

CONTROLLED

RING-OPENING POLYMERISATION

USING MICROWAVE HEATING

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ABSTRACT

This thesis reports the synthesis of linear and star polycaprolactone *via* the ring-opening polymerisation of ϵ -caprolactone using $-OH$ / tin octanoate as the initiator / catalyst system. The aim of the work carried out in this thesis is to study the polymerisation when conducted using both conventional and microwave heating and develop new synthetic methods for the synthesis of structural polymers *via* ring-opening polymerisation.

Chapter 1

This chapter discusses the fundamentals of polymers and ring-opening polymerisation. This chapter also provides an insight to the background and theory of microwave heating mechanisms and applications.

Chapter 2

This chapter discusses the equipment, synthetic methods and polymer characterisation techniques employed in the work conducted in this thesis.

Chapter 3

This chapter discusses the synthesis of linear polycaprolactone *via* ring-opening polymerisation of caprolactone using microwave heating with a CEM reactor operated at 2.45 GHz and conventional heating with an oil bath. Kinetics of polymerisation using both conventional and microwave heating methods, process optimisation and polymer characterisation are reviewed in this chapter. Results

showed enhanced rates of polymerisation when microwave heating was utilised compared to conventional heating due to the reduction / elimination of the induction time and selective heating of the catalyst.

Chapter 4

This chapter reports the synthesis and characterisation of 3-arm and 4-arm star polycaprolactone using multifunctional initiators. Polymerisation was conducted using both conventional and microwave heating. Kinetics of polymerisation, structural characterisation of the star polymers, process optimisation techniques and effects of both heating methods on reaction kinetics and structures are also discussed in this chapter.

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Chapter 5

This chapter discusses the synthesis of polycaprolactone in tuned and untuned microwave systems using CEM and Miniflow microwave reactors. Comparison between tuned and untuned systems, energy efficiency and polymer characterisation are reported in this chapter. Time and power optimisation in ring-opening polymerisation for the preparation of scale-up using a 2 kW microwave generator is also discussed in this chapter.

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ABBREVIATIONS AND ACRONYMS

BnOH	Benzyl alcohol
C_p	Specific Heat Capacity (J/g K)
$CDCl_3$	Deuterated Chloroform
CL	ϵ -Caprolactone
$\bar{D}$	Dispersity Index
d_p	Penetration Depth
DCM	Dichloromethane
DP	Degree of Polymerisation
DSC	Differential Scanning Calorimetry
ϵ'	Dielectric Constant
ϵ''	Dielectric Loss
ϵ^*	Complex Permittivity
ϵ_s	Static Permittivity
f_c	Relaxation Frequency (RxF)
FDA	Food and Drug Administration
g	Gram
GPC	Gel Permeation Chromatography
h	Hour
k_{app}	Apparent Rate Constant of Polymerisation
k_d	Rate constant of Depropagation
k_p	Rate constant of Propagation

kW	Kilowatt
MALDI-TOF	Matrix-assisted Laser Desorption/ Ionisation Time of Flight
MeOH	Methanol
Min	Minute
M_n	Number Average Molecular Weight
MROP	Microwave-assisted Ring-opening Polymerisation
MS	Mass Spectroscopy
MW	Molecular Weight
M_w	Weight Average Molecular Weight
MWD	Molecular Weight Distribution
NMR	Nuclear Magnetic Resonance
OctH	Octanoic Acid
PCL	Polycaprolactone
PLA	Poly(lactic acid)
ppm	Part per Million
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PTOL	Pentaerythritol
PTOLE	Pentaerythritol Ethoxylate
R	Gas Constant ($8.4144 \text{ JmolK}^{-1}$)
ROP	Ring-opening Polymerisation
$\text{Sn}(\text{Oct})_2$	Tin (II) Ethyl Hexanoate or Tin Octanoate
$\tan\delta$	Loss Tangent or Energy Dissipation Factor

TFA	Trifluoroacetic Acid
T _g	Glass Transition Temperature
THF	Tetrahydrofuran
T _m	Melting Temperature
TMP	Trimethylolpropane
TMPE	Trimethylolpropane Ethoxylate
W	Watt
°C	Celsius Degree
η	Intrinsic Viscosity
τ	Relaxation Time
ω	Angular Frequency
ΔG	Free Energy of Polymerisation

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CHAPTER 1 INTRODUCTION

1.1 Polymer Fundamentals

1.1.1 Polymer Structures

Polymers are the main building block and one of the most important materials used in everyday life. The word *polymer* is extracted from Greek context “poly”, which means many and “meros”, meaning parts or units. Thus, polymer is referred to a structure built from multiple repeating units, or monomers. The fundamentals of polymers can be studied across various disciplines such as biophysics, material science and macromolecular science.³

Polymers are commonly formed by covalent bonds linked between monomers through polymerisation reaction. A macromolecule that is composed from a single species of monomer is known as homopolymer, or simply referred to as polymer. Polymers that involve two types of monomers are known as copolymers, while three different monomers involved result in a terpolymer. According to Cowie and co-workers, copolymers composed from bifunctional monomers can be further divided into four key categories as described as follows:¹

1. Alternating copolymer: monomers have regular placement along the chain



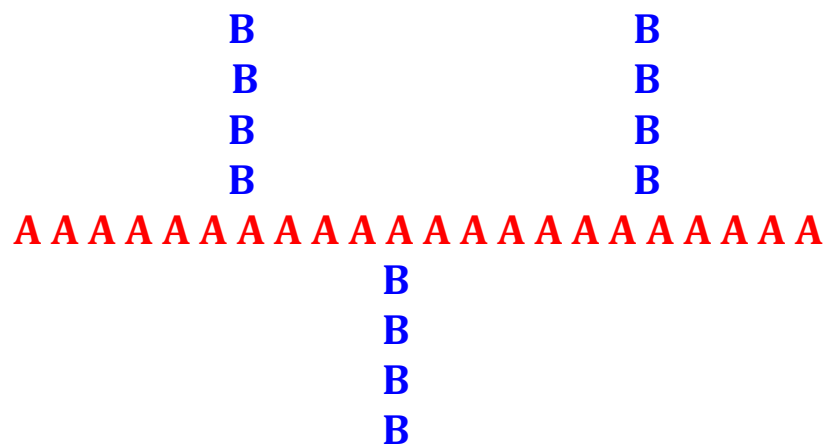
2. Statistical copolymer: random distribution of the monomers along the chain



3. Block copolymer: substantial sequence or blocks of monomers along the chain



4. Graft copolymer: blocks of one monomer are grafted like branches on the backbone of the other block of monomer



Alternating, statistical and block copolymers can be typically classified as linear polymers. However, many various and novel polymer structures have been successfully synthesised over the past two decades which include star polymers, hyper-branched polymers, dendritic and cross-linked polymers. In general, polymers can be described using a combination of any of the division as mentioned previously. This has led to an increased research interest in the field of polymer science as different polymer structures with different architectural aspects are directly correlated to the polymer's physical properties, mechanical properties and chemical reactivity. Figure 1.1 below shows a diagram of typical polymer structures namely linear, star and hyper-branched polymers.

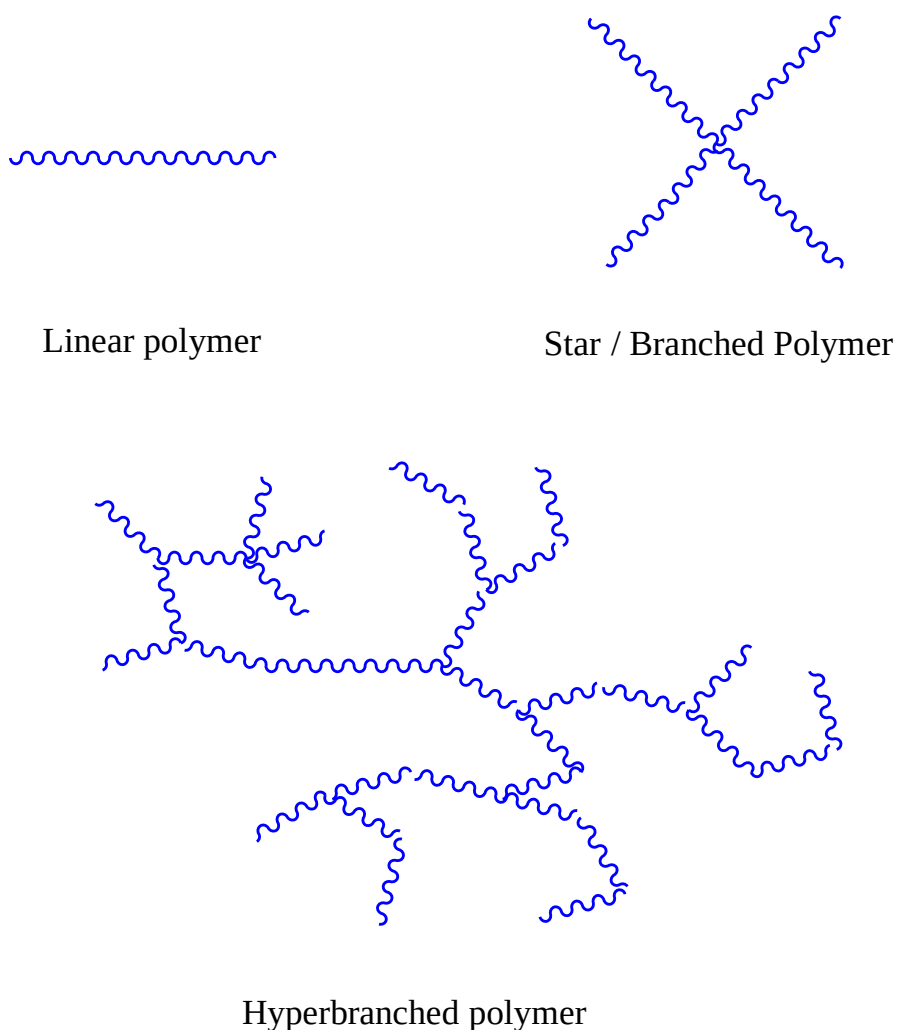


Figure 1.1 Structures of linear, star and hyper-branched polymers

Star and branched polymers have gained popularity over the years as they have been shown to exhibit useful rheological and mechanical properties with respect to linear polymers. As a specific example, star polymers exhibit a smaller hydrodynamic radius and a lower melt viscosity than their corresponding linear counterparts of the same M_n and composition, therefore these star polymers can be easily moulded at low temperatures. Other advantages of the branched architecture also include improved toughness and higher reactivity which allows them to be used for practical applications in the pharmaceutical industry.⁴

1.1.2 Mechanisms of Polymerisation

In general, the two key polymerisation methods are step-growth polymerisation and addition / chain growth polymerisation.^{1, 3} The step-growth mechanism is used for monomers with bi- or multi-functional groups and is commonly but not always present in condensation reactions. A molecule is typically eliminated during step-growth polymerisation therefore most of the polymers synthesised using this method differ slightly from the original monomer. Step-growth polymerisation is a step reaction that involves the formation of dimers, trimer, tetramers and so on until a long polymer chain is formed, which eventually closes indicating the end of the polymerisation. Figure 1.2 below shows the synthesis of terylene using ethylene glycol and terephthalic acid, an example of step-growth polymerisation.¹

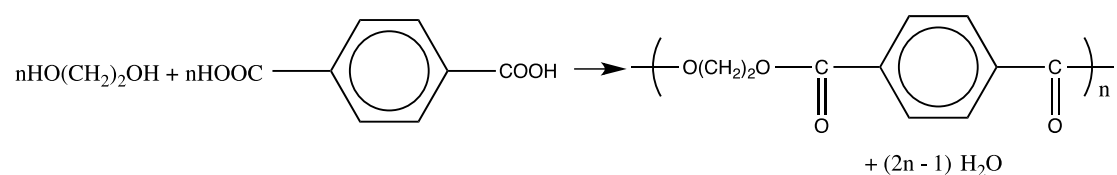


Figure 1.2 Step-growth polymerisation in the synthesis of terylene (Cowie et al.)¹

Addition or chain-growth polymerisation involves the conversion of monomer into polymer by using a free radical or initiator to initiate the opening of the double bond, thus the polymer product has the same composition as the original monomer. The reaction typically involves a series of stages that follow the completion of one another which include initiation, propagation and termination. In this method of polymerisation, an initiating species (R) with an active centre that stimulates the initiation stage is formed from an organic molecule with a relatively small M_n . This reactive species then attacks and reacts with the first monomer unit, resulting in the initiation of the chain growth process. Subsequently in the propagation stage, monomers are added to the reactive centre forming the propagating species. This step is repeated until all the monomer in the system is completely consumed. When one or more reactions remove the reactive centre of the propagating species, the propagating step is terminated. Figure 1.3 below shows an example of chain growth polymerisation involving the initiation, propagation and termination stages.¹

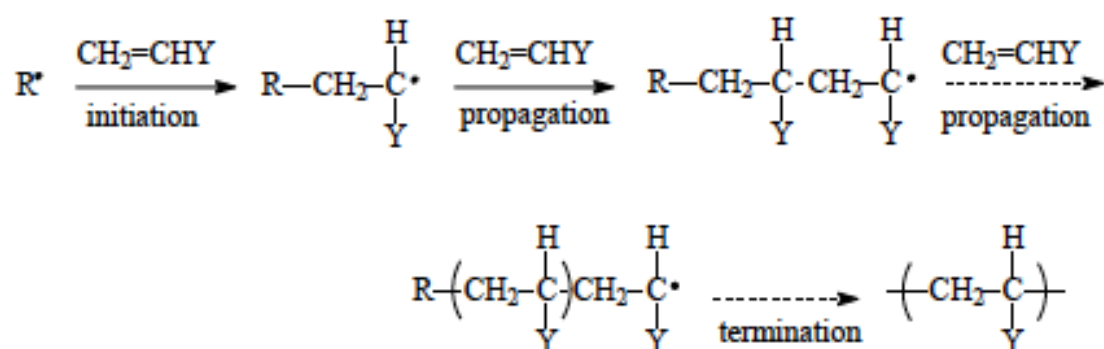


Figure 1.3 Initiation, propagation and termination in the chain growth polymerisation of vinyl monomers (Cowie et al.)¹

In chain growth polymerisations, reaction only takes place at the growing chain end where monomer reacts with the propagating species because

monomer cannot react with monomer. This is the key attribute that differentiates chain growth polymerisation from step-growth polymerisation, both exhibiting very different polymer growth profiles (Figure 1.4).

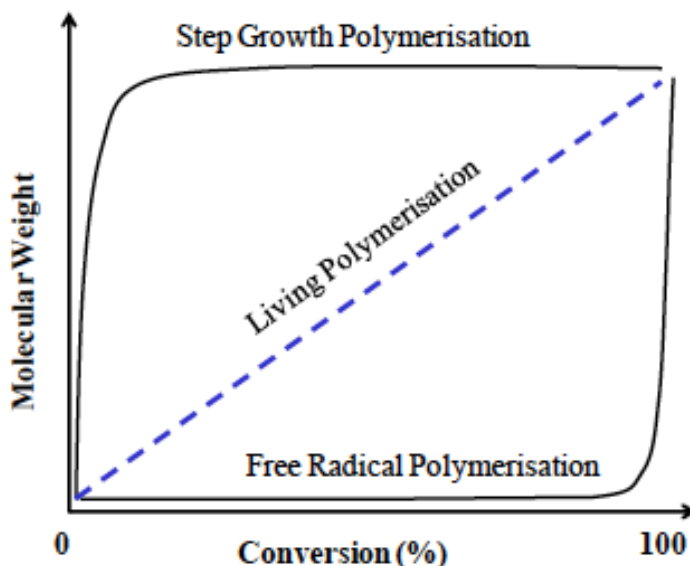


Figure 1.4 Molecular weight vs monomer conversion comparing step-growth and chain growth polymerisation²⁵

Furthermore, chain growth polymerisations that include the initiation, propagation and termination stages can be further subdivided into one of the categories as follows:

- Free radical polymerisation
- Anionic polymerisation
- Cationic polymerisation
- Pseudo-living / controlled / living radical polymerisation

Pseudo-living / controlled polymerisation is the main polymerisation mechanism focused on in this chapter. In pseudo-living polymerisation, the molecular weight of the polymer formed increases linearly with monomer conversion while low dispersity index ($\bar{D}$) can be obtained. The sequential

addition of monomers can result in the synthesis of block copolymers. In this research, controlled ring-opening polymerisation will be further discussed in the following sections.

1.2 Ring-opening Polymerisation

This study is focused on the ring-opening polymerisation (ROP) of cyclic monomers. ROP has been characterised as a type of chain polymerisation, however various polymer scientists including Odian have classified it as an independent mode of polymerisation as different cyclic monomers adopt specific mechanisms.³ Figure 1.5 shows various cyclic monomers that have been evaluated for ROP which include ethers^{3, 6}, lactams and esters^{8-9, 11-12}.

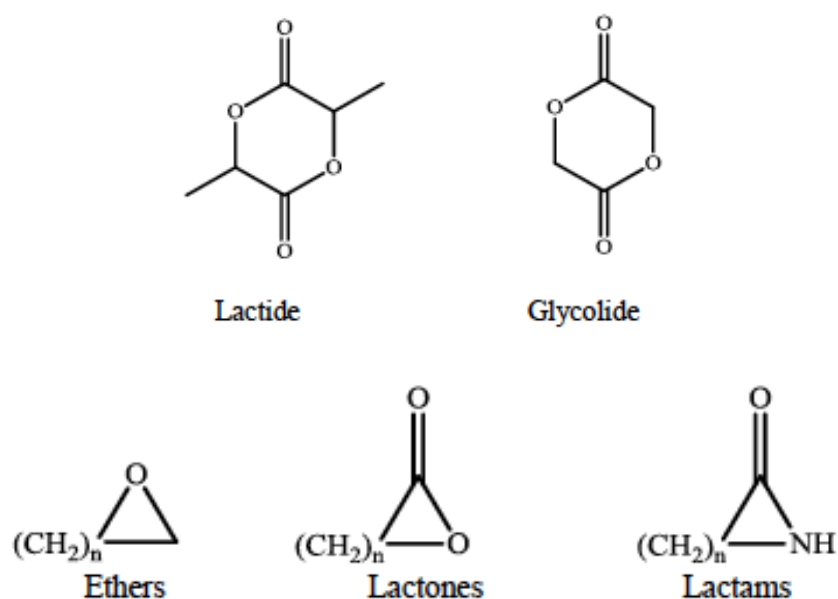


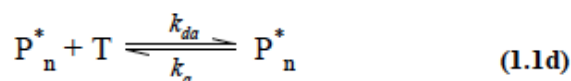
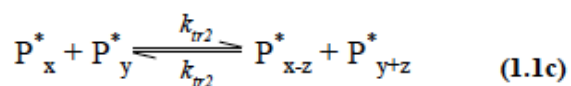
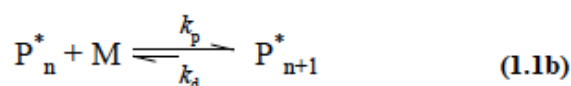
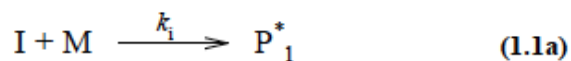
Figure 1.5 Cyclic monomers evaluated for ring-opening polymerisation³

Some of the factors that affect the polymerisation of cyclic monomers into linear chains include kinetic and thermodynamic characteristics of the structure. Thermodynamic factor plays a greater role in monomer conversion, however

this does not directly determine the reactivity of the monomer.⁵ Studies have shown that monomer reactivity is also dependent on the kinetics of propagation. In a study conducted by Duda and coworkers using 6, 7, 9, 12, 13, 16 and 17 member lactones monomer and zinc 2-ethylhexanoate / butyl alcohol as the catalyst / initiator system, it was shown that monomer reactivity was proportional to the ring strain. However, monomer reactivity decreased as the ring size increased due to the increase in thermodynamic stability of the monomer ring, hence it was less likely for the monomer ring to be opened and be polymerised.¹⁸ In this study, the hydrophobicity of the lactone was the key factor in the formation of the catalyst-initiator complex. Complex formation was kinetically favoured, making this stage the rate-determining step. In other cases where cyclic monomers with high hydrophobicity are involved, the propagation step becomes the rate-determining step hence resulting in different monomer reactivity. This shows the influence of kinetics on cyclic monomers in ROP.

1.2.1 Kinetics of Living Ring-opening Polymerisation

The kinetics scheme of reversible, pseudo-living ROP as described by Duda et al. exhibits the initiation and propagation stages, as well as reversible or temporary termination reactions as shown in Figure 1.6.⁵



Where,

P^*_i : living macromolecule / propagating species

(e.g. $P^*_1, P^*_n, P^*_{n+1}, P^*_x, P^*_y, P^*_{x-z}, P^*_{y+z}$)

T : deactivating agent

P_n : temporary deactivated species

k_i, k_p, k_d : rate constant of initiation(i), propagation(p), depropagation(d)

k_{tr2} : rate constant of transfer to polymer

k_a, k_{da} : rate constant of temporary activation and deactivation

Figure 1.6 Kinetics of pseudo-living ROP as depicted by Duda and coworkers⁵

It is assumed that the initiation process in this system occurred more rapidly than the propagation stage in order to meet the requirements of controlled pseudo-living ROP, disregarding any side reactions that may take

place.⁵ Furthermore, the rate constant of propagation can be expressed as follows (assuming that k_p is independent of degree of polymerisation (DP) and that $k_i \gg k_p$):

$$R_p = -\frac{d[M]}{dt} = k_p \sum [P_n^*] [M] - k_d \sum [P_n^*] \quad (\text{Equation 1.1})$$

Therefore, the integration of Equation 1.1 generates a semi logarithmic equation describing the relationship between monomer concentration and polymerisation time (assuming that process efficiency is 100%, i.e. $\sum [P_n^*] = [I]_0$).

$$\ln \frac{[M]_0 - [M]_{eq}}{[M] - [M]_{eq}} = k_p \sum [P_n^*] t = k_p [I]_0 t \quad (\text{Equation 1.2})$$

Unlike the polymerisation of unsaturated monomers, it is inevitable that an amount of un-reacted monomer ($[M]_{eq}$) is present at equilibrium in reversible ROP reactions. The theoretical values of $[M]_{eq}$ in polymerisations can often be found in literature, but the specific value of $[M]_{eq}$ under detailed polymerisation conditions must first be determined in order to conduct an accurate analysis.⁵ Thus when the value of $[M]_{eq}$ is unknown, the following equation is used:

$$\ln \frac{[M]_0}{[M]} = k_p \sum [P_n^*] t = k_p [I]_0 t \quad (\text{Equation 1.3})$$

Hence the theoretical degree of polymerisation (DP) can be calculated using the following simple linear function of conversion (assuming $k_i > k_p$):

$$DP = \frac{[M]_0 - [M]}{[I]_0} = \frac{[M]_0}{[I]_0} \times \frac{[M]_0 - [M]}{[M]_0} \quad (\text{Equation 1.4})$$

Or, $DP_{theo} = DP_{target} \times \text{Conversion}$

In summary, linear plots of $\ln([M]_0/[M])$ vs time and DP (or M_n) vs monomer conversion ($([M]_0 - [M])/[M]_0$) depicts the controlled characteristics of pseudo-living ROP.⁵

1.2.2 Mechanisms of Living Ring-opening Polymerisation

In general, both ionic and coordinative initiators can be used in ROP. Depending on the type of initiator involved in the reaction, ROP can be subdivided into the mechanistic categories as follows:

- Anionic ROP
- Cationic ROP
- Activated monomer ionic polymerisation
- Coordination-insertion ROP

In anionic ROP, anionic centres are formed at the initiation stage followed by the nucleophilic attack of the anion on the monomer during propagation.^{3,8}

Figure 1.7 below shows a diagram of an anionic ROP.

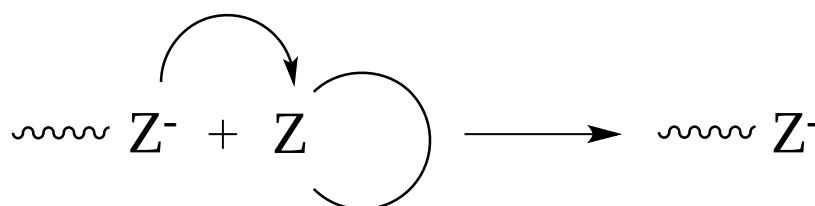


Figure 1.7 Example of anionic ROP as depicted by Odian et al.³

Similarly in cationic ROP^{3,6}, oxonium ions are formed at the initiation stage followed by the nucleophilic attack on the monomer by the oxonium ions in the propagation stage. Figure 1.8 below shows a diagram of a cationic ROP.

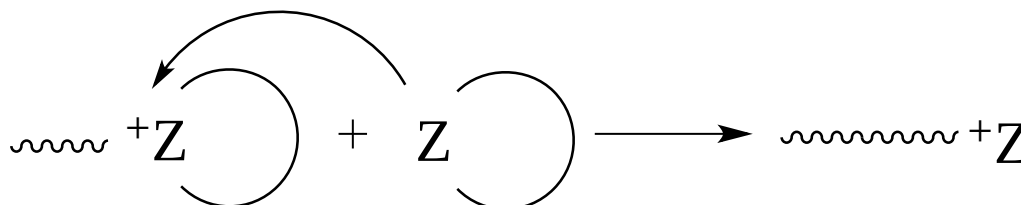


Figure 1.8 Example of cationic ROP as depicted by Odian et al.³

Activated monomer is another type of ROP mechanism.^{3,13} In activated monomer ROP, an anionic or cationic species may be derived from the monomer. However, monomers are not directly involved in the propagation process. Instead, the active ionic species derived from the monomer will react with the functional end group of the polymer. Figure 1.9 below shows an example of activated monomer polymerisation, in which the cation formed between the monomer and catalyst reacts with the functional end group on the propagating chain.

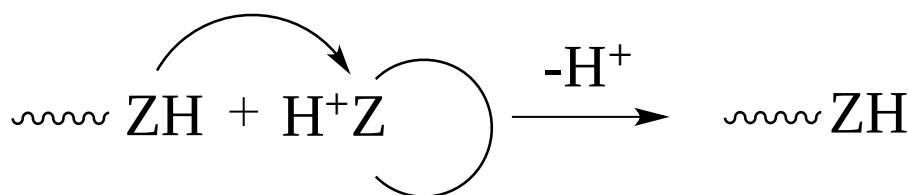


Figure 1.9 Example of activated monomer cationic ROP as depicted by Odian et al.³

Lastly, some ROP follow the coordination-insertion mechanism.^{7,19} This mechanism is named coordination-insertion as it involves the coordination of the metal centre of the catalyst with the monomer followed by the insertion of the initiator ligand, resulting in the ring-opening of the cyclic monomer. The

coordination process remains throughout the propagation stage where every newly coordinated monomer is inserted into the growing polymer chain. This thesis will focus on coordination-insertion ROP and this mechanism will be detailed in the following section. Figure 1.10 below shows an example of coordination-insertion ROP.

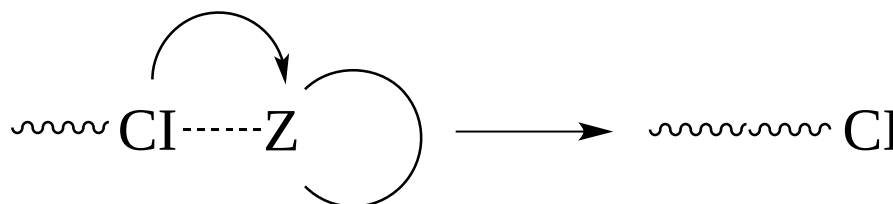


Figure 1.10 Example of coordination-insertion ROP using catalyst/initiator (CI) as depicted by Odian et al.³

1.2.3 Coordination Polymerisation

In general, only monomers with the ability to coordinate with the active site of the catalyst can be polymerised in coordination polymerisation reactions using a specific coordination catalyst / initiator system.⁷ The key feature in coordination polymerisation is the reciprocal activation between the catalyst and monomer.^{7, 19} However, both the active site of the catalyst and covalent bond of the growing chain must be stable without the presence of monomer. When the monomer is present, the covalent bond of the catalyst and the respective bond of the monomer are more susceptible to reacting, leading to ring-opening and then propagation. Kuran mentioned that the term 'coordination polymerisation' should be differentiated from cationic, pseudo radical and pseudo ionic polymerisation.^{7, 19}

Heterocyclic and unsaturated hydrocarbon monomers are the two main monomer categories that can be involved in coordination polymerisation but this

study will focus on heterocyclic monomers. The catalysts involved in the coordination polymerisation of these heterocyclic monomers include various metal complexes with a metal centre that exhibits relatively high Lewis acidity and substituent X with sufficient nucleophilicity.⁷ High Lewis acidity is favoured in the coordination mechanism involving cyclic monomers as this enhances the nucleophilicity of the alkoxide, resulting in the nucleophilic attack on the monomer. Some common catalysts used in the polymerisation of heterocyclic monomers include aluminium, zinc, iron, lanthanum and yttrium.^{7, 19} Figure 1.11 shows a simple example of coordination polymerisation of cyclic monomers (ethers and lactones).

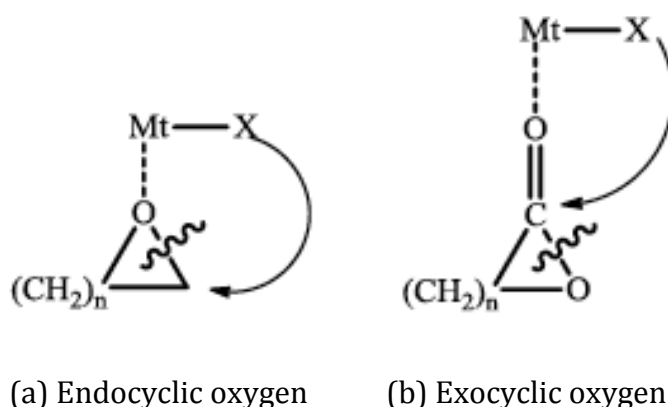


Figure 1.11 Coordination polymerisation of cyclic ethers and lactones. The metal centre of the catalyst coordinates with the endocyclic oxygen (a) in ethers and exocyclic oxygen (b) in lactones, resulting in the insertion of substituent X via nucleophilic attack, adapted from Odian and coworkers.³

Oxacyclic, thiacyclic, azacyclic and phosphacyclic are some of the heterocyclic monomers that have been successfully polymerised via coordination ROP, these monomers contain oxygen, sulphur, nitrogen and phosphorus heteroatom respectively. Some oxacyclic monomers include cyclic ethers and esters, carbonates and lactams. A large variety of cyclic esters have been studied within the study of coordination polymerisation by Duda and

Kuran.^{5, 19} However, the coordination ROP of lactones is the main area of research interest in this thesis.

1.3 Synthesis of Biodegradable Polyesters

A wide variety of biodegradable polyesters have been successfully synthesised, of which poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA) are more commonly produced at industrial scale. However, this thesis will focus on the synthesis of PCL.

PCL is a semi-crystalline aliphatic polyester with a melting temperature (T_m) of 56-65°C and glass transition temperature (T_g) of (-65)-(-60)°C. PCL is biodegradable within the period of several months to years depending on the environment of degradation, degree of crystallinity and molecular weight of the polymer. PCL can be produced using two key methods namely polycondensation of 6-hydroxycaproic (6-hydroxyhexanoic) acid and the ring-opening polymerisation (ROP) of cyclic ϵ -caprolactone (CL) monomer.¹⁶

Polycondensation

PCL has been successfully synthesised under vacuum by Braud and coworkers² via the polycondensation of 6-hydroxyhexanoic acid. Water was removed during this process hence shifting the equilibrium towards polymer formation. Polymerisation was completed within 6 hours using a maximum temperature of 150°C without the addition of a catalyst. There are several disadvantages using polycondensation in the synthesis of PCL, one of which is the lengthy reaction time and high reaction temperature requirement in order to achieve high conversion rates. The removal of reaction by-products must also be

Figure 1.13 below shows various cyclic monomers mentioned that have been successfully used for ROP.

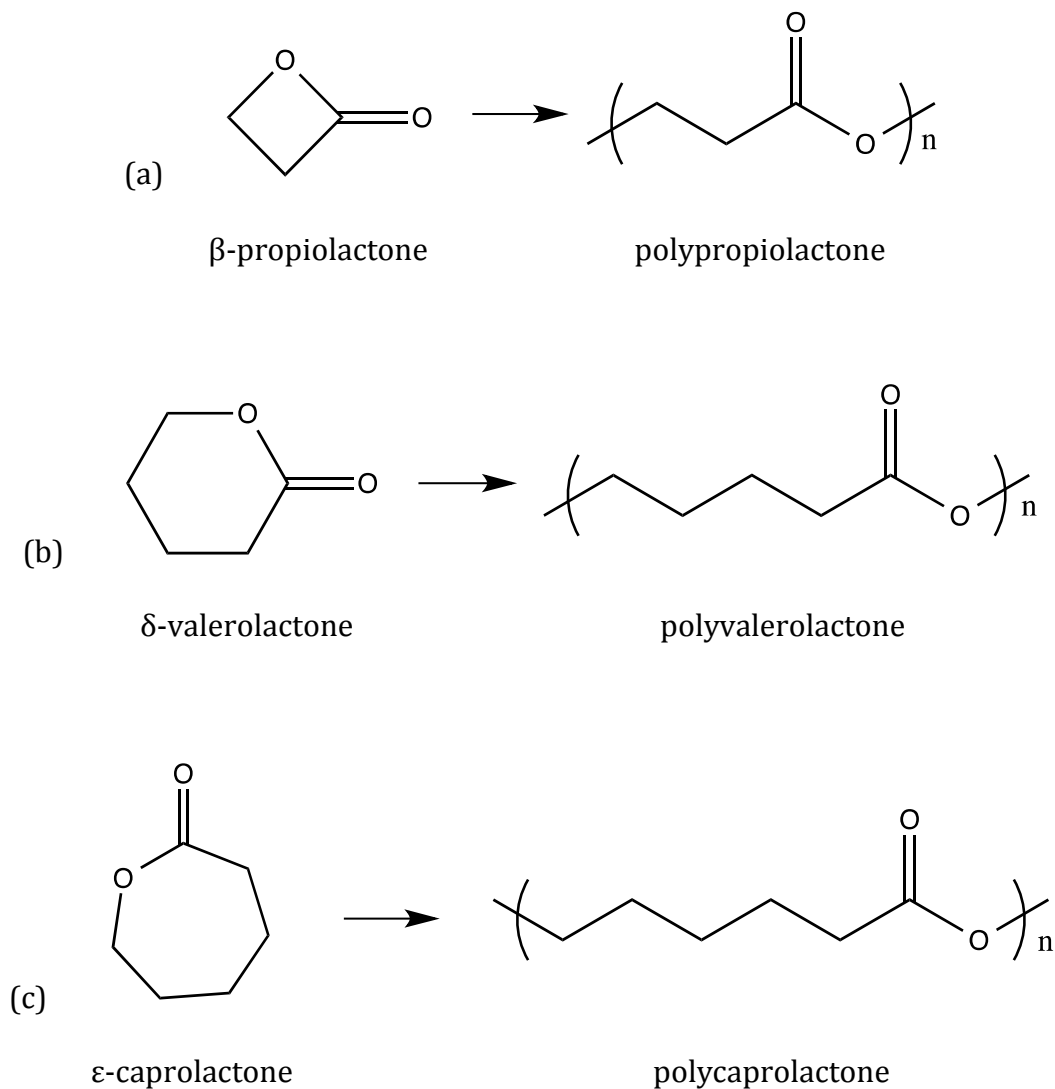


Figure 1.13 Various cyclic monomers successfully used in ROP: (a) β -propiolactone in synthesis of polypropiolactone^{8, 19}, (b) δ -valerolactone in the synthesis of polyvalerolactone¹⁹ and (c) ϵ -caprolactone in the synthesis of polycaprolactone^{11, 12, 19}

1.4 Ring-opening Polymerisation using Conventional Heating

As mentioned in Section 1.2.2, the ROP of CL can be further divided into several mechanistic categories depending on the type of catalyst used namely anionic ROP, cationic ROP, activated monomer ionic polymerisation and coordination-insertion ROP. Coordination-insertion ROP is most commonly used in the commercial synthesis of PCL. Various metal derived catalysts such as aluminium alkoxides and tin alkoxides are widely used in the ROP of CL. In the practical work conducted in this thesis, the synthesis of PCL was performed using R-OH and tin octanoate ($\text{Sn}(\text{Oct})_2$) as the initiator/catalyst system. $\text{Sn}(\text{Oct})_2$ is widely used in the batch synthesis of PCL commercially as $\text{Sn}(\text{Oct})_2$ has been approved by the US Food and Drug Administration (FDA) as food additive. The usage of $\text{Sn}(\text{Oct})_2$ was first reported in 1960s²², however the advantages of using $\text{Sn}(\text{Oct})_2$ have been studied more recently. Figure 1.14 below shows the structure of $\text{Sn}(\text{Oct})_2$.

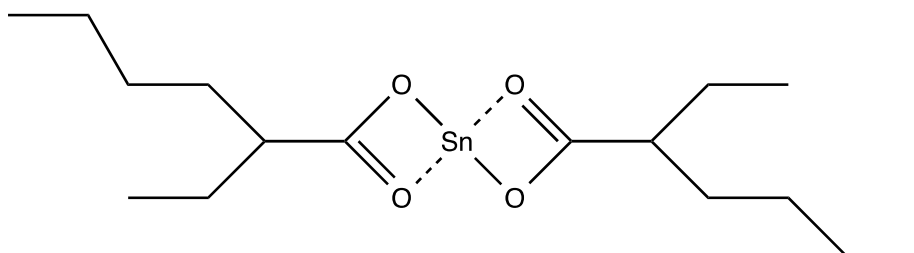


Figure 1.14 Structure of tin octanoate ($\text{Sn}(\text{Oct})_2$)

1.4.1 Mechanism of Ring-opening Polymerisation using $\text{Sn}(\text{Oct})_2$

The actual function of $\text{Sn}(\text{Oct})_2$ in the ROP of lactones has been studied and various contradicting results have been reported in literature. However, two key mechanisms have been suggested namely direct catalytic and coordination-

insertion.^{12, 22} In direct catalytic mechanism, the monomer is activated by the catalyst via coordination-insertion followed by the nucleophilic attack from the R-OH initiating compound.¹³ However, the coordination-insertion mechanism has been more frequently reported in the recent years. In the coordination-insertion ROP, the Sn(Oct)₂ catalyst serves as a co-initiator with the purposely added R-OH initiator. Firstly, an activated alkoxide species is formed between Sn(Oct)₂ and hydroxyl group. Polymerisation then begins with the coordination of the monomer to the metal centre and insertion of the alkoxide species to the carbon atom of the carbonyl group.^{12-13, 18, 20}

Kowalski and coworkers¹² studied the kinetics of CL polymerisation using Sn(Oct)₂ catalyst in tetrahydrofuran (THF) solvent at 80°C. CL monomer was selected as it is easily purified. It was concluded that octanoic acid (OctH) was released from the formation of the alkoxide species between butyl alcohol and Sn(Oct)₂ catalyst.

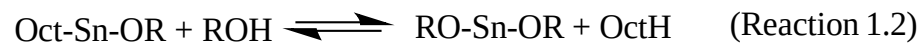
A second alkoxide species (tin dialkoxide) is formed from the reaction between the first alkoxide species and hydroxyl group as shown in Reaction 1.2 in Figure 1.15. The ROP study conducted by Kricheldorf and coworkers³⁰ focused on the role of the second octanoate species in the coordination-insertion process and the significance of the presence of tin dialkoxide in order for polymerisation to proceed. In addition, a detailed analysis was conducted on the Sn(Oct)₂/benzyl alcohol (BnOH) catalyst initiator system using ¹³C NMR immediately after both materials were mixed together at room temperature. It was observed that the signal of CO from Sn(Oct)₂ was shifted from 189.1 ppm to 182.3 ppm which is closer to that of the OctH. It was also observed that there was an increase in the shift when the molar ratio of BnOH was increased. These

observations suggest the formation of alkoxide species between BnOH and octanoate forming tin dialkoxide, which is the true initiator.³⁰

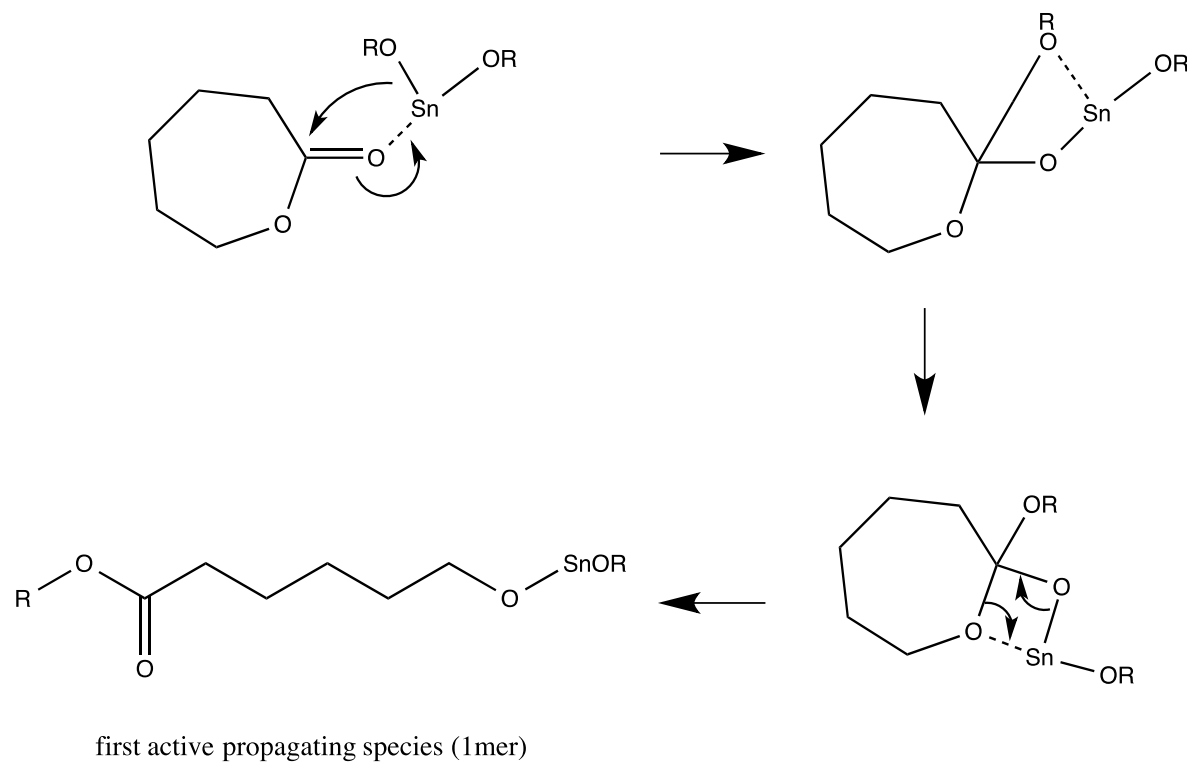
A more recent study conducted by Storey and coworkers²² suggested a complete mechanism for the ROP of CL using $\text{Sn}(\text{Oct})_2/\text{R-OH}$ as the catalyst/initiator system as shown in Figure 1.15. It was proposed that in the first stage of polymerisation (Reaction 1.1), reaction occurred between $\text{Sn}(\text{Oct})_2$ and the R-OH initiator to form the first tin alkoxide species and octanoic acid (OctH). The first tin alkoxide species then reacts with a second equivalent R-OH to form tin dialkoxide and another equivalent OctH (Reaction 1.2). This is then followed by the coordination-insertion mechanism between the tin dialkoxide species and monomer, forming the first active propagating species that contains a fragment of the R-OH from the initiator and an active propagating centre. The formation of the first active propagating species is the beginning of polymerisation. In an alternative case, intermolecular exchange can occur with the tin alkoxide species, in which the reaction will be likely from the R-OH of initiators that remain. The exchange between the activated and deactivated chain forms a dynamic equilibrium, which eventually consumes the remaining, unreacted R-OH initiator. Theoretically, the number of propagating species is dependent on the mole equivalent of R-OH initiator in the system. Therefore, the degree of polymerisation (DP) can be fixed by adjusting the molar ratio of monomer: initiator.

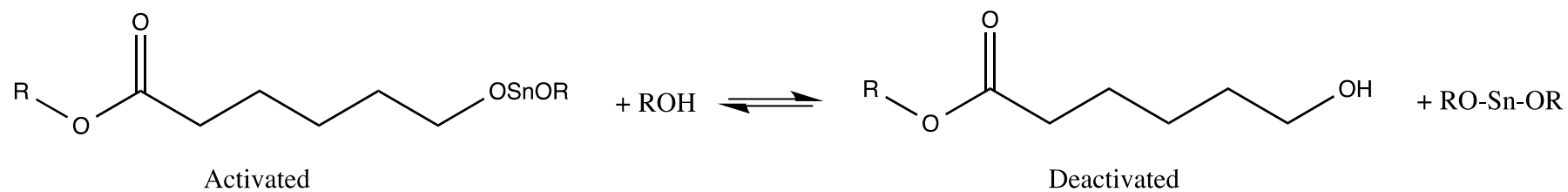
During propagation, the monomer is added to the active centre of the catalyst and this process is repeated until all the monomer units are consumed. The polymer chain is terminated when equilibrium is achieved between the polymer active species and the polymer chain containing R-OH .

'In-situ' Catalyst Formation:

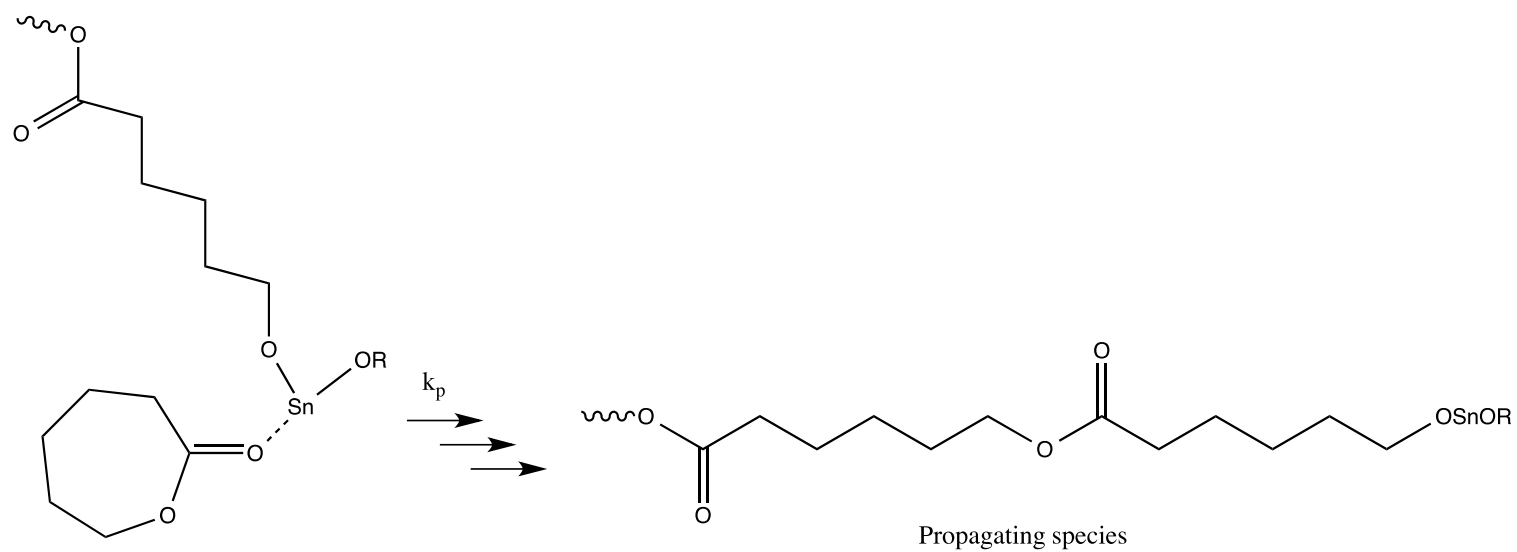


Initiation:

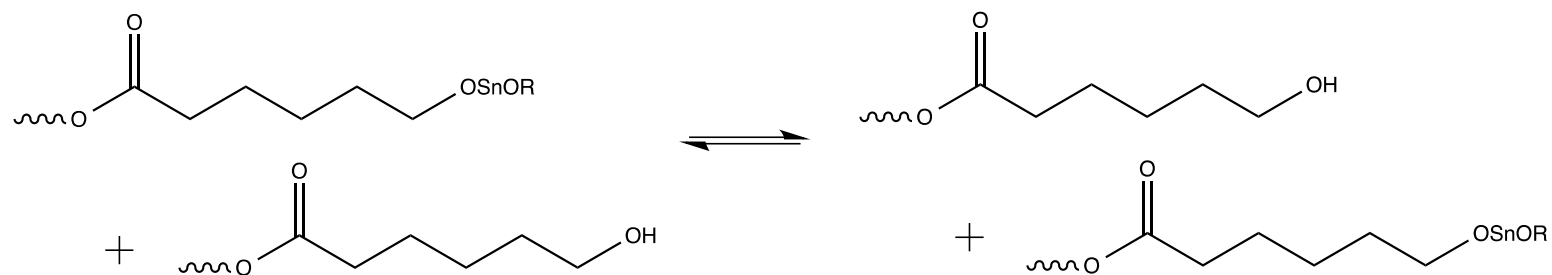




Propagation:



Molecular chain transfer of active chain ends



Deactivation of active centre by water

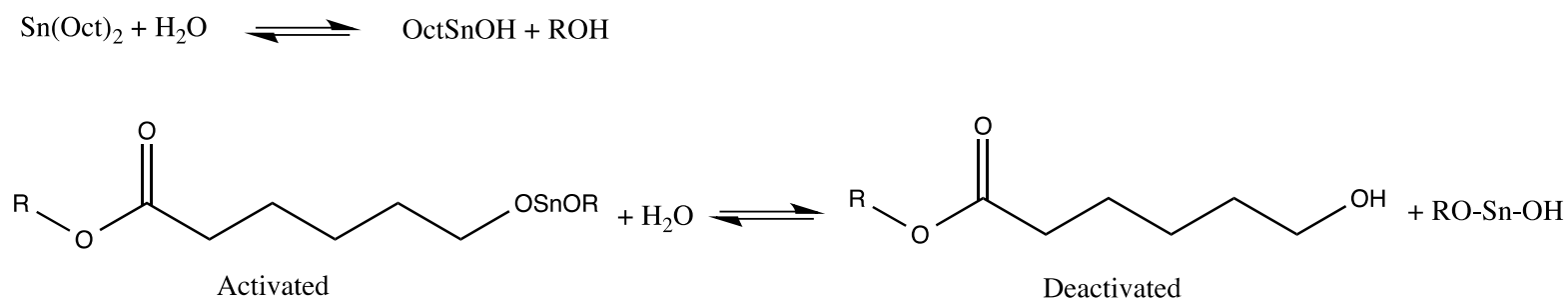


Figure 1.15 ROP of CL using $\text{Sn}(\text{Oct})_2$ catalyst and R-OH initiator as depicted by Storey and coworkers²²

Furthermore, Storey and coworkers depicted the deactivation of the tin active species using water.²² The deactivation process can take place during the initiation stage, or propagation stage, or both. The presence of water can produce a tin alcohol derivative and lower the initiator concentration due to the derivative being more thermodynamically stable than the alkoxide and dialkoxide species.^{22, 30}

1.4.2 Kinetics of ROP of CL using Sn(Oct)₂ and R-OH Initiator

Separate kinetic studies on the ROP of CL have been successfully conducted by Kowalski et al. and Storey et al. using Sn(Oct)₂ and R-OH initiator. Kowalski and coworkers conducted the ROP of CL using Sn(Oct)₂/BnOH as the catalyst/initiator system in THF solvent at 80°C.¹² Storey and coworkers conducted the ROP of CL using Sn(Oct)₂ catalyst and ethylene glycol (EOH) as the initiator at 130°C.³⁷ Both studies suggested that the rate of polymerisation was found to be dependent on the catalyst concentration, as the catalyst concentration is determined by concentration of the active chain ends containing the active tin alkoxide species. However, in order for the concentration of the active chain to be independent of the R-OH initiator concentration, $[ROH]/[Sn(Oct)_2] > 2$ which is the minimum R-OH required in excess to form the true catalytic species.²² Therefore, the molar ratio of -OH required to react with Sn(Oct)₂ is 2:1 for the formation of the tin dialkoxide species.

The presence of excess R-OH favours the formation of the tin alkoxide species. When all the R-OH groups have reacted with the catalyst, no more active species can be formed. The excess R-OH then becomes the chain transfer agent, which is able to form more polymer chains. However once a chain is formed, it

becomes deactivated in order for the number of active chains to remain constant. Hence, it is possible to control the number of polymer chains by controlling the amount of R-OH in the system.^{12, 22} It is then possible to determine the degree of polymerisation (DP) using the following calculation:

$$D_P = \frac{[CL]_0}{[ROH]_0} \quad (\text{Equation 1.5})$$

Where, $[CL]_0$ = initial concentration of CL monomer

$[ROH]_0$ = initial concentration of R-OH

Once again Storey and coworkers studied the relationship between the concentration of R-OH and DP.²² Whilst keeping the ratio of monomer/catalyst constant, it was observed that the rate of polymerisation did not vary when the molar ratio of R-OH/Sn(Oct)₂ was adjusted. It was reported that the experimental molecular weights obtained were well correlated to the theoretical values calculated, hence concluding that DP can be determined by adjusting the molar ratio of CL/R-OH initiator.

Both studies conducted by Storey et al. and Kowalski et al. showed that the rates of polymerisation were significantly affected by the concentration of Sn(Oct)₂ catalyst. In the ROP of CL conducted at 130°C, Storey and coworkers²² found that when the concentration of R-OH initiator remained constant, the rate of polymerisation decreased when the concentration of Sn(Oct)₂ decreased. A similar trend was observed in the ROP of CL conducted by Kowalski and coworkers¹², where the rate of polymerisation increased with the increase in

catalyst concentration while the concentration of BnOH initiator remained constant.

Furthermore, Storey et al. also investigated the effect of the presence of water in the system on the rate of polymerisation. It was observed that the rate of polymerisation decreased when the amount of water increased. Induction periods were also observed in the beginning of polymerisation, which was attributed to slow heat transfers and delay in the formation of the co-initiator. The authors suggested that the delayed interaction between the initiator and pre-catalyst could be due to the initiator being a diol. The diol may also act as a bidentate ligand, hence reducing the efficiency of the catalyst by interfering with the formation of tin dialkoxide during the initiation stage. This concludes that water deactivates the catalyst by decreasing the number of active chains.²²

1.5 Fundamentals of Microwave Heating

1.5.1 Conventional Heating vs Microwave Heating

Heating is widely used in engineering, chemical and food industries for distillation, drying, promoting physical or chemical changes and many other purposes. It is the most common operational unit utilised in chemical processing.²⁴ In general, heating is normally conducted via convection, conduction or radiation. In this thesis, both conventional and microwave heating methods will be studied and compared. In the practical experiments conducted, conventional heating was carried out using a hot oil bath while microwave reactors were used in microwave volumetric heating.

When a material is heated conventionally, all the forward energy has to pass through the surface of the medium. Hence, conventional heating is slow,

imprecise and difficult to control. In the conventional heating experiments conducted in this study, the heating rate is limited by the temperature of the heating fluid (hot oil) in the oil bath, thermal diffusivity and heat distribution within the reaction flask.

Due to the disadvantages of conventional heating as mentioned, alternative heating methods have been discovered and utilised to improve heating efficiency in processes. Microwave heating has been widely used since post-Second World War for domestic and industrial purposes but it has gained more research interest in the recent years as microwave equipment that is safe to use in a laboratory is more readily available. Microwave heating is usually applied to existing reactions conducted using conventional heating to reduce the reaction time by using an electrical source.

Microwave energy has the ability to couple directly with the molecules inside the reaction mixture, resulting in efficient heating especially when the chemical components in the bulk have a high ability to transform electromagnetic radiation into heat. Microwave irradiation can therefore heat the reaction mixture homogeneously and raise the temperature of the entire volume simultaneously. Unlike conventional heating, factors such as heat flow, thermal conductivity, heat transfer coefficients and material wall thickness do not need to be taken into account when using microwave heating. Microwave heating can be applied to any material, given that the material is neither a perfect electrical conductor nor a perfect insulator.

1.5.2 Microwave Heating

In this section, the fundamental theories of microwave heating will be discussed. As a result of the benefits of volumetric electrical heating as mentioned in the previous section, microwave heating has been used in a wide range of applications at laboratory scale such as drying, food processing and various chemical reactions.^{24, 32} In this thesis, the comparison between both conventional and microwave heating in the synthesis of PCL via ROP will be investigated.

Microwave energy consists of electric and magnetic fields that are perpendicular to each other but heating is mainly caused by the electric component that leads to wave-material interactions (Figure 1.16).²⁵ Materials that do not contain a magnetic component will only respond to the electric field of the microwave.

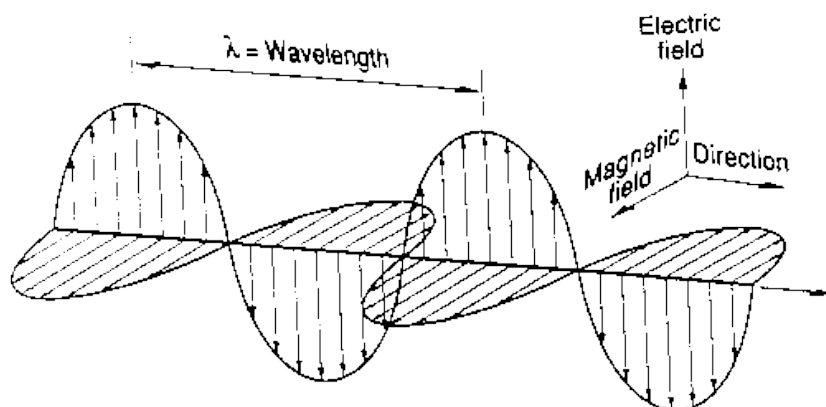


Figure 1.16 Electric and magnetic field components that are perpendicular to each other in microwaves²⁵

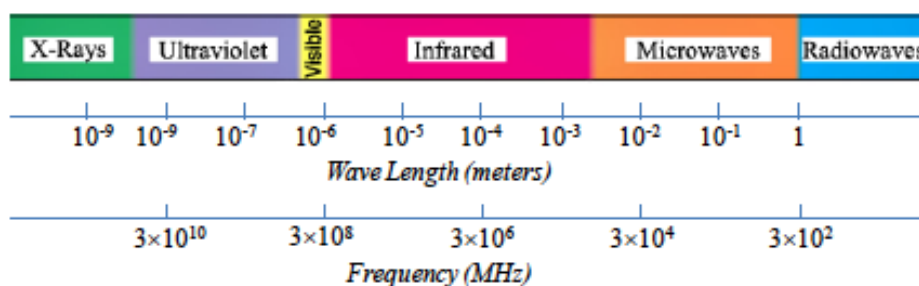


Figure 1.17 The electromagnetic spectrum²⁵

The microwave region falls in between radio and infrared frequencies in the electromagnetic spectrum with a frequency range of 0.3 to 300 GHz with corresponding wavelengths of 1cm to 1m, which is mostly used for telecommunication and radio transmissions. Microwave heating is generally conducted at a frequency of 2450 MHz (± 50 MHz) which has a corresponding wavelength of 12.25 cm or other frequencies that have been designated as ‘industrial, scientific and medical’ (ISM) frequencies for safety reasons and to minimise interference with telecommunication services. However, organic synthesis conducted using microwave heating at frequencies other than 2450 MHz is extremely uncommon. A list of ISM microwave frequencies is listed in Table 1.1.

Table 1.1 ISM microwave frequencies and their corresponding wavelengths, adapted from Nuchter et al.²⁶

Frequency (MHz)	Wavelength (cm)
433.92 $\pm$ 0.2	69.14
915.13 $\pm$ 13	32.75
2450 $\pm$ 50	12.24
5800 $\pm$ 75	5.17

1.5.3 Mechanisms of Dielectric Heating

The heating mechanism in which a material has the ability to absorb microwave energy and convert it into thermal energy is known as microwave dielectric heating. Dielectric heating is an efficient form of heating used in chemical processes.²⁴⁻²⁵ Depending on the physical nature of the material heated, the dielectric mechanisms used for dielectric heating can be subdivided into dipolar rotation and ionic conduction.^{25, 27}

Materials that follow a dipolar rotation mechanism when heated must have a dipole moment to interact with microwave radiation, these dipoles have the ability to align themselves with the electrical field applied.²³⁻²⁵ Depending on the physical nature of the material and microwave frequency, the dipoles can realign themselves with the electric field as it oscillates.²⁷⁻²⁸ The molecules are able to rotate with the oscillating electric field if they exist in a liquid or gaseous state, this is however restricted if the molecule is in solid state. No heating occurs at extremely low microwave frequency as these dipoles can completely adapt to the field variation. Similarly at high frequency, the molecules are unable to rotate quickly enough to adapt to the rapid oscillation change, resulting in no dielectric heating. These dipoles are able to rotate and respond to the electrical field in the microwave frequency region (300 MHz – 300 GHz) but the electrical field changes so rapidly that a lag is formed in between the rotation and oscillation, resulting in a phase difference that produces thermal energy via frictional force between the molecules.²⁴⁻²⁵

In the ionic conduction mechanism, ions rotate with the oscillating microwave electrical field and cause friction with other molecules or atoms within the system. Heat is produced as a result of the collision between these

particles. Most chemical processes follow the dipolar rotation mechanism unless the microwave heating of ionic liquids is involved.

1.5.4 Microwave Dielectric Heating Theory

1.5.4.1 Dielectric Properties

The dielectric properties of a material define the heating characteristics of the material. When microwaves couple with a material, the energy is partially reflected from the material and the other part is absorbed leading to dielectric heating.²⁹ The dielectric property of a material is expressed as the complex relative permittivity and can be determined using the following equation:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (\text{Equation 1.6})$$

Where, ϵ^* : complex relative permittivity of material

ϵ' : dielectric constant

ϵ'' : dielectric loss

j: imaginary component

The dielectric loss (ϵ'') indicates the efficiency of which microwave energy is converted into thermal energy and ϵ' is the dielectric constant that expresses the polarisability of the molecules in an electric field.^{25, 28} But instead of probing the complex relative permittivity, the ability of a material to convert microwave energy into thermal energy at a set temperature and frequency is more often depicted by the loss tangent, $\tan \delta$.^{25, 27} The loss factor can be expressed as the following equation:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (\text{Equation 1.7})$$

The loss factor, $\tan \delta$ is a convenient indication of the efficiency of a material to convert microwave energy into heat energy. In order to achieve efficient microwave absorption and heating, a large value of $\tan \delta$ must be obtained through a compromise between the dielectric constant (ϵ') and dielectric loss (ϵ''). As an example water has a $\tan \delta$ of 0.123 as the ϵ' of water is 80.4 at room temperature with a low ϵ'' . Kappe et al. have listed the $\tan \delta$ values of various organic materials as shown in the table below:

Table 1.2 Tan δ values of some common organic solvents (20°C, 2.45 GHz)²⁵

Solvent	Loss Factor ($\tan \delta$)
Water	0.123
Chloroform	0.091
Tetrahydrofuran (THF)	0.047
Toluene	0.04
Ethylene Glycol	1.35
Ethanol	0.941
Methanol	0.659
Acetic Acid	0.174

1.5.4.2 Temperature and Frequency Dependency of ϵ' and ϵ''

Both temperature and frequency are important parameters that control the ability of molecules to rotate and align with the dielectric field in microwaves, which ultimately affect the dielectric constant (ϵ') and dielectric loss (ϵ'') values. Hence it is important to investigate the dependence of ϵ' and ϵ'' on these factors in order to achieve accurate dielectric heating results. This can be expressed using the Debye equation below in terms of complex relative permittivity.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_S - \epsilon_\infty}{1 + j\omega\tau} \quad (\text{Equation 1.8})$$

Where, ϵ^* : complex relative permittivity of material

ϵ_S : static permittivity at very low frequency ($\ll \tau^{-1}$)

ϵ_∞ : infinite permittivity at very high temperature ($\gg \tau^{-1}$)

ω : angular frequency ($\omega = 2\pi f$, f is referred to frequency in Hz)

τ : relaxation time

j : imaginary component

Equation 1.8 can be separated into real and imaginary parts. The derivation for both ϵ' and ϵ'' can be expressed as follows:

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_S - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (\text{Equation 1.9})$$

$$\epsilon'' = \frac{\epsilon_S - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (\text{Equation 1.10})$$

The relaxation time (τ) and the corresponding relaxation frequency (f_c) are essential parameters used to determine the efficiency of microwave energy being converted into heat energy. When microwave energy is applied to a material, the molecules align themselves to the dielectric field. When the dielectric field is switched off, the molecules require a certain amount of time to revert from their rotated positions to their original randomised state. This time is referred to relaxation time, while the microwave frequency at which the molecules are in the relaxation state is known as the corresponding relaxation frequency. Since both these parameters are correlated, the corresponding relaxation frequency can be determined using $\tau = 1/(2\pi f_c)$. It is theoretically possible to determine the value of τ at a particular f_c as at this point, ϵ'' is at its maximum while ϵ' is at half of its declining value between ϵ_s and ϵ_∞ . Figure 1.18 below shows an example of frequency dependence of ϵ' and ϵ'' in the heating of water.

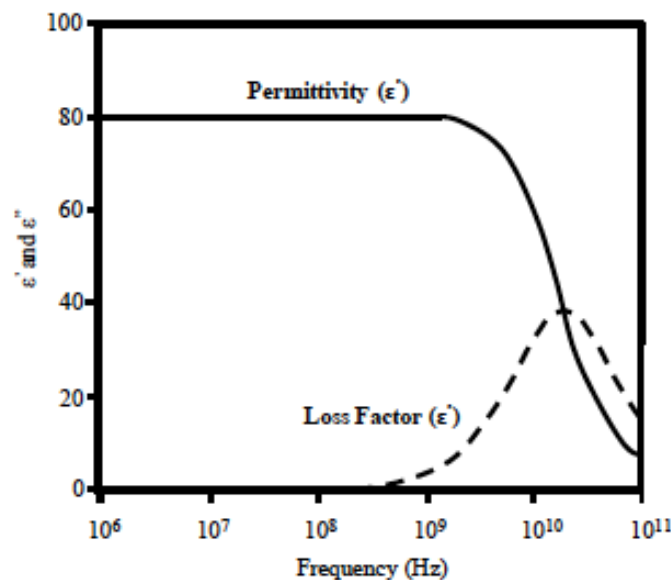


Figure 1.18 Frequency dependence of dielectric constant (ϵ') and dielectric loss (ϵ'') in the heating of pure water at 20°C, depicted by Gabriel et al.³¹

As shown in the plot in Figure 1.18, the water is not heated at a very low frequency ($\epsilon' \ll \tau^{-1}$) because the water molecules are able to rotate at a similar pace with the oscillating dielectric field. The plot also shows that the value of ϵ'' is at its maximum when ϵ' is at half of its declining value between ϵ_s and ϵ_∞ , this enables the estimation of τ to be 9×10^{-12} seconds as the corresponding relaxation frequency is approximately 18 GHz when determined from the maximum value of ϵ'' . The maximum value of ϵ'' indicates that maximum dielectric heating efficiency is located within this frequency region. Hence a reactor that operates at a frequency of 18 GHz would be able to heat water up more rapidly than at 2.45 GHz. When a microwave frequency of 2.45 GHz is used, the corresponding τ is estimated to be 65 picosecond. At this point, ϵ'' would not be at its maximum value resulting in less efficient dielectric heating at this frequency. However, the $\tan \delta$ for water is higher than 0.01 when using a microwave frequency of 2.45 GHz, indicating that dielectric heating is still efficient just not ideal.²⁸

1.5.4.3 Penetration Depth

Penetration depth (D_p) is one of the most important parameters used in microwave engineering. Metaxas and Meredith have defined penetration depth as the depth into the material at which point the microwave power has fallen to 37 % of the initial power forwarded.^{24-25, 26, 29} Penetration depth must always be taken into account when microwave-related experiments are being conducted as it is an indication of whether energy is evenly distributed within the heated medium, which is key in any scaled-up chemical reactions. Penetration depth is a function of dielectric constant (ϵ') and dielectric loss (ϵ''), as given by Meredith in the simplified equation as follows:

$$D_p \approx \frac{\lambda_0 \sqrt{\epsilon'}}{2\pi \epsilon''} \quad (\text{Equation 1.11})$$

In Equation 1.11, λ_0 is referred to free space microwave wavelength for microwave frequencies of 2.45 GHz (12.2 cm) and 915 MHz (32.7 cm). To ensure uniform heat distribution within a reactor, the cross-sectional area should be twice the penetration depth.

1.6 Summary of Chapter

In conclusion, literature studies have shown that the ROP of CL can be achieved using a tin catalyst and an alcohol as initiator at relatively high temperatures using conventional heating. Therefore, the aim of the work conducted in this thesis is to synthesise PCL using microwave heating. The objective is to conduct ROP using CL monomer and $\text{Sn}(\text{Oct})_2$ / R-OH as the catalyst / initiator system in a microwave reactor, and to study the effects of microwave heating on ROP. Additionally, microwave heating has been efficiently used to accelerate chemical reactions and reduce reaction time. However, the effect of microwave heating on the ROP of lactones, specifically of CL, is still poorly described.

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CHAPTER 2 EQUIPMENT AND ANALYTICAL METHODS

In order to interpret the experimental results accurately, the most relevant equipment parameters and characterisation techniques involved in this research work are discussed in this chapter. Experimental procedures relevant to the specific polymerisation methods discussed in each chapter will be presented in the introduction section of each chapter.

2.1 Microwave Reactors

Microwave reactors can typically be divided into two categories (a) single-mode and (b) multi-mode.

Microwaves are created by the magnetron prior to being directed into the cavity of the reactor. In the case of multi-mode microwave reactors (i.e. domestic kitchen microwave) the microwaves are distributed by the mode stirrer and are then reflected from the wall prior to interacting with the material. As a result, variable energy intensity (multi-mode energy) is created within the cavity, which leads to irregular dielectric heating. Therefore, the material is rotated within the cavity in order to achieve a more uniform energy distribution.

Single-mode microwave reactors provide better energy concentration than multi-mode reactors as the microwave generated by the magnetron are directed to the cavity through a waveguide that can be controlled in such a way as to produce a single, highly homogenous energy field of high power intensity.¹⁻²

2.2 CEM Discover

A CEM Discover microwave reactor was utilised in this study, the specific features of the CEM are as follows:³

- The microwave frequency is 2.45 GHz
- The maximum power output is 300W, supplied power is adjustable from 0-300 W with 1 W increment
- Self-tuning; single-mode cavity
- Temperature measurement via infrared (IR) sensor by Neoptix Inc, which measures the surface of the reactor

In the experimental work detailed in this thesis, an external optical fibre (OF) thermocouple was fitted into the bulk of the reaction medium to obtain a direct temperature measurement for comparison to the IR sensor during the reactions. The OF sensor was placed in the centre of the reaction vessel to record the temperature of the reaction material throughout polymerisation. The forward power was supplied continuously or by pulse depending on the temperature requirement. Reactions can be carried out under high pressure up to a maximum pressure of 2.07×10^6 Pa, but the polymerisations conducted in this study were carried out in an open vessel at ambient pressure. The CEM reactor was connected to a computer using a RS 232 cable and Chem Driver Version 2.6 was used as the computerised controller and recorder for all the reaction parameters in the experiments.

All the microwave-heated polymerisations conducted in this thesis were conducted in an open vessel while microwave heating was supplied continuously with a maximum forward power of 300 W. An overhead mechanical stirrer was

fitted to the open vessel to ensure that stirring was maintained as the polymerisation solution became more viscous, the impeller shaft and blades were constructed from glass and PTFE as metal elements cannot be used in the cavity. The reaction temperature was set using Chem Driver to heat the reaction material from room temperature to target temperature (i.e. 150 °C). During the ramp time, the forward power was automatically increased to ensure the target temperature was reached within the set period. Once the target temperature was achieved, the hold time started and the forward power was regulated to maintain the target temperature throughout the reaction time. A typical CEM setting for polymerisation conducted at 150 °C is shown in Table 2.1.

Table 2.1 Settings for a typical ROP conducted in a CEM at 150 °C using continuous microwave heating

Stage	1	2	3	4	5
Power (W)	300	300	100	100	100
Ramp Time (min)	10	0	0	0	0
Hold Time (min)	60	60	60	60	60
Temperature (°C)	150	150	150	150	150

The microwave and apparatus set-up are as shown in the photograph in Figure 2.2. An overhead mechanical stirrer was fitted into the reaction vessel to ensure the contents of the vessel are stirred vigorously.

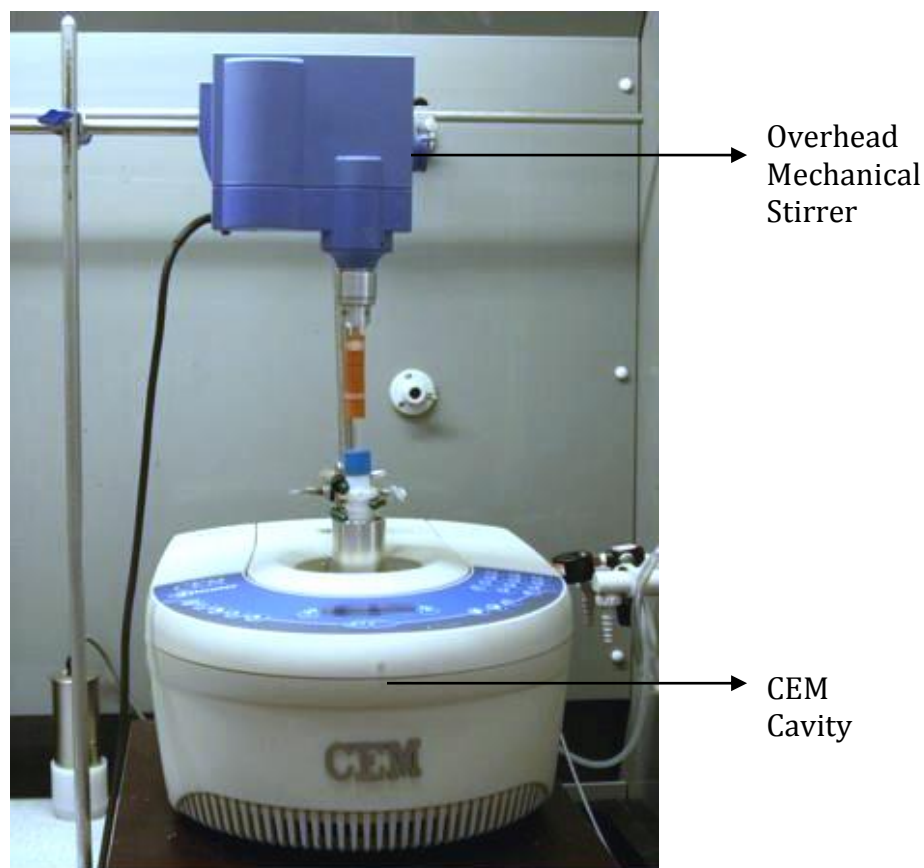


Figure 2.1 CEM microwave with an overhead mechanical stirrer for bulk polymerisations

2.3 Miniflow 200SS

A second microwave reactor was employed in this study, known as the Miniflow 200SS (Sairem). The specific features of the Miniflow are as follows:

- The microwave frequency is 2.45 GHz (no magnetron)
- The maximum power output is 200 W, supplied power is adjustable from 0-200 W with 1 W increment
- Manual tuning required to minimise reflected power (close to 0)
- No built-in temperature measurement system. An external OF thermocouple was connected to the microwave reactor for temperature recording, temperature of the reaction material was measured directly

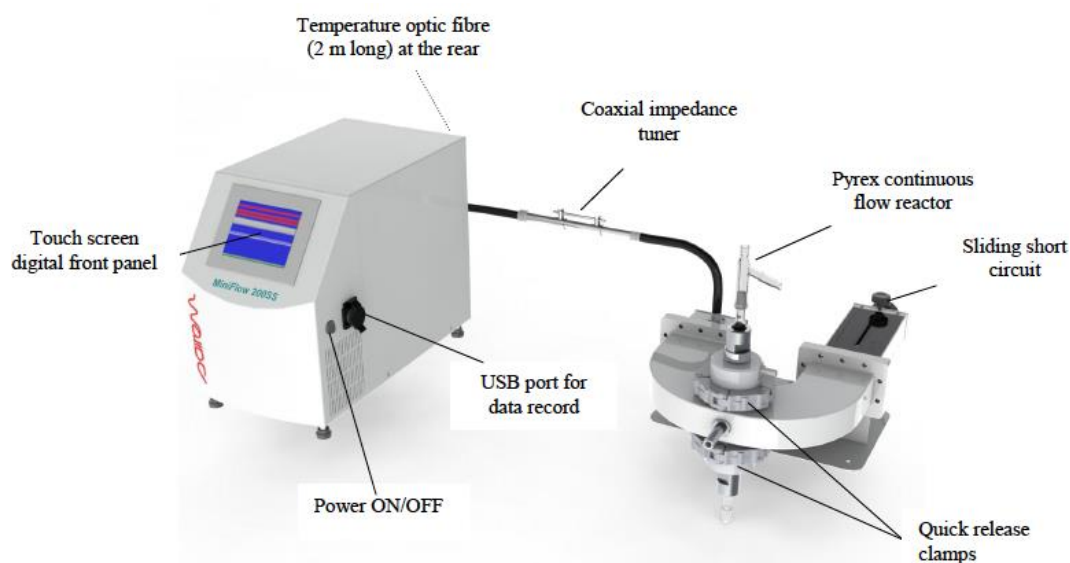
- Polymerisation can be conducted in either batch or continuous mode.
In this study, reactions were conducted in batch mode
- Delivered with 2 microwave cavities: TE (transversal electric) or U-waveguide cavity and TM (transversal magnetic). In this study, U-waveguide and TM was utilised

Similar to the CEM, the forward power of the Miniflow was controlled automatically based on the temperature feedback from the OF measurement to produce continuous or pulse microwave irradiation. Once again, reactions were conducted in an open vessel where the OF thermocouple was directly immersed into the reaction material where temperature was measured from the centre of the reaction flask. The OF thermocouple was directly connected to the microwave reactor where the temperature and forward power were controlled using the touch screen set-up panel on the Miniflow.

The heating stages were controlled using the Miniflow panel, which also recorded all reaction parameters. During the ramp time, the forward power was automatically increased to ensure the target temperature was reached within the set period. Once the target temperature was achieved, the hold time started and the forward power was reduced and regulated to maintain the target temperature throughout the reaction time. Unlike the CEM, the Miniflow requires manual tuning prior to polymerisation in order to control the reflected power and ensure the reflected power is close to 0. Fine tuning ($\sim 1-5$ W) can be carried out throughout the reaction. A typical Miniflow setting for polymerisation conducted at 150 °C is shown in Table 2.2.

Table 2.2 Settings for a typical ROP conducted in the Miniflow at 150 °C using continuous microwave heating

Stage	1	2
Power (W)	200	100
Ramp Time (min)	10	0
Hold Time (min)	60	60
Temperature (°C)	150	150

**Figure 2.2 Diagram of the Miniflow 200SS reactor, adopted from Sairem's Miniflow 200SS instructions handbook**

2.4 2 kW Single-mode Microwave Reactor

In this study, a 2 kW single-mode microwave generator (Sairem) was also employed in order to produce heat profiles as preparation for the scale-up of PCL synthesis. The specific features of this reactor are as follows:

- The microwave frequency is 2.45 GHz
- The maximum power output is 2 kW, supplied power is adjustable from 0-2000 W. The recommended minimum power output is 100 W
- Automatic tuning via software to minimise reflected power (close to 0)
- No built-in temperature measurement system. An external OF thermocouple was connected to the microwave reactor for temperature recording, temperature of the reaction material was measured directly
- Polymerisation can be conducted in either batch or continuously. In this study, experiments were conducted in batch mode

Similar to the Miniflow, the forward power was adjusted automatically based on temperature feedback from the OF thermocouple immersed in the reaction flask and recorded by the Neoptix. Inc software upon a dedicated PC. Heating of the materials was conducted in an open vessel using a magnetic stirrer for agitation as it had been shown that at the target reaction temperature the solution viscosity was sufficiently low to allow good mixing with the magnetic stirrer. Prior to setting the forward power and heating time, calculations were made based on the specific heat and mass of the materials to achieve an estimate of how much energy the material is able to absorb. In this study, all heating / reactions

were completed in less than 5 minutes, hence only one heating stage was set due to the short heating period.

A typical 2 kW single-mode reactor setting for polymerisation conducted at 150 °C is shown in Table 2.3.

Table 2.3 Settings for a typical ROP conducted in the 2kW single mode microwave generator at various power levels and heating time

Power (W)	Time (s)	Average Temperature (°)
450	60	185
900	30	162

Table 2.4 Summary of comparison between the CEM, Miniflow and 2kW single-mode microwave reactors

Instrument	CEM	Miniflow	2kW Single-mode
Tuning	Automatic	Manual; more accurate	via software
Cavity	Enclosed cavity, no physical observations can be done throughout reaction	Cavity has a "view-hole", physical observations can be done throughout the reaction	Cavity has a "view-hole", physical observations can be done throughout the reaction
Heat-loss	Enclosed cavity, minimum heat loss to the surroundings	U-shape waveguide, heat loss from the reaction to the surroundings	Not enclosed, but less heat-loss than MiniFlow
Temperature Control	IR and Fibre-Optic	Fibre-Optic only	Fibre-Optic only
Reflected Power	No details provided	Details provided. Microwave effects on material can be studied	Details provided. Microwave effects on material can be studied
Maximum Power Output	300W	200W	2000W
Stirring	Built-in magnetic stirrer	No. But a magnetic stir-plate can be placed under cavity	No. But a magnetic stir-plate can be placed under cavity
Others		Reflected power must be kept below 30W to avoid damage to generator	Sufficient training and supervision required

2.5 Polymer Structure Characterisation

Molecular weight determination is one of the most important stages in polymer synthesis as the physical properties, mechanical properties and biodegradability of a polymer are determined by the molecular weight of the polymer. Unlike a small molecule, a polymer consists of a mixture of different molecular weights. Due to this dispersity or heterogeneity in molecular weights, it is hence important to consider both the average molecular weight and molecular weight distribution of the polymeric material taking into account the spread of chain lengths present in the particular sample.⁴

Various analytical techniques can be utilised to determine the average molecular weight of a polymer. The method used to determine the polymer molecular weight is dependent on the properties related to the polymer molecule sizes, as some methods are tailored to analyse molecules with low molecular weights more accurately while others are favoured for molecules with high molecular weights.¹⁰ However, it is important to understand the following terms that are commonly used in polymer chemistry when describing molecular weights, these include:

- Number average molecular weight (M_n)
- Weight average molecular weight (M_w)
- Dispersity index ($\mathcal{D}$)
- Degree of polymerisation (DP)

The number average molecular weight (M_n) of a polymer is the total weight of the polymer divided by the number of moles in the polymer. The number of moles in the polymer can be measured by calculating the number of molecules that are present in the polymer sample. M_n can be expressed using the following equation:

$$M_n = \frac{w}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x}$$

Where, N_x : Number of molecules of weight M_x

w : Total weight of the polymer sample

The weight average molecular weight (M_w) can be determined by dividing the total weight of the polymer sample by the total number of polymer molecules as expressed in the following equation:

$$M_w = \sum w_x M_x = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

Where, w_x : Weight fraction of molecules of weight M_x

The average molecular weight of a polymer can be fully characterised by plotting the molecular weight distribution (MWD) using the values of M_n and M_w , as shown in Figure 2.3 below:

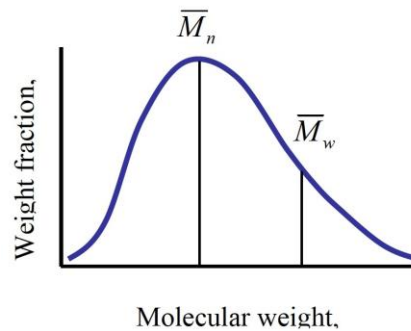


Figure 2.3 Molecular weight distribution curve for a typical polymer

As shown in the molecular weight distribution plot in Figure 2.3, M_n is leaning towards a lower molecular weight while M_w is leaning towards a higher molecular weight.¹⁰ The width of the molecular weight distribution curve is determined by the ratio of M_w/M_n , also known as the dispersity index or polydispersity ($\bar{D}$) of the polymer. In real examples the value of M_w will always be greater than M_n for any given polymer. Theoretically the value of $\bar{D}$ should be 1 for an ideal polymer, suggesting that all the molecules in the polymer have the same molecular weight. However, experimental values of $\bar{D}$ can vary depending on the polymerisation.¹⁰ In practical experiments, the average molecular weight, $\bar{D}$ and molecular weight distribution can be determined using gel permeation chromatography (GPC) which will be discussed in the latter section.

Besides molecular weight, the degree of polymerisation (DP) is another commonly used term often used to describe the chain length of a polymer. DP can also be defined as the average number of monomer units in a polymer chain.^{4, 6} In practical experiments, the value of DP can be determined via end-group analysis using ^1H Nuclear Magnetic Resonance (^1H NMR) or Matrix-assisted Laser Desorption/Ionisation Time of Flight Mass Spectroscopy (MALDI-TOF MS) which will be further discussed in the following sections.

2.5.1 Nuclear Magnetic Resonance (NMR)

NMR was a primary technique used in this research work to determine the structure of the resultant polymer. In this study, NMR was mainly used to determine the chemical structures of known polymers. The chemical shifts of these polymers were identified from the polymer handbook¹² and other literature. The most common NMR methodologies used in polymer synthesis and cited in the literature are ^1H and ^{13}C NMR.

In practice, the analytical sample was made up of 1 mg : 1 mL polymer sample and deuterated chloroform solution prior to being placed in a Bruker DPX-300 for NMR analysis.

A magnetic nucleus possesses a small number of quantised energy levels when placed in a magnetic field, and NMR is essentially the chemical structure information derived from the interaction between the magnetic nucleus of an atom and a magnetic field of an electromagnetic pulse. A nucleus that has an odd number of protons and neutrons is able to provide NMR information due to the presence of angular momentum. However, a nucleus that consists of an even number of protons and neutrons is lacking angular momentum and therefore no NMR spectra can be derived. The resonance frequency given off by each nucleus in the magnetic field is different due to the different magnetic characteristic of each nucleus, therefore this information is used to distinguish each nucleus. The environment in which the molecular nucleus is in also determines the resonance frequency and chemical shift, which is used to obtain information on the chemical structure.⁵

2.5.1.1 Proton NMR (^1H NMR)

^1H NMR was used in this study to determine the monomer conversion throughout the reactions and to identify the end-group of the polymer. To calculate the monomer conversion, the chemical shifts of the methylene proton resonance adjacent to the oxygen of the carbonyl group and polymer were identified and the integrals were compared. For end-group analysis, benzyl alcohol (BnOH) and glycerol were determined as the initiator/ polymer end-group in Chapter 3 and Chapter 4 respectively. The specific calculations are presented in each relevant chapter.

2.5.2 Gel Permeation Chromatography (GPC)

GPC was used in this study to determine the molecular weight and polydispersity of the resultant polymer. GPC is also commonly known as size exclusion chromatography (SEC) as the macromolecules are separated based on the hydrodynamic volume or size of the analytes. The analytes are allowed to pass by the column packed with porous beads where the smaller analytes pass through the pores of the beads more easily than their larger counterparts, this increases the retention time of the smaller analytes in the pores. Figure 2.4 below shows a simplified instrumentation of a PL-GPC 120 by Polymer Laboratories as used in the practical work conducted in this study.

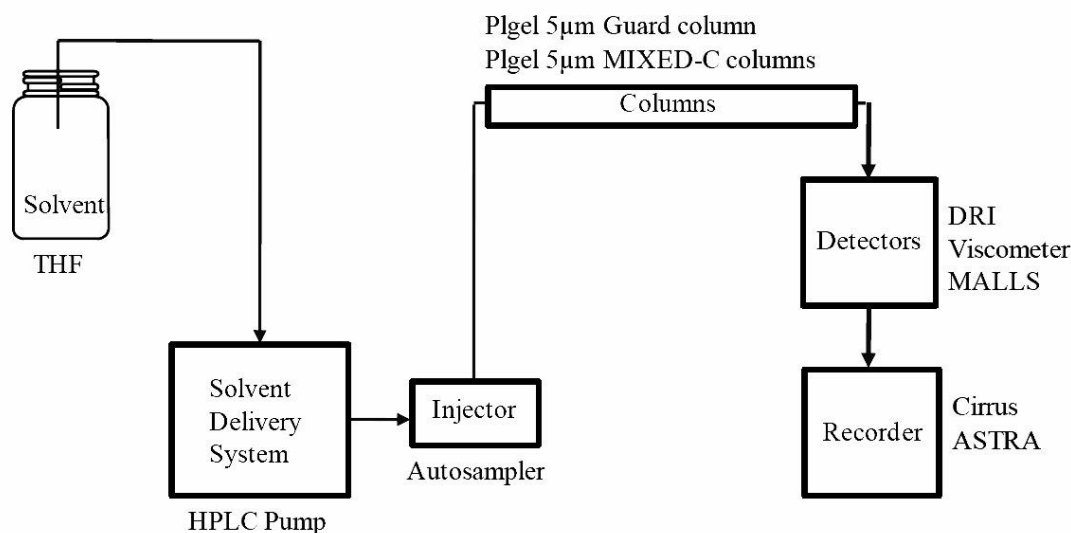


Figure 2.4 Schematic diagram of PL-GPC 120 by Polymer Laboratories¹¹

To prepare an analytical sample for GPC, 7 mg of polymer in 1 mL THF was made up in a GPC vial prior to being injected into the GPC column via an autosampler. There are a total of three columns where the polymer solution was transported through. The first one was the Guard column (PLgel 5 µm, Polymer Laboratories). The second and third columns were the Mixed-C columns (PLgel 5 µm, Polymer Laboratories) where separation of the polymer samples occurred. Samples were analysed after the polymer was separated into fractions, allowing the determination of molecular weight (M_n and M_w) and polydispersity ($\mathcal{D}$).

In the synthesis of star PCL mentioned in Chapter 4, GPC was not used to analyse the polymer product due to the nature of the star polymers chemical structure. The branched nature of the structure means that the various arms are composed of various molecular weights that may themselves act in the GPC as linear polymers. This may lead to inaccurate determination of molecular weight and polydispersity of the star polymers. The molecular weight of the star polymers with lower DPs were analysed using MALDI-TOF MS instead.

2.5.3 Matrix-Assisted Laser Desorption/Ionisation-Time of Flight Mass Spectroscopy (MALDI-TOF MS)

In this study, MALDI-TOF MS was used to determine the molecular weight and end-group of the DP21 star polymers. A Bruker Ultraflex III spectrometer was used to conduct this analysis.

Matrix-Assisted Laser Desorption (MALDI) comprises an ionisation method and TOF MS detection for polymer analysis while using a compound consisting of a matrix and salt. In this study, dithranol and sodium trifluoroacetate were used as the matrix and supporting salt for ionisation respectively. The polymer is deposited onto the matrix, which supports vaporisation by absorbing the laser energy, prior to being carried into a gas phase. In the gas phase, the supporting salt assists ionisation of the polymer via cationisation.⁷

Time of Flight Mass Spectroscopy (TOF MS) is an analytical technique commonly associated with MALDI. A high voltage ~25 kV is applied to accelerate the ions prior to being drifted in an evacuated tube. In this study, MALDI-TOF MS analysis was conducted using a reflectron mode to slow down the ions in order to produce spectra with high resolution.

2.5.4 Differential Scanning Calorimetry (DSC)

In this study, DSC was used to determine the melting temperature (T_m) and glass transition temperature (T_g) of both linear and star PCL in order to compare both polymers.

In a typical DSC analysis, 3 mg of polymer was weighed onto a pan. The pan was then transferred to a DSC cell where the reference pan was placed. A DSC Q2000 was used to conduct this thermal analysis, which is connected to a PC. Data was analysed using TA analysis software.

DSC utilises a thermal analytical technique to determine the properties of a polymer in the function of temperature. During the analysis, the temperature of the polymer was measured continuously alongside a reference. The heat used to maintain the temperature of the polymer in order to match the temperature of the reference was also recorded as heat flow in the form of heat gain or heat loss.⁸ Results were plotted onto a graph as heat capacity against temperature, and the inflection points of the plotted curve were used to determine both T_m and T_g .

2.6 Summary of Chapter

The aim of this chapter is to achieve a comprehensive understanding of the equipment, synthesis methods and polymer characterisation techniques employed in the work conducted in this thesis. The CEM, Miniflow and 2 kW Single Mode microwave reactors were studied in detail in order to compare the features of each reactor and to determine the effect of these different features on the synthesis of PCL. Resultant polymers were characterised using ^1H NMR, GPC, MALDI-TOF and DSC to ensure the quality of the PCL was consistent across different equipment used.

2.7 References

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CHAPTER 3 SYNTHESIS OF LINEAR POLYCAPROLACTONE USING MICROWAVE HEATING

3.1 Overview

This chapter will discuss the synthesis of linear poly-(ϵ -caprolactone) using microwave heating. This study aims to investigate the ring-opening polymerisation (ROP) of ϵ -caprolactone (CL) using benzyl alcohol (BnOH) and tin octanoate ($\text{Sn}(\text{Oct})_2$) as the initiator / catalyst system.

The first section of this chapter consists of the literature findings on previously reported polymer synthesis using microwaves as a heating method. Microwave effects on previously reported ROP are summarised in this section.

This is followed by the results obtained from the practical work conducted within this study, where a direct comparison of kinetic studies of ROP reactions conducted using both conventional and microwave heating at different reaction temperatures and using different synthetic methodologies are presented, leading to the overall conclusion on the effect that microwave heating has upon this polymerisation system. In greater detail, the pseudo-living characteristics of the ROP of CL in both conventional and microwave heating systems were investigated and compared. Kinetic studies were conducted on the formation of the actual alkoxide active species in the induction / initiation stage of ROP. Induction period and propagation rates were studied to understand the microwave effects on the system. Conventional heating reactions were conducted using an oil bath while the microwave-heated experiments were conducted with a CEM Discovery reactor.

3.2 Literature Review

3.2.1 Ring-opening Polymerisation of CL using Microwave Heating

In recent years, there has been a growth in level of research interest in utilising microwave heating as an alternative heating method for the production of polymers.^{1,2} Based on the research work conducted so far, there has been conflicting reviews on the benefits of using microwave heating over conventional heating. Beneficial effects like rate enhancement have been reported in some studies^{1,2}, but others have reported negative effects (i.e. reduction in rate of polymerisation) when microwave heating was used in place of conventional heating methods.³

The ROP of CL using microwave heating has been conducted using a wide range of methods, which include the utilisation of different types of catalysts and microwave equipment.³⁻¹⁶ In this introduction, prior microwave ROP work using different catalysts and microwave reactors will be discussed first, followed by a more specific review of PCL and the synthesis of polymers using alcohol initiators and $\text{Sn}(\text{Oct})_2$ catalyst, as these are the reaction systems used for the ROP of CL in the experimental work conducted and discussed in this thesis chapter.

In the last decade, studies have been dedicated into improving the ROP process by developing various catalysts and exploring compounds such as tin, aluminium, zinc and other rare earth metals.⁷⁻¹⁶ Albert et al. successfully synthesised PCL using titanium tetrabutylate as a catalyst and microwave radiation as the heating source.⁴ Polymerisation was heated isothermally at 180°C using a single mode (TE_{10}) microwave reactor at 2.45 GHz and these microwave generated results were compared to those conducted using thermal heating in a thermostat.

The conversion, viscosity build-up and growth in polymer molecular weight were determined for the reactions.

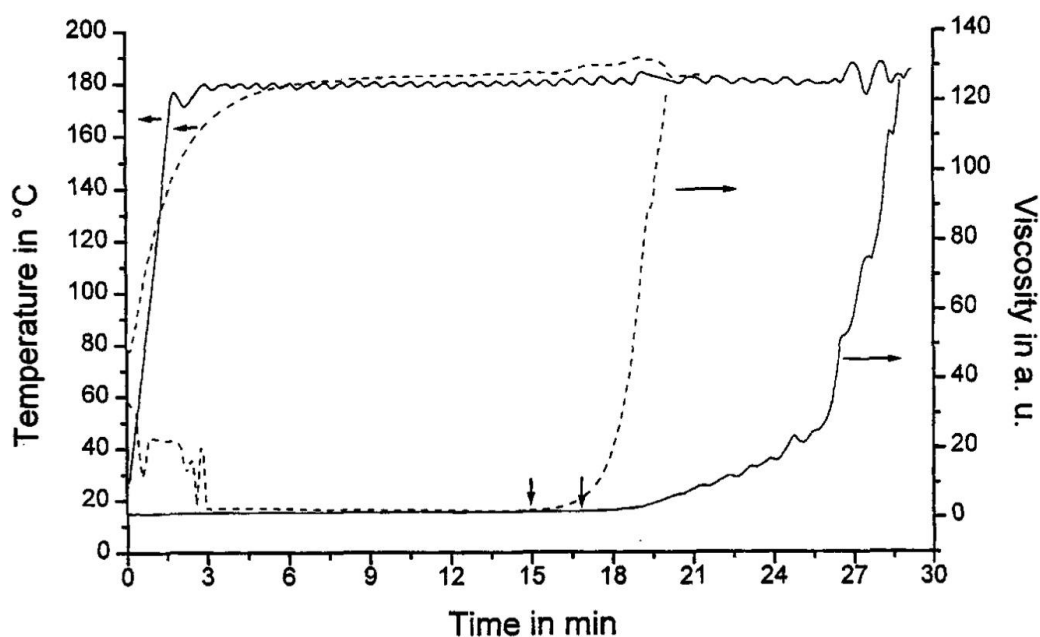


Figure 3.1 Temperature and viscosity of the reaction mixture over time in the microwave (full line) and thermostat (dashed line), extracted from study by Albert et al.⁴

The single mode microwave reactor allowed the measurement of power input, transmitted power and reflected power to be determined. The power output by the microwave reactor was 300 W for the system during the period where the reaction mixture was progressing to the target temperature, after the set point was reached the power was then gradually decreased during the reaction to maintain the reaction temperature at 180 °C. The reflected power was observed to increase towards the end of polymerisation and this was attributed to the high viscosity and the low microwave absorption of PCL compared to its monomer counterpart.

Polymerisations were conducted using three different CL to titanium tetrabutylate ratios, but results obtained were similar for each scenario and conversions fell within the range of 89 to 99 %. Minor differences in viscosity build up and molecular weights of the final polymer were determined but the author

claimed that there were no significant improvements observed when microwave heating was used over conventional heating.

Liu and coworkers⁷ investigated the ROP of CL initiated by benzoic acid. The polymerisation was conducted using a 2.45 GHz Whirlpool-VIP275 multimode microwave oven and results were compared to the reactions conducted using conventional heating. A maximum power of 850 W was applied to the reaction in this study and the reaction temperature was measured with a tin-grounded thermocouple. It was concluded from this study that the rate of propagation was significantly enhanced by microwave heating. However, the conclusion was drawn based only on the comparison of the polymer molecular weights from both microwave and conventional heating systems. As an example, PCL of $M_w = 4000$ g/mol was obtained after 30 mins in the microwave (340 W) at 160 °C (Figure 3.2) while it took 240 mins to obtain $M_w = 3100$ g/mol when conventional heating was used at 155 °C but no kinetic data was presented to support these conclusions.

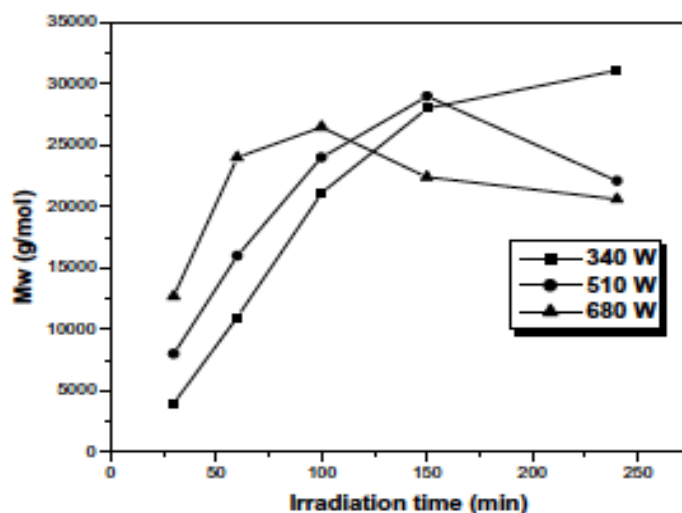


Figure 3.2 Effect of microwave power on M_w of PCL, extracted from study by Liu and coworkers⁷

Liao et al. studied the synthesis of PCL using zinc powder as a catalyst.⁵ The microwave reactor used in this study operated at 2.45 GHz but the detailed model

and design were not described. The microwave heating system was supplied with constant powers of 170, 340, 510 and 680 W while the reaction temperature ranged from 80 °C to 210 °C. It was observed that when the power output was increased, the reaction temperature also increased. It was concluded that microwave heating enhanced the ROP of CL compared to when conventional heating was used. Once again, this conclusion was based only on the M_w of the polymer product from both heating systems. Kinetic studies and rate constants were not presented while the reaction temperatures used were not identical, for example, the M_w of the PCL product obtained when zinc was used was 79200 g/mol at 150 °C using 510 W in the microwave, while the M_w of PCL in the conventional heating system was 27000 g/mol and the polymerisation was conducted for 48 hours at 120 °C. Due to the fact that the reaction temperatures in both heating systems were not determined, comparison between the rates of polymerisation may be deemed invalid.

Ring-opening Polymerisation of CL using $\text{Sn}(\text{Oct})_2$ catalyst

$\text{Sn}(\text{Oct})_2$ is one of the most commonly used catalysts in the industrial production of PCL as it is accepted by the US Food and Drug Association (FDA) as a food additive and also favoured in terms of biomedical applications. As the ROP of CL has been applied commercially, the application of $\text{Sn}(\text{Oct})_2$ in the reaction is a key interest in this study.^{5,10-13,15,16}

Liao et al. conducted the ROP of CL using $\text{Sn}(\text{Oct})_2$ to investigate the heating characteristics of the polymerisation when microwave heating was used.¹¹ In this study, a 2.45 GHz multimode Whirlpool-JA203 microwave with a maximum forward power of 850 W was applied and the reaction temperature was monitored

and measured using a thermocouple that was inserted into a self-made ampoule. The authors made an observation that the mass of CL present in the reaction had a strong influence on the reaction temperature. For experiments conducted at the same power level in the microwave, the reaction temperature was noted to increase when the amount of monomer was increased.

In a separate study, the same authors investigated the ROP of CL using only $\text{Sn}(\text{Oct})_2$ without the presence of an alcohol initiator using both microwave and “flash” conventional heating.¹² A hot salt bath at 240 °C consisting of KNO_3 , NaNO_2 and NaNO_3 was utilised as the method of “flash” heating, the results obtained were compared to those conducted using a National NN-S570-MFS microwave oven operating at 2.45 GHz with a power output of 700 W for a pre-determined heating time. When polymerisation was conducted using the “flash” conventional heating method, the reaction temperature reached 213 °C in 3 minutes while it took 6 minutes in the microwave at 700 W. A difference in monomer conversion was also observed in both heating systems. For example at 213 °C, a 99 % conversion was achieved in 8 minutes when “flash” conventional heating was used while this conversion was only 62 % in the microwave. The semi logarithmic kinetic plot showed that the propagation rate constant (k_p) of the reaction conducted using “flash” conventional heating was 4.48 times faster than the reaction using microwave heating. Even though the concentration of the propagating species was not taken into account, the data is still deemed valid in terms of rate of polymerisation.

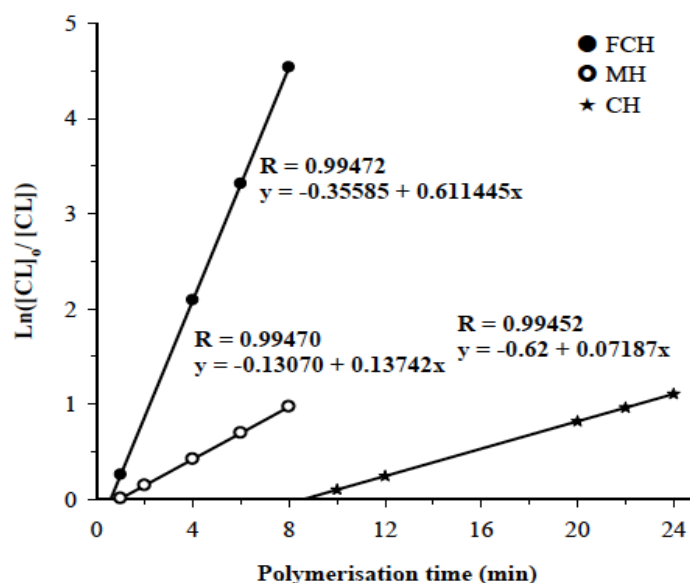


Figure 3.3 Semi Logarithmic kinetic plot from study by Liu et al.¹²

Furthermore, the same authors examined the thermal and non-thermal effects of microwave by further investigating the kinetics of polymerisation using both “flash” conventional and microwave heating at a range of different reaction temperatures. It was concluded that the reactions conducted using conventional heating obeyed the Arrhenius Law, which states that the rate of polymerisation increases when temperature increases, and is therefore a thermal effect. The microwave-heated reactions however did not obey the Arrhenius Law, which suggested the non-thermal effect of microwave heating on ROP in this study (Figure 3.4).

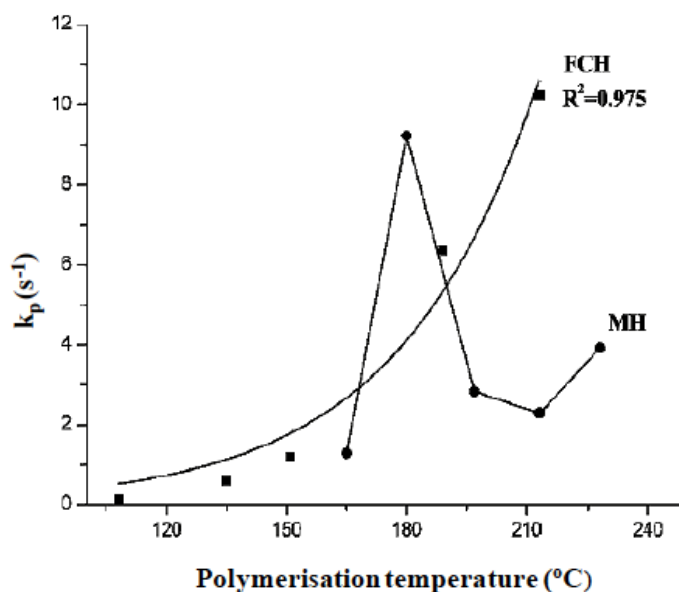


Figure 3.4 Dependence of k_p on polymerisation temperature using “flash” conventional heating (FCH) and microwave heating (MH) from study by Liu et al.¹³

In a more recent study, Liu and colleagues also investigated the scaled-up ROP of CL.¹⁴ A multimode WLD6S-01 microwave oven operating at 2.45 GHz with a maximum power output of 600 W was specially designed for this study, the temperature of the system was monitored by means of infrared (IR) measurement. Polymerisations were conducted using different microwave power levels of 850, 1700 and 2550 W. A conversion of 93 % was obtained in 40 minutes and the M_w of the PCL product ranged between 66000 and 12200 g/mol. It was observed that when the masses of CL monomer and microwave power were increased, the reaction temperature also increased.

The ROP of CL using microwave heating was also conducted by McCarthy et al. in the presence of $\text{Sn}(\text{Oct})_2$ under non isothermal conditions.¹⁰ However, the microwave reactor information were not specified in this publication. Polymerisations were conducted at different microwave power levels and monomer conversion was observed. The authors claimed that the reactions did not

initiate when the power level was below 200 W while close to 100 % monomer conversion was achieved in 1 minute when 500 W was applied. However, the PCL product obtained from the reaction completed in 1 minute at 500 W exhibited lower M_w and $\bar{D}$ values. The authors did not provide an explanation for this rapid rate of polymerisation but attributed it to interchange reactions between polymer chains.

Lastly, Fang and coworkers conducted the ROP of CL using 1, 4-butadienol / $\text{Sn}(\text{Oct})_2$ as the initiator / catalyst system with different microwave frequencies.¹⁶ The authors did not make a direct comparison between the reactions using both conventional and microwave heating in terms of kinetics of polymerisation and properties of PCL. A LT502XB Lambda microwave reactor was used with a pulse power on-off cycle utilised to control the temperature at constant level. ROP was conducted with and without the initiator at 120, 150, 180 and 200 °C. It was observed that high conversions were achieved in 2 hours in the microwave between 150 and 200 °C, with and without the initiator. The rates of polymerisation were not followed but the authors concluded that microwave heating has enhanced the rate of polymerisation in this study based on previous work conducted with $\text{Sn}(\text{Oct})_2$ using conventional heating at 120-140 °C which offered conversions of 92 – 99 % over 16 to 18 hour periods. It was also observed that lower M_w values were obtained when initiator was added into the reaction compared to those without the initiator, but these values were in good agreement with the theoretical M_w for the pre-determined monomer / initiator molar ratio. This was attributed to the varying water content in the monomer which served as the initiator in the reactions conducted without 1, 4-butadienol.

3.3 Aims and Objectives

Based on the literature review, the key aim of the work discussed in this chapter is to compare and contrast the ring-opening polymerisation (ROP) of CL with benzyl alcohol / tin octanoate as the initiator / catalyst system using both conventional and microwave heating. It will be sought to confirm the hypothesis that microwave heating accelerates the rate of polymerisation in the synthesis of linear poly(caprolactone) [PCL]. Secondly, this study aims to verify the pseudo-living characteristics of ROP in the synthesis of linear PCL. Lastly, this study also aims to determine if microwave heated reactions obey the Arrhenius Law, and thus to clarify whether microwave heating exerts a thermal effect.

The first objective is the synthesis of linear PCL using both conventional and microwave heating at a temperature range of 140°C to 180°C, to compare and contrast both heating methods. The second objective is to determine the relationship between M_n of the growing PCL chain over time at a temperature range of 140°C to 180°C, using both conventional and microwave heating. The last objective is to compare the apparent (k_{app}) and propagation (k_p) rate constants for polymerisations conducted using both conventional and microwave heating, this will determine whether microwave heating is similar to conventional heating, which exerts a thermal effect.

3.4 Experimental

3.4.1 Materials

ϵ -caprolactone (99 %, Acros) and anhydrous benzyl alcohol (99.8 %, Sigma Aldrich) were purchased and used as received without further purification. A stannous octanoate stock solution was prepared by dissolving 2.45 g of $\text{Sn}(\text{Oct})_2$ (96 %, Sigma-Aldrich) in 50 ml of dry toluene. Toluene was distilled prior to being dried over molecular sieves in the School of Chemistry.

3.4.2 Polymer Characterisation

3.4.2.1 Determination of Monomer Conversion using ^1H NMR

^1H NMR spectra for kinetic samples were recorded in CDCl_3 using a Bruker DPX-300 spectrometer operating at 300 MHz. Spectra were obtained using sample concentrations of 20-30 mg/mL in deuterated chloroform (chloroform-D) as the solvent and tetramethylsilane as the internal reference in 5 mm o.d. tubes at room temperature. Chemical shifts were displayed in units of parts per million (ppm). ^1H NMR spectra generated by ChemBioDraw Ultra 12.0 software was used to determine monomer conversion and end-group analysis.

Monomer conversion was determined by comparing the integrals of the methylene proton resonance adjacent to the oxygen of the ester group for both CL monomer ($-\text{CH}_2\text{OCO}-$, $\delta = 4.24$ ppm) and PCL polymer ($-\text{CH}_2\text{OCO}-$, $\delta = 4.07$ ppm). Monomer conversion was then calculated by inserting these integral figures into the following equation (Equation 3.1):

$$\text{Conversion (\%)} = \frac{\text{Polymer}}{\text{Monomer} + \text{Polymer}} \times 100 \% \quad (\text{Equation 3.1})$$

A sample calculation to determine monomer conversion is shown as follows:

$$\text{Conversion} = \frac{1}{1 + 0.04} = 96 \%$$

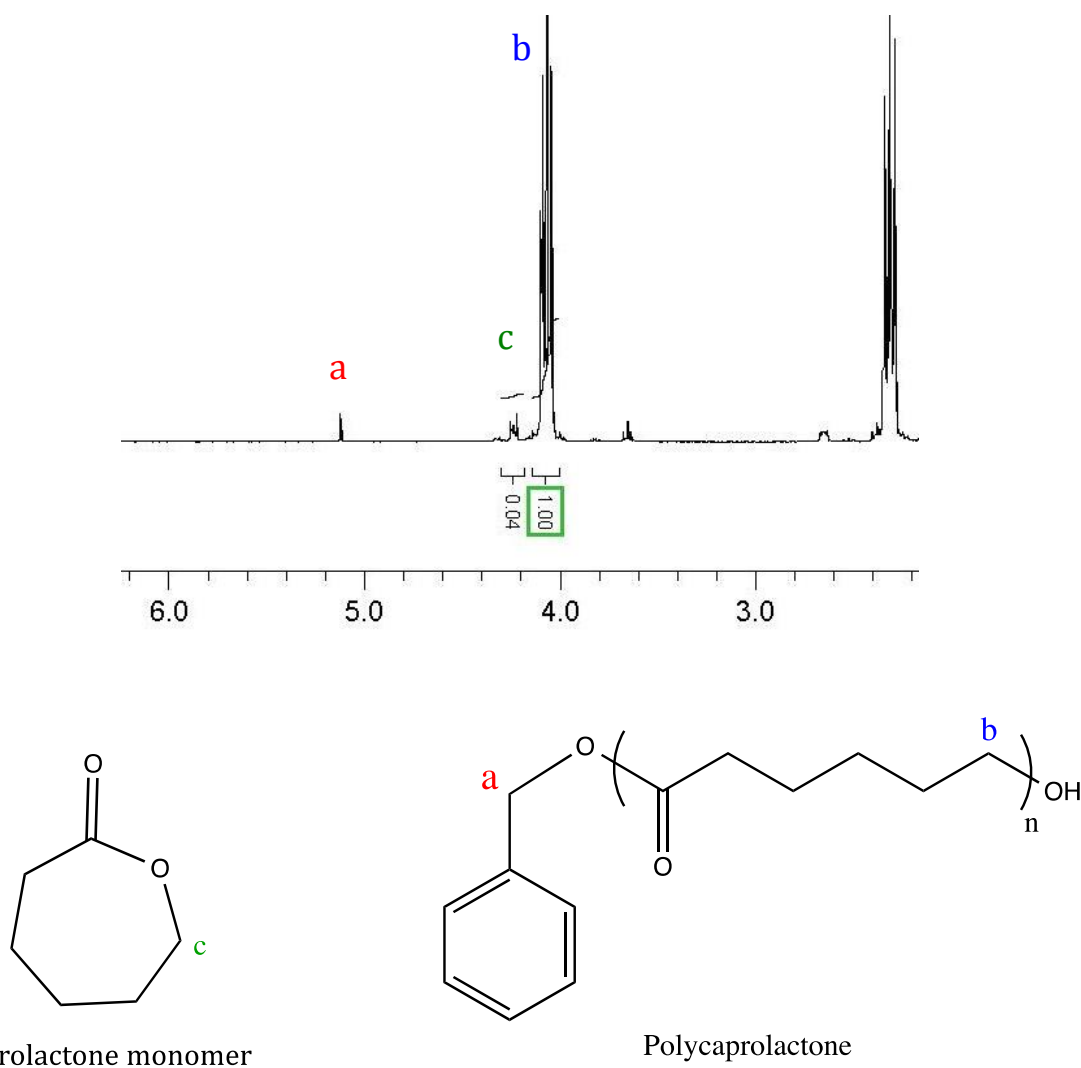


Figure 3.5 ^1H NMR for a typical kinetic sample of ROP of CL using $\text{BnOH}/\text{Sn}(\text{Oct})_2$ as the initiator/catalyst system. Sample was taken after 3 hours using conventional heating at 160°C

The ^1H NMR spectra in Figure 3.5 shows that benzyl alcohol is indeed the end-group of the polymer as indicated by the methylene proton resonance adjacent to the ester group ($\delta = 4.1$ ppm) and methylene proton ($\delta = 5.1$ ppm) that belongs to the benzyl ester end group.

3.4.2.2 Determination of Molecular Weight using Gel Permeation Chromatography (GPC)

Average molecular weight (M_w), number average (M_n) and polydispersity ($\bar{D}$) of the polymers were determined using Gel Permeation Chromatography (GPC) on PL-120 Polymer Labs equipment comprising a refractive index (RI) detector. In a typical procedure for preparation of a GPC sample, a polymer solution sample of 5-10 mg/mL of PCL in HPLC THF was filtered through a 0.2 μm sieve to a GPC vial. These samples were then placed into the GPC column using PS standard. The columns were calibrated with polystyrene standards and HPLC grade THF as the eluent at a flowrate of 1 mL/min at 40 °C.

3.4.2.3 Determination of Thermal Properties using Differential Scanning Calorimetry (DSC)

In a typical procedure, a polymer sample of 3 mg was weighed into a standard pan. An empty pan was used as a reference. The heating profile was set from -65 °C to 60 °C with a heating rate of 20 °C/min. Measurements were conducted under a nitrogen atmosphere. DSC results for linear PCL were reported in Chapter 4 as a direct comparison with star PCL.

3.4.3 Experimental Procedures

All polymerisations conducted in this section were performed as bulk reactions without further purification of the reaction materials. The procedures for ring-opening polymerisation conducted using conventional and microwave heating were as follows:

3.4.3.1 Ring-Opening Polymerisation using Conventional Heating

The typical procedure for the synthesis of PCL using conventional heating consisted of weighing 6.25 g of ϵ -caprolactone (54.8 mmol, 98 mol%) into a 50 ml flask. 68 μ L of BnOH (0.63 mmol, 1 mol%) and 28.7 μ L of Sn(Oct)₂ (0.24 mmol, 0.4 mol%) were then added into the reaction flask using a syringe. A target DP = 87 was selected in order for results to be comparable to the work that was previously conducted by the group.³⁸

The flask was also equipped with an external overhead mechanical stirrer operating at approximately 300 rpm to ensure the content was stirred homogenously. The flask was then immersed into a pre-heated oil bath at reaction temperature throughout the entire polymerisation time during which the content was stirred continuously.

To follow the kinetics of polymerisation and molecular weight growth over time, the overhead mechanical stirrer was paused at set times and samples were collected during these intervals using a polyethylene Pasteur pipette for ¹H NMR and GPC analysis. Polymer product became a solid once it had cooled down.

3.4.3.2 Ring-Opening Polymerisation using Microwave Heating

The typical procedure for the synthesis of PCL using microwave heating consisted of weighing 6.25 g of ϵ -caprolactone (54.8 mmol, 98 mol%) into a 50 ml flask. 68 μ L of BnOH (0.63 mmol, 1 mol%) and 28.7 μ L of Sn(Oct)₂ (0.24 mmol, 0.4 mol%) were then added into the flask using a syringe. A target DP = 87 was selected in order for results to be comparable to the work that was previously conducted by the group.³⁸

A glass stirrer rod attached to a PTFE paddle through a PTFE barring was fitted into the reaction flask. The flask was then placed into the cavity of a CEM Discover reactor and the stirrer rod was attached to an overhead mechanical stirrer operating at approximately 300 rpm to ensure the content of the reaction vessel was stirred homogenously throughout the entire reaction. The CEM reactor was connected to a computerised controller, which recorded the infrared (IR) temperature and forward power readings throughout the reaction. The IR temperature measurement only measured the temperature of the reaction vessel, hence an external temperature measurement apparatus known as a fibre optic (OF) probe was immersed into the reaction mixture to measure the actual temperature readings of the reactants throughout the experiments.

To follow the kinetics of polymerisation and molecular weight growth over time, the overhead mechanical stirrer was paused at set times and samples were collected during these intervals using a polyethylene Pasteur pipette for ^1H NMR and GPC analysis. Polymer product became a solid once it had cooled down.

The same procedure was carried out for the reactions conducted in the Miniflow microwave reactor. However, the reflected power was manually tuned to be as close to zero prior to the start of polymerisation. Unlike the CEM, the Miniflow does not have a built-in IR temperature sensor hence an external OF temperature probe was placed directly into the centre of the reaction material in the flask to measure and record the temperature throughout polymerisation.

3.4.3.3 Thermal Effect on ROP using Conventional and Microwave Heating

To investigate the effect of temperature on ROP, reactions were conducted at 140 °C, 150 °C, 160 °C, 170 °C and 180 °C using both conventional heating and microwave heating.

The experiments were prepared in the same manner by mixing 6.25 g of CL, 68 μ L of BnOH and 28.7 μ L of Sn(Oct)₂ in a 50 ml reaction flask. For experiments that were heated conventionally, the flask was equipped with an overhead mechanical stirrer before being immersed into the hot oil. For experiments that were heated in the microwave, an overhead mechanical stirrer and a fibre optic probe was placed in the flask before being positioned into the CEM cavity. Samples were collected at regular time intervals via pipette to determine monomer conversions via ¹H NMR and molecular weight distributions via GPC.

3.4.3.4 Effect of Pre-heated Monomer on ROP using Conventional and Microwave Heating

To investigate the effect of pre-heating CL monomer on ROP, reactions were conducted at 180 °C using both conventional heating and microwave heating.

For the experiment using conventional heating, 6.25 g of CL was placed into a 50 ml reaction flask which was heated in an oil bath at 150 °C for 15 minutes. After the flask was removed from the oil bath, 68 μ L of BnOH and 28.7 μ L of Sn(Oct)₂ were added to the pre-heated CL and the flask was equipped with an overhead mechanical stirrer before being immersed into the oil bath once again and the reaction time was started. The same procedure was repeated at 180 °C.

For the experiment using microwave heating, 6.25 g of CL was placed into a 50 ml flask which was heated in an oil bath at 150 °C for 15 minutes. After the flask

was removed from the oil bath, 68 μL of BnOH and 28.7 μL of $\text{Sn}(\text{Oct})_2$ were added to the pre-heated CL. An overhead mechanical stirrer was equipped into the flask before being positioned into the cavity of the CEM and the reaction time was started. The same procedure was repeated at 180 $^{\circ}\text{C}$. Samples were collected at regular time intervals via pipette to determine monomer conversions via ^1H NMR.

3.4.3.5 Effect of Pre-heated Initiator with 1 mol Equivalent Monomer on ROP using Conventional and Microwave Heating

To investigate the effect of pre-heating the co-initiator with 1 mol equivalent of CL monomer, reactions were conducted at 160 $^{\circ}\text{C}$ using both conventional heating and microwave heating.

For the experiment using conventional heating, 35 μL of CL, 68 μL of BnOH and 28.7 μL of $\text{Sn}(\text{Oct})_2$ were placed into a 50ml reaction flask which was heated in an oil bath at 160 $^{\circ}\text{C}$ for 15 minutes. After the flask was removed from the oil bath, 6.25 g of CL was added to the pre-heated reactants and the flask was equipped with an overhead mechanical stirrer before being immersed into the oil bath once again and the reaction time was started.

For the experiment using microwave heating, 35 μL of CL, 68 μL of BnOH and 28.7 μL of $\text{Sn}(\text{Oct})_2$ were placed into a 50 ml flask which was heated in an oil bath at 160 $^{\circ}\text{C}$ for 15 minutes. After the flask was removed from the oil bath, 6.25 g of CL was added to the pre-heated reagents. An overhead mechanical stirrer was placed into the flask before being positioned into the CEM cavity and the reaction time was started. Samples were collected at regular time intervals via pipette to determine monomer conversions via ^1H NMR.

3.5 Results and Discussion

The aim of this study is focused on the bulk ring-opening polymerisation (ROP) of ϵ -caprolactone (CL) and benzyl alcohol (BnOH)/Sn(Oct)₂ as the initiator/catalyst system. Bulk ROP was carried out using both conventional and microwave heating. The target degree of polymerisation (DP) was obtained by adjusting the molar ratio of [CL]:[BnOH] as [87]:[1] for DP = 87. Relative molar ratio of [CL]:[Sn(Oct)₂] was kept constant at [1]:[1.40 × 10⁻⁴]. The reaction scheme is shown in Figure 3.6.

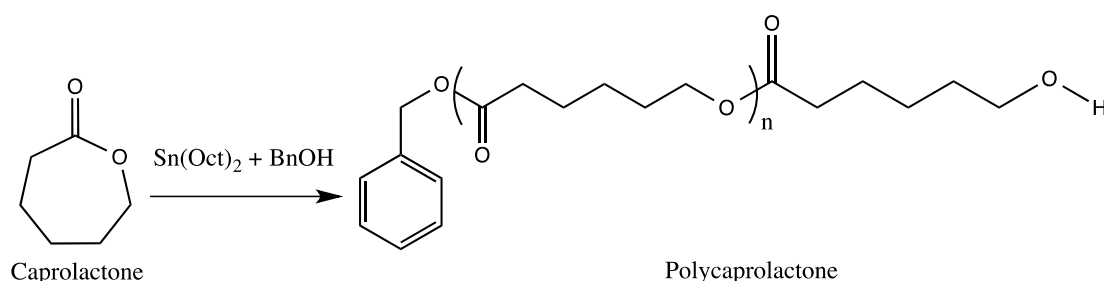


Figure 3.6 Ring-opening polymerisation of CL using BnOH/Sn(Oct)₂ as the initiator/catalyst system

ROP was carried out in bulk as previous literature findings had shown that bulk-ROP generally proceeds faster than reactions that involve solvents. Furthermore, it has been shown that a more effective and controlled pseudo-living ROP can be achieved through bulk polymerisation and also it has been shown to give the maximum opportunity to observe difference related to microwave heating.³⁹ Bulk ROP is also a greener process as it eliminates the usage of volatile solvents that are often toxic, therefore making bulk ROP a sustainable methodology for polymer production. Sn(Oct)₂ catalyst was chosen in this study as it is widely used in the industrial production of PCL and PLA because it has been approved by the Food and Drug Administration (FDA). Lastly, BnOH was selected as the initiator as it is favourable for M_n determination via ¹H NMR analysis. When the benzyl ester

becomes the head group of the resultant PCL, the methylene proton resonances (-CH₂) present are clearly differentiated from those of the polymer backbone, making it useful to define M_n. The points of discussion in this chapter can be summarised as follows:

- (a) Determination of the effect of temperature on ROP
- (b) Polymerisation kinetics study and direct comparison of ROP conducted using both conventional and microwave heating
- (c) Determination of the pseudo-living characteristic of ROP and controlled growth of M_{wt}.
- (d) Detailed study on the initiation stage of ROP and effect on polymerisation kinetics using various polymerisation preparation methods

3.5.1 Thermal Effect on Rate of Polymerisation using Conventional and Microwave Heating – Effect of Preheating Feed Materials

Polymerisation was conducted at a range of different temperatures from 140 °C to 180 °C using both conventional and microwave heating to investigate the effect of temperature on the rate of conversion from monomer to polymer and establish a view to determine which heating method provides better control over the system and a faster rate of reaction. ¹H NMR was used to follow the rate of monomer consumption. Figures 3.7 and 3.8 follow the kinetics of polymerisation and show how the rate of monomer conversion increased over time as the reaction temperature increases.

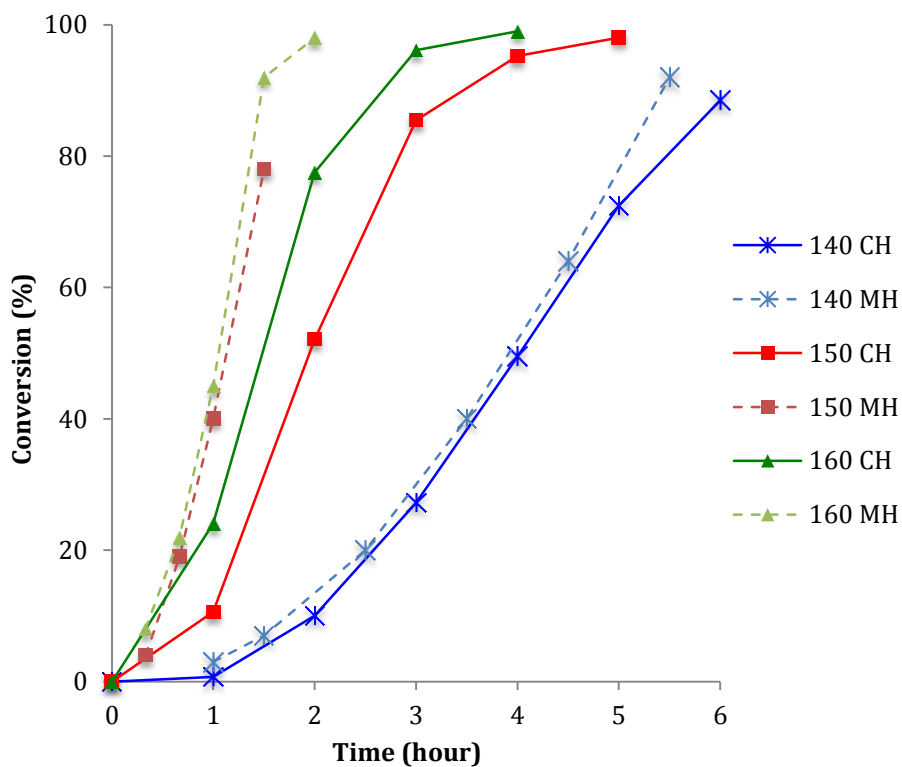


Figure 3.7 Conversion against time for ROP of CL with BnOH and Sn(Oct)₂ at 140 °C, 150 °C and 160 °C using conventional (CH) and microwave heating (MH)

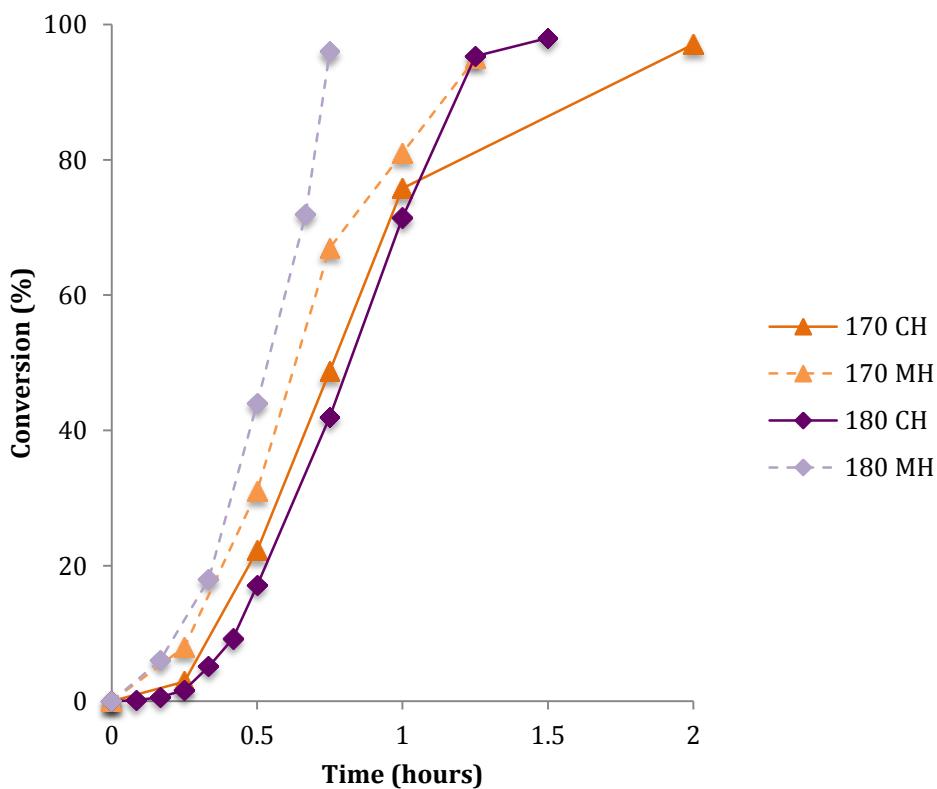


Figure 3.8 Conversion against time for ROP of CL with BnOH and Sn(Oct)₂ at 170 °C and 180 °C using conventional (CH) and microwave heating (MH)

Reactions were conducted between the temperature range of 140 °C and 180 °C as the boiling point (T_B) of the reaction mixture is at approximately 200 °C. Temperature measurements were recorded using the OF temperature probe which was placed directly in the centre of the reaction mixture in the flask.

When conventional heating was used, the reaction required 6 hours to achieve a 90 % conversion at 140 °C, 5 hours to achieve 98 % conversion at 150 °C, 4 hours to achieve 99 % conversion at 160 °C, 2 hours to achieve 97 % conversion at 170 °C and 90 minutes to achieve 98 % conversion at 180 °C. When microwave heating was used, the reaction required 5 hours to achieve a 90 % conversion at 140 °C, 90 minutes to achieve 80 % conversion at 150 °C, 2 hours to achieve 99 % conversion at 160 °C, 90 minutes to achieve 95 % conversion at 170 °C and 45 minutes to achieve 96 % conversion at 180 °C.

Overall, monomer conversion occurred more rapidly when microwave heating was used compared to conventional heating. It was observed that the propagation rates were similar in both heating systems but the induction periods were significantly reduced when microwave heating was used. These observations were in agreement with the conclusion drawn by Nguyen et al. which suggests that microwave irradiation selectively heats the catalytic species $\text{Sn}(\text{Oct})_2$ and reduces the induction period, which leads to a shorter overall reaction time.³⁶ A series of different polymerisation methods were conducted as an attempt to reduce the induction period as mentioned in the following sections.

3.5.2 Effect of Pre-heated Monomer on Polymerisation using Conventional and Microwave Heating

Figures 3.7 and 3.8 from Section 3.5.1 confirm the presence of a variable length induction period in the reactions, this stage involves the formation of the organometallic species or “true” catalyst from the reaction between $\text{Sn}(\text{Oct})_2$ and BnOH initiator prior to the propagation stage, which is the linear relationship between conversion and time. The mechanism for the induction period will be further discussed in detail in Section 3.5.6.1. In this section, the objective is to investigate the effect of pre-heated monomer on ROP, focusing on the formation of the true catalyst and enhancing the rate of reaction using this polymerisation method by reducing or completely eliminating the induction period. The reactions were conducted using conventional heating and results were compared and contrasted with a set of CEM microwave generated results from other coworkers in the group³⁸ to determine which heating method will reduce the induction period and overall reaction time.

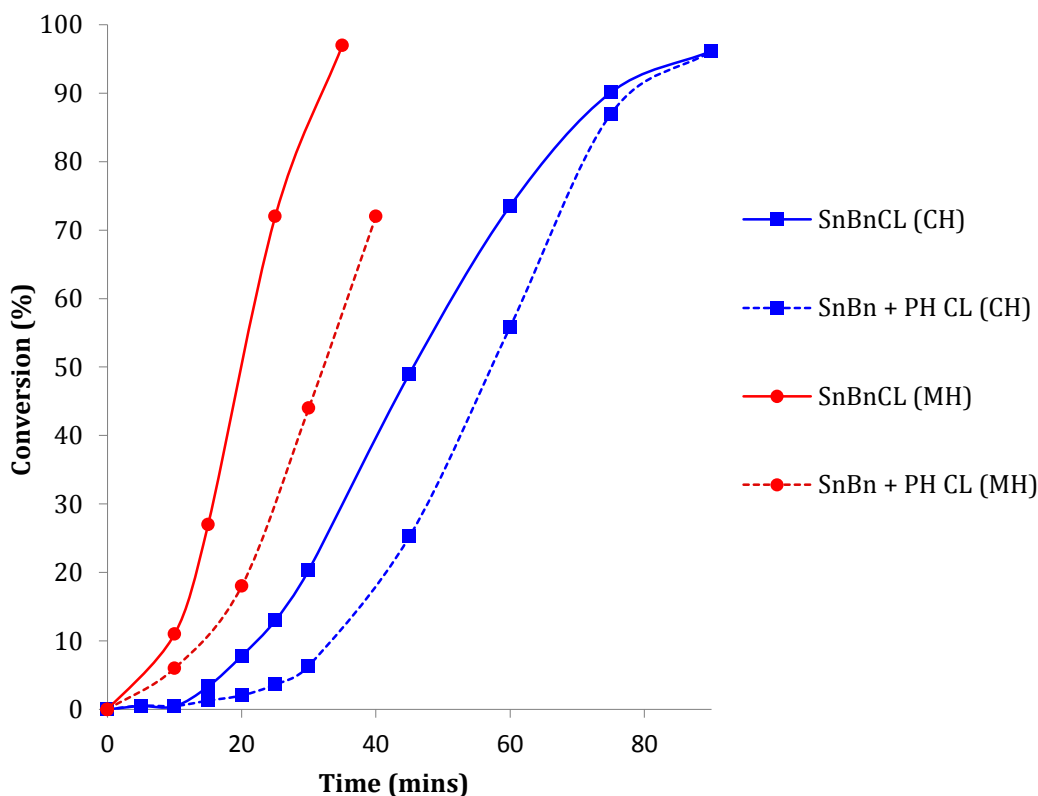


Figure 3.9 Conversion against time for ROP of CL with BnOH and Sn(Oct)₂ with and without pre-heated monomer (PH CL) using conventional (CH) and microwave heating (MH) at 180 °C

Figure 3.9 shows that the rate of reaction was greater for polymerisations without pre-heated CL monomer when using both conventional and microwave heating. When conventional heating was used, the reaction took 60 minutes to achieve 74 % conversion without pre-heated monomer. Using the same heating method, the conversion was only at 56 % after 60 minutes with pre-heated monomer. However, the induction time was approximately the same ~5 minutes for the reactions that were conventionally heated. When microwave heating was used, it took 35 minutes to achieve 97 % conversion without pre-heated monomer, while only 57 % conversion was achieved in the same amount of time with pre-heated monomer. Additionally there seems to be an extended period after polymerisation has commenced where the polymerisation is progressing by at a reduced rate prior to true propagation starting.

This showed that heat energy is essential during the induction stage of ROP for reaction to take place between BnOH and $\text{Sn}(\text{Oct})_2$ to form the true catalyst prior to propagation. Pre-heating CL monomer separately prior to adding it to the rest of the reaction mixture did not assist in the formation of the organometallic species and is therefore unnecessary, as monomer cannot interact with monomer without the presence of the true catalyst.

It was also observed that the reactions conducted using microwave heating exhibited a higher rate of propagation compared to those conducted using conventional heating. When microwave heating was used, 97 % conversion was achieved in 35 minutes without pre-heated monomer. The same conversion was achieved in 90 minutes without pre-heated monomer when conventional heating was used. Microwave heating reduced the overall reaction time by 55 minutes. When microwave heating was used, induction occurred so quickly that this stage was completely eliminated as shown in Figure 3.9. Nguyen et al. suggested that microwave irradiation selective heats the catalytic species $\text{Sn}(\text{Oct})_2$ and reduces the induction period, which leads to a shorter overall reaction time.³⁶ Also the segment of reduced rate polymerisation observed just after induction / initiation was also shorter in the microwave ROP's.

3.5.3 Effect of Pre-heated Initiator with 1 mol Equivalent of Monomer on ROP using Conventional and Microwave Heating

After the induction stage takes place in ROP, the propagating species is formed by the reaction between the true catalyst and monomer. The formation of this first propagation species is essential in ROP, which explains the vital presence of monomer during this stage. The objective of the experiments in this section is to

show if pre-heating the co-initiator along with 1 mol equivalent of monomer will affect the rate of reaction. The first set of experiments were conducted by pre-heating BnOH and Sn(Oct)₂ in the absence of monomer for 15 minutes prior to adding the CL monomer at room temperature into the co-initiator mixture, while the second set of experiments were conducted by pre-heating the co-initiator together with 1 mol equivalent of CL monomer for the same period of time before adding the rest of the monomer at room temperature into the reaction mixture. The reactions were conducted at 160 °C using conventional heating and results were compared and contrasted with a set of CEM microwave generated results from other coworkers in the group to determine which heating method provides a shorter overall reaction time and induction period.⁴⁰ In Section 3.5.2, the microwave-heated reactions at 180 °C were so rapid that the induction period could not be observed, therefore 160 °C was selected as the reaction temperature in this section as the reaction time was lengthy enough for the induction period to be observed in detail. The data from these experiments are detailed in Figure 3.10.

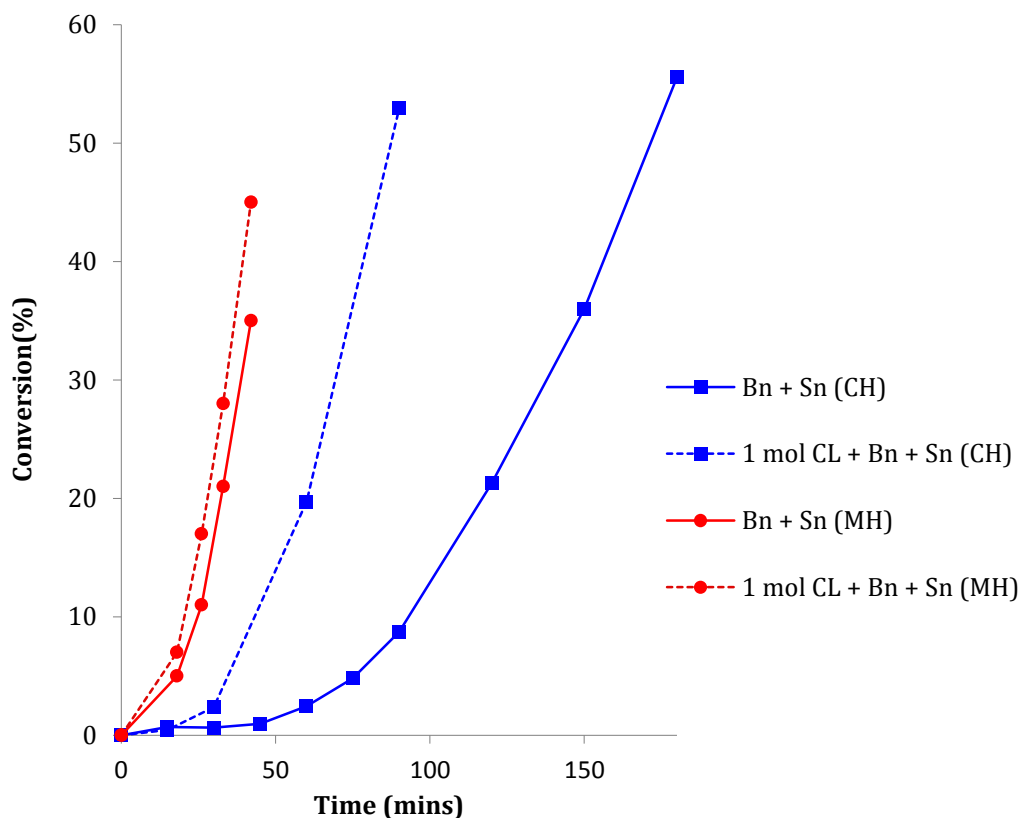


Figure 3.10: Conversion against time for ROP of CL with BnOH and Sn(Oct)₂ with pre-heated co-initiators (Bn+Sn) and pre-heated co-initiators with 1 mol equivalent of monomer (1 mol CL+Bn+Sn) using conventional (CH) and microwave heating (MH) at 160 °C. Microwave heated reactions were generated from other coworkers in the group.⁴⁰

Figure 3.10 shows that the overall reaction time for ROP conducted with pre-heated co-initiator and 1 mol equivalent of monomer were shorter than the reactions conducted with pre-heated co-initiator only. The introduction of 1 mol equivalent of CL monomer during the induction stage had enhanced the rate of reaction. When conventional heating was used, it took 60 minutes to achieve 3 % conversion without monomer at the beginning, while 20 % conversion was achieved in the same amount of time with the introduction of 1 mol monomer during the induction stage. A similar trend was observed for microwave-heated reactions. When microwave heating was used, 35 % conversion was achieved in 40 minutes without the presence of monomer at the beginning while a 45 %

conversion was achieved in the same amount of time with the introduction of 1 mol monomer during the induction stage. However, it was noted that the difference between these different procedures was much smaller than the difference between the conventionally heated equivalents.

When the differing sections of the reaction were investigated in greater detail, it was observed that the induction period at the beginning of the reaction was 40 minutes without the presence of monomer in the pre-heated mix when conventional heating was used. However, the induction period was reduced by half with the presence of monomer at the beginning of the reaction using the same heating method. A similar trend was observed for the reactions conducted using microwave heating. When microwave heating was used, the induction period was 10 minutes without the presence of monomer at the beginning of the reaction while this period was reduced to 5 minutes when 1 mol monomer was introduced during the induction stage. Results show that the presence of monomer is essential during the induction stage because CL is efficient at converting the absorbed microwave energy into heat, thus speeding up the formation of the “true” catalyst and first propagating species in their coordination-insertion mechanism.

The reactions conducted using microwave heating had a shorter overall reaction time than those that were conventionally heated suggesting microwave heating to be a more efficient heating method. When microwave heating was used, 45 % conversion was achieved in 40 minutes while a conversion of 7 % was achieved in the same amount of time when conventional heating was used. It was proposed that this confirmed the conclusion made by by Nguyen et al. that microwave selective heats the $\text{Sn}(\text{Oct})_2$ catalytic species during the induction period and enhances the rate at which the co-initiator and first propagating species

(1mer) are being formed,³⁶ the overall reaction time was also reduced because the propagation rate was also observed to be higher in the microwave reactions..

3.5.4 Temperature and Power vs Polymerisation Time in CEM

In a typical microwave-heated polymerisation conducted at 160 °C, the CEM microwave reactor parameters were set as follows (Table 3.1):

Table 3.1 CEM reactor settings for ROP of CL

Stage	1	2	3	4	5
Power (W)	300	300	100	100	100
Ramp Time (min)	10	0	0	0	0
Hold Time (min)	60	60	60	60	60
Temperature (°C)	160	160	160	160	160

Microwave energy was introduced into the system continuously during the reaction, while a maximum power of 300 W was applied to the reaction vessel. The CEM was set to heat the reaction following several stages, where the first stage is generally when power is forwarded into the system to take the reaction temperature up to target temperature, followed by the hold time in the latter stages where the target temperature is held constant throughout the reaction. The ramp time was set for 10 minutes to raise the temperature of the reaction materials in the vessel from room temperature to the target reaction temperature (e.g. 160 °C). In practice however, the temperature control algorithm of the microwave system increased the forward power from 0 to 80 W, which caused the temperature of the reaction mixture to reach 160 °C in less than 2 minutes. Once the target temperature was achieved, the hold time automatically started and the system was observed to display a drop in forward power. The forward power was regulated at

25 W throughout the hold time period to maintain the reaction temperature at 160 °C. As mentioned in Section 3.4.3.2, temperature measurement was recorded throughout polymerisation with a built-in IR temperature sensor that is located outside the microwave cavity, which measures the temperature of the reaction flask. A separate OF temperature probe was placed in centre of the reaction flask, which records the actual temperature of the reaction material throughout the reactions.

An example of a temperature / power profile of the ROP at 160 °C is as shown in Figure 3.11, similar profiles were obtained for the other reaction temperatures.

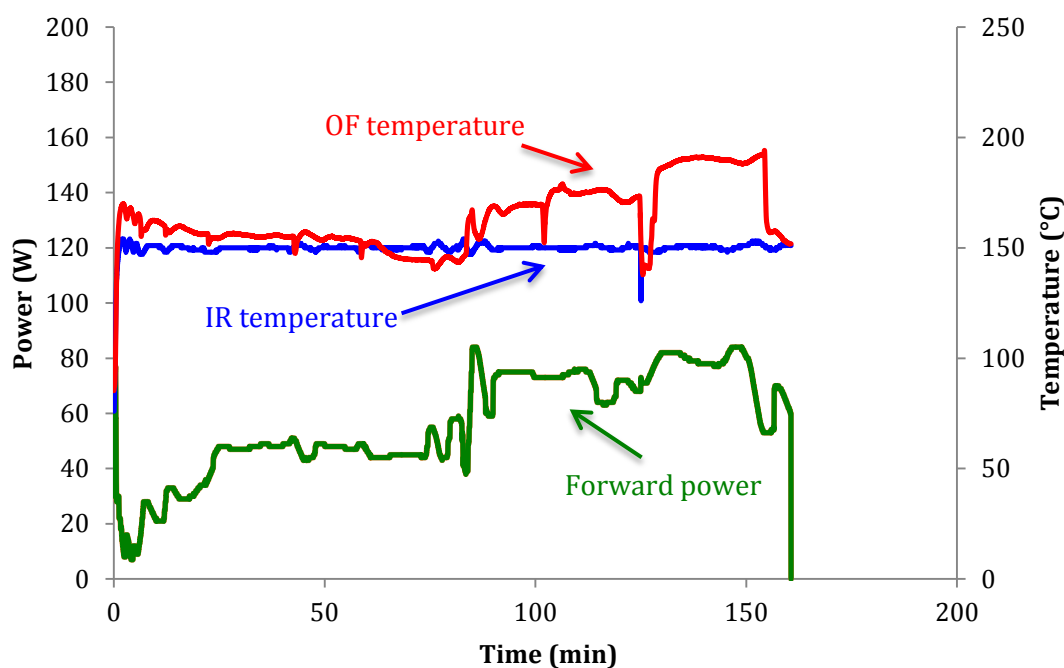


Figure 3.11 A typical temperature / power profile vs time. Mass of CL is 6.25 g, relative molar ratio of CL:BnOH:Sn(Oct)₂ = 90:1:0.012. ROP was conducted at 160 °C using microwave heating. Temperature was measured using IR and OF probe

Figure 3.11 shows that in order for the reaction temperature to be maintained at 160 °C, the set temperature had to be 150 °C as the temperature reading of the reaction mixture was generally 10 °C above the reaction vessel

temperature reading. It was also observed that a generally low average power of ~25 W was required to achieve 98 % conversion in 2 hours (refer to Figure 3.11), this signifies that the usage of microwave heating in the synthesis of these polymers could be a highly sustainable process as very low input energy levels are required for the majority of the reactions cycle time.

However, the differences seen in the IR and OF temperature readings indicate that the power and temperature control of the CEM reactor is unpredictable and difficult to manipulate, as the forward power cannot be tuned. There is also no indication of how much power was absorbed by the reaction. Another microwave reactor known as the Sairem Miniflow 200SS holds these features that the CEM reactor is lacking, and will be further discussed in Chapter 5.

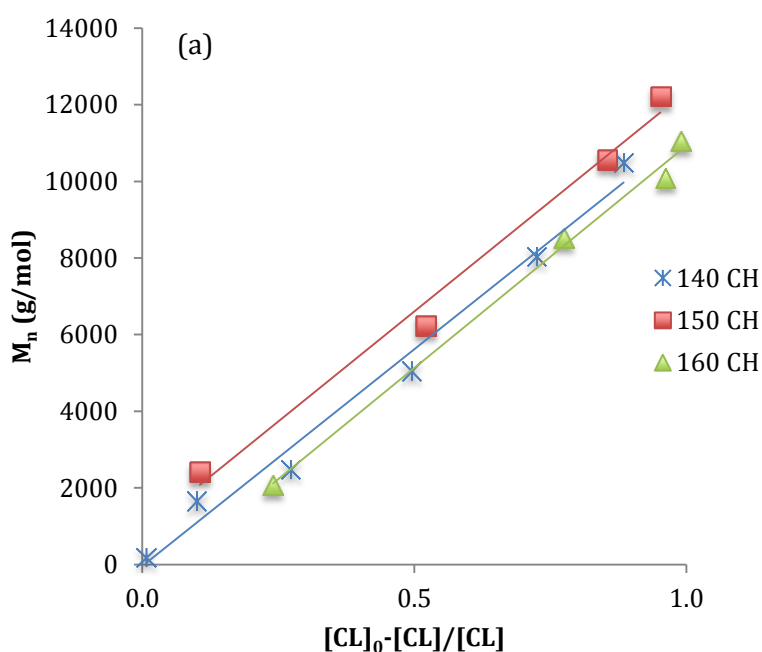
3.5.5 Pseudo-living Polymerisation using Microwave Heating

As mentioned in Chapter 1, the relationship between molecular weight and time or conversion is a key indication as to whether a polymerisation exhibits pseudo-living characteristics. Therefore, as the chemical mechanism for a microwave ROP may be different from those using conventional heating, the pseudo-living characteristic of the microwave-heated reactions was studied by following the kinetics of polymerisation of this particular heating system, and comparing the results directly to those using conventional heating. The following list defines several assumptions that were made in order to ensure the accuracy of the kinetic analysis:

- (a) $[M]_{eq}$ is assumed to be 0 and the depropagation step is negligible
- (b) The total concentration of the active species $[P^*]$ throughout the entire reaction must be defined along with the slope of the plot in order to calculate

the rate constant of propagation. The slope can be obtained by following the kinetics of polymerisation, but P^* must be calculated using the equation $[I]_0 = \Sigma[P^*]$. The initial concentration of BnOH initiator must be taken into account and the initiation efficiency must be assumed to be 100%.

The kinetics of the ROP's of CL using $\text{Sn}(\text{Oct})_2$ and BnOH as the catalyst / initiator system over a temperature range of 140 °C – 180 °C using microwave heating were followed. A linear relationship was observed between the M_n of polymer and degree of polymerisation for these systems when using both conventional and microwave heating as shown in Figures 3.12 and 3.13. Therefore, it can be concluded that the ROP of CL using $\text{Sn}(\text{Oct})_2$ catalyst and BnOH initiator does exhibit pseudo-living characteristics when either heating method is adopted..



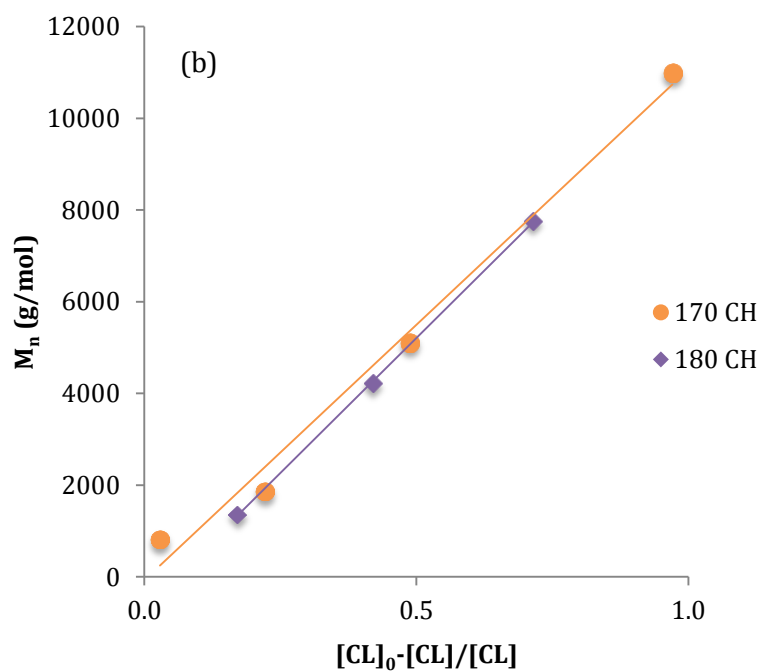
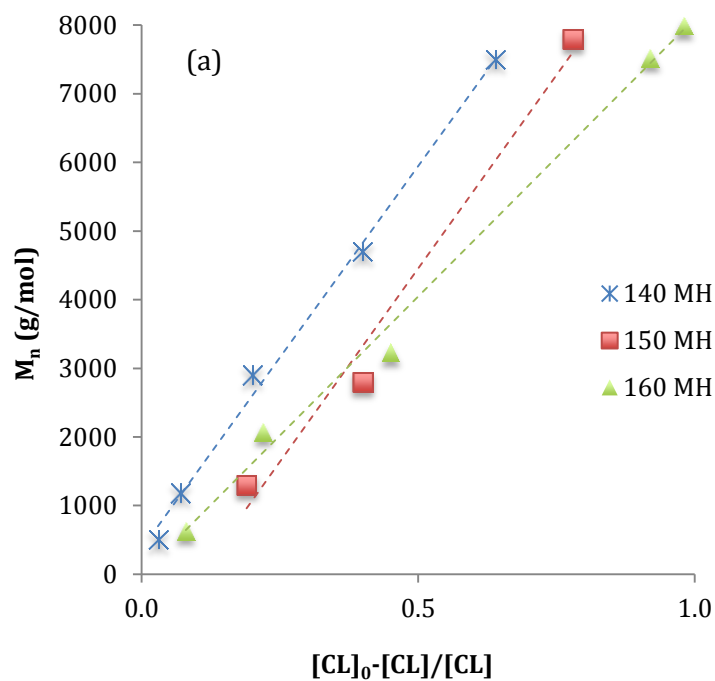


Figure 3.12 Linear relationship between polymer M_n and degree of conversion for ROP at (a) 140 °C to 160 °C and (b) 170 °C to 180 °C using conventional heating (CH)



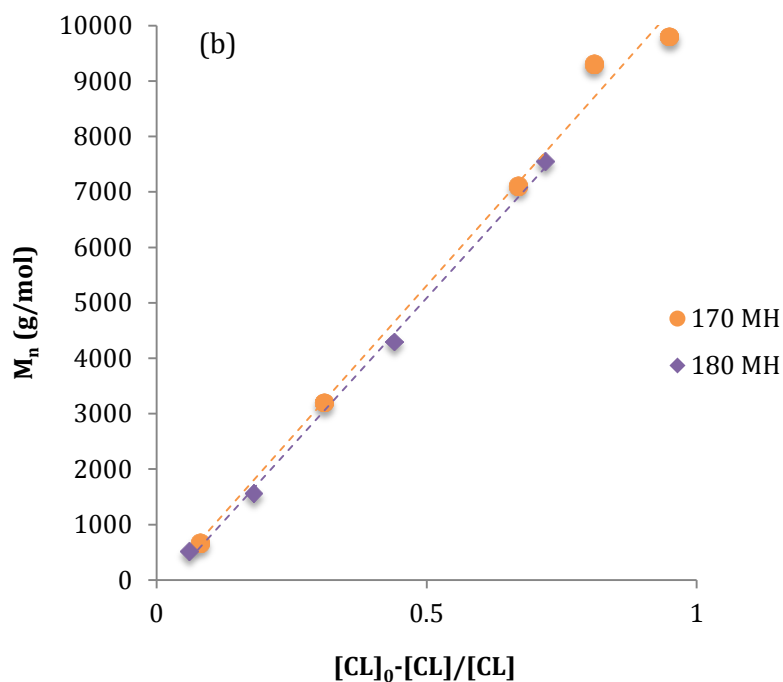
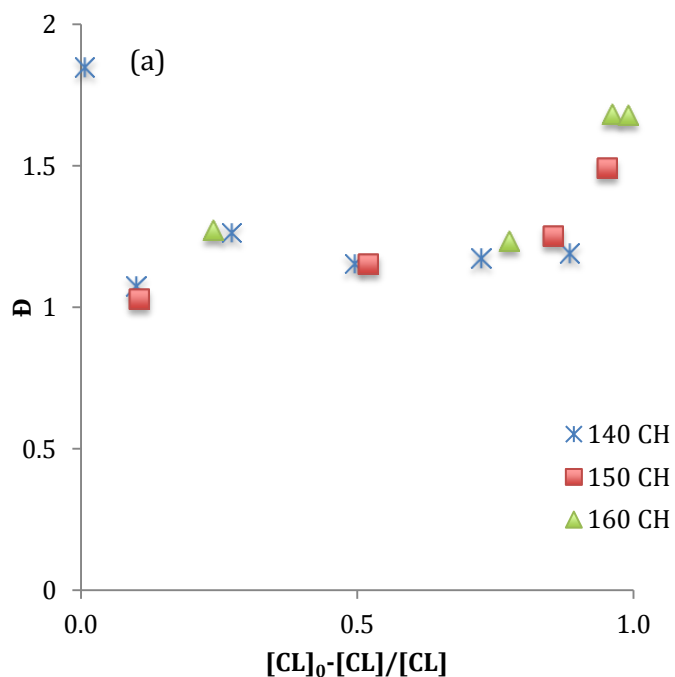


Figure 3.13 Linear relationship between polymer M_n and degree of conversion for ROP at (a) 140 °C to 160 °C and (b) 170 °C to 180 °C using microwave heating (MH)

Figures 3.14 shows that the polydispersities ($\bar{D}$) fluctuate between 1.03 – 2 for the conventional heating system, while Figure 3.15 shows that these values were between 1.2 -3.25 for the microwave heating system.



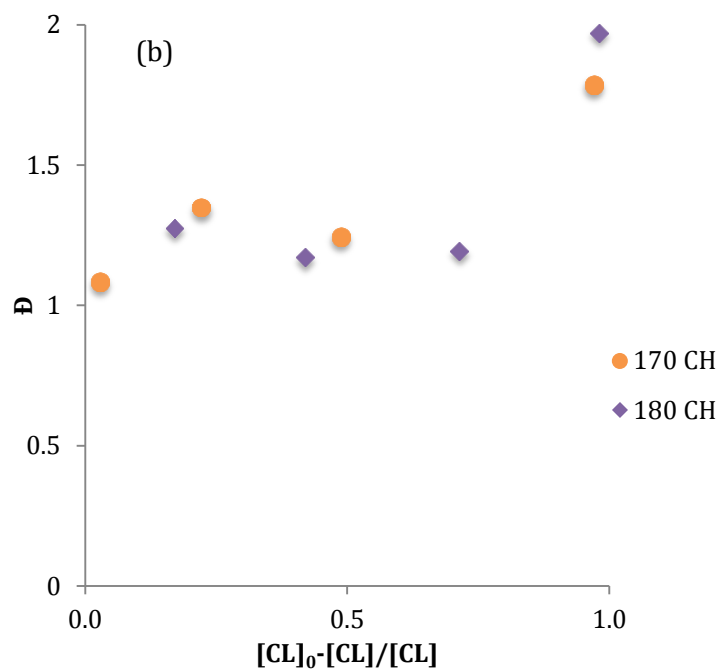
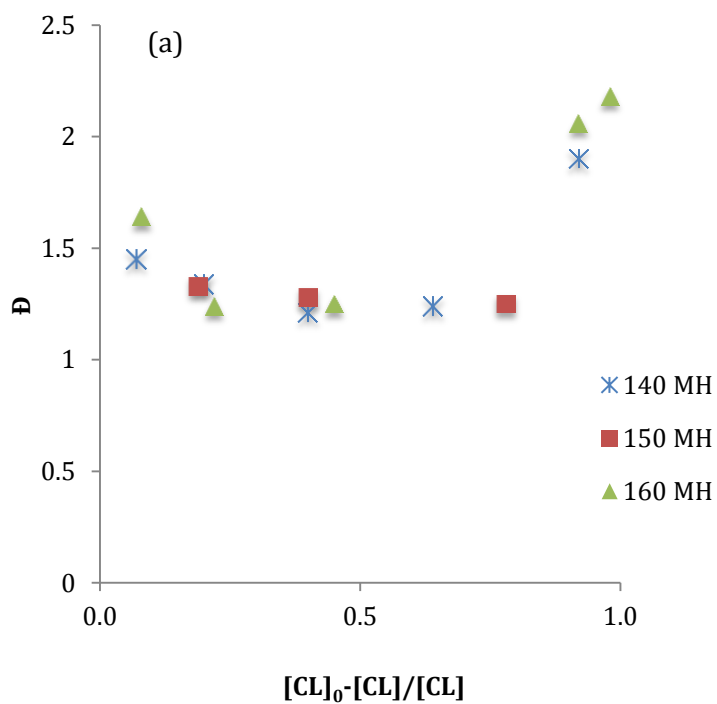


Figure 3.14 Dependence of dispersity index (M_w/M_n) on degree of conversion for ROP at (a) 140 °C to 160 °C and (b) 170 °C to 180 °C using conventional heating (CH). Dispersities were determined via GPC using PS standard



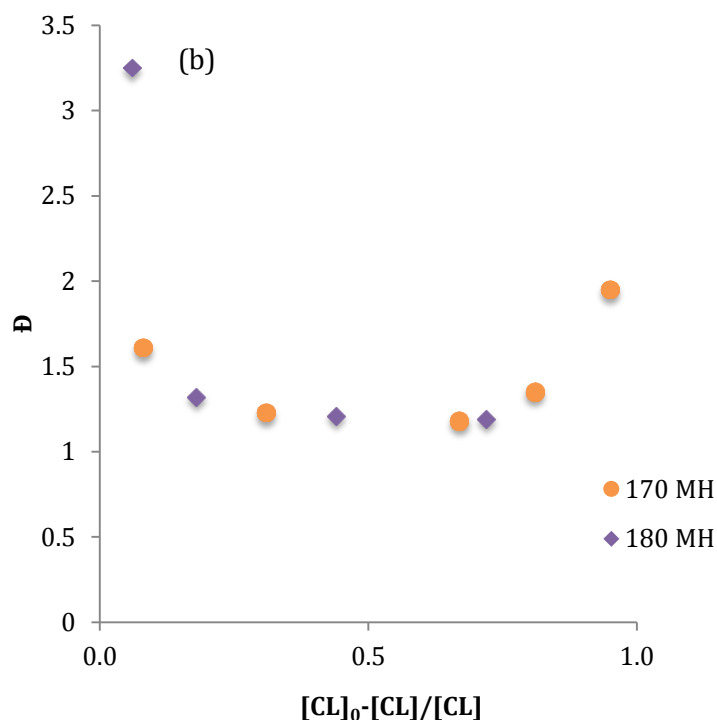
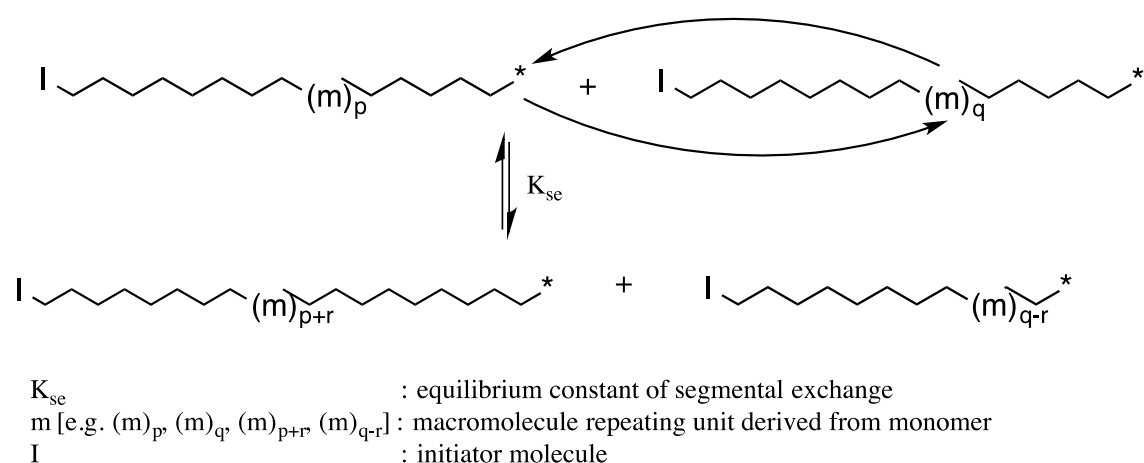


Figure 3.15 Dependence of dispersity index (M_w/M_n) on degree of conversion for ROP at (a) 140 °C to 160 °C and (b) 170 °C to 180 °C using microwave heating (MH). Dispersities were determined via GPC using PS standard

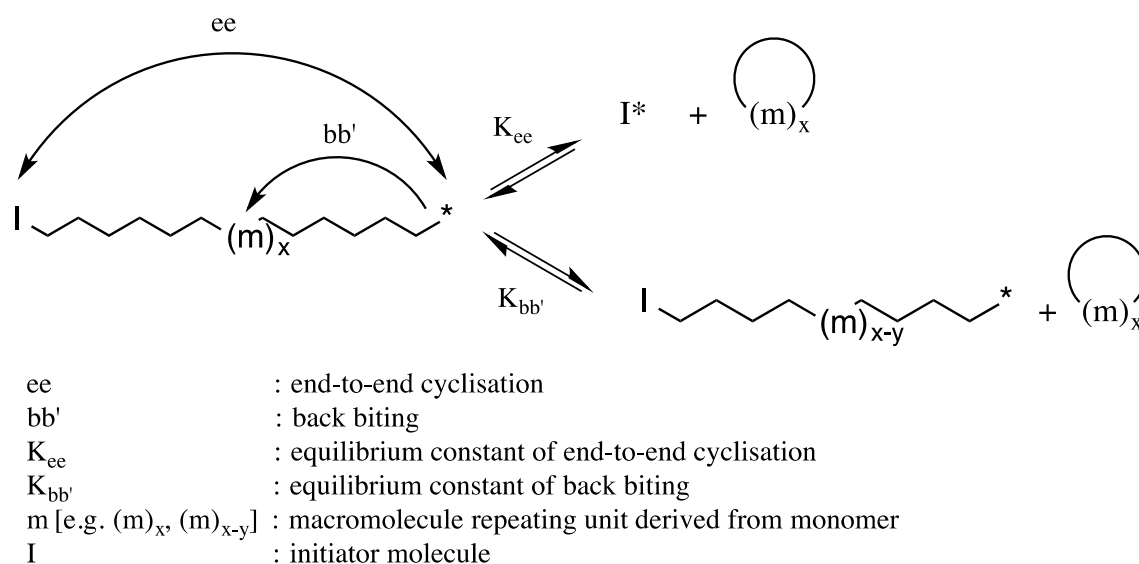
At the beginning of polymerisation (~5 % conversion) after the induction period is completed, high $\bar{D}$ values (1.85 for 140 °C using conventional heating; 3.25 for 180 °C using microwave heating) were observed. This is due to the lack of accuracy in measurements as the molecular weights of the product were very low thus the materials lie outside the calibration zone of the GPC. Once the kinetics of polymerisation have become well established, the molecular weights started to grow with time and the $\bar{D}$ values fell within the GPC calibration zone. These $\bar{D}$ values were observed to fall between 1.1 and 1.3 for both conventionally and microwave-heated reactions. However, these $\bar{D}$ values were shown to increase to ~1.98 towards the end of the reactions when conversions were close to 100 %. These results suggest that other processes such as transesterification are occurring during the ROP at higher conversion levels (see discussion below). This broadening

may also be related to the increase in viscosity of the reaction medium at high conversion introducing diffusion issues which allow termination processes to occur and the control agents will find it hard to find and interact with the chain ends to protect them from following alternative reaction pathways.

It was reported by Duda et al. that the increase in $\bar{D}$ in conventionally heated processes was normally caused by the presence of side reactions, including the segmental exchange of macromolecules and macrocyclisation. These are also known as inter- and intra- molecular transesterification respectively for cyclic esters as shown in Figure 3.16.²⁸ These transesterifications have been observed in polymerisations involving various monomers.²⁷ Intermolecular transesterification is thought to be the primary reason for the broadening of the molar mass distribution. Results show the increase in $\bar{D}$ values in both conventional and microwave systems, suggesting that these side reactions may have occurred in both heating systems. However, it should be noted that the PCL product with low $\bar{D}$ values (~ 1.25 - 1.35) could be obtained when monomer conversion is around 80 %.



(a) Segmental exchange / Intermolecular transesterification



(b) Macrocyclisation / Intramolecular transesterification

Figure 3.16 General scheme for ROP side reactions adapted from Duda et al.²⁷
(a) Segmental exchange or intermolecular transesterification and
(b) Macrocyclisation or intramolecular transesterification

3.5.6 Conventional Heating vs Microwave Heating in ROP

The main objective of this study is to determine whether microwave heating can enhance the rate of ROP reactions. In both conventional and microwave heating systems, an overhead stirrer was attached to the apparatus to ensure rigorous stirring within the open-vessel reactor. This was to ensure that the reaction mixture in both heating systems was stirred uniformly and subjected to identical temperature and pressure conditions. Hence, any potential high-pressure thermal effects of microwaves on ROP (e.g. bulk superheating caused by high pressure build up when vessel is sealed²⁶) can be minimised. All polymerisations were conducted in bulk to maximise the differences in the reactions that result from mass heating effect of microwave dielectric heating.

The kinetics of polymerisation data from both conventional and microwave heating systems by using $\text{Sn}(\text{Oct})_2$ (0.05 g of 4.98×10^{-1} g/mL) and BnOH as the catalyst / initiator system of DP 87 at a reaction temperature range of 140 °C – 180 °C (Section 3.5.1, Figure 3.7 and 3.8) were compared in detail. Results are summarised in Table 3.2.

Table 3.2 Summary of results for ROP of CL using $\text{Sn}(\text{Oct})_2$ (0.05 g of 4.98×10^{-1} g/mL) and BnOH as the catalyst/initiator system at 140 °C – 180 °C using conventional and microwave heating

Entry	Heating Method	Temperature (°C)	Induction Period (min)	Overall Reaction Time (min)	Conversion (%)
1	Conventional	140	60	360	89
2	Conventional	150	30	300	98
3	Conventional	160	20	240	99
4	Conventional	170	16	120	97
5	Conventional	180	15	90	98
6	Microwave	140	40	330	92
7	Microwave	150	20	90	78
8	Microwave	160	10	120	98
9	Microwave	170	5	75	95
10	Microwave	180	3	40	72

Table 3.2 clearly shows that the rates of polymerisation were enhanced when microwave heating was used. For example at 160 °C, the overall reaction time was 240 minutes to achieve a conversion of 99 % using conventional heating while it took half the time (120 minutes) to achieve a 98 % conversion when microwave heating was used. A similar trend was observed for the reactions conducted at the other reaction temperatures.

Initial analysis demonstrated that these faster polymerisation rates can be partially attributed to a more efficient heating system delivered by microwaves. In a typical conventional heating system, conductive heating with an oil bath as an external source was used to heat up the reaction mixture. Hence, energy was

transferred into the system via conduction and convection processes. Thus it took several of minutes for the reaction bulk to reach the reaction temperature. By comparison, a more efficient volumetric heating process of the medium was achieved in the microwave heating system. When microwave heating is used, energy is instantaneously introduced into the system via electromagnetic waves through the entire bulk, eliminating any conduction and convection processes as observed in the conventional heating system.^{26,29} Therefore, this typically results in a reduced time for the microwave experiments to reach the reaction temperature. Furthermore, this is a difference that gets larger as the set point temperatures are greater

The initial analysis can be supported by the calculation of penetration depth and temperature measurements for both heating methods. As an example for temperature measurement analysis, it took approximately up to 5 minutes for the reaction mixture to reach 150 °C when conventional heating was used while the same reaction temperature was achieved within a minute using microwave heating. The penetration depth (Chapter 1, Equation 1.11) is a function of dielectric constant (ϵ') and dielectric loss (ϵ'') and by definition, penetration depth (d_p) is the point at which 37 % of the initially input microwave power is still present in the material.^{26,29} Hence dielectric heating can be produced within the width of $2 \times d_p$, while dielectric heating is less efficient when outside this width. The d_p value of CL is 3.34 cm based on the dielectric data at 150 °C ($\epsilon' = 24.17$, $\epsilon'' = 2.85$)³⁸. The reaction vessel used in these experiments has a maximum diameter of 3.5 cm, which is less than $2 \times d_p = 6.68$ cm. Therefore, it can be concluded that a more efficient heating system can be achieved when microwave heating is used.

3.5.6.1 Effects of Microwave Heating on Induction Period

These differences are further analysed in the following subsections focusing on the individual polymerisation stages (i.e. induction and propagation). Induction periods were observed in the initiation step when conventional heating was used while the propagation stage relates the reaction to its apparent (k^{app}) and propagation (k_p) rate constants.

Figures 3.7 and 3.8 (Section 3.5.1) confirm the presence of induction periods. These induction periods were reduced as the temperature was increased. It was also observed that the induction periods were significantly reduced or eliminated when microwave heating was used. These induction periods were followed by a linear relationship of conversion with time, also known as the propagation stage.

The presence of induction period seen in conventionally heated experiments can be explained by several reasons, (a) slower heat transfer into the system as this method is dependent on conductive heating, the slow heat transfer was no longer an issue when microwave heating was used as dielectric heating is more efficient. (b) selective heating of individual components in the system leading to the possibility of instantaneous heating and higher temperatures at local points of certain species in the bulk. The elimination of these induction periods observed has to be explained by taking into account the effect of selective heating on the mechanism of polymerisation which was defined to have affected all possible reactions that occur before the propagation process (Figure 3.17).³⁶

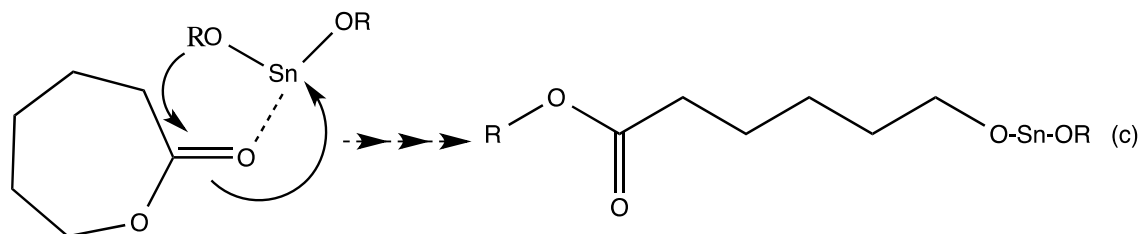
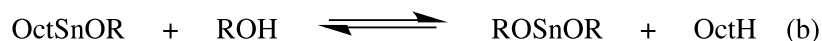
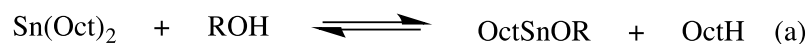


Figure 3.17 Mechanism of the formation of (a) monoalkoxide (b) dialkoxide (c) first propagation species of the ring-opening polymerisation process.

As shown in Figure 3.17, the formation of the first active monoalkoxide catalyst is followed by a second equilibrium to form the true initiator, which is a tin dialkoxide. The initiator opens up the monomer ring via coordination-insertion to form the first species (1mer) of the polymerisation. The remaining monomer will continue to ring open during the propagation stage until all the monomer is consumed and there is no monomer left in the system.

The presence of an induction period was observed by Storey et al. when diols were used as initiators. It was suggested that this period was due to slow heat transfer and strong interaction between the diol and $\text{Sn}(\text{Oct})_2$ catalyst.¹⁹ In the presence of $\text{Sn}(\text{Oct})_2$, diols act as a bidentate ligand hence producing a strong complexation with the catalyst, also known as the true catalyst or co-initiator. However, this resulted in a slow initiation process within the induction period.

When $\text{Sn}(\text{Oct})_2$ and BnOH was used as the catalyst / initiator system specifically, Kricheldorf et al. reported that $\text{Sn}(\text{Oct})_2$ and BnOH formed a strong complex even at room temperature via ^1H NMR, ^{13}C NMR and ^{119}Sn NMR analysis^{21,30,31}, this was indicated by the downfield shift of the CH_2 and OH protons of BnOH . These shifts were greater when the molar ratio of $\text{Sn}(\text{Oct})_2$ / BnOH

increased. They have also shown in their ^{13}C analysis that the C-O signal of $\text{Sn}(\text{Oct})_2$ (189.1 ppm in CDCl_3 / TMS) was shifted towards the free OctH at 183.6 ppm when BnOH initiator was added to the catalyst, thus proving the presence of this complexation.

The slow formation of the initiator equilibrium or strong complexation of the BnOH initiator may have also contributed to the slow initial coordination insertion process, leading to a slow initiation process when conventional heating is used. The linear / controlled characteristics observed during polymerisation after the induction period was over proposed that the coordination insertion process did not seem to commence until the true initiator was completely formed. This would suggest that this stage was the rate-determining step of the process and was significantly longer for the formation of the true catalysts in-situ using conventional heating over microwave heating. Therefore, it may have been this stage that was significantly altered when microwave heating was used.

Once the first propagation species (1mer) is formed, the polymer chain will continue to grow by propagating with the Sn attached to the chain end via the coordination insertion process for each new chain unit. However, the chain's interaction with BnOH could result in an inactive species and re-produce the actual dialkoxide initiator which ring opens the monomer. This process could repeat itself until all free BnOH is completely consumed and thus would slow down the polymerisation.

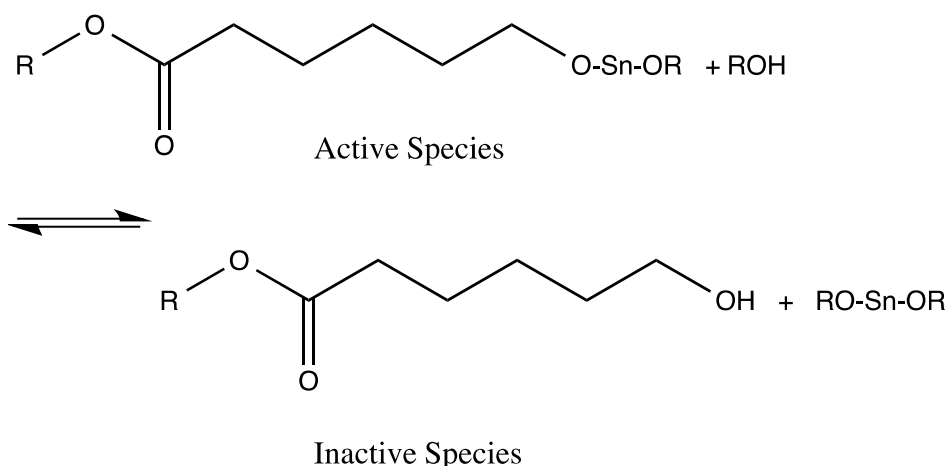


Figure 3.18 Equilibrium of active species and free BnOH

In order to determine the microwave heating effects on induction period, Nguyen et al. followed the kinetics of BnOH consumption using ^1H NMR up to the point where induction was completed.³⁶ The ^1H NMR spectra was based on the ROP of CL at 150 °C for a target DP = 20 so that a clear methylene proton resonance in free BnOH was achievable as the catalyst loading is greatest producing the best signal to noise ratio. The analysis depended on the depletion of the methylene proton close to the -OH group of free BnOH ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, $\delta = 4.69$ ppm) and that of the benzyl ester as the end-group of the polymer chain ($\text{C}_6\text{H}_5\text{CH}_2\text{OCO}-$, $\delta = 5.11$ ppm). Figure 3.19 shows that no monomer was converted in the first 30 minutes of polymerisation, this was identified as the induction period. It was observed that the methylene proton resonance of the free BnOH was decreased while that of the benzyl ester end group increased during this induction period. The conversion of BnOH into the benzyl ester end group was at 14 % after 10 minutes and increased to 48 % after 30 minutes, followed by the propagation stage where monomer conversion started.

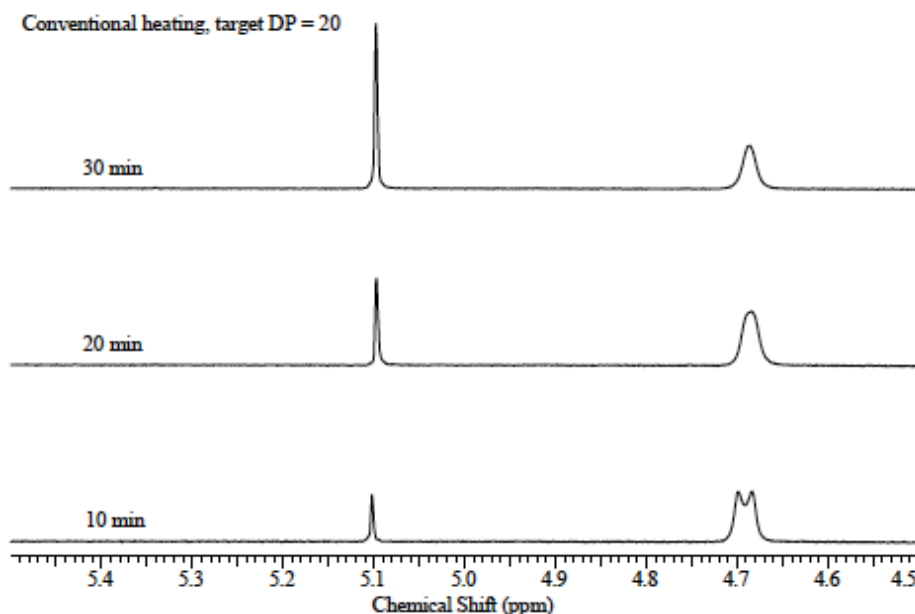


Figure 3.19 ^1H NMR for the induction period of ROP using conventional heating at DP20. Samples were taken at 10 min intervals (a) 10 min (b) 20 min (c) 30 min. Measurements were conducted in Bruker 300 in CDCl_3 . Chemical shifts indicate the signal of CH_2 of benzyl ester end group ($\delta = 5.11$) and free BnOH ($\delta = 4.70$)³⁶

Figure 3.20 shows that in the microwave heating system, approximately 100 % of the free BnOH was converted to form the benzyl ester end group only after 10 minutes.

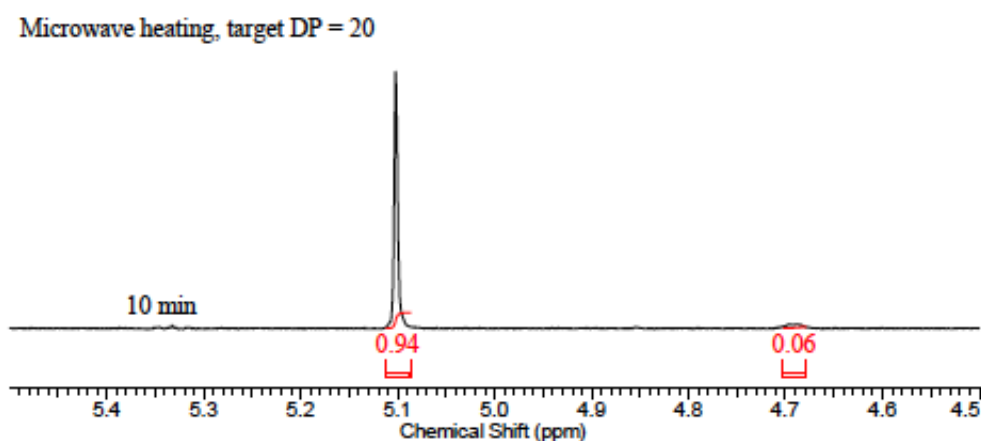


Figure 3.20 ^1H NMR for the 10 min sample from ROP using microwave heating at DP 20. Measurement was conducted in Bruker 300 in CDCl_3 . Chemical shifts indicate the signal of CH_2 of benzyl ester end group ($\delta = 5.11$) and free BnOH ($\delta = 4.70$)³⁶

It is concluded that the BnOH consumption rate was faster when microwave heating was used, which leads to the faster formation of the initiator and tin complex and first propagating species. Furthermore, the presence of an induction period as seen in conventional heating polymerisations was due to the poor interaction between BnOH and $\text{Sn}(\text{Oct})_2$, this induction period could be reduced / eliminated by using microwave as the heating source. They have proposed that this is due to selective heating of the tin species and the monomer such that catalyst formation is occurring more quickly at more dilute catalytic concentrations.

3.5.6.2 Effects of Microwave Heating on Rate Constant

In this study, it was proposed that, if the tin species and the monomer are being selectively heated, then the propagation stages should also be affected. This is because both of these species are involved in chain growth. Therefore, to further investigate whether the proposed microwave influence on the $\text{Sn}(\text{Oct})_2$ catalyst species was due to a thermal effect and extended to the propagation stage, the conventional heating results were compared and contrasted with a set of CEM microwave generated results from the group.⁴⁰

Results from this comparison drawn from the data from Figures 3.7 and 3.8 in Section 3.5.1 showed that reactions conducted using microwave heating displayed enhanced rates of conversion compared to those conducted using conventional heating. At 160 °C, the reaction took 4 hours to achieve 99 % conversion when conventionally heated while it took half the time to achieve the same conversion in the microwave. A similar trend was observed for the reactions conducted at 140 °C, 150 °C, 170 °C and 180 °C.

These simple plots of conversion versus time were then converted into semi-logarithmic kinetic plots of polymerisations (i.e. $\ln[M]_0/[M]$) versus time to determine and compare the apparent rate constants (k_{app}) using both conventional and microwave heating. As significant induction periods were observed when conventional heating was used compared to the microwave-heated polymerisations, these kinetic plots for polymerisations conducted at a temperature range of 140 °C – 180 °C were therefore plotted and compared in order to investigate any similarities in propagation rates. Once again, the relationship between $\ln([M]_0/[M])$ and time show the pseudo-living characteristics of the polymerisation.

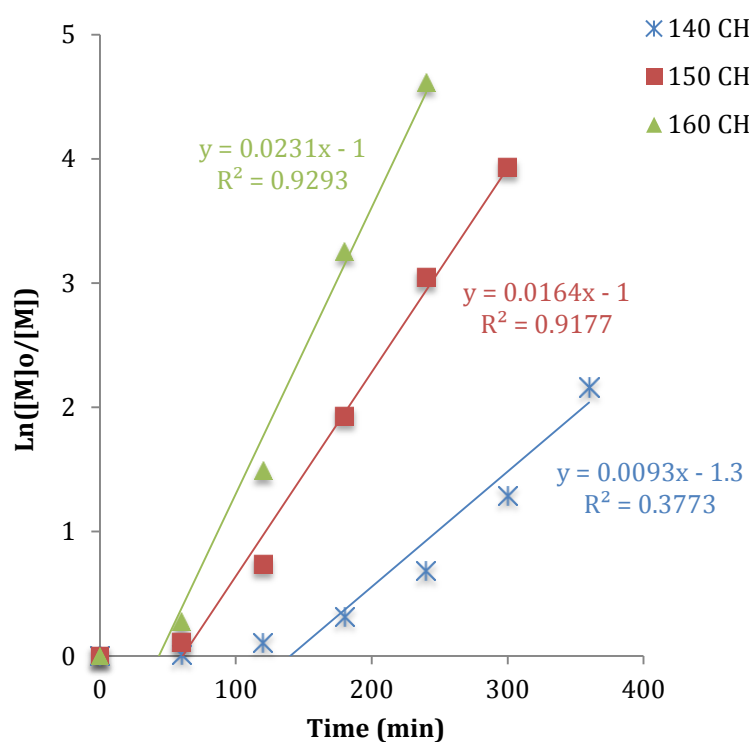


Figure 3.21 Temperature dependence of the reaction apparent rate constants (k_{app}) at 140 °C, 150 °C and 160 °C. ROP was conducted using conventional heating (CH) for a target DP 87 with CL: BnOH: Sn(Oct)₂ relative molar ratio = 87: 1: 0.012. Mass of CL was 6.25 g

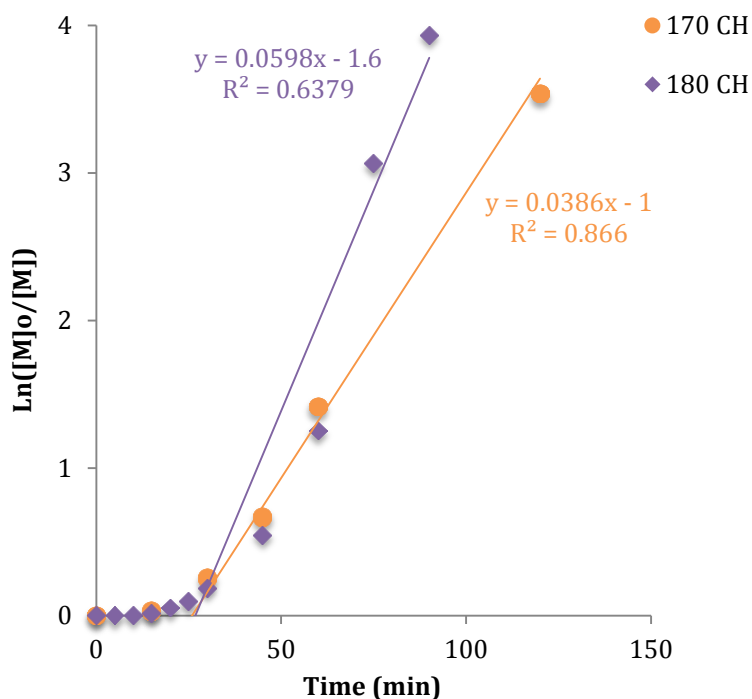


Figure 3.22 Temperature dependence of the reaction apparent rate constants (k_{app}) at 170 °C and 180 °C. ROP was conducted using conventional heating (CH) for a target DP 87 with CL: BnOH: Sn(Oct)₂ relative molar ratio = 87: 1: 0.012. Mass of CL was 6.25 g

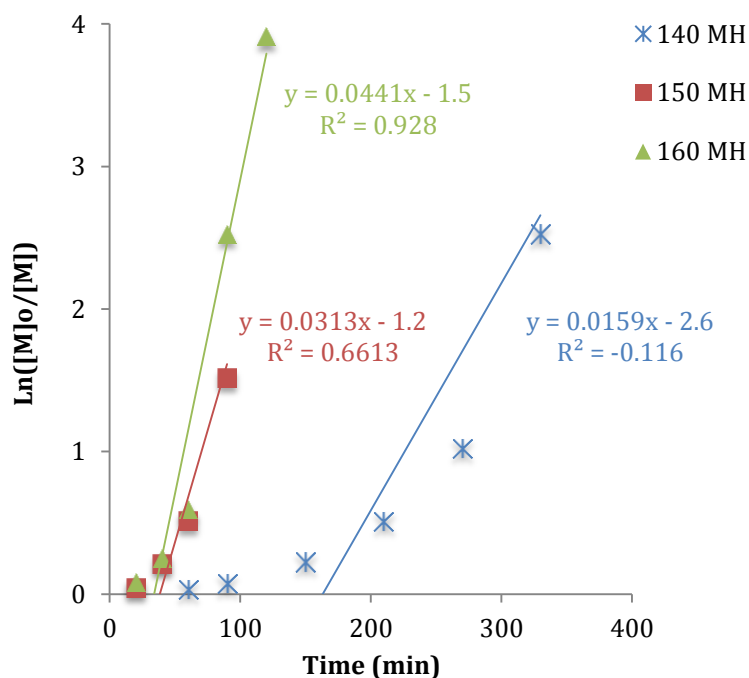


Figure 3.23 Temperature dependence of the reaction apparent rate constants (k_{app}) at 140 °C, 150 °C and 160 °C. ROP was conducted using microwave heating (MH) for a target DP 87 with CL: BnOH: Sn(Oct)₂ relative molar ratio = 87: 1: 0.012. Mass of CL was 6.25 g

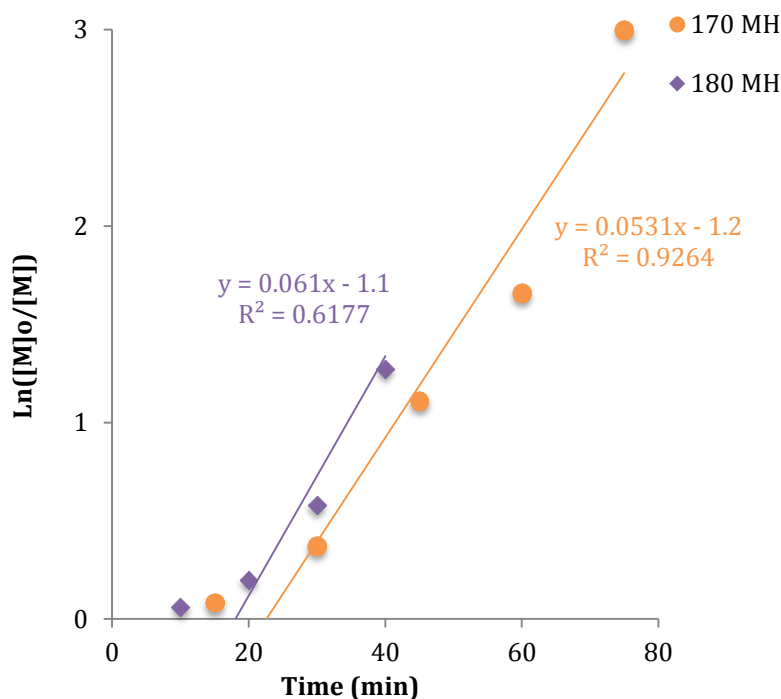


Figure 3.24 Temperature dependence of the reaction apparent rate constants (k_{app}) at 170 °C and 180 °C. ROP was conducted using microwave heating (MH) for a target DP 87 with CL: BnOH: Sn(Oct)₂ relative molar ratio = 87: 1: 0.012. Mass of CL was 6.25 g

The apparent rates of polymerisation (k_{app}) were derived from the slope of the kinetic plots as presented in Table 3.3. When microwave heating was used, k_{app} values were noted to be higher than those of conventional heating. When the reaction temperature was at 160 °C, the k_{app} of the microwave-heated reaction was exactly 2 times faster than the conventionally heated equivalent. The increase in $\text{Ln}([M]_0/[M])$ over time confirms the pseudo-living properties exhibited by the polymerisations.

Table 3.3 Apparent and propagation rate constants of propagation for polymerisation conducted using both conventional and microwave heating for target DP = 87 ($[\text{BnOH}]_0 = 0.103 \text{ mol L}^{-1}$) at 140 °C – 180 °C

Entry	Temperature (°C)	$k_{app} \text{ (min}^{-1}\text{)}$		$k_p \text{ (Lmol}^{-1}\text{min}^{-1}\text{)}$	
		Conventional	Microwave	Conventional	Microwave
1	140	0.0093	0.0159	0.0010	0.0016
2	150	0.0164	0.0313	0.0017	0.0032
3	160	0.0231	0.0441	0.0024	0.0045
4	170	0.0386	0.0531	0.0040	0.0055
5	180	0.0598	0.0610	0.0062	0.0063

The rate constant of propagation (k_p) was calculated from the equation:

$$k_p = k^{app} / [\text{BnOH}]_0 \quad (\text{Equation 3.2})$$

It was assumed that,

$$[\text{CL}]_0 \approx 0$$

$$[\text{BnOH}]_0 = 0.103 \text{ molL}^{-1}$$

When microwave heating was used, k_p values were also noted to be higher than those of conventional heating. Therefore it can be concluded that the propagation rates for the reactions were also increased when microwave heating was used, which resulted in faster overall rates of polymerisation. The difference in k_p values confirms the hypothesis that microwave selectively heats the co-initiator active species leading to the increase in rate of polymerisation.

Based on a literature review on dielectric heating in polymerisations, there are three general effects that microwave irradiation have on enhancing the rate of reactions: (a) purely thermal / kinetic effects, (b) specific effects and (c) non-thermal effects.^{26, 32} As proposed by Kappe et al., most of the enhancements in rate of reaction observed were caused by thermal / kinetic effects as the actual reaction temperatures were higher than the temperatures expected in closed systems. It was suggested that the efficient heating of microwave absorbing materials and pressure build up in the reaction vessel has led to the observation of these high temperatures. But for the polymerisations conducted in this study, an open vessel with rigorous overhead stirring was utilised to prevent any pressure build up within the system that could possibly lead to overheating. The bulk temperature of the reaction material in the microwave cavity was also monitored using an optical

fibre (OF) temperature measurement apparatus that was directly immersed into the centre of the reaction vessel as opposed to the infrared (IR) thermometer that reads the temperature of the reaction vessel wall. The temperature / power profiles suggested that the reaction temperature was maintained at the set temperature throughout polymerisation, therefore the reduction / elimination of the induction period and the enhancement in rate of polymerisation could be explained by other microwave effects (i.e. specific thermal effects).

Kappe and coworkers defined specific microwave effect as the acceleration of chemical transformations in a microwave field that cannot be achieved or duplicated by conventional heating, but essentially are still thermal effects. These specific microwave effects could be a result of the selective heating of a microwave-absorbing material in a less microwave-absorbing material that is not directly heated. Rather, only the microwave-absorbing component is heated and the heat is then transferred to the less microwave-absorbing component.³² If this theory is applied to the system in this study as the $\tan \delta$ values for both CL monomer and $\text{Sn}(\text{Oct})_2$ catalyst at 160 °C are approximately 0.11 and 0.13 respectively as presented in Figure 3.25. These similar values suggest that the microwave energy absorbed by both components can equally be transferred into heat efficiently. Based on the dielectric properties assessment of the individual reaction components, only BnOH was expected to not heat efficiently within the system. As either CL monomer or $\text{Sn}(\text{Oct})_2$ catalyst are responsible for the equilibrium reactions involved in the system, it is likely that selective heating has influenced the polymerisation mechanisms.

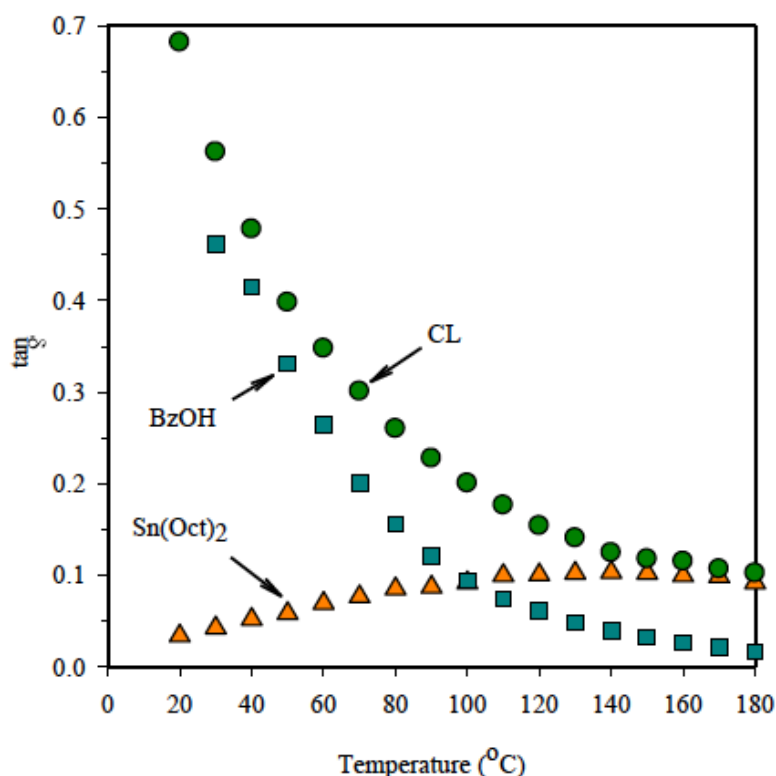


Figure 3.25 Temperature dependence of $\tan \delta$ at 2.45 GHz of CL (●), BzOH (■) and $\text{Sn}(\text{Oct})_2$ (▲). These values were calculated using the equation $\tan \delta = \epsilon'' / \epsilon'$ ³⁸

It was proposed this in this case it was unlikely selective heating of the CL monomer is the dominant factor in the change of mechanism here, although it can't be conclusively discounted. This was because it represents the major component in the system (6.25 g of CL, 68 μL of BzOH and 28.7 μL of $\text{Sn}(\text{Oct})_2$) but the bulk temperature was not significantly higher than the set temperature. Therefore, after analysing all the possible effects as mentioned previously, a common factor that resulted in the presence of a lengthy induction period and fast propagation rate is the tin active species. Therefore, it is proposed that the efficiency of $\text{Sn}(\text{Oct})_2$ was greatly enhanced by microwave heating which selectively heated the tin active species. The target temperature of the bulk was achieved rapidly due to the dielectric heating properties of the CL monomer, which assisted the selective heating process.

Summary of the effects of microwave heating on induction period

As a conclusion from this section, the reduction / elimination of the induction period as observed in the polymerisations conducted using microwave heating was due to the following effects which in turn was likely caused by the selective heating of the tin active species:

- (a) Faster formation of monoalkoxide and dialkoxide co-initiator
- (b) Faster formation of the first propagating species (1mer) via coordination-insertion mechanism
- (c) Faster re-activation of dormant species by free catalyst

3.5.7 Factors Affecting the Control over ROP

3.5.7.1 Reaction Temperature (Arrhenius Equation)

To further investigate whether the selective heating of the tin species is due to thermal or non-thermal effect, the characteristics of microwave heating was examined by applying the Arrhenius equation (Equation 3.3) to the experimental results derived from this temperature study.

$$k = Ae^{\frac{-E_a}{RT}} \quad (\text{Equation 3.3})$$

Where,

k: rate coefficient

A: Arrhenius constant

E_a: activation energy

R: universal gas constant, $8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1}$

T: temperature (K)

According to the Arrhenius law, rates of reactions, including those catalysed by enzymes, will increase with a rise in temperature. For most reactions, raising the temperature usually increases the rate constants and the Arrhenius equation represents the temperature dependence of reaction rates of such first order reactions. The temperature dependence of rate constants was determined by plotting the logarithm of kinetic constant, $\ln k$ against inverse temperature, $1/T$. This was then compared with reactions using conventional heating therefore allowing any thermal factors obtained from microwave effects on polymerisation to be identified. Table 3.4 shows the k_{app} values of polymerisation conducted using both heating methods at various reaction temperatures that were previously derived from the slopes from Figures 3.21, 3.22, 3.23 and 3.24 in Section 3.5.6.2.

Table 3.4 Temperature study of polymerisation conducted using both conventional and microwave heating for target DP = 87 with relative molar ratio of CL:BnOH:Sn(Oct)₂ = 87:1:0.012. Mass of CL was 6.25 g

Entry	Heating Method	Temperature (°C)	Time (mins)	Conversion (%)	$k_{app} \times 10^{-3}$ (min ⁻¹)
1	Conventional	140	360	89	9.3
2	Conventional	150	300	98	16.4
3	Conventional	160	240	99	23.1
4	Conventional	170	120	97	38.6
5	Conventional	180	90	98	59.8
6	Microwave	140	330	92	15.9
7	Microwave	150	90	78	31.3
8	Microwave	160	120	98	44.1
9	Microwave	170	75	95	53.1
10	Microwave	180	40	72	61.0

The results from this experiment agree with the Arrhenius law as it was shown that the time required for each polymerisation to be completed was reduced as temperature increased. When microwave heating was used, it took 330 minutes to achieve 92 % conversion at 140 °C (Table 3.4, Entry 6) while it took 120 minutes

to achieve 98% conversion at 160 °C (Table 3.4, Entry 8). When the temperature increased to 170 °C, it only took 75 minutes to achieve 95 % conversion (Table 3.4, Entry 9).

It should be emphasized that these temperature study experiments were conducted under the same conditions and the concentration of the reaction components was kept constant while only the temperature varied, hence the discussion on the effect of temperature is focused mainly on k_{app} instead of k_p which is calculated by taking into account the initial concentration of BnOH. In this experiment, $[BnOH]_0$ was held constant. When microwave heating was used, the k_{app} values were observed to increase as the reaction temperature increased. When the reaction temperature was increased from 140 °C to 150 °C, k_{app} was increased 1.97 times from 0.0159 to 0.0313 respectively. However when 30 °C was increased from 140 °C to 170 °C, k_{app} was only 3.34 times higher from 0.0159 to 0.0531 respectively.

Liu and coworkers proposed that microwave heating in polymerisation is a non-thermal effect in their study because the increase in rate constants using microwave heating did not obey the Arrhenius Law.¹² However in Figure 3.26, the plot of $\ln(k_{app})$ against $1/T$ exhibits a profile that is similar to the profile obtained for the reaction heated using “flash” conventional heating by Liu et al. (Figure 3.4, Section 3.2.1).¹³ The increase in rate constants when microwave heating was used fitted the Arrhenius Law, which suggests that the selective heating of tin species using microwave heating is purely due to thermal effect. In other words, microwave heating enhances the rate of polymerisation by selectively heating the tin active species, resulting in faster formation of the co-initiator, faster coordination-insertion process and propagation rate because the temperature of

the tin centre is much higher than the temperature of the bulk. The overall bulk temperature was not drastically affected due to the small quantity and concentration of the tin catalyst.

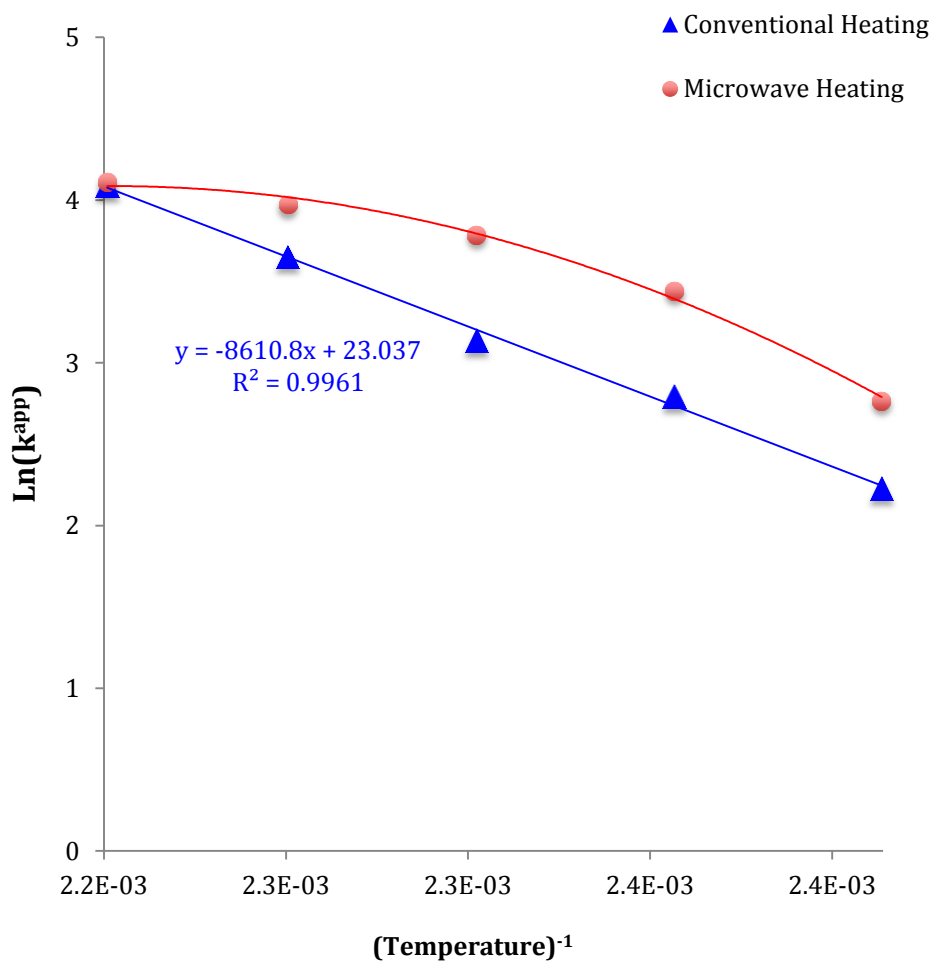


Figure 3.26 Dependence of apparent rate constant (k_{app}) on polymerisation temperatures using conventional (■) and microwave (●) heating at 140 °C-180 °C

3.6 Conclusions and Further Work

The ROP of CL using BnOH and Sn(Oct)₂ as the initiator / catalyst system was successfully conducted using both conventional and microwave heating. The overall reaction time was reduced when microwave heating was used compared to conventional heating. The enhancement observed in the rate of polymerisation was caused by the selective heating of tin active species because it is a susceptible microwave absorbing material (i.e. CL monomer). This hypothesis was built based on the dielectric properties assessment on the individual components and kinetic characteristics of polymerisation. The controlled of M_n over time shown in the Arrhenius plots conducted at 140 °C-180 °C conclude that microwave heating is more energy efficient than conventional heating, hence the reduction / elimination of induction period and the faster rate of polymerisation.

Firstly, the temperature study of ROP showed that the overall reaction time was reduced and enhanced rate of polymerisation was observed when reaction temperature increases. The presence of CL monomer was proved to be very important during the induction period resulting in the formation of the first propagating species (1mer).

Secondly, the ROP of CL was shown to exhibit pseudo-living characteristics as shown by the 2 plots, (a) M_n versus conversion and (b) $\ln ([M]_0/[M])$ versus time. Furthermore, low $\bar{D}$ values around 1.4 were obtained when the monomer conversion is less than 80 %. At higher conversions, high $\bar{D}$ values were seen arising likely due to transesterification reactions. However, control over the molecular weight growth of PCL was successfully achieved resulting in high conversions >97 %.

Kinetic studies were conducted for both conventional and microwave heating systems and microwave-heated reactions showed enhanced rate of polymerisation. This was attributed to the reduction / elimination of the induction period that is always present in conventionally heated processes and faster propagation rate achieved via microwave heating. The induction period is the stage in which in-situ formation of the “true” catalyst occurs. The reduction / elimination of induction period was explained by ^1H NMR studies, which were conducted previously by the group focusing on the complex formation during induction period and throughout polymer growth. ^1H NMR spectra showed that free BnOH was converted to form the benzyl ester end group as part of the polymer chain at a faster rate when microwave heating was used, this resulted in the significant reduction / elimination of the induction period found in all conventional heating processes as the tin active species was selectively heated by microwave irradiation. Furthermore, the presence of monomer increased the rate of these reactions when microwave heating was used compared to the conventional counterparts as CL monomer is efficient at converting absorbed microwave energy into heat.

The comparison of both k_{app} and k_p values for conventional and microwave systems show that faster propagation rates were observed for microwave-heated polymerisations. Again, this was attributed to the selective heating of the tin species and the importance of CL and $\text{Sn}(\text{Oct})_2$ in the coordination-insertion mechanism. Furthermore, microwave heated polymerisations were found to exert a thermal effect as the reactions obeyed the Arrhenius equation, similarly to the conventional heating results.

Future Work

It was observed that when CL, BnOH and Sn(Oct)₂ was used for ROP, the formation of PCL was faster in the microwave. This suggested that CL is a strong microwave-absorbing medium for the selective heating of the tin species. Further study is required to confirm this hypothesis, therefore ROP should be conducted using BnOH and Sn(Oct)₂ with other types of cyclic monomer that demonstrate less efficiency in absorbing and converting microwave energy into heat.

The understanding of the ROP of CL using BnOH and Sn(Oct)₂ has been obtained by using laboratory scale CEM and Miniflow microwave reactors. Following this understanding, it would be important to investigate any differences when conducting these experiments with different microwave reactors (e.g. single mode microwave), which will be needed for scaling up the polymerisation.

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CHAPTER 4 SYNTHESIS OF 3-ARM AND 4-ARM STAR POLYCAPROLACTONE USING MICROWAVE HEATING

4.1 Overview

The synthesis of 3-arm and 4-arm star PCL via ROP using multifunctional initiators and $\text{Sn}(\text{Oct})_2$ catalyst conducted using microwave heating will be discussed in this chapter. This chapter contains a literature review focusing on ROP and similar processes using conventional heating, a presentation and discussion of the experimental results related to:

- (a) Polymerisation kinetics for each 3-arm star PCL concentrating on the synthesis of these polymers using microwave heating.
- (b) Structural characterisation of the polymers using various analytical methods.
- (c) Polymerisation methods employed to reduce the overall reaction time and induction period.
- (d) A comparison between the conventional and microwave heating methods.

This section also discusses the effects of utilising different heating methods on the reaction kinetics and polymer structures produced.

4.2 Literature Review

In recent years, there has been an increased level of research interest in the field of biodegradable star polyesters. In this case the term star refers to branched polymers that consist of more than two linear polymer arms attached to a core (Figure 4.1). These polymers have generated increased interest over the last 15 years because they have been shown to exhibit differentiated and beneficial rheological and mechanical properties with respect to linear polymers of similar molecular dimensions.⁶⁻²² For example, star polymers exhibit a smaller hydrodynamic radius and a lower melt viscosity than their linear counterparts of the same M_n and composition, hence these star polymers can be moulded at lower temperatures. This polymer structure type is of interest to this study, which is focussed on the use of PCL as a biodegradable/bioresorbable polymer, because PCL is a polymer with a low thermal stability, therefore it has been proposed that it would be more preferable to utilise star polymers in moulding processes.²² Additionally, biodegradable star PCL show great potential in biomedical applications due to the higher levels of (a) polymer mass that can be achieved for a particular melt viscosity and (b) functionality per unit volume.^{1, 13}

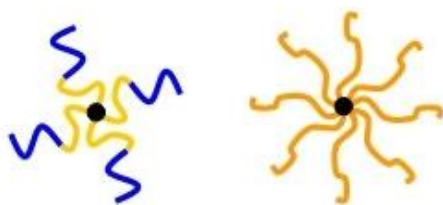


Figure 4.1 Diagram of star polymers

There are three key approaches of which star polymers can be synthesised⁶, the first method being (a) Core-first – in which polymeric arms are built away from a multifunctional initiator serving as the core of the structure, (b) Arm-first – where pre-synthesised linear polymers are coupled with a multifunctional terminator or pre-existing multifunctional reactive species, the latter which becomes the core upon interaction with the pre-synthesised arms and lastly (c) Direct Oligomerisation – which is a direct, controlled polymerisation of macromonomers that contain a functional group which is able to participate in a second polymerisation to a low degree of polymerisation (i.e. an oligomerisation) (DP), and it is the oligomeric backbone that forms the core of the structure in this case.^{6, 16} Of these three, the “core-first” approach has typically been the most extensively employed method for the preparation of biodegradable polymers such as PCL and polylactide [poly(lactic-acid) (PLA)]. Consequently, with the use of many different core molecule structures which contain multiples of a particular reactive functional species have been detailed in the literature for the synthesis of star structures.⁶ For example, multifunctional initiators such as 2-ethyl-2-hydroxymethyl-1,3-propanediol (otherwise known as trimethylolpropane, TMP), pentaerythritol (PTOL), glycerol have been reported to take part in the synthesis of star PLA via ROP with Sn(Oct)₂ serving as a catalyst.^{8, 9, 14, 17}

The polymerisation studies reported in the previous chapter focused on applying various polymerisation methods to identify the effect(s) that microwave heating had upon on ROP to synthesise linear PCL, this work utilised benzyl alcohol (BnOH) as the initiator and Sn(Oct)₂ catalyst. Hence the synthesis of 3-arm and 4-arm star PCL using both conventional and microwave heating

will be discussed in this chapter to further expand these studies on polymer formation using different heating types. The literature review in this chapter will therefore only focus on the synthesis of star PCL by employing $\text{Sn}(\text{Oct})_2$ and a multifunctional initiator. Polymerisations conducted using conventional heating will be reviewed exclusively as there have been very few studies which have reported for the synthesis of star polymers using microwave heating.

Feng et al.¹⁴ reported that the synthesis of 3-arm and 4-arm star PCL were successfully conducted and the star polymers served as a macroinitiator for the preparation of star block copolymers using lactides and glycolides.¹⁵ The ROP of CL was conducted in bulk using multifunctional initiators such as TMP and PTOL with $\text{Sn}(\text{Oct})_2$ at 110 °C and the molar ratio of $[\text{CL}]:[\text{Sn}(\text{Oct})_2] = 1000$. High monomer conversions of 95 – 99 % were achieved in the star polymer synthesis with both initiators during a 24-hour polymerisation. The structures of the polymer products were determined using NMR analysis and were reported to be consistent with the theoretical M_n and that the hydroxyl moiety was confirmed as the end group as expected from the proposed mechanism. Narrow molecular weight distributions, i.e. low $\bar{D}$ values of between 1.09 and 1.26 were also successfully obtained. Similarly, the use of multifunctional initiators PTOL,⁸⁻⁹ glycerol, aminopropanediol and aminohydroxy methylpropanediol¹⁰ have been reported in the synthesis of star PLA via ROP with $\text{Sn}(\text{Oct})_2$ as the catalyst.

A subsequent study by Kricheldorf et al reported the successful synthesis of 3-arm and 4-arm star PCL using TMP and PTOL initiators and $\text{Sn}(\text{Oct})_2$ catalyst.¹⁷ In this study, bulk polymerisations were conducted at 100°C with a molar ratio of $[\text{CL}]:[\text{Initiator}] = 20$ to achieve polymers with a total target DP = 20. The ROP was studied over a large range of reaction times (4 to 16 hours) but

it was reported that 4 hours was sufficient to achieve high monomer conversions. A conversion of 93 % obtained after 4 hours in TMP initiated reactions, while a conversion of 88 % was obtained within the same time frame when PTOL was used as the initiator. The star structures were analysed using ^1H NMR, MALDI-TOF MS and solution viscosity and it was concluded that the length of the polymeric arms were aligned with the target theoretical figures although no M_n and $\bar{D}$ values or data were mentioned in the study. However, these conclusions based upon the polymer structures were confirmed via MALDI-TOF MS analysis and this technique also demonstrated the absence of cyclic oligolactones, suggesting that no trans-esterification normally associated with common, linear polymerisation systems at high conversions had occurred.

Another study reported by Lang et al.¹³ showed that 3-arm star PCL was successfully synthesised by the ROP of CL in the presence of glycerol initiator and $\text{Sn}(\text{Oct})_2$ catalyst. These 3-arm star polymers were then converted into double-bond functionalised 3-arm star PCL with maleic anhydride in the melt at 130 °C. Polymerisation was carried out at 130 °C for over 48 hours and high conversions of >93 % were reportedly obtained. The star polymer products were then analysed using GPC, FTIR, ^1H NMR, ^{13}C NMR and differential scanning calorimetry (DSC). The latter method was conducted by measuring the thermal properties of the polymer product and the results were presented in direct comparison with the linear PCL equivalent. However, the DSC was inconclusive because the apparatus had a – 50 °C limitation and the glycerol-initiated PCL did not show a significant enough raise in glass transition temperature (T_g) to be detected in the study.

In a more recent study, the synthesis of star polymers containing various

numbers of polymeric arms and lengths was carried out by Choi et al.²³ The M_n values of the polymer were assessed using ^1H NMR, GPC-DRI and MALDI-TOF MS by end group determination of the polymer product. It was reported that the resonances in ^1H NMR spectra of the methylene chain end ($-\text{CH}_2\text{OH}$, $\delta = 3.65$ ppm) and the methylene proton adjacent to the C=O group ($-\text{CO}-\text{CH}_2-$, $\delta = 2.31$ ppm) were successfully located and their ratio was calculated to give the DP value of each polymeric arm. The authors found that the DP data obtained in this way were in good agreement with the target DP. However, the efficiency of the initiation was calculated from the ratio of $\text{DP}_{\text{theo}} / \text{DP}_{\text{NMR}}$ to have low values for short arm polymer chains (89-94 %). Additionally, whilst the M_n values determined via ^1H NMR and MALDI-TOF were in close agreement, those obtained via GPC-DRI were shown to have lower values than predicted. The authors attributed this to the lower hydrodynamic radius of star polymers with respect to the linear equivalents due to the presence of the “star-centre”.

As mentioned previously, there are no reports to date on the ROP of CL utilising microwave heating which have multifunctional alcohols and $\text{Sn}(\text{Oct})_2$ serving as the initiator/catalyst system. In this chapter, the fundamental understanding of the ROP of CL using microwave heating processes will be discussed and compared to the application of conventional heating. This study extends the study reported in the previous chapter on the synthesis of linear PCL to the production of 3/4-arm star PCL using various multifunctional initiators and $\text{Sn}(\text{Oct})_2$ catalyst at 150 °C with two different target DPs (approximately DP 20 and DP 90).

4.3 Aims and Objectives

The work discussed in this chapter extends the scope of the study reported in the previous chapter, which was focused on the synthesis of linear PCL with $\text{Sn}(\text{Oct})_2$ / BnOH as the catalyst / initiator system using both conventional and microwave heating. In this chapter, the key aim is to investigate the influence of the physical form of the initiator on the ROP of CL on the synthesis of 3-arm and 4-arm star PCL. In the previous chapter, it was shown that microwave heating exerts thermal effect and selectively heats the $\text{Sn}(\text{Oct})_2$ catalyst in the reaction. This study aims to investigate how the dielectric properties of the initiator affect the characteristics of the synthetic process and whether the heating method used has an effect on the macro-structuring of the polymers formed.

The first objective is the synthesis of 3-arm and 4-arm star PCL using multi-functional hydroxyl initiators and $\text{Sn}(\text{Oct})_2$ utilising both conventional and microwave heating. The second objective is to synthesise these core corona star structures using an increased concentration of $\text{Sn}(\text{Oct})_2$ catalyst. The final objective is to characterise these macrostructures using analytical methods such as ^1H NMR, MALDI-TOF, GPC and DSC.

4.4 Experimental

4.4.1 Materials

ϵ -Caprolactone (99 %) was purchased from Acros and used as received without further purification. Karl-Fisher titration determined its water content to be 67 ppm. Tin 2-ethylhexanoate (96 %) (SnOct_2), anhydrous benzyl alcohol (99 %) (BnOH), glycerol (98 %), trimethylolpropane ethoxylate ($M_n \sim 450$), pentaerythritol ethoxylate ($M_n \sim 270$) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Toluene was distilled at the School of Chemistry then stored over molecular sieves to be dried.

4.4.2 Polymer Characterisation

4.4.2.1 Determination of Monomer Conversion by ^1H NMR

^1H NMR spectra on kinetic/non-precipitated samples were recorded in CDCl_3 using a Bruker DPX-300 spectrometer (300 MHz). For purified polymers, a Bruker DPX-400 spectrometer (400 MHz) was used. Number-average Molecular weight (M_n) was determined by end-group analysis using ^1H NMR analysis by comparing the integral of methylene proton resonance adjacent to the carbonyl group (H_a , 4.1 ppm, to that of methylene proton (H_x , 5.1) belong to benzyl alcohol end group. The monomer conversion was determined by comparing the integral of the proton resonance of the methylene moiety adjacent to oxygen of the carbonyl group for both the monomer ($-\text{CH}_2\text{OCO}-$, $\delta = 4.24$ ppm) and polymer ($-\text{CH}_2\text{OCO}-$, $\delta = 4.07$ ppm).

4.4.2.2 Determination of Molecular Weight via GPC

In a typical procedure, a polymer solution of 7 mg/mL PCL in HPLC THF was prepared and filtered through a 0.2 μm sieve into a GPC vial. The samples were then injected into a GPC calibrated using poly(styrene) standards ranging from 580 to 377,400 g/mol, for a typical time of 24.5 min. In the assessment of control over molecular weight (M_{wt}), all samples were precipitated in MeOH prior to GPC analysis. All GPC equipment and standards were supplied by Polymer Laboratories (Varian) and the data analysed using the Cirrus software package.

4.4.2.3. Determination of End Group using Matrix-assisted Laser Desorption/ Ionisation-Time of Flight Mass Spectroscopy (MALDI-TOF MS)

MALDI-TOF MS was performed using dithranol as the matrix and sodium tetrafluoroacetate (NaFTA) as the supporting sodium salt for ionisation. 10 mg/mL of various solutions in THF of dithranol were prepared along with 1mg/mL of NaTFA and 2 mg/mL of polymer. A mixture of individual components at a volume ratio of 7/1/1 v/v/v was formed and then placed on a stainless steel plate prior to being air-dried.

4.4.2.4 Determination of Thermal Properties using Differential Scanning Calorimetry (DSC)

In a typical procedure, a polymer sample of 3 mg was weighed into a standard pan. An empty pan was used as a reference. The heating profile was

set from -65 °C to 60 °C with a heating rate of 20 °C/min. Measurements were conducted under a nitrogen atmosphere.

4.4.3 Experimental Polymer Synthesis Procedures

All polymerisations conducted in this section were performed as bulk reactions without further purification of the reaction materials. The procedures for ring-opening polymerisation conducted using conventional and microwave heating were as follows:

3-Arm Star PCL Synthesis:

For the synthesis of PCL with a target DP of 90, CL (50 g, 438 mmol) and glycerol (0.45 g, 4.87 mmol) were weighed into a 50 g long-neck round bottom flask. Sn(Oct)₂ catalyst (0.05 g of a 4.98x10⁻¹ g/mL stock solution) was then added via syringe. The flask was then equipped with a magnetic stirrer bar, sealed and heated for the set reaction time at 150 °C in either an oil bath or a microwave reactor. Reaction temperatures were assessed by a direct measurement of the reaction bulk via a fibre optic probe inserted into the reaction medium. Other DPs were obtained by following the same method and adjusting the monomer to initiator ratio accordingly (Table 4.1).

For other core species, the polymerisations were repeated using equal amount of reactants but replacing glycerol with the same molar quantity of trimethylolpropane (TMP) (1.40 g, 1.04 mmol), trimethylolpropane ethoxylate (TMPE) (2.19 g, 4.87 mmol) and glycerol ethoxylate (GE) (4.86 g, 4.87 mmol) instead to achieve 3-arm star PCL. The molar ratio of [CL]/[initiator] was varied for each target DP and the specific molar ratios adopted to achieve each target

DP are specified in Table 4.1. The concentration of $\text{Sn}(\text{Oct})_2$ remained constant at $[\text{CL}]:[\text{Sn}(\text{Oct})_2] = [1]:[2.80 \times 10^{-4}]$ in all ROP reactions with the exception of a small series of reactions conducted with an increased $\text{Sn}(\text{Oct})_2$ concentration, where a $[\text{CL}]:[\text{Sn}(\text{Oct})_2]$ concentration ratio of $[1]:[2.87 \times 10^{-3}]$ was applied.

4-arm Star PCL Synthesis:

A typical procedure for the synthesis of 4-arm star PCL is similar to that of the 3-arm star PCL. For a target DP of 90, CL (50 g, 438 mmol) and (1.31 g, 4.87 mmol) of pentaerythritol ethoxylate (PTOLE) were weighed into a 50 g long-neck round bottom flask. $\text{Sn}(\text{Oct})_2$ catalyst (0.05 g of a 4.98×10^{-1} g/mL stock solution) was then added via syringe. Likewise, specific molar ratio of the components for each target DP is specified in Table 4.1. The concentration of $\text{Sn}(\text{Oct})_2$ remained constant in all polymerisations while the molar ratio of $[\text{CL}]/[\text{initiator}]$ was varied for each target DP.

Table 4.1 Summary of target DP and the corresponding molar ratios of the ROP components.

Initiator	Total Target DP	DP of each arm	Relative molar ratio $[\text{CL}]:[\text{Initiator}]$
Glycerol	21	7	21 : 1
Glycerol	90	30	90 : 1
TMP	21	7	21 : 1
TMP	90	30	90 : 1
TMPE	21	7	21 : 1
TMPE	90	30	90 : 1
PTOLE	20	5	20 : 1
PTOLE	88	22	88 : 1
GE	21	7	21 : 1
GE	90	30	90 : 1

4.5 Results and Discussion

This chapter discusses the synthesis of 3-/4-arm star polymers using a multi-ols/ $\text{Sn}(\text{Oct})_2$ combination as the initiator/catalyst system. The DPs for the polymers were targeted as close as possible to 21 and 90, this is so that the polymer properties can be compared with the linear equivalent as mentioned in Chapter 3. Table 4.1 summarises the specific DP required on each polymer arm to achieve the total target DP.

4.5.1 Synthesis of 3-arm Star PCL

4.5.1.1 Polymerisation Kinetics

3-arm star PCL was firstly synthesised with a trifunctional initiator glycerol and $\text{Sn}(\text{Oct})_2$ as catalyst using microwave heating (see Figure 4.2).

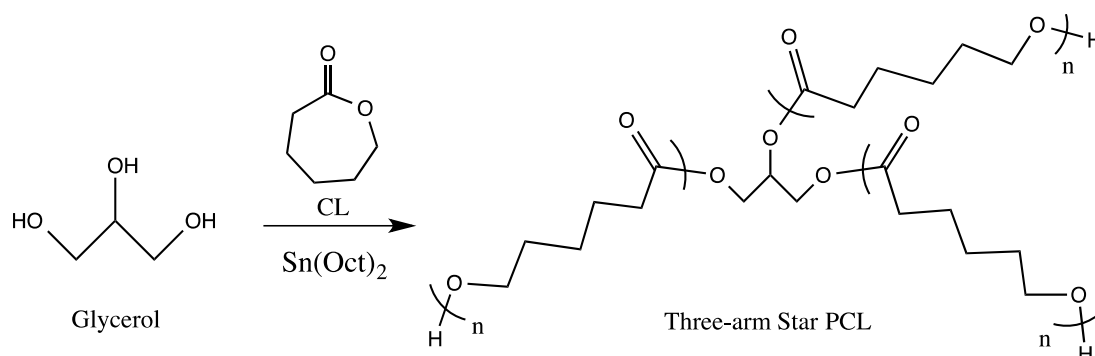


Figure 4.2 Synthesis of 3-arm star PCL using conventional and microwave heating with glycerol as the initiator and $\text{Sn}(\text{Oct})_2$ catalyst.

Bulk polymerisations were conducted using both microwave and conventional heating at 150 °C. The total target DP of the polymers were obtained by adjusting the molar ratio of $[\text{CL}]:[\text{glycerol}]$ to be $[21]:[1]$ for DP = 21 and $[90]:[1]$ for DP = 90, this would result in DP = 7 and DP = 30 for each arm respectively. Relative molar ratio of $[\text{CL}]:[\text{Sn}(\text{Oct})_2]$ was kept constant at $[1]:[2.80 \times 10^{-4}]$.

Kinetic experiments for both conventional and microwave polymerisations were conducted for both DPs by taking samples at individual set points throughout the reaction, this data was then compared in Figure 4.3.

As discussed in Chapter 3 on linear polymerisation work, the induction period was noted to be the section of the polymerisation that was subject to the greatest changes when different heating methods were used. Consequently, the induction period for both conventional and microwave polymerisations were compared throughout the experiments to define if this was also the case with star polymer synthesis. For PCL with DP 90, the induction period was 25 minutes when conventional heating was used and 10 minutes with microwave heating (Figure 4.3a). A similar trend was observed for PCL with DP 21, the induction period was 60 minutes when conventionally heated and 25 minutes when microwave heating was used (Figure 4.3b). Repeated experiments showed that the induction period was generally shorter (typically less than half of the conventional equivalent) for reactions carried out using microwave heating at this catalyst concentration, regardless of the target DP.

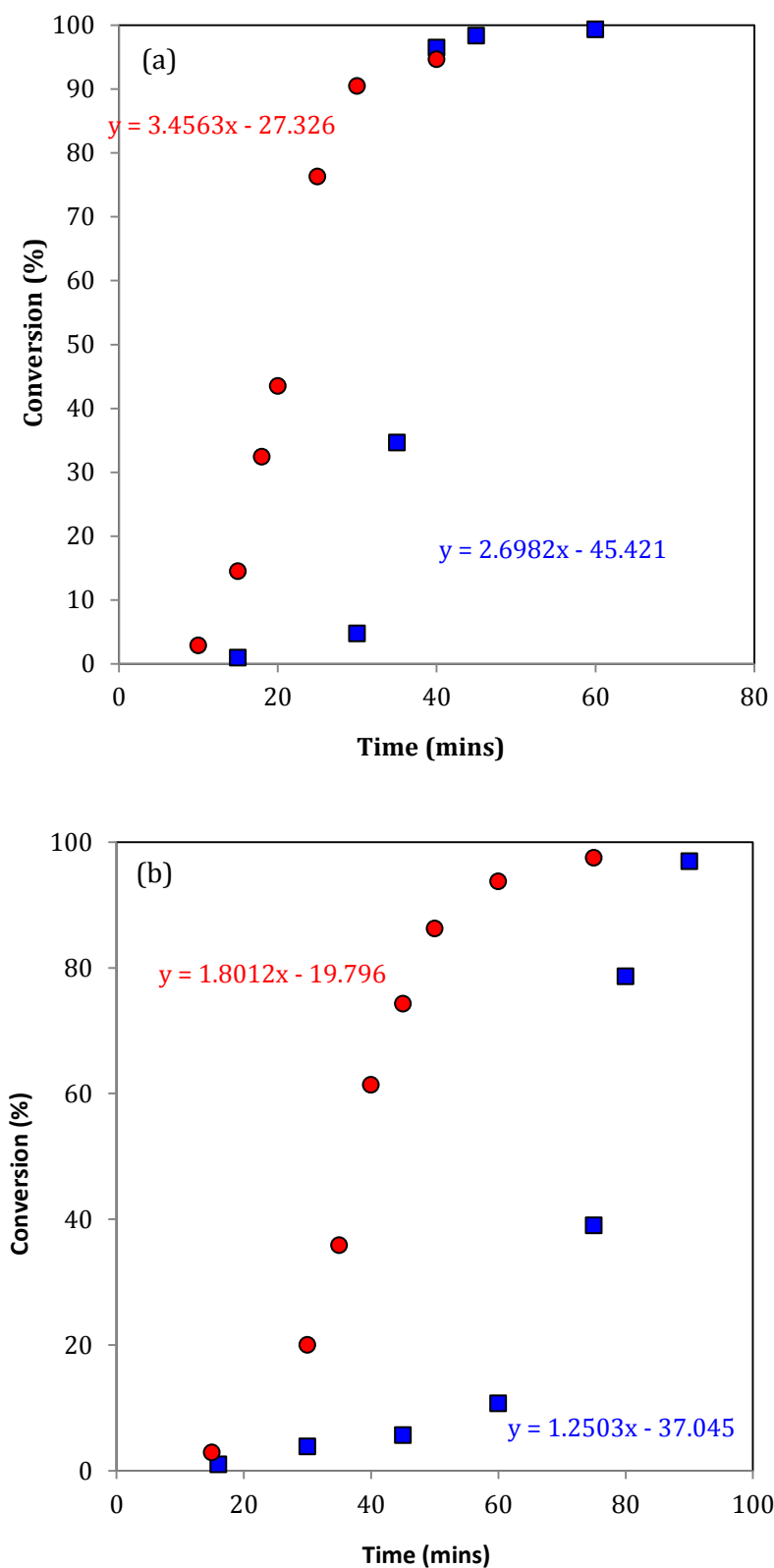


Figure 4.3 Polymerisation kinetics using conventional (■) and microwave (•) heating for a total target (a) DP 90, for each DP = 30 arm, and (b) DP 21, for each DP = 7 arm. All polymerisations were conducted at 150°C using glycerol initiator, 25 g CL and [CL]:[Sn(Oct)₂] = [1]: [2.80x10⁻⁴].

In addition, it was noted that the induction period for the synthesis of PCL with DP 21 was generally longer than those of DP 90. A greater period of time was required for the synthesis of polymer with shorter arms as significantly more initiator is present in the reactions targeting the lower DP, therefore much more reaction to form the catalyst co-initiator species has to be achieved at the beginning stage of the polymerisation prior to propagation commencing.

Post induction reaction profiles were also compared for these conditions, propagation rates were defined by the slope of the graphs. For PCL with DP 90, the propagation period was observed to be 20 mins when conventionally heated and a conversion of 99 % was achieved. When microwave heating was used, the propagation rate was faster (slope = 3.46) than the conventional heating reaction (slope = 2.7) over a shorter period of 15 mins and a conversion of 95 % was achieved. Similarly for PCL with DP 21, after the end of the induction period, it took 75 mins to achieve 97 % conversion (slope = 1.25) when conventional heating was used and 45 mins (slope = 1.8) to obtain the same conversion when microwave heating was used.

Thus, it can be concluded that both induction and propagation periods are shorter when microwave heating was used. Faster propagation rates were also observed in microwave-heated reactions compared to those that were conventionally heated. The shorter induction periods observed in microwave-heated reactions are attributed to similar effects that were highlighted for linear materials in Chapter 3. This was related to a faster complexation of both the initiator and the first monomer species due to selective heating of the organometallic species. In practice however, even after the alkoxide monomer

species have completely formed in the induction period, the propagation stage of the polymerisation was observed to proceed more quickly when microwave heating was applied as a result of the continued selective heating of the tin complex.

4.5.1.2 Determination of 3-arm Star Structure

Therefore, it was shown that 3-arm star polymer had been successfully produced in both conventionally and microwave heated polymerisations using glycerol as an initiator and $\text{Sn}(\text{Oct})_2$ catalyst. The molecular structures of these 3-arm star PCL materials were then subjected to a range of polymer analysis techniques to (a) verify that a 3-arm star structure was successfully produced and (b) to observe any molecular structural differences when microwave heating was used compared to conventional heating. To do this, the star structures of the polymers produced were subjected to ^1H NMR, GPC, MALDI-TOF and DSC analysis. The data analysis from ^1H NMR, GPC and MALDI-TOF will be presented in this section while the data from DSC analysis will be discussed using a direct comparison with linear PCL of the same molecular weight.

^1H NMR Analysis

Determination of monomer conversion and end-group analysis was conducted using ^1H NMR as the initiator moiety on the polymer chain is a main focus point in the PCL star structure determination. The polymer product was first precipitated in MeOH and left to dry overnight under reduced pressure to ensure that the polymer product was free of impurities prior to end-group

analysis via NMR. Figure 4.4 shows an example of one of the ^1H NMR spectra obtained from the PCL that has the proposed 3-arm star structure.

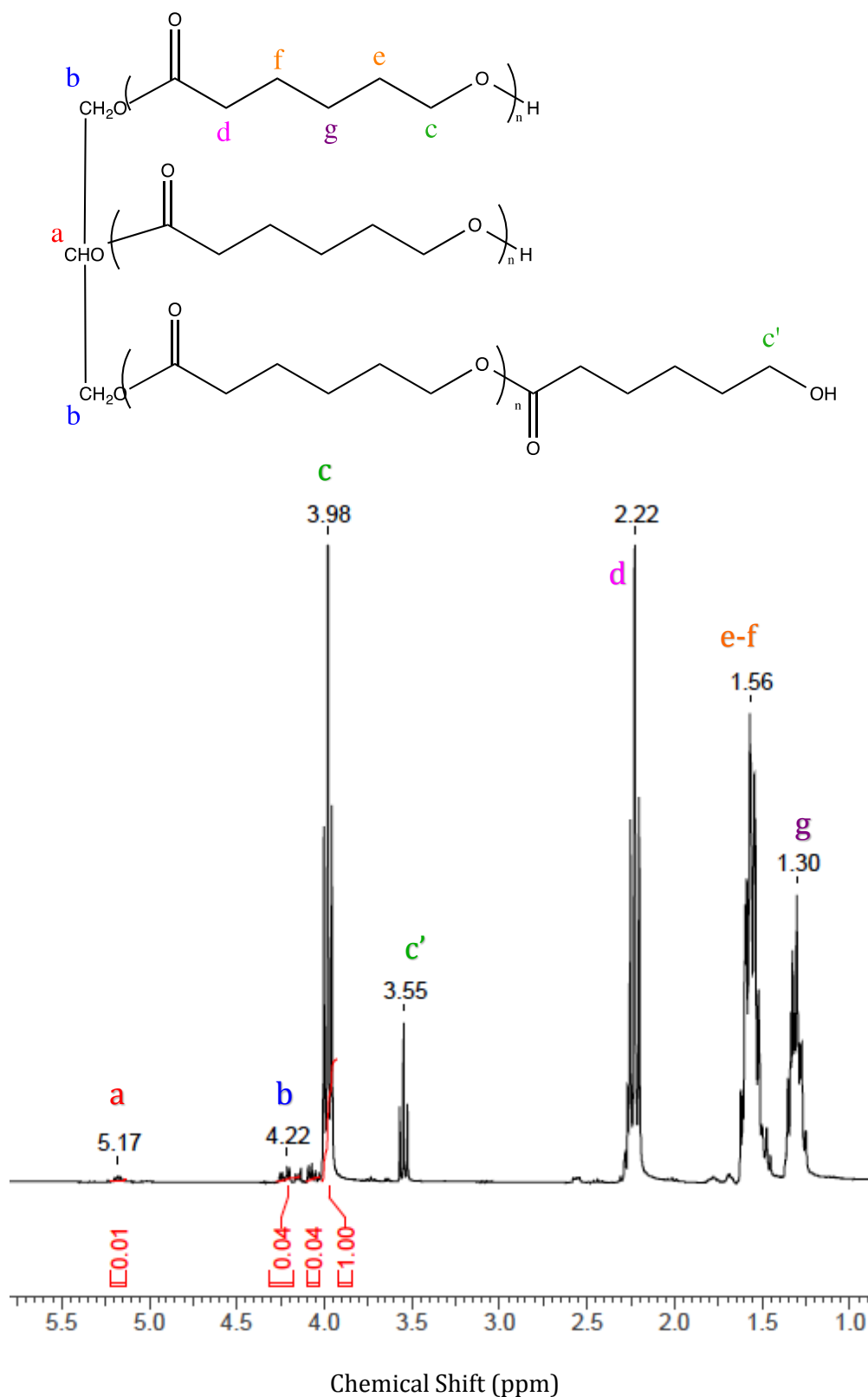


Figure 4.4 ^1H NMR spectrum of 3-arm star PCL initiated by glycerol, which was recorded in CDCl_3 using a Bruker 300MHz.

The ^1H NMR spectra clearly showed that the glycerol initiator had been incorporated as the end-group of the polymer as indicated by the shift in the resonance of the protons from $\delta = 3.77$ ppm for CHOH (glycerol secondary hydroxyl) and $\delta = 3.55\text{--}3.65$ ppm for the two CH_2OH groups (glycerol primary hydroxyls) to $\delta = 5.17$ ppm for CHO of polymer (ethers of secondary hydroxyl) and $\delta = 4.22$ ppm for the two CH_2O groups (ethers of primary hydroxyls) of glycerol end-group of the PCL polymer chain. Additionally, the magnitude of the monomer resonance suggests that there's close to no monomer present in the final product and that all the primary hydroxyl groups of the glycerol have been completely initiated to form the polymer chains. However, the fact that the resonance for the methylene associated with the secondary hydroxyl group in the monomer (~ 4.1 ppm) are obscured by other peaks meant that polymer chain growth on all three available hydroxyl sites could not be confirmed via ^1H NMR analysis and thus require further investigation via other analytical methods. Figure 4.20 in later Section 4.6 shows an additional ^1H NMR spectrum of 3-arm star PCL initiated by glycerol using both conventional and microwave heating.

Monomer conversion was determined by comparing the integral of the proton resonance of $\delta = 4.1$ ppm (CL) and $\delta = 3.98$ ppm (PCL) as shown in Figure 4.4. A sample calculation to determine monomer conversion is shown as follows:

$$\text{Conversion} = \frac{\text{Polymer}}{\text{Monomer} + \text{Polymer}} \times 100\%$$

$$\text{Conversion} = \frac{1}{1 + 0.04} \times 100\% = 96\%$$

MALDI-TOF MS Analysis

MALDI-TOF is a highly efficient analytical method used to confirm end-group functionalities of polymers. MALDI-TOF was used to characterise the glycerol initiated PCL structure by determining the combined molecular weight of the end groups present in the polymer. The MALDI-TOF spectra as shown in Figure 4.5 shows the proposed 3-arm star PCL initiated by glycerol with an overall target DP = 21. Unfortunately, no spectra could be obtained for DP = 90 polymers using the same method as the molecular weights were too large and the polymer was unable to be transported into the analytical section of the apparatus.

Practical data can be interpreted and used to calculate the molecular weight of the end group based on the equation below:

$$M_{\text{obs}} = n(M_{\text{ru}}) + M_{\text{end}} + M_{\text{ion}} \quad (\text{Equation 4.1})$$

Where,

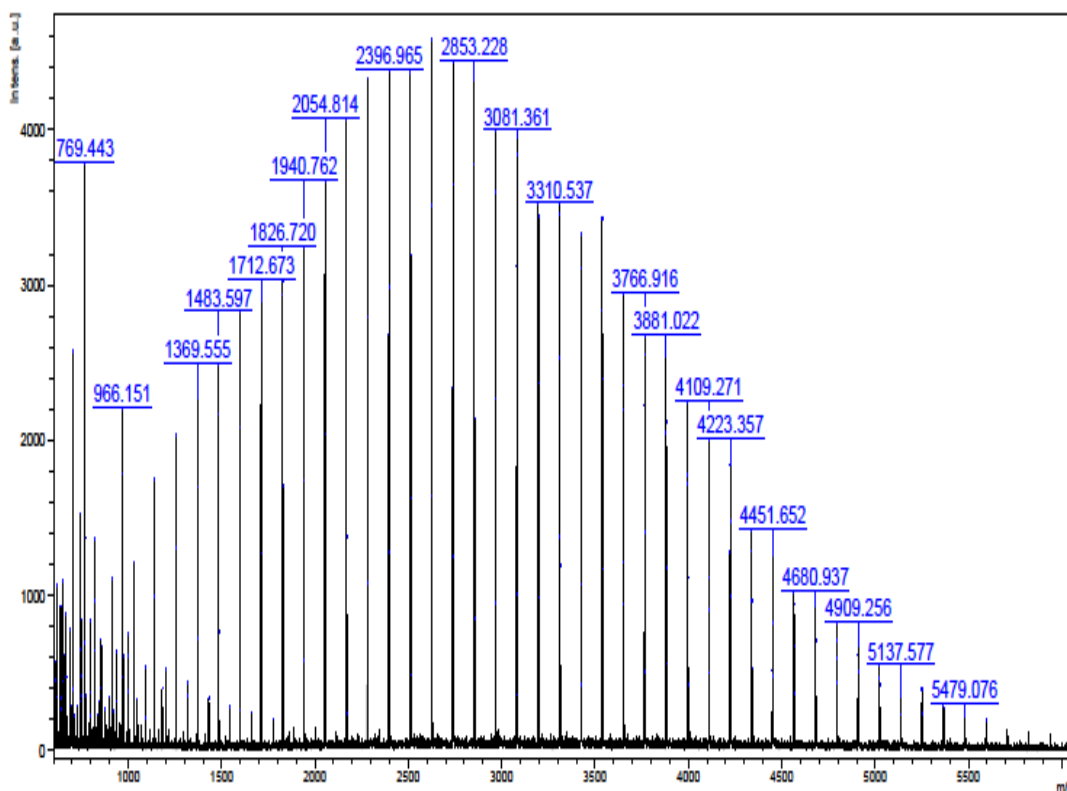
M_{obs} : the observed molecular weight by MALDI-TOF,

n : the number of repeating units (or DP)

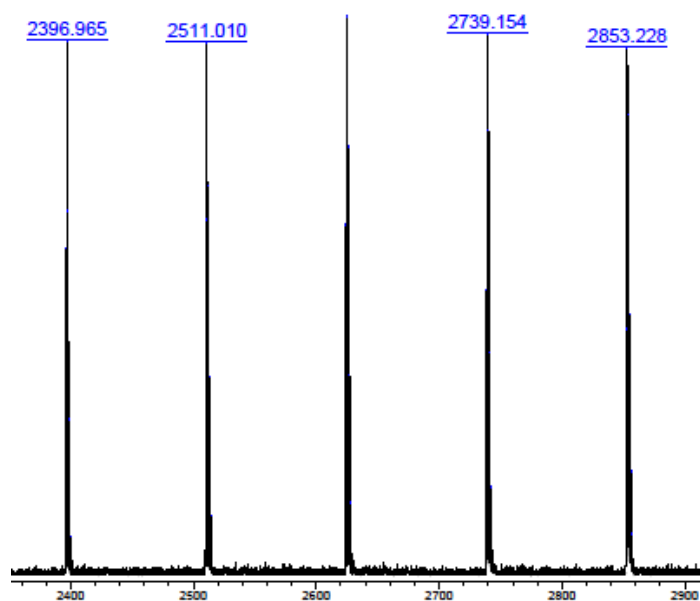
M_{ru} : molecular weight of the repeating unit, in this case $M_{\text{CL}} = 114.14$

M_{end} : molecular weight of the combination of end groups on the polymer

M_{ion} : molecular weight of the ion attached to the polymer chain



(a) Full MALDI-TOF MS spectrum



(b) Zoom-in section

Figure 4.5 The MALDI-TOF MS spectra of 3-arm star polymer with the overall target DP = 21. Dithranol and NaTFA were used as the matrix and ionization supported salt, respectively. The polymer was dissolved in THF and characterisation was carried out using Bruker Ultraflex III spectrometer.

Firstly, variables such as n , M_{ru} and M_{ion} must be defined in order to calculate M_{end} . The value of M_{ion} is dependent on the mode of ionisation utilised during the MALDI-TOF characterisation as the polymer was ionised by complexation with the salt that occurs via several different mechanisms. PCL was reported to achieve complexation via cationisation with NaTFA being the cation source used, therefore the value of M_{ion} is equal to the MW of a Na^+ moiety that is 22.99 g/mol.

When glycerol is assumed as the end group with $M_{end} = (M_{glycerol} - 3H) + 2H = 91.09$. The H species are defined as the H's that are added to the ring open monomer for the hydroxyl groups terminal groups at the other end of the polymer chain, whilst the abstraction of 1 H during cationisation was compensated, which was then replaced by Na^+ . Therefore, M_{theo} was calculated to be 2511.02 by using Equation 4.1. Table 4.2 shows that the observed M_n value with each corresponding number of repeating unit was in good agreement with the theoretical M_n values, within a margin of error of $\pm 5\%$. This suggests that the end group of the star PCL is glycerol and the structure is that of a 3-arm star PCL.

Table 4.2 Summary of the theoretical M_n calculated by assuming $M_{end} = M_{glycerol} - 1H$, M_n observed by MALDI-TOF MS and the corresponding number of repeating units.

Repeating Unit	M_{theo}	M_{obs}
10	1255.5	1255.5
11	1369.6	1369.5
12	1483.8	1483.5
13	1597.9	1597.6
14	1712.0	1712.6
15	1826.2	1826.7
16	1940.3	1940.7
17	2054.5	2054.8
18	2168.6	2168.8
19	2282.7	2282.9
20	2396.9	2396.9
21	2511.0	2511.01
22	2625.2	2625.08
23	2739.3	2739.2
24	2853.4	2853.2
25	2967.6	2967.3
26	3081.7	3081.4
27	3195.9	3195.4
28	3310.0	3310.5
29	3424.1	3424.6
30	3538.3	3538.7

GPC Analysis

The polymer product was also characterised using GPC analysis.

Monomodal GPC traces were observed for both target DPs and both heating methods applied, as shown in Figure 4.6.

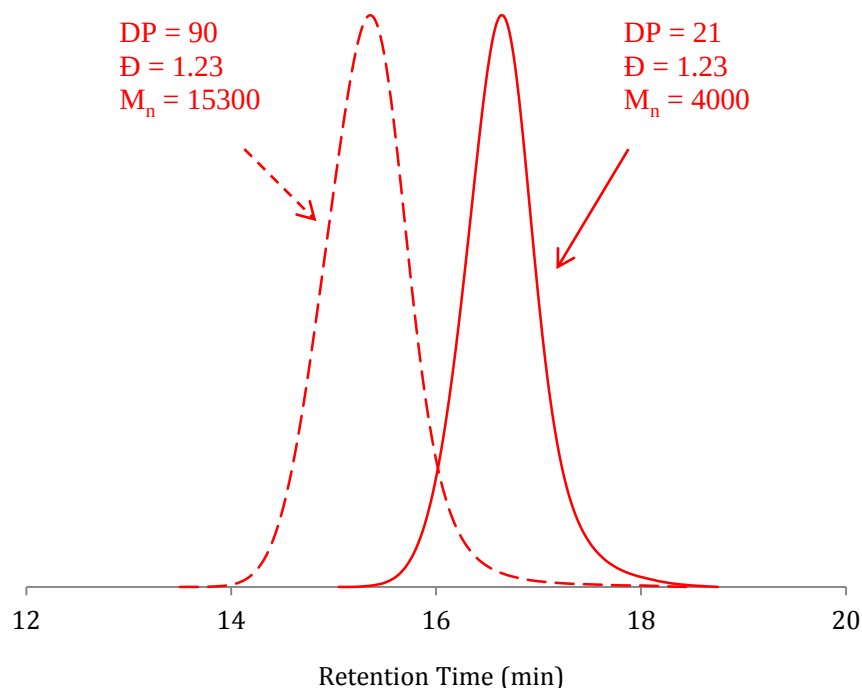


Figure 4.6 GPC traces of 3-arm star PCL DP = 90 (---) and DP = 21 (—) initiated by glycerol. PS standard used for calibration. M_n values were corrected via the Mark-Houwink-Sakurada relationship using $K = 1.09 \times 10^{-3} \text{ dLg}^{-1}$ and $\alpha = 0.6021$. Mark-Houwink-Sakurada equation is defined by $[\eta] = KM^\alpha$, from which the molecular weight (M) of a polymer can be determined from the intrinsic viscosity (η).

The value of $\bar{D}$ was narrow, defined to be 1.23 for both DP 21 and DP 90.

However, GPC is not a reliable analytical method used to determine the MW of star polymers as the hydrodynamic volumes of star polymers are different from linear polymers and PS calibration standards used. Therefore, the GPC was largely used for comparison between the products of the two heating methods in this study rather than to derive definitive MW's for the stars.

DSC Analysis

DSC was utilised to analyse the thermal properties of the comparative 3-arm star and linear PCL. PCL is a semi-crystalline polymer which has been reported to exhibit a T_m in the range of 56 to 65 °C and a T_g in between -65 to -

60 °C. DSC results on the glycerol-initiated 3-arm star PCL and benzyl alcohol-initiated linear PCL are shown in Figures 4.7 and 4.8.

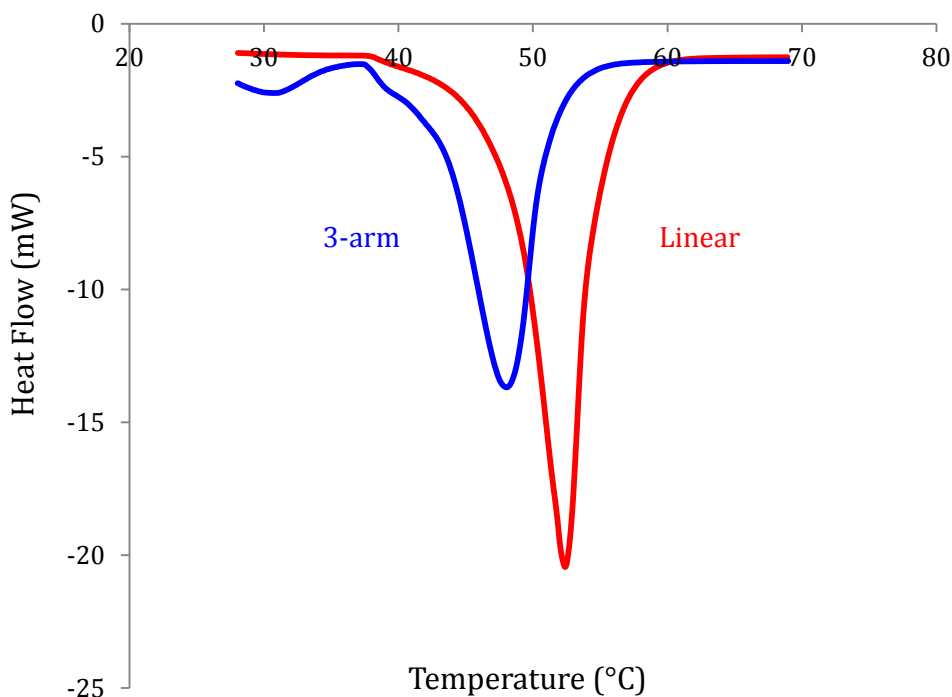


Figure 4.7 DSC traces showing the melting transition of linear (-) and 3-arm (-) star PCL for target DP 21

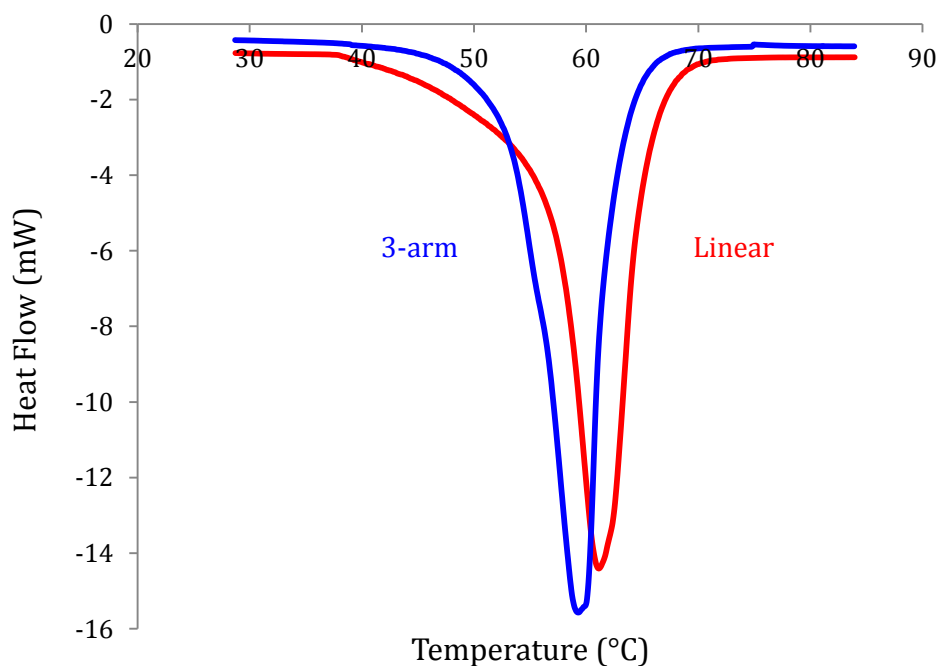


Figure 4.8 DSC traces showing the melting transition of linear (-) and 3-arm (-) star PCL for target DP 87 and 90 respectively

Figures 4.7 and 4.8 show that the melting transition of PCL moved towards a lower temperature as the polymer arm length decreases (DP = 21). For PCL with a target DP = 21, T_m of the linear PCL is 52.42 °C while the 3-arm star equivalent exhibits a T_m of 47.57 °C. A similar trend was observed for linear PCL with target DP = 87 and 3-arm star PCL with target DP = 90 with T_m = 61.35 °C and T_m = 59.39 °C respectively. This was to be expected because there is an increased number of chain ends with the reduced the M_n value of the polymer. Chain ends are relatively free in motion and less energy is required to stimulate chain movement and melting, therefore the T_m is lowered. Additionally, as the MW of the polymer drops there is less chain entanglement which may also lead to a reduction in T_m .

Additionally, it was observed that the 3-arm star polymers exhibit a lower T_m than the linear equivalent. Several factors that affect T_m , these include symmetry, intermolecular bonding, tacticity, branching and molar mass. In the case of the branched PCL structures, these have irregular chain orders which contain definitive “bends” in the chains, hence these polymers do not pack well and so are likely to have less chain chain interaction as a result. By comparison, linear PCL crystallites achieve close packing by Van der Waals forces between the chains that provide stability to the polymer structure. Interactions between the chains hold the structure together more firmly and raise the melting temperature. Thus it was proposed that the 3-arm star PCL structures have reduced packing efficiency and low crystallinity, hence these polymers have a lower density and T_m when compared to linear PCL.

Conclusions for the Synthesis of 3-arm Star PCL with Glycerol

3-arm star PCL was successfully synthesised via ROP of CL using glycerol and $\text{Sn}(\text{Oct})_2$ for both target DP 21 and DP 90. Overall, a shorter amount of time was required to achieve a high conversion (>98 %) when microwave heating was used compared to conventional heating. As in the case of the linear polymers, this was shown to be principally due to a reduction in the induction time exhibited by a polymer system. Smaller stars were also shown to exhibit a longer induction time, which was related to the quantity of initiation steps that were required to achieve that particular arm MW. The 3-arm star structures of the polymers were confirmed using ^1H NMR and MALDI-TOF MS, in which glycerol was proven as the core group in the MALDI-TOF analysis. Both analytical methods show that glycerol is indeed present in the polymer. GPC analysis was conducted and monomodal GPC traces were observed for polymers of both target DPs. The $\bar{M}_w/\bar{M}_n$ value is 1.2 for both DPs which suggests that similar good quality structures have been synthesised using both heating methods. DSC analysis was utilised and the data obtained served as a direct comparison between linear and 3-arm star polymers of the same molecular weight. In general, 3-arm star PCL of both target DP = 21 and DP = 90 have a lower T_m when compared to linear polymers due to the lower crystallinity and packing efficiency.

4.5.2 Effects of the Physical State of Initiator on Polymerisation

Up to this point glycerol had been the key initiator used in the initial synthesis of 3-arm star PCL, at room temperature this is in a liquid state and has a melting point of 17-18 °C, and it was observed that glycerol initiator was soluble in CL monomer. During the analysis of the polymerisation using kinetic experimental approach, which takes samples from the reaction mixture for analysis at set points throughout the reaction, it was noted that no initiator is present in the reaction mixture at the end of each induction period. Thus it was proposed that the solubility of the initiator in monomer may be one of the factors that contributes to the presence and the length of an induction period observed. Thus, a series of reactions were carried out using a solid initiator to compare the effect of the physical state of initiator on the length of induction period.

Table 4.3 Physical Characteristics of multifunctional initiators.

Initiator	Formula Weight (g)	Melting Point (°C)	Room Temp Physical Form	Compatibility with Organic Solvents/Monomers	Tanδ at 150 °C
BnOH	108.14	-15	Liquid	Miscible	0.40
TMP	134.17	58	Solid (Flake)	Partial	0.20
PTOL	136.15	260	White Solid	Limited	0.01
TMPE	~450 ^a	NA ^b	Liquid	Limited	-
PTOLE	~270 ^a	NA ^b	Liquid	Limited	-
G	92.09	18	Liquid	Miscible	0.25
GE	~1000 ^a	NA ^b	Liquid	Miscible	0.10

^a As quoted by supplier, ^b Data not available from supplier

Trimethylolpropane (TMP) was selected as the trifunctional solid initiator used to synthesise 3-arm star PCL. TMP appears in a solid state with a melting temperature of 56-58 °C, it was also observed that TMP was not completely miscible in CL. Therefore, TMP was used as a comparison for

synthesising 3-arm star PCL. Nam Nguyen conducted all reactions using TMP as the initiator and the results he obtained were used as reference in this section.³⁵

Similarly, the synthesis of 3-arm star PCL using TMP was also conducted in solvent-free, bulk reactions like those polymerisations previously reported which used glycerol as the initiator. All polymerisations were progressed using both conventional and microwave heating at 150 °C and were targeted to obtain polymers with target DP = 21 and DP = 90, i.e. theoretical arms of DP = 7 and DP = 30 respectively. The total target DPs of the polymers were achieved by adjusting the molar ratio of [CL]:[TMP] as [21]:[1] for DP = 21 and [90]:[1] for DP = 90. The relative molar ratio of [CL]:[Sn(Oct)₂] was kept constant at [1]:[2.80 x 10⁻⁴].

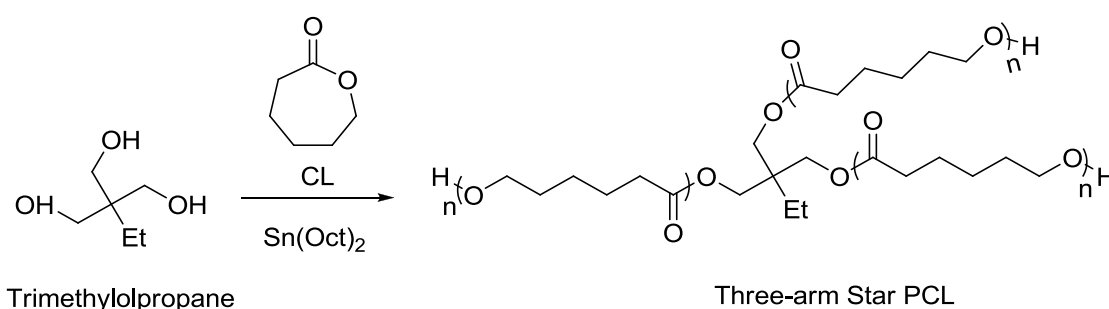


Figure 4.9 Synthesis of 3-arm star PCL using conventional and microwave heating with Trimethylolpropane (TMP) as the initiator and Sn(Oct)₂ catalyst.

Polymerisation kinetics for both DPs using conventional and microwave heating were followed and samples were taken at set points throughout the reactions, and all data is compared in Figure 4.10. The induction periods were observed closely in the polymerisations utilising both heating methods. For DP 90, the induction period was 90 mins when conventional heating was used and 60 mins when heated in the microwave. For PCL with DP 21, the induction

period was 180 mins with conventional heating and 150 mins when microwave heated. Thus it was concluded solid TMP was used as the initiator, the induction period was generally 30 mins shorter using microwave heating than those reactions conducted using conventional heating. As observed with glycerol, the induction period for DP 21 polymerisations were longer than those of DP 90 as it takes a greater amount of time to produce shorter arm chains due to the larger amount of initiator required.

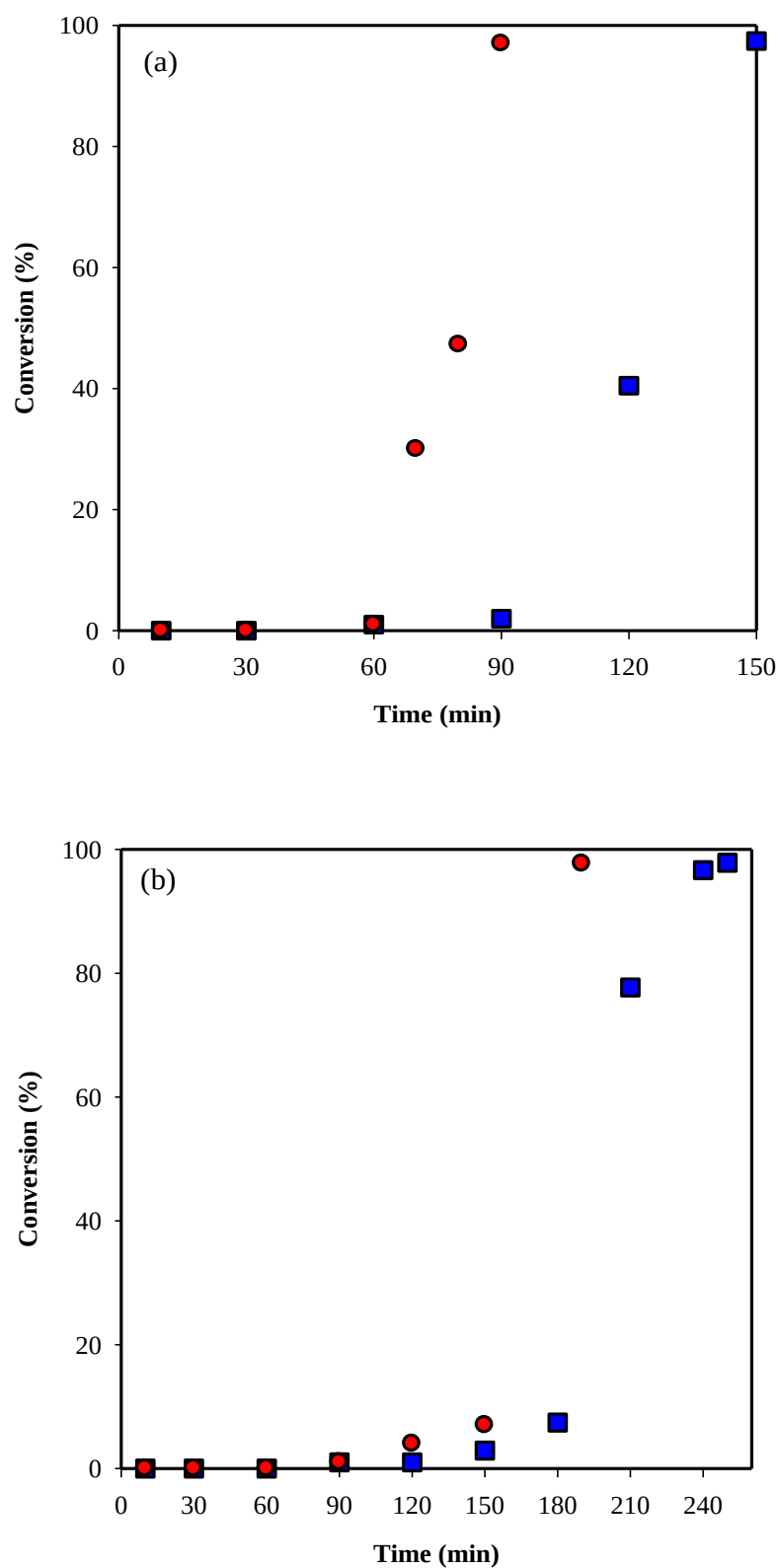


Figure 4.10 Polymerisation kinetics using conventional (■) and microwave (●) heating for a total target (a) DP 90, for each DP = 30 arm, and (b) DP 21, for each DP = 7 arm. All polymerisations were conducted at 150 °C using TMP initiator, 25 g CL and [CL]:[Sn(Oct)₂] = [1]: [2.80x10⁻⁴].

Thus it was observed that similar trends in both the presence and the nature of an induction period was observed for polymerisations carried out with both liquid glycerol and solid TMP initiator respectively relative to the changes in M_{wt} and heating method. However, the induction periods observed were to be very different in time length. Repeat experiments show that the induction period was generally longer when solid TMP was used as the initiator regardless of the heating source and target DP. As mentioned previously, TMP was observed to not be completely miscible with CL monomer and does not dissolve in the reaction mixture immediately. The reaction mixture was completely depleted of “free” TMP at the end of the induction period. Therefore, it was proposed that the poor solubility of TMP in the reaction mixture was one of the contributing factors leading to the lengthened induction period in these polymerisations.

In addition, it was shown that the use of a solid initiator reduced the differentiation in induction time that could be achieved between the different heating methods applied. The reductions achieved in the TMP induction times by moving to microwave heating were significantly less than when using glycerol. It is known that solid organic materials do not couple with incident microwave energy efficiently as the physical form of solid material leads to internal dipole rotation restrictions such that they cannot follow the phase of the incident energy.³² Thus, TMP whilst still in a solid form will not contribute as significantly to the selective heating of the reaction system compared to liquid glycerol when microwave heating is used. This effect is exemplified by review of the dielectric property data for TMP as detailed in Figure 4.11, which shows that TMP does not show a significant response to the applied field until it is in liquid form above its melting point.

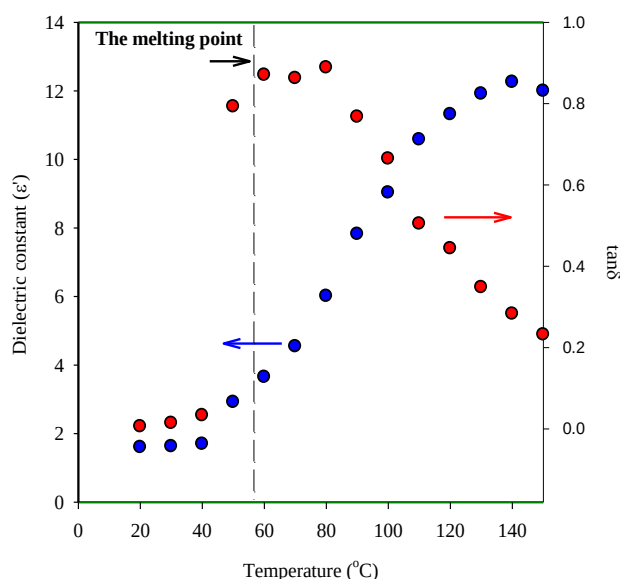


Figure 4.11 Plot of dielectric properties: dielectric constant, ϵ' (●) and $\tan \delta$ (●), against temperature for TMP.³⁵

Thus it was proposed that as conventional heating relies on convection it was not as affected by the physical form of the initiator so the differentiation between them is reduced. However, a longer induction period was also observed when TMP was used in conventionally heated polymerisations. This suggests that the catalytically active tin alkoxide species was formed more slowly compared to when liquid glycerol was used. It was proposed that when TMP was used, the steric barrier to forming the “true” catalytic species via ligand exchange was increased, hence slowing the complexation. However, the fact that there is still a single distribution in the GPC (Figure 4.12) observed from the polymer produced by the polymerisation and the MW of the polymer was observed to grow linearly with time in the propagation stage (Figure 4.10) lead to the conclusion that the polymerisation was exhibiting a pseudo-living characteristics.

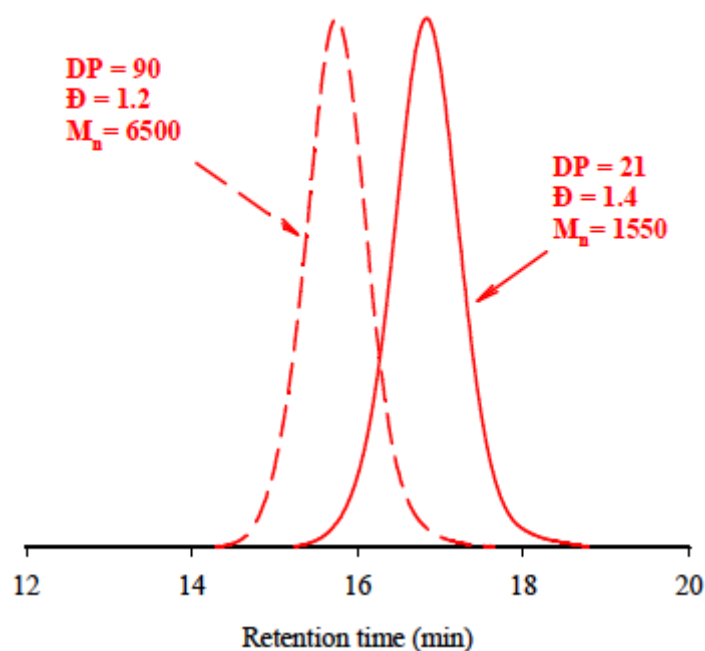


Figure 4.12 GPC traces of 3-arm star PCL DP = 90 (---) and DP = 21 (—) initiated by TMP. PS standard used for calibration. M_n values were corrected via the Mark-Houwink-Sakurada relationship using $K = 1.09 \times 10^{-3} \text{ dLg}^{-1}$ and $\alpha = 0.6021$.³⁵

Post induction period reaction profiles were then compared and it was observed that for the DP 90 PCL, a propagation period of 130 mins was required to achieve 97 % conversion when conventional heating was used and this period was 90 mins to achieve the same conversion when microwave heating was used. Similarly for PCL with DP 21, a 98 % conversion was achieved within a 240 mins propagation period when conventional heating was used and 200 mins in the microwave to achieve the same conversion. This suggested that there was also an advantageous influence from using microwave heating on the reaction during the propagation stage of the polymerisation. This was consistent with the previous chapter on linear polymer work, where it has been proposed that these differences were attributed to the fact that microwave heating could be selectively heating the organometallic species and monomer because both materials exhibit similar dielectric properties at 150 °C.

Consequently, the experimental work conducted in this chapter has shown that similar quality 3-arm star PCL polymers had been successfully synthesised using TMP as the initiator and $\text{Sn}(\text{Oct})_2$ as the catalyst via both heating methods as defined by GPC analysis. Once more, the molecular structures of these polymers must be further analysed to verify the 3-arm star structure.

4.5.3 Effects of using Ethoxylated Initiators

Synthesis of 3-arm and 4-arm Star PCL using TMPE and PTOLE

To further investigate the hypothesis that the physical form of the initiators has a significant effect of the reactions, especially when the organometallic species and monomer are selectively heated during the induction period, polymerisations were carried out using partially polymerised initiators. The synthesis of 4-arm star PCL using solid pentaerythritol (PTOL) initiator with DP = 88 has been previously conducted by Nam Nguyen and the data will be used as reference and comparison in this section.³⁵

Both trimethylolpropane ethoxylate (TMPE) and pentaerythritol ethoxylate (PTOLE) contain partially polymerised arms, the former consists of 6-7 polyethylene glycol (PEG) units on each arm from a TMP core while the latter consists of 3-4 PEG arm units from a PTOL core. The ethoxylated counterparts of TMP and PTOL were selected as the main initiators for the reaction, all of which exhibit liquid state at room temperature. Therefore, these are liquid multi-ol initiators, which should be less sterically hindered (specifically around the initiating hydroxyl which will now be located significantly further way from the branched centre). Hence, these changes

should improve the miscibility of both the initiator in the monomer and increase the potential of achieving the selective heating of the initiator in the microwave. In a subsequent series of experiments, star polymers were synthesised using TMP ethoxylate (3-arm) and PTOL ethoxylate (4-arm). The usage of these liquid initiators will result in the formation of amphiphilic core corona star polymers that consist of a hydrophobic core (PEG) and a hydrophobic outer corona (PCL). The synthesis of 3-arm star PCL initiated by TMPE and PTOLE is illustrated in Figure 4.13.

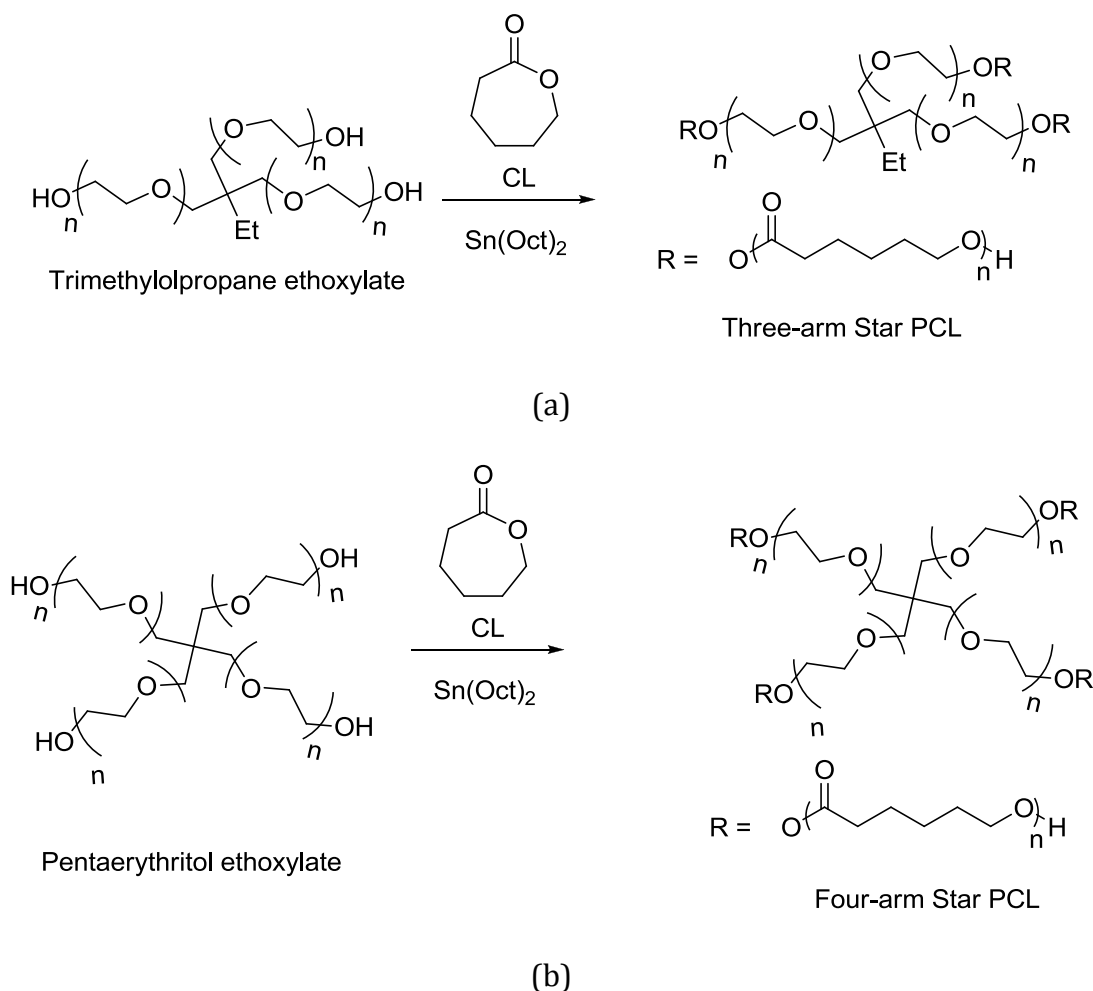


Figure 4.13 Synthesis of 3-arm (a) and 4-arm (b) star PCL using conventional and microwave heating with TMPE (a) and PTOLE (b) and $\text{Sn}(\text{Oct})_2$ as the initiator/catalyst system.

As in previous star experiments, all polymerisations were conducted at 150 °C using both conventional and microwave heating and the total target DP of the polymers were obtained by adjusting the molar ratio of [CL]:[TMPE] as [21]:[1] for DP = 21 and [90]:[1] for DP = 90, this resulted in DP = 7 and DP = 30 for each arm respectively, whilst [CL]:[PTOLE] was adjusted to [88]:[1] to achieve target DP = 88 resulting in DP = 22 for each arm. The relative molar ratio of [CL]:[Sn(Oct)₂] was kept constant at [1]:[2.80 × 10⁻⁴].

It was proposed that the adoption of these liquid initiators in the synthesis of 3-arm and 4-arm star polymers would reduce the influence on the length of the induction period of the physical form/ miscibility of the initiator and also the reduced the steric crowding due to the increased flexibility in initiator structures and intermolecular distance between hydroxyl functional groups. The results from these polymerisations are summarised in Table 4.4.

Table 4.4 Summary of results for the synthesis of 3-arm and 4-arm star PCL using conventional (CH) and microwave heating (MH) with TMPE and PTOLE

Initiator	Target DP	Heating method	Time (min)	$M_{n(theo)}$ (g mol ⁻¹)	$M_{n(GPC)}^a$ (g mol ⁻¹)	PDI ^a
TMPE	90	CH	50	10700	13500	1.24
TMPE	90	MH	50	10700	13600	1.21
TMPE	21	CH	60	2800	2300	1.33
TMPE	21	MH	60	2800	2400	1.37
PTOLE	88	CH	60	10500	14400	1.27
PTOLE	88	MH	60	10500	14800	1.30

Polymerisation conditions: [CL]:[Sn(Oct)₂] = [1]:[2.80×10⁻⁴], 150 °C. All monomer conversions > 95 %. ^a Measured by GPC in THF (40 °C) using PS standards and corrected by applying the appropriate correcting factor (0.56)

The kinetics of polymerisation were determined by taking samples at set periods and this data showed that the overall time taken for the polymerisations to achieve a conversion >95 % was shorter when TMPE and PTOLE was used in

place of TMP and PTOL. However, in the case of the ethoxylated initiators, the overall reactions times were also noted to have become aligned when both conventional and microwave heating was used such that the final cycle times are very similar.

Furthermore, it was observed that when the physical form and molecular structure of the initiator were changed, polymers with the lower target DP were more significantly affected compared to those with a larger target DP. When conventional heating was used, the overall reaction time for the DP 21 reaction with TMPE was a quarter of the time required for the TMP equivalent (Figure 4.10), while this time was only reduced to approximately a third for the DP 90 PCL equivalent. Induction periods were still observed in all polymerisations with ethoxylated initiators as shown in Figure 4.14.

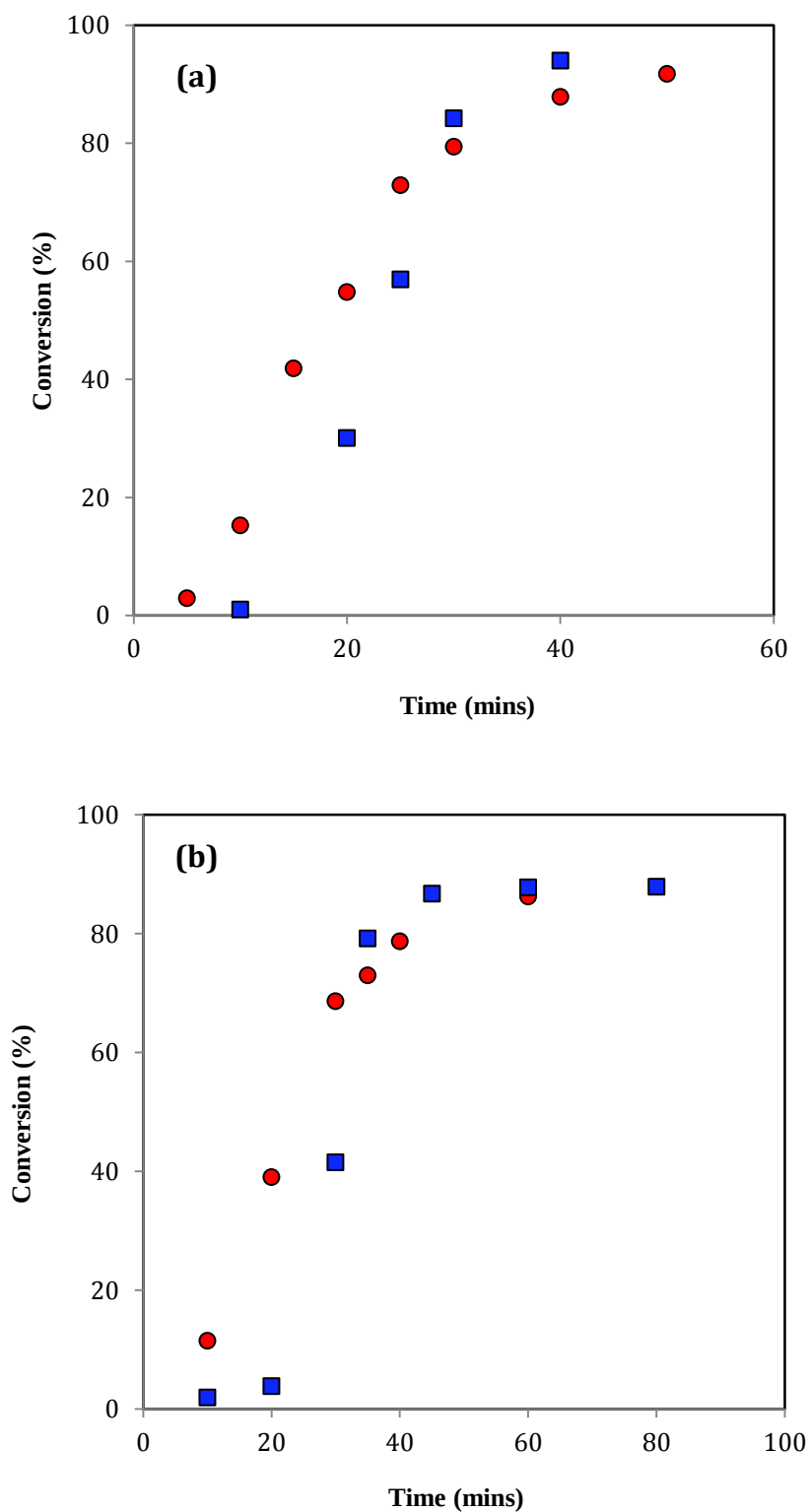


Figure 4.14 Polymerisation kinetics using conventional (■) and microwave (●) heating for a total target (a) DP 90, for each DP = 30 arm, and (b) DP 21, for each DP = 7 arm. All polymerisations were conducted at 150 °C using TMPE initiator, 25 g CL and [CL]:[Sn(Oct)₂] = [1]: [2.80×10⁻⁴].

It was observed that the induction periods for the polymerisations with ethoxylated initiators were always significantly shorter (a) the ethoxylated initiators and (b) microwave heating was used rather than conventional heating. When conventional heating was used, the induction periods for the polymerisations with TMPE were 15 and 20 minutes for both DP = 90 and DP = 21 while this period was 5 and 10 minutes respectively for DP = 90 and DP = 21 in the microwave. These induction periods were significantly shorter than when solid TMP was used as the initiator (Section 4.5.2). The induction periods for the TMP initiated polymerisations were 60 mins (DP = 90) and 90 mins (DP = 21) when microwave heating was used and 90 mins (DP = 90) and 180 mins (DP = 21) when conventionally heated. A similar trend was observed in the PTOLE initiated reactions where the induction periods were significantly reduced when compared to the reactions using PTOL (Figure 4.15).

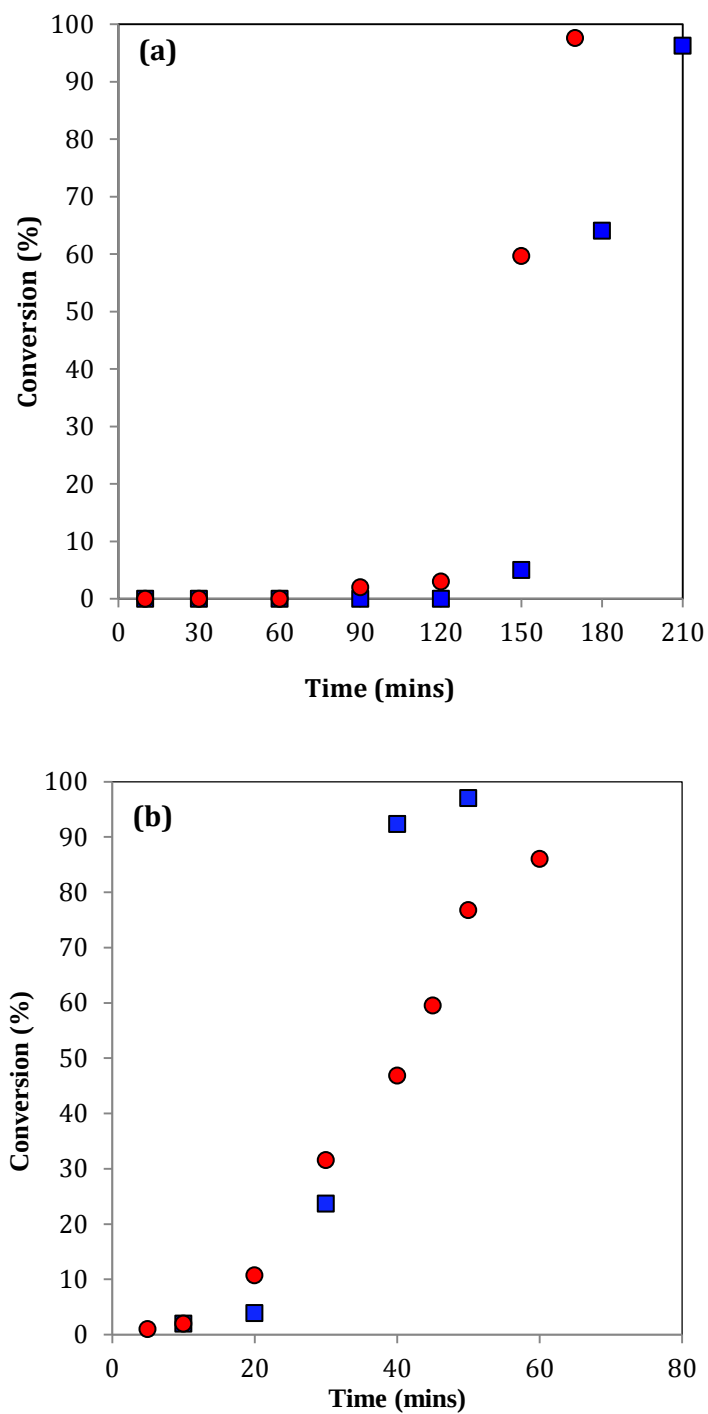


Figure 4.15 Comparison of the kinetics of the ROP initiated with (a) PTOL³⁵ and (b) PTOLE, conducted in a round bottom flask using CH (■) and MH (●) (150 °C, DP 88).

Therefore it was concluded that the change in physical form and reduced steric hindrance had led to the expected reduction in induction periods by

enabling greater availability for the initiator to take part in the formation of the “true” catalytic species and the reaction with the first monomer.

An interesting trend was observed in both cases, whilst induction period reductions were noted in the reactions with both heating methods. a different trend was noticed at high conversions when compared with the solid initiator equivalents. When solid initiator was used, the rate of propagation for the microwave-heated reactions, which is defined by the slope of the linear relationship plot of conversion against time, was found to be greater than the conventionally heated reactions. However, when the ethoxylated initiators were used, microwave heated reaction plots showed faster propagation rate at lower conversions, but the slope of these plots were observed to reduce and move away from the ideal linear relationship more quickly than the conventionally heated reaction plots, i.e. microwave-heated reactions start more quickly but conventionally heated reactions finish more strongly. This suggests that the microwave-heated polymerisations were also affected by the initiator type at high conversion as well as during the induction stage.

The main difference between the initiators is the presence of the ethoxylated polymer arms. Steric effects caused by these partially polymerised arms on the initiators was unlikely to affect the electromagnetic polarisation and ROP mechanisms at high conversions due to the reaction centres being at opposite ends of the long PCL chain by the time the differences in the propagation rate were observed. Hence this difference was attributed to the changes in the macrostructure within the reaction mixture as a result of the amphiphilic core corona star polymer products where the PEG arms are hydrophilic while the growing PCL arms are hydrophobic. This amphiphilic

environment comprises a small central hydrophilic region being surrounded by a large hydrophobic polymer corona (Figure 4.16).

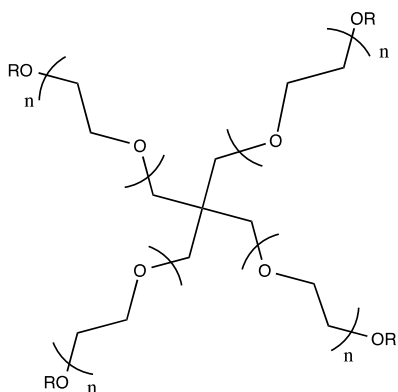


Figure 4.16 Illustration of a central hydrophilic region being surrounded by a large hydrophobic polymer corona

It was proposed that the presence of such a structure could lead to the generation of extended order in the reaction mixture where the hydrophobic polymer arms interact more preferentially with themselves in order to minimise their interaction with the hydrophilic core. Alternatively, the amphiphilic star polymers may display a “pseudo-micellar” behaviour where the PCL folds around the core forming the “micelle”, thus leading to the chain ends being separated from free monomer as they are more hydrophilic (hydroxyl species) and so prefer to be collocated with the core. As a consequence of either of these scenarios, it would be more difficult for the tin reactive species to come in contact and react with free monomer or the hydroxyl functional ends of a dormant chain due to the presence of the extended structure. This would be a much more significant effect with microwave selective heating where the organometallic species is the key element being heated as there would be less energy introduced to the ordered polymer structure to disrupt the macro-structuring. Conventional heating will produce convection heating currents imparting more heat into the polymer so disturbing the order and producing a

higher reaction rate. This effect becomes more marked at higher molecular weight with microwave heating because (a) the chain is long enough to create the order and (b) the polymer is becoming increasingly microwave transparent as its molecular weight increases and the dipole restriction becomes more marked.

This conclusion was supported by the observation that the heating profiles of these reactions with ethoxylated initiators also showed that the temperature of the reactions conducted in the microwave started to decrease at higher conversions leading to the drop in rate of reaction. The temperature drop at high conversions is also one of the reasons why microwave heating systems were affected more than the conventional heating systems as it is less likely for the chain end tin species to be selectively heated due to the core-corona structures that are present. Therefore, the extended structures have reduced the ability and efficiency of the dipoles that interact with the incident microwave energy.

Synthesis of 3-arm Star PCL using glycerol ethoxylate

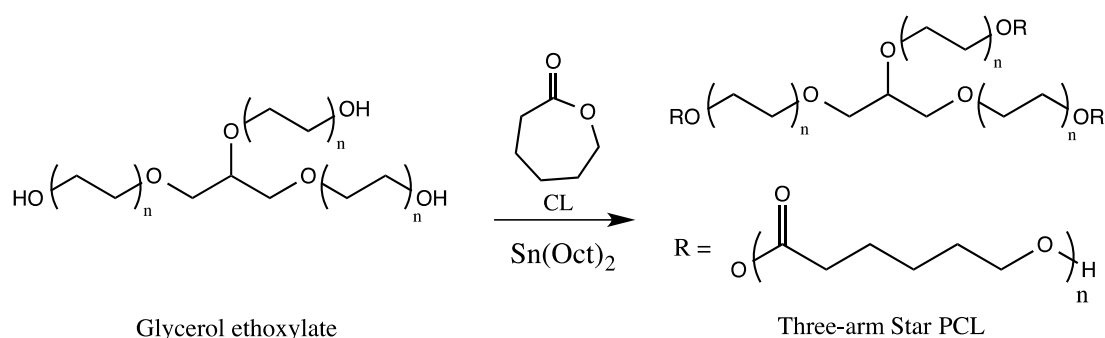


Figure 4.17 Synthesis of 3-arm star PCL using conventional and microwave heating with glycerol ethoxylate and Sn(Oct)₂ as the initiator/catalyst system.

The glycerol initiated polymerisations from Section 4.5.1 served as comparisons to the liquid ethoxylated initiators discussed in this section.

Therefore, these investigations were extended in order to verify the hypothesis of extended structures by synthesising 3-arm star PCL using glycerol ethoxylate (GE) initiator, which also exhibits a liquid state at room temperature. This is because whilst both glycerol and glycerol ethoxylate structures contain an identical hydroxyl core which means that, glycerol should form completely hydrophobic star polymers with CL. GE, due to the absence of ethoxylate arms, should form amphiphilic star polymers when reacted with CL due to the presence of hydrophilic PEG arms. As a result, it would be unlikely for the glycerol initiated star polymers to create an extended structure as mentioned previously, hence all stages of polymerisation should proceed faster when microwave heating is used over conventional heating. The plots for glycerol ethoxylate initiated reactions should be aligned for both microwave and conventional heating systems if the hypothesis of extended structures is valid. In addition to that, these reactions should also explain if the lengthy induction period observed in TMP and PTOL initiated polymerisations were due to the influence of physical and dielectric properties of the initiator or the steric environment and reactivity of the functional groups around the core, because the hydroxyl functional groups on glycerol are in closer proximity than those of glycerol ethoxylate, TMPE and PTOLE while the centre hydroxyl group in glycerol is a secondary hydroxyl and should therefore have a lower reactivity compared to the primary functional groups on the other ethoxylated initiators. The synthesis of 3-arm star PCL using glycerol and glycerol ethoxylate initiators were conducted under the same conditions as the previous polymerisations using TMPE and PTOLE. The polymer products obtained from the reactions

were compared, data was collected from both crude and purified material and the results are summarised in Table 4.5.

Table 4.5 Results of the ROP of ϵ -caprolactone initiated by glycerol (G) and glycerol ethoxylate (GE) using conventional (CH) and microwave heating (MH).

Initiator	Target DP	Heating system	Time (min)	$M_{n(theo)}$ (g mol ⁻¹)	$M_{n(GPC)}^a$ (g mol ⁻¹)	PDI ^a
G	90	CH	45	10300	13500	1.37
G	90	MH	35	10300	15300	1.23
G	21	CH	90	2400	6100	1.15
G	21	MH	60	2400	4000	1.23
GE	90	CH	50	11300	12335	1.31
GE	90	MH	70	11300	12218	1.27
GE	21	CH	70	3400	2792	1.28
GE	21	MH	70	3400	2618	1.32

Polymerisation conditions: [CL]:[Sn(Oct)₂] = [1]:[2.80×10⁻⁴], 150 °C. All monomer conversions > 95 %. ^a Measured by GPC in THF (40 °C) using PS standards and corrected by applying the appropriate correcting factor (0.56)

The results showed that, as expected, the reactions carried out with liquid glycerol and glycerol ethoxylate initiators have both shorter induction times and overall reaction time when compared to the reactions conducted with solid initiators. Furthermore, when glycerol was used, the reaction did exhibit a faster induction and propagation and the overall time taken to achieve >95% conversion in both conventional and microwave heating systems were similar with both DP21 and DP90 systems. Additionally, it was observed that the overall reaction time for the glycerol initiated polymerisations were always shorter than the glycerol ethoxylate equivalents. Kinetics of polymerisation for both conventional and microwave reactions were followed for both DPs and samples were taken at individual set points to monitor the trend at both induction and high conversion periods, this data was then compared in Figure 4.18.

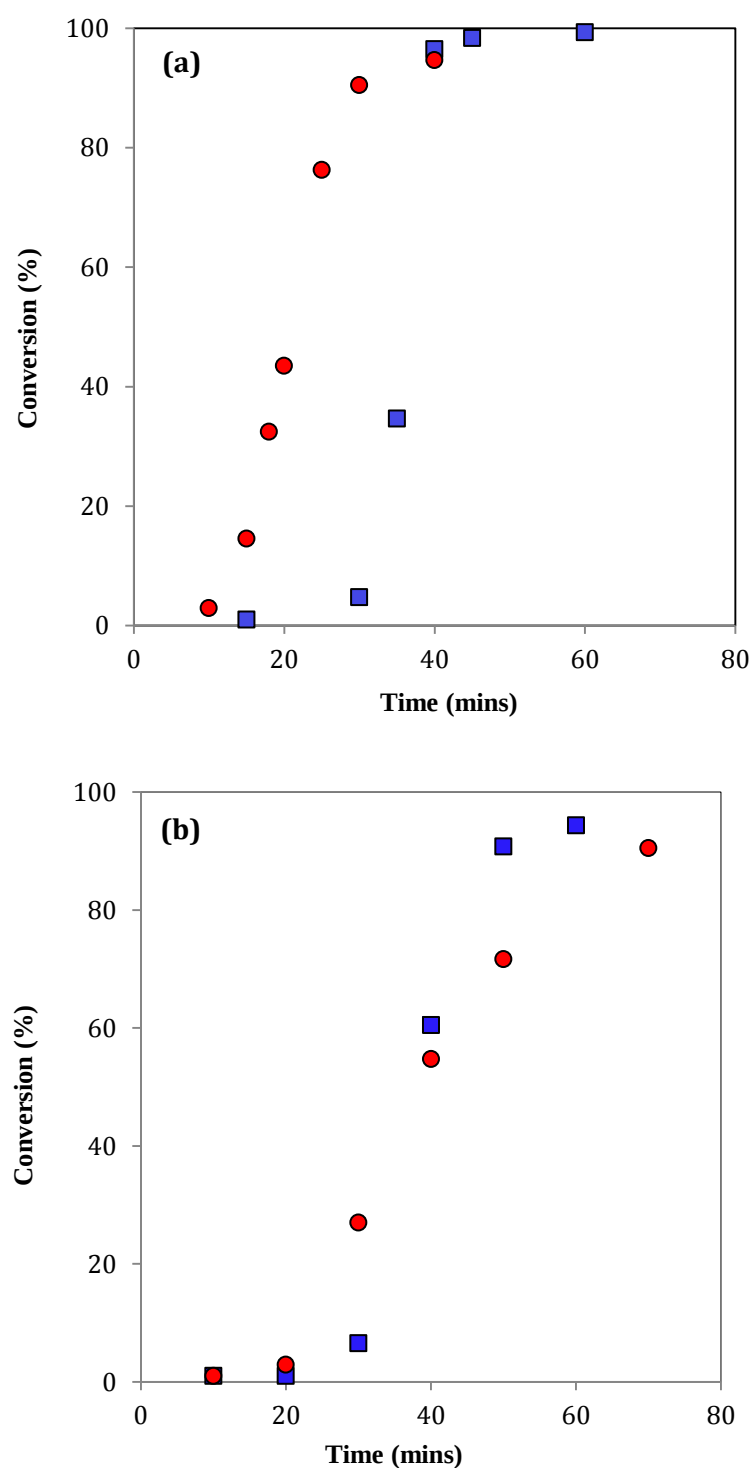


Figure 4.18 Polymerisation kinetics using conventional (■) and microwave (●) heating for a total target DP 90, for each DP = 30 arm. All polymerisations were conducted at 150°C using glycerol (a) and glycerol ethoxylate (b) initiator, 25 g CL and [CL]:[Sn(Oct)₂] = [1]: [2.80x10⁻⁴].

When microwave heating was used, the induction periods for both glycerol and glycerol ethoxylate initiated reactions were shorter than when conventional heating was used. Furthermore, a significantly shorter induction period was observed when glycerol was used in the microwave while the difference in induction period when glycerol ethoxylate was used was less prominent and the drop in propagation rate at high conversions also indicated at higher conversion such that the overall cycle time for the polymerisation was at best aligned, if not slightly longer, with microwave heating. This again supported the conclusion that these differences were due to the presence of the proposed amphiphilic nature of the polymeric species produced from ethoxylated initiators in the reaction. Results confirmed that the presence of ethoxylated species lead to the overall reaction time being aligned in the glycerol ethoxylate, TMPE and PTOLE initiated polymerisations. Although ethoxylated initiators have shown to be able to produce well-controlled amphiphilic core corona star PCL that contain a hydrophilic core and hydrophobic shell, no advantages were gained in terms of improving the overall polymerisation time with the use of microwave heating alone. It was then proposed that the best method to improve the overall polymerisation time was to utilise microwave heating during the induction period followed by a complete conventional heating system post induction, this was shown to reduce the overall reaction time from 70 minutes to 50 minutes. The repeating kinetic trend observed with ethoxylated and non-ethoxylated initiated ROPs were found to be consistent regardless of the physical state, functional group reactivity and steric environment showed that the key similarity was due to the formation of

macrostructures in the reaction mixture as the molecular size of the hydrophobic corona in the amphiphilic polymers increased.

The induction and propagation stages were significantly affected by the physical state of the initiators, this suggested that the dielectric properties of the reaction mixture played a more significant role in the overall polymerisation time rather than the functional group reactivity. It was observed that the time difference in the induction period was directly related to the magnitude of the $\tan \delta$ of the initiators as shown in Table 4.2, this supports the hypothesis that the lengthy overall reaction time in TMP and PTOL initiated polymerisations were caused by poor miscibility of the initiator in the reaction mixture thus leading to poor heating efficiency, low availability to take part in the initiating reaction mechanisms. Glycerol initiated reactions showed a shorter induction period when microwave heating was used compared to the glycerol ethoxylate equivalents (conventional and microwave heated), this demonstrated that microwave heating had managed to overcome the steric crowding of the hydroxyl groups and the reactivity of the secondary hydroxyl site in glycerol that reacts more readily than when conventional heating was used. It was observed that the induction period of the reaction initiated with glycerol ethoxylate in the microwave was increased compared to the glycerol equivalent and the plots had become aligned with those obtained from reactions that were conventionally heated. Therefore, this led to the conclusion that microwave heating was able to overcome steric hindrance and functional group reactivity more efficiently than conventional heating. However, the dielectric properties of the initiators could also lead to any differences observed between microwave and conventionally heated reactions as glycerol has a greater $\tan \delta$ value than

glycerol ethoxylate as shown in Table 4.3, indicating that glycerol initiated reactions respond more efficiently to microwave heating.

Molecular structure results of the star polymer in Table 4.5 showed that the ethoxylate initiated data demonstrated a similar trend to those initiated by solid initiators. The M_p and M_w values for both ethoxylate and non-ethoxylate products derived from using the two heating sources were very similar while the M_n values exhibited a small variance relative to the different PDIs observed. In general, polymers initiated by liquid initiators showed lower PDIs which supports the proposal that better miscibility was achieved with liquid initiators, leading to a more efficient induction process as all initiator functional groups were more readily available to interact with the tin species in the reaction mixture from the beginning of the reaction, hence the target [initiator]:[catalyst]:[monomer] ratio could be achieved more accurately.

4.5.4 Effects of Varying $\text{Sn}(\text{Oct})_2$ Catalyst Concentration

The synthesis of star PCL was conducted with an increased $\text{Sn}(\text{Oct})_2$ catalyst concentration as a proposed means to overcome any catalyst separation issues that might present in the type of segregated system proposed for the amphiphilic core corona star polymers. The catalyst concentration was increased as an attempt to (a) further reduce the induction time, (b) additionally increase propagation rate when microwave heating is used and (c) reduce any catalyst diffusion issues by increasing the concentration of selectively heated species in the medium. The concentration of $\text{Sn}(\text{Oct})_2$ was increased to a ratio of $[\text{CL}]:[\text{Sn}(\text{Oct})_2] = [1]:[2.87 \times 10^{-3}]$. Polymerisations were carried out at 150 °C

using both conventional and microwave heating with a target DP = 90. Kinetics of polymerisation was followed and results are shown in Figure 4.19.

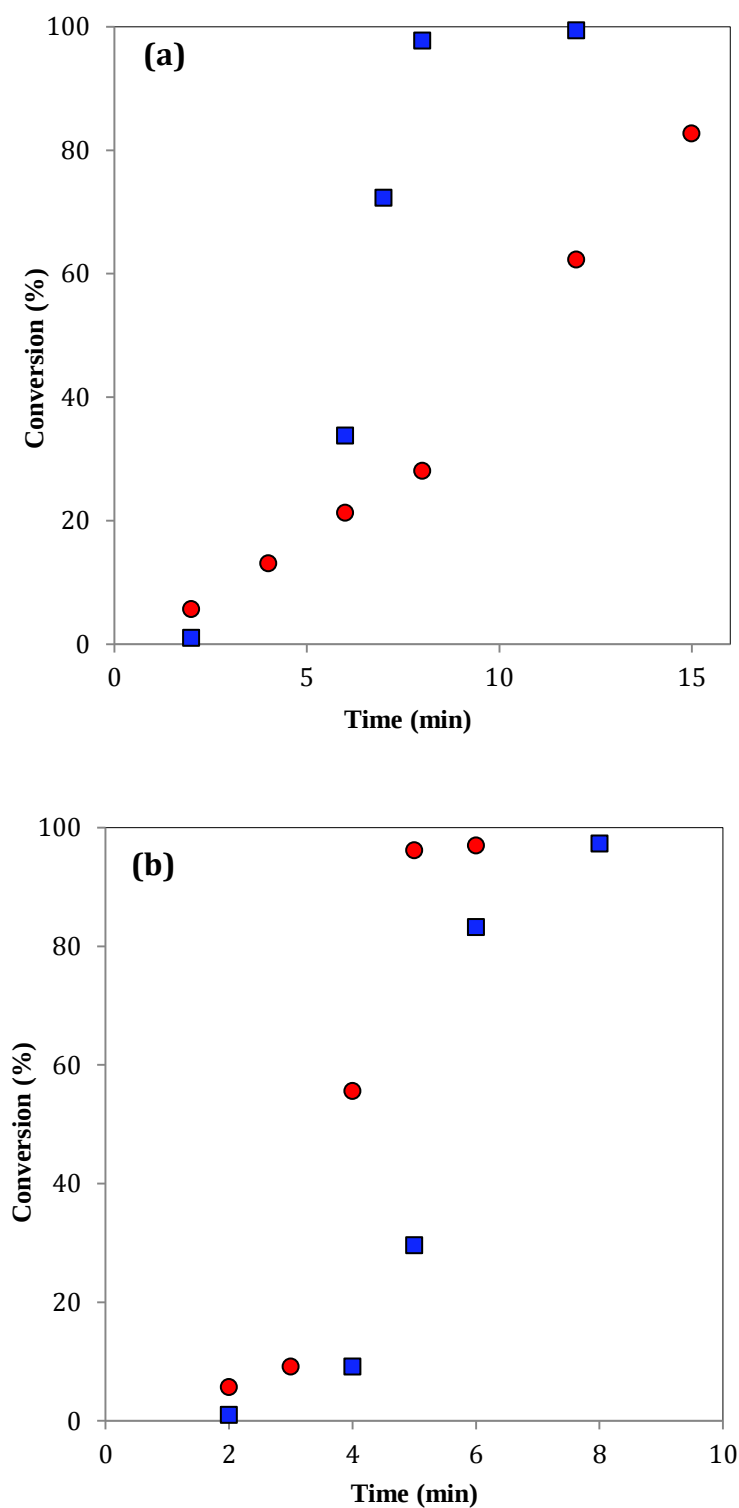


Figure 4.19 Comparison of the kinetics of the ROP initiated with (a) solid TMP and (b) liquid TMPE using conventional heating (■) and microwave heating (●) (150 °C, DP 90) with a higher catalyst concentration ([CL]:[Sn(Oct)₂] = [1]:[2.87×10⁻³]).

Results show that when the concentration of $\text{Sn}(\text{Oct})_2$ was increased, the overall reaction time in all cases was reduced as predicted. When solid TMP was used, the conventionally heated reaction showed a greater reduction in overall reaction time compared to the microwave-heated reaction. A 95 % conversion was achieved in 8 minutes when conventional heating was used while it took 18 minutes in the microwave to achieve the same conversion. This was attributed to the poor selective heating of the TMP, which is a solid with low miscibility hence reducing the overall availability of the TMP to interact with the tin species present. The convection heating methods have induced greater levels of heating of the polymeric structures to overcome solvation issues of TMP and aiding the increased tin concentration to overcome the partitioning in the system. However, perhaps more surprisingly the propagation rate that followed on post-induction was also observed to be exhibiting a slower rate and may also reflect lower efficiency of the induction process due to lower levels of selective heating. In addition to that, the selective heating of TMP might have been reduced due to the microwave penetration depth being affected at high $\text{Sn}(\text{Oct})_2$ concentration levels. However when liquid TMPE was used, the overall reaction time was reduced for both conventional and microwave processes for this liquid initiator and once again the overall reaction time for the microwave-heated polymerisation was lower than that of the reaction that was conventionally heated. Additionally the propagation rate was now higher with microwave heating. Thus using higher tin concentrations with liquid TMPE as the initiator, a similar trend was observed where the overall reaction time was significantly reduced, i.e. 50 minutes to 5 minutes in the microwave and 40 minutes to 8 minutes using conventional heating. However in this case, the microwave-

heated reaction did not demonstrate a significant difference in overall reaction time when compared to the conventional equivalent and no aligned plots were observed. It can therefore be concluded that the increase in selectively heated species had overcome any hindrance in the polymerisation caused by different molecular structures present in the reaction mixture. This conclusion supports the proposal that any hindrance reported in the polymerisation with lower $\text{Sn}(\text{Oct})_2$ levels are due to miscibility problems which was then solved by the increase in selectively heated species. Further work will need to be carried out to determine the structures produced using conventional and microwave heating with different multifunctional initiators at these high level of $\text{Sn}(\text{Oct})_2$ concentrations.

4.6 Comparison of the Star PCL Structures Synthesised using Conventional and Microwave Heating

In this last section of the chapter, an essential comparison between the polymer structures produced using conventional and microwave heating will be presented. ^1H NMR, GPC and MALDI-TOF MS will be means of comparing the molecular structures of the PCL products. Reactions conducted with solid TMP initiator, ethoxylated initiators and increased $\text{Sn}(\text{Oct})_2$ concentration were carried out with the key purpose of investigating the differences in kinetics of polymerisation including the induction and propagation processes, hence structures produced by these different polymerisation methods will not be compared in this section. Therefore, the comparison of molecular structures in this section will be narrowed down to the DP 21 star PCL initiated by glycerol.

^1H NMR spectra for the DP 21 star PCL synthesised using conventional and microwave heating are shown in Figure 4.20. The figure shows that the ^1H NMR spectra are similar for both star PCL produced using conventional heating and microwave heating respectively. Figure 4.20 shows that (a) the NMRs for both conventional and microwave heated polymers are essentially identical indicating very similar structures have been produced and (b) the glycerol initiator was the end group of the polymers synthesised via both heating methods as indicated by the resonances of H_1 of glycerol at $\delta = 5.17\text{ppm}$ and H_2 of glycerol at $\delta = 4.22\text{ppm}$ which is shifted from its monomer resonance position of 3.55ppm to 3.98ppm has also shown to be essentially fully depleted indicating that no unreacted primary hydroxyl on the glycerol is left.

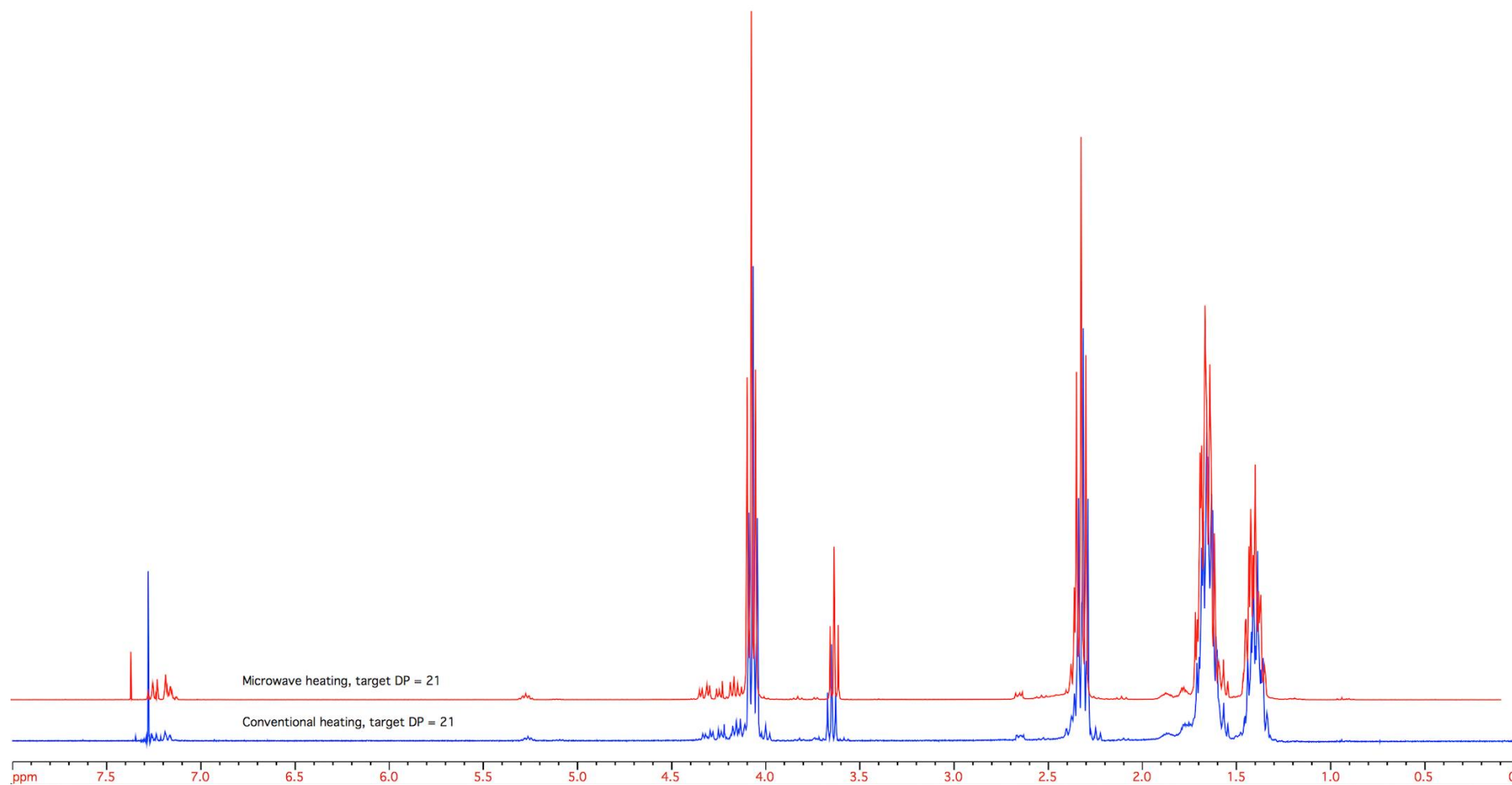


Figure 4.20 ¹H NMR spectra of 3-arm star polymer for the target DP = 21 by using conventional heating (blue) and microwave heating (red) via ROP using Glycerol/Sn(Oct)₂ at 150°C.

The molecular structures of the 3-arm star PCL synthesised via both conventional and microwave heating were also characterised using GPC. Figure 4.21 shows the GPC traces of all the star polymers produced by both heating methods. Overall, the MW distribution is similar for both heating methods at specific target DPs. The $\bar{D}$ values for both heating methods are similar for both heating methods, except for the DP 90 3-arm star PCL produced by conventional heating which has a $\bar{D} = 1.4$ which is slightly higher than all the star polymers.

For target DP = 21 polymers, the M_n values are 6100 and 4000 for conventional and microwave heating respectively, while for target DP = 90 polymers, the M_n values are 13500 and 15300 for conventional and microwave heating respectively. In general, the differences in M_n values for all DP 21 and DP 90 3-arm star PCL synthesised via conventional and microwave heating are ± 2000 and do not show any particular trend. It should be emphasised that the M_n values obtained from GPC analysis are not entirely accurate as this GPC analytical method relies on measuring the hydrodynamic volume of linear polymers. This has contributed to the differences in M_n values of the 3-arm star polymer achieved via this method, while the $\bar{D}$ values do not seem to be affected. Therefore, it can be concluded that both heating methods have produced similar star structures based on the similarity in $\bar{D}$ values and practical DP per polymer arm when molecular structure were compared.

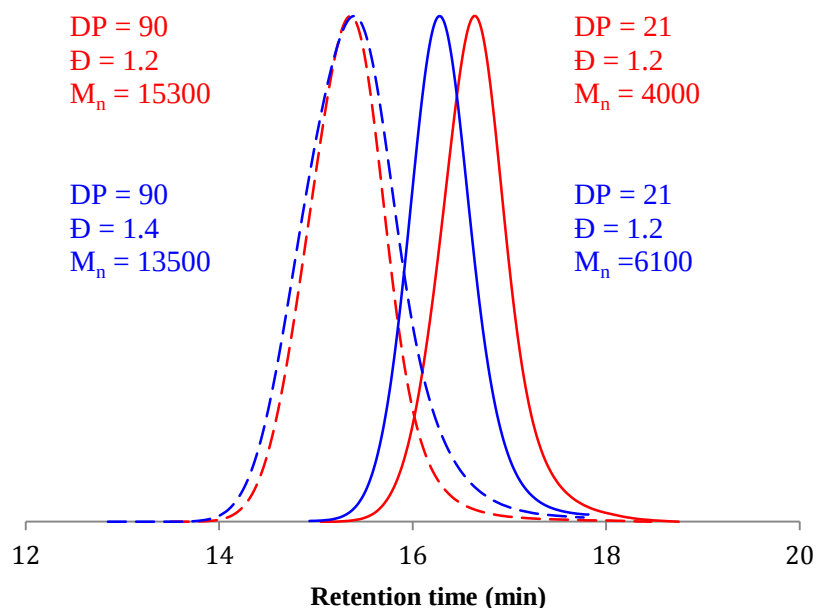


Figure 4.21 GPC-DRI traces of 3-arm star PCL. The traces were compared via using conventional (blue) and microwave (red) heating. GPC-DRI was employed and the calibration was carried out using PS standard. The M_n values were corrected via the Mark-Houwink-Sakurada relationship using $K = 1.09 \times 10^{-3} \text{ dLg}^{-1}$ and $\alpha = 0.6021$.

Figure 4.21 shows that the synthesis of 3-arm star PCL using both microwave and conventional heating has produced polymer products of similar dispersities that are close to $\bar{D} = 1$.

Finally, MALDI-TOF MS was conducted for the 3-arm star PCL produced using both conventional and microwave heating with the target DP = 21. Both Figures 4.22 and 4.23 show the MALDI-TOF spectra for the polymers produced via conventional and microwave heating respectively. As expected, only one distribution was observed in both spectra and the M_n values observed are similar for both heating methods, concluding that both conventional and microwave heating have produced similar polymers.

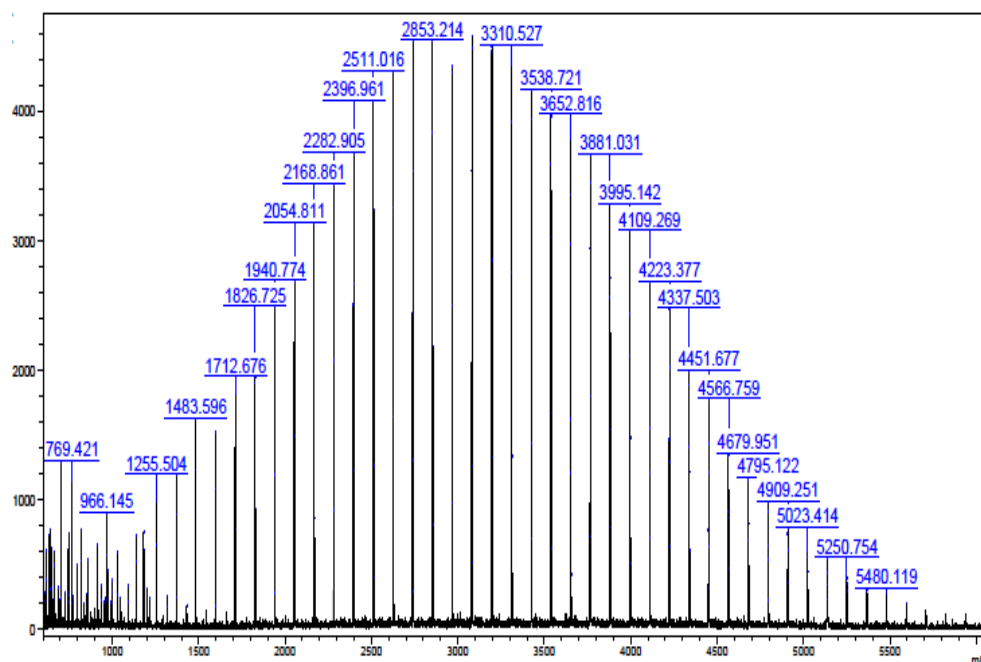


Figure 4.22 MALDI-TOF MS spectra of 3-arm star PCL with the overall target DP = 21 using conventional heating. Dithranol and NaTFA were used as the matrix and ionisation supported salt respectively. The polymer was dissolved in THF and characterisation was carried out using Bruker Ultraflex III spectrometer.

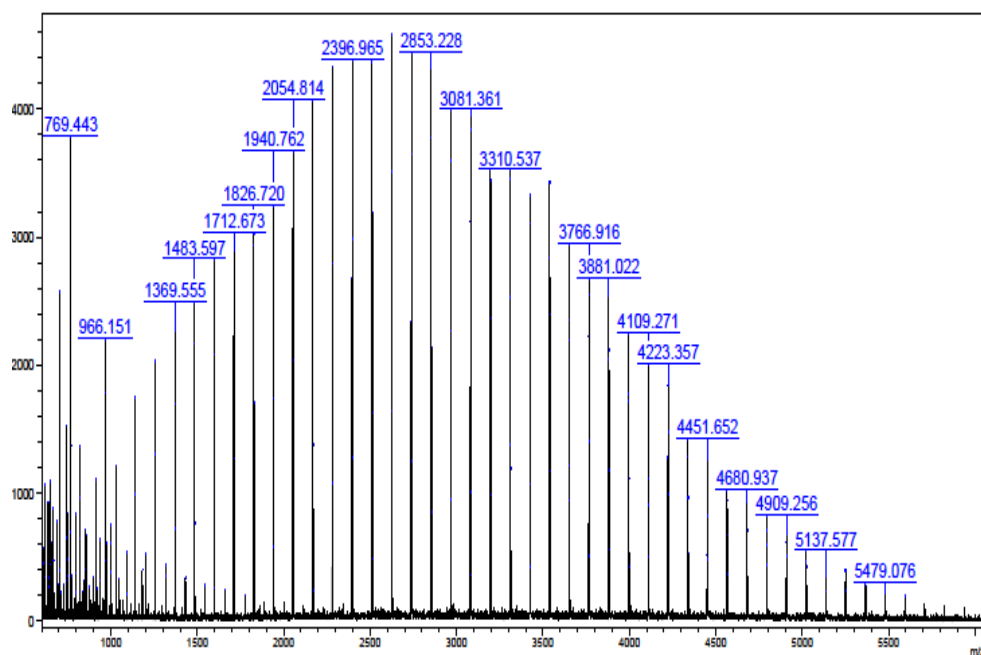


Figure 4.23 MALDI-TOF MS spectra of 3-arm star PCL with the overall target DP = 21 using microwave heating. Dithranol and NaTFA were used as the matrix and ionisation supported salt respectively. The polymer was dissolved in THF and characterisation was carried out using Bruker Ultraflex III spectrometer.

4.7 Conclusions and Future Work

The key aim of the work presented in this chapter was to investigate the synthesis and molecular characterisations of 3-arm star PCL using conventional and microwave heating. ROP of CL was conducted in bulk in the presence of a multifunctional alcohol with $\text{Sn}(\text{Oct})_2$ serving as the initiator/catalyst system. The synthesis of 3-arm star PCL was successfully carried out via both conventional and microwave heating methods and the molecular structures of the polymer products were analysed via several characterisation methods. The multifunctional glycerol initiator was confirmed as the end group of the polymer using ^1H NMR and MALDI-TOF MS. In addition to that, the thermal properties of the polymers were studied and a direct comparison between the star PCL and their linear counterparts was conducted. DSC analysis showed a significant difference in the T_m values of the linear and 3-arm star PCL, which supports the claim that the star polymers possess a structure that consist the proposed number of polymeric arms.

The kinetics of polymerisation using both conventional and microwave heating were followed and results demonstrated that the polymerisation was faster when microwave heating was used when compared to conventional heating. This suggests that the adoption of microwave heating to reduce manufacturing time presents great commercial potential when extended to industrial scales.

Polymerisations conducted using ethoxylated initiators showed that the change in physical form of the initiator from solid to liquid can reduce the induction time and steric hindrance by enabling greater availability for the initiator to take part in the formation of the “true” catalytic species.

The structural characterisation of the star PCL products synthesised using conventional and microwave heating were conducted with ^1H NMR, GPC and MALDI-TOF MS. Polymer products processed via both heating methods were compared and it can be concluded that both conventional and microwave heating processes successfully lead to polymers of similar properties.

Future Work

All reactions in this chapter carried out using microwave heating were conducted in a laboratory scale CEM microwave reactor hence for the purpose of scaling up the processes from a laboratory scale to more significant industrial volumes, the synthesis of these star polymers should be processed in a specially designed single mode microwave reactor as a next step. Material and energy balances need to be calculated prior to the design of this large scale microwave reactor.

Secondly, structural characterisation should to be carried out for the polymers produced using solid and ethoxylated initiators, as well as the polymer product from the high $\text{Sn}(\text{Oct})_2$ concentration reaction to verify that similar polymer properties can be achieved with these various methods. Since it has been proven that it is more difficult to obtain MALDI-TOF and ^1H NMR data from the ethoxylated initiators and the subsequent chain extended PCL stars, dielectric assessment can be used to determine the molecular structural similarities/differences between the 3 and 4 arms materials.

Lastly, lower dispersity values have been observed for higher DP polymers, which suggest that this method of synthesis is suitable for the production of branched polymers with high molecular weights. Therefore,

studies should be expanded targeting higher DPs as materials with larger molecular weights should deliver good mechanical properties while retaining their melting viscosities, hence allowing them to be processed more easily than the linear counterparts.

4.8 References

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CHAPTER 5 COMPARISON OF TUNED AND UNTUNED REACTOR SYSTEMS AS AN APPROACH TO MAXIMISE EFFICIENCY FOR SCALE-UP

5.1 Overview

This chapter will discuss the synthesis of PCL using microwave heating in different microwave reactor systems. This study aims to investigate the differences in polymerisation when conducted using tuned and untuned microwave reactors in order to determine specific microwave parameters that yield ideal polymerisation results for the purpose of scale-up.

The first section of this chapter will include the literature findings on previously reported microwave-heated synthesis using various tuned and untuned microwave reactors including the CEM Discover and Sairem Miniflow 200SS reactors utilised in this study.

This is followed by the comparison of the tuned and untuned microwave systems used in the experimental work conducted in this thesis. The ROP of CL conducted in both CEM and Miniflow will be compared and the energy efficiency will be calculated in this section followed by the characterisation of the PCL synthesised in both tuned and untuned systems.

Lastly, a 2 kW single-mode microwave reactor will be introduced into this study to allow a comparison between the CEM, Miniflow and 2 kW microwave generator. The power density in the systems was studied for the synthesis of PCL which represents the first step toward scale-up of this chemistry using microwave heating.

5.2 Literature Review

In recent years, microwave heating has become a popular alternative to conventional heating in many sections of industry due to its potential to deliver timesaving and more sustainable manufacturing processes based on reduced energy usage. At the laboratory scale microwave reactors such as the CEM and Miniflow have been widely used to conduct small-scale research in the areas of engineering, materials science, organic chemistry, etc. Furthermore, as interest in the use of microwave heating has increased, so have the level of research devoted toward comparing the performance of differing microwave reactor designs. For example, Wang and Lee¹ conducted a series of experiments for the synthesis of SnO₂-graphite nanocomposites, which is utilised as the material for anodes in Li-ion batteries. Reactions conducted using microwave heating in a CEM were compared to those conducted in a household microwave oven and conventional heating. The SnO₂-graphite nanocomposites were prepared *via* urea-mediated homogenous hydrolysis of SnCl₄, which was heated using microwave heating in a single-mode CEM microwave reactor at medium power and a multimode household microwave oven for 1 minute. The reactions were also conducted using conventional heating in a water bath at 85 °C for 3 hours. Synthetic graphite was also introduced in the preparation stage to allow for the formation of SnO₂-graphite composites. The nanoparticle products were then extensively analysed and characterised using XRD, ICP, FE-SEM, SEM and TEM/SAED. The SnO₂ particles prepared in the CEM had the smallest size and narrowest size distribution of 1-3 nm. The particles prepared in the multimode household microwave oven and oil bath had a size distribution of 2-5 nm and 3-9 nm respectively. Thus the authors concluded that microwave heating in the CEM

provided better control over both particle size and distribution, resulting in substantially better composites than those prepared using conventional heating.¹

In another study involving SnO₂ conducted by Cavaliere et al., a Miniflow 200SS was utilised in the preparation of Pt nanoparticles. A solution consisting of hexachloroplatinic acid and ethylene glycol was brought to pH11 using NaOH and was heated for 6 min under reflux conditions (130 °C) whilst blanketed with a N₂ atmosphere in the microwave. The resulting Pt nanoparticles were purified and characterised *via* TEM.² Whilst in another related study, Savych and coworkers³ utilised microwave heating in the synthesis of nanocatalyst particles using a Miniflow 200SS. The synthesis procedures used were similar to the practical work conducted by Cavaliere et al.² with the reaction solution being heated at 120 °C for 6 min and the resulting nanoparticles being analysed *via* FE-SEM. The conclusion from both of these studies was that the use of microwave heating has significantly reduced the synthesis time required for the preparation of these materials.

Outside of the laboratory, high power microwave heating has been used to replace conventional manufacturing and assembling processes such as welding, soldering and brazing. Microwave heating overcomes limitations inherent in conventional heating in processes like these, such as long processing times, high energy requirements, high setup costs and significant levels of defects in product.⁴ Siores and Do Rego⁵ reported successfully work on joining thin sheets of steel with thickness of 0.1-0.3 mm using microwave heating in a 2 kW multimode microwave generator. Meanwhile, Srinath et al.⁶ successfully created a novel approach of using microwave heating for the metallurgical bonding of highly conductive copper metal. The process was conducted at atmospheric condition using high power (900 W) microwave heating in a 1 kW multimode generator

operating at 2.45 GHz. Charcoal was used to facilitate the microwave hybrid heating (MHH), see Figure 5.1.

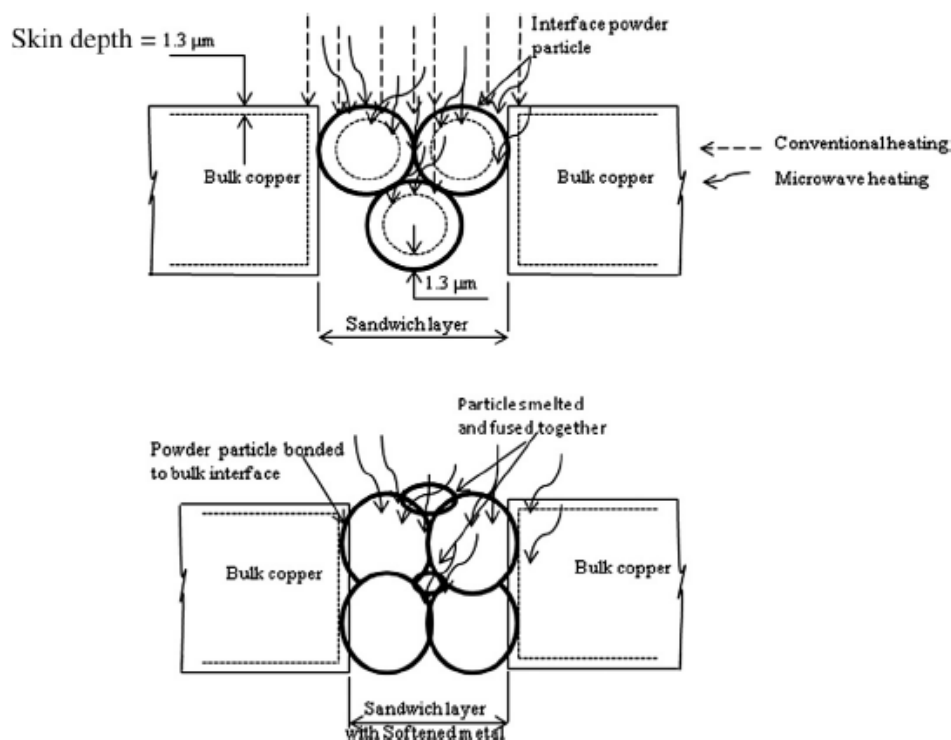


Figure 5.1 Schematic diagrams showing the interactions of microwaves with bulk and powder particles; and the fusion of molten particles with bulk pieces at the interface as depicted by Srinath et al.⁶

Copper coins and plates were successfully bonded using microwave heating within 900 s of heating time. A copper layer with thickness of 0.5 mm was introduced in between the two surfaces forming a sandwich layer. Metallurgical bonding of the bulk occurred when the powder particles were completely melted after being exposed to microwave heating. The resulting material was subjected to characterisation *via* elemental and phase analysis, measurement of microhardness, tensile strength testing and porosity sizing. X-ray diffraction (XRD) analysis indicated that the copper powder particles were partially transformed into copper oxides, which enhanced the coupling of microwaves with

the powder, resulting in faster heating and better bonding with the bulk. A dense uniform microstructure with good metallurgical bonds was achieved. The hardness of the joint area was 78 ± 7 Hv and the porosity in the joint was 1.92 %, while the ultimate tensile strength of the copper joint was observed to be 164.4 MPa.⁶

5.3 Aims and Objectives:

The aim of the work conducted in this chapter is to compare a tuned microwave reactor (Miniflow) with an untuned microwave reactor (CEM) that was previously used in the experimental work discussed in Chapter 3 and Chapter 4. The objective is to study the effect of tuning on the ROP of CL by comparing the induction periods and propagation rates of each polymerisation in a tuned Miniflow and an untuned CEM.

A literature review has shown that high power microwave heating has successfully delivered energy and timesaving processes. The synthesis of PCL was conducted in batch throughout this project. Hence time and power optimisation in ROP using a 2 kW microwave generator was discussed in this chapter for the preparation of scale-up, shifting this microwave heating system from batch to continuous flow, which will be favourable in industrial polymer processing.

5.4 Comparative study of the ROP of CL using Microwave Heating in Different Microwave Reactors

5.4.1 Comparison of Tuned and Untuned Microwave Systems featuring CEM and Miniflow

As reported in the previous chapters of this study, the main microwave reactor used in the synthesis of linear and star PCL was the CEM Discovery. However, a Miniflow 200SS microwave reactor was introduced into this study to investigate and compare the polymerisations conducted in both microwave systems. The specific features of both reactors are detailed in Chapter 2, Sections 2.1 (CEM) and 2.2 (Miniflow). The advantages and disadvantages of the features in both reactors are as described in Table 5.1 as follows:

Table 5.1 Comparisons between CEM and Miniflow Reactors

Microwave	CEM	Miniflow
User-friendliness	User-friendly. No manual tuning required.	Less user-friendly compared to CEM but still relatively simple to operate.
Cavity	Enclosed cavity, no physical observations can be done throughout reaction.	Cavity has a "view-hole", physical observations can be done throughout the reaction.
Heat-loss	Enclosed cavity, minimum heat loss to the surroundings. Possibly easier to keep material at temperature with less power.	U-shape waveguide, heat loss from the reaction to the surroundings.
Temperature Control	IR and Fibre-Optic	Fibre-Optic only
Details on Absorbed/Reflected Power	No details provided	Details provided. Microwave effects on material can be studied.
Maximum Power Output	300W	200W
Stirring Features	Built-in magnetic stirrer	No. But a magnetic stir-plate can be placed under cavity.

A key conclusion from Table 5.1 is that the CEM features an untuned system. Hence even though the CEM is user-friendly, it does not provide details on reflected microwave power as offered by the Miniflow. The Miniflow features a tuning system that allows reflected power to be tuned in order for the absorbed power to match the forward power. Reflected power data can be utilised to determine the energy efficiency of the system by calculating the actual amount of power absorbed by the material rather than comparing reaction results simply based on the amount of power input into the system.

Furthermore, as the level of reflected power is displayed by the Miniflow in real time, this data can be used to manually tune the microwave input both prior to and throughout the reactions, to ensure that the reflected power is as close to 0 W as possible. The maximum power output of the CEM is 300 W, which is 100 W more than the maximum power output of the Miniflow. Therefore both the CEM and Miniflow were set manually to generate a maximum forward power of 150 W to ensure that the results from both systems could be compared. In addition, reaction temperature readings were made using a fibre-optic (OF) probe directly inserted into the bulk of the reaction medium. This has been shown to provide a more accurate representation of the temperature of the reaction materials compared to the data provided by the internal IR sensor within the CEM which measures the temperature of the reaction flask wall. Hence the OF temperature readings from both reactors will be focused on in the following sections instead of the IR readings.

5.4.2 Comparison of ROP of CL in Tuned and Untuned Microwave Systems

5.4.2.1 ROP of CL using Microwave Heating in a CEM and Miniflow

The ROP of CL was conducted in bulk using CL monomer and BnOH / Sn(Oct)₂ as the initiator / pre-catalyst system. As described in the previous chapters of this thesis, the target degree of polymerisation (DP) was obtained by adjusting the molar ratio of [CL]:[BnOH] as [87]:[1] for DP = 87. Relative molar ratio of [CL]:[Sn(Oct)₂] was kept constant at [1]:[1.40 x 10⁻⁴]. The reaction scheme is as shown in Figure 5.2.

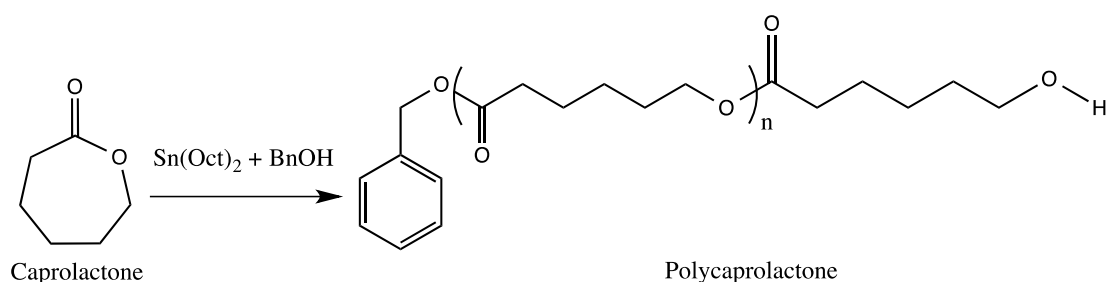


Figure 5.2 ROP of CL using BnOH/Sn(Oct)₂ as the initiator/catalyst system

The polymerisations in this investigation were conducted at a range of different temperatures from 160°C to 180°C utilising microwave heating which was achieved using both CEM and Miniflow to investigate any differences in polymerisation trends (i.e. rate of polymerisation, polymer quality etc) that was related to the reactor type and the ability to tune the power input to give minimal reflected power. ¹H NMR was used to follow the rate of monomer consumption and these results are shown in Figure 5.3.

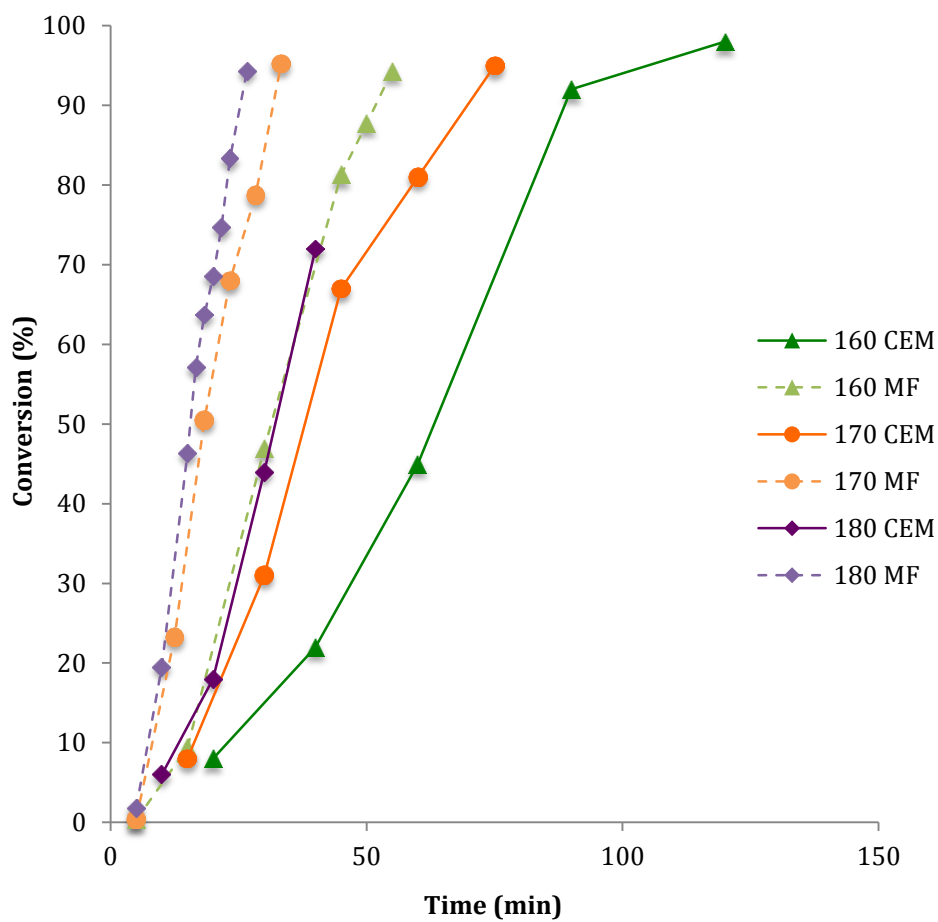


Figure 5.3 Conversion against time for ROP of CL with BnOH and Sn(Oct)₂ at 160°C - 180°C using microwave heating in the CEM and Miniflow (MF) microwave reactors

A similar and expected trend was observed in polymerisation time for the reactions in the Miniflow as had been observed previously in the CEM generated results by the group, i.e. the overall reaction time was shorter with increase in reaction temperature.¹¹ However, Figure 5.3 shows that even when microwave heating was used in all reactions, there was a significant difference in the rate of polymerisation for the reactions conducted in the CEM and Miniflow reactor formats. In all cases the tuned Miniflow experiments exhibited shorter reaction times. In the CEM at 160°C, the reaction required 2 hours to achieve 98% conversion but only 55 minutes were required to achieve 95% conversion in the Miniflow at the same temperature. Likewise at 170°C, it took 75 minutes to

achieve 95% conversion in the CEM, but this time was 33 minutes in the Miniflow to achieve the same conversion. Finally at 180°C, the reaction took 27 minutes to achieve 95% conversion in the Miniflow.

As the overall power had been reduced from 300 W to 150 W to allow for comparison between the results obtained from the different reactor formats, the studies were extended to look at the effect of varying input power on the polymerisations.

5.4.2.2 Investigation of Varying Temperature and Power within a Tuned and Untuned Microwave System

In a typical microwave-heated polymerisation conducted at 160°C and using 150 W of input power, the CEM microwave reactor parameters were set as follows (Table 5.2):

Table 5.2 CEM reactor settings for ROP of CL

Stage	1	2	3	4	5
Power (W)	150	150	100	100	100
Ramp Time (min)	10	0	0	0	0
Hold Time (min)	60	60	60	60	60
Temperature (°C)	160	160	160	160	160

Microwave energy was introduced continuously into the system while a maximum power of 150 W was applied to the reaction vessel. The initial ramp time to raise the temperature of the reaction materials within the vessel from room temperature to the target reaction temperature (e.g. 160 °C) was set for 10 minutes. In practice however, the temperature control algorithm of the microwave system increased the forward power from 0 to 80 W, which caused the temperature of the reaction mixture to reach 160 °C in less than 2 minutes.

Once the target temperature was achieved, the hold time automatically started and the system was observed to display a drop in forward power. Even though the forward power was set at 100 W during the hold time period, the forward power was automatically regulated at ~25 W throughout this period to maintain the reaction temperature at 160 °C.

The parameters set in the Miniflow for a typical polymerisation at 160°C is as described in Table 5.3.

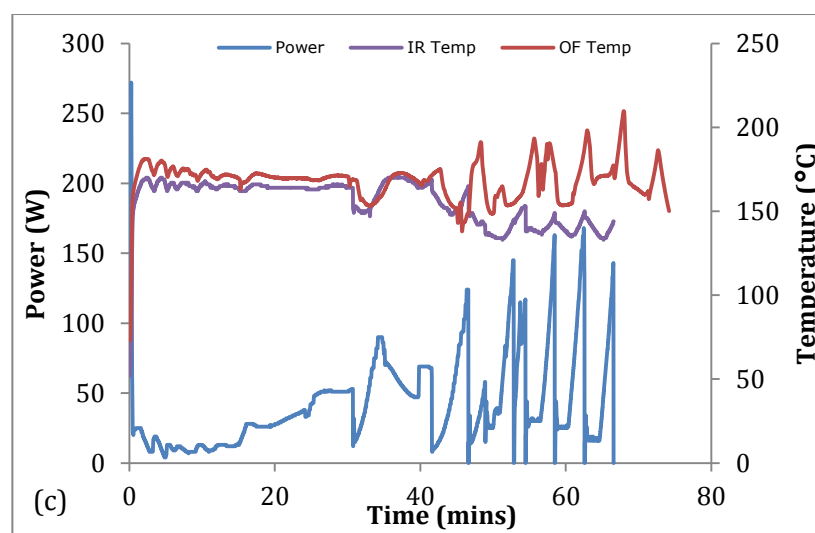
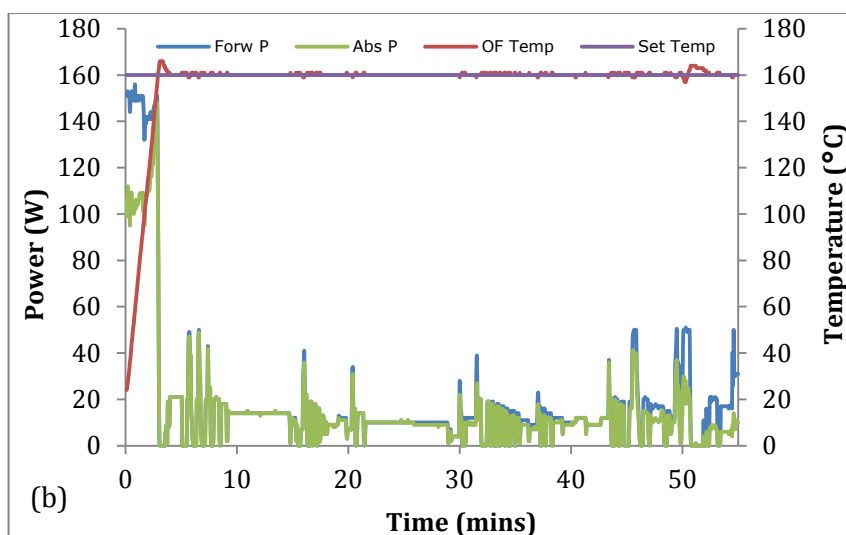
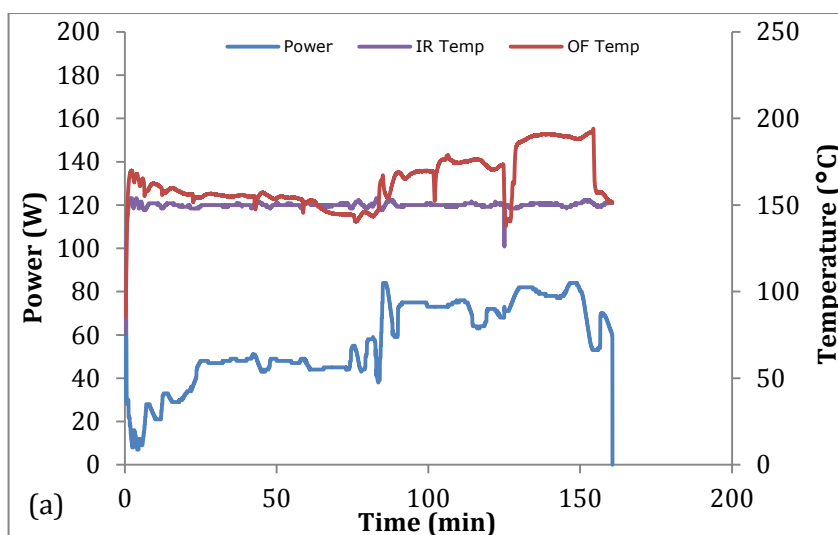
Table 5.3 Miniflow microwave reactor settings for ROP of CL

Stage	1	2
Power (W)	150	100
Ramp Time (min)	10	0
Hold Time (min)	60	60
Temperature (°C)	160	160

Once again, microwave energy was introduced continuously into the system throughout the experiment. The same ramp time of 10 minutes was set for the Miniflow to raise the temperature of the reaction material to the target reaction temperature (i.e. 160 °C). In practice however, the temperature control algorithm of the Miniflow system increased the forward power from 0 to 150 W, which caused the temperature of the reaction mixture to reach target reaction temperature in less than 2 minutes. Once the target temperature was achieved, the hold time automatically started and the system was observed to display a drop in forward power. Even though the forward power was set at 100 W during the hold time period, the forward power was automatically regulated at ~25 W throughout this period to maintain the reaction temperature. The temperature readings were recorded throughout the reactions using an OF temperature probe. Additional data that was gained from the built-in controller of the Miniflow which

recorded the forward and reflected power readings throughout the reaction.

Figure 5.4 below shows the temperature / power profiles of the ROP conducted in the CEM and Miniflow at 160 °C – 180 °C so direct comparisons between the reactors could be made.



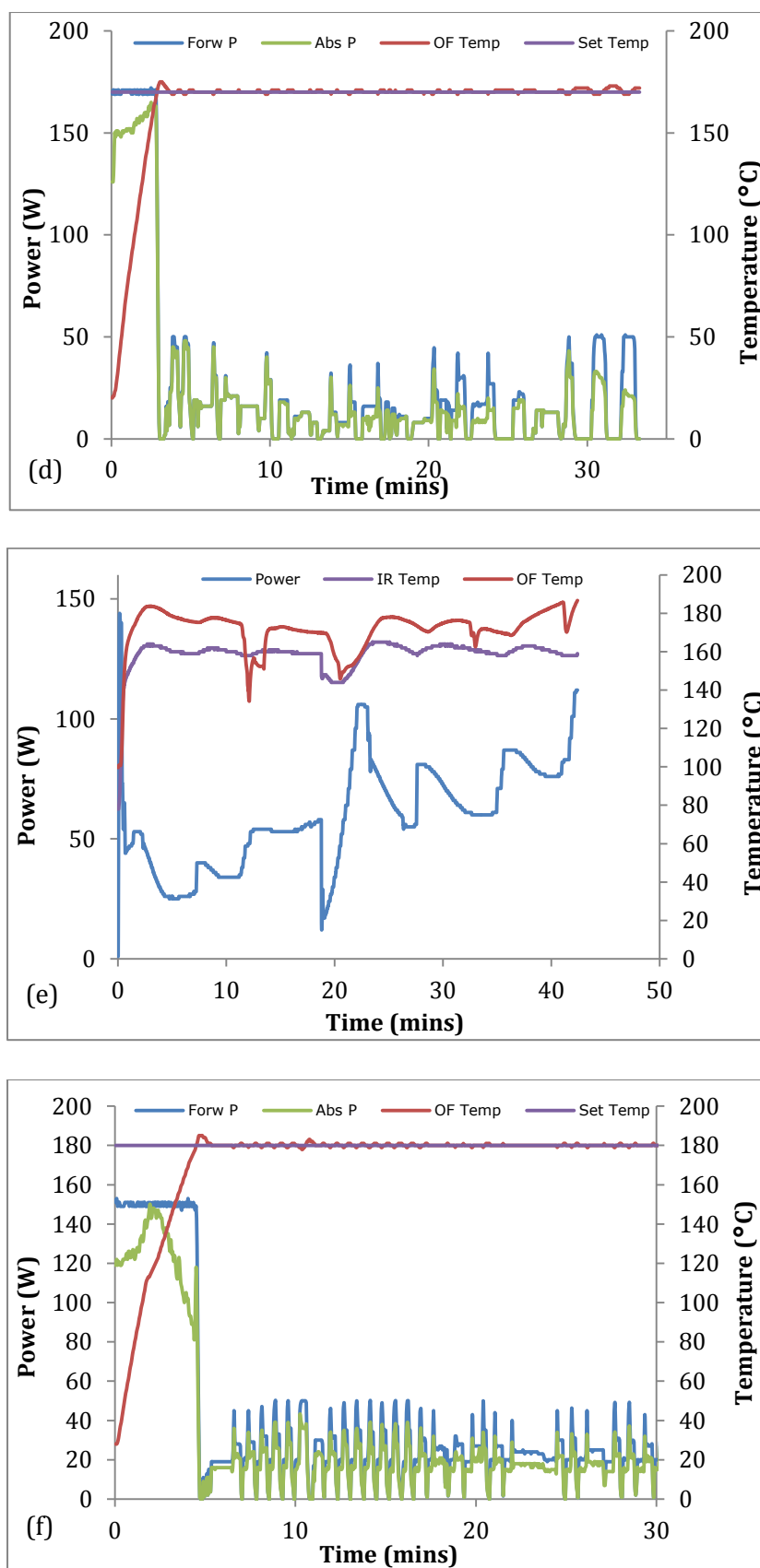


Figure 5.4 Temperature / power profiles for ROP conducted in the CEM (a) and Miniflow (b) at 160 °C; CEM (c) and Miniflow (d) at 170 °C; CEM (e) and Miniflow (f) at 180 °C.

As mentioned previously, the CEM reactor does not record the absorbed power level. However, the Miniflow utilises manual tuning to regulate the reflected power so that the reflected power is as close to zero as possible. When reflected power is minimised, most of the forward power by the Miniflow is absorbed by the reaction material, therefore increasing the energy and heating efficiency of the system.

The fact that the rate of polymerisation for the reactions were slower in the CEM even though the reaction temperature in both systems were approximately the same suggests that not all the power forwarded in the CEM was absorbed by the reaction material. This is reflected in the much more variable temperature profile throughout the reaction when in the untuned system. Thus the data from these experiments clearly demonstrated that tuning the system is essentially achieving good levels of control over the experimental conditions and so achieving repeatable and consistent reactions. This improved control is attributed to the fact that in the Miniflow, the reflected power was regulated throughout the reaction *via* manual tuning which ensured that close to all the forward power was absorbed by the reaction material.

However, it was also observed that towards the end of polymerisation (i.e. when conversion > 80%), the reflected power level started to increase and manual tuning was unable to minimise the reflected power at this stage. It was proposed that this is due to the fact that the reaction vessel is made up of more than 80% of PCL polymer, which does not absorb microwave energy as well as the CL monomer counterpart. Therefore, this polymer loading leads to difficulties in coupling the input energy into the sample to keep it at the desired set point temperature. Consequently the system will try to add more power in an attempt

to maintain the reaction temperature. Again, this rise in power in the untuned CEW led to an undesirable increase in sample temperature at the end of the reaction, such that it is significantly above the set point. This additional thermal energy may accelerate unwanted transesterification reactions (see Chapter 3.4.5) which will result in broadening of the Đ and reducing the quality of the polymer product. Meanwhile, whilst it was proven difficult to control reflected power in the tuned system, it was observed that there was little or no temperature increase observed in the high conversion polymer stage so the thermal pathway that the materials undergo is far more stable and predictable.

Thus it was also concluded that in larger scale production, where monitoring of viscous polymer solutions is more difficult than the increase in reflected power observed from the power measurement readings is also a sign that represents that the polymerisation is close to completion. Similar predictions of reaction completion have also been achieved by using dielectric property measurements within the microwave research group at Nottingham.^{14, 15, 16}

Thus it was concluded that a tuned microwave reactor (Miniflow) provides a more predictable, efficient and repeatable energy / heating to a ROP reaction than an untuned system (CEM). This was attributed to the additional manual tuning feature ensuring that almost all the power forwarded into the system has been absorbed by the reaction material within the vessel, resulting in the reduction / elimination of induction period and enhanced rate of polymerisation. It was proposed that the selective heating of the tin active species that is responsible for the presence of induction period was affected by the power absorbed by the component which lead to an increase in temperature of the tin

centre, supporting the hypothesis that microwave selective heating is a thermal effect as suggested in Chapter 3, Section 3.5.7.1.

5.4.2.3 Structural Characterisation of PCL Produced in a Tuned and Untuned Microwave System

It was shown that linear PCL was successfully synthesised in both tuned CEM and tuned Miniflow microwave reactors using BnOH as an initiator and Sn(Oct)₂ as the catalyst. The molecular structures of these linear PCL were then analysed to observe any differences in polymer quality (i.e. M_n and $\bar{D}$), when a tuned microwave system was used compared to an untuned microwave system. The polymer product was analysed using Gel Permeation Chromatography (GPC) analysis, results from both CEM and Miniflow microwave reactors were summarised in Table 5.4 as follows:

Table 5.4 GPC results showing conversion corrected M_n ($M_{n(\text{Theo})}$), experimental M_n ($M_{n(\text{GPC})}$) and $\bar{D}$ of PCL from the ROP of CL using tuned (Miniflow) and untuned (CEM) microwave reactors at 160 °C, 170 °C and 180 °C

System	Temperature (°C)	Time (min)	Conversion (%)	$M_{n(\text{Theo})}$	$M_{n(\text{GPC})}$	$\bar{D}$
CEM	160	120	98	9732	7990	1.6
Miniflow	160	55	95	9368	8643	1.4
CEM	170	75	95	9434	9800	1.9
Miniflow	170	33	95	9458	9512	1.1
CEM	180	40	72	7150	7550	1.2
Miniflow	180	27	95	9368	8788	1.4

The GPC results summarised in Table 5.4 show that the M_n values obtained from the tuned Miniflow system were closer to the target / conversion corrected theoretical M_n values compared to those obtained from the untuned CEM system, with exception of the reactions conducted at 180 °C as the tuned reaction achieved a further 23% conversion compared to the untuned counterpart. In

addition, the $\bar{D}$ values obtained in the tuned system were generally better (closer to 1) than those obtained in the untuned system. This suggests that ROP conducted in a tuned system produced polymers of better quality with desirable molecular weights and polydispersities.

5.4.3 Energy Efficiency within a Tuned and Untuned Microwave System

Once the amount of power absorbed can be determined, then the heating efficiency of the system can be calculated. Therefore, only the heating efficiency of the polymerisation reactions conducted in the Miniflow could be investigated as it features a tuning system, while the CEM does not. The energy absorbed by the material can be derived from the reflected power data obtained from the Miniflow and calculated using a spreadsheet by computing the power data collected from the reactor, and summing up the total amount of power absorbed (area under graph) that was recorded every second during polymerisation *via* the Trapezium Rule. The absorbed energy values can therefore be compared with the theoretical energy values as shown in Table 5.5 below:

Table 5.5 Forward, absorbed and theoretical energy for the ROP of CL in CEM and Miniflow at 160°C for the synthesis of DP21 and DP90 PCL

Run	Equipment	Forward Energy (J)	Absorbed Energy (J)	Theoretical Energy (J)
DP21	CEM	31700	-	10861
DP21	MiniFlow	17995	17457	11378
DP90	CEM	35237	-	10947
DP90	MiniFlow	17597	15045	10775

Table 5.4 shows that for the synthesis of DP21 PCL in the Miniflow, 97 % of the forward energy was absorbed. For DP90 PCL, 86 % of the forward energy was absorbed.

The theoretical energy for each system was calculated using the following formula:

$$Q = mC_p\Delta T \quad (\text{Equation 5.1})$$

Where,

Q:	Energy (J)
m:	Mass of Material (g)
C _p :	Specific Heat Capacity of CL (1.72 J/ g K)
ΔT:	Target temperature – Starting Temperature (°C)

In general, the experimental absorbed energy values were calculated to be higher than the theoretical values, which indicate that the system obeys the laws of thermodynamics. The energy absorbed by the material in the CEM cannot be determined and comparisons with theoretical values cannot be made unless it is assumed that 100 % of the power is absorbed by the material which is not accurate. However, it is clear that the inability to tune the system has a drastic effect on the efficiency of the system. Consequently, it was concluded that for a scale up process of a ROP reaction to be successful on both an economic, batch to batch repeatability and product quality basis (see data on product quality in Table 5.4), that such a large scale system will need to be tunable.

5.5 2 kW Single-Mode Microwave Reactor

The final section of this study aimed to determine microwave parameters that produce ideal polymerisation results for the purpose of scale-up by investigating the power density profiles of the reaction systems. To do this, a 2 kW single-mode microwave reactor was used to increase the microwave power level in the synthesis of PCL *via* the ROP of CL. This polymerisation procedure was identical to those of the reactions conducted in Section 5.4.2.1 to synthesise PCL with a target DP = 90 but the BnOH initiator was replaced with glycerol to produce 3-arm star PCL in order to reduce the material viscosity within the system. ^1H NMR was used to follow the rate of monomer consumption.

In a typical microwave-heated polymerisation, the 2 kW microwave generator parameters were set as follows (Table 5.6):

Table 5.6 2 kW single-mode microwave generator settings for ROP of CL

Power (W)	450			900		
Time (s)	60			30		
Run	1	2	3	1	2	3

Similar to the Miniflow, the 2 kW microwave generator provides information on the reflected power, which allows the calculation of the amount of energy absorbed and heating efficiency. In this study however, reactions were conducted at a fixed forward power of 450 W and 900 W for 60 s and 30 s respectively. Three runs were conducted at each power level to ensure results are reproducible. The power levels were specifically selected to raise the temperature of the reaction to 180 °C within 30 s based on the C_p of CL = 1.72 J / g K to ensure the formation of polymers at the end of the reaction.

A forward power of 450 W was selected and utilised to heat 50 g of material for 60 s in bulk. The reaction was then repeated at 900 W for 30 s in order for the same amount of energy to be forwarded into the system and results from each polymerisation run were summarised and compared.

5.5.1 Study for the ROP of CL in a 2 kW Microwave Reactor

The polymerisation results generated from the 2 kW single-mode microwave reactor were summarised in Table 5.7 below. The experimental values for energy absorbed were also calculated using a spreadsheet by summing up the total amount of power absorbed by the system based on the power data collected from the reactor every second during polymerisation and summarised in the table of results as follows:

Table 5.7 Summary of results for the ROP of CL using glycerol at 450 W and 900 W in a 2 kW single-mode microwave reactor

Power (W)	450			900		
Time (s)	60			30		
Trial	1	2	3	1	2	3
Temperature (°C)	186	184	187	159	169	160
Conversion (%)	4	8	8	5	15	8
T_{plateau} (°C)	220	227	226	213	232	223
t_{plateau} (mins)	02:34	02:27	02:30	02:14	01:39	02:05
Conversion (%)	93	93	96	83	82	93
Energy Absorbed (J)	25449	25374	25449	23819	25012	24617
Average Energy (J)	25424			24482		
M_n	3690	3311	2814	3569	4547	3552
Đ	1.7	1.7	2.0	1.7	1.6	1.9
Physical state	White Solid			White Solid		

The summary of results in Table 5.7 shows that PCL was successfully synthesised when 450 W and 900 W was used to heat the system for 60 s and 30 s respectively. For the reaction conducted at 450 W, an average of 25424 J of energy was absorbed and the average energy absorbed by the reaction conducted at 950 W was 24482 J. The resultant PCL synthesised from all 6 runs conducted at 450 W and 950 W show similar M_n and $\bar{D}$ values even though the forward power used in the latter reactions was double the initial amount of forward power used. It can be concluded that the ROP of CL in the 2 kW microwave generator is driven by energy density. This is favoured in the approach to scaling-up these reactions as the same amount of energy can be absorbed by the system in a shorter amount of time to produce polymer product of the same quality.

As an approach to scale-up, the ROP of CL must be conducted in a continuous flow manner. In continuous flow reactions, the exposure time of the flowing material to microwave heating will only be a couple of seconds. Therefore, carrying out power density study provides accurate calculation of how much power and heating time is required in order for the system to absorb sufficient energy resulting in the successful formation of polymer. Another parameter that needs to be taken into account includes penetration depth, which is affected by the diameter of the pipe used in the construction of the microwave flow reactor.

Table 5.8 Comparison between CEM, Miniflow and 2kW microwave reactor

Microwave	CEM	Miniflow	2kW Single-mode
User-friendliness	User-friendly. No manual tuning required.	Less user-friendly compared to CEM but still relatively simple to operate.	Less user-friendly than CEM, more user-friendly than Miniflow as tuning can be controlled automatically using software.
Cavity	Enclosed cavity, no physical observations can be done throughout reaction.	Cavity has a "view-hole", physical observations can be done throughout the reaction.	Cavity has a "view-hole", physical observations can be done throughout the reaction.
Heat-loss	Enclosed cavity, minimum heat loss to the surroundings. Possibly easier to keep material at temperature with less power.	U-shape waveguide, heat loss from the reaction to the surroundings.	Not enclosed, but less heat-loss than Miniflow
Temperature Control	IR and Fibre-Optic	Fibre-Optic only	Fibre-Optic only
Details on Absorbed/Reflected Power	No details provided	Details provided. Microwave effects on material can be studied.	Details provided. Microwave effects on material can be studied.
Maximum Power Output	300W	200W	2000W
Stirring Features	Built-in magnetic stirrer	No. But a magnetic stir-plate can be placed under cavity.	No. But a magnetic stir-plate can be placed under cavity.

5.6 Conclusions and Further Work

A direct comparison was carried out for the microwave features between the untuned CEM and tuned Miniflow reactor where the difference between both reactors is the tuner that allowed the reflected power to be regulated so that the reaction material will absorb all the power forwarded by the microwave generator. Even though the CEM is a user-friendly reactor, it does not provide sufficient information for the calculation of energy absorbed by the heated material. The amount of energy absorbed can be used to determine the heating efficiency of the system.

Miniflow generated results showed enhanced rates of polymerisation compared to the reactions conducted using the CEM even though the reaction temperature was observed to be the same. The lower rates of polymerisation in the CEM indicate that the heated material did not absorb all the power forwarded into the system. Furthermore, the more uniform and predictable reaction temperatures and power profiles combined with the ability to largely mitigate the increase in reflected power displayed by the Miniflow towards the end of polymerisation when the reaction is approaching total depletion of monomer demonstrated that the tuned Miniflow was a more batch to batch repeatable process that gave rise to better quality product (reduced Transesterification) and more energy efficient reactor. Furthermore, there is the potential to use to increase in reflected power to monitor the end point of the reaction.

A 2 kW single-mode microwave reactor operating at 2.45 GHz was introduced into this study for the preparation of scale-up. ROP of CL was conducted at fixed high power levels to determine the energy and heating time required for polymer formation. The ROP of CL using microwave heating is driven

by power density as PCL was successfully synthesised within 30 s using 900 W of forward power in the 2 kW microwave generator, which is ideal in a continuous flow process. Other parameters that need to be determined for the construction of a continuous flow microwave rig include penetration depth and pipe diameter.

5.7 References

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CHAPTER 6 OVERALL CONCLUSIONS

The fundamentals of polymers and ring-opening polymerisation (ROP) were discussed in Chapter 1. The kinetics and mechanisms of living ROP using –OH / tin octanoate ($\text{Sn}(\text{Oct})_2$) as the initiator / catalyst system were investigated in reference to previously reported literature. The fundamentals and mechanisms of microwave dielectric heating, which include dielectric properties, theory of dielectric heating and penetration depth were summarised in the latter section of the chapter. All the equipment and analytical techniques utilised in the work conducted in this thesis were reported in Chapter 2.

The key aim of this research is to study the effect of using microwave heating on the controlled ROP of ϵ -caprolactone (CL) using mono and multifunctional –OH initiators and $\text{Sn}(\text{Oct})_2$ catalyst. As a result, linear and star PCL were successfully synthesised by employing microwave heating. In general, polymerisations were compared and contrasted with those conducted using conventional heating.

In Chapter 3, linear PCL was successfully synthesised using benzyl alcohol (BnOH) and $\text{Sn}(\text{Oct})_2$ catalyst. Microwave-heated reactions were conducted using a CEM reactor operating at 2.45 GHz while the conventionally heated reactions were conducted using an oil bath. Polymerisations have shown to exhibit controlled / pseudo-living characteristics. Reactions conducted using microwave heating showed enhanced rates of polymerisation when compared to those conducted using conventional heating. The enhanced rate of polymerisation was caused by the selective heating of the tin active species, as it is a susceptible microwave absorbing material based on the dielectric properties

assessment conducted on the individual components. Microwave heating was found to be purely thermal effect by increasing the temperature of the tin active species, resulting in faster coordination-insertion process and propagation.

Chapter 4 discusses the synthesis of 3-arm and 4-arm PCL using multifunctional –OH initiators and $\text{Sn}(\text{Oct})_2$ catalyst. Polymerisation was conducted using both conventional and microwave heating. Once again, enhancement in the rate of polymerisation was observed when microwave heating was used. The effect of the physical state of the initiator on polymerisation was studied by introducing ethoxylated initiator (liquid counterparts) into this study. Results showed that the change in the physical form of the initiator has reduced steric hindrance leading to the reduction in induction periods by enabling greater availability for the initiator to take part in the formation of the co-initiator / “true” catalytic species. Analytical methods namely ^1H NMR, Matrix Assisted Laser Desorption / Ionisation – Time of Flight Mass Spectroscopy (MALDI-TOF MS), Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC) were used to characterise the resultant PCL, confirming that the star structure consists the proposed number of polymeric arms and showing that both conventional and microwave heating methods produced polymers that exhibit similar structures.

Lastly, Chapter 5 investigates the difference in polymerisation using microwave heating in a tuned and untuned system. The CEM reactor features an untuned system while the Miniflow reactor features a tuned system. Miniflow generated results showed enhanced rates of polymerisation compared to the CEM at the same reaction temperature suggesting that all / most of the power forwarded by the Miniflow was absorbed by the material. Unlike the Miniflow,

the CEM does not provide sufficient information for the calculation of energy absorbed by the heated material. The increase in reflected power displayed by the Miniflow towards the end of polymerisation (conversion > 80%) shows that there is potential to use the reflected power as an indication of the end point of a reaction. GPC analysis demonstrated that the tuned system produced polymers of better quality with desirable M_n and $\bar{D}$ values. ROP was conducted at higher power levels using a 2 kW single-mode microwave generator as a preparation for scale-up by reducing the reaction time significantly. Star PCL was successfully synthesised within 30 s using 900W of forward power in the 2 kW microwave generator operating at 2.45 GHz.

In summary, this thesis has provided a better understanding in the ROP of CL using microwave heating. Controlled / pseudo-living characteristics were observed in polymerisations conducted using both conventional and microwave heating. Selective heating of the tin active species in the system when microwave heating was used has proven to enhance the rates of polymerisation and reducing / eliminating the induction period. Physical state of the initiator has shown to affect the induction period and overall polymerisation trend. A tuned microwave reactor system has shown higher energy efficiency compared to an untuned reactor. As an approach to maximise system efficiency for the scale-up of PCL production, a 2 kW microwave generator was introduced into this study. As a result, PCL of good quality was successfully synthesised within 30 s using high microwave power levels, which is ideal in a continuous flow process in a scaled-up reaction.