetate was partially controlled by chain length, providing further confirmation that termination is a diffusion controlled process.

1.3.3 Precipitation Polymerisation

This is an example of a heterogeneous polymerisation, with the initiator only being soluble in the initial reaction mixture and not in the polymer, which eventually precipitates out into a separate phase. However it is possible for the monomer and solvent, along with the initiator, to be absorbed into a polymer particle, meaning polymerisation can potentially continue in the polymer phase.[5]

An in-depth investigation examining the precipitation polymerisation of acrylic acid in toluene discovered that the rate of polymerisation was equal in both the continuous and polymer phases,[68] contradicting similar studies which stated that polymerisation only occurred in the polymer phase.[69] Termination as a result of polymer precipitation affecting the radical concentration was present but determined to be negligible, with the vast majority of termination occurring as a consequence of disproportionation of the polymer radicals.

1.3.4 Suspension Polymerisation

Suspension polymerisation uses the monomer suspended as droplets in a continuous phase such as water, with coalescence being prevented through a combination of agitation of the mixture and the presence of a low concentration of suspension stabilizers. The initiator selected should

only be soluble in the monomer droplets, meaning each droplet can be treated as a mini bulk polymerisation system, therefore the kinetics should be similar to those seen in bulk.[5]

1.3.5 Emulsion Polymerisation

This is a similar system to suspension polymerisation, except the initiator is soluble in the continuous phase rather than the monomer. When the monomer is first added it is mostly in droplet form, with a minority of the monomer forming small particle micelles, but eventually the number of micelles will greatly exceed the number of droplets in the reaction mixture.[70] The initiator that is used should be capable of entering both the droplets and micelles.[71]

As the micelles are swollen with polymer chains, they are constantly replenished by diffusion of monomer species in the form of droplets. After approximately 50 % conversion these monomer droplets will have disappeared and consequently the polymerisation process occurs entirely within the micelles.[6] Polymer chain length can easily be increased without affecting reaction rate by either altering temperature or the concentration of initiator.

1.3.6 Dispersion Polymerisation

The monomer and initiator used for a dispersion polymerisation are soluble in the reaction medium but the resultant polymer is insoluble, using conditions that are identical to those required for precipitation. The major difference is the presence of a stabiliser which allows the

polymerisation to occur in two different phases throughout the reaction time.[5] At the beginning of the polymerisation the reaction mixture is homogeneous as any polymer formed is still soluble in the chosen reaction medium, however as chain length increases there is a critical point where the polymers become insoluble, at which point precipitation occurs.[72]

The polymer chains then start to collect together and form particles, at which point the stabiliser groups are able to anchor to the particle surface to prevent further aggregation *via* a steric effect.[73] This separates the particles so that the attractive van der Waals forces between the polymer chains are too weak to cause further accumulation. Initiator, monomer and short polymer radicals can then diffuse into these particles, which are now in a separate heterogeneous phase, therefore polymerisation can continue, causing the particles to swell and increase in size.[74] An example of this process is provided (Figure 1.16).

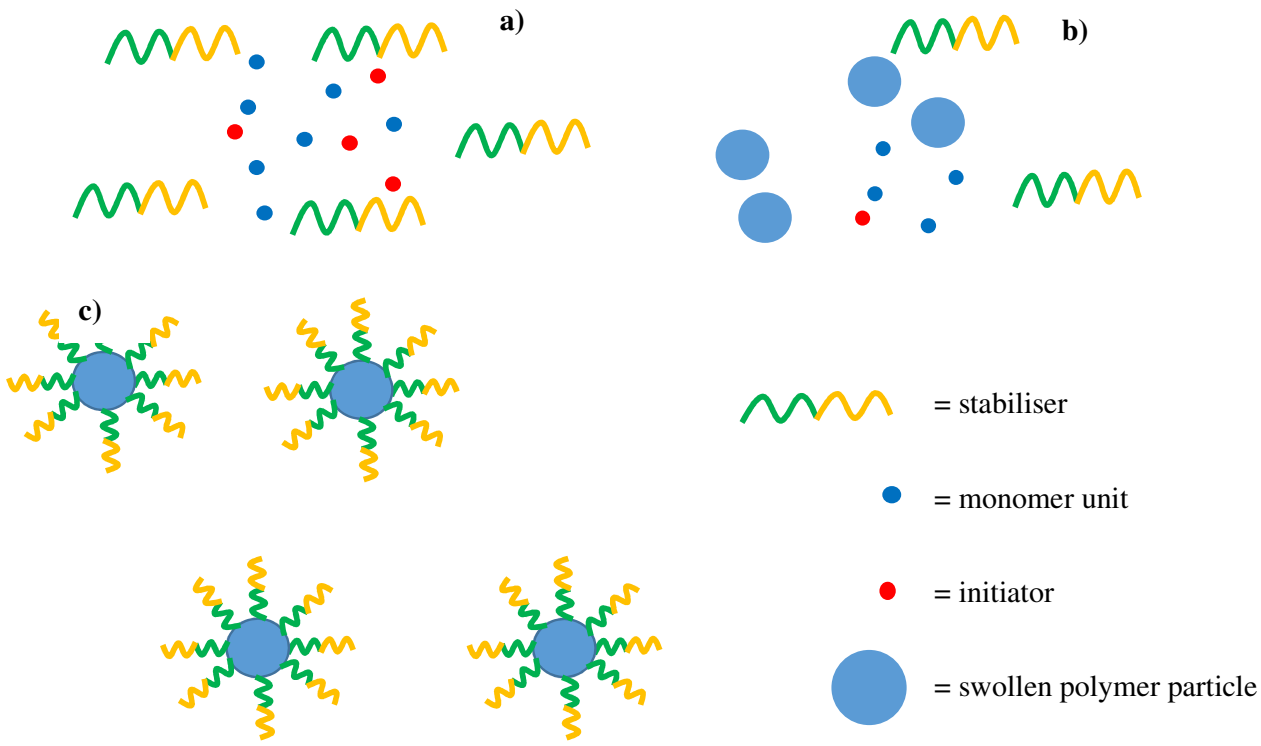


Figure 1.16 - a) shows the presence of all the reactants, monomer, initiator and stabilisers. In b), the polymer has begun to coagulate as large particles. c) shows the stabiliser anchored to the polymer particle surface. The presence of stabiliser groups leads to well defined particles and steric stabilisation prevents further coagulation of the polymer

1.4 **Supercritical Fluids (SCFs)**

1.4.1 Introduction

There has been a shift in recent years to make chemical processes more sustainable, with one increasingly popular method being the application of supercritical fluids. A fluid reaches its supercritical phase when it is taken above its critical pressure and critical temperature, as shown for the phase diagram of carbon dioxide (Figure 1.17).

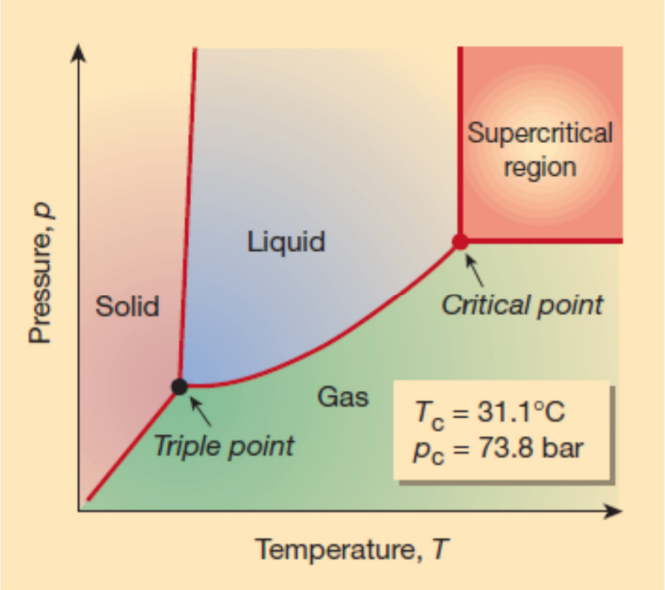


Figure 1.17 - Phase diagram for carbon dioxide with the conditions required to reach the supercritical phase shown[75]

At the critical point (Figure 1.17) there is no boundary between the liquid and gas phases, therefore SCFs are often described as having hybrid properties of a gas and a liquid.[76]

These unique properties give supercritical fluids numerous advantages when used in place of conventional solvents such as lower viscosity, where the high diffusivity can result in

producing faster reaction rates for a variety of chemical processes.[77, 78] Another distinguishing characteristic when using SCFs is the 'tuneable' nature of the density, as small changes in temperature and pressure can have a significant influence on the density, therefore the reaction environment can be altered for various situations.[79]

These properties give SCFs a wide array of potential uses such as for extraction,[80] fractionation and spray coatings.[81, 76] The application being focussed on in this study is with regard to chemical synthesis, where the selection of the SCF used could have various effects. Water, alcohols and amines are all possible considerations, however the variation in mass and intermolecular forces can affect whether a particular reaction can be successfully carried out.

1.4.2 Supercritical CO_2 ($scCO_2$)

One of the most popular SCFs in use is supercritical CO_2 as it is non-toxic, non-flammable and inert to a wide variety of chemical procedures. These properties, combined with being readily available and inexpensive, makes CO_2 highly appealing as an alternative to conventional solvents.[82]

Supercritical CO_2 has proved effective with a number of techniques such as extractions, purifications and is particularly effective for the synthesis and processing of polymers. [76, 83, 84, 85] This is a result of the high diffusivity of $scCO_2$ facilitating the manipulation of a large variety of polymers for processes such as impregnation and chemical modification.[86, 87]

The use of $scCO_2$ has also been successfully applied to various polymerisation synthesis techniques such as using free radicals. Additionally a large proportion of polymers are

insoluble in CO_2, therefore when the CO_2 is vented off at the end of a reaction, impurities such as unreacted monomer are removed, leaving a pure polymer product.[88]

1.4.3 Homogeneous Polymerisation in $scCO_2$

The most commonly applied chain growth technique for homogeneous polymerisations in CO_2 involves the use of free radicals, although it is possible to utilise other methods such as cationic polymerisation.[89, 90] Owing to the unique properties associated with supercritical fluids, numerous investigations have examined what effect the use of $scCO_2$ has on the polymerisation process. Investigations examining AIBN in CO_2 discovered that the rate of decomposition was noticeably slower compared to conventional solvents, which was attributed to the lower dielectric constant.[91] In contrast, the initiator efficiency was found to be as high as 80 % when using CO_2. This was a result of the high diffusivity allowing a higher proportion of radicals to initiate a monomer molecule, instead of undergoing other processes such as self-termination.[92]

An investigation into homogeneous free radical polymerisation in CO_2 focussed on the production of polystyrene, where a series of experiments looked at the effect of varying reactor pressure and concentrations of various reactants. [93] The rate of propagation was unaffected by the presence of CO_2, which was supported by previous research examining polymerisation of styrene and methyl methacrylate.[92] Another investigation determined that applying low temperatures and pressures during the experiments subsequently made CO_2 a poor solvent for the reaction, and thus lowered the rate of propagation.[94]

However one aspect for the polymerisation of styrene that could be altered was the termination rate. The poor quality of CO_2 as a solvent meant that increasing the polymer concentration

subsequently led to an increase in the mutual diffusion coefficient, which is a result of forming more tightly coiled chains.[93-95] These tightly packed chains cause an increase in the termination rate, which is assumed to be a consequence of a large concentration gradient between the inner and outer regions of the coil, allowing fast diffusion of the radical chain end to the surface of the polymer coil. Therefore, a homogenous reaction mixture when producing polystyrene could only be maintained by targeting low molecular weights and conversions.

This poor solubility observed for polymers with higher molecular weights and conversions is typical for almost all polymers in CO_2. A homogenous phase polymerisation has only been maintained to near full conversion and high molecular weights with amorphous fluoropolymer and polysiloxanes. [85, 96, 97] The excess shifts of peaks observed in ^{19}F NMR spectroscopy confirmed the presence of a specific solute-solvent interaction when fluorinated groups are present, therefore increasing the solubility in CO_2.[98]

When considering hydrocarbon based polymers, Poly (vinyl acetate) (PVAc) is considered one of the most highly soluble in CO_2.[99, 100] This is owing to a number of interactions both with the acetate and carbonyl groups present, as well as the lack of any significant steric bulk, thus making these groups easily accessible to the CO_2 molecules.[101] However, the number of interactions is rapidly reduced as polymer chain length increases.[102, 103]

An investigation examining the free radical polymerisation of vinyl acetate in CO_2 determined that lowering the reaction pressure led to an increase in the final conversion and molecular weight obtained after 4 hours.[104] This demonstrated noticeably different behaviour compared to methyl methacrylate and styrene, possibly owing to the low T_g and highly reactive nature of PVAc.

Another study looked at the effect of CO_2 on the propagation rate for vinyl acetate,[105] where it had been expected that the rate would drop compared to using conventional solvents, as had

been observed with other monomers owing to the presence of polar groups.[94, 95] However virtually no change in the propagation rate was observed, therefore it appeared that CO_2 was an effective solvent for both the polymer and monomer.

1.4.4 Heterogeneous Polymerisation in CO_2

Most polymers are insoluble in CO_2, therefore a heterogeneous reaction mixture is observed during the synthesis process. A number of investigations have looked at the precipitation polymerisation of poly (acrylic acid) in CO_2, with one example showing that CO_2 compared favourably as a dispersing media for the polymer formed compared to conventional solvents.[106] A certain degree of control over molecular weight could also be obtained when ethyl mercaptan was used as a chain transfer agent.

Another precipitation polymerisation in CO_2 examined the production of PMMA,[107] where use of no controlling agent produced a polymer with a moderately high molecular weight. After using a variety of different methods to control the growth of the polymer, it was determined that the highest degree of control was obtained when using controlling agents which were soluble in CO_2.

An investigation into the dispersion polymerisation of vinyl acetate highlighted how, unlike with some polymers such as PMMA, there was no sign of increase in reaction rate or molecular weight when using a dispersion polymerisation.[91] This was attributed to the low T_g of PVAc (30 °C), which reduces the viscosity within the dispersed particles. In addition, the high solubility of CO_2 in PVAc means the particles are swelled with a high concentration of CO_2 which increases the diffusion rate of the polymer radical chains. A combination of these effects

prevents the Trommsdorff effect occurring within these particles as was observed with PMMA, therefore no acceleration is induced.

Another aspect that required consideration for dispersion polymerisations of PVAc was with regard to stabiliser choice, as there was no formation of a stable latex of dispersed particles when using Poly(dimethylsiloxane) (PDMS) as a stabiliser, which is often used for dispersion polymerisations of PMMA. At the start of the reaction, the vinyl acetate monomer is able to act as a co-solvent which allowed the formation of stable particles. As the monomer is consumed, the dielectric constant for the reaction mixture drops which affects the solubility of the PDMS chains in CO_2 and causes them to collapse, meaning the PVAc particles are no longer stabilised. This drop in the dielectric constant does not occur with PMMA.

1.5 Microwave Heating

Microwaves are part of the electromagnetic spectrum, with wavelengths between 0.01-1 m, resulting in a frequency range of 0.3-300 GHz. For the purposes of laboratory experimentation, a frequency of 2.45 GHz is most commonly used. The photon energy at this frequency (1.6234×10^{-24} J) is considerably lower than that required to break a chemical bond such as C-C (347 $kJ.mol^{-1}$), thus microwaves cannot be used to initiate a chemical reaction. However microwaves can interact with materials in other ways, therefore allowing a particular material to be classified as either transparent, reflective or absorbent.

A transparent material demonstrates virtually no change upon being exposed to microwave energy. This can be a result of the molecules being too far apart, such as in a gas, or that the

molecules are restricted in their movement. Examples of transparent materials include quartz, Teflon and glass, making them highly suitable materials for reaction vessels in microwave reactors.

Reflective materials, which are often highly conductive materials such as metals, show only a marginal coupling with the microwave energy on the material surface.

An absorbent material can effectively absorb the energy from the microwaves and convert it into heat, usually as a consequence of interactions with the electric component of the microwave, although there has been research utilising the magnetic field.[108] However in order for this heating to occur the material must possess a dipole moment, which allows the molecules to align themselves with the electric field. The oscillation of this field subsequently makes the dipoles rotate, causing heat to be generated *via* molecular friction. The frequency of microwaves is ideally suited in this regard, as it is not so high that the molecules do not have time to realign, while also not being so low that molecular friction does not occur. There are two main mechanisms by which microwaves can heat a molecule: dipole polarisation and ionic conduction.

Ionic conduction involves microwaves causing the charged particles in a particular sample to oscillate, thus creating heat as a result of particles collisions as well as molecular friction. This is particularly relevant to work involving ionic liquids, as is discussed in more detail later (Chapter 3). Similarly, with strongly conducting materials, it is possible that the use of microwaves can cause a flow of electrons on the surface, therefore heating the sample through resistance heating.[109]

The other mechanism by which a sample can be heated is *via* dipole polarisation, where the material is required to have either a permanent or induced dipole in order to interact with the electric field.[110] The nature of this interaction with any dielectric material can be determined by examining two parameters; the dielectric constant and dielectric loss. The dielectric constant (ε') defines the ability of the material to absorb the microwave, whereas dielectric loss (ε") measures the efficiency by which this energy is converted and remitted as heat.[111] These properties can then be used to calculate the loss tangent (tanδ = ε"/ ε'), which provides an indication for the ability of a material to absorb and remit microwave energy.

A diagram demonstrating the differences between ionic conduction and dielectric heating is shown (Figure 1.18).

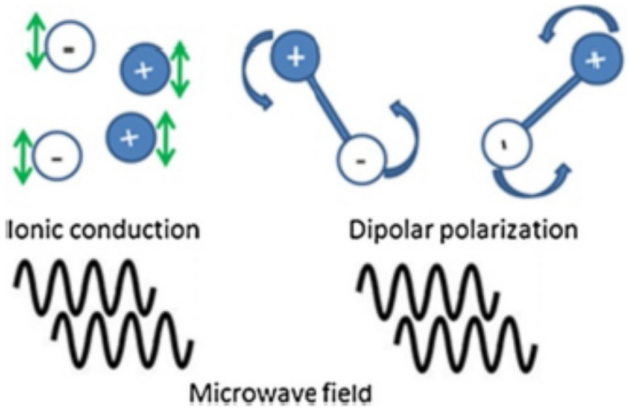


Figure 1.18 - Different molecular movements for materials with ionic conduction or dipolar polarisation

1.5.1 Dielectric Properties: Temperature and Frequency Dependence

An important factor for effective dielectric heating is the frequency of the electromagnetic energy that is applied. At low frequencies the molecules remain perfectly in phase with the

oscillation of the electric field, resulting in a minimal transfer of energy, thus the change in temperature is negligible. Similarly, applying a high frequency means the molecular dipoles are unable to respond and rotate, therefore no temperature increase is induced.[111]

The use of microwaves provides ideal conditions for dielectric heating, where molecular rotation is enabled by the electric field, therefore the material is able to absorb the microwave energy. However this rotation is slightly out-of-phase compared to the electric field as a consequence of intermolecular interactions such as friction, which leads to generating heat.[110] This frequency dependence for both dielectric parameters is demonstrated (Figure 1.19).

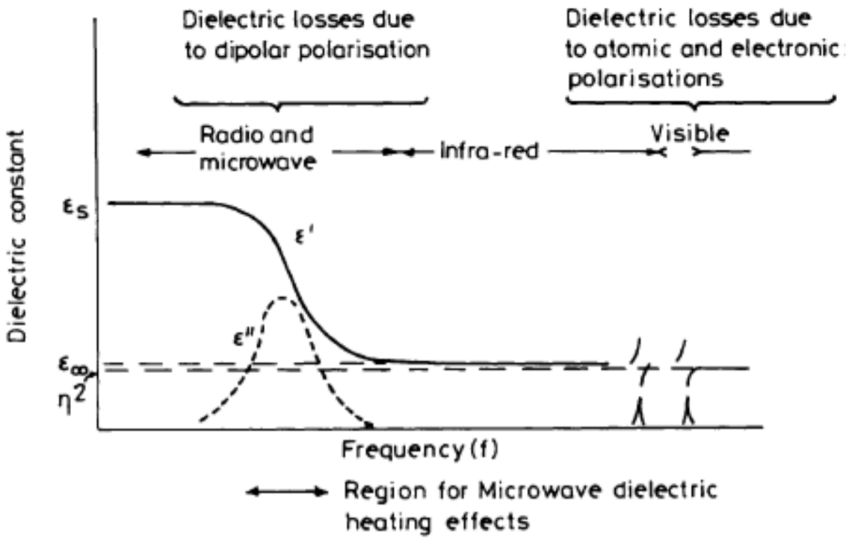


Figure 1.19 – Demonstrating how the frequency of an electromagnetic wave can effect dielectric properties[111]

The dielectric properties are also influenced by variations in temperature. A vast majority of organic materials show a decrease in dielectric constant, as the increased kinetic energy of the molecules reduces their ability to be polarised and rotate with the electric field (Figure 1.20).

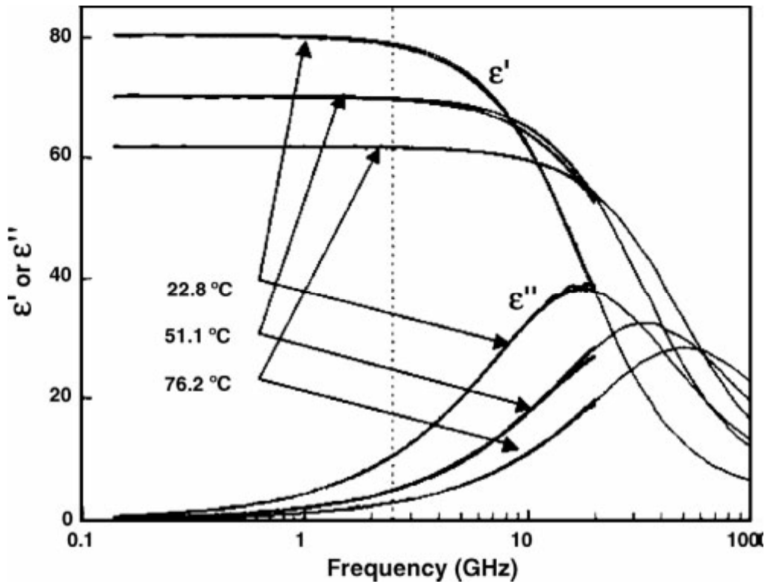


Figure 1.20 - Effect of temperature variation for water on both the dielectric constant and loss[109]

The dielectric loss is also proven to be affected by increasing the temperature of the material. The maximum possible value for ε" is observed to decrease as a higher temperature increases the distance between the molecules, therefore there are fewer interactions from friction to generate heat. The frequency required to reach the peak ε" value is also shown to increase with rising temperature.

However this scenario is not always applicable, such as for organic solvents that have long relaxation times i.e. the time taken for the molecules to change from polarised to having randomised motion once the electric field is switched off. This causes the loss tangent value to increase as temperature rises, thus potentially leading to a thermal runaway.[112]

1.5.2 Microwave Induced Acceleration

One of the key aspects throughout this thesis is the application of microwave heating to accelerate chemical synthesis, an area of research that is gaining more attention as it presents numerous advantages. Conventional heating methods such as using oil baths require a combination of convection and conduction to transfer heat to a reaction *via* thermal gradients, whereas the microwave energy interacts with the reactants and is converted into heat energy.[113] This direct coupling to the reactant molecules allows reactions using microwaves to be heated in a rapid and uniform manner leading to higher yields, reduced reaction times and fewer side reactions.[114]

Various theories have been applied in an attempt to explain the differences observed compared to conventional methods. One possibility is the presence of a non-thermal effect which induces the acceleration of the reaction rate,[115] however investigations where this is observed often have issues such as the application of unreliable temperature measurement techniques. The use of Infra-Red (IR) energy is a simple method to measure the reaction mixture temperature, however the measurements can be proven to be inaccurate, particularly during periods showing a rapid rise in temperature.[116] Therefore it is frequently discovered that these non-thermal effects can be explained by factors such as variable temperature readings.[117] The methods for recording temperature when using microwaves are covered in greater detail later in this thesis (Chapter 3).

Another important aspect to consider is the development of the microwave equipment that has been used. Early experiments used microwave ovens which, even when modified for chemical synthesis had issues with consistency, resulting from multi-mode heating and the potential danger occurring from hot spots.[110, 118, 119] The development of single mode microwave

instruments has led to reaction heating profiles being reproducible, thus providing a means to obtain reliable data.[109, 120]

Microwave heating has been proven to be beneficial for a widely diverse set of organic reactions ranging from rearrangements and hydrogenations to Friedel-Crafts, as well being applied to reactions using transition metals and organometallics.[113, 114, 120-122] Additionally, considerable success has been achieved involving polymers, as microwaves have been proven to show several advantages over conventional methods for a variety of polymerisation techniques. A more in-depth study on the application of microwave heating with polymers is covered later on (Chapter 3).

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Chapter 2 - Equipment and Analytical Techniques

2.1 Outline

The purpose of this chapter is to introduce the various laboratory apparatus, experimental procedures and analytical techniques used during this study. This includes a description of the microwave and high pressure reactors used for polymer synthesis.

2.2 Materials

Vinyl acetate (≥ 99 %, Sigma-Aldrich), 2,2′-Azobis(2-methylpropionitrile) (AIBN) (98 %, Sigma-Aldrich), 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (Wako), Toluene (98%, Fischer), HPLC Chloroform (≥ 99.9 %, Sigma-Aldrich), d-cholroform (99.8 %, Sigma-Aldrich), Vinyl pivalate (99 %, Sigma-Aldrich), Methanol (99.8 %, VWR Chemicals), Ethyl 2- bromopropionate (99%, Sigma-Aldrich), Ethanol (99.5 %, Fischer), Potassium ethyl xanthate (98%, Alfa Aesar), Dichloromethane (≥ 99.5 %, Sigma-Aldrich) and Magnesium Sulfate (99%, Fisher) were all used without further purification

2.3 Microwave Equipment

2.3.1 CEM Reactor

All the microwave reactions in this study were conducted using a CEM Discover SP (Figure 2.1)



Figure 2.1 - Image of the CEM Discover reactor taken from the CEM website, www.cemmicrowave.co.uk/

The CEM reactor provided a continual reading for the power level input for the reaction mixture during each experiment, with a maximum power rating of 300 Watts. There was also an internal infra-red temperature sensor, however for the purposes of this study a fibre optic probe was used to record the internal bulk temperature, which was inserted through a septum directly into the reaction vessel while being contained within a glass sleeve. This sleeve was necessary to protect the probe from being damaged by the various chemical reagents in the reaction mixture. This procedure was adopted as previous published data had proven that the readings from CEM internal IR sensor can deviate from the actual reaction temperature, particularly during periods with a rapid rise in temperature.[1, 2]

In a typical experimental procedure, the CEM reactor was programmed to input the maximum 300 W to rapidly heat the reaction mixture to the desired temperature as quickly as possible, after which the reactor automatically applied the minimum required power to maintain the reaction temperature (10-20 W). Particular experiments required the use of a lower initial power setting (50 W) to ensure a slower heating rate in order to avoid a temperature overshoot. However once the set temperature had been reached in these reactions, the apparatus reduced the input power such that it applied a minimal degree of power to sustain the required temperature.

2.3.2 Reaction Procedure when applying microwave heating

A typical reaction was conducted following the typical procedures detailed below:

1. A schlenk tube containing a mixture of vinyl acetate monomer, V-70 and xanthate RAFT agent was subjected to 3 freeze pump thaw cycles to ensure a minimal amount of oxygen was present. A glass sleeve inserted through the septum was present during this process, which was suspended above the reaction mixture. The schlenk tube was then purged with argon during which the glass sleeve was moved into the reaction mixture.
2. The schlenk tube was placed into the CEM reactor and clamped in place, after which the fibre optic probe was inserted into the glass sleeve to monitor temperature.
3. The desired temperature was programmed into the CEM, with the power set to either 50 or 300 W to determine the rate at which the reaction would be heated.
4. Once the reaction temperature was reached, a minimal power level (~10-20 W) was continually applied to maintain this temperature.

5. When sampling, a long needle was degassed 3 times in argon before taking samples for NMR and GPC at the required times. The power was momentarily turned off as the metal needle could potentially cause arcing, but was set back to the minimal level once the sample was taken.

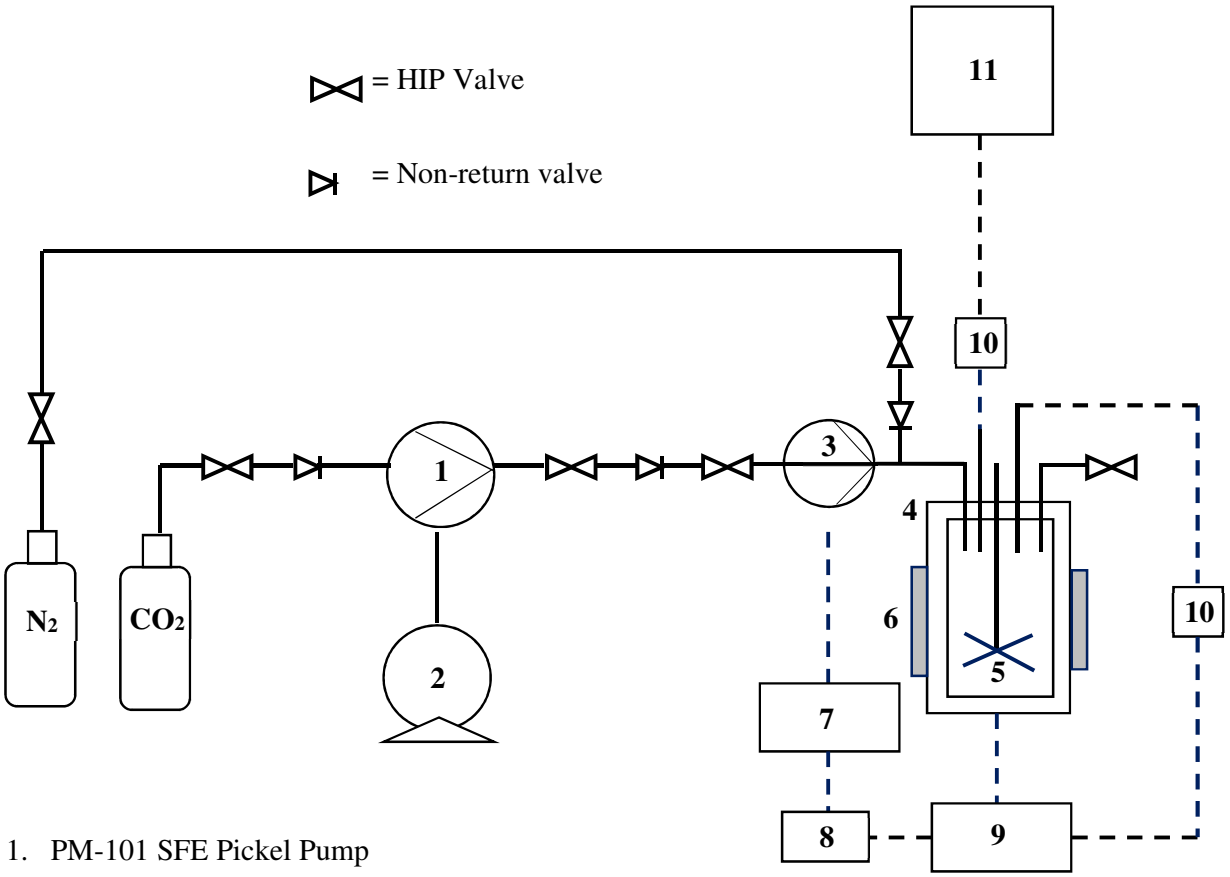
2.4 **High Pressure Equipment**

2.4.1 CO_2 Pump

The compressed CO_2 was delivered to the high pressure vessels using a PM-101 SFE Pickel Pump, with a gas inlet valve and refrigerator unit in order to liquefy the CO_2. Pressure output by the apparatus was controlled using compressed air, which compresses the liquefied CO_2 using a high surface area piston setup (111:1). It is designed such that the compressed air drives a large piston, which is connected to a smaller piston, where the different surface areas of these two pistons allows the relatively low pressure air to compress the liquid CO_2.

2.4.2 Generic High Pressure Equipment

A line diagram of the general apparatus use for the high pressure is shown in Figure 2.2.



1. PM-101 SFE Pickel Pump
2. Compressor
3. Piezoelectric Transducer
4. Mark III 20ml Clamp Seal Autoclave
5. Overhead Stirrer
6. Heating Jacket
7. Pressure Monitor
8. Trip
9. Temperature Control / Monitor
10. K-Type Thermocouple
11. Temperature Log

Figure 2.2 - Labelled schematic diagram for autoclave setup

The pressurised CO_2 was passed through 1/16 inch piping in order to deliver the liquefied CO_2 for the compression system, which was fitted with non-return valves to ensure no material could contaminate the main CO_2 line. This 1/16 inch pipe was connected to 1/8 inch pipe for transferring CO_2 directly into the autoclave. Both sets of pipes were constructed from stainless streel pipes supplied by Swagelok to ensure no issues arose from corrosion with use over time. High Injection Pressure (HIP) valves were used to control the flow of CO_2 so that the autoclave pressure could be altered without affecting the pressure within the main line.

2.4.3 Mark III Clamp Seal Autoclave

The polymerisation reactions carried out in CO_2 were performed using a 20 ml stainless steel Mark III autoclave (Figure 2.3).

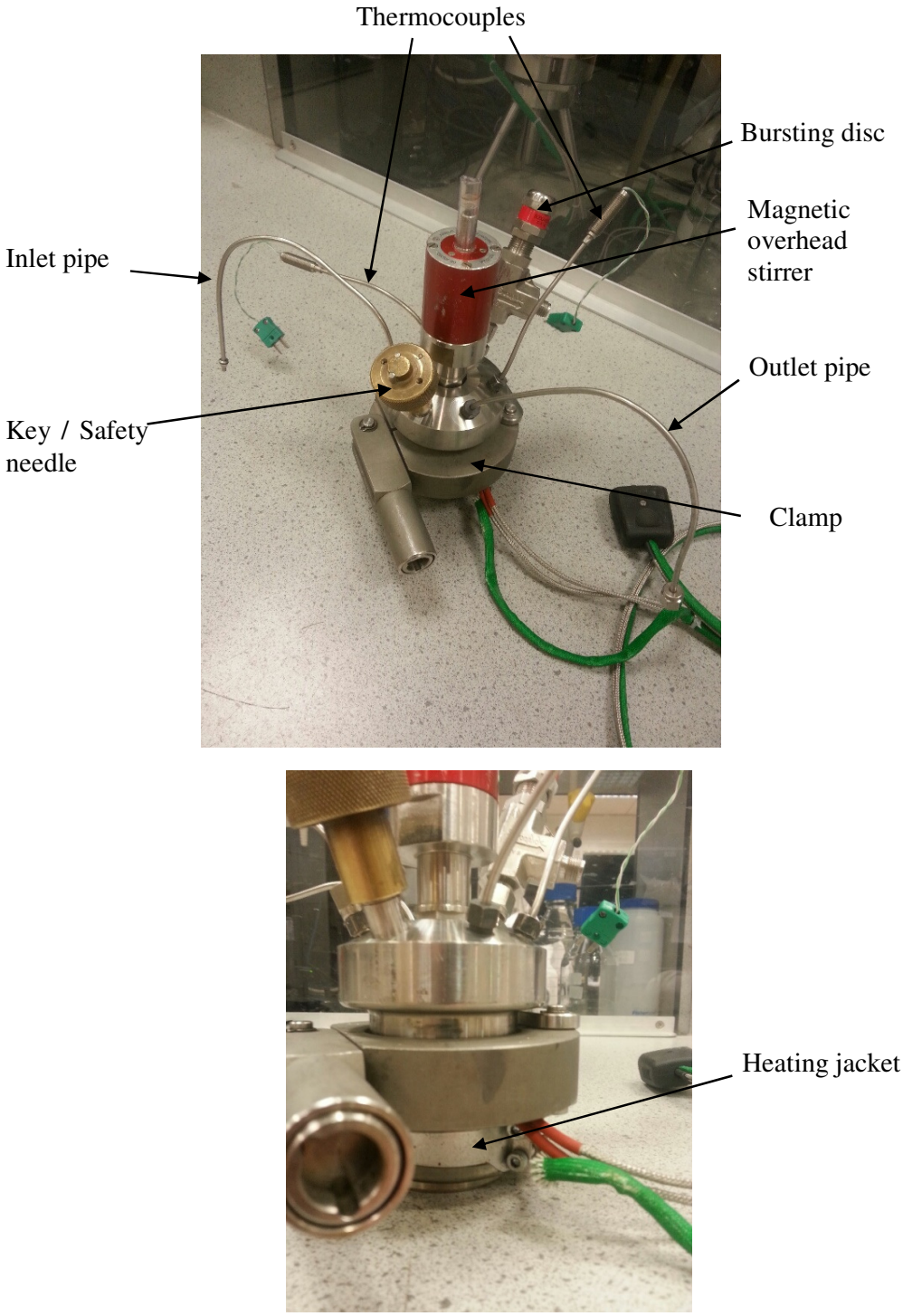


Figure 2.3 - Pictures showing various components of the autoclave reactor

The autoclave was designed and built internally at the University of Nottingham. There are two main components, the stainless steel base and the head attachment. The head attachment contains the inlet and outlet pipes for CO_2, as well as an assembly to allow a magnetic overhead stirrer to be introduced into the vessel to ensure effective mixing during the reactions. Two thermocouples were used, one attached to the heating box to control temperature and another for recording temperature data. A bursting disc was attached to ensure the autoclave pressure cannot reach dangerous levels (Figure 2.3).

A valve for a safety needle is also part of the head attachment, with a small hole built in to allow the slow release of CO_2 in the case of over pressuring during a reaction. The removal of the safety needle meant any residual CO_2 remaining after depressurisation could be vented, ensuring that the autoclave could be opened safely at the end of the reaction. At the start of the process, the reaction mixture is injected into the autoclave through the safety valve before the safety needle is secured in place (Figure 2.4).

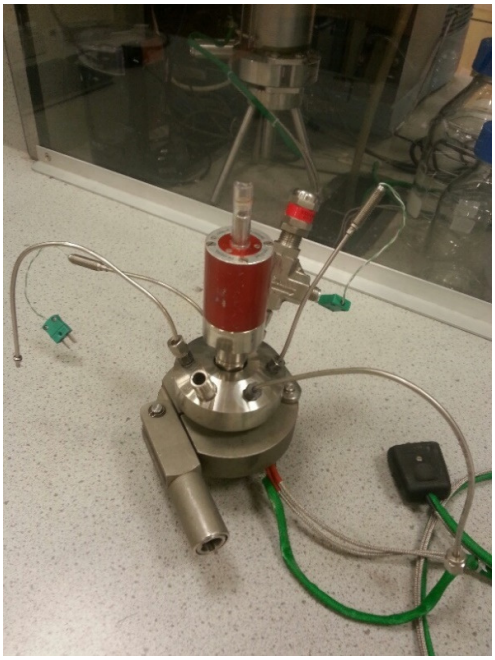
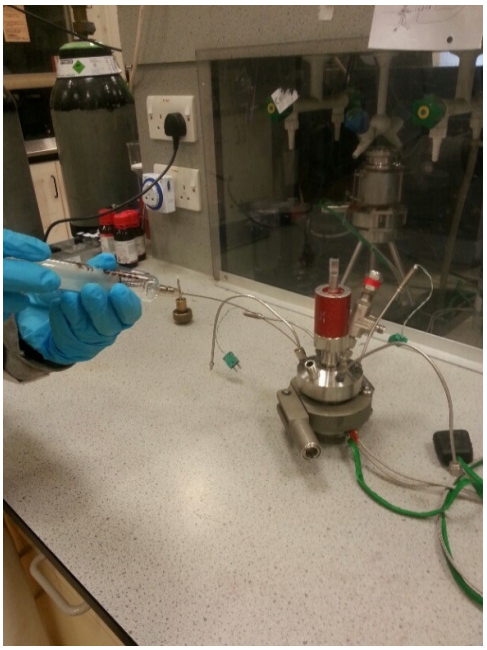
a)  b) 

Figure 2.4 - a) autoclave with the safety needle removed. b) showing how to inject the reaction mixture

During these reactions it was found that the PVAc frequently foamed when venting off the CO_2 which blocked the outlet pipe. In order to remove the remaining CO_2, a mixture of dry ice and acetone was used to lower the temperature, which subsequently lowered the pressure within the autoclave. These conditions also ensured that the polymer was in a solid form, thus removing the safety needle would not allow more foaming polymer to escape. Once ambient pressure had been reached, the autoclave was then allowed to reach room temperature before being opened to extract the final polymer product.

An ethylene propylene diene monomer (EPDM) o-ring was placed into a groove in the autoclave body, which provides a seal between the head attachment and autoclave body that can safely withstand the high pressures used. A clamp system was used to secure the two autoclave components together, where the key to open and close the clamp forms part of the

needle valve for the autoclave head. Each clamp and key/safety needle are uniquely tailored as a pair so that a specific safety key is required for any individual clamp, thus ensuring that the clamp could only be opened once the safety needle had been removed (Figure 2.5).



Figure 2.5 - Each key / safety needle is tailored to fit the corresponding clamp for the autoclave

Therefore there should be no residual CO_2 in the autoclave when the clamp is opened, allowing the polymer product to be extracted in a safe manner.

A piezoelectric transducer was used to monitor the pressure. The strain from pressure being applied to the quartz crystal in the transducer is directly related to its electrical output, known as the piezoelectric effect. This output is then registered by a digital readout which gives an accurate indication of the pressure in the autoclave. A Watlow heating jacket (Figure 2.4) was designed to fit specifically around the autoclave base to provide uniform heating during the synthesis of the polymers in CO_2. A K-type thermocouple was used to monitor the internal temperature, which was connected to a CAL Instruments 3300 heating controller to allow the

temperature to be altered, with a separate thermocouple providing accurate temperature data over time to a computer. A trip box was connected to the pressure readout and the temperature controller with a pressure limit of 345 bar, which if exceeded would cut out the power to the heating jacket.

The magnetically coupled overhead stirrer was attached to the autoclave head, using a EPDM o-ring to ensure the autoclave remained sealed even under high pressure. A small stirrer blade was used to ensure uniform distribution of the reactants within the autoclave, while a stirring motor was used to control the speed of mixing.

2.4.4 Standard experimental procedure for an expanded phase CO_2 reaction

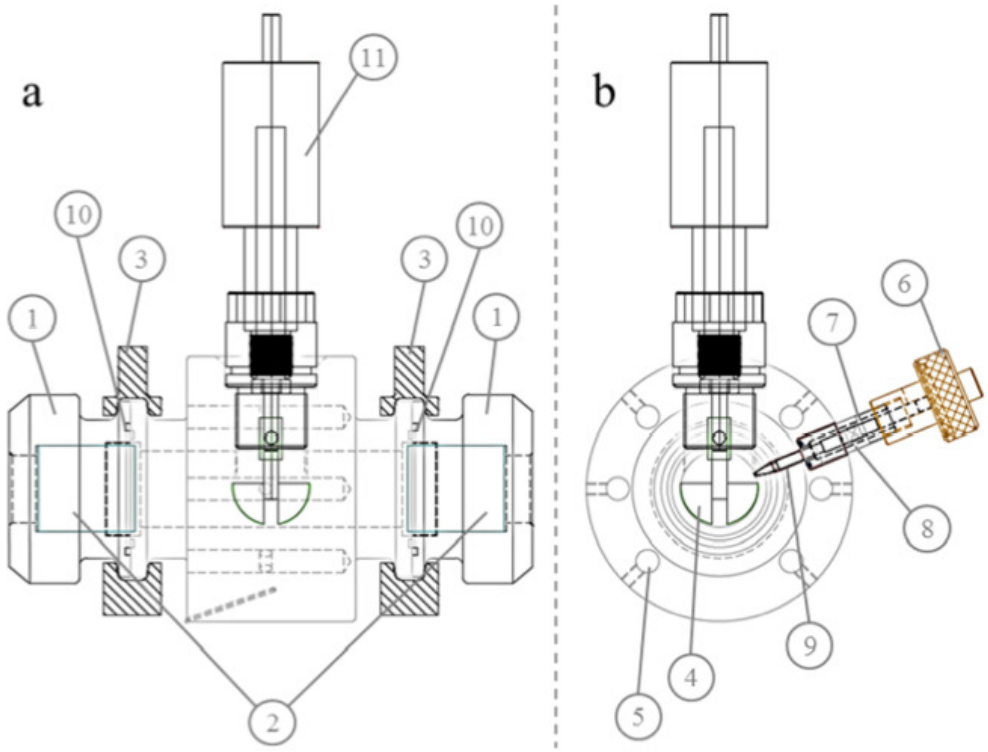
The same procedure was used for each expanded phase reaction using vinyl acetate. Only the reactant amounts and the ratio of RAFT agent to initiator were altered.

1. Before any reaction a thorough leak test was carried out to ensure no fittings or pipes would leak CO_2 during the reaction.
2. An example for targeting 35,000 $g.mol^{-1}$ for a PVAc homopolymer used a mixture of vinyl acetate (15 ml, 0.1627 moles), xanthate RAFT (89 mg, $4.002x10^{-4}$ moles) and AIBN (32.9 mg, $2.001x10^{-4}$ moles).
3. Prior to the reactants being added, the autoclave was purged with a small flow of CO_2 (~30 psi) for half an hour.
4. A syringe and needle was purged 3 times with argon, then used to extract the reactants and add them to the autoclave.
5. The safety needle was used to seal the autoclave, after which the stirring rate was set to 300 rpm, then the pressure was increased to ~650 psi.
6. The temperature was set to 65 °C. It is at this point the reaction is deemed to have started. Once the autoclave reached this temperature, the pressure was increased until it reached ~2000 psi.
7. Once the target reaction time had been reached, the heating jacket was removed and then the autoclave was placed in dry ice to stop polymerisation occurring as quickly as possible. Acetone was added to the dry ice to cool the autoclave to very low temperatures (~ -40 °C) to lower the pressure as much as possible.
8. The pressure was vented out very slowly to prevent the pipes from being blocked owing to the PVAc foaming.

9. Once no more CO_2 would vent through the outlet pipe, the safety needle was very carefully removed so the autoclave could reach atmospheric pressure.
10. The autoclave was allowed to heat back to room temperature. Then the clamp was removed and the polymer product extracted.

2.4.5 Experimental procedure for determination of reagent solubility in a high pressure view cell

The solubility of the various components used for the CO_2 experiments were determined using the high pressure view cell that was designed and built at the University Of Nottingham chemistry. A schematic diagram for this view cell is shown (Figure 2.6).



1. Ends of view cell with portholes
2. Sapphire Windows
3. Clamps
4. Stirrer
5. Heating cartridges
6. Key for clamps
7. Safety needle
8. Screw thread to secure safety needle
9. Safety needle
10. EPDM O-rings
11. Motorised stirrer

Figure 2.6 - Schematic diagram for the view cell used for determining the solubility of the vinyl acetate monomer and PVAc

In this case, the body of the view cell has two similar open ends. These ends both have grooves for an o-ring to ensure the system can maintain the high pressures required when the equipment is assembled. Each end contained a thick sapphire window, with one end used to observe what was happening to the solubility sample, and the other window allowing an external light source to illuminate the inside of the view cell. Each window required two O-rings in order for the view cell to safely withstand the high pressure experiments.

Heating elements were placed into the main body so the view cell could achieve the appropriate internal temperature. Finally, both ends of the view cell had a metal head which was used to clamp the window assembly onto the main body, using an identical safety clamp system to that used for the autoclave, where the key required to close the clamps is unique.

The temperature was measured with a K-type thermocouple inside the view cell wall, with a second thermometer protruding into the view cell to both gave similar temperature readings. A CAL Instruments 3300 heating controller was used to monitor and control the temperature, while a piezoelectric transducer connected to a digital readout was used to monitor the pressure. The trip for the view cell was set up so that if the pressure inside rose too high, the power to the temperature controller would cut out. A magnetically coupled overhead stirrer was used to ensure effective mixing.

2.4.6 Standard procedure for view cell solubility experiments

1. A thorough leak test was conducted prior to charging the vessel to ensure to no fittings or pipes would leak during pressurisation of the view cell.
2. For the testing of PVAc, at this point a vial containing the polymer sample under study would be secured to the bottom of the view cell.
3. The o-rings were then placed upon the sapphire windows and view cell, the windows were inserted and secured using clamps at either end of the view cell.
4. For the solubility study of vinyl acetate, 70 ml of the monomer was then added to the view cell through the safety valve.
5. The key was used to seal the autoclave after which the stirring rate was set to 300 rpm, then the autoclave pressure was increased to 800 psi. (The stirrer was not present when testing the solubility of the PVAc sample.)
6. The autoclave target temperature was set to 45 °C, and once this had been attained, the system was left for several minutes to allow the view cell conditions to equilibrate.
7. The view cell pressure was then increased to 4000 psi, and left for several minutes to equilibrate at the chosen conditions.
8. After the observations had been made, the controller was used to lower the view cell to room temperature.
9. The remaining CO_2 was then vented and the view cell opened.

2.5 Characterisation Techniques

2.5.1 Gel Permeation Chromatography (GPC)

GPC was utilised to determine the molecular weight values for the polymer samples obtained during this study. This procedure requires the polymer to be dissolved in a solvent and passed through a column packed with a porous material. The time taken for a particular sample to reach the end of the column is determined by the hydrodynamic volume; the volume occupied by the polymer when in solution. This volume is determined by two factors; the solubility parameters of the polymer within the chosen solvent and polymer chain length. Each sample in this study used HPLC chloroform during GPC analysis, therefore any differences observed were entirely owing to varying chain lengths.

In order to obtain molecular weight values, the column and RI detector required calibration using polymer standards in the desired solvent which have known molecular weights, usually calculated using light scattering. Standards were not available for PVAc, therefore Poly Methyl Methacrylate (PMMA) standards were used instead, meaning the GPC data was comparable but did not provide absolute values.

Longer polymer chains within a single sample pass through the column quickly, whereas short chains pass through more pores, which increases the time taken to reach the RI detector. Therefore as well as molecular weight values, GPC analysis can also determine the uniformity of polymer chain length within each sample, known as the dispersity (Đ). GPC spectra were collected upon a Polymer Laboratories GPC-50 Plus using PLGel Mixed-D polystyrene column in chloroform (Sigma-Aldrich 99.8%) and a flow rate of 1ml.min^{-1}. The final molecular weight values were calculated using an RI detector and compared to PMMA standards. Each

sample was ~5 mg/ml and allowed to mix for at least an hour to ensure all the material had dissolved, before passing through a 0.2 μm PTFE GPC filter into the sample vial.

GPC chromatograms were collected upon a Polymer Laboratories GPC-50 Plus using PLGel Mixed-D polystyrene column in chloroform (Sigma-Aldrich 99.8%) and a flow rate of 1ml.min^{-1}. The final molecular weight values were calculated using an RI detector and compared to PMMA standards. Each sample was ~5 mg/ml and allowed to mix for at least an hour to ensure all the material had dissolved, before passing through a 0.2 μm PTFE GPC filter into the sample vial.

2.5.2 Nuclear Magnetic Resonance (NMR)

NMR spectra were used as a means for determining conversion for the kinetic experiments throughout this thesis, and in the specific case of the block copolymer reactions, it was also used to calculate the block ratios. The NMR analysis was carried out using either a Bruker DPX-300 or AV-400 (300 MHz) spectrometer using $CDCl_3$ as the solvent. Chemical shifts are reported relative to $SiMe_4$ and determined by reference to the residual ^1H solvent peak.

When producing the PVAc homopolymer, conversion was calculated by comparing the integrals of a monomer hydrogen in the CH_2 group within the vinyl bond (-CH_2-, δ = 4.47 ppm) and the combined monomer and polymer peak (-CH_2- and –CH-, δ = 4.8 ppm).

For the block copolymer, the conversion for the PVPi block was calculated by comparing the integrals of a monomer hydrogen from the CH_2 group within the vinyl bond (-CH_2-, δ = 4.51 ppm) and the combined monomer and polymer hydrogens from the ^{t}Bu group (-^{t}BuCOO-, δ = 1.25 ppm). Once the block copolymer had been precipitated, the ratio of the PVAc and PVPi

block could be calculated by comparing the integrals of the ^{t}Bu hydrogens (-^{t}BuCOO-, δ = 1.25 ppm) with a combination peak from the CH_3 group and CH_2 in the polymer backbone for PVAc and a CH_2 group in the polymer backbone for PVPi (-CH_3COO-, -CH_2- & -CH_2-, δ = 1.9 ppm) The integrals for all the NMR data was carried out using ACD/Labs software.

2.5.3 Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis technique where two pans, one which contains a known mass of the chosen sample and one empty to act as a reference, are heated at the same rate. The difference in energy required to maintain the heating rates can then be related to the change in enthalpy for the sample. DSC analysis was conducted to measure the glass transition temperature (T_g); the temperature at the physical form of a polymer sample changes from hard and brittle to soft and pliable, representing a significant change in its properties.

Different molecular structures within a polymer means that the T_g values will vary, which was of particular importance for the research regarding block copolymers of PVAc and Poly (vinyl pivalate) (PVPi). A single T_g in the analysis would imply that a polymer blend had been formed upon the addition of the second monomer, meaning the polymer properties would be owing to a mixture of the two polymers. However the presence of two T_g values within a sample would indicate the presence of distinctive polymer blocks. This phase separation allows the formation of varying molecular structures and can have different applications compared to a polymer blend.

The DSC analysis was conducted using a TA-Q2000 DSC (TA Instruments) was used for the T_g analysis. The heating rate for both the sample and reference pans was 10 ºC/minute, using a

temperature range of 0 – 100 ºC and a nitrogen flow of 50 mL/minute. Aluminium pans were used with a sample mass between 2-3 mg. The T_g was measured as the change in heat capacity in the 2nd run.

2.6 References

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Chapter 3 - Accelerated RAFT Polymerisation of Vinyl Acetate using Microwave Heating

3.1 Introduction

Over recent decades, the number of papers utilising the application of microwave heating to chemical reactions has been steadily increasing.[1-4] Initial experiments used modified domestic microwave ovens,[5, 6] however using these multimode cavities produced hotspots within the reaction and therefore led to inconsistent results.[7] The inefficient nature of these devices when used for small scale experiments meant that new technology was required for effective chemical synthesis when applying microwave energy. The subsequent design of single mode instruments has led to reproducible heating profiles, as well as enhanced energy efficiency.[9] Consequently microwave heating has been shown to be capable of reducing reaction times, increasing yields and improving selectivity for a wide range of organic reactions. [1, 10]

3.1.1 Principles of Microwave Heating

Conventional heating methods apply either conductive, convective or radiative transfer of energy in order to heat a reaction. This can be a slow process, requiring the energy to penetrate through several different materials including the reaction vessel itself.[11] In contrast, microwave heating uses the energy from an alternating electric field to directly couple with the "microwave absorbent" molecules in the reaction mixture. This is referred to as selective heating of the

reactants,[12] which allows for the internal temperature to be both raised and maintained rapidly in an evenly distributed manner, i.e. there are much lower/no thermal gradients throughout the reaction medium.[13] However, for this heating to be effective a suitable microwave transparent material for the reaction such as quartz, glass and Teflon must be used.[14]

There are two main mechanisms by which microwave heating can occur; dielectric polarisation and ionic conduction.[14] In either scenario, a dipole must be present within the target material, which are able to align themselves with the electric field from the microwaves. This field continuously oscillates, which therefore causes the molecules to be in constant motion (Figure 3.1).

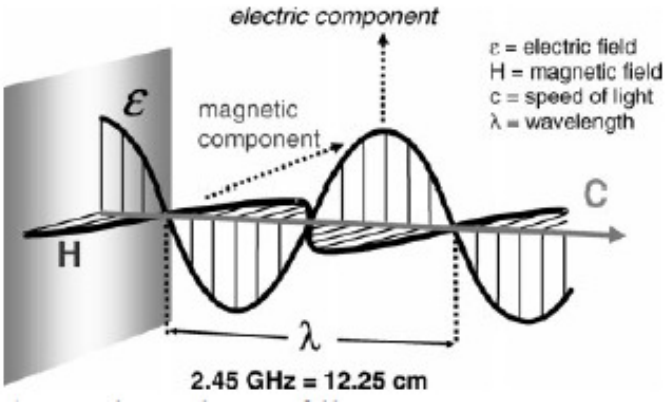


Figure 3.1 - Diagram of the electric and magnetic fields generated by a microwave [14]

The energy generated by this oscillation is transferred and stored within the molecules as they continually realign themselves. Eventually this energy is dissipated *via* dielectric loss and internal resistance, caused by molecular friction with other molecules surrounding those being selectively heated.[15]

Ionic conduction requires the use of ionic atoms/molecules to generate heat *via* molecular friction. [16] This mechanism is more relevant to other work such as ionic liquids, which can offer numerous advantages such as stability, low vapour pressure and solubility for a wide

range of compounds.[17] Applying microwave heating with these ionic liquids has led to improved yields and lowered contamination in the final product for numerous reactions.[18]

The advantages of ionic liquids have also been exploited in polymer manufacture, both during production and as additives.[19] Using microwaves has been proven to provide a faster and more environmentally friendly means of polymer synthesis and modification.[20] Increased yields and reduced reaction times during free radical polymerisation have been shown to be a consequence of an increased propagation rate and lowering of termination caused by hydrogen bonding between the monomer molecules, radical chains and ions.[21, 22] However, the application of microwaves is not always beneficial, as one study found the rate of polymerisation was lowered compared to conventional methods as a consequence of a disturbance in the interaction between the radical and ions.[20, 23]

By analysing the dielectric properties of the various materials present within a reaction mixture, it is possible to predict how effectively a reaction will be heated by the application of microwave energy. Electromagnetic energy can interact with molecules in a material *via* three procedures; absorption, transmission and reflection.[24] The dielectric properties for a particular material can be obtained from evaluating the two components of its complex permittivity;[25] the real part (the dielectric constant ε') which determines the capacity of the material to store energy from the electric field, and the imaginary part (the dielectric loss ε") that defines the ability to disperse this stored energy into heat for the reaction. Using these parameters, the loss tangent can be calculated as shown (Equation 3.1).

Equation 3.1 - Loss Tangent (tanδ) = ε"/ ε'

This gives an indication for the potential of the material to be heated by microwaves, but these values are subject to variation, as they are dependent on the conditions that the material is subject to. Lowering the density by raising the temperature of a sample generally causes a non-linear decrease in loss tangent, as the molecules in the material move further apart. Therefore the use of microwave heating is less effective as the level of molecular friction is reduced, as was observed during the dielectric analysis shown later in this thesis (Section 3.3). [13]

The frequency of the electromagnetic wave is also a vital consideration for ensuring reliable heating profiles. Low frequencies are ineffective as the rotation of the molecules is too low to have significant effect in order to increase the temperature. However, when the frequency is too high, the molecules are unable to realign with the field fast enough, therefore little change is observed.[14] In the microwave region, the speed of rotation for the particles is only fractionally slower than the electric field, therefore the molecules are constantly producing heat from molecular friction, causing a temperature increase. However, owing to the many other commercially exploited uses of microwaves such as communication, a specific band of the spectrum is assigned for use in chemical synthesis, known as the Industrial, Scientific and Medical (ISM) allowed frequencies.[26] Thus all the reactions in this thesis are carried out at 2.45 GHz.

An additional factor when using electromagnetic energy is the penetration depth; defined as the depth at which only 37 % (1/e) of the microwave power remains.[24] As the microwave energy passes further through a substance, a certain percentage of the power will be lost owing to interactions such as absorption, therefore there is a point for any material where the loss of energy will be large enough to result in non-uniform heating. Therefore, when designing a microwave reaction vessel, the penetration depth for the desired material should be considered to ensure even heat distribution (Equation 3.2)

Equation 3.2 - $$D_p = \frac{\lambda_0 \sqrt{\varepsilon'}}{2\pi\varepsilon''}$$

As demonstrated, the value of 1/e is inversely proportional to tanδ, therefore it is also influenced by the material conditions such as temperature, frequency and viscosity.[27] When examining laboratory scale synthesis, the loss in power can usually be overcome by ensuring effective mixing. Materials with very high penetration depths such as glass and quartz are microwave transparent, so are suitable choices when designing microwave reaction vessels.[28]

3.1.2 Conventional vs. Microwave Heating

The reason differences can be observed with the different methods of heating illustrated (Figure 3.2).

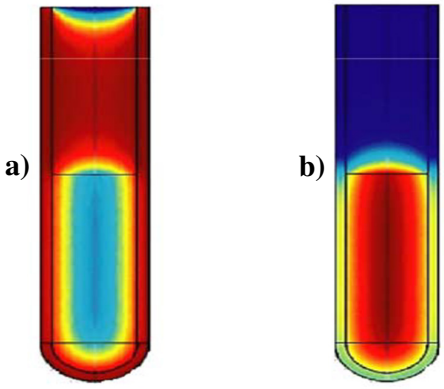


Figure 3.2 – Predictive models showing the difference between a) conventional and b) microwave heating, with red indicating a heated region and blue showing a cold region[8]

The image on the left (Figure 3.2a) demonstrates a heating profile for when using a conventional heating method such as an oil bath, where heat passes to the reactants using convection currents *via* the walls of the reactor.[29] This results in the outside of the reaction vessel being at a considerably higher temperature than the centre of the reaction mixture, thus creating a significant thermal gradient, which can influence the chemistry within different regions of the mixture. Such uneven heating profiles can lead to increased batch-to-batch variability as the exact conditions are difficult to reproduce.

The image on the right (Figure 3.2b) shows a predictive thermal scan of a reaction heated using microwave energy, which assumes the overall reaction mixture offers suitable dielectric properties to produce uniform, volumetric heating. Therefore the temperature of the entire volume can be raised simultaneously in a reproducible manner, when using a suitably microwave-transparent material for the reaction vessel.[30] Furthermore, selectively heating the reactants rather than the entire reactor demonstrates how microwave heating can be a more energy efficient process.

3.1.3 Temperature Measurement

One factor that alters between conventional and microwave heating systems is the method of recording temperature. When using conventional equipment there can frequently be a noticeable difference in temperature between the heat source and the reaction mixture, indicating the presence of thermal gradients as a result of the slow transfer of heat *via* conduction and convection.[8, 10] In this work both the oil temperature and the internal reaction

mixture temperature of the conventional reaction were measured using K-type thermocouples, which confirmed that the oil bath had to be set several degrees higher than the desired reaction temperature.

Safely measuring the internal reaction temperatures within microwave reactors is a more complex procedure, as inserting metal thermocouples into the reactor can potentially lead to: (a) arcing (discharge of energy concentrated within the inserted element) that can result in fires;[31] (b) leakage of microwave energy from the reactor into the environment due to the insert acting as an antenna; and (c) damage of the insert which becomes inoperative.[32] Consequently, two techniques have been developed for measuring the temperature in a microwave reactor (Figure 3.3).

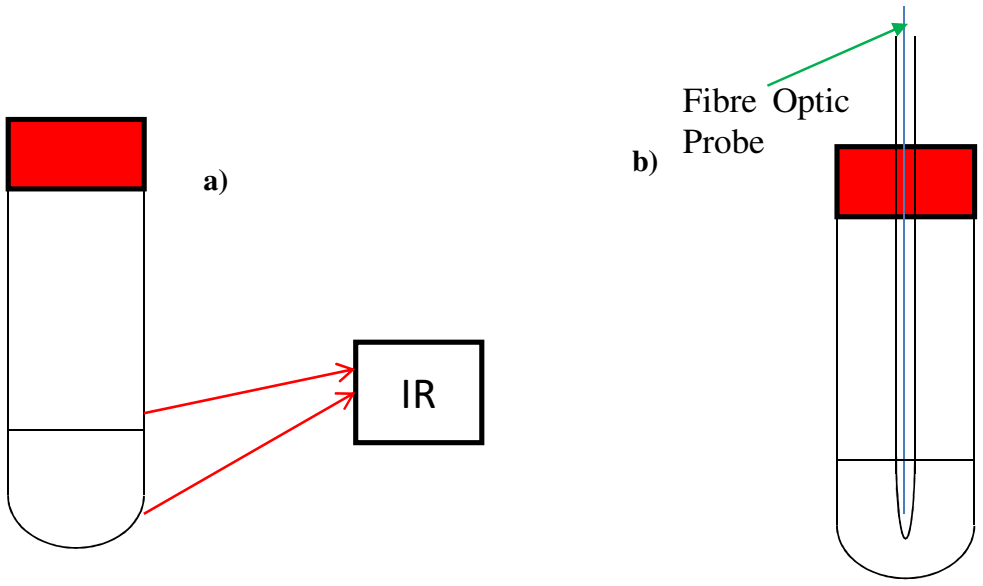


Figure 3.3 – Showing the different methods for measuring temperature when using a microwave reactor. a) demonstrates temperature measurement using IR energy emission. In b) a fibre optic probe is used to determine the reaction temperature

In the first methodology shown (Figure 3.3a) an Infra-Red (IR) sensor is used to measure the temperature of the external reactor wall of the reactor; this has the benefit of avoiding the introduction of an external probe into the microwave cavity, thus mitigating the issues detailed in the previous paragraph. However, a major drawback discovered when applying this method is that there can be a significant deviation from the actual bulk temperature, since the reactors are made of microwave transparent materials and so are only heated *via* conduction/convection from the reaction mixture.[33]

Therefore it takes time for the external temperature to equilibrate and accurately reflect the temperature of the internal reaction mixture. This has led to false reports of faster reactions and higher yields/conversions due to the presence of a non-thermal microwave effect, which have subsequently been proven to a result of the recorded temperature being significantly lower than the actual bulk temperature (Figure 3.2b).[34] This thermal deviation can be even greater when external cooling is applied during a reaction.[14, 35] When accurate bulk temperature measurements were made using the probe methods discussed below, these non-thermal effects were proven to be a result of applying higher temperatures.[36]

The alternative to IR thermal monitoring is the use of a fibre optic probe located inside the bulk solution (Figure 3.3b). These are K-type quartz probes, which have a protective sleeve for added longevity of the probe – i.e. protecting it from the reagents which may damage the adhesives and sealants used in its construction. The optical radiation directed into the fibre is modulated so that the properties of light in the fibre are altered by changes in the temperature to which it is subjected. This provides a high responsivity and accuracy in respect of the temperature of the reaction mixture, as well as offering fast response to unexpected changes in temperature, such as when auto-acceleration is occurring.[33]

3.1.4 Microwaves and Polymerisations

The production of poly(vinyl acetate) (PVAc) is of great importance to the chemical industry as it has a wide range of uses such as in adhesives and paints.[37-40] It is also used as a precursor in the preparation of poly(vinyl alcohol) which has applications in a variety of different industries including papermaking, textiles and a variety of coatings.[41-43] In addition to this, PVA is widely used as a protective colloid in poly(vinyl chloride) production.[44]

PVAc is most commonly produced using free radical polymerisation to ensure fast production times, but the lack of control over the growth of the polymer chains results in high dispersity values.[45, 46] The use of controlled polymerisation techniques has allowed a variety of polymers to be produced with targeted molecular weights and low dispersities, providing higher quality and therefore more reliable application performances. This enhanced degree of control over the polymerisation process also allows the production of copolymers,[47-49] as well as providing a route to three dimensional molecular structures such as star and comb-graft polymers.[50-52]

Consequently, there have been numerous reports where controlled radical polymerisation techniques have been applied to the synthesis of vinyl acetate, particularly with regards to Reversible Addition Fragmentation Chain Transfer (RAFT) / Macromolecular Design via the Interchange of Xanthates (MADIX). However, while control has been achieved with these methodologies, a major issue stems from the extended reaction time required to obtain high conversions due to the level of interaction that these controlling agents exhibit with the radicals in the system. This increase in reaction time can be several hours or even potentially days if the RAFT agent induces a significant induction period; a length of time at the outset of a reaction where no polymerisation occurs, which is particularly relevant to Less Activated Monomers (LAMs) such as vinyl acetate.[53] Theoretically when using a RAFT agent the

polymerisation rate for the reaction should be identical to that of a standard free radical process,[54] however experimental observation has revealed lengthening of the overall reaction time as the radicals spend significant periods of time in a "dormant" state.

Slow reaction kinetics have also been observed in respect of the other controlled polymerisation techniques, making them undesirable for use in industry. A study of Atom Transfer Radical Polymerisation (ATRP) determined a significantly high concentration of the copper species provided narrow dispersities, but subsequently led to a lowered reaction rate as a consequence of slow initiation.[55] Similarly, an investigation into Nitroxide Mediated Polymerisation (NMP) discovered that tailoring the rate of dissociation to the chosen monomer was vital when using an alkoxyamine species in order to prevent retardation of the reaction.[56]

Microwave heating has been shown to increase yields and shorten reaction times for a wide variety of reactions,[9, 17, 57] including controlled polymerisation techniques. A preponderance of papers have studied the polymerisation of methyl methacrylate (MMA) with regards to ATRP while using microwave energy,[58-61] although other monomers have also been used.[5] It had been determined that the use of microwaves led to increased reaction rates and narrow dispersities, as well as significantly lowering the amount of catalyst required compared to conventional methods, while still being able to control the growth of the polymer chains.

However other research has shown little noticeable difference when using microwave heating with ATRP and MMA.[62] This could be as a consequence of the particular reagents used in this specific case, or may potentially be a result of the different microwave set up having a significant influence. The papers which demonstrated an induced acceleration of the polymerisation rate had notably used a modified microwave oven, while the research showing little change had used monomode-microwave reactors. It is therefore possible that factors such

as thermal gradients arising as a result of hotspots could have influenced the reaction in the modified oven, causing the observed acceleration.

Several papers have studied how the use of microwave heating can influence NMP. An investigation into the polymerisation of acrylamide showed no significant acceleration of the polymerisation rate with microwave heating. However the investigation highlighted the importance of selecting appropriate temperature measurement techniques. As the viscosity rose, the IR sensor gave increasingly inaccurate temperature readouts, whereas the fibre optic technique was capable of providing consistently accurate temperature data, which is particularly important for high conversion bulk polymerisations.

Another paper examining the polymerisation of alkyl acrylates with NMP also showed no distinct increase in polymerisation rate when using microwave heating. However there were several beneficial effects in comparison to the use of a conventional oil bath.[63] Polymers were produced with narrow dispersities for high conversion levels, as well as results being reproducible as a consequence of the uniform heating profile.

However, there has been research where an increase in polymerisation rate was observed when applying microwave energy. A group observing the NMP for acrylamides initially found no obvious acceleration of polymerisation rate when using a high power level from the microwave reactor at the start of the reaction, as observed in previous work.[64] However a significant acceleration was seen when applying pulsed microwave energy, which still demonstrated narrow dispersity values as expected from NMP. The use of a pulse system also involved the use of simultaneous external cooling with compressed air, allowing higher energy levels to be applied to the reaction mixture. This increase in reaction rate occurred as the viscosity of the system rose, leading to either an increase in propagation rate or a reduction in the persistent radical species, thus inducing the observed acceleration.

A miniemulsion of styrene using NMP found that using microwave heating produced polymers with molecular weights closer to those predicted theoretically compared to conventional methods, as well as having lower dispersities.[65] Additionally using microwave heating was observed to produce smaller particles and therefore increased the rate of polymerisation.

A theoretical study looked at determining the exact nature of the acceleration of styrene polymerisation while maintaining control using NMP.[66] The most accurate theoretical model assumed the existence of a microwave induced initiation step, where production of additional radicals is instigated by the decomposition of monomer molecules from the application of microwave heating.

While microwave heating has proven to be beneficial when applied to NMP and ATRP, there are limitations to these methods. ATRP always requires a metal component which would be a contaminant during further processing, while NMP can still be a slow process unless using high temperatures, thus making it more energy intensive. In the literature many papers have focussed on the acceleration of RAFT polymerisations using microwave energy, with the variable nature of both the Z and R groups within the control agent making RAFT polymerisation highly versatile and therefore applicable to a variety of monomers,[67-69] including vinyl acetate.[53, 70]

Sumerlin *et al* provided a review of several RAFT polymerisations which have been accelerated using microwave heating.[7] One group investigated the RAFT polymerisation for N,N-Dimethylacrylamide (DMA) and N-Isopropylacrylamide (NIPAM).[71] Both monomers showed an acceleration of the polymerisation rate when using microwaves, as indicated by the increase in the apparent propagation rate (k_p^{app}), which could be enhanced even further with simultaneous cooling. These observations were assigned to a rapid rise in temperature leading to an overshoot and thus causing an increase in radical production. Furthermore the application

of microwaves demonstrated numerous other advantages over conventional heating, including higher conversions, shorter reaction times and the removal of the inhibition period. The high retention of the RAFT end group functionality was confirmed by the successful growing of a second polymer block.

Another research group examined the application of microwave heating for the RAFT polymerisation of methyl methacrylate (MMA), methyl acrylate (MA) and styrene.[72] The polar nature of the MMA and MA monomer caused an enhanced dielectric heating effect, leading to faster rates of polymerisation, whereas the non-polar styrene exhibited no difference from the conventional heated reaction. This microwave enhancement could also be applied to various synthesis techniques, such as the formation of nanostructured hydrogels.[73]

The slow reaction rate of PVAc production when using RAFT polymerisation makes it less desirable than standard free radical polymerisation for an industrial process,[53] therefore being able to accelerate the process while maintaining control would be a significant improvement. This is particularly relevant to applications using PVAc as a stabiliser, where regulating molecular weight is vital in order to produce a high quality product.

It has been reported that the RAFT polymerisation for vinyl acetate microwave heating led to an overshoot of nearly 10 °C in the initial 5 minutes, before cooling to the programmed temperature at 70 °C, which could be caused by either the exothermic nature of the polymerisation or a lack of control from the microwave reactor.[74] However, attempts to replicate this temperature overshoot with an oil bath produced lower k_p^{app} values than when using microwaves, thus indicating that an additional effect caused the observed acceleration when applying microwaves. Additionally, lower dispersity values implied that microwave heating aided in increasing the degree of control over molecular weight.

A similar study by Brown *et al* also found that microwave energy could accelerate the RAFT polymerisation of vinyl acetate while maintaining good control over molecular weight, which was attributed to increasing the rates of propagation and addition-fragmentation during chain transfer.[75] A second polymer block confirmed that a majority of the PVAc chains retained the RAFT end group.[74, 76]

The focus of this chapter is to carry out an in-depth study as to why this combination of reduced cycle time and enhanced molecular structure control has been observed for vinyl acetate when applying microwave heating to RAFT polymerisation. Kinetic studies and various analysis techniques will be utilised to determine which reaction parameters influence the observed acceleration.

3.2 Experimental

Materials: Vinyl acetate (99%, Alfa Aesar), 2,2'-Azobis(4-methoxy-2.4-dimethyl valeronitrile) (V-70) (Wako), Ethyl 2-bromopropionate (99%, Sigma-Aldrich), Ethanol (Fischer), Potassium ethyl xanthate (98%, Alfa Aesar), Dichloromethane (Fisher) and Magnesium sulfate (99%, Fisher) were used without further purification. The xanthate RAFT agent was synthesised as previously reported.[77]

NMR Analysis: ^{1}H NMR samples were prepared in deuterated chloroform to a concentration of 3 mg.ml^{-1} and analysed using a Bruker DPX 300 MHz spectrometer. All the experiments used the same resonances to determine conversion. An example of a typical NMR spectrum for PVAc is shown (Figure 3.4).

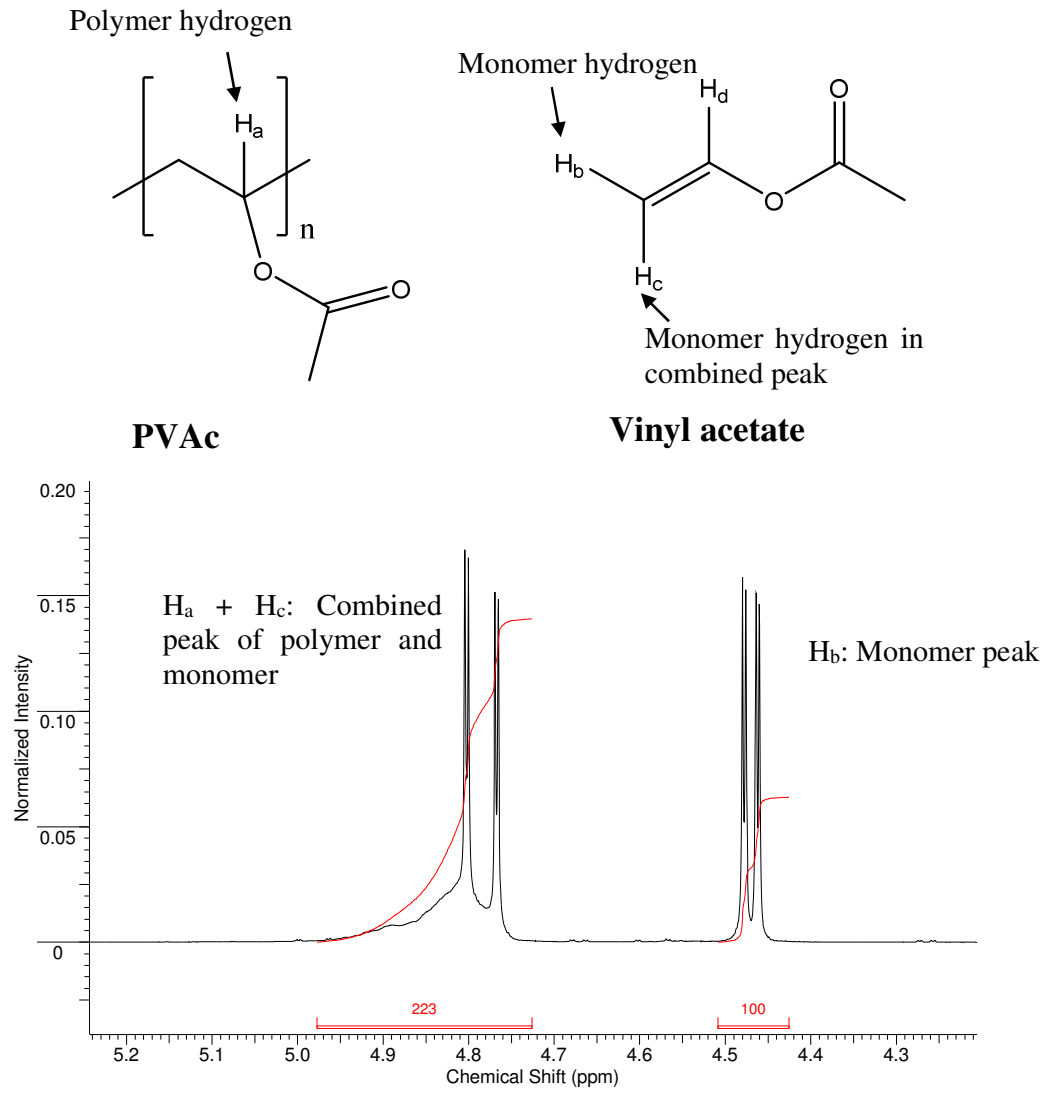


Figure 3.4 – ^{1}H NMR spectrum of a kinetic sample during a RAFT polymerisation, shown with structures of vinyl acetate and PVAc

Both NMR peaks are doublets as they are split by the adjacent proton, which subsequently form double doublets, with the further splitting occurring owing to proton on the other side of the C=C bond (H_d). The larger J coupling for the combined monomer and polymer peak confirm that this must be from a proton in a trans position.

GPC Analysis: GPC chromatograms were collected upon a Polymer Laboratories GPC-50 Plus using PLGel Mixed-D polystyrene column in chloroform (Sigma-Aldrich 99.8%) at a flow rate of 1ml.min^{-1}. The final molecular weight values were calculated by comparing to PMMA standards with a molecular weight range between 465,000 – 162 g.mol^{-1}. Each sample was made with a concentration of 5 mg.ml^{-1}.

Synthetic Procedures: All microwave reactions were conducted using the CEM Discover SP system. A fibre-optic temperature probe was used to ensure the temperature was measured accurately. Each reaction was heated using the maximum 300 W power input for the initial heating stage. Once the desired reaction temperature was reached, a minimal amount of power was used to maintain these conditions. The internal temperatures of the conventionally heated reactions were measured with a K-type thermocouple. All reactions were subjected to at least 3 freeze pump thaw cycles before degassing with argon.

Dielectric Analysis: All materials were measured using a cavity perturbation technique. A detailed description of this technique is given by Meredith,[78] while Lester *et al* describes the methodology used for each material analysis.[79] Firstly the empty tube was weighed and measured 4 times to ensure it had the same dielectric properties of air and therefore contained no contaminant. A small volume of the substance (~0.5 ml) was measured out. The tube was reweighed in order to see determine the exact weight of the sample. The dielectric properties for the sample were measured four times to ensure consistent results at room temperature.

At this point a temperature range had to be determined. A limit of 20 °C below the boiling point was chosen as the upper limit. This ensured that the sample would not boil as this could be dangerous and would provide inaccurate results.

Example Bulk RAFT polymerisation: V-70 (66.6 mg, $2.2x10^{-4}$ mol) was weighed out and added to the schlenk tube. The xanthate RAFT agent (120 mg, $5.4x10^{-4}$ mol) was weighed out and then vinyl acetate (20 ml, 0.22 mol) was added to it, after which this mixture was shaken. This was found to be important as this mixing before adding to the schlenk tube ensured consistent results. Once all the reactants were in the schlenk tube it was subjected to three freeze pump thaw cycles before being degassed thoroughly with argon. After this, the tube was placed in the oil bath / CEM microwave reactor for 6 hours targeting 35,000 $g.mol^{-1}$ at 35 °C and 45 °C.

Solvent RAFT polymerisation: V-70 (66.6 mg, $2.2x10^{-4}$ mol) was weighed out and added to the schlenk tube. The toluene (10 ml, $9.4x10^{-2}$ mol) was also measured and added. The xanthate RAFT agent (120 mg, $5.4x10^{-4}$ mol) was weighed out and then vinyl acetate (20 ml, 0.22 mol) was added to it and this mixture was shaken. Once all the reactants were in the schlenk tube it was subjected to three freeze pump thaw cycles before being degassed thoroughly with argon. After this, the tube was placed in the oil bath / CEM microwave reactor for 6 hours targeting 35,000 $g.mol^{-1}$ at 45 °C. The amount of toluene and V-70 was altered for various experiments. All other conditions were kept constant.

Synthesis of O-Ethyl-S-(1-ethoxycarbonyl) ethyldithiocarbonate RAFT Agent

Ethyl 2-bromopropionate (11.1 g, 0.06 mol) was dissolved in ethanol (100 ml) in a 250 ml flask. Potassium ethyl xanthate (10.1 g, 0.07 mol) was then added over 30 minutes. The mixture was degassed thoroughly and then stirred at room temperature for 24 hours, after which the solvent was removed under reduced pressure to obtain a yellow liquid. This was extracted with DCM (100 ml), washed with water (3 x 75 ml) and then dried using $MgSO_4$. Once this was filtered the final product was dried for at least 24 hours, with the structure confirmed using

NMR and IR spectroscopy. Examples of ideal spectra for the xanthate RAFT agent are shown (Figure 3.5a-c).

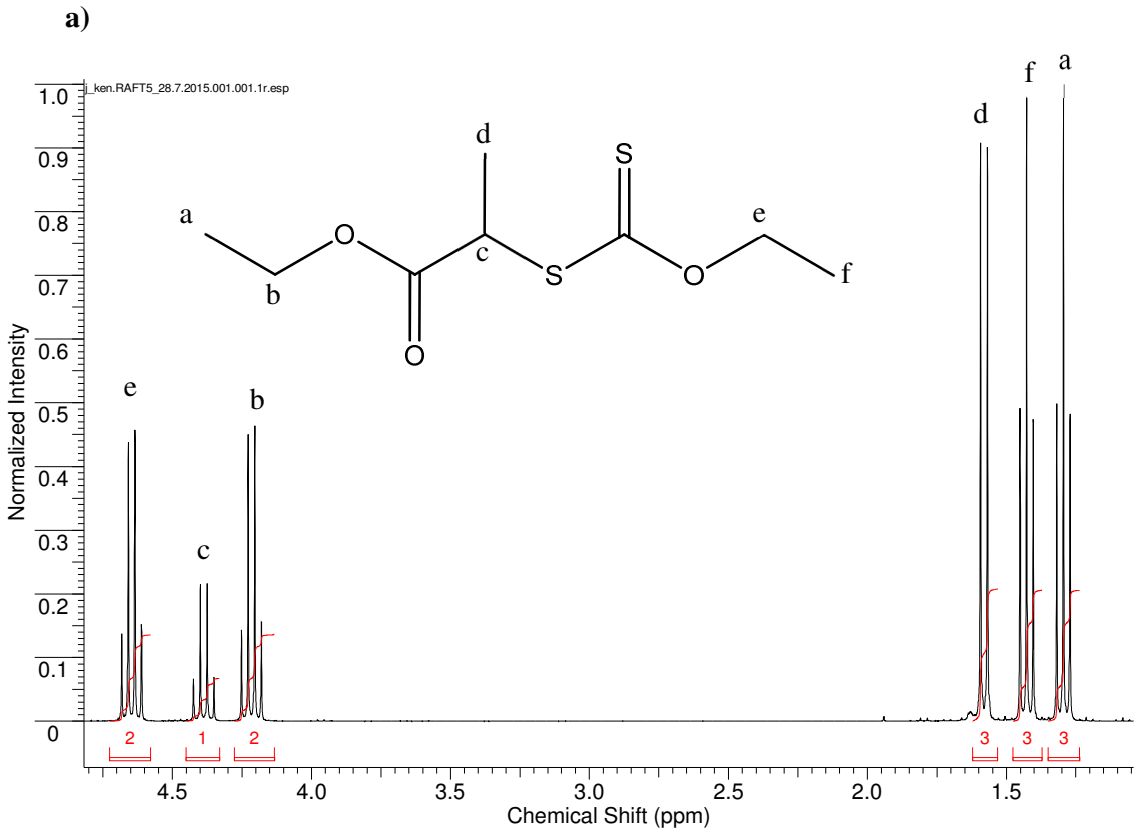


Figure 3.5a – ^{1}H NMR spectrum and molecular structure of the xanthate RAFT agent

b)

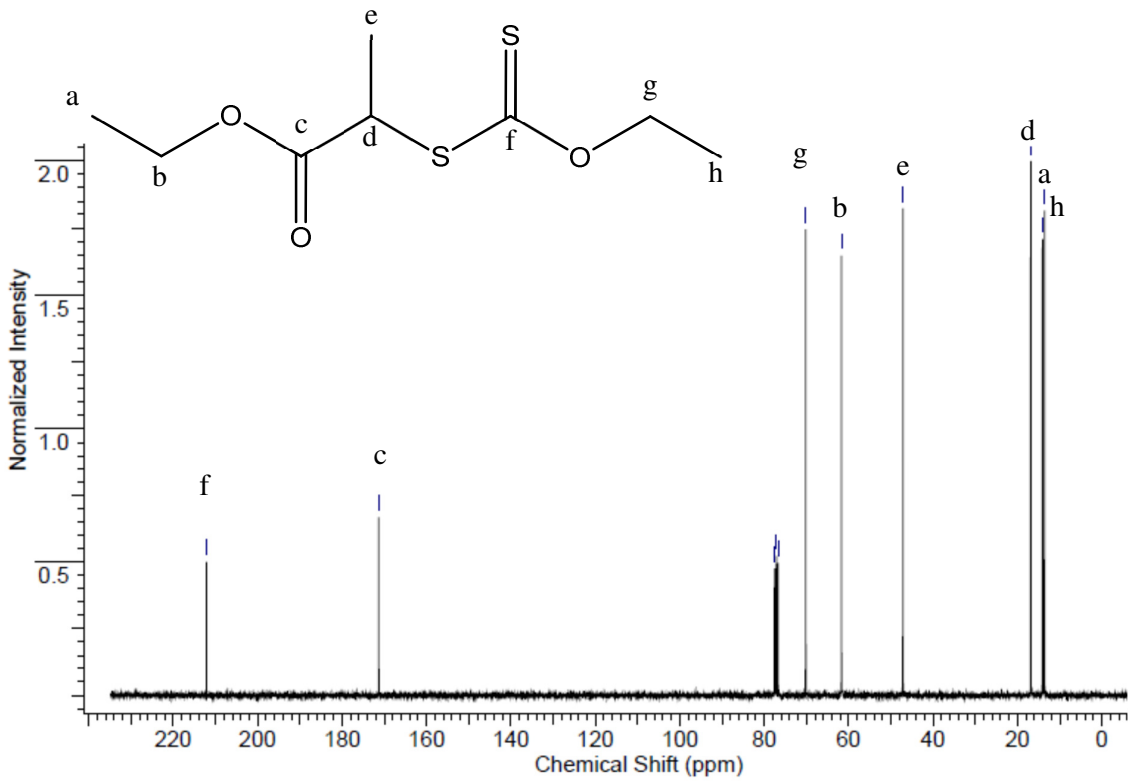


Figure 3.5b –^{13}NMR spectrum of the xanthate RAFT agent

c)

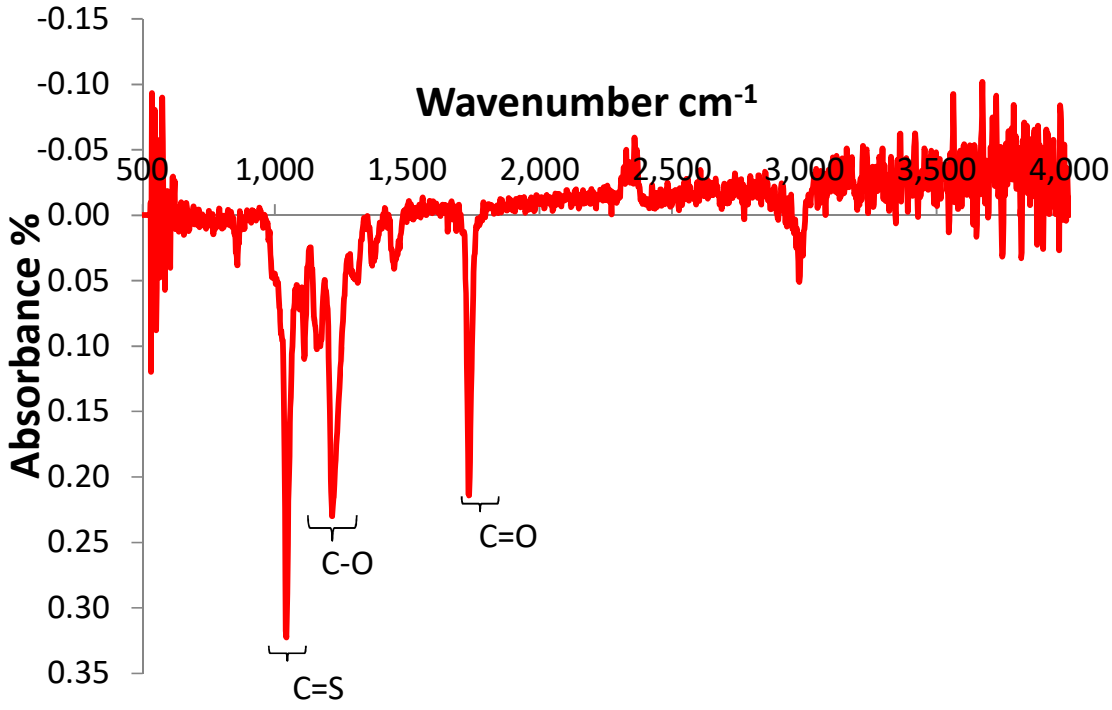


Figure 3.5c – IR spectrum for the xanthate RAFT agent.

3.3 **Results and Discussion**

3.3.1 Dielectric Analysis

In order to gain a greater understanding of the rate enhancement previously reported in the literature, the dielectric properties of the various reactants were measured. Two materials that were present in each of the reactions were the vinyl acetate monomer and the xanthate RAFT agent (Figure 3.6).

Vinyl Acetate **Xanthate RAFT agent**

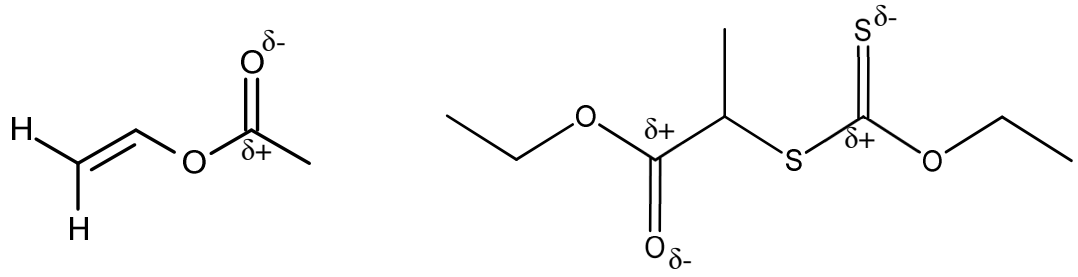


Figure 3.6 - Structure of vinyl acetate monomer and xanthate RAFT agent
Dipole moment of vinyl acetate = 1.79

The molecular structures of both the monomer and the RAFT agent indicate they have the potential to be heated by microwaves owing to the presence of dipoles. Both reactants are also in a liquid form, allowing the molecules to freely move and follow the electric field. As mentioned previously, the magnitude of the tanδ value for a particular material is often regarded as giving an indication of whether a material will heat effectively in a microwave (i.e. >0.1 microwave absorbent, <0.1 microwave transparent) and is a function of two different

parameters; the dielectric loss and the constant as shown in Equation 3.1. The dielectric properties of these materials, along with those of toluene across a range of temperatures, are shown (Figure 3.7). The process by which these values are measured is described in previous research.[80]

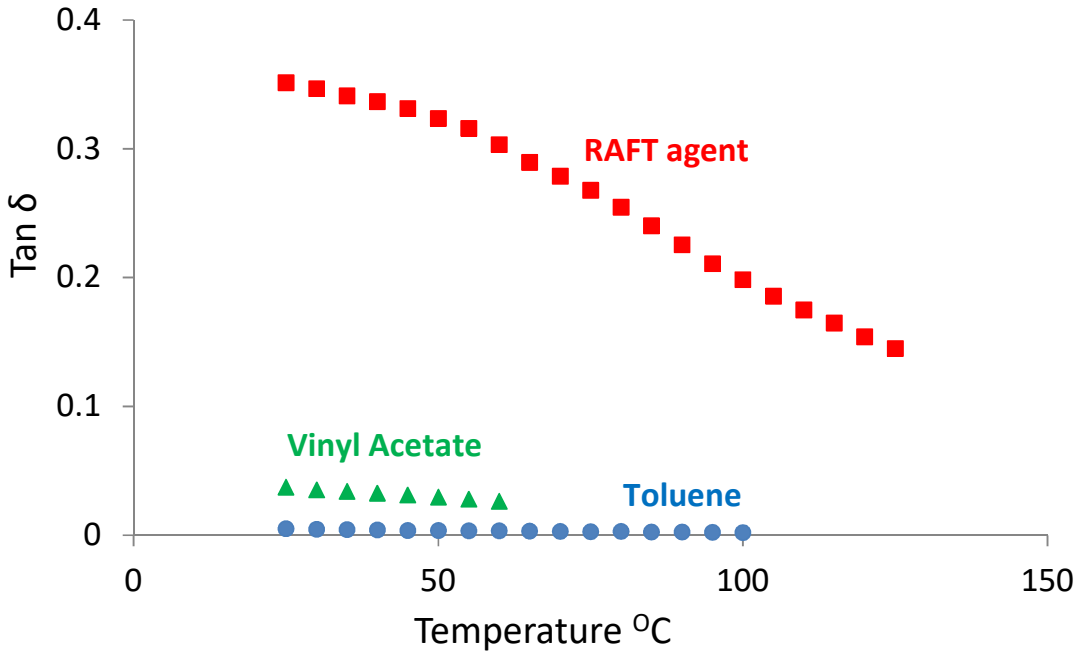


Figure 3.7 - A plot of the variation in tanδ with temperature for the key polymerisation reactants using the cavity perturbation technique

The tanδ values measured for vinyl acetate were low, indicating that it would not be selectively heated by microwave energy, even with a significant dipole present (Figure 3.7). In contrast, the xanthate RAFT agent showed considerably higher tanδ values across the whole temperature range investigated (Figure 3.7). This could be a consequence of the RAFT agent having two strong dipoles, as well having slightly larger structure than the monomer, meaning that the viscosity will be higher. When considering the dielectric properties for a particular material,

viscosity plays a significant role. If a material has a low viscosity the molecules are far apart, therefore when the molecules rotate with the microwave field there is less friction between the molecules in the medium, so they cannot transfer the microwave energy to heat as efficiently.

Conversely, if the molecular size is too great it could potentially give rise to a very viscous material, where the molecules cannot effectively align themselves with the field as their movement is restricted by the additional bonding (both intra and inter molecular) that exists around the dipole. Therefore, while the increase in viscosity from vinyl acetate to RAFT agent is only small, it could have a significant influence with regard to the difference in the dielectric properties. A key conclusion from this study of the dielectric property data was that the high tan δ measured implied that the RAFT agent would be the most likely of the reagent species to undergo selective microwave heating during the polymerisation, which could have a significant effect on the polymerisation process.

The initiator primarily used in this study was V-70, the structure of which is shown, along with the mechanism for the formation of the initiating radicals (Figure 3.8).

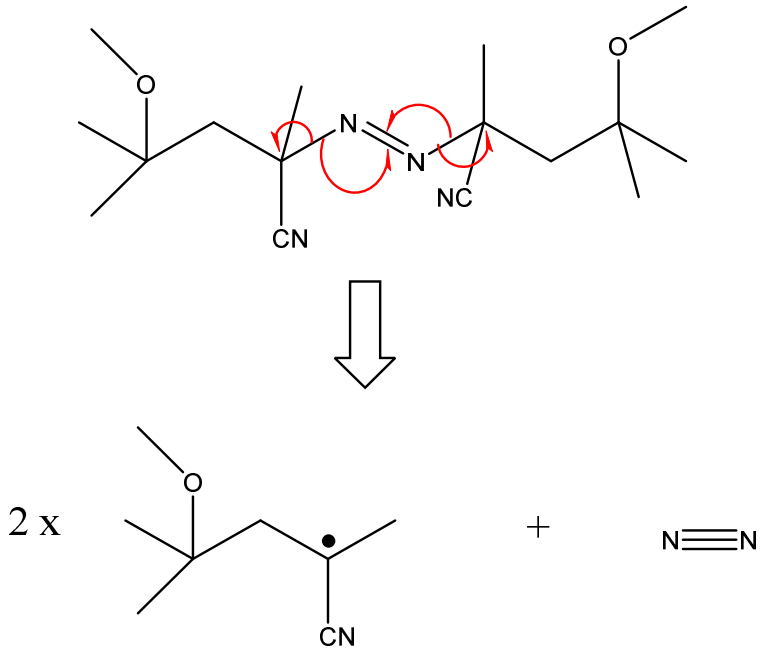


Figure 3.8 – Decomposition of the V-70 initiator into free radicals

The study of thermal initiators when increasing temperature must be carried out with great care with regard to potential hazards. The measurements for dielectric analysis have already been examined at the University of Nottingham (Figure 3.9).[81]

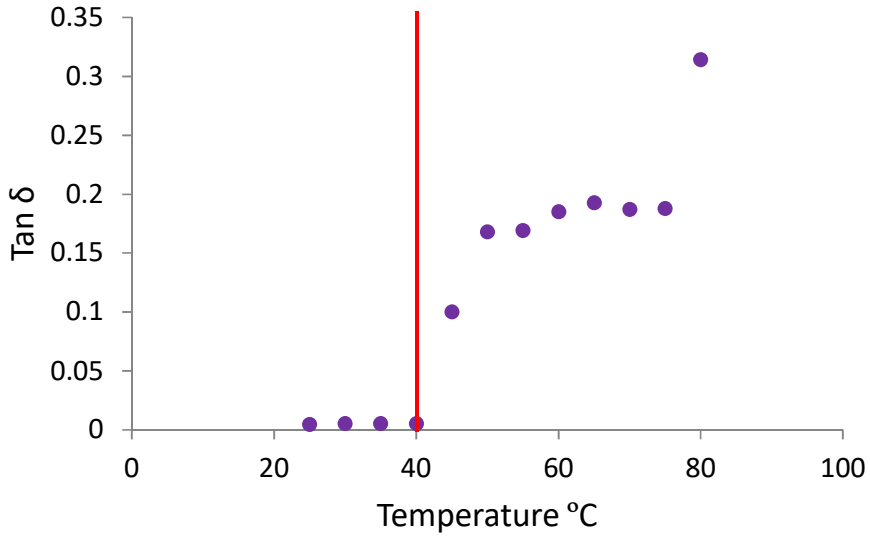


Figure 3.9 – A plot of the variation of tanδ with temperature for V-70 initiator. The red line indicates the 1 hour half-life at 40°C [81]

At the lower temperature range between 20-40 °C, tanδ is extremely low, confirming that the initiator is almost completely microwave transparent. An important factor relating to those experimental data is that the initiator is in a solid form, therefore the dipoles are restricted in their ability to align themselves with the electric field of the microwaves. Further consideration is also required for the rate of radical production, as a study by Adlington *et al* had shown that the free radicals are highly microwave absorbent species, and could be influential in inducing an acceleration of the polymerisation rate. However the radical production rate is rather slow at these temperatures, therefore there are fewer radical species present.[82]

Once the temperature had reached 40 °C, the dielectric properties of V-70 were observed to increase dramatically, which was attributed to two factors; the V-70 starts to melt, thus giving the dipoles more freedom to move (as mentioned with regard to the vinyl acetate monomer and xanthate RAFT agent). Additionally this increased temperature decreases the half-life time for

V-70 to 1 hour, leading to a significant increase in radical generation. This rise in the concentration of microwave absorbing species further contributed to the rise in the tanδ values.

Further work required the use of a solvent to lower the viscosity of the reaction medium to prevent any issues regarding diffusion of the reactants. When considering which solvent to use it was important to consider its dielectric properties, as several reports of using highly microwave absorbing solvents such as ionic liquids have shown an increase in the polymerisation rate.[19] However this will potentially lead to a problem with penetration depth, as all the microwave energy may be absorbed by the solvent close to the walls of the reactor; therefore nullifying any potential benefits that may arise from selective heating of particular reactants. Furthermore using a material with a high dielectric constant can affect the electric field applied to the reaction mixture, resulting in an alteration to the field distribution.[11] Therefore in this study the selected strategy was to include a solvent which was microwave transparent, in order to promote selective heating of the RAFT agent and radicals rather than invoking a bulk heating effect. Toluene is a non-polar solvent and the very low tanδ values measured in the dielectric analysis indicated that it would a suitable choice for the solution polymerisations (Figure 3.7).

3.3.2 Bulk RAFT Polymerisation

The xanthate RAFT agent employed throughout this thesis was selected as previous research had confirmed its suitability for controlling the polymerisation of vinyl acetate.[53] A 10:1 ratio of RAFT:initiator was applied in bulk conditions to determine the influence of microwave heating compared to conventional methods. This ratio was chosen to provide a low number of radicals within the reaction mixture, which should reduce the probability of producing 'dead

chains' *via* irreversible termination, as well as ensuring that the transfer rate to the RAFT agent is higher than the rate of propagation. This combination of factors was designed to provide optimum controlled growth of molecular weight with narrow dispersity values.

AIBN was chosen as the source of radicals as several investigations had produced successful RAFT polymerisations of vinyl acetate, including numerous reactions which had induced an acceleration of the polymerisation rate while maintaining control with microwave heating.[74, 83] These initial reactions were carried out at 65 °C, with a half-life time for the thermal decomposition of the AIBN initiator of 10 hours, providing a low concentration of radicals during the reaction with both heating methods (Figure 3.10).

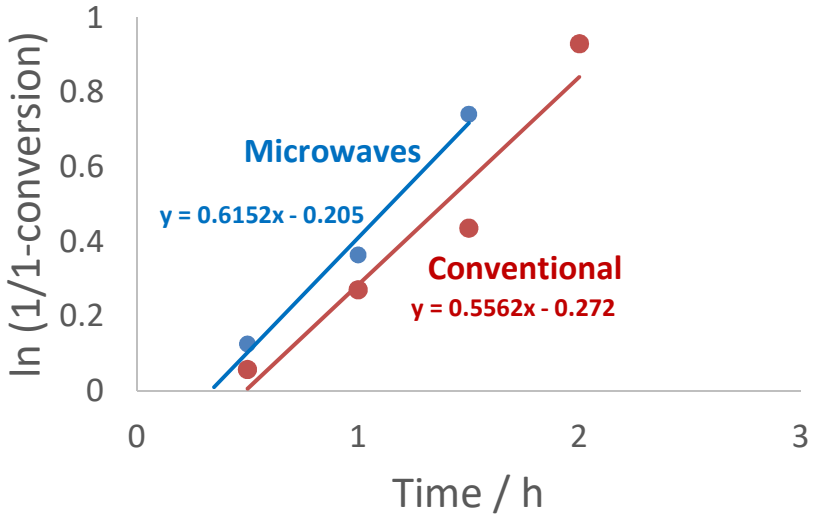


Figure 3.10 - Conversion over time for the RAFT polymerisation of vinyl acetate when applying microwave and conventional heating with AIBN initiator at 65°C. The trendlines for both sets of data confirmed a linear increase of conversion over time

Examples of NMR and GPC analysis from these experiments are given (Appendix 1 and 2). Both sets of data displayed narrow dispersity values and a linear trend of molecular weight increasing with conversion, indicating that a controlled polymerisation had occurred. However the difference in polymerisation rate in terms of the rise in conversion over time (Figure 3.10)

was negligible, therefore the effect of varying the reaction conditions was studied in order to determine the optimum conditions for the application of microwave energy.

One aspect to consider is the concentration of radicals in the system or 'radical flux', which can be altered by various aspects such as altering initiator concentration or changing the initiator decomposition rate.[84] These initial reactions employed a low radical concentration to minimise the level of termination, but this simultaneously results in a low rate of polymerisation, as there are only a relatively small number of polymer radical chains able to propagate. A proposal based on the dielectric properties for V-70 (Figure 3.9) had stated that acceleration could be induced by selectively heating free radicals. However such a low radical concentration may have resulted in reduced levels of energy being coupled into the system, hence providing little differentiation from conventional heating.

AIBN is a thermal azo-initiator, therefore applying higher temperatures would increase the rate of decomposition, leading to faster production of radicals at the start of the reaction. However the boiling point of VAc is 72 °C, thus a further increase in reaction temperature would have provided complications as a result of a reflux system, and would be likely to affect whether the microwave energy could be applied effectively. Therefore the initiator was altered to V-70 (Figure 3.8), another azo-initiator but with a 10 hour half-life temperature at 35 °C. Changing the initiator allowed the temperature, and therefore the initiator decomposition rate, to be altered without changing the nature of the reaction.

When considering a standard free radical polymerisation, an increase in temperature also leads to a rise in the termination rate, causing a significant loss of control and consequently producing

broad dispersity values as a result of a rise in the number of dead polymer chains. But with a RAFT agent present, there is also the formation of a dormant (i.e. temporary coupled non-propagating radical intermediate) radical species. Higher temperatures should mean a shorter lifetime for these dormant radicals (i.e. they will "shuttle" back to becoming "live" radicals) in a shorter period of time, thus reducing retardation and side reactions, and therefore control should still be maintained with the increased initiator decomposition.[85]

A set of experiments was conducted to confirm that the results of slow radical production still applied when using a 10 hour half-life for V-70 (Figure 3.11).

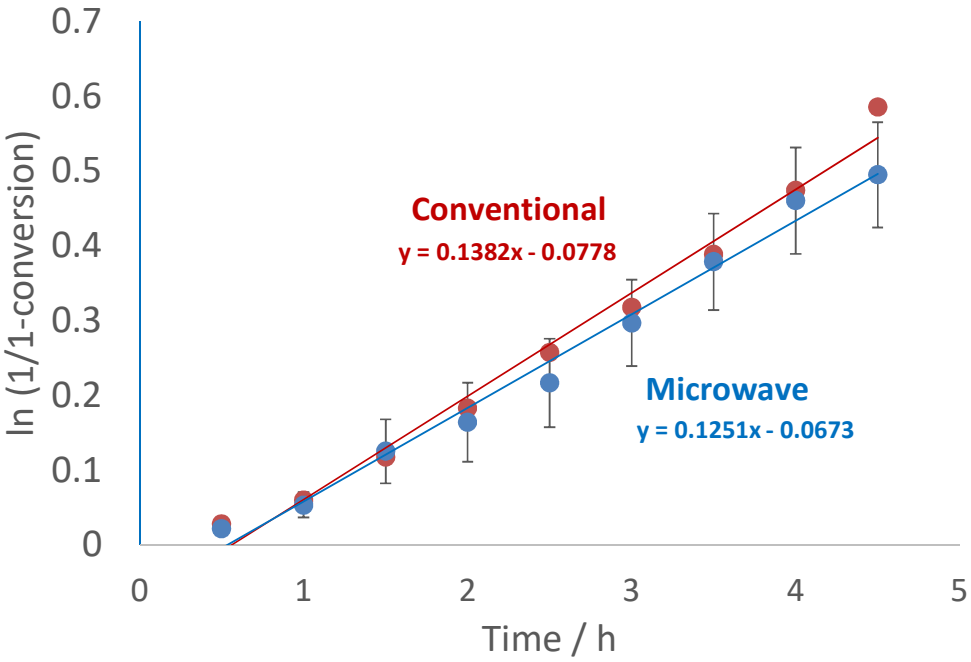


Figure 3.11 – Conversion over time for V-70 at 35 °C. Error bars represent the standard deviation from multiple repeat reactions. The trendlines for both sets of data confirmed a linear increase of conversion over time. Error bars that cannot be seen are within the region of the data point

Examples of NMR and GPC analysis from these experiments can be observed (Appendix 3 and 4). As expected, the difference between the two heating methods was negligible when a

low radical flux was used with V-70 (Figure 3.11), showing almost identical behaviour to that seen when using the AIBN initiator (Figure 3.10). In order to observe the influence of a more rapid production of radicals over the reaction, the temperature was increased to 45 °C, reducing the half-life for radical production with V-70 to 30 minutes. The dielectric data also showed that the ability of the V-70 initiator to absorb microwave energy is significantly improved at this higher temperature (Section 3.3.1). This increase in the number of microwave absorbing radical species could potentially induce an acceleration. A comparative graph of the RAFT polymerisation with V-70 showing both heating methods at different reaction temperatures is shown (Figure 3.12).

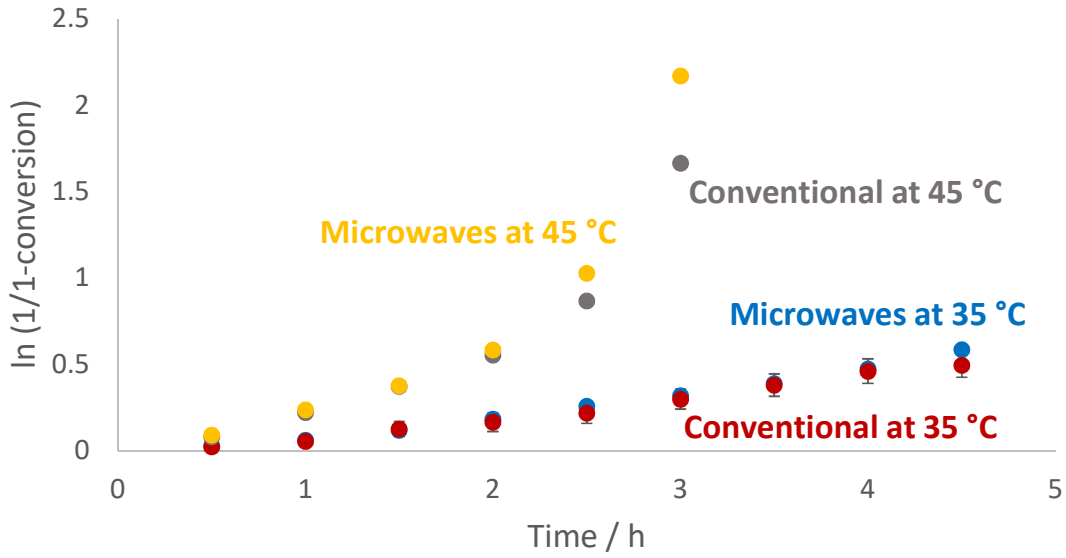


Figure 3.12 – Comparison of reactions at 35 °C and 45 °C using a RAFT:V-70 ratio of 10:1 for both microwave and conventional heating. Error bars represent the standard deviation from multiple repeat reactions. Error bars that cannot be seen are within the region of the data point

Increasing the decomposition rate of the initiator led to a significant increase in the reaction rate for both heating methods (Figure 3.12), as was expected when lowering the half-life time to produce a larger number of radicals at the start of the reaction, as the presence of more

radicals increases the probability of propagation occurring. Furthermore a slight increase in reaction rate towards the end of the reaction time was observed when using microwave heating (Figure 3.12), which was attributed to the rise in viscosity as the conversion continues to increase, therefore proving that mixing and heat transfer into the bulk were less effective for conventional methods. An improved result when using microwaves suggested that selective heating was being achieved, therefore the issues regarding heat transfer were reduced, resulting in effective control over molecular weight with the more rapid initiator decomposition. However, this small difference was still not enough to justify the application of microwaves on a commercial basis, thus it appeared that further modification of the reaction conditions was required to increase the rate of propagation for the RAFT reaction.

Another aspect to consider with regards to radical flux is the initiator concentration, which is controlled by the ratio of the relative proportions of RAFT agent to initiator, and determines the balance of different radical types and "states" in the reaction.[84, 86, 87] Firstly there are active radical species which are capable of propagating, which can be from the initiator ($I^{\bullet}$), RAFT agent leaving group ($R^{\bullet}$) or polymer chains ($P_n^{\bullet}$). A higher initiator concentration means more $I^{\bullet}$ radicals, which will eventually produce more $R^{\bullet}$ and $P_n^{\bullet}$ radicals and subsequently lead to an increase in the rate of reaction, which is referred to previously when describing the mechanism of RAFT polymerisation (Chapter 1).

However there are other consequences that arise as a result of increasing initiator concentration, as a larger number of radicals can increase termination levels in the system, which can have various consequences with regards to reaction rate (Chapter 1). Active radical species are also capable of undergoing addition to the RAFT agent, creating intermediate non-propagating dormant radical species.[85] The stability of these intermediate radicals is influenced by the Z and R groups on the RAFT agent, and can subsequently alter the nature of the reaction kinetics.

Reactions with highly stable dormant polymer species are retarded with increasing concentration of the RAFT agent.[84]

Intermediate dormant radicals which have low stabilisation show little to no retardation of the polymerisation process, so the kinetics are largely dependent on the initiator concentration, the initiator rate of decomposition and the propagation rate.[84] Previous experiments shown in this chapter reveal no obvious signs of retardation, even when using high RAFT agent concentrations, implying the intermediate radicals for these polymerisations have low stability, as expected, since vinyl acetate has a highly reactive radical in standard free radical polymerisations.

But as with the active species, there can also be termination caused by the addition of a radical species to these non-propagating radicals, which decreases the initiator efficiency, leading to fewer chains being able to propagate and therefore lowering the overall rate of reaction.[88, 89] The terminating radical can come from several sources including the initiator and the RAFT agent leaving group, therefore it is beneficial to have a fast rate of fragmentation for the non-propagating radical. [84]

Taking these influences into account, the initiator concentration was doubled to give a RAFT:V-70 ratio of 5:1 in order to increase the number of radicals that were present at the start of the reaction. The conversion over time for microwave and conventional heating is shown and compared with using the lower initiator concentration (Figure 3.13).

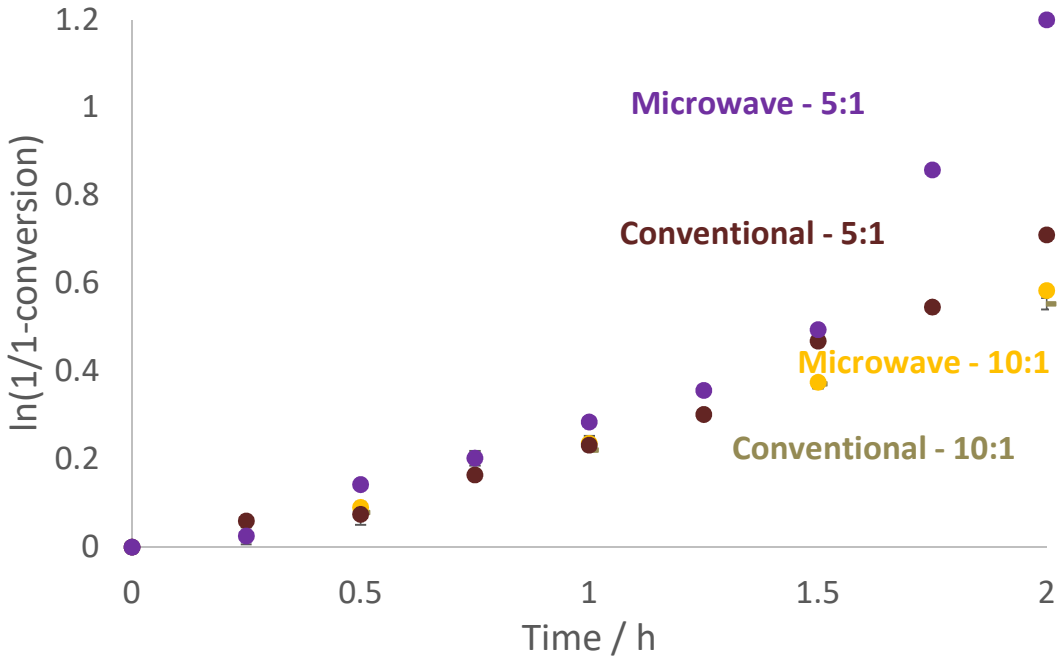


Figure 3.13 – Comparison of microwave and conventional heating for 10:1 and 5:1 ratios of RAFT:V-70 for bulk RAFT polymerisation. Error bars represent the standard deviation from multiple repeat reactions. Error bars that cannot be seen are within the region of the data point

Examples of GPC analysis from these experiments are given (Appendix 5 and 6). As observed with the lower initiator concentration, there is little difference in respect of reaction rate when using the 5:1 ratio between the two heating methods at the outset of the reaction. However, a definite increase in the reaction rate was observed after 1.5 hours upon the application of microwave heating (Figure 3.13) implying that the higher initiator concentration, and therefore having a larger number of radicals present in the reaction, does effect the polymerisation process. The observed delay for this increase may owing to a build-up of radical species being required in order for selective heating to be effective.

Several theoretical papers have attempted to model how the application of microwaves results in the observed acceleration of the polymerisation rate. An initial study from Hernandez-Ortiz

et al suggested that microwaves cause a more rapid decomposition of the initiator,[90] resulting in producing more chains that are able to propagate. However this scenario would ultimately lead to a loss of control owing to increasing termination and reduced molecular weight. Smith *et al* have also shown that it is unlikely that microwave heating induces a lower temperature decomposition of the radical, therefore the observed effects could be linked to more rapid bulk heating when using microwaves, compared to the slower rise in temperature with conventional heating techniques.[91]

Zetterlund and Perrier have theorised that microwaves enhance the rate of propagation while termination is unaffected, allowing the reaction to maintain good control of molecular weight and promote low dispersity values. [92] However this model could not replicate the experimental data exactly, as the theoretical dispersity for the reaction was shown to increase, therefore the exact reason for the observed controlled acceleration of the reaction is still unknown.

An acceleration with increased initiator concentration was a significant result, but it was vital that control of chain growth was maintained, therefore the GPC data were studied comparatively with the conversion data for the 5:1 ratio (Figure 3.14).

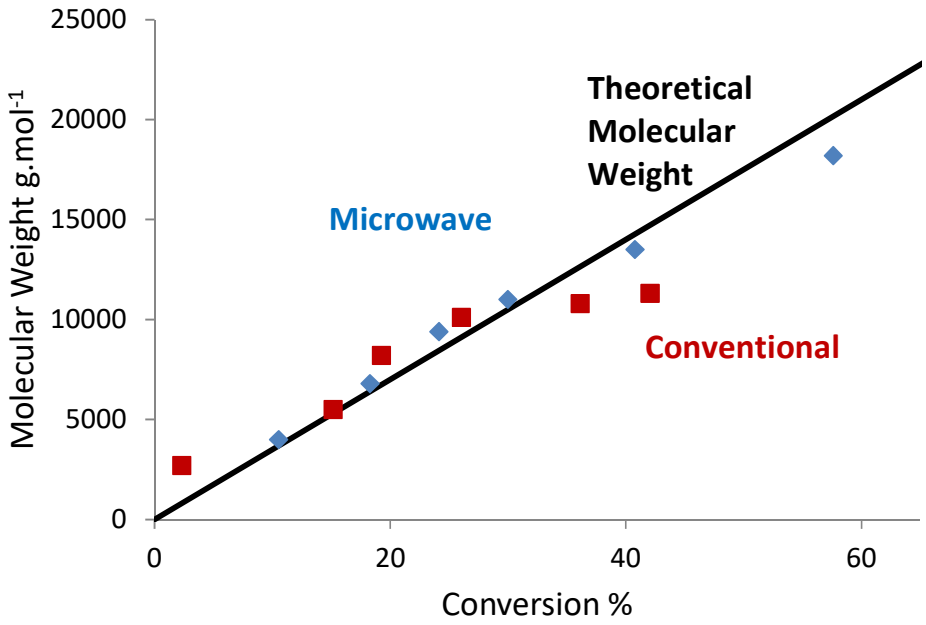


Figure 3.14 – Molecular weight and conversion data for bulk RAFT polymerisation with 5:1 ratio of RAFT:V-70 at 45 °C

The dispersity values for both heating methods were below 1.4 even during the period of microwave acceleration, providing further confirmation of the control when using the RAFT agent, as ineffective regulation over polymer chain growth during the acceleration of the reaction rate would have resulted in higher dispersity values. Additionally the microwave heated reaction demonstrated superior retention of polymerisation control, as the data still followed the theoretical growth at 60 % conversion, whilst the conventional system diverged from this ideal trend at around 35 %.

These results obtained within the initial 2 hours of the bulk RAFT polymerisations looked very promising, however the main issue centred on the increase in viscosity as conversion increases. After 2 hours the reaction mixture became too viscous to sample, therefore additional kinetic samples could not be collected until the reaction was terminated after 5.5 hours, after which both heating methods had reached higher conversion levels and molecular weights, as would

be expected. However the M_n values measured were observed to be noticeably larger than predicted, implying a lack of control over the polymerisation process as a consequence of the increasing viscosity of the reaction medium. This was further confirmed by the broad dispersities of the final GPC peaks.

The rise in viscosity is to be expected in a bulk polymerisation as the monomer acts as the solvent, therefore as monomer is depleted with increasing conversion, the reaction mixture becomes more viscous. In these circumstances it would be expected for conversion to continue, as propagation is a chemically controlled bimolecular process, allowing the radicals to continue to react as the viscosity increases.[84] Large dispersity values prove that the reaction is no longer controlled by the RAFT chain transfer equilibrium at this point, indicating that this is a diffusion controlled process, and is therefore ineffective once the reaction becomes too viscous.[87, 93]

Termination, as another diffusion controlled process, is also reduced with higher viscosity levels, further decreasing the regulatory control of molecular weight during the reaction. Therefore these bulk polymerisation procedures would not be suitable for the industrial applications intended for this project, as the purpose of applying a controlled polymerisation technique is to be able to regulate polymer chain growth. The dielectric data (Figures 3.7 and 3.9) proved that selective heating of both the RAFT agent and the V-70 radicals was taking place during these reactions, and causing the rate enhancement noticed in these bulk RAFT polymerisations. However the issues arising from the increasing viscosity needed to be addressed.

3.3.3 Solution RAFT Polymerisation

The major drawback with the bulk reactions was the significant increase in viscosity as the process proceeds, which not only prevents effective control being exercised over the polymerisation, but it can also be potentially dangerous. When viscosity is too high, the RAFT reaction behaves more like a free radical polymerisation rather than being controlled. An associated reduction in diffusion means that the radicals cannot become dormant or terminate but can continue to propagate, causing a further rise in viscosity which will eventually lead to the Trommsdorff effect.[94, 95]

The simplest alternative to reduce viscosity was to introduce a solvent into the reaction medium, which would ensure that the overall viscosity would remain low, even with high levels of monomer conversion. As shown in the dielectric analysis (Figure 3.7), toluene was confirmed as a suitable option with low tanδ values, confirming it was microwave transparent and therefore would not inhibit the effects induced by selective heating. The same RAFT : initiator ratio was used from the bulk reactions (5:1), with a 2:1 ratio of vinyl acetate:toluene (Figure 3.15).

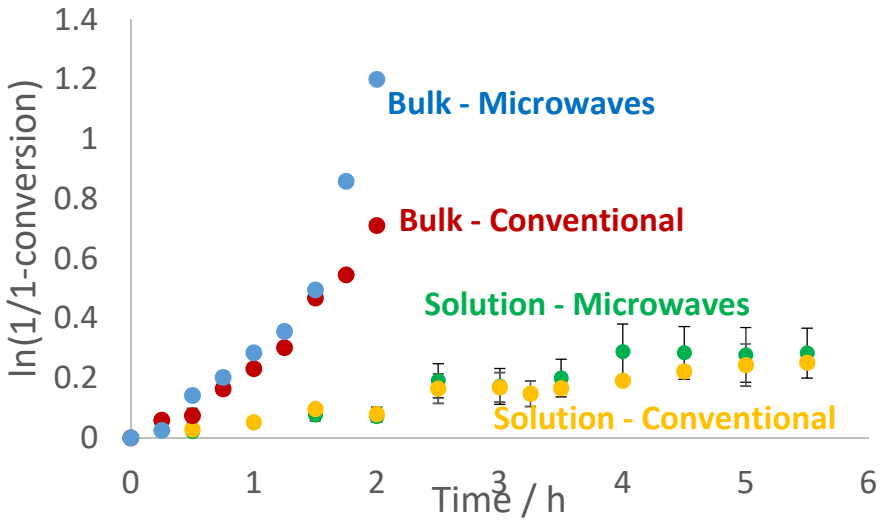


Figure 3.15 – Comparison of bulk and solution RAFT kinetic data for a RAFT:V-70 ratio of 5:1 at 45 °C. Error Bars are based on the standard deviation from multiple repeat experiments. Error bars that cannot be seen are within the region of the data point

Examples of NMR and GPC analysis for the experiments using 10 ml of toluene are given (Appendix 7-9). A significant difference in the data presented (Figure 3.15) can be seen when compared to that of the previous bulk reactions, including a noticeable reduction in the final conversion reached for both heating methods. This indicated that the high proportion of solvent present had a significant impact on the reaction rate, as the radicals have a lower probability of reacting with an available monomer molecule in order to continue propagation compared to a bulk polymerisation. The selective heating of particular reactants using microwave energy was also affected, as the presence of solvent actually seemed to retard the microwave reaction.

In an attempt to counteract the observed effects caused by the presence of toluene, the initiator concentration was increased further for a RAFT:initiator ratio of 2.5:1, while maintaining the level of solvent. This would ensure a higher radical concentration during these reactions, which

has been proven to provide faster reaction rates in previous research regarding free radical polymerisation.[86] A graph summarising these data is shown (Figure 3.16).

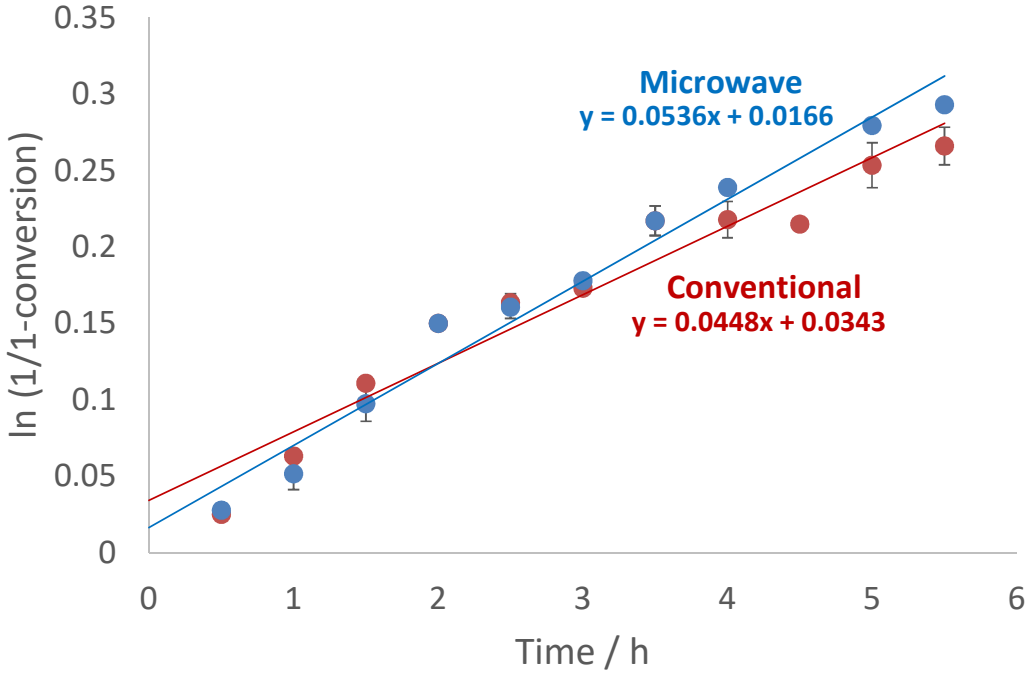


Figure 3.16 – Kinetic data for solution RAFT polymerisation using 10 ml toluene with RAFT:V-70 ratio of 2.5:1. Error Bars are based on the standard deviation from multiple repeat experiments. The trendlines for both sets of data confirmed a linear increase of conversion over time. Error bars that cannot be seen are within the region of the data point

Increasing the radical concentration was shown to prevent the retardation of the microwave heated RAFT polymerisation seen previously (Figure 3.15), however there was only a minor increase of 3% in the final conversion observed when using microwave heating compared to the conventional equivalent (Figure 3.16). This change in conversion, albeit small, has shown that increasing the radical concentration is a vital consideration with regards to microwave induced acceleration. The molecular weight of the polymer also demonstrated a linear relationship with conversion for both methods of heating, confirming that the RAFT agent was

able to regulate the polymer chain length through the reaction. The tables (Tables 3.1 and 3.2) and graph (Appendix 10) further prove the degree of control over the polymerisation process with the increase in initiator concentration

Tables 3.1 and 3.2 - GPC data for solution RAFT polymerisations with RAFT:V-70 ratio of 2.5:1

Conventional Heating

Conversion % [a]	$M_{n,th}$ g.mol^{-1} [b]	M_n g.mol^{-1} [c]	Đ [c]
7	2,500	2,100	1.48
6	2,400	2,850	1.43
9	3,200	3,750	1.38
12	4,200	4,600	1.33
14	5,000	5,200	1.32
19	6,700	6,600	1.3
23	8,200	7,200	1.3

Microwave Heating

Conversion % [a]	$M_{n,th}$ g.mol^{-1} [b]	M_n g.mol^{-1} [c]	Đ [c]
3	1,400	1,700	1.47
5	2,100	2,500	1.45
11	4,100	3,800	1.38
11	3,900	4,500	1.34
20	7,000	6,700	1.3
21	7,400	6,800	1.32
21	7,700	7,000	1.3
25	8,800	7,400	1.3
27	9,500	7,800	1.33

[a]Calculated from NMR analysis, an example is shown in Figure 3.4

[b]Calculated using equation

$$\textbf{Equation 3.3;} \qquad M_{n,\,theo} = \frac{[M]_0 - [M]_t}{[RAFT]_0} \times m_M + m_{RAFT}$$

Where $[M]_0$ = initial monomer concentration, $[M]_t$ = monomer concentration at time t, $[RAFT]_0$ = initial RAFT agent concentration, m_M = molecular weight of monomer and m_{RAFT} = molecular weight of RAFT agent

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

While these results were potentially promising, the difference between the two heating methods in terms of reaction rate was still minimal, therefore further modifications were required to the reaction system in order to see any potential advantage in utilising the application of microwave heating. As it was regarded as unsafe to increase the initiator level further in case it triggered a reaction runaway, the amount of toluene was reduced by half to a 4:1 ratio of vinyl acetate : toluene, while still using the higher ratio of 2.5:1 for the RAFT:V-70 (Figure 3.17).

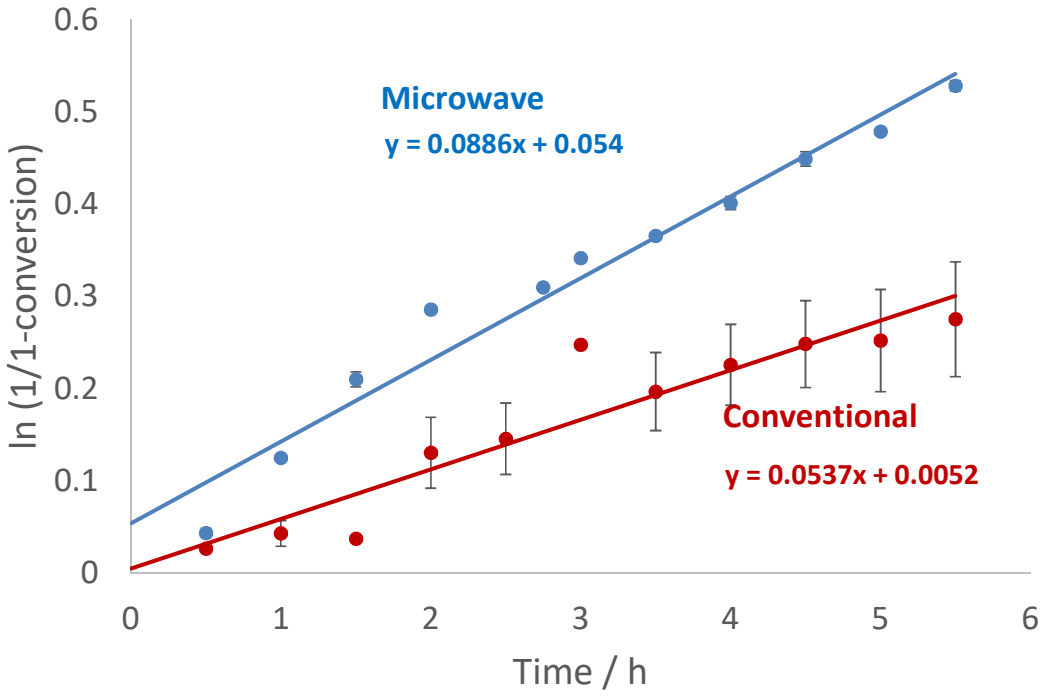


Figure 3.17 – Kinetic data for solution RAFT polymerisation using 5 ml toluene with RAFT:V-70 ratio of 2.5:1 at 45°C. Error Bars are based on the standard deviation from multiple repeat experiments. The trendlines for both sets of data confirmed a linear increase of conversion over time. Error bars that cannot be seen are within the region of the data point

An example of NMR analysis from these experiments is also provided (Appendix 11). The reduction in solvent volume resulted in a significant increase in the final conversion when employing microwave heating, with the gradients for the kinetic data (Figure 3.17) confirming that the reaction rate had almost doubled upon the application of microwaves compared to

conventional heating. The molecular weight and dispersity data for these reactions further confirmed that the reaction was controlled by the RAFT agent, with both heating methods demonstrating low dispersity values. This continues to support previous research, where lowering solvent levels led to increasing yields with microwave heating.[82]

Unlike the bulk reactions, the difference between the methods of heating can be observed from the very start of the reaction. Both the high radical concentration and the lower solvent level appear to induce an acceleration of the propagation rate when using microwave energy. The effect of microwaves is supported by the theory relating to 'hot radicals'; where a radical species is selectively heated by the microwave but the energy absorbed is not all removed during propagation.[96] This temporarily creates an excited vibrational radical and, if there is a high enough excess of energy, further propagation can occur. When using large amounts of solvent, there is a lower probability of these excited molecules causing further polymerisation. Lowering the solvent level means there is a decreased possibility of a selectively heated molecule hitting a non-heated molecule such as toluene, therefore less vibrational energy is lost heating cooler material.

These experiments had successfully demonstrated the acceleration of the polymerisation rate, however it was still necessary to determine whether the RAFT agent could still maintain control over the growth of the polymer chains over time with both the molecular weight and dispersity measured (Figure 3.18).

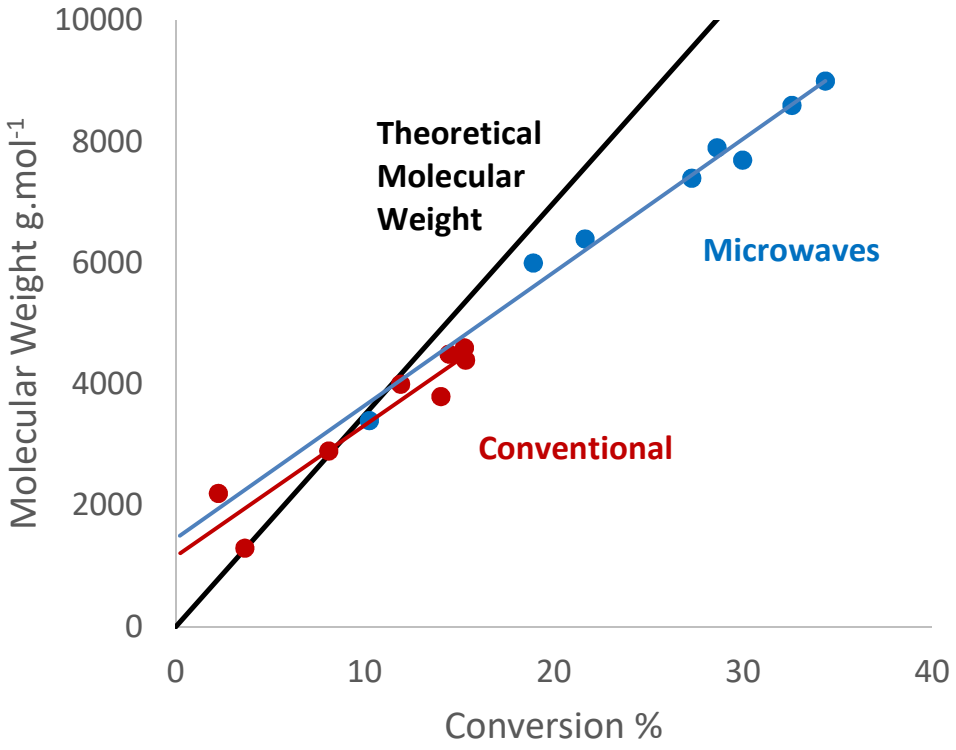


Figure 3.18 - Molecular weight and conversion data for solution RAFT polymerisation using 5 ml toluene with 2.5:1 ratio of RAFT:V-70. The trendlines for both sets of data confirmed linear growth for the PVAc throughout the reaction

The narrow dispersities confirmed that, even during the period of microwave acceleration, the RAFT equilibrium was able to effectively control molecular weight (Figure 3.18). This implied that the chain transfer of the RAFT end group onto radical polymer chains was enhanced, although the deviation from the ideal linear growth suggested that there was polymer chains were still undergoing irreversible termination. The experimental error levels for the conventional reactions were also observed to be significantly larger than for the microwave reaction, which could be attributed to the reproducibility of the heating techniques. Microwave energy directly heats the reaction mixture with an even distribution, whereas the conventional reactions are heated by conduction and convection which engenders a much slower rate of heat transfer, as described in detail previously (Figure 3.2). Thus the microwave heating profile

was proposed to exhibit greater batch-to-batch repeatability which, combined with a faster rate of heating compared to the conventional system, aided in minimising variation from multiple kinetic reactions. The difference between the two heating methods is highlighted further when studying the temperature profiles of both sets of reactions (Figure 3.19).

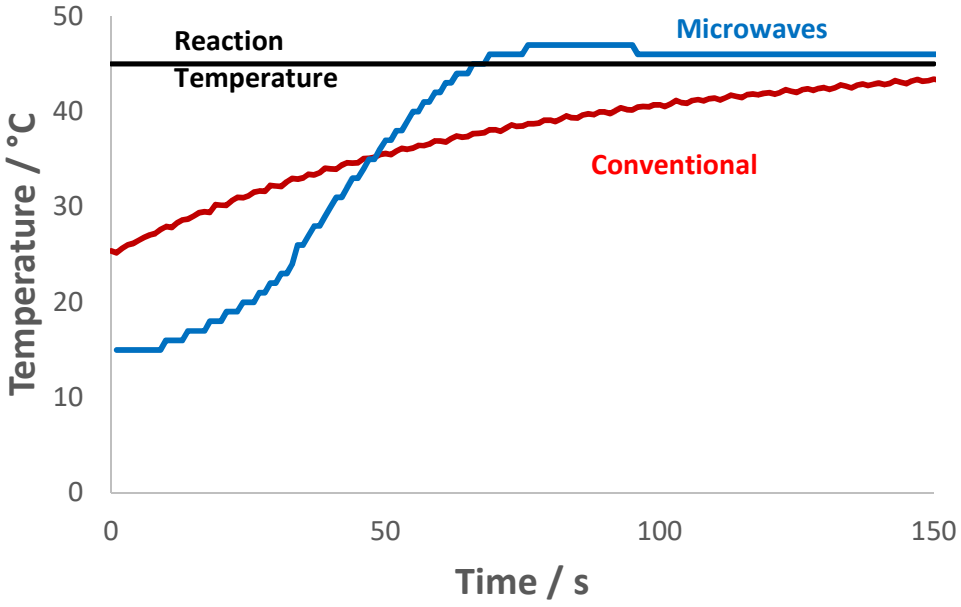


Figure 3.19 - Temperature profiles for solution RAFT polymerisation using 2.5 ml toluene and RAFT:V-70 of 2.5:1 at 45°C

In the experimental procedures, the oil bath had to be programmed in advance to allow time to equilibrate at the desired temperature, which still led to a slow rise in temperature for the reaction medium observed during use of the conventional heating method; this could cause a variation in the decomposition of the initiator, making it difficult to replicate the exact reaction conditions, In comparison, the microwave reaction reached the reaction temperature in a significantly faster time than when using the oil bath (Figure 3.19), as the reactants are directly heated throughout the entire medium. Therefore the rate of heating is much faster using microwaves, meaning the decomposition rate is increased, providing more reproducible reaction conditions and therefore more consistent results.

It had previously been reported in the literature that applying high power levels in the initial stage of a reaction can lead to an increase in conversion.[97, 98] A typical power input profile from the CEM reactor during these RAFT polymerisations is demonstrated (Figure 3.20).

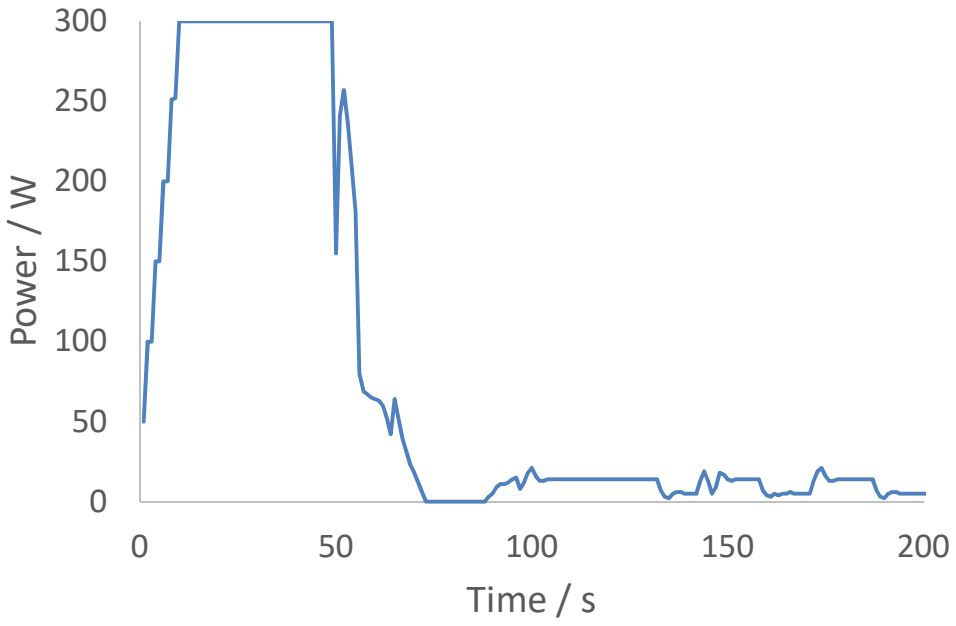


Figure 3.20 – Power profile over time for standard RAFT polymerisation heated using microwave energy

At the start of each reaction, the maximum 300 W input from the CEM reactor was applied in order to reach the desired temperature as quickly as possible. However, it was important to monitor this process as rapid heating of the reaction could potentially lead to an overshoot.[99] When considering radical polymerisation, a higher than expected rise in temperature may lead to increased initiator radical termination, which could inhibit the propagation process and therefore little to no polymer would be formed. The temperature profile for microwave heating confirmed that no overshoot occurred in the initial reaction stage (Figure 3.19).

After this initial rapid heating, a minimal power input between 10-20 W was required to maintain the reaction temperature. This potentially suggested that the microwave polymerisation may be a more sustainable process, as the differences reported in the reactions were achieved with low levels of input power, although a similar power input reading would be necessary during an oil bath reaction for confirmation. These findings also proved that relatively low levels of microwave energy were needed to produce significant differences in the mechanistic behaviour .

With the previous reduction in solvent level showing a considerable increase in rate for the microwave reaction, the solvent level was lowered further to an 8:1 ratio of vinyl acetate : toluene to observe whether this trend continued (Figure 3.21).

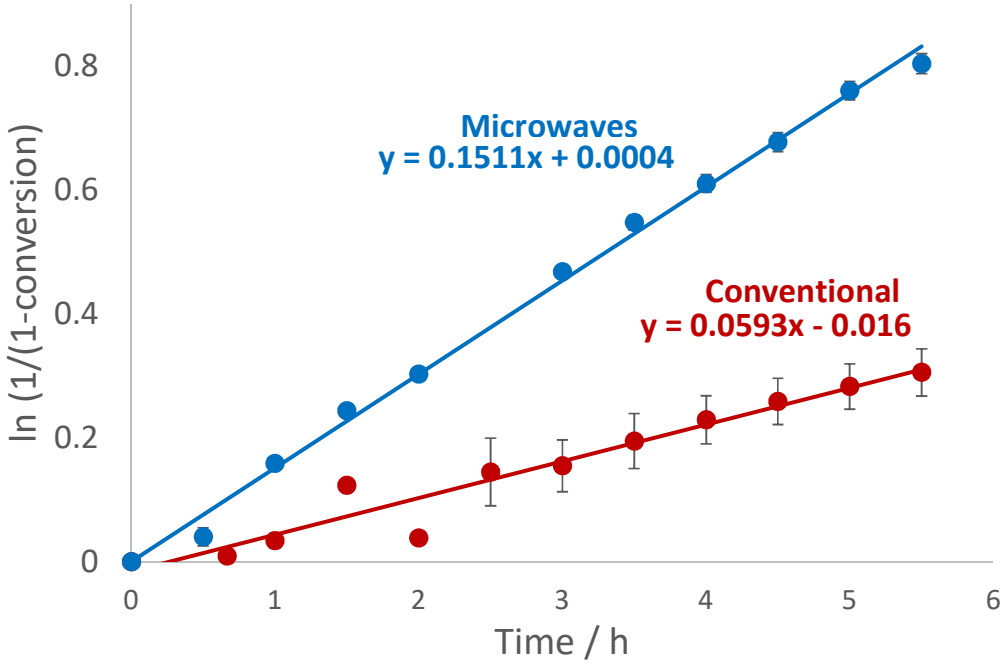


Figure 3.21 - Kinetic data for solution RAFT polymerisation using 5 ml toluene with RAFT:V-70 ratio of 2.5:1 at 45°C. Error Bars are based on the standard deviation from multiple repeat experiments. The trendlines for both sets of data confirmed a linear increase of conversion over time. Error bars that cannot be seen are within the region of the data point

Examples of NMR and GPC analysis of for these experiments are also provided (Appendix 12 and 13). The reaction rate has more than doubled when applying microwave energy (Figure 3.21), confirming an increased rate of reaction for the polymerisation process when lowering the solvent volume, providing further evidence towards a dilution effect. Additionally, the difference was observed to be more pronounced with the minimal solvent level (Figure 3.21) than with the bulk reactions (Figure 3.13).

The trend in the solution polymerisation from the selective heating of radicals would appear to imply that using bulk conditions should provide the optimal reaction parameters for the microwave induced accleration. However the drastic increase in viscosity at higher conversion levels could be diminishing these effects, demonstrating how important diffusion control is over these particular RAFT polymerisations. It was also concluded that reducing the level of solvent produced better conformity to the theoretically predicted performance in both heating systems. Whilst this is also the case for the conventional reaction, this is because the conversion is still too low to generate a divergence.

As mentioned previously, the regulation of polymer chain length was still a vital consideration during the enhanced polymerisation rate when using microwave energy (Figure 3.22).

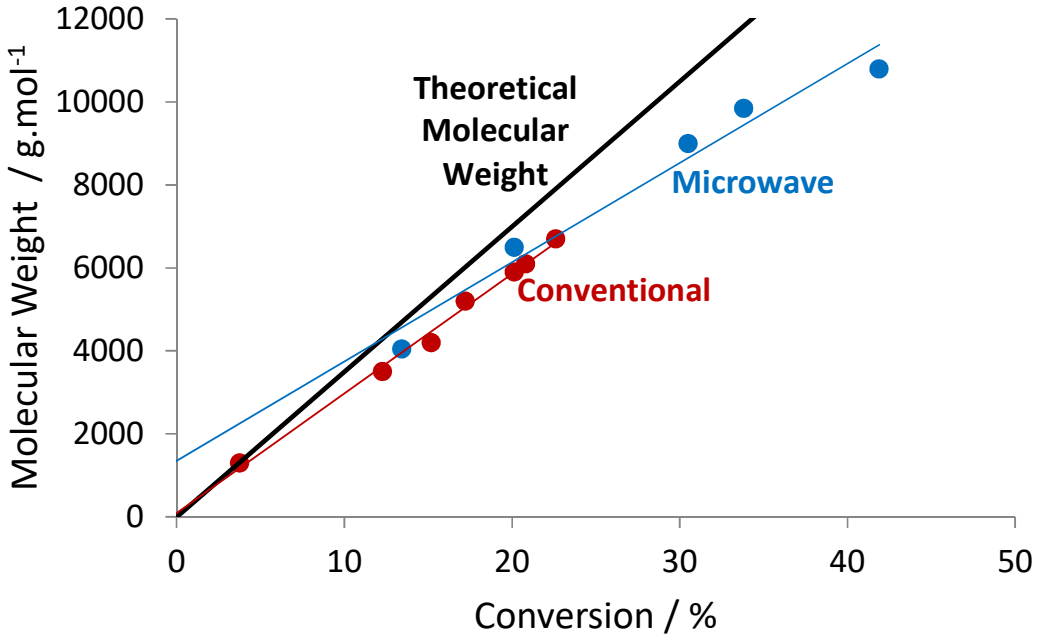


Figure 3.22 - Molecular weight and conversion data for solution RAFT polymerisation using 2.5 ml toluene with 2.5:1 ratio of RAFT:V-70. The trendlines for both sets of data confirmed linear growth for the PVAc throughout the reaction

The GPC data proved that even with the acceleration of the reaction rate when using microwaves, there is a linear relationship of molecular weight with conversion (Figure 3.22). This confirmed that throughout the reaction time, the growth of the polymer chains is controlled by the RAFT agent.

Further evidence for the degree of control provided over the polymerisation when using the RAFT agent can be seen when examining the GPC traces (Figure 3.23).

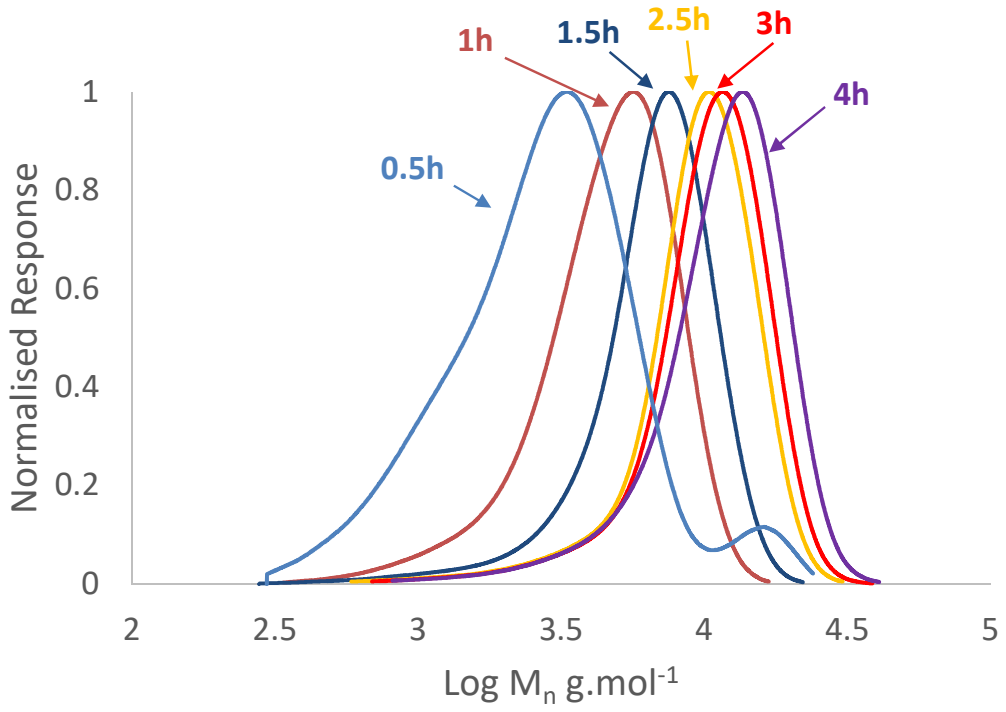


Figure 3.23 - GPC traces showing growth of polymer over time for a microwave heated RAFT polymerisation using 2.5 ml of toluene with a RAFT:V-70 ratio of 2.5:1 at 45°C

The traces (Figure 3.23) demonstrate the progression of polymer growth, where the initial molecular weight and dispersity values can be seen to be quite high. This is usually a result of slow fragmentation of the RAFT agent,[100] meaning propagation occurs before the reaction is under steady state kinetics and therefore produces irreversibly terminated chains, which increase the dispersity value. The small shoulder peak observed in the early stages is as a result of small polymer chains undergoing rapid termination. After 1 hour, the dispersity values are noticeably narrower, indicating a higher proportion of polymer chains are in a dormant state. At this point, the RAFT equilibrium is effectively controlling the polymerisation process, ensuring uniform growth of the polymer chains.

The GPC traces for conventional heating highlights the significant differences in polymer growth between the employed heating methods (Figure 3.24).

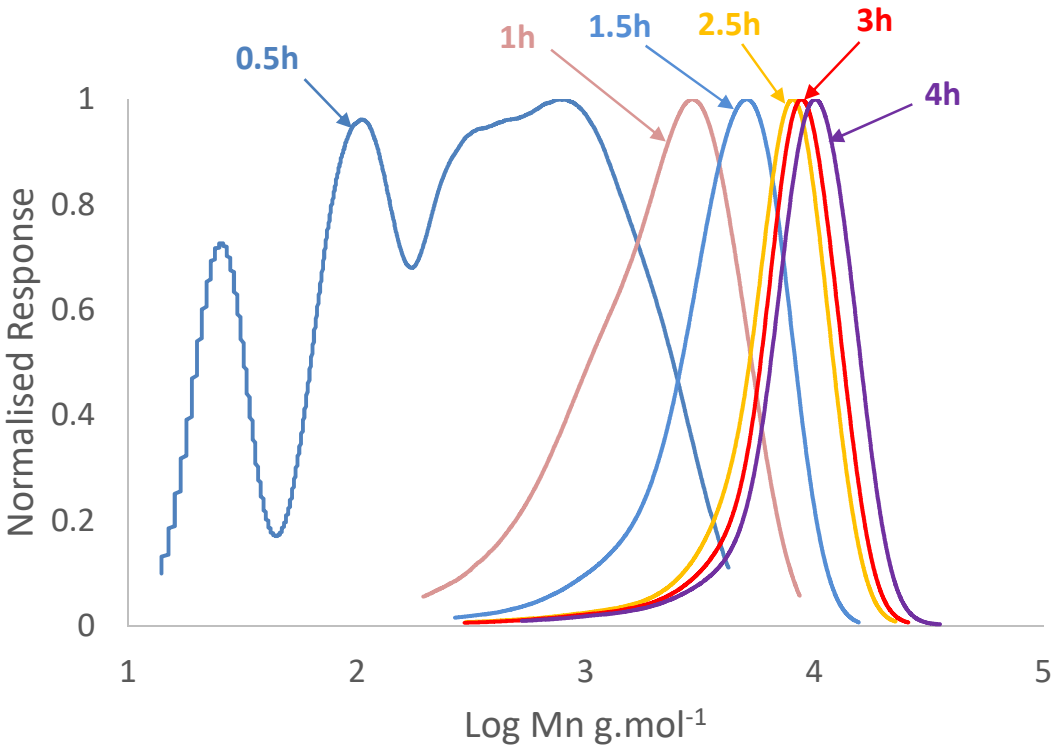


Figure 3.24 - GPC traces showing growth of polymer over time for a conventionally heated RAFT polymerisation using 2.5 ml of toluene with a RAFT:V-70 ratio of 2.5:1 at 45°C

The first kinetic sample provided a very broad dispersity, low molecular weight and a poorly defined peak (Figure 3.24), in contrast to the first GPC peak for microwave heating (Figure 3.23). The GPC traces for conventional heating do eventually demonstrate narrower dispersities, however there is a noticeable lowering in polymer chain growth after 3 hours, as was also observed from the graph of molecular weight against conversion (Figure 3.22). In comparison the molecular weight when using microwaves continues to rise at a steady rate, further displaying the advantages over conventional heating methods.

The trend in the dispersity values over time can also be seen in the tables below.

Tables 3.3 & 3.4 – GPC data for solution RAFT polymerisations with RAFT:V-70 ratio of 2.5:1

Conventional Heating

Conversion % [a]	$M_{n,th}$ g.mol^{-1} [b]	M_n g.mol^{-1} [c]	Đ [c]
1	1,800	1,200	2.39
1.5	3,800	3,900	1.32
2.5	6,800	6,500	1.3
3	7,600	7,400	1.24
4	9,400	8,600	1.24

Microwave Heating

Conversion % [a]	$M_{n,th}$ g.mol^{-1} [b]	M_n g.mol^{-1} [c]	Đ [c]
0.5	1,700	2,600	1.74
1	4,400	4,400	1.3
1.5	6,500	6,300	1.25
2.5	9,800	8,919	1.23
3	10,800	9,700	1.23
4	13,300	10,600	1.26

[a]Calculated from NMR analysis

[b]Calculated using Equation 3.3;

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

These were important results, demonstrating a combination of significantly increasing the polymerisation rate while retaining the desired level of control upon the application of microwave heating.

One of the important factors contributing towards this observed acceleration with microwave energy was use of a high initiator concentration, therefore we decided to see whether there was the potential to further enhance the polymerisation process by increasing the concentration of V-70. This was investigated further by applying a RAFT : initiator ratio of 1:1, and a ratio of 2:1 for vinyl acetate : toluene to maintain a low viscosity level (Figure 3.25).

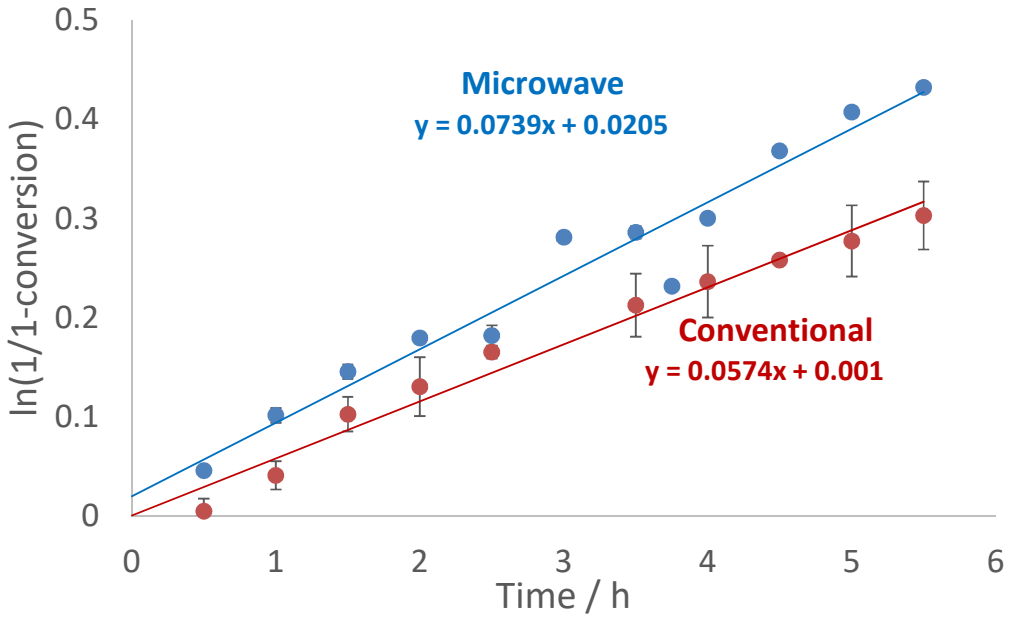


Figure 3.25 - Kinetic data for solution RAFT polymerisation using 10 ml toluene with RAFT:V-70 ratio of 1:1 at 45°C. Error Bars are based on the standard deviation from multiple repeat experiments. The trendlines for both sets of data confirmed a linear increase of conversion over time. Error bars that cannot be seen are within the region of the data point

These initial results showed that the microwave heated reaction reached a higher conversion compared to using an oil bath (Figure 3.25). The GPC data confirmed a linear growth in molecular weight for conventional heating and in the initial stages when applying microwaves (Figure 3.26).

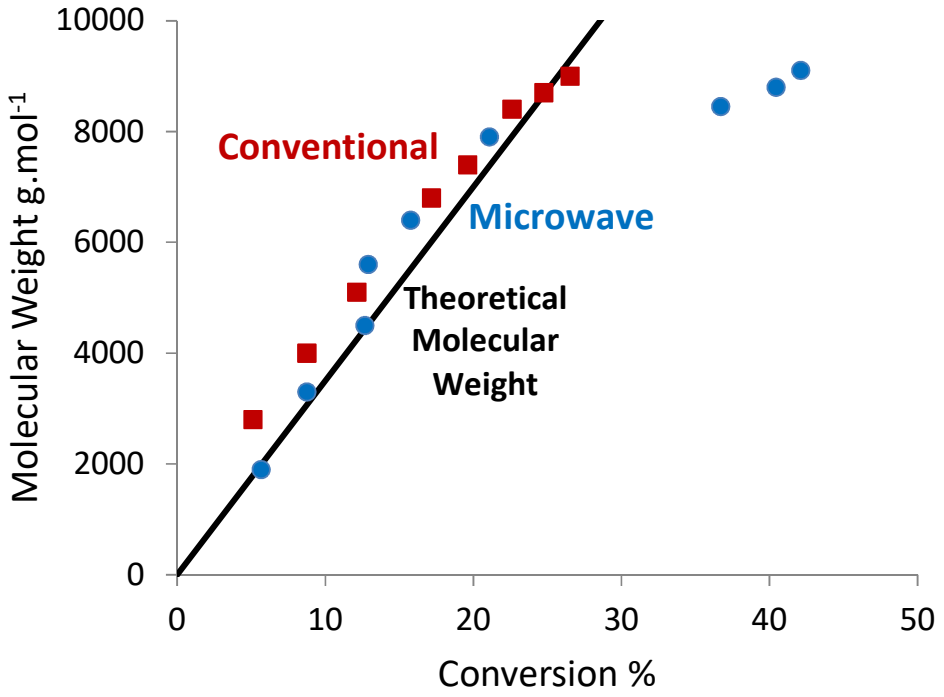


Figure 3.26 – Molecular weight and conversion data for solution RAFT polymerisation using 10 ml toluene with 1:1 ratio of RAFT:V-70

An increase in termination interactions for the microwave heated reactions could potentially result in the non-linear growth of the molecular weight with higher conversion values observed (Figure 3.26). The expected trends based on the previous sets of data (Figure 3.21) was that a ratio of 8:1 for vinyl acetate : toluene should provide the optimum conditions for an induced acceleration using microwave energy (Figure 3.27).

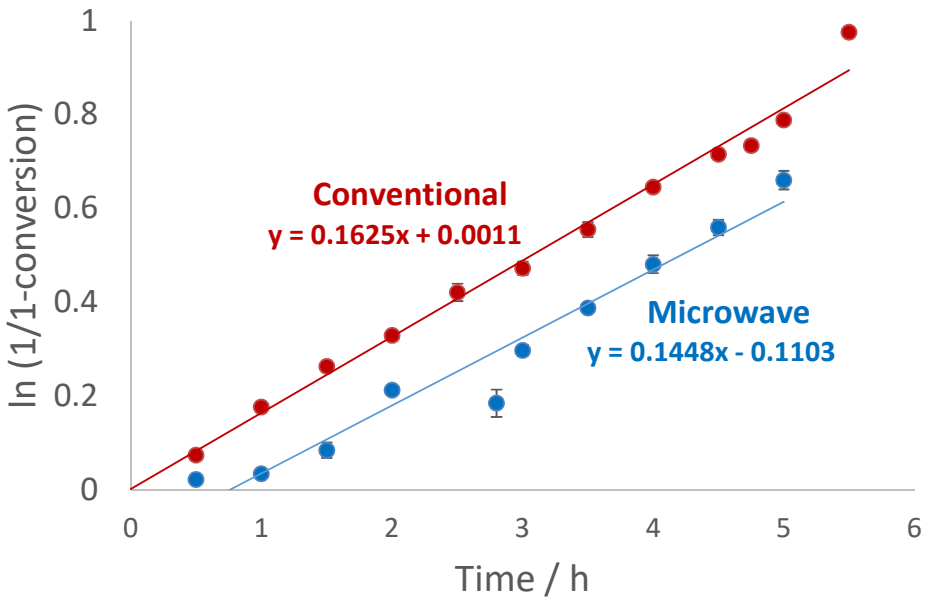


Figure 3.27 - Kinetic data for solution RAFT polymerisation using 2.5 ml toluene with RAFT:V-70 ratio of 1:1 at 45°C. Error Bars are based on the standard deviation from multiple repeat experiments. The trendlines for both sets of data confirmed a linear increase of conversion over time. Error bars that cannot be seen are within the region of the data point

An example of NMR analysis from these experiments is also provided (Appendix 14). The data showed that overall conversion for both heating methods had increased as expected, however lowering the volume of toluene in this case had led to the oil bath reactions reaching noticeably higher conversions with a faster reaction rate. This appeared to contradict the findings from previous experiments, where lowering the solvent volume led to a significant acceleration when using microwaves. The GPC data were examined to see whether the conventional reaction was still able to maintain control of the chain growth (Figure 3.28).

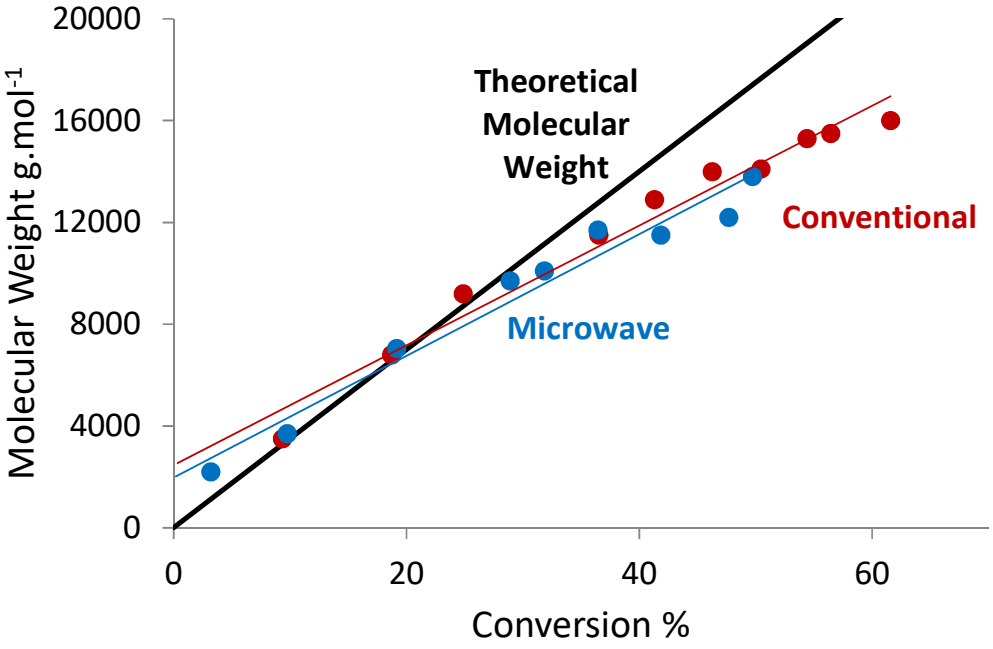


Figure 3.28 – Molecular weight and conversion data for solution RAFT polymerisation using 10 ml toluene with 1:1 ratio of RAFT:V-70. The trendlines for both sets of data confirmed linear growth for the PVAc throughout the reaction

The molecular weight data for both sets of reactions appeared to demonstrate good control provided by the RAFT agent, with a clear linear trend for both heating methods and thus indicating controlled growth of the polymer chains. This was observed up until approximately 30 % conversion, after which both heating methods were found to diverge from the ideal growth trend. This is indicative of an increase in termination and side reactions, which is detailed in Chapter 1 regarding controlled polymerisation kinetics (Section 1.2.3).

This alteration in the kinetic reaction profiles could also be distinguished when comparing the dispersity values.

Tables 3.5 & 3.6 – GPC data for solution RAFT polymerisations with RAFT:V-70 ratio of 2.5:1

Conventional Heating

Conversion % [a]	$M_{n,th}$ g.mol^{-1} [b]	M_n g.mol^{-1} [c]	Đ [c]
0.5	3,100	3,500	1.34
1	6,100	6,800	1.25
1.5	8,000	9,200	1.24
2.5	11,600	11,500	1.28
3	13,100	12,900	1.3
3.5	14,700	14,000	1.32
4	16,000	14,100	1.36
4.5	17,200	15,300	1.34
5	17,900	15,500	1.37
5.5	19,400	16,000	1.39

Microwave Heating

Conversion % [a]	$M_{n,th}$ g.mol^{-1} [b]	M_n g.mol^{-1} [c]	Đ [c]
1	1,200	2,200	1.42
1.5	3,300	3,700	1.36
2	6,200	7,050	1.25
3	9,200	9,700	1.24
3.5	10,200	10,100	1.28
4	11,600	11,700	1.28
4.5	13,300	11,500	1.33
5	15,100	12,200	1.35
5.5	15,800	13,800	1.37

[a]Calculated from NMR analysis

[b]Calculated using Equation 3.3;

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

Tables 3.5 and 3.6 showed high dispersity values at the start, which initially decreased as the reaction progressed, as was seen with the previous reactions using the 2.5:1 ratio for RAFT:V-70. However after 3-4 hours, the dispersity values continuously rise until the reaction had finished.

This suggested that the reactions were no longer being controlled by the RAFT agent, which can be linked to the increased initiator concentration. While this can produce faster polymerisation rates, the increasing number of radicals can also lead to further irreversible termination of the polymer chains.

It has been stated previously that there are different radical types which affect different parts of the polymerisation process. A high radical concentration, combined with a slow fragmentation rate for the RAFT agent, can lead to the initiator radicals self-terminating rather than reacting with a monomer molecule. This would mean that there would be a reduction in propagation and therefore a slow initial polymerisation rate, as was observed for the microwave heated reactions (Figure 3.27). It is possible that exciting the high concentration of $I^{\bullet}$ radicals with microwave energy led to more termination, and therefore the rate of propagation was hindered at the start of the reaction.[84]

Similarly, fewer $R^{\bullet}$ group radicals impede the ability of the RAFT agent to reinitiate polymerisation, meaning a further reduction in the propagation rate. A combination of all these effects from increased radical concentration, including increased irreversible termination, had noticeably negative effects on these controlled polymerisations. This may be why the use of microwaves in this scenario produced a considerably slower rate of reaction compared to the conventional method (Figure 3.27).

These data demonstrated that applying a radical concentration that is too high can result in the selective heating effect being diminished in favour of a bulk heating effect, suggesting that there may be an ideal concentration of a selective species to achieve the desired acceleration. This is similar to the discussion on using microwave absorbent solvents earlier in this chapter, and would explain the striking similarities in the results from the two heating methods.

3.4 **Conclusions**

A significant increase in conversion rate of up to 50% has been observed when using microwave heating for RAFT polymerisation while maintaining the desired control. Studying the dielectric properties has shown that this is attributed to effective selective heating of the RAFT agent and the radicals produced by the V-70 initiator in the reaction. This consequently led to an investigation into the influence of the rate of initiator decomposition and the RAFT:V-70 ratio. Initial reactions confirmed that a high rate of decomposition was required to benefit from the use of microwave heating, which could be enhanced further with a high initiator concentration, thus producing more species which could be selectively heated to induce an acceleration of the polymerisation rate *via* the concept of 'hot radicals'. However, an additional finding was there was a limit to this, where too high a concentration of the initiator eventually replicated a bulk heating effect and ultimately showed no benefit when using microwave energy.

Use of a toluene solvent had proven to be influential on the rate of conversion *via* a dilution effect, but also benefitted the use of microwave heating with lower amounts of toluene to reduce viscosity by inducing an acceleration of the polymerisation rate. Furthermore, it was discovered that good control of the molecular weight growth was still maintained, whereas bulk conditions showed only a minimal difference between the two heating methods, thus confirming that viscosity was an important factor to consider for RAFT polymerisation.

However, this acceleration was observed as a result of using a microwave transparent solvent such as toluene, which facilitated the continued selective heating of particular reactants. A microwave absorbent solvent such as an ionic liquid would have resulted in bulk heating of the

reaction mixture, therefore potentially losing the induced acceleration upon the application of microwave energy.

The reaction profiles of the RAFT reactions suggest that the reaction using microwave heating did not have a single rate, but exhibited multiple reaction zones, particularly for the bulk reactions. Initial reaction rates are very fast, with the low amount of toluene (Figure 3.21) leading to the elimination of the induction period observed in the CH reactions. In bulk reactions a third zone is identified in which little conversion is observed; this is thought to be related to diffusion issues in the very viscous reaction medium. This is an area that will require further study.

3.5 References

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Chapter 4 – Application of supercritical CO_2 for the RAFT polymerisation of Vinyl Acetate

4.1 Aims and Objectives

The previous chapter showed the successful acceleration of the RAFT polymerisation of vinyl acetate (VAc). It was confirmed that the optimal reactive conditions required a 12.5 % ratio of toluene compared to the mass of monomer to reduce viscosity and a 2.5:1 ratio of RAFT : initiator. These parameters gave the largest increase in reaction rate when employing microwaves compared to conventional heating whilst maintaining tight control over molecular weight. However, the use of toluene cannot be considered to be environmentally friendly. Additionally, increasing viscosity at high yield levels proved detrimental to the control over the polymer chain length. The focus of the work described in this chapter was an investigation of the application of CO_2 as a viscosity modifier in the RAFT polymerisation of vinyl acetate in $scCO_2$.

4.2 Introduction

One technique that has become increasingly popular in RAFT polymerisation chemistry is the use of $scCO_2$ as a viscosity modifier. CO_2 presents many advantages over previous strategies, such as offering low toxicity, low cost and a negligible environmental impact. As a supercritical

fluid, its properties can also be "tuned" by altering the pressure and temperature parameters and this allows the reactive envelope to be manipulated.

The combination of CO_2 and microwave heating could potentially provide an acceleration of reaction rate with a high degree of control while maintaining a low viscosity throughout. However, it was necessary to undertake a preparatory investigation into the effect of using CO_2 to observe how altering various conditions affected the RAFT polymerisation of vinyl acetate. This included aspects such as the RAFT : initiator ratio and the molecular weight of the product. In addition, there were specific technical aspects to consider when using a high pressure autoclave reactor, such as the monomer loading, the variation of viscosity with temperature and pressure and the consequences of introducing a metal reaction vessel. Kinetic trials for the CO_2 experimental sequence would allow comparative analysis of reactions using both conventional and microwave heating. These comparisons could then indicate what the requirements might be for an optimised reaction system.

4.2.1 $scCO_2$ and controlled polymerisation

Since the use of CO_2 had been so successful in promoting free radical polymerisations,[1-3] there has naturally been an interest in applying it to controlled processes. When carrying out a standard or a controlled free radical process in CO_2, it is important to recognise where the polymerisation process takes place. The conclusions of various studies have determined that the continuous CO_2 phase is the initial locus of polymerisation.[4, 5] This continues until the polymer reaches its J_{crit} value; the molecular weight at which the polymer forms insoluble particles in CO_2. The particles can then only grow in size *via* precipitation of polymer onto a particles' surface. The locus of polymerisation only changes when a high proportion of the

monomer has been consumed and large polymer particles have been produced, at which point the polymerisation continues within the particles.[5, 6] However, polymerisation does not necessarily continue after precipitation occurs, as it is dependent on numerous factors such as temperature and pressure, both of which influence viscosity and therefore alter the effectiveness of CO_2 in its role as a polymerisation medium.

A detailed investigation of NMP with styrene using N-tert-butyl-N-[1-diethylphosphono (2,2-dimethylpropyl)] nitroxide (SG1) as the controlling agent demonstrated that higher monomer loading levels in the reactor led to significantly faster polymerisation rates.[7] The excess of the SG1 also influenced the final polymer product; lower amounts of SG1 produced high levels of yield but resulted in polymers with higher than expected M_n values and broad dispersities. Finally, the highest yield reached was at 95 % using a monomer loading of 60 % (w/v) and a 30 % excess of SG1 after 48 hours. This yield was considerably higher than the 26 % observed for the standard free radical polymerisation of styrene in CO_2. The presence of SG1 meant that a majority of the chains were in a dormant state as shown in the mechanism for NMP (Chapter 1). This consequently led to fewer polymer chains being in the form of radicals, which slowed the rate of propagation but also lowered the probability of termination occurring, therefore increasing the final yield that could be attained.

ATRP has also been studied using a CuBr complex with various macroligands to polymerise MMA.[8] A comparative study between using CO_2 and benzotrifluoride as a solvent produced polymers with similar molecular weight and dispersity values, but with a much slower polymerisation rate in CO_2, probably as a result of slow complexation of the CuBr in CO_2. Additionally, the initiator efficiency measured was higher when using CO_2, which could be a result of the low viscosity of the reaction medium.

A study for the ATRP of VAc in $scCO_2$ used a CuBr/terpyridine complex and showed that monomer loading appeared to have little effect on the yield reached after 24 hours.[9] This is very different from the NMP of styrene with SG1 using CO_2, where a higher monomer loading led to a noticeable increase in yield as the larger monomer volume increased the solubility of the polymer in the reaction medium. However as the monomer dissolved in the CO_2 phase, rather than the expanded polymer phase, it is possible that the local monomer concentration was depleted.

Increasing the density of the continuous CO_2 phase by using a higher pressure dissolved the initial reactants more effectively. This increased both the propagation rate and the equilibrium constant while decreasing the rate of termination,[10] and this accelerated the rate of polymerisation and produced high molecular weights. An additional effect of the high pressure was a rise in the number of active polymer chains present in the reaction which produced lower dispersities.[11] A higher pressure also increased the J_{crit} value for Poly(vinyl acetate) (PVAc) in CO_2, meaning a longer reaction time was required before precipitation of the polymer occurred. Furthermore, using a higher pressure induced greater plasticisation after the PVAc becomes insoluble in CO_2, enhancing the diffusion of monomer into the polymer phase and allowing polymerisation to continue.

Kinetic studies showed that the polymerisation rate was initially high, but slowed in the latter stages being consequential upon a combination of increased termination rate and poor solubility of the polymer in CO_2. A linear relationship throughout the reaction between molecular weight and yield implied good control from the CuBr complex, but an increasingly large dispersity was observed over time as a result of frequent chain transfer reactions. The indications were that improved control might be provided by using a catalyst with a higher equilibrium constant and deactivation rate to prevent these side reactions occurring.[12] A higher

initiator concentration reduced the M_n value as expected but to a lesser extent compared to the bulk ATRP system, thus providing further evidence of how CO_2 affects initiator efficiency.

An investigation into the RAFT polymerisation of MMA in CO_2 showed that at low yield propagation occurred as expected,[13] but after 24 hours the final yield was still low as a result of polymer precipitation. When aggregation of these precipitated polymer particles was prevented by the introduction of a stabiliser to give a dispersion polymerisation, it became possible to approach 100 % yield. Poor control regarding precipitation polymerisation of PMMA when not using a stabiliser has also been found when using ATRP.[14, 15] The RAFT polymerisation of styrene in CO_2 was compared to that observed when using toluene as the solvent (Figure 4.1).[16, 17]

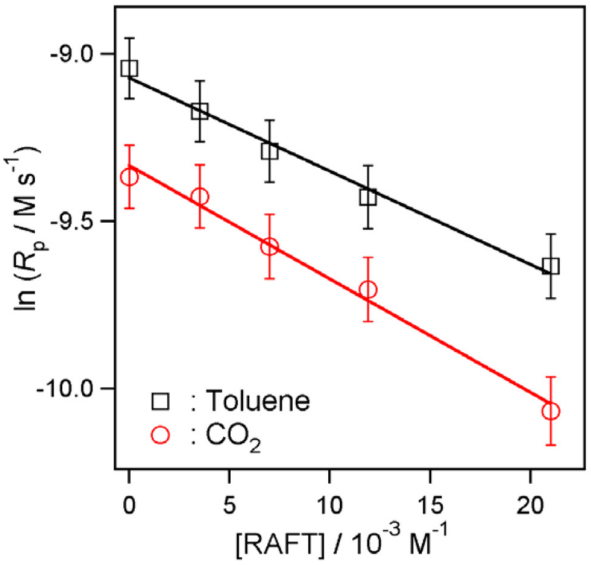


Figure 4.1 – Rates of polymerisation of styrene when using CO_2 and toluene as the solvent[16]

A clear drop in polymerisation rate when using CO_2 was attributed to an enhancement of the rate at which the termination occurred as the poor solvent quality of CO_2 for polystyrene caused the polymer chains to be more tightly coiled, which has been proven to cause an increase in

termination.[18] This is enhanced further by the depleting monomer being continuously replaced by CO_2 over time,[19] and would be expected to produce polymers with broad dispersities from a higher number of so called "dead" polymer chains. Surprisingly, the measured dispersity values when using CO_2 were narrower than with toluene, possibly as a result of increased mobility of the molecules from the low viscosity of CO_2 which allowed more effective mass transfer of monomer to reach the radical species.

A comparative study of the RAFT polymerisation of methyl acrylate in toluene and CO_2 found that the number of chains produced was almost identical for either solvent, confirming that the termination rate was virtually unaffected by the use of CO_2.[17] Termination in Poly(methyl acrylate) occurs by segmental diffusion of the entangled chains, where shielding of the radical chain end provided by side groups can potentially slow the rate of termination. The methyl group in Poly(methyl acrylate) is poor at shielding, resulting in a high probability that termination will occur and therefore the lower viscosity provided by using CO_2 has little effect.

However, as with the RAFT polymerisation of styrene, the presence of CO_2 caused the rate of polymerisation for methyl acrylate to be lower than when using toluene, which results from the propagating radical species forming stabilising complexes with CO_2.[20] These complexes lower the local monomer concentration around the radical centres which slows the rate of propagation.

The RAFT polymerisations of both styrene and methyl acrylate showed that increasing the RAFT agent concentration produced narrower dispersities as well as lower molecular weights in CO_2 compared to toluene. The low viscosity of CO_2 increased the rate of addition for propagating radicals adding to the RAFT agent, confirming that this is a diffusion controlled process. But, as in conventional reaction media, higher RAFT agent concentration also slowed down the rate of polymerisation.

The presence of a stabiliser during RAFT polymerisations in CO_2 has been shown to produce polymers with uniform particle size whilst maintaining the desired control over molecular weight and dispersity.[13, 21] Various copolymers have also been successfully produced in CO_2 using RAFT which will be covered in greater detail later (Chapter 5).

An investigation into the RAFT polymerisation of vinyl acetate in CO_2 used two different PVAc macro-RAFT agents to control the rate of polymerisation.[22] Increasing the concentration of either RAFT agent lowered the molecular weight as there was a higher probability of a polymer radical species being transferred to the RAFT agent, as seen with styrene and butyl acrylate. Increased RAFT agent concentration led to better control over the polymerisation process as was confirmed by the low dispersity values and the linear relationship between molecular weight and yield (Figure 4.2).

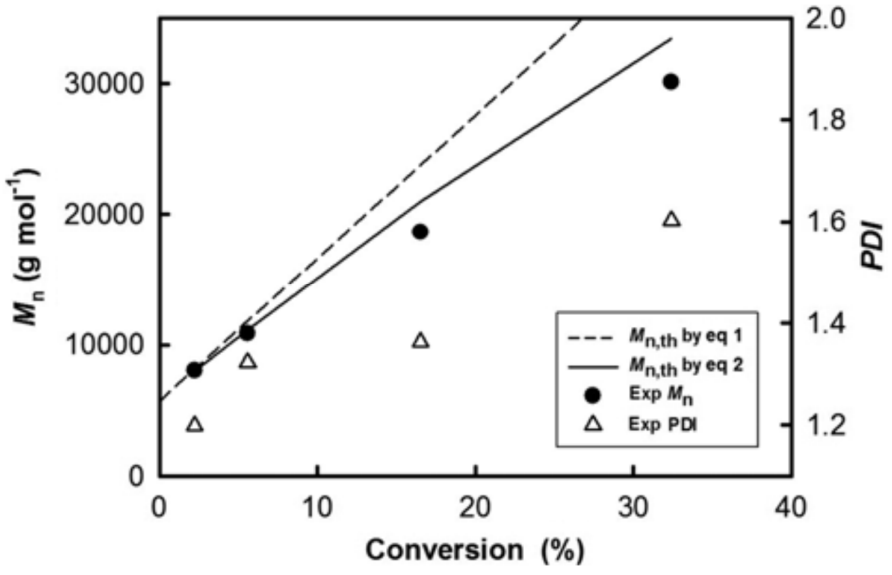


Figure 4.2 – Theoretical and experimental values of molecular weight and yield compared for PVAc macro-RAFT agents[22]

A slight deviation from ideal linear growth (Figure 4.2) was partly caused by polymer chains being formed which derived from the initiator rather than the RAFT agent. The effectiveness of the initiator when using CO_2 also contributes to this divergence from ideal polymer growth which is explained in greater detail later in this chapter. This research also proved that increasing the initiator concentration led to broader dispersity values as yield rose and this was attributed to chain transfer to the monomer and polymer.

4.2.2 Solubility of polymers in CO_2

The quadrupole moment of CO_2 has a significant role with regard to polymer solubility. Although any quadrupole-dipole interaction is only effective over a short distance, any degree of polarity in a molecule can enhance its solubility in CO_2.[23-25] However if this polarity is too high the polymer can become insoluble as dipole-dipole interactions are considerably stronger than quadrupole-dipole interactions, therefore solute-solute interactions between the polymer chains will be stronger than those between the solute and the CO_2 solvent.[26]

Dipole-dipole interactions with a solvent are a key factor in determining solubility, however, the dipole on a CO_2 molecule is virtually non-existent, so any solute-solvent interactions derive from the large quadrupole moment. The strength of these interactions with CO_2 can be altered by changing either the pressure or the temperature, therefore knowing whether a material will be soluble in CO_2 can be difficult.[27] The most effective way of determining the solubility of a particular material in CO_2 is by looking at the polarisability/volume, which is calculated by dividing the molecular polarisability of a particular molecule by the molar volume,[28] and gives an indication of the number and the strength of van der Waals interactions between the solute and CO_2.

There has been an investigation to compare the polarisability of CO_2 to that of various solvents.[29] A graph comparing CO_2 with ethane and fluoroform (Figure 4.3) explores this.

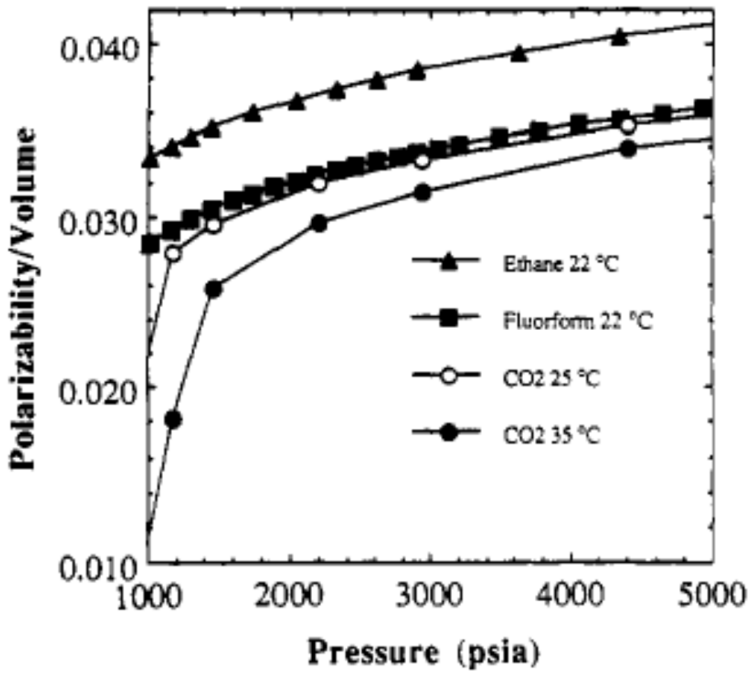


Figure 4.3 - Polarisability/volume for ethane, fluoroform and CO_2 at varying pressures[29]

The graph shows that under appropriate conditions, CO_2 can demonstrate similar behaviour to these solvents with regard to the polarisability/volume. This also emphasises how the pressure and temperature values selected when using CO_2 have a significant influence on solubility.

Kazarian *et al* studied the solubility of various carbonyl containing polymers such as PVAc in CO_2 using FT-IR spectroscopy.[30] The strong electron withdrawing effects of the oxygen in CO_2 caused the molecule to exhibit Lewis acid-base sites, which allow CO_2 to have numerous interactions with a polymer chain. The carbonyl oxygen in a PVAc chain is able to have a Lewis acid-base interaction with the CO_2 (Figure 4.4a), unlike with other similar polymers such

as Poly(methyl acrylate), where the carbonyl group is hard to access.[31] Further work by Raveendran *et al* confirmed the presence of a weaker but still significant interaction of the acetate hydrogen in PVAc with an oxygen atom in CO_2 (Figure 4.4b) which accounts for the higher solubility of PVAc in CO_2 compared to a wide range of other polymers.[32] The surface tension for a polymer in CO_2 also plays a role in its solubility as a lower value means the energy density is closer to that of CO_2, making the polymer more soluble.[31]

There is also evidence from theoretical calculations that the presence of the ester oxygen in PVAc provides another means of interaction with the CO_2 molecules as well as potentially offering a degree of rotation, making the carbonyl group more easily accessible (Figure 4.4c) and further enhancing its solubility.[24]

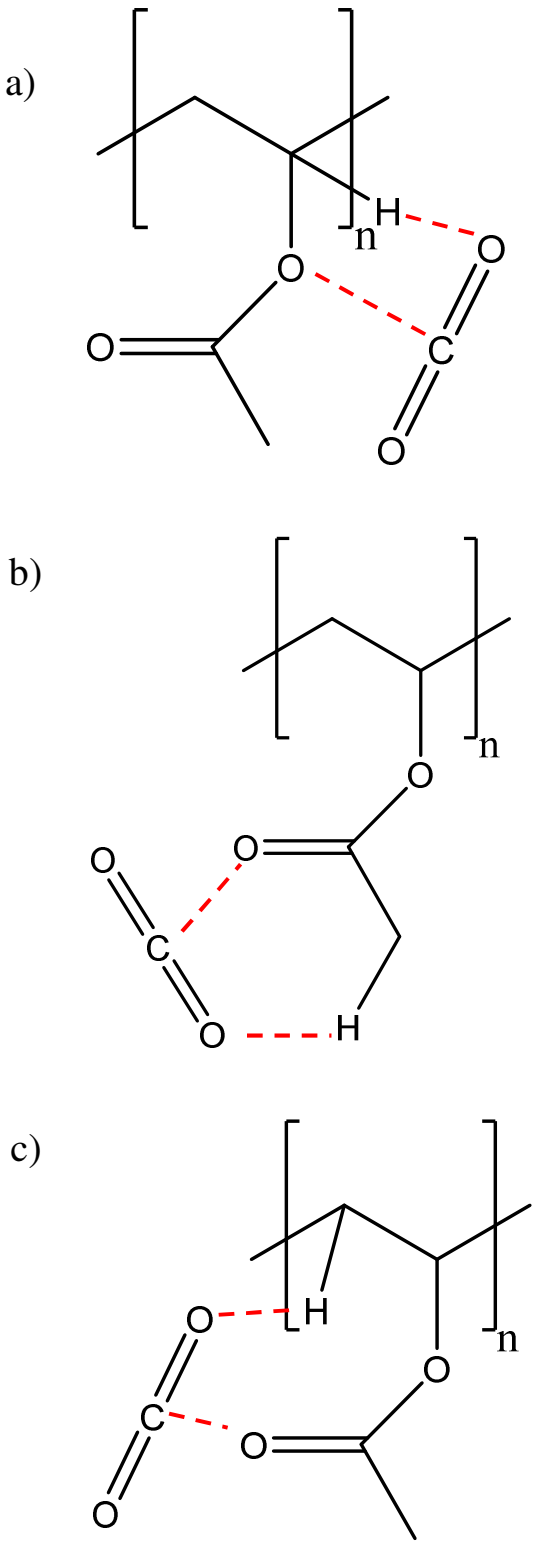


Figure 4.4 - Representation of the possible Lewis acid-base interactions between poly(vinyl acetate) and CO_2

4.3 **Experimental**

Vinyl acetate solubility

Vinyl acetate monomer (70 ml) was added to the fixed volume view cell (100 ml). This was pressurised to 5.5 MPa, at which point the heating cartridges were set to 45 °C based on the temperature used previously during the solution and bulk RAFT polymerisations. Once the temperature had equilibrated, the pressure was increased to 27.6 MPa, which is a high value but still well within the pressure safety limit for the autoclave. This specific pressure level/point was based on multiple studies into the solubility of polymers such as PMMA and Polystyrene, which confirmed that higher pressures enhanced their solubility in CO_2. Once the appropriate images had been taken the vessel was allowed to cool to ambient temperature, at which point the view cell was depressurised to remove the remaining CO_2.

Poly (vinyl acetate) solubility

A 1 g sample of PVAc (M_n ~ 20,000 $g.mol^{-1}$) was placed in a small glass vial within the view cell The pressure was increased to 800 psi, at which point the heating cartridges were set to 45 °C. Once the temperature had equilibrated, the pressure was slowly increased up to 27.6 MPa. Once images had been taken, the vessel was allowed to cool to ambient temperature, after which the view cell was depressurised to remove the remaining CO_2.

Example RAFT Polymerisation

A mixture of vinyl acetate (15 ml, 0.1627 moles), xanthate RAFT (89 mg, 4.002×10^{-4} moles) and AIBN (32.9 mg, 2.001×10^{-4} moles) was subjected to three freeze pump thaw cycles in a Schlenk tube, then purged with argon. The autoclave reactor was purged with a flow of CO_2 at 30 psi for at least 25 minutes to remove oxygen, which would inhibit the polymerisation. A 20 ml glass syringe and needle were degassed with argon 3 times, before being used to transfer the reaction mixture from the Schlenk tube and inject it into the autoclave, which was then sealed. At this point the stirring was set to 300 rpm and the pressure increased to ~4.8 MPa. The internal temperature for the autoclave was then set to 65 °C, at which point the reaction was deemed to have started. Once the autoclave temperature had equilibrated, the pressure was increased to 13.8 MPa.

After the reaction time had elapsed, the heating jacket was removed. The formation of polymeric foams was a potential safety concern during depressurisation, therefore the autoclave was placed in a mixture of dry ice and acetone to cool down to temperatures around -40 °C. This reduced the pressure in order to lower the solubility of the polymer and allowed the safe removal of the safety needle, which meant the autoclave could warm up to room temperature whilst reducing the risk of blocking the outlet pipe. Once ambient conditions were reached, the PVAc could then be safely removed.

Polymer Yield

In the previous chapter, yield was measured with NMR by comparing polymer and monomer peaks. However, this is not possible with reactions performed in CO_2 as unreacted monomer can be lost when the autoclave is depressurised. Therefore yields for the polymers obtained

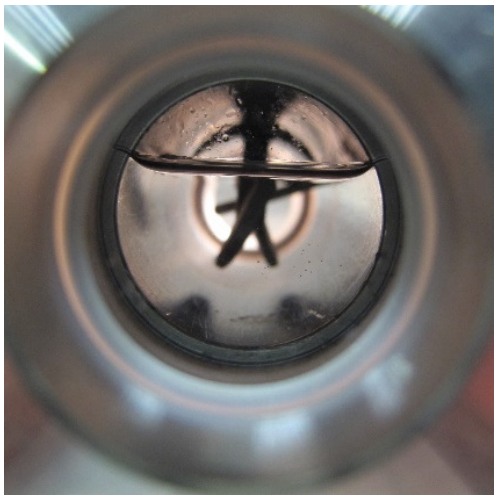
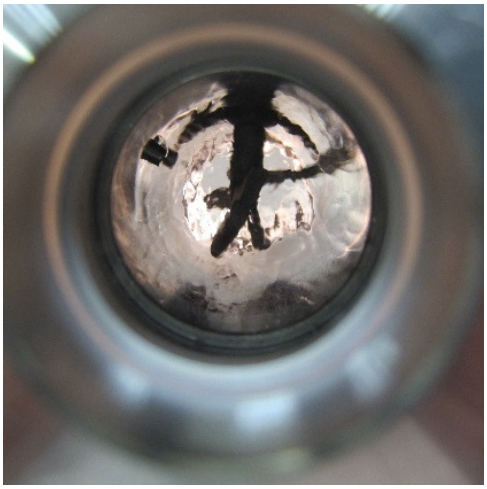
were determined gravimetrically. To ensure accuracy the polymers were dissolved into DCM and then precipitated into hexane with a 1:20 volume ratio. This material was dissolved and precipitated again to ensure the removal of any residual monomer. The polymer product was then left to dry in the room temperature vacuum oven overnight before being weighed.

4.4 **Solubility studies**

4.4.1 Vinyl acetate

Initial experiments investigated the solubility of the vinyl acetate monomer in CO_2 which would help determine the conditions used for the CO_2 experiments. Vinyl acetate monomer (70 ml) was added to simulate the autoclave reaction condition, using a high monomer loading in the view cell (100 ml). The pressure was set close to the upper limit allowed for CO_2 experiments at 27.6 MPa, with a temperature of 45 °C to be used with the V-70 initiator.

It is known that increasing pressure results in increased solubility, but if the reactions could be performed at a lower pressure, it would make the polymerisation a more ecologically secure and more sustainable process, as the energy required to reach and maintain 13.8 MPa is considerably lower than for 27.6 MPa.[9]

a)   b)

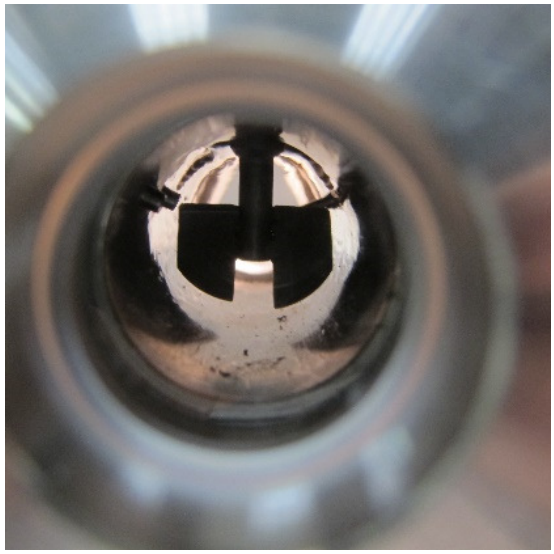
c) 

Figure 4.5 – View cell images showing the vinyl acetate monomer with a) ambient conditions b) 5.5 MPa, room temperature c) 38 °C, 12.4 MPa

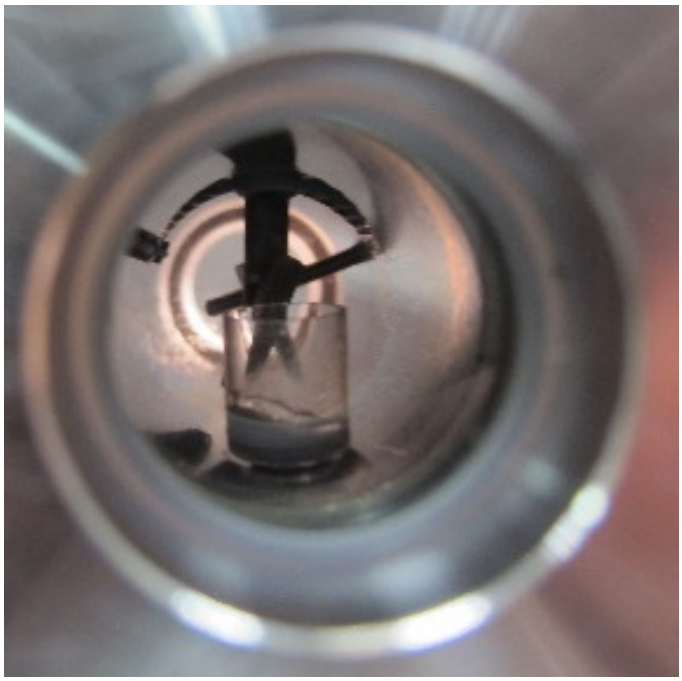
The vinyl acetate monomer is shown in its liquid form at room temperature and pressure (Figure 4.5a). As the view cell was pressurised (Figure 4.5b), the vinyl acetate was expanded by the CO_2 to fill the entire view cell and proved to be miscible with CO_2 even at lower pressures. Once the view cell reached 5.5 MPa the temperature was increased, during which it was observed at 38 °C (Figure 4.5c) that the monomer had become fully soluble, as there was no phase separation between the monomer and CO_2.

When the view cell reached the set temperature at 45 °C the pressure was registered at 13.8 MPa. This was increased to 27.6 MPa to observe the influence of applying high pressure, but no visible change could be observed within the view cell. The high solubility for the vinyl acetate monomer was expected, as it is well known that small molecules such as aliphatic hydrocarbons are highly soluble in CO_2.[33, 34]

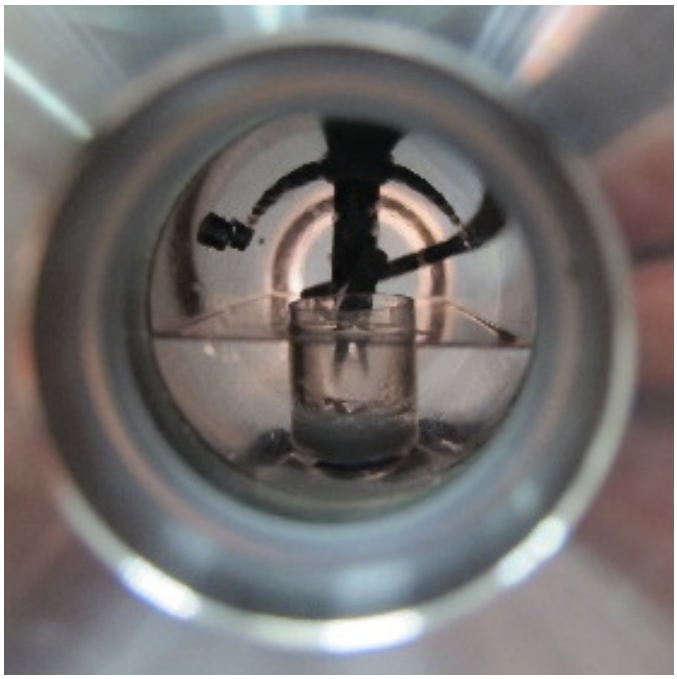
4.4.2 Poly (vinyl acetate)

Numerous factors including backbone flexibility and end group functionality determine whether a polymer will be soluble or insoluble in CO_2. [23, 35] Applying high pressure CO_2 to multiple polymers induces plasticisation. Lowering of the glass transition temperature (T_g) causes a reduction in viscosity, re\sulting from increased molecular mobility and large distances between the polymer chains.[36] These effects are caused by Lewis acid-base interactions between CO_2 and functional groups in the chains (Figure 4.4), which liquefy the polymer and thus replicate the process of heating.[37] This enhanced mobility allows polymerisation to continue even at high yield levels. An appreciation of the changing conditions required for plasticisation of the chosen polymer, in this case PVAc, and the effect of this behaviour provides vital information required prior to starting the reaction.

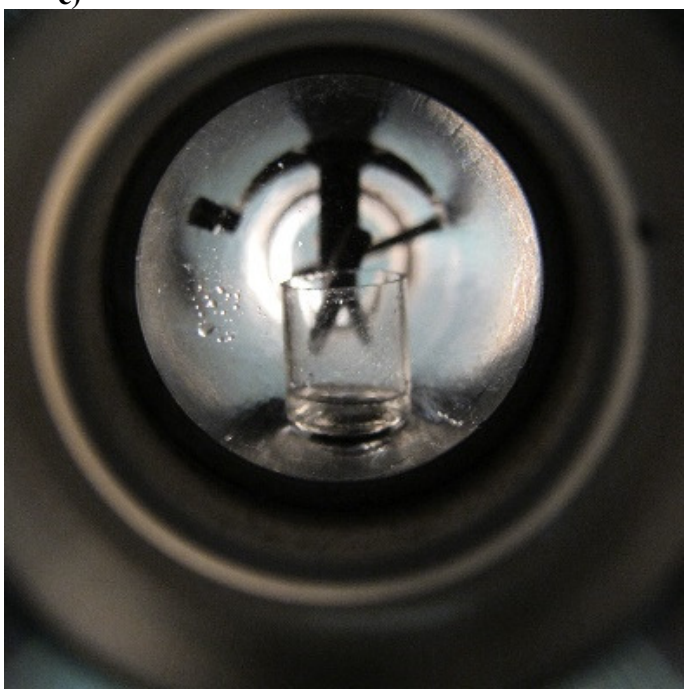
a)



b)



c)



d)



Figure 4.6 – View cell images of PVAc at a) 4.8 MPa, room temperature, b) 45 °C, 5.5, c) 45 °C, 13.8 MPa and d) after venting

The PVAc sample was a polymeric powder, and neither the application of a low pressure of CO_2 (Figure 4.6a) or increasing the temperature to 45 °C at 5.5 MPa (Figure 4.6b) produced an obvious physical change. It was only when the pressure in the view cell was increased to 13.8 MPa that a significant change in the PVAc sample was observed (Figure 4.6c).

Increasing the pressure leads to a higher concentration of CO_2 dissolving in the PVAc, thus increasing the number of CO_2-polymer interactions. When the pressure of a system is sufficiently high, these interactions have a similar order of magnitude to those between the polymer chains.[38] Additionally CO_2 can easily diffuse between the polymer segments owing to its small molecular size, increasing both the distance between the polymer chains and the free volume fraction.[39] These factors, combined with a higher polymer chain mobility, led to the plasticisation of PVAc (Figure 4.6c). An increase in pressure to 27.6 MPa had no further visible effect on the polymer sample (Figure 4.6d). Both solubility studies indicated that the RAFT polymerisation experiments at 45 °C could be performed at 13.8 MPa, thus making it a safer and less energy intensive process. This is advantageous compared to other CO_2 reactions such as dispersion polymerisations using PDMS (Poly dimethylsiloxane), which is conducted under high pressure to prevent coagulation of the polymer.[40]

Finally, when depressurising the view cell, the PVAc sample was observed to demonstrate a significant degree of foaming once the CO_2 had been removed from the view cell (Figure 4.6d). This was caused by pores continually nucleating within the PVAc sample during depressurisation, which can grow in size *via* two mechanisms; diffusion of CO_2 from the polymer into the pores and boiling of liquid CO_2 dissolved in the polymer at reduced pressure which causes expansion.[41-43] Additionally, the low T_g of PVAc (~30 °C) further enhances the increase in pore size and leads to significant foaming of the sample in the view cell.

The forming of foams while depressurising the reaction system resulted in the introduction of a safety protocol whereby, when a polymerisation was finished, the autoclave was cooled to very low temperatures (around -40 °C) using a mixture of dry ice and acetone, which lowered the pressure significantly so the remaining CO_2 could be safely removed, in order for the autoclave to be opened to obtain the final polymer product. This lower temperature also solidifies the PVAc in the autoclave to prevent the polymer flowing into the pipes when the CO_2 is vented.

An additional consideration for producing PVAc in CO_2 is how the polymer chain end group can influence solubility.[35, 44] In an ideal RAFT polymerisation for vinyl acetate, a vast majority of the chains would be in a dormant state, and are therefore capped by the xanthate RAFT end group. This could potentially interfere with the CO_2-polymer interactions, and reduce the capability of the CO_2 to plasticise the PVAc. However, an investigation by Lee *et al* showed that the presence of a RAFT group should only have a minor effect on reducing solubility.[3] It is actually possible to enhance solubility by having CO_2-philic groups present in the RAFT agent.[45]

4.5 V-70 and VAc in CO_2

Research into the solution RAFT polymerisation of vinyl acetate in Chapter 3 had determined that the application of V-70 at 45 °C accelerated the polymerisation rate when using microwave heating. This happened as a consequence of rapid radical production in the initial stages of the reaction enhancing selective heating. A pressure of 13.8 MPa was applied as the solubility

experiments (Section 4.4.2) had proven that PVAc would be plasticised under these conditions, increasing molecular mobility so that polymerisation could continue as the concentration of polymer increased. These initial reactions were carried out for 24 hours to achieve a high level of yield, but multiple experiments yielded virtually no polymer. Previous investigations using V-70 for RAFT polymerisations in CO_2 had successfully produced a high polymer yield. However, these experiments frequently used lower temperatures and / or higher pressure, implying that slower production of radicals or increased molecular mobility may be essential to ensure a high yield level.

Furthermore, a previous study carried out by Canelas *et al* investigated the application of low temperature initiators for dispersion polymerisations of vinyl acetate at room temperature.[46] This determined that a number of initiators, including V-70, produced very low levels of yield. When using CO_2 as a polymerisation medium there are more variables to consider compared to traditional solvents. For example, pressure and temperature changes alter the density which affects the polarisability/volume (Figure 4.3). The tuneable properties of CO_2 can also affect the polymerisation in a number of ways such as altering the rates of propagation and termination, as well as influencing the initiator efficiency which is covered in greater detail later in this chapter.[19, 47]

4.6 **AIBN and CO_2**

The lack of polymer obtained with V-70 necessitated the selection of an alternative radical source. AIBN had been successfully used as an initiator in the bulk RAFT polymerisations of vinyl acetate (Chapter 3), as well as being successfully employed in RAFT reactions of VAc in $scCO_2$.[22] An additional consideration from the reaction with V-70 was that the rapid radical

production induced a number of side reactions such as self-termination. The reaction temperature was set to 65 °C, therefore ensuring a slow introduction of the initiator radical species over a longer period of time to allow continuous polymer production. Subsequent experiments detailed in this chapter proved that AIBN was able to successfully polymerise vinyl acetate in CO_2.

4.7 **RAFT : Initiator Ratio**

During the solution RAFT experiments (Chapter 3) an important factor was the RAFT : initiator ratio, where a high initiator concentration was required to induce an acceleration of the polymerisation rate while maintaining the desired control. These first experiments were designed to study the effect of altering the RAFT : AIBN ratio for the final yield obtained in CO_2, as well as monitoring the degree of control over molecular weight and dispersity values.

Table 4.1 - Comparing different RAFT : Initiator ratios. All reactions used 10 ml VAc, targeting 10,000 g.mol^{-1} in CO_2 at 13.8 MPa and 65 °C for 24 hours

Entry	RAFT:Initiator	Gravimetric Yield / %[a]	$M_{n,\,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
1	2:1	63	6,500	27,200	1.27
2	2:1	61	6,300	19,100	1.43
3	2:1	57	5,900	17,400	1.46
4	5:1	48	5,000	16,300	1.18
5	5:1	58	6,000	16,500	1.24
6	5:1	49	5,100	14,000	1.18

[a]Calculated after precipitation into excess hexane;

[b]Calculated using equation

$$\textbf{Equation 4.3;} \qquad M_{n,\,theo} = \frac{[M]_0 - [M]_t}{[RAFT]_0} \times m_M + m_{RAFT}$$

Where $[M]_0$ = initial monomer concentration, $[M]_t$ = monomer concentration at time t, $[RAFT]_0$ = initial RAFT agent concentration, m_M = molecular weight of monomer and m_{RAFT} = molecular weight of RAFT agent

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

An example of GPC analysis from these experiments is also provided (Appendix 15). The first set of experiments (Table 4.1, Entries 1-3) used a higher concentration of initiator in a 2:1 ratio of RAFT : AIBN, ensuring a high number of radicals were present, hence increasing the probability of propagation occurring and thus leading to an increase in polymerisation rate and higher final yields.[48, 49]

However, further analysis showed that the application of these conditions also produced broad dispersity values. A high initiator concentration produces more polymer radicals, but also increases the number of other radical species, such as from the initiator (I$^{\bullet}$) and from the RAFT agent leaving group (R$^{\bullet}$). Therefore there is an increased probability of forming initiator-RAFT derived species, meaning fewer RAFT molecules are available to control the synthesis of the polymer chains. Additionally a large number of polymer radicals also increases the number of radical-radical interactions, causing irreversible termination and lowering the degree of control of polymer chain growth, which is confirmed by the broad dispersities. Furthermore an excess of radicals increases the rate of side reactions, such as chain transfer to both the monomer and the polymer.[22, 50]

The lower initiator concentration for the RAFT:AIBN ratio of 5:1 was observed to produce lower yields (Table 4.1, Entries 4-6). This is as a result of the higher concentration of RAFT agent producing a larger proportion of polymer chains with RAFT end group functionality, which therefore lowers the rate of propagation. However, the increase in the deactivation rate provides a higher degree of control over the growth of the polymer chains, which is confirmed by the lower dispersity values.).

One observation from all the reactions (Table 4.1) was that the M_n values measured by GPC were noticeably higher than the $M_{n,th}$ calculated using Equation 4.1, where the measured gravimetric yield was used as the $[M]_0 - [M]_t$ term. A potential factor that could contribute to

this lack of control is the influence of CO_2 on the rate of decomposition of AIBN.[51] When forming a polymer using a solvent, the radicals formed by decomposition of the AIBN molecule pass through a polar transition state. This can be stabilised by dipole-dipole interactions with the solvent, which lowers the energy barrier for initiator decomposition. However, CO_2 has a very low dielectric constant resulting in poor dielectric strength, therefore the decomposition rate of AIBN measured in CO_2 is significantly lower than that of other solvents.[52] Slow radical production results in fewer AIBN initiated polymer chains, which has been proven by previous research to result in higher than expected M_n values in RAFT polymerisations.[49]

The presence of CO_2 also has a noticeable effect on the initiator efficiency. When radicals are formed they are described as being in a "solvent cage",[53] which radicals can then either react within to form adducts, or diffuse out of to initiate the polymerisation process. The larger the percentage of initiator radicals which can begin the formation of a polymer chain, the higher the efficiency. In CO_2 the efficiency for an AIBN radical reacting with a monomer molecule has been measured to be as high as 80%, whereas in benzene the efficiency can be as low as 53%.[47] The low viscosity when applying CO_2 allows radicals to diffuse apart rapidly rather than remain in close proximity where they can undergo recombination.[51, 52] A high initiator efficiency results in an increased number of radical species, derived from both the initiator and polymer chains, which increases the probability of termination and lowers the molecular weight.[54]

These CO_2 experiments were undertaken with the objective of potentially combining CO_2 and microwave heating in future polymer syntheses. Previous research in Chapter 3 determined that a high initiator concentration was required to induce an acceleration of the polymerisation rate when using microwave heating as a solution for RAFT reactions. This produced narrow

dispersities and high yields (Table 4.1) in CO_2, thus the higher ratio of 2:1 for the RAFT : AIBN ratio was applied for the subsequent reactions.

4.8 **Monomer loading**

One of the major issues with the initial experiments in CO_2 was the significant difference between the theoretical molecular weight values expected based on the ratio of monomer : RAFT agent used and the actual M_n values measured using GPC (Table 4.1). A possible cause for this discrepancy is the solubility of the PVAc in CO_2 which is determined by the J_{crit} value; the molecular weight at which the polymer becomes insoluble and precipitates out, resulting in the formation of discrete continuous and polymer phases.[55] The partitioning of separate phases in CO_2 has been proven to reduce the control over molecular weight growth for controlled polymerisations.[55] Monomer volume has a significant effect on the J_{crit} value, and subsequently influences the time in which the reaction is in a single homogeneous phase. Several experiments were designed using an increased initial volume of the vinyl acetate monomer to determine the influence on the final yield and molecular weight (Table 4.2).

Table 4.2 - Results varying monomer loading. All reactions used RAFT : Initiator = 2:1, targeting 10,000 g.mol^{-1} in CO_2 at 13.8 MPa and 65 °C and 24 hours.

Entry	Monomer / ml	Gravimetric Yield / % [a]	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
1	10	63	6,500	27,200	1.27
2	10	61	6,300	19,100	1.43
3	10	57	5,900	17,400	1.46
4	15	70	7,200	9,700	2.13
5	15	81	8,300	12,700	1.95

[a]Calculated after precipitation into excess hexane;

[b]Calculated using Equation 4.1

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards

The results showed that applying a larger monomer volume (Table 4.2, Entries 4 & 5) produced gravimetric yields that were 10-20% higher than those using the lower vinyl acetate concentration (Table 4.2, Entries 1-3). This was attributed to the higher monomer loading in the autoclave, raising the J_{crit} value and therefore increasing the polymer solubility in CO_2.[56] A more soluble polymer results in the reaction mixture being in a single phase for a longer duration of the reaction time, therefore there are fewer issues caused by radical partitioning upon the formation of the heterogeneous polymer phase, which slows the rates of initiation and propagation.[13] This decrease in the polymerisation rate induced by the phase separation would

be expected to produce a lower gravimetric yield when using a lower monomer volume, as was observed in the final results (Table 4.2, Entries 1-3). Additionally, an increase in the rate of deactivation can be induced with a decreased monomer loading, therefore further slowing the production of the polymer.[56] However, this increased deactivation of the polymer chains also contributes to the narrow dispersities that were measured.

Analysis of the molecular weight values further demonstrates the influence of the initial monomer concentration. The M_n values measured when applying the higher monomer loading (Table 4.2, Entries 4 & 5) were considerably closer to the $M_{n,theo}$ calculated using the yield in Equation 4.1 compared to the lower monomer volume (Table 4.2, Entries 1-3). Shorter polymerisation times are required to reach a low J_{crit} value, which results in a proportion of AIBN being unable to decompose,[57] leading to higher than expected M_n values (Table 4.2, Entries 1-3).

The increased final yields when using the higher monomer loading (Table 4.2, Entries 4 & 5) implied a low rate of deactivation, therefore the equilibrium favoured the formation of the polymer radical species, thus allowing more monomer units to add to the radical chains and therefore increasing the rate of propagation. A RAFT polymerisation regulates molecular weight growth through an equilibrium between the active radical and dormant polymer species. This lowered deactivation rate also results in poorer control over molecular weight, producing broad dispersity values, however a noticeable similarity between the theoretical and experimental M_n values when using the higher monomer loading (Table 4.2, Entries 4 & 5) implied that the RAFT agent was able to regulate the growth of the polymer to a certain extent. A complete lack of control would have led to a free radical process, which would have produced significantly higher molecular weight values.

This difference in the monomer volume used is further enhanced by partitioning of the controlling RAFT agent. The majority of polymer chains in an ideal RAFT polymerisation are in a dormant state, in order to control the molecular weight. However, it is possible that the RAFT agent is not able to effectively control the molecular weight in the separate polymer phase once J_{crit} has been reached. The use of a lower monomer volume means the J_{crit} value is reached faster[56] and there is less control over the polymerisation for a longer time period.[7, 55] This partitioning implies that the equilibrium for the formation of these dormant polymer chains with RAFT end functionality is a diffusion controlled process.[56]

An additional observation determined that the ratio of RAFT : initiator had a significant influence on the polymerisation process when using a lower monomer loading. Earlier experiments (Table 4.1, Entries 1-3) showed that the 2:1 ratio of RAFT : initiator with vinyl acetate (10 ml) led to an increase in yield over that obtained from the 5:1 ratio (Table 4.1, Entries 4-6), but at the cost of having poorer control as proven by the higher than predicted M_n values.[7] When using the 2:1 ratio with the higher monomer loading (Table 4.2, Entries 4 & 5), the molecular weights measured from GPC were observed to be similar to the predicted M_n values.

The difference in the physical appearance between the products created by the two variations in monomer loading was also noticeable. The use of a lower monomer concentration produced a polymer with a slight adhesive quality, as there was a considerable amount of unreacted monomer remaining. Conversely a coarse, dry polymer powder was obtained when using a higher monomer loading, which confirmed a significant reduction in the monomer impurity.

An interesting observation for certain reactions was seen through the effect of foaming. As was observed in the solubility experiments, PVAc is liquefied when in CO_2 meaning that if the outlet tap for the autoclave was opened while the PVAc was still plasticised, some

polymeric material would be lost, which would lower the final yield that was recorded. There is also the potential hazard of blocking the outlet pipe. Therefore the temperature of the autoclave had to be reduced to around -40 °C, then carefully vented to ambient pressure, at which point the key was removed to allow the trapped CO_2 to escape while the autoclave reached room temperature. However, during this time there were occasions when the polymer would begin to foam and would quickly fill the internal volume of the autoclave. As the foaming continued, the polymer would then escape via the key-hole (Figure 4.7).

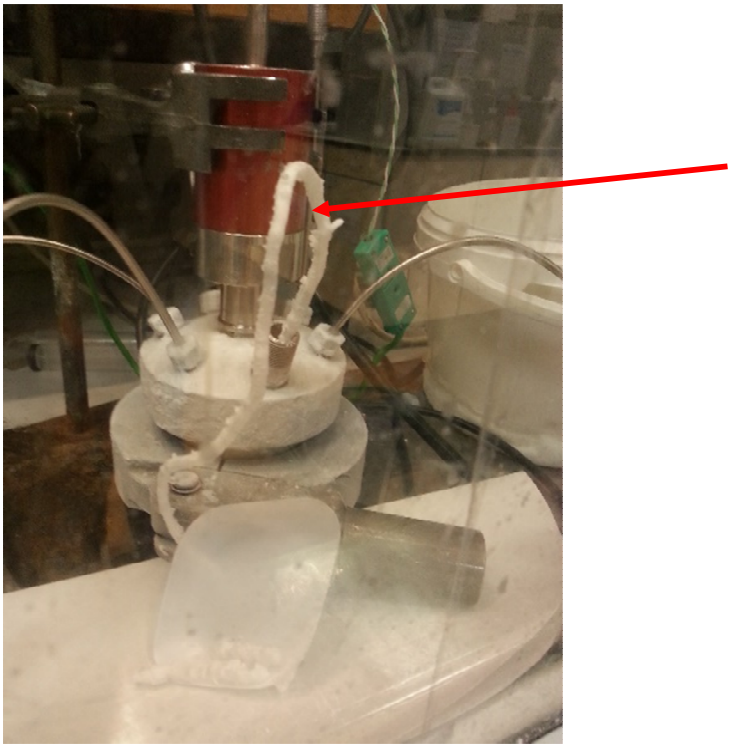


Figure 4.7 – Picture of the autoclave reactor, with an arrow indicating the foaming PVAc coming out once the key had been safely removed

The reactions using 10 ml of vinyl acetate showed a higher degree of control, as confirmed by the narrow dispersity values measured. However the higher monomer loading at 15 ml provided a noticeable increase in the gravimetric yield, as well as lowering the level of

monomer impurity in the final product (Table 4.2). The increase in yield can be related to the equation regarding RAFT polymerisation kinetics in Chapter 1.

Equation 4.2 = $\frac{-d\,[M]}{dt}$ **= k_p [P*] [M]**

Where [M] = monomer concentration, t = time, k_p = propagation rate constant, [P*] = polymer radical concentration

A higher monomer concentration increases the rate of monomer consumption which consequently produces higher yields, as observed when varying the monomer loading for the RAFT polymerisations of vinyl acetate in CO_2 (Table 4.2).

4.9 Molecular Weight

Another consideration for RAFT polymerisations in CO_2 is to determine what would be the effect of altering the target molecular weight, and how that would influence the final polymer produced, the results of which have been summarised (Table 4.3).

Table 4.3 – Varying target molecular weights by altering the ratio of monomer:RAFT agent with the following conditions - 15 ml VAc, 2:1 RAFT:AIBN at 65 °C in CO_2 for 24 hours

Entry	Gravimetric Yield % [a]	Target M_n	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
1	70	10, 000	7,200	9,700	2.13
2	81	10, 000	8,300	12,700	1.95
3	68	20, 000	13,300	29,600	1.96
4	54	20, 000	10,500	22,900	2.10
5	75	30, 000	22,700	43,700	2.07
6	79	30, 000	23,700	44,600	2.04

[a]Calculated after precipitation into excess hexane;

[b]Calculated using Equation 4.1;

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards

A majority of the reactions (Table 4.3) produced high final gravimetric yields, implying that the polymerisation rate was unaltered by changing the ratios of monomer to initiator or monomer to RAFT. This is to be expected, as the RAFT : initiator ratio controls the

concentration of propagating species, which is unchanged for this set of experiments.[54] The concentration does change relative to the monomer volume depending on the target molecular weight, but this was proven to have a negligible effect on the final yield. Each reaction also produced broad dispersity values for the final polymer, implying a low rate of deactivation compared to the propagation rate. This can be observed in examples of the GPC analysis (Appendix 16 and 17). As described previously (Section 4.8), this produces high yields as result of a high rate of propagation, but there is also a reduction in control over molecular weight growth.

The major disparity when varying the concentration of the xanthate RAFT agent was the correlation between the M_n and $M_{n,th}$ values. When targeting 10k (Table 4.3, Entries 1 & 2) the experimental M_n values were close to those calculated using the gravimetric yield in Equation 4.1 ($M_{n,th}$), implying a level of control over the polymerisation process, even with the broad dispersity values. However when the target molecular weight was increased (Table 4.3, Entries 3-6), there was a significant difference between the experimental and theoretical molecular weights, confirming that chain length affects the degree of control over the polymerisation process in CO_2.

The chain length of a polymer in CO_2 is a vital consideration with regard to solubility.[58] Small chains require a minimal amount of energy to maintain a linear formation, but as the molecular weight rises there is an increase in the number of polymer-polymer interactions, which cause the chain to coil round to adopt a more favourable entropic configuration.[59] These complex forms are often stronger than the interactions between the polymer and CO_2, which are further hindered by the forming of polymer 'coils' (Figure 4.8).[35]

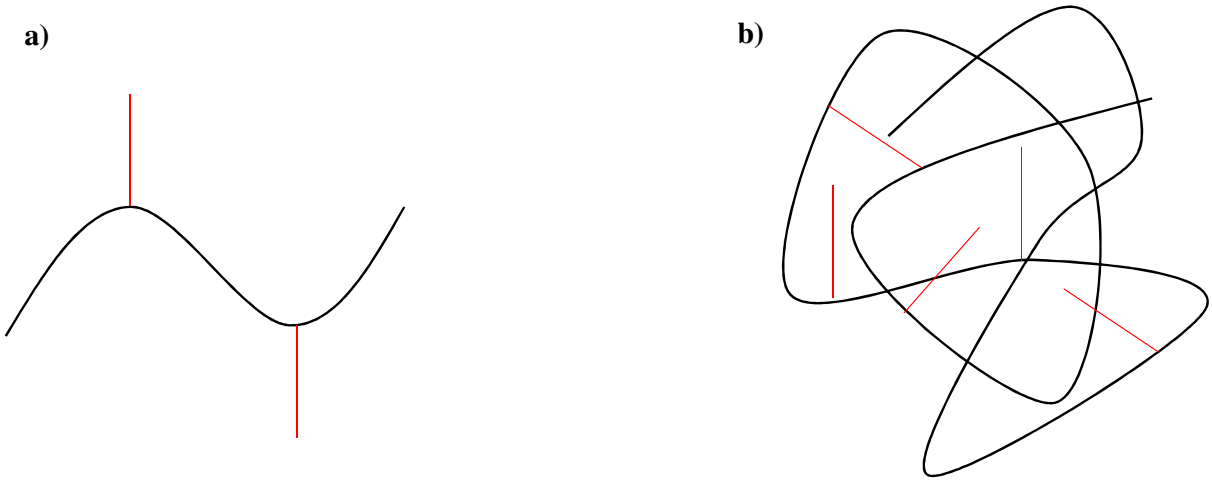


Figure 4.8 – A representation of polymer chains (black) and polar acetate groups (red). a) shows a short polymer chain with accessible acetate groups. b) demonstrates a longer polymer chain where the acetate groups are much more difficult to access.

These increasingly complex arrangements of the polymer chains limit the number of interactions between the acetate groups and the CO_2 owing to the presence of a larger number of non-polar linking segments of the macromolecule (Figure 4.8).[60] An increase in the intermolecular forces between the polymer chains also reduces the flexibility of the polymer backbone, causing a further lowering in solubility.[44]

PVAc is regarded as highly CO_2-philic compared to many polymers, as the various interactions between the CO_2 and the polar groups (Figure 4.4) result in the chains remaining soluble at higher molecular weights.[31] However the solubility of PVAc in CO_2 is still much lower compared to fluorinated and silicone based polymers, and once the molecular weight reaches the J_{crit} value, the solubility of PVAc drops dramatically.[44, 61] This phase separation can lead to complications such as radical partitioning, as was observed for the experiments investigating the influence of monomer loading (Table 4.2).

Another potential cause for the deviation in M_n and $M_{n,th}$ values when targeting higher molecular weights is related to viscosity. As polymer chain length increases, the viscosity of

the reaction mixture rises, therefore polymerisation processes such as propagation and termination become controlled by diffusion.[62] As termination has a low activation energy, it is influenced at lower viscosities compared to initiation and propagation. A rise in viscosity also limits polymer chain movement, reducing the number of radical-radical interactions required for termination.[63] In bulk or highly concentrated solution radical polymerisations, it is possible that a continuous rise in viscosity can reduce effective heat transfer, leading to a build-up of radicals in the system and rapid growth in molecular weight, known as the Trommsdorff-Norrish effect. The presence of CO_2 means viscosity should be lowered, however it is possible that a slight reduction in molecular mobility when targeting higher molecular weights could result in a lower degree of control over polymer chain length.

4.10 **Kinetics for RAFT polymerisation of vinyl acetate in CO_2**

4.10.1 A comparison of RAFT polymerisations of vinyl acetate in CO_2 targeting 10k and 35k

One of the most important criteria for a controlled polymerisation is maintaining a linear relationship between molecular weight and yield percentage throughout the duration of the reaction. In order to determine whether such a correlation might be established for the RAFT polymerisations in CO_2, a series of experiments was designed to obtain kinetic data over 24 hours.

The first kinetic study for the yield over time targeted 10,000 $g.mol^{-1}$ (Figure 4.9).

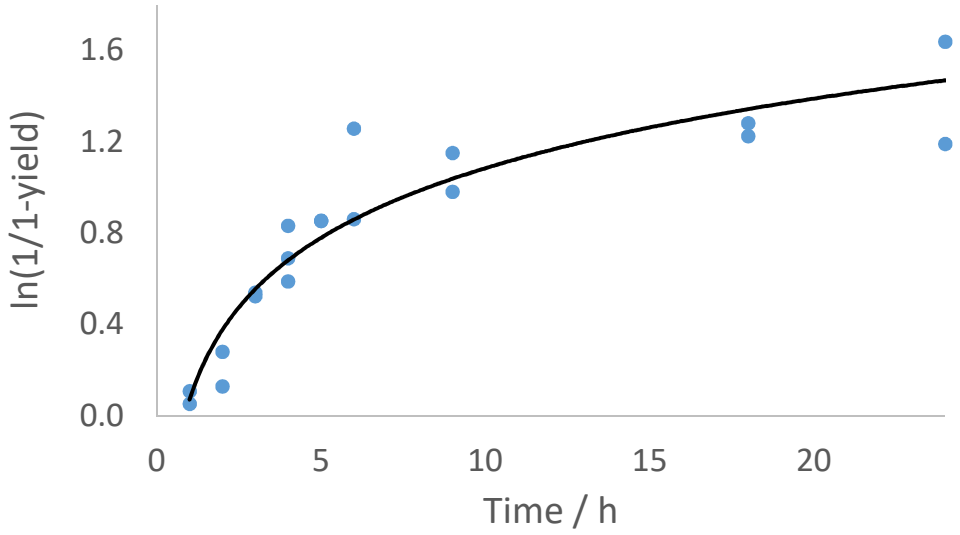


Figure 4.9 – Kinetic data obtained using yield from multiple experiments for the synthesis of 10k PVAc in CO_2 at 65 °C, 15 ml vinyl acetate and a 2:1 ratio of RAFT : AIBN. A logarithmic curve fit accurately depicts the initial rapid rise then levelling off observed for the yield over time

The initial stage of the reaction (Figure 4.9) showed a period of linear growth. This is expected for a RAFT polymerisation as shown with the following graph regarding monomer consumption, assuming a constant polymer radical concentration (Figure 4.10).

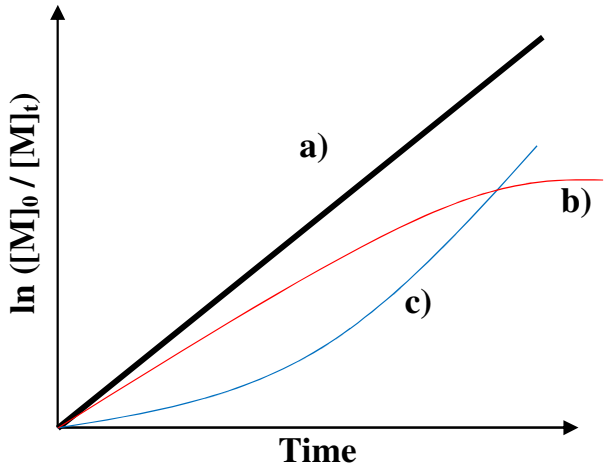


Figure 4.10 - Relationship between monomer consumption over time with varying conditions. a) ideal controlled polymerisation, b) high number of termination and / or side reactions and c) slow initiation

An ideal RAFT polymerisation would demonstrate a linear relationship with monomer consumption over time until full yield was reached (Figure 4.10a). However this was only observed during the first 6 hours when targeting 10k g.mol^{-1} (Figure 4.9), when the reaction had reached 65 % yield. The rate of reaction was then lowered considerably, producing a final yield of 75 % after 24 hours, which suggests an increase in termination and / or side reactions in the latter stages of the polymerisation (Figure 4.10b). One reason for this rate change could be a change in the solubility of the PVAc in the CO_2 monomer-rich phase over the course of the 24 hour reaction time.

One of the most important conclusions when investigating the variation in monomer loading (Table 4.2) was how monomer concentration influenced the J_{crit} value for PVAc. The higher monomer loading should mean that the reaction is in a single phase for a longer time period; however, the noticeable change in reaction rate after 6 hours (Figure 4.9) could relate to the PVAc reaching the J_{crit} value and forming a separate polymer phase, which lowers the rate of propagation.

Further analysis of the kinetics for the RAFT polymerisation of vinyl acetate can be carried out by examining the GPC data (Figure 4.11).

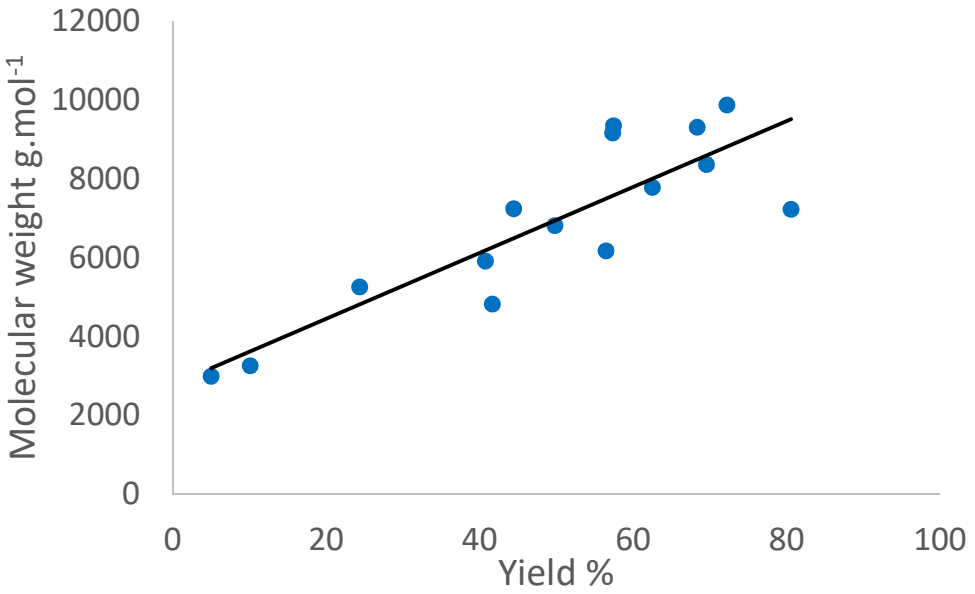


Figure 4.11 – Molecular weight and yield data obtained from multiple experiments targeting 10,000 g.mol^{-1}. The trendline confirms a linear relationship between the molecular weight and yield as expected with RAFT polymerisation

A linear trend between the molecular weight and the yield level was observed throughout the entire reaction time (Figure 4.11), providing further evidence that there is control provided by the RAFT agent, despite the lowering of the reaction rate after the first 6 hours (Figure 4.9).

The lack of consistency in the molecular weight data (Figure 4.11) was a consequence of the sampling procedure that was required when working with $scCO_2$. Unlike the sampling of RAFT polymerisations when using either conventional or microwave heating (Chapter 3), where samples can be taken during the reaction, the highly soluble nature of PVAc and vinyl acetate in CO_2 meant that taking samples *in-situ* would not be possible. As a consequence, each sample was taken from an individual reaction and despite considerable effort being expended to

provide identical conditions for each reaction, there was clearly a degree of variation between experiments, as may be gauged from the results collated in Table 4.4.

Table 4.4 – GPC data from multiple experiments targeting 10,000 g.mol^{-1}

Gravimetric Yield[a] / %	Predicted M_n[b] / g.mol^{-1}	M_n[c] / g.mol^{-1}	Đ [c]
5	720	3,000	1.43
10	1,200	3,300	1.42
24	2700	5,300	1.51
41	4,300	5,300	1.85
42	4,400	4,800	3.18
44	4,700	7,300	2.25
50	5,200	6,800	2.04
56	5,900	6,200	2.41
57	6,000	9,200	2.2
57	6,000	9,400	2.15
62	6,500	7,800	2.94
68	7,100	9,300	2.69
70	7,200	8,400	2.54
72	7,400	9,900	2.43
81	8,300	7,200	3.57

[a]Calculated after precipitation into excess hexane;

[b]Calculated using Equation 4.1;

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards

Additional GPC data with regards to the reaction over time can be observed (Appendix 18 and 19). The high dispersity values measured confirmed that the use of a high initiator concentration in the RAFT : AIBN ratio has an effect even with low yields, offering a fast overall polymerisation rate but while also lowering the level of control provided by the xanthate

RAFT agent.[48] Additionally there are noticeable inconsistencies regarding the correlation between the M_n and $M_{n,th}$ values. However the linear trend in the molecular weight data (Figure 4.11) implied that the RAFT equilibrium maintained a degree of control over the growth of the polymer chains.

This set of experiments provided significant data in respect of the kinetics of RAFT polymerisation for vinyl acetate in CO_2, but only across a limited molecular weight range. Therefore another series of kinetic reactions was designed targeting 35,000 g.mol^{-1}. This would demonstrate whether the reaction profile for the polymerisation is modified with longer chain lengths. Furthermore, this would allow the CO_2 reactions to be comparable with conventional and microwave heated RAFT polymerisations which had also targeted 35,000 g.mol^{-1}. A graph summarising the results is shown (Figure 4.12).

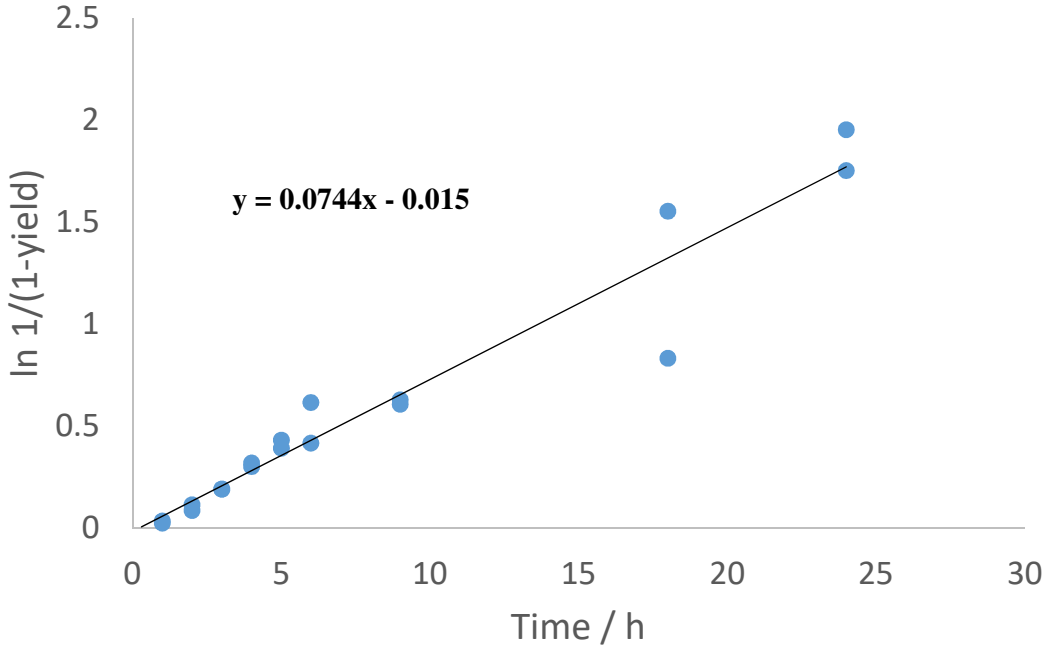


Figure 4.12 – Kinetic data obtained using yield from multiple experiments for the synthesis of 35k PVAc in scCO$_2$ at 65 °C, 15 ml vinyl acetate and a 2:1 ratio of RAFT : AIBN. The trendline confirms a linear increase of yield over time as expected for an ideal RAFT polymerisation

A continuous linear increase in yield throughout the reaction time (Figure 4.12), indicates a high level of control provided by the RAFT agent. However there appears to be no change in the reaction rate i.e. the rate at which monomer is converted into polymer, which was in contrast to the behaviour observed for the 10k reaction (Figure 4.9). Further comparison between the two sets of kinetic data is warranted and detailed analysis is presented later (Section 4.10.2). An investigation into the relationship between molecular weight and yield provided further evidence regarding the level of control over the growth of the polymer chains that is afforded by the RAFT agent (Figure 4.13).

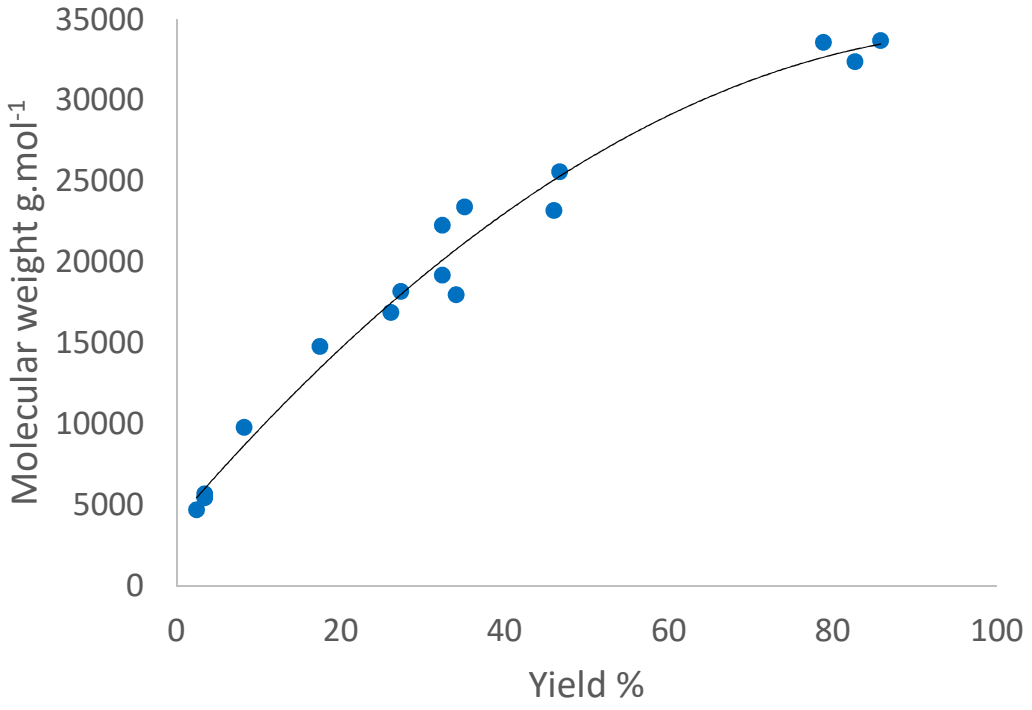


Figure 4.13 – Molecular weight and yield data obtained from multiple experiments targeting 35,000 g.mol^{-1}. A polynomial curve demonstrated that the growth of the PVAc deviates from an ideal linear trend for the higher yield values

There was a general rise in the molecular weight values as the yield for the polymer increased, although the relationship was not linear as would be expected for an ideal RAFT polymerisation, indicating only a limited degree of control over the polymerisation process was maintained when altering the concentration of RAFT agent. This appears to present a disparity with the findings from previous experiments (Table 4.3), where targeting a higher molecular weight resulted in significant discrepancies between the M_n and $M_{n,theo}$ values which implied a lack of control.

The kinetic experiments also demonstrated differing trends when comparing the theoretical and experimental data measured using GPC chromatography (Table 4.5). An example of a GPC from these experiments is also provided (Appendix 20).

Table 4.5 - GPC data from multiple experiments targeting 35,000 g.mol^{-1}

Gravimetric Yield / % [a]	$M_{n,\,theo}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
2	800	4,700	1.43
3	1,000	5,450	1.25
8	2,100	9,800	1.5
17	4,300	14,800	1.35
26	6,300	16,900	1.28
27	6,500	16,700	1.25
32	7,800	19,200	1.33
34	8,200	18,000	1.33
35	8,400	19,800	1.32
45	10,800	27,000	1.58
46	11,000	23,200	1.4
47	11,100	25,600	1.44
79	18,600	33,600	1.65
83	19,500	32,400	1.72
86	20,200	33,700	1.68

[a]Calculated after precipitation into excess hexane;

[b]Calculated using Equation 4.1;

[c]Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards

When targeting 10 kg.mol^{-1} (Table 4.4) there were major inconsistencies between the theoretical and experimental M_n values, as well a broad range of dispersities. In contrast, the molecular weight data for 35k demonstrated a constant rise in molecular weight over time and narrower dispersities, implying that the longer chain length resulted in improved control (Table 4.5). Previous investigations had determined that the rate of termination is influenced by chain length, as the lifetime of the polymeric radical increases with higher molecular weights,[64, 65] thus reducing the probability of termination occurring in the reaction.[66] Targeting a molecular weight of 35k results in a much faster rise in molecular weight compared to targeting shorter polymer chains of 10 kg.mol^{-1}, which consequently lowers the rate of termination of the reaction.

4.10.2 Comparison of kinetic experiments in CO_2

A comparison of both sets of kinetic experiments over time highlights the differences observed in the reaction profiles (Figure 4.14).

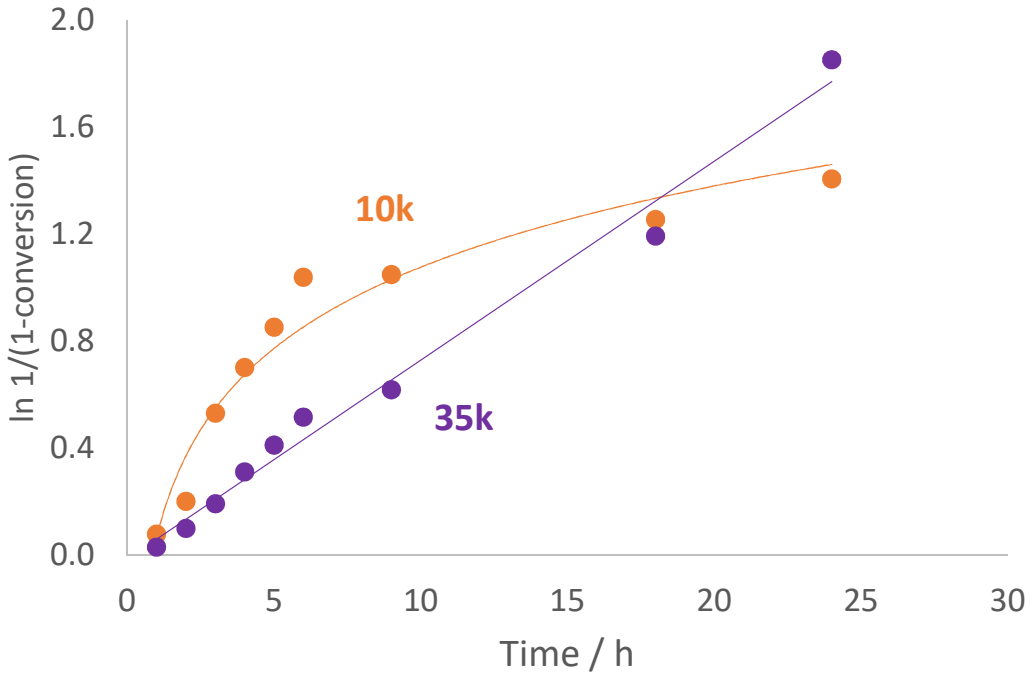


Figure 4.14 - Comparison of kinetic data in $scCO_2$ targeting 10,000 and 35,000 $g.mol^{-1}$. Data points are averages from kinetic data targeting both molecular weights

Comparison of both sets of kinetic data confirmed that the 10k reaction had a faster rate of reaction in the initial stages (Figure 4.14). A higher RAFT concentration is required compared to targeting 35k, however, previous RAFT polymerisations using $scCO_2$ with styrene and methyl acrylate had demonstrated that this can retard the polymerisation rate.[16] Therefore the differences in polymer chain length appear to be influential in the observed variation in reaction kinetics, as has been theorised with multiple model simulations.[65-67] Shorter chains allow for faster rates of propagation, but this effect is progressively diminished as the target molecular weight rises. The GPC data (Figure 4.11) showed that the molecular weight during the 10k reaction remains low throughout the reaction, whereas the rise in molecular weight is significantly faster when targeting 35k (Figure 4.13), as would be expected. This difference in reaction rate relating to target polymer chain length can be enhanced further using elevated temperatures.[67]

A further disparity between the two sets of kinetic data occurred after the 6 hour point. The 10k reaction showed a sudden lowering of the reaction rate, whereas targeting 35k showed a constant rise in yield for the entire 24 hour reaction period (Figure 4.14). It had been expected that the higher molecular weight reaction would have the slower rate of polymerisation, based on the investigation into the effect of varying monomer loading (Table 4.3).

Targeting a significantly higher molecular weight results in longer polymer chains being produced at lower yield levels, which is confirmed by the GPC data (Figure 4.13), therefore phase separation occurred earlier in the reaction. The level of monomer would increase the solubility within the autoclave but even at high yield rates, where most of the monomer would have been consumed, the kinetics for the reaction hardly change.

4.11 Comparison of Kinetic experiments using Conventional and Microwave Heated Reactions with CO_2

The CO_2 kinetic experiments targeting 35 $kg.mol^{-1}$ molecular weight applied similar reaction conditions to the solution RAFT polymerisations using a 4:1 ratio of monomer : solvent. Comparing the yield and molecular weight data would determine which method produced the fastest polymerisation rate whilst maintaining the desired level of control over the reaction (Figure 4.15).

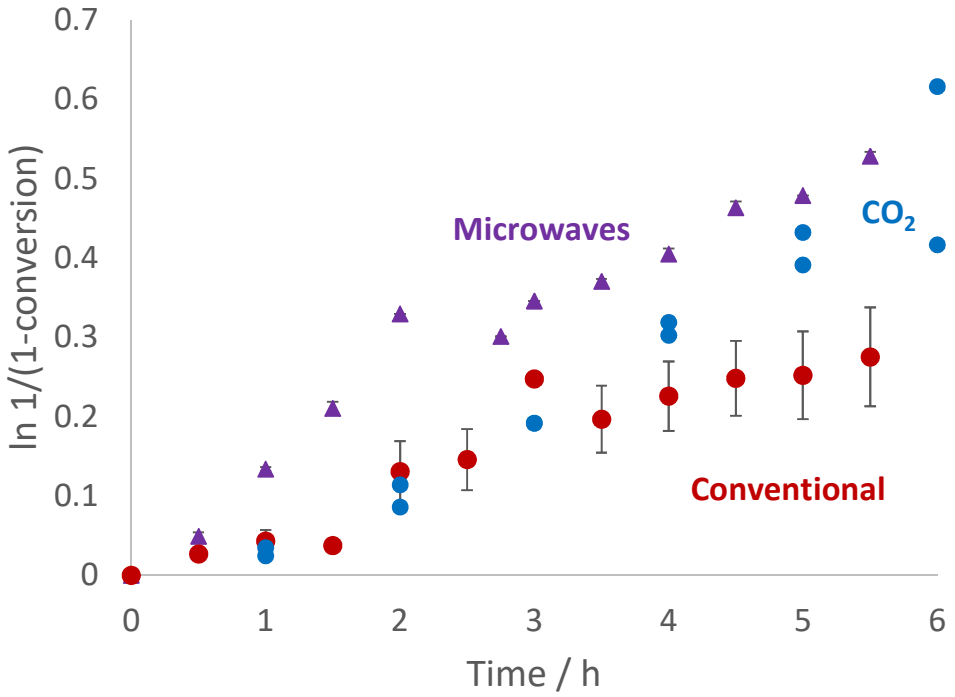


Figure 4.15 - Comparing the different reaction methods for targeting 35,000 g.mol^{-1}.

Conventional & Microwave heating; 2.5:1 RAFT:V-70, 45 °C, 4:1 vinyl acetate:toluene at 45 °C, 20 ml VAc

CO_2; 2:1 ratio RAFT:AIBN, 65 °C, 15 ml VAc

Error bars that cannot be seen are within the region of the data point

The CO_2 reactions and those using conventional heating for the solution RAFT polymerisations were observed to have similar kinetic profiles in the initial stages (Figure 4.15). However, as the reaction progresses, the reaction rate with conventional heating is observed to be reduced, whereas when using CO_2 the rise in yield remains constant. This difference in the kinetic data is linked to the changing viscosity of the reaction over time. As the yield increases, a larger quantity of polymer is formed which, combined with continuous monomer consumption, gradually increases the viscosity in the conventional reaction and lowers the rate of

polymerisation. However, increased molecular mobility as a result of the low viscosity of CO_2 prevents a rapid increase in viscosity, therefore the reaction rate remains principally unaffected.

The microwave reaction was proven to have the faster reaction rate, despite being 20 °C lower in temperature than when using $scCO_2$. This indicated how influential the application of selective heating is on the RAFT process; this has been highlighted further in previous work (Chapter 3). Further investigation into the different reaction techniques compared the relationship between molecular weight and yield (Figure 4.16).

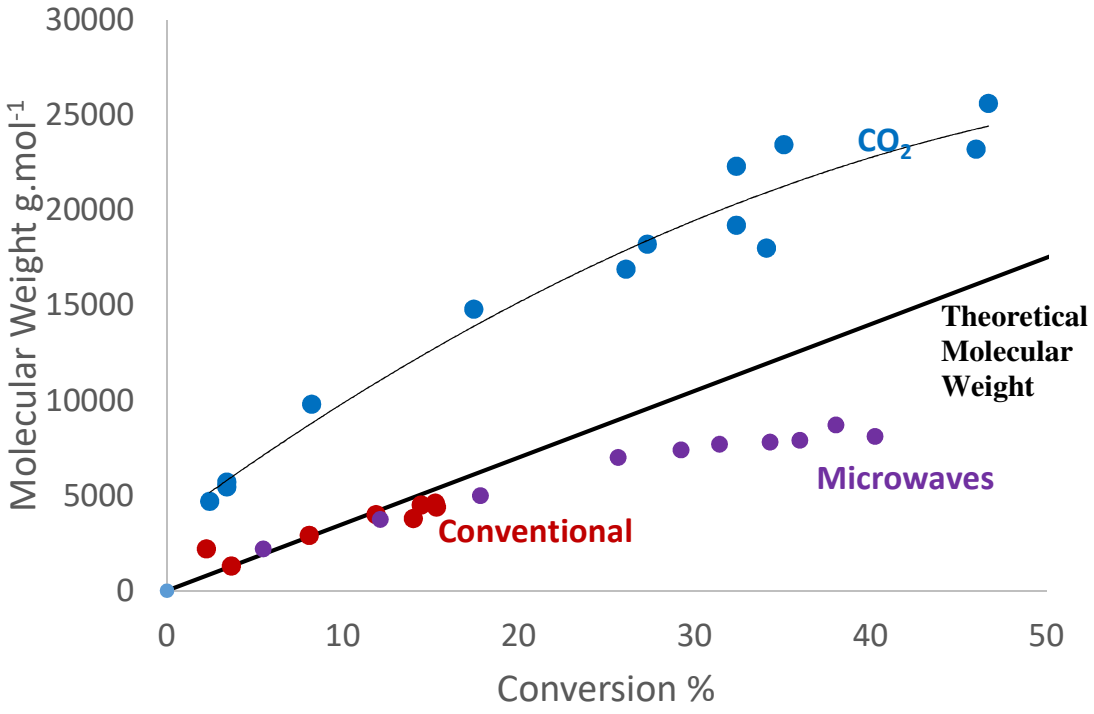


Figure 4.16 - Molecular weight data for each technique applied to RAFT polymerisation of VAc targeting 35,000 g.mol^{-1}

The reaction using conventional heating is shown to follow ideal growth for specific molecular weights. However, as seen from the yield data (Figure 4.15) the reaction rate is lowered over time, which is reflected by a slower rise in molecular weight after 15 % yield. The GPC data

have already been discussed earlier in this chapter with regard to using $scCO_2$ (Section 4.10.1). Comparison of the molecular weight data showed that the values measured were considerably higher than the ideal RAFT polymerisation (Figure 4.16), however, there was still a clear overall linear trend between molecular weight and yield over a long time frame.

When applying microwave heating there was a linear rise in molecular weight with higher yield rate, even with the increased rate of reaction (Figure 4.16). There does appear to be a slight deviation from the ideal chain growth in the latter part of the reaction period, but this was not seen in the other microwave heated reactions with the same RAFT : V-70 ratio, which were performed whilst varying the volume of toluene. Repeating the reaction using these conditions would confirm whether this deviation occurs again.

Combining the data from previous experiments has determined that the optimal conditions for the RAFT polymerisation of vinyl acetate would require a combination of $scCO_2$ and microwave heating. The benefit of this can be highlighted further when comparing the CO_2 experiments at 35k, with the minimal solvent system when applying microwaves, which used a 8:1 ratio of monomer:solvent (Figure 4.17).

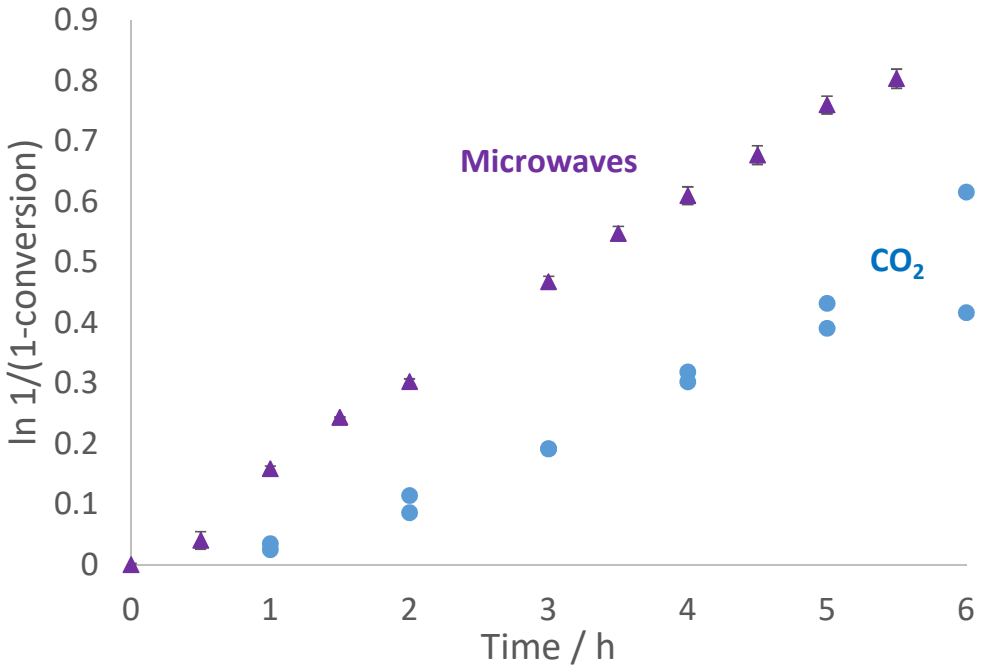


Figure 4.17 – Comparison of kinetic experiments using CO_2 and microwave heating when targeting 35,000 g.mol^{-1}. Error bars that cannot be seen are within the region of the data point

The difference between microwave and $scCO_2$ is far more noticeable when using these optimum conditions (Figure 4.17), where the microwave reaction used the 2.5:1 ratio of RAFT : V-70 but with 2.5 ml of toluene. This minimal solvent level assisted in inducing a significant increase in reaction rate, whilst maintaining a high degree of control over molecular weight. However, the use of toluene, which has a high boiling point, requires the use of an energy intensive process in order to obtain a final pure polymer product. An ideal scenario would involve combining the use of microwave heating with a $scCO_2$ reactor. This would be particularly useful over longer time periods as bulk RAFT polymerisations of vinyl acetate had shown that at high yields, the microwave and conventionally heated reactions showed broad dispersity values, proving that a rise in viscosity in the reaction system eventually causes a loss of control over the reaction.

Using such a small solvent volume for the microwave reactions results in the polymerisation being comparable to a bulk system, therefore there will be issues regarding viscosity when reaching high yield levels (Figure 4.17). The application of CO_2 during these experiments using microwave heating would result in an improved control over viscosity while obtaining the advantages from selective heating of the reactants. The practicality of this future work is covered in greater detail later in this thesis (Chapter 6).

4.12 **Conclusions**

The RAFT polymerisation of vinyl acetate showed how the presence of $scCO_2$ can exert a significant effect on the polymerisation process. As observed with the bulk and solution RAFT polymerisations, the ratio of RAFT : initiator was important in terms of successfully balancing an increase in reaction rate but also needing to maintain the desired control over the final molecular weight and dispersity values, as seen previously (Chapter 3). However, analysing other aspects has shown additional considerations when using $scCO_2$.

Investigations into varying the target molecular weight and monomer concentration were observed to have significant effects on the final polymer regarding final yields and molecular weight control. These were confirmed to be linked to polymer solubility, as varying the J_{crit} value using different reaction conditions can significantly alter the polymerisation rate. Additionally, the kinetic experiments showed that the chain length of the polymer radicals controlled the rate of reaction, as well as affecting the dispersity values.

Future work for the kinetic experiments could potentially monitor the reactions using a view cell to confirm whether a phase change could be observed as the reaction rate is lowered when

targeting molecular weights in the region of 10 kg.mol^{-1}. This is potentially challenging, as the standard procedure required to vent the autoclave requires dry ice and acetone to attain the very low temperatures required to remove the CO_2 while minimising the loss of PVAc. However this reduced temperature would damage the sapphire windows of the view cell, therefore further consideration would be required regarding the venting of CO_2.

Another possibility for furthering this research would be to take more kinetic samples and extend the reactions over a longer time period. The current data (Figure 4.14) showed that few samples were taken after the change in reaction rate when targeting 10 kg.mol^{-1}, therefore having more data could help determine the exact nature of this variation. A longer reaction time would also confirm whether it is possible to get closer to full yield whilst controlling the growth of the polymer chains. Furthermore, a higher temperature could be used to induce the rapid production of radicals. This would demonstrate what would happen were all the polymer chains to be initiated in the early stages of the reaction time, as seen with previous experiments (Chapter 3).

4.13 **References**

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Chapter 5 Making block copolymers of PVAc-b-PVPi using RAFT polymerisation

5.1 Introduction

5.1.1 Block copolymers using controlled polymerisation

The lifetime of a radical in a standard free radical polymerisation is approximately one second, therefore the production of any type of copolymer with only an initiator present is virtually impossible.[1] Introducing a controlling agent significantly reduces the number of radicals in the reaction system by using a reversible process to form dormant polymer chains (Figure 5.1).

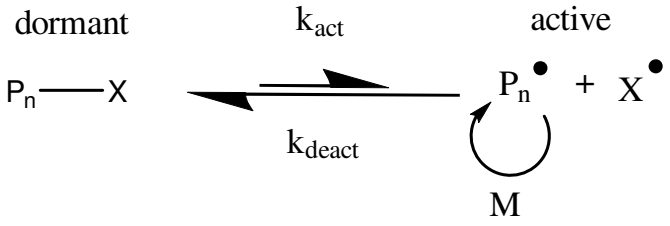


Figure 5.1 - General scheme for controlled radical polymerisations. Pn = polymer molecule, M = monomer unit and X = group capable of undergoing reversible termination without acting as initiator

This favoured dormant state allows the introduction of another monomer to form a second polymer block, producing what is known as a block copolymer (Figure 5.2).

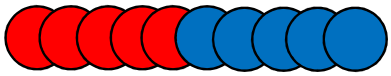


Figure 5.2 – Diagram demonstrating the structure of a diblock copolymer

Block copolymers can be advantageous compared to homopolymers as they allow the combination of two or more polymers which have distinctive properties, and can therefore have numerous applications in a wide range of industries such as cosmetics, pharmaceuticals and stabilisers for dispersion polymerisation.[2, 3] The presence of a controlling agent can also provide pathways to other copolymer structures, which are detailed in Chapter 1.

A number of research groups have examined the production of block copolymers using both Nitroxide Mediated Polymerisation (NMP) and Atom-Transfer Radical-Polymerisation (ATRP).[4-8] An investigation by Kim *et al* examined how glass transition temperature values (T_g) were dependent on the polymers chosen and the type of copolymer formed when using NMP. A derivative heat flow graph measured using Differential Scanning Calorimetry (DSC) for the various copolymers produced is shown (Figure 5.3).[4]

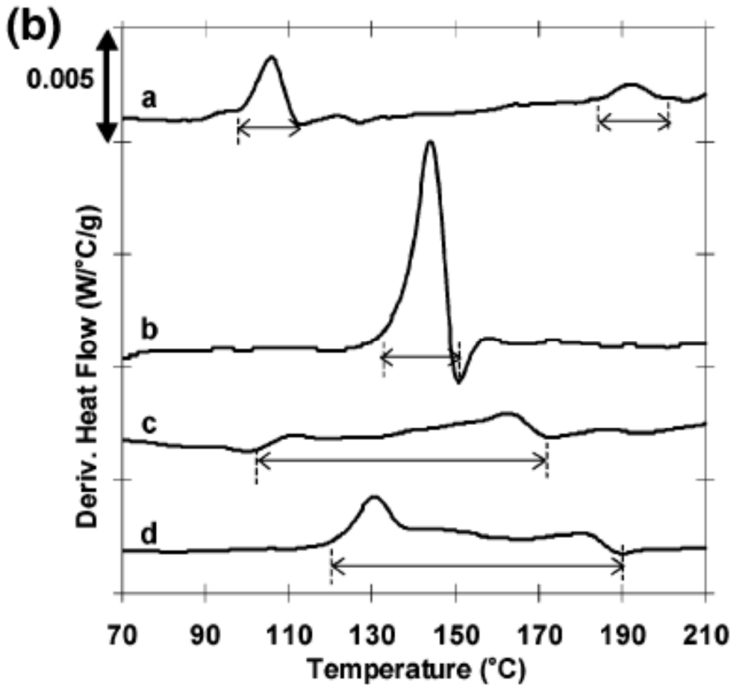


Figure 5.3 - Heat flow graph for various copolymers of styrene and 4-hydroxystyrene. a is from a block copolymer, b is a random copolymer and c-d are gradient copolymers[4]

A block copolymer formed from styrene and 4-hydroxystyrene showed two distinct narrow T_g peaks which were comparable to their separate homopolymers (Figure 5.3a), indicating the presence of a well-defined internal structure as a result of phase separation of the two blocks. The mole fraction of styrene used during the production of the random copolymer (Figure 5.3b) was in the range of 0.56-0.58, therefore the T_g measured was approximately halfway between the T_g values for the separate homopolymers. For gradient copolymers the monomer composition is predominantly from one polymer, which slowly changes to the other polymer along the length of the copolymer chain, therefore the T_g peaks observed (Figure 5.3 c&d) are considerably broader. Block copolymers do not always have such narrow T_g peaks as seen in this investigation, as the presence of a large proportion of homopolymer from one block broadens the T_g.[8]

Further research by Benoit *et al* determined that using (2,2,6,6-Tetramethylpiperidin-1-yl)oxidanyl (TEMPO) for the polymerisation of dienes led to poor control over polymer chain growth owing to a build-up of excess nitroxides.[9] However the use of an alkoxyamine initiator with the corresponding nitroxide led to the successful production of tert-butyl acrylate, which was capable of forming a diblock copolymer structure with poly (isopropene). A variety of different polymers were also examined to determine how influential the order of monomer addition was on the final copolymer structure. When making block copolymers with polystyrene and poly (isopropene), the final block copolymer formed was determined to have controlled molecular weight growth and narrow dispersities regardless of which polymer was used as the macro-initiator. However for poly (acrylate) the order of monomer addition was observed to be highly significant when forming copolymers with either polystyrene or poly (isopropene). Experiments where poly (acrylate) was added as the second block showed ineffective growth resulting in a large amount of homopolymer impurity.

An investigation by Gan *et al* examined the application of ATRP in the production of block copolymers with poly(2-(Dimethylamino)ethyl methacrylate) (DMAEMA) and poly(tert-Butyl Methacrylate) (t-BMA),[10] using bromine as the transferable group in the macro-initiator for the growth of the 2nd block. It was determined that the 'long tail' at the end of the Gel Permeation Chromatography (GPC) peaks represented the macro-initiator, confirming a lack of control. This was either a result of poor blocking efficiency, where the loss of end group functionality prevents the growing of the second polymer block, or incomplete functionalisation of bromine onto the first block. However, by changing the transferable group to chlorine, the results obtained were significantly improved as block copolymers could be synthesised, with both DMAEMA and t-BMA being a suitable macro-initiator for the first block. Both were also capable of producing block polymers which had low molecular weight and narrow dispersity values.

An additional study of block copolymers using ATRP was carried out by Yang *et al,* which applied (Me_6[14]aneN_4) as the catalyst/ligand to successfully produce a homopolymer of poly (4-vinylpyridine) (P4VP) with a chlorine transferable group.[11] This catalyst was able to provide M_n values similar to those taken from theoretical calculations, resulting from strong co-ordination with the copper ions in the initiator. The use of poly (P4VP) as a macro-initiator was proven by the successful growing of a second block of polystyrene, as confirmed using GPC (Figure 5.4).

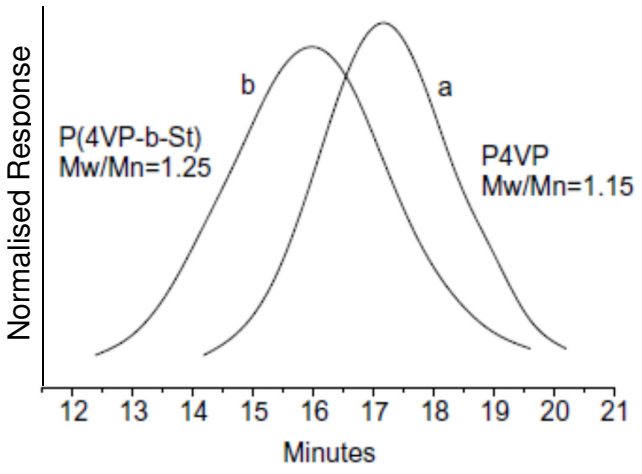
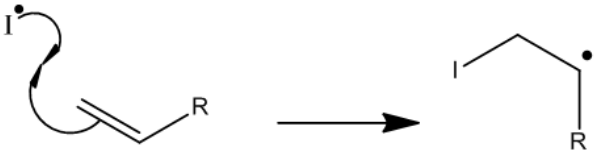


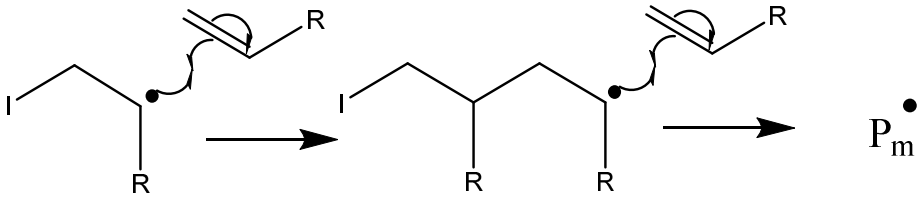
Figure 5.4 - GPC trace showing successful growth of polystyrene on P4VP macro-initiator*[11]*

However, the focus in this chapter is on the use of RAFT polymerisation, where the versatility of this technique towards a wide range of monomers allows the production of numerous block copolymer stuctures.[6] A general scheme for a successful block copolymerisation using RAFT is shown (Figure 5.5).

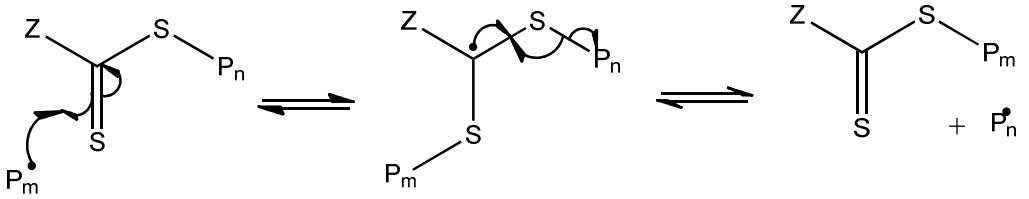
Initiation



Propagation



Chain Transfer



Re-initiation

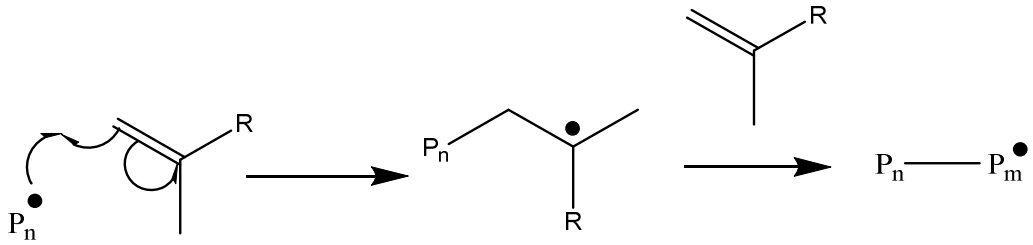


Figure 5.5 - Example of forming a block copolymer where P_m represents the polymer for the 2nd block and P_n is the first polymer block making the macro-RAFT agent

Selecting a RAFT agent to produce a well-defined block copolymer requires careful consideration, as the reactivity towards both monomers needs to be similar, which is partly determined by the choice of Z group on the RAFT agent.[12, 13] A low chain transfer constant with either of the selected monomers could affect the final polymer formed, resulting in a high degree of impurity in the reaction steps owing to the formation of homopolymer.[14] This decreases the number of block copolymer chains present, as well as producing broad dispersity values. A guideline to suitable Z groups for various monomer types is presented (Figure 5.6).

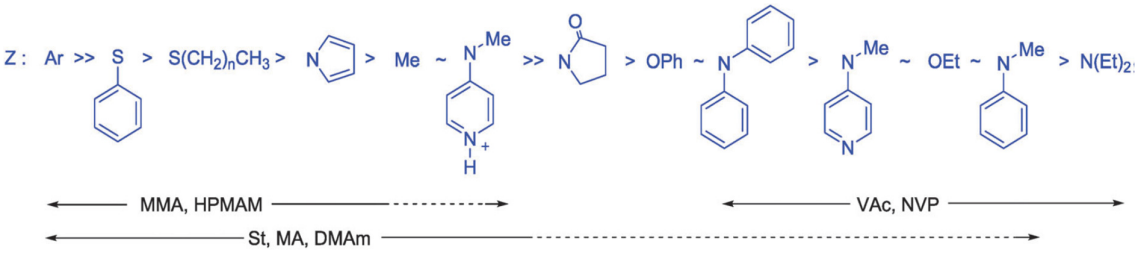


Figure 5.6 - Showing the suitability of Z groups in a RAFT agent towards particular monomer types[14]

The choosing of compatible monomers is also important, as research detailed previously has proven the influence of monomer addition on the structure of the final block copolymer produced. As demonstrated in Figure 5.5, the first block formed is used as a macro-RAFT agent to grow the second block, therefore the polymer selected for this first block is required to be a comparable or better leaving group than the second polymer.[15] Additionally, this polymer radical leaving group must also be capable of re-initiating further propagation of the second block (Figure 5.5).[16] Therefore the optimal conditions would use a monomer which has a high degree of steric stabilisation for the radical, meaning it is a more effective leaving group.[17]

These requirements restrict the compatibility of particular monomers to successfully forming block copolymers, as is shown (Figure 5.7).

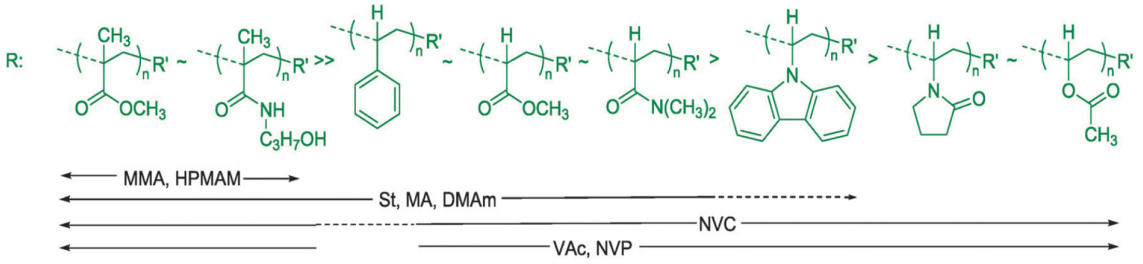


Figure 5.7 - Showing which RAFT agent polymer R groups suit various monomer types[14]

Another influencing factor on the forming of block copolymers is the initiator used for radical production.[14] There will be a certain number of polymer chains that are derived from the initiator rather than the R group from the RAFT agent, which can potentially alter end group functionality. Furthermore, potential issues can arise with the application of a high initiator concentration, as an increased presence of radicals leads to a higher probability of polymer chains becoming irreversibly terminated.

This consequently leads to the homopolymer impurity that is inevitably created during the synthesis of a block copolymer, therefore low initiator concentrations tend to be used to decrease the number of active radical species present.[12] However, this also lowers the rate of propagation and thus increases the time taken to reach high conversion levels. Therefore the reactivity of the monomers should be considered in order to balance the initiator concentration, taking into consideration the rate of polymerisation whilst maintaining a low degree of homopolymer impurity.[18]

Each subsequent block addition will produce more polymer chains that have been irreversibly terminated, therefore there are fewer chains with RAFT end group functionality capable of

continuing the propagation of another block. Subsequently only di-block and tri-block copolymers are commonly synthesised, although it is possible to have more.[19] Another way to ensure a lower homopolymer impurity is to maintain a low conversion level for each block, as there is an increasing probability of radical-radical termination occurring as more monomer is consumed.[14] Other reaction parameters also require consideration as with any RAFT polymerisation, such as the monomer : RAFT agent ratio which determines the degree of polymerisation and the theoretical M_n that will be targeted.[20, 21]

The rules regarding the compatibility of particular RAFT agent groups (Figure 5.5 and 5.6) apply when reacting together two monomers of similar reactivity. More active monomers (MAMs) such as methyl methacrylate (MMA) form very stable intermediate radicals, therefore a suitable RAFT agent would require a fast chain transfer rate, such as dithioesters and dithiobenzoates. Whereas less active monomers (LAMs) produce rapidly propagating radicals, therefore the chosen RAFT agent should have a low chain transfer rate; this includes xanthates and dithiocarbamates. The major difference between these monomer categories is the Z group, which controls the reactivity of the RAFT agent,[13, 22] therefore the concept of reacting together MAM and LAM monomers to produce a block copolymer is more complicated.

The most common means of achieving this is to use a "universal" RAFT agent, which involves the use of dithiocarbamate RAFT agents which are able to alter the electronic structure of the Z group.[23, 24] An example of this is shown (Figure 5.8).

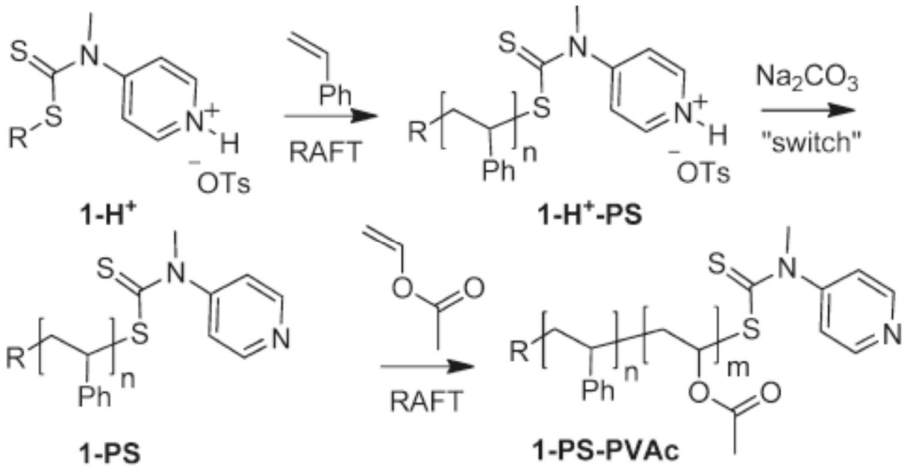


Figure 5.8 - Example of producing a MAM-b-LAM block copolymer[25]

The "switchable" nature of the Z group drastically alters the transfer rate of the RAFT agent, thus making it able to control the polymerisation of both types of polymer (Figure 5.8). Other means of making block copolymers with polymers of differing reactivity involve using a combination of controlled polymerisation techniques such as RAFT and click chemistry,[26] which provides an alternative pathway to forming well-defined block copolymers.

5.1.2 Block copolymer Synthesis using microwaves

As with the production of homopolymers, various synthesis techniques have been investigated with regard to the formation of block copolymers; this includes the application of microwave heating to increase reaction rates while maintaining the desired control.[27] There are very few examples of microwave heating being used for the formation of block copolymers using either NMP or ATRP. The growing of a second block is often used to confirm the homopolymer

produced using microwaves can function as a macro-initiator to grow a second polymer block,[28, 29] however this second block is not necessarily grown using microwaves.

In comparison, there are numerous examples of microwave heating being utilised during the synthesis of block copolymers using RAFT polymerisation. An investigation by Roy *et al* examined the potential of using both poly(N-isopropyl acrylamide) and poly(N, N-Dimethyl acrylamide) as polymer macro-RAFT agents.[30] Both of these polymers, when synthesised with microwaves, displayed increased rates of polymerisation and produced low dispersity values, therefore indicating the presence of a high number of polymer chains with RAFT end group functionality. This was subsequently confirmed by the successful growing of a second block, using polymers such as methyl and tert-butyl acrylates. Employing microwave heating during the growth of the second block continued to induce an accelerated polymerisation rate with narrow dispersities for the final polymer, as well demonstrating a high blocking efficiency to lower the level of homopolymer impurity.

Similar studies have confirmed that this acceleration for RAFT polymerisations upon the application of microwave heating was also observed with various other monomers including benzyl methacrylate and N-isopropylacrylamide.[31, 32] Additional benefits when using microwaves were also demonstrated such as improved control over molecular weight, higher final conversions, narrow dispersities and reproducible results.[33]

PVAc has also been applied as a macro-RAFT agent for the formation of block copolymer using microwave heating.[34] As shown in multiple previous investigations, PVAc homopolymer can be produced with microwaves, demonstrating an accelerated reaction rate and lower dispersities compared to conventional methods.[35, 36] The successful synthesis of a second polymer block with both vinyl pivalate and vinyl benzoate confirmed that, even with the rapid reaction rate, there is a high retention of the RAFT end group functionality. The use of

microwave heating for the production of this second polymer block continued to show an increase in polymerisation rate, narrow dispersities and high blocking efficiencies.

5.1.3 Block copolymer synthesis using CO_2 as a reaction medium

A review paper on the use of ATRP in $scCO_2$ studied the potential of producing block copolymers, using poly (1,1-dihydroperfluorooctyl methacrylate) (FOMA) as the macro-initiator, with MMA and DMAEMA as the chosen second blocks.[37] In both experiments, it was possible to grow the second block with reasonable agreement between the theoretical and experimental M_n values. One observation confirmed that the PFOMA homopolymer was soluble in CO_2, making it a suitable choice as a macro-initiator. However, the forming of the second block reduced the solubility of the copolymer, making it necessary to apply higher pressures and temperatures to make the block copolymer either partially or entirely soluble in CO_2.

Another paper studied the application of NMP to synthesise block copolymers in $scCO_2$.[38] Macro-initiators of poly (dimethylacetamide) (DMA), poly (*t*-BA) and polystyrene were synthesised in $scCO_2$ using N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)]nitroxide (SG1) as the controlling agent. Each macro-initiator was subjected to an inverse suspension polymerisation, with poly (*N*-isopropylacrylamide) (NIPAM) being used at various concentrations for the second block. The dissociation rates varied depending on the macro-initiator that was selected, where using poly (t-BA) showed an induction period as a result of the equilibrium favouring the formation of the dormant polymer species, whereas a more rapid dissociation rate for poly (DMA) led to the forming of the second polymer block even in the early stages of the reaction time.

The steady state kinetics of NMP meant that changing the ratio of the macro initiator : [SG1] had no effect on the rate of polymerisation. Each block copolymer synthesised showed good agreement between M_n calculated from NMR and GPC analysis, with narrow dispersities for a majority of the final polymers, indicating that a high level of control was maintained throughout.

Several research groups have examined the potential of using CO_2 during the production of block copolymers with RAFT polymerisation. An investigation by Thurecht *et al* studied the RAFT-controlled dispersion polymerisation of PMMA using a high pressure autoclave reactor.[39] Chain extension of the polymer chains was observed upon the addition of more MMA monomer, thus proving that the chains with RAFT end functionality could continue to propagate. The use of styrene with the PMMA macro-RAFT agent confirmed this technique could also be applied to produce block copolymers in $scCO_2$, although it was important to include additional stabiliser and initiator when adding the second monomer to ensure that the spherical particle morphology was maintained.

Low viscosity and high diffusivity results in $scCO_2$ being an excellent plasticiser for the PMMA particles, allowing easy access for the second monomer to initiate the formation of a block copolymer. Various other monomers have also been successfully used with the PMMA macro-RAFT agent in $scCO_2$, including benzyl methacrylate (BzMA) and DMAEMA.[40] Altering the ratio of the blocks was shown to have an effect on the internal morphologies of the particles on examination using Transmission Electron Microscopy (TEM) (Figure 5.9).

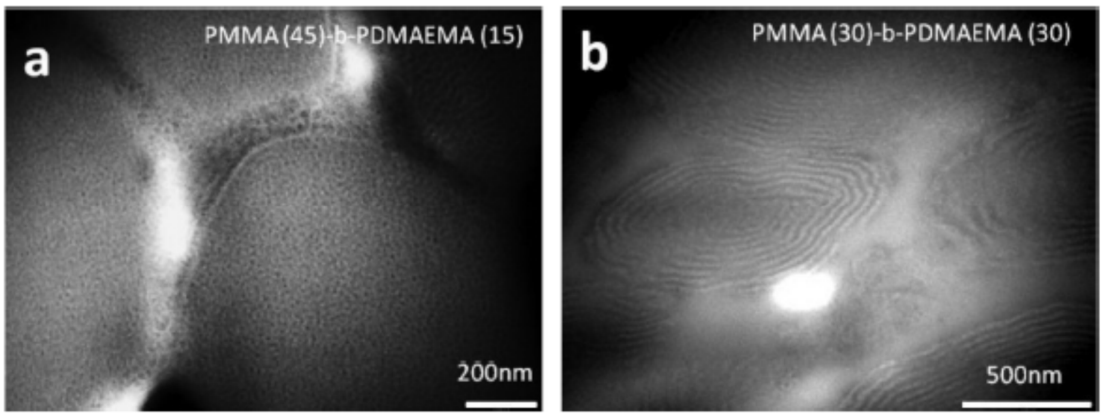


Figure 5.9 - TEM analysis showing how varying the ratio for the monomer concentrations can affect the final block copolymer morphology[41]

A more in-depth analysis of this technique found that the use of CO_2 presented other advantages over other reaction media.[41] It was possible to achieve high levels of monomer conversion for both blocks, and the utilisation of flushing CO_2 through the system facilitated the removal of unreacted monomer and other impurities. Additionally, using suitable conditions could produce a high blocking efficiency, as well as being able to obtain the final product as a free flowing white powder.

PVAc has been successfully used as a macro-RAFT agent for a block copolymer with PVPi when using CO_2,[42] with a good linear relationship between molecular weight and conversion throughout the reaction with narrow dispersities. However, the PVAc macro-RAFT agent was synthesised in a conventional oil bath rather than in CO_2.

One of the objectives of these experiments was to confirm how the production of the PVAc macro-RAFT agent is affected by the application of conventional and microwave heating. Chapter 3 had shown how the use of microwaves could accelerate the polymerisation rate, while maintaining the desired control and low dispersity expected when using a RAFT agent.

However, by growing a second polymer block, this would prove whether the observed acceleration successfully maintained the RAFT end group functionality on the polymer chains, as it is possible that the acceleration observed with microwave heating may be increasing the rate of termination, leading to a higher proportion of 'dead' chains. This would therefore produce a higher degree of homopolymer impurity from the 2nd PVPi block.

Additionally, different methods would be applied during the synthesis of the PVPi block. This would include using conventional and microwave heating, as well as using CO_2 as a reaction medium. A comparison of these various techniques would ascertain which approach allowed the most effective production of the final block copolymer. The analysis would include aspects such as the conversion and the level of homopolymer produced, which would aid in determining the reaction parameters for future experiments.

5.2 **Experimental**

5.2.1 Synthesis of macro-RAFT agents produced by Conventional and Microwave Heating

A Schlenk tube containing a mixture of vinyl acetate (20 ml, 0.022 moles), xanthate RAFT agent (830 mg, 3.7×10^{-3} moles) and V-70 (230 mg, 7.4×10^{-4} moles) was subjected to three freeze pump thaw cycles and then purged with argon. For conventional reactions, the tube was then placed in an oil bath pre-set to 45 °C. Using microwave heating, the fibre optic temperature probe was placed in a glass sleeve which reached into the reaction mixture, at which point the CEM was set to 45 °C.

The reactions for both heating methods were terminated after 2 hours. Once sufficiently cooled, the reaction mixture was dissolved in dichloromethane (DCM), then the polymer was precipitated out in hexane with a 1:20 ratio. This precipitation was repeated again before the polymer was left to dry overnight in the room temperature vacuum oven.

5.2.2 Synthesis of PVAc-b-PVPi block copolymers by conventional and microwave heating

A Schlenk tube containing a mixture of vinyl pivalate (5 ml, 0.03378 moles), PVAc macro-RAFT agent (0.87 g, 8.7×10^{-5} moles), V-70 (10.7 mg, 3.47×10^{-5} moles) and toluene (5 ml, 0.047 moles) was subjected to three freeze pump thaw cycles and then purged with argon. For conventional reactions, the tube was then placed in an oil bath pre-set to 45 °C. Using microwave heating, the fibre optic probe was placed in a glass sleeve which reached into the reaction mixture before the CEM reactor was programmed to 45 °C.

Both heating methods had a 7 hour reaction time with kinetic sampling being carried out starting at 2 hours, and then every subsequent hour. To obtain the ratio data for the block copolymer, the final product was dissolved in DCM, then precipitated into a cold mixture of methanol : water in a 4 : 1 ratio. A rotary evaporator was then used to obtain the final block polymer.

5.2.3 Synthesis of PVAc-b-PVPi block copolymers using CO_2

A Schlenk flask containing a mixture of vinyl pivalate (13.5 ml, 0.092 moles), PVAc macro-RAFT agent (2.35 g, $2.4x10^{-4}$ moles) and V-70 (29 mg, $9.4x10^{-5}$ moles) was subjected to three freeze pump thaw cycles and then purged with argon. The autoclave reactor was purged for 25 minutes with a CO_2 flow of ~30 psi. The reaction mixture was extracted with a purged 20 ml syringe and needle and injected into the autoclave. Once the autoclave was sealed the stirring rate was set to 300 rpm, and then the pressure increased up to ~700 psi. The internal temperature was set to 45 °C after which, having allowed time for the reactor to equilibrate at this temperature, the pressure was further increased to 2,000 psi.

When the 7 hour reaction was complete, the reactor was cooled to around -40 °C using a mixture of dry ice and acetone, after which the outlet tap was slowly opened vent the remaining CO_2 until the autoclave was at ambient pressure. The reactor was then left to reach room temperature before the final polymer could finally be removed and analysed.

5.2.4 Synthesis of PVAc-b-PVPi block copolymers by conventional and microwave heating with the microwave synthesised macro-RAFT agent

A Schlenk tube containing a mixture of vinyl pivalate (5 ml, 0.034 moles), PVAc macro-RAFT agent (0.64 g, $9.1x10^{-5}$ moles), V-70 (10.7 mg, $3.5x10^{-5}$ moles) and toluene (5 ml, 0.047 moles) was subjected to three freeze pump thaw cycles and then purged with argon. For conventional reactions, the tube was then placed in an oil bath pre-set to 45 °C. Using microwave heating,

the fibre optic probe was placed in a glass sleeve which reached into the reaction mixture before the CEM reactor was programmed to 45 °C

Both heating methods had a 7 hour reaction time with kinetic sampling being carried out starting at 2 hours, and repeated every subsequent hour. To obtain the ratio data for the block copolymer, the final product was dissolved in DCM, then precipitated into a cold mixture of methanol : water in a 4 : 1 ratio. A rotary evaporator was then used to obtain the final block copolymer.

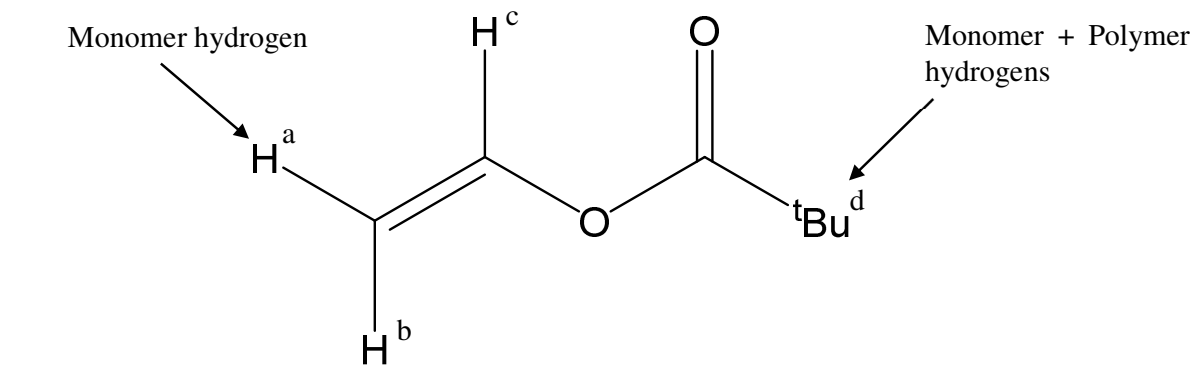
5.2.5 Synthesis of PVAc-b-PVPi block copolymers using CO_2 and the microwave synthesised macro-RAFT agent

A Schlenk flask containing a mixture of vinyl pivalate (14 ml, 0.095 moles), PVAc macro-RAFT agent (2.09 g, 2.8×10^{-4} moles) and V-70 (35 mg, 1.1×10^{-4} moles) was subjected to three freeze pump thaw cycles and then purged with argon. The autoclave reactor was purged for 25 minutes with a CO_2 flow of ~30 psi. The reaction mixture was extracted with a purged 20 ml syringe and needle and injected into the autoclave, then having sealed the autoclave, the stirring was set to 300 rpm and the pressure was increased up to ~700 psi. The internal temperature was set to 45 °C, with the reactor being allowed to equilibrate before increasing the pressure up to 2,000 psi.

When the 7 hour reaction was complete, the reactor was cooled to around -40 °C using a mixture of dry ice and acetone, the outlet tap was then opened to slowly vent the remaining CO_2 until the autoclave was at ambient pressure. The reactor was left to stabilise at room temperature before the final polymer could then be removed and analysed.

5.2.6 NMR Analysis

Nuclear Magnetic Resonance (NMR) was used to determine conversion for the kinetic samples. A typical NMR spectrum from a kinetic sample is shown along with a diagram for vinyl pivalate (Figure 5.10).



Vinyl pivalate

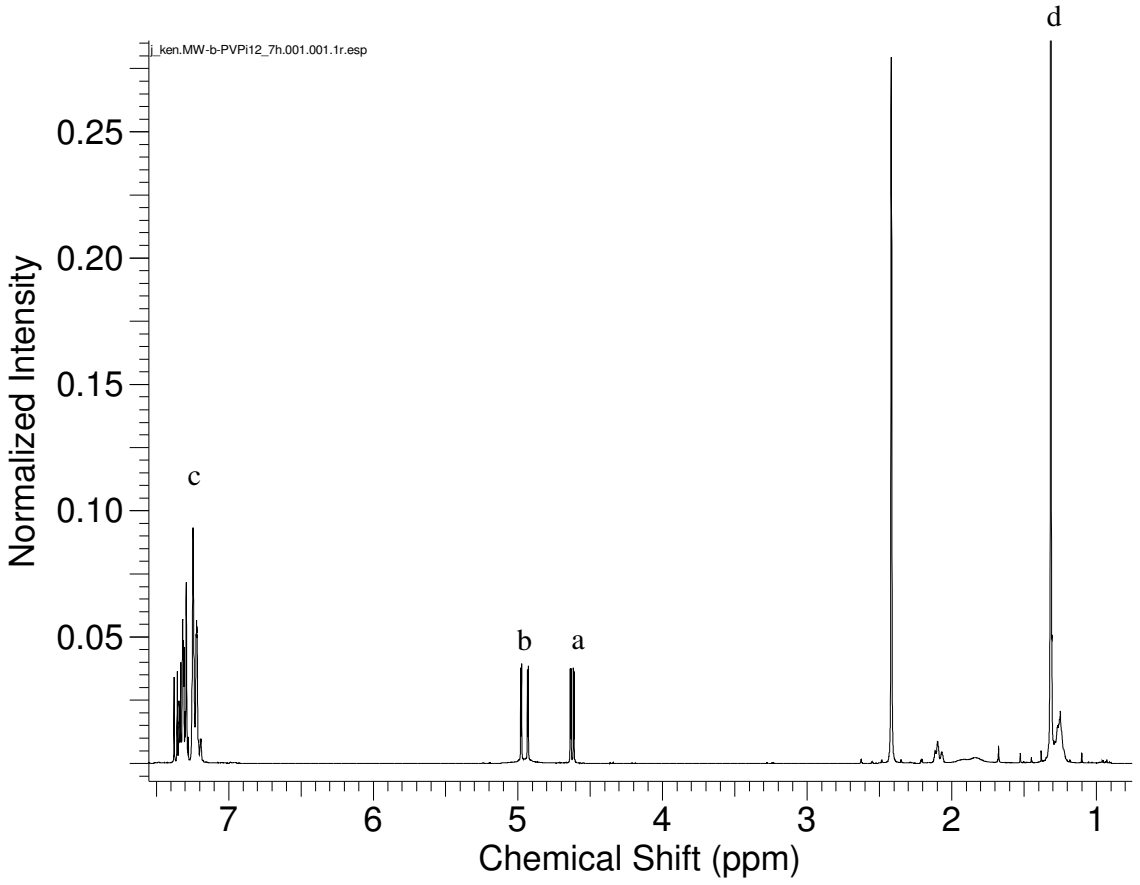


Figure 5.10 – Diagram of vinyl pivalate and ^{1}H NMR spectrum for kinetic sample of block copolymer

When calculating conversion it was important to choose appropriate peaks owing to the similarity of the vinyl pivalate and vinyl acetate structures (Figure 5.11).

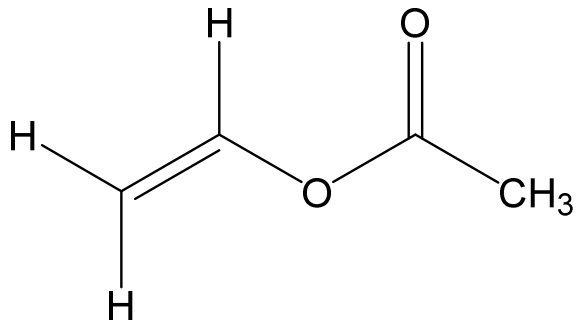


Figure 5.11 - Diagram of vinyl acetate

The similarity in molecular structure meant certain NMR peaks could be from both monomers and polymers, therefore it was important to select appropriate peaks for analysis. The peak marked **a** (Figure 5.10, -CH_2-, δ = 4.51 ppm) is unique to the specific monomer hydrogen indicated in vinyl pivalate. Peak **d** was chosen as the combined monomer and polymer peak as the ^{t}Bu group is only present in vinyl pivalate (Figure 5.10, -^{t}BuCOO-, δ = 1.25 ppm), therefore no alteration observed in these peaks would be as a consequence of the PVAc macro-RAFT agent. An example of the integration required to calculate conversion is demonstrated (Figure 5.10 and Equation 5.1).

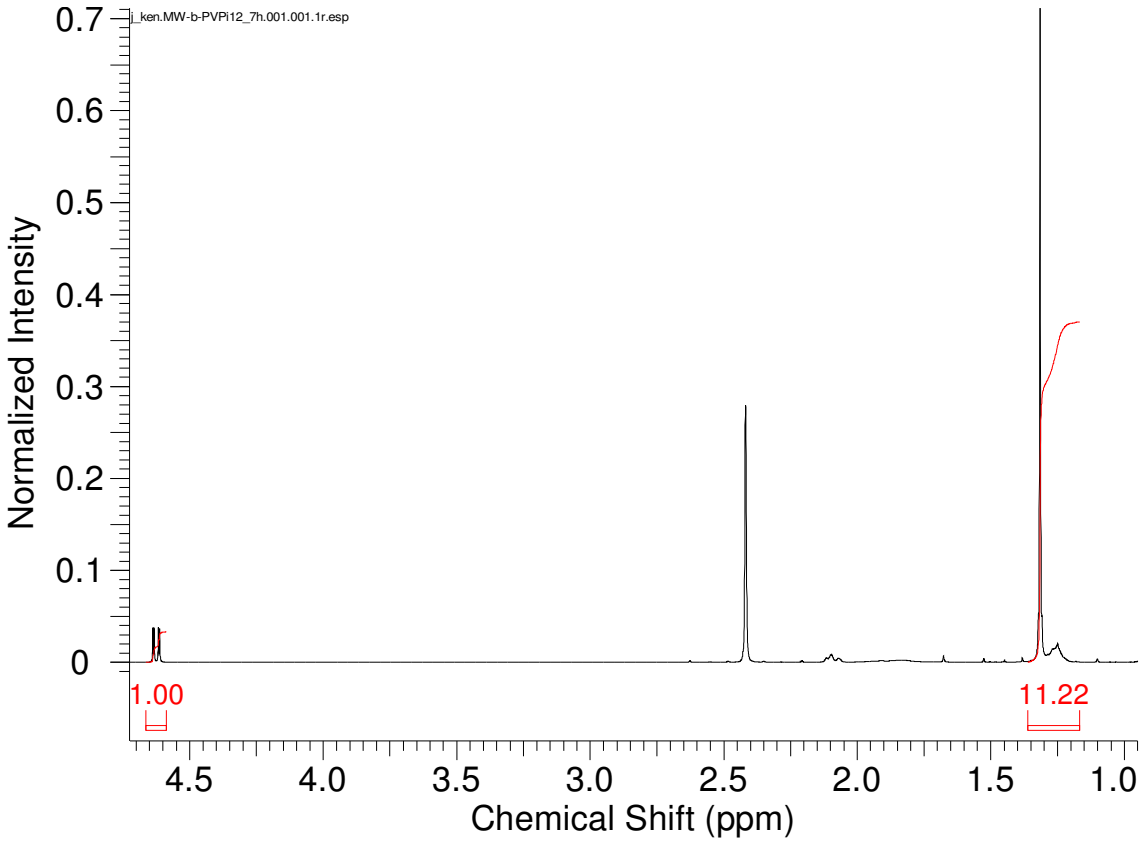


Figure 5.12 – Example ^{1}H NMR spectrum with integrals of PVAc-PVPi product before precipitation used to calculate conversion

Conversion can then be calculated with the following equation.

Equation 5.1 $$\textbf{Conversion \%} = \frac{(11.22/9) - 1}{[\,1+(11.2/9)\,]} \times 100 = 11\ \%$$

The combined monomer and polymer peak at 1.25 ppm represents each hydrogen within the ^{t}Bu group and therefore needs to be divided by 9. The minus one represents removing the monomer hydrogen from the peak at 4.4 ppm.

Once the polymer had been precipitated and dried to remove any residual impurities, the NMR analysis could be used to calculate the ratio of the block copolymer (Figure 5.13).

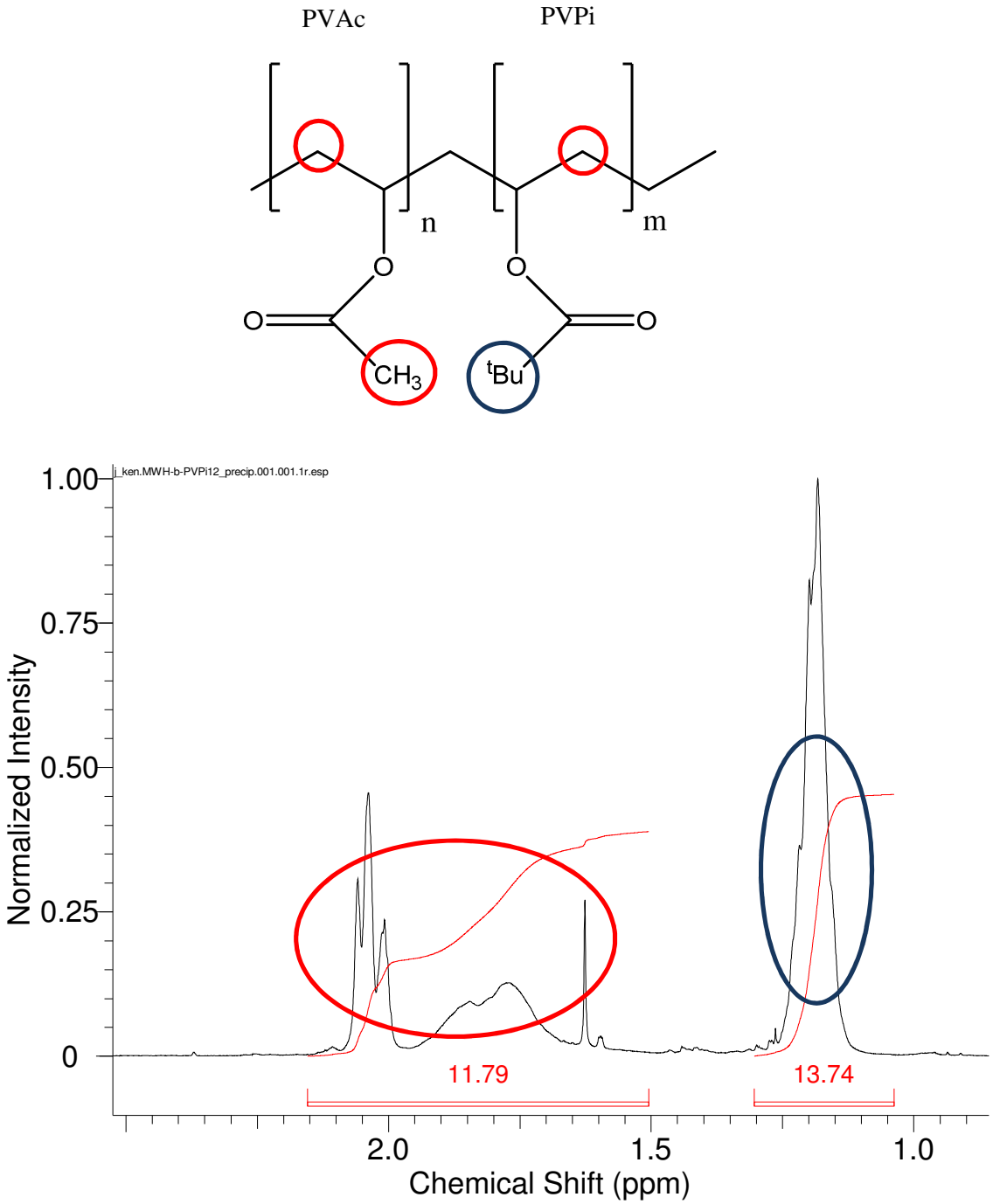


Figure 5.13 - Example ^{1}H NMR spectrum of PVAc-PVPi product after precipitation with integrals used to calculate block ratios

The peak on the right (-^{t}BuCOO-, δ = 1.25 ppm) now solely represents the ^{t}Bu group of PVPi as any unreacted monomer will have been removed during precipitation. The peak on the left (-CH_3COO-, -CH_2- & -CH_2-, δ = 1.9 ppm) is produced as a combination of the CH_3 group of vinyl acetate and the CH_2 hydrogens from both polymer backbones (Figure 5.13).

Using the spectrum in Figure 5.13 as an example, the equivalent of one PVPi hydrogen is determined:

Equation 5.2 - Block copolymer ratio **9 PVPi = 13.74**

PVPi = 1.53

The peak at 1.9 ppm is known to be composed 5 hydrogens from PVAc and 2 hydrogens from PVPi, therefore;

11.79 = 5 PVAc + 2 PVPi

The value calculated for the equivalent of one hydrogen from PVPi can then be entered into this equation;

11.79 = 5 PVAc + (2 x 1.53)

5 PVAc = 8.73

PVAc = 1.75

Finally, these can be compared and then entered into a ratio.

PVAc = (1.75 / (1.75+1.53) = 0.53

PVPi = (1.53 / (1.75+1.53) = 0.47

PVAc : PVPi

0.53 : 0.47

1.13 : 1

5.2.7 DSC

A TA-Q2000 DSC (TA Instruments) was used to measure T_g values for the block copolymers. Each sample was between 2-4 mg, and was weighed into an aluminium pan, using an empty pan as the reference. Every sample was taken to 0 °C, then heated to 200 °C at a rate of 10 °C per minute. This process was repeated, as a second cycle ensured that any T_g peaks observed were not as a result of contamination by the previous sample. An example of a typical DSC analysis is given (Figure 5.14).

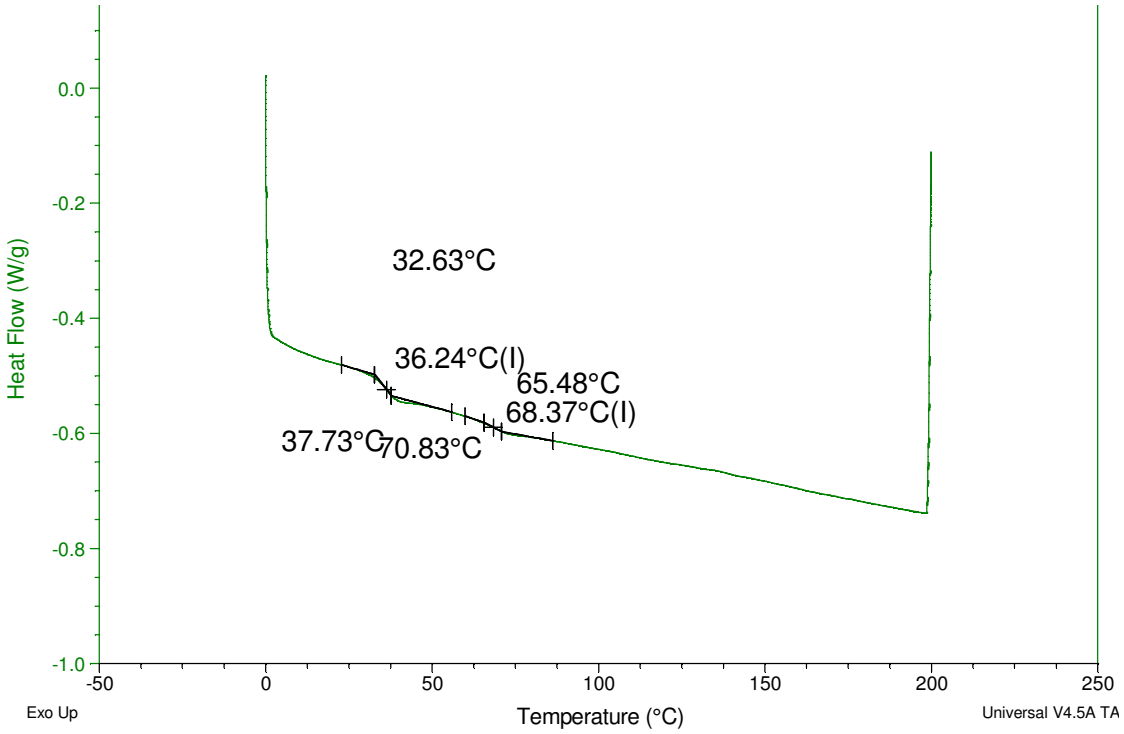


Figure 5.14 - Example of DSC analysis for PVAc-PVPi product, showing the presence of two T_g values

The presence of two distinct T_g values in each sample run showed that there could potentially be distinct blocks of Poly (vinyl acetate) and Poly (vinyl pivalate) present, but GPC analysis is required for confirmation.

5.2.8 Gel Permeation Chromatography Analysis

GPC spectra were collected upon a Polymer Laboratories GPC-50 Plus using a PLGel Mixed-D polystyrene column in chloroform (Sigma-Aldrich 99.8%) and a flow rate of 1ml.min^{-1}. The

final molecular weight values were calculated by comparing to PMMA standards with a molecular weight range between 465,000 and 162 $g.mol^{-1}$. Each sample was made with a concentration of $5mg.ml^{-1}$.

5.3 Results and Discussion

5.3.1 Production of macro-RAFT agents

As proven by previous investigations, it was important to consider all aspects of the reaction to ensure the successful synthesis of a block copolymer. An important factor to determine was the order of monomer addition, as there could potentially be little to no growth of the second block if the polymer macro-RAFT agent selected cannot control the polymerisation process. An investigation by Birkin *et al* regarding block copolymers using PVAc and PVPi determined that having PVAc as the macro-RAFT showed improved control over molecular weight and dispersity, compared to using PVPi for the first block.[3]

Another consideration was the choice of RAFT agent, as it was important that it should be capable of controlling the polymerisation of both monomers. Vinyl acetate and vinyl pivalate are both classified as LAMs and demonstrate comparable polymerisation rates, therefore both should be compatible with RAFT agents that have low chain transfer rates, as proven in previous investigations.[43, 44] The xanthate RAFT agent that has been used during this research to successfully control the synthesis of PVAc homopolymer should also be suitable for VPi, and should therefore be capable of synthesising the PVAc-b-PVPi block copolymers.[45]

The macro-RAFT agents were both produced using bulk conditions and a 5 : 1 ratio of RAFT : V-70, as previous reactions under these conditions had been proven to produce high levels of

conversion for both heating methods, coupled with a short reaction time. There was even an indication of acceleration of reaction rate when using microwaves, however it was important to stop after the reaction had reached around 70 % conversion. At this point the viscosity levels slowed the rate of termination while propagation continues which, combined with uneven heat distribution, results in a lack of control over the polymerisation process. Furthermore past studies have indicated that as conversion approaches 100 %, there is an increase in irreversible termination,[14] therefore a higher number of the polymer chains no longer have RAFT end group functionality, resulting in fewer chains being capable of growing a second polymer block.

The optimum conditions discovered during Chapter 3 for synthesising PVAc demonstrated a significant increase in reaction rate while maintaining good control over molecular weight for the RAFT polymerisation of PVAc when using microwave heating. This involved using a higher concentration of initiator in a 2.5 : 1 ratio of RAFT : V-70, combined with 2.5 mL of toluene to reduce viscosity. However, while these conditions provided improved results when applying microwave heating, the conversion after 5.5 hours when using conventional heating was low.

Therefore several batch reactions would be required in order to synthesise enough macro-RAFT agent for the planned block copolymer experiments. Each reaction would have differing final results in terms of dispersity and M_n values, hence the data between the two heating methods would not be comparable. It was therefore decided to use bulk conditions to produce the macro-RAFT agents, which had been shown to produce high conversion levels in a short reaction time for both heating methods (Chapter 3).

The purpose of using macro-RAFT agents produced with the different heating methods was to observe how the subsequent block copolymer synthesis was affected, such as the level of homopolymer produced and whether low dispersity values were maintained. There were

several samples from previous RAFT polymerisations of PVAc that had targeted higher molecular weights at 35,000 g.mol^{-1}. However, these macro-RAFT agents would have necessitated using large amounts in order to form a second block with reasonably low molecular weight values, therefore both heating methods targeted 5,000 g.mol^{-1}. Tabulated results confirming the GPC analysis for the macro-RAFT agents are compiled in Table 5.1.

Table 5.3 –GPC analysis for PVAc macro-RAFT agents produced using conventional and microwave heating targeting 5,000 g.mol^{-1}

Heating Method	M_n / g.mol^{-1}	M_w / g.mol^{-1}	Đ
MWH	7,400	8,440	1.14
CH	10,000	14,800	1.48

Table 5.1 showed that the macro-RAFT agent produced using microwave heating demonstrated a higher degree of control compared to the conventional reaction, with an M_n value closer to the 5,000 g.mol^{-1} that was targeted, as well as a much narrower dispersity. This implied that a larger proportion of the chains had retained the RAFT end group functionality, therefore a higher number of polymer chains would be capable of growing a second block. Examples of NMR and GPC analysis from the macro-RAFT agents is also provided. (Appendix 21 and 22).

5.3.2 Block copolymers synthesised with conventionally synthesised macro-RAFT agent

The first reaction using the PVAc macro-RAFT agent produced in the oil bath examined using conventional heating to grow the second block (Figure 5.15).

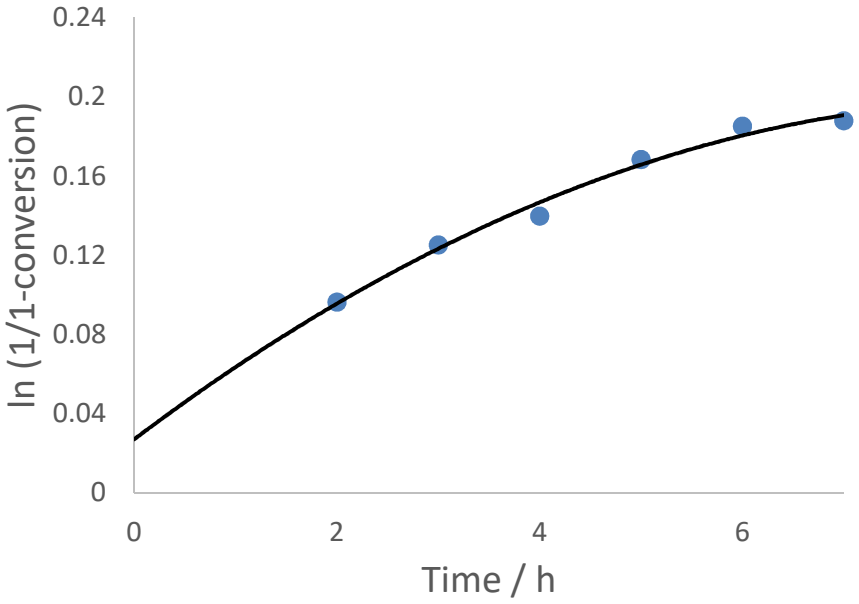


Figure 5.15 – Conversion over time for PVAc-PVPi block when applying conventional heating and the PVAc-macro RAFT agent produced using conventional heating. A polynomial curve demonstrates the very gradual rise in conversion over time

Initially a steady rise in conversion was observed, which was lowered towards the end of the reaction time (Figure 5.15). No further samples were taken after 7 hours owing to time constraints when using the microwave reactor, therefore comparative samples could not be taken. An example of NMR analysis is also provided (Appendix 23).

The slow rate of reaction observed throughout the reaction time may be a consequence of applying a 1 : 1 ratio of monomer:solvent. Initially the experiments to produce block copolymers involved using bulk conditions, which offered the simplest reaction system with fewer reactants. However it was observed that the amount of macro-RAFT agent required did not dissolve in the small volume of monomer, therefore the presence of a solvent was required to ensure a single phase system at the start of the reaction. Toluene was chosen as it had been successfully used in the previous RAFT polymerisations for vinyl acetate, using a 1 : 1 ratio which was sufficient to ensure effective mixing of the reactants. Additionally, dielectric

analysis carried out previously had confirmed toluene would not interfere with any effects as a result of selective heating when applying microwave energy.

However the use of a solvent meant that there was an additional component in the mixture that was not directly involved in the reaction, which could lower the rate of propagation and introduce side reactions such as chain transfer,[46] therefore producing a polymer with a low final conversion. Further analysis can be carried out when studying the GPC data (Figure 5.16).

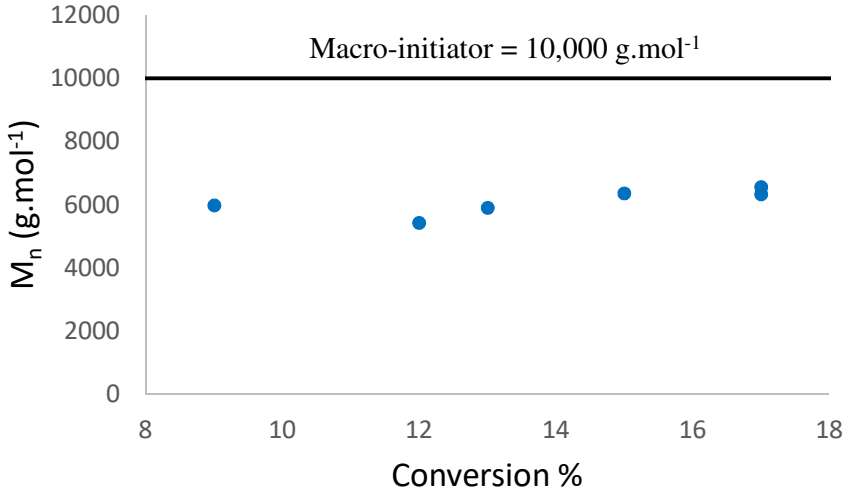


Figure 5.16 - GPC analysis for PVAc-PVPi product when applying conventional heating using PVAc-macro RAFT agent produced using conventional heating

Figure 5.16 indicated that there was little change to the molecular weight throughout the course of the reaction, in contrast to the homopolymer RAFT synthesis of PVAc, where conversion and molecular weight demonstrated a linear growth relationship as was expected. A more in-depth analysis can be determined when studying the data from the GPC (Table 5.2).

Table 5.2 - GPC data for PVAc-PVPi product when applying conventional heating using PVAc-macro RAFT agent produced using conventional heating. Macro-RAFT agent = 10,000 g.mol^{-1}. Macro-RAFT agent = 10,000 g.mol^{-1}

Conversion % [a]	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
9	14,600	6,000	1.71
12	15,900	5,400	2.03
13	16,500	5,900	1.97
15	17,700	6,400	1.89
17	18,400	6,300	2.02
17	18,500	6,600	1.96

[a] Calculated from NMR, an example is shown in Equation 5.1

[b] Calculated using Equation 5.3; $$M_{n,theo} = \frac{[M]_0 - [M]_t}{[RAFT]_0} \times m_M + m_{RAFT}$$

where: $[M]_0$ = initial monomer concentration, $[M]_t$ = monomer concentration at time t, $[RAFT]_0$ = initial RAFT agent concentration, m_M = molecular weight of monomer and m_{RAFT} = molecular weight of RAFT agent

[c] Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

There was a noticeable difference between the theoretical values and those measured by GPC, as well as broad dispersity values, implying a low degree of control (Table 5.2). However a complete loss of control from the RAFT agent would have produced a standard free radical

polymerisation reaction profile and produced high molecular weight polymer, therefore it appeared the presence of the PVAc macro-RAFT agent had a limited degree of control over the growth of the PVPi polymer chains. A more in-depth analysis requires studying the overlap of the final block copolymer peak with the macro-RAFT agent from GPC (Figure 5.17).

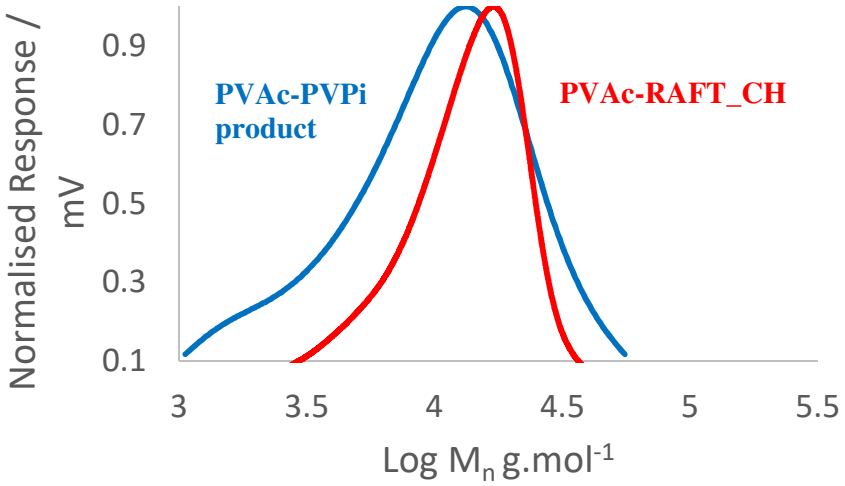


Figure 5.17 – GPC peaks for the PVAc-PVPi product when applying conventional heating and the PVAc macro RAFT agent produced using conventional heating

The broad dispersity was expected as the macro-RAFT agent itself had a dispersity of 1.48, which is high for a controlled polymerisation, implying that there were fewer chains which had the RAFT end functionality required for the growing of the 2nd PVPi block. This was proven by the broad dispersities measured (Table 5.2), confirming there was limited control for the growth of the 2nd polymer block.

Another factor influencing the large dispersity values observed throughout this reaction was the high concentration of initiator used, as previous work had indicated a small amount of initiator minimised the amount of homopolymer impurity producing while forming the 2nd

polymer block.[14] However in order to ensure consistency with previous work throughout this study, the ratio for the RAFT : V-70 was set to 2.5 : 1 and therefore resulted in introducing a high concentration of radicals, increasing the number of termination interactions and consequently producing more 'dead' polymer chains.

DSC analysis was employed to provide additional confirmation for the successful synthesis of a diblock copolymer. The presence of two distinct T_g values in the final polymer product would potentially indicate a well-defined internal morphology with distinct phase separation of the blocks, however the GPC data was still required for confirmation. Each block copolymer throughout this study was produced similar graphs during the DSC analysis to the standard example shown (Figure 5.14), with the presence of two T_g values, although it is a possible that this is a result of two homopolymers being present. The first T_g value at 30 °C was attributed to the PVAc-macro RAFT agent, while a second T_g value was observed at approximately 65 °C. This second peak could derive from the PVPi homopolymer, however the value measured was lower than would be expected (~86 °C). The PVPi present within the block copolymer chains may be affected by inter or intra molecular interactions, which would cause the T_g value to be lowered.

Once the polymer had been precipitated in the methanol:water mixture, it was then possible to calculate the ratio of PVPi : PVAc in the block copolymer chains using an NMR spectrum (Figure 5.12) and applying the subsequent calculation required (Equation 5.2). The ratio was measured as 1 : 1.82, compared to a theoretical ratio calculated of 1 : 1.52 using the final M_n value in Table 5.2. This ratio indicated a small PVPi block, as was expected with the low level of conversion produced within the reaction time.

The next reaction was designed to determine the influence of microwave heating towards the kinetic synthesis of the PVPi block (Figure 5.18).

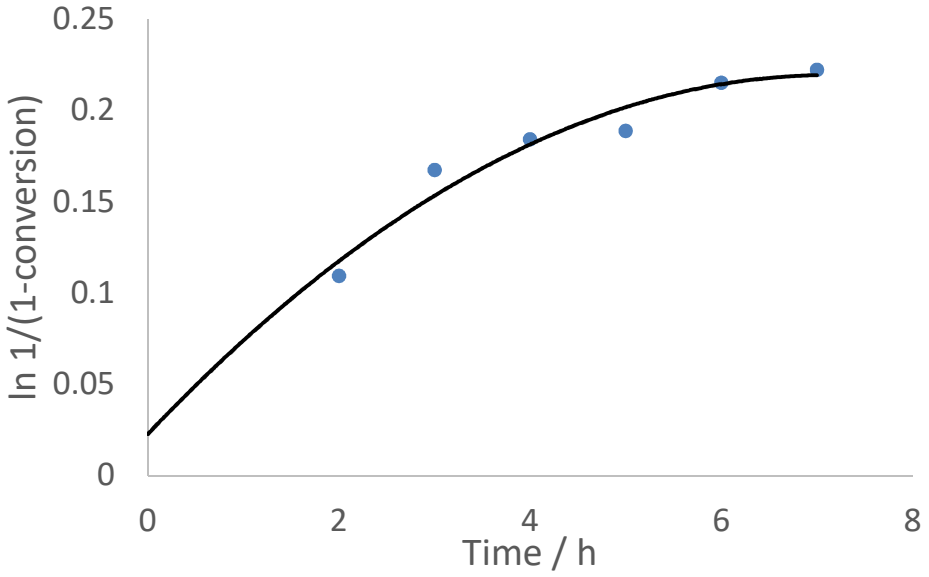


Figure 5.18 – Conversion over time for PVAc-PVPi block when applying microwave heating and the PVAc-macro RAFT agent produced using conventional heating. A polynomial curve demonstrates the very gradual rise in conversion over time

The trend for the rise in conversion (Figure 5.18) was observed to be almost identical compared to that when using conventional heating, with no indication of any acceleration for the rate of polymerisation. The reaction mixture itself had been observed to be highly microwave absorbent, as analysis of initial reactions using microwaves had produced little to no polymer after 7 hours. This was attributed to a temperature overshoot in the early stages of the reaction, which resulted in 'initiator burn-out'; where the rapid radical production results in self-termination and therefore does not initiate propagation of the monomer molecules. This overshoot was a consequence of applying the maximum 300 W of power at the start of the reaction in attempt to rapidly reach the desired reaction temperature, which was subsequently lowered to 50 W.

This high absorbance of microwaves could potentially have produced 'hot radicals', a theory which has been detailed previously in this study regarding microwave heating for the RAFT polymerisation of vinyl acetate (Chapter 3). However the exact cause for this rapid temperature rise when using 300 W of power cannot be determined without the relevant dielectric data, where each reactant present would be analysed in order to determine whether they could effectively absorb and re-emit the microwave energy as heat.

No significant increase in the polymerisation rate of PVPi was induced when using microwave heating, as was also observed when using a 1 : 1 ratio of monomer:solvent for the solution RAFT polymerisations of PVAc (Chapter 3). These previous studies for the formation of PVAc homopolymer used a solvent to lower viscosity and ensure effective mixing. However it was determined that a minimal volume of solvent compared to the monomer, in an 8:1 ratio, was required to enhance the reaction rate when using microwaves while also maintaining the desired control over molecular weight and the dispersity.

Another variance compared to the synthesis of PVAc homopolymer was the RAFT controlling agent that was used. Dielectric analysis in Chapter 3 had confirmed that the xanthate RAFT agent used to produce the PVAc homopolymer could undergo dielectric heating when exposed to microwave energy. It is possible that the PVAc macro-RAFT agent is not capable of efficiently absorbing microwaves, therefore decreasing the probability of inducing an acceleration.

Another difference between the two heating methods applied for synthesising the PVPi was observed when studying the GPC data (Figure 5.19).

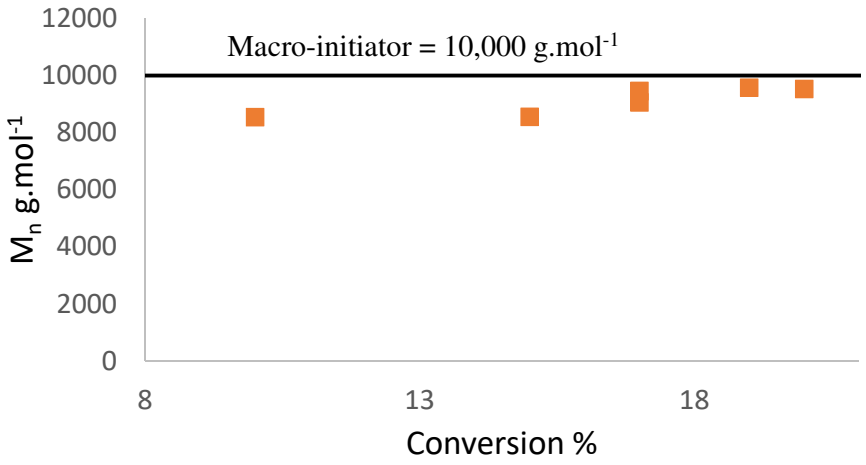


Figure 5.19 - GPC analysis for PVAc-PVPi product when applying microwave heating using PVAc-macro RAFT agent produced using conventional heating

The GPC data (Figure 5.19) appeared to show little difference compared to using conventional heating, as the molecular weight was still largely unchanged throughout the reaction time. However, a more significant change can be seen when looking at Table 5.3.

Table 5.3 – GPC data for PVAc-PVPi product when applying microwave heating using PVAc-macro RAFT agent produced using conventional heating. Macro-RAFT agent = 10,000 g.mol^{-1}

Conversion % [a]	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
10	15,200	8,500	1.36
15	17,700	8,600	1.46
17	18,400	9,100	1.44
17	18,600	9,500	1.4
19	19,600	9,600	1.46
20	19,900	9,500	1.5

[a] Calculated from NMR

[b] Calculated using Equation 5.3;

[c] Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

The higher molecular weight values implied that a larger number of chains present in the reaction mixture have formed block copolymers compared to using conventional heating. This was supported by the lower dispersity values than those measured in Table 5.2, potentially indicating a lower amount of homopolymer impurity from PVPi. However, after 17 % conversion, the observed broadening of the dispersity indicates a lack of control over the

polymerisation in the latter stages. The difference between the $M_{n,th}$ and experimental M_n was also proven to increase as the conversion rose.

Overlapping the GPC peaks of the PVPi block synthesised in the microwave reactor with the PVAc macro-RAFT agent provides further confirmation of the differences in comparison to using conventional heating methods.

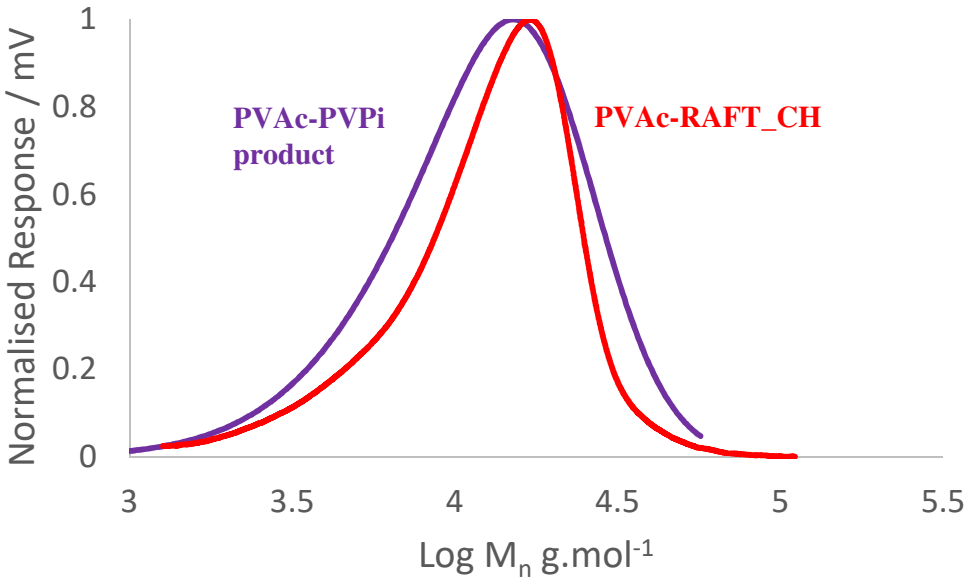


Figure 5.20 - GPC peaks for the PVAc-PVPi product when applying microwave heating and the PVAc macro RAFT agent produced using conventional heating

The narrower GPC peak (Figure 5.20) compared to using conventional heating for the PVPi block (Figure 5.17) confirmed the lower dispersity value for the final block copolymer when applying microwave heating. This therefore implying a higher degree of control for the RAFT polymerisation, as was also observed when producing PVAc homopolymer using microwaves.

Two T_g peaks were observed in the DSC analysis at 30 °C and at 65 °C, identical to those seen when using conventional heating; this would appear to confirm the presence of block copolymer for this reaction.

Using Equation 5.2 from the NMR analysis of the final precipitated polymer, the PVPi : PVAc ratio was determined to be 1 : 1.4, compared to a 1 : 1.05 ratio based on the experimental GPC data. The ratio measured implicated the two blocks were of similar size in the final polymer chain. This demonstrated that, while no acceleration of the polymerisation rate was observed, analysis of the data had highlighted other benefits from the application of microwave heating while synthesising the PVPi block.

Several alterations were made to the experimental procedure when utilising CO_2 during synthesis, as previous work for the RAFT polymerisations of vinyl acetate had shown that applying a high monomer loading led to increased conversion levels. To ensure these experiments were comparable to the production of PVAc in CO_2 (Chapter 4), 11 ml of PVPi was used. All other aspects of the reaction conditions such as the RAFT : initiator ratio were unchanged.

Data from the CO_2 reactions was far more limited, as the highly soluble nature of both the monomer and polymer in CO_2 prevented any kinetic samples being taken throughout the reaction time. The calculation for the final conversion was also affected when using CO_2, as the venting process removed any unreacted vinyl pivalate monomer still present. While this is advantageous to obtain a purer polymer product, it was not possible to calculate conversion from NMR analysis. Therefore the gravimetric yield of the final precipitated polymer was used as shown in Table 5.4.

Table 5.4 – Yield and GPC data for PVAc-PVPi product while applying CO_2 and the PVAc macro RAFT agent produced using conventional heating. Macro-RAFT agent = 10,000 g.mol^{-1}. Macro-RAFT agent = 10,000 g.mol^{-1}

Gravimetric Yield / % [a]	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
24	22,300	18,600	1.21

[a] Calculated after precipitation into methanol : water mixture

[b] Calculated using Equation 5.3

[c] Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

The reaction produced a moderate yield within the 7 hour reaction time, whereas using similar reaction conditions to produce PVAc homopolymer showed little/no conversion after 24 hours. The only differences between the reactions were the monomer and the use of a polymer macro-RAFT agent for the PVPi block. Both monomers have similar reactivity, therefore the use of the polymer macro-RAFT agent could be influencing the polymerisation process.

The application of a polymer macro-RAFT agent has a significant impact on reaction kinetics, as it removes one of the slowest steps in a RAFT polymerisation; the addition of the RAFT agent to the polymer radicals.[14] The slow nature of this step can result in induction periods where no polymerisation occurs, which is more commonly observed when using highly reactive monomers such as vinyl acetate, as the RAFT agents have low chain transfer constants in order to control polymer chain growth.[45] Using a macro-RAFT agent eliminates this step

and therefore will have increased the rate of reaction for the polymerisation in CO_2. The presence of PVAc may also have increased the solubility of the RAFT agent, meaning it could work more effectively during the reaction.

The gravimetric yield shown in Table 5.4 indicated an increase in the polymer yield compared to using conventional and microwave heating. This was a result of the low viscosity of the mixture when using CO_2 which increased diffusivity of the reactants, and could potentially lead to an increase in polymerisation rate. The reaction conditions were also optimised further compared with the other reactions by using a larger volume of monomer to obtain higher conversion levels.

However, as with the other experiments for synthesising the PVPi block, the final yield obtained (Table 5.4) was noticeably lower compared to the reactions of vinyl acetate within the same time period. The effect of CO_2 on various aspects of the polymerisation such as initiator efficiency implies numerous possibilities for the differences observed. Further experiments would need to be planned to determine the exact cause for the varying polymerisation rates.

The M_n measured using GPC was observed to be noticeably higher than those measured using either conventional or microwave heating (Table 5.4), as well as good agreement compared to the theoretical molecular weight value calculated from the polymer yield. This suggested a higher proportion of block copolymer chains was produced in this reaction, as indicated by previous work into block copolymer synthesis in CO_2, where an increase in the blocking efficiency reduced the level of homopolymer impurity.[41]

A possible explanation for these improved results is that the application of high pressure slowed the rate of irreversible radical-radical termination, leaving a larger number of chains being controlled by the RAFT process.[47] This is supported by the narrow dispersity value measured,

indicating the presence of a small amount of homopolymer impurity. Further confirmation of the results when applying CO_2 was found when analysis the overlapping GPC peaks (Figure 5.21).

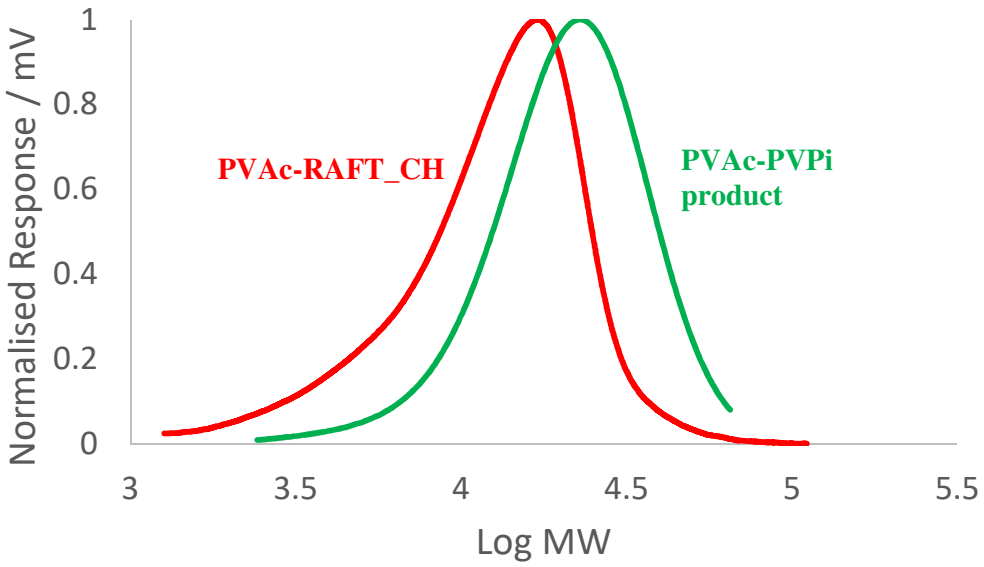


Figure 5.21 - Comparison of PVPi block synthesised in CO_2 with macro-RAFT agent showed the absence of low molecular weight polymer in PVPi

The higher molecular weight and narrow dispersity observed (Figure 5.21) both implied a higher proportion of chains were controlled by the macro-RAFT agent to form block copolymer. These numerous factors supported findings which had shown that the use of CO_2 as a reaction medium meant a higher blocking efficiency when forming the PVPi block, resulting in a much larger proportion of the chains forming block copolymers compared to using either conventional or microwave heating. As with the other reactions, the two T_g values were observed at 30 °C and 65 °C, providing further evidence that the forming of a block copolymer had been successful.

The calculated ratio of PVPi : PVAc from NMR analysis was found to be 1.47 : 1, compared to a 2.23 : 1 ratio based on the final M_n from the GPC analysis. This confirmed the presence of

a larger PVPi block in the final copolymer compared to PVAc, highlighting further differences compared to the experiments with conventional and microwave heating.

5.3.3 Block copolymers synthesised with microwave macro-RAFT agent

One of the aims for these experiments was to observe whether the macro-RAFT agent produced using microwaves demonstrated a higher degree of control over the growth of the 2nd PVPi block. When using microwave heating, the final macro-RAFT agent had lower values for molecular weight and dispersity, which implied a high number of polymer chains had retained the RAFT end group functionality, and should therefore produce a higher quality block copolymer. This initial experiment examined using conventional heating to produce the PVPi second block (Figure 5.22).

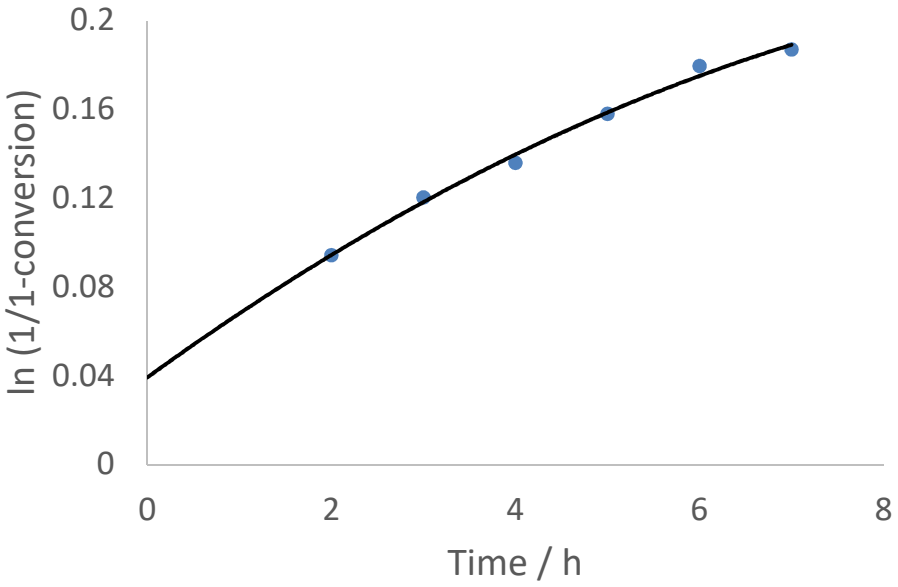


Figure 5.22 - Conversion over time for PVAc-PVPi block when applying conventional heating and the PVAc-macro RAFT agent produced using microwave heating. A polynomial curve demonstrates the very gradual rise in conversion over time

The rise in conversion observed appeared to show an almost identical trend compared to the first macro-RAFT agent used. This was as expected as no reaction conditions influencing the effecting the polymerisation rate, such as temperature or the RAFT : V-70 ratio, were altered when using the macro-RAFT agent produced using microwave heating. The GPC data also confirmed virtually no change in the molecular weight values over time (Figure 5.23).

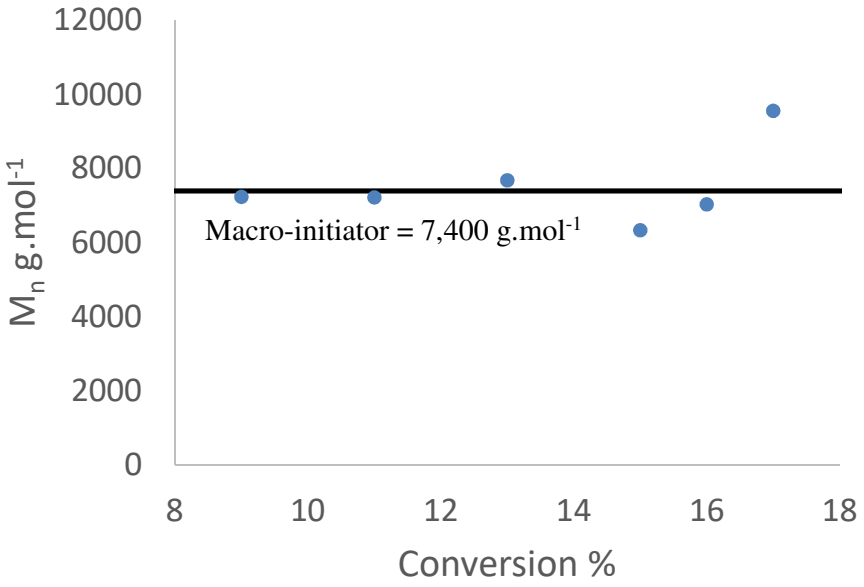


Figure 5.23 – GPC analysis for PVAc-PVPi product when applying conventional heating using PVAc-macro RAFT agent produced using microwave heating

As with the other macro-RAFT agent, it appeared that there was virtually no change in the molecular weight value for the polymer throughout the course of the reaction time. Further analysis of the reaction can be derived when looking at Table 5.5, which summarises the GPC analysis over time.

Table 5.5 – GPC data for PVAc-PVPi product when applying conventional heating using PVAc-macro RAFT agent produced using conventional heating. Macro-RAFT agent = 7,400 g.mol^{-1}

Conversion / % [a]	M_n / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
9	11,500	7,200	1.48
11	12,600	7,200	1.60
13	13,200	7,700	1.60
15	14,100	6,300	1.89
16	14,900	7,000	1.80
17	15,200	9,600	1.43

[a] Calculated from NMR

[b] Calculated using Equation 5.3;

[c] Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

The experimental M_n values measured (Table 5.5) showed an improved agreement with the theoretical calculation compared to the previous results with conventional heating (Table 5.2), as well as a majority of the kinetic samples showing narrower dispersities. The improved retention of the RAFT end functionality in the PVAc macro-RAFT agent appeared to

demonstrate a higher degree of control over the growth of the PVPi block. This was also observed when analysing the overlapped GPC peaks (Figure 5.24).

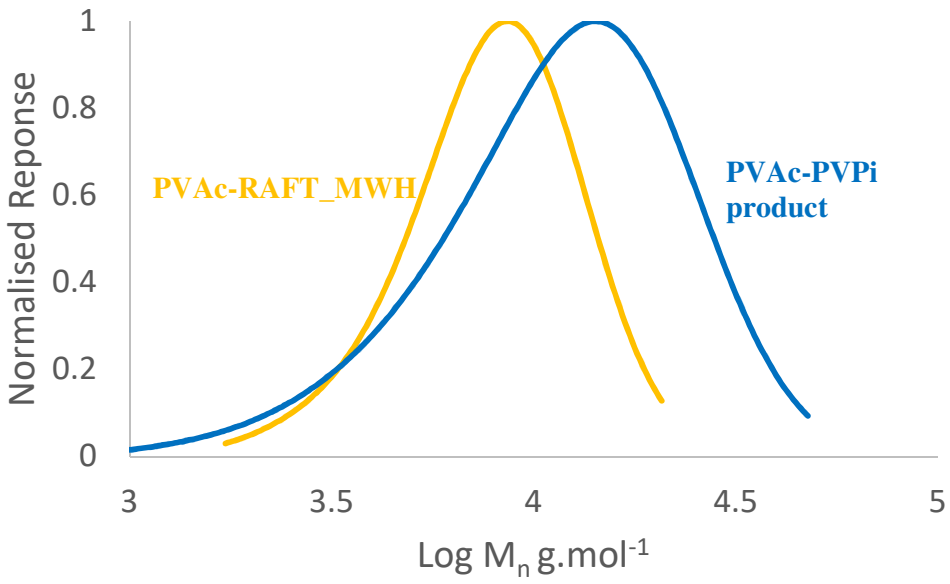


Figure 5.24 - GPC peaks for the PVAc-PVPi product when applying conventional heating and the PVAc macro RAFT agent produced using microwave heating

There was a noticeable reduction in lower molecular weight material with the microwave synthesised macro-RAFT agent in the final block copolymer. This implied that, while PVPi homopolymer was still present, the amount produced during the reaction had been reduced compared to the previous reaction using conventional heating (Figure 5.17). Therefore the use of the macro-RAFT agent synthesised using microwaves demonstrated improved control over the block copolymer synthesis.

The PVAc : PVPi ratio calculated from NMR was 1.32 : 1, however the experimental ratio from the GPC values was 1 : 1.3 ratio, indicating a larger PVPi block in the final copolymer. The ratio from NMR showed a significant difference compared to the first macro-RAFT agent

used, as was expected since the macro-RAFT agent synthesised using microwaves had a noticeably lower molecular weight. The final M_n value was also higher for the PVPi block than had been observed in the previous reaction with conventional heating, therefore a change in the block copolymer ratio would be expected. The NMR analysis used to calculate the block copolymer ratio is provided (Appendix 24).

Microwave heating was also examined for producing the PVPi block with the other PVAc macro-RAFT agent.

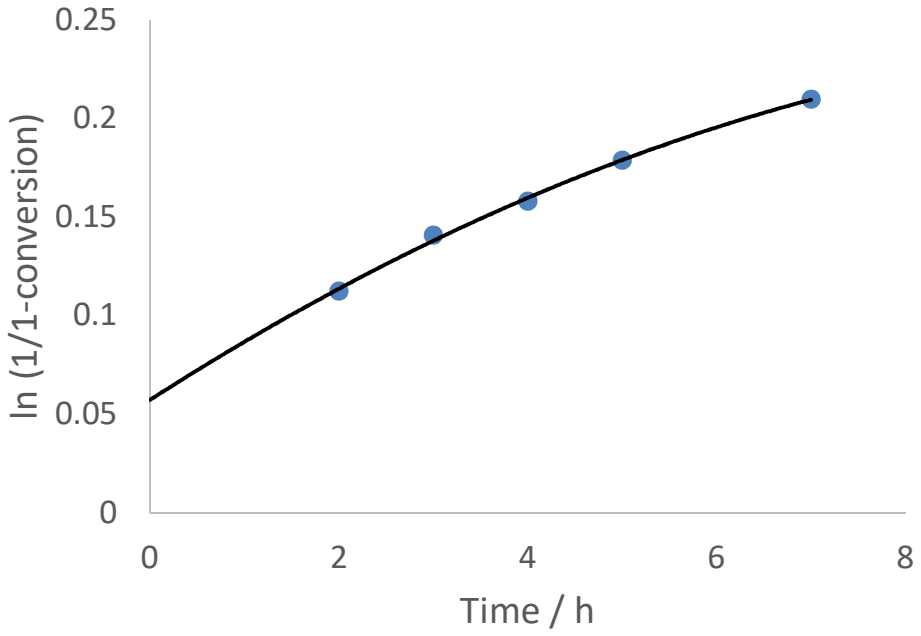


Figure 5.25 – Conversion over time for PVAc-PVPi block when applying microwave heating and the PVAc-macro RAFT agent produced using microwave heating. A polynomial curve demonstrates the very gradual rise in conversion over time

There was virtually no difference in the rate of conversion (Figure 5.25) compared to using the first macro-RAFT agent with microwave heating, as expected. The experimental M_n values over time were also observed to be similar to those seen previously (Figure 5.26).

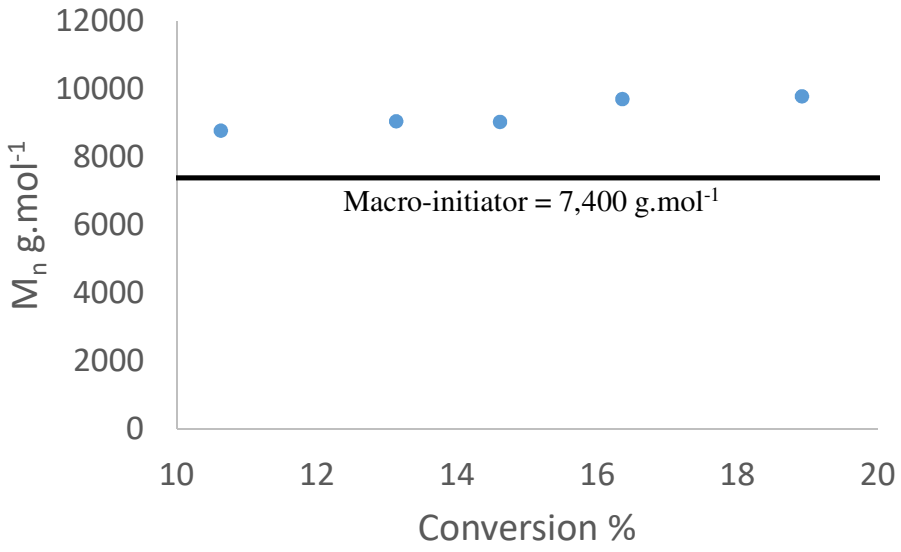


Figure 5.26 - GPC analysis for PVAc-PVPi product when applying microwave heating using PVAc-macro RAFT agent produced using microwave heating

The molecular weights of the material produced throughout the reaction appeared to be almost unchanged. There was also little difference between these results and those applying microwave heating for the PVPi block while using the conventionally produced macro-RAFT agent. The table of results summarised the findings for the PVPi block produced with microwaves (Table 5.6).

Table 5.6 – GPC data for PVAc-PVPi product when applying microwave heating using PVAc-macro RAFT agent produced using conventional heating Macro-RAFT agent = 7,400 g.mol^{-1}

Conversion % [a]	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
11	12,243	8,800	1.39
13	13,383	9,100	1.44
15	14,059	9,000	1.48
16	14,855	9,700	1.46
19	16,023	9,800	1.51

[a] Calculated from NMR

[b] Calculated using Equation 5.3;

[c] Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

The use of microwave heating appeared to have little effect on the values measured using GPC for the final block copolymer compared to those observed for conventional heating (Table 5.5). This demonstrated that the selection of macro-RAFT agent had a significant influence on the properties of block copolymer. The improved control provided by using a macro-RAFT agent with a high retention of the RAFT end group functionality resulted in the heating method having less influence for the synthesis of the PVPi block. Overlapping the peaks also demonstrated the influence of using a different PVAc macro-RAFT agent (Figure 5.27).

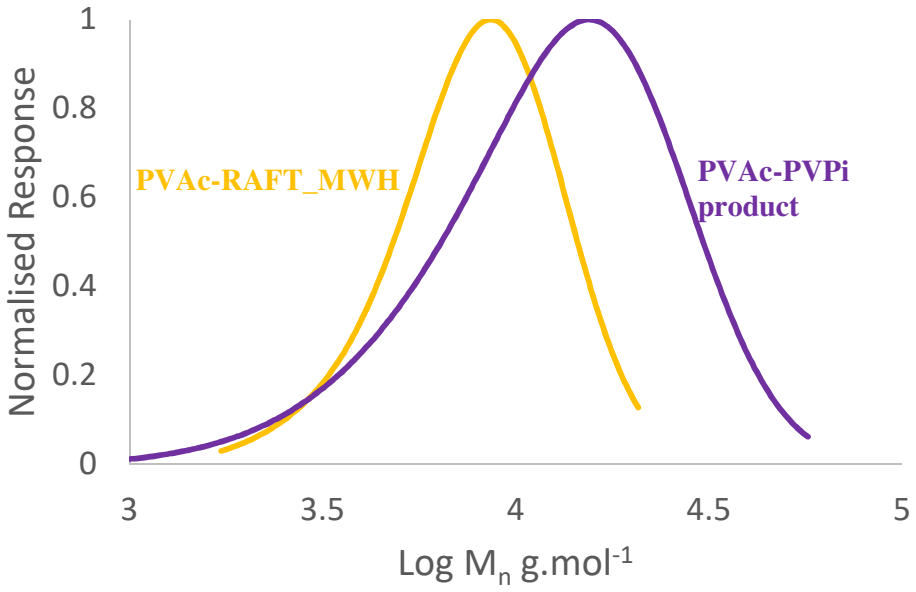


Figure 5.27 - GPC peaks for the PVAc-PVPi product when applying microwave heating and the PVAc macro RAFT agent produced using conventional heating

As observed with conventional heating, there appeared to be a reduction in the amount of low molecular weight material produced, which would indicate a higher degree of control from the PVAc macro-RAFT agent. However the rising dispersity as the reaction progressed suggested there was still some homopolymer impurity present.

The ratio of PVAc : PVPi from NMR was 1.13 : 1 compared to 1 : 1.32 from the experimental GPC data. As mentioned previously, the M_n values shown (Figure 5.26) were very similar to those using the first macro-RAFT agent when applying microwave heating, however the lower molecular weight for the macro-RAFT synthesised with microwaves resulted in the block copolymer ratio being altered.

The macro-RAFT agent synthesised was also used for growing the 2nd PVPi block in the CO_2 autoclave (Table 5.7)

Table 5.7 – Yield and GPC data for PVAc-PVPi product while applying CO_2 and the PVAc macro RAFT agent produced using conventional heating. Macro-RAFT agent = 10,000 g.mol^{-1}. Macro-RAFT agent = 10,000 g.mol^{-1}

Gravimetric Yield %	$M_{n,th}$ / g.mol^{-1} [b]	M_n / g.mol^{-1} [c]	Đ [c]
24	17,900	15,200	1.65

[a] Calculated from NMR

[b] Calculated using Equation 5.3;

[c] Experimental M_n and Đ obtained from GPC-RI detector using PMMA standards.

The results with the CO_2 experiments showed almost no difference compared to using the conventionally produced macro-RAFT agent, as Table 5.7 confirmed that the conversion and molecular weight results measured were very similar to the previous CO_2 experiment. Even the calculated block copolymer ratio from NMR of 1 : 1.46 for PVAc : PVPi was virtually unchanged, although GPC suggested a much larger PVPi block with a ratio 1 : 2.05. One difference observed was the improved agreement between the experimental and theoretical molecular weight values, indicating a higher degree of control when using the PVAc macro-RAFT agent produced with microwaves. However, the dispersity was observed to be higher than with the macro-RAFT agent produced using conventional heating, which may imply that a higher proportion of PVPi homopolymer was produced. Further analysis was derived from studying the overlapped GPC peaks (Figure 5.28). NMR analysis used for the block copolymer ratio and DSC data are provided (Appendix 25 and 26).

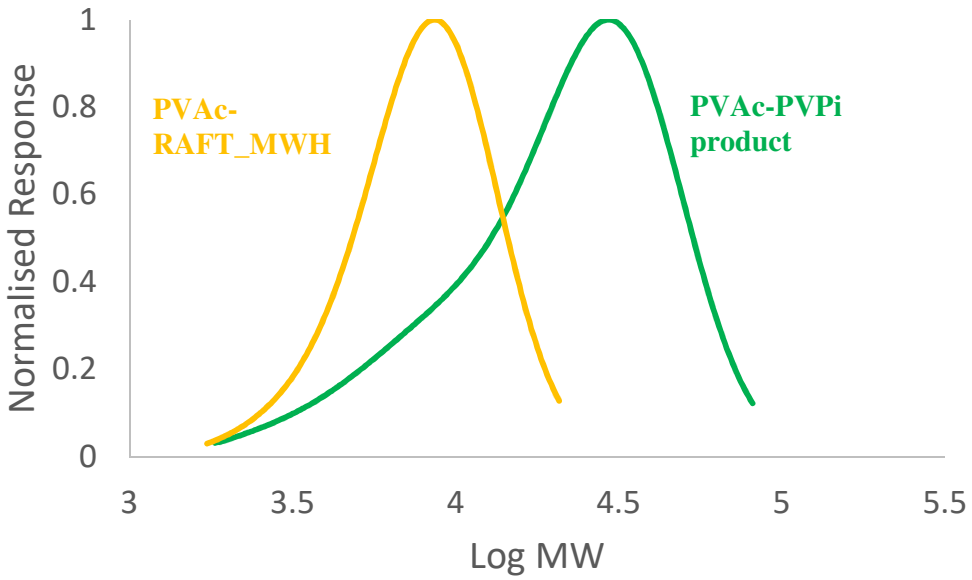


Figure 5.28 - Comparison of PVPi block synthesised in CO_2 with macro-RAFT agent showed the absence of low molecular weight polymer in PVPi

The GPC final polymer peaks with the macro-RAFT agent produced using microwave heating (Figure 5.28) showed only a small amount of overlap. The broader dispersity measured (Table 5.7) was unexpected as both conventional and microwave reactions demonstrated improved control for PVPi with the second macro-RAFT agent synthesised using microwaves. However, the use of CO_2 still demonstrated closer agreement between the theoretical and experimental molecular weight values for the 2nd PVPi block compared to both conventional and microwave heating.

5.4 **Conclusions**

These are only preliminary results regarding the production of block copolymers, but early indications suggested that the use of microwaves was able to provide better control compared to conventional heating methods, as shown by the lower dispersities measured using GPC. However, the acceleration of the polymerisation rate with microwaves seen with the RAFT polymerisation of PVAc was not observed. The application of CO_2 as the reaction medium was proven to produce narrow dispersities, good agreement between the experimental and theoretical M_n values and a high proportion of macromonomer is successfully inserted when synthesising the PVPi block.

The choice of synthesis technique for producing macro-RAFT agent was also demonstrated to have a significant influence over the properties for the final block copolymer. The PVAc produced with microwave heating had lower molecular weight and dispersity values than that produced when using an oil bath for temperature regulation, which consequently led to improved control and lowered the amount of hompolymer impurity formed when applying either microwave or conventional heating for synthesising the second PVPi block.

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Chapter 6 – Conclusions and Future Research

6.1 Microwave Heating and RAFT

The work in Chapter 3 determined that the RAFT : initiator ratio had a significant influence over the polymerisation process when comparing the use on microwave heating to conventional heating. A high initiator concentration in a 2.5:1 ratio of RAFT:V-70 was found to be vital to induce the acceleration seen when using microwave heating. However, it was observed that there was a limit to the magnitude of this effect which was proposed to be as a result of the initiator could led to an increase in termination. For example using the 1:1 ratio was observed to led to high dispersity values for both heating techniques. The general conclusion was that the use of microwaves produced an accelerated reaction rate while maintaining the desired level of control, as well as having reproducible results, as proven by the small degree of error.

An additional discovery was the importance of using an appropriate solvent, as well as controlling the level of solvent for these microwave heated polymerisations. The results from the bulk RAFT reactions showed only a minor increase in reaction rate when using microwaves, even when a 2.5:1 ratio for RAFT : initiator was adopted. It was only after introducing toluene as a solvent that a significant increase in the polymerisation rate was observed when applying microwave heating, therefore confirming that molecular mobility was a key factor in inducing an acceleration. However a minimal volume of toluene was needed, otherwise this acceleration effect was diminished. This was attributed to the stored energy introduced to the selectively heated species *via* the microwave energy was being dissipated into the solvent as heat rather than being focused into driving a chemical transformation.

Further research is required in order to understand the exact cause for this observed increase in reaction rate. One step to understanding this would be continuing analysis using dielectric data. Currently, each reactant has been individually studied to determine which were microwave absorbent species, and this data would suggest that it is the selective heating of both the transient radical and the RAFT agent that leads to the acceleration observed in the polymerisation. However, this does not give an entirely accurate representation of how the reaction mixture is heated/excited as it does not reveal how the reaction systems species interact with the incident energy when the radical and/or RAFT agent are attached to a growing polymer chain. Thus, analysing how various reaction mixtures behave in the electric field could potentially confirm observed trends, such as how decreasing the level of solvent caused a greater acceleration of the reaction rate when using applying microwave heating with the 2.5:1 ratio of RAFT : V-70.[1] For example, kinetic dielectric data could also give provide a more in-depth understanding of the reaction behaviour over time. At the starting point in the reaction, the radicals present would be mainly derived from the V-70 initiator and the vinyl acetate monomer. As more monomer is consumed, a higher proportion of the radicals would be in the form of polymer radical chains. Over time these chains will get increasingly longer, therefore it would be interesting to observe whether these radicals are still capable of effectively absorbing and remitting the microwave energy as heat.

This data could also provide an explanation as to why there are differing kinetic zones observed in the microwave heated RAFT polymerisation. These zones may simply result from differing reaction mixture conditions etc, changes in diffusion, viscosity. Alternatively it could indicate the onset of phase segregation as have been observed in start polymerisation studies.[2] Alternatively, it could be as a result of the altering system dielectric properties as the chains grow in length. A rigorous study of the dielectric properties of the entire reaction would provide

a greater understanding of the reaction mechanism, and therefore provide more substantial evidence as to why an acceleration of the polymerisation rate is induced.

Another area of future work would be related to broadening of this work in order to study microwave heated RAFT polymerisations of other monomers. It would be envisaged that this would be commenced by using the idealised reaction parameters defined from with study with other monomer which would be compatible with the same xanthate RAFT agent and initiator, such as vinyl pivalate. This could be used to indicate whether these conditions induce a similar degree of acceleration when using microwaves.[3] These optimal reaction parameters could also be applied to more active monomers (MAMs) such as methyl methacrylate. The difference in reactivity would mean the use of a suitable RAFT agent which would need analysing to determine whether it is microwave adsorbent.[4]

6.2 **Supercritical CO_2**

The work using CO_2 found that multiple factors had an influence over the polymerisation process involving the reagents and conditions studied. A high monomer loading was found to have a strong influence on the properties of the final polymer, leading to higher final yields and good agreement between the theoretical and experimental M_n values.[5, 6] Additionally, a high initiator concentration was observed to increase the polymerisation rate, but while also lowering the degree of control over molecular weight growth.

Kinetic studies examined the polymerisation over time when targeting 10,000 and 35,000 $g.mol^{-1}$ in CO_2. While both achieved high levels of conversion after a 24 hour period, the reaction profiles were noticeably different. Targeting 10,000 led to a faster initial rate of

reaction which slowed down significantly after 6 hours, whereas the reaction rate for 35,000 was relatively constant throughout the entire reaction time. Further repeat reactions are required to confirm these trends observed with the kinetic data correct and thus allow for an accurate comparison between the synthesis of PVAc homopolymer in CO_2 conducted by applying microwave heating and targeted 35,000 $g.mol^{-1}$. The key issues that was investigated when designing the CO_2 experiments were addressing the issues regarding rising viscosity levels. The $scCO_2$ polymerisations generally demonstrated a linear relationship between molecular weight and yield, which indicated that a high level of molecular mobility was retained and meant that the viscosity of the media were low even when a high volume of monomer was consumed. This was the desired result and so indicated that the experimental design had been successful.

Therefore being able to prove that consistent results are obtained when using CO_2 could lead towards reactions which would combine the application of CO_2 and microwave heating during the synthesis of PVAc homopolymer. This could potentially lead to optimum conditions that could utilise the acceleration induced with microwaves and retained control, with the high molecular mobility when applying CO_2 as a viscosity modifier. This would involve employing the 2 kW microwave cavity, as this would allow easiest access with regard to using a high pressure reaction vessel (Figure 6.1).

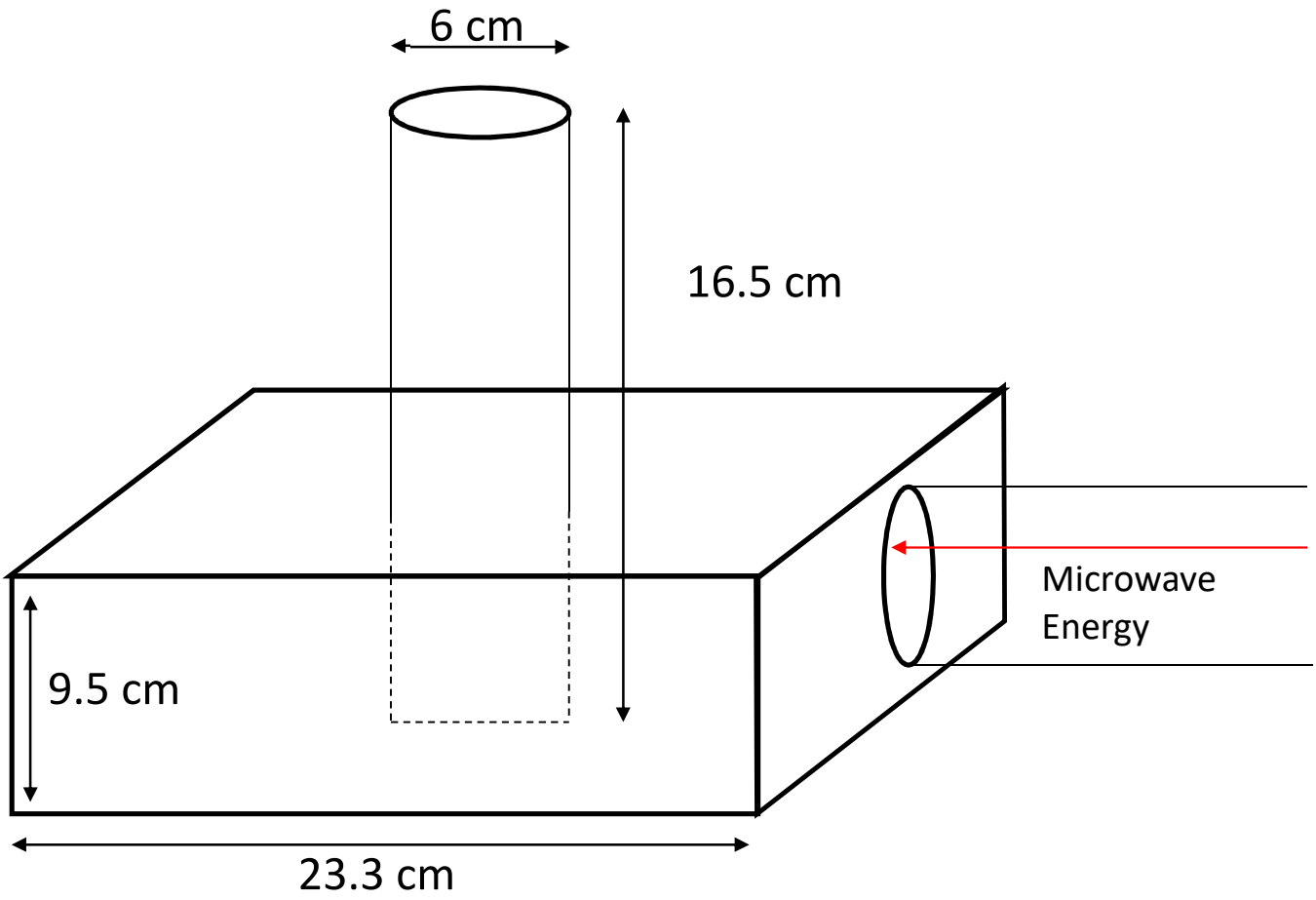


Figure 6.1 - Measurements from 2 kW microwave cavity required for production of microwave transparent high pressure autoclave.

Thus a further topic for future work would be building of a specialist autoclave to allow a combination of CO_2 and microwaves polymerisation during the production of PVAc. Dielectric analysis has proven that CO_2 is a microwave transparent substance, thus it will not interfere with any selective heating effects regarding accelerating the polymerisation rate with microwaves.[7] Therefore reactions in this autoclave could optimise the increase in reaction rate with a high level of control, as well as having low viscosity in order to obtain a high final yield. A significant level of collaborative work will be required for the design of the reaction vessel, which would have unique requirements in order to successfully accommodate the application

of microwave heating. A simple solution would be to build the base and component parts that will be exposed to microwave energy prom of Polyether Ether Ketone (PEEK). This polymer is transparent to microwave energy and therefore does not interfere with any selective heating effects, while also having the capability of withstanding the high temperature and pressures necessary to use CO_2. The use of a standard metal autoclave head will mean fewer custom made PEEK parts are needed and can therefore be easily replaced when necessary. A diagram demonstrating this is shown (Figure 6.2).

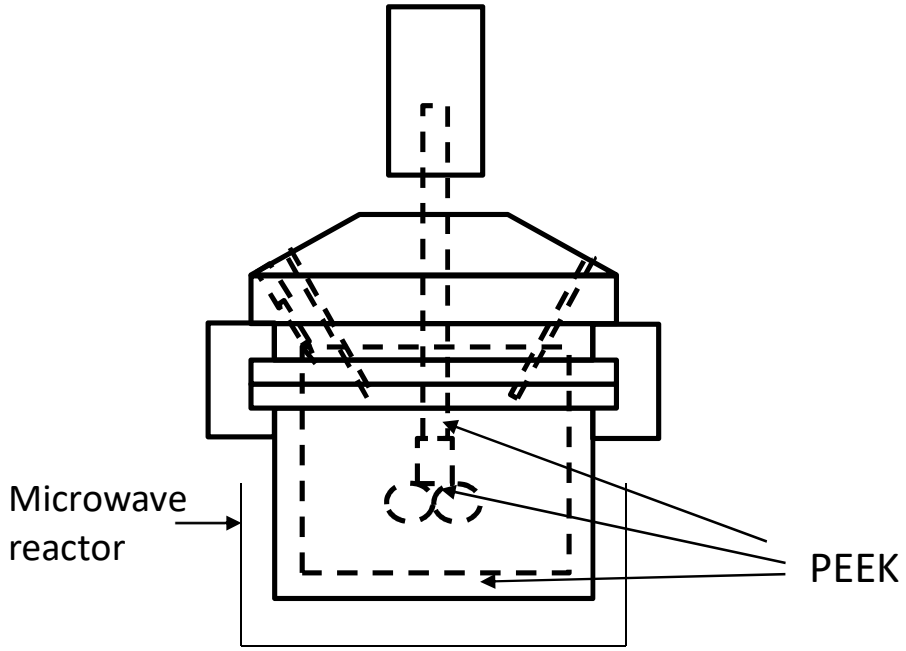


Figure 6.2 - A diagram of the CO_2-microwave autoclave inside the microwave reactor, which would utilise both PEEK and metal parts

The dimensions of the reactor will require a significant level of design effort as the required condition may lead a limited volume for the reaction mixture within the vessel. While the diameter of the tube in the 2 kW reactor is 6 cm (Figure 6.1), the thickness of the base wall in the PEEK autoclave required to withstand the high pressure for the reactions must be

considered, meaning the inner diameter will be smaller. Using a metal autoclave head also requires the height of the base for this autoclave to be a located outside the microwave cavity to prevent arcing, i.e direct large discharge of the energy to the reaction lid.

One issue that requires further consideration is the use of V-70 as the initiator. The experiments which demonstrated an induced acceleration of the polymerisation rate (Chapter 3) determined that a rapid radical production rate was required, therefore V-70 was used at 45 °C, providing a half-life time of 30 minutes. However when the same conditions were used in the high pressure autoclave (Chapter 4), virtually no polymer had been made even after 24 hours, therefore an alternative means of producing radicals quickly would be required. One possibility would be to continue using AIBN as had been done previously (Chapter 4), but with a high temperature (~80 °C) to decrease the initiator half-life time. It is possible that another initiator could be used for vinyl acetate, although this would require further research using CO_2 to determine a suitable alternative.

Furthermore, a greater understanding of the RAFT polymerisation in CO_2 could be gained by observing the reactions within the view cell. As has been mentioned previously (Chapter 4), PVAc is considered to highly soluble in CO_2 compared to a wide variety of other polymers, but the degree of solubility is limited as molecular weight increases. Observing the phase behaviour of the kinetic reactions targeting 10,000 and 35,000 $g.mol^{-1}$ using the view cell would confirm the point at which the polymer is no longer soluble in CO_2.[8-10] This could then subsequently be related to the molecular weight measured at this point, as well as the volume of monomer that is consumed.

6.3 **Block Copolymers**

The work with block copolymers found the use of microwave heating provided a higher degree of control when producing the PVAc macro-RAFT agent compared to conventional methods, which was reflected with subsequent the improved results for the 2 stage synthesis of the PVPi block. Narrower dispersities were also observed when producing the 2nd PVPi block with microwaves, however there was no indication of any induced acceleration as was seen for producing the PVAc homopolymer. The optimal results in producing a block were obtained. There was less discrepancy between the theoretical and experimental M_n values, narrower dispersities observed in the final polymer which indicated good control over the growth of polymer chains. There also appeared to be an efficient blocking efficiency, leading to a low amount of PVPi homopolymer impurity.

One aspect that should not be investigated is the use of varying levels of initiator. As mentioned previously (Chapter 5), in order to help reduce the amount of homopolymer when producing block copolymers a small amount of initiator is used compared to the RAFT agent, such as a 10:1 ratio of RAFT:V-70.[11] The use of a high initiator concentration for these PVAc-b-PVPi block copolymers was to induce a faster polymerisation rate for the 2nd block. However low levels of conversion were seen regardless of the method of polymerisation that was applied. Therefore reducing the initiator concentration could reduce the level of PVPi homopolymer while having a minimal influence on the final polymer conversion.

The potential use of a PVAc macro-RAFT agent produced in CO_2 could also be considered. When producing the PVPi block, the use of CO_2 was shown to produce the 2nd PVPi block with a low dispersity, indicating a high degree of control provided by the RAFT agent. It is possible that the use of CO_2 may also be successful for the macro-RAFT agent. If this could be done to

a high conversion level, it could be possible to add the vinyl pivalate monomer and additional initiator *in situ,* avoiding the need to depressurise the autoclave to produce a 2nd block.

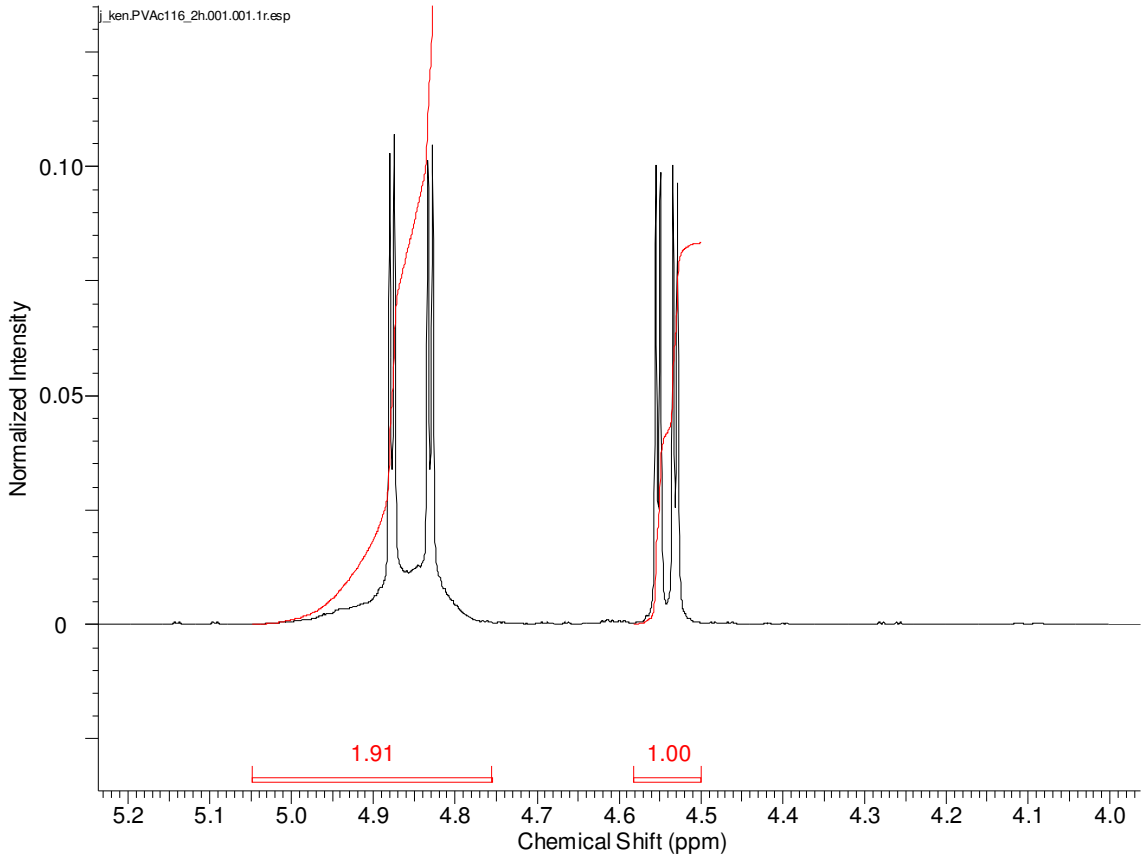
Another possible set of experiments would utilise the PEEK autoclave, which would be compatible with microwave heating. The use of microwave heating was capable of producing a low dispersity macro-RAFT agent which had a higher proportion of chains with end group functionality capable of growing a 2nd polymer block. While using CO_2 for the 2nd block was found to also have low dispersity, reduced homopolymer impurity and produced a higher final yield. A combination of these two effects could provide a high degree of control for the PVPi block, as well as the potential for a one pot synthesis to produce the block copolymer.

6.4 References

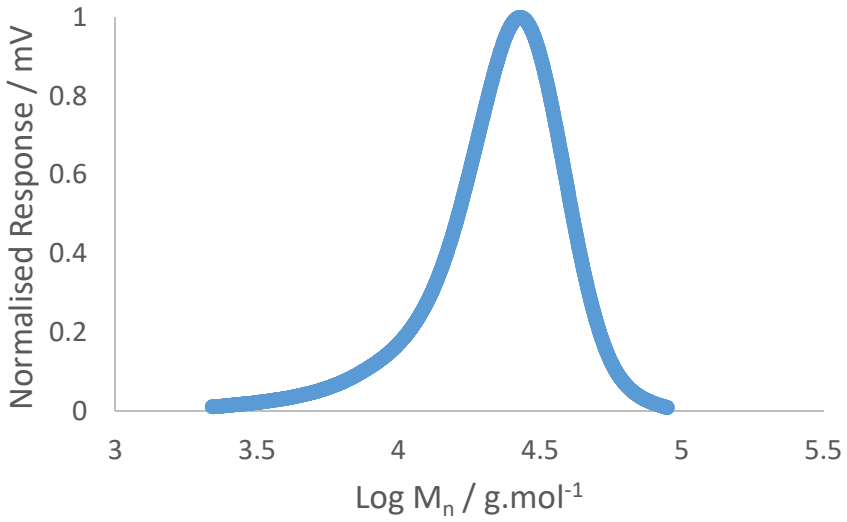
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Appendix

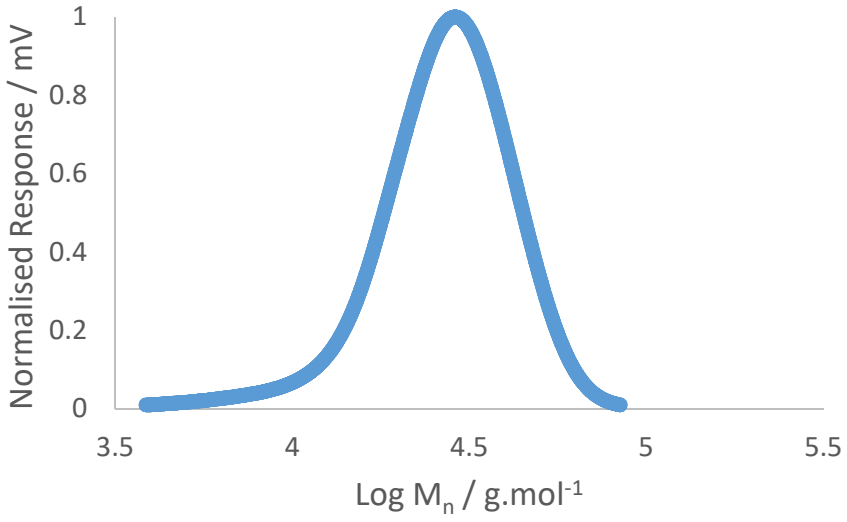
Appendix 1 – Chapter 3; NMR analysis 10:1 ratio RAFT:AIBN, 65°C, Conventional Heating, 2 hours



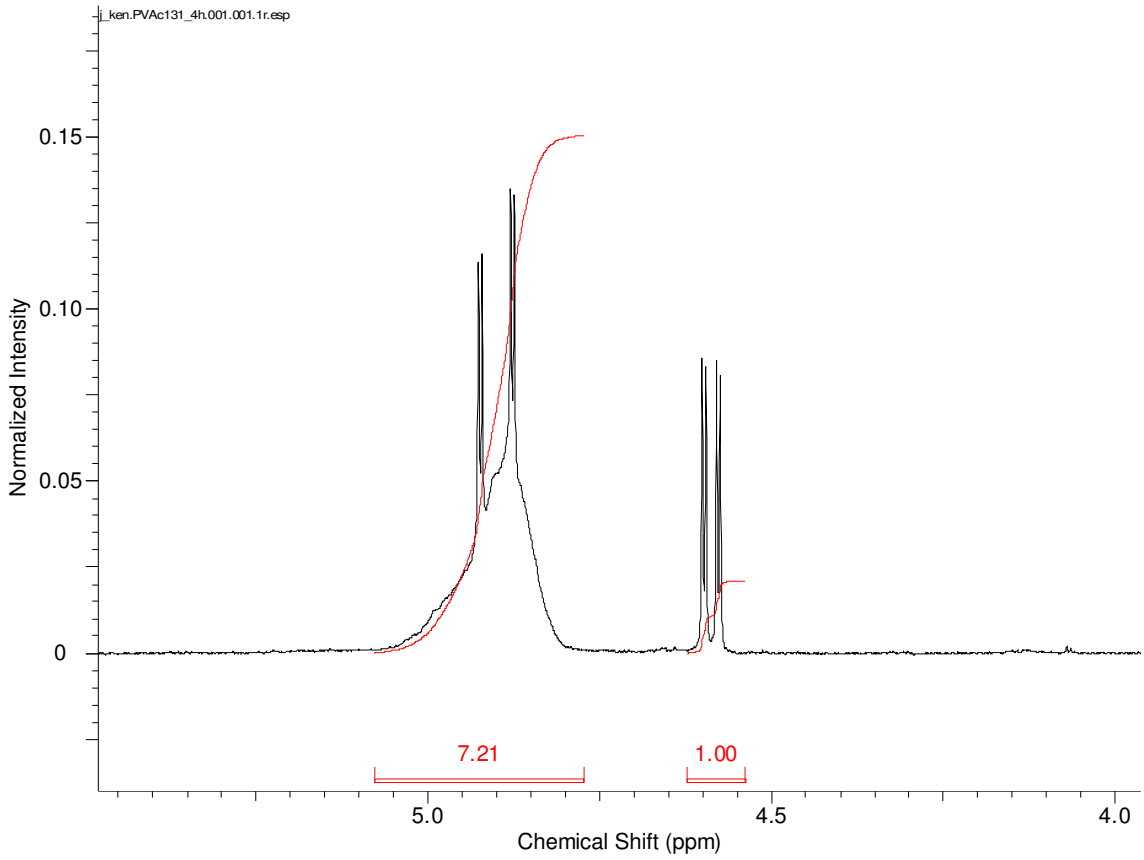
Appendix 2 – Chapter 3; GPC analysis 10:1 ratio RAFT:AIBN, 65°C, Conventional Heating, 2 hours, Đ = 1.37



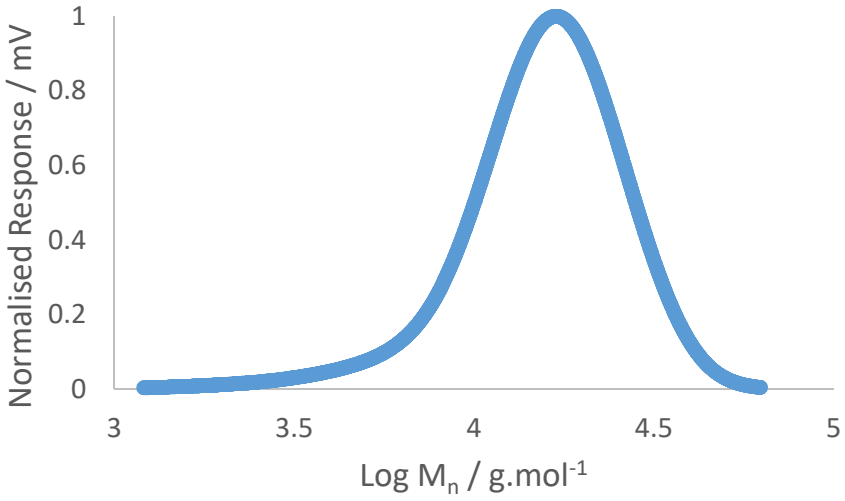
Appendix 3 – Chapter 3; GPC analysis 10:1 ratio RAFT:V-70, 35°C, Conventional Heating, 4 hours, Đ = 1.22



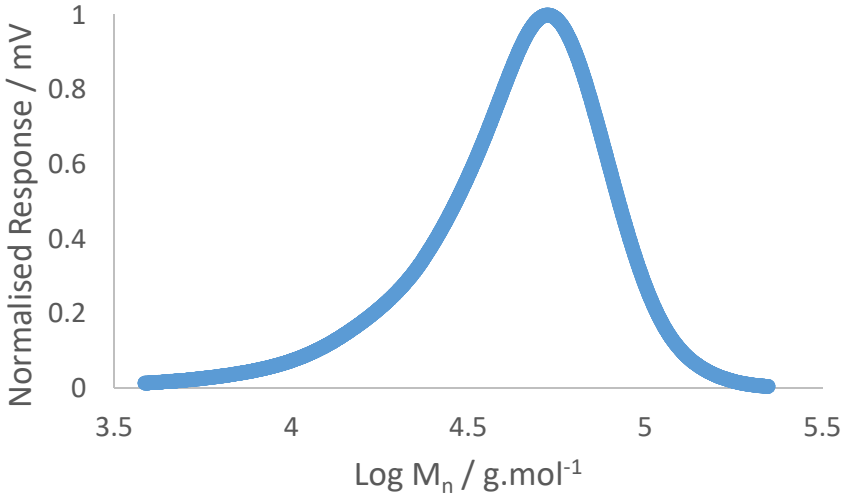
Appendix 4 – Chapter 3; NMR analysis 10:1 ratio RAFT:V-70, 35°C, Microwave Heating, 4 hours



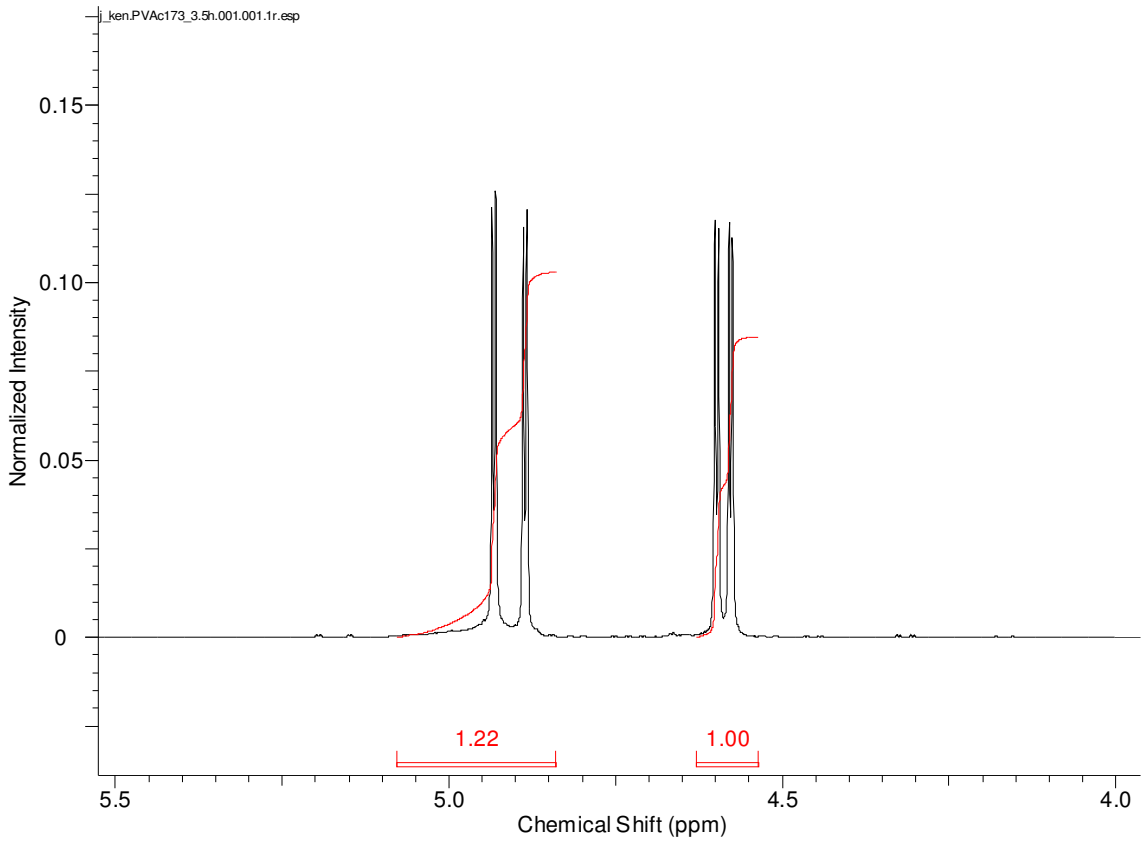
Appendix 5 – Chapter 3; GPC analysis 5:1 ratio RAFT:V-70, 45°C, Conventional Heating, 1.5 hours, Đ = 1.33



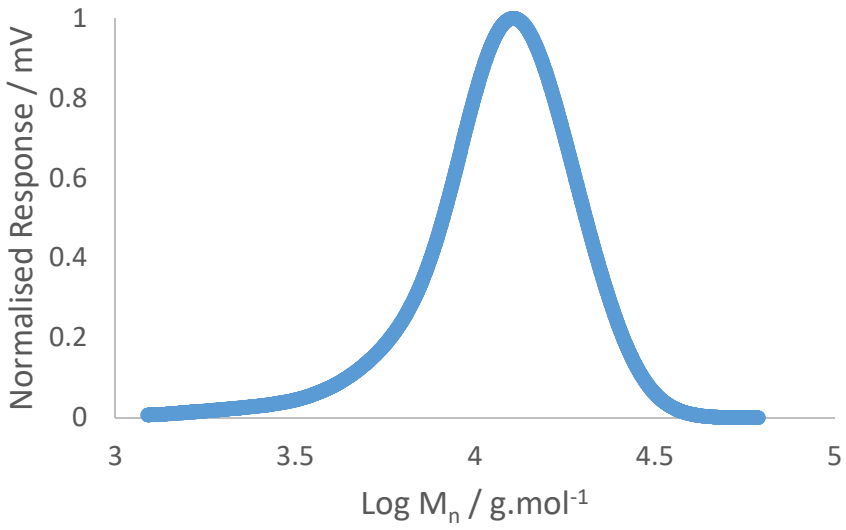
Appendix 6 – Chapter 3; GPC analysis 5:1 ratio RAFT:V-70, 45°C, Microwave Heating, 1.5 hours, Đ = 1.46



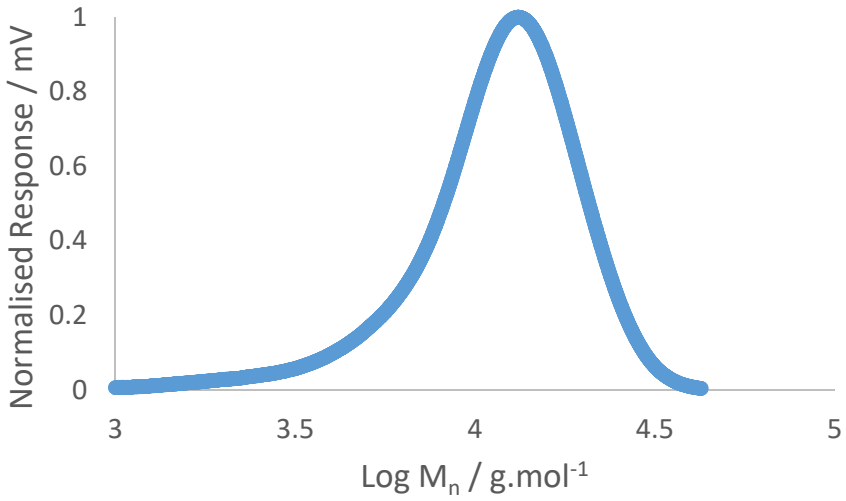
Appendix 7 - Chapter 3; 5:1 ratio RAFT:V-70, 45°C, Conventional Heating, 3 hours – 10 ml Toluene



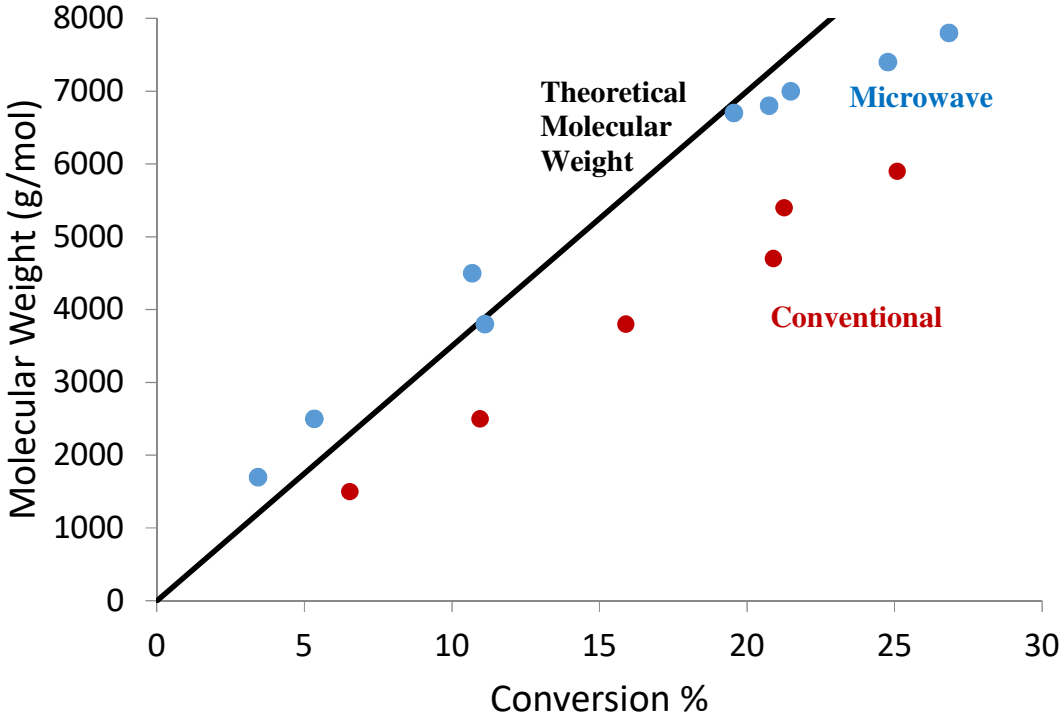
Appendix 8 - Chapter 3; GPC analysis 5:1 ratio RAFT:V-70, 45°C, Conventional Heating, 3 hours – 10 ml Toluene, Đ = 1.29



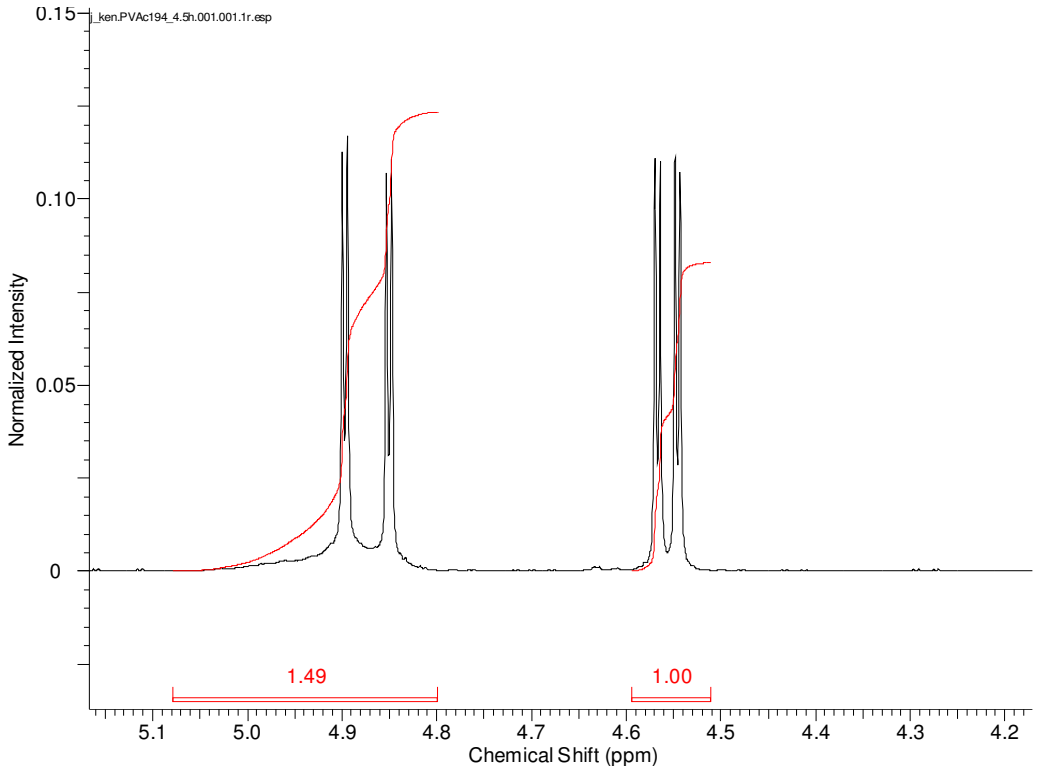
Appendix 9 - Chapter 3; 5:1 ratio RAFT:V-70, 45°C, Microwave Heating, 5 hours – 10 ml Toluene, Đ = 1.34



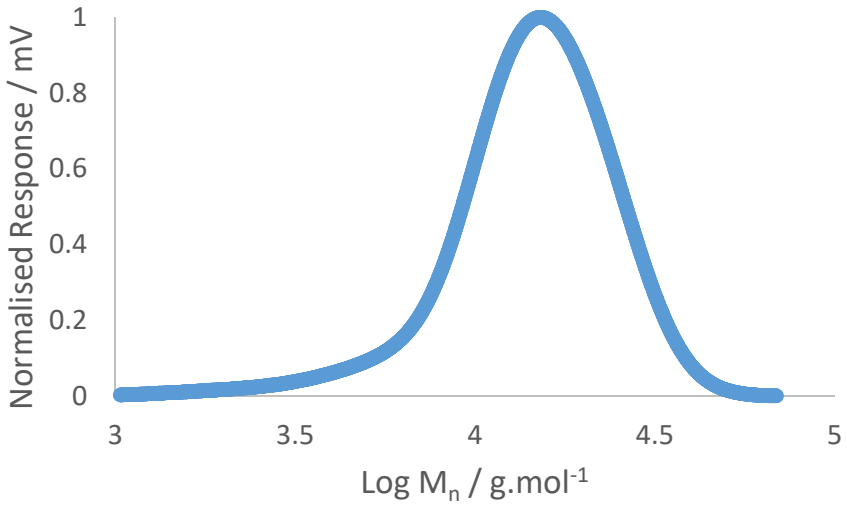
Appendix 10 - Chapter 3; 2.5:1 ratio RAFT:V-70 – 10 ml Toluene



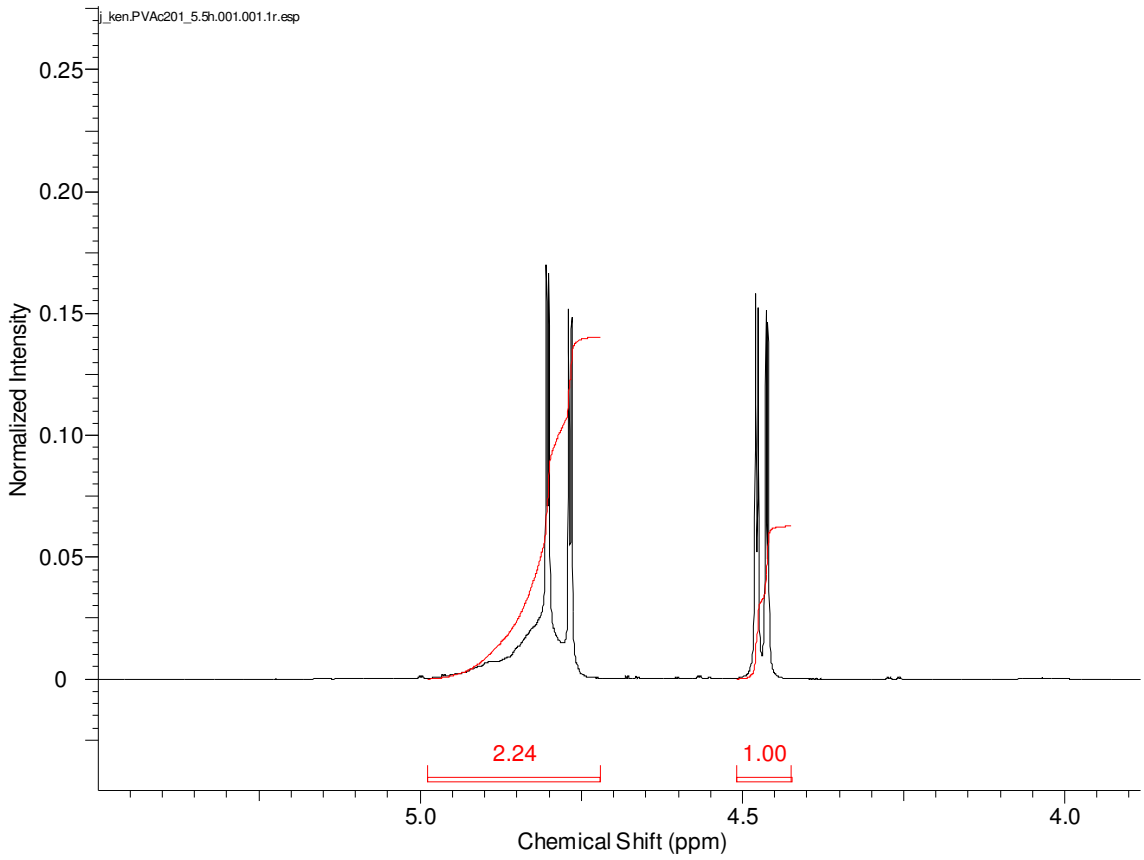
Appendix 11 – Chapter 3; NMR analysis, 2.5:1 ratio RAFT:V-70, 45°C, Microwave Heating, 4.5 hours – 5 ml Toluene



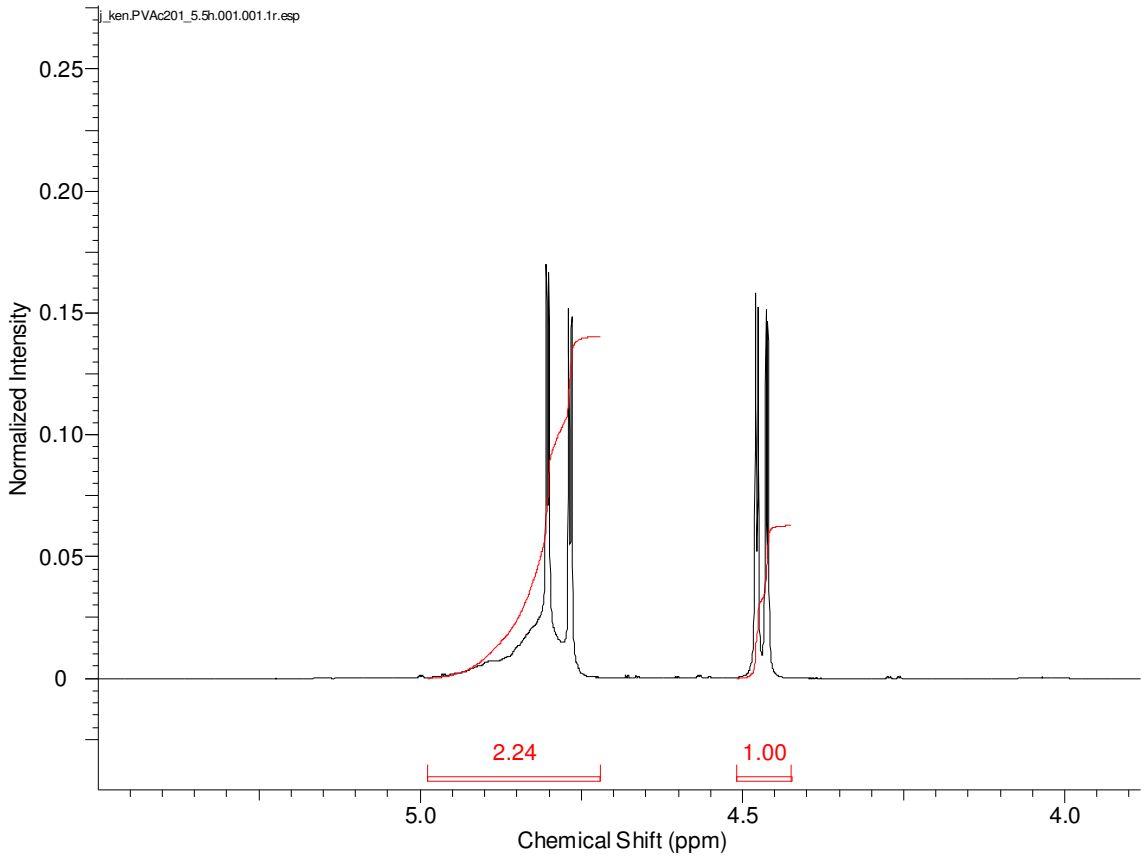
Appendix 12 – Chapter 3; GPC analysis 2.5:1 ratio RAFT:V-70, 45°C, Conventional Heating, 4 hours – 2.5 ml Toluene, Đ = 1.34



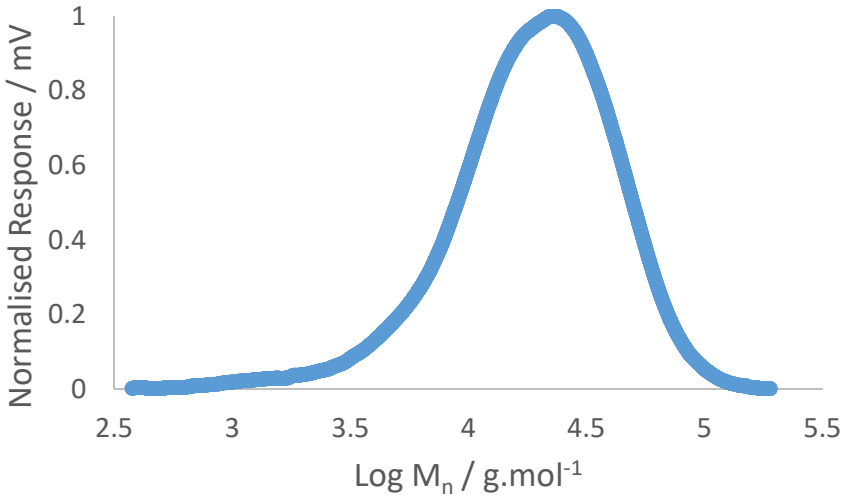
Appendix 13 – Chapter 3; NMR analysis 2.5:1 ratio RAFT:V-70, 45°C, Microwave Heating, 5.5 hours – 2.5 ml Toluene



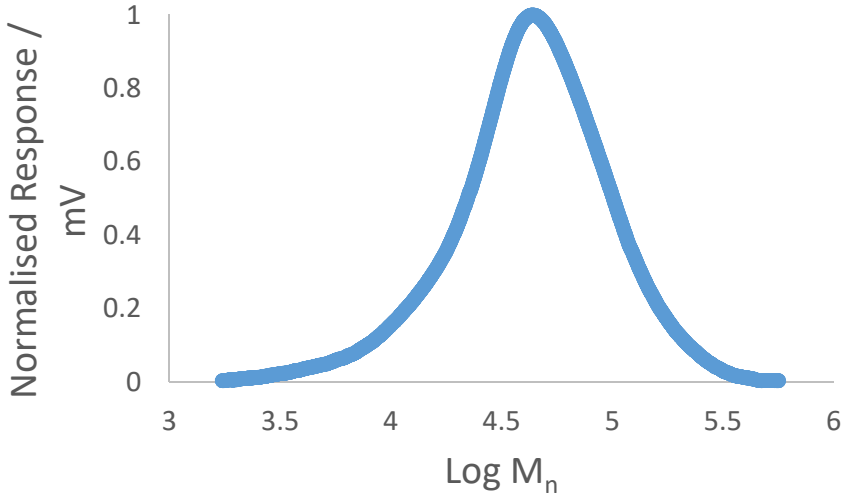
Appendix 14 – Chapter 3; NMR analysis 1:1 ratio RAFT:V-70, 45°C, Microwave Heating, 5.5 hours – 2.5 ml Toluene



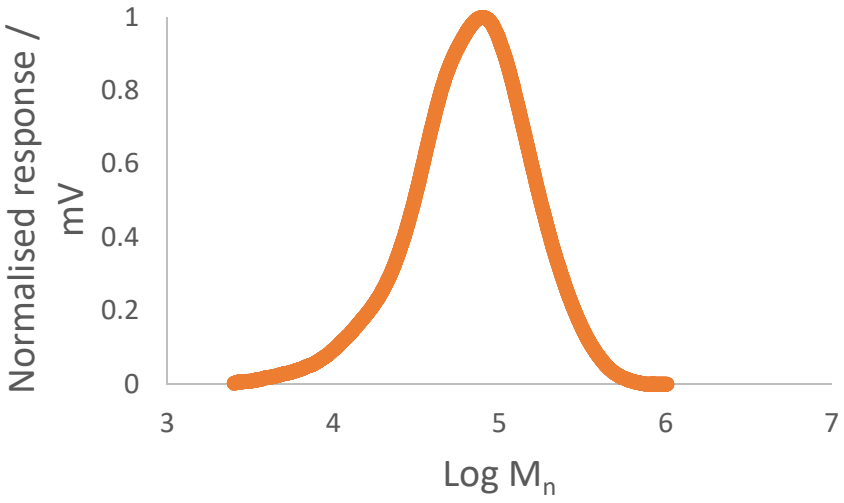
Appendix 15 – Chapter 4; GPC analysis 10,000 g.mol^{-1}, 5:1 ratio RAFT:AIBN, 65°C, 24 hours, Đ = 2.00



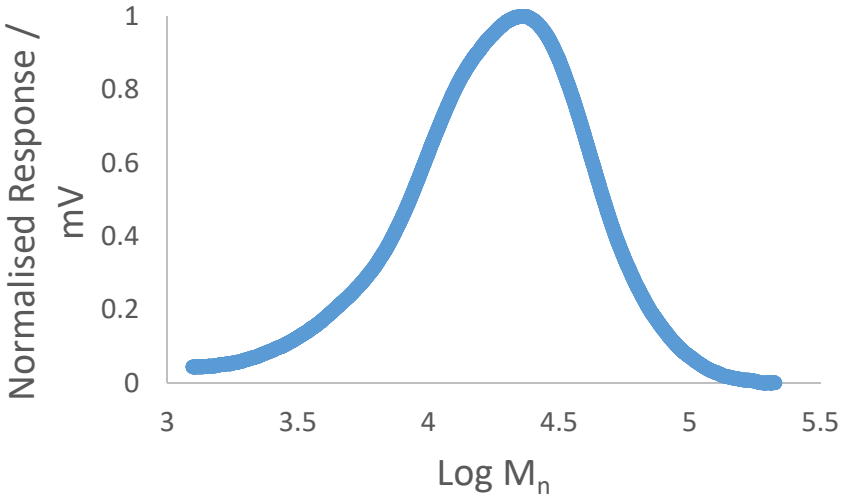
Appendix 16 - Chapter 4; GPC analysis 20,000 g.mol^{-1}, 2:1 ratio RAFT:AIBN, 65°C, 24 hours, Đ = 1.96



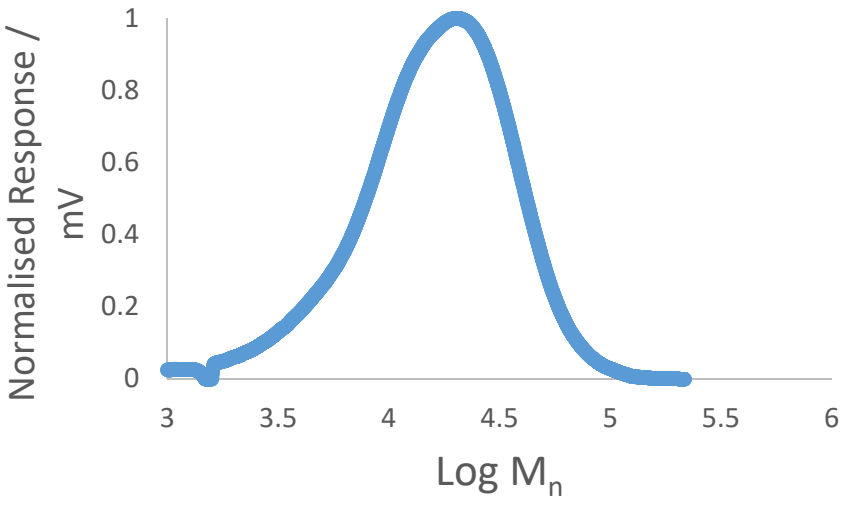
Appendix 17 - Chapter 4; GPC analysis 30,000 g.mol^{-1}, 2:1 ratio RAFT:AIBN, 65°C, 24 hours, Đ = 2.05



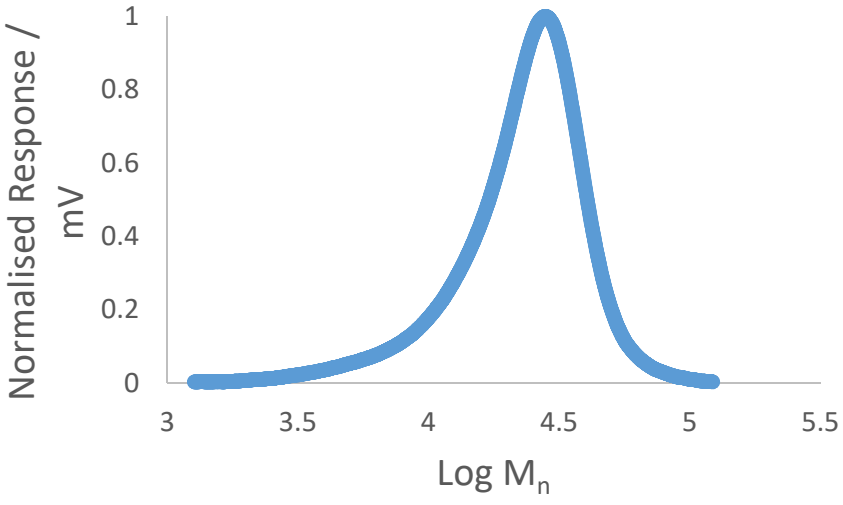
Appendix 18 - Chapter 4; GPC analysis 10,000 g.mol^{-1}, 2:1 ratio RAFT:AIBN, 65°C, 18 hours, Đ = 1.98



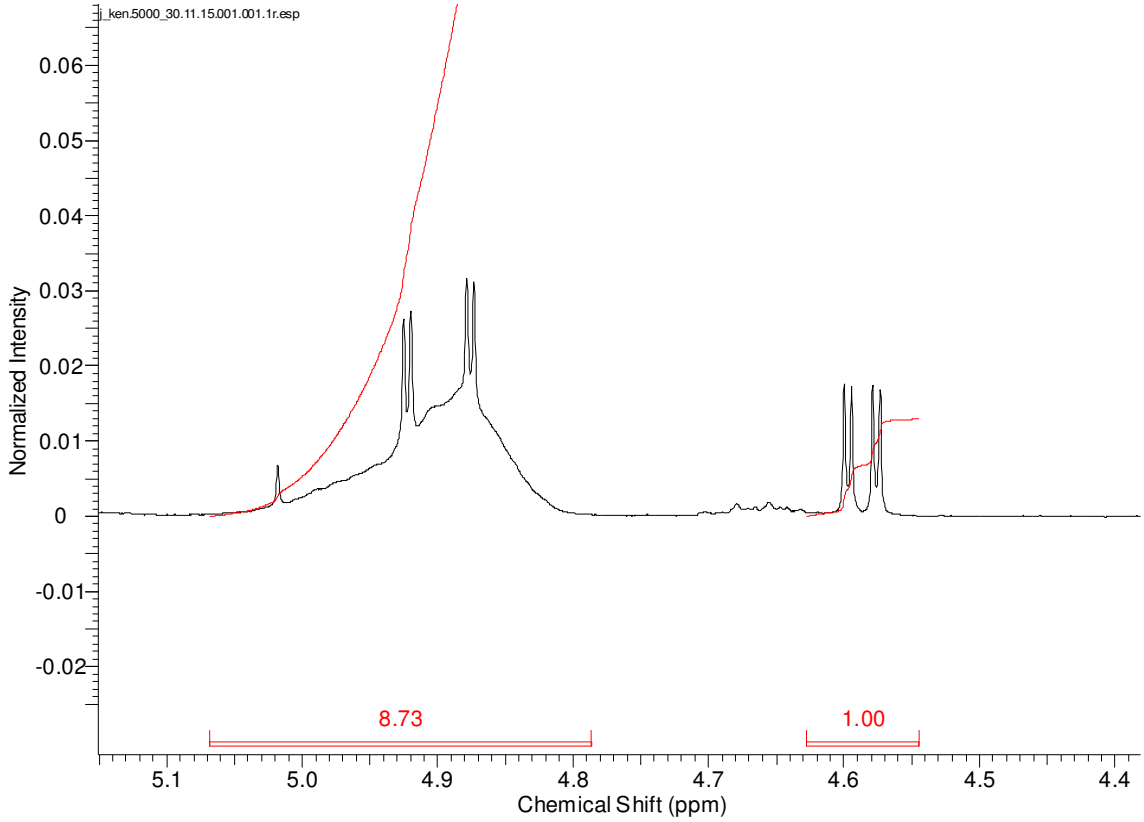
Appendix 19 - Chapter 4; GPC analysis 10,000 g.mol^{-1}, 2:1 ratio RAFT:AIBN, 65°C, 24 hours, Đ = 2.13



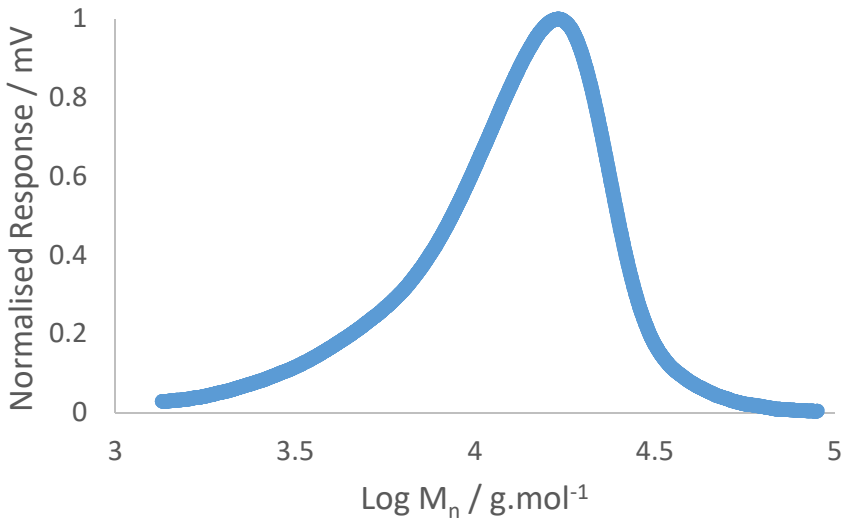
Appendix 20 - Chapter 4; GPC analysis 35,000 g.mol^{-1}, 2:1 ratio RAFT:AIBN, 65°C, 4 hours, Đ = 1.43



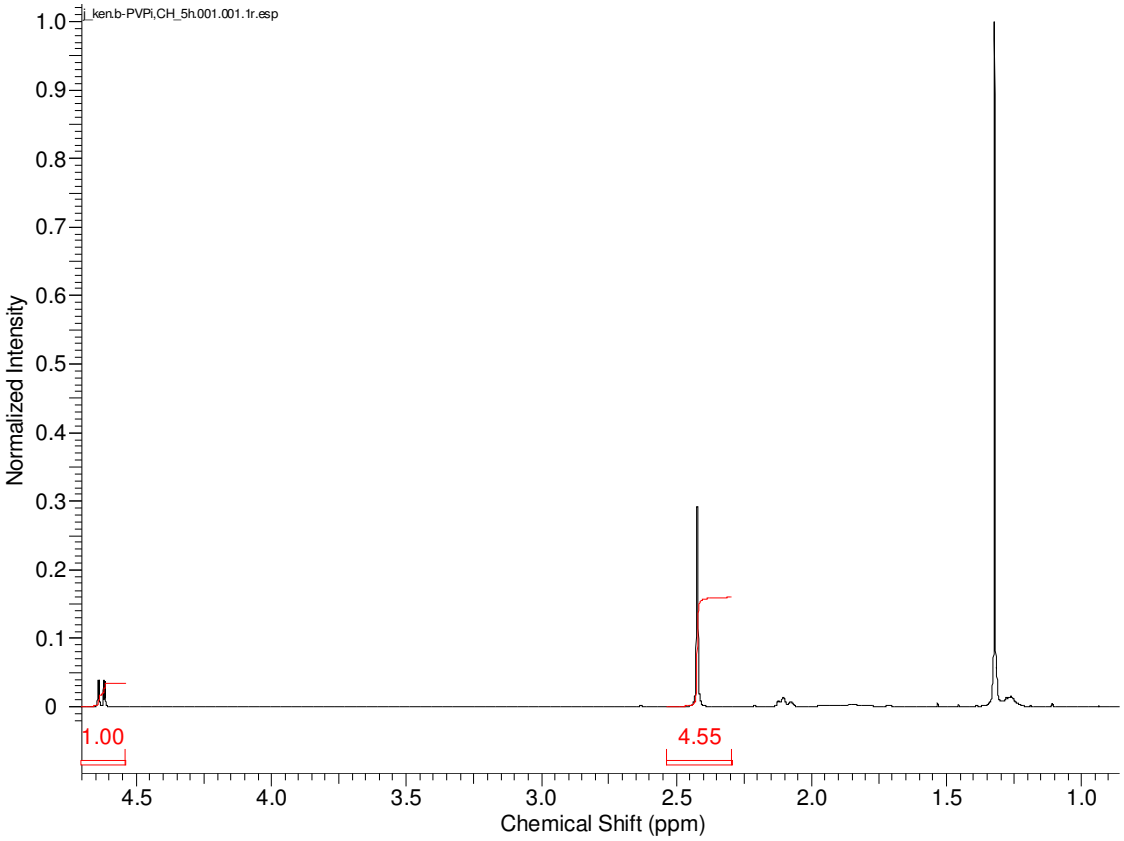
Appendix 21 – Chapter 5; NMR analysis, PVAc macro-RAFT agent, 5:1 ratio RAFT:V-70, 7,400 g.mol^{-1}, 2 hours



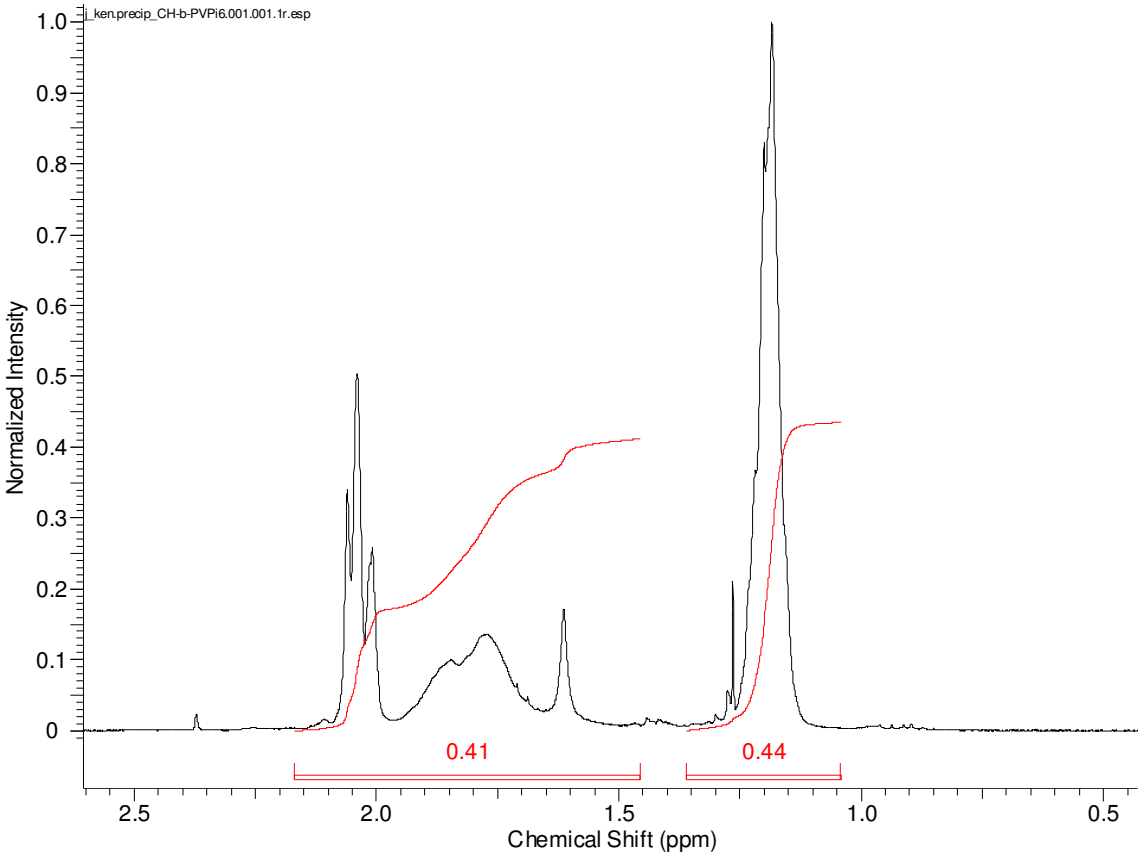
Appendix 22 – Chapter 5; GPC analysis, PVAc macro-RAFT agent, 5:1 ratio RAFT:V-70, 7,400 g.mol^{-1}, 2 hours, Đ = 1.53



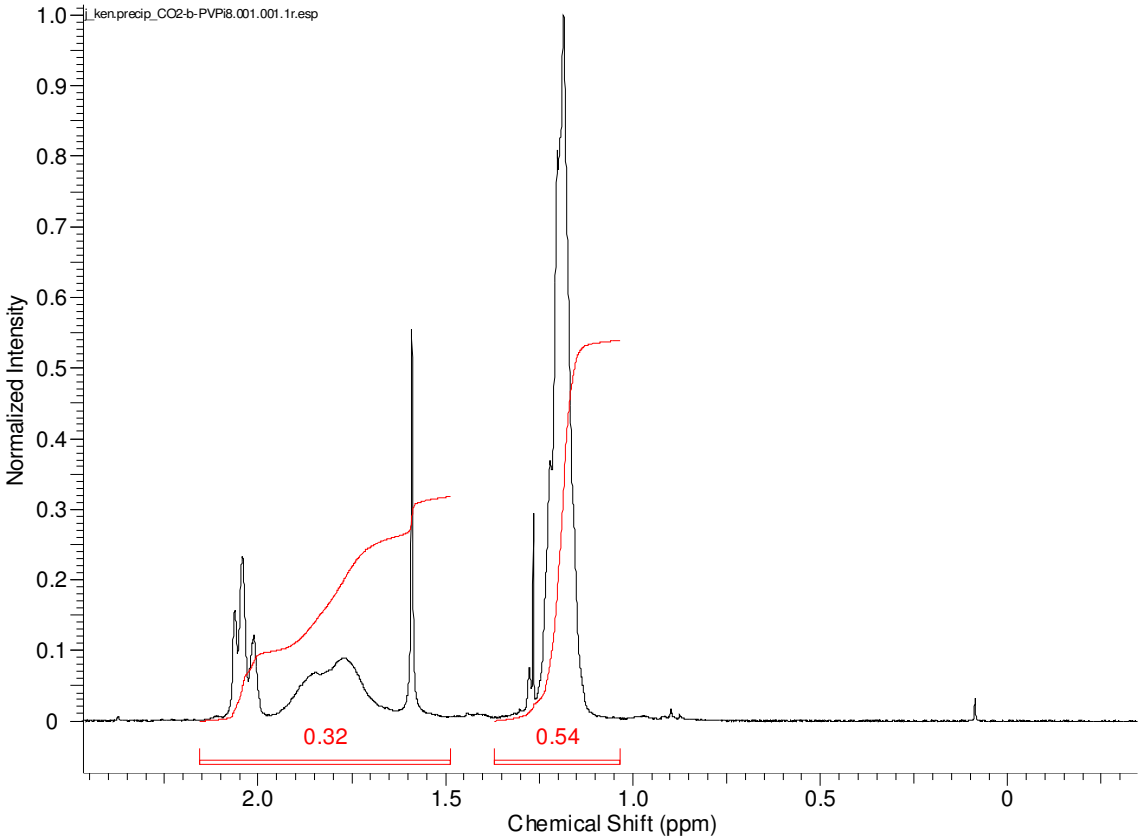
Appendix 23 – Chapter 5; NMR analysis, PVAc-PVPi product, Conventionally produced macro-RAFT agent, 2.5:1 ratio macro-RAFT:V-70, Conventional heating, 5 hours



Appendix 24 – Chapter 5; NMR analysis, PVAc-PVPi product, Microwave macro-RAFT agent, 2.5:1 ratio macro-RAFT:V-70, Conventional heating PVAc:PVPi ratio



Appendix 25 – Chapter 5; NMR analysis, PVAc-PVPi product, Microwave macro-RAFT agent, 2.5:1 ratio macro-RAFT:V-70, CO_2, PVAc:PVPi ratio



Appendix 26 – Chapter 5; DSC analysis, PVAc-PVPi product, Microwave macro-RAFT agent, 2.5:1 ratio macro-RAFT:V-70, CO_2, T_g values = 36.17 °C and 63.89 °C

