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Continuous flow microwave catalytic chain transfer polymerisation of methyl methacrylate oligomers

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Abstract

The aim of this project was to develop and compare microwave at 2.45 GHz and conventional heating processes to produce low molecular weight methyl methacrylate oligomers. The required level of conversion for this process to be successful was 40 %. Batch and flow processes were investigated for both heating methods, and conversions of up to 70 % in batch and 55 % in flow were achieved.

A large number of publications conclude that microwave heating can lead to significant improvements in conversion, rate and product quality when compared to conventionally heated reactions. In many cases this has been attributed to a non-specific thermal effect due to material interactions with the electric field component of the microwave. In many cases these conclusions stem from inaccurate temperature measurement in a microwave environment, and comparisons with conventional heating being carried out under different conditions. In this work a robust methodology was developed to compare microwave and conventional heating for oligomer production.

Initial work was carried out at 30-50 cm³ using a CEM Discover SP (300 W) microwave, a conventionally heated stirred oil bath and a single mode cavity. Investigation into the effects of temperature, heating rate and reaction time on conversion were carried out, and it was found that the target material could be produced to 70% conversion in less than 5 minutes. From the understanding gained using small scale batch reactions a set of design

requirements were produced for larger scale flow systems using microwave and conventional heating, and these systems were constructed as part of this project. This apparatus allowed for repeatable production of the target material at flow rates of up to 36 kg/hour when operated using a 2 kW microwave generator with automated tuning. Conventional comparisons were carried out at in flow with the use of apparatus of the same physical geometry under the same conditions.

This is the first work published to carry out direct comparisons between conventionally heated and microwave reactions under the same conditions. It was found that at all scales and under all the conditions investigated that there were no quantifiable benefits in conversion or product quality offered by the use of microwave heating. It was concluded that such benefits concluded elsewhere are likely to result from poor control and rigour in experimental comparisons.

Acknowledgements

Dedication

Dedicated to both of my parents, Dad and Siân.

Thank you, for your unwavering support and for always being there.

I wouldn't be where I am now without you.

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λ_{od}	Excitation wavelength	(m)
λ_{co}	Cut off wavelength	(m)
P_d	Power density	(W/m³)
ε'	Relative dielectric constant	(-)
ε''	Relative loss factor	(-)
ε_0	Permittivity of free space	(F/m)
ε^*	Complex relative permittivity	(-)
E	Electric field	(V/m)
H	Magnetic field	(A/m)
f	Frequency	(Hz)
μ_0	Permeability of free space	(H/m)
μ'	Relative permeability,	(H/m)
λ	Wavelength	(m)
$\tan \delta$	Loss tangent	(-)
CEM	300 W single mode microwave generator	(-)
cP	Centipoise	(Pa.s/1000)
Da	Dalton-molecular mass	(-)
Cp	Specific heat capacity	(J/g.K)
ρ	Density	(kg/m³)
T_{min}	Minimum temperature	(°C, K)
T_{max}	Maximum temperature	(°C, K)
$T_{1/2}$	Half-life temperature	(°C, K)
C_s	Chain transfer coefficient	(-)
N	Rotational speed	(Hz)

D	Characteristic dimension of agitator	m
μ	Viscosity	(Pa.s)
A	Pre-exponential factor	(s^{-1})
k	Rate constant of chemical reaction	(-)
Ea	Activation energy	(kJ/mol)
R	Ideal gas constant	(J/K.mol)
ΔH_f	Standard enthalpy of formation	(kJ/mol)
OD	Outside diameter	(m)
ID	Internal diameter	(m)
GC	Gas chromatography	(-)
MS	Mass spectrometry	(-)
NMR	Nuclear magnetic resonance	(-)
GPC	Gel permeation chromatography	(-)
TGA	Thermo gravimetric analysis	(-)
MMA	Methyl methacrylate	(-)
MMA_2	Methyl methacrylate dimer	(-)
MMA_3	Methyl methacrylate trimer	(-)
SiC	Silicon Carbide	(-)
AIBN	Azobisisobutyronitrile	(-)
BPO	Benzoyl peroxide	(-)
THF	Tetrahydrofuran	(-)
VOC	Volatile organic compounds	(-)
THF	Tetrahydrofuran	(-)
PhCoBF	Bis[(fluroboryl)diphenylglyoximato]cobalt(II)	(-)
CCTP	Catalytic chain transfer polymerisation	(-)

NMP   Nitroxide-mediated radical polymerisation   (-)

ATRP   Atom transfer radical polymerisation   (-)

RAFT   Reversible   addition–fragmentation   chain-transfer   (-)

polymerization

1 Introduction

1.1 Background Chemistry

This Section will concentrate upon presenting a background discussion upon free radical polymerisation controlled by catalytic chain transfer. It will primarily focus upen detailing the mechanisms, uses and limitations of this technique.

1.1.1 Project focus

Within this project methyl methacrylate (MMA) was exclusively used, the molecular structure shown below in Figure 1-1. This is a commonly used monomer within both industry, and academia; there is a wide range of works reported. It is more commonly seen in its polymer form as clear plastic sheets (Perspex™, Plexiglass™, Lucite™). In its polymer for it is also used in many medical applications for such applications as targeted drug delivery, or as cement for denture fixing and joint replacements (Shlosberg, Goodacre et al. 1989; Schwarz 2011; Battencourt and Almeida 2012).
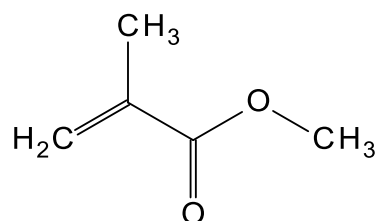
Figure 1-1: Structure of methyl methacrylate ($C_5H_8O_2$)

Polymers are defined as any material composed of repeated monomer units. All known plastics are polymeric in nature, but all polymers are not plastics. Polymers exist in nature in materials such as carbohydrates and cellulose, which are both polymers of glucose (O'Sullivan 1997).

When polymers were originally discovered and produced, the view of the scientific and engineering community was that "the bigger the better", meaning that the higher the molecular weight the better the macro material

properties of the polymer would be. As understanding developed and the range of applications that scientists attempted to utilise polymers for increased. It became clear that greater control over the molecular weight, and molecular structure had to be matched with the demands of the growing range of applications (Young and Lovell 2011). Leading to development of techniques which could successfully control the molecular weights and distributions produced. There has been movement towards different architectures such as branched, star and co-polymers; functionalization of the polymeric materials. Allowing for development of a wide variety of physical properties and potential applications (Cowie and Arrighi 2008).

In the work reported here, the target materials were short chain molecules; which are more commonly referred to as oligomers. These were the target material as there is no current viable process for their manufacture. The other advantage in producing oligomers is that they remain liquid rather than polymeric material which is solid. This allows for simplified designs, whilst developing a flow system. The term oligomer can be used to define a wide variety of molecular weights depending upon the application used. Typically it can refer to material with up to 100 repeat units, for MMA polymer this equates to an overall molecular weight of 10,000 g/mol (Adlington, Jones et al. 2013). In this project, the target materials are 2 and 3 repeat units. 2 and 3 repeat unit oligomers are referred to as MMA_2/MMA_3 (where the subscript denotes the number of repeat units) or as dimer/trimer. These short length oligomers were formed by the use of catalytic chain transfer polymerisation to control the length of the polymer chains formed. The mechanism for this method of chain length control will be discussed in greater detail within this Chapter.

The purpose of producing these short chain oligomers is that as of yet there is no industrially viable process for their manufacture. With increasing environmental legislation and economical pressure to improve environmental emissions companies are looking for ways to improve, these materials are a potential way of improving the automotive paints industry. They allow for

development of low volatile organic compound (VOC) coatings (Adamsons, Blackman et al. 1997; Huybrechts, Bruylants et al. 2002). When produced using catalytic chain transfer (explained later within this Chapter) the mechanism produces polymers with a vinyl group at the end, this unsaturated bond allows for the species to remain active, thus allowing for further polymerisation and use in other applications. These materials can be used as chain transfer agents and for the formation of hyper-branched materials (Moad, Moad et al. 1996; Hutson, Krstina et al. 2004). For these materials to retain their use it is required that in many cases they be within a monomer solution with a 40:60 ratio. Therefore for this process to be successful it is required that a conversion of 40 % or greater be achieved (Cowie and Arrighi 1991; Saldivar-Guerra and Vivaldo-Lima 2013).

1.1.2   Polymer growth mechanisms

There are three main mechanisms by which polymers chains grow, these are; step growth, chain growth and living/controlled growth polymerisation.

Typically chain growth polymerisation occurs *via* free-radical mechanisms. During the chain growth stage of the polymerisation, the radicals are located at the end of a small number of polymer chains. These chains rapidly grow to give high molecular weight; consequently this mechanism gives very rapid formation of high molecular weights at low levels of conversion. Therefore it is clear that chain transfer will have to be used to produce low molecular weight products (Dotson, Galvan et al. 1995; Peacock and Calhoun 2006; Ravve 2012).

1.1.3   Free radical polymerisation

This is the method by which MMA and many other vinyl monomers, such as styrene are routinely polymerised in both academia and industry (Allen and Patrick 1961). A free radical is defined as an atom or molecule that has an unpaired valence electron, making for a highly reactive species. These free radicals are commonly introduced into the chemical process *via* the use of an initiator. The radicals are typically generated by the application of UV-light or

thermal energy (Ozay, Ekici et al. 2009; Akzo-Nobel 2010; Sigma-Aldrich 2013). In certain cases controlled self-initiation is utilised, i.e. the direct generation of radicals from the monomer. A good example of this is the polymerisation of styrene (Khuong, Jones et al. 2005). However, in general initiators are used because they generate radicals at lower temperatures and give a more controlled release, than a self-initiated process.

1.1.4 Radical initiators

Initiators are materials which typically contain within their structure "weak" or thermally/UV sensitive bonds. This means that they can decompose in a controlled manner, for example at a set temperature. The method of bond decomposition is also very specific, instead of the more normal heterolytic bond fission process, which involves a bond breaking in a manner where the 2 electrons that form the bond being broken become located within one of the fragments, shown in Figure 1-2 below. This creates two ions which carry a different charge (Shriver, Atkins et al. 2009).

$$X \overline{} Z \longrightarrow X^{\delta-} + Z^{\delta+}$$
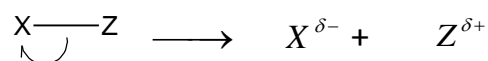
Figure 1-2: Heterolytic bond fission

The free radical initiator decomposes *via* a process of homolytic bond fission. In this case one electron from the broken bond is singly location within each of the molecular fragments, shown in Figure 1-3 below. Creating 2 radicals, which carry a similar charge, generated by the unpaired electron.

$$X \overline{} Z \longrightarrow X^{\bullet} + Z^{\bullet}$$
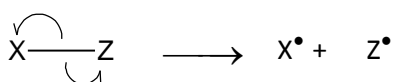
Figure 1-3: Homolytic bond fission

The commonly used initiators generally exhibit a well-known relationship between half-life ($T_{1/2}$) time and temperature half-life temperature (Akzo-Nobel 2010). The half-life represents the time taken for half the material to decompose to form radicals. It is normally assumed that the process is

4

complete after four half-lives. This is because the commercial advantage of keeping the reaction medium at temperature for this time is not justified, for such low levels of remaining initiator (6.25 %).

The temperature at which radicals are formed is a direct function of the molecular structure of the material. The decomposition of these initiators takes the form of an exponential decay, similar to that experienced by a radioactive species. An example of a decay curve can be seen in Figure 1-4 below.
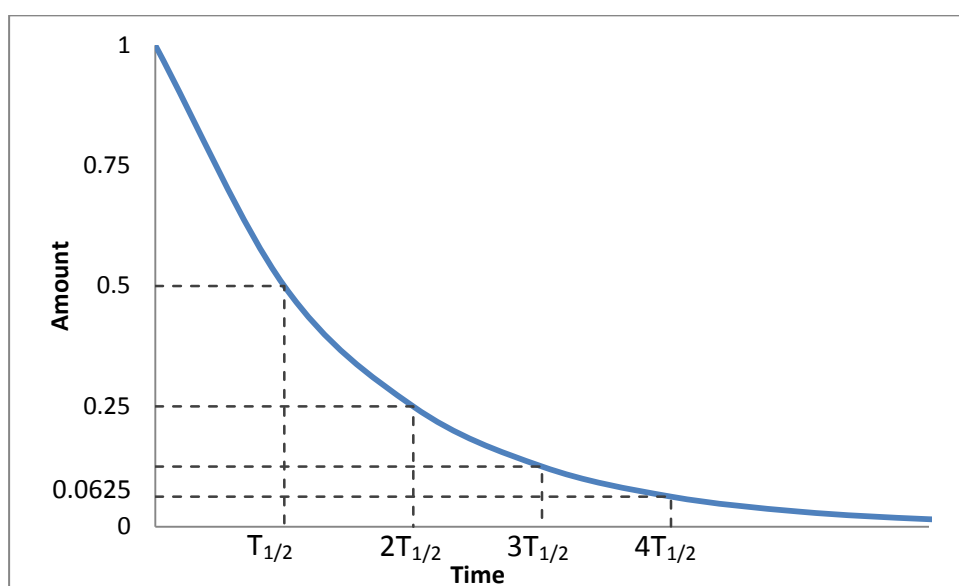
Figure 1-4: Exponential decay curve for a generic initiator, no units on time axis. 4 half-lives are shown.

The most commonly used initiator families or based upon the molecular structure are azo and peroxides. An example of the azo initiator, which is the primary initiator used within this work is azobisisobutyronitrile (AIBN), shown in Figure 1-5.
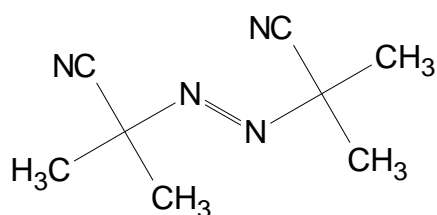
Figure 1-5: Chemical structure of AIBN ($C_8H_{12}N_4$)

These species have a susceptible C-N bond within their structure. Upon being exposed to thermal energy this bond undergoes homolytic fission shown in Figure 1-6. This process generates 2 carbon centred radicals, evolving N_2 gas as by-product.
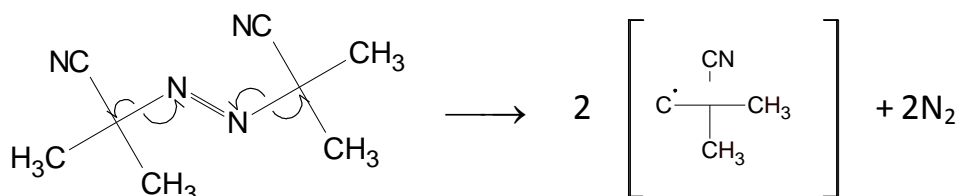
Figure 1-6: Homolytic fission of AIBN to produce radical and nitrogen

The second initiator used within this work was, benzoyl peroxide (BPO), structure shown in Figure 1-7 below. This was chosen due to the fact that it exhibits a similar half-life temperature to that of AIBN (Table 1-1).
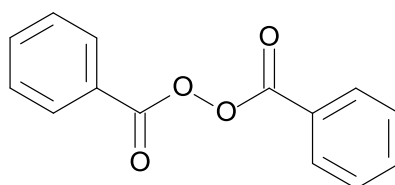
Figure 1-7: Chemical structure of benzoyl peroxide ($C_{14}H_{10}O_4$)

Table 1-1: Shows half-life times of initiators used against temperature (°C) (Akzo-Nobel 2010) (Sigma-Aldrich 2005).

	AIBN	BPO
10 hour	66	77
1 hour	84	93
0.1 hour	102	110
1 sec	147	152

In the work reported within this thesis, BPO has been used as a secondary initiator. Unlike a carbon centred radical, oxy radicals are known to actively deactivate cobaloxime type CCT catalyst, this was utilised in a specific set of experiments shown later.

In this case the thermally sensitive linkage is the O-O bond located at the centre of the structure. The mechanism for decomposition in this case is shown in Figure 1-8; it can be a 2-step process with this type of molecule.
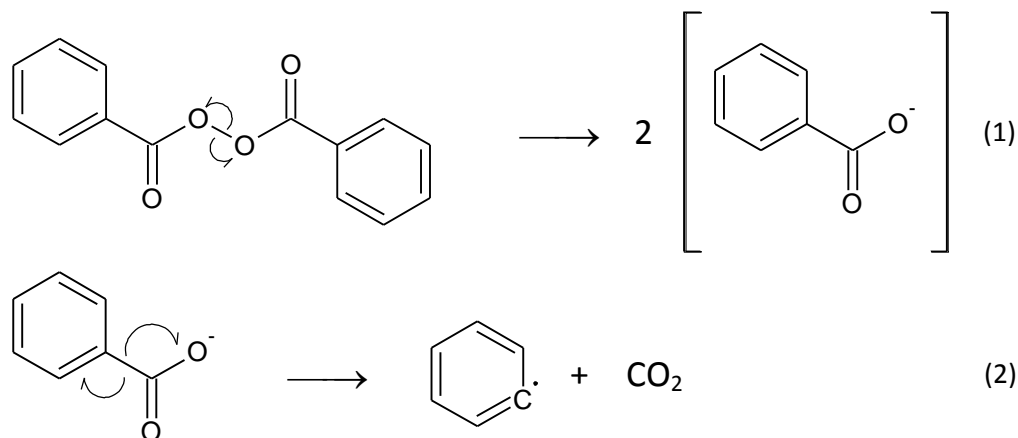
Figure 1-8: Homolytic fission for decomposition of BPO. (1) shows decomposition to form the radical used for initiation. (2) shows further decomposition of the radical.

Step 1 produces oxygen centred radical directly from the homolytic decomposition of the O-O bond. **Step 2** can occur if the radical is not relatively quickly involved in an initiation process. If it remains within solution for enough time a further homolytic rearrangement will occur to produce a new carbon centred radical with the formation of CO_2 by-product.

1.1.5 Conventional chain transfer polymerisation

Chain transfer is used as a method to reduce the average molecular weight of products produced in a polymerisation reaction. Chain transfer works by transferring the activity of a growing polymer chain to another. Chain transfer can occur as an unwanted side reaction during polymerisation between the growing polymer chain and the monomer, and in some cases the solvent used. To further reduce the molecular weights, chain transfer agents are used. These are materials which contain a weak bond, such as thiols (R-S-H) or carbon tetrachloride (CCl_4) (Cowie and Arrighi 2008).

The radical at the end of the growing polymer chain reacts with the transfer agent, abstracting a hydride terminating the polymer chain. This mechanism for termination leaves the polymer chain with an unsaturated C=C double bond. This forms a sulphur based radical which in a second stage initiates a new monomer unit. This process is shown below in Figure 1-9.

$$P_n^\bullet + H - SR \quad \xrightarrow{k_{td}} D_n \quad +^\bullet SR \qquad (1)$$

$$^\bullet SR + M \quad \xrightarrow{k_{rein}} RS - M^\bullet \qquad (2)$$
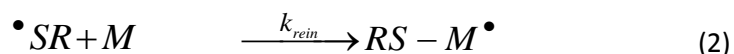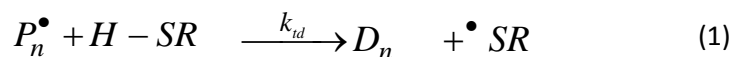
Figure 1-9: Chain transfer with the use of a thiol (1) hydride is removed from the thiol species to the growing chain. (2) The sulphur radical initiates a new polymer chain.

The main disadvantage of this process is that the chain transfer agent is only able to transfer one growing chain. Therefore to achieve low molecular weights large quantities of the material are required. With the use of thiols and chlorine containing compounds it causes contamination, thiols are highly odorous and can produce an unpleasant characteristic smell if used with volatile compounds (Müller, Adelsberger et al. 2012).

1.1.6 Catalytic chain transfer polymerisation

Catalytic chain transfer (CCT) is commonly carried out by the use of ppm levels of an organocobalt catalyst. This is advantageous when compared to chain transfer with the use of thiols or CCl_4. As a catalyst the material is not consumed during the reaction, it is rather re-generated in a 2-stage mechanism.

CCT was first discovered in the early 80's, (Burczyk, O'Driscoll et al. 1984; Gridnev 1988; Sanayei and O'Driscoll 1989). The suggested mechanism for the occurrence for CCT is shown below in Figure 1-10, over the years this has become widely accepted amongst the scientific community.

$$(1)$$

$$(2)$$
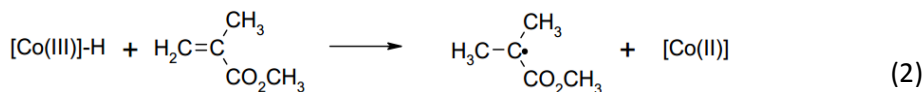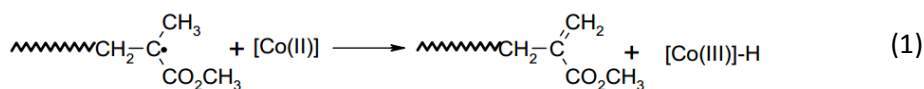
Figure 1-10: CCT mechanism, (1) the chain transfer and abstraction of hydrogen from a growing polymer chain. (2) is the re-initiaton of monomer and regeneration of the catalyst species (Pierik 2002).

In the first step a low spin Co (II) species abstracts a hydride from the α-methyl group of the growing polymer chain. This results in the formation of a vinyl terminated polymer chain and the formation of a cobalt hydride species. In step 2 this cobalt hydride then re-initiates a new chain, and in turn re-generates the Co(II) complex, allowing for the process to be repeated.

CCT as with conventional chain transfer produces polymers terminated with a vinyl group. Thus allowing for functionalization or further polymerisation, making these short chains ideal for use as CCT agent, or replacements for VOCs in the automotive coatings industry (Adamsons, Blackman et al. 1997; Huybrechts, Bruylants et al. 2002).

The measure of how effective a material is as a chain transfer agent is defined by the chain transfer constant (C_s) This is theoretically defined for a specific system as being the ratio of the rate constant for chain transfer (k_{tr}) against that for propagation (k_p). There are many different materials which can be used as CCT catalysts, the most common of these are Vitamin B12 derived cobalt complexes, this is due to their very high chain transfer constant, in the order of 10^4, when compared to other compounds such as thiols or mercaptans which are in the order of 10^1 (Heuts, Davis et al. 1999).

The catalyst used in this work was Bis[(fluroboryl)diphenylglyoximato]cobalt(II) –PhCoBF, structure shown in Figure 1-11 below. This material has a chain transfer coefficient of 2.5 x 10^4 in methyl methacrylate at 60 °C (Heuts, Forster et al. 1999).
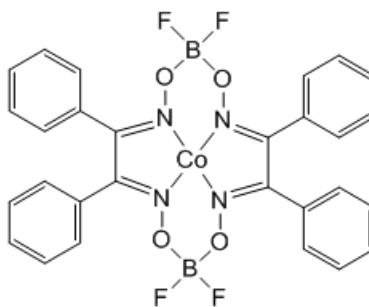
Figure 1-11: Chemical structure of organometallic cobaloxime CCT catalyst used.

1.1.6.1 Catalyst deactivation

Catalyst deactivation can proceed *via* several mechanisms; Co(II) is the only cobalt complex that can take part in the reaction. If this is either oxidised or reduced to Co(III) or Co(I) respectively, this will lead to an overall reduction in catalytic reaction. The most common form of catalyst deactivation is *via* the use of peroxides initiator, such as BPO, or by the presence of oxygen. To minimise catalyst deactivation all experiments should be thoroughly degassed prior to dissolution of catalyst (Pierik 2002).

1.1.7 Reaction cascade

Figure 1-12 below is the reaction cascade for CCT, free radical polymerisation. The first 3 steps in this cascade represent the key stages that form the backbone of standard free radical polymerisation, the identity and characteristics of these individual stages will be discussed in greater detail below, in brief they represent the chemical processes involved in free radical generation through to chain growth. Steps 4 and 5 represent the typical chain termination processes which are responsible for terminating the growth of polymer chains in "uncontrolled" free radical polymerisation i.e. those in which CCT is not employed. These are the stages which are replaced by the CCT chain transfer stages (6 and 7) when a CCT agent is deployed (Cowie and Arrighi 2008).

$$I-I \xrightarrow{k_d} 2I^\bullet \tag{1}$$

$$I^\bullet + M \xrightarrow{k_i} I-M^\bullet \tag{2}$$

$$P_n^\bullet + M \xrightarrow{k_p} P_{n+1}^\bullet \tag{3}$$

$$P_n^\bullet + P_m^\bullet \xrightarrow{k_{tc}} D_{n+m} \tag{4}$$

$$P_m^\bullet + P_n^\bullet \xrightarrow{k_{td}} P_m + D_n \tag{5}$$

$$P_n^\bullet + \left[Co(II)\right] \xrightarrow{k_{tr}} D_n + \left[Co(III)\right] - H \tag{6}$$

$$\left[Co(III)\right] - H + M \xrightarrow{k_{rein}} I-M^\bullet + \left[Co(II)\right] \tag{7}$$

$$P_n^\bullet + H - SR \xrightarrow{k_{td}} D_n + {}^\bullet SR \tag{8}$$

$${}^\bullet SR + M \xrightarrow{k_{rein}} RS - M^\bullet \tag{9}$$
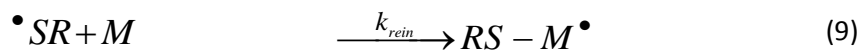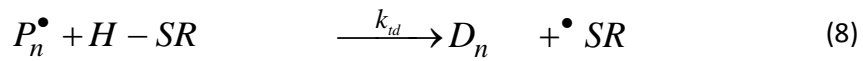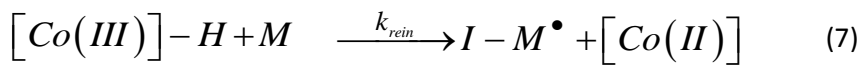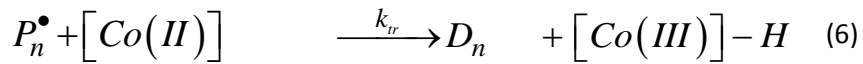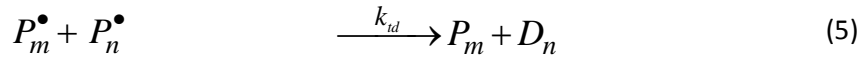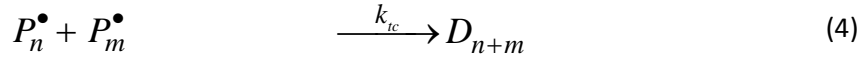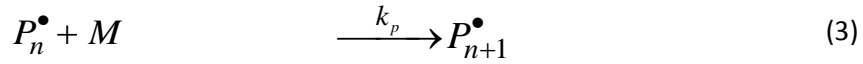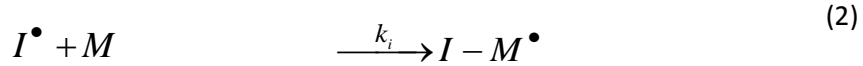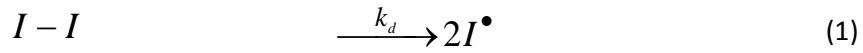
Where

I	:	Radical species
M	:	Monomer
$P_n^\bullet$	:	Propagating species
D_n	:	Deactivated species
H-SR	:	Thiol CTA
k_d	:	Rate constant for initiator decomposition
k_i, k_p	:	Rate constant for initiation and propagation
k_{tc}, k_{td}, k_{tr}		Rate constant for termination by combination, disproportionation, and chain transfer respectively
k_{rein}	:	Rate constant for re-initiation

Figure 1-12: Reaction cascade for free-radical polymerisation.

1.1.7.1 Chain transfer polymerisation reaction cascade

Steps 1 - decomposition: this represents radical generation *via* homolytic bond fission as discussion in Section 1.1.4. This stage is defined as the rate determining step; it has the slowest rate of all the steps within the reaction cascade.

Step 2 - initiation: this step represents the start of the chain growth process. It involves the attack of the initial initiator radical upon the carbon-carbon double bond (C=C) of the first monomer. As radicals contain an unpaired valence electron, this species is regarded as a very strong electrophile, it seeks areas of high electron density, in order to find an electron in which to create a spin-coupled pair. Such areas of electron density are the double bonds within a molecule which contains a bond formed by the pairing of 2 π electrons, which are loosely held in place by the nuclei of the bond, when compared to the second δ-bond. This process of initiation is shown in Figure 1-13.
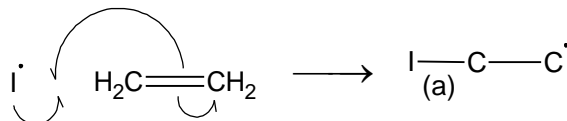
Figure 1-13: Electron movement during initiation of monomer.

Thus in initiation, the initiator radical valence electron, interacts with one of the π electrons from the C=C bond to create a new δ bond; bond (a) shown in Figure 1-13. The second π electron transfers to the second carbon atom which initially formed part of the C=C bond. This ensures that the new initiated monomer species retains the reactive radical group, so can repeat this double bound interaction process in order to extend the chain.

Step 3 – propagation or chain growth: Represents multiple repeats of the C=C double bond attack described in Step 2, increasing the chain length by one repeat unit each time.

Step 4 and 5 – termination: describes any process by which chain growth is stopped. This is usually as a result of the loss of the chain and reactive group. Typically, this process occurs by two key mechanisms.

Step 4 - combination. Two radical containing chains meet and the radicals present at the chain ends spin-couple to create a new bond between the two chains, as a results a larger combined weight dead polymer chain is formed.

Step 5- disproportionation, involves hydride abstraction by the chain end radical from a second individual polymer chain. This results in the generation of saturated chain end on the polymer chain end which has "done" the abstracting. Meanwhile, the polymer which has had the hydride abstracted from it gains a vinyl double bond as a chain end group. This group has the same structure that is introduced by the CCT chain transfer mechanism.

Step 6 and 7 are CCT chain transfer processes discussed in Section 1.1.6. Steps 8 and 9 are the standard non-catalytic chain transfer steps which were discussed in Section 1.1.5. The extent to which these steps occur is related to the presence and the efficiency of chain transfer agent (CTA) used. If no CTA is present steps 4 and 5 will dominate the termination steps. If a conventional CTA is added in sufficient concentration then steps 8 and 9 will dominate termination. Similarly if a CCTA agent is added then steps 6 and 7 will dominate.

1.1.8 Effect of temperature upon a conventional free radical reaction cascade

Shown below in Table 1-2 are the rate equations for the different stages within the reaction.

Table 1-2: Rate equation and relative rates of each step in the free radical polymerisation reaction.

Rate equation	Speed of step
$R_d = k_d [I]$	Slow
$R_i = k_i [M][I]$	Fast
$R_p = k_P [M][M^\bullet]$	Fast
$R_{tr} = 2k_t [M^\bullet]^2$	Very Fast[1]

Analysis of the relative rates and components of the rate equations of each of these steps is important in order to understand why specific steps dominate so that long chain polymers are generated. Temperature can have a significant effect upon these steps, affecting the outcome and safety of the process.

As previously shown, initiator decomposition is the rate determining step within the cascade. This therefore limits the input of radicals into the system. The fastest reaction stage within the cascade is termination; therefore long polymers should not be produced.

However because the concentration of radicals is kept low and the rate of termination is dependent upon $[M^\bullet]^2$, whereas the rate of propagation is dependent upon both $[M]$ and $[M^\bullet]$, it remains dominant and long polymer chains are formed.

Increasing temperature will increase the rate of decomposition, thus increasing radical concentration within the system, which will mean that

---

[1] Where k_t includes, combination and disproportionation.

termination becomes more dominant, giving a reduction in both yield and molecular weight.

Introduction of a CCT agent into the system has the effect of introducing another termination step and another route for initiation.

$$R_{tr} = k_{tr}[M^{\bullet}][Co(II)]$$

$$R_i = k_i [M][I]$$

It would be expected that as the reaction temperature is changed the required levels of CCT catalyst would have to be altered to maintain the target molecular weight. This is however not usually the case, the high efficiency of the catalyst is great enough, that in many cases it can overcome the increased influx of radicals. Thus further reducing the overall molecular weight and yield achieved. This can allow for reactions to be carried out at higher temperatures than those without CCT, as the catalyst reduces the viscosity therefore preventing the temperature rise leading to thermal runaway (Cowie and Arrighi 1991).

1.1.9 Heat of reaction for methyl methacrylate polymerisation

Many polymerisation reactions are exothermic in nature; because of the large numbers of chemical bonds being created in the formation of the polymer chains. Calculation of heat of reaction is difficult in polymer systems because there is a wide range of chain lengths formed.

This can be demonstrated by a simple example: if at one extreme a system containing 100 monomer units were to react to form 1 chain with $Dp_n=100$, this would contain 99 bonds between these individual units. At the other end of the scale if dimer were to be formed exclusively only 49 bonds would be formed.

In this work the target material is MMA_2/MMA_3. Therefore the heat of reaction calculation carried out *via* Hess cycle has been simplified to assume

that the reaction is exclusively forming MMA_2. All other heat sources such as initiator decomposition and chain transfer have been assumed to be 0.

A Hess cycle calculation was carried out using the heat of formation to infer the heat of reaction at standard conditions: -40 kJ/mol for formation of dimer, thus showing that this is a highly exothermic reaction. For full details of Hess cycle see Section 9.1.1. If this reaction were to occur to 100 % conversion within an adiabatic system this heat of reaction could produce a temperature change of up to 157 °C, calculation shown in Appendix 9.1.1.

1.1.10 Thermal runaway

Slight increases in temperature can lead to dramatic increases in the rate of reaction; this coupled with a highly exothermic reaction can lead to potentially severe consequences.

One of the most significant problems encountered when conducting polymerisation is thermal runaway, gel effect or Trommsdorff Norrish effect. This refers to the loss of control over the highly exothermic polymerisation reaction due to being able to retain thermal control. As the polymerisation occurs the temperature within the mixture increases, greater levels of radicals are produced resulting in more polymer being formed. As this occurs the viscosity of the material increases, reducing heat transfer. In a large reaction system the mean path for heat transfer can be long, in the order of metres; this coupled with the increased viscosity means that it becomes increasingly difficult to remove heat from the process. This increase in temperature within the system leads to an increased rate of polymerisation and further increases viscosity. This viscosity increase also reduces molecular diffusion within the system, reducing the ability of the chains to terminate, as a result forming higher molecular weight materials further increases viscosity. This can form a cycle where heat generation within the system increases exponentially such that the system loses control, potentially leading to large build up in pressure and loss of containment (Dionisio, Mahabadi et al. 1979; O'Neil and Torkelson 1997).

The way in which this is most often prevented in industrial reactors is *via* the use of lower operating temperatures. This leads to a slower release of radicals giving higher control, it however has the disadvantage of slowing the rate of reaction and increasing residence times required.

Thermal runaway can be prevented by the adoption of CCT, and by limiting conversion (<50 %). This ensures that the viscosity remains low and does not significantly inhibit heat transfer or chain termination. Therefore using this method it is possible to carry out the reaction at higher temperatures, allowing for access to much higher rates of reaction. This could potentially allow for polymerisation to be carried out in minutes or seconds, rather than hours. This intensification coupled with continuous flow processing techniques could lead to a viable process for industrial production.

1.1.11 Polymerisation ceiling temperature

Ceiling temperature is defined as the temperature at which the rate of polymerisation and rate of depolymerisation become equal, hence allowing for no further gain of polymer. Ceiling temperature is defined thermodynamically based upon the concentration of monomer present, and the end group structure of the polymer. The ceiling temperature for poly methyl methacrylate is 220 °C, therefore it is important to ensure that reaction temperature remain below this to ensure that it is not causing limitations in conversion achieved (Cowie and Arrighi 1991; Mark 2007).

1.1.12 Product characterisation of polymers

With a specific molecular weight target it is important to carry out analysis of products formed to ensure that the target material has been produced, and to ensure quality of the product produced and the conversion achieved. In this work conversion has been defined as the % consumption of monomer (Cowie and Arrighi 1991; Nguyen 2012).

In terms of characterisation of a linear molecular structure here are two main factors used, molecular weight and poly dispersity (PDI).

In larger weight polymers, molecular weight is determined by a distribution, of all the molecular weights present. Due to their being 100,000s of repeat units there is often a wide variation. There are two main different averaging techniques used when analysing polymeric materials, the number average molecular mass (M_n) and the weight averaged molar mass (M_w).

$$M_n = \frac{\sum M_i N_i}{\sum N_i} \qquad (1)$$

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \qquad (2)$$

M_n is the arithmetic (normal) mean distribution of molecular weight and is more sensitive to low molecular mass chains; M_w is more sensitive to higher molecular weight chains. This gives a variation between the two averages; the ratio between the two is known as polydispersity (PDI), equation (3) shown below. This dimensionless number is a measure of the spread within the distribution of molecular mass present, where 1 would mean only one molecular mass is formed (Nguyen 2012).

$$PDI = \frac{M_w}{M_n} \qquad (3)$$

Due to the very low molecular weight products being formed in this work, PDI will not be used. Instead relative abundances of the target materials will be stated, with such a narrow distribution PDI would become statistically irrelevant (Gridnev, Ittel et al. 1995).

Product characterisation was mostly carried out using two techniques, NMR and GPC. Some samples were further analysed with the use of GC-MS and TGA to help validate results given by the other two techniques. Explanation of these techniques can be found in methodology Section 4.5.

1.2 Introduction to chemical reactors

There are many economic and environmental drivers pushing industry towards cleaner and more efficient processing technologies. Rising costs have a push effect on companies to increase efficiency, thus in large scale industries small improvements can lead to big savings. Environmental legislation put in place by governments; and guidelines created by professional bodies such as the Institute of Chemical Engineers (IChemE) and the American Institute of Chemical Engineers (AIChE) have forced companies to improve. Improvements in processing and management can have a pull effect; businesses are much more likely to improve a process of their own volition if the changes made result in financial benefits.

Adaptation of new processing techniques and the use of novel systems can be used to drastically improve a process, potentially giving significant benefits. In the case of large scale polymer manufacture, continuous processing could help overcome many of the limitations of batch systems (Wiles and Watts 2012).

1.2.1 Batch reactor overview

The term 'batch reactor' is defined as a reactor in which all feed material is placed into the reactor before the reaction commences and remains within until completion or the required level of conversion is reached, with the products being subsequently removed and purified. The vessel then requires cleaning before the next use.

The earliest types of batch reactors consisted of clay pots and were used for the fermentation of grapes to produce wine, meaning that the fundamentals of this technology have been around for thousands of years. Modern day batch reactors are used globally for a huge variety of industrial and academic purposes, from the brewing of hundreds of thousands of pints at once, down to a pharmaceutical scale where milligrams of high value product are formed

(Euzen, Trambouze et al. 1993; Trambouze and Euzen 2004; Fogler 2006; Sinnott and Towler 2009).

There are numerous advantages to this type of technology, however there are also many disadvantages. It is a very well understood process, allowing for simple design concepts based upon reaction kinetics. With modern control and monitoring technologies very precise control can be achieved within the vessel, as high levels of mixing allow for very high repeatability and product quality making this method attractive in many industries such as pharmaceuticals or speciality polymers (Evans 2013). This technology also allows for ease in switching between products, as if a plant is required to produce different materials the same reactor can often be used (Zlokarnik 2006).

There are however several inherent disadvantages with this technology. In high volume industries, such as the bulk polymer industry, there is the requirement for high throughput that is hindered by the slow reaction time typically associated with batch processing. This leads to the requirement of either a large number of reactors operating in parallel, or the use of very large reactors, often containing thousands of litres of material. This leads to large geometry reactors being produced which can present several challenges, especially when processing polymeric materials.

For example, the polymerisation of methyl methacrylate to a relatively high molecular weight, it has been shown in the previous Section that this presents several challenges. This highly exothermic reaction requires an initial heat input to initiate the reaction by initiator decomposition, and once the reaction starts the high rate of propagation gives rapid heat generation and an associated viscosity increase. In order to main precise control of the reaction, both thermally and in terms of product quality, high levels of mixing and effective heat removal from the system are required.

Heat transfer within a liquid is directly related to the Reynolds number (Perry and Green 2008); this dimensionless number is a measure of the turbulence

within the material and is directly proportional to the viscosity. The equation below shows the Reynolds number equation for fluid within a stirred tank:

$$\mathrm{Re} = \frac{\rho N D^2}{\mu}$$

Where:

ρ : density

N : rotational speed

D : characteristic dimension of agitator

μ : viscosity

From this it can be seen that if the rate of stirring (N) is maintained as constant throughout the reaction, the Reynolds number will fall due to the increasing viscosity. The subsequent heat transfer will also fall; this coupled with long heat transfer paths can give potential for heat build-up within a reactor. Reduced efficiency of mixing could also hinder the reaction and result in poor quality products.

To ensure safe operation the conditions within the reactor are closely controlled. This control can come in several forms; reduced operating temperature reduces the rate of initiator decomposition giving a slower, more controlled reaction. Implementing different chemistries, for example the use of CCT which, as explained previously, has been shown to be able to overcome the risk of thermal runaway. Using this method could allow for operation at higher temperatures and pressure, in order to increase the rate of reaction; this is known as process intensification.

1.2.2 Continuous flow reactor overview

The basis of a continuous flow reactor is that it is operating in a steady state. Steady state is defined as when the system is operating with no accumulation in terms of heat flow, temperature, mass flow, or conversion. All parameters

within the continuous flow system should be at steady state with no change over time.

Over the years, more and more processes have adopted the use of continuous flow reactors. With increasing economical driving factors and improvements in control and monitoring technology this type of processing has become more viable, and it has even started to make in-roads into the pharmaceutical industry, which has always traditionally been a batch processing industry. There will however always be certain chemical reactions which are impossible to carry out in flow (Donati and Paludetto 1999; Wiles and Watts 2012; Evans 2013).

Continuous flow reactors or plug flow reactors are constructed on the principle of changing concentration along the length of a pipe; the length required is dependent upon the rate of reaction and overall conversion required. Therefore it is advantageous to have a rapid reaction, as this allows for reduced pipe lengths.

Continuous processing in all reacting systems offers advantages and improved safety compared to batch equivalents. In batch processing, all the reactants are mixed together prior to initiation. In continuous systems the materials are mixed together throughout the reaction; this gives much more control of the reaction, giving an inherently safer process. There are also reduced volumes of material reacting at any one time, as a plug flow reactor can be assumed to be lots of small reactors in series, with little or no interaction between different units within the pipe. This means that there is a significantly reduced risk of effects arising from large volumes. The flow system has improved mixing, induced by the fluid movement and increased heat transfer from the larger surface area.

This combination of increased heat transfer and smaller reaction volumes in flow reactors allows for the use of more extreme operating conditions to utilise thermal effects and achieve higher reaction rates. This could potentially

lead to significant reductions in energy requirement and reduced processing time compared to batch processes.

Other benefits of flow processes are the reduced solvent requirements, as in batch systems it is required that the reactor be cleaned between each reaction. In a continuous process this is avoided as the process is not shut down at the end of a single reaction.

The disadvantages of continuous flow processing in a polymer system arise from the stability of the current methods and industry not wanting to invest large sums of money to adopt a new technique that may only give marginal benefits. With access to higher reaction rates and newer control technology, higher operating costs and more stringent environmental legislation; continuous processing may find its way into the bulk polymer industry in the future, although it is not currently widely utilised.

2 Microwave fundamentals

Microwaves are a form of non-ionising electromagnetic radiation in the frequency range 300 MHz to 300 GHz, giving wavelengths between 1 m and 1 mm. The electromagnetic spectrum can be split into several different regions, shown in Figure 2-1 below.

Dominant heating mechanism	Space charge		Orientation		Atomic		Electronic				
Spectrum classification	Radio				Microwave		Infrared (IR)		Visible	Ultra violet (UV)	X ray and gamma
Frequency (Hz)	10^3		10^6		10^9		10^{12}		10^{15}		10^{18}

Figure 2-1: Electromagnetic spectrum, reproduced from (Meredith 1998)

With all electromagnetic radiation there are restrictions upon the frequencies, and what purposes they can be used for, to prevent interference between equipment and disruption of communications. There are however frequencies that can be used for heating purposes, termed Industrial Scientific and Medical (ISM) frequencies. These vary globally, according to national legislation; the most common of these used in microwave heating applications are at 896 MHz and 2.45 GHz, giving wavelengths of 32.8 and 12.2 cm in air (BERR 2008).

Electromagnetic radiation has two components, electric field (E, V/m) and a magnetic field (H, A/m). These two fields are always perpendicular and in phase to each other, as shown in Figure 2-2. Electromagnetic radiation propagates at the speed of light (c), $3x10^8$ m/s in free space. The relationship between speed, frequency (f, Hz) and wavelength (λ, m) is given by:

$$f = \frac{c}{\lambda}$$

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Wavelength is defined as the length for the electromagnetic wave going through one full oscillation (Staelin, Morgenthaler et al. 1994).
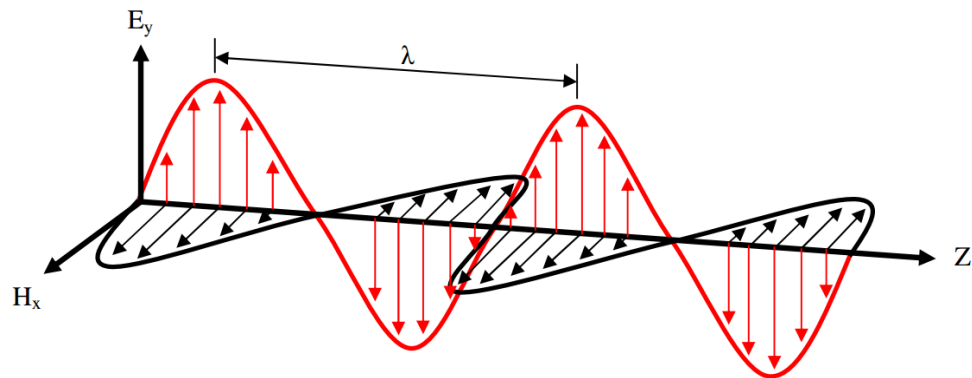
Figure 2-2: Diagram showing electromagnetic wave with perpendicular, in-phase electric and magnetic fields, λ indicates one wavelength (Hamilton 2009)

2.1 Material interactions

Microwave heating is part of a group of heating techniques known as electroheat, these include induction, infrared (IR), conductive/direct resistance, and radio frequency (RF). These techniques utilise specific sectors of the electromagnetic spectrum and are each suited to heating different types of materials (Barber 1983; Metaxas 1996). Heating within the microwave range occurs mainly by two mechanisms, dipolar polarisation and conduction; the other mechanisms become more dominant at other frequencies; explained in further detail later (Al-Harahsheh 2005).

Within single phase materials classification of material interaction can be simplified into three groups:

1. Transparent: low loss materials such as Quartz, Alumina, PTFE or air. Microwaves propagate through the material with minimal heating occurring.
2. Absorbent: high loss materials such as water or MMA. Microwave energy is absorbed as it propagates through the material causing heating. More details on this shown below.

3. Reflective: highly conductive materials such as metals. Microwave energy is reflected, high magnetic field may induce Eddy currents within the material up to the skin depth causing heating at the surface.

This simplification does not work when looking at multi-component materials, one of the components could be transparent whilst another being highly absorbent; thus allowing for heating of one component whilst minimal energy transfer occurs to the transparent material. This is known as selective heating, and can be a significant benefit to the use of microwave heating.

A good example of this occurring in a solid is processing of vermiculite, a layered microwave transparent mineral with microwave absorbent water physically bound between layers. In its processed (exfoliated) form it can be used as a fire retardant insulation in construction. This process carried out conventionally is highly energy inefficient with heating of the entire material required. Microwave heating selectively heats the water, significantly reducing energy requirement (Folorunso, Dodds et al. 2012).

2.2 Dielectric properties

Dielectric materials are those which can be polarised by an applied electric field, this can be by the presence of a permanent or an induced dipole within the material. The complex permittivity is a measure of how a material interacts with an electromagnetic field, and is dependent upon both frequency and temperature. It is well established that when a dielectric material is placed within an electric field that the electric field intensity is increased within the material (Metaxas and Meredith 1983). The extent to which the field intensity is increased is based upon the complex permittivity of the material, shown below:

$$\varepsilon* = \varepsilon' - j\varepsilon''$$
(2-1)

Where $\varepsilon*$ is the complex permittivity, ε' is the dielectric constant and ε'' is the loss factor (Meredith 1998).

Dielectric constant is the measure of the ability of the material to be polarised by an electric field. Loss factor is the measure of how effectively the energy stored *via* polarisation, can be converted into heat. The overall dielectric loss is contributed to by several different mechanisms, this relationship is shown below:

$$\varepsilon_{eff}^{"} = \varepsilon_d^{"} + \varepsilon_e^{"} + \varepsilon_a^{"} + \varepsilon_{MW}^{"} \qquad (2\text{-}2)$$

Where subscripts d, e, a, and MW refer to dipolar, electronic, atomic and Maxwell-Wagner respectively (Metaxas and Meredith 1983). The contribution of each mechanism is dependent upon the material and the frequency of the applied wave. Under microwave heating the dipolar mechanism is dominant and causes a significant portion of heating.

Commonly the dielectric loss angle (δ) is used to define a materials, 'lossyness', or how well it will be heated by an electromagnetic field. It is calculated using:

$$\delta = \tan^{-1}\frac{\varepsilon^{"}}{\varepsilon'} \qquad (2\text{-}3)$$

Figure 2-3 below shows materials of varying dielectric properties measured at ambient temperature. Materials to the right of the chart are seen as 'lossy' and would be expected to heat within an electromagnetic field. Materials to the left are low loss and would not be expected to heat. Important materials to note are PTFE which is used within microwave cavities to retain sample, and MMA which is the monomer used for this body of work.
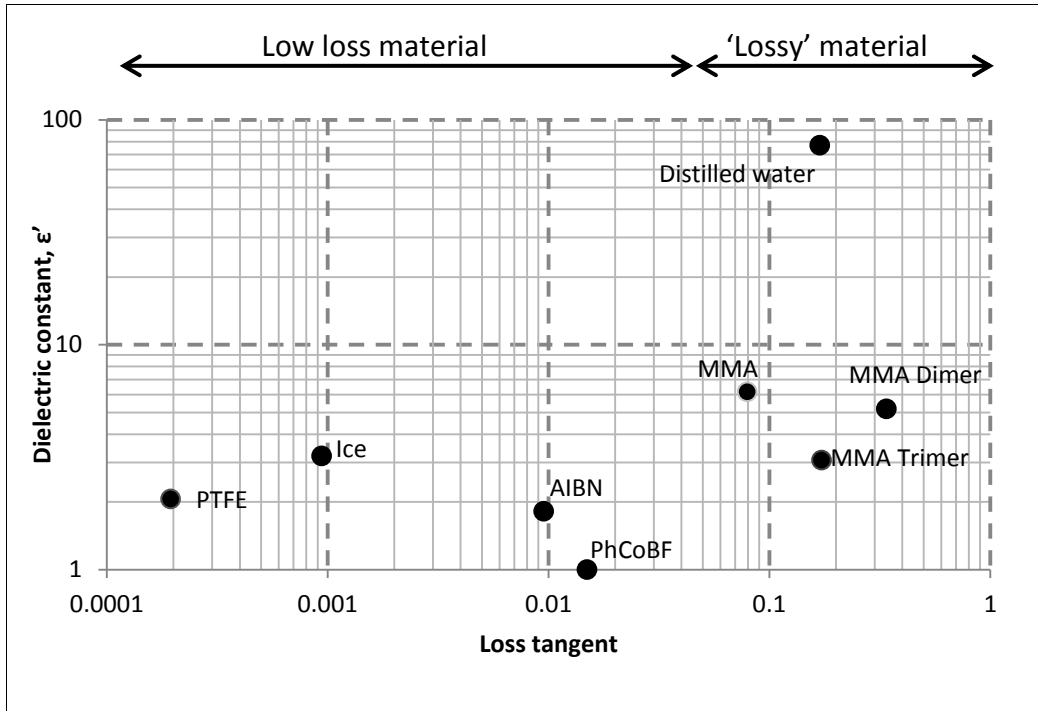
Figure 2-3: Dielectric properties of materials at ambient temperatures, 2.45 GHz, redrawn from (Meredith 1998), others added from(Robinson, Kingman et al. 2010).

2.2.1 Power density

Dielectric heating is affected by three factors; the extent of the polarisation occurring (amplitude), frequency of polarisation and the strength of the applied electric field E. The multiplication of these two factors can be calculated as a power, this relationship is given from the dielectric heating/power density equation shown below.

$$P_d = 2\pi f \varepsilon_0 \varepsilon'' E^2 \qquad\qquad (2\text{-}4)$$

Where

P_d :   Power density, P_d (W/m³)

ƒ   :   frequency (Hz),

ε_0 :   permittivity of free space,

ε'' :   dielectric loss factor of the material

E   :   electric field strength (V/m).

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With frequency restricted by ISM bands and dielectric properties fixed by the material, the main method in which power density can be increased is by increase in E, this can be done by increasing the power output of the microwave generator. From this equation it would indicate that loss factor is the only contributor to heating, however the dielectric constant has an effect upon the electric field strength within the material.

This equation can be modified to calculate the temperature change within the material given by this power density.

Temperature rise with respect to time from heat input is given by:

$$\frac{dT}{dt} = \frac{P_d}{C_p.\rho}$$

(2-5)

Where C_p is the specific heat capacity (kJ/kg.K), and ρ is the material density (kg/m³).

Equation (2-4) is analogous to:

$$Power\ transfer = frequency \times amplitude\ of\ polarisation$$

Where the amplitude of polarisation is the contribution to the heating based upon the extent to which the material is polarised. From this the relationship between heating and frequency can be understood.

Shown in Figure 2-4 below is a graphical representation of the contribution to heating provided by both frequency. At low frequencies the material is fully polarised by all mechanisms, due to the low rate of oscillation in the applied field. This low frequency gives lower levels of heating due to reduced friction.
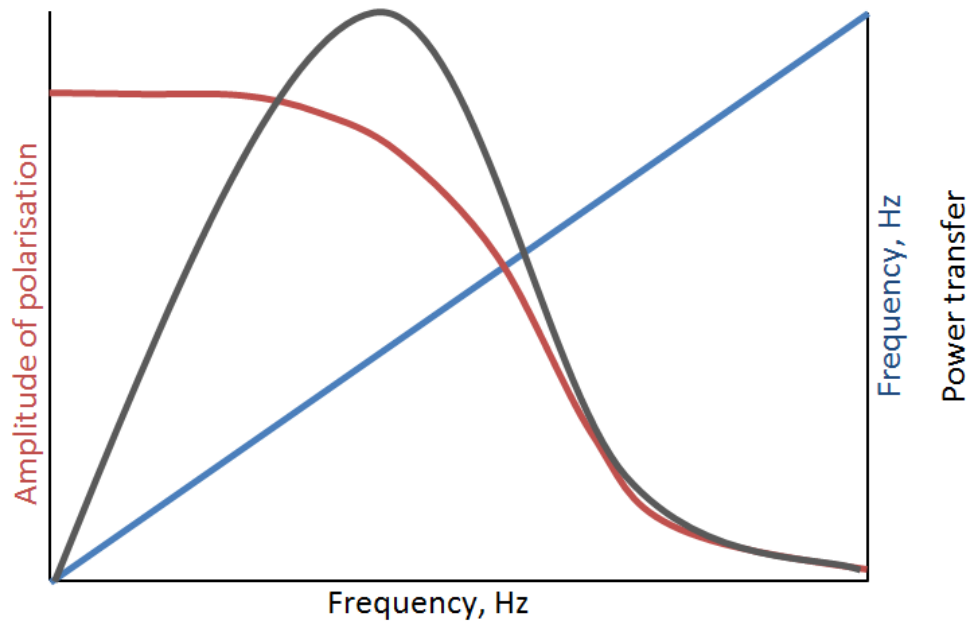
Figure 2-4: Graphical representation of the contribution to overall power transfer provided by polarisation and frequency

As frequency increases the amplitude of the polarisation falls slightly, as the material cannot remain in phase with the applied field. The contribution to heating from the frequency is increased therefore giving a much higher power transfer. This maximum in power transfer occurs at a specific frequency for different materials at different temperatures, and is known as the relaxation frequency (s^{-1}) (Agilent 2006). As frequency increases further the amplitude of polarisation falls further, and therefore the rate of heating falls again.

2.2.2   Loss mechanisms

Microwave heating arises from polarisation, forcing the molecules, atoms or electrons within a material to align with the oscillating electric field. This oscillation produces heat due to friction caused by the movement. The main types of polarisation are orientation, space charge (Maxwell-Wagner), atomic and electronic (Von Hippel 1954).

2.2.2.1   Dipolar polarisation

Dipolar or orientation polarisation occurs in dielectrics containing permanent dipoles due to asymmetric charge distribution within the molecule, such as water. This means that under a time-alternating electric field they are highly

sensitive and re-orientate themselves to remain in phase with the oscillating electric field.

At intermediate frequencies, such as microwave; the relaxation time after polarisation is similar to that of E-field oscillation (6.9×10^{-7} s), thus giving high levels of heating at these frequencies. This re-orientation under an electric field is shown in Figure 2-5 below. At microwave frequencies this mechanism gives the largest contribution to heating.
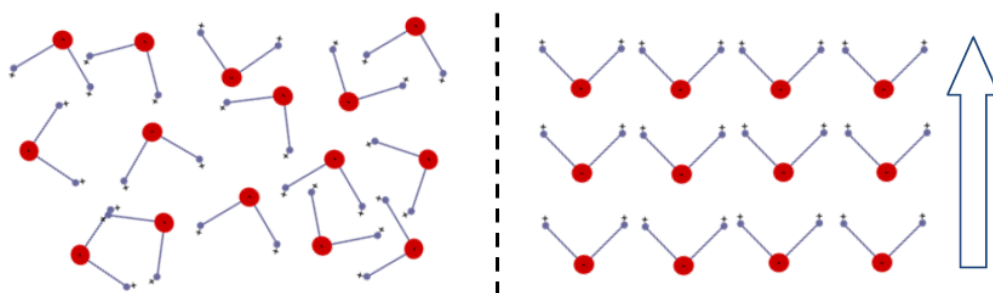
Figure 2-5: Graphical illustration of dipolar polarisation of water under an applied electric field (right), arrow indicates direction of the applied field (AlSayegh 2012).

2.2.2.2 Electronic polarisation

Atoms are composed of a positively charged nucleus and a negatively charged electron cloud. This cloud is an area in which the electrons are most likely to be. Under normal conditions (no applied electric field) the electrons can be assumed to be evenly distributed with equal probability of an electron being at any location around the nucleus; this can be simplified to a 2 dimensional structure which is shown in Figure 2-6(left). Application of an oscillating electric field can cause a shift in this electron density, inducing a temporary dipole within the atom. This is shown in Figure 2-6(right). This type of polarisation occurs rapidly, thus significant contributions to the overall loss are only found at frequencies higher than that of microwave heating (visible light or ultraviolet) (Meredith 1998).
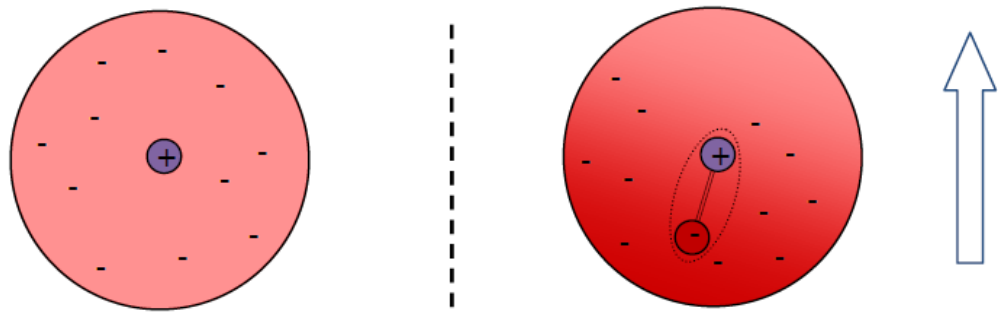
Figure 2-6: Graphical representation of electronic polarisation of an atom under an electric field (right), arrow indicates direction of the applied field (AlSayegh 2012).

2.2.2.3 Atomic polarisation

When atoms bond to form molecules such as (HCl or NaCl), there will be a positive and negative atom, and it is the attraction between these that causes a bond to form. The electrons within the bond will always be attracted to the electronegative (Cl^-) side of the molecule causing the atoms to behave like a permanent dipole. Under an applied electric field this dipole will cause the molecule to stretch, vibrate and align with the electric field, shown in Figure 2-7 below. Much like electronic polarisation the occurrence and decay of atomic polarisation is rapid, with significant contribution to dielectric loss occurring at higher than microwave frequencies (infrared).
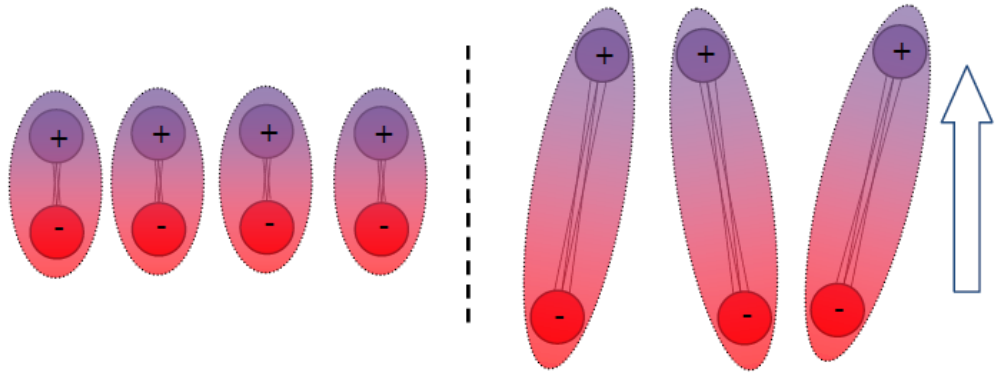
Figure 2-7: Graphical representation of atomic polarisation of a molecule under an electric field (right), arrow indicates direction of the applied field (AlSayegh 2012).

2.2.2.4 Maxwell-Wagner (interfacial polarisation)

Interfacial polarisation or space charge polarisation arises due to the build-up of charge between the interface of conducting and non-conducting heterogeneous solids such as a mixture of metallic and non-metallic powders. This build-up of positive and negative charge can contribute to the overall polarisation of the material and contribute to the dielectric properties. This mechanism takes place at frequencies of usually less than 50 MHz (Metaxas and Meredith 1983).
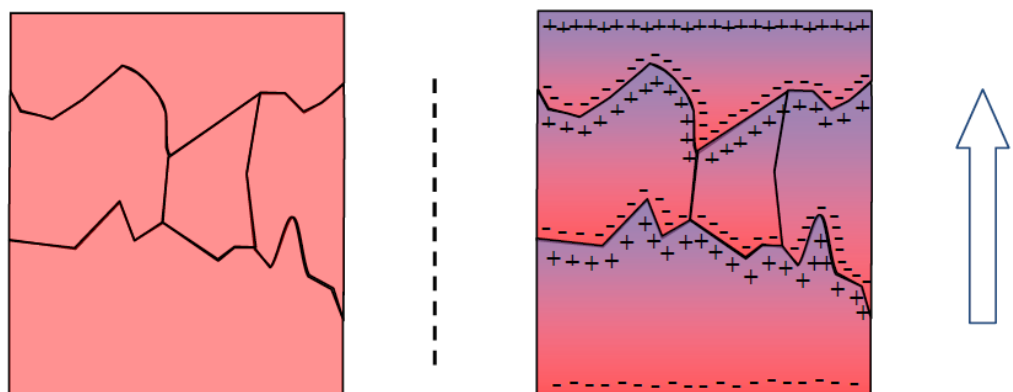
Figure 2-8 Graphical representation interfacial polarisation of a multi-phase material under an electric field (right), arrow indicates direction of the applied field (AlSayegh 2012).

2.2.2.5 Ionic conduction

When an electrical conductor is subjected to microwave irradiation, charge conductors (ions or electrons) flow in phase with the electric field. The induced current causes direct heating due to electric resistance, with this type of heating occurring within metals and in those with dissolved ions such as brine. The high electric field can induce eddy currents upon the surface of the material, causing a current to flow in the opposite direction of the original current; this is known as the skin effect.

Under microwave heating water is known to heat almost exclusively by dipolar rotation, the addition of a charge carrier such as NaCl increases its conductivity allowing to heat by ohmic heating simultaneously with the dipolar mechanism.

2.2.3 Frequency dependence of dielectric properties

Figure 2-9 below shows the effect of frequency upon dielectric properties, within an ideal material exhibiting all types of polarisation. At low frequencies ionic conduction is the only mechanism contributing to the loss factor. The constant is high because all the different polarisation mechanisms are contributing to full polarisation of the material. At these low frequencies the low rate of polarisation allows for all forms of polarisation to occur in phase with the incident wave.
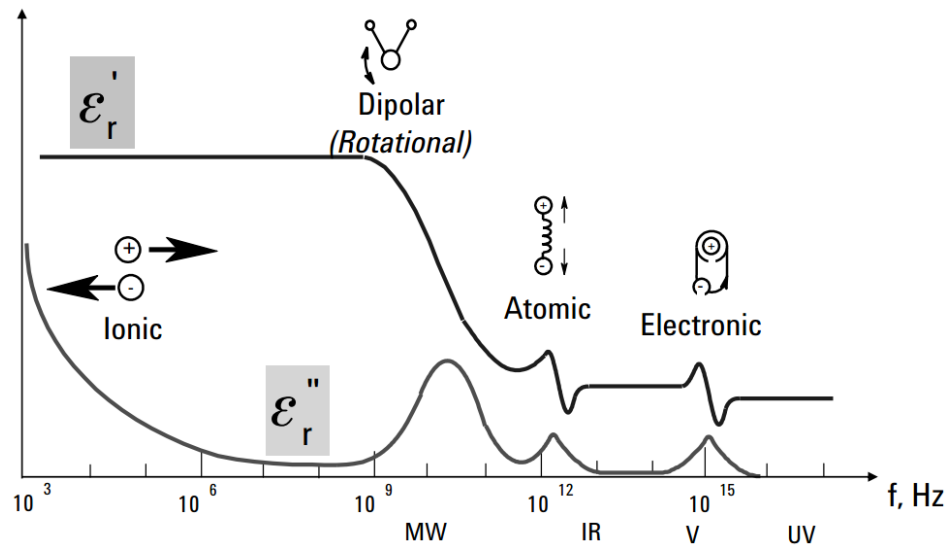
Figure 2-9: Effect of frequency upon dielectric heating mechanism (Harrop 1972), reprinted by (Agilent 2006)

As frequency is increased into the microwave region (10^9 Hz), dipolar polarisation begins to lag behind the frequency of the oscillating wave. This lag causes the reduction in constant due to reduced degree of polarisation. The peak in loss is at the relaxation frequency for this mechanism (22×10^9 Hz for water). As frequency is further increased both atomic and electronic polarisation reach their relaxation frequencies at 10^{12} and 10^{15} Hz. Past this frequency, the rate of oscillation of the incident wave becomes so high that no polarisation occurs.

2.2.4 Temperature dependence of dielectric properties

The ability for a material to become polarised is based upon the way in which the molecule moves. Temperature has a direct effect upon this, and can either help or hinder the way in which the material is heated under electromagnetic radiation.

The effect that temperature has is highly dependent upon the type of material. Increased temperature often gives a reduction in viscosity and a reduction in density; allowing a material to be fully polarised up to a higher temperature, thus giving an increase in the dielectric constant, and the relaxation frequency of the material; which leads to an increase in the overall level of heating. This is highlighted in Figure 2-10, where increasing the

temperature (dotted lines) has shifted the graph to the right, giving an increased maximum in power transfer.
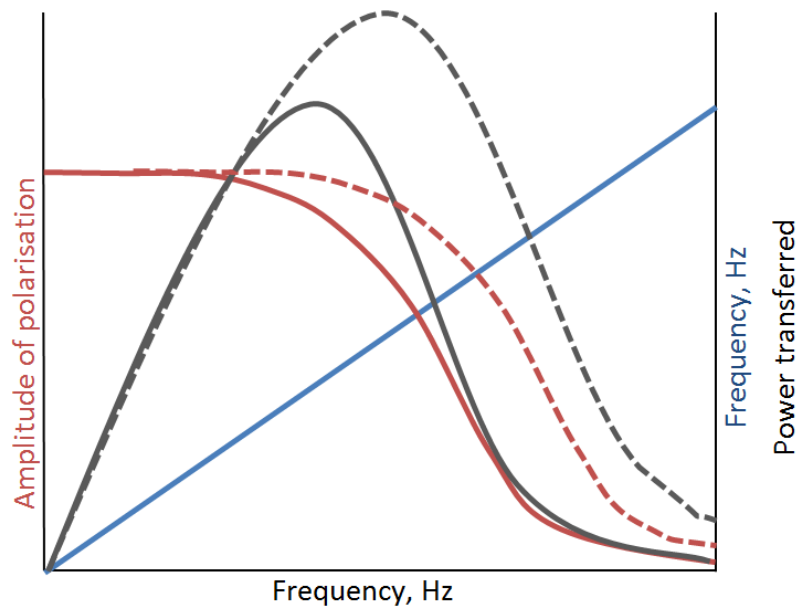
Figure 2-10: Graphical representation of the effect of temperature on polarisation of the material and the power transfer to the material. The higher temperature system is shown in dotted lines

In complex materials made up of a mixture of components, or those undergoing a phase change, dielectric properties are of significant importance. It may be found that a phase change can give rise to a significant change in dielectric properties, due to changes in the chemical bonding occurring, such as ice to water Figure 2-3. If a chemical reaction is occurring within the system, materials can be produced which will affect the physical and dielectric properties.

2.2.5 Attenuation

Attenuation is the process by which energy intensity (power) is lost from a propagating wave. This can be caused by propagation into a microwave absorbent medium, or propagation along a waveguide which is below cut-off frequency (explained in Section 2.4.7).

2.2.6 Penetration depth

As an electromagnetic wave penetrates through a dielectric material, its amplitude diminishes due to absorption of energy. The rate at which this decay occurs is dependant both upon ε' and ε''. Penetration depth D_p is defined as the depth into a material at which power flux reaches $1/e$ (36.8 %) of the surface value (Meredith 1998). It is calculated using the following equation:

$$D_p = \frac{\lambda_0}{2\pi\sqrt{2\varepsilon'}} \frac{1}{\sqrt{\left[\left\{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2\right\}^{0.5} -1\right]}}$$

(2-6)

Where λ_0= wavelength in free space (m), ε'=dielectric constant, ε''=dielectric loss.

If $\varepsilon''<\varepsilon'$ the equation can be simplified to:

$$D_p \approx \frac{\lambda_0\sqrt{\varepsilon'}}{2\pi\varepsilon''}$$

(2-7)

2.2.7 Dielectric property measurement

There are many techniques used for the measurement of dielectric properties, with the technique used being dependent upon several factors; the type of material, whether the material is low or high loss, phase of material, temperature range required, and the frequency range required. Two of the most common techniques at microwave frequencies are cavity perturbation and co-axial probe (Agilent 2006).

During this project dielectric property measurements of all the materials used had been carried out and published by a previous student at the University of Nottingham; the data is fully presented within the following publication by Robinson, Kingman et al. (2010). The work was assessed and reproduced at a limited scale to check the accuracy; it was found that the analysis was carried out rigorously. Therefore for the purposes of this project no further

measurements were taken and results were taken from the publication referenced above. Materials were obtained from the same supplier and were all analysed via NMR to ensure purity before use. It was therefore assumed that the dielectric properties remained constant.

2.3 Advantages and disadvantages of microwave heating

Industrially heat transfer is provided conventionally, this being either by the use of electrical heat, high pressure steam, heating oil or direct heating in a furnace (Coulson, Richardson et al. 1999; Sinnott and Towler 2009). This type of heating has several advantages; it is cheap, readily available and well understood. For a microwave system to be viable, the advantages offered by the system must be great enough to outweigh the increased cost involved with the electrically complex equipment. Advantages of microwave processing over conventional processing include:

- Selective heating
- Volumetric heating
- Reduced thermal inertia
- Reduced foot print
- Non-contact
- Reduced fouling
- Reduced temperature gradients
- Increased energy efficiency
- Rapid heating
- Flexible operating window

The main disadvantages of microwave heating are the capital high costs, the complex electrical equipment is expensive and high electrical costs also contribute. A major cost is also in R&D, as most microwave systems require a bespoke cavity to handle the materials in a specific situation, which can lead to significant costs being encountered.

2.4　Microwave equipment

Microwave systems can be simplified and represented by the layout shown below in Figure 2-11. In different systems these parts may take different forms but are in essence the same. Each part will be explained in detail within the next Section.
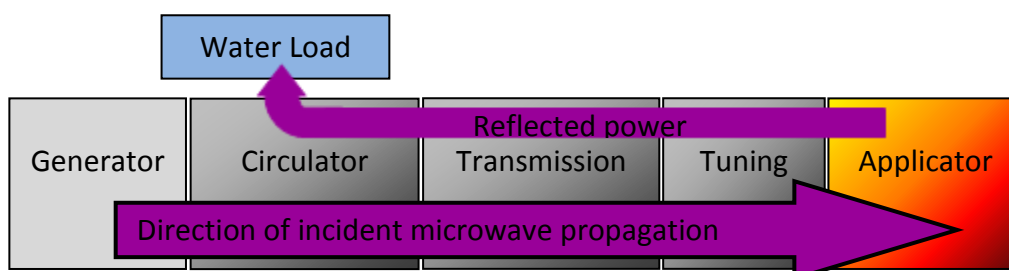
Figure 2-11: Simplified diagram showing basic components in a microwave heating system, redrawn from (AlSayegh 2012).

2.4.1　Generator

Generators are used to produce electromagnetic energy for use in communication, radar and heating systems. Both communication and radar applications use almost zero power. Historically, industrial microwave heating applications have been >10 kW.

2.4.1.1　Magnetron

The most common type of generator used in microwave heating is the magnetron; other types include the klystron and solid state generation. Klystrons are a device for wave amplification; high costs mean they are not commonly used within laboratory environments. Solid state devices were more commonly used for low power applications, <10 W, but there are now systems available at 200 and soon to be up to 2000 W, as these systems allow for very precise control and can give constant frequency output at almost 0 power output (Sairem 2012). These are not discussed further as they have not been used within this work.

The popularity of the magnetron is due to the simplicity and cheapness of manufacture, its uses in domestic equipment have led to large reductions in

price. These domestic magnetrons however do not give precise control of power or frequency, so research and industrial equipment utilises higher quality equipment to give better results and repeatability.

Figure 2-12 below shows a diagram of a standard magnetron. A cylindrical metal cathode (blue) is heated at the centre; this is surrounded by a circular anode (red) containing radial slots. A high strength magnetic field is produced parallel to the cathode/anode assembly, in low power systems this is by a fixed magnet; at high powers an electromagnet is used. This assembly is enclosed within a vacuum of 10^{-6} mm Hg. An antenna is connected to the slotted anode to transmit the generated microwaves.
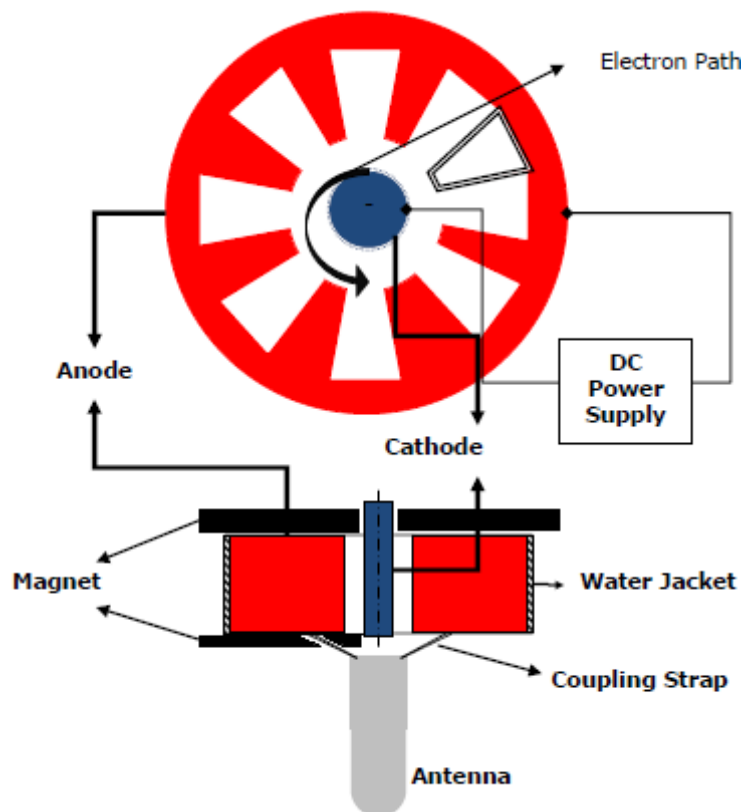
Figure 2-12: Magnetron used for producing electromagnetic radiation (AlSayegh 2012).

During operation, a high electron potential is applied between the anode and cathode (2-20 kV) depending on power output. Electrons are released from the heated cathode. Due to the presence of the magnetic and electric field; they are forced into a spiral motion around the cathode to the anode.

As electrons pass the slots within the anode they cause the cavity to resonate, with the frequency of the resonance being dependent upon the slot geometry and the circumferential velocity. Once a high enough circumferential velocity is achieved a standing wave is produced within the cavity. Energy is transferred to this wave by high velocity electrons, as they contact the wave they are slowed, transferring their kinetic energy. Residual energy is transferred to the anode, causing heat build-up; water cooling is commonly used, although at low power levels air cooling can be utilised. This high power field is transferred to the transmission line *via* the antenna (Thostenson and Chou 1999).

Magnetrons allow for high energy efficiency, at 2450 MHz giving 70 % conversion from DC to microwave, at a reduced frequency of 900 MHz this efficiency increases to 90 %.

2.4.2 Circulator

If power transfer to the sample is below 100 %, power will be reflected, as shown in Figure 2-11. This power could potentially reach the magnetron and cause excess heating of the delicate equipment reducing its operable life. To prevent this, a circulator is used; this has the purpose of allowing incident power to be transmitted forward to the sample, whilst preventing any reflected power reaching the generator.

This type of equipment can have different designs, in relatively low power, when compared to industrial microwave equipment, systems such as domestic microwave or the CEM Discover. The cavities are coated with absorbent paint to absorb any excess energy, with the energy then dissipated as heat within the walls. In other low power systems such as the Sairem MiniFlow reflected power is absorbed into a solid absorbent and heat dissipated by air cooling.

At higher power levels (e.g. >300 W) this becomes unsuitable, as there is the potential for high levels of power to be reflected. The use of static magnets and physical geometry allows for the incident wave to be transmitted, whilst

any reflected power is directed into a flowing water load, shown below in Figure 2-13. This heat is then rejected in a heat exchanger. Most lab and scientific equipment has a built-in measurement of forward and reflected power, coupled with interlocks that will limit incident power if high levels of reflected energy are detected.
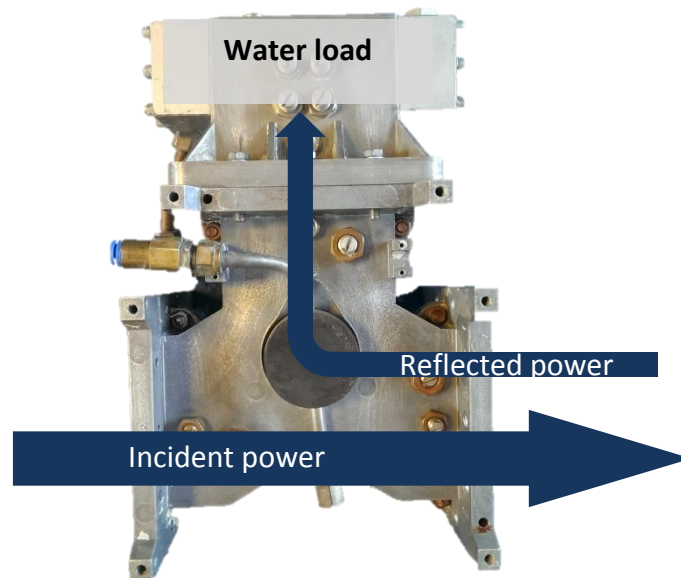
Figure 2-13: Photograph taken of circulator for protecting generator from reflected power, including directions of travel for energy.

2.4.3 Transmission line

Transmission lines are the method by which the generator, tuner and cavity are connected. These can come in many different forms, waveguides, co-axial lines, parallel plates and open wires (Meredith 1998). The most commonly used within microwave heating systems are coaxial lines and open waveguides; this is due to their ability to carry higher power levels.

2.4.3.1 Coaxial line

Are constructed from a metal core surrounded by a dielectric insulator (can be air). This is the surrounded by another metallic shield and finally insulated with a plastic sheath.
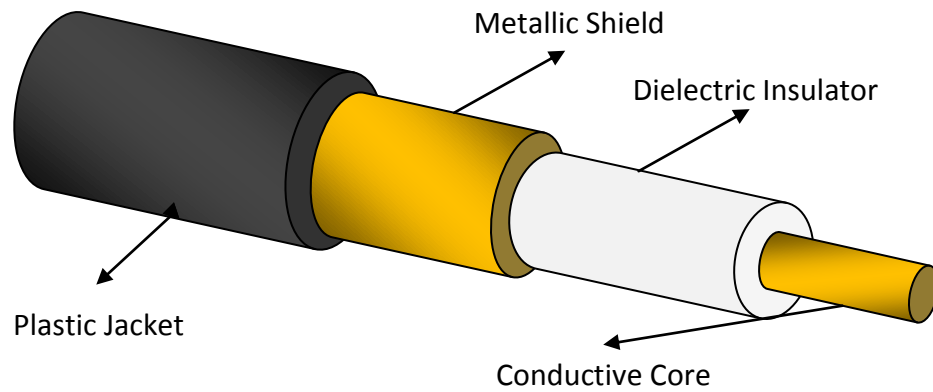
Figure 2-14: Coaxial cable, copied with permission from (AlSayegh 2012)

This design allows the electromagnetic wave to transmit along the insulated Section. Coaxial cables are commonly used in low power applications such as solid state generators <200 W in power or network analysers.

The problems with coaxial cables are that as power is increased, losses within the line due to skin depth become high, and heating of the cable occurs. At higher power levels it is more common to use open waveguides.

2.4.3.2 Open waveguide

These open tubes are commonly used to transfer high levels of power with low loss of energy along the transmission line. These hollow, most commonly metallic structures are usually rectangular, circular waveguides are also used in some applications.

Microwaves propagate along the air within the waveguide. This offers an advantage over coaxial cables as air losses are lower than the dielectric insulators used, and very low levels of attenuation are caused by Joule heating of the walls due to induced electrical current. This is however negligible at microwave frequencies.

This type of structure can be used to transfer hundreds of kW of energy. Precision fabrication and machining is required to minimise losses. The dimensions of the waveguide used are dependent upon the frequency used, the lower the frequency the larger the waveguide. Below microwave

frequencies these sizes become prohibitive, here coaxial cables are more commonly used (Metaxas and Meredith 1983; Meredith 1998).

2.4.4 Modes of propagation

When microwave radiation is contained within a structure such as a rectangular waveguide, maxima and minima in electric and magnetic field begin to form, which is due to constructive and destructive interference. These patterns are known as modes, of which there are three main types:

- TM mode (transverse magnetic): no magnetic field in the direction of propagation
- TE mode (transverse electric): no electric field in the direction of propagation
- TEM (transverse electric and magnetic) mode: no electric or magnetic field in the direction of propagation

Patterns within a waveguide are described using a 2 dimensional mode number, in the format TEM_{ab}, where a and b are the mode numbers indicating the numbers of half wavelengths in the vertical and horizontal direction (Pozar 2011). Throughout this work WR340, rectangular waveguides operating in the TEM_{01} mode, were used. WR340 is a standard size rectangular waveguide, 340 indicates a width of 3.400 inches with 1.700 inches height.

2.4.5 Tuning

In most systems efficiency is important to reduce costs, improve throughput and minimise environmental and economic impact.

Electronic theory states that power dissipation from the energy source is maximised when the impedance of the generator is matched to that of the system. The system is defined as everything attached to the generator, transmission lines, tuning devices, cavity and load. If impedance is not matched energy will be reflected back to the generator, reducing efficiency and the operational lifetime of the magnetron. Impedance is matched by the

use of different tuning devices, which is done by changing the impedance of the system to match that of the generator (Rizzoni and Hartley 2007).

2.4.5.1 Short circuit tuner

Short circuit tuners are commonly used in single-mode resonant systems, and this type of tuning was used extensively in this work. This device works by having a sliding plate, placed at the end of the microwave cavity. This plate is adjusted by a piston. The purpose of this type of tuning is to superimpose the reflected wave upon the incident wave, such that the standing wave produced has a maximum centred within the sample. The location of the short circuit will have to be adjusted on a sample-to-sample basis, due to compression of the wavelength caused by the dielectric constant of the sample.

2.4.5.2 Stub tuner

Two, three or four stub tuning devices are commonly used in systems utilising waveguides for power transfer. These are available as manually or automatically operated devices, throughout this work an automated HOMER tuner from S-team was used; this is equipment that gives rapid matching of impedance to maximise energy transfer, and also allows for recording of forward and reflected power on a millisecond basis.

Stub based tuning devices are inserted into the waveguide between the generator and the load; operation is by the insertion of metallic stubs at different lengths into the waveguide. This type of tuning works by changing the impedance of the load to match that of the generator.

Care should be taken when using automated tuning devices, as arcing or plasma generation within the system can lead to the system becoming de-tuned and further power being transferred to the arc. In higher power systems where this is likely, arc sensors should be used with an interlock to ensure safe operation.

2.4.5.3 Alternative impedance matching devices

Other common impedance matching devices are the iris and the E-H tuner; these are both used with waveguides. In some low power systems, co-axial cables are used rather than waveguides, and can be tuned using a co axial tuner (Meredith 1998).

2.4.5.4 Un-tuned systems

Low power systems such as domestic microwaves and the CEM Discover do not operate with active tuning such as those mentioned above. Rather, excess power is absorbed by the walls and is lost; this gives a lower energy efficiency. At this low power, the equipment such as the CEM is not used to generate products efficiently, but for the research of reaction mechanisms, so energy efficiency is not a concern. Domestic microwaves are like this to minimise costs and allow for ease of use.

2.4.6 Microwave cavities

There are many different types of microwave cavity. These can vary from a simple box used as a multi-mode oven, all the way through to bespoke designed microwave cavities for specific purposes.

2.4.6.1 Multi-mode

This is the most common type of microwave cavity used both domestically and scientifically. This type of cavity is constructed of a metallic box with at least 2 wavelengths dimension in two axes, to allow for formation of multiple modes, as shown in Figure 2-15 below.
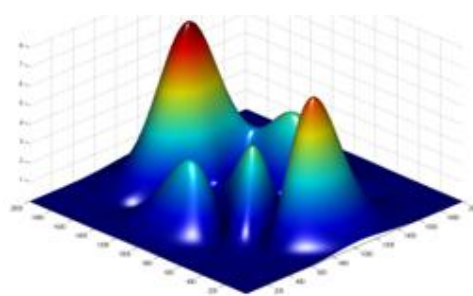
Figure 2-15: E-field intensity within a multi-mode microwave cavity of dimensions 200x200x200mm at 2.45 GHz (AlSayegh 2012).

This type of design is simple to use and allows for the processing of large volumes of material, when compared to a single mode cavity (explained in following Section). This increase in productivity is caused simply by the increased cavity size.

There are several disadvantages to this type of equipment; the formation of several modes of propagation can cause hot spots within the sample, as shown in Figure 2-15, however there are two different methods used to prevent this and to homogenise heating. Firstly, the addition of a mode stirrer, which is a metallic object rotated within the cavity to change the cavity geometry causing the modes within to move, and secondly rotating the sample. The latter is the more commonly used method, as witnessed in domestic equipment. This type of cavity is commonly used within the food processing industry where low power densities and low heating rates are required to maintain food quality. Uneven heating and uncertainty of location of high field intensities make this type of cavity unsuitable for highly temperature sensitive chemical reactions as uneven heating could have a dramatic effect upon the reaction occurring (Chan and Reader 2000).

2.4.6.2 Single-mode cavities

A single mode cavity, as the name suggests is designed in such a way that it can only support one mode of propagation. This allows for well-defined heating zones and can be used to achieve very high heating rates. The very nature of this means that there is uneven field distribution within the sample, with some regions of the sample experiencing zero heating whilst others heating rapidly.

Resonant single-mode cavities

This type of cavity is commonly used in batch and flow processing as it allows very high E-field intensities to be achieved at relatively low power levels, this is caused by superimposition of the incident and reflected wave giving access to high heating rates and selective heating effects (Figure 2-16).
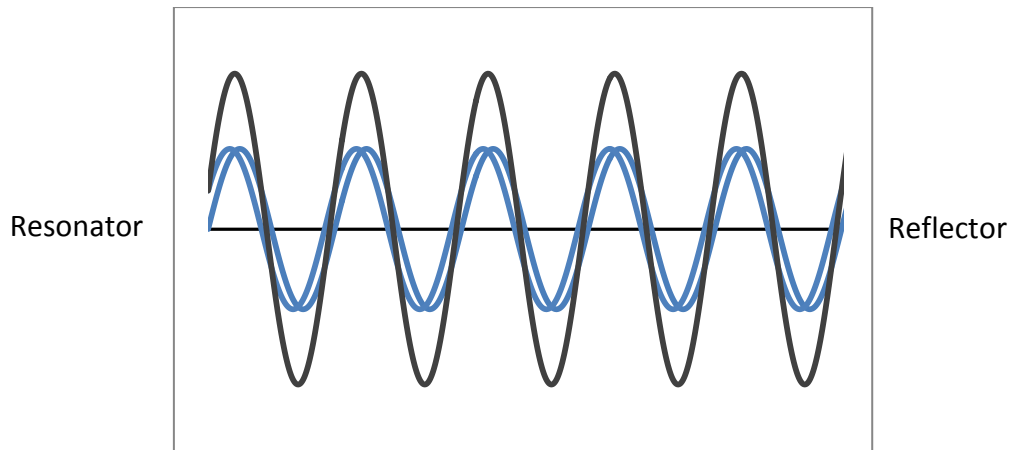
Figure 2-16: Formation of a standing wave, blue indicates the incident and reflected wave, grey the superimposed wave of the two combined. Redrawn from(Morschhäuser, Krull et al. 2012)

This Section will concentrate on one type of resonant cavity, sometimes known as a plasma generation cavity, shown in Figure 2-17. This cavity is a waveguide with a choke allowing for insertion of a sample.
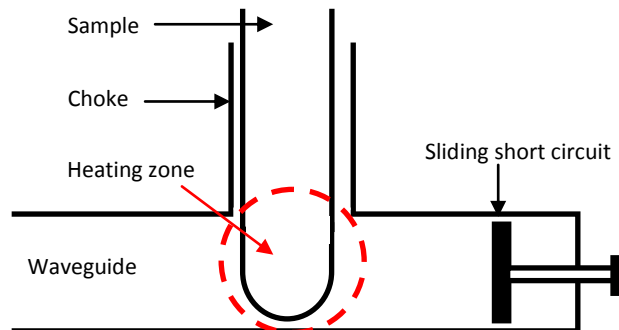
Figure 2-17: Diagram showing single mode resonant cavity used for batch experimentation.

This type of cavity allows for formation of a standing wave along the waveguide, due to the incident wave resonating off the short circuit tuner and imposing the reflected wave upon the incident. Adjustment of the short-circuit, allows for this maxima in field intensity to be placed directly at the centre of the sample, allowing for high heating rates and energy transfer efficiency of >99 %.

The disadvantage of this type of cavity is the small geometry, if used for batch experiments this allows for a maximum volume of 50 cm³. This type of cavity can be adapted for use in a flow system by passing a tube through the cavity, which is explained fully in Appendix 6.1.1.

When using this type of cavity very high heating rates with small samples can be achieved, for example: heating of 50 cm³ water with an incident power of 2000 W. Assuming 100 % energy transfer, the sample would boil in under 8.5 seconds. Energy balances should be calculated prior to experimentation to prevent overheating or thermal runaway.

Arcing should also be taken into consideration, with such high E-field intensities it is possible for arcing to occur on rough edges or corners due to charge build up.

Slotted single mode cavity

A good example of this type of cavity is the CEM Discover SP, which is referred to simply as "CEM" throughout this work. This equipment was used for carrying out batch experimentation. The single mode TM cavity gives a well-defined area of high intensity, and the slotted waveguides allow for a self-tuned system, without the addition of moving impedance matching devices. Tuning is provided by power being transmitted into the region surrounding the sample, as is shown in Figure 2-18, which is then transmitted to the sample through the slots. Depending upon the sample placed within the cavity, power is transmitted through different slots maximising efficiency and power transfer. Reflected power is absorbed by the walls of the cavity to protect the magnetron.
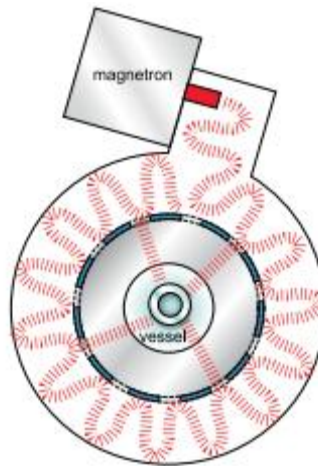
Figure 2-18: CEM Discover SP from above showing electromagnetic field and energy entering sample through slots within the cavity (CEM 2010).

There are several advantages and disadvantages to this type of equipment. The equipment is easy to use due to the self-tuning cavity, allowing for experiments to be carried out rapidly with the use of different materials. The problem with slotted waveguides is low efficiency due to the self-tuning absorbent cavity and inability for scale up. With the use of higher power levels (>2 kW), arcing can occur in the slots making this design prohibitive.

Equipment detail

This equipment operates at a maximum 300 W incident power at 2.45 GHz, adjustable by 1 W increment. Built in PID control utilises either infrared (IR) or optical fibre (OF) temperature measurement. In almost all experiments optical fibre temperature measurement was used, due to poor accuracy of IR with high heating rates. This microwave system does not however allow for measurement of reflected power, making it impossible to carry out precise energy balances.

The CEM is controlled *via* PC using the 'Synergy' software package, within this software there is full control of the variables being used, temperature, pressure, power, stirring, temperature measurement source.

2.4.6.3 Travelling wave applicator

This type of applicator is relatively straight forward, in its simplest form the sample is placed within the waveguide, any energy that passes through the sample is then absorbed by a water load, rather than being reflected by a short-circuit.
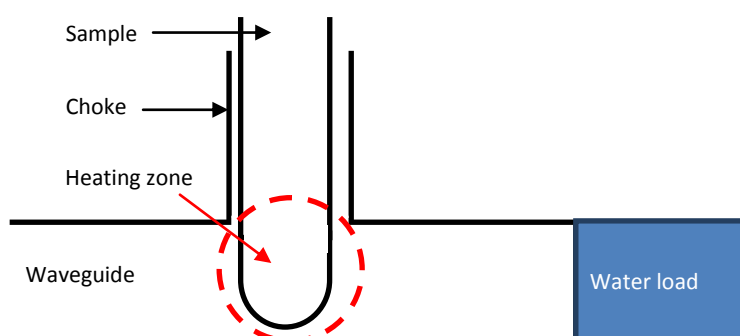
Figure 2-19: Travelling wave applicator with water load.

The advantages of this type of process are that heating can be carried out at a lower rate than in a resonant cavity, by application of energy in stages. The problems are that if low loss materials are used the number of passes required becomes prohibitive. Further examples of this type of cavity used in flow are shown in Section 3.1.4.

2.4.7 Electromagnetic chokes

These are physical devices used to attenuate or reflect the electric field such that propagation into the surrounding atmosphere is below legislative levels of 5 mW/cm² (BERR 2008). In batch or liquid flow systems these can take the form of cylindrical tubes below the cut off length at the frequency used, and with sufficient length to allow for attenuation to occur.

Electromagnetic waves propagate at the speed of light at a constant frequency, when the wave enters a dielectric material this speed is reduced relative to its dielectric constant, and can be calculated using:

$$v = \frac{1}{\sqrt{\varepsilon_0 \varepsilon' \mu_0 \mu_r}}$$ (2-8)

Where

ε_0 permittivity of free space (8.85 x 10^{-12} F/m)

ε' relative permittivity

μ_0 permeability of free space (1.26 x 10^{-6} H/m)

μ' relative permeability, 1 for non-magnetic materials

From the velocity of the wave at a set frequency, the excitation wavelength (λ_{od}) can be calculated. This wavelength is important in the design of chokes for flow systems where the material is passed through the microwave cavity. To ensure that electromagnetic propagation out of the cavity is controlled, the diameter of these chokes should be below the cut-off length of the wave. Cut off length within a circular choke is defined as $\lambda_{od}/4.413$, the narrower the diameter of the tube the faster the attenuation (Meredith 1998).

2.5   Temperature measurement in electromagnetic fields

In conventionally heated systems, temperature measurement is relatively straight forward; many different techniques can be used depending upon the material being measured and the temperature range used. Within a high intensity electric field such as a microwave system, the range of techniques available becomes limited.

2.5.1   Contactless temperature measurement

Techniques such as infrared pyrometers or laser thermometers can be used to give measurement of temperature without contact with the medium measured.

Temperature is inferred by the measurement of radiation emitted by the material; this is most commonly in the IR spectrum. This technique assumes the material is a blackbody or a near approximation. The term 'blackbody' means that the material absorbs all electromagnetic energy at all frequencies

and that no energy is reflected, however this is a theoretical phenomenon and no materials offer these perfect conditions. If the material is reflective, such as glass, this can give false readings due to reflection of radiation from other heat sources nearby (Boyd 1983).

This technique can be used to give spot temperature measurement at a specific location on a material, or by the use of a pyrometer to give a thermal image showing temperatures for the entire surface of a material. The main advantage of this in microwave processing is that it has no contact requirement, just line of sight with the sample. Insertion of probes into the microwave field can present several challenges, highlighted in the following Section.

The main drawback of this technique is that the temperature measurement is a surface measurement only and does not represent the whole material. When using a homogenous medium, in terms of temperature and composition, contained within a vessel this could lead to a large error in measurement, as the IR is measuring a combination of the outer wall of the glass vessel combined with any radiation internally reflected or from other heat sources. In fluid processing it is often more accurate to have direct internal measurement of the sample.

2.5.2 Direct-contact internal measurement

A more commonly used technique is the use of a thermocouple, which is based upon contact between two different metals joined together producing a voltage when heated. The most common type of thermocouple used for general purposes is 'K-type' - this consists of two alloys joined together, which produce a well-defined and reproducible voltage that corresponds with change in temperature. The advantage of using thermocouples is that they are low cost, wide varieties are available and they have high durability.

The implications of insertion of metal probes into electric fields are numerous, as arcing can occur around the tip of the thermocouple due to high skin voltages. If inserted through a standard choke significant

electromagnetic leakage could occur, due to the choke acting as a co-axial cable with the air within acting as the insulator, see Section 2.4.3.1. This can perturb the electric field pattern within the cavity, therefore affecting the system in which the temperature is being measured. This makes the use of thermocouples within microwave cavities complex and potentially dangerous (Wiesbrock, Hoogenboom et al. 2004).

An alternative technique for temperature measurement is the use of optical fibres, which utilise a thin glass tube to transmit light rather than voltage. The use of thin glass tubing (ε' approximately 5) (Meredith 1998) with a PTFE sheath allows for minimal perturbation of the electromagnetic field. The advantages of optical fibres are high response time, chemical stability due to the protective PTFE sheath, minimal electromagnetic impact, and high flexibility. They are however expensive, costing around an order of magnitude more than a thermocouple. They also have a much narrower range of operation, from approximately -270-250 °C, compared to -200-1375 °C for a K-type thermocouple. This method is ideal for use in the type of batch experimentation detailed in this work. The main disadvantage of this type of technique is that it is a point measurement; therefore it cannot be a representative measurement for the sample. To counter this, it is important to ensure that the sample remains well agitated throughout, which is ensured *via* high agitation.

Internal temperature measurement is more accurate due to high reduced thermal gradients within the fluid; it is flexible, allowing for use in different systems and geometries. During a polymerisation reaction there is the potential risk of high viscosities occurring, so to protect the delicate optical fibre sealed glass sheathes were used. This slows the thermal response of the measurement, but adds a layer of safety.

2.5.3   Inference from pressure

In liquid phase systems temperature can be directly inferred from the pressure within the system. There is well published data regarding the

relationship between vapour pressure and temperature of pure components (Perry and Green 2008). This technique becomes more complex if there is a reaction occurring, as changes in the mixture composition will affect this relationship.

2.5.4 Energy control

In flow systems it is possible to determine temperature without the requirement for measurement within the microwave cavity. The following equation can be used:

$$\Delta T = \frac{Q}{m.C_p}$$

With accurate control of both the power transferred to the sample and the mass flow rate, the temperature change can be accurately calculated. This method is preferable in flow systems as it allows for un-obstructed flow within the microwave cavity and removes any perturbation by insertion of probes.

3 Previous studies in microwave polymerisation

This review of this rapidly evolving field will concentrate on the past five years of research. A brief introduction to the origins of microwave synthesis and the path to the current state of the art will be outlined.

The review can be split into sections; initially it will focus upon small scale batch reactions and then move on to cover approaches to scale up, including both batch and flow systems. The term scale up varies depending upon whom the work was carried out by; it can mean increasing throughput to a few 100 g or several kg.

Throughout this review close attention will be paid to the so called 'non-thermal' effects witnessed by some researchers and the methodology and conditions which were used to quantify these. Organic synthesis will be included within this field, as this much larger field is closely linked with polymerisation and often similar methodologies and conclusions are drawn by researchers.

3.1.1 Review of batch microwave processing

The first publications relating to microwave synthesis were published in 1986 by Gedye et al. (1986), with the use of a domestic microwave. Throughout the 90s there was a wide range of polymerisation reactions carried out with the use of "modified" domestic microwaves. The term modified has been used to describe a wide variety of changes. A common modification is to cut a hole in the top of the cavity to allow for glassware to be inserted into the cavity, allowing for refluxing to occur (Cheng, Zhu et al. 2003; Bao and Zhang 2004; Gao, Zhang et al. 2004). A good example of this is shown in Figure 3-1 below, this one example highlights many of the modifications made.
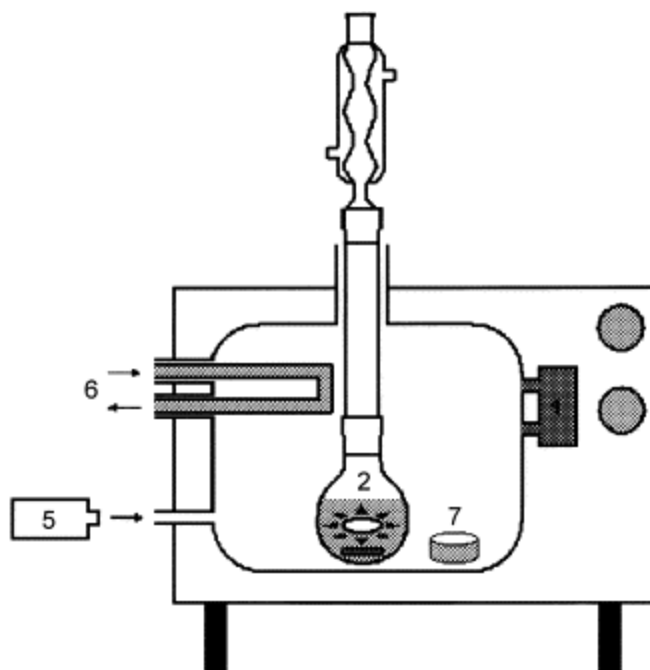
Figure 3-1: Modified domestic microwave. (2) reaction mixture with magnetic stirrer; (5) infrared pyrometer; (6) circulating water in a glass tube; (7) solid dielectric absorbent (Klán, Hájek et al. 2001).

This is a typical example, it can be seen that there have been apertures cut into the system to allow for refluxing, temperature measurement *via* IR and for cooling. This system has had a solid absorbent and a flowing water loop to absorb excess energy; this highlights two major problems with this type of system. The high levels of energy within the cavity, and the low levels of control available; thus making it difficult to draw any accurate conclusions.

Gedye et al. (1986) used a domestic microwave (720 W maximum), where reaction temperature was inferred by the pressure within the sealed 150 cm³ PTFE vessels. It was shown that when carrying out 5 cm³ reactions at 65 psi, in methanol, that a 240 fold increase in rate was discovered, when compared to conventionally heated experiments, reducing reaction time from 16 hour to under 4 min. Conventionally heated experiments were carried out at atmospheric pressure under reflux; this means that the pressurised microwave reaction was 55 °C hotter (Gedye, Smith et al. 1986; Gedye, Smith et al. 1991).

This temperature variation was caused entirely by the experimental design. Microwave heated experiments were carried out within a pressure vessel allowing for increased temperatures to be achieved without boiling, whilst the atmospheric conventional experiment did not. This temperature variation is likely the primary source of the rate increase witnessed. Incomparable experiments were used. This same experimental design is commonly used in current comparative works, as highlighted in the following review by Kappe and Dallinger (2009).

The conclusions provided by the authors of this work were that this increased rate was "merely a thermal effect and can be attributed to the higher temperatures used in microwave reactions". As the first publication in this soon to be a rapidly expanding field, this conclusion is of significant importance. As is to be shown later, researchers drew very different conclusions as to the causes of the rate increase (Hoogenboom and Schubert 2007).

Since then the field has expanded rapidly with almost exponential growth in publications year on year (Kappe and Dallinger 2009). During this time the methods, techniques and equipment have improved significantly. Throughout the 90s, work was carried out with the use of modified domestic microwaves, often using small sample sizes (5 cm³), within a sealed reaction vessel (Shlosberg, Goodacre et al. 1989; Dotson, Galvan et al. 1995; Jacob, Chia et al. 1995; Chia, Jacob et al. 1996; Ming, Changxi et al. 1996; Jacob, Chia et al. 1997).

Due to the high demand for microwave systems in chemical synthesis and polymerisation, companies developed bespoke apparatus for laboratory use. Research with this sort of equipment started appearing around 2000-2002. This new equipment offered, more precise control of power, improved field homogeneity, the use of single-mode cavities, and in some cases built in temperature control using infrared (David 2003; Kappe 2004; Wiesbrock,

Hoogenboom et al. 2004; Wiesbrock, Hoogenboom et al. 2004; Kempe, Becer et al. 2011).

The continuous theme throughout the large majority of the work carried out, up to this point is a "non-thermal, or microwave-effect". This phenomenon that researchers witnessed, vastly improved reaction rate, conversion or product purity with the use of microwave irradiation when compared to conventional heating. Several potential mechanisms for this have been proposed: selective heating of one or more compounds present, localised superheating of solvents used, selectively heating specific functional groups within a molecule increasing affinity to react (Kappe and Larhed 2005; Koopmans, Iannelli et al. 2006).

In recent years, as understanding of microwave equipment and the mechanisms by which microwave heating occurs has improved, the general standard of research has risen with researchers carrying out experiments with the use of more precise equipment and procedures. Such as the use of significantly larger reaction volumes, that allow for increased power transfer, giving improved repeatability and reproducibility (Moseley, Lenden et al. 2007). Currently more than 90 % of published microwave synthesis and polymerisation is carried out within single mode reactors at elevated pressure (Kappe and Dallinger 2009; Moseley and Kappe 2011).

The use of pressurised vessels allowed for increased reaction temperatures to be achieved. This has led to a much higher reaction rate, thus increased yield within a shorter reaction time. Some researchers have noted improved purity and poly-dispersity of products with reduced by-product formation (Moseley and Kappe 2011). There are several hypotheses put forward by different researches to explain these improvements:

Selective heating effects arising due to differential dielectric properties within the material used, this selective heating allows for localised selective heat of catalysts or initiators vastly improving the rate and selectivity whilst maintaining a lower bulk temperature (Rosana, Tao et al. 2012). This method

of heating also has the potential to allow for microwave transparent materials to be heated by either addition of a microwave absorbent dopant such as an ionic liquid, or the use of a catalyst which readily heats (Porcelli, Cacciapuoti et al. 1997; Kappe, Pieber et al. 2013).

Several researchers state that there is a non-thermal effect that is provided by the use of microwave heating, yet there is no explanation of what is causing this effect on a molecular level. There is however a growing body of work, the aim of this has been to dispel the myth of magic microwave heating effects and give evidence to support these unrepeatable thermal effects (Adlington, Jones et al. 2013; Kappe, Pieber et al. 2013).

Theory supporting the fundamentals of microwave heating has been covered previously in Chapter 1. From this and knowledge of experimental design and temperature measurement, several potential explanations for these enhancements can be postulated. More even/rapid heating occurring within microwave heated small-scale batch systems: when compared to a poorly stirred conventionally heated system this could create a significant variation due to more of the material reacting sooner. At the extreme, this could allow for localised superheating within the reaction mixture, due to higher temperatures at the centre, and lack of nucleation sites. In the case of polymerisation where the product material has an increased boiling point, this could allow for the reaction to be carried out at atmospheric pressure, with the polymeric product formed preventing boiling. This type of heating is not possible to reproduce with the use of conventional heating, due to the nature of heat transfer (Coulson, Richardson et al. ; Perry and Green 2008; Damm, Glasnov et al. 2009).

Historically laboratory scale polymerisation reactions were carried out with the use of atmospheric pressure under reflux conditions. As previously stated over 90 % of microwave synthesis reactions were carried out with the use of pressurised vessels, allowing for achievement of higher reaction temperature. This increased reaction temperature could potentially be opening new

reaction pathways, allowing for cleaner synthesis giving purer higher quality products (Bardts, Gonsior et al. 2008).

Recent publications by (Kappe, Pieber et al. 2013) have stated that these so-called 'non-thermal effects', are in fact all thermal effects, but that they cannot be reproduced with the use of conventional heating. It has been argued, for example, that the presence of an electric field affects the orientation of dipolar molecules or intermediates and hence changes the pre-exponential factor *A* or the activation energy (entropy term) in the Arrhenius equation;

$$ k = Ae^{-Ea/(RT)} $$

Where:

k	:	Rate constant of the reaction
A	:	Pre-exponential factor
Ea	:	Energy of activation
R	:	Ideal gas constant

This is a hypothesis and no evidence has been shown to prove this (Bogdal, Penczek et al. 2003; Kappe 2004).

3.1.2 Review of temperature measurement and non-thermal effects

From detailed analysis of the research published within this field, there are some common features between publications; these are independent of whether basic domestic equipment or modern single-mode apparatus was used.

Several notable researchers within the field have shown that many of the so-called 'microwave effects' are caused exclusively by inaccurate temperature measurement and the use of incomparable conventional experiments (Obermayer and Kappe 2010). The vast majority of work is carried out with the use of IR temperature measurement for feedback control.

Feedback is used to allow a system to achieve a specific set point variable without overshoot. In the case of microwave heating, the power supplied is adjusted to precisely achieve the temperature set point. An example of this is shown below in Figure 3-2, it can be seen that as the temperature increases the forward power is reduced proportionally, thus slowing the heating rate and not overshooting the temperature set point. It is unknown as to which algorithm is being used to control the temperature, this was unavailable within the control software and the suppliers declined to provide.
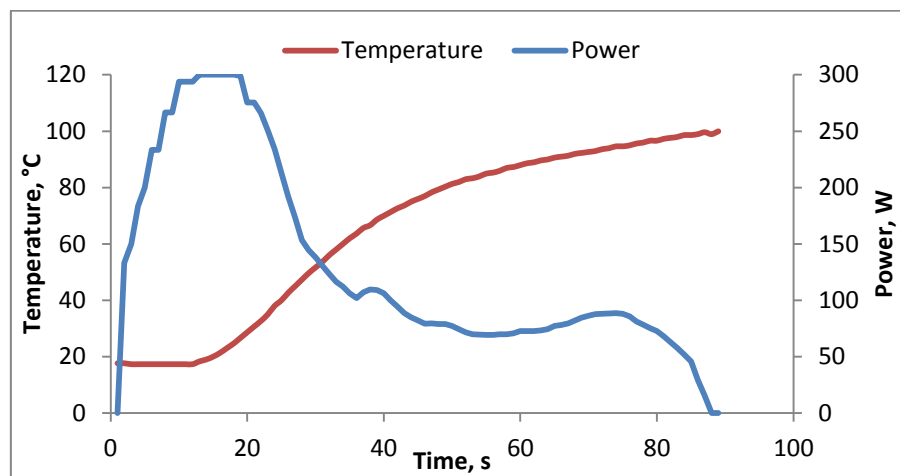
Figure 3-2: Demonstrates how the CEM adjusts power levels to achieve a temperature set point. Heating of 30 cm³ water at 300 W to a temperature set point of 100 °C.

For this method to give accurate control, it is required that there is accurate measurement of the process variable (temperature). It has been shown that by the adoption of optical fibre direct temperature measurement that there is more precise, accurate and higher speed measurement; IR measurement can entirely miss rapid temperature changes and lead to inaccurate conclusions being drawn (Albert, Warth et al. 1996; Kappe 2013), this is shown experimentally in Section 5.3.1. Further details comparing these two techniques are given in Section 2.5.

Many microwave systems produced have built in IR temperature measurement rather than the costly OF. With new equipment costing 1000s, researchers have in several cases opted to monitor the temperature with OF,

externally to the temperature feedback/control loop (Adlington, Jones et al. 2013). This has been shown by Adlington et al. (2013). This work was carried out at the University of Nottingham and the results of which have been used directly as the start point of this thesis. In this body of work methyl methacrylate was polymerised to form low molecular weight oligomers, at 30 cm³ under reflux conditions, using conventional and microwave heating. Conventional heating was carried out within a stirred oil batch, microwave heating in a CEM Discover equipped with IR temperature sensor. Reaction temperatures were further monitored with the use of an optical fibre. This rigorous work used direct comparisons in terms of equipment geometry and experimental methodology; it was shown however that there was a significant increase in rate and conversion when microwave heating was used. This work has since been repeated with the use of a newer microwave generator CEM Discover SP-D, equipped with optical fibre control. It has been found that there was no quantifiable difference between conventional and microwave reactions, shown in Chapter 5.

Kappe et al. (2010/2013) have attempted to separate thermal and non-thermal effects by the use of silicone carbide (SiC) tubes instead of Pyrex. The purpose of this was to try and exclude the electric field within the sample whilst utilising the highly microwave absorbent SiC to achieve the high heating rates offered by microwave heating; it was shown by the use of electromagnetic modelling that the SiC tube did not exclude the E-field and a mixture of dielectric heating of the sample and the SiC occurred (Robinson, Kingman et al. 2010). Liquid temperatures were monitored and control feedback was given from optical fibre. This work has shown that when using SiC as an intermediate to heat the reaction, that there were no differences in the reactions tested between conventional and microwave heating (Obermayer, Gutmann et al. 2009; Robinson, Kingman et al. 2010; Kappe 2013). This equipment is acting as hybrid heating apparatus, with energy being supplied to the SiC *via* microwave and then conventionally to the sample. The accurate temperature control provided by the optical fibre

feedback was likely the main cause of no microwave effect occurring, and not the SiC reactor.

This has become a subject of heated debate between two research groups; with one publishing improved rates of reactions when using microwave heating, compared to conventional heating (Rosana, Tao et al. 2012; Dudley, Stiegman et al. 2013). This data was published with the use of IR temperature measurement, upon repeating this work with OF it was published as a reply that there was no enhancement provided by microwave heating (Kappe 2013; Kappe, Pieber et al. 2013). This recent debate has been highlighted in externally published articles (King 2013), it is important as it shows that there is still no clear conclusions drawn by the academic community with regard to the source of the rate improvements caused by microwave heating.

3.1.3 Summary of microwave polymerisation carried out at the gram scale

From the review of work carried out above there are several key factors which appear to have contributed to the large variation between conventional and microwave heated reactions; temperature measurement, experimental design and variation in equipment used for comparison. In some cases there may be a benefit offered by microwave heating, with the current methodologies used by the majority of researchers it is not, however, possible to quantify these.

1. **Temperature measurement:** infrared techniques only allow for measurement of surface temperature, thus introducing an inherent inaccuracy and thermal lag with the technique. Optical fibre can be used to give a rapid, direct internal measurement of the reactant. This technique however, only gives measurement at a single point within the material; with the potential for high heating rates in potentially localised regions this could produce error. High levels of mixing or multiple measurement points should be used.

2. **Comparison with conventional heating:** many researchers change more than just the heating mechanism used. Experiments are designed with the use of different reactor geometries, stirring rates, reaction volumes, heating/cooling rates and pressures are used. Pressure is a major factor as it allows for huge variations in temperature, the contribution of the other factors should not however be overlooked as these can all give a significant contribution to error.

It is clear from this work that any experimentation carried out must involve a well-designed comparison to allow for quantification of any differences between conventional and microwave heating.

3.1.4 Routes to scale up of chemical reactions

Up to this point, this review has concentrated on small scale reactions (<50 cm³).There are two ways in which reactions can be scaled up; batch and continuous flow. It has been shown in several publications, that when scaling up reactions the benefits shown in small scale batch microwave cannot often be duplicated in larger multi-mode equipment (Damm, Glasnov et al. 2009). This can be due to several factors, reduced heating rates and uneven heating caused by the heterogeneous field distribution, low levels of heating within the sample due to limitations in the penetration depth of the material used (10 cm for MMA at 20 °C) (Adlington, Jones et al. 2013). Increasing the system volume often reduces the pressure ratings of equipment as significantly thicker walls are required, this reduced pressure gives reduced maximum temperatures available (Bowman, Holcomb et al. 2007; Kappe, Dallinger et al. 2009; Strauss 2009).

Many of these limitations could potentially be overcome with the adoption of a flow system. Flow often removes the requirement for large vessels, with reactions occurring within the piping. This allows for higher pressure rated equipment, and can remove the problems encountered with penetration depth and heat transfer.

3.1.4.1 Review of batch polymerisation carried out at the kilogram scale

Scale up *via* the use of multi-mode microwave reactors has been demonstrated at scales up to 2.5 kg with the use of different equipment types. Domestic microwave have been used up to a scale of 400 cm³ with the use of reflux or pressurised vessels.

More interesting is the work carried out by Xu, Zhang et al. (2010), the use of a 6 kW microwave generator operating at up to 2550 W to polymerise up to 2.5 kg ε-caprolactone with the use of custom built multi-mode reactor. They showed that the large scale reactions behaved in a manner similar to that of the small scale reactions, in terms of molecular weight, yield and rate. Temperature measurement was carried out with the use of IR probes rather than OF. The work makes no mention of penetration depth, which at this scale could become problematic, reactions were carried out in vessels with 10 cm diameter, where the penetration depth in the monomer used is <1 cm at ambient conditions. No conventionally heated comparisons were made, the purpose was to demonstrate that the reaction could be scaled up with no effect upon the reaction.

Scale up of organic synthesis in a multi-mode batch system operating at up to 12 litre has been shown with the use of a purpose built reactor utilising 3x2500 W magnetrons, operating at 2.45 GHz. Comparisons were made to smaller scale microwave systems, the purpose was to show that scale up could be accomplished without penetration depth or other factors affecting the process. Comparable conversions were found in several reactions, when scaling up by 1000 times (Schmink, Kormos et al. 2010). This drew attention to the penetration depth issues presented with batch scale up, in this work it was concluded that the increase in scale had no effect upon the conversions or rates witnessed.

There are problems associated with batch scale up using microwave heating, penetration depth becomes prohibitive; potentially introducing large temperature gradients and reducing the benefits of microwave heating

(Moseley, Lenden et al. 2007). This is graphically highlighted in Figure 3-3 below, a simplified example showing different vessel sizes within an electromagnetic field. It can be seen that the small vessel which has a geometry blow 2x the penetration depth of the material, has heating throughout the vessel. As the geometry increases, it can be seen that at the largest size there is a large region within the vessel that is not effectively heated.

Penetration depth within the material
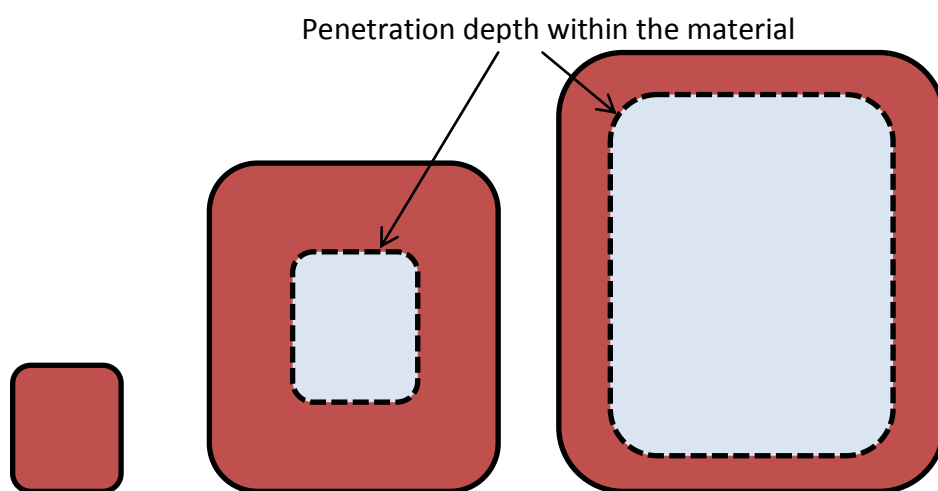
Figure 3-3: Penetration depth within, three various sized electromagnetically transparent vessels containing a dielectric material (not drawn to scale).

Reducing frequency to 900 MHz can help overcome this but requires larger equipment and compliance with stricter electromagnetic compatibility (EMC) regulations (Moseley, Lenden et al. 2007; BERR 2008; Bowman, Schmink et al. 2008; Strauss 2009; Schmink, Kormos et al. 2010).

3.1.4.2   Review of flow polymerisation

The majority of works published into continuous flow microwave processing focus on organic synthesis rather than polymerisation.

Ring opening polymerisation was carried out by Paulus, Erdmenger et al. (2007) as a direct scale up of work shown by Hoogenboom, Paulus et al. (2006). Investigation into a variety of different continuous flow reactors within a CEM Voyager microwave cavity was carried out. Different reactor

geometries were used, a 200 cm³ continuous stirred tank reactor (CSTR) and two continuous flow coils with 5 and 10 cm³ volume. Reaction times were kept constant, with flow rate adjusted appropriately it was found that the CSTR gave the narrowest PDI, the reaction coils giving a broader peak. It was proposed that this was caused by the variations in turbulence within the system, the tubular reactors were stated as being laminar whilst the CSTR turbulent. It was not possible to calculate the Reynolds number from the data presented. No comparisons with batch or conventionally heated systems were shown.

Diehl, Laurino et al. (2010) have taken a different approach. The work compared microwave heated batch reactions with conventionally heated continuous flow; it is believed that the purpose of this was to show that the benefits of microwave processing can be reproduced conventionally. They have carried out microwave heated batch RAFT polymerisation within an unspecified reactor at unspecific conditions (approx. 130 °C). It was found that this gave increased conversion when compared to conventional heating. It was stated that the scale up of batch reactions in a microwave was "difficult if not impossible". Their approach to scale up was to then carry out conventionally heated flow polymerisation and compare this to microwave heated batch reactions. Conclusions drawn are that, under the same conditions, flow polymerisation is faster than conventionally heated batch reactions, but similar to that of microwave; it is also concluded that continuous flow polymerisation and scale up was possible with conventional heating but not with microwave.

Improved rates of reaction and conversion were stated; in this case caused by both the microwave batch reactions and conventionally heated flow, when compared to conventionally heated batch reactions. There is no justification or quantification of the causes of these improvements. No explanation of the batch reactors used in this work was made, it was however suspected that the use of atmospheric conventionally heated batch reactors, was compared to high pressure sealed vessels used in flow and microwave heated reactions;

thus potentially contributing to the rate increases. Flow experimentation was carried out on ml scale in a 0.75 mm tube, therefore it would from high rates of heat transfer, similar to those which are offered in small scale microwave processing (Cléophax, Liagre et al. 2000).

Several studies have used similar reactor geometries, often with the use of narrow bore (<3 mm) coiled PTFE or glass tubes within an off-the-shelf commercially available piece of equipment modified for flow operation (Baxendale, Hayward et al. 2007; Glasnov and Kappe 2007; Paulus, Erdmenger et al. 2007; Damm, Glasnov et al. 2009; Glasnov and Kappe 2011). These publications present similar conclusions of it being possible to scale up the reactions from batch with no effect upon the conversion achieved. Some state improved rate of reactions but have stated that this was due to process intensification. Process intensification is the use of more extreme operating conditions (temperature, pressure, chemicals) to allow for enhanced rate of reaction or improved conversion. The most interesting of these publications is by (Damm, Glasnov et al. 2009), included within are conventionally heated batch reactions, microwave batch reactions and microwave flow reaction. The conclusions have linked the data together and used engineering principles to explain the variations noticed; this level of detail has not been seen elsewhere (Glasnov and Kappe 2007; Paulus, Erdmenger et al. 2007; Diehl, Laurino et al. 2010; Razzaq and Kappe 2010; Glasnov and Kappe 2011; Hornung, Guerrero-Sanchez et al. 2011; Wilson, Osuma et al. 2012).

A large scale process for microwave heated organic reactions has been shown by Wharton (2011). The process allows for continuous operation at (20 bar. 250 °C), with the use of a 2.5 kW, 2.45 GHz generator. Power is transferred to the sample within a 40 mm OD quartz tube, the cavity used was a travelling wave applicator, as shown in Figure 3-4 below. This type of cavity has the advantage of allowing for large material volumes within the microwave cavity; giving the potential for increased energy transfer and potential maximisation of any potential microwave effect due to increased interaction. The use of a travelling wave applicator has several disadvantages; lower power density

compared to resonant cavities gives reduced heating rate and reduced power transfer, 39-57 %. No dielectric property data was presented within this work; this could potentially give insight into the cause of this low efficiency. This is a low energy transfer efficiency, in microwave systems it is often possible to achieve >99 % (Wharton 2011) (CTech 2011).
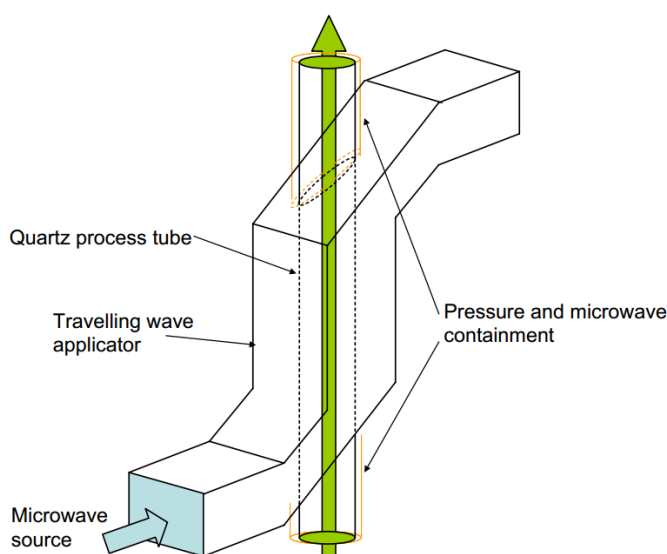
Figure 3-4: Travelling wave applicator used for microwave flow reactions (Wharton 2011)

Results have been presented showing three different chemical syntheses, conventional comparisons were carried out in flow; no details of the design of equipment used were presented. In these conventional comparisons, increased yield, enhanced rate and energy savings were presented in the microwave heated system. Comparisons were carried out at different temperatures, with the microwave experiments being carried out 10-15 °C hotter; no mention of this is made in the conclusions. It is not known if this was due to poor control or by choice. Impossible conclusions have been drawn in places; such as 100 % reductions in material used. Throughout the work published there are discrepancies with the numbers quoted; maximum flow rates of 10 kg/day to 1 tonne/day quoted, giving some uncertainty of the level of rigour within the work. In the microwave heated experiments, temperature overshoots and poor control were shown in two of the

examples, this was caused by power level being varied to achieve the temperature set point during start up, this indicates poor temperature feedback control; a 20-30 °C overshoot was shown.

Morschhäuser, Krull et al. (2012) have produced a flow system that operates using a 6 kW, 2.45 GHz generator with maximum conditions of 60 bar, 310 °C. The equipment has a maximum theoretical throughput of 20 l/hour, but is however operated for synthesis at 3-5 l/hour for ease of materials handling. The cavity designed is described as a "transmission line resonator"; this is similar to that shown in Figure 3-4 above. However, instead of a water load a short circuit is used, creating a resonant cavity with a standing wave. The volume of material within the microwave cavity is significantly smaller; 10 mm ID Alumina tube is used to contain the pressurised material. Important to note is that the equipment contains an adjustable 'residence time coil' after the microwave cavity and prior to cooling. This allows for the same residence times to be used at different flow rates, an important feature as it can be used to decouple power density effects from residence time.

Presented within the work are efficiency curves for heating of water and methanol at different flow rates, it is not mentioned if these experiments were carried out at constant power or energy per gram. This importantly shows that there is power transfer efficiency of 25-75 % from microwave to heat; this is again a low value, similar to that shown by Wharton (2011).

The equipment presented by (Wharton 2011; Morschhäuser, Krull et al. 2012) is of interest as it is similar to the scale at which this work will be carried out. Other flow publications were made on equipment operating at the mg-g scale with low microwave power equipment.

Both of these publications have several similarities between them:

- **Similar cavity design**: both use an applicator with the electromagnetic field travelling parallel to the fluid flow. Wharton (2011) used this as

travelling wave rather than Morschhäuser et al. (2012) which presented the use of a resonant cavity.

- **Low energy transfer efficiency**: the cavity design is likely to be the cause of the low efficiency, it should be expected to achieve >99 %. In the case of Morschhäuser et al. (2012) heating of "lossy" materials such as methanol and water was carried out which indicates a flaw in the cavity design. Very high efficiency would be expected with these materials.

- **Batch comparisons:** Morschhäuser et al. (2012) stated that small scale microwave experiments were carried out to understand the reactions to ensure safe operation on large scale. There was however no comparisons drawn between those batch reactions and data achieved in flow. Wharton (2011) carried out no small scale reactions as a comparison, some collaborative data with Croda was presented, this however appears to be generic non-specific, energy data.

- **Conventional comparisons:** Direct comparison between conventional and microwave systems is required to quantify any potential benefits offered by microwave heating, this has not been shown in a rigorous manner in any of the works reviewed. Wharton (2011) presented limited data on this, but however it was non-specific and carried out at a different temperature rendering the comparison invalid. Morschhäuser et al. (2012) gave no mention of conventional comparison.

3.1.5 Literature review conclusions

A review of the current techniques for microwave polymerisation and organic synthesis has shown that the majority of batch scale reactions are carried out using purpose built microwaves, such as the CEM Discover/Voyager, with only a small minority of publications made using domestic microwaves.

Many researchers have shown that the use of microwave heating gives significant benefits when compared to conventional heating. These benefits given are: improved rate; conversion; selectivity; reductions in energy and by-

product reduction. Several hypotheses as to the cause of these benefits have been proposed, most of which refer to microwaves selectively heating one or more of the materials present, causing localised superheating whilst allowing for a lower bulk temperature.

The majority of published works that show these improvements did not carry out conventionally heated comparisons under the same conditions. Often comparing microwave reactions carried out in pressurised vessels to those carried out under reflux conditions. This build-up of pressure allowed for significantly increased reaction temperatures without boiling, thus the so-called "microwave effect" witnessed is caused by the experimental design rather than the microwave heating. Another common feature is the use of IR temperature measurement, this technique is inaccurate and gives surface temperature measurement rather than that of the bulk liquid; once again allowing for reactions to be carried out at higher temperatures than those measured. Discussion on temperature measurement techniques within microwave cavity can be found in Section 2.5.

It is proposed that these benefits offered by microwave heating are purely thermal in nature and arise in many cases due to poor experimental design. Review articles have been published stating this, but no work has been found with direct conventional comparisons carried out with the use of accurate temperature measurement within the microwave cavity. To allow these comparisons to be drawn, all variables should be kept constant when comparing heat sources: heating rate, reaction time, temperature, pressure, volume, vessel geometry, stirring rate, cooling rate.

Batch chemistry with microwave heating has been shown to be successfully scalable to the 10 kg scale, with certain materials. it is hard to see how this could be used to scale up much further. Above this point, penetration depth becomes an issue and many of the potential benefits offered by microwave heating are lost. With low loss materials and the use of 896 MHz, this could however be increased as the penetration depth issues would be reduced.

Continuous flow processing has been shown to be scalable to the 10s of litres per hour scale, unlike batch processing it is possible to overcome penetration depth issues allowing for further scope. Overcoming these issues in batch processing can be difficult or near impossible due the reduced surface are to volume ratios which are inherently present in large batches. The use of continuous processing also allows for process intensification, the use of more extreme operating conditions, to give higher reaction rates. The large scale systems shown, both utilised cavities with the electromagnetic energy travelling in parallel to flow, in both cases this gave low levels of energy transfer <75 %.

To date there is no work presented which shows all stages of scale up, from batch to either large scale batch or flow; including direct comparisons between conventional and microwave heating. No work has been shown to scale up polymerisation in this manner, it has been published that it is not possible to use microwave heating to carry out polymerisation in flow, very little justification for this statement was given (Strauss 2009; Diehl, Laurino et al. 2010).

3.2 Aims and objectives

The aim of this work was to design and produce a system which could be used to produce low molecular weight methyl methacrylate oligomers. These materials are used as chain transfer agents in the production of macro monomers, or as replacements for VOCs in paints. There is currently no economically viable process for their production, therefore VOCs are still in use in many applications. For this project to be successful these products are required to be economically produced with a conversion of 40 %, any conversion over this level is a benefit.

Continuous flow microwave processing will be used to achieve this aim, with a lab scale process that can produce kg/hour. In order to achieve this level of scale up, small scale batch experiments will be carried out to better understand the physical and chemical conditions required to allow for scale

up. In this small scale, investigation will be made into the effects of temperature, catalyst concentration and heating rate.

Heating rate experiments will be carried out using microwave heating only, by varying power levels. The purpose of this is to determine and quantify any potential microwave selective heating effects. Many researchers have shown that microwave processing can lead to significant benefits to the process, it is hypothesised that these are purely caused by poor control of experiments and comparisons being made between incomparable experimental conditions.

In developing a new process it is important to understand the effects of all variables. As part of this direct, rigorous comparison between conventional and microwave heating will be carried out, using batch and flow processing. To date, this level of comparison has not been presented within the literature and will make a contribution to the field.

4 Methodology

This Chapter will detail the experimental methods utilised for the preparation of reagents; batch and flow synthesises; and analysis of products formed during polymerisation of methyl methacrylate via CCT polymerisation. Detailed descriptions and operational parameters of the experimental equipment are included.

All experiments were carried out at least in triplicate to ensure repeatability and allow for variation analysis. Variation was calculated as the standard deviation in the data, and has been included with all figures presented.

4.1 Materials used

Methyl methacrylate (MMA), azobisisobutyronitrile (AIBN), chloroform HPLC grade (99%), tetrahydrofuran (THF) HPLC Grade 99 %, and chloroform-d (99.8 atom % D) were all purchased from Sigma Aldrich. bis[(fluroboryl)diphenylglyoximato]cobalt(II) –PhCoBF (purity unknown) catalyst purchased from DuPont. All chemicals were used as supplied without further purification.

4.2 Batch CCT polymerisation reactions

Batch experiments were conducted at three different scales, with the use of three different types of laboratory equipment. To ensure that the results were comparable, the material preparation methods for each experiment were kept the same. The reaction volumes used were 30, 50 and 250 cm³. 30 cm³ was used for the majority of experiments as this scale afforded the best comparison between conventional and microwave heating methodologies.

4.2.1 Preparation of batch polymerisation mixtures

In a typical reaction a MMA stock solution was created, in order to minimise the weighing errors. To prepare these stock solution, 250 cm³ MMA was added to 500 cm³ round bottom flask, which was sealed using rubber septum; this was then stirred and degassed, with flow of N_2 for 30 min. PhCoBF was

weighed and then transferred to a second 500 cm³ round bottom flask where it was degassed for 30 min. Monomer was transferred to the vessel containing catalyst *via* N_2 flushed syringe. The solution was then placed within an ultra-sonic bath for 20 s to ensure dissolution of catalyst.

For a 30 cm³ reaction (1 w/w%, 2.35 g, 14.31 mmol) AIBN was weighed, placed within reaction vessel, and sealed with a rubber septum. The tube was then degassed using N_2 for 30 min. 30 cm³ 600ppm catalyst/ monomer solution was then transferred *via* degassed syringe to the reaction vessel.

A sealed glass tube was inserted through the septum as a thermo-well, to protect the optical fibre used for temperature measurement. The optical fibre was inserted such that the tip was submerged within the liquid but not interfering with the stirrer.

Table 4-1: Reaction compositions used in batch reactions

ID	Monomer, cm³	Catalyst ppm	Catalyst mass, g	Initiator	Initiator mass, g
1	30	600	0.0169	AIBN	0.282
2	30	300	0.0085	AIBN	0.282
3	30	60	0.0017	AIBN	0.282
4	50	600	0.0282	AIBN	0.470
5	250	600	0.1412	AIBN	2.350

Reactions were carried out inside three different vessel types, these are shown below:

4.2.2 Reaction vessels used in batch polymeristaion

Four different vessel geometries were used. 30 cm³ reactions were carried out within a straight sided Quickfit boiling tube. 50 cm³ reactions were carried out in two different vessel types specified in text as to which was used; Long-neck round bottom flask, and CEM pressure vessel. 250 cm³ reactions were carried out using a standard 1-neck 500 cm³ round bottom flask.

Vessels were equipped with a magnetic stirrer bar and sealed with a rubber septum to maintain O_2 free environment and allow for slight pressure build up during reaction. Septum was carefully pierced and temperature measurement device inserted, for conventional reactions this was a 3 mm stainless steel thermocouple, in microwave experiments a glass sheath was inserted to allow for optical fibre to be inserted. The temperature probes were inserted such that the tip was in the centre of the liquid present. Further detail on temperature measurement techniques can be found in microwave fundamentals 2.5.

Pressure vessel

50 cm^3 reactions within the CEM, were carried out with the use of a 50 cm^3 pressure vessel supplied with the CEM Discover. The vessel was equipped with direct internal measurement capability *via* optical fibre, maximum pressure rating of 20 bar, and automated pressure relief to ensure safety.

The use of this reactor did not allow for maintenance of O_2 free environment, as the glass vessel connected *via* a thread and the reaction mixture had to be poured in giving contamination.

4.2.3 Equipment used

Three different types of heating equipment were used to supply energy in the batch experiments, CEM Discover SP and a single-mode microwave system were used, a stirred oil bath was used for conventional.

4.2.3.1 Heated oil bath

A standard laboratory thermostatic oil bath, containing 1 litre of silicone oil was used. Stirring within the oil was maintained at 700 rpm to ensure a stable vortex within the sample to maximise heat transfer rates. Temperature within the oil was monitored and logged continuously *via* thermocouple to ensure stable and accurate temperature was maintained during experiments.

4.2.3.2 CEM Discover SP

The CEM Discover SP herein referred to as the 'CEM' is an off the shelf laboratory microwave primarily designed for microwave accelerated acid

digestion. This simple to use microwave apparatus is used world-over for research into synthesis, polymerisation and many other reactions (Brzezinska 2011; CEM-Corporation. 2011).

Post reaction all experiments were cooled to 100 °C and 0 barg by passing compressed air through the microwave cavity. Subsequently reactions were quenched with an iced bath; samples were taken and placed directly into freezer; with analysis being carried out as soon as possible.

4.2.3.3   2 kW microwave generator

As a first stage of scale up a larger scale microwave generator with the use of precise measurement and tuning was used coupled with a high Q microwave cavity. This allowed for investigation of power density and heating rate upon the reaction, precise energy balances were also carried out.

A Sairem 200-2000 W microwave generator operating at 2450 MHz was used. The generator was attached to a simple single mode TE_{10} cavity. Tuning was provided by the use of a manually operated sliding short-circuit, impedance matching was carried out automatically by the use of an S-team HOMER tuning device. Direct temperature measurement was taken by the use of an optical fibre inserted directly into the reaction medium through the septum. Stirring was applied to the sample *via* magnetic stirring plate placed below the microwave cavity. Temperature and power levels were logged continuously and saved *via* PC. Microwave energy was supplied and controlled manually, until the bulk temperature reached 100 °C.

Once experiments were completed reactions were quenched with an iced bath, samples were taken and placed directly into freezer; with analysis being carried out as soon as possible.

4.3   Method used for carrying out polymerisation in flow

Flow experiments were carried out using two different designs, 1 and 8 litre, both were operated using either conventional or microwave heating as the energy source. The methods used for preparation, filling and operation are

the same for each. In the larger scale system there was the added capacity of sampling material at the cavity exit.

Initial flow experimentation investigated the effects of two variables upon the polymerisation reaction, power density and energy input.

4.3.1 Material preparation for flow polymerisation

For a typical 4 kg reaction the following composition and procedure was used for preparation of samples. The same method was used for all.

10 litre 3-neck round bottomed flask with Quickfit fittings was placed upon 2 d.p. balance, 4 kg MMA monomer was weighed out. Material was degased *via* ¼ inch nylon tubing, Swagelok connected to gas supply for 1 hour.

Due to the large quantity used it was not possible to purge CCT catalyst within another vessel and transfer monomer across. (2.40 g, 600 ppm) Catalyst was transferred into the degassed monomer as a powder, O_2 contamination was minimised by the presence of high N_2 flow rate within the vessel. The mixture was then degassed for a further 30 min prior to vessel being placed within sonic bath for 60 s to ensure dissolution of catalyst.

40 g, 1 w/w % AIBN was weighed using 4 d.p. balance and transferred to the reaction mixture *via* powder funnel. Mixture was homogenised and degassed for a further 30 min.

Table 4-2: Mass compositions for reactions carried out in flow.

Monomer volume, litres	Catalyst ppm	Catalyst mass, g	Initiator mass, g
F1	600	0.564	9.40
F4	600	2.256	37.60
F8	600	4.512	75.20

4.3.2 Charging the feed vessel for flow polymerisation experiment

Experimental apparatus was flushed with N_2 at 0.2 bar, flow rate uncontrolled, for 30 min to ensure inert atmosphere.

Feed vessels were isolated from the rest of the system and internal pressure vented, the 3-neck flask was connected to the vessel feed port *via* ¼ inch tubing, connected with Swagelok fittings. Material was transferred *via* the cannula to the high pressure feed vessel by application of slight (<0.5 bar) N_2 pressure to the glass vessel.

4.3.2.1 Power density and energy calculations for flow polymerisation

Power density (W/m³) is a fundamental variable in scale up of this type of flow system. Increasing the power density has a direct scale up effect upon throughput of the system, four different levels were used, this covered the full operation range of the generator used. Details are shown in Table 4-3 below. In order to maintain constant energy input, flow rate was adjusted along with power level.

Table 4-3: Matrix of experiments carried out in flow. Energy input and mass flow rates of MMA required to achieve set point temperature at different power levels are given.

Temperature, °C	Energy input, J/g	Power, W			
		250	500	1000	2000
80	152	1.6	3.3	6.6	13.1
90	178	1.4	2.8	5.6	11.2
100	203	1.2	2.5	4.9	9.8

Energy and temperature are intimately linked; increasing energy input increases the temperature. Three set point temperatures were investigated, the energy level required to achieve this temperature can be simply calculated, shown below, an assumed start temperature of 20 °C was taken.

$$Specific\ energy\left(\frac{J}{g}\right) = C_p \Delta T$$

$$Specific\ energy\left(\frac{J}{g}\right) = 2.54(100-20) = 203$$

Mass flow rate at 500 W:

$$Q = mC_p\Delta T$$

$$m\left(\frac{g}{s}\right) = \frac{Q}{C_p\Delta T} = \frac{Q}{Specific\ energy}$$

$$m\left(\frac{g}{s}\right) = \frac{500}{203} = 2.5\ g/s$$

Where

Q=   :   microwave power (W)

m=   :   mass flow rate of fluid (g/s)

C_p :   specific heat capacity[2] (J/g.K)

ΔT   :   temperature change (K)

Conventionally heated experiments were carried out at 1 power level (1050 W) with flow rate adjusted to vary energy input. Flow rate required was determined experimentally by heating of pure monomer.

During experiments mass flow rate was monitored with the use of 2d.p. balance, control was carried out manually. Auto tuning of forward power was carried out using a HOMER tuner, this simultaneously recorded and logged forward and reflected power. Temperature within the equipment was monitored and logged to give understanding of how equipment operated. Samples were taken at 2 min intervals, throughout flow experiments, these were quenched within an ice bath before storage in a freezer, analysis was carried out as soon as possible.

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[2] Specific heats of common compound can be found in (Perry and Green, 2008) and can be taken as 4.18 and 2.5J/g.K for water and MMA respectively.

4.4   Method for recovering monomer and oligomers formed

Recovery of monomer was carried out upon large scale reactions to reduce waste and maximise usage of raw materials. Due to the large variation in boiling points between the products it was possible to separate very high purity monomer from the other products by the use of rotary evaporation, a form of distillation. The recovered monomer was re-inhibited with 30 ppm hydroquinone, as was originally supplied. Recycled monomer was then checked for purity by NMR before use, large scale reactions used no more than 50:50, recycled: new monomer, to ensure there was no potential build-up of contaminants. Pure samples MMA_2 and MMA_3 were purified by a college using vacuum distillation.

4.5   Product characterisation techniques

Analysis of products formed was primarily carried out using two techniques ^{1}H-NMR and GPC. GC-MS and TGA were used on a set of samples to validate the results given by NMR analysis.

4.5.1   Nuclear Magnetic Resonance (NMR)

NMR is a commonly used technique for the determination of the structure of molecules; the most commonly used are ^{1}H and ^{13}C NMR. Spectrographs produced are analysed and compared to literature values to determine structure.

Within this work a Bruker DPX-300 MHz was used, samples were typically prepared *via* dissolution in deuterated chloroform ($CDCL_3$) at a concentration of 1 mg/1 cm³. highly viscous samples were dissolved in dichloromethane (DCM). Analysis was carried out using ACDLABS 12 software.

NMR works upon the principle of interactions between a magnetic atom nucleus and a magnetic field. Magnetic nuclei are defined as those with an odd number of protons and neutrons. Those with an even number of protons or neutrons have no angular moment and give no NMR spectra. When a magnetic field is applied to a magnetic nuclei, the nucleus aligns itself with the magnetic field and adopts orientations at different energies. Each nucleus

has characteristic magnetic moment and resonance frequency, under a given magnetic field. The higher the magnetic field the larger this becomes, superconducting magnets 1-20 tesla are used to maximise this differential. This resonance frequency can be used to determine to determine each nucleus. The resonance frequency is also dependent upon the shielding applied by surrounding electrons. This shielding affects the resonant frequency of the nucleus. Resonant frequencies are often expressed as a chemical shift, this is defined as the frequency difference between nuclei in differing chemical environments (Atkins and de Paula 2010; Barker 2011).

^{1}H-NMR was used to determine conversion and relative abundance of products formed. Conversion is defined as consumption of monomer and was calculated by integration and comparison of the peak given by the (O-C**H**$_3$) δ=3.70 for monomer, compared to the (O-C**H**$_3$) for all other higher molecular weight material present δ=3.75-3.50.

Figure 4-1 below shows integrated NMR trace, and the method used for determination of conversion. Peak areas for monomer 1, 1.02 for all higher order oligomers. % conversion is defined as the ratio between the peak areas

$$\% \ Conversion = 1 - \frac{Monomer}{Monomer + Oligomer} = 1 - \frac{1}{1+1.02} = 50.5\%$$
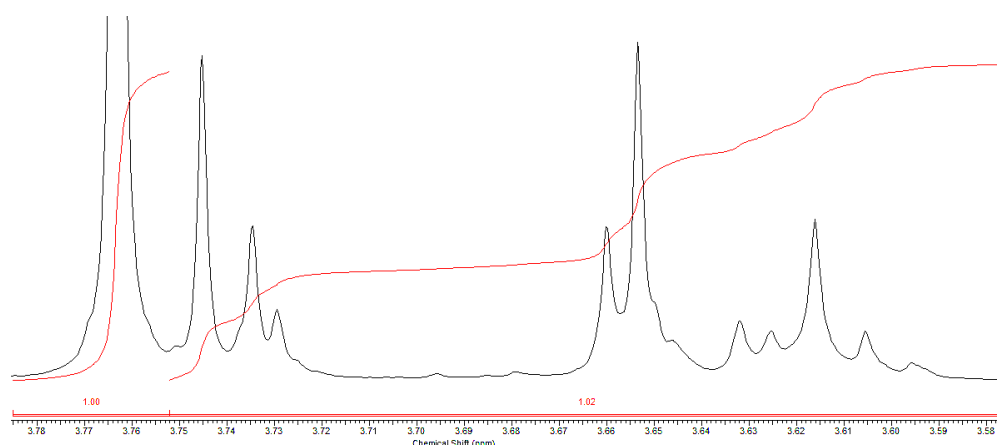
Figure 4-1: NMR trace of a typical reaction carried out at 600 ppm, integration traces used for determination of conversion of monomer.

Relative abundance of the oligomers MMA-MMA$_4$ were calculated by similar method, as DP$_n$ increased, varying shielding around the (O-C$\mathbf{H}_3$) on different monomer units caused shift of the peaks. Peaks produced by each oligomer, shown in Figure 4-2 below, Table 7-4 shows the chemical shift for each (O-C$\mathbf{H}_3$) in the materials.
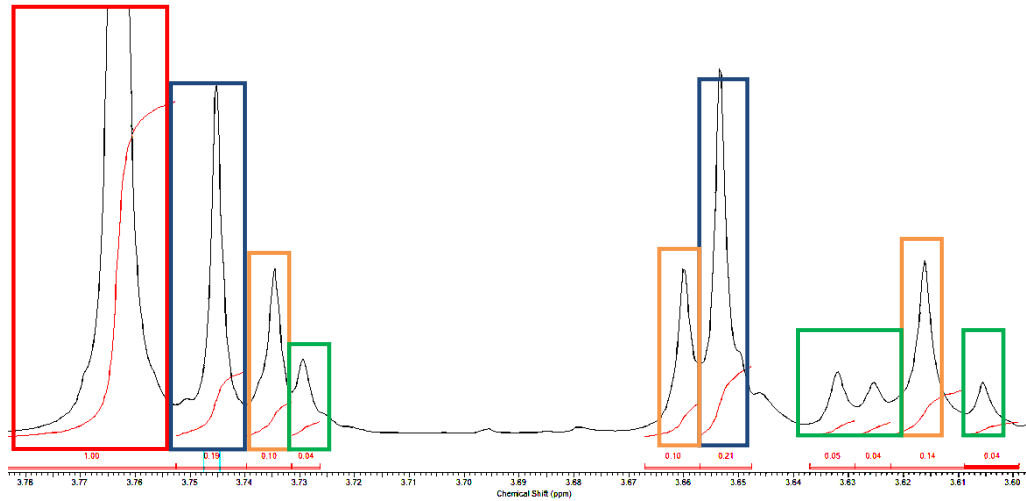
Figure 4-2: NMR trace showing peaks for the (O-C$\mathbf{H}_3$) group on different length MMA oligomers, Red: MMA, Blue: MMA$_2$, Orange: MMA$_3$, Green: MMA$_4$

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Table 4-4: Chemical shifts for MMA-MMA$_4$ produced by the (O-CH$_3$) nucleus on each monomer unit.

	δ of (O-CH$_3$) peak			
MMA	3.700	-	-	-
MMA$_2$	3.745	3.655	-	-
MMA$_3$	3.735	3.660	3.615	-
MMA$_4$	3.726	3.635	3.625	3.605

Above tetramer it was not possible to differentiate between molecular weights by NMR, this was due to all further increased units having the same shielding as the peak produced at 3.635, thus giving a large/broad peak on the NMR trace.

4.5.2 Gel permeation chromatography

Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) is a commonly used technique for analysis of polymers. A fundamental characteristic of a polymer is its molecular weight and molecular weight distribution.

GPC separates polymer samples based upon the hydrodynamic volume of each individual chain present, this is defined as the size of the polymer when fully solvated. This is achieved by dissolving a sample within a solvent (THF), and passing the solution through a column packed with immobile porous material. This immobile phase is often constructed of a cross-linked inert polymer, containing a range of pore sizes.

As the sample moves through the column, smaller molecules enter pores within the stationary phase, whilst the larger molecules cannot, as a result the larger molecules experience a shorter time within the column and are eluted first. The range of pore sizes within the column leads to separation of the sample, allowing molecular weight distributions to be produced. Definition of molecular weight distributions, and their analysis, are shown in Chapter 1.

Within this work the targeted materials are very short chain oligomers with 2-4 repeat units; this presents a problem with analysis. The GPC equipment available has a column with minimum calibration of 690 Da, this is above the range of products produced. Therefore analysis of these low molecular weights was carried out with the use of NMR, GPC analysis was used to ensure no higher molecular weight material was formed (Gridnev, Ittel et al. 1995).

Equipment used for carrying out GPC analysis
Varian GPC50 operating at 40 °C, coupled with a PLgel 3 μm guard column and two PolarGel 5 μm Mixed-D coupled with a refractive index detector using HPLC grade THF as the mobile phase at a flow rate of 1.0 cm^3/min. The calibration of the equipment was performed using poly(methyl methacrylate) narrow distribution standards (supplied by polymer laboratories) which ranged from 690-1,944,000 Da. Data was analysed using Cirrus GPC offline software package.
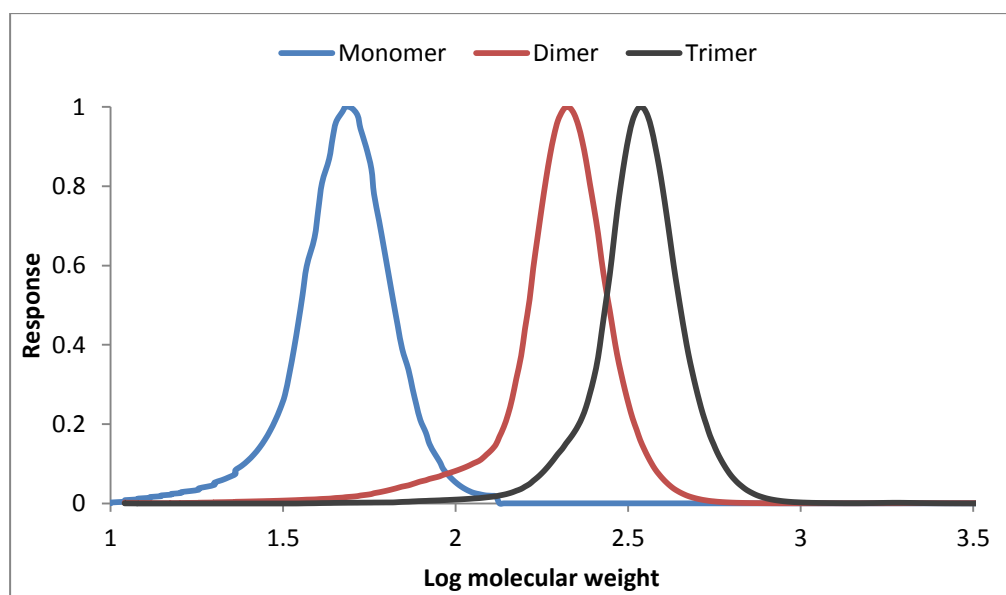
Figure 4-3: GPC trace for pure samples of MMA, MMA$_2$, MMA$_3$

4.5.3 Thermo-gravimetric analysis (TGA)

TGA is used to determine the mass change of a material as a function of temperature within a controlled inert atmosphere. Commonly in use with polymers this is used to determine degradation temperatures. The aim of its use in this work was to use this technique to separate products based upon their relative volatilities, in order to determine percentage composition of materials present. This technique can be coupled with further analytical techniques such as mass spectrometry, to analyse products as they are released. It is well as to what materials are present in the mixtures tested, analysed by NMR and GC-MS. The purpose of this is to give a physical measure of the relative quantities.

4.5.4 Method used for carrying out Thermo-gravimetric analysis (TGA)

A stepwise isothermal method was developed which could separate MMA monomer, MMA_2, MMA_3, MMA_4, it was not possible to separate higher order oligomers due to low % presence and high viscosities on the pan preventing separation.

Analysis was carried out using a Q5000 IR (TA instruments). Samples were in liquid form, 1 drop with mass between 2-10 mg, was placed within a cleaned, platinum pan. Platinum was used as it is chemically inert with the materials tested, has high thermal conductivity and is non-porous.

To create the method, pure samples were heated at a constant rate of 10 °C/min from ambient to 250 °C. Nitrogen flow rate 75 ml/min was used as the carrier gas, this high flow rate was used to encourage turbulence around the sample and promote evaporation.

All experiments were carried out in triplicate to ensure accuracy. Figure 4-4 below shows the curves produced when heating pure samples of monomer/MMA_2/MMA_3, it is clearly shown that these materials can be separated based upon temperature.
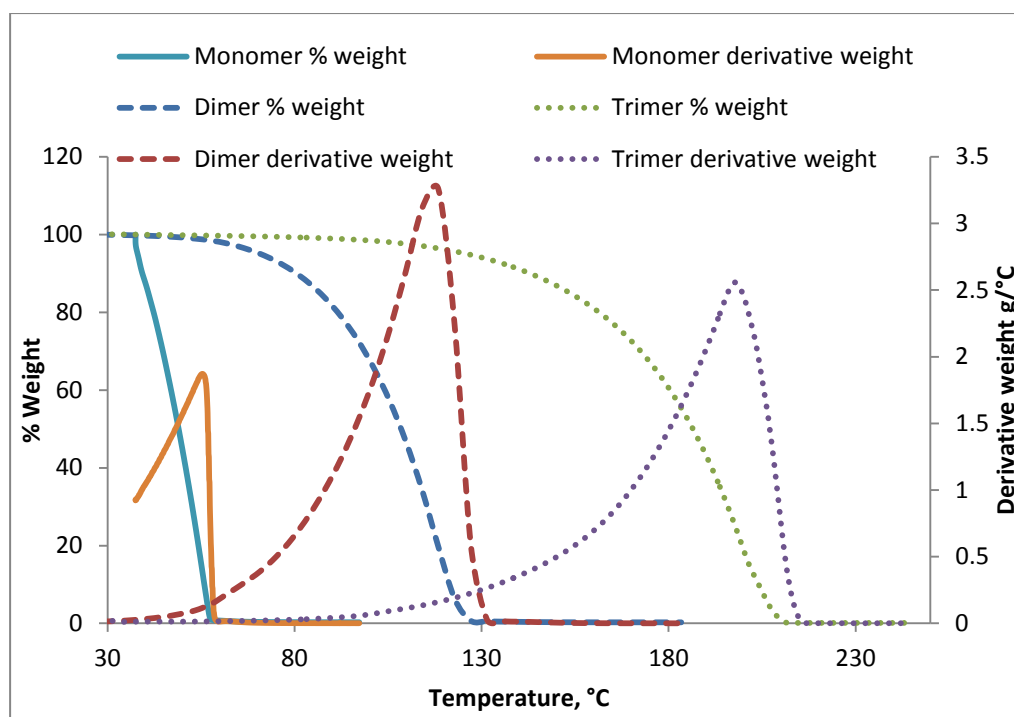
Figure 4-4: Thermal decomposition, calibration curves for pure MMA/MMA$_2$/MMA$_3$ in TGA at 10 °C/min up to 250 °C

Through trial and error of temperatures and isothermal duration the following method for separation was used:

> Method Log:
> 1: Isothermal for 30.00 min
> 2: Jump to 85.00°C
> 3: Isothermal for 60.00 min
> 4: Jump to 140.00°C
> 5: Isothermal for 90.00 min
> 6: Jump to 205.00°C
> 7: Isothermal for 90.00 min
> 8: Jump to 500.00°C
> 9: Isothermal for 5.00 min
> 10: End of method

Data collected was exported to Microsoft EXCEL where it was then analysed and % abundance calculated.

4.5.5 Coupled Gas chromatography with Mass Spectroscopy (GC-MS)

Gas chromatography is an analytical technique that is used to separate and analyse mixtures by separation into their individual components. Coupled with mass spectroscopy this is an extremely powerful analysis technique.

The sample is injected in the GC equipment a mobile phase carrier gas (He) drives the sample through the column. Compounds that react heavily with the column will elute from the column at a slower rate than those that have very little interaction. To achieve good separation a large length column is often required (>10 m). as individual compounds elute from the column the concentration is detected; the time taken between injection and detection is known as the retention time.

Calibration of the detector is required as different compounds can give a different response at the same concentrations; this is not always a linear relationship and should be taken into account when carrying out quantitative analysis of samples. This response factor is determined by analysis of pure samples at a known range of concentrations; this is shown in Figure 4-5 below. It is clearly shown that for the three samples used that the relationship was linear.
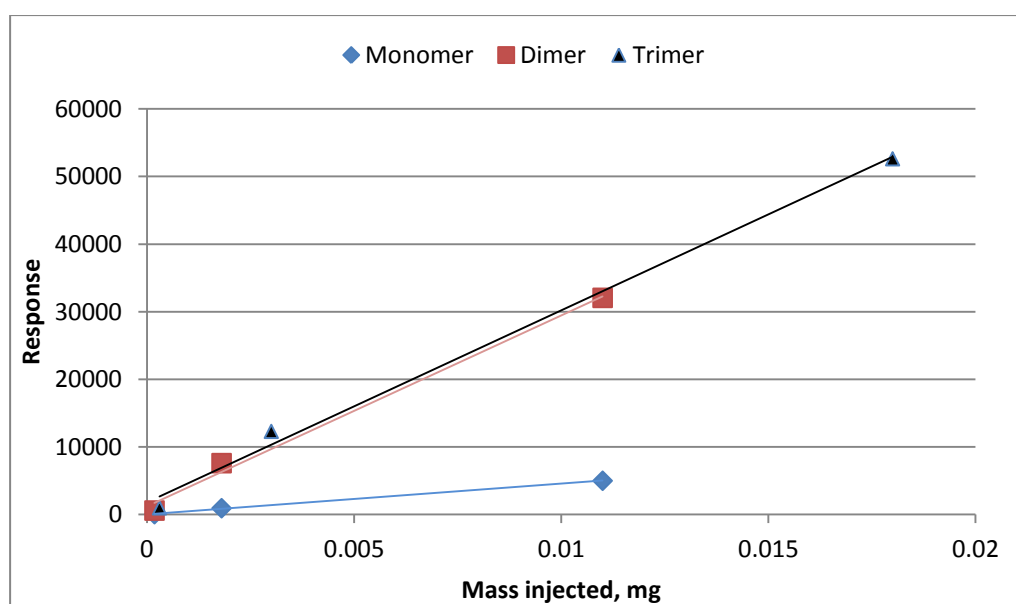
Figure 4-5: Linearity check for responses of pure samples within GC detector.

Mass spectroscopy is an extremely powerful tool, coupled with GC this allows for near perfect separation and analysis of samples. As samples elute they are passed into the MS for analysis.

This technique is the perfect analysis tool for the products used as it allowed for clear separation of all products produced, with precise quantitative analysis possible. However, due to availability of the equipment it was not possible to analyse all samples in this way, a select group of samples were used for comparison and validation of the other techniques used. NMR and GPC were used simultaneously to analyse samples in the majority of experiments.

Figure 6-29 below shows an example chromatograph produced using GC. It can be clearly seen that there is good baseline separation between the different length oligomers; abundance was calculated based upon the relative peak areas.
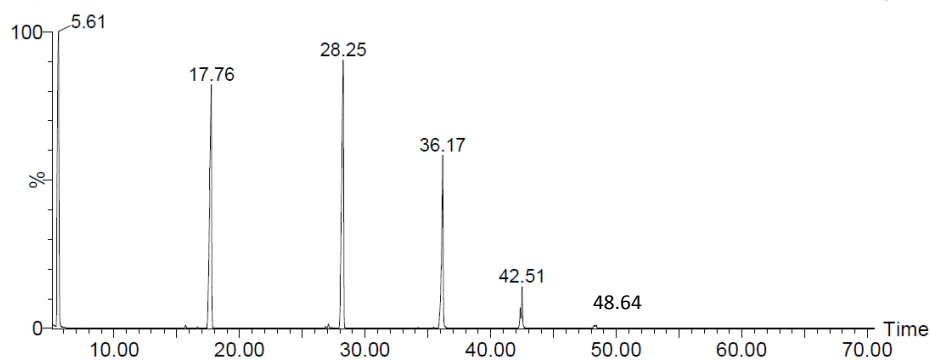
Figure 4-6: GC chromatograph for a typical polymerisation reaction, showing peaks for the different MMA oligomers present.

Figure 4-7 below show MS data for MMA monomer, the peak at 99 is caused by the loss of one H atom, 85.02 loss of CH_3, 69.02 (C_4H_5O), 59.01 ($C_2H_3O_2$).
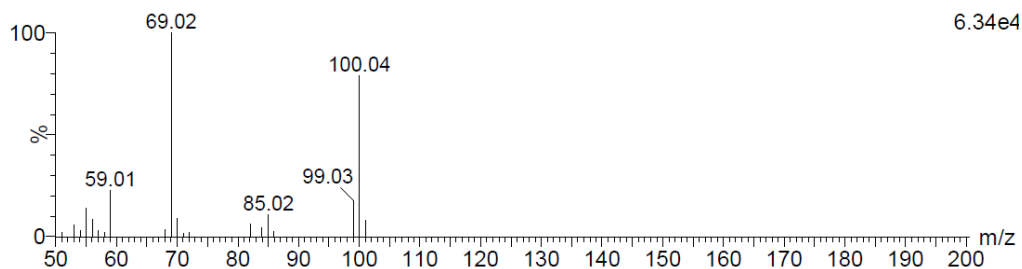
Figure 4-7: Mass spectometer output for methyl methacrylate monomer

Equipment used for GC-MS analysis

Products were analysed *via* GC/MS on a Waters Autospec Micromass VG. The instrument was fitted with a BP-1 GC column (15 m, 0.25 mm, 0.25 µm), using Helium as the carrier gas (100 KPa). The gradient was set to 50 °C (3 min) to 300 °C (20 min) at 6 °C/min.

0.01 g sample was solvated with 1 ml HPLC grade dichloromethane. 100 µl sample was further diluted with 500 µl DCM, 1 µl was then injected as sample.

5 Accelerated batch synthesis of low molecular weight methyl methacrylate oligomers

This Chapter details initial work conducted using small scale batch polymerisation experimental procedures. The purpose of these experiments was to establish an understanding on the empirical methodologies of the polymer chemistry that were to be studied, and then to use this understanding to quantify the thermal, kinetic and physical characteristics of the reaction system which is to be investigated.

Additionally, comparative reactions conducted using conventional reactor formats which utilise standard heating methodologies were required to establish a base line for comparison with the work carried out with microwave experimentation. These comparisons were carried out in such a way that all variables including reactor geometry, stirring rate and heating rate were kept constant throughout. This would ensure that any difference observed was directly related to the use of microwave heating and not caused by other variables.

Typically, commercial polymerisation reactions are conducted in large batch reactors at moderate temperatures. The reaction temperatures applied are often set to be between the 10-hour and 1-hour initiator half-life temperature, within this study AIBN was used as the initiator in most cases, giving a temperature range of 60-80 °C. The strategy usually applied required this temperature to be maintained isothermal for the duration of the process. This method was adopted because it gave a slow, controlled, continuous release of radicals throughout the reaction. The purpose of this was to increase the control over the reaction. Free-radical polymerisation reactions are often highly exothermic (40-80 kJ/mol for MMA), giving significant risk of thermal runaway.

However, it has been shown that adoption of more extreme operating conditions has resulted in increased rates of reaction, higher selectivity and

reduced by-product formation (Bogdal 2005; Bogdal and Prociak 2007; Moseley and Kappe 2011). As previously stated, attempting to employ these more extreme conditions can be difficult within a batch system. Alternatively, use of a continuous flow system presents a real opportunity to enable these more extreme conditions to be achieved in a safe and repeatable manner. However, to successfully transfer the polymerisation system from batch to continuous flow, a significantly reduced reaction time was required. Therefore, to define if this could be achieved, the experimental programme discussed in this thesis was carried out using small scale batch reactions.

5.1.1 Conventional and microwave heated batch heating profiles of MMA monomer

As stated previously an objective of this work was to allow for direct comparison between both conventional and microwave heating. A variable that has often overlooked by researchers is heating rate (Obermayer and Kappe 2010; Kappe, Pieber et al. 2013). Heating rate can be affected by several parameters such as, stirring rate, vessel geometry, temperature gradient, fluids/materials used.

Investigation was carried out to determine what volume of material and vessel geometry was required to give comparable heating time in conventional and microwave heating. Conventional heating experiments were carried out within an oil bath; reactions were carried out using two different vessel geometries: a straight sided reaction flask containing 30 cm³ monomer, and a long neck round bottom flask containing 50 cm³. Both vessels were observed to take approximately 300 s to heat to the target temperature of 100°C. Consequently, it was noted that there was an increased surface area to volume ratio in the round bottom flask which was proposed to explain the higher heating rate per gram within this geometry.

The preferable option of these vessels was to use the round bottom flask as the same vessel could be used with a larger maximum capacity. When heated in the CEM at 300 W it was seen that it took 90 s to achieve 100 °C. However,

it was found that with reduced material volume that there was no effect upon the heat up time; making this vessel unsuitable for use in comparing heating sources in this instance.

In conventionally heated experiments, temperature was measured with the use of a K-type thermocouple; in microwave heating an optical fibre was used. In all experiments the reaction mixture was well stirred to ensure homogenous, temperature was measured at the centre of the sample.

When using a straight sided vessel (30 mm OD, 150 mm long, 100 cm³) unlike in the round bottom flask, it was found that the heating time changed when the volume of reagents was varied. This relationship can be seen in Figure 5-1 below; it was found that when using 30 cm³ that the heating time in both conventional and microwave heating was comparable.
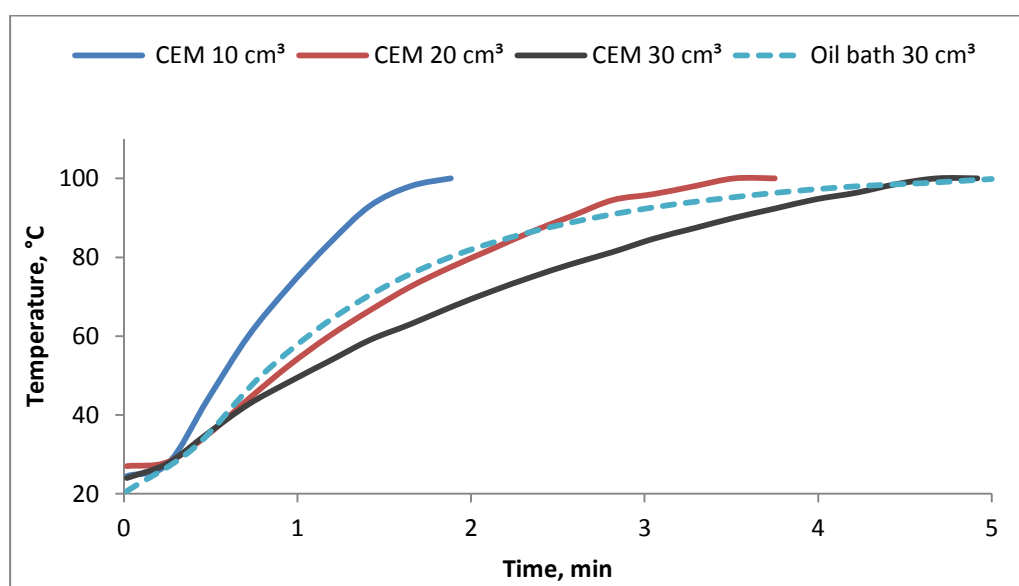
Figure 5-1: Temperature profiles for heating different volumes of pure MMA in straight sided tube within CEM and oil bath.

Therefore for the majority of experiments, unless otherwise specified, this vessel geometry and reaction volume was used. However, it was observed that this relationship only held when heating pure MMA monomer in the CEM at 300 W.

5.2 Conventional CCT polymerisation

Initially batch polymerisation reactions were carried out in the straight walled 30 cm³ tubes discussed above and heat was applied *via* the use of stirred oil bath. The vessels were sealed with a rubber septum to allow for elevated pressure to be achieved within, and so allow temperature to exceed the normal atmospheric boiling point of the monomer (100°C). Temperature within the reaction vessels was continuously monitored and recorded with the use of thermocouples, these were inserted through the rubber septum.

These initial experiments were focussed upon investigating the effect that varying reaction conditions had upon a standard CCTP reaction. Therefore, unless stated otherwise the standard procedure reactions contained 600 ppm CCT catalyst (PhCoBF) and 1 w/w% initiator (AIBN) and were conducted following the experimental procedure detailed in Chapter 6. Additionally, these polymerisations were conducted without the use of solvent. High boiling point solvents such as toluene are commonly used in research applications to reduce the rate of reaction and to allow for more control at increased operating temperatures. Therefore, the use of solvents is undesirable in a process which is focussed on rate acceleration. Furthermore, it adds a separation stage which can lead to contamination.

5.2.1 Batch polymerisation with temperature maintained at or above set point

As one key aim of this study was to achieve and increased reaction rate, the initial reaction strategy investigated was to conduct the polymerisation at an increased temperature.

AIBN was chosen as the initiator in this process as it is typically used industrially in the polymerisation of MMA. Thus because these first experiments were to be reacted at the 1 hour half-life (84 °C) then it was calculated that 5 hours are required to decompose 97 % of the initiator. Increasing temperature to 90 or 100 °C reduces the half-life to 28 and 7.6 minutes respectively (Sigma-Aldrich 2005; Akzo-Nobel 2010). This large

increase in rate of decomposition also increases the levels of initiation and propagation occurring. However, it can also significantly increase initiator – initiator termination. This is undesirable as it tends to result in the isolation of reduced yield of inferior quality product and is often referred to as "initiator burn-out" (Cowie and Arrighi 1991).

Reaction vessels were placed within the pre-heated oil bath at the required temperature, (80, 90, 100 °C) for 1-hour. 1 cm³ samples were taken *via* syringe at 5, 30 and 60 min; these were then quenched and stored in a freezer prior to analysis.

Results and discussion for polymerisation with maintained temperature
Figure 5-2 and Table 5-1 below, show temperature and conversion data for the three reaction temperatures.
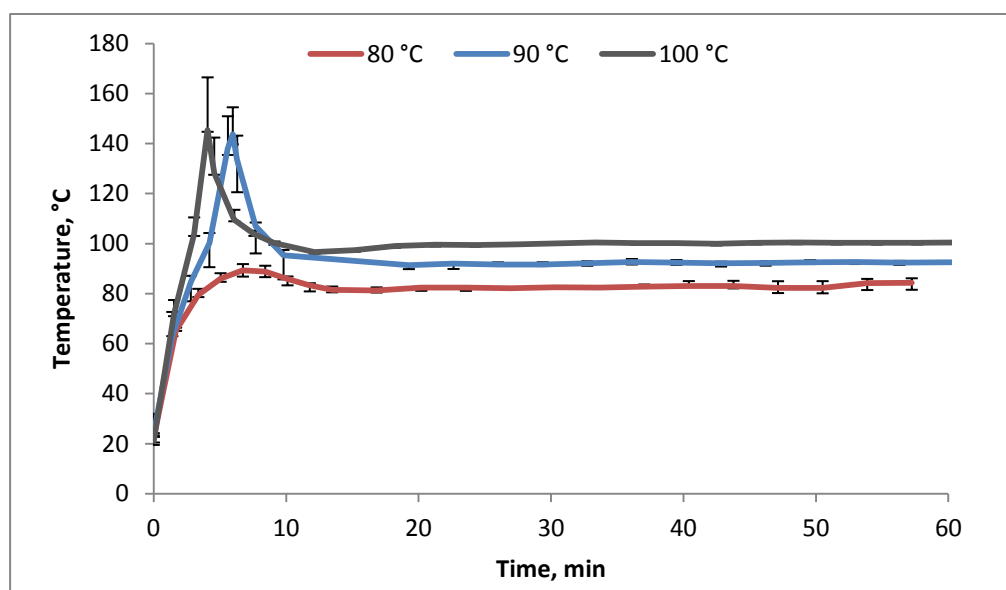
Figure 5-2: Temperatue profile of conventionally heated 30 cm³ CCT polymerisation, sample was held within isothermal oil bath for 1 hour.

Table 5-1: % Conversion for conventionally heated reaction maintained at temperature set point for 1 hour.

Set point temperature, °C	% Conversion		
	5 min	30 min	60 min
80	26±3	41±2	43±8
90	66±1	66±1	63±3
100	63±1	61±2	63±1

From Figure 5-2 it can be observed that, at 80 °C, after the temperature set point was reached, there was a small temperature overshoot above the set point. The temperature peaked at 89 °C, after which the temperature then slowly returned to the set point (after approximately 15 minutes). This was attibuted to the heat of reaction generated from the bond formation process. Investigating the conversion to polymer achieved by the reaction as it progressed at this temeprature, it is observed that between 5 and 30 min there was a further 20 % increase in conversion, though there was no observed increase in temperature. The isothermal temperature was likely caused by the lower rate of reaction reducing heat generation such that the heat transfer to the oil being high enough to maintain the constant set point temperature.

In the case of the reactions conducted at 90 and 100 °C, it was observed that a conversion of 65 % was achieved after 5 min in both cases. However, it was also noted that there was no further increase in conversion past this point. This was concluded to indicate that the reaction was no longer progressing and that chain generation and growth had effectively ceased. Both the 90 and 100 °C reactions were also observed to exhibit a significant reaction exotherm, achieving peak temperatures of approximately 140 °C. After reaching this maxima the temperature then cooled rapidly back to the set point, where the return to the target temperature in both cases was achieved in a similar time to that of the 80 °C experiment. From these observations it was concluded that, it may be possible to carry out the reaction without the

requirement for temperature to be maintained, the high rate of reaction and heat generation could potentially sustain the reaction.

The varying times taken for the peak temperature rise were caused by the increased rates of initiator decomposition within the system and was direclty related to the thermal performance of the AIBN. Initiator decomposition, is known to be the rate determining step of the reaction system, thus increasing will have a large effect upon the overall rate observed. It will also potentially lead to increased "early" termination of radicals (i.e. initator burn out) which can potentially reduce overall conversion.

In the cases of both 90 and 100 °C it is unknown at what point the reaction achieves its final conversion, it is hypothesised that this point was reached once the reaction had achieved its maximum temperature. This was postulated due to the rapid rate of cooling that was observed to occur after the peak temperature had been reached. Therefore, It was proposed that, if the reaction were continuing, that this cooling effect would be slowed by heat generation from the bond forming reaction involved in chain growth. However, it was not possible to sample the reactions earlier in the process because of the high pressure (4 bar), maintained within the tube caused by the elevated temperature.

Analysis of products formed by NMR showed that at all three temperatures mixtures of MMA_2/MMA_3/MMA_4 were formed in a 4:2:1 ratio. GPC analysis (Figure 5-3) showed that no high molecular weight material was formed with <1% higher molecular weights present in the samples of material.
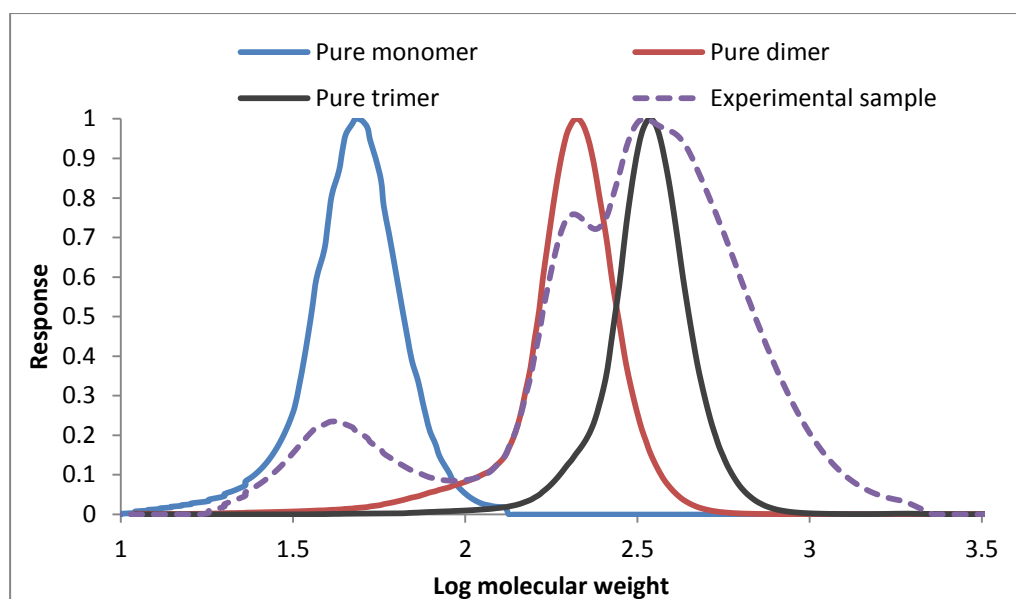
Figure 5-3: Sample GPC trace for conventional batch polymerisation carried out at using conventional heating at 100 °C, traces for pure products overlaid.

In the reactions carried out at 90 and 100 °C the same peak conversion of 65 % was reached, this indicates that the system is self limited. This could potentially have been caused by two mechanisms both potentially linked to a signiifcant increase in vioscosity of the reaction medium resulting from the high rate of polymer production achieved:

1. Initiator burn-out: the initiator produced radicals at such a high rate that the reaction became diffusion limited and very high rates of initiator-initiator termination occurred.

2. The CCT catalyst is limiting the conversion, the high efficiency of the catalyst is preventing further conversion, further investigation into this is shown in Sections 5.3.7-5.3.8.

Further experimentation was required to determine which of these effects was limiting conversion within the system. These further investigations are fully discussed later in Section 5.3.8.

5.2.2 High temperature conventionally heated batch reactions with no maintained temperature set point

It had been shown by the previous experiments that polymerisations with a set point of 90 and 100 °C gave rise to significant exotherms. However, it was also noted that the overall reaction temperature returned to the set point after approximately 10 - 15 minutes. Therefore, it was proposed that this internally generated energy could be utilised to sustain the reaction and remove the requirement for continued heat input.

In order to prove this, 30 cm³ reactions were prepared *via* method 1 shown in methodology Chapter. These were heated to the same temperature set points (80, 90, 100 °C) within an oil bath, upon reaching this temperature they were then removed from the heating fluid. The vessel was not insulated after removal from the oil bath to ensure that the method was comparable with microwave heated experiments. Microwave heated experiments were not insulated as it was not possible to place insulation within the CEM microwave cavity. The reactions were stirred for 1 hour, and the temperature within the vessel was monitored using a thermocouple throughout. Samples were taken *via* syringe at 5, 30 and 60 min; these were then quenched and stored in a freezer prior to analysis.

Results and discussion of the effect of not maintaining the reaction temperature at or above the set point

By comparison of the data in Table 4-1 above and Table 4-2 below, it was noted that there were significant differences between the two reaction regimes. In the reactions where the temperature was not maintained at the set point, there was no trend of increasing conversion, after 5 min at all three temperatures.

Table 5-2: % Conversion for conventionally heated reaction, once heated to set point no further energy added.

Temperature, °C	% Conversion		
	5 min	30 min	60 min
80	10±2	11±4	10±4
90	20±2	20±2	20±2
100	65±3	65±1	66±2

However, from close examination of the temperature profiles in Figure 5-4 this trend in conversion could be predicted.
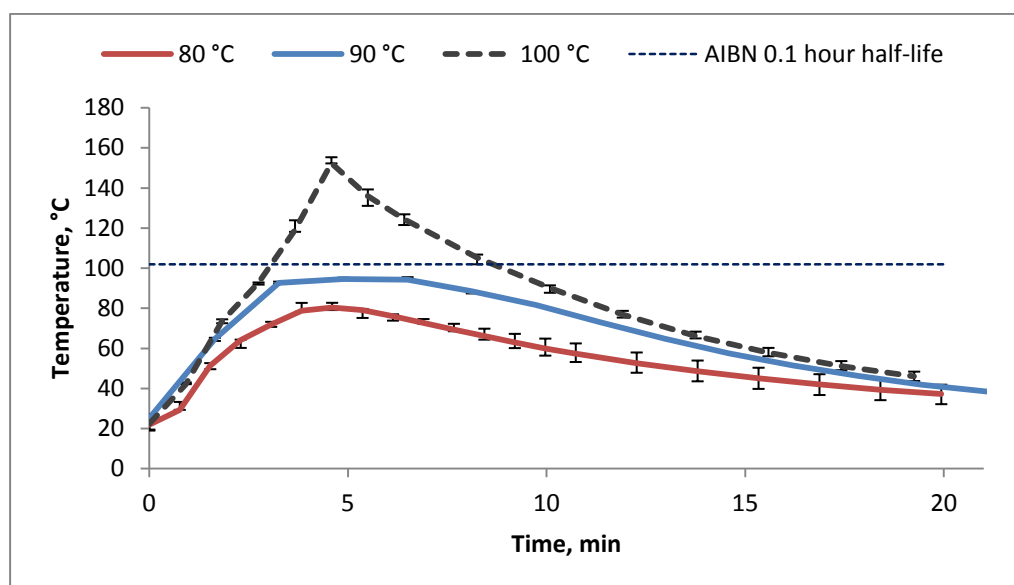
Figure 5-4: Temperature profile for conventionally heated 30 cm³ batch polymerisation, once heated to set point no further energy was added.

At 80 °C, 4 °C below the 1 hour initiator half-life, there was no temperature increase and the reaction cools at a rate similar to that of pure monomer. This result differed from the reaction where the temperature was maintained, there was a slight but measureable exotherm and 15 % increased conversion after 5 min.

At 90 °C, 6 °C above the 1 hour half-life, there was a different temperature profile to that of the temperature maintained reaction. In this case, there was a slight increase in temperature, the temperature then maintained at 90 °C for 3 min before cooling. There was no large increase in temperature

observed. Consequently, the level of conversion was also noted to have dropped significantly. This shows that, under these conditions, the reaction was temperature sensitive, and that the small losses in heat by removing from the oil were enough to quench the reaction both preventing the exotherm and decreasing conversion.

At 100 °C a significant exotherm was observed, almost identical to that in the previous Section. This indicated that, at these high temperatures, the polymerisation occurred at a high enough rate to sustain itself and achieve the same conversion and product distribution as that found with additional heat was input.

NMR analysis of products formed showed that at all three temperatures MMA_2/MMA_3/MMA_4 was formed in a 3.7:2:1 ratio. GPC analysis showed that no high molecular weight material was formed with <2% higher molecular weight oligomers.

5.2.3 Batch scale up

It is well established that scale up of reactions can have significant effects upon reaction conditions (Fogler 2006; Sinnott and Towler 2009). Small scale reactions can allow for almost perfect mixing and increased rates of heat transfer, due to short transfer distances involved. Therefore, to investigate the influence of scale up on the types of system being studied in this section of work, scaled up experiments were carried in which the reaction volume and vessels were increased: 30, 50, 250 cm³.

5.2.3.1 50 cm³ conventionally heated polymerisation

50 cm³ reactions were prepared *via* method 4. Reaction vessels were placed within the pre-heated oil bath at 100 °C. Once the temperature set point had been achieved, the reaction vessel was removed from the oil batch and stirred for a further 5 min; samples were then taken and quenched prior to analysis.

It was found that there was no variation between reactions carried out at 30 and 50 cm³. Both the conversion and product distributions of the 50 cm³ polymerisation were found to be identical to that of the 30 cm³ equivalent. It had been proposed that there may be an increased maximum temperature observed when this increased volume was involved. This was due to increased thermal mass and reduced heat losses from the vessel. However, the temperature profiles were observed to be near identical to the 30 cm³ case, with the time taken to achieve the maximum temperature and the magnitude of the peak being comparable. The only notable difference came in the initial heating of the mixture. It took longer to heat the larger volume, this was expected, and was due to the way in which conventional heating occurs.

5.2.3.2   250 cm³ conventionally heated batch polymerisation

250 cm³ reactions were prepared *via* method 5 shown in methodology Chapter. Reaction vessel was held within the oil bath until the set point temperature was reached; vessel was then removed and stirred for the duration. The reaction vessel was contained within a bund, to that in the case of loss of containment that any material was caught safely.

During the initial heating of the mixture, which took 4 min, there was an inflection point at 85 °C, where the heating rate increased. This indicated that polymerisation had started and that energy was being released as a result of the onset of the bond forming processes.

Figure 5-5 contains pictures which were taken from a high resolution video. These stills highlight key points during the reaction, after it was removed from the oil bath.
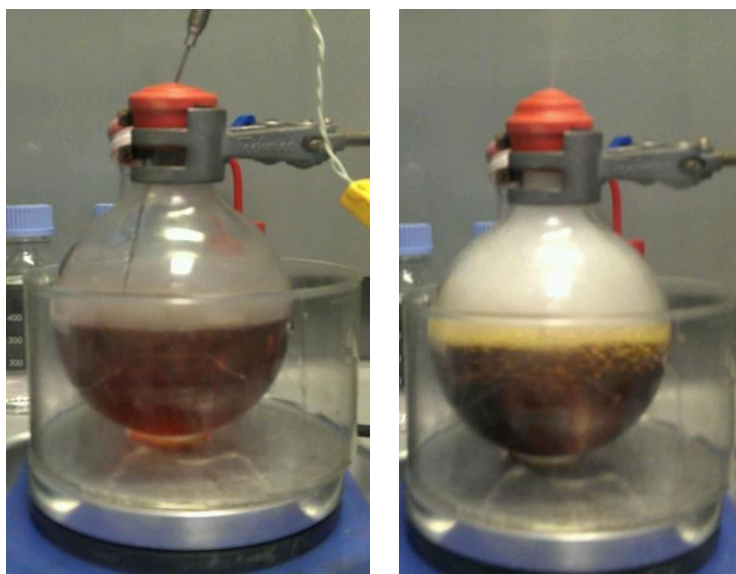
Figure 5-5: 250 cm³ conventionally heated reaction at 100 °C, (left) shows reaction with thermcouple in place. (right) internal pressure build up has forced thermoucple out, and mixture is uncontrollably boiling

It was observed that 30 s after removal from the oil bath the sample began to boil. At this point the bulk temperature was found to have increased to 160 °C. The calculated internal pressure for these conditions was 4.5 bar. After 40 s the pressure within the vessel forced the thermocouple out of the vessel, allowing vapour release (Figure 5-5 (right). The two pictures Figure 5-6 were taken less than 1 s apart.
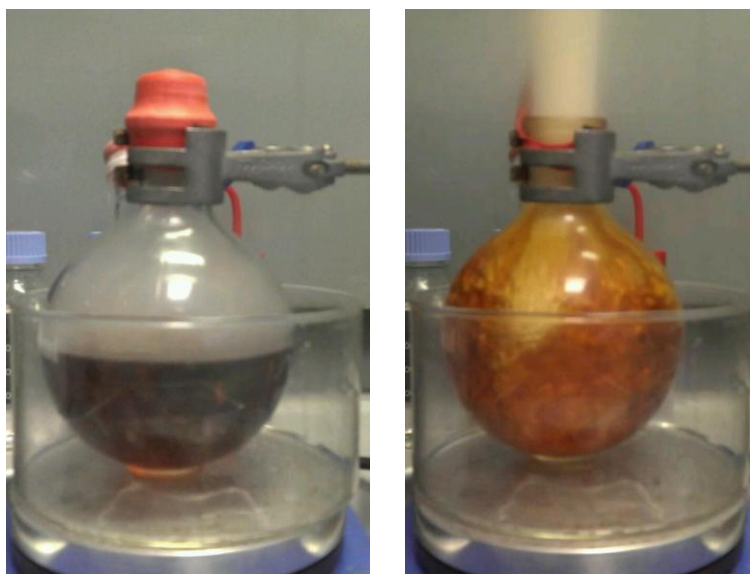
Figure 5-6: 250 cm³ conventionally heated reaction at 100 °C, (left) deformed septum due to elevated pressure. (right) failure of septum resulting in sudden release of material.

It can be seen that the rubber septum was clearly deformed due to pressure within the system. In the next photo there was a clear catastrophic failure of the septum. Allowing for a material eruption from the vessel, this occurred 90 s after the sample reached the 100 °C set point. Vapour release did not occur within the smaller scale reactions, this can be explained by the larger mass of material used. As has been shown industrially and scientifically, increasing the scale of reactions can have a large impact upon the safety of the reaction.

This vapour release was caused by the reaction retaining more heat, resulting in a higher temperature being reached; this consequently gave an increased pressure. In the smaller reactions a peak temperature and pressure of (140 °C, 2.9 bar), was reached, it is unknown what pressure was produced in the larger reaction as the thermocouple was ejected, this occurred at 160 °C, it can be surmised that the temperature and pressure continued to rise once the septum sealed and material was no longer vented.

After the eruption of material, approximately 30 cm³ material remained within the reaction vessel. This experiment highlights the risks involved in scaling up batch polymerisation systems and demonstrates why industrial batch systems operate under more controlled conditions with the use of high

pressure apparatus. By adopting these procedures, the rate of reaction, reducing heat evolution and the inherent risks involved with this.

An alternative strategy for preventing such a reaction runaway would be to adopt a flow system. Such a reaction geometry allows for reactions to be carried out using more extreme conditions, this is possible because of the smaller volumes of material reacting at any time. Additionally, this system, by definition, is not a sealed system therefore internal residence times and pressure can be more accurately/easily controlled

Summary and conclusions from batch conventionally heated experiments

It has been shown that, at small scale <50 cm³, a CCT polymerisation can be carried out at a very high rate, to achieve the set targets for the reaction (i.e. ~ 40 % conversion to dimer and trimer) in under 5 min.

To achieve this when heat was continually applied to the reaction, a reaction set temperature of 90 to 100 °C was required. It was found that the bulk temperature within the reaction achieved approximately 150 °C. When carried out adopting a strategy of removing heat input after the peak temperature had been attained, it was found that a temperature of 100 °C was required.

Moderate scale up to 250 cm³ was shown to have a significant effect upon the reaction leading increased temperature and pressure resulting in vapour release and equipment failure; thus highlighting the importance of proper design and control within a system, both of which could be provided by the adaption of flow.

5.3   Microwave batch processing

In order to draw conclusions about any potential microwave benefits for this reaction system, direct comparisons with the conventional batch experiments that utilised microwave heating were required. Many researchers who have published studies on microwave heating have not done this rigorously in the

past. For example they have often compared microwave systems with conventional reactions that had different stirring rates, vessel geometries, reaction volumes, pressure, temperature, heating rates etc. In the experiments reported in this thesis, all reaction conditions and apparatus, other than the heating source, were kept constant between the comparisons. It was hoped with the use of precise experimental design, valid quantifiable comparisons between the two heating sources could be achieved

Batch microwave experiments were carried out using two systems: (a) a 'CEM Discover SP', a commercially purchased item of research equipment and (b) larger scale, batch microwave specifically built at the University of Nottingham capable of operating at up to 2 kW, details of equipment can be seen in Section 5.4. It was planned that this latter apparatus was to be used to provide a scale up link with the larger scale flow system, the design of which was one of the aims of the project.

5.3.1 Investigating effects of temperature measurement method upon polymerisation

As previously shown in the literature and in the microwave fundamentals Chapter, accurate temperature measurement is essential to ensure validity of results achieved when comparing the outcome of comparative microwave and conventional experiments The use of inaccurate temperature measurement techniques which do not directly measure the bulk temperature, such as the indirect IR in a CEM reactor, can lead to incorrect conclusions regarding the effects of microwave heating upon the reaction.

In conventionally heated systems temperature can be measured with the use of thermocouples, these are robust, accurate, compact, respond rapidly to changes and give precise measurement. However, these cannot be used under normal conditions within an electromagnetic field, as they are metallic and can conduct the electric field or cause arcing. The most commonly used technique in microwave heated systems is infrared (IR); there is growing use

of optical fibre (OF) techniques; further details of these two techniques can be found in Section 2.5.

Method for investigating the effect of temperature measurement technique
This experiment was designed to highlight the temperature differential between the bulk internal temperature and that of the external vessel wall. To achieve this 50 cm³ pressure vessels, provided with the CEM Discover were used. The same reaction composition as used previously in Section 5.2 was used. This offered the largest reaction volume that it was possible to introduce within the microwave cavity. As shown in Section 5.3.4, this gave the highest heating rate. This vessel is rated to 250 °C and 21 bar, with a 5 mm thick wall. This increased thickness compared to 2 mm wall Quickfit, is advantageous as it further highlights the variation between the two techniques due to heat conduction.

50 cm³ reactions were prepared *via* method 4. Reaction vessels were then placed within the CEM cavity and heated to 90 °C. The temperature was monitored *via* the chosen technique, IR or OF, and controlled by the built in temperature control software. Once the set point was achieved the reaction was stirred for 5 min before quenching and sampling. 90 °C was chosen as the temperature set point, as the reaction was shown in Section 5.2 to be more sensitive to changes in temperature.

IR controlled experiments were carried out by using the IR sensor built into the CEM. Temperature was also monitored independently *via* Neoptix™ optical fibre to quantify temperature differentials. OF controlled experiments used the CEM's built in OF controller, it was not possible to output the IR signal simultaneously.

Results showing the effect of temperature measurement technique
Figure 5-7 below shows the temperature profile when operating under OF control when the mixture is heated from ambient to 90 °C set point in 71 s. The reaction was allowed to occur for 5 min while under continuous stirring and temperature monitoring. It was observed that a slight exotherm

occurred, with the mixture reaching 92 °C. After this, the mixture then maintained its own temperature at approximately 88 °C for the duration of the study. NMR analysis showed that 18±1 % conversion had been achieved, compared to 20±2% when heating conventionally under the same conditions (at 30 cm³). NMR method and sample preparation shown in Section 4.5.1.
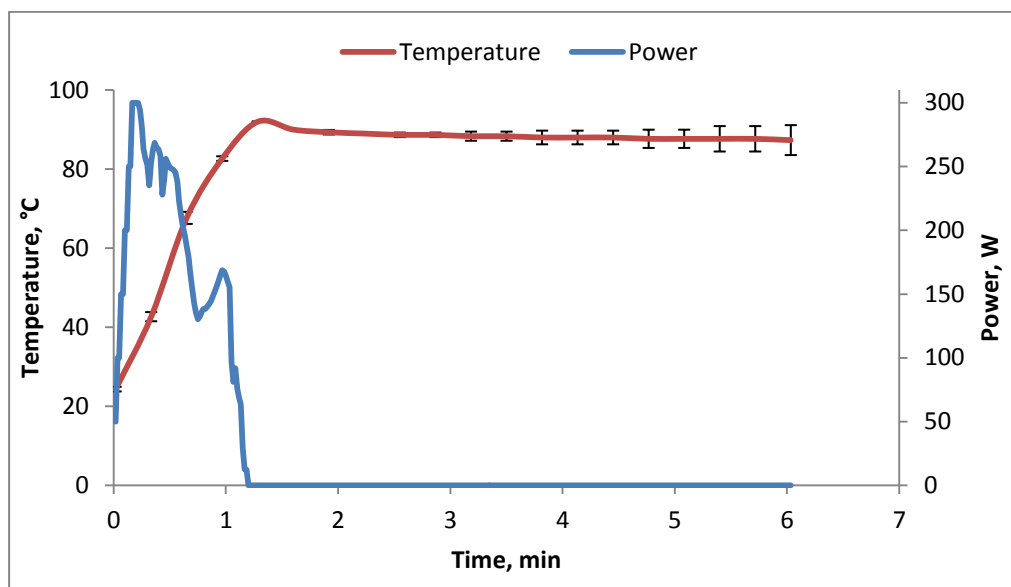
Figure 5-7: Temperature profile and power trace for optical fibre controlled 50 cm³ reaction carried out using CEM pressure vessel at 90 °C.

Figure 5-8 shows reaction temperature for that controlled via IR feedback, overlaid is the data shown previously in Figure 5-7.
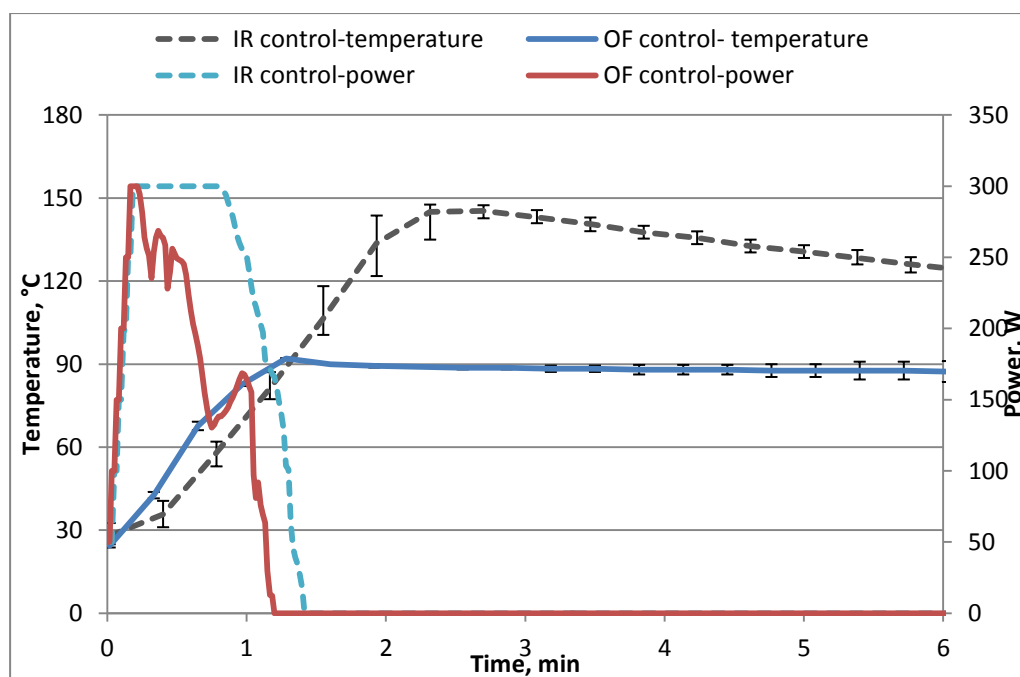
Figure 5-8: Temperature profiles comparing reaction temperature monitored by infrared and optical fibre within CEM.

The data taken from the additional OF monitor is not included, this data is presented in Figure 5-9 later. It can be clearly seen that there are two different temperature profiles. In the initial heating, the temperature measured *via* IR was lower than that of the OF experiment, this temperature then exceeds that of the OF controlled reaction to achieve a maximum of 148 °C compared to 92 °C. if only using IR data without the use of IR it could be concluded that there is 65 % conversion achieved in microwave heating compared to 20 % in conventional, data for this is shown previously in Section 5.2.3. If using the OF controlled experiment it is seen that 20 % conversion was achieved, similar to that of the conventional.

Analysis of the power traces shown in Figure 5-8 shows that with IR control more energy is used and for a longer duration. This would indicate that the equipment was heating to a higher temperature. Numerical integration of the power traces shows that when using OF and IR energy levels of 260 J/g and 390 J/g were input; 50 % more energy was input under IR control compared to OF. If it were assumed that 100 % energy transfer to the sample occurred this equates to a temperature rise of 50 °C.

Figure 5-9 which directly compares the two temperature measurement techniques, shows that when the temperature measured by IR is recorded as 90 °C, the internal temperature of the reaction vessel was in fact 132 °C, giving a 42 °C error.
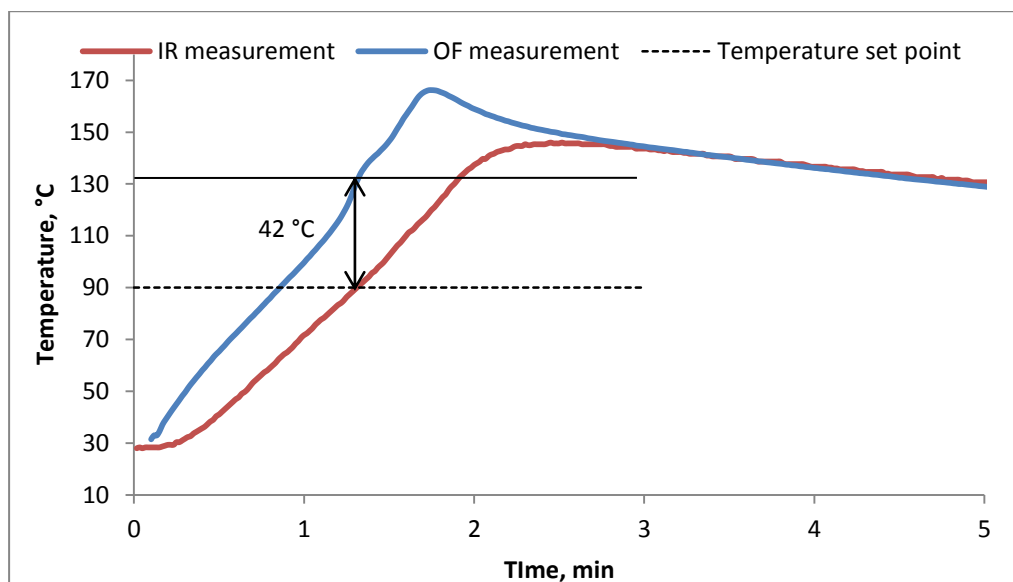
Figure 5-9: Temperature profiles highlighting variation between IR and OF techniques in a reaction controlled using IR.

It can then be noted that a peak temperature of 168 °*C* was measured *via* OF at 1 min 40 s, compared to the IR techniques estimate of a maximum of 151 after 2 min 30 s. This thermal lag was caused by the time taken for the walls of the reaction vessel to be heated by the liquid within. The reduced peak temperature was caused by a combination of the heat losses from the vessel and the location of the IR sensor. The IR sensor within the CEM Discover is at the base of the cavity, directly below the vessel and is angled vertically. Thus it is likely to be taking its readings from the lowest and likely coldest point. After approximately 3 min the temperatures measured by the two techniques equilibrates with no variation. This simple experiment has highlighted that, when using a system such as the CEM, temperature measurement techniques can significantly affect the results. When high rates of change in temperature occur the IR measurement lags behind both in time and temperature, giving an under reading; with slower temperature changes such as in the cooling phase the techniques agree.

This experiment was designed to highlight this discrepancy and has been effective. It has shown that when using accurate temperature control (OF) there was no variation between products formed and conversion achieved when compared to a conventionally heated system. Thus direct measurement of the bulk temperature is required in order to make rigorous comparisons between microwave and conventionally heated reactions.

5.3.2 Microwave heated batch polymerisation maintained at a temperature set point

Direct comparisons with conventionally heated reactions were carried out within the CEM. 30 cm³ reactions were prepared *via* method 1 shown in methodology Chapter. Reaction vessels were placed within the CEM cavity and heated to the required temperature and then held at that temperature for 1 hour.

Figure 5-10 below shows temperature profiles for reactions carried out 80, 90, 100 °C.
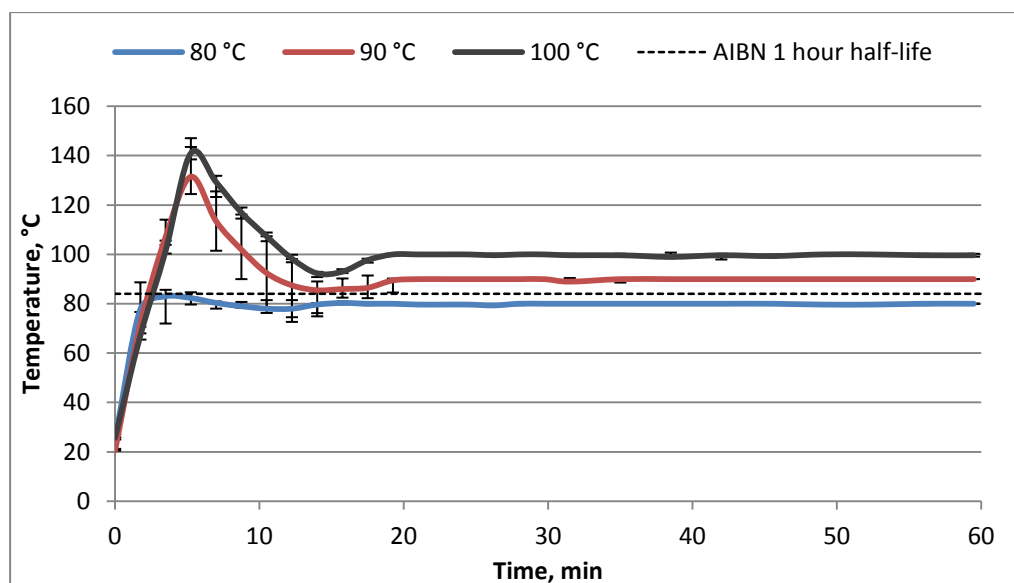
Figure 5-10: Temperatue profile of 30 cm³ microwave heated reaction maintained at temperature set point for 1 hour

At 80 °C a slight exotherm peaking at 84 °C was noted, before cooling back to the set point. Meawhile, with both 90 and 100 °C set point the temperature profiles exhibited significant exotherms, with reactions self heating at 0.5 °C/s

up to maximum peak temperature of 130 and 140 °C repectively. In both cases, once the maximum temperature was reached, the temperature was observed to return to the set point. This is the same trend as was obseerved in conventionally heated reactions shown in Section 5.2.

Analysis of products formed showed that MMA_2/MMA_3 was the principle product manufactured during all of these reactions. Small amounts of MMA_4 are present in the final product. This was comparable to the conventional system. GPC analysis confirmed no formation of higher molecular weight oligomers resulted from using the microwave heating methods. GPC methods shown in Section 4.5.2. When comparing conversion between the conventionally heated experiments (Table 5-3), similar trends were noted. With approximately 65 % achieved at 90 and 100 °C set point reactions. There was some variation when comparing reactions at 80 °C, with slightly higher conversions oberved conventionally, the differences were within experimental error thus not significant.

Table 5-3: % Conversion comparison between microwave and conventionally heated reactions held at a minimum temperature set point for 1 hour.

Set point temperature, °C	Microwave	Conventional
80	36±2	43±8
90	66±1	63±3
100	65±2	63±1

A more detailed comparison of the exotherm within the 100 °C set point experiment when conducted by conventional and microwave heating is contained in Figure 5-11.
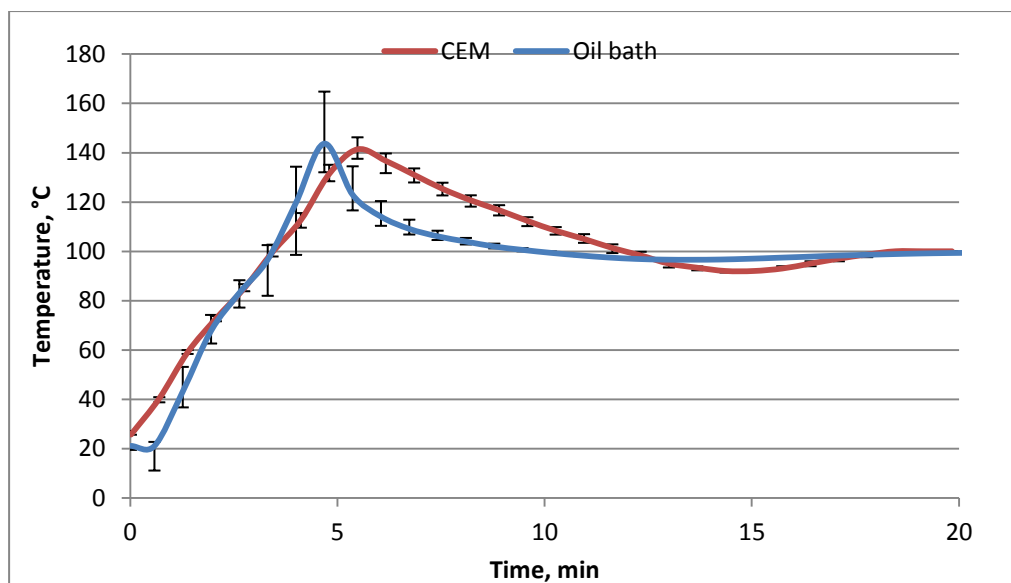
Figure 5-11: Temperature profile comparison between CEM and conventionally heated, 100 °C reaction maintained above the set point temperature.

In the oil bath, the peak temperature was reached more rapidly and it also returned to the set point temperature more rapidly. This was due to the vessel being immersed within hot oil for the duration of the experiment. Thus, this means that thermal energy is still being input into the system. By comparison, in the microwave case there was no energy input during this time. Once the peak temperature was reached more rapid cooling was noticed, this was due to much higher heat transfer coefficient of the oil compared to the air, with the cooling in the CEM there was a slight undershoot in temperature, this was due to the PID controller not resuming heating soon enough.

GPC analysis of the final products defines that all of these reactions exclusively produced MMA_2/MMA_3/MMA_4 in a 4:2.2:1 ratio, with less than 2 % higher molecular weight material formed (no material above M_n 700 was observed). Thus this reaction was clearly still under chain transfer control and could not therefore be classified as thermal runaway. This conclusion indicated that these reactions could be controlled whilst they exhibited these types of exotherm, and that there is potential for energy recovery.

5.3.3 Increased reaction rate CCT polymerisation with the use of high initial temperatures

30 cm³ reactions were prepared *via* method 1, shown in Chapter 4. Reaction vessels were placed within the CEM cavity and heated to the required temperature and then stirred for 1 hour with no further energy input, similar to the "heat and remove" reactions carried out conventionally.

Inspection of the data in Table 5-4 below, defined that there were once again significant differences between the two reaction regimes.

Table 5-4: Conversion data for 30 cm³ polymerisation carried out in CEM at different temperature set points.

Set point temperature, °C	Heat and remove	Temperature maintained
80	9 ± 0	36±2
90	25 ± 1	66±1
100	65 ± 2	65±2

As in the conventionally heated reactions (Section 5.2), it shows that when the target set point was 80 and 90 °C, it was observed there was reduced conversion in the heat and remove experiments. However, at the 100 °C set point the same conversion was achieved in both regimes and the same as that in conventional processing. Products formed were MMA_2/MMA_3/MMA_4 in a 4:2:1 ratio.

The previous two sections have shown that there were no variation between the reactions carried out in conventional and microwave processing. Reactions carried out at 100 °C have been shown to produce the target materials at the highest levels of conversion without further energy input. This reaction regime will be used throughout the remaining work, the other temperatures will not be further investigated.

5.3.4 Increased volume microwave polymerisation

5.3.4.1 Temperature profiles

A change in vessel geometry was required to accommodate the increased reaction volume involved in these scale up experiments. Thus temperature profiles for heating of pure monomer were produced in the new reactor geometry. The geometry of the vessel used was given previously in Section 4.2.

Figure 5-12 shows heating profiles for pure monomer, achieved with the CEM at 300 W, for 2 monomer volumes (30 and 50 cm³). 30 cm³ samples was heated in straight walled tube, 50 cm³ was heated in long necked round bottom flask.
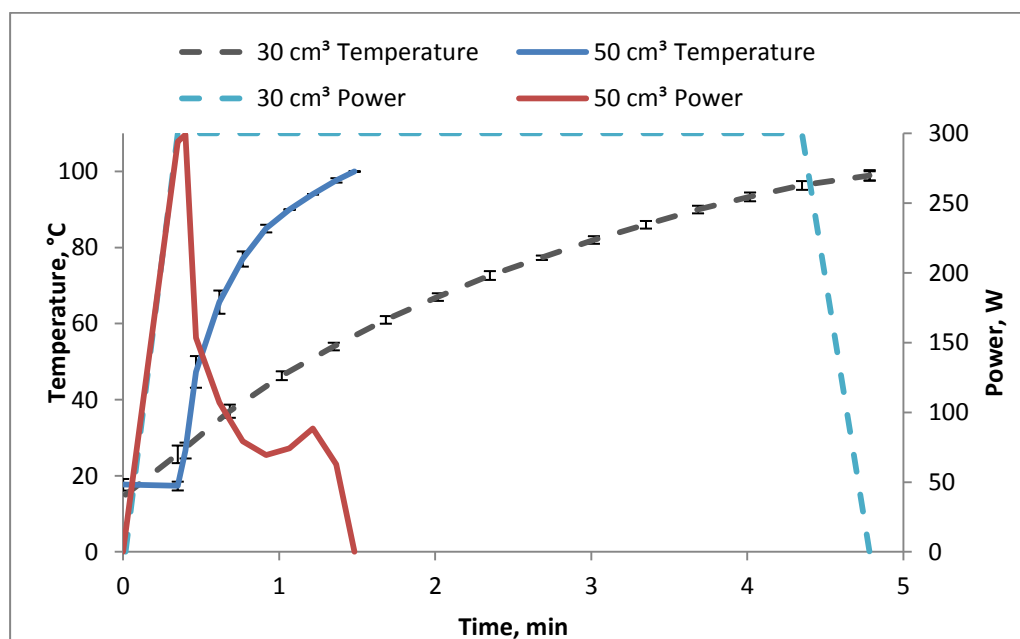
Figure 5-12: Temperature profile and power traces for heating of 30 and 50 cm³ monomer to 100 °C in CEM.

The data showed that there was a different trend exhibited to that which had been expected. Rather than the increase in volume resulting in an increased time required to heat the sample to the target temperature, a 3.5 min reduction was observed. It was proposed that this increase in heating rate was caused by the changes in vessel geometry allowing a better match with the microwave generator, giving increased power transfer. This would lead to

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an increase in the heating efficiency of the system. To quantify this, a simple energy balance was conducted. Theoretically to heat 30 and 50 cm³ monomer from 20 – 100 °C requires, 6.01 and 10.01 kJ respectively. In practice the CEM used 84 kJ for 30 cm³ and 11 kJ for 50 cm³ during these experiments. From this efficiency of energy transfer can be calculated, giving 7 % energy transfer for 30 cm³and 92 % for 50 cm³. Thus supporting the conclusion that the change in geometry has changed the mode pattern within the microwave cavity, increasing energy transfer to the sample.

5.3.4.2 Comparison of 30 and 50 cm³ microwave polymerisation

The implication of this increased heating rate is that direct comparison with conventional heating was not possible, conventional heating took 5 min to reach the temperature set point. This is not however a problem, as this 50 cm³ reaction can be compared with the 30 cm³ microwave reaction which in turn can be compared to the conventionally heated.

50 cm³ reactions were prepared *via* method 4 in the experimental Section. Reaction vessels were placed within the CEM cavity and heated to the required temperature and then stirred for 5 min before sampling. This data is shown in Figure 5-13.
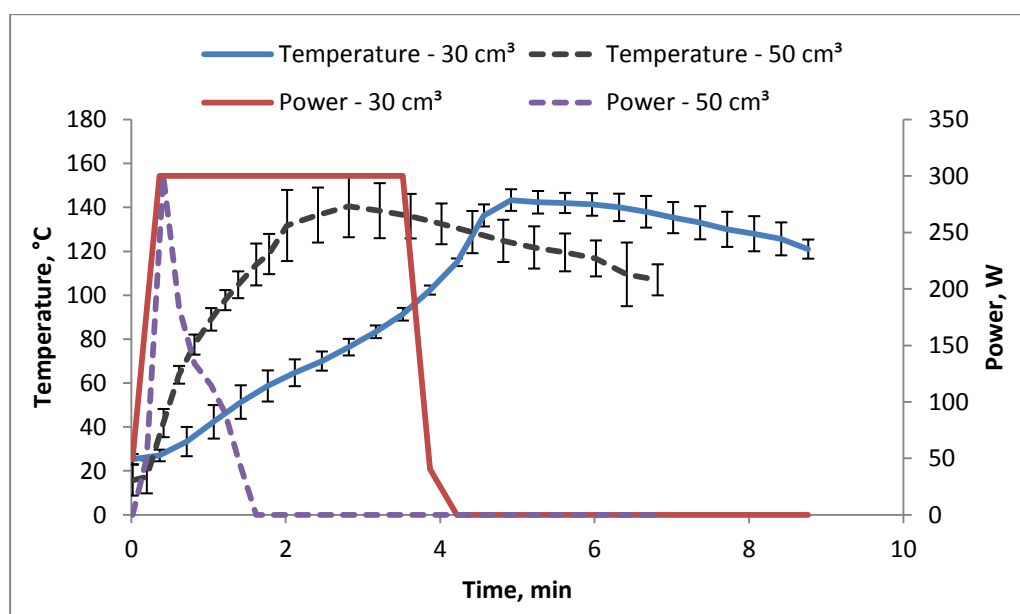
Figure 5-13: Temperature profile and power traces for 30 and 50 cm³ reactions carried out at 100 °C in CEM.

Comparing reaction temperature profiles between 30 and 50 cm³ experiments in Figure 5-13, the main difference between the two was in the heat up phase, i.e. from ambient to 100 °C. Once this set point is reached the exotherms are very similar, with both reactions achieving a peak temperature of 140 °C.

There was a slight variation in conversion between the two systems, 65±3 and 71±2 for 30 and 50 cm³ respectively. This increased conversion was not witnessed with the conventionally heated reaction.

5.3.5 Microwave polymerisation with heat removal

When designing reaction systems/process, the inherent safety of the design is of highest importance. In order for a process to be used industrially it must be producible in a safe, controlled manner. This aim of this was to show that scale up of CCT polymerisation from batch to flow systems was possible. Therefore, it was important, even at these early stages, to ensure that the reaction could be controlled.

The CEM has the capacity to cool the sample by passing compressed air through cavity at ambient temperature. This provides low levels of cooling, as heat exchange is gas based rather than utilising a specific heat transfer liquid or heat exchanger.

50 cm³ reactions were prepared *via* method 4 as defined in the experimental Chapter. Reaction vessels were placed within the CEM cavity and heated to the required temperature, samples were stirred throughout the experiment to ensure homogenous. Once the set point was reached, no further energy was input and cooling of the reaction was commenced by passing compressed air through the microwave cavity at 18 °C and continued for five minutes. Reaction was then sampled for analysis.

Results of carrying out microwave polymerisation with simultaneous heat removal

Figure 5-14 shows temperature profiles for the two reaction methods, cooled and uncooled, 12 % and 65 % conversion achieved respectively. The uncooled reaction data has been presented previously in Section 5.3.4.2.
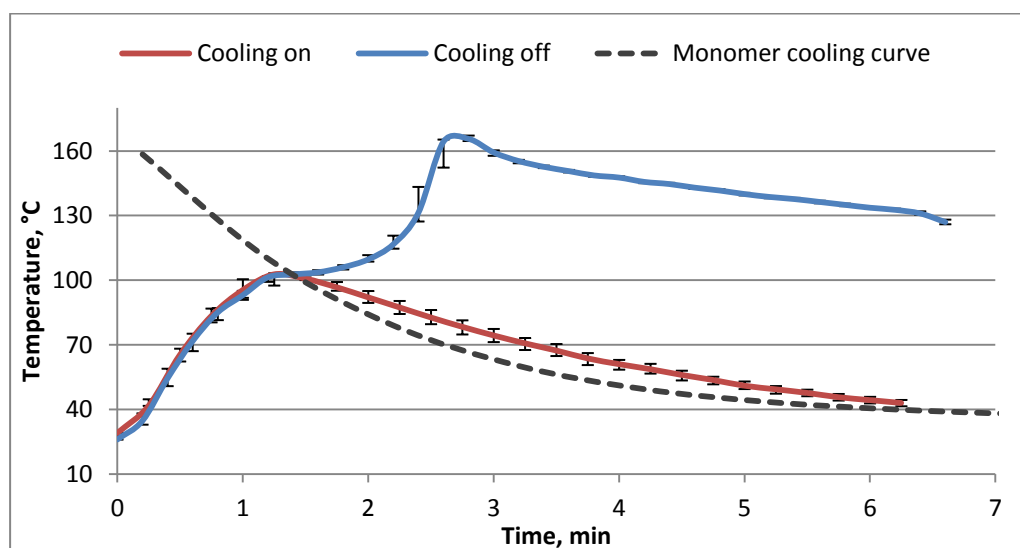
Figure 5-14: Temperature profiles for polymerisation carried out in the CEM with and without cooling activated

The curve for the experiment which heated pure monomer then applied cooling has been overlaid onto the top of that with the reaction occurring. The data showed that the behaviour between the two mixtures was similar, with the only noticeable difference being a slightly lower rate of cooling in the reacting system. This was expected due to the fact that heat evolution in this system is related to the exothermic nature of polymerisation reaction. Additionally, there will be an increase in the reaction medium viscosity, only in the polymerisation case (related to molecular weight increase) which will reduce the efficiency of heat transfer from the system.

The key conclusion from this data was that, when cooling gas was applied, there was no increase in overall system temperature. The application of compressed air cooling prevented the temperature increase observed when active cooling was not conducted. Thus demonstrating that the reaction was

controllable at this scale. This does not imply that this reaction is safe to carry out in large scale with this type of cooling system.

5.3.6 Isothermal microwave polymerisation

Up to this point in the study, the CCT reactions of MMA have been carried out by utilising the reaction exotherm to increase the rate and allow rapid product formation. Cooling had only been used to demonstrate that the reaction can be controlled. Microwave heating offers the option of conducting reactions using practical strategies that cannot be achieved using conventional heating. For example, the reaction mixture can be volumetrically heated whilst the walls of the reactor are being simultaneously cooled. The advantage of this such a strategy is that microwave volumetric energy input may increase the localised molecular energy of specific reactive species within the process medium and so potentially achieve a set rate of reaction at a lower bulk temperature. In doing so, particularly for reactions that are prone to self-acceleration, such as polymerisation, the inherent safety of the process would be increased.

Method for isothermal microwave heated polymerisation
30 cm³ reactions were prepared *via* method 1 as described in the experimental Section. Reaction vessels were placed within the CEM cavity and heated to the required temperature. Once the set point was achieved compressed air cooling was activated, this was kept constant for the duration of the experiment. Power levels were automatically adjusted to maintain the reaction isothermal at 100 °C.

Results for isothermal microwave heated polymerisation
Figure 5-15 below, shows the temperature and power profiles for a typical reaction conducted by this method.
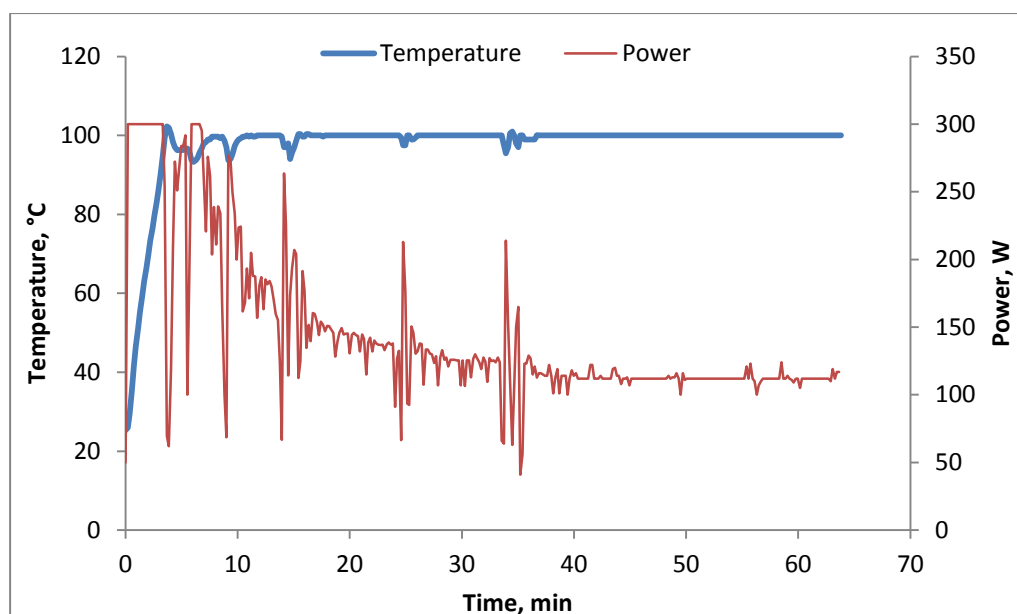
Figure 5-15: Temperature profile and forward power for 30 cm³ isothermal, 1 hour reaction carried out at 100 °C in CEM.

In the first five minutes full power (300 W) was used to heat the reaction to the 100 °C set point and once this was achieved cooling was activated. Initially the temperature was not maintained at the set point, it was proposed that this was due to energy transfer by the cooling exceeding the energy transferred by the microwave. After two minutes the temperature once again reaches the set point, this was caused by formation of products *via* the exothermic reaction. Additionally, dielectric property assessment of the products has shown that, low molecular weight MMA oligomers are able to absorb electromagnetic energy at a greater level than monomer, due to increased dielectric loss (data shown in Appendix 9.3), heat of reaction also contributed energy. Throughout the experiment there are small, spiked reductions in temperature, these were caused by sampling. In order to sample the mixture microwave power was shut off to ensure safety. This was also the source of the large spikes in forward power, as the CEM returned the mixture to its set point. Figure 5-16 shows that as conversion to product increased the levels of forward power reduced, this was due to higher energy absorption and reduced reflected power.
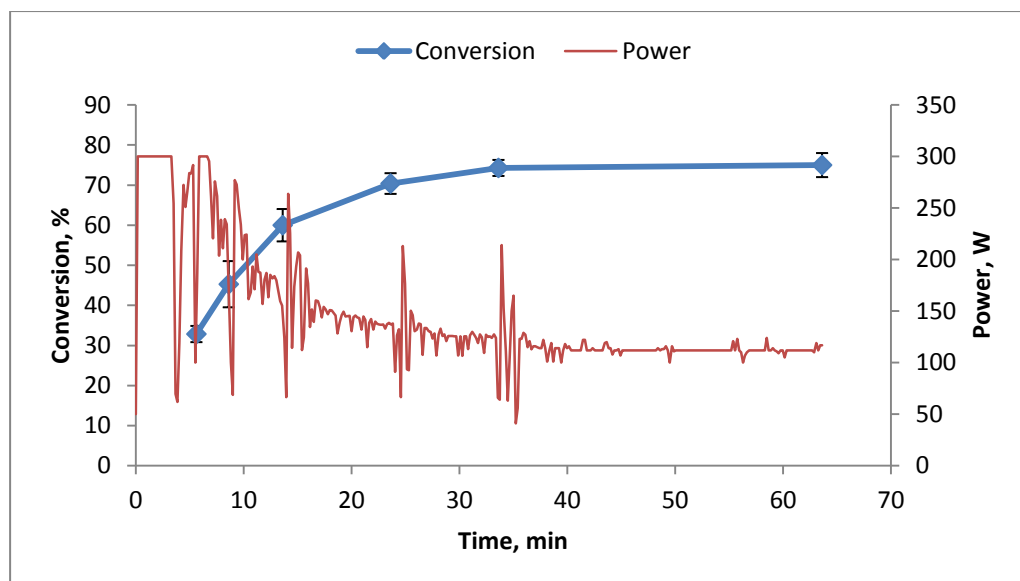
Figure 5-16: Forward power and conversion, conversion was mesuared using NMR analysis, for 30 cm³ isothermal 1 hour reaction carried out at 100 °C in CEM.

This shows that the reduced power requirement was not caused by heat generation from within the reaction, but by increased capacity to absorb electromagnetic radiation. Conversion reached steady state of 74 % after 30 min, where the conversion was limited due to the presence of the CCT catalyst, as has been discussed previously. By comparison with the reactions with uncontrolled temperature there was an observed increase in conversion, i.e. 73 % up from 65 %. This was likely caused by the more controlled way in which radicals were produced, reducing radical-radical termination and increasing the level of monomer initiation.

Analysis of products formed by NMR showed that at all three temperatures MMA_2/MMA_3/MMA_4 was formed in a 4:2:1 ratio with <1% higher molecular weights. Additionally, GPC analysis showed that no high molecular weight material was formed.

This kind of system with heating against cooling was simple to carry out at this scale but would be challenging in a larger scale environment. In order to retain efficiency, heat transfer liquids would be required. There is the added complication of using microwave transparent solvents such as hexane or

toluene. These are highly flammable and present a hazard if arcing were to occur.

The rate at which products were produced is lower in this reaction than in reactions with an uncontrolled exotherm, this is expected as the lower temperature reduces rate of propagation. There was a slight increase in conversion (8 %), this was due to the higher levels of control in the reaction and the reduced rate of radical formation per unit time, leading to less radical terminator (or initiator burn out). Additionally, it was noted that to realise this slight increase in conversion significantly higher levels of energy and more complicated system design would be required.

5.3.7 Microwave polymerisation with reduced catalyst concentration

The aim of this project was to produce a flow system which can produce MMA_2/MMA_3. These very low molecular weights have been chosen as there is currently no commercially viable process for their production. Their material properties also present several benefits when designing a new flow system. There is only a small change in viscosity, 0.5 cP MMA to 250 cP MMA_3 at 20 °C, where 250 cP equates to a viscosity similar to that of motor oil. This allows for simplification of design and removes extra complications such as fouling and blocking.

From work carried out by (Adlington, Jones et al. 2013), it has been shown that MMA_2/MMA_3 can be produced in bulk phase using 600 ppm PhCoBF as the CCT catalyst. They also carried out work at different catalyst levels to determine the effectiveness of the catalyst at different concentrations. This data was determined at lower operating temperatures than are to be used in this system. Therefore, tests were carried out to find out whether lower catalyst loadings could be used to produce the same products within a higher temperature flow process. Catalyst concentrations were reduced by 50 and 90 %, to give concentrations of 300 and 60 ppm respectively. This limited range of variables was used as the purpose of the study was to give an assessment of the effects and not fully investigate them.

Results and discussion of the effect of reduced catalyst concentration

30 cm³ reactions were prepared *via* method 1, 2, 3; in the experimental Section depending on catalyst concentration required in the experiment. Reaction vessels were placed within the CEM cavity and heated to the required temperature. The reaction was then continually stirred before sampling at 5, and 20 min intervals, all samples were quenched prior to sampling.

It was expected that as catalyst concentration was reduced, conversion and molecular weight would increase because the presence of the CCT agent is known to retard the reaction rate. This is because as the catalyst: monomer ratio increased, chain transfer increased. This results in increased instances of monomer being terminated by the catalyst, before it comes into contact with monomer, effectively stopping propagation. The data in Table 5-5 confirms this proposal.

Table 5-5: Conversion against time at different catalyst concentrations; carried out at 100 °C in CEM.

Catalyst loading, ppm	% Conversion	
	5 min	20 min
60	73±8	81±7
300	67±3	67±6
600	65±2	65±2

At 60 ppm a conversion of 81 % was achieved while at 600 ppm a maximum of 65 % was observed. However, the data in Figure 5-17 shows the trend in the reaction temeprature with catalyst concentration was different from that expected. It was expected that as catalyst levels were reduced the rate of reaction would increase, due to reduced control, and that there would be a larger temperature rise.
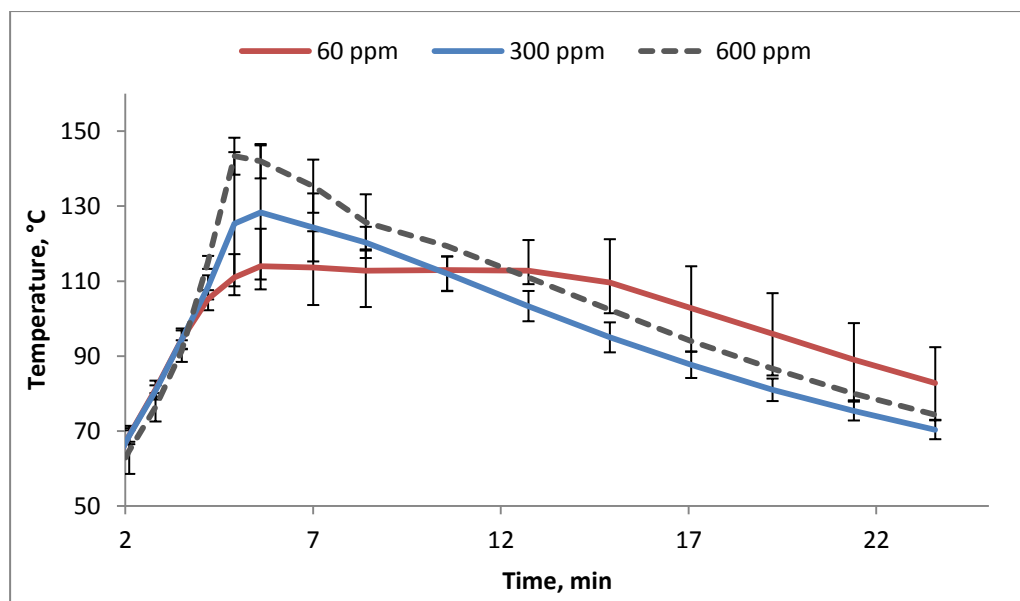
Figure 5-17: Temperature profile for 30 cm³ reactions containing different catalyst concentrations, carried out at 100 °C in CEM.

However, it was observed that at 600 ppm there was a large exotherm resulting in a sharp peak. Due to the high operating temperatures (>100 °C), it was concluded that very high rates of initiator decomposistion gave higher radical concentration. At low catalyst concentration, due to increased viscosity, this lead to radical-radical termination giving a reduced rate of reaction, hence the reduced reaction exotherm. This is a highly inefficienct reaction as it leads to wastage of initiator. Addition of high levels of catalyst, >300 ppm, reduces radical-radical termination by reducing viscosity and promoting propagation.

Furthermore, GPC analysis shows that the molecular weights produced were consistent throughout the experiment, indicating that the catalyst remained efficient throughout the reaction (see Table 5-6).

Table 5-6: Degree of polymerisation and poly dispersity (PDI) of products produced with reduced catalyst concentration under microwav eheating at 100 °C minimum temperature set point. D_p quoted when average molecular weight was higher than 300(MMA$_3$/Trimer)

	5 min	20 min
60 ppm	D_p=11, PDI=1.5	D_p=11, PDI=1.5
300 ppm	D_p=4, PDI=1.5	D_p=4, PDI=1.75
600 ppm	MMA$_2$/MMA$_3$	MMA$_2$/MMA$_3$

Figure 5-18 below shows the same data as above with increased resolution, also included is the temperature profile for a reaction carried out with 0 ppm catalyst present.
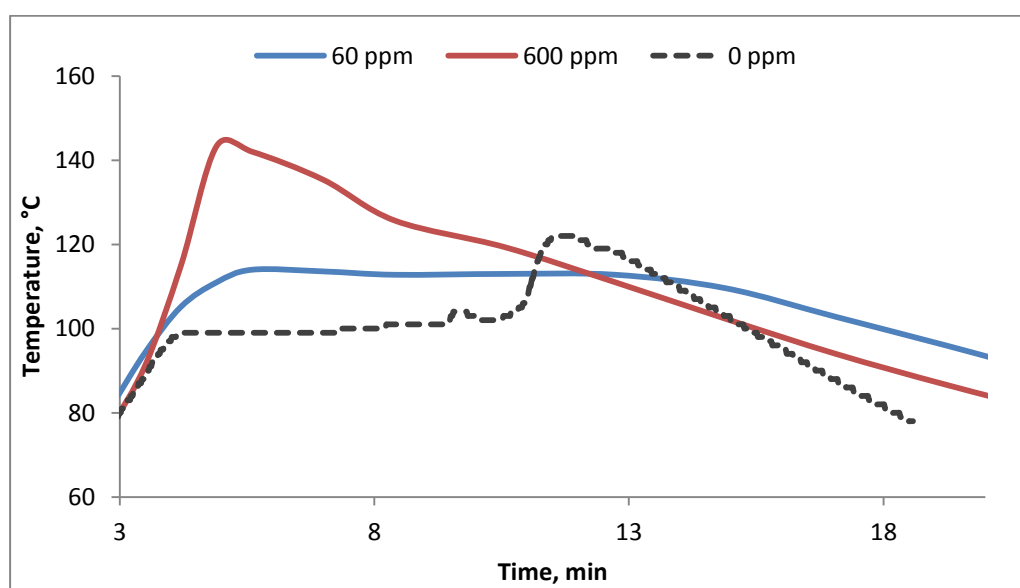
Figure 5-18: Temperature profile for 30 cm³ reactions containing different catalyst concentrations, carried out at 100 °C in CEM.

This reaction was carried out to confirm that the catalyst presence caused the large reaction exotherm. After the initial heating section there was 4 min of the reaction maintaining its temperature. At 10 min there was a slight temperature spike, this was caused by the reaction foaming, producing the solid mass shown in Figure 5-19, this phase change was completed before the large temperature spike occurring at 11 min. Foaming is caused by the monomer and low molecular weight material in system boiling, whilst the

higher molecular weight material forms the solid phase of the polymeric foam. This shows that temperature measurement alone is not a suitable measure for evidence of the reaction undergoing auto acceleration. As there was no significant change in viscosity in the CCT reactions, it is concluded that the reaction is undergoing a large exotherm or a selective heating induced temperature rise and not undergoing a Trommsdorff-Norrish effect.

Figure 5-19: Polymer foam formed when carrying out 30 cm³ non-CCT controlled MMA polymerisation within CEM Discover at 100 °C

This has shown that the presence of CCT catalyst has three effects upon the reaction: limiting overall conversion, increasing rate of reaction by reducing viscosity and molecular weight from the order of hundred s of thousands to a few thousand.

5.3.8 Re-initiation to investigate the effect of CCT catalyst on overall conversion

It is noted that in previously presented batch experimentation that conversion did not exceed 65-70 % . It is hypothesised that this was caused by the presence of the CCT catalyst. As conversion increased, monomer concentration dropped and subsequently the PhCoBF concentration increased. This increase is believed to be effectively stopping the reaction, due to the rate of chain transfer being significantly higher than propagation.

5.3.8.1 Effect of re-initiation on the overall conversion within an already reacted batch polymerisation

A second hypothesis for limited conversion was proposed: the reaction temperature was too high and caused initiator burn-out. All initiator decomposes in milliseconds and forms radical-radical by-products, rather than carrying out an initiation step. This is caused by the levels of decomposition being higher than the rate of diffusion within the system.

In order to determine which of these effect was responsible for the conversion cap, 30 cm³ reactions containing 600 ppm CCT catalyst and 1 w/w% AIBN were heated to 100 °C, the mixture was then stirred for 5 min before quenching. Reactions were carried out using both the CEM and oil bath in four different combinations, these combinations are shown below. These four experimental permutations were carried out to determine any variation between conventional and microwave heating.

At the end of the primary reaction a 5 cm³ sample was removed and analysed by NMR to determine conversion (65 %). Reaction was then re-initiated by the injection of 5 cm³ monomer containing 600 ppm CCT catalyst and 0.129 g AIBN. All material was maintained oxygen free to prevent catalyst deactivation. The mass of AIBN added, was determined as the number of moles required to give the same 1 w/w% monomer/initiator concentration as in the first reaction. Concentration was calculated as follows:

$$Monomer\ volume = (1 - 0.650)\,25 + 5 = 13.750 cm^3$$

$$Monomer\ mass = (0.940)\,13.750 = 12.925 g$$

$$AIBN\ mass = \frac{12.925}{100} = 0.129\,g$$

Reaction mixture was then placed within the CEM and stirred for 60 s to ensure homogenous; it was then heated to 100 °C and stirred for 5 min before sampling.

Batch re-initiation results and discussion

As can be seen in Table 5-7 below, the conversions achieved in all reactions was similar which was further indication of no differentiated microwave effect upon these reactions.

Table 5-7: Conversion data for 30 cm³ re-initiation reactions carried out using AIBN.

Heating method			First reaction	Second reaction
Microwave	→	Conventional	66±1	60±1
Conventional	→	Conventional	69±0	59±0
Microwave	→	Microwave	67±1	64±1
Conventional	→	Microwave	65±2	63±1

After the first reaction the conversion was 66 %, with a slight drop to 62 % after re-initiation. The data from the first reactions was the same as that previously described in earlier Sections. When investigating the second reactions there was a clear drop in conversion, injection of 5 cm³ monomer reduces the overall conversion to 50 %.It was expected that after re-initiation the conversion would increase to above the level produced in the first reaction. This was however not the case, a 5% overall reduction occurred. When comparing reaction, exotherms shown in Figure 5-20 it is shown that once the set point was achieved the there was a much smaller exotherm occurring in the re-initiated reaction.
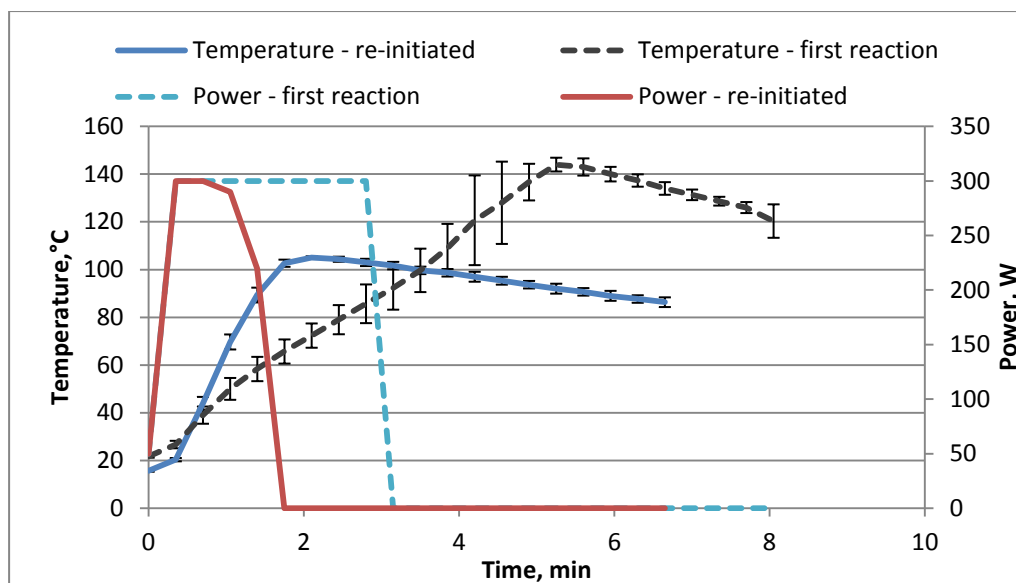
Figure 5-20: Temperature and power profile for 30 cm³ reaction at 100 °C, including profile for the same material re-initiated using AIBN.

This could be caused by several factors, including: increased viscosity reducing diffusion and limiting the rate of reaction; reduced monomer concentration due to oligomer presence; consequently reducing the rate of propagation due to the very high catalyst concentrations (1450 ppm) within the mixture. GPC analysis of products from all the reactions shows no variation, all reactions produced dimer/trimer/tetramer.

It should be noted that there was a significant increase in heating rate, when using microwave heating, between the first and second reaction. The increased rate was caused by the presence of MMA oligomers, which are more effective absorbers of microwave energy than monomer (Robinson, Kingman et al. 2010).

This data indicated that the conversion was being limited by the catalyst concentration and that initiator burn-out was not a factor in the limitations. To further validate this conclusion, a series of experiments were conducted where, rather than re-initiation by addition of 5 cm³ monomer containing 600 ppm catalyst. The reaction mixture was halved and 15 cm³ monomer containing 0.19 g AIBN injected. This has the effect of reducing the catalyst concentration from 1100 ppm in the above reaction to 450 ppm.

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After re-initiation with 15 cm³ monomer solution, the oligomer concentration is 33 %, compared to 50 % with addition of 5 cm³. After the secondary reaction the conversion was found to be 74±1 %, this is a 10 % point increase on that achieved in the initial set of reactions. Again there was no difference in the molecular structure of the products produced; this provides further evidence of the catalyst limiting the reaction.

5.3.8.2 Effect of re-initiation with an oxygen centred radical

In order to test whether the catalyst was the limiting factor and not viscosity and/or initiator-initiator termination, a different initiator was used for the re-initiation. Rather than AIBN which is a carbon centred radical, benzoyl peroxide was chosen, and the same molar ratio of both initiators was used. Oxygen centred radicals, are known to disrupt the catalytic cycle of the CCT agent being used, so rendering the catalyst inert. It use should therefore allow further reaction and increased molecular weight formation.

30 cm³ MMA, 600 ppm catalyst, 1 w/w % were heated within the CEM to 100 °C and stirred for 5 min prior to samples being taken, samples were quenched prior to analysis.

5 cm³ reaction mixture was removed and the remaining 25 cm³ was re-initiated with 5 cm³ monomer, 600 ppm catalyst, 0.0113 g benzoyl peroxide. Throughout all steps of the reaction it was ensured that the reaction mixture remained oxygen free, to ensure that the deactivation was caused by the initiator and not contamination.

Required benzoyl peroxide concentration was calculated as follows:

$$Monomer\,volume = (1 - 0.65)\,25 + 5 = 13.75\,cm^3$$

$$Monomer\,mass = (0.94)\,13.75 = 12.925\,g$$

$$AIBN\,mass = \frac{12.925}{100} = 0.129\,g$$

Where M_w AIBN and benzoyl peroxide are: 164.21 and 242.23 g/mol respectively (Sigma-Aldrich 2013).

$$Benzoyl\ peroxide\ mass = 0.129 \times \frac{242.23}{164.21} = 0.190g$$

Reaction mixture was heated to 110 °C for re-initiation, this temperature was used in order to give the same 0.1 hour initiator half-life.

Results for BPO re-initiation
From inspection of Figure 5-21 below, it was clear that there was a reaction occurring after re-initiation in this experiment.
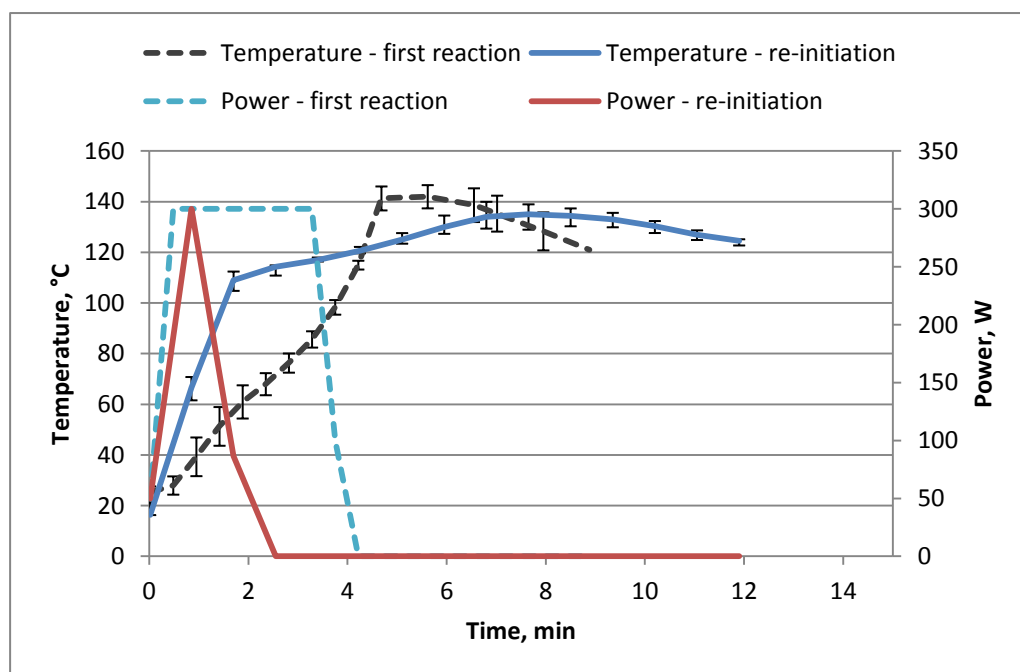
Figure 5-21: Temperature and power profile for 30 cm³ reaction at 100 °C, including profile for the same material re-initiated using benzoyl peroxide.

There was a significant reaction exotherm resulting in a maximum temperature of 135 °C, this exotherm was however much flatter than in the first reaction. It is proposed that this was caused by a reduced rate of reaction related to increased viscosity and reduced monomer concentration, both of which reduced the rate of propagation. The conversion achieved was increased from 63 % in the first pass reaction to 93 % after the second. Determination of molecular weight showed that after the first reaction

MMA$_2$/MMA$_3$ is formed; after re-initiation the composition is 60 % D$_p$ 26 with PDI of 1.5. The remainder of the mixture consisting of MMA$_2$-MMA$_4$. This elevated molecular weight was due to the oxygen centred radical poisoning the catalyst, allowing for formation of higher molecular weights. The nature of the polymer present indicates that there was still CCT catalyst present and chain transfer was occurring. It was not possible to rigorously determine the extent to which the catalyst was poisoned.

5.4 Single mode microwave batch processing

When scaling up a process it is important to have information about all aspects of the process. The most important and fundamental being the mass and energy balances. In a sealed batch system the mass balance is simple as the entire initial mass remains with varied composition. However, the energy balance is also very important, because energy efficiency must be maximised in order to make the process as sustainable and economically viable as possible.

When attempting to carry out energy balances using the CEM it is clear that this apparatus is unsuitable, it has been designed as an 'off the shelf, plug and play piece of equipment, that could be used by those without access to more complex apparatus or the knowledge regarding microwaves equipment.

While the equipment can operate with precise temperature control, when using optical fibre, it does not give adequate measurement of energy. The system does not have any active forms of tuning, the only method for tuning is *via* the geometry of the vessels used; as shown in Section 5.3.4.1. Precise measurement of forward power is provided by the equipment, it however does not measure reflected power. This can be calculated by carrying out a theoretical energy balance based upon energy required to give a specific temperature rise within the material vs. experimentally measured temperature rise.

In order to scale up this system it was important to carry out experiments in which the energy transfer can be maximised and in which incident and reflected power were monitored to calculate absorbed power. The apparatus used differs significantly from the CEM used previously. Microwave energy was produced using 2 kW magnetron operating at 2450 MHz, with minimum operating power of 200 W. The cavity used was single-mode cavity, tuning was given by manual sliding short and automated 3-stub tuner. All equipment was connected using waveguides.

This type of cavity allows for very high power densities, giving potential for very high heating rates to be achieved within the sample. More information on this is provided in Chapter 2. The addition of automatic tuning, provided by the 3-stub tuning device, with incorporated power monitoring, allowed for maximised energy transfer.

This system however does have limitations; this generator did not have the capacity to receive feedback to allow for automated temperature control. In order to achieve a specific set point temperature, manual cycling of the forward power was used, this was less precise than automated control, acceptable levels of control (±5 °C) were achieved via this method.

Using a generator with increased power output it was possible to investigate the effects of power density upon the system, changing the power density within the material can be used to vary the heating rate. Higher power gives a higher heating rate. This can be used to highlight any potential "selective heating" effects within the material, by rapidly heating a multi-component material it can be possible to preferentially heat certain components based upon their dielectric properties. By increasing the heating rate, the temperature differential between specific components and the bulk temperature could be increased, potentially leading to a benefit over conventionally heated systems.

Results and discussion for high power batch polymerisation

30 cm³ and 50 cm³ reactions were prepared *via* method 1 and 4 in the experimental Section. Reaction vessel was placed within the cavity and heated to the required temperature and then stirred for 5 min. Reactions were exposed to constant energy at different power levels, 330, 500, 1000 and 2000 W.

To highlight the differences between heating with a more specific, optimised system and the CEM heating profiles were produced. The automated tuning device was used, and set such that it had a power threshold for activation of 300 W to ensure that it operated continuously. In practice the power was increased by 10 % to 330 W, this still allows comparison with the CEM whilst it ensured stable operation.

To allow simple comparisons of absorbed power (W) at different incident power levels, it is converted to an absorption coefficient, defined as:

$$Absorption\ coefficient = \frac{Absorbed\ power}{Incident\ power}$$

Figure 5-22 below shows the temperature curves for the heating of monomer from 20 °C to 100 °C in the new system, it is shown that 330 W heating occurred at a much higher rate than in the CEM, as it took 300 s, compared to 50 s in single mode to reach the 100 °C set point temperature.
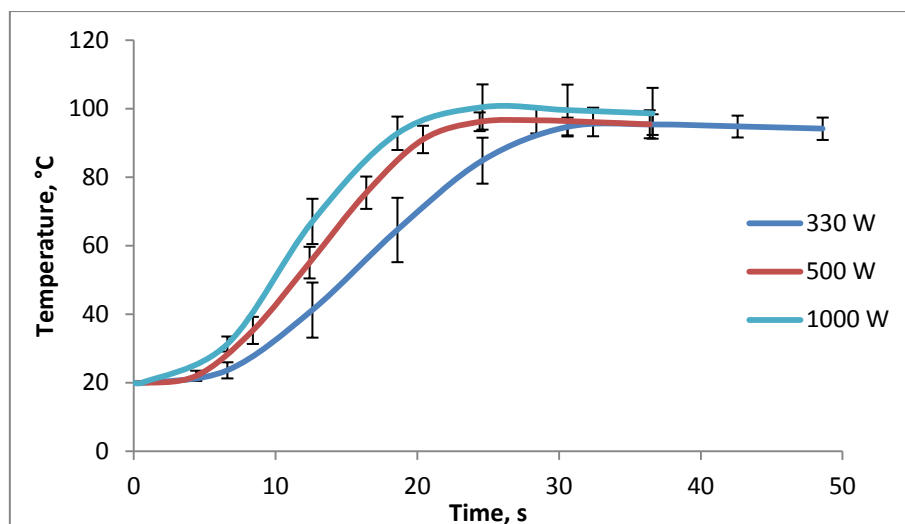
Figure 5-22: Temperature profile for heating of 30 cm³ monomer in single-mode microwave cavity at different power levels
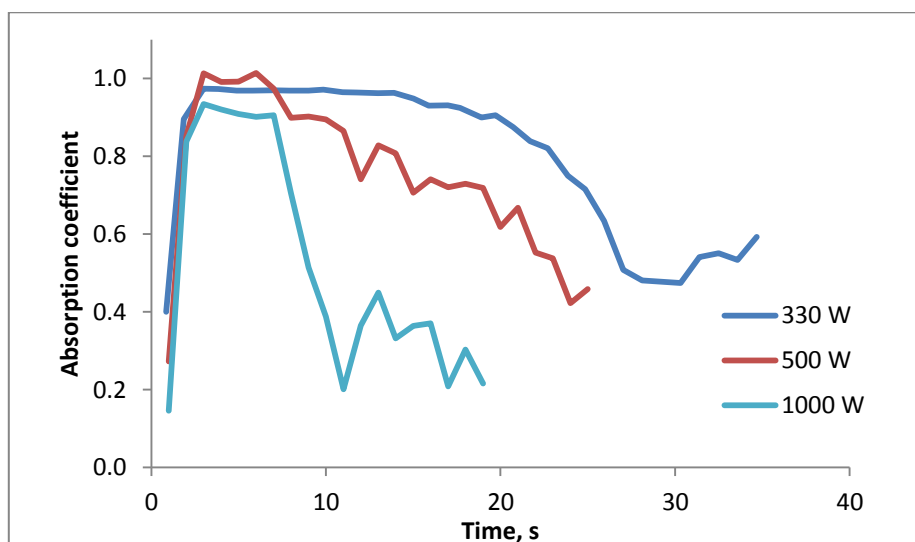
Figure 5-23: Energy absorption coefficients for heating 30 cm³ monomer in single-mode, microwave cavity at different power levels

Some of this increased rate can be attributed to the slightly elevated power levels. Looking at the energy absorption in Figure 5-23 shows that between 20-50 °C more than 95% of energy was absorbed. Past this point, energy transfer reduced, falling as low as 50 % as the sample reached 100 °C. This drop in energy transfer could be caused by the ability of the material to absorb microwave energy dropping as the temperature increased. As shown in Appendix 9.3, as temperature increases the constant and loss of monomer both decrease, confirming this fact. Vapour formation could also be a factor, as the liquid is heated bubbles formed, increasing the void fraction, this

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increased the volume of material present forcing a portion of the liquid out of the area of high electric field within the cavity. The higher power level was observed to increase the heating rate. However, this link was not a linear relationship as expected. As the power level was increased the percentage of energy absorbed reduced, this was attributed to the limitations in the cavity design and the mass of material in the cavity. A given mass of material under fixed conditions can only absorb a finite amount of power, once this point is reached the remaining power is wasted and returned to the generator as reflected power. This is highlighted when looking at Figure 1-28
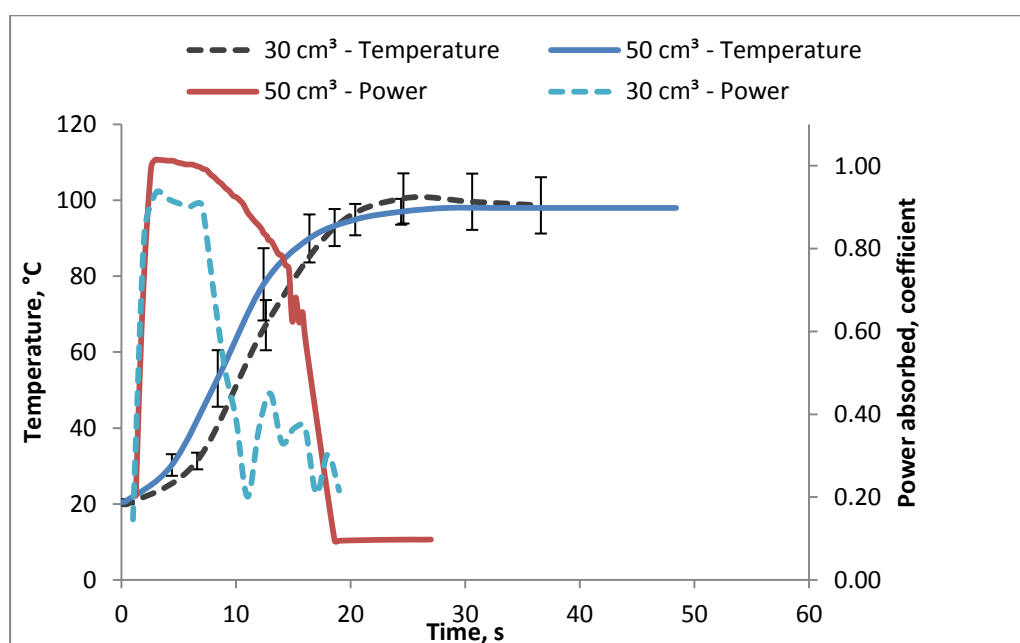
Figure 5-24: Shows the differences in temperature and power absorption traces for heating of 30 and 50 cm³ monomer at 1000 W incident power in single mode microwave.

This data demonstrated that by increasing the mass of material present in the cavity, energy transfer efficiency was increased. This resulted in comparable heating times being achieved for both the 30 and 50 cm³ monomer samples, at the same power level. Had energy balances not been carried out this could be overlooked. If this process were to be scaled up based solely on the energy information gathered using the CEM, it could lead to a design being produced which gave an energy requirement of 83 kJ/g, when calculated as a

temperature rise this gives 1100 °C. This could potentially lead to catastrophic failure of components.

It should be noted that both heating time and power are variables within this experiment, to decouple these it would requires the use of various sized samples or the application of simultaneous cooling whilst heating would be required. Using this system this was not possible, as the cavity had fixed dimensions and would not allow for increased sample size above the current 50 cm³.

There are several ways in which cooling could be applied to a microwave system. These include passing gas through cavity where helium is regarded as being the most appropriate choice due to its high thermal conductivity. Equipment could be designed to allow for the flow of microwave transparent liquids, such as hexane, over the surface of the reactor vessel to remove heat. However, hexane is highly flammable and could present a risk if arcing were to occur. Dry ice is another option; this can be placed relatively easily within a waveguide to give cooling. However, it has low thermal conductivity and gives a large volume change upon vaporisation. With this in mind a change in heating time is going to remain a variable within this set of experiments, as it is not straightforward to decouple using this experimental apparatus. Figure 5-25 contains the temperature profiles for reactions conducted using the single-mode apparatus at four different power levels.
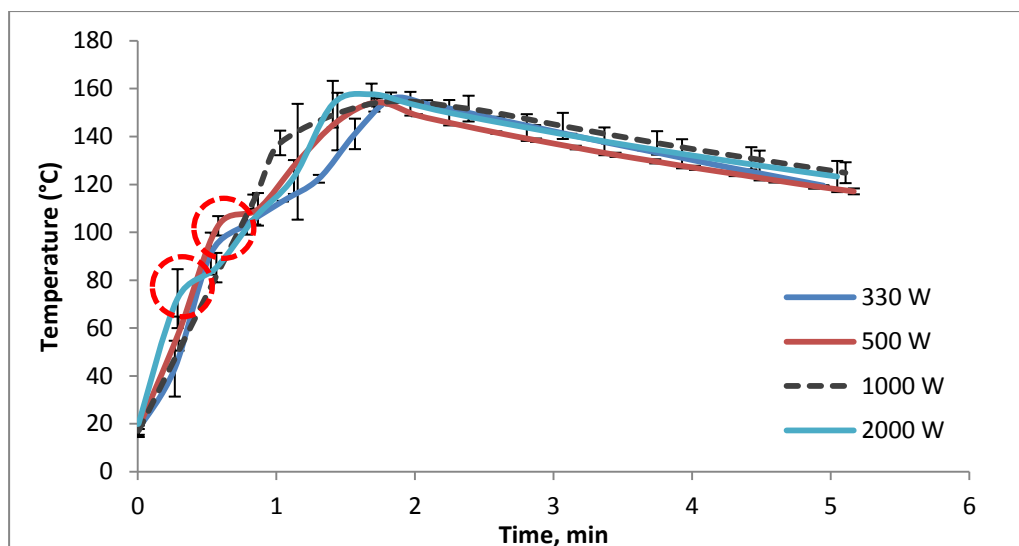
Figure 5-25: Temperature profiles for 50 cm³ reactions carried using single mode microwave as energy source, at four different power levels. Red circles indicate systematic errors caused by manual temperature control.

As shown, they are all similar where the initial heating times of the reactions vary by approximately 20 s. This was the expected result, as it had been concluded from the monomer heating trials that excess power was reflected and not absorbed by the sample. Within the initial heating section, inflection points were also highlighted. It was proposed that these were caused by the cycling of forward power to reach the temperature set point (100 °C). The reaction exotherms present were also noted to be of the same magnitude as those seen previously in both conventionally and CEM heated experiments. This indicates that similar reaction pathways and rates were occurring in these reactions, and resulted in comparable levels of conversion.

Table 5-8 below shows conversion data for the reactions carried out, it can be seen that there was no significant change in conversion with respect to volume or microwave power used.

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Table 5-8: % Conversion data for single mode microwave polymerisation carried out at different volumes and power levels, constant set point temperature of 100 °C used.

Power, W	Volume used	
	30 cm³	50 cm³
330	58±7	62±6
500	61±5	62±2
1000	65±3	62±2
2000	-	66±8

Analysis by NMR shows all reactions formed MMA_2/MMA_3/MMA_4 in a 4:2:1 ratio, with <3 % higher molecular weight formed, GPC showed no material >600. Low power (330 W) experiments were carried out to give a direct comparison with the CEM and oil bath experiments, whilst the higher power experiments were used to determine the effects of heating rate and the capacity of the sample to absorb microwave energy.

30 cm³ 2000 W reactions were also conducted, but it was found that the sample used was too small to give repeatable results, due to high levels of energy reflected. Comparing data with the CEM it is clearly seen that this system gave much higher energy transfer at 30 cm³, 71 % compared to 7 % when using the CEM. At 50 cm³, energy transfer is comparable between the CEM and single mode, giving 95 % efficiency.

Thus it was concluded that increasing the power level had no quantifiable effect on the conversion, reaction exotherm or products produced. This gives more evidence that the reaction is temperature driven, and is not benefiting from selective heating effects offered by the microwave. This indicates that the reaction could be scaled up into flow with increased power levels; these increased power levels are required to give higher throughput at constant energy per gram, without affecting the products formed.

From this data it can be concluded that, in order to maximise energy transfer, a large sample is required within the microwave cavity. The reaction is

temperature driven, and that higher power levels and heating rates are only required such that the flow rate can be scaled up.

5.5   Summary of microwave batch polymerisation data

The aim of this section of work was to gain a better understanding of how the polymerisation occurred, and under what conditions the reaction was most suited to scale up and utilisation of flow. Therefore, throughout the work direct comparisons were been made between conventional and microwave heated experiments.

Initial experiments using different temperature measurement techniques within the microwave showed that, if this was not accurately monitored incorrect conclusions regarding efficiency and conversion could be drawn. This was largely due to a lack of control over the energy input and/or direct internal temperature assessment. Once the control strategies had been defined, it was observed that throughout the work there were no quantifiable differences between the conventionally and microwave heated reactions. The only variation found was variation in the heat up times of the reactions. This is caused purely by the physical geometry of the vessels and the nature in which the two mechanisms transfer energy.

It is concluded that using this specific chemistry that there was no 'microwave effect' which has been suggested by many researchers, rather improvements seen by these researchers was by the poor application of energy and monitoring of temperature within the reaction.

The use of two different microwave systems, CEM Discover SP and a single mode resonant cavity, gave interesting insight into the nature of the reaction and how the use of microwave energy can be utilised for scale up. The CEM is a low power density cavity with a low heating rate, where the single-mode can give high heating rates. It was found that this had no effect upon the reaction.

5.6 Summary and conclusions for batch polymer processing

It has been shown that it is possible to carry out CCT reactions to high conversion in less than 60 s by operating outside of the moderate operating conditions used industrially, or in many research applications. Increasing the pressure under which the reaction was carried out allowed for the achievement of higher temperatures, which coupled with high catalyst loading (600 ppm), allowed for high rates of reaction to be achieved.

Investigation of catalyst concentration showed that this high loading was required to handle the high levels of radicals present and manage the viscosity, at the increased operating temperature. The maximum possible conversion was restricted by the presence of the CCT catalyst. As conversion increased monomer concentration drops, giving an increase in the catalyst/monomer ratio. A point was reached at which the rate of chain transfer became sufficiently high that initiated monomer was terminated before propagation occurred. This was proved by re-initiation with an oxygen centred initiator which is known to inhibit the catalytic cycle.

5.7 Considerations for scale up and design of a flow system

From the understanding given from this work there are clear and important lessons to be taken forward in the design of a flow system. The use of a slotted waveguide, such as that in the CEM is unsuitable, there is no application for tuning or the scope for increased throughput due to the geometry of the cavity; a single-mode cavity is more suitable as it allowed for high power use, up to 30 kW at 2.45 GHz; very high power density, giving high energy dissipation; large bore tubes can be passed through the cavity in order to maximise material volume and improve energy transfer. Accurate temperature control is required, the reaction is highly temperature sensitive and slight variations have a significant effect upon conversion. Heat of reaction was found to give significant increases in temperature of the reaction; this in turn gives increased pressure. It is required that any system

designed is able to handle these pressures and maintain the reaction in a single liquid phase to ensure stability of flow and energy transfer.

6 High flow rate continuous flow polymerisation of low molecular weight oligomers

There are several limitations regarding the use of large scale batch systems on industrial scale. These limitations are derived from the physical geometries (large diameter vessels), and the physical and chemical properties of the reactants used. These limitations often require that reactions be carried out under moderate temperatures (<80°C), to reduce the rate of reaction and maintain control to ensure safe operation. A strategy by which these limitations can be overcome, in a safe manner, is to carry out these reactions under more extreme conditions with the adoption of a continuous flow system.

This Chapter presents results from the highly exothermic polymerisation of methyl methacrylate to produce oligomers, under steady, or near steady state conditions. A purpose built experimental apparatus constructed to withstand the high pressure required and temperature produced by the highly exothermic reaction (10 bar, 220 °C), was used.

Experiments using this equipment were carried out to investigate the effects of power density, flow rate (2.5-10 g/s), residence time, reaction temperature, and to quantify any benefits or variations arising from the use of conventional or microwave heating. It will be shown how the adoption of flow processing can help to overcome some of the limitations encountered with the use of batch reactors, and that the use of more extreme operating conditions can lead to reduced reaction times, minutes not hours, whilst maintaining control and safe operation.

Throughout this Chapter, as with the batch experimentation, direct comparison between conventional and microwave heated experiments were carried out. The purpose of this was to allow for accurate comparison of the

reaction rate, conversion and product spectrum between the two heating methods and to quantify variation.

From the small scale (30 cm³) batch experiments carried out in Section 5.3, a clear understanding of the reaction behaviour, and the effects that several variables have upon the conversion, rate and residence time required has been achieved. Using this information the following hypotheses for the use of flow are proposed:

1. Use of flow within high pressure equipment will allow for scale up of the reaction from 30 cm³ (28.2 g) batch reactions with a 1 min heating time and 5 min reaction time, to a flow system at 2.5-10 g/s. It is expected that there will a reduction in the heating time of the mixture and a drop in the residence time, this is inherent with changing to flow and was impossible to avoid. This change in residence time is likely to cause a reduction in conversion, but is not expected to affect the reaction in any other way.

2. The use of microwave heating offers no quantifiable variations to the polymerisation, when directly compared to conventional heating under the same conditions.

3. Power density (W/m³) has no effect upon the reaction provided that the energy input per gram is comparable.

4. Increased power allows for use of increased flow rate with no quantifiable effect upon the reaction, or the distribution of products formed.

5. The reaction is temperature dependent; increasing the reaction temperature from 80 to 100 °C in the flow system will lead to increased rate and conversion.

6.1   Design of flow heating equipment

A design of this type has to meet several requirements: transfer microwave energy efficiently to the sample material; give controlled and measureable mass flow rate (g/s) *via* real time measurement; be constructed of suitable

materials to handle the temperature (200 °C), pressure (10 bar) and viscosity (0.03 Pa.s), similar to that of light oil. Above all it must be able to operate in a safe manner; this is not just during use, but must include considerations for materials handling, vapour extraction during filling and emptying of the equipment.

6.1.1 Microwave cavity design

Microwave energy is transferred from the waveguide to the material within a microwave cavity. A standard WR340 single-mode resonant cavity was used. This was chosen for its simplicity and ease for modification This type of microwave cavity is covered in more detail in Section 2.4.6.

Within the microwave cavity it is required that there be interaction between the electromagnetic field and the flowing material whilst maintaining a safe environment. Metallic materials are unsuitable for this as they are electromagnetic conductors and would not allow any energy transfer. An alternative material was required, there are many materials which could fulfil the requirements for this system, these are commonly plastics or ceramics such as: Glass/quartz, PEEK (Polyether ether ketone), HDPE (high-density polyethylene), PTFE, borosilicate or alumina.

The drawback with use of glass or quartz is strength, it has low pressure resistance, compared to steel, and can require structural support, complex joints are required to connect the glass tubing to the steel. Borosilicate and alumina are good materials for use in microwave cavities, these are used in a wide range of applications where mechanical durability and chemical resistance are required, it is again difficult to connect these to metal joints without specialised fittings. PEEK is an ideal material for this kind of system, it is strong, rigid has high thermal and chemical resistance, can be connected *via* the use of compression fittings. The aforementioned materials all offer advantages and disadvantages in use, a major drawback with them is cost, especially with the ceramics. A less costly option which offers all of the above properties is PTFE (polytetraflouroethylene) ; it is chemically inert, can be

connected directly to Swagelok by the use of modified fittings, thermally resistant up to 220 °C, rigid, cheap and available off the shelf in a wide variety of sizes. This allowed for flexibility in the design phase, sections could be changed without significant cost arising.

It was found when using compression fittings to connect PTFE to metal that over time the joints began to leak. Upon inspection it was found that the O-ring used to seal the joint were compressing the tube such that it became deformed. To prevent this, brass inserts were fabricated and inserted within the PTFE tube at each end, shown below. This increased the strength of the material without entering the electric field or disturbing fluid flow.
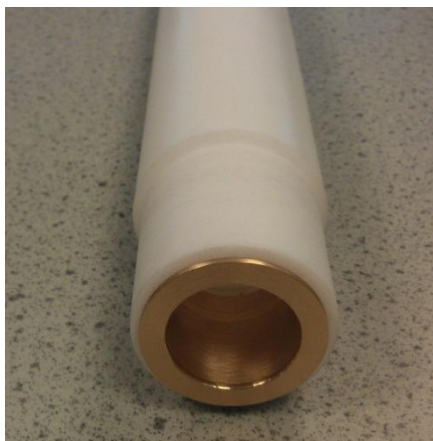
Figure 6-1: Machined PTFE tube used in cavity, shown with brass insert used to prevent deformation of tube under compression.

When using microwave systems it is essential that the electromagnetic field is contained, this is to conform with EU legislation (BERR 2008). At 2.45 GHz, 50 mm ID aluminium cylinders can be used as choke, this is below the cut off wavelength and gives attenuation of the electric field. This is based upon the assumption of the choke being empty.

In a flow system it is required that material be passed into the cavity, heated, and then pass out again. Insertion of a dielectric material into the choke

changes the wavelength of the wave by changing the speed at which it propagates. This is shown below:

$$v = \frac{1}{\sqrt{\varepsilon_0 \varepsilon_r \mu_0 \mu_r}}$$

Frequency remains constant as the wave propagates, the reduced velocity causes compression of the wave, reducing wavelength, the higher the dielectric constant the more higher the compression. In materials with high ε', such as water the wavelength is as low as 1.5 cm. In methyl methacrylate (ε'=6.17, 20 °C) the wavelength is 4.9 cm, this gives a cut off length of 1.1 cm, calculated using the relationship $\lambda_{co}=\lambda_{od}/4.413$ (Metaxas and Meredith 1983). this is clearly smaller than the 42 mm ID tube used. This shows without carrying out experimentation that standard 50 mm chokes are unsuitable for use in this case.

In the initial design a smaller PTFE tube was used (10 mm ID) this was only used for the investigation into preventing leakage as it required simpler connections and was lower cost to replace. Several different methods were used with the aim of stopping leakage; the first of these was to fabricate metal caps to go over the end of the existing chokes, shown below in Figure 6-2.
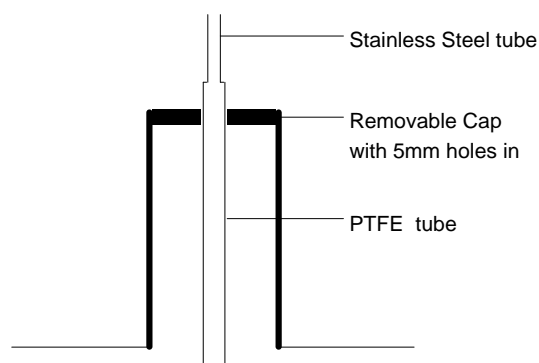
Figure 6-2: Diagram showing the initial choke pattern used on one side of the cavity, the choke on the other side of the cavity was identical.

As shown above, this effectively reduced the aperture size in the choke from 50 mm to 15 mm. This however did not prevent propagation out of the cavity.

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As a second iteration to this design, a sliding choke section was created to slide over the existing choke, giving a second 55 mm tube, shown in Figure 6-3. This significantly reduced leakage, although not low enough to meet regulations. The final design iteration was to add a second cap, this connected directly to the stainless steel tube giving a solid metal connection at the end of the choke, effectively encasing the microwave cavity reducing leakage below detectable levels. 5 mm holes were drilled in the caps, this was to prevent any pressure build up within the waveguide, caused by heating, or to allow for any liquid to escape should there be failure of the PTFE tubing.
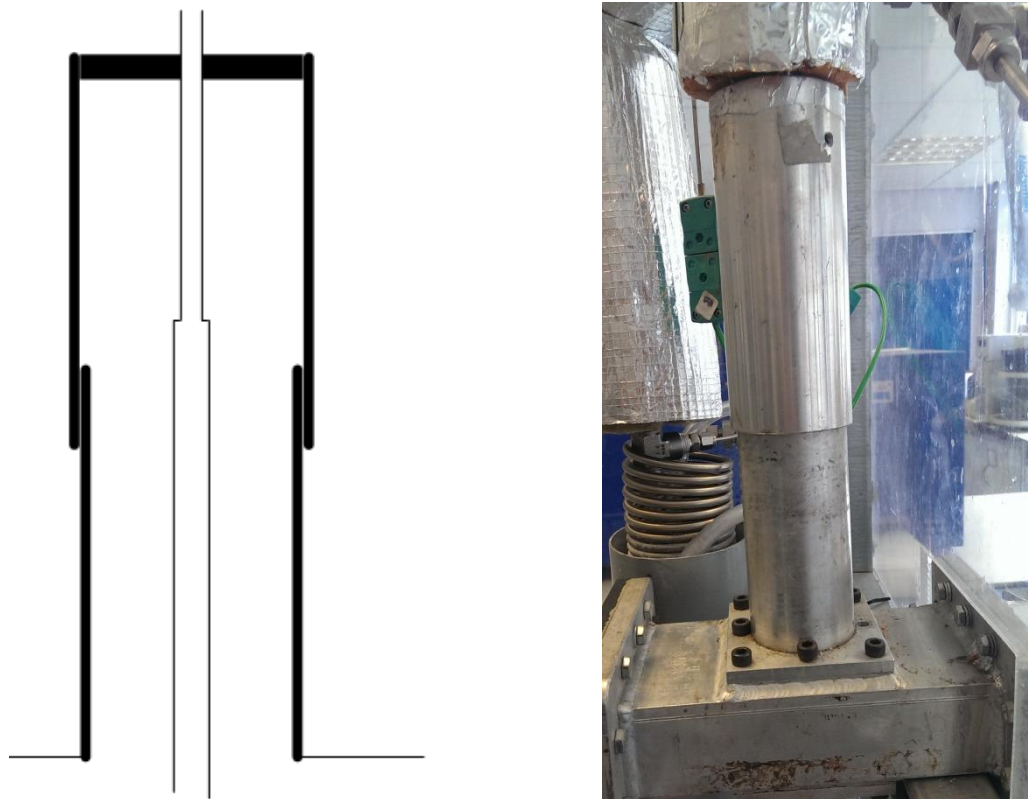
Figure 6-3: Diagram showing electromagnetically sealed choke used as final design.

Scale up of the tube within the microwave cavity gave a slightly different final design, the concept used was however the same. The lower cap was removed; the sliding section of choke was fabricated such that it gave a contact fit with the brass fittings used to connect PTFE to steel. The same

design was used top and bottom and was found to stop electromagnetic leakage.

6.1.2 Flow production and control

Flow is induced by the application of pressure to a fluid, this can be done in many ways, commonly pumps are used. This system was used with a maximum microwave power input of 200-2000 W, by carrying out an energy and mass balance using $Q = m.C_p.\Delta T$ it can be seen that the flow rates required within the system operate within the range of 1 – 13 g/s.

The wide range of flow rates required makes selection of flow equipment challenging. It was decided that the method which produced the most stable flow was by direct contact of the material with N_2 from a 220 bar cylinder. Within an industrial system this would be an unsuitable method, as it is costly and inefficient, however for a laboratory it is ideal. Pressure is applied with no noise, caused by the pump action, very wide range of pressure and flow rate can be used, no requirement for use of soft pipes (peristaltic pump), the inert atmosphere provided is required for the chemistry used.

Flow rate was calculated on a mass basis as volumetric flow is can be affected by changes in density within the fluid. which affect the density and the accuracy of volumetric measurement. Flow rate was measured using a 2 d.p. balance with bespoke LabView software, this outputs mass flow rate and total mass collected in numerical and graphical format to allow feedback and mass flow control. Flow rate is controlled using a manually operated 12.7 mm needle valve. Shown below is the diagram of the feedback loop used.

6.1.3 Temperature control

In batch systems temperature is controlled by direct measurement and feedback to the heat source. This is required as the system is dynamic, heat losses and material properties are changing over time.

Once steady state is achieved, there are no significant variations in any of the variables within the system. With this in mind it is feasible to control

temperature set point by feed-forward control of the energy input rather than feedback of measured temperature.

In this system power (W) was supplied by the heating equipment, either microwave or conventional, was maintained as constant throughout any individual experiment. Energy input to the sample was controlled by adjustment of the mass flow rate; increasing flow rate reduces energy per unit mass (J/g). Temperature was measured in the system but was not used as a control, it was for monitoring only.

This method removed the requirement for temperature measurement within the electromagnetic field, which as previously demonstrated is a complex problem.

Temperature within the system was monitored at several locations; this was to ensure safe operation and control. To maximise efficiency and minimise heat losses, the hot sections of the system are insulated with 30 mm RockWool™ piping insulation, seen in Figure 6-4.

6.1.4 Heating equipment

Two types of heating have been used in this flow experimentation. Microwaves are provided using 2 kW magnetron operating at 2.45 GHz. Power can be adjusted in 1 W increments with a minimum stable output of 200 W. Tuning was carried out by two devices, manually operated short circuit and 3 stub impedance matching device. In initial experiments, a manual device was used, this was found to give low power transfer. An automated system was then used throughout. This provided higher levels of power transfer (>99 %), compared to approximately 80 % with manual tuning, and allowed for real-time monitoring of forward and reflected power.

Conventional heating was carried out using rubberised heating tape operating at 1050 W with maximum temperature set point of 150 °C, this temperature was used in order to maximise thermal gradients and increase heat transfer.

6.1.5   Piping layout

The following equipment was used within the system:

- Piping and connections: Swagelok™/Ham-Let™ pipes and fittings used throughout unless specified below (207 bar at 37 °C)

- PTFE tube within microwave cavity (47 bar, 200 °C) (Du-Pont 2011)[3]

- Stainless to PTFE connection: brass fitting. Swagelok not used as not available in compatible sizes (10 bar, 200 °C).
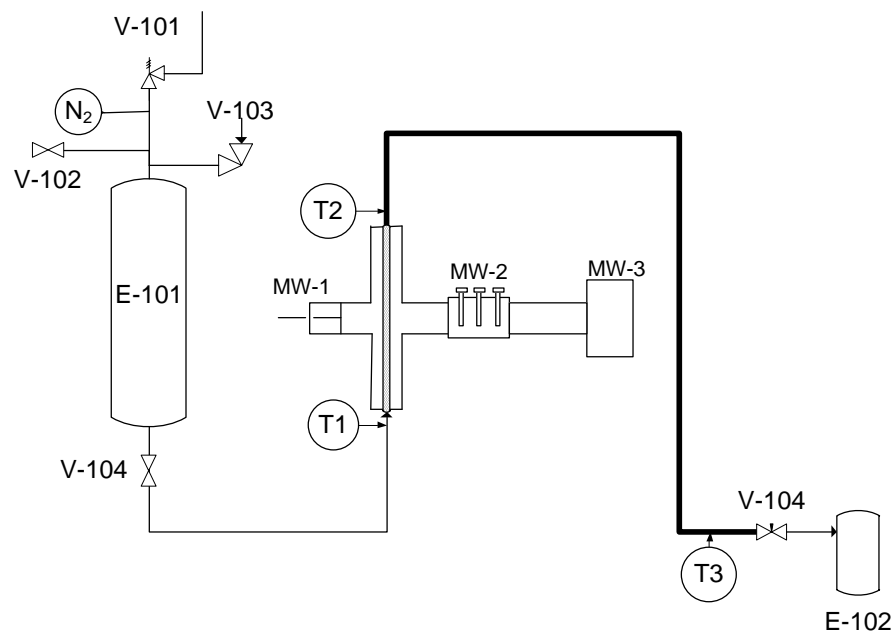
Figure 6-4: Piping diagram for flow system used for microwave heating

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[3] Calculated assuming a tensile strength of 10 MPa, the lowest value found in literature, if the average value were taken this would be 70 bar.

Table 6-1: List and description of equipment used in flow system.

ID	Description	Purpose
V-101	¼ inch relief valve	Spring loaded pressure relief
V-102	¼ inch ball valve	Bleed valve
V-103	½ inch ball valve	Fill point
V-104	½ inch ball valve	Isolation
V-105	½ inch needle valve	Flow control
T1-T3	Thermocouple	Temperature measurement
N_2	Gas inlet (4 bar)	
E-101	1 litre pressure vessel	Contains feed material
E-102	Glass collection vessel	Contains products (low pressure)
MW-1	Manual short-circuit tuner	
MW-2	Automated 3 stub, HOMER tuner	
MW-3	2 kW microwave generator	
———	Un-insulated stainless steel piping	
▬▬▬	Thermally insulated stainless steel piping	
⁄⁄⁄⁄⁄⁄⁄⁄⁄	PTFE pipe within microwave cavity	

6.1.6 Safety considerations

There were several safety considerations taken into account when designing this system:

1. **Temperature:** there are two sources of heat within this system; the energy input from the heat source (conventional/microwave) and the heat evolved from the reaction. In the worst case scenario this could produce a temperature rise of ~300 °C, this was calculated via a Hess cycle, assuming that all monomer formed into one chain, therefore giving the maximum number of polymerisation steps. Increased temperature can lead to thermal runaway and increased pressure due to temperature exceeding the monomer boiling point (100 °C, 1 atm).

2. **Pressure:** pressure is directly applied from N_2 cylinder to produce flow within the system; pressure within the system can be increased by temperature exceeding the boiling point of the monomer. Boiling point is

defined as the point at which the vapour pressure of the liquid is equal to or greater than the total pressure of the system. Relationship between vapour pressure of MMA and temperature shown in Figure 6-5.
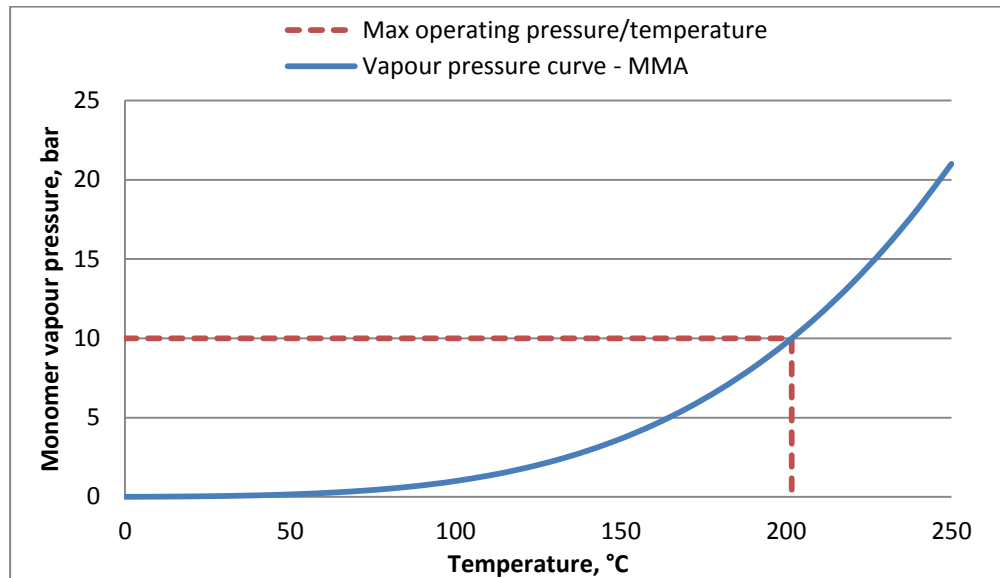
Figure 6-5: Vapour pressure of MMA against temperature, calculated using the Antoine equations with constants taken from (Perry and Green 2008). Highlighted are the maximum operating conditions of the equipment used

3. **Viscosity:** with a polymerisation reaction occurring there will be viscosity increases within the system, with high molecular weight formation this could be in the order 10,000 cP compared to 0.6 cP for MMA monomer at ambient conditions, potentially causing blockages and fouling.

4. **Electromagnetic leakage:** there are legal restrictions in place regarding power levels which can be allowed to propagate from any equipment (5 mW/cm², 50 mm from source).

5. **Contamination:** could be in liquid or vapour form. Potentially carcinogenic materials such as MMA must be contained to prevent exposure.

To control these potential hazards several systems were implemented within the design. Temperature at several points within the equipment was continuously recorded to monitor the system. Mass flow rate was controlled with the use of a balance (precision 0.00g), coupled with a manual feedback loop. Power transfer was continuously tuned and monitored with the use of a

HOMER tuner. This precise monitoring of both mass and power gave control of energy input, hence direct control of the temperature achieved within the system. Pressure relief was provided by the use of variable release spring operated valves. The entire system was contained within a 5 mm Perspex enclosure, and surrounded by a bund to ensure any fluid spillage was contained. With this polymerisation CCT catalyst was used, this had a dual effect of limiting the chain length, thus reducing the levels of heat evolved, and the viscosity of the product material. Electromagnetic radiation was continually monitored, with a safety interlock connected to the generator. To ensure any leakage was maintained below the legal requirement, the system was designed to ensure that zero leakage occurred.

6.2   Effect of power and energy on heating of pure monomer in flow

Experiments were carried out with the use of pure monomer, without initiator or catalyst added. The purpose of this was to determine the effects of the different variables upon the system. The primary variables were:

- Temperature set point: this was used to determine the specific energy (J/g) required to achieve the temperature set point, according to the relationship $Q=m.C_p.\Delta T$. Where C_p for MMA =2.55 J/g.K
- Power level: controlled directly by the microwave generator, could be varied between 200-2000 W

The link between these two variables was mass flow rate (g/s); from this the residence time within the microwave cavity could also be calculated.

6.2.1   Investigation of mass flow rate against time

Figure 6-6 below shows the measurement of cumulative mass collected against time. This was carried out without heating, the flow rate used were calculated based upon a 100 °C (200 J/g) set point. It can be seen that the three flow rates used lay within the operating limits of the system, the operating limits are defined as the operation at 200 and 2000 W power output. These experiments were each repeated three times and the standard

deviation of the three was found to be 5 %. When calculated as a temperature change this gives ±4 °C against the set point.
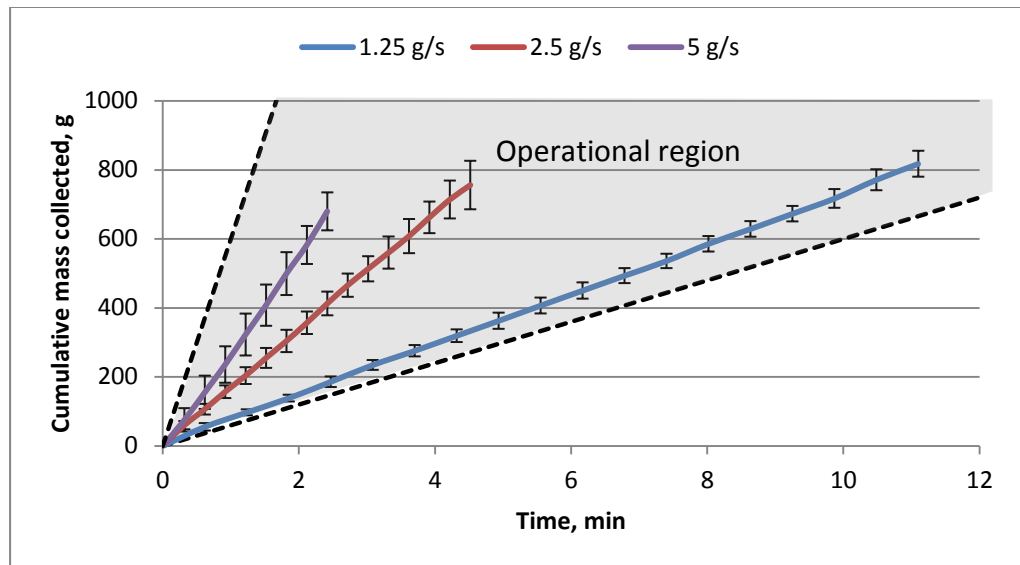
Figure 6-6: Mass collected against time for flow experiments using monomer, carried out at three different flow rates. Flow rates calculated assuming 100 °C (200 J/g) set point. Operational region is shaded grey.

6.2.2 Mass flow rate against energy input

Figure 6-7 below shows the mass flow rate required to achieve a specific, energy level or temperature, at different power levels. The grey area highlights the region in which this equipment was operated.
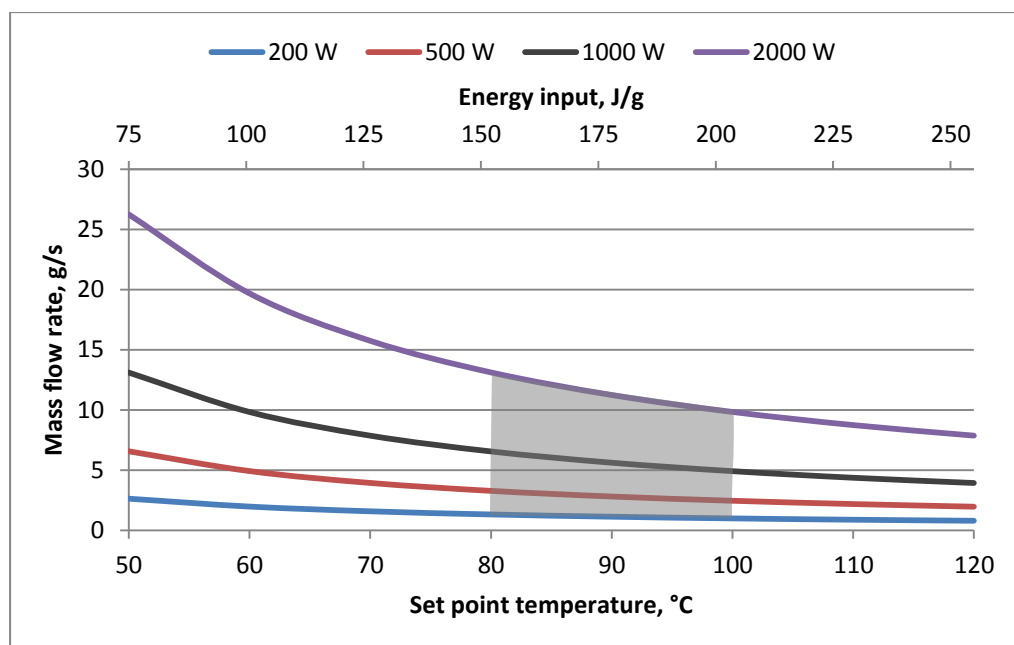
Figure 6-7: Relationship between the temperature set point and the required mass flow rate, at various different power levels using microwave heating in flow. Operational region is shaded grey.

6.2.3 Residence time within microwave cavity

The residence time within the microwave cavity is directly linked with the volumetric flow rate; the cavity has a fixed volume of 320 cm³. Shown below is the relationship between the residence time and temperature set point at different power levels. Highlighted in grey is the area in which the equipment has been operated.
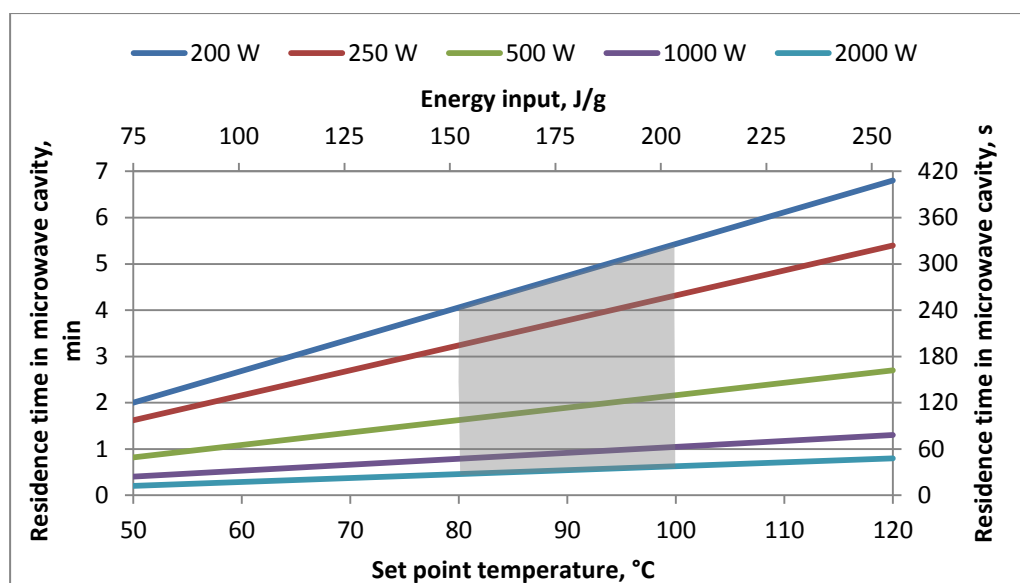
Figure 6-8: Residence time within the microwave cavity to achieve a specific temperature/energy input at various power levels used. Operational region is shaded grey.

6.2.4 Temperature profiles for heating monomer in flow

Temperature profiles for heating of pure monomer were carried out at constant energy input of 130 J/g giving a temperature set point of 70 °C. Three different power levels were used; mass flow rate was adjusted to maintain this constant energy input. Monomer temperature profiles are important as they can be used to compare with experiments where polymerisation is occurring and can be subsequently used to quantify any variation in the temperature profiles caused by the reaction exotherm.

Figure 6-9 below shows heating profiles, temperature measurement was carried out at the exit of the microwave cavity, location shown in Figure 6-4. Inspection of the 250 W temperature profile shows that there is a trend of increasing temperature over time from ambient at the start. After around 8 minutes the temperature becomes constant at the 70 °C set point.
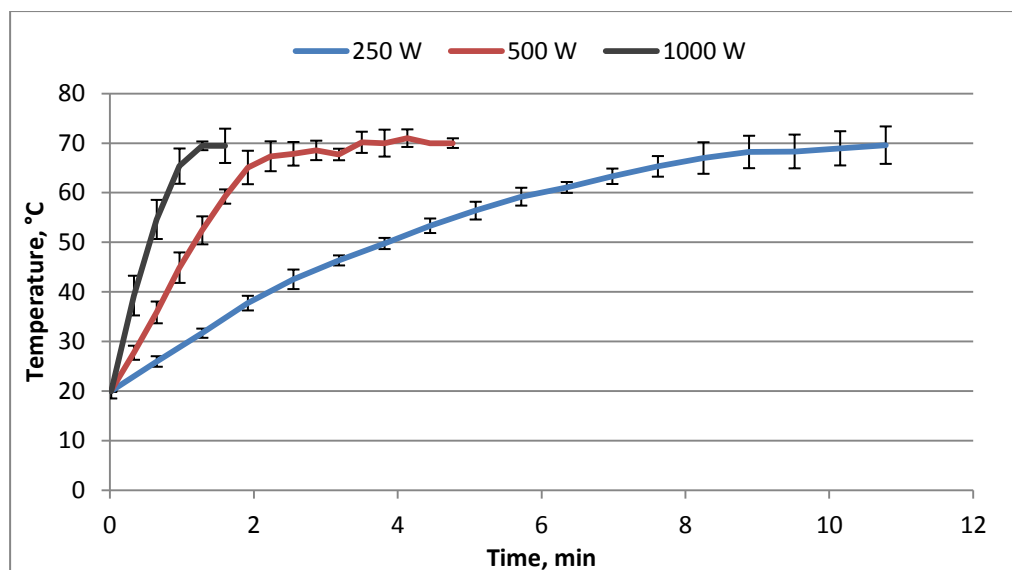
Figure 6-9: Temperature profiles, heating of monomer in flow using microwave system at different power levels, with constant energy input 130 J/g. Energy is held constant by adjusting the mass flow rate.

This long period for heat up was expected, and was caused by two factors. At the start of the experiment the 320 cm³ PTFE tube within the microwave cavity was filled entirely with monomer. As flow is started and microwave power introduced material flows out of the microwave cavity, it is clear that material at the top of the microwave cavity does not have the full residence time within the cavity, and thus does not receive the full amount of energy per gram. As time progresses more and more material passes through the cavity until such a point is reached that 1 full volume of the cavity has passed through, all subsequent material then receives the full energy input. At 250 W, 130 J/g this takes approximately 4 min to occur. The remaining 4 minutes before steady state was achieved is caused by heat losses from the system. As the material flowing warms up, heat is lost from the liquid to the surrounding piping and equipment, as the fluid directly comes into contact with approximately 5 kg of fittings and pipe, which in turn is in contact with the thin walled aluminium chokes (3 mm). This acts as a radiator, removing heat from the system. Over time this equipment warms up until equilibrium with the surroundings is achieved and the fluid temperature becomes constant.

As the power level and flow rate was increased, it can be seen that the time taken to achieve steady state was reduced. This was due to reduced residence time within the microwave cavity and improved heat transfer allowing for equipment to be heated more rapidly than at 250 W. The experimental duration was reduced due to the fixed volume of material in the feed vessel.

6.3 Operating limits

Table 5-2 show a summary of the conditions under which the system can operate, the residence times are shown for the temperature range of 80-100 °C used within this work.

Table 6-2: Summary of maximum and minimum operating conditions for flow system.

Variable	Limits	Description
Flow rate	0 - 20 g/s	Limited by pressure drop in system
Temperature	220 °C	Safe limit of PTFE
Pressure	10 bar	Safe limit of PTFE-steel connectors
Power		
Microwave	200-2000 W	
Conventional	1050 W at 150 °C	Maximum power available
Residence time		
200 W	4-5.4 min	At 80 and 100 °C set point
2000 W	24-32 s	At 80 and 100 °C set point
Feed capacity	1 litre	

6.4 Flow polymerisation of methyl methacrylate oligomers

6.4.1 Effect of energy upon polymerisation in flow

Batch experimentation carried out focussed upon discovering the energy/temperature at which the polymerisation gave the highest conversion. Conversion is defined as consumption of monomer, which, as opposed to yield, is the least ambiguous means of quantifying the extent of a reaction forming multiple products.

Flow experiments were conducted at the same temperature set points as the batch experiments, (80, 90, 100 °C). This was done in order to quantify any potential effects or changes in the conversion or products produced by scaling up the reaction and moving from a batch reactor to flow.

Three different power levels were used, 250, 500 and 1000 W. Different power levels were used as a direct scale up, in order to increase the material throughput, increased power levels were required to maintain constant energy input and hence temperature. The experimental matrix is shown below in Table 6-3. These power levels were used as 250 W was the lowest level at which the generator could output a stable signal, 1000 W was used as the maximum due to limitation of the feed capacity. Increasing the power beyond this gave experimental durations too short to approach steady state.

Table 6-3: Matrix of experiments for determination of the effects of energy/temperature and power upon polymerisation. Effect is determined by measurement of conversion.

Temperature, °C	Power level, W		
	250	500	1000
80	-	-	-
90	-	-	-
100	-	-	-

1 litre MMA containing 600 ppm catalyst and 1 w/w% initiator was prepared and charged to feed vessel by method shown in Section 4.3.2.

Results and discussion
Polymerisation experiments were first carried out at low power and temperature (250 W, 80 °C). This was done as a safety precaution, as it had previously been shown during batch experiments there was a significant temperature rise (maximum theoretical temperature 140 °C) due to the heat of reaction when carrying out the reaction at 100 °C. At 80 °C there were low levels of conversion achieved (5 %), and the temperature exotherm caused by the heat of reaction was small (<10 °C). With 320 cm³ material within the heated reactor at one time the reduced operating temperature was to ensure

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safe operation; it has previously been shown that scale up to 250 cm³ in batch could lead to pressure build up and vapour release (see Section 5.2.3.2).

Once it was found that the system operated in a safe and repeatable manner at the reduced temperature and throughput, the temperature and power levels were subsequently increased.

Figure 6-10 below shows the temperature profiles for a polymerisation reaction and a temperature profile for heating of monomer, carried out with a 100 °C temperature set point, 2.5 g/s flow rate and microwave forward power 500 W. Temperature was measured using thermocouple T2 at the cavity outlet, location can be seen on page 146.

It can be clearly seen below that there are two distinct trends between the reacting and non-reacting system. Up to approximately 2 min there is very little variation between the two temperature profiles, this is due to the material already within the microwave cavity, having a reduced residence time and subsequently lower levels of heating; explained further in Section 6.2.4 above.
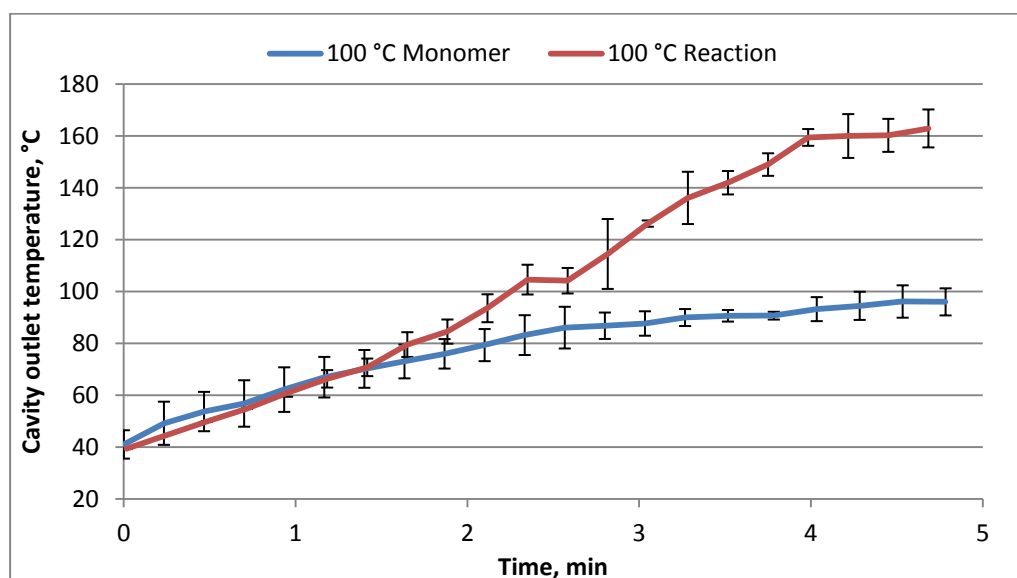
Figure 6-10: Temperature profiles for polymerisation reaction and heating of pure monomer, carried out at 100 °C temperature set point, 2.5 g/s flow rate and microwave forward power 500 W.

This trend was found in all experiments carried out, to allow for clearer presentation of data the initial 2 min of experimental time will be removed from the temperature traces. This will be carried out for all data presented forthwith.

It can now be clearly seen in Figure 6-11 below that there was a large temperature differential between the two experiments. This was expected; it has been previously shown in 30 cm³ batch that there was a 40 °C temperature rise due to the exothermic reaction achieving 65 % conversion, support calculations shown in Appendix 9.1.1. Samples were taken in this flow experiment after 4.5 min once the reaction had achieved steady state; conversion was measured at 55 %. Analysis of molecular weight by NMR showed that MMA_2/MMA_3 was produced in a 3:2 molar ratio, GPC showed no higher weight polymer materials formation.
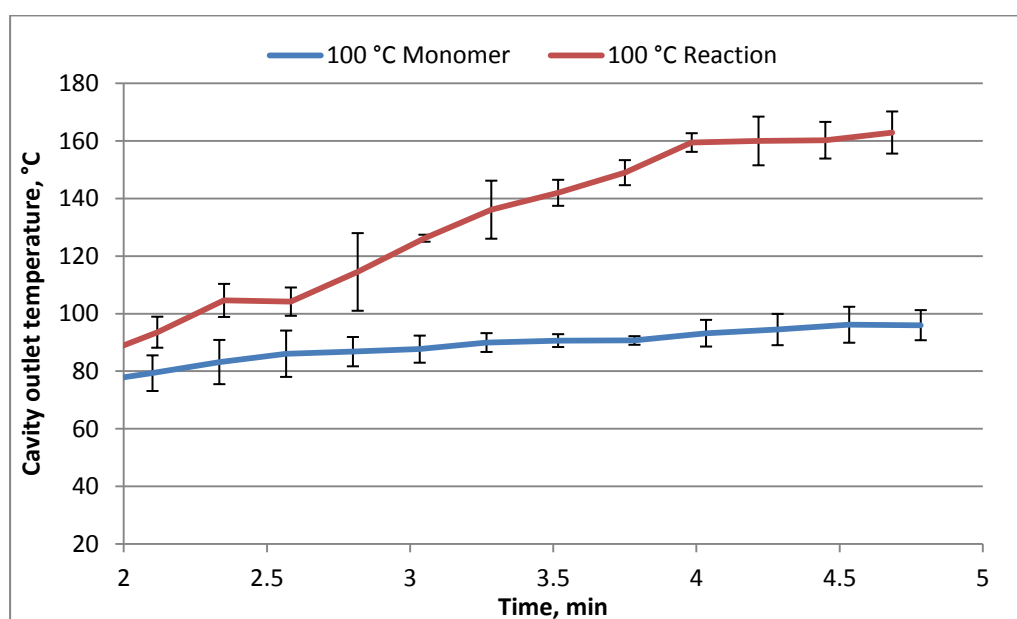
Figure 6-11: Temperature profiles for polymerisation reaction and heating of pure monomer, carried out at 100 °C temperature set point, 2.5 g/s flow rate and microwave forward power 500 W.

The maximum temperature in flow was 160 °C (55 % conversion), when carried out in 30 cm³ batch reactions the maximum achieved was 140 °C (65 % conversion). It would be expected that the temperature rise due to the heat of reaction in the batch experiment would be higher due to the slightly

higher levels of conversion. The increased temperature in flow was caused by the highly insulated steady state system having reduced thermal losses.

One of the aims carrying out the reaction inflow was to show that this reaction regime had no effects upon the conversion, rate, product distribution or energy requirement of the reaction. This has however been shown to be false, there was a 10 % point drop in conversion, products formed remained constant. It is postulated that this reduced conversion was caused by the reduced residence time within the reactor, in batch experiments this was 5 min, 2.5 min in flow. The residence time is based upon the volume of the microwave cavity plus all the piping and equipment after the cavity. It also assumes that the set point temperature was reached at the half-way point within the cavity; justification of this assumption is explained in further detail in Figure 6-22 on page 184. Further investigation of the effects of residence time on the levels of conversion are covered in Section 6.8.2.

Figure 6-12 below shows temperature profiles for the three reactions carried out at different energy input per gram. Once again it can be seen that the temperature profiles for the reaction deviate from those of pure monomer. This temperature rise was directly proportional to level of conversion achieved.
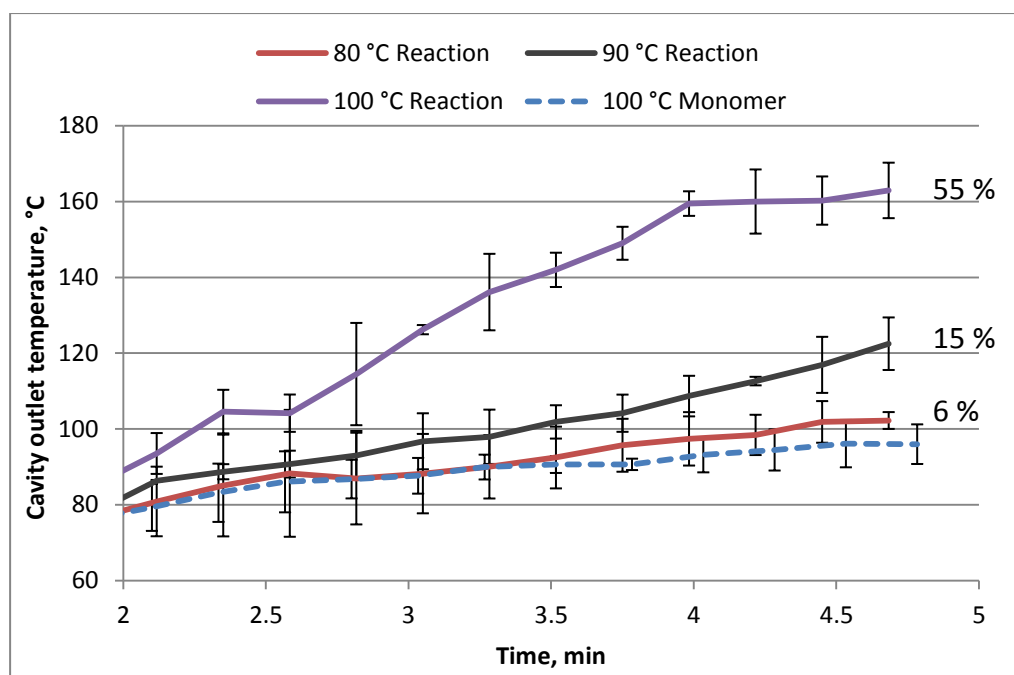
Figure 6-12: Temperature profiles for reactions carried out at different temperature set points, microwave power kept constant at 500 W, energy levels/temperature controlled by adjustment of flow rate. Annotations show % conversion from monomer.

As was previously shown there was reduced levels of conversion at all temperature set points when compared to batch reactions, shown in Table 6-4 below. It is proposed that this reduced conversion was due to the reduced residence times in the flow reactor (2 -2.5 min), when compared to batch (5 min).

Table 6-4: % Conversion for both microwave heated batch and flow reactions. Batch reactions carried out in CEM at 300 W with 5 min residence time. Flow reactions carried out at 500 W.

Temperature set point, °C	Energy input, J/g	% Conversion	
		Batch	Flow
80	152±5	9±2	6±2
90	178±6	25±2	15±3
100	203±5	65±3	55±2

It was shown above in Figure 6-12 that there were different steady state temperatures for the three reactions. Within the reaction there are two

sources of heat, the energy input to the system by the microwave heating and the heat evolved from the exothermic reaction; Table 6-5below shows a break down of these and their contribution to the overall temperature (ΔT).

Table 6-5: Sources of heat within the system with reaction occurring, at different microwave energy inputs, carried out at constant power level of 500W.

		Temperature set point, °C		
		80	90	100
Conversion, %	%	6	15	55
ΔT, microwave energy	˚C	60	70	80
ΔT, heat of reaction	˚C	9	46	59
Theoretical maximum (Tmax$_t$)	˚C	89	114	193
Experimental maximum (Tmax$_e$)	˚C	102	122	160
Tmax$_t$- Tmax$_e$	˚C	-13	-8	33

Important to note is that there was an inversion in the relationship between the theoretical and experimentally measured maximum temperature. At both 80 and 90 °C the theoretical temperature rise was lower than was achieved experimentally. The energy balance calculations for heat of reaction assume formation of dimer, whereas in practise there is a mixed molecular weight distribution, thus the heat contributed by the heat of reaction was higher in practise than in theory. Calculation for temperature rise caused by heat of reaction, shown in Appendix 9.1.1. At 100 °C the theoretically calculated temperature was 33 °C higher than that measured experimentally. This was caused by increased heat losses from the system to the surroundings; this increased heat loss was caused by the larger temperature differential between the reacting material and ambient conditions. There was also a reduced flow rate, used to achieve the higher energy input at constant power level 3.25 g/s at 80 °C, 2.5 g/s at 100 °C; giving increased residence time and heat losses.

6.5 Effect of power and increased flow rate

The above experiments were repeated with the use of different power levels to show how this affected conversion; flow rate was adjusted to ensure that constant energy levels per unit mass (J/g) were used. As shown in Table 5-6 below, there was minimal variation when comparing conversion against power level.

At all three power levels investigated it is clearly shown that energy input and subsequent temperature set point had a significant effect upon the reaction. It can be seen that at 100 °C there was a slight drop in conversion as power and flow rate were increased. This was caused by reduced residence times within the system (40 s – 4 min), giving shorter reaction times. This effect was not found at 80 and 90 °C, it is likely that this was caused by the low levels of polymerisation occurring and that there was not high enough resolution on the NMR analysis to give a more precise measurement of conversion, minimum detection ~5 %.

Table 6-6: Effect of power and energy input upon the % conversion achieved in flow.

Temperature set point, °C	Energy input, J/g	Power input		
		250 W	500 W	1000 W
80	152	10±2	10±2	9±3
90	178	14±2	15±2	16±2
100	203	56±2	55±2	50±2

6.6 Comparison between conventional and microwave heated reactions in flow

As was shown in the previous Chapter, direct comparison between conventional and microwave heated systems was essential in the determination of potential benefits offered by either heating mechanism. In batch reactions this was carried out with the use of a stirred oil bath, the reactor geometries, pressures, stirring rates and heating rates were kept

constant. This is highly important as many researchers carry out conventional comparisons with the use of different operating conditions, thus often drawing inaccurate conclusions.

In order to ensure the validity of the work, the PTFE tube used within the microwave cavity was changed and replaced with a stainless steel tube with the same internal dimensions. This was then wrapped with rubberised heating tape operated at 150 °C 1050 W, heating zone A, shown below in Figure 6-13. It was found that the reaction temperatures could not be achieved with flow rates (>0.5 g/s), this was caused by the laminar flow (Re=20) within the system giving poor heat transfer characteristics. At this low flow rate it made comparison with microwave heating impossible, therefore the ½ inch stainless tubing prior to the reactor (heating zone B) was also heated.

This design enabled the similar flow rates to be used, the same physical vessel geometry, same flow characteristics and same residence times. The addition of heating zone B was unavoidable; it was however a minor change compared to the microwave heated equipment. It is known that the temperature profiles within the system are not the same when comparing conventional to microwave heating, this is however impossible to avoid. This variation was caused by the way in which the two mechanisms transfer heat being significantly different, conventional heating relies on convection and conduction through the fluid; whilst in microwave heating the energy is directly applied to the fluid volumetrically.
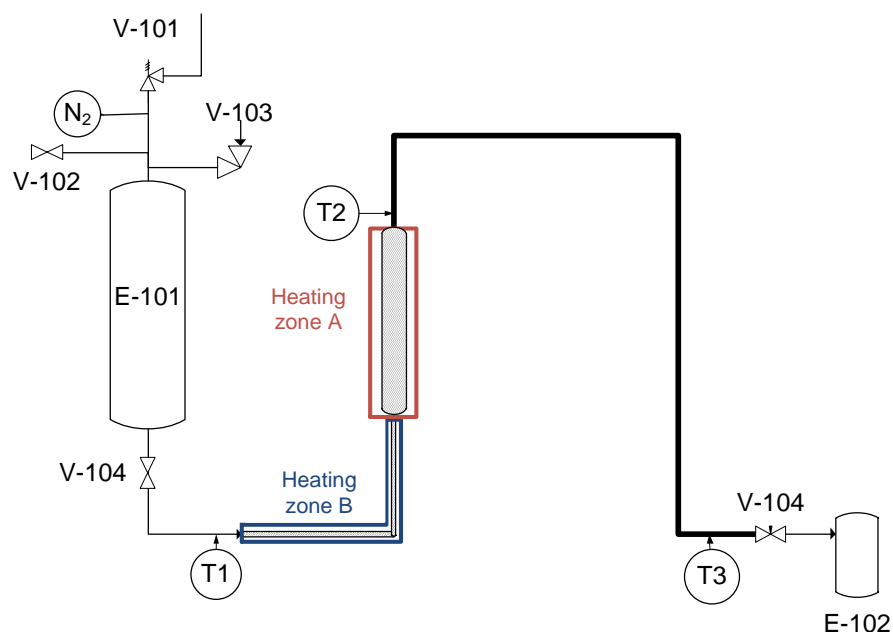
Figure 6-13: Piping diagram of equipment used for conventional comparison with microwave heated equipment; equipment list can be seen on page 146.

As stated above it was not as simple to achieve the target temperatures conventionally. In the microwave system this was achieved by carrying out an energy balance to calculate flow rate. In the conventional system a wide range of flow rates were tested (1.5-3 g/s) to find which gave the required temperatures. The same level of control could not be achieved with conventional heating as with microwave heating, this was due to the poor heat transfer characteristics of the heat source; due to this conventional comparisons were only carried out at 80±5 °C and 100±6 °C.

It was not possible to investigate the effects of power as with the microwave system; this was due to the fixed surface area for heat transfer and the maximum power and operating temperature of the heating tape already reached. Conventional comparisons were carried out at flow rates similar to those at 500 W when using microwave heating.

6.6.1 Temperature profile-monomer

80 and 100 °C monomer set point temperatures were achieved using flow rates of 2.7 and 1.4 g/s; this is lower than the flow rates used with microwave

heating. It was not possible to get the flow rate closer without making significant changes to the equipment geometry.

Figure 6-14 below shows temperature profiles for monomer heated to 80 °C. It can be clearly seen that wall temperature remained constant throughout, with fluctuations of around ±5 °C. An energy balance shows that approximately 410 W was transferred to the fluid, with the remaining 640 W lost to the surroundings.
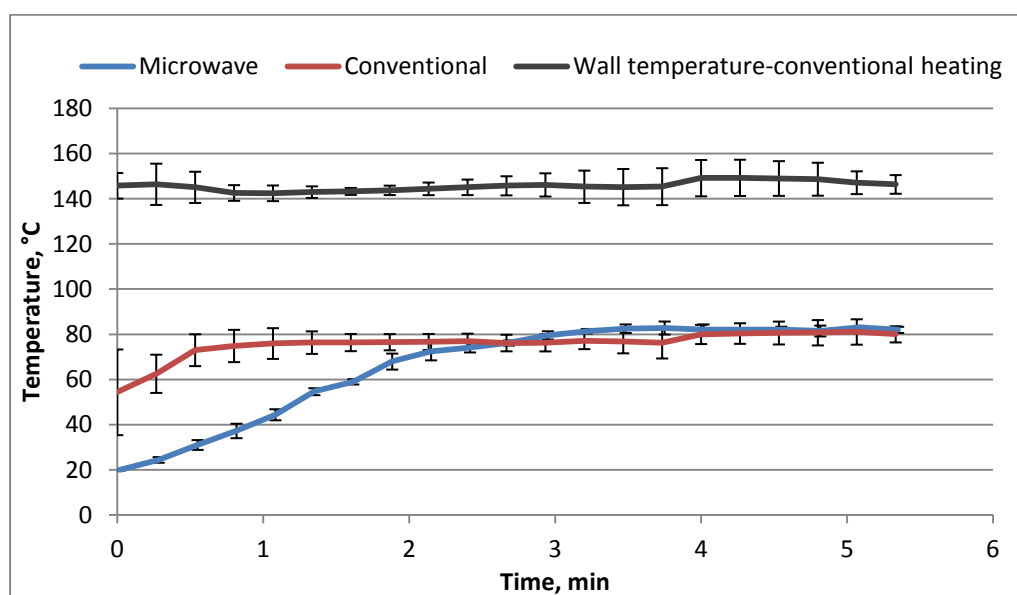
Figure 6-14: Temperature profile for monomer heated to 80 °C using both conventional and microwave heating (500 W) in flow, flow rates of 2.7 and 3.3 g/s respectively.

Comparing the temperature profiles for the conventional and 500 W microwave heating it can be seen that the conventionally heated experiment achieved steady state two minutes before the microwave. In the conventionally heated system, heat was transferred to the fluid through the walls of the pipes. Whereas in the microwave heating the energy was applied directly to the fluid and heat was then transferred outwards through the walls of the pipes. This leads to lower heat losses from the fluid in the conventional heating, hence steady state being achieved more rapidly.

6.6.2 Conventional flow polymerisation

1 litre MMA containing 600 ppm catalyst and 1 w/w% initiator was prepared and charged to feed vessel by method, F1.

As with the microwave experiments, polymerisation was first carried out at the lower reaction temperature of 80 °C, this was as a safety precaution.

Conventionally the reaction produced 13 % conversion compared to 8 % in the microwave, both produced MMA_2/MMA_3 with no higher molecular weight polymeric product formed. Figure 6-15 below shows temperature profiles for conventional and microwave heated experiments carried out at the same energy input (150 J/g). It is noted that in the conventionally heated reaction there does not appear to be any temperature rise caused by the heat of reaction, unlike with the microwave reaction.
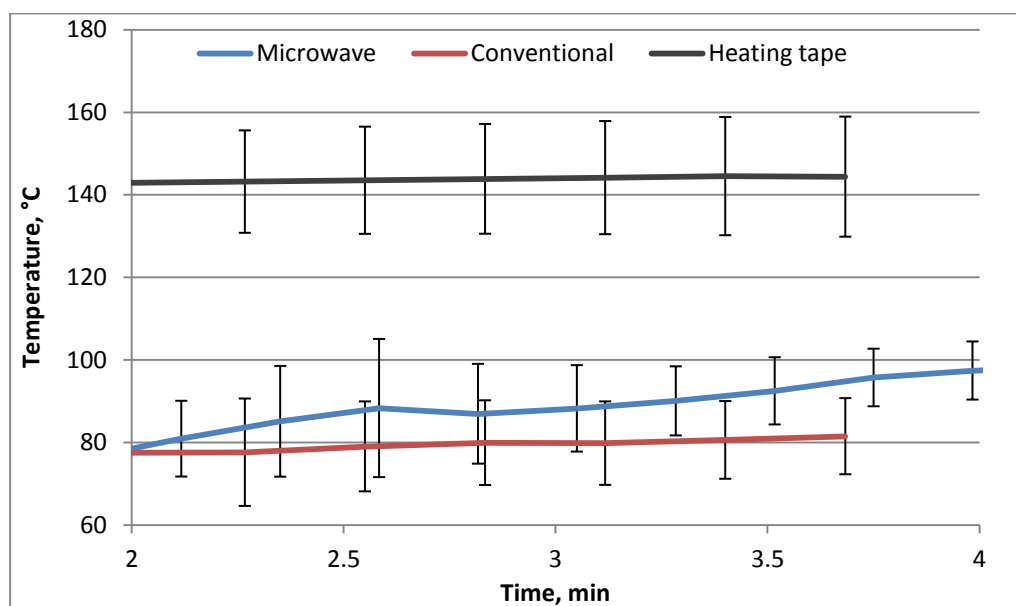
Figure 6-15: Comparison of temperature profiles for polymerisation carried out in flow using conventional and microwave heating, at 80 °C temperature set point.

It is proposed that this was caused by the temperature profile within the reactor. In the microwave system it was expected that the set point temperature was achieved near the centre of the reactor, further detail and explanation given in Section 6.8.2.1, giving approximately 48 s reaction time

before the temperature was measured, thus allowing time for the reaction to occur. In the conventionally heated system the reaction does not achieve the set point temperature until the exit of the reactor. Hence the temperature rise caused by the heat of reaction was not witnessed at the thermocouple. This is however unproven and this temperature discrepancy could be caused by changes in viscosity reducing the overall heat transfer to the fluid and hence the temperature.

Increasing the operating temperature to 100 °C it can be seen that once again there was a significant reaction exotherm (Figure 6-16), similar to that witnessed in the batch and microwave flow experiments, with a steady state temperature of 152 °C being achieved. When comparing both conventional and microwave experiments it is seen that the temperature profiles achieved are almost identical, with a slightly higher mean steady state temperature in the microwave experiment (155 °C). This is however within experimental variation. Product analysis showed that both reactions gave 55 % conversion, with MMA_2/MMA_3 formed with no higher molecular weight material.
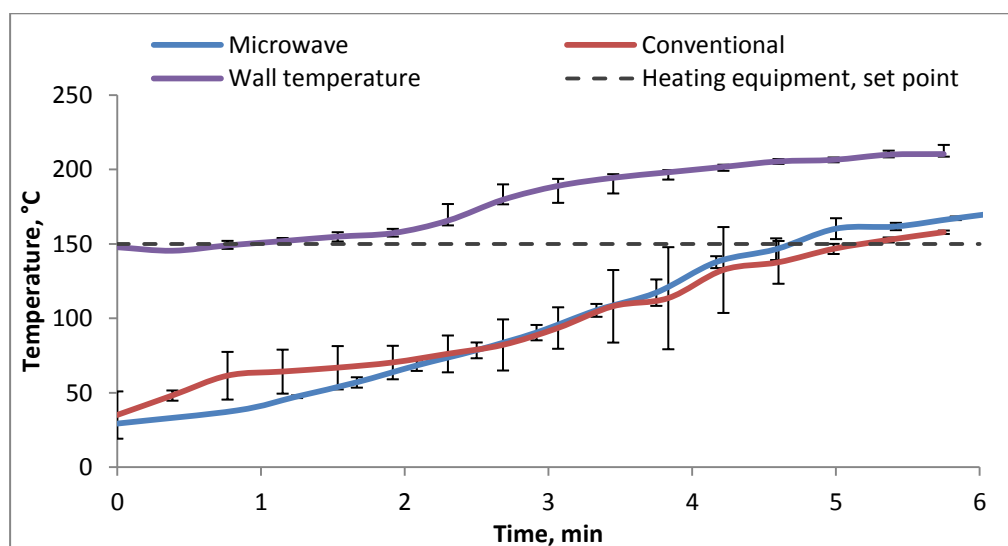
Figure 6-16: Comparison of temperature profiles for polymerisation carried out in flow using conventional and microwave heating (500 W), at 100 °C temperature set point.

It is clearly seen above, that during the experiment the wall temperature rose above that of the set point of the heating equipment, it was also 40 °C higher

than that of the fluid within the centre of the pipe. This indicates a significant temperature gradient over a distance of 1 cm, highlighting the design challenges encountered with scaling up polymerisation reactions. This indicates that there was uneven heating and that there was therefore uneven levels of polymerisation occurring. This phenomenon was not identified during microwave experiments, showing that more even heating occurred within the sample. There was however no effect upon the conversion or products formed, indicating a potential advantage of microwave heating if this were to be scaled up further.

6.7 Summary and conclusions for flow polymerisation using initial design

This Section of work used an initial design concept to carry out large scale polymerisation of methyl methacrylate in flow. The aim of which was to determine whether the reaction could carried out in continuous flow without any effect upon the reaction, when compared to batch.

Microwave heated polymerisation investigating both the effects of energy and power; found that the same relationship existed in flow when compared to batch. Increasing the reaction temperature from 80-100 °C gave a rise in conversion from 10-55 %, 10 % point drop in conversion to that achieved in batch reactions. It is hypothesised that this was caused exclusively by the reduction in residence time within the flow system and not a by-product of increased scale or reaction regime.

Increasing power levels were found to have no effect upon the reaction, other than to allow for increased throughput. This helps to add further evidence to the fact that the reaction is purely driven by energy and temperature and that there are no selective heating effects offered by microwave heating.

Direct comparison between conventional and microwave heated flow polymerisation was carried out at two different temperature set points. The aim of this was to determine and quantify any differences between the two heating sources. It was found at the lower temperature used 80 °C that there

was a slightly elevated conversion achieved with conventional heating 13 % compared to 9 %. At 100 °C this was not witnessed, 55 % conversion was achieved using conventional heating with the same product distributions and identical temperature profile. The 100 °C reaction is more important than that carried out at 80 °C as it gave a much higher yield of the target materials.

From this it is once again shown that there are no quantifiable differences when comparing conventional and microwave heating with this specific chemistry. There were however some less quantifiable benefits from using the microwave heating: there were higher levels of control, with the capacity to finely tune energy transfer; more rapid shut down to reduced thermal inertia; and improved flexibility, when compared to the conventional heating equipment used.

From this work there are some clear modifications and improvements that could be made to the equipment to improve the quality of the results and allow for higher flow rates and power levels to be investigated. These modifications are highlighted below.

6.8   Design modifications for increased feed capacity

Modifications made to the equipment were based upon improved materials handling, increased capacity, and better safety and control. The microwave cavity and conventional heating zone were kept constant throughout.

The purpose of a continuous flow system is to operate for extended periods of time in a steady state mode; it was clear from inspection of previously presented data that this system did not have the available feed capacity to achieve this. When reactions were being carried out it can be seen that there was only a short region of steady state operation. It was also found that the system could not operate successfully above 1 kW as the experimental duration was too short. Feed capacity was increased from a 1 litre single vessel feed, to an 8 litre dual vessel feed. The advantage of this is that the feed vessels could be isolated, allowing simultaneous filling and emptying; allowing for truly continuous operation as required.

In the initial design, hot samples were taken at the outlet. The samples were then quenched prior to analysis. With 1 litre total material reaction, the hot liquor was flowed into an atmospheric pressure 10 litre collection vessel and allowed to cool naturally. With increased capacity and the potential for temperature reaching 200 °C this was no longer viable. A heat exchanger was designed and introduced to the system, giving two advantages. It cooled the reactor effluent to <20 °C giving safer materials handling, whilst also effectively stopping the reaction at a well-defined point, giving a known residence and reaction time.

It was found in some experiments that there was slight surging in the measured flow, and that simultaneously there were spikes in reflected power. It is postulated that this was caused by the liquid within the system boiling. To prevent this, the operating pressure of the system was increased from 4 to 10 bar, giving a maximum single phase operating temperature of 200 °C.

The design has two different reaction zones, the cavity, and the piping leading to the outlet. It was unknown at what point within the system the reaction occurred. To provide further insight and improve understanding, an extra sample point was introduced. This allowed for samples to be taken directly from the cavity outlet as well as at the outlet.

Figure 6-17 below shows a diagram of the experimental apparatus after modifications. The microwave cavity remained constant throughout with the modifications occurring before and after, allowing for direct comparisons between the two systems. Temperature monitoring, mass flow monitoring and control, microwave generator, HOMER tuner, microwave cavity, conventional heating apparatus were all kept constant.

Red: ¼ inch piping. Black: ½ inch piping and fittings. Blue: Heat exchanger loop. Green: low pressure collection vessel.
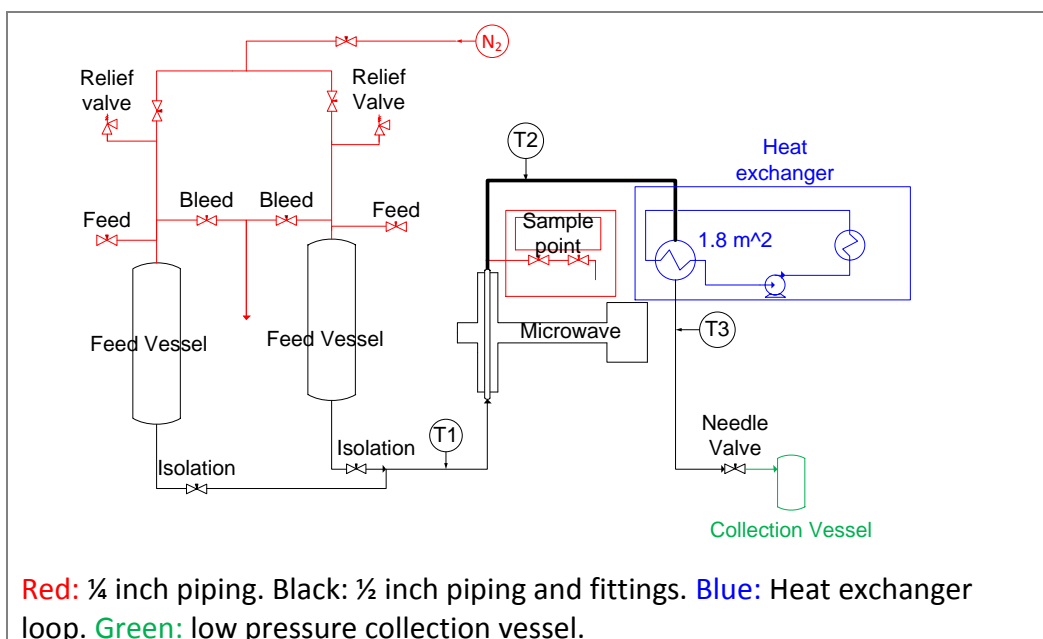
Figure 6-17: Simplified diagram of modified flow system. Different zones within the system are highlighted, fully detailed diagram can be found in Appendix 9.2.

6.8.1 Temperature profiles in flow with microwave heating

To reduce material usage and wastage, experiments were carried out at 4 litre scale; with the full 8 litre feed capacity only used where required.

From the work carried out previously in batch and flow, it has been shown that formation of MMA_2/MMA_3 was maximised at 100 °C (203 J/g). In this increased capacity system this was the only energy level investigated. To test the system after modifications, it was operated in the same manner as before; temperature profiles were produced at power levels of 500, 1000 and 2000 W.

Temperature profiles for heating of monomer to 100 °C are shown in Figure 6-18 below. It can be clearly seen that the system achieved steady state in terms of temperature measurement at the cavity outlet. Cavity outlet was defined as temperature measured at T2, shown in Figure 6-17.
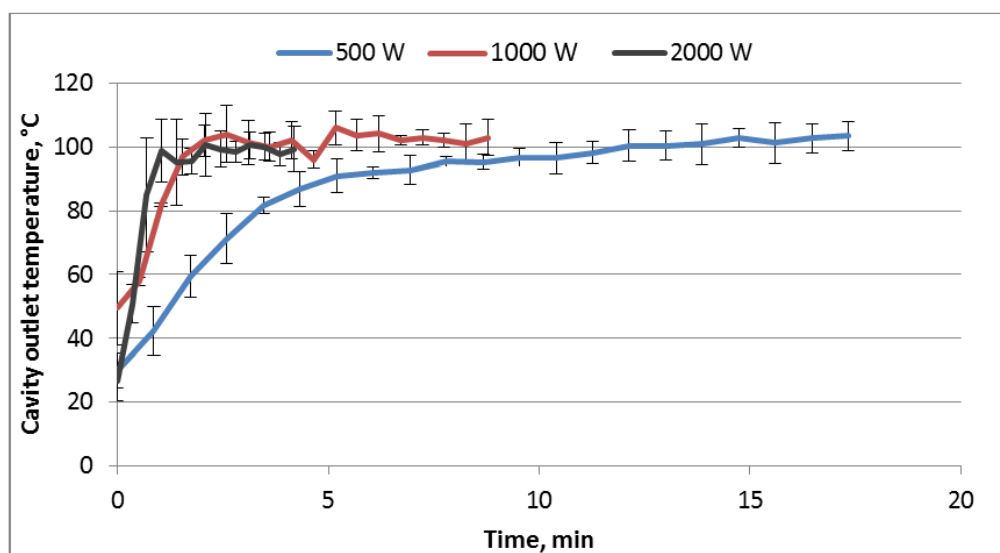
Figure 6-18: Temperature profiles, for heating of monomer using different microwave power levels, constant energy of 200 J/g.

As was shown previously in Section 6.2.4, there was an initial temperature gradient; caused by the material within the cavity not having the full residence time and consequently being heated to a lesser extent. As power level and flow rate were increased the system achieved steady state more rapidly, this was due to increased energy transfer and reduced residence time. It can be clearly seen that the system achieves steady state for several minutes at all three power levels investigated.

6.8.2   Flow polymerisation using modified design

Large scale reactions were carried out using 4 kg feed material at three different power levels 500, 1000, 2000 W. Energy input was kept constant at 200 J/g by variation of flow rate; 2.5, 5, 10 g/s respectively.

With the previous design, the small feed capacity only allowed for short experimental duration, because of this samples were only taken at the end of the experiment once steady state was achieved. With the larger feed capacity and additional sample point added to the system, the sampling frequency was increased. Samples were taken at 2 min intervals from both sample points; time corrections have been added to the results to take into account the time

delay for material passing between the two sample points, shown in Figure 6-19.
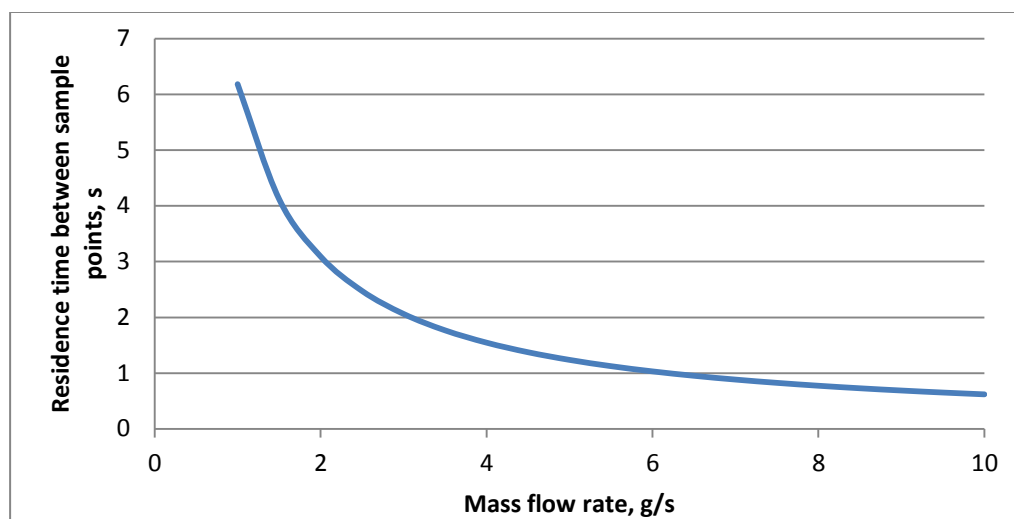
Figure 6-19: Time correction used to take into account the delay in material passing between the sample points at different mass flow rates.

6.8.2.1 Flow polymerisation at 500 W

Four litres reaction mixture was prepared by method, F4, and processed at 200 J/g 2.5 g/s at 500 W incident power.

Temperature profiles and conversion are shown below in Figure 6-20. Comparison between the two temperature profiles shows a similar trend to that previously shown in Section 6.2.1. With polymerisation occurring, the temperature continued to rise up to a steady state temperature of 185 °C, whilst for heating of pure monomer the temperature reached steady state at 100 °C.
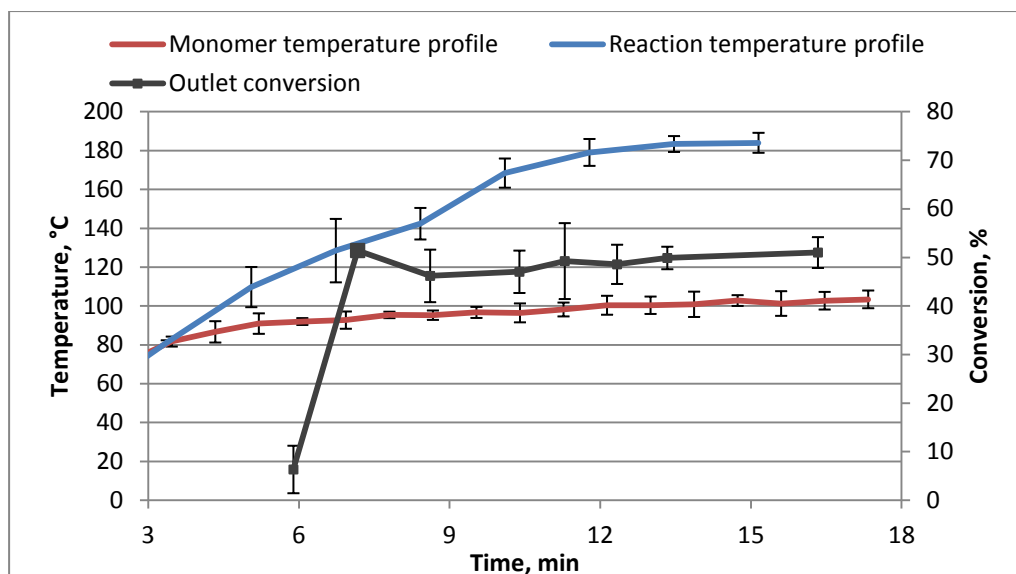
Figure 6-20: Polymerisation and monomer temperature profile, carried out at 500 W, 2.5 g/s at 100 °C temperature set point.

It is clearly shown that steady state conversion was rapidly achieved once the temperature reached 100 °C. Steady state conversion was achieved before temperature, this is as expected; it is not possible for steady state temperature to be achieved prior to conversion becoming constant. This is due to the temperature being dependent upon the energy contributed from the heat of reaction. Analysis of products formed showed that throughout the reaction MMA_2/MMA_3 was formed in the ratio 3:2, with <5 % higher tetramer present; GPC analysis showed no higher molecular weight oligomers present.

The steady state temperature achieved in this reaction was higher than that in both the 1 litre flow experiment, and in batch. Table 6-7 below shows data comparing these three systems, it is clearly seen that there is a drop in conversion as the scale was increased. It is proposed that this reduced conversion is not caused by the transition to flow, but rather by a number of factors:

1. **Reduced residence time:** as shown in Table 6-7 below there was a reduction in the volume of the reaction zone, reducing the reaction time before cooling.

180

2. **Reduced heat losses:** transition from batch to flow allows for reduced heat losses due to reduced surface area to volume ratio, and the system is at steady state due to the surround equipment being pre-heated.

3. **Bubble formation:** in the initially designed flow system a pressure of 4 bar was used, this could potentially allow for bubble formation, removing energy from the system *via* latent heat.

4. **Increased temperature:** the reduced heat losses and longer experimental duration allow for higher temperatures to be achieved, similar to that which would be expected from the theoretical temperature rise at 50 % conversion, see Table 6-5. This increased temperature is approaching the ceiling temperature of 220 °C causing depolymerisation to occur simultaneously.

From the above four options, it is most likely the reduced residence time that was causing the reduced conversion. This was due to this variable changing the most between experiments therefore having a larger impact.

Table 6-7: Conversion, temperature and residence time data for comparison between microwave batch experiments and flow carried out at 100 °C.

Experiment type	Conversion, %	Peak temperature, °C	Residence time, s	
			Cavity	After cavity
Batch	65±3	140	300	
1 litre flow[4]	55±2	160	64	89
4 litre flow[1]	50±2	185	64	26

Within the flow equipment there were two reaction zones, the microwave/conventional heating cavity and the piping from the cavity through to the outlet. In the larger system the reaction zone after the microwave cavity was reduced in volume due to the addition of post reactor cooling.

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[4] Power input: 500 W, flow rate: 2.5 g/s

With the large system it was possible to sample material at the cavity outlet, simultaneously to the piping outlet. This allowed for determination of where the bulk of the reaction occurred within the system. It is clearly shown in Figure 6-21 that 45 % of the conversion occurred entirely within the microwave cavity, a further 5 % then occurred in the 26 s between the exit of the cavity and the heat exchanger. This confirms the conclusions that were drawn from the temperature measurement at the cavity outlet; if the reaction were not occurring within the cavity the high temperatures would not be measured.
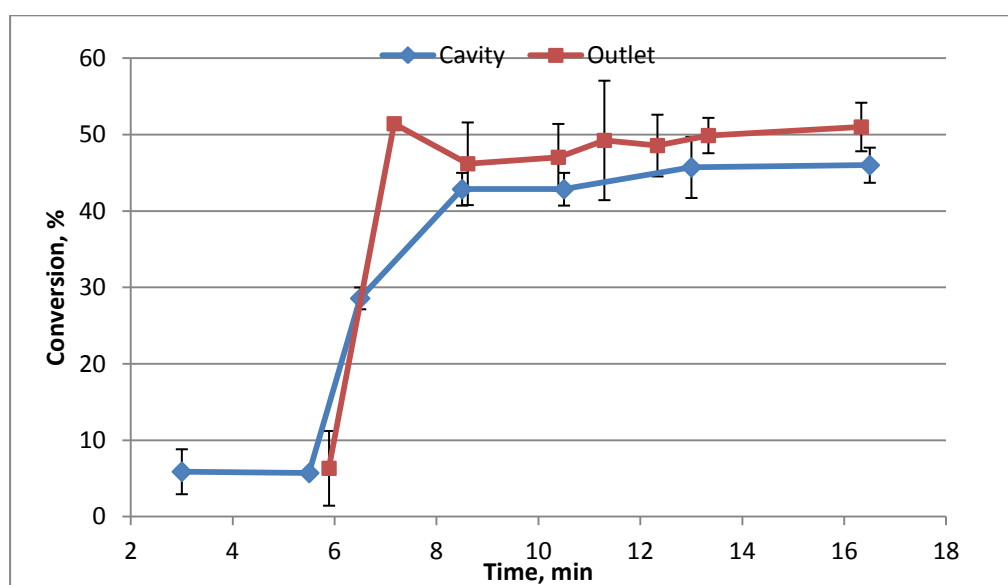
Figure 6-21: Conversion achieved within the microwave cavity and at the equipment outlet, carried out at 500 W, 200 J/g.

With the current design it was not possible to determine at what point within the microwave cavity the reaction occurred. It is not known at what point vertically within the reactor that the 100 °C temperature set point was reached. From microwave theory and knowledge of how single mode cavities work, it is hypothesised that the bulk of the heating occurs at the centre point of the cavity with some propagation of the electric field along the tube.

From the batch experiments carried out, it was shown that it took approximately 60 s for the reaction to reach its peak temperature once the 100 °C set point was reached, further detail was given in Section 5.2.2. When

calculated as a volume in flow this equated to 150 cm^3 at a flow rate of 2.5 g/s. assuming the same rate of reaction in both systems it can therefore be assumed that a 150 cm³ system volume is required to achieve the peak temperature. The total volume of the microwave cavity is 320 cm³, thus 150 cm³ measured back from the thermocouple calculates back to just above the centre of the cavity, thus helping to confirm the above hypothesis. This is shown in Figure 6-22 below, the temperature profile is a theoretical profile derived from batch heating experiments.
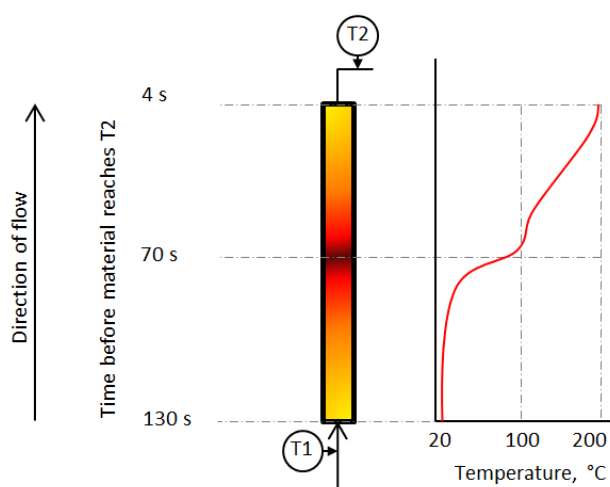
Figure 6-22: Graphical representation of temperature profile and residence times within microwave cavity at 2.5 g/s, 500 W with 100 °C temperature set point. Yellow indicates regions with low levels of heating, red indicates high heating rate.

The best way in which this could be proved is by the addition of temperature measurement within the cavity, the use of optical fibre at different height positions within the cavity could give a temperature gradient. The other alternative would be to model the system; this would require a highly complex model involving electromagnetics, fluid properties and reaction kinetics. This is however beyond the scope of this work.

6.8.2.2 Flow polymerisation at 1000 W

Four litres reaction mixture was prepared by method F4 defined in methodology Chapter, and processed at 200 J/g 2.5 g/s at 500 W incident power.

Scale up to 5 g/s, 1000 W, 200 J/g was found to give similar results to that at 500 W. Figure 6-23 shows similar trend to that in Figure 6-20 with conversion rapidly achieving steady state once the temperature exceeded 100 °C. It takes a further 6 min before temperature achieves steady state at 185 °C, the same as that found at 2.5 g/s.

Analysis of products formed showed that throughout the reaction MMA_2/MMA_3 was formed in the ratio 3:2, with <5 % higher tetramer present; GPC analysis showed no higher molecular weight oligomers present.

Figure 6-23: Temperature profile and conversion data, for flow polymerisation carried out at 1000 W, 5 g/s at 100 °C temperature set point.

Importantly it is noted that the total conversion achieved was lower than that at 500W, 2.5 g/s, 43 % compared to 50 %. This helps to confirm the hypothesis that the conversion was being limited by the residence time within the system; increasing the throughput to 5 g/s halves the residence time to 45 s.

Analysis of samples taken directly from the microwave cavity showed that there was 38 % conversion, this was higher than expected, due to the short reaction times at this point. This higher than expected conversion could be caused by the delay between sampling and quenching of the sample, at these extreme temperatures a few seconds can allow for a large change in composition.

If the hypothesis of reduced conversion due to shorter residence times is true, it would be expected that scaling up the reaction to 2 kW, 10 g/s would once again reduce conversion as the residence time would be <25 s. From the batch experiments and examination of the temperature profile, it would be expected that there would be very little conversion achieved; in batch it was shown to take 1 min for the peak temperature to be achieved.

6.8.2.3 Flow polymerisation at 2000 W

Eight litres reaction mixture was prepared by method F8 defined in methodology Chapter, and processed at 200 J/g 2.5 g/s with 500 W incident power.

Figure 6-24 shows temperature profiles for both 1000 and 2000 W reactions carried out at 200 J/g and 5 and 10 g/s respectively. The 2000 W reaction was carried out using 8 litres of monomer to maximise experimental duration. There are some clear and significant differences noted. At 2 kW there was oscillation in temperature between 100-180 °C. From these temperatures it indicates that the system is oscillating between reacting and not reacting.
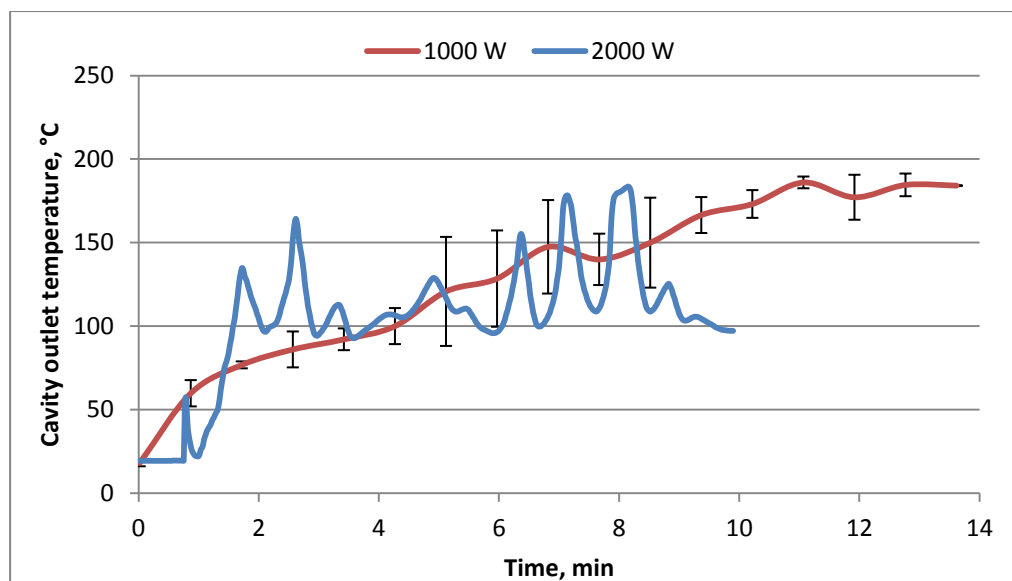
Figure 6-24: Temperature profile comparing 1000 and 2000 W microwave flow polymerisation.

A closer inspection of temperature and flow rate in Figure 6-25 below, shows that these are intimately linked. Peaks in temperature correspond to troughs in flow rate. This level of variation in flow rate was found in all experiments; however it had a significant effect at 2 kW indicating the inherent instability at this throughput. This shows that the residence time within the microwave cavity is too low (16 s) for the reaction to occur, hence there was no rise in temperature. When the flow rate was reduced the residence time (20 s) became long enough for there to be a measureable temperature increase.
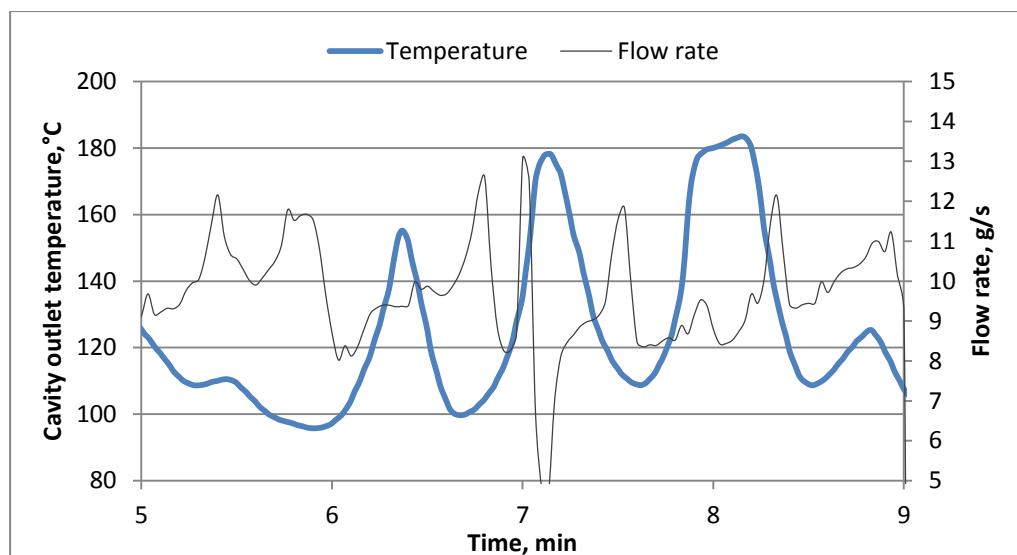
Figure 6-25: Temperature and mass flow rate for 2000 W flow polymerisation experiment

Analysis of conversion gave wide variation, samples taken were found to have 25±17 % conversion. This is a significantly larger variation than that found in previous experiments. It is proposed that this variation was caused by the residence time within the cavity being too low, therefore not allowing for conversion to occur.

To reduce the variation within this result and to allow for further scale up of flaw rate, it would be required to increase the volume of the system prior to cooling. Thus allowing for increased residence time before cooling occurred. This would have a double advantage of allowing for investigation into the effects of residence time upon conversion, at lower flow rates.

6.8.3 Conventionally heated large scale flow polymerisation

As has been carried out all the way through this project, direct comparisons were made between conventional and microwave heating. As with previous conventional flow experiments, heating was provided using rubberised heating tape with a maximum energy output of 1050 W, the tape was operated at a 120 °C temperature set point throughout.

Conventional experiments were carried out at one flow rate and energy input, the required flow rate was determined experimentally as 2.0 g/s to give 100

°C, by heating of pure monomer. Four litres reaction mixture was prepared by method, F4, and processed at 200 J/g at 500 W incident power.

Conventionally heated flow polymerisation results

Figure 6-26 below shows temperature and conversion data for the reactions carried out. With the flow rate used, this reaction is similar to that of a 500 W microwave reaction. Similar trends to those found in microwave heating were witnessed. The conversion rapidly achieved steady state, with temperature achieving a slightly higher steady state value of 200 °C.
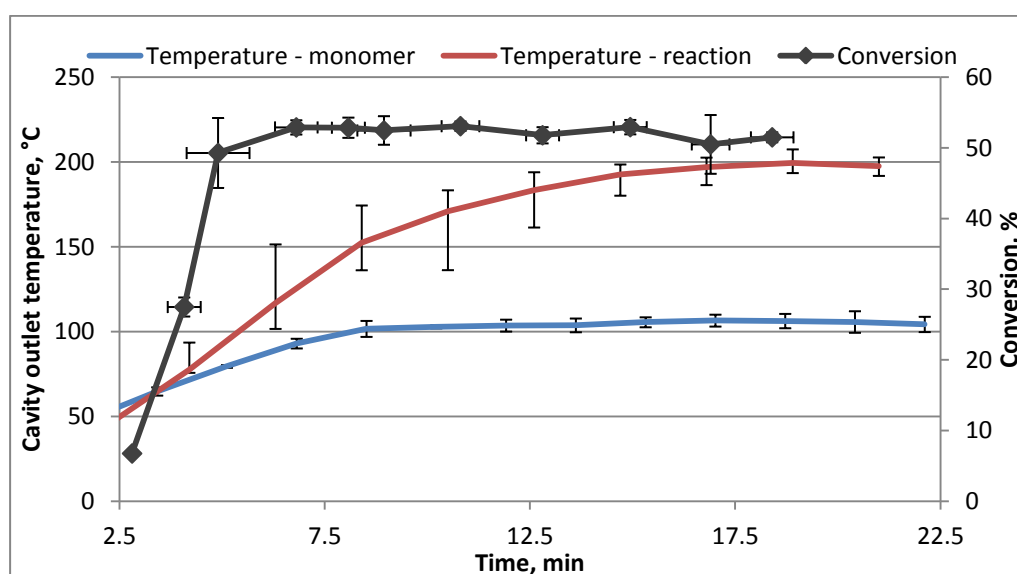
Figure 6-26: Temperature and conversion data for conventionally heated flow polymerisation.

When directly comparing microwave and conventional reactions in Figure 6-27 it can be seen that there was very little difference between the two systems, there was however a longer experimental duration with conventional heating. This was caused by the reduced flow rate of 0.5 g/s.

It can be seen that there was a slight increase in conversion in the conventional system (1-2 %) and that there was an increased steady state temperature (≈15 °C), these variations are however within experimental variation. It is expected that this increase in conversion was caused entirely by the reduced flow rate giving an 80 s residence time within the cavity rather than 64 s.

Analysis of products formed showed that throughout the reaction MMA_2/MMA_3 was formed in the ratio 3:2, with <5 % higher tetramer present; GPC analysis showed no higher molecular weight oligomers present.
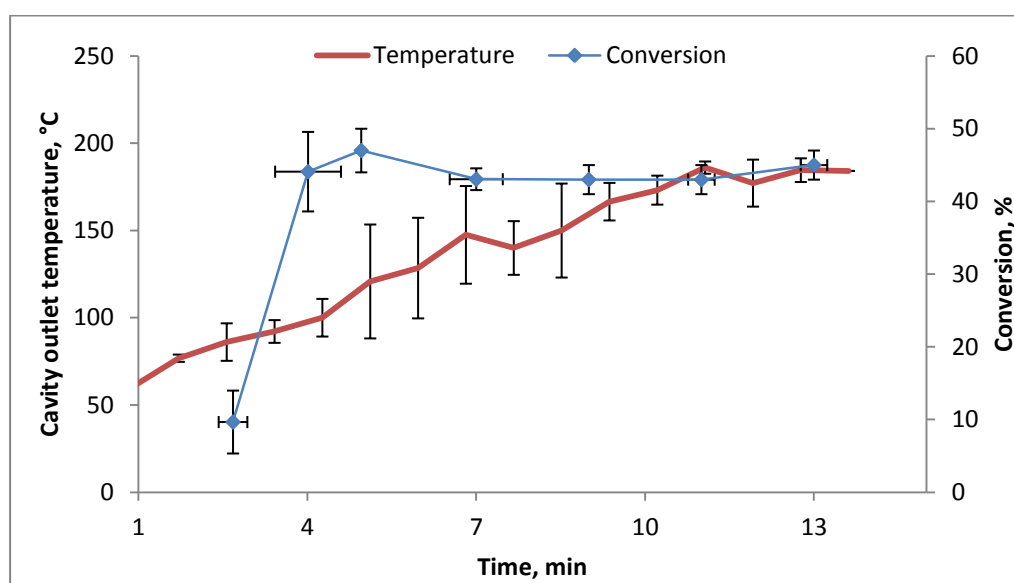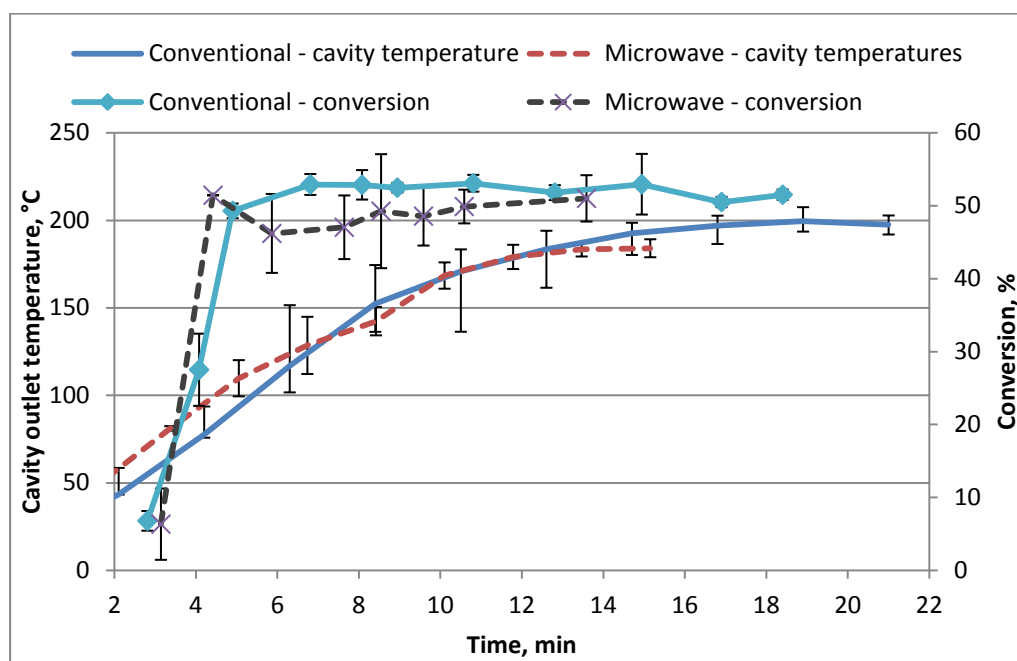

Figure 6-27: Comparison of temperature profile and conversion achieved between conventional and 500 W microwave flow experiment at 100 °C set point.

This gives further evidence that the use of microwave heating over conventional has no quantifiable effect upon the reaction.

6.9 Modified flow design summary and conclusion

This Section has taken the original design concept and modified it in order to allow more data to be gathered about the reaction, with the addition of an extra sample point. It also allowed for longer experimental duration and operation at increased power level. In order to operate at 2 kW further modifications to the system would be required.

It has been shown that in the scale up from a batch to flow system there was a reduction in conversion achieved from 65 to around 50 % (at 500 W, 2.5 g/s). This can be explained by the significant reductions in residence times within the system; this was also confirmed when comparing this design and

the initial flow design, as the modifications gave reduced residence time caused by the addition of cooling 55 % compared to 50 %. Scaling up the reaction from 2.5 g/s to 5 g/s helped to confirm this, as a further reduction in conversion was witnessed. It is therefore hypothesised that this can be used as a control method to achieve a specific level of conversion. Increasing or reducing this volume can be used to control the product produced.

Direct comparison using conventional heating was carried out, this closely matched the experiments carried out at 500 W. It was found that there was a very slight increase in conversion achieved, this was however caused by the increased residence time and was not a benefit offered by the heating mechanism.

NMR and GPC analysis of products formed has shown that in all of the reactions carried out there was no significant variation in product distribution, and that in all reactions the target materials were produced, with no higher molecular weight polymeric material formed.

6.10 Verification of product analysis

Throughout this work product analysis was carried out *via* the use of nuclear magnetic resonance to determine conversion and relative abundances of MMA_2-MMA_4. Gel permeation chromatography (GPC) was used to ensure no higher molecular weight products were formed, these cannot be determined by NMR due to similar H^1 environments.

In order to verify the results shown by these two well defined and understood techniques, further analysis using both coupled gas chromatography with mass spectroscopy (GC-MS) and thermo gravimetric analysis (TGA) was carried out.

Twelve samples were chosen for further analysis:

1. Microwave 4 litre scale flow at 500 W, 100 °C temperature set point
   a. 2 cavity outlet samples
   b. 2 outlet samples

2. Conventional 4 litre scale flow at 100 °C temperature set point.

   a. 2 cavity outlet samples

   b. 2 outlet samples

Analysis of the 12 samples by NMR and GPC showed that there was very little variation between them, there was slight variation in conversion achieved, as discussed previously in Section 6.8.3 Figure 6-28 below shows abundances of the different components in the samples taken, it can be clearly seen that there are similar yields of dimer/trimer with small amounts of tetramer formed.
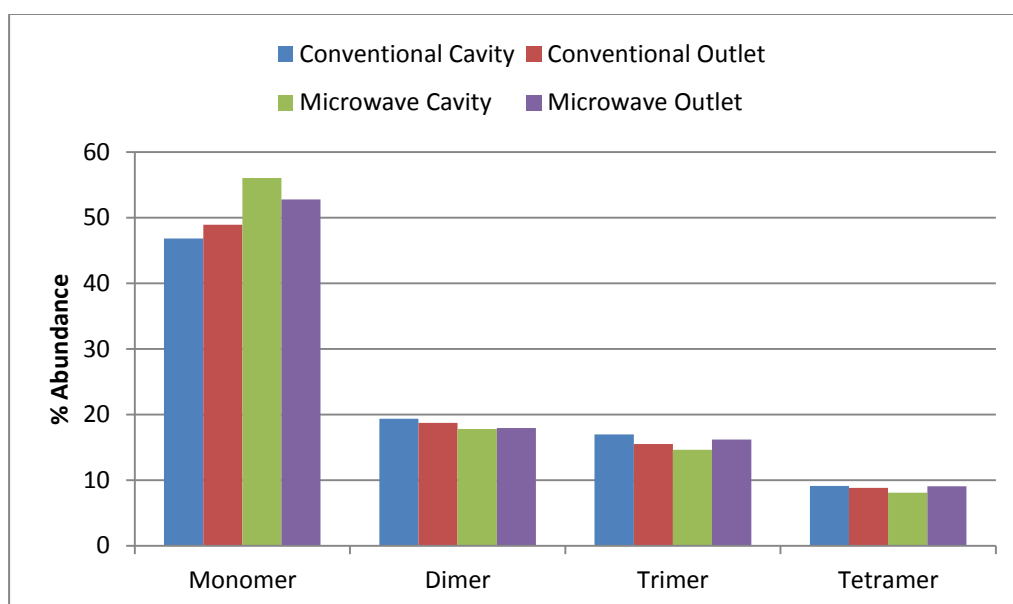
Figure 6-28: Product analysis by NMR for microwave and conventionally heated flow experiments carried out at 100 °C.

6.10.1 Determination of product composition by gas chromatography (GC)

Gas chromatography was used with mass spectroscopy. Samples were prepared and analysed using the method set out in Section 4.5.2. This technique is ideal for analysis of these short chain oligomers; this was due to the high resolution available and the clear separation of the products, with determination available up to hexamer. It was not possible to use this technique for the majority of samples produced; this was due to the lack of availability of the equipment.

Figure 6-29 below shows an example chromatograph produced using GC.
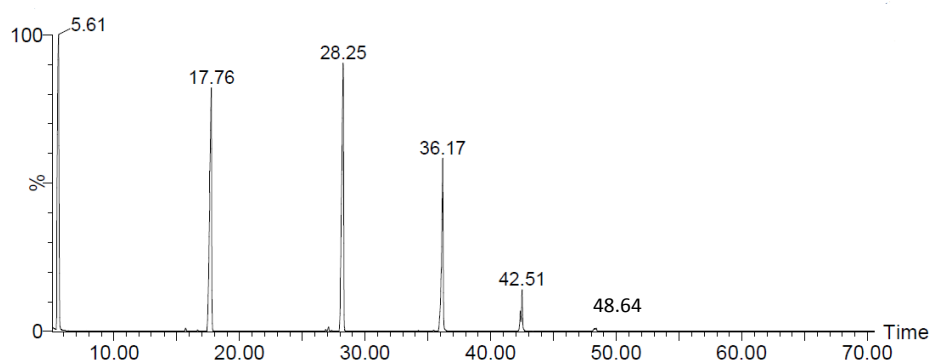
Figure 6-29: GC chromatograph for a typical polymerisation reaction, showing peaks for the different MMA oligomers present.

Table 5-8 shows residence time for the various compounds within the mixture. It can be clearly seen that there was good baseline separation between the different molecular weight oligomers, relative abundance was calculated based upon the relative peak areas.

Table 6-8: Elution time of methyl methacrylate oligomers in GC column, and molar composition of 4 litre microwave flow reaction carried out at 500 W and 100 °C temperature set point

	Elution time	Peak area	% abundance (molar basis)
Monomer	5.61	26187	44
Dimer	17.76	37352	32
Trimer	28.25	30679	17
Tetramer	36.17	11049	5
Pentamer	42.51	6153	2
Hexamer	48.64	1003	0.3

Analysis of pure samples (MMA, MMA_2, MMA_3), was carried out to investigate the linearity of response against conversion, samples were prepared by serial dilution within DCM. Higher order pure samples were unable to be produced *via* distillation with the vacuum available in the lab (Moon 2013). It was found that the chemicals responded linearly, shown in Section 4.5.2.

When comparing conventional and microwave product compositions, Figure 6-30, it can be clearly seen that there was no significant variation between the conventional and microwave reactions, with similar product distributions.
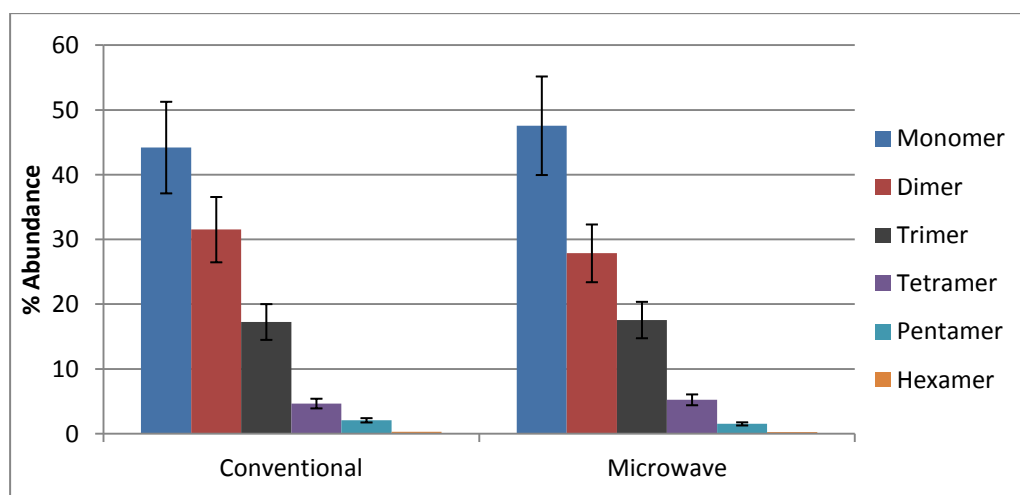
Figure 6-30: Product analysis by GPC for microwave and conventionally heated 4 litre flow experiments carried out at 100 °C.

6.10.2 Determination of product composition by thermo-gravimetric analysis (TGA)

TGA is used to determine the mass change of a material as a function of temperature within a controlled inert atmosphere. Commonly with polymers this is used to determine degradation temperatures. The aim of its use in this work was to separate products based upon their relative volatilities, in order to determine percentage abundance of materials present. Within this technique there was a risk of the samples polymerising during heating, it is however proposed that this did not occur due to no initiator present, and monomer evaporating at low temperatures. With this equipment there was no method of analysing the vaporised product, it was however well know as to what compounds were present, this was determined via NMR, and GC-MS. The purpose of this was to give a physical measure of the relative quantities.

Using the method for separation explained in Section 5.4, separation of products was achieved up to tetramer. Figure 6-31 below shows total mass and derivative mass change (mass/time) as temperature was stepped up and held isothermally. It can be clearly seen that after temperature was stepped there was a large spike in the derivative mass loss (mass/time) this then dropped significantly to below 0.1, where mass loss became a constant. Zero mass loss was not achieved, due to the relative vapour pressures. To achieve a higher level of precision smaller temperature steps and longer isothermal times would have been required. This method was a trade-off against time, and was found to give adequate precision to compare with other techniques. It was not possible to achieve separation of oligomers higher than MMA_4, this was due to the small mass present and the high viscosity of the remaining sample inhibiting mass transfer, over 95 % of the sample mass was separated.
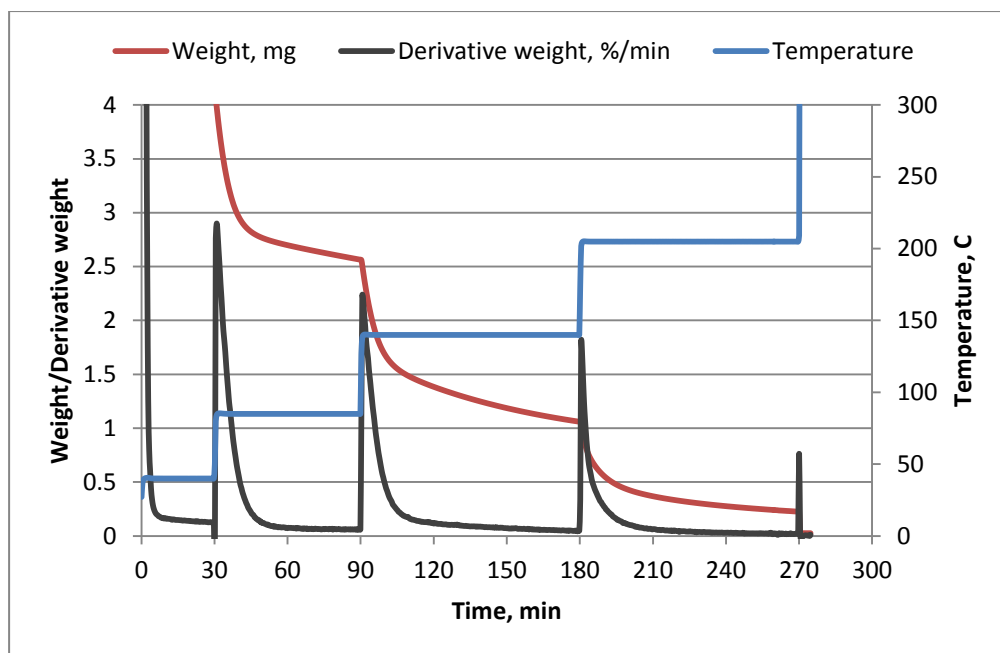
Figure 6-31: TGA data output for method used to separate products formed in a typical flow polymerisation reaction.

Comparison between the four samples, as with NMR and GC shows that there was no significant variation in product composition between the four samples taken.
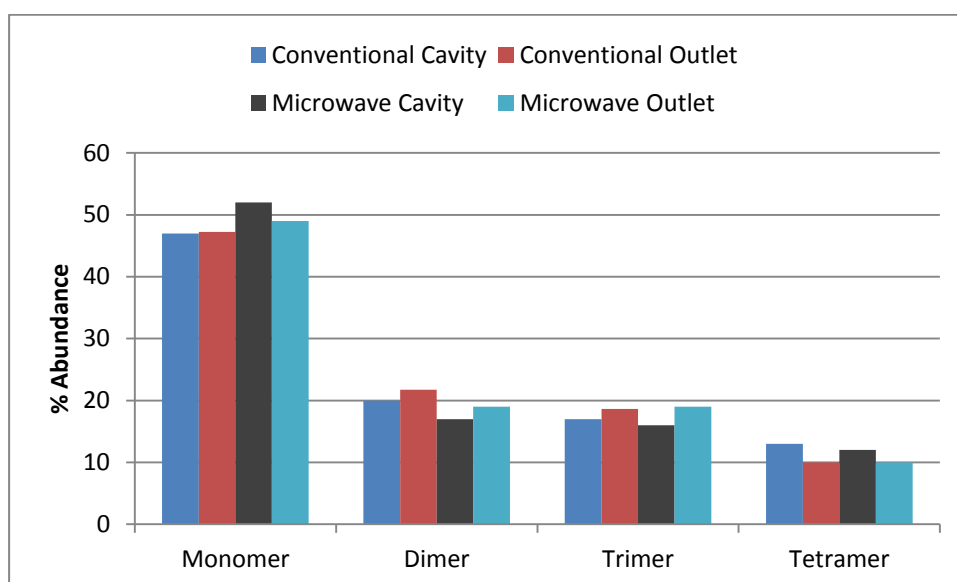
Figure 6-32: Product analysis by TGA for microwave and conventionally heated 4 litre flow experiments carried out at 100 °C.

6.10.3 Summary of product analysis results

Analysis using the three techniques has shown that in all 8 samples taken there was no significant variation in composition between them.

When comparing the three techniques used there were some variations in results achieved, in Figure 6-33 below it can be seen that both NMR and TGA give a very similar measure of content. GC gave reduced measure of monomer (8 %) and increased dimer (8 %); it then gave close approximation with the other techniques for trimer and tetramer. It is postulated that this was caused by evaporation of sample, due to the mcg samples taken in GC preparation, evaporation of monomer would cause this effect. The advantage of the GC is that it can account for >99 % of the sample mass, resolving composition up to that of hexamer, whereas NMR and TGA only account up to tetramer.
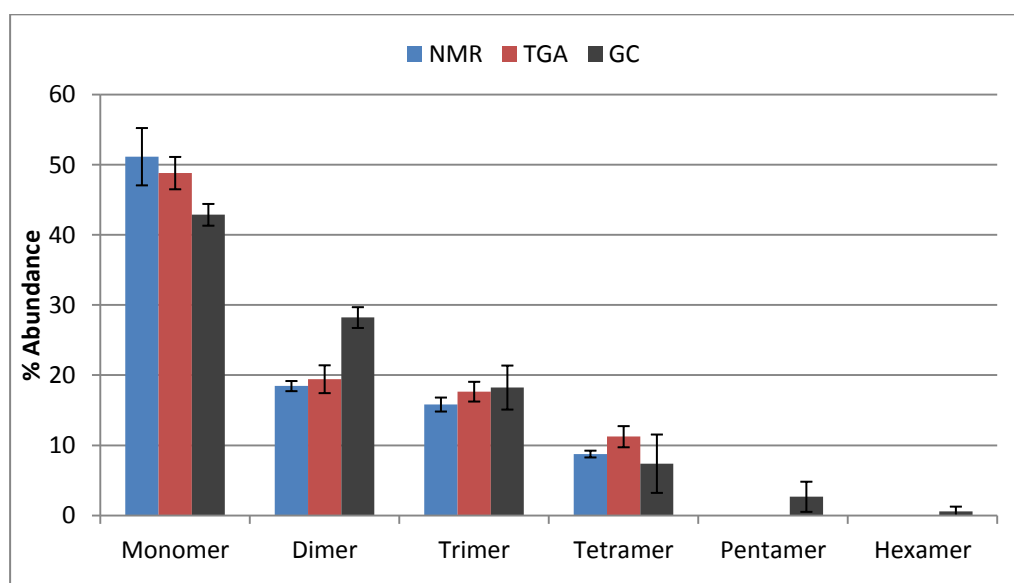
Figure 6-33: Comparison between average product distributions produced using NMR, GPC, and TGA.

This analysis of a limited number of samples by two other independent techniques has shown that NMR is suitable for analysis of the products formed, hence validating the use of this technique within this work.

6.11 Flow polymerisation summary and conclusions

The aim of this project was to design and create a flow system that was able to produce short chain methyl methacrylate oligomers in a continuous, safe and repeatable manner. From this the aim was to carry out direct comparison between conventional and microwave heating, the purpose of which was to determine any potential benefits offered by either heating source. As part of this scale up process small scale, highly controlled batch experiments were carried out to determine the optimum operating conditions for the reaction. Comparison with these small scale reactions was essential as it determined the effects of adopting flow upon the chemistry.

A successful flow apparatus was created, in which flow polymerisation was carried out at 250, 500, 1000 and 2000 W, at three different energy inputs; with mass flow used to control the energy input. It has been demonstrated that the equipment can operate in a repeatable manner, allowing for conventional comparisons to be carried out.

Comparison of results achieved in flow compared to batch have shown that the flow system could produce the same target materials in a continuous manner, thus allowing for production of up to 36 kg/hour at 1000 W. Analysis of conversion showed that there was a reduction in conversion achieved, this reduction was caused entirely by the reduced residence times; as was proven by increasing the power level and flow rate. Modification of the system should allow for 65 % conversion to be achieved, this is the maximum achieved in batch. No further conversion could be achieved due the nature of CCT polymerisation, (see background chemistry Sections 1.1.6.1-1.1.7. for further detail).

Direct comparison between conventional and microwave heating at increased scale has shown that there was no quantifiable variation between the two energy sources. The same levels of conversion, product formation, rate of reaction and energy input were achieved.

There were some slight variations in the physical geometry of the heating Sections used in both systems, with the conventional system having a longer heating zone. This is not a significant benefit offered by microwave energy; it is purely a function of heat transfer and surface area. It was found during experiments that the use of microwave energy gave more control than conventional heating; energy input could be adjusted almost instantaneously at 1 W increments. This was not possible with conventional heating, with the equipment used. With a more optimised conventional heating zone it is expected that these benefits would be reduced.

In conclusion, it has been shown that with this chemistry that there were no quantifiable benefits offered by the use of microwave heating over conventional. The reaction has been shown to be scaled up safely and repeatable from small scale batch to relatively large scale lab flow equipment. 50-55 % conversion to the target materials could be achieved in a continuous and repeatable manner.

7 Conclusions and further work

7.1 Conclusions

The aim of this work was to create a process which could safely, efficiently and repeatably produce low molecular weight methyl methacrylate oligomers at a minimum of 40 % conversion. Investigation into microwave and conventional heating, with the use of batch and continuous flow reactor geometries was undertaken. Throughout all scales of the work direct comparisons were made between both heating sources, which has not been shown by any other researcher. The purpose of this was to quantify any potential variations between both heating sources and those caused by the transition from batch to flow.

7.1.1 Batch experiments

It was hypothesised at the start of this work that the microwave effect shown by numerous researchers was caused in many cases due to poor temperature measurement and poor understanding of the way in which microwaves heat. This gave poor experimental design and comparisons being drawn between incomparable conventional and microwave experiments. Often one or many of the parameters below were not kept constant during these comparisons: different reaction conditions (temperature, pressure), reactor geometry, stirring rate, heating rate or cooling rate.

IR is a commonly used technique for measurement of temperature, as it is non-contact, easy to use and low cost; because of this it is fitted as standard to a large majority of off-the-shelf microwave equipment. Experiments were carried out at 50 cm³ scale to investigate the effect of IR against optical temperature measurement, when compared to conventional heating. It was found that when using optical fibre control there was no variation between microwave and conventionally heated reactions; this has been demonstrated under a wide range of operating conditions. IR measurement was found to

give a -42 °C error in temperature measured, hence giving a 60 % increase in conversion.

Investigation into, and quantification of any potential selective heating effects were carried out with the use of a single mode resonant cavity coupled with automatic impedance matching and power recording at 330-2000 W. It was shown that power had no effect upon the reaction, other than to increase the heating rate. From this it was expected that if there were any selective heating effects that increased power density would have highlighted them.

This batch work has shown that with this specific chemistry, that when rigorous comparison between conventional and microwave heating was carried out there was no "microwave effect". No microwave effects, that have been shown by other researchers could be reproduced, these microwave effects that have been shown are increased rate, conversion, or improved product purity.

7.1.2 Scale up and use of flow

It has been clearly shown in this work that this highly exothermic reaction can be successfully scaled up by the adoption of flow (38 litre/hour maximum), using pressurised equipment. It was shown that when attempting to scale up this reaction in batch with the use of conventional laboratory glassware that it was not possible due to pressure build up and sudden vapour release.

It was shown that scale up of flow rate led to a reduced overall conversion; it is proposed that this was caused by the reduced space time within the reactor. This could be investigated with the addition of increased volume to the reaction Section; this was not however covered within this work.

Direct comparison between conventional and microwave heating was carried out with both flow designs. It has been shown that in flow, when comparing microwave heating to conventional, there were no quantifiable benefits in conversion, rate of reaction or product quality.

It has been shown rigorously that with this type of chemistry that there were no quantifiable benefits offered by the use of microwave heating when compared to conventional. This was shown by investigation using direct comparison and investigation into the effects of power density upon the reaction.

This work has demonstrated that for the first time at this scale, that polymerisation can be carried out with the use of microwave heating. It was shown that scale up of flow rate and power had no effect upon the products formed when compared to the small scale batch reactions. Any reductions in conversion achieved are hypothesised to be caused by the reduced residence time within the reactor.

7.2   Further work

The main aim of this work was the development of a continuous flow microwave polymerisation system. From this work some key areas for further investigation have been highlighted.

It was found that when carrying out flow experiments with increased power and flow rate that there was a reduction in conversion; it was hypothesised that this was caused by the reduced reaction times in flow compared to batch, this hypothesis was produced as it was found that as flow rate was increased, the residence time and conversion both dropped. Quantification of this is important as the viability of this technique is dependent upon conversion being maximised. It is proposed that this could be proven by increasing the volume of the reaction zone, thus increasing residence time prior to quenching of the reaction.

This phenomenon of reduced conversion could be further investigated at small scale. Batch experiments were heated to temperature set point and allowed to react for 5 min before sampling. This was carried out as a safety precaution to for the reaction to cool and pressure to drop. Examination of temperature profiles indicates that the reaction is completed significantly faster than this. Using liquid nitrogen to quench reactions could be a viable

method of determining a more precise relationship between time and conversion. This, coupled with the above modifications to the flow system, would allow for increased confidence of the effects of residence time upon the reaction.

This flow system was designed with the aim of producing low molecular weight methyl methacrylate oligomers; from an academic and industrial view point it would be of interest to investigate how this system could be modified for production of higher molecular weights. There are significant challenges faced with this, primarily from increased viscosity, the current design would be unsuitable as fouling and blockage of piping could occur. Re-design with the use of extrusion as the pumping mechanism could allow for high molecular weight polymer formation. This would require a complete remodel of the system, with the removal of the expansion and contraction in piping, which would cause blockage.

The current microwave cavity, choke and tube design in use was not designed with the use of electromagnetic models; it was created using an iterative design process, based upon a pre-existing microwave cavity. This design has been found to give efficient energy transfer (>99 %). It is believed that the main heating within the cavity occurred within the central zone. It is however possible that due to presence of the dielectric within the chokes, there could be propagation within the entire length of tube within the cavity. It would be interesting to better understand this as it could lead to a more compact and better design. This could be carried out using the following approaches:

Electromagnetically model the system - This would be a highly complex model as the dynamic system includes a chemical reaction and a wide range of temperatures. This gives changes in the physical and dielectric properties of the material. This would require dielectric measurements to be carried out at an extensive range of compositions and temperatures.

Internal temperature measurement - Direct measurement of the material within the microwave cavity, with the use of optical fibres at different axial

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and radial locations within the cavity, would give a more detailed understanding of where the heating occurred. The complications of this are ensuring material and electromagnetic containment.

There are several ways in which this system could be optimised to improve efficiency and reduce plant footprint, these are however beyond the scope of this work and don't apply as an academic venture. There is significant energy released during this reaction as heat, this could be recovered and used to heat the initial feed significantly reducing energy requirement, if it is assumed that the specific heat capacity of the products are the same as the feed and that there is 100 % heat recovery this could allow for a self-sustaining reaction. Product separation is of further interest, with 50-60 % conversion being achieved there is still large amounts of monomer present in the reactor effluent, if this material were to be passed into a single stage separation vessel at low pressure, the existing energy within the system could be used to vaporise and separate a large portion of the monomer present.

Efficiency improvements come from the adaption of precise monitoring and control techniques; it has been shown that there is a large change in dielectric properties between the start material and the products. This would make it possible to monitor the reaction in real time with the use of dielectric properties; this has been shown to work well with batch reactions but has not yet been tested in flow.

The major drawback with CCT polymerisation is the use of cobalt catalysts which are highly active and have a characteristic dark brown colour. For this product to be viable it would be required to remove this catalyst. It has been shown to be possible to remove MMA_2/MMA_3 *via* distillation techniques. This is a highly energy and time intensive process and does not remove all products formed. It would be advantageous to strip the catalyst from the products rather than the products from the catalyst. This may be achievable with the use of a chemical stripping or washing process; it is however beyond the scope of this work.

For this process to be scaled up to a meaningful size it would be required that the process is economic. It has been shown that there were no selective heating effects or benefits found when using microwave heating, therefore the advantage of the use of high cost microwave processing are negated. It may be viable to carry out this process as a conventional system. Analysis of the potential markets and analysis of the product values would be required, the high cost of the feed stocks make this an unlikely prospect.

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9 Appendices

9.1 Material properties

Table 9-1: physical properties of methyl methacrylate at ambient conditions (Rowley, Wilding et al. 2007).

	Value	Unit
Molecular mass	100.116	
Density	940	kg/m³
Normal boiling point	100	°C
Specific heat capacity	2.54	J/g.K

Physical properties were calculated using the following equations, with the use of pre-defined constants Table 9-2. These were taken from (Rowley, Wilding et al. 2007).

$$Vapour\ pressure\,(P\ psi) = \exp\left[C1 + \frac{C2}{T} + C3\ln(T) + C4 \times T^{C5} \right]$$

$$Density\,(\rho\,mol\,/\,dm^3) = C1\,/\,C2^{(1+(1-T/C3)^{C4})}$$

$$Specific\ heat\ capacity\,(C_p\ J\,/\,kmol.K) = C1 + C2T + C3T^2$$

Table 9-2: constants for calculation of physical properties of methyl methacrylate, minimum and maximum temperatures included (Rowley, Wilding et al. 2007).

Constant	Vapour pressure, psi	Density, mol/dm³	Specific heat capacity, J/kmol.K
C1	107.36	0.7761	255100
C2	-8085.35	0.25068	-938.4
C3	-12.72	566	2.413
C4	8.33E-06	0.29775	-
C5	2	-	-

T_{min} (°C)	-48	-49	-49
T_{max} (°C)	293	293	100

9.1.1 Heat of reaction

Heat of reaction for formation of dimer from MMA can be calculated with the use of a Hess cycle. The Hess cycle is based upon Hess' law which states that the total enthalpy change during a reaction is the same whether the reaction is made in one or several steps. Therefore allowing for the overall heat of reaction to be calculated *via* an alternative route, the use of heat of formation for specific bonds. This is shown below:

$$MMA \longrightarrow 0.5\,MMA_2$$
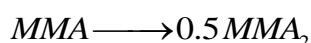
Bond	ΔH_f	Monomer		Dimer	
		N_b	$\Delta H_f \times N_b$	N_b	$\Delta H_f \times N_b$
C-H	413	8	3304	16	6608
C-O	358	2	716	4	1432
C=O	805	1	805	2	1610
C-C	347	2	694	6	2082
C=C	614	1	614	1	614
Total	-		6133	-	12346

$$\Delta H_{reaction} = \Delta H_{f\,(products)} - \Delta H_{f\,(reactants)}$$

$$\Delta H_{reaction} = 6133 - 0.5(12346) = -40kJ\,/\,mol$$

This reaction is highly exothermic; if higher molecular weight products are formed the heat of reaction can be as high as -80 kJ/mol.

From this heat of a reaction, if 100 % conversion to dimer is achieved within an adiabatic system, a theoretical temperature rise can be calculated.

$$\Delta H = -40kJ\,/\,mol = -40000J\,/\,mol$$

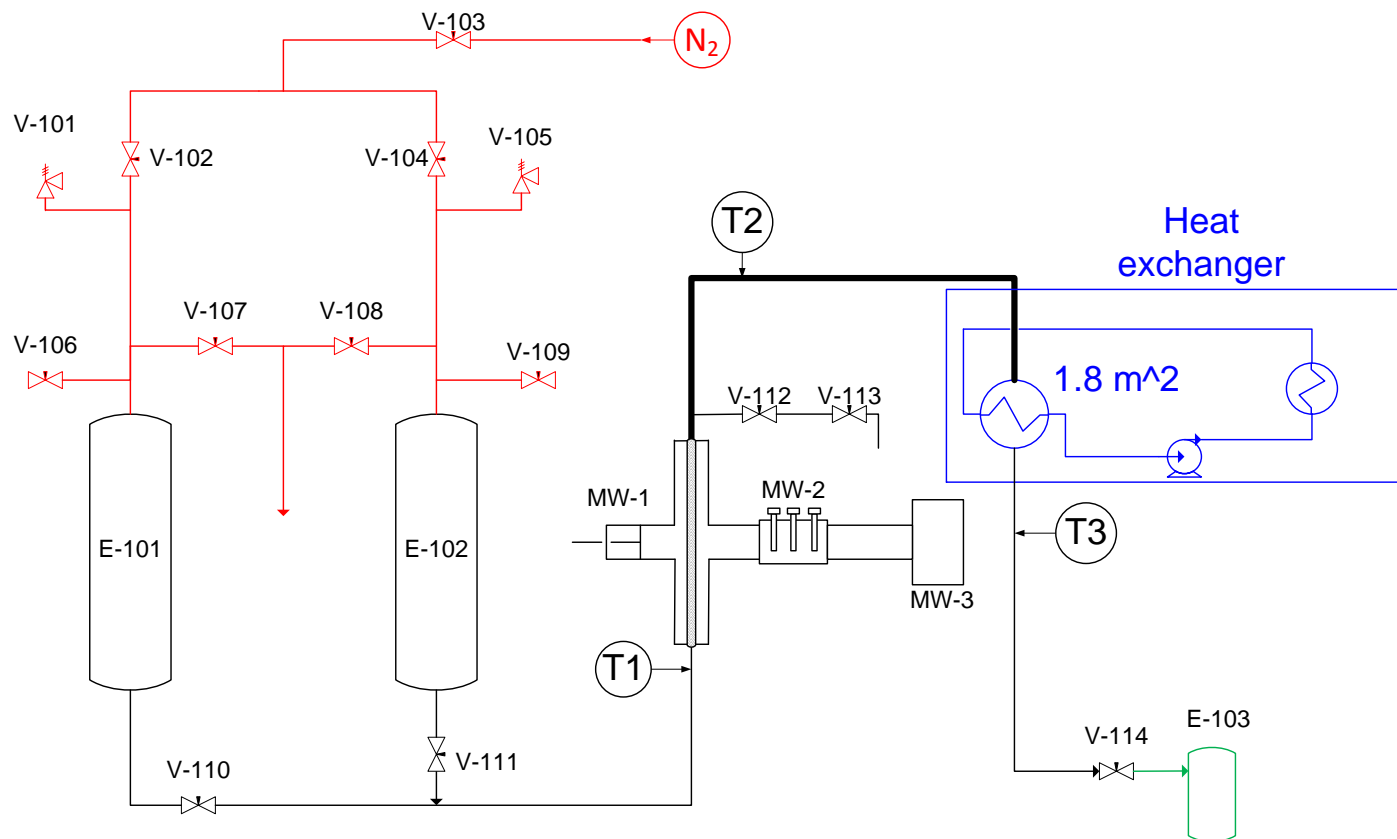$$C_p = 254 J/mol.K$$

$$\Delta T = \frac{\Delta H}{C_p} X$$

$$\Delta T = \frac{40000}{254} 1 = 157.5^{o} C$$

Where

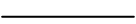|		
X	:	Conversion
ΔT	:	Temperature rise (°C, K)
ΔH	:	Heat of reaction (J/mol)
C_p	:	Specific heat capacity (J/mol.K)

9.2   Piping layout for redesigned flow apparatus

Diagram and table shown below.

Red: ¼ inch piping. Black: ½ inch piping and fittings. Blue: Heat exchanger loop. Green: low pressure collection vessel.

Figure 9-1: Detailed diagram for modified flow system, coloured zones are detailed above.

Table 9-3: Equipment list for modified flow system.

ID	Description	Purpose
V-101	¼ inch relief valve	Pressure relief
V-102	¼ inch ball valve	Pressure isolation
V-103	¼ inch ball valve	Pressure isolation
V-104	¼ inch ball valve	Pressure isolation
V-105	¼ inch relief valve	Pressure relief
V-106	¼ inch ball valve	Feed port
V-107	¼ inch ball valve	Bleed point
V-108	¼ inch ball valve	Bleed point
V-109	¼ inch ball valve	Feed port
V-110	½ inch ball valve	Flow isolation
V-111	½ inch ball valve	Flow isolation
V-112	¼ inch ball valve	Sampling
V-113	¼ inch ball valve	Sampling
V-114	½ inch needle valve	Flow control
T1-T3	Thermocouple	Temperature measurement
N_2	Gas inlet (4 bar)	
E-101	4 litre pressure vessel	Contains feed material
E-102	4 litre pressure vessel	Contains feed material
E-102	Glass collection vessel	Contains products (low pressure)
MW-1	Manual short-circuit tuner	
MW-2	Automated 3 stub, HOMER tuner	
MW-3	2 kW microwave generator	
—————	Un insulated stainless steel piping	
━━━━━	Thermally insulated stainless steel piping	
⟋⟋⟋⟋⟋⟋	PTFE pipe within microwave cavity	

9.3 Dielectric properties of methyl methacrylate and its oligomers

Shown below are dielectric properties for methyl methacrylate monomer used throughout this work, also shown are the properties of the oligomers

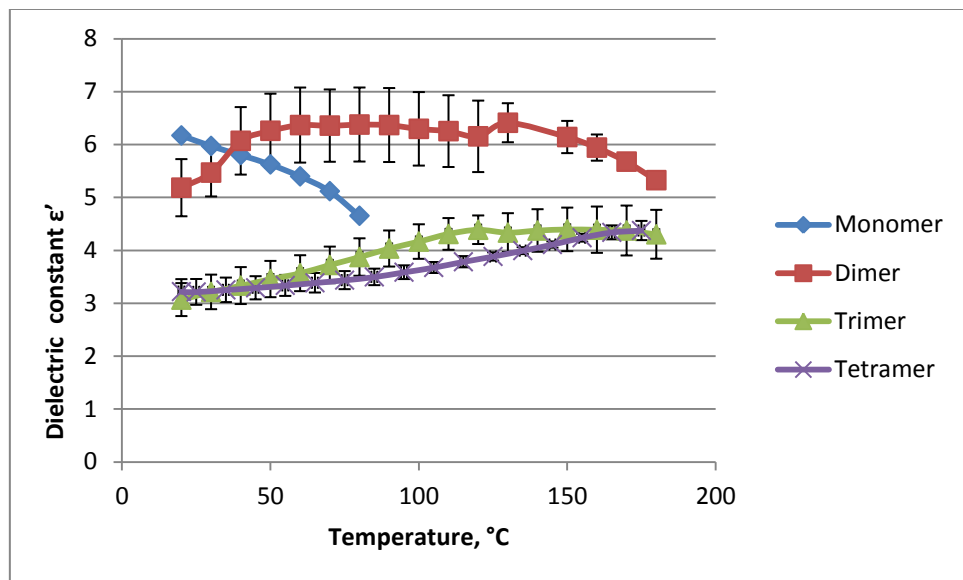produced (Adlington, Jones et al. 2013). Data was measured using cavity perturbation technique at 2.45 GHz.

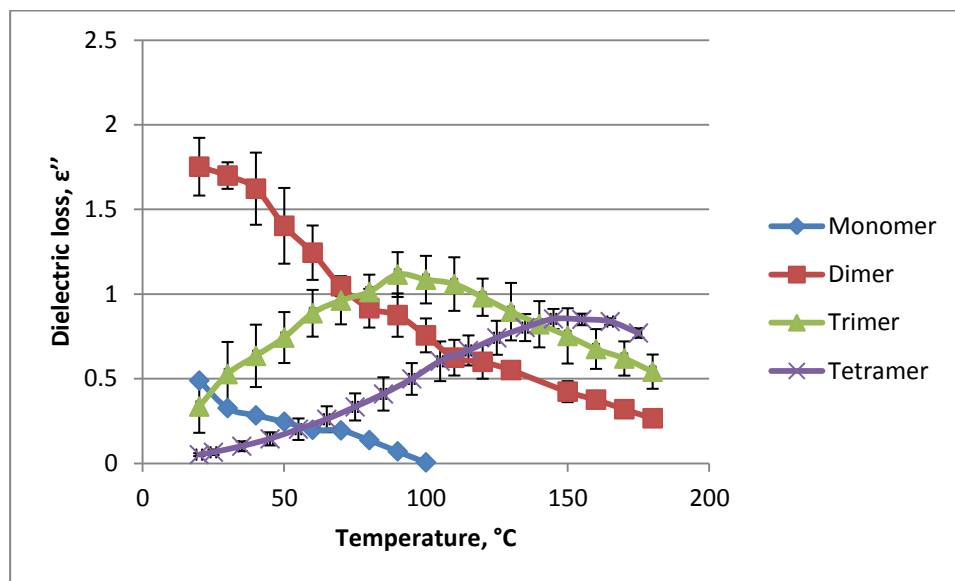*Figure 9-2: Dielectric constant of materials used, measured at 2.45 GHz.*

Figure 9-3 Dielectric loss of materials used, measured at 2.45 GHz