

Ring Opening Polymerisation of

ε-Caprolactone Using Microwave Electric

and Magnetic Heating

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Declaration

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

Signed..... Date.....

Kaiyang Wang

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List of Conferences and Publications

Kaiyang Wang, Georgios Dimitrakis, Derek J. Irvine, "Exemplification of catalyst design for microwave selective heating and its application to efficient in situ catalyst synthesis", 2017, Chemical Engineering and Processing: Process Intensification;

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Abstract

The work presented in this thesis aims to highlight the differences in heating methods, which are conventional, microwave electric, and microwave magnetic heating, for the ring opening polymerisation of ε -caprolactone, as well as the development of an alternative catalyst that is specifically used in microwave magnetic heating to replace the current benchmark catalyst.

Chapter 1 introduces the background of this thesis. There is also an overview of various types of biodegradable polymers, polymerisation techniques, and catalysts used in the polymerisation. An introduction into the basics of microwave and microwave electric and magnetic heating is also provided in this chapter.

Chapter 2 goes on to explain the analytical techniques that are used to characterise the polymer and the dielectric properties. Procedures in locating the reaction vessel at the microwave electric and magnetic dominant positions in the microwave reactor are described. Experimental procedures that are used throughout this thesis are also explained.

Chapter 3 investigates the dielectric properties of various types of metal complexes in both solid powder form and when dissolved in a solvent, to study the factors that affect the interaction between these complexes and the microwave electromagnetic field. Then further investigation into a series of heating experiments of solutions containing these complexes is carried out, to see if the empirical observations follow the same trend as predicted from the dielectric property results. Chapter 4 explores the first application of microwave magnetic heating to the ring opening polymerisation of ε -caprolactone catalysed by metal halides, and compares this to the conventional and microwave electric heating, and investigates the effects of different heating methods have on the overall polymerisation. This chapter also investigates various metal halides that experienced different response to the microwave electric and magnetic heating to see how this affects the polymerisation process.

Chapter 5 describes the development of novel organometllic catalysts that can be used in the ring opening polymerisation of ε -caprolactone with the application of microwave magnetic heating, and possibly replace the existing benchmark catalyst Sn(Oct)₂. The use of various heating methods is also investigated to see what effects they have on the overall process.

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Abbreviations

Å	Ångström	(10 ⁻¹⁰ m)
AIBN	Azobisisobutyronitrile	(-)
BzOH	Benzyl Alcohol	(-)
СН	Conventional Heating	(-)
CL	ε-Caprolactone	(-)
Cyclo	Cyclohexanone	(-)
DMG	Dimethyl Glyoxime	(-)
DP	Degree Of Polymerisation	(-)
DPG	Diphenyl Glyoxime	(-)
ε'	Dielectric constant	(-)
ε''	Dielectric loss factor	(-)
٤*	Complex permittivity	(-)
E-field	Microwave Electric Field	(V/m)
EH	Microwave Electric Heating (Heated by Microwave where	(-)
	the Electric field is at dominant)	
EMF	Electromagnetic Field	(-)
FRP	Free Radical Polymerisation	(-)
GPC	Gel Permeation Chromatography	(-)
H-field	Microwave Magnetic Field	(A/m)
HH	Microwave Magnetic Heating (Heated by Microwave where	(-)
	the Magnetic field is at dominant)	
ISM	Microwave frequencies for industrial, scientific and medical	(-)
	use	
$\mathbf{k}_{\mathrm{app}}$	Rate constant of chemical reaction	(min ⁻¹)
[M]/[C] ratio	Monomer To Catalyst Molar Ratio	(-)
[M]/[I] ratio	Monomer To Initiator Molar Ratio	(-)
M_n	Number Average Molecular Weight	(g mol ⁻¹)
$M_{\rm w}$	Weight Average Molecular Weight	(g mol ⁻¹)

M_p	Peak Molecular Weight	(g mol ⁻¹)
MW	Microwave	(-)
MWH	Microwave Heating	(-)
MWt	Molecular Weight	(-)
NMR	Nuclear Magnetic Resonance	(-)
PCL	Poly(Caprolactone)	(-)
PhCoBF	Bis-[(Difluoroboryl) Diphenylglyoximato] Cobalt (II)	(-)
Đ	Polydispersity Index	(-)
ROP	Ring Opening Polymerisation	(-)
tanδ	Loss tangent	(-)
TE	Transverse Electric	(-)
T _g	Glass Transition Temperature	(°C)
TGA	Thermogravimetric Analysis	(-)
THF	Tetrahydrofuran	(-)
T _m	Melting Point	(°C)
ТМ	Transverse Magnetic	(-)
W	Watt	(W)

Chapter 1 Introduction

1.1 Background of the Study

In the field of green chemistry, the study of the development of material based on non-petroleum sources has gained popularity during the last decade.^[1, 2] In particular, polymers have become attractive alternatives thank to their abundant resources and versatile applications.^[3, 4] On top of this, there has been significant interest in developing environmental friendly and biodegradable polymers with reduced manufacturing cost over the last decades, which has led to an exponential increase in research into various monomers, catalyst systems, and processing techniques.^[5-7]

Among different monomers, aliphatic polyesters synthesised from cyclic esters were seen to have great potential, due to their versatility as well as good biocompatibility and biodegradability.^[7-10] With the aid of different catalysts, successful polymerisation reactions were conducted, where superior catalytic efficiencies were found for catalysts based on expensive metals (such as palladium) or more toxic metals (such as aluminium), compared to catalysts based on the relative cheap, earth-abundant and low toxicity metals (such as iron). ^[11-15] However, due to the nature of the polymerisation, the removal of the involved catalyst is difficult, and additional processes are required. ^[15, 16] Therefore, there is a need for improving the catalytic efficiency of the cheap and low toxicity catalysts, so that they can compete and replace the expensive and toxic ones. To achieve this goal, novel processing techniques were developed to improve the catalytic performance of these cheap and low toxic metal catalysts. i.e. light activated polymerisation ^[17-19] and microwave-assisted polymerisation. ^[20-23]

In particular, microwave-assisted polymerisation was found to be a promising technique because of its ability to heat the material directly *via* an electromagnetic field. As a result, it can raise the reaction bulk temperature rapidly and volumetrically. ^[24, 25] Additionally, it was found that the catalyst could potentially experience selective heating which could potentially elevate the catalyst surrounding and/or surface temperature much higher than the bulk temperature.^[26] As a result, significant improvements in reaction rate and produced polymer quality, as well as reductions in induction time and polydispersity were reported by different researchers. ^[20-23] From these empirical observations, pioneering studies found that it was possible to enhance the catalytic efficiency by exploiting the microwave selective heating on catalyst when the processes were conducted using the microwave. ^[23, 27, 28]

Despite the benefits associated with the microwave-assisted processing, the major problem associated with the microwave heating is the dielectric property of the material, if a material can interact with the electromagnetic field efficiently, the microwave energy will be absorbed as it penetrates through the material. Thus, the energy that can be delivered to the centre of the bulk is limited by the penetration depth of the electromagnetic field, and the potential of commercialisation the process is restricted. ^[29] Methods for avoiding such problem were investigated, for example, using radio frequencies which offer greater penetration depth or using high input power so that energy can be delivered to the centre of the bulk to achieve volumetric heating. ^[30, 31] Recently, it was found that the magnetic susceptible material can be heated efficiently by
the microwave magnetic field. ^[28, 32, 33] However, this was not fully exploited in the chemistry field, especially in the polymer industries. Therefore, this thesis has investigated the potential of applying microwave magnetic heating to polymerisation reactions. Additionally, by understanding how the microwave electromagnetic field heats the catalysts, it could help to design a catalyst that can be specifically used in a process associated with microwave electromagnetic heating.

In this thesis, the dielectric property of different metal halide and organometallic catalysts based on iron, cobalt, and tin were studied. The reason these three metals were chosen was due to their distinct dielectric and magnetic properties, and their catalytic efficiencies. Heating experiments of these samples using microwave radiation, where the electric field was dominant (microwave electric heating), were then performed to exemplify the selective heating effects. These results were then compared to identical experiments that were done using microwave radiation where the magnetic field was dominant (microwave magnetic heating). After identifying the heating behaviour of these catalysts when heated by the microwave electric or magnetic heating, these catalysts were used in the synthesis of poly (*\varepsilon*-caprolactone) via the ring opening polymerisation of ε-caprolactone using various heating methods. For the first time, the microwave magnetic heating is applied to such polymerisation reaction, and the results were compared with the identical reactions that have done with conventional and microwave electric heating. Therefore, any differences between each heating methods could be identified and allow for investigating the origin of these observations. By identifying the factors that affects the selective heating of the catalysts, it is possible to design a cheap and non-toxic catalyst that has catalytic efficiency comparable to, or superior to, the benchmark catalyst when being selectively heated by the microwave.

1.2 Introduction to Polymers

A polymer is a large molecule containing many repeated subunits. The subunits that are used to make up the repeat units are called monomers, which are able to add to each other *via* a process called polymerisation to form polymers.

The first recognised synthetic polymer was back in 1866 by Berthelot. ^[34, 35] However, before the 1930s, the concept of the polymer was thought to be aggregates of monomer molecules. But later, it was found the polymers are in fact very long molecules made up of many monomer units which was first proposed by Staudinger in the early 20th century. ^[34-36]

The World War II era facilitated the development of synthetic polymers due to the limited supply of natural materials such as silk and rubber. ^[34, 35] The economic importance of polymers has stimulated growth in research and understanding of the properties of these materials in industry and academia.

A requirement for small molecules to be qualified as a monomer is to possess two or more bonding sites through which other monomers can bond covalently to form a polymer chain. ^[37] In polymer macromolecules, bending and rotations can occur around these bonds. There are three main types of polymer chain structures: linear, branched and cross-linked or network polymers, as shown in Figure 1.1.



Figure 1.1 Different possible chain structures for polymers (a) linear, (b) branched, and (c) crosslinked.

The linear polymer is made up of one monomer molecule after another, hooked together in a long chain. Conversely, a branched polymer has monomers with two or more functional groups or a mixture of mono and multifunctional monomers. In cross-linked polymers, adjacent linear chains are actually connected by covalent bonds, for example, vulcanisation of rubber using sulphur.

1.3 Biodegradable Polymers

With the development of polymer science and a wide range of applications for these polymers, they have become indispensable materials in various fields such as food, packing, painting, medical applications, and etc. However, specific waste disposal and processing (i.e. incineration) are required when their lifetime come to an end. The severe environmental problems associated with these processes have raised concerns all over the world. Especially for the landfill disposal, because these polymer wastes will remain in landfills for years without degradation.^[5, 6, 38]

In order to provide solutions to the problems of such polymers, the idea of biodegradable polymers as an alternative to non-biodegradable polymers are proposed and gaining more and more interest. The biodegradable polymer is able to be degraded by the action of naturally occurring microorganisms such as bacteria, fungi and algae. ^[5, 6, 38] This distinct advantage allows the biodegradable polymers to be degraded over time when disposed in landfills.

The biodegradation occurs in two stages as shown in Figure 1.2. The first stage involved the depolymerisation of the macromolecules into shorter chains. Followed by the second stage corresponds to the mineralisation, that small polymer fragments are transported into cells where they are bioassimilated by the microorganisms and then mineralised. ^[39, 40]



Figure 1.2 Diagrammatic representation of the chemistry of biodegradation ^[41]

1.3.1 Linear Aliphatic Polyesters

Most degradable and biodegradable polymers contain hydrolysable linkage, namely, ester, orthoester, anhydride, carbonate, amide, urea, and urethane, in their backbones. The ester bond-containing aliphatic polyester (such as poly(glycolic acid) and poly(lactic acid), see Table 1.1), are particularly interesting because of their outstanding biocompatibility and variable physical, chemical, and biological properties. ^[7, 9]

Polymer	Acronym	Chemical structure
poly(glycolic acid)	PGA	
poly(lactic acid)	PLA	$ \begin{bmatrix} 0 \\ CH \\ H_{3}C \end{bmatrix}_{n}^{O} $
poly(hydroxyl butyrate)	PHB	$\begin{bmatrix} CH_3 & O \\ CH & CH_2 \\ CH_2 & D \\ n \end{bmatrix}$
poly(valerolactone)	PVL	$\begin{bmatrix} O - CH_2 & CH_2 \\ CH_2 & CH_2 \\ U & 0 \end{bmatrix}$
poly(ɛ- caprolactone)	PCL	$\begin{bmatrix} O & CH_2 & CH_2 & CH_2 \\ CH_2 & CH_2 & CH_2 & CH_2 \\ CH_2 & CH_2 & CH_2 \\ O & n \end{bmatrix}$
poly(ε-decalactone)	PDL	$\begin{bmatrix} O & CH_2 & C$

Table 1.1 Various biodegradable aliphatic polyesters ^[6, 42]

The biodegradability of these polyesters originates from their main chain structures and their hydrophilicity. ^[43-45] Recent studies showed that lipases are an important group of esterases for biodegradation of aliphatic polyesters. These enzymes are found to be able to hydrolyse aliphatic polyesters in contrast to aromatic polyesters because of the flexibility of the main chain. High hydrophilicity of aliphatic polyester also allows intimate contact between the polyester chain and the active site of lipases. This is significantly in contrast to the rigid main chain and hydrophobicity of aromatic polyesters. ^[10] For example, in the most common polyester, polyethylene terephthalate (PET), whose chemical structure is shown in Figure 1.3, it has an aromatic ring in its main chain structure. As a result, it is not readily biodegradable.



Figure 1.3 The chemical structure of polyethylene terephthalate (PET)

1.3.2 Poly (ε-caprolactone)

In the green chemistry field, studies in alternative polymeric materials to those based on non-renewable petroleum resources has been an attractive subject in the recent years. On top of this, the desire of environmental benign biodegradable plastics has surged impetus towards the polymerisation of cyclic esters. Aliphatic polyesters possess good biodegradability and biocompatibility, become attractive as alternative environmental friendly polymers, which has facilitated its use as commodity plastics for environmental protection.^[5] In particular, polylactones is a popular candidate because of their permeability, biocompatibility, and biodegradability.

Poly(ε-caprolactone) (PCL) is currently one of the most important and widely studied degradable polymers, the use of which can be tracked back to 1930s.^[6] It is a saturated aliphatic polyester with hexanoate repeat units. The first time PCL gained attention was when it was discovered that PCL could be completely degraded by bacterial and fungal enzymes, and thus making it particular interest in biodegradable material applications.^[7]

PCL has a glass transition temperature (T_g) of -60 °C and melting point (T_m) between 56 to 66 °C, which enables easy formability at relatively low temperature. Its high thermal stability also makes it easy to use in melt processing.

PCL shows good resistance to water, oil, and alcohols, ^[46] but also displays a rare property of being miscible with many other polymers, such as poly(vinyl

chloride) and poly(styrene-acrylonitrile), and other polycarbonates, nitrocellulose and cellulose butyrate. Additionally, it is also mechanically compatible with a wide range of other polymers, such as polyethylene and natural rubber.

PCL can be biodegraded within several months to several years depending on the molecular weight, the degree of crystallinity of the polymer, and the condition of degradation. ^[47, 48] Its degradation is autocatalysed by the carboxylic acids liberated during hydrolysis, and this process can be accelerated by many enzymes.

The low melting point of PCL, exceptional blend-compatibility, controlled degradability, and biocompatibility makes PCL a very useful polymer and has stimulated extensive research into its potential application in various fields.

1.4 Polymerisation Techniques

Various polymerisation techniques have been developed throughout the history of polymer science, but it is not the intention that a detailed survey of these methods is to be included in this study. However, in-depth review and studies of these methods can be found from pioneer researchers. ^[36, 49-52] This study will be focusing on the techniques relevant to the ring opening polymerisation (ROP). However, a brief introduction of the general polymerisation methods is essential. There are two main polymerisation methods which are step growth polymerisation and chain growth polymerisation.

1.4.1 Step Growth Polymerisation

The step-growth or condensation polymerisations proceeds through stepwise reactions between monomers that contain functionalities. In this mechanism, there are two monomers present containing different functionalities which a reaction can take place between these functionalities. Such polymerisation follows a similar route as conventional condensation reactions in which a small molecule (i.e. water) is formed as the polymer is synthesised.

In step growth polymerisation, there is only one reaction mechanism for the formation of the polymer.^[53] During the initial stage, monomers are consumed rapidly to form the initial oligomers like dimer and trimer. As a result, the molecular weight of the polymer chain builds up slowly until 80-90% monomer conversion. After this point, an exponential increase in the polymer molecular weight is observed as shown in Figure 1.4. For example, PCL can be prepared by the condensation of 6-hydroxyhexanoic acid with the release of water. However, the major drawback is the removal of water during the polycondensation to favour the production of polymer. This disadvantage becomes more significant as the polymerisation reach higher conversion due to high viscosity at high molecular weight.



Figure 1.4 Graph of molecular weight versus conversion comparing between Chain growth, step growth, and controlled/pseudo living polymerisation.

1.4.2 Chain Growth Polymerisation

The chain growth polymerisation involves a sequence of individual monomer adding to the active site of a growing polymer chain. Such polymerisation mechanism is divided into three major steps: initiation, propagation, and termination.

The initiation step starts with the decomposition of the initiator which produces initiating species, R[•]. The species has an active centre capable of inducing the initiation step. The initiating species, which can be a free radical, anion or cation, are then subsequently added to the first monomer (RM[•]) to start the propagation process

During the propagation process, monomers are added stepwise to the reactive centre (RM[•]) in a head to tail addition to produce the growing polymer chain. In this stage, only the reactive centre can react with monomers, whereas monomers

cannot react with each other. Thus the reaction can only occur at the growing chain end. As a result, a distinguished growth profile for the resultant polymers can be observed compared to step growth polymerisation from Figure 1.4.

The termination step occurs *via* reactions between the growing polymer chains that removes or combines the reactive centre leading to a dead polymer without the existence of free radicals.

All chain growth polymerisation can be categorised into one of the followings:

- Free radical polymerisation
- Anionic polymerisation
- Cationic polymerisation
- Controlled/pseudo living polymerisation

1.4.3 Free Radical Polymerisation

Free radical polymerisation (FRP) is tolerant to impurity and various function groups, and thus makes it the most widely used chain growth polymerisation technique in industry. Such polymerisation proceeds in three steps as mentioned previously: initiation, propagation and termination.

The initiation step involves the decomposition of a radical initiator such as peroxide or azo compounds, to give free radicals R· with a rate constant of decomposition k_d . The free radicals are then added to the vinyl group of the monomer (M) with a rate constant of initiation k_i to give RM· as shown in Figure 1.5.



Figure 1.5 Step of initiation of a monomer

After the monomers are initiated, the propagation reaction takes place in which the monomers are added stepwise to further the initiated monomer in a head to tail addition manner to produce a growing polymer chain. In this stage, the process of electron transfer and consequent motion of the active centre down the chain proceeds.

Termination of reaction stops the further propagation of chains by either combination or disproportionation processes leading to a dead polymer in which no free radicals exist. The combination process occurs when two growing polymer chains react in a head to head manner and form a single chain (Figure 1.6 a). In the disproportionation process, a hydrogen atom is abstracted from a growing polymer chain by a free radical to form hydrogen and vinyl ended polymers (Figure 1.6 b).



Figure 1.6 Chain termination reactions.

1.4.4 Anionic and Cationic Polymerisation

The anionic polymerisation encompasses the polymerisation of vinyl monomer with strong electronegative groups. Such polymerisation are commonly used in the production of synthetic polydiene rubbers, solution styrene-butadiene rubber (SBR), and thermoplastic styrenic elastomers. The initiators used in this polymerisation are either electron transfer agent or strong anions. The transfer or an electron from the initiator to the vinyl monomer leads to the formation of an anion radical or so-called carbanion. Typical initiators are alkali metals, such as lithium or sodium.

In cationic polymerisation, a cationic initiator transfers charge to a monomer to activate the monomer. The polymerisation reaction is very sensitive to the solvent selection as free ions in the solvent will affect the reactivity of the propagation cationic chain. The more polar the solvent is, the faster the propagation process proceeds.

1.4.5 Controlled Polymerisation

Controlled/*pseudo* living polymerisation is a polymerisation process that the molecular weight of the polymer increase linearly with conversion (see Figure 1.4). The target molecular weight can be achieved with a low polydispersity index (\oplus <1.5). The precise control over the polymerisation also allows for the synthesis of polymers with complex structures *via* sequential addition of second monomers. This is particularly important for many of the novel/special properties of polymers result from their polymer structure and molecular weight. This type of reactions will be discussed in greater details with a specific focus on controlled ring opening polymerisation.

1.4.6 Ring Opening Polymerisation

Ring opening polymerisation can be considered as a chain growth polymerisation (addition of monomer to a growing chain end). Many ROP methods are found to exhibit a controlled/pseudo living characteristics. However, it is still recognised as an independent mode of polymerisation by many polymer scientists. This is because the rate of ROP does not benefit from the enthalpy difference between single and double C-C bond, which is in contrast to the enthalpy lost as a result of chain growth polymerisation. Rather, the driving force for ROP is the ring strain and associated steric considerations.

A variety of polymers based on cyclic monomers have been synthesised *via* ROP, such as cyclic ethers, amides, and esters like lactones and lactide. Many polymers of industrial importance are also produced using ROP, i.e. polycycloocetene, polynorbornene, polyphosphazene, etc.

The ROP reactions can be initiated by both ionic and coordinative imitators. Depending on the type of catalyst, ROP can be categorised into four main mechanisms:

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

In anionic ROP, an anionic species is formed as a result of initiation. During the propagation stage, the monomer is ring opened by an attack of the anionic species on the carbonyl carbon of the monomer (anionic ROP of caprolactone is shown in Scheme 1.1). The main drawback of this method is the presence of

significant intramolecular transesterification, also called 'backbiting', at high polymer conversion.



Similarly, cationic ROP involves the formation of a cationic species during the initiation step, followed by propagation of monomers *via* the cationic ions, which is nucleophilically attacked by the carbonyl oxygen of the monomers (see Scheme 1.2).



Scheme 1.2 Mechanism of cationic ROP

In activated monomer ROP, the monomer is activated from a combination of a catalyst and an initiator, which breaks the carbonyl bond and opens the ring of the monomer. This 'active' monomer then reacts with the neutral functional end group in other monomers to form propagating polymer chain (see Scheme 1.3).



Scheme 1.3 Mechanism of activated monomer ROP

Coordination-insertion ROP is the most common technique used. It involves coordination of the monomer to the catalyst, followed by the insertion of the monomer into a metal-oxygen bond of the catalyst. As a result, the first ring opened monomer is formed, which then continues by the coordination of a second monomer. The newly coordinated monomer is then inserted into the growing chain *via* a migratory insertion rearrangement of this transition species. The mechanism is shown in Scheme 1.4.

Scheme 1.4 Mechanism of cooperation-insertion ROP

During the ROP, side reactions can take place in the form of intramolecular transesterification (see Scheme 1.5) and/or intermolecular transesterification (see Scheme 1.6). The intramolecular transesterification takes place where the active site in the polymer react with its polymer chain and results in a cyclic macromolecule, this reaction is often called "back-biting". Conversely, the intermolecular transesterification is the side reaction taking place between two polymers, resulting in expansion of the Đ value. ^[26-30]



Scheme 1.5 Mechanism of intramolecular transesterification



These side reactions become significant during the later stage of the polymerisation (i.e. conversion >80%), particularly at high temperature. As a result, broadening in a polydispersity of the obtained polymer, and loss of control over the polymerisation could be observed.

1.5 Catalysts Used in ROP Reactions

The ROP can be conducted using different catalytic systems, namely, metalbased, enzymatic, and organic systems.

The metal-based catalyst system is the most widely used catalytic system for ROP because they are readily available and highly active. They are able to catalyse the ROP with or without the presence of a solvent. ^[38, 43, 46, 49]

Enzymatic catalyst system can successfully perform ROP reactions in mild conditions (i.e. room temperature), but very slow (i.e. 1100 h to reach 81%). ^[54] Another drawback is that low temperature (below 70 °C) is required to keep enzymes active.

Organic compounds, like 1,5,7-trizabicyclo[4,4,0]dec-5-ene (TBD) and phosphazene bases, can be used as catalysts as well. ^[55] However, either a cocatalyst or long reaction time (14% after 10 days using BEMP as the catalyst at 80 °C) was required. Organic acids have also been used as the catalyst. This catalytic system was found to be reusable up to two times, and can be used without the presence of initiators. However, a high catalyst load of [M]:[C] ratio of 40:1 was normally used.

Although all these catalytic systems are able to perform ROP successfully, the metal catalytic system is the catalyst system focused on within this thesis. Thus, the metal-based catalytic system is discussed in more details in the next section.

1.5.1 Alkali and Alkaline Based Catalyst

Alkali metal-based catalyst (i.e. lithium and potassium) are able to conduct ROP successfully, but these catalysts are ionic, and the ROP follows the anionic mechanism. ^[8, 43] As a result, significant transesterification during ROP are

observed, and thus loss control over the polymerisation. Additionally, the alkali catalysts tend to form aggregates when mixed with monomers, thus reduce the solubility of the catalyst. ^[8]

ROP of ε -caprolactone (CL) using lithium based catalyst was successfully conducted by Rajendran *et al.*. ^[56] The polymerisation performed for 5 to 10 minutes at 60 °C with and without the presence of BzOH. High molecular weight up to 10.7×10^4 g mol⁻¹ was obtained with Đ spanning from 2.24-5.38. The addition of BzOH was found to provide control to the polymerisation and reduced Đ to 1.52-1.86. However, the mechanism of the reaction remained unclear.

Similarly, Satti *et al.* also performed the ROP of CL using lithium catalyst at 50 °C for over 24 hours at [monomer] to [catalyst] ratio of 800 to 1, the molecular weight of the product was around 9100 g mol⁻¹ with a narrow polydispersity of 1.14. ^[57] The mechanism was believed to follow an anionic ROP mechanism as shown in Scheme 1.7.

Nucleophilic attack to the carbonyl group



Scheme 1.7 Nucleophilic attack on the carbonyl group and subsequent propagation reaction of ε -CL from alkoxide species.

Compared to Alkali based catalysts, the alkaline based catalysts are more attractive due to their high activity and low toxicity. The most common alkaline catalysts are based on magnesium and calcium. Both metals are essential elements in plants and animals, as a result, they are biologically benign. ROP using alkaline based catalysts are found to follow monomer-activated and coordination-insertion mechanisms, and some of the catalysts provided 'living' character to the polymerisation. ^[58]

Shueh *et al.* performed ROP of CL using magnesium based catalysts at 50 °C, the polymerisation was able to complete within 3h with molecular weight up to 24100 g mol⁻¹ with narrow dispersity index. ^[58] The relationship between monomer:catalyst ratio and the molecular weight was found to be linear, suggested a "living" character to the polymerisation.

Calcium based catalysts were also applied to the ROP of CL by Piao and coworkers. A two steps mechanism was proposed with the first step of forming active species between the calcium catalyst and the initiator, followed by a coordination-insertion mechanism. ^[59, 60]

1.5.2 Poor Metal Based Catalysts

The poor metal based catalyst is the most popular catalysts used to catalyse ROP. The most commonly used catalysts in this group are based on aluminium and tin. Aluminum is less active compared to other metals, but it is widely used because it provides good control over the polymerisation. The main drawback is the toxicity of the residue metal after the polymer is decomposed, which could induce pollution to soil and underground water reservoir.

Tin based catalyst, especially Stannous (II) ethylhexanoate (also called tin octanoate) is the most often used catalyst for ROP of cyclic esters. It is effective, commercially available, easy to handle and soluble in the most commonly used organic solvents. ^[43, 61] It must be used with a nucleophilic compound (usually an alcohol) to initiate the reaction in order to provide controlled characteristic to the polymerisation. The drawback associated with tin octanoate are that high temperature is required, which facilitates side transesterification reactions and broadens the polydispersity of the product polymer. ^[61]

When tin octanoate is used in ROP, the first step of the polymerisation involves the production of the active alkoxide species by reacting the catalyst with alcohol (Scheme 1.8). The equilibrium between alcohol/catalyst and active alkoxide exists throughout the polymerisation. Thus, an excess amount of alcohol (i.e. [initiator]:[catalyst] ratio ([I]:[C] molar ratio) of 5:1) is added to drive the reaction in favour of the active alkoxide species. Without the nucleophilic initiators, there will be no control of the polymerisation.



Scheme 1.8 Mechanism of formation of the active alkoxide species

The active species then initiates the monomer *via* the coordination-insertion mechanism to generate the first active monomer ready for propagation (Scheme 1.9). Such monomer consists of an active propagation centre which can further propagate the polymerisation *via* the coordination-insertion mechanism.



Scheme 1.9 Mechanism of coordination-insertion ROP of CL using Sn(Oct)₂

Water present as impurities in the reaction could react with the active alkoxide species and will reduce the concentration of the active species and produce a tin alcohol derivative. This derivative is more thermodynamically stable than the alkoxide and is a less efficient initiator. Thus the formation of such derivatives will reduce the efficiency of the catalytic system.

1.5.3 Transition Metal Based Catalysts

Rare earth metals like Scandium and lanthanum are used in ROP due to their good catalytic efficiency. However, the low availability and high expense in recycling these catalysts is the major drawback for the application of such catalysts. As a result, more researchers are looking into the earth abundant transition metals as preferred catalyst systems. The most commonly used transition metal for ROP is titanium and zinc, but recently, the less toxic metals like Co and Fe are more preferential and attracting more interests. Cobalt salts were successfully applied to ROP of CL by Rajashekhar and Chakaraborty at 150 °C. ^[62] High conversion and molecular weight were achieved within few hours with low dispersity index (\oplus <2). The mechanism was believed to follow a monomer-activated route. Additionally, hydrated cobalt catalyst was found to be superior to an anhydrous system with BzOH. It was suggested that the presence of H₂O in hydrated catalyst facilitated the ROP process.

O'Keefe *et al.* have found that iron (III) alkoxide complexes can be effective catalysts for ROP of CL. ^[63] The polymerisation can achieve 95% conversion within 2 h, and the molecular weight of the produced polymer was up to 55000 g mol⁻¹ with D < 2. The mono-Fe complex was found to be more sensitive to impurity than the di-Fe complex, due to higher D values.

In the more recent study, Gowda *et al.* found FeCl₂ and FeCl₃ could be an effective catalyst for conducting ROP of CL at room temperature. ^[15] However, FeCl₃ provided faster reaction rate with higher molecular weight polymer product. They found that using alcohol as the initiator improved molecular weight and reduced Đ compared to water, however, longer reaction time was required to reach completion.

Similarly, Hege and Schiller also conducted ROP of CL using iron halides at room temperature. ^[16] FeCl₃ was found to be able to reach completion within 2.5 h (for [monomer]:[catalyst] ratio of 200:1 and 400:1), whereas over 80 h were required for FeBr₃ to reach over 60% conversion. The efficiency of the initiator was found to follow the order: 2-allyl phenol>isopropyl alcohol>BzOH>H₂O. The 2-allyl phenol was found to form a metal complex with iron (III) salts before participating in ROP process, and the produced complex was believed to be more effective in initiating the reaction.

1.6 Microwave-Assisted ROP

Studies in identifying the efficiencies of various catalyst systems have solidified the understandings in the catalysis of the ROP of CL. However, several drawbacks were found for these catalyst systems, for example, long induction time ranging from minutes to hours, along with the polymerisation reaction finishing in hours even days. Moreover, such polymerisation reactions were normally conducted at an elevated temperature which makes the process possesses disproportionate energy consumption (i.e. reacting at 160 °C for 90 hours).

To overcome this problem and make the process energy efficient, novel processing techniques were utilised. Recent studies have focused their interest towards microwave (MW) heating.^[21-23, 64] In MW heating, energy is delivered volumetrically and directly into the sample, unlike the convection/conduction heating in conventional heating. By doing this, rate enhancements in ROP reactions were claimed by some MW studies. ^[20, 65] However, negative effects such as yield reduction and promotion of side reactions were also highlighted by other studies. ^[21] To fundamentally understand the effects MW heating offers, studies on various catalysts, MW instruments, and solvents were conducted by different researchers.

Fang and co-workers studied the microwave assisted ROP of CL using different input power and temperatures. ^[66, 67] The CL monomer can easily reach the set temperature with MW heating, and over 90% yield was obtained after 2 hours of reaction. The glass transition temperature (T_g), melting temperature (T_m), and

thermal stability was found equivalent to that were synthesised with conventional heating. However, the polymer can be produced by microwave heating within 2 hours, compared to more than 12 by the commercial thermal process.

Albert and his group compared the ROP results using conventional heating and MW heating. However, no substantial improvements in reaction conversion or product quality were found in MW irradiated reaction when compared to conventional studies. ^[68]

Liao *et al.* studied the effects of MW input power on the ROP of CL. ^[22] Dependence between molecular weight and input power level was found. Additionally, a significant reduction in reaction time was also found when compared to conventionally heated experiments.

The kinetics of ROP of CL were studied by Sivalingam *et al.* with different cyclic heating pulses. ^[69] Because the temperature varied during the reaction, a model was proposed, and the activation energy was determined based on the model. The results indicated that the microwave heating increases the polymerisation rate by lowering the activation energy.

Nguyen and his group studied and compared the ROP of CL between microwave and conventional heating at identical conditions. ^[23] They found the induction period and reaction time was significantly reduced when microwave heating was applied. They found such observation was potentially originated from the microwave selective heating on the organometallic catalyst that accelerates the formation of the "true" catalyst. By doing the heating experiment with the microwave, they exemplified the selective heating effects on the organometallic catalyst as a temperature overshoot was noticed when the catalyst was added to the bulk.

From these pioneering studies, the microwave was found to be a promising heating method for ROP of CL. Beneficial effects such as accelerating reaction rate, improving product quality, and reducing induction time were observed. However, to apply microwave to chemical reactions, it is essential to have fundamental understandings about microwave before designing such microwave process.

1.7 Fundamentals of Electromagnetic Heating

Conventional heating methods like oil bath and hot plate are commonly used for heating chemical reactions. Generally, the surface of the sample is heated either by radiation, conduction, or convection. The heat energy is then transferred to the centre depending on the temperature difference, the thermal diffusivity of the medium, and the level of the mixing. This leads to poor control of the temperature and slow heating.

Conversely, the heating of a medium can also be achieved by the volumetric heating from the electromagnetic field. In such electromagnetic heating, the entire reaction medium can be heated instantaneously and with the identical heating rate. Therefore, the heating of the medium does not depend on the heat energy transfer like in conventional heating. Since 1986 when reactions were firstly carried out using microwave irradiation, the use of microwave as the heating method has become more and more popular in both industrial and academic research areas. Microwaves are a form of electromagnetic radiation that has frequencies spamming from 0.3 GHz to 300 GHz corresponding to the wavelength from 1cm to 1m, respectively. The corresponding photon energy is 0.0016 eV at 2.45 GHz which is not high enough to induce bond cleavages and thus cannot directly induce chemical reactions.

Microwaves are applied in various fields such as radio transmission and telecommunications. In order to avoid interference with these frequencies, specific frequencies of 915 MHz and 2.45 GHz have been assigned for use in microwave heating by ISM (industrial, scientific and medical use). The corresponding wavelengths are 32.75 and 12.24 cm, respectively.

The microwave electromagnetic field consists of an electric field and a magnetic field components, which are perpendicular to each other. This can be seen in Figure 1.7, the position where the maximal electric field is located, the corresponding magnetic field is at its minimal, and *vice versa*. For the most purpose of microwave heating, it is the electric field that is used in the heating process. Such heating process is normally called dielectric heating. Conversely, the heating with the magnetic field is referred to magnetic heating.



Figure 1.7 Illustration of the (a) electric field and (b) magnetic field distribution in a microwave electromagnetic field.^[70]

1.7.1 Microwave Heating at the Electric Field Dominant Position

In dielectric heating, the heating is caused due to the dielectric loss which originates from dipolar polarisation and ionic conduction.

In dipolar polarisation, the material must contain a dipole moment to interact with the electric field. These dipoles can rotate and align themselves with the applied electric field, and as the field oscillates, these dipoles then re-align with the field. The restricted rotation of the molecules during this process is called the relaxation process. During the relaxation process, energy is given off in the form of heat (Figure 1.8 a).

However, this process is strongly dependent on the physical form of the material and the field frequency. In aqueous and gas phase, the dipoles are able to rotate with the alternating field but are restricted in solid form. If the frequency is too low, the alignment of molecules can keep the same pace as the alternating field, and thus no heating occurs. Conversely, if the frequency is too high, the molecules cannot rotate quickly enough to keep up the alternating field, and leads to no heating.

In the microwave frequency region, the dipole are able to respond and rotate with the electric field, but they cannot perfectly align with the field. Therefore, there is always a phase difference between the orientation of the field and that of the dipoles. This phase difference allows thermal energy to be generated *via* frictions and collisions among the molecules. As a result, such heating mechanism is not very effective in the gas phase due to the molecules being too far apart from each other. The second heating mechanism is ionic conduction. In this mechanism, the charged species orientate with the alternating field and collide with their neighboring molecules or atoms and generating heat (Figure 1.8 b).



Figure 1.8 Dielectric heating mechanism: a) dipolar polarisation and b) ionic conduction.

In the dielectric heating, the heating characteristics of material depend on dielectric properties of the material. The fundamental dielectric property is the complex relative permittivity of material, ε^* , which can be expressed as:

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

Where j is the imaginary component, ε ' is the dielectric constant which determines the ability of the molecule to rotate with the oscillating field, and ε '' is the dielectric loss factor which identifies the efficiency of the material to convert the electromagnetic energy into heat.

The loss tangent is often used to describe the potential behaviour of material within an electromagnetic field at a specific temperature and frequency. It is expressed as:

$$tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

A high tand value indicates efficient electromagnetic energy absorption and rapid heating. However, there is always a compromise between ε ' and ε ''. For

example, water has high ε ' values (ε ' = 80.4 at 25 °C) but low ε '' results in a tan δ of only 0.123. In comparison, ethanol has a significant lower ε ' value (ε '=24.3 at 25 °C) but has a higher tan δ value (0.941) due to its high ε '' value. When a material has tan δ of 0.1 or greater, it is considered to be able to heat efficiently in a microwave, whereas a material with tan δ less than 0.1 is recognised as microwave transparent.

As discussed previously, frequency has a critical impact on the dielectric properties of material. The dielectric properties of water are shown in Figure 1.9 to demonstrate the frequency dependence. When at low frequency, water molecules can keep up with the rotation of the field perfectly, and thus no heating occurs as indicated by the low ε '' value. As the frequency increase, the ε '' reaches its maximum at the frequency of 18 GHz. The dielectric heating will be most effective at this frequency as a result of the maximum ε ''. At the frequency of 2.45 GHz, the heating of water is not as efficient as that at 18GHz due to the low ε ''.



Figure 1.9 Dielectric properties of water at various frequencies [83]

The penetration depth is also an important term to be considered when applying dielectric heating. The penetration depth is defined as the point where 37% of

the initial microwave power is still present in a material. This indicates the heat distribution within a material throughout its bulk. It is especially important when scaling up a process to maintain even heat distribution.

The simplified penetration depth (dp) equation is expressed as:

$$d_p = \frac{\lambda_0 \sqrt{\varepsilon'}}{2\pi \varepsilon''}$$

Where λ_0 is the free space microwave wavelength.

Ideally, a reactor should have a diameter less than twice of the penetration depth in order to maintain even heating throughout its bulk.

1.7.2 Selective Heating in Microwave Electric Heating

The efficiency of dielectric heating changes according to the dielectric properties of a substance, therefore, when a mixture of several different materials presents within the electric field, a material with higher dielectric properties has greater potential to interact with and dissipate heat energy from the alternating field. Such difference in heating response between different materials is called selective heating.

This selective heating has been noticed by several researchers when a transition metal compound or organometallic compound was used in the reaction as a catalyst. Hu and Cheng demonstrated that the conversion in a MW-induced degradation of atrazine reaction is significantly higher when using transition metals (copper and iron species) compared to alkali (sodium species) and alkaline (calcium and magnesium species) metals. ^[71, 72] Nguyen *et al.* have also identified the existence of MW selective heating on the Sn(Oct)₂ catalyst in ring opening polymerisation of caprolactone. ^[23] Such selective heating was found to enhance the reaction conversion and accelerate the formation of the active

alkoxide species. Adlington *et al.* observed a rapid formation of cobalt '*in situ*' catalysts using MW heating. ^[73, 74] Additionally, they found a critical concentration of species susceptible to MW heating was required to show the significance of the selective heating effects.

In a heterogeneous system, such selective heating on metallic catalysts has also been demonstrated. For example, Suttisawat *et al.* compared the dehydration of decalin and tetralin between MW and CH, increasing in conversion were observed in MW, and a large temperature gradient from catalyst surface to surrounding species was also noticed in MW experiment. ^[75] They proposed that such phenomenon induce faster molecular desorption (of product species) or enhance species transportation within the system and resulted in exquisite results when using MW.

Previous research demonstrated the benefits could be exploited from the MW selective heating effects. However, if the sample is irradiated with MW of a superfluous input power, hot spots could be formed on the catalyst surface and could lead to deactivation of the catalyst. ^[28]

1.7.3 Microwave Heating at the Magnetic Field Dominant Position

Heating by microwave is not only dielectric heating, other types of heating can also be induced by microwave magnetic field called magnetic loss heating. Magnetic losses occur in the microwave region for magnetic materials that are ferromagnetic or paramagnetic depending on their magnetic properties. ^[76] Such losses are induced by electron-spin and domain wall.

Magnetic properties based on the magnetic susceptibility (χ) of a material, which is the ratio of induced magnetisation (M) to the applied magnetic field (H). Without an applied external magnetic field, the magnetic moments in a material are randomly orientated, and thus possess no magnetisation. Once the external magnetic field is applied, the magnetic moments tend to align with the field and produce a bulk magnetisation. When all particles align their magnetic moments along the direction of the magnetic field, the magnetisation of the material saturates. ^[77] The magnetic susceptibility of these materials are also dependent on their atomic structures, temperature, and external field (H). ^[78]

If a material possesses magnetic susceptibility when an external magnetic field is applied, it is characterised as ferromagnetic or paramagnetic material. The magnetic moments in ferromagnetic materials tend to orient parallel to each other even in the absence of the applied field. Whereas for paramagnetic materials, when the applied field is removed their magnetic moments start to randomise, cancelling their magnetic moments and reducing the bulk magnetisation. ^[78]

Similar to dielectric heating, heat dissipation from magnetic particles results from the delay in the magnetic relaxation moment. There are two types of magnetic relaxation process: the Néel relaxation and the Brownian relaxation.

The Néel relaxation refers to the delay in the magnetic moment rotation within the particle (i.e. unpaired spins in the d-orbital of a metal). Conversely, the Brownian relaxation is the delay in the magnetic moment rotation of the particle itself (i.e. domain wall). When magnetic particles are exposed to a magnetic field with a reversal times shorter than the magnetic relaxation times of the particles, magnetic heating of the particles can be observed. The Néel (τ_N) and Brownian (τ_B) magnetic relaxation times of a particle can be calculated *via* the following equations ^[79-82]:

$$\tau_N = \tau_0 exp \, \frac{\kappa v_M}{kT} \tag{1}$$

$$\tau_B = \frac{3\eta V_H}{kT} \tag{2}$$

$$\tau_N = \frac{\tau_B \tau_N}{\tau_B + \tau_N} \tag{3}$$

Where τ_N is the Néel relaxation time, τ_B the Brownian relaxation time, τ the effective relaxation time, $\tau_0=10^{-9}$ s, K the anisotropy constant, VM the volume of the particle, k the Boltzmann constant, T the temperature, η the viscosity and VH the hydrodynamic particle volume.

However, because the Brownian relaxation is related to the rotation of the particle, the heat dissipation through Brownian relaxation is strongly affected by the viscosity of the medium, whereas the Néel relaxation does not influence by the viscosity. If a medium has high viscosity and the particle rotation is suppressed, the heat dissipated from Brownian relaxation could be either diminished or seized. Similarly, if magnetic materials are attached to polymer chains, the Brownian rotation will be restricted, and the Néel mechanism becomes dominant. ^[77, 78]

1.8 Microwave Reactor

A Sairem MiniFlow 200SS microwave reactor with a single mode cavity is used as the microwave reactor in this study. An optical fibre temperature sensor was connected to the MiniFlow and was introduced directly into the reaction bulk *via* a quartz tube on a stopper as shown in Figure 1.10. This provides immediate feedback on temperature to the MiniFlow.



Figure 1.10 Sairem MiniFlow 200SS.

1.9 References

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Chapter 2 Methodology and Experimental

This chapter detailed the experimental methods used in characterising the polymer products and dielectric properties, and heating of samples. Additionally, experimental procedures for the preparation of materials, heating experiments, polymer synthesises, and analysis of the product formed during the polymerisation of ε -caprolactone *via* the ROP reactions were provided. Detailed description and operational parameters of the experimental equipment were also included.

2.1 Methodology

2.1.1 Characterisation of Polymers

Molecular weight is one of the important measurements used to describe the polymer obtained and the efficiency of the process in polymer synthesis and characterisation. Several important properties like mechanical property and biodegradability are strongly dependent on its molecular weight.

Five important terms related to the average molecular weight are usually used in polymer science:

- Number average molecular weight (M_n)
- Weight average molecular weight (M_w)
- Peak molecular weight (M_p)
- Polydispersity index (Đ)
- Degree of polymerisation (DP)

The number average molecular weight determines the number of molecules of the individual macromolecules. It is measured by counting the number of polymer molecules in a polymer sample.

$$M_n = \frac{\sum M_i N_i}{\sum N_i}$$

Where Mi is the molecular weight of the molecules and Ni is the number of molecules.

Compared to M_n , The weight average molecular weight (M_w) takes into account the molecular weight of a chain in determining contributions to the molecular weight average.

$$M_{w} = \frac{\sum M_{i}^{2} N_{i}}{\sum M_{i} N_{i}}$$

The peak molecular weight (M_p) determines the molecular weight of the highest peak.

The polydispersity index determines the molecular weight distribution of a polymer. It is obtained by dividing the weight average molecular weight by the number average molecular weight.

$$\mathbf{D} = \frac{M_w}{M_n}$$

The best \tilde{D} can be obtained is 1 meaning that all of polymer molecules have exactly the same molecular weight. In this study, M_n , M_p and \tilde{D} values are obtained by gel permeation chromatography (GPC).

Degree of polymerisation (DP) refers to average number of monomer units in a polymer chain. DP is determined by end-group analysis using ¹H nuclear magnetic resonance (NMR) in this study.

$$DP = \frac{polymer\ molecular\ mass}{monomer\ molecular\ mass}$$

2.1.1.1 Gel Permeation Chromatography (GPC) GPC is frequently used in characterisation of polymer molecular weight. The

GPC separates macromolecules based on size exclusion principles.

Columns containing cross-linked polymer beads such as cross-linked polysterene / poly(divinyl bznzene) porous beads are used as stationary phase, while solvent such as tetrahydrofuran (THF) or chloroform are used as the mobile phase. Small molecules diffuse in and out of pores of the beads in the column and thus taking longer time to pass through the column. Conversely, large molecules spend less, or no time, in the pores of polymer beads and are detected by the analyser first (as demonstrated in Figure 2.1).



Figure 2.1 Illustration of Gel Permeation Chromatography mechanism.

After the separation, the polymer fractions are analysed by the detector. In this case, a differential refractive index (RI) detector is used. Characterisation of the polymer is achieved by comparing the sample molecular weight against narrow molecular weight of polystyrene standards of known molecular weight with a Đ close to 1.00.

2.1.1.2 Nuclear Magnetic Resonance (NMR)

NMR is widely used to identify the chemical structure of a polymer. The principle of NMR is based on the alignment of active nuclei (i.e. ¹H, ¹³C,

¹⁵N, etc) when an external magnetic field (B_o) is present. Each nucleus has its own magnetic field and the direction of these magnetic fields are random. However, when an external magnetic field is applied, the nuclei spin state are exited and split into α or β state. The spins at α state orientate and align with the external field, whereas those at β state are opposed to the external field. The frequency of such precession is called resonance frequency and is characteristic to the individual nuclei.

When the field is removed, the spins return to its ground state and the absorbed energy is then emitted at the same level with a frequency equivalent to the resonant frequency. The emitted frequency signal is then recorded by the NMR spectrum. The resonant frequency, absorbed energy, and the emitted signal are strongly dependent on the external magnetic field strength in a proportional manner (as shown in Figure 2.2). Therefore, strong magnetic field is always necessary.



Figure 2.2 Illustration of energy difference between the two spin states of a hydrogen atom as the strength of external magnetic field changes.

However, similar proton nuclei still behave differently in different compounds due to the electron(s) surrounding the proton. Because these electrons are negatively charged particles, they response to the B_0 and generate a secondary magnetic field that opposes the much stronger applied field. This secondary field shields the nucleus from the applied field and reduces the magnetic field at the nucleus. As a result, a stronger external field is required to compensate for the induced shielding field, and to achieve the same level of resonance. Thus the emitted frequency shifts to higher frequency for the more shielded nuclei. This shift in NMR frequency is known as the chemical shift.

If a nucleus is surrounded with higher electron density, its chemical shift will move towards lower chemical shift (upfield region). Conversely, when less electrons are shielding the nucleus, then the chemical shift will move to higher chemical shift (downfield). By understanding the shielding effects from nucleus surrounding environment, its structural information can be obtained. Tetramethylsilane (TMS), ((CH3)₄Si), is normally used as a reference compound with a chemical shift of 0 ppm.

The interactions between the spins of neighbouring nuclei (equivalent or less than 3 bond length) in a molecule may cause the splitting of the NMR signal. The separation between the spins are always constant, and is called the coupling constant (J) (as shown in Figure 2.3). This effect is called spin-spin coupling or J coupling. The splitting pattern is related to the number of equivalent H-atom at the nearby nuclei.



Figure 2.3 Example of splitting of the NMR signal from spin-spin coupling. NMR can also be used to calculate the conversion of a polymerisation by comparing the NMR peak of the same function group between monomer and polymer. This will be further discussed in Sectuin 2.3.4.

2.1.2 Characterisation of Dielectric Property

2.1.2.1 Cavity Perturbation Method

The dielectric properties were measured using the cavity perturbation method. The cavity perturbation method is based on measurement of change in quality factor (or Q factor) and resonant frequency when a sample is inserted. This method has been extensively applied for measuring the dielectric properties of low loss materials. ^[1, 2] A schematic of the cavity perturbation experimental apparatus is showed in Figure 2.4.



Figure 2.4 Schematic of the cavity perturbation experimental apparatus

The cavity resonates in transverse magnetic (TM) mode at a frequency of 2470 MHz. This frequency is used because it closely matched to the frequency allowed for industrial and domestic operation in UK. A sample is inserted into the longitudinal axis of the TM cavity which possesses a uniform electric field. In TM cavities, the electric field is parallel to the longitudinal axis of the perturbed sample and will diminish in the radial direction as showed in Figure 2.5. ^[1, 2] Therefore, as the electromagnetic field orientates in the cavity, the magnetic field in a TM cavity is zero along its longitudinal axis, so the mode distribution around the sample is purely electric. ^[1, 2]



Figure 2.5 The electric and magnetic fields for TM mode cavity^[3]

When a material is introduced into a resonant cavity, the cavity field distribution and resonant frequency changes depending on the shape, electromagnetic properties, and the position of that material in the cavity. The sample was adjusted to the maximum electric field location of the cavity. To apply the cavity perturbation method, it is assumed that the sample volume is small with respect to the volume of the resonant cavity so that the sample does not disturb the internal field significantly. This means that the electromagnetic field in the cavity should be approximately identical with and without the insertion of the sample. ^[4] The measurement can then be performed by determining the changes in the resonant frequency and Q factor of the cavity before and after sample insertion. ^[5] The alternation within the cavity was detected by a vector network analyser. The dielectric property was calculated from the measured frequency shift and change of Q factor using Maxwell's equation developed from the perturbation theory ^[2, 6]:

$$\varepsilon' = 1 + 2j_1^2(X_{1,M}) \frac{\delta J}{f_0} \frac{V_c}{V_s}$$
$$\varepsilon'' = J_1^2(x_{1,m}) (\frac{1}{Q_s} - \frac{1}{Q_0}) \frac{V_c}{V_s}$$

Where $J_1(x_{1,m})$ is the first order Bessel function, $x_{1,m}$ is the mth root of the first order Bessel function, V_c is the volume of the cavity (mm³), V_s is the volume of the sample (mm³), f_0 is the resonance frequency of the empty cavity (Hz), δf is the shift in resonant frequency (Hz), Q_0 and Q_s are quality factor of the empty cavity and the cavity with a sample.

To ensure that perturbations in the field were only caused by insertion of the sample, the resonant frequency and Q factor of the cavity containing empty quartz tube were measured as a reference. Thus, the observed shift in frequency and changed in Q factor when the sample was introduced into the cavity was solely due to presence of sample.

The furnace above the cavity was used to heat the sample to desired temperature in order to determine how the dielectric properties change with temperature. The sample was adjusted to the optimal position in the cavity and then sent to the furnace with an electric motor. Additional 5 min after the sample reached set temperature was allowed to assure the sample temperature was equilibrated to the set temperature. The sample was then injected back to the cavity by means of the automated motor. After the measurement was completed, the sample was sent back into the furnace to be heated to the next set temperature. The measurement took less than 10 s, so the sample should not cool during measurements. In practice, the average time for same to reach next set temperature was about 10 min at a rate of 2 °C/min with a temperature overshoot of no more than 3 °C.

2.1.2.2 Coaxial Probe Method

The coaxial probe technique includes an Agilent 8753 ES VNA (100-5000 MHz) network analyser, a flexible coaxial cable and a 7 mm coaxial probe. The probe is made from Inconel steel can operate at temperature range from -40 to 250 °C, consists a 7 mm coaxial line with an inner conductor of 3 mm. The end of the probe is attached to a radiating annular aperture with a metallic flange.

Calibration of the probe was done using three different calibration standards: open line, short circuited line and a reference liquid of known dielectric response, which is ethanol in this case. ^[7]

Good contact between the probe and sample is essential for accurate measurements. For this reason, bubbles between the probe and liquid samples were carefully avoided in the experiments.

A swept frequency signal was transmitted from the VNA into the sample *via* the coaxial line. The reflection coefficient (Γ) of the material is monitored. The values of ε ' and ε '' of that material can be then determined based on the phase and amplitude of Γ using a modal analysis. ^[8-10]

An on-site oil bath was placed below the probe for heating the sample to desired temperature without need of transferring the sample.

2.1.3 Single-Mode Cavity vs. Multi-Mode Cavity

There are two major types of microwave cavities used for microwave heating,

single-mode cavity and multi-mode cavity.



Figure 2.6 a) Diagram showing single mode resonant cavity used for heating experiments ^[11]. An example of b) E-field and c) H-field component of the microwave radiation inside a waveguide in the single mode operation resonant condition ^[12].

The single-mode cavity allows for formation of a standing wave along the waveguide, due to the incident wave resonating off the short circuit tuner and imposing the reflected wave upon the incident (shown in Figure 2.6 (a)). Adjustment of the short-circuit, allows for the maxima in field intensity to be placed directly at the centre of the sample, giving access to high heating rates and high electric field (E-field) or magnetic field (H-field) intensities as showed in Figure 2.6 (b).



Figure 2.7 *E*-field intensity within a multi-mode microwave cavity of dimensions $54 \times 52 \times 52$ mm at 2.45 GHz. ^[13]

In a multi-mode cavity, at least 2 wavelengths dimension in two axes are applied to allow for the formation of multiple modes, as showed in Figure 2.7. This type of cavity is simple to use and allows for the processing of large volumes of materials. This increase in productivity can be done by simply increasing the cavity size ^[11].

The reasons of choosing single-mode cavity over multi-mode cavity are: (a) reflected power can be obtained in the single-mode cavity (MiniFlow) which allows for a direct and quantitative comparison of power absorption between samples; (b) based on the geometry of a single-mode cavity, regions with high E-field or H-field intensity can be identified, and allows for comparison between the electric heating and the magnetic heating; (c) the formation of several modes of propagation in an multi-mode cavity can cause hot spots within samples as showed in Figure 2.7, and this will affect experimental results.





Figure 2.8 Details of the tube positioning in a single-mode microwave resonator: (i) maximal position of the E-field density and (ii) maximal position of the H-field density.

The sample positioning for heating experiments in a single mode transverse electric (TE) cavity is illustrated as showed in Figure 2.8. The position where E-field was at dominant was obtained by tuning the short circuit until the lowest reflected power was obtained (Figure 2.8 (i)). The position where the H-field was at dominant then obtained by shifting the obtained optimum E-field position by quarter of the microwave wavelength (λ_g) as showed in Figure 2.8. The MiniFlow used in this study is a standard WR-340 waveguide (4.3cm × 8.6 cm), which gives an electromagnetic field with a group wavelength (λ_g) of 174.28 mm at 2.45 GHz. ^[14] Therefore, the short circuit was shifted by 43.57 mm to allocate the sample at the position where H-field was dominated (Figure 2.8 (ii)). Because the optimum E-field position changed as the sample various due to the dielectric property of the sample, therefore, the system was tuned every time a new sample was introduced. Similarly, the procedure in determining the H-field dominated position was performed when a new sample was introduced.

However, due to the tuning process in the TE cavity, two separate tuning processes were required for the magnetic heating experiments to achieve the magnetic field dominant position. This could potentially introduce experimental errors and inconsistent results were obtained. To avoid this, a single mode TM cavity was used for the magnetic heating experiments. The physical set up of a TM cavity is shown in Figure 2.9.



Figure 2.9 Photo of the TM cavity.

In the single mode TM cavity, the maximum level of the electric field was located in the centre of the cavity. However, as the sample was inserted to the centre of the cavity without tuning, due to the differences in the dielectric property, the maximum electric field was shifted and the magnetic component of the electromagnetic field was believed to become dominant. To justify if the sample was located at the magnetic field dominant position, a simulation in predicting how the field propagates within the TM cavity was conducted.

The simulation was performed using CONCERTO, and was ran on a Lenovo Thinkpad with intel core i5-42000U 1.6 GHz processor and 8 GB RAM by Adam Dundas. The schematic of the geometry of the TM cavity was shown in Figure 2.10 with 3,000,000 cells for 30,000+5,000 iterations each. The input power used in the simulation was 100 W at 2.45 GHz. The metal part of the cavity was assumed to be perfect conductor, and the physical properties of ϵ -caprolactone used in the simulation were summarised in Table 2.1.

Table 2.1 Physical properties of ε*-caprolactone*

ε'	27.48 @150 °C
ε"	0.153 @150 °C
Heat capacity	196.8 J/mol K @20 °C
Density	1.03 g/cm^3



Figure 2.10 Schematic of the geometry of the TM cavity. Lime green shows metal, light blue shows PTFE and dark blue shows ε -caprolactone.

First, the simulation of the propagation of the E-field was performed as shown in Figure 2.11, whereas the simulation for the propagation of the H-field was shown in Figure 2.12.



Figure 2.11 E-field propagation slice taken at XY = 25 mm and XZ = -10 mm, Left: a 'birds-eye' view of the geometry, right: a side view of the geometry.

From the figures above, it was obvious that most of the E-field propagated around the inlet of the energy source, and was not propagating through the sample at the centre as shown by the dark regions at the centre of the cavity. This simulation clearly demonstrated that there were no E-field propagated within the sample in the TM cavity.



Figure 2.12 H-field propagation slice taken at XY = 25 mm and XZ = -10 mm, Left: a 'birds-eye' view of the geometry, right: a side view of the geometry.

Inspecting Figure 2.12, the simulation showed that the H-field propagated around the inlet of the energy source, as well as at the centre of the cavity where the sample located. And this suggested that a substantial amount of magnetic energy were presented within the sample when heating the sample in the TM cavity. Combining the simulation results of both E- and H-field, it showed that when performing the microwave heating in the TM cavity, the heating of the sample should primarily be magnetic heating.

A simulation of the power density within the cavity was also shown in Figure 2.13.



Figure 2.13 Power density plot for the TM cavity at XY=25 mm and XZ= -10 mm. Left: a 'birds-eye' view of the geometry, right: a side view of the geometry.

The power density figures above showed that the power density at the area where the sample located was at the highest, suggesting that the energy was focused at the location where the sample was placed.

From the simulations, it was found that the heating of the sample in the TM cavity should mainly be the magnetic heating. In order to validate the simulation with empirical observations, magnetic heating experiments comparing the heating performance of various solutions between TE cavity at magnetic dominant position and TM cavity were conducted. If similar results was obtained between heating experiments in the TE and the TM cavity, this would suggest that the heating of the sample in the TM cavity should be primarily magnetic heating.

2.1.5 Heating Experiments Using H-Field Heating in TE and TM Cavities H-field heating (HH) experiments of cyclohexanone neat solvent and cyclohexanone containing FeCl₃ were conducted to compare the heating performance between the TE and TM cavities. Identical conditions were applied to all experiments. A maximum input power of 150 W was used for all heating

experiments. The summary of temperature profiles and power profiles are shown in Figure 2.14 and Figure 2.15, respectively. The derivatives for all temperatures were less than ± 4 °C, and ± 10 W for all power readings.



Figure 2.14 Comparison of heating profile of HH experiments of cyclohexanone (cyclo) and cyclohexanone with FeCl₃ samples between TE (dot lines) and TM (solid lines) cavities.

The Figure 2.14 demonstrated the microwave magnetic heating profiles of cyclohexanone and cyclohexanone solution containing FeCl₃ when conducted in TE and TM cavity. From the graph, it was found that the temperature profiles between TE and TM were very close with differences less than 3 °C for both cyclohexanone and cyclohexanone with FeCl₃. This suggesting that although in TM cavity, the electric component is located in the centre, but the electric field shifted as sample was introduced into the system and magnetic field become dominant at this position. The relative higher bulk temperature in TM cavity. But inspecting the overall temperature profile, it can be seen that HH experiments conducted in TM cavity were identical to those were done in TE cavity.



Figure 2.15 Comparison of power profile of HH experiments of cyclohexanone (cyclo) and cyclohexanone with $FeCl_3$ samples between TE (dot lines) and TM (solid lines) cavities.

From the MiniFlow, the reading of input and reflected power can be obtained, and the difference between the two readings is the power absorbed by the sample, therefore, the amount of microwave power absorbed during the heating can be calculated as shown in Figure 2.15. The absorbed power against time plots for both TE and TM experiments followed the same trend with a difference around 10 W and 5 W for cyclohexanone with FeCl₃ and cyclohexanone, respectively. These results again suggested that the tuning for both methods were similar and thus gave similar results regarded to temperature and power profiles. Therefore, for all the HH experiments, the TM cavity was used.

2.2 Experimental Section for Chapter 3

2.2.1 Materials

Cobalt (II) chloride (98%, Aldrich), Cobalt (II) bromide (98%, Aldrich), Cobalt (II) iodide (98%, Aldrich), Iron (II) floride (98%, Aldrich), Iron (II) chloride (98%, Aldrich), Iron (II) bromide (98%, Aldrich), Iron (II) Iodide (98%, Alfa Aesar), Iron (III) floride (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) bromide (98%, Aldrich), Iron (III) chloride (98%, Aldrich), Iron (III) chloride (98%, Ilon (98%, Ilon

Aldrich), diphenyl glyoxime (98%, Aldrich), ASA (80% from synthesis), and cyclohexanone (98%, Aldrich), were used as supplied without further purification. The ASA ligands were synthesised as described in the literature ^[15, 16].

2.2.2 Reactor Geometries

All heating experiments were conducted in a Sairem MiniFlow (maximum power 200 W) microwave reactor. An optical fiber temperature sensor was introduced directly into the solution bulk *via* a septum using a cylindrical choke fitted to the reactor to arrest any microwave leakage. All heating experiments were carried out at the frequency of 2.45 GHz.

2.2.3 Dielectric Property Measurements

Samples were granulated into fine powders in order to reduce voidages within the tube during dielectric measurements. In addition, because the best compaction process could only yield samples that were about 50% dense, it should be aware that the air phase was present in the mixture as dispersed inclusions in a continuous (background) medium or environment phase. Therefore, the density of the sample powder was considered and accounted for when analysing the dielectric property of samples.

Extra care was taken to obtain similar heights and densities of samples in order to gain reproducible results. Each sample was carried out with 5 repeats. After each run, sample tubes were cleaned at least twice and placed in oven for about one hour to make sure tubes were well cleaned and dried. To make sure all results were representative, volumes of sample was measured at each set temperature. Thus, volume changes from any phase transformations were included during the dielectric property calculation. For the dielectric property measurements of dry samples, because of the hygroscopic natural of cobalt, zinc, and nickel, their halide complex can absorb moisture very quickly. This made it hard to avoid sample to absorb moisture during transferring sample into tubes. Therefore, instead of drying samples in oven then transfer to tubes, the sample was first sent to tube followed by heating to the final set temperature (220 °C) in the furnace above the cavity. The new height and volume after dried was recorded and dielectric properties were performed from high temperatures to low temperatures.

2.2.4 Synthesis of Organometallic Complexes

2.2.4.1 Synthesis of CoCl₂DMG

Cobalt (II) chloride (14.3 mg, 0.1 mmol) with dimethyl glyoxime (DMG) ligand (25.5 mg, 0.2 mmol) in a mole ratio of 1:2 were added to the selected stirred solvent (40 mL) at room temperature. After 30 min, a light green solution was obtained and used directly for heating experiments.

2.2.4.2 Synthesis of CoCl₂DPG

Cobalt (II) chloride (14.3 mg, 0.1 mmol) with diphenyl glyoxime (DPG) ligand (52.7 mg, 0.2 mmol) in a mole ratio of 1:2 were added to the selected stirred solvent (40 mL) at room temperature. After 30 min, a dark green solution was obtained and used directly for heating experiments.

2.2.4.3 Synthesis of CoBr₂DMG

Cobalt (II) bromide (35.9 mg, 0.1 mmol) with DMG ligand (25.5 mg, 0.2 mmol) in a mole ratio of 1:2 were added to the selected stirred solvent (40 mL) at room temperature. After 30 min, a light green solution was obtained and used directly for heating experiments.

2.2.4.4 Synthesis of CoBr₂DPG

Cobalt (II) bromide (35.9 mg, 0.1 mmol) with DPG ligand (52.7 mg, 0.2 mmol) in mole ratio of 1:2 were added to the selected stirred solvent (40 mL) at room temperature. After 30 min, a dark green solution was obtained and used directly for heating experiments.

2.2.4.5 Synthesis of FeCl₂ASA

Iron (II) chloride (17.8 mg, 0.1 mmol) with the ASA ligand (39.7 mg, 0.1 mmol) in a mole ratio of 1:1 were added to the selected stirred solvent (40 mL) at room temperature. A period of 30 min was given to the mixture and a colour change from yellow to light brown was observed.

2.2.2.6 Synthesis of FeCl₃ASA

Iron (III) chloride (29.7 mg, 0.1 mmol) with the ASA ligand (39.7 mg, 0.1 mmol) in a mole ratio of 1:1 were added to the selected stirred solvent (40 mL) at room temperature. A period of 30 min was given to the mixture and a colour change from yellow to dark brown was observed.

2.2.4.7 Synthesis of FeBr₂ASA

Iron (II) bromide (23.6 mg, 0.1 mmol) with the ASA ligand (39.7 mg, 0.1 mmol) in a mole ratio of 1:1 were added to the selected stirred solvent (40 mL) at room temperature. A period of 30 min was given to the mixture and a colour change from yellow to light brown was observed.

2.2.4.8 Synthesis of FeBr₃ASA

Iron (III) bromide(32.5 mg, 0.1 mmol) with the ASA ligand (39.7 mg, 0.1 mmol) in a mole ratio of 1:1 were added to the selected stirred solvent (40 mL) at room temperature. A period of 30 min was given to the mixture and a colour change from yellow to dark brown was observed.

2.2.5 Heating Experiment Procedures

The synthesised solutions described above were sent to the MiniFlow. Before conducting the heating experiment, a sacraficial solvent sample of identical volume was used for tuning the system so that maximum electric field was located at the sample position. Low input power (10-20 W) was applied to the sample to obtain a stable signal for tuning. A sliding short tuner at the back of the waveguide was slid in and out to find the location with lowest reflected power as shown in Figure 2.16. After the tuning process, the sample should be allocated at the optimised position. The position of sample was rechecked every time a new sample was introduced by observing the reflected power. Heating of the sample was achieved by positioning the tube at position of maximum E-field as described in Section 2.1.4. Each sample was repeated three times with three sets.



Figure 2.16 Sample position and tuning in a MiniFlow TE waveguide.

2.3 Experimental Section for Chapter 4

2.3.1 Materials

FeCl₃, CoCl₂, and SnCl₂ were bought from Sigma Aldrich. All samples were dried in an oven for one day before moving into desiccator for storage at room temperature. The caprolactone monomers and Benzyl alcohol were bought from Sigma without further purification.

2.3.2 Reactor Geometries

All microwave electric heating ROP reactions were conducted in a MiniFlow microwave reactor with TE cavity equipped with an OF probe thermometer. The OF probe was inserted directly into the reaction mixture for accurate and immediate temperature feedbacks.

In microwave magnetic heating ROP reactions, a MiniFlow with TM cavity was used. An OF probe was again used for temperature detection.

In conventional heating ROP reactions, a standard oil bath was used where oil temperature was controlled by a thermocouple in the oil bath. The temperature was also cross referenced to an internal bulk temperature measurement using an OF probe.

2.3.3 ROP Reaction Procedure

In a typical conventional heating (CH) ROP reaction, catalyst were weighted for specific [M]:[C] ratio (i.e. 36, 18 and 9 mg of FeCl₃ were weighted for [M]:[C] ratio of 400:1, 800:1, and 1600:1, respectively). These catalysts were then transferred into reaction vessel, which was sealed with a rubber stopper, for degasification with argon. In the meantime, Benzyl alcohol (BzOH) with C/I (catalyst to initiator) ratio of 1/5 were prepared for each catalyst load (i.e. 0.12, 0.06, and 0.03 mL of BzOH for [M]:[C] ratio of 400:1, 800:1, and 1600:1, respectively). The obtained BzOH was then mixed with 10 g of caprolactone monomers and were degassed under argon. After 10 min of degasification, monomer and initiator mixture were transferred into a reaction vessel which contained the catalyst. The vessel was then immersed in an oil bath, which was preheated to the set temperature, to start the reaction.

During the kinetic study, 0.2 mL of the sample was sampled using a syringe. The obtained sample was transferred into glass sample container and stored in the fridge at -20 °C.

Identical procedures were performed for CoCl₂ and SnCl₂. 57.2, 28.6, and 14.3 mg of CoCl₂ were weighted for [M]:[C] ratio of 200:1, 400:1, and 800:1, respectively. Conversely, 43.1, 21.5, and 10.3 mg of SnCl₂ were weighted for [M]:[C] ratio of 400:1, 800:1, and 1600:1. BzOH with [C]/[I] ratio of 1/5 were used for each catalyst load: 0.24, 0.12, 0.06, and 0.03 mL for [M]:[C] ratio of 200:1, 400:1, 800:1, and 1600:1 respectively.

In a typical microwave electric field heating reactions, a quartz tube (diameter of 3 mm) with open at the top was inserted into the rubber stopper on the sealed reaction vessel for the insertion of optic fibre (OF) thermometer before degasification. After this, identical preparation procedures as described in CH were conducted. The reaction vessel was then sent to a single mode MW cavity (Sairem MiniFlow 200SS) instead of an oil bath. The internal bulk temperature was continuously monitored using an OF thermometer inserted directly into the reaction mixture *via* the quartz tube on the stopper. The experimental set up for microwave EH reaction can be seen in Figure 2.17. In these MW experiments, the temperature measurements from OF probe was used to control the power input required to keep the bulk temperature constant at the target set point.



Figure 2.17 Experimental setup for EH reactions.

Similarly, in microwave magnetic heating reactions, the sample solution was transferred into a quartz reaction vessel (diameter 2 cm) with open at the top. The vessel was sealed with a rubber stopper where a quartz tube with an open at the top was inserted for the access of OF thermometer before degasification. After the degasification, the vessel was located in a TM cavity connected to the MiniFlow microwave reactor instead of the TE cavity used in EH reactions. The OF thermometer was inserted directly into the reaction mixture *via* the quartz tube. The experimental set up is shown in Figure 2.18.



Figure 2.18 Experimental setup for HH experiments

2.3.4 Analytical Characterisation Procedure

Gel Permeation Chromatography (GPC) GPC characterisation experiments were performed on a Polymer Labs GPC-120 instrument at 35 °C equipped with a PLgel 5μm Guard column and two PLgel 5μ MIXED-E columns in series coupled with a refractive index detector using HPLC grade THF as the mobile phase at a flow of 1.0 cm³·min⁻¹. The GPC was calibrated with polystyrene narrow Đ standards close to 1.00. All GPC equipment and standards were supplied by Polymer Laboratories (Varian). GPC data was analysed using the Cirrus GPC offline software package.

Approximately 3 mg samples were dissolved into 5 mL of HPLC grade THF. The sample vail was located on an orbital shaker with smooth circular shaking motion at 400 revolution per minute (RPM) for 30 min to make homogenous solution. The vail was then sent to GPC for analysis.

Nuclear Magnetic Resonance (NMR)

¹H NMR spectra were recorded at 25 °C using a Bruker DPX-300 spectrometer (300 MHz). Chemical shifts were recorded in $\delta_{\rm H}$ (ppm). Samples were prepared as solutions in CDCl₃ to which chemical shifts were referenced (residual chloroform at 7.26 ppm). Analysis of the spectra was carried out using ACDLABS 12 software.

The monomer conversion was determined by comparing the integral of methylene proton resonance adjacent to oxygen of the carbonyl group for the monomer (-CH2OCO-, δ =4.24 ppm) and polymer (-CH2OCO-, δ =4.07 ppm). An end group analysis can also be done to identify the degree of polymerisation (DP). It was done by comparing the integral of methylene proton resonance adjacent to the carbonyl group (Hx, δ =4.1 ppm) to that of methylene proton of benzyl alcohol (H_x, δ =5.1 ppm). The correspondingmolecular weight from NMR can then be calculated by multiplying DP with molecular weight of CL monomer.

2.4 Experimental Section for Chapter 5

2.4.1 Materials

Sn(Oct)₂ was bought from Sigma Aldrich without further purification. Fe(Oct)₃, 50 weight % (wt. %) mineral spirits was bought from Alfa Aesar. Co(Oct)₂ 65 wt.% in mineral spirits was bought from Sigma Aldrich. Both Fe(Oct)₃ and Co(Oct)₂ solutions were transfered to evaporating dish and located in vaccum oven at 35 °C for at least 2 weeks until weight of the sample remain constant. After removal of mineral spirits, the sample was collected into glass vail and ready to use in ROP reactions. The caprolactone monomers and Benzyl alcohol were bought from Sigma without further purification.

2.4.2 Reactor Geometry

All microwave electric heating ROP were conducted in a MiniFlow with TE cavity equipped with an OF temperature sensor. The microwave magnetic heating experiments were conducted using a MiniFlow with TM cavity. Comparative conventional heating experiments were conducted using a standard oil bath method where the oil temperature was by a thermocouple in the oil bath controlling the temperature of the heating fluid. The temperature was also cross referenced to an internal bulk temperature measurement using another thermometer at side.

2.4.3 Characterisation

Gel Permeation Chromatography (GPC) was performed on a Polymer Labs GPC instrument at 35 °C equiped with a PLgel guard column and two agelent PLgel mixed E columns with mixed pore size of 3µm. The GPC was calibrated with poly(styrene) narrow Đ standards ranging from 690-194400 gmol⁻¹. THF was used for providing the mobile phase at a flow of 1.0 cm³ min⁻¹. GPC data was analysed by ASTRA software.

Nuclear Magnetic Resonance (NMR) was used to identify the monomer conversion and DP of the polymerisation. ¹H NMR spectra were recorded at 25 °C using a Bruker DPX-300 spectrometers (300MHz). Chemical shifts were
recorded in δ (ppm), and were analysed using ACDLABS software. Samples were dissolved in HPLC grade CHCl₃ to which chemical shifts were referenced (δ =7.26 ppm).

2.4.4 ROP Reaction Procedure

In a typical conventional heating (CH) ROP reaction, catalyst were weighted for specific [M]:[C] ratio (i.e. 108, 54 and 27 mg of Fe(Oct)₃ were weighted for [M]:[C] ratio of 400:1, 800:1, and 1600:1, respectively). These catalysts were then transferred into reaction vessel, which was sealed with a rubber stopper, for degasification with argon. In the meantime, Benzyl alcohol (BzOH) with C/I (catalyst to initiator) ratio of 1/10 were prepared for each catalyst load (i.e. 0.24, 0.12, and 0.06 mL of BzOH for [M]:[C] ratio of 400:1, 800:1, and 1600:1, respectively). The obtained BzOH was then mixed with 10 g of caprolactone monomers and were degassed under argon. After 10 min of degasification, monomer and initiator mixture were transferred into a reaction vessel which contained the catalyst. The vessel was then immersed in an oil bath, which was preheated to the set temperature, to start the reaction.

During the kinetic study, 0.2 mL of the sample was sampled using a syringe. The obtained sample was transferred into glass sample container and stored in the fridge at -20 °C.

Identical procedures were performed for Co(Oct)₂ and Sn(Oct)₂. 76, 38, and 19 mg of Co(Oct)₂ were weighted for [M]:[C] ratio of 400:1, 800:1, and 1600:1 respectively. Conversely, 91.4, 45.7, and 22.9 mg of Sn(Oct)₂ were weighted for [M]:[C] ratio of 400:1, 800:1, and 1600:1.

2.5 Summary

In this chapter, the analytical techniques in characterising the polymer product were introduced. The fundamental for techniques used in dielectric property characterisation were also summarised. Detailed descriptions in conducting experiments in E-field and H-field dominant positions were included. Additionally, a TM cavity was used for the HH experiments. In order to prove that the heating in the TM cavity was primarily HH, simulations and heating experiments were conducted, and found that the heating of the sample in the TM cavity was mainly HH.

The sample preparations and experimental procedures for experimental works conducted in each chapters were also included in this chapter. Details for dielectric properties measurements, heating experiments, synthesises of polymer, analytical procedures for characterising the polymer were also provided.

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Chapter 3 Investigation and Comparison of the Dielectric Property of Metal Halide and Organometallic Catalysts

3.1 Aim and Objective

This chapter identifies the dielectric properties of simple metal halides and organometallic containing various metal centre. The dielectric property measurements were conducted in solid powders forms and later were measured after dissolving in a solvent (cyclohexanone). From the dielectric property measurements, the predictions of how these solutions would be heated by microwave can be made. Therefore, series of heating experiments of these solutions were conducted using a single mode microwave reactor (MiniFlow). From the heating experiments, the predictions from dielectric property measurements can be justified.

3.2 Introduction

In microwave heating (MWH), materials within the electromagnetic (EM) field tend to rotate with the alternating field. This response can be quantified in the term called "dielectric property" which defines the ability of the material to both: interact with/store energy from such alternating field in the case of dielectric constant, ε ', and then convert an amount of the stored energy into heat in regards to the dielectric loss factor, ε ''. As the dielectric properties predict the ability of a material interacts with the EM field, it is essential to identify the dielectric properties of materials involved in a typical process to establish a basic understanding of the heating behaviour of the materials. The dielectric properties vary with temperature and frequency; thus it is vital to understand the variation in the dielectric properties across a broad range of conditions to fully characterise the behaviour of the materials in an applied EM field. Similarly, in a chemical reaction, the physical state, chemical composition, and temperature of the system can change, so it is important that considerations of experimental conditions need to be taken into account when carrying our dielectric property measurements (i.e. temperature, pressure, material concentrations).

In this chapter, dielectric property measurements of three different metal based powder materials were performed which were cobalt (II), iron (III), and tin (II), both in their inorganic halide form and organic liganded organometallic form. As these complexes were dissolved in monomer to participate polymerisation reactions as a catalyst, a mixture of the complex with a solvent were also carried out in order to understand the interactions between the EM field and metal catalysts when dissolved in a solvent. In a typical organic liganded organometallic complex, organic ligands were attached to the metal centre. To identify how organic ligands affect the organometallic omplexes regarding the response of an applied EM field, organic ligands were measured when on their own, mixed with a solvent, and attached to a metal centre. Additional to the dielectric property measurements, MW heating experiments using the identical molar concentration were conducted to justify the prediction from the dielectric property measurements, and to compare the heating behaviour between each sample.

3.3 Results and Discussion

In this section, plots of dielectric property measurements and TGA results against temperature for various cobalt halides were shown. The relationship between the dielectric property and factors such as temperature, frequency, physical properties, and molecular structures were also identified.

3.3.1 Dielectric Property Measurements for Cobalt Complexes

3.3.1.1 Hydrated Inorganic Cobalt Halides

The metal halides system containing cobalt metal centre were first investigated. The hydrated cobalt halides include CoCl₂, CoBr₂, and CoI₂. The dielectric constant and loss factor of these samples were measured at a frequency of 2470 MHz, because this is the frequency most close to the ISM (industrial, scientific and medical use) frequency. The plots of the dielectric properties of these samples were shown in Figure 3.1, Figure 3.3, and Figure 3.5, and the corresponding TGA plots showing sample weight against temperature were shown in Figure 3.2, Figure 3.4, and Figure 3.6. All derivatives of the dielectric constant were below 3%, while all derivatives of the loss factor were below 5% of the average value.



Figure 3.1 Dielectric properties of CoCl₂.



Figure 3.2 TGA reading for CoCl₂.

The dielectric property measurements and TGA readings of CoCl₂ were shown in Figure 3.1 and Figure 3.2. The dielectric constant and loss factor increased gradually as the temperature rose till 140 °C where both dielectric constant and loss factor reached a maximum and began to decline. Two peaks for loss factor at 100 and 140 °C was also observed, this was due to the bonded water of crystallisation left the metal centre as the temperature increased. Thus these water molecules were able to rotate freely to follow the alternating field. These free water were detected by the cavity and increment in the loss factor were observed. From TGA readings, mass losses were found to be significant at around 90 and 140 °C where two peaks in the derivative weight were observed, this increment in weight derivative indicated that the mass of the sample was reduced significantly at these two temperature ranges due to the loss of free water and bound water, respectively. It can be observed by the colour change of the sample that changed from light pink (colour of hydrated sample) to blue (colour of anhydrous sample). This confirmed the observation of increment in the loss factor was due to the loss of water of crystallisation.



Figure 3.3 Dielectric properties of CoBr₂ at 2470 MHz.



Figure 3.4 TGA reading of CoBr_{2.}

The dielectric property measurements of CoBr₂ were shown in Figure 3.3 along with a TGA data showed in Figure 3.4. The hydrated CoBr₂ was a dark purple coloured solid sample at room temperature. Both dielectric constant and loss factor increases dramatically after 40 °C as it turns into liquid form at around 45 °C. The sample colour changed into dark blue. The increment in dielectric properties was a two-step growth with the first peak at 60 °C and a second peak at 140 °C. After 140 °C, the dielectric properties started to drop as most coordinated waters was evaporated. CoBr₂ turned into light green solid form at around 175 °C. A similar trend was also obtained in the TGA reading where the mass loss rate was at its maximum at around 60 and 140 °C due to the loss of the

free water and the bound water, respectively. A 35% mass loss was obtained at 220 °C; this was equivalent to around 6 moles of water molecules per mole of CoBr₂ sample.



The dielectric property measurements and TGA results of CoI₂ were presented in Figure 3.5 and Figure 3.6. Similar observations to the CoBr₂ were obtained in both the dielectric properties and TGA readings. The dielectric constant and loss factor increased dramatically after 40 °C and reached the maximum between 120 and 140 °C, followed by a drop till 160 °C where sample became anhydrous based on TGA results. Both dielectric constant and loss factor then remained

constant up to 220 °C. However, unlike CoBr₂, there were no observations of transformation from solid to liquid. Therefore, there were no abrupt changes in dielectric property across the temperature range. The mass of sample underwent a constant decreasing with high mass loss rates at around 80 and 140 °C as a result of the loss of free water and bound water.

In the above results, free water and bound water were noticed for all samples. Free water is moisture exist in the sample. However, bound water is water molecules that stick at boundaries to hydrophilic surfaces of the cobalt molecules. The orientation and rotational polarisation of these bound water were hindered to a lesser degree. As a result, these adsorbed water molecule did not respond to the alternating electromagnetic field, and its dielectric property was considerably less than that of water molecules in liquid form. ^[1] Therefore, as the bound water becomes free water and started to leave the system at a higher temperature, it enhanced the dielectric response of the sample as the orientation and rotation of water molecules were no longer hindered (details will be further discussed in Section 3.3.1.4).

A table summarising the dielectric properties at room temperature and final temperature were shown in Table 3.1. The notable temperature showed in the table was obtained from TGA readings. Also, the dielectric constant and the loss factor for all samples undergo various degrees of changes at these notable temperatures as shown in previous graphs. However, it should be emphasised that CoBr₂ and CoI₂ are very hygroscopic and tend to absorb water molecules from surroundings. In a typical TGA measurement, samples will be held for up to 20 min; this could cause a greater level of water presences in TGA readings.

Sample	Notable temperature	Dielectric properties at 20 °C		Dielectric properties at 220 °C	
		ε'	ε"	ε'	ε"
CoBr2 5.8H2O	Melted at 45 °C 80 °C lose 1.3 mol water; 180 °C became anhydrous	5.45	1.256	3.859	0.00517
CoCl ₂ 0.7H ₂ O	100°C lose 0.24 mol of water; 160 °C became anhydrous	2.90 0.0019		2.938	0.0019
CoI2 4.9H2O	100 °C lose 1.1 mol of water; 200 °C became anhydrous	4.39	0.04	4.37	0.068

Table 3.1 Summary table of the dielectric properties at initial and final temperature.

It can be seen that although the dielectric properties change significantly after the water of crystallisation became free water, but once all the water evaporated from the sample, the dielectric properties became identical as which when it was in solid form. This change in dielectric property could be due to (a) presence of water molecules that provided an additional physical form to the sample and dissolved the sample which made it freer to interact with the EM field. (b) Transformation of cobalt halides from a solid form to solvated form, this provided a greater degree of freedom in molecular rotation and would be similar to the condition they were presented during a reaction. This would be further explained in the following sections.

3.3.1.2 Relationship Between the Dielectric Properties and the Physical State It was noticed that during the heating of CoBr₂, the sample turned into the liquid form at around 45 °C. This was due to the water of crystallisation became free water that converts CoBr₂ sample into CoBr₂+water solution. In the meantime, both dielectric constant and loss factor underwent a dramatic growth. This could potentially be due to the fact that in solid form, the molecular movement was restricted due to the presence of relatively strong intermolecular force, and hence the molecule was unable to align with the alternating electric field significantly. ^[2] Therefore, only the electronic and the ionic polarisation could contribute to the overall polarisation when the sample was presented in the solid form. ^[2] However, as the sample melted into liquid form, molecules were capable of moving more freely due to the weaker intermolecular restriction force. As a result, the degree of the ionic polarisation and electronic polarisation was expected to increase to give a greater dielectric constant. Also, once the sample was transferred into liquid form, the orientation polarisation started to participate to the total polarisation. Thus, resulted in better interactions between molecules and the electromagnetic field, and increased the dielectric constant. ^[2] At the same time, due to the presence of a force exerted by adjacent molecules, the attempted alignment with the electric field was not perfectly in phase. This gave rise to heat losses due to intermolecular friction within the material so as the loss factor. ^[3] Therefore, the samples in liquid form were expected to show greater values in the dielectric constant and the loss factor.

The reduction in the dielectric properties after 120 °C in the CoBr₂ sample could result due to the loss of the coordinate water which in turn reduced a number of polar molecules presented in the sample. This could also be due to the prohibition of the reorientation of molecules from the chaotic oscillation at high temperature. The chaotic oscillation became significant as temperature rise; this reduced the degree of orientation to align with the alternating field. Therefore, molecules were less likely to change its orientation to align with the shifting field.^[4] Additionally, the reduction in loss factor could also relate to the decreasing in viscosity resulted from rising temperature. This was because that friction between rotating molecules and surrounding environment were expected to reduce as well. Thus, the ability to generate heat from friction was reduced so as the loss factor. ^[3]

3.3.1.3 Relationship Between Dielectric Properties and Temperature From the dielectric property measurement plots showed in the results section,

the dielectric constants for all solid samples (except CoBr₂ which turns into a liquid at 48 °C) tends to increase as temperature rises. However, as samples reached a certain temperature, the dielectric constants started to decrease as the temperature increased gradually. This could be due to the change in the ionic polarisation since these samples were bonded by the ionic bonding between the metal centre and two ligand atoms. In these ionic solids, the dielectric constant arised from the shift of ions, which gives rise to ionic polarisation, was more significant than the electronic shift that causes electronic polarisation. ^[2]

As previously mentioned, this kind of polarisation was due to the applied field displacing cations in one direction and anions in the opposite direction, which gives rise to a net dipole moment. ^[5] As temperature rises, the dielectric constant of an ionic solid tends to decrease due to the reduction in the number of molecules per unit volume as the sample expands. However, at the same time, the greater separation of ions produced by the increase in volume weakened the force between them, thus increased their ease of displacement and the ability to be polarised by the ionic polarisation. ^[2] The following gradual decreasing in dielectric constant at a higher temperature may result from the chaotic thermal oscillations of molecules. Although the energy required for displacing ions was reduced at high temperature, in the meantime, the energy required for ions to follow the alternating field was raised due to chaotic thermal oscillations. Therefore, the displacement of ions was prohibited and could no longer contribute to the overall polarisation, leading to a drop in the dielectric constant. ^[3]

However, the increment and reduction in dielectric constant could also be related to the presence of coordinated water (i.e. CoI₂). Because the dielectric constant of water was high (ε'_{water} =78 at 25 °C at 2.45 GHz⁷²). Thus the moisture content may significantly affect the overall dielectric constant of the sample. Also, as coordinated water evaporates, reduction of dielectric constant was also expected. This would be further discussed in the next section.

3.3.1.4 Effects of Coordinate Water on the Dielectric Properties

High water contents were noticed in various samples except CoCl₂ and FeBr₂. This was because of the hygroscopic nature of cobalt. ^[4] The presence of free water and bound water could influence the dielectric properties significantly due to its high dielectric constant and loss factor ($\varepsilon'_{water} \approx 78$, $\varepsilon''_{water} \approx 10$ at 25 °C at 2.45 GHz ^[6, 7]). Therefore, a large dielectric constant and loss factor was obtained for CoBr₂ (CoBr₂ 5.8H₂O $\varepsilon' = 5.45$, $\varepsilon'' = 1.256$), CoI₂ (CoI₂ 4.9H₂O, $\varepsilon' = 4.39$, $\varepsilon'' = 0.04$). In solid form, the presence of a polar structure of coordinated water contributed to the enhancement in dielectric constant. Due to strong restrictions in solid samples and strong bonding with metal atoms, the water molecule could not rotate with the alternating field to provide reorientation polarisation.



Figure 3.7 Dielectric properties of CoI₂.





From dielectric property measurements and TGA reading plots showed in the results section, it was noticed that when samples mass loss rate was high, a slight increase in dielectric constant and a peak in loss factor was observed as showed in Figure 3.7 and Figure 3.8 as an example. Among these samples, CoI₂ were found to have an abrupt change in the dielectric properties without phase transformation when sample lost mass. The tanð of the CoI₂ was found to increase from 0.01 to 0.3 as it started to lose mass, which then dropped back to 0.01 after the mass loss. The observations showed that when the temperature was sufficiently high to release the adsorbed water, the bound water was activated

and became free water, which then started to participate in microwave interaction as it evaporated. The released bound water became free water.

The increment in the dielectric properties could also be caused by the formation of vacancy or disorder within solid material due to evaporation of water. For metal halide presents in MX₂ structure, it occurs as strongly bonded twodimensional X-M-X layers with weak interlayer coupling. ^[8] Therefore, the evaporation of water could cause disorder between different layers due to weak interlayer forces. The transition of samples from order to disorder solid cause greater mobility and separation of ions which further enhances ionic polarisation and dielectric constant. ^[2] The following decreasing in dielectric constant and loss factor were due to loss of free water. After all the coordinated water was vaporised, dielectric constants and loss factors dropped to values similar to which before the formation of free water.

The above observation was similar to results obtained from Hu and Cheng ^[9, 10] who concludes the selective heating of catalyst was due to the selectively heating of the coordinated water attached on the catalyst. Therefore, when heating metal halides with the microwave irradiation, instead of selective microwave heating on metal halides, it could be that the coordinated water was selectively heated and then transfers the thermal energy on to the surface of metal halides.

3.3.1.5 Effects of Chemical Structure on the Dielectric Properties

A colour change was observed when the CoBr₂ melted into liquid form. The colour of the CoBr₂ was purple when it was in solid form, but changed to dark blue when it transferred into a liquid state. The colour change was caused by the change in chemical structure of CoBr₂.



Figure 3.9 Chemical structure of CoBr₂ hexahydrate. ^[11]

The colour observed for CoBr₂ was associated with electrons in d-orbitals. The electron configuration of cobalt ion was [Ar] 3d7 with 7 electrons in the d-orbital that will be located to $t_{\rm 2g}$ and $e_{.g.,}$ orbital. $^{[12]}$ The structure of solid CoBr_2 hexahydrate was found to have Co ion being octahedrally coordinated by four equivalent water molecule O atoms and two equivalent Br ions (as showed in Figure 3.9), while having another two water molecules present as free water.^[13] Because of the weak ligand field of bromide and coordinate water, the energy of transferring an electron from t_{2g} orbital to e.g., orbital was lower than paring electrons in a single occupied orbital. Thus cobalt electrons in d-orbital would occupy $t_{2g} \mbox{ and } e_{.g.,}$ before paring with other electrons in a single orbital. As a result a high spin state was obtained for CoBr₂.^[8] Therefore, the cobalt ion will have two paired electrons and three unpaired electrons in the d-orbital as shown in Figure 3.10. According to crystal field theory, as the Br and O ion attached to the cobalt ion, repulsion between the lone pairs of attaching ions and the metal electrons affectd the metal d orbitals and caused an energy difference between the sets of d orbitals. This energy difference was comparable to the energy of visible light. Therefore, a purple colour was observed in solid CoBr₂. ^[12]



Figure 3.10 Spin state diagram of CoBr₂.

However, as CoBr₂ melted, the water of crystallisation transferred into free water. Thus the number of water molecules bonded to cobalt ion was reduced. Thus the energy differences in d orbital changed and caused a change in colour. It was found that when the CoBr₂ was presented in octahedral structure, it showed a purple to pink colour. When it was in tetrahedral structure, a blue colour was observed. ^[14] In solid form, the bond angle of Br-Co-Br was found to be 180°, O-Co-O (angle between water of crystallisation in opposite direction) was 180°, and the Br-Co-O (angle between water of crystallisation and bromide) was about 90°, therefore, the symmetrical octahedral structure resulted in a relatively low dielectric properties. ^[13] However, when the structure changed to tetrahedral, its asymmetry further enhanced the reorientation polarisation of CoBr₂. ^[15, 16] Therefore, the rise in the dielectric properties of CoBr₂ after it meltd could also relate to the transformation from the symmetrical octahedral structure into the asymmetrical tetrahedral structure as it lost the water of crystallisation.



Figure 3.11 FT-IR spectra of CoBr₂.

To verify the structure transformation resulted from the loss of coordinate water rather than loss of bromide ion from ligand substitution, FT-IR spectra were performed for CoBr₂ at various temperatures (50, 90, 150 and 190 °C) as shown in Figure 3.11. The band at 1600 cm⁻¹ corresponded to the cobalt-bromide bond. ^[11] The area under the curve was found to be similar at different temperatures. Thus the bond between cobalt and bromide was not broken during heating, and the transformation to the tetrahedral structure was related to loss of bonding between the cobalt atom and the oxygen atom from the water of crystallisation. The peak at 700 cm⁻¹ for results of 50, 90 and 150 °C was related to the cobalt-oxygen bond, which could be due to the presence of cobalt oxide and also Co-O bonding from the water of crystallisation. The CoBr₂ was bought with 99% purity as previously mentioned. Thus the amount of cobalt oxide should not over 1%. It was found that the area under the curve at 700 cm⁻¹ was obtained to be greater than 1% (for 50, 90, and 150 °C readings), so the peak also included the presence Co-O bond between cobalt and water of crystallisation. However, peaks at 650 and 750 cm⁻¹ for the 190 °C reading were related to the presence of cobalt oxide. ^[18]

3.3.1.6 Anhydrous Cobalt Halides

The dielectric properties of all anhydrous samples were presented in Table 3.2. Because no abrupt changes in the dielectric properties were observed, plots of the dielectric properties were not presented here. All derivatives of the dielectric constant were below 3%, while all derivatives of the loss factor were below 5% of the average value.

Sample	Dielectric properties at 20 °C		Dielectric properties at 220 °C		
	ε'	ε"	ε'	ε"	
CoCl ₂	2.77	0.0017	2.75	0.0018	
CoBr ₂	3.57	0.002	3.80	0.00318	
CoI ₂	4.04	0.013	4.37	0.068	

Table 3.2 Summary of dielectric property of anhydrous samples.

Comparing Table 3.1 and Table 3.2, significant reduction in both the dielectric constant and the loss factor were noticed after samples were dried. The loss factor for all anhydrous samples was found to be one order of magnitude smaller compared to hydrated samples. It was also observed that the presence of water of crystallisation enhances a dielectric property of cobalt halides in both solid and liquid form, the extent of this influence depended on the degree of hydration of the cobalt halide. It was also worth mentioning that for anhydrous samples, no abrupt change in the dielectric properties was observed across the whole temperature range. Therefore, this suggests that the significant change in the dielectric properties of bound water to free water and loss of free water.

Comparing the dielectric properties of anhydrous samples containing different halides, it was found that the attached halide could potentially affect the cobalt halide in interacting with the alternating field. Also, it was found that the size of halides affected the dielectric properties significantly (dielectric constant $\varepsilon'_{CoCl_2} < \varepsilon'_{CoBr_2} < \varepsilon'_{CoI_2}$ follows the trend of size of halide Cl (167 picometer (pm)) < Br (182 pm) < I (206 pm)). ^[19] This was because the increase in halides size reduces the charge density on the halide which further reduces the electronegativity of the halide (electronegativity of halide: Cl(3.16) > Br(2.96) > I(2.66).^[19] The ionic bonding between metal and halides depended on the electronegativity between ions with opposite charges. Thus, the reduction in electronegativity lowered the binding force between ions with opposite charges. As previously discussed, the ionic polarisation relied on the motion between cations and anions; the less binding force between them allowed them to move more freely with the alternating field. The reduction of electronegativity and the growth in halide size also influenced the bond length and the electron attraction. As the bonding force between oppositely charged ions reduced, the ions would be more separate and further increases degree of freedom of ions, which in turn enhanced the ionic polarisation of the cobalt halide. Therefore, growth in dielectric constant should be expected as ligand size increases (CoCl₂<CoBr₂<CoI₂).

3.3.1.7 Organic Ligands for Cobalt Based Catalyst

Dimethyl glyoxime (DMG) and diphenyl glyoxime (DPG) are two common organic ligands that are attached to cobalt halides to form an organometallic catalyst. To identify how the attachment of organic ligands to the cobalt halides affected the dielectric property of the catalyst, the dielectric property of organic ligand on its own was measured. All derivatives of the dielectric constant were below 3%, while all derivatives of the loss factor were below 5% of the average value.



Figure 3.12 Dielectric properties of dimethyl glyoxime at 2470 MHz.



Figure 3.13 TGA result for dimethyl glyoxime.

Figure 3.12 and Figure 3.13 showed the dielectric property and TGA results for dimethyl glyoxime (DMG). The loss in weight was due to the decomposition of the organic ligand from 90 °C. As a result, the dielectric property dropped as the mass of the sample reduced.



Figure 3.14 Dielectric properties of diphenyl glyoxime at 2470 MHz.



Figure 3.15 TGA result of diphenyl glyoxime.

From Figure 3.14 and Figure 3.15, the results for dielectric property and TGA readings of diphenyl glyoxime (DPG) were shown. Similar to DMG, as DPG started to decompose after 90 °C, a drop in dielectric property was observed.

Comparing the dielectric property between DMG and DPG, DPG had a relatively higher dielectric constant and loss factor than DMG. The dielectric constant was up to 2%, and the loss factor was up to 60% greater for DPG. This could be due to the replacement of methyl groups to cyclic phenyl groups that were attached to the ligand. This provided additional electrons to the ligand, and

therefore, was better in interacting with EM field and converting the energy into heat.

In the results, reduction in both dielectric constant and loss factor was also noticed as the sample started to decompose. When DMG and DPG decomposed, the main decomposed products were NO and additional CO/CO₂ for DPG ^[20]. These gas phase producted leave the system as soon as they were generated.

3.3.2 Different Approach in Identifying the Dielectric Properties of the Cobalt Complexes

In a typical chemical reaction, metal halides or organic ligands would be dissolved into the bulk solvent/monomer. In this case, the dielectric property obtained from solid powder samples would not be representable. As discussed previously, the physical formation of the sample had significant effects on the dielectric properties because the degree of freedom in rotation and orientation could be affected significantly. Therefore, it may have significant different dielectric properties when solvated by solvent molecules as they were more free to interact with the EM field.

Thus, additional dielectric properties were carried out with these samples after mixed with a solvent. Cyclohexanone was chosen as the solvent because it provided high solubility for samples used in this study, without possessing strong response to MW. A strong MW absorbent solvent could experience fast MW heating, and any selective heating on the catalysts could be masked^[20, 21]. Additionally, the highly absorbent solvent could attenuate the EM field and limited the MW energy that could be absorbed by the catalyst. In a less MW absorbent solvent, the selective heating of the catalyst was related to its relaxation process within the solvent.



Figure 3.16 Molecular structure of a) Cyclohexanone, b) ε -Caprolactone.

The other advantage of using cyclohexanone was that it had a similar chemical structure as ε -caprolactone (which will be the monomer for polymerisation reactions in next two Chapters) without the ability to be polymerised. Thus, the dielectric property measurements could be safely taken without the introductions of newly formed polymer chains. From Figure 3.16, the structure of cyclohexanone consists a six carbon cyclic molecule, whereas caprolactone has a cyclic ring with 6 CH₂ groups and an oxygen atom in it, both rings also have a ketone function group. Therefore, it was expected that solute would experience similar intermolecular interactions when present in Cyclohexanone and ε -Caprolactone.

3.3.2.1 Cobalt Halides

An assessment of dielectric properties of cyclohexanone and mixtures of this solvent containing the cobalt halides was conducted to aid in understanding/predicting the interactions between EM field and the materials within these multi-component solutions. The plots of dielectric constant and loss factor were shown in Figure 3.17. All derivatives of the dielectric constant and loss factor were below 5% and 8%, respectively, while all derivatives of the tanð were below 8% of the average value.



Figure 3.17 Plot of the temperature dependence of dielectric constant (ε ') and loss factor (ε '') of cyclohexanone (cycloh) and a mixture of different cobalt halides.

From Figure 3.17, inspection of the results in ε ' suggested that all cobalt halides exhibited very similar interactions with EM field regarding the energy that can be stored in their structure across the full temperature range. The trend in ε ' with temperature revealed that the total polarisation of all the samples/mixtures was dominated by the presence of cyclohexanone with the catalyst and precursors having only a minor effect, which was attributed to the very small amounts of cobalt halides present in the mixture. By contrast, higher ε '' value were obtained when cobalt halides were added to the solvent (up to 14% for CoI₂, 8% for CoBr₂, and 4% for CoCl₂). The behaviour of ε '' indicates that the presence of the cobalt halides (even in a small amount) contributed to the total amount of the stored energy that can be converted into heat in the samples/mixtures. The CoI₂ had the highest ε '' value suggests that it had the best efficiency in converting the energy into heat. This again agrees that the greater size of the cobalt halide enhanced intermolecular frictions/interactions with the medium, and thus resulted in higher MW heating efficiency.

Comparison of the tan δ values were also presented in Figure 3.18. This predicted the relative capability of the materials contributed to the heating of the medium when introduced to an EM field.



Figure 3.18 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of different cobalt halides at a concentration of 240 ppm.

Figure 3.18 summarised the tan δ of different cobalt halides when mixing with cyclohexanone. The tan δ of solvent/cobalt halide mixture follows the similar trend as which of cyclohexanone across the whole temperature range. Closer

inspection of the data showed that both CoBr₂ and CoI₂ produced measureable increases in tan δ even at this low concentration (240 ppm). Conversely, CoCl₂ showed an almost identical tan δ value as cyclohexanone. Comparing the tan δ of cobalt halide mixtures to the solvent, the additional cobalt halides raised the tan δ value up to 9% for CoI₂, 6% for CoBr₂, and 2% for CoCl₂, respectively. Again, the result agreed with the previous hypothesis that the greater size of the cobalt halide provides enhancement in dielectric response. This could be due to (a) greater polarity within the molecule producing additional dielectric interactions; (b) greater chance of intermolecular interactions with surroundings. Therefore, adding cobalt halides could potentially enhance the solution's overall ability to interact with MW energy and so undergo stronger microwave heating (MWH).

3.3.2.2 Organic Ligands

Similar to the previous section, organic ligands were mixed with the selected solvent were conducted. Results of tanð, dielectric constant, and loss factor were summarised in Figure 3.19 and Figure 3.20. All derivatives of the dielectric constant and loss factor were below 5% and 8%, respectively, while all derivatives of the tanð were below 8% of the average value.



Figure 3.19 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of different organic ligands at a concentration of 240 ppm.

Figure 3.19 summarised the comparison between tano value for the solvent and solution with DMG and DPG ligands. In general, the addition of DPG had a greater enhancement in tano of the solution (up to 4%) comparing to DMG (up to 2%). Inspecting details in dielectric constant and loss factor (shown in Figure 3.20), both DMG and DPG exhibited identical ε ' across the temperature range (less than 2% differences), whereas, the ε '' value had greater differences for DPG (5%) than DMG (3%). This enhancement in dielectric property of DPG could be due to the additional cyclic phenyl ring that was attached to the ligand as discussed in Section 3.3.1.7.



Figure 3.20 Plot of the temperature dependence of dielectric constant (ε ') and loss factor (ε '') of cyclohexanone (cycloh) and a mixture of different organic ligands.

Although differences were observed in tano results when DMG and DPG were added to the solvent, the differences were not as significant as which of the cobalt halides. Therefore, if both organic ligand and cobalt halide were presented in a solution, it was expected that the cobalt halides would experience strong MW selective heating than the ligand.

3.3.2.3 Cobalt Organometallic Complex

After the dielectric property of the cobalt halides and organic ligands were examined, the next step of this study was to identify the dielectric property of the organometallic that was synthesised with the cobalt halides and the ligands. These cobalt organometallics were used as catalysts in Catalytic Chain Transfer Polymerisation (CCTP).

Currently, the most frequently cited of these cobalt CTA's is bis-[(difluoroboryl) diphenylglyoximato] cobalt (II) (PhCoBF), because it exhibits the best balance between activity and stability. However, it is synthesised in a two-step process that is not highly atom efficient. The first step involves the reaction of two-mole equivalents of the diphenylglyoxime (DPG) ligand with cobalt (II) acetylacetonate to form cobaloxime which contains two bidentate DPG ligands (See Figure 3.21, structure (a)).



Figure 3.21 Molecule structure of: (a) Cobaloxime with DPG ligands, (b) Cobaloxime with DMG ligands, (c) PhCoBF, (d) CoBr₂DPG₂ (e) CoBr₂DMG₂.

This procedure has also been reported with the dimethylglyoxime (DMG) version of the ligand (as shown in Figure 3.21, (structure (b))) and both of these products have been shown to be active CCTP catalysts in their right. However, they are sensitive to being deactivated by oxidation and hydrolysis. The second step involves reacting this step 1 product with boron trifluoride diethyl etherate (BF.OEt₂) to generate a single tetradentate ligand as shown in Figure 3.21, (structure (c)) ^[22, 23]. This enhances the complexes' stability towards oxidation and hydrolysis and allows it to be handled readily in the air in solid form. However, the yield from this second stage was typically only in the region of 40% and so requires purification stages to be added to the manufacturing process, increasing both the cost and the environmental footprint of the process ^[24].

Consequently, Kevin *et al.* (2013) had investigated the synthesis of alternative catalysts that were more economically and higher catalytic efficiency. They had reported a successful adaptation of the existing PhCoBF synthesis, which generated the cobalt halide/glyoxime catalyst of the type shown in Figure 3.21 (structure (d)) ^[25]. Similarly, an alternative catalyst with DMG ligands was also synthesised (as shown in Figure 3.21 structure (e)). The bromide member of this family had been shown to demonstrate levels of activity and stability similar to those of PhCoBF, but it was synthesised using a single step and without the need to be ring closed to achieve the greater level of stability. Thus, this catalyst was significantly more atom efficient, sustainable and potential industrial applicable than PhCoBF. Furthermore, adopting a single stage process could potentially enable the use of in situ catalyst manufacture and continuous flow processing. By doing so would further increase the sustainability and intensification of the process, because it reduced waste by; (a) removing the catalyst pre-preparation

process form the overall manufacturing cycle, (b) eliminating catalyst deactivation during storage and (c) minimising inter-batch cleaning of the polymerisation.

From previous sections, it was hypothesised that providing additional dipole and size to the cobalt halide may lead to an increase in the dielectric properties of the bulk system that contains the substance. By attaching different ligands to the cobalt centre, the size and dipole present on the catalyst may vary, and different results may be observed between different catalysts. Therefore, by studying the dielectric property of different cobalt organometallics listed above, it could assess how the selective heating changes as the ligands coordinated to the cobalt centre are modified. Thus developed a fundamental understanding and prediction about how MWH can be influenced by these transformations and enabled the design of improved catalyst structures which maximised the benefits of MWH.

The *in situ* catalysts was synthesised by mixing CoBr₂ and the chosen ligand with cyclohexanone which was then directly used for dielectric property measurements. Figure 3.22 details the trend in the tanδ values for the cyclohexanone solvent and mixtures of solvent and catalyst/precursor over the temperature range from 20 to 120 °C. All derivatives for the dielectric constant and loss factor were below 5% and 8%, respectively, while all derivatives of the tanδ were below 8% for the average value.



Figure 3.22. The plot of the temperature dependence of tand of cyclohexanone (cycloh) and cyclohexanone solutions of different organometallic catalysts at a concentration of 240 ppm.

From Figure 3.22, it was observed that tand value for all samples follows similar behaviour before 60 °C that the tan dropped as temperature raise. In all cases, the addition of the organometallic complexes to cyclohexanone produced measurable increases in tand even at this very low concentration. Furthermore, above 65 °C the values of tan of the solution containing the organometallic additives were noted to exhibit increased deviation from both: (a) the behaviour of the solvent and solvent ligand mixture and (b) from one another. This demonstrated that all the organometallic precursors should undergo selective MWH at these low concentrations and potentially contribute to the heating of these mixtures and the promotion of a chemical transformation within that medium. Furthermore, the influence that specific cobalt complexes would potentially be more differentiated above 65° C, where the magnitude of the tan δ value between the various metal containing additives was noted to be greater. Inclusion of the organic liganded catalysts raised the tan δ values to a greater extent (up to 80% for CoBr₂DPG₂, 55% for PhCoBF, 30% for CoBr₂DMG₂ where these figures are the increases relative to the value exhibited by the solvent

alone) than did the cobalt halide precursors (up to 6% for $CoBr_2$ found in Section 3.3.2.1).

These data supported the initial hypothesis that adding these organically liganded metal catalysts into a solvent should enhance the solutions' overall ability to interact with EM energy and so undergo stronger MWH. This was attributed to the combination of increased solvation of the metal centre and the introduction of additional dipoles into the structure upon the addition of the organic soluble ligands. A greater tand value was found when comparing between CoBr₂DMG₂ and CoBr₂DPG₂. This agrees with the previous hypothesis that replacing methyl groups with larger phenyl groups enhances the efficiency in converting MW energy into heat. Thus, this proposes that the phenyl functionality must produce greater solvation and a greater level of dipole/EM field interactions within the DPG ligand, which leads to the phenyl complexes outperforming the methyl version. By comparing CoBr₂DPG₂ and PhCoBF, the data also supported the proposal that different ligand structures affected the dielectric properties to different levels because the tand of bidentate CoBr₂DPG₂ was indeed shown to be greater than that of the more rigid tetradentate molecular structure of PhCoBF. This effect was linked to the fact that the coordinated CoBr₂DPG₂ /cyclohexanone structure was more flexible and so the dipoles in the structure were freer to align with the E-field orientation of the EM energy. Thus the response of an organometallic material to EM field clearly determined by a number of key molecular factors.


Figure 3.23. The plot of the temperature dependence of dielectric constant and loss factor of cyclohexanone (cycloh) and a mixture of different catalysts.

Inspection of results in ε ' in Figure 3.23, suggested that all samples possessed similar ability in storing MW energy from EM field across the full temperature range. However, the ε '' value showed similar trends to that of tan δ , especially after 60 °C where significant differences were noted. The behaviour of ε '' indicates that the presence of the organometallic species (even in small amounts) contributes to the total amount of the stored energy that can be converted into heat in the samples/mixtures. The increased differentiation above 65 °C was attributed to the additional compatibility with the medium (solvation) and the greater flexibility enabling more facile molecular motion.

Furthermore, review of the dielectric data suggested that the most effective temperature range for the solvent to be influenced by the MW energy was below 40 °C. After the point, the solvent starts to get retarded in absorbing MW energy or converting it into heat. However, with the addition of organometallics, the solution shows a better potential to be heated by MW. Therefore, it was expected that at a higher temperature (after 40 °C), solutions with organometallics would experience stronger MWH compare to the solvent and thus results in different readings in temperature.

3.3.3 MW Heating Experiments of Cobalt Halides and Organometallics

From the previous section, the predictions of how solutions heat with MW were made based on the dielectric property measurements. The next step was to justify these predictions by conducting series of MW heating experiments of these samples. A 40mL of selected solution was transferred into an MW transparent quartz tube. A constant power of 150 W from the MiniFlow was transmitted into the sample. From these experiments, it was allowed to (a) identify factors that affect how the solutions heated by MW, (b) define if similar trends can be observed as which in the dielectric property. In Figure 3.24, the temperature profiles and corresponding power profiles for the heating experiments of cyclohexanone containing cobalt halides were shown. In these graphes, the reproducibility of the experimental measurement for power absorption was ± 6 W and for all temperature measurements were less than ± 2 °C. The power absorption was calculated as the difference between the incident and the reflected power during the experiment. It must be noted that impedance matching was only carried out during the onset of the heating trial and was not maintained continuously throughout the experiment. Therefore, the power absorption data may also be influenced by any differences in the reflected power due to impedance "mismatch" that potentially took place during the duration of the experiment as the samples were heated up and their ε ' values changed with temperature. Additionally, because each sample was manually tuned before experiments with different input powers, the temperature of the sample after tuning was approximately 30 °C, therefore, the best tuning of the sample occurred at around 30 °C instead of at 20-25 °C which was the start temperature of the experiments, and thus peaks in power profiles were observed in all graphs.



Figure 3.24. Top: Temperature profiles of the precursors in cyclohexanone (cycloh). Bottom: Corresponding power profiles. From Figure 3.24, differences in heating response were observed when CoCl₂,

CoBr₂, and CoI₂ were dissolved into cyclohexanone. The heating performance follows an order as CoI₂>CoBr₂>CoCl₂, which has the same order as observed in dielectric property results that as temperature increased, CoI₂ became best in MW heating followed by CoBr₂. As the halide atom moves down the periodic table, the halide atom would have additional surrounding electron shells. The iodide halide has one additional electric shell than bromide, and two additional electric shells than chloride, thus greater atom size was obtained for iodide (atom diameter of chloride, bromide, and iodide was 1.75, 1.87 and 2.04 Å, respectively ^[28]). These additional electron shells caused an increasing in distance between the metal centre and halide atom which potentially creat greater dipole moment within the molecule. Additionally, the increment in atom size reduced attractions on electrons from its nucleus and causing reduction in restrictions of electrons around the iodide atom than that around the chloride atom. This would potentially allow electrons around iodide atom to be more freely to interact with the electromagnetic field. Furthermore, the different heating performance in cobalt halides could also be related to the additional electron shell when changing the halide atom from chloride to iodide. This allows for the halide ligand to have more electrons to interact with the MW field. This heating result supported the conclusion in the previous section that the increment in the solute molecular size allows for better intermolecular interactions with the surroundings which enhance the ability in dissipating heat.

Inspecting the power absorption profile in Figure 3.24, additional absorbed power was found for CoCl₂, CoBr₂ and CoI₂ (up to 5, 15 and 25 W, respectively). This could be attributed to that additional dipole moment introduced to the cobalt halides allows for better interactions with MW field. Therefore, additional power was able to be absorbed by the sample. Moreover, because these cobalt halides became better in MW heating as temperature raised, thus different final temperatures were obtained from these heating experiments.

The next step was to identify if the ligands experience MW heating when dissolved in the solvent. Results in cyclohexanone can be found below in Figure 3.25. The reproducibility for all samples was ± 1 °C and ± 4 W.



Figure 3.25. Top: Temperature profiles of the ligands in cyclohexanone (cycloh). Bottom: Corresponding power profiles.

Insignificant differences in temperature and power profile were found between the ligands solution and the solvent itself. The ligand heating results indicated that the ligands neither absorb additional MW power like cobalt halides nor experience MW heating when dissolved in the solvent. This was identical to the dielectric property results obtained in Section 3.3.2.2 that both ligands were MW transparent.

After identifying the heating behaviour of cobalt halides and organic ligands, the next step was to identify how the combined organometallic catalysts were heated by MW. From the dielectric property section, it was found that the synthesised organometallic catalysts showed greater potential to be heated by MW. Therefore, greater heating rates may be observed for these samples. The heating results were shown in Figure 3.26 where the reproducibility of the experimental measurement for power absorption was ± 8 W and for all temperature measurements were less than ± 3 °C.



Figure 3.26 Top: Temperature profiles of cyclohexanone (cycloh) and cyclohexanone plus catalysts and/or precursors. Bottom: Corresponding power profiles.

Figure 3.26 (a) and (b) showed the temperature profiles and absorbed power variation with time during the MWH experiments for all samples. Again, the changes in the power profiles was due to the impedance "mismatch" of the field.

Figure 3.26 (a) demonstrated that the heating profiles of the cyclohexanone and cyclohexanone/DPG solutions were very similar, indicating that a limited level

of system heating resulted from the presence of the ligand precursor alone. By comparison, the solutions containing the halide precursor, premade PhCoBF and CoBr₂DPG₂ as well as *in situ* synthesised CoBr₂DPG₂ catalysts were noted to produce measureable increases in the heating rate and achieved higher bulk temperatures than neat cyclohexanone. However, the profile of the organically liganded catalysts showed greater differences in both of these characteristics than that of the halide pre-cursor. Comparing this result with previous results of cobalt halides and organic ligands from Figure 3.24 and Figure 3.25, the profile of the organically liganded catalysts showed greater differences in both of these characteristics than that of the halide precursor. Meanwhile, the heating rates of all samples were found to decrease progressively with time this could be expected from the results of Figure 3.19 as the *tan* δ values had been shown to decrease with increasing temperature. Table 3.3 contains additional, more detailed data from the same experiments that were reported above.

Entry	Catalyst	Temperature Overshoot at 240ppm [°C]	Additional ^a Absorbed Power at 240ppm [W]	Temperature Overshoot at 1100ppm [°C]
1	DPG	1±2	1±6	3±2
2	CoBr ₂	4±2	10±6	13±3
3	CoBr ₂ DPG ₂ in situ	17±2	19±6	N/A
4	CoBr ₂ DPG ₂	11±2	20±6	25±5
5	PhCoBF	11±2	20±6	16±5

Table 3.3 Detailed data for heating experiments using cyclohexanone.

^a Additional absorbed power and temperature overshoot were defined as the maximum absorbed power and temperature difference between the sample and the cyclohexanone solvent that occurs throughout the experiment.

The halide precursor was noted to absorb approximately 10 W more than the neat solvent, and those of both the pre-made and *in situ* catalysts absorb

significantly more (~20 W) than the solvent at the 240 ppm level. Relating these data to the levels of energy input the cyclohexanone absorbs about 87% of the applied MW power at its maximum, but with the addition of the catalysts, this rose to 99% of the MW power. Thus, it was clear that the addition of the premade organic liganded catalysts (PhCoBF, CoBr₂DPG₂) significantly improved the MW absorption of the mixture, and illustrated that the sample with higher absorbed power would reach higher temperatures. However, Figure 3.22 predicted that the more flexible bidentate CoBr₂DPG₂ would eventually outperform the PhCoBF due to its greater dipole mobility which resulted in a more efficient conversion of MW energy into heat after 80 °C because it exhibited a greater differential in tan δ in its favour. The *in-situ* formed CoBr₂DPG₂ exhibited better power absorption characteristics than the preformed catalysts, however, at present, the underlying mechanism that resulted in that response was unclear.

Furthermore, while both pre-made PhCoBF and CoBr₂DPG₂ were observed to exhibit a peak simultaneously in the absorbed power after 18 s, the time for this peak exhibited by the *in situ* formed CoBr₂DPG₂ was noted to be different, namely 32 s. This delay potentially could attribute to the time required to synthesise the catalyst in the in situ case. Once the synthesis of the catalyst was completed, then the absorbed power variation was determined by the impedance mismatch as influenced by the changing dielectric properties of the *in situ* CoBr₂DPG₂ with temperature. Furthermore, by cross referencing this to the temperature profile, it can be defined that the bulk temperature was only in the region of 45 °C by the time that the catalyst had been synthesised (see black correlation arrows in Figure 3.26 (a)). This was well below the 1-hour half-life temperature of the initiator that has been used in the previously reported *in situ* polymerisation papers (2,2'-Azobis(2-methylpropionitrile) (AIBN) - 1-hour half-life temp = 82 °C)^[29]. This confirmed that the catalyst would be synthesised and fully available to control the polymerisation before the polymerisation commencing.

Considering that catalyst concentrations were in parts per million (ppm) level, this level of additional system heating *via* the catalyst indicated that the intermolecular friction between organometallic complex and solvent would be significant in order to result in such an increase in the solvent bulk temperature. To confirm that this heating rate differential was due to the presence of the organometallic species, the second series of heating trials were conducted where the organometallic concentration was raised to 1100 ppm as shown in Figure 3.27. The reproducibility of the experimental measurement for all temperature measurements were less than ± 5 °C.



Figure 3.27 Comparison of the plots of temperature increase with time for cyclohexanone (cycloh) solutions containing 200 and 1100 ppm of organically liganded catalysts.

In Figure 3.27, the results of heating experiments organometallic with increased concentration were shown. These experiments exhibited an increased rate of

heating, achieved a higher final temperature, and the differential between the level of the trend in the CoBr₂DPG₂ was increased.

To investigate the effect of ligand structure further, a second *in situ* catalyst was prepared to contain the dimethylglyoxime ligand (DMG). In this case, the ligand's phenyl functional groups were replaced by methyl groups. The MWH data comparison with the DPG complex was shown in Figure 3.28. The reproducibility of the experimental measurement of power absorption was \pm 7 W and for all temperature measurements were less than \pm 4 °C.



Figure 3.28 Top: Temperature profiles of cyclohexanone (cycloh) and cyclohexanone plus CoBr₂DPG₂ and CoBr₂DMG₂. Bottom: Corresponding power profiles.

The DMG ligand was expected to be more flexible than the phenyl version because of the reduced steric hindrance associated with the bulky aromatic groups. However, Figure 3.28 showed that the DMG complex was observed to exhibit lower heating characteristics than the DPG equivalent empirically. Thus, it was proposed that the phenyl functionality must produce greater solvation and/or a greater level of dipole/EM field interactions within the DPG ligand, which leads to the phenyl complexes outperforming the methyl version. Thus the design of MWH responsive complexes will clearly require a balancing of a number of key molecular factors.

3.3.4 Iron Systems

After identifying the dielectric properties and heating behaviours of the cobalt halides and organometallics, the next step was to do the same for the iron system. In this section, iron samples with the metal centre of Fe (II) and Fe (III) were used. The iron (II) halides include FeCl₂, FeBr₂, and FeI₂, whereas the iron (III) halides include FeCl₃ and FeBr₃.

3.3.4.1 Iron Halides

Catalysts using iron as the metal centre are also very attractive as an alternative to replacing rare metals ^[30-33]. This was because of the commercial availability, and its minimal environmental and toxicological impact. So, it was attractive to find if the selective heating can be obtained in the iron system which can allow us to further investigate whether the selective heating of the iron species offers similar benefits to the rare metal catalyst regarding the catalytic behaviours. Additionally, during the catalytic reaction of the cobalt/glyoxime system, the cobalt oxidation state will alternate in-between cobalt (II) and Cobalt (III). Unfortunately, distinguishable cobalt (II) and Cobalt (III) samples were not able to be obtained. However, with the iron/diimine system, Iron (II) and Iron (III)

organometallic catalyst can be synthesised with the corresponding Iron (II) and Iron (III) precursors. Identically structured catalysts with different oxidation state can thus be obtained (as shown in Figure 3.29). Therefore, it was possible to identify how the oxidation state of a metal centre can affect the selective heating of the catalyst.



Figure 3.29. Structures of the iron/diimine system. Left: synthesised via Fe(II) precursors; Right: synthesised via Fe(III) precursors^[34].

Same as the cobalt system, an assessment of dielectric properties of cyclohexanone and mixtures of this solvent containing the iron halides was conducted to aid in understanding/predicting the interactions between EM field and the materials within these multi-component solutions. Comparison of the tanð values was conducted to predict the relative capability of the materials contribute to the heating of the medium and/or enhancement of a chemical transformation when introduced to an EM field. The first series of the experiments characterised the tanð results for neat cyclohexanone and its solutions containing various iron (II) halides and iron (III) halides. The plot of the corresponding tanð results were shown in Figure 3.30 and Figure 3.31, respectively. In these graphs, all derivatives for tanð were below 8% for the average value.



Figure 3.30 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of different iron (II) halides at a concentration of 240 ppm.

From Figure 3.30, the tanð of iron (II) halides was plotted. Similar to the cobalt halides results, the FeI₂ showed the highest tanð (19% greater than cyclohexanone) followed by FeBr₂ (10% greater than cyclohexanone), and FeCl₂ showed the lowest tanð value(3% greater than cyclohexanone). Again, the iron halide with iodide ligands showed the highest MW response. This again proved that the metal halide with the larger ligands attached would be expected to be heated better by MW. The differential between solvent and solutions became greater as the temperature went up, this was due to the retardation of the solvent to be heated by MW and became less competitive in absorbing MW power at high temperature. Thus, the solution with the addition of iron halides started to heat better at a higher temperature than the neat solvent.

Cross-referencing the iron (II) halides results with cobalt (II) halides, with identical halide ligands, the iron (II) version showed greater tanδ comparing to the cobalt ones. For example, regarding tanδ value, FeI₂ was 9% greater than CoI₂, FeBr₂ was 4% greater than CoBr₂, and FeCl₂ was 1% greater than CoCl₂.

This again agreed previous finding that the molecules with larger molecular size possessed a greater ability to interact with the MW field.



Figure 3.31. Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of different iron (III) halides at a concentration of 240 ppm.

Similarly, the iron (III) halides showed an increment in tanð value as temperature raise. Cross-referencing with the iron (II) halide results, it was found that the solutions with iron (III) halides possessed a greater tanð value than iron (II) halides. FeBr₃ and FeCl₃ showed an increment of 63% and 42% comparing to cyclohexanone, respectively. This greater increment than iron (II) halides could be related to the additional halide ligands that was attached to the metal centre. The additional ligand (a) enlarged the size of the molecule, (b) introduced additional dipole to the molecule, (c) providing additional electrons to the molecules to interact with MW field. Since the ligand atoms wee identical, the introduction of the additional ligand atom would provide an increment in molecular size by about 40% for both precursors, thus allowed for a greater degree of steric interactions with surrounding molecules. Additionally, in Fe (II) species, the angle between two halide atoms was almost 180° (as showed in Figure 3.32 left), so the dipole momentum cancels out with each other. But the

trihedral structure in Fe (III) species allowed for a greater level of polarity within the molecule (as showed in Figure 3.32 right), thus, the molecule could have stronger interactions with the alternating electromagnetic field. Furthermore, the additional halide atom provided additional electrons to be able to interact with the MW field. With the aid of increased molecular size, the degree of freedom in electron movements becomes greater, and thus has stronger ability in interacting with the alternating field.



Figure 3.32. Chemical structures of Iron bromide. Left: iron (II) bromide; Right: iron (III) bromide.

3.3.4.2 Organic Ligands

The organic ligands for iron catalysts were used differently compared to cobalt catalyst. The FeDMG₂ or FeDPG₂ complex are very air sensitive and unstable even in the complete absence of oxygen. A base and a reducing agent was required in order to keep the complexes stabilised. However, doing this will introduce additional function groups which will affect the dielectric data. Therefore, another organic ligand ASA produced by the group were used as organic ligands for the Iron system study. The tanδ results of cyclohexanone containing ASA were shown in Figure 3.33, and the all derevatives for tanδ values were below 4% of the average value.



Figure 3.33 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of organic halides at a concentration of 240 ppm.

Inspecting Figure 3.33, again when the organic ligand was presented in the solvent, insignificant differences were noticed between the solution and the neat solvent. The results suggested that the organic ligands alone were not responding to MW when dissolved in the solvent. However, once the ligands were attached to the metal centre and formed an organometallic, it would enhance the MW heating on the organometallic. Moreover, the size of the ligands could also affect the heating performance of the organometallic because the size of the siz

3.3.4.3 Iron Organometallic Complexes

After identifying the tan δ values for iron halides and organic ligand, the next step was to determine the tan δ values for the organometallic systemesised via the combination of the iron halides and organic ligand. The results of tan δ of this experiments were shown in Figure 3.34, and all derevatives for the tan δ values were 6% below the average value.



Figure 3.34 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of iron (III) organometallics at a concentration of 240 ppm.

From Figure 3.34, the tanδ of the synthesised organometallic were plotted. Again, the solution with the organometallic showed greater tanδ value than the neat solvent (up to 45%). Comparing this with the cobalt organometallics, the organometallic based on iron showed a lower tanδ value compared to the cobalt organometallics. This could be due to that the in the cobalt organometallics, there were two ligands attached to the metal centre, whereas the iron organometallics only had one ligand. Therefore, the molecular size of the iron organometallic was expected to be smaller than the cobalt ones, and thus a lower tanδ value was found.

3.3.5 MW Heating Experiments of Iron Halides and Organometallics

Heating experiments of iron halides and organometallics were conducted in order to testify the prediction of the dielectric property. All samples were dissolved into cyclohexanone within MW transparent tubes. The heating profiles and correspond power profiles for iron (II) halides and iron (III) halides were shown in Figure 3.35 and Figure 3.36, respectively. The reproducibility of the experimental measurement for power absorption was ± 6 W and for all temperature measurements were less than ± 2 °C.



Figure 3.35. Top: Temperature profiles of the Iron (II) precursors in cyclohexanone (cycloh). Bottom: Corresponding power profiles.

Inspecting Figure 3.35, again, in cyclohexanone, the iron (II) halides with Iodide halides exhibited the greatest heating response (up to 8 °C higher than the cyclohexanone), and the FeCl₂ has the lowest MW heating response. This again suggested that the effect of the selective heating on a solute was determined by its molecule size if the solute was susceptible to the MW heating. Similarly,

looking at the power profile, the addition of iron halides into the solvent enhance the solution to absorb additional MW energy.



Figure 3.36. Top: Temperature profiles of the Iron (III) precursors in cyclohexanone (cycloh). Bottom: Corresponding power profiles.

Interestingly, from Figure 3.36 it was found that with an additional halide atom attached to the metal centre, FeBr₃ experienced better heating performance as FeI₂, while FeCl₃ was heated in a similar fashion as FeBr₂ comparing to Figure 3.35. This could be related to (i) the increased size of the additional halide atom; (ii) the increased dipole moment.

The above results demonstrated that adding iron halides to cyclohexanone could potentially improve the heating rate of the solution. The next step was to identify how the iron organometallics that were synthesised from these iron halides were heated with MW. The heating profiles and power profiles of these experiments were shown in Figure 3.37. The reproducibility of the experimental measurement for power absorption was ± 8 W and for all temperature measurements were less than ± 5 °C.



Figure 3.37. Top: Temperature profiles of the Iron (III) catalysts in cyclohexanone (cycloh). Bottom: Corresponding power profiles.

From Figure 3.37, the heating performance of iron organometallics was summarised. Similar to the cobalt/glyoxime catalysts, the combination of the ligands and metal precursor showed a stronger MW selective heating comparing to iron halides. The organometallic synthesised from FeBr₃ showed the highest temperature overshoot, followed by FeCl₃. The organometallic based on FeBr₂ had the least temperature overshoot. These results verifyed the conclusion made in the previous section that the MW heating on organometallics could be amplified by the attachment of the ligands, and this was depended on the size of the overall size.

However, the enhancement in heating response for iron catalysts (up to 10 °C higher than the cyclohexanone) was not as strong as the Cobalt/glyoxime catalysts which had temperature differences up to 20 °C. This could be due to that two glyoxime ligands were attached to the cobalt metal centre in a cobalt/glyoxime catalyst, whereas only one ligand was attached to the iron metal centre in an iron/diimine catalyst. The growth in molecular size for the cobalt catalyst was much greater than the iron catalyst; therefore, a greater degree of steric interactions would be expected in the relaxation process of the cobalt catalyst. For this reason, a higher temperature rise was observed in the cobalt catalyst than the iron catalyst.

Although no systematic comparisons could be made between the cobalt and the iron system, yet common observations could still be obtained from the above results. These results confirmed that the addition of ligands to the metal centre increases its steric interactions and this allowed for more heat dissipation to take place during its relaxation process. However, it was not possible to identify how the catalyst relaxation process can be influenced by alternating its metal centre from cobalt to iron, or *vice versa*. Therefore, additional experiments in relating the cobalt and iron system were planned to be performed.

Heating experiments with lower input power (60 W) were also conducted in order to identify the effects of input power on the selective heating of the catalyst by comparing results with which done at 150 W input power. The results of low power heating experiments were presented below in Figure 3.38. The reproducibility for all samples was ± 1 °C and ± 3 W.



Figure 3.38. Top: Temperature profiles of the Iron precursors and catalysts in cyclohexanone (cycloh) at 60W input power. Bottom: Corresponding power profiles.

From the low power heating results as shown in Figure 3.38, there were no significant differences observed for samples which were otherwise heated at a different rate at higher power (150 W). This can be explained by the power density (Pd) equation $Pd = 2\pi f \varepsilon_0 \varepsilon''[E]^2$ where f is the frequency, ε_0 is the permittivity of free space (8.85×10-12 F/m), ε ' is the dielectric loss factor and E is the electric field strength (V/m) ^[35]. The power density is the power dissipated per unit volume based on the electric field strength. The greater in input power, the stronger electric field strength will present within the electromagnetic field. Therefore, more power will be dissipated to the selective heated molecules and magnify the selective heating effects. Conversely, low input power offers less energy dissipation within the system, and thus insufficient energy for molecules to overcome the steric restrictions during its relaxation process. This suggested that besides the fact that the solvent and the catalysts could have significant effects in the selective heating of the catalyst, it could be concluded that the selective heating was also related to the input power of the system.

Comparing both low power and high power heating profiles, it was obvious that the selective heating phenomena are more significant at higher power because more energy was delivered to the selectively heated molecules. Therefore, it was reasonable that to fully exploit the selective heating mechanism, a high input power is required. However, in most MW assisted chemical reactions, a continuous input MW power was applied to the system to heat samples to a set temperature, and a minimum input power (less than 100 W) was then put into the system afterwards to maintain the temperature, as shown in Figure 3.39 (a). Thus, the selective heating effects of catalysts may be minimised during these processes and resulted in insignificant product yield when compared to the corresponding conventional process.



Figure 3.39. Example of heating profile and power profile in MW assisted reaction. (a): An input power of 300 W was applied to elevate the temperature to 150 °C, and an input power of 30-40 W was applied to the system afterwards to maintain the bulk temperature $[^{36]}$. (b): Temperature profile (blue line) and

microwave power (green line) as a function of time for a pulse process with the cooling system, a pulse power of 300 W were sent to the system every $30 \text{ s}^{[37]}$.

A pulsed process has recently been applied to MW processes (as shown in Figure 3.39 (b)), and improvements in product yields were reported. Durand-Reville et al. ^[38] observed an enhancement in reaction yield under conditions in which the application of MW energy was carried out in a series of pulses. In the Claisen rearrangement of a substituted propargylic enol ether into an azadirachtin precursor reaction, a 17% higher yield was obtained in the pulsed system (300 W) compared to which was carried out by a continuous irradiated system. Similarly, Chen et al. [37] also applied the pulsed system (with an input power of 300 W) for an ApNE claisen rearrangement reaction and observed a significant improvement in the reaction yield and reaction rate compared to a continuous MW irradiating system. These observations agreed with the suggestion that continuous exposure to high MW power allowed for a greater level of exploitations of the selective heating on a catalyst. Moreover, this could potentially provide enhancement in reaction yields better than a continuous MW irradiation system with a low input power during the process.

3.3.6 Tin Systems

Similar to the previous sections, the dielectric property of tin system was also measured when mixed with cyclohexanone. In these experiments, the tin (II) iodide was not able to obtain, so no data were included. Because there was no glyoxime liganded organometallic for the tin system, therefore tin octanoate was used as organometallic with the tin metal centre. Additionally, because the octanoate ligands were not obtainable, therefore, no dielectric property measurements for organic ligands were conducted in this section.

3.3.6.1 Tin Halides

The results of this section started with measurements of tan δ values for cyclohexanone containing tin halides including SnCl₂ and SnBr₂. The results of tan δ values were ploted and shown in Figure 3.40. All derivatives for the tan δ values were less than 5% of the average value.



Figure 3.40 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of tin halides at a concentration of 240 ppm.

In Figure 3.40, the tano for a mixture of cyclohexanone and tin (II) halides were plotted. The dielectric property of the tin halides was found to follow the trend of the neat solvent (dropped as temperature rise), however, with a greater value. SnCl₂ showed an increment up to 5% whereas SnBr₂ possessed an increment of 12% comparing to cyclohexanone. Again, the metal halide with bromide ligands showed greater potential to be heated by MW than chloride ligands, due to the additional electron orbital and greater molecular size of the bromide molecule.

Conversely, cross-referencing the metal halides with identical halide ligands, the tin system showed superior susceptibility to MW heating than iron and cobalt system. This could be due to that the tin metal centre is one row down in the periodic table, this means that the tin metal centre has an additional electron shell than cobalt and iron. This provides (a) additional electrons to interact with EM field, (b) greater size in the metal centre and overall molecular to enhance intermolecular interactions.

3.3.6.2 Tin Organometallic Complex

The tand values for the tin organometallics were also characterised and shown in Figure 3.41. The deravatives for the tand values were below 9% of the average value.



Figure 3.41 Plot of the temperature dependence of $tan\delta$ of cyclohexanone (cycloh) and cyclohexanone solutions of tin octanoate at a concentration of 240ppm.

Inspecting Figure 3.41, the addition of tin organometallic significantly enhanced the dielectric property of the solution up to 100% at 120 °C. Again this increment was more significant compared to the tin halides, suggested that the replacement of small halide ligands to larger organic ligands improved the potential of the organometallics to be heated by MW. Additional, this showed that tin octanoate would expect to experience stronger MW heating than tin halides. Therefore, the

tin organometallic would be expected to experience stronger MW heating than its halides when conducting an MW heating trial.

3.3.7 MW heating experiments of tin halides and organometallics

After predicting the heating performance of cyclohexanone solution containing tin halides and organometallics from the dielectric property measurements, the heating experiments of these samples were then conducted. The heating profiles and power profiles of these experiments were shown in Figure 3.42. The reproducibility of the experimental measurement for power absorption was ± 9 W and for all temperature measurements were less than ± 5 °C.



Figure 3.42 Top: The heating experiment of cyclohexanone (cycloh) and cyclohexanone containing Tin halides and organometallics, Bottom: The corresponding power profile.

In Figure 3.42, the summary of heating experiments of tin halides and organometallic were showed. The heating results again showed that the addition of tin halides and organometallics would enhance the solution heating performance. Additionally, the tin organometallic solution experienced the strongest MW heating and resulted in the highest final temperature than the ones containing tin halides. This was identical to the dielectric property measurements. The results again proved that it was possible to predict the heating behaviour of samples using the dielectric property measurement.

Conversely, inspecting the power profiles of the heating experiments, additional power was found to be absorbed by solutions containing tin halides and organometallics. This suggested that these additional power absorbed by the solute were contributed to the heating of the overall solution, and the differential in heating performance was originated from the addition of these solutes.

3.4 Conclusion

In this chapter, the dielectric property of metal halides and organometallics when dissolved in cyclohexanone were presented. Moreover, heating experiments of a solution containing different samples were conducted to identify any differences in the heating performance among all samples.

It was found that the addition of metal halides and organometallics to the solvent enhance its ability to convert absorbed MW power into heat to different extent. The choice of the attached ligand and the choice of the metal centre were found to be critical in affecting these results. This was due to different ligands, or metal centre would result in (a) differences in overall molecule size, (b) number of electrons available to interacting with EM field. Therefore, from the results, it was found that the organometallics would always have greater $tan\delta$ values than their metal halides.

Finally, heating experiments of these samples in solvent were conducted to testify results obtained from dielectric property measurements. Inspecting the temperature profiles, the addition of metal halides and organometallics improved the heating performance of the solution follow the same trend as predicted from dielectric property measurements. This suggesting that the dielectric property measurement could be a useful tool in predicting the heating performance of a sample. Based on the power profile, it was found that additional power was absorbed by metal halides and organometallics. This additional power allowed solutes to be selectively heated by MW and contributed to the overall heating of the solution. Considering the solutes were present in ppm (parts per million) level, the solutes would experience strong MW heating in order to raise the overall solution temperature to be significant extents. Again, this was identical to the predictions made from the dielectric property measurements that the tanð of solutes was greater than the solvent, especially for organometallics.

3.5 Future Work

Future work to be investigated in this area is to see if the dielectric properties of the catalyst when involved in an ROP reaction can be identified. Additionally, investigations of the catalyst temperatures when heated with MW can be conducted to identify to what extent the selective heating affect the catalyst surface temperature. Future reaction experiments with pulsed MW system can also be investigated to identify if the pulsed system provide more benificial effects than MW system with constant input power.

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Chapter 4. Investigation into the Comparison of the Effect of Electromagnetic Field Has on the Inorganic Metal Catalyst in Ring Opening Polymerisation of ε -caprolactone

4.1 Aims and Objectives

This chapter reports work conducted to investigate the causes behind the empirically observed acceleration of ring opening polymerisation (ROP) of ε -aprolactone catalysed by metal halides when using electromagnetic heating (EMH). Three different sets of catalysts based on iron, cobalt, and tin were studied, because each metal possesses distinct magnetic properties namely ferromagnetic, paramagnetic, and diamagnetic, respectively. By establishing systematic comparisons of ROP reaction results between conventional heating (CH), Electric or E-field heating (EH), and Magnetic or H-field heating (HH), it was possible to identify the potential effects of these heating methods have up on the ROP reaction based on both their dielectric and magnetic properties. As the use of EH has already been reported to accelerate the ROP of caprolactone, the overall goal of this work was to investigate if the ROP reaction results with HH could outperform EH when using catalysts that are susceptible to HH. ^[1, 2]

This work was conducted with ε-caprolactone monomer which have been extensively studied by academia and industry.^[3, 4] Various metal halides were applied to the ROP reaction to act as the catalyst. The application of EMH in these processes has also been studied; however, the scaling up from lab scale to pilot scale was hindered, due to the limitation in penetration depth of the microwave (MW) (varied from 0.58 to 8.4 cm at 100% conversion at 2.45GHz). However, in the magnetic heating method, because the monomer and polymer

are not susceptible to magnetic heating, the bulk of monomer and polymer would have limited interactions with the magnetic field, while the catalyst could be effectively heated. By doing so, the penetration depth limitation could be overcome and thus has greater potential for commercialisation.

4.2 Introduction

Among the biodegradable polymers, poly(ε -caprolactone) (PCL) has gain significant attentions due to its mechanical properties, miscibility with a large range of other polymers and biodegradability. PCL can be produced by polycondensation reactions of 6-hydroxycaproic (6-hydroxyhexanoic) acid as shown in Scheme 1 a. ^[3] Under vacuum condition, water produced during the reaction are removed and the equilibrium is shifted toward polymer formation. The most commonly used method for large scale synthesis of high molecular weight (Mwt) and low dispersity polymers, is *via* ring-opening polymerisation (ROP) of the seven numbered ring cyclic ester of ε -caprolactone (CL) (as shown in Scheme 1 b).^[3, 8, 9]. This process can be initiated by a large variety of species and can be catalysed using metal complexes, nucleophilic organocatalysts, and enzymes. Metal complexes based on tin and aluminum are particularly effective in preventing transesterification side reactions and allowing very high Mwt PCL with low polydispersity of around 1.1.^[3]

a) Direct condensation

$$\begin{array}{c} 0 \\ HO \end{array} \xrightarrow{(n-1)} H_2O \xrightarrow{(n-1)} O \\ HO \xrightarrow{(n-1)} H_2O \xrightarrow{(n-1)} O \\ HO \xrightarrow$$

b) Ring opening polymerisation



Although these metal catalysts are excellent in synthesising PCL, it is very difficult to remove the metal catalyst from the polymers after the synthesis due to the fact that they solvated in the same phase as the polymer. Therefore, the cytotoxicity associated with such residues limits the utility of these polymers. In spite of the fact that the concentration for such catalysts is low (normally in ppm levels), the residues of these catalysts from the decomposed polymers could accumulate in the compost and potentially cause negative impacts on terrestrial and aquatic microorganisms when in agricultural use and mammalian cells in tissue engineering applications. However, the harmful effects may be suppressed or avoided by using bio-acceptable compounds, for example, iron compounds. Most of the commercially available iron compounds have been regarded as 'lowtoxic', and iron compounds are furthermore substances frequently occurring in nature.^[10] Conversely, cobalt has been included to investigate the properties of metal centres that exhibit differing magnetic properties. However, it is also a key constituent of cobalamin, also known as vitamin B₁₂, which is the primary biological reservoir of cobalt as an 'ultra-trace' element assisting to the existence of life. Therefore, the alternative catalyst based on iron and cobalt would be potentially environmentally benign compared to the tin catalysts.

H. R. Kricheldorf and his coworkers used iron (III) oxide as a catalyst for ROP of lactide in 1985.^[11] These experiments were done at a range of different temperatures, with the iron (III) oxides found to be useful only at the highest

polymerisation temperature (180 °C). In 1997, the same author used Fe (II) salts as catalysts and whilst they did lead to polymerisation, the iron (II) salts investigated were found to require long reaction time (around 90 hours to reach 80% conversion).^[12] Anders Sodergard and Mikael Stolt investigated the feasibility of performing bulk polymerisation of PLA in the presence of various commercially available iron compounds as catalysts.^[10] Again, the catalysts were considered to exhibit low efficiencies (required up to 24 hours for completion), and high polymerisation temperatures were required. Additionally, a long initiation period was also noticed by the authors. W. B. Tolman and his coworkers also found simple iron salts lead to sluggish reactions.^[13] However, Gowda, et al. found that when using specific combinations of alcohols as initiators, the iron chloride could be the efficient catalyst to perform fast ROPs yielding PCL with high Mwt.^[14] In a more recent study, Hege and Schiller were able to perform controllable ROP of PCL in the presence of iron (III) halides and alcohol at room temperature.^[15] However, the time required to achieve high conversion (>80%) was very variable spanning from few hours to 150 hours.

Meanwhile, reports on catalysts based on cobalt are very limited. Rodriguez and co-workers tested cobalt octanoate catalyst as an alternative to the current benchmark catalyst - tin octanoate in the bulk ROP of lactone and lactide.^[16] However, the activity of cobalt octanoate was observed to be low due to its solubility in the molten monomers, thus the catalyst was found to be not effective. Tolman and coworkers reported a dicobalt complex that was able to provide high PLA yield (>80%) of low Mwt oligomers in a controlled fashion.^[17] Recently, Rajashekhar and Chakraborty successfully performed controlled ROP of cyclic esters using cobalt (II) salts.^[18] The catalysts were found to be effective even at

high monomers to catalyst ratios. And the system was suggested to be superior regarding reaction time and yield than other that had been reported.

These studies have paved the way for applying environmental benign metal halides and organometallics as catalysts to produce PCL via ROP mechanism. However, most ROP reactions required cycle times that were measured in hours or even days, making these process less favored due to the time consuming and disproportionate energy consumption involved (i.e. maintain the reaction temperature at 160 °C for 90 hours). As a result, recent studies have also focused their interest towards alternative processing techniques, including microwave (MW) heating, to determine if they could deliver improvements in PCL production. In MW heating, volumetric heating mechanisms replaces the convection/conduction heating pathways of delivered by conventional heating. With volumetric heating, rate enhancement in ROP reaction have been claimed by some MW studies.^[19, 20] However, negative effects such as yield reduction and promotion of side reactions were also highlighted by other studies.^[21] To understand the effects of MW upon the ROP of caprolactone, studies on applying various catalyst, MW instruments, and solvents have been conducted by different groups.

Albert and co-workers successfully conducted microwave-assisted ROP of caprolactone at 180 °C.^[22] A continuous input power up to 200 W at a frequency of 2.45 GHz was applied to raise the mixture temperature to the set point, followed by pulsed MW power up to 40 W to maintain the temperature. However, when compared to conventional studies that have done in identical conditions, no substantial improvement relating to the use of MW irradiation was identified.

Liu *et al.* studied and compared ROP of caprolactone using tin octanoate between MW and conventional heating.^[23] Four different MW power inputs (170, 340, 510, and 680 W) at a frequency of 2.45 GHz were used to carry out MW-assisted ROP. Significant improvement in product Mwt and reduction in reaction time were noticed with MW heating when compared to conventional heating. The PCL synthesised with MW have a Mwt at least three times greater than those samples synthesised conventionally. The reaction reached completion in 270 min using MW heating rather than 48 h in conventional heating. Increasing the input power was found to have a beneficial effect on product yield and Mwt.

In 2003, Sivalingam and coworkers studied the kinetics of synthesising PCL when MW was pulsed into the reaction.^[24] They found the activation energy for MW heating was four times less than conventional heating, and the MW acceleration in polymerisation rate was achieved by lowering the activation energy. However, because the temperature varied with reaction time, the actual reaction temperature was unable to be identified. Thus could lead to a miscalculation in finding the activation energy.

Lanthanide halides have also used as a catalyst in the MW-assisted synthesis of PCL by Baudry *et al.*. Accelerated rate compared to conventional heating was also reported.^[25] Additionally, they suggested that fast heating inhibited secondary transfer reactions, and resulting in lower polydispersity index (Đ).

Therefore, beneficial effects such as accelerated yield/rate have been claimed with the implementation of MW heating to PCL synthesis. In such MW heating processes, the energy has been delivered by an electromagnetic field. However, in most of the reported studies, they focused on the dielectric materials and their interactions with the electric field. In this respect, it is also important to remember the presence of a magnetic field (H-field) in an electromagnetic field as discussed in Chapter 1 (Section 1.7).

In 1994, Cherradi and coworkers reported their preliminary work in which they showed that the H-field must make substantial contributions to the heating of superconducting materials.^[26] But due to the size of the sample (120 mm in length), where in some cases, the sample was exposed to both magnetic and electric field simultaneously, it resulted in a combination of heating from the alternating electric and magnetic field.

Later in 2001, Cheng *et al.* showed that they were able to locate the positions where the E-field and the H-field dominated in a 2.45 GHz single-mode waveguide.^[27] Consequently, they reported significant differences in the heating behavior of solids delivered by the E-field and H-field when applied individually. In fact, in both this article and later in a patent, the authors showed that the heating with the E-field and the H-field in a 2.45 GHz MW reactor behaved very differently depending on the magnetic property of the sample. They demonstrated for the first time that the MW field itself, independent of temperature, profoundly affected the thermodynamics of any system where electrons have unpaired spins.

Studies in MW heating of ferrofluids and aqueous electrolyte solutions have also conducted. Rosensweig formulated and computed the heating rate in ferrofluids when subjected to an alternating H-field, and showed substantial heating rates were achievable.^[28] He also noticed that an optimum particle size that resulted

in maximum heating existed and that this was nearly independent of the applied field intensity. Horikoshi and Sumi investigated and compared the heating characteristics of aqueous electrolyte solutions with conditions where either the E-field or H-field was dominant. The heating rates from H-field energy input at high electrolytes concentration (0.125 M to 0.50 M) was observed to exceed the rates from E-field input, this was attributed to the limitation of the penetration depth of the microwaves in the E-field.^[29]

Magnetic heating was also tested in situations where chemical reactions were involved and found to have great potential both in laboratory and industrial processes. Kirschning and coworkers demonstrated the first application of magnetic nanoparticles as "heatable" media in an electromagnetic field for chemical synthesis.^[2] A continuous flow process was designed with a magnetic inducting reactor and it was shown that nanoparticles based on Fe, and principally other transitional metals such as Co, and Ni could be heated efficiently by this process.

Serpone *et al.* examined the heterogeneous Suzuki-Miyaura coupling reaction of 4-methylbiphenyl in the presence of Pd catalyst with both E and H-field.^[30] Chemical yield of the 4-methylbiphenyl with the H-field was 2-fold greater than those with the E-field at identical temperatures and reaction time. They found that in E-field heating, hot spots were noticed which impacted negatively on this coupling reaction. But by heating with H-field, the formation of hot spots was avoided, and thus resulted in better yield.

Sosnowchik, *et al.* successfully synthesised carbon nanotubes by using radio frequency (RF) inductive heating. However this was done by heating a substrate

supporting the catalyst particles.^[31] Ruoff and co-workers also performed RF inductive heating in graphene synthesis with a copper substrate by heating the metal substrates directly by the H-field.^[32] The quality of graphene products were shown to be comparable to, or higher than that produced *via* conventional synthesis techniques.

The direct heating of metals by an H-field provides fast and selective magnetic heating compared to the conventional heating methods, which is similar to that have been observed in E-field heating. But in contrast to the technical complexity of the apparatus, as well as safety issues, associated with MW E-field, which has hampered their broad application of such technology in flow systems so far, the reactor concept in H-field heating is simple and so can be adapted to other flow systems relatively easily. Given the dramatic increase in interest in flow chemistry, this new heating technology is believed to have prospects both in academia and industry.^[33] The H-field heating is also found to be less dangerous in long term exposure. MW E-field is known to have harmful effects in body tissues because they can be heated by the alternating field.^[34] But this not the case for the pure induction H-field heating. Ivkov et al. examined the physical effects of induction on tissue from the application of an alternating pulsed magnetic field, at 153 kHz, on nude mice.^[35] They found that for field strengths below 700 Oe (with a 20 min exposure), no adverse effects were observed. In fact, the magnetic heating has already been proved to be an effective tool for cancer curing known as magnetic hyperthermia. The treatment is found to only heat magnetic nanoparticles that are injected into cancer cell, while the rest of body tissues remain unharmed.^[36]

Therefore, with these advantages, magnetic heating could have a great potential for large scale production, with better energy efficiency and healthier working environment than the direct MW E-field. It should also be noticed that to date, such heating technique have not been reported to have been applied to the synthesis of polymers. Furthermore, as many processes involve the usage of metal catalysts, there is a great opportunity and potential to implement and develop magnetic heating in the polymer industries.

In this chapter, the ROP of caprolactone was conducted with simple metal halides catalysts namely FeCl₃, CoCl₂ and SnCl₂ using conventional heating (oil bath). The identical reactions were then carried out adopting E- and H-field heating. The kinetic of the reactions and the product polymers isolated from using different heating methods were characterised and compared to each other. By doing this, it enabled a fundamental understanding of the potential effects various heating methods have up on the reaction to be established. Additionally, as these selected catalysts have different magnetic properties, this study allowed potential differences in catalytic efficiency among each catalyst when they are subjected under the alternating H-field to be identified.

4.3 Results and Discussion

The goal of this work is to identify if the potential E-field selective heating of the catalyst (discussed from the previous chapter) which could affect the rate of synthesis and/or yield of PCL in ROP reactions. Additionally, it was also planned to test the feasibility of the same reaction if carried out with H-field. Ultimately, establishing a fundamental comparison between conventional, E-field heating (EH), and H-field heating (HH), and by achieving this goal define it is possible and desirable to develop a novel H-field heating process. Consequently, before the development of such H-field heating process, comparisons between batch experiments using the different heating methods with simple metal halide catalysts were initially conducted. An additional reason behind the decision was that the batch PCL synthesis is a relatively well-studied process, thus this will aid in a better understanding of the empirical observations.

4.3.1 Synthesis of PCL using FeCl₃ as catalyst

Before conducting any reactions, the alteration in heating performance caused by adding FeCl₃ complex into monomer (CL) was first investigated by conducting a heating experiment similar to those described in the previous chapter. The initial heating experiments using EH and HH were conducted in a single mode Sairem MiniFlow 200SS at 150 W, operating at 2.45 GHz.

The initial heating experiments were aiming to investigate and compare the heating performance of the bulk of monomer both with and without the addition of FeCl₃ complex. From the previous chapter, it was found that the addition of metal halides to solvent could enhance the heating of the solvent. The origin of this was attributed to the fact that the metal halides were potentially being selectively heated by E-field, and thus additional heat was dissipated into the solvent and causing the observed temperature differences. А [Monomer]: [Complex] ratio of 800:1 was used in these heating experiments. Without any addition of initiator, no polymerisation should have been initiated during this heating experiment. The temperature profile was monitored with time by the use of optical fibre (OF) temperature sensor, which has been reported to be able to achieve a direct measurement of the reaction medium bulk temperature by previous researchers.^[37-40]



Figure 4.1 Example of typical temperature profile and power profile of CL and CL+FeCl₃ mixture using EH at 150 W input power, where PA is Power Absorbed.

In Figure 4.1 the blue line in Figure 4.1 showed the heating profile of monomer on its own when no complex or initiator was present, whilst the red line was for monomer with complex. This heating profile demonstrated that efficient bulk volumetric heating of the neat monomer using EH could be achieved. However, when FeCl₃ was present, it was observed that the additional FeCl₃ enhanced the heating of the bulk with EH. A temperature difference up to 20 °C was obtained from the heating profile. Additional, by cross-referencing of this data with power profile, it was found that the sample with FeCl₃ absorbed an average of additional 19 W. The additional absorbed power suggested the observed temperature difference may be as a result of achieving the selective heating of FeCl₃ within the bulk. Comparing the results obtained from cyclohexanone (Figure 3.36 in Chapter 3, Section 3.3.5), a larger temperature difference was obtained for the CL sample. This could be due to greater viscosity in CL than cyclohexanone, which will lead to a greater level of intermolecular friction as the EH interacts with FeCl₃, thus increasing the efficiency by which the E-field will heat the medium. Alternatively, because CL has better dielectric properties, its ability in coupling with the E-field is better, and thus this may have enhanced the observed selective heating effect.



Figure 4.2 Example of typical temperature profile and power profile of CL and CL+FeCl₃ mixture using HH at 150 W input power where PA is Power Absorbed.

Meanwhile, reviewing the heating profile of the same samples heated using an H-field as shown in Figure 4.2, an even greater temperature differences (up to 33°C) was observed for the sample containing FeCl₃. However, the power profile indicated that an average power of only 30 W and 10 W were absorbed for CL containing FeCl₃ and CL neat solvent, respectively. This was concluded to be because the sample was located at an area of weak E-field, where H-field was at the dominant at that position. At this position, the sample was primarily exposed to a strong H-field, whereas the corresponding E-field was weak. Due to the fact that the H-field power absorption cannot be measured, and only the E-field power absorption reading was found compared to E-field heating experiments. Additionally, this weak E-field heating was potentially may be partially responsible for the heating of CL sample in these HH experiments. To identify

if the observed temperature difference was related to weak EH or strong HH, another series of low power EH experiments were conducted, and the temperature and power profiles were shown in Figure 4.3.



Figure 4.3 Example of typical temperature profile and power profile of CL and CL+FeCl₃ mixture using EH at 50 W input power where PA is Power Absorbed.

As shown in Figure 4.3, the power profile of CL containing FeCl₃ was similar to which obtained from the H-field heating shown in Figure 4.2. However, it took around 120 s to reach 120 °C which only required the 60 s with H-field heating. This obviously suggested that the FeCl₃ experienced significant H-field selective heating and resulted in significant heating enhancement comparing to CL with the influence of the H-field.

From the comparison of the EH and HH experiment results, it was observed that the heating of CL alone with H-field took double the time required with E-field. This was because the CL cannot interact with the H-field and was only heated by the weak E-field in HH, which was not as efficient as when it was located at the E-field dominant position, as a result, longer heating time was observed. Conversely, CL containing FeCl₃ only required an additional 15 s to reach the same temperature when heated with HH. Such significant reduction in heating time suggested that heating of CL containing FeCl₃ with H-field could achieve similar heating performance to EH, but rather than a significant portion of this heating coming from interaction with the bulk monomer in the case of the application of the E-field, it was proposed that the catalyst was being selectively heated by the H-field and only a relatively minor part in this case was related to the bulk was heated as it was only exposed to a weak E-field.

Initial batch reactions involving bulk ROP of caprolactone were then conducted with FeCl₃ as catalyst and benzyl alcohol (BzOH) as an initiator using oil bath as conventional heating, and MiniFlow for EH and HH. BzOH was chosen as initiator because it is the most common alcohol used as the initiator in ROP reactions. Additionally, Nguyen *et al.* found that at 150°C, which was the common temperature for ROP reactions, the BzOH was essentially MW transparent.^[39] Therefore, it would not involve in competing in absorbing MW energy. Furthermore, Hege and Schiller found that ROP using FeCl₃ performed best with BzOH as an initiator.^[15] Therefore, BzOH was selected to be the initiator for all ROP reactions.

The influences of reaction conditions, including temperature, [Monomer]:[Catalyst] ratio ([M]:[C] molar ratio), the level of MW power on the ROP of CL initiated by FeCl₃ were investigated. Several researchers found that the ROP of CL could be performed at room temperature when FeCl₃ was used as a catalyst. Therefore, a wide range of temperature from 50 °C to 150 °C, the latter of which is a typical operation temperature for ROP polymerisation, was selected as reaction temperatures. In this study, the [M]:[C] ratios used were 400:1, 800:1, and 1600:1. For the study of different MW powers, six different input power were selected which were 25, 50, 75, 100, 125, and 150 W.

4.3.1.1 ROP of CL with FeCl₃ at [M]:[C] ratio of 400:1 Firstly, ROP of CL using FeCl₃ were conducted at [M]:[C] ratio of 400:1 with various heating methods. This catalyst concentration was used to establish direct comparison with ROP that were done with at room temperature by Hege and Schiller^[15].

Table 4.1 Average results of ROP of CL with $FeCl_3$ and BzOH at various temperature at [M]:[C] ratio of 400:1.

Entry	Temperature (°C)	time (min)	heating method	M _n ^a (gmol ⁻¹)	M _p ^a (gmol ⁻¹)	Đ ^a	Conversion ^b (%)
1	50	25	СН	3200	5000	1.42	59.2
2	50	25	EH	3500	5400	1.27	88.5
3	50	25	HH	4700	6600	1.37	91.5
4	75	25	СН	3900	6300	1.43	97.0
5	75	25	EH	4500	6200	1.33	99.9
6	75	25	HH	5000	8000	1.39	99.9
7	100	25	СН	3700	6700	1.31	84.3
8	100	25	EH	4200	8300	1.68	99.9
9	100	25	HH	4700	9700	1.55	96.3
10	125	25	СН	2500	5300	1.66	64.2
11	125	25	EH	3100	7100	1.97	76.6
12	125	25	HH	4300	9400	1.66	83.7
13	150	25	СН	1900	4900	1.81	62.1
14	150	25	EH	2700	6200	1.87	73.3
15	150	25	HH	3100	7900	1.83	81.7

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

The initial ROP reactions were conducted with the monomer to FeCl₃ to BzOH molar ratio ([M]:[C]:[I] ratio) of 400:1:5 in conventional oil bath heating methods. At 50°C, an 59% conversion was achieved after 25 min (Table 4.1, entry 1). Cross-referencing to the same experiments conducted by Hege and Schiller at 27 °C ^[15], a faster yield was achieved by increasing the temperature from 27 to 50 °C. This suggested it was beneficial to perform the reaction at an elevated temperature. Therefore, the temperature was increased to 75 °C, and the polymerisation reactions were able to achieve 97% conversion within 25 min (Table 4.1 entry 4). However, as the temperature was further increased to 100,

125, and 150 °C, the polymerisation started to lose control and the conversion dropped to 84, 64 and 62%, respectively (Table 4.1 entry 7, 10, 13) at 25 min mark. This could be due to the undesired transesterification or depolymerisation side reactions occurred at elevated temperature. In such polymerisation reaction, it is well known that transesterification takes place at elevated temperature or at long reaction time.^[41-45] These observations could be further explained by referring to Mwt results.

Comparing the Mwt of the produced polymer at each set temperature, an increased Mwt, regarding M_n and M_p , were found as temperature increased to 100 °C. The M_n represents the number average molecular weight of the polymer, and Mp identifies most frequently recorded molecular weight value for polymers and is located at the top of the distribution peak. As temperature increased from 50 to 75 °C, similar Mwt were achieved (M_n =4300 gmol⁻¹ at 50 °C, and M_n =3900 gmol⁻¹ at 75 °C) but in a shorter period (reduced from 45 to 25 min). Further increasing the temperature to 100 °C, the M_p value increased from 6300 to 6700 gmol⁻¹, suggesting higher molecular weight was achieved at 100 °C. However, at 125 and 150 °C, the Mp value dropped to 5300 and 3900 gmol⁻¹, respectively. This again proves the detrimental effects from the transesterification/depolymerisation side reactions. The GPC traces of the produced polymers at various temperatures were shown in Figure 4.4.



Figure 4.4 Comparison of the GPC traces of the product polymer synthesised using FeCl₃ at different temperatures with CH.

Inspecting the GPC profiles in Figure 4.4 for PCL produced *via* CH, the peak of the GPC trace started to shift to left as the temperature raised from 50 to 100 °C, followed by shifting back to the right side at 125 and 150 °C. As previously mentioned that in GPC technique, as the polymer mixture passes through the column(s), molecules with small hydrodynamic volumes were partially retained by the pores of the polymer beads, therefore, taking longer time to pass through the columns leading to a longer retention time. Conversely, molecules with larger hydrodynamic volumes spend little or no time in the pores and were therefore eluted quickly. Therefore, the left-shifting peak represented an increment of Mwt as reaction temperature raise up to 100 °C, followed by a drop in Mwt and right shifting peaks for 125 and 150 °C.



Figure 4.5 Comparison of the GPC traces of the product polymer synthesised using $FeCl_3$ at different temperatures with (a) EH, and (b) HH.

Similarly, inspecting Figure 4.5 for the GPC profiles of PCL produced *via* MWH, it was found that the peak of the GPC trace shifted to the most left as the temperature raises to 100 °C. Inspecting the peak distributions, the peaks became broadened as the reaction temperature increased, indicating the presence of undesired transesterification/depolymerisation reactions. Moreover, this side reaction accelerates as the reaction temperature rise and eventually causing expanded peaks, for example, the D results increased from 1.31 at 50 °C to 1.82

at 150 °C. From these Mwt resssults, it was identified that the temperature between 75 and 100 °C might be the optimised temperature range for the ROP to be carried out for high conversion and low Đ.

From the conventional heating (CH) results, it was found that the reaction bulk temperature accelerated the conversion rate and improved the polymer Mwt, however, at the cost of magnification of side reactions and the widened Đ. Series of comparative reactions were then carried out using electromagnetic heating (EMH) including EH and HH.

It was observed that there was an increase in conversion from 85% in the CH case to 99% with EH and HH at 50 °C (Table 4.1 Entry 1, 2 and 3). Additionally, the reactions conducted in E- and H-field followed the same trend as CH experiments going from low Mwt to high Mwt as temperature rising to 100 °C (i.e. the M_p value increased from 6600 and 8200 gmol⁻¹ at 50 °C, to 8300 and 9700 gmol⁻¹ at 100 °C for EH and HH, respectively). Moreover, further increasing the temperature showed a reduction in polymer conversion and Mwt, for example, the Mp value dropped to 6200 and 7900 gmol⁻¹ at 150 °C for EH and HH, respectively. Reduction in conversion (only 73% and 82% conversion were achieved at 150 °C at identical reaction time for EH and HH, respectively) and broadening in Đ (up to 1.87 and 1.83 at 150 °C in EH and HH cases) were also observed as temperature rise which were identical to CH results.

Directly comparing Mwt results between CH, EH and HH, both EH and HH showed an improvement in Mwt of produced polymer, in terms of M_n and M_p , e.g. at 150°C, the M_n value for EH and HH were 2700 and 3100 gmol⁻¹ which was 35% and 55% higher than the M_n value of 2000 gmol⁻¹ in CH. This improvement was found to be more significant in HH than EH (typically \sim 15-30% greater at each point).

When EMH was used as the heating source, it was found that higher conversion was achieved compared to CH even at high temperature. For example, it was noticed that at 125 °C and 150 °C, both EH and HH showed higher production conversion than CH (i.e. 64% in CH comparing to 77% in EH and 84% in H-field heating at 125 °C). This could be due to the selective heating of the mixture found in previous heating experiment, causing potentially greater reaction site temperature than CH, as a result promotes propagation reactions and suppressed side reactions.

Thus, a series of kinetic studies were then conducted with three heating methods to determine the conversion with time adopting these varying conditions. Figure 4.6, Figure 4.7, and Figure 4.8 demonstrates the results of these kinetic experiments.



Figure 4.6 Conversion versus time plots for ROP of CL at different temperatures with CH. Condition: [CL]:[FeCl₃]=400:1.



Figure 4.7 Conversion versus time plots for ROP of CL at different temperatures with EH. Condition: [CL]:[FeCl₃] = 400:1.



Figure 4.8 Conversion versus time plots for ROP of CL at different temperatures with HH. Condition: [CL]:[FeCl₃] = 400:1.

Inspecting Figure 4.6, the conversion increased as reaction proceeded. Comparing Figure 4.6, Figure 4.7 and Figure 4.8, confirmed that the trends exhibited in the conversion against time plots were similar among CH, EH, and HH. Comparison of these results against different temperatures showed that it too tracks the same trend as found previously that 75 °C to 100 °C was the optimum temperature range for the reaction to achieve high conversion and Mwt.

In CH experiments, it was found that above 100°C, the conversion started to level out after reaching 82%, 67% and 57% at 100°C, 125°C, and 150°C,

respectively. This again identified that the side reactions at high temperature became dominant with detrimental effects in polymer conversion. But in EMH methods, the conversion was able to reach a greater degree before leveled out, i.e. ~10% and ~20% higher than CH at 150 °C for EH and HH, respectively. This again suggested that using EMH could potentially reduce detrimental effects from side reactions.

Kinetic studies comparing how conversion changes as reaction progresses at 50 °C and 100 °C were then conducted as shown in Figure 4.9. By doing so, it could identify the effects of reaction temperature have upon the conversion when using different heating methods.



Figure 4.9 Comparison of conversion versus time plots for ROP of CL using $FeCl_3$ between 50 ^{o}C and 100 ^{o}C .

From Figure 4.9, two temperatures namely 50 and 100 °C were used for direct comparison between CH and EMH in conversion. Interestingly, it was found that at 50 °C, the initial reaction conversion (at 5 min) between CH and EMH was only around 10%, whereas, at 100 °C, the initial reaction conversion was 40% higher for EMH than CH. This observation could be due to the high input

power (up to 150W) initially been pulsed to the sample. Two typical power profiles were presented in Figure 4.10 and Figure 4.11.



Figure 4.10 Power profile of ROP of CL using $FeCl_3$ at 50 °C at [M]:[C] ratio of 400:1 with EH (-) and HH (-). PA: power absorbed.



Figure 4.11 Power profile of ROP of CL using FeCl₃ at 100 °C at [M]:[C] ratio of 400:1 with EH (-) and HH (-). PA: power absorbed.

In Figure 4.10 and Figure 4.11, the amount of power being absorbed by the sample during the reaction in both EH and HH were identified. These results showed that only 20 s were required to raise the temperature to 50 $^{\circ}$ C at the

maximum input power (150 W), whereas 50 s was required to raise to 100 °C with identical input power. Therefore, longer exposure to EM field was required to reach higher reaction temperature, and this could be the potential origin of the observed different initial conversion between CH and EMH. This will be discussed in more detail in later of this section in the study of different input power.

From the kinetic studies, it was possible to calculate the rate of propagation (k_{app}) for each heating methods from plots taken at various temperature. The kinetic plots of $ln(M_0/M)$ versus reaction time were detailed in Figure 4.12, Figure 4.13, and Figure 4.14.



Figure 4.12 Kinetic plots of $ln(M_0/M)$ versus time at different temperature using CH with best fit line (BFL). Condition: $[CL]:[FeCl_3]=800:1$.

Analysis of data in Figure 4.12 showed a straight-line relationship holds for $\ln(M_0)/M$ as a function of reaction time at 50 to 100 °C. This linear relationship identified that the polymerisation was a controlled first order reaction. However, this relationship deviated from the trend line at 125 and 150 °C. This was due to the competition in side reactions causing the reaction lost its control.



Figure 4.13 Kinetic plots of $ln(M_0/M)$ versus time at different temperature using EH with best fit line (BFL). Condition: $[CL]:[FeCl_3]=400:1$.

Figure 4.13 shows the kinetic plots of the polymerisation with EH. A Linear relationship was found for reactions at 50, 75, and 100 °C, whereas deviations from trend line were found at 125 and 150 °C.



Figure 4.14 Kinetic plots of $ln(M_0/M)$ versus time at different temperature using HH with best fit line (BFL). Condition: $[CL]:[FeCl_3]=400:1$.

Finally, the kinetic plots of H-field heated polymerisation were summarised in Figure 4.14. Again, a linear relationship was found in $\ln(M_0)/M$ plots for 50-100 °C. The observed trends in a linear relationship were identical among all three heating methods. These results demonstrated the mechanism of the polymerisation was not affected by applied heating methods, and the induced

differences in conversion were resulted from thermal effects. The polymerisation rate constant from the kinetic studies, was summarised in Table 4.2 for all three heating methods, Where the k_{app} values was derived from the gradient of the kinetic plots of the reaction (Figure 4.12, Figure 4.13, and Figure 4.14).

Table 4.2 Summary of rate constant (k_{app}) at different temperatures using CH, EH, and HH. Condition [CL]:[FeCl₃]=400:1.

	СН	EH	HH
Temperature (^o C)	k _{app} (min ⁻¹)	k _{app} (min ⁻¹)	k _{app} (min ⁻¹)
50	0.035	0.07	0.059
75	0.130	0.156	0.154
100	0.173	0.332	0.220
125	0.111	0.210	0.195
150	0.083	0.176	0.192

Analysis of the data in Table 4.2 leads to the conclusion that the k_{app} value of all EH and HH were at least 1.4 and 1.1 times that of the CH experiments at the identical bulk temperature, respectively.

The fact that the k_{app} value was greater for EH and HH than CH at the equivalent temperature suggests that the EMH (both EH and HH) was directing energy directly into reaction species. In this case, EH heats both the monomer and the catalyst (reaction site) directly, while HH primarily heats the catalyst, both direct heating results in a raised local reaction rate. This potentially infers that the local temperature of reacting site was above the measured temperature for the bulk. However, the higher k_{app} value in EH experiments suggested that the acceleration in the propagation process was more significant in EH than HH, which could potentially be due to efficient heating of the monomer and polymers in EH.

To investigate this further, the plots of $ln(k_{app})$ versus 1/T for identical bulk temperature EMH and CH ROP reactions were compared, where k_{app} was

derived from the gradient of the kinetic plots of the reaction (Figure 4.12, Figure 4.13, and Figure 4.14). However, in this study, only k_{app} at 50 °C, 75 °C, and 100 °C were used because the control of the reaction was lost at 125 °C and 150 °C due to the competitions in side reactions.



Figure 4.15 The relationship between lnk_{app} versus the reciprocal of absolute temperature with best fit line (BFL). Condition: [CL]:[FeCl₃]=400:1.

$$k = Aexp(-\frac{Ea}{RT_{eff}})$$
 Equation 1

The plot of ln k_{app} versus 1/T was noted to have similar gradients among three heating methods. From the plot, it was able to calculate the activation energy (E_a) and pre-experimental factor (A) from the Arrhenius equation (shown in Equation 1) by measuring the gradient of the linear relationship as shown in Figure 4.15. There were no significant differences of E_a between all heating methods. Indeed, the E_a calculated for CH, EH, and HH was 32.5, 31.3, and 31.1 kJ/mol, respectively.

Using the calculated E_a and A values in CH, it was possible to calculate the effective temperature of reaction site with EMH by introducing the k_{app} value calculated in EMH into the Arrhenius equation of CH as shown in Equation 2.

$$k_{MW} = A_{CH} exp(-\frac{Ea_{CH}}{RT_{eff}})$$
 Equation 2

Rewriting the equation allows the calculation of the effective temperature of the reaction:

$$T_{eff} = \frac{-E}{Rln(k_{MW}/A)}$$
 Equation 3

With this method, the temperature gradients between the reaction site (T_{eff}) and the bulk temperature (T_b) were estimated. The bulk temperature was the temperature which the reaction was carried out. The difference between both values quantifies the potential "heat concentration" around/at the catalyst transition states and was listed in Table 4.3.

Table 4.3 Estimation of effective temperature of reaction in EH and HH at $[CL]:[FeCl_3]=400:1$. (T_b : the bulk temperature the reaction is conducted at; T_{eff} : the effective temperature of the reaction estimated based on Arrhenius plot).

	E	H	HH		
T _b (°C)	T _{eff} (°C)	ΔT (°C)	T _{eff} (°C)	ΔT (°C)	
50	65.76	15.77	60.81	10.81	
75	91.48	16.48	90.98	15.98	
100	119.22	19.22	111.89	11.89	

Analysis of Table 4.3 demonstrated a local temperature difference might be at least 15 °C and 11 °C above the bulk temperature in EH and HH, respectively. Comparing results of EH and HH, EH showed greater temperature differences to bulk temperature than which of HH. Throughout the reaction, as both monomer and catalyst were heated by EH, this could potentially have been able to create local heat concentration if generated from the selective heating of both species. Whereas in the HH, heat concentration were created around catalyst while monomer remains 'cold'. From this study, it was able to quantitatively identify that in EMH method, a higher local temperature could exist when the bulk temperature was identical to CH method. It was observed in early of this chapter that when applying EMH to the reaction, higher initial conversion were achieved. It was hypothesised that this was due to the initial high input power in EMH. Therefore, to define how input power affects the conversion of these EMH experiments, a series of short reactions were conducted at different input powers. This change would also help to explain the reason for different initial conversion differences between different heating methods. Two sets of short reactions were conducted. the first set of reactions stopped right after the reaction reach the set temperature (100°C) to investigate how the heating rate could affect the polymer yield. The other set of reactions was continued for 180 s after reach set temperature, to identify how the input power could affect the reaction for identical reaction time. The characteristics and yield data related to both EH and HH were contained in Table 4.4 and Table 4.5 while a typical GPC data of the product polymer at 150 W was shown in Figure 4.16.

Table 4.4 Average results of ROP of CL with FeCl₃ and BzOH using various input power at [M]: [C] ratio of 400:1 to reach 100 °C with EH.

	EH				
input	time ^a	M_n^{b}	M_p^{b}	Ðb	Conversion ^c
power	(s)	(gmol ⁻¹)	(gmol ⁻¹)		(%)
25W	133	1380	1750	1.14	31.97
50W	63	1000	970	2.00	28.57
75W	55	1070	1110	1.09	25.37
100W	37	910	970	1.83	24.81
125W	34	1290	1700	1.14	48.98
150W	29	1290	1680	1.13	50.00

^a time required to raise the bulk temperature to 100 °C.

^b determined by GPC, measured in THF at 35 °C

^c determined by ¹H-NMR

	НН				
input	time ^a	Mn ^b	Mp ^b	Ðb	Conversion ^c
power	(s)	(gmol ⁻¹)	(gmol ⁻¹)		(%)
25W	234	2370	3740	1.27	39.39
50W	97	1820	3110	1.29	32.43
75W	70	1690	980	1.42	44.75
100W	48	1480	970	1.32	39.39
125W	43	1670	1100	1.42	38.27
150W	30	2240	3700	1.29	50.50

Table 4.5 Average results of ROP of CL with FeCl₃ and BzOH using various input power at [M]: [C] ratio of 400:1 to reach 100 °C with HH.

^a time required to raise the bulk temperature to 100 °C.

^b determined by GPC, measured in THF at 35 °C

^c determined by ¹H-NMR

In Table 4.4 and Table 4.5, the time required to reach the set temperature was reduced as the input power increased for both EH and HH. Indeed, the time required to reach 100 °C was reduced from 133 s to 29 s as input power was increased from 25 W to 150 W for EH, whereas an even more significant reduction in time from 234 s to 30 s was found in HH. The time required to heat the bulk in HH was 75% longer than EH at 25 W, but was significantly reduced and achieved comparable heating time to EH when the input power was increased to 150 W. This result suggested that the H-field selective heating was more significant at high input power which used almost identical time as EH to reach 100 °C at 150W. Moreover, this could also because the bulk was also heated by the weak E-field in HH experiments. Therefore, during HH at high input power, the weak EH was still effective in heating the bulk. Whereas at 25 W input power, the weak EH was not enough to raise the bulk temperature efficiently.

As the input power was increased, the reactants spent less time with the EM field applied. However inspection of Mwt results shown in Table 4.4, it was found that polymer with similar Mwt or improvement in Mwt was obtained as input power was increased. For example, PCL produced at 50W and 100W with the EH have almost identical M_n (the achieved M_n value was 1000 and 910 gmol⁻¹ at 50W and 100W, respectively), but the reaction time for 100 W was 40% less than which at 50 W. Moreover, in the HH experiments, the PCL product produced at 150 W has identical Mwt as which produced at 25 W, but the time was reduced by approximately eight times than which at 25 W. Additionally, similar or higher product yield was found for high input power for both EMH methods, e.g. with the EH, the reaction time was halved as input power increased from 25W to 50W, but similar conversions (32% at 25 W and 29% at 50 W) were achieved. Similarly, in HH, identical conversions were obtained at 25 W and 100 W, but the reaction time was 4.8 times shorter at 100 W. These results clearly identified that the input power of EMH has significant beneficial effects on product yield and quality.

Comparing the results between both EMH methods, both experiments observed to exhibit similar reaction characteristics, e.g., improved Mwt as the input power increased. However, by cross-referencing the Mwt results between each heating methods from 25 W to 150 W, PCL produced with HH has higher Mwt than those with EH ranging from 25% at 125W to 80% at 50W. This could be explained by the different time that the reactants were subjected with EM field, e.g. at least 25% more time was spent in HH than in EH at input power of 25 W to 125 W. However, at 150 W which the reactants were subjected to EH and HH with identical time, PCL produced with HH showed greater Mwt (75% greater in Mn) than EH with the identical conversion and a typical GPC trace was demonstrated in Figure 4.16



Figure 4.16 Comparison of the GPC traces of typical PCL product from short ROP reactions with E-field (solid line) and H-field (dot line) heating at power of 150W.

Inspection the GPC traces as shown in Figure 4.16, GPC started to detect signal trace from 11.5 min mark for PCL produced using HH with peaks at around 12.5 min, 14 min, and 15 min. Whereas in EH, the signal trace started from around 12.5 min and the first peak located at around 14min which overlays with the second peak in H-field heating. The results exhibited identical trend as previous ROP studies showed in Table 4.1 where PCL produced using HH showed improvement in Mwt than which was done with EH.

These result demonstrated that the HH delivered promotions in Mwt growth which was different from EH. The previous heating experiments showed that the catalyst was primarily selectively heated in HH whereas both monomer and catalyst were heated in EH. Without competition in selective heating when using HH, the selective heating on the reaction site (catalyst) could potentially promote both the initiation process and the chain growth process (propagation reaction), thus greater Mwt was obtained. The series of experiments discussed above had clearly demonstrated that input power and heating methods could potentially affect the PCL yield and Mwt. Therefore, a series of short experiments at different input power but with identical reaction time 180 s were then conducted to further investigate the reasons behind the observed differences between EH and HH. Table 4.6 and Table 4.7 summaries the characteristic and yield data, and a typical GPC trace plot was shown in Figure 4.17.

Table 4.6 Average results of ROP of CL with FeCl₃ and BzOH using various input power at [M]: [C] ratio of 400:1 for 3min with EH.

	ЕН					
input power	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)		
25W	2100	2630	1.19	54.33		
50W	2300	2900	1.21	65.63		
75W	1620	2750	1.5	64.15		
100W	2430	3040	1.23	71.67		
125W	2460	3110	1.23	76.41		
150W	2260	3080	1.31	79.67		

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

Table 4.7 Average results of ROP of CL with FeCl₃ and BzOH using various input power at [M]:[C] ratio of 400:1 for 3min with HH.

	НН						
input	Mn ^a	Mp ^a	Ða	Conversion ^b			
power	$(gmol^{-1})$	(gmol ⁻¹)	D	(%)			
25W	2090	2070	1.41	50.73			
50W	2210	3400	1.39	55.15			
75W	2580	4360	1.38	67.32			
100W	2700	4000	1.31	82.30			
125W	2700	4060	1.53	82.72			
150W	3020	3870	1.37	83.22			

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

From the results shown in Table 4.6 and Table 4.7, improvements in Mwt and conversion of the produced PCL were obtained when input power was elevated from 25 W to 150 W in both heating methods. For example, as the input power

was increased from 25W to 150W, the M_p value increased from 2600 and 2100 gmol⁻¹ to 3100 and 3900 gmol⁻¹ for EH and HH, respectively. However, a greater enhancement in M_n and M_p from 25 W to 150 W was found in HH (Table 4.7) compared to in EH (Table 4.6). For example, the increment in M_n and M_p in HH from 25W to 150W were 45% and 95%, respectively, compared to 17% and 18% when using EH. Additionally, comparing results between two heating methods, the Mwt results at 25W in EH outperformed which in HH i.e. PCL produced in both heating methods have identical M_n, but M_p of the product with EH was 27% more. However, this observation was reversed as input power was further increased, for example, the M_n value for PCL produced using HH was 10% and 9% greater than that using EH at 100 W and 125 W. And the M_p value was 32% and 31% greater for PCL produced using EH and HH was shown in Figure 4.17 to illustrate the differences in the Mwt results.



Figure 4.17 Comparison of the GPC trace of the product polymer synthesised with idnetical reaction time with E-field (solid line) and H-field (dot line) heating at power of 150W. Condition: $[CL]:[FeCl_3]=400:1$.

Inspecting the graph of GPC trace shown in Figure 4.17, a greater Mwt in PCL was found for HH where the peak in GPC trace for PCL using HH shifted further

left than that using EH. This again agrees that the HH provides more significant impact on product yield and quality at a greater power level. For example, the increment in M_n and M_p were up to 45% and 95%, respectively, when the input power was increased from 25 W to 150 W. Conversely, the differences in Mwt at different input power were below 20% in EH. Such results potentially suggested that the catalytic efficiency of the iron halide was improved as it experienced significant selective heating from HH, which resulted in more notable increment in Mwt results than in EH experiments.

However, it should be remembered that in EMH, it was not possible to separate E-field and H-field, therefore, a weak E-field presents in HH, and *vice versa*. Although it was called microwave heating where H-field or E-field was dominated, it was still a combination of both fields heating the sample. Therefore, the observed outperformance in HH could be combination effects of strong HH and weak EH. The previous results showed that only strong HH provided significant impact on product yield and quality, whereas weak EH could still improve reaction rate and Mwt. This suggested that HH was a more beneficial heating method. Because both beneficial effects from strong HH and weak EH could be applied to reaction process during HH. Conversely, weak HH during EH would only had limited or negligible effects to the reaction process.

4.3.1.2 ROP of CL with FeCl₃ at [M]:[C] ratio of 800:1

A series of identical experiments but with lowered [M]:[C] ratios namely 800:1 were then conducted to identify the impact of catalyst concentration in different heating methods. Table 4.8 summarised the characteristic and yield of PCL produced using different heating methods.
Entry	Temperature (°C)	time (min)	heating method	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	conversion ^b (%)
1	50	45	CH	4800	5700	1.07	20.6
2	50	45	EH	4700	7600	1.26	40.5
3	50	45	HH	4300	7700	1.15	47.0
4	75	45	СН	5500	9100	1.31	49.0
5	75	45	EH	5500	9900	1.38	78.3
6	75	45	HH	6500	10000	1.23	64.3
7	100	45	СН	5000	7900	1.56	63.6
8	100	45	EH	5700	9800	1.46	76.4
9	100	45	HH	6300	11000	1.44	79.1
10	125	45	СН	3500	7100	1.66	51.1
11	125	45	EH	5200	8500	1.47	72.1
12	125	45	HH	5500	9700	1.51	70.2
13	150	45	СН	2900	5800	1.67	59.1
14	150	45	EH	4800	6900	1.47	64.2
15	150	45	HH	4800	7000	1.25	69.4

Table 4.8 Average results of ROP of CL with $FeCl_3$ and BzOH at various temperature at [M]: [C] ratio of 800:1.

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

Halving the concentration of the catalyst significantly increased the reaction time required to reach similar Mwt. For example, at 50°C for 45 min, the M_p value was only reached to 5700 gmol⁻¹, while it achieved 6800 gmol⁻¹ in M_p at [M]:[C]=400:1 for the same amount of time. Reduction in conversion was also noticed at lower catalyst concentration because fewer reaction sites were available for reaction and more monomers were able to attach to a polymer chain. As a result, higher Mwt results were able to be achieved at identical conversion when less catalyst was used. For example, in EH at similar conversion, M_p of 8500 gmol⁻¹ was reached in [M]:[C]=800:1 (Table 4.8 entry 11) whereas M_p was only 7100 gmol⁻¹ in [M]:[C]=400:1 (Table 4.1 entry 11).

The influence of the temperature on the bulk ROP of PCL at [M]:[C] ratio of 800:1 exhibited similar trends to those observed at [M]:[C] = 400:1 in CH. In fact, the temperature was noted to have a great impact on the polymerisation. It

was found that at 50°C, the reaction proceeded very slowly, where only 20% conversion was reached after 45 min in CH. Increasing the temperature to 75 °C and 100 °C significantly improved the product yield and Mwt with a reduction in reaction time. Further increasing the temperature to 125 °C and 150 °C, the M_n value reduced by 30% and 39% compared to that at 100 °C in CH, respectively. This attributed was again to the transesterification/ depolymerisation reactions as it was also observed that D of PCL expanded at elevated temperature. Figure 4.18 displayed the GPC trace of the PCL obtained in CH at various temperatures.



Figure 4.18 Comparison of the GPC trace of the product polymer synthesised using FeCl₃ at different temperatures. Condition: [CL]:[FeCl₃]=800:1.

It was noted that the curves showed a tendency to move towards the region of high molecular weight as temperature increased from 50 to 100 °C, while a shifting towards low molecular weight was noticed at 125 and 150 °C. At the same time, the molar mass distribution was broader and the presence of multi-modal GPC results were observed, suggesting the occurrence of transesterification side reactions. This again suggested high temperature above 100 °C has a detrimental effect on the reaction.

By comparison, the EMH experiments were observed to exhibited similar trend as CH but achieved greater yield. At least 13% higher conversion was achieved using both EMH methods compared to CH. Again, 75 to 100 °C was the best temperature range for the ROP reaction, above this temperature range reduction in Mwt and broadening in D were observed. For example, the M_n value dropped from 5700 to 4900 gmol⁻¹ and 6300 to 5300 gmol⁻¹ for EH and HH as the temperature increased from 100 to 150 °C. In a comparison between EH and HH, the differences in Mwt were typically around 8% to 18% at each point which was not as significant as that observed in [M]:[C]=400:1. Such results suggested the beneficial effects from EMH could be potentially affected by changing the catalyst concentration.

A series of kinetic studies were also conducted to determine the conversion achieved with time adopting the temperature change. Figure 4.19 demonstrated a typical time-conversion curves for the ROP reaction at various temperature using CH.



Figure 4.19 Kinetic study of ROP of CL using FeCl₃ at different temperatures using CH. Condition [CL]:[FeCl₃]=800:1.

Inspecting the conversion against time plots above, the conversion was found to increase with reaction time. The conversion versus time plots exhibited similar trend as which done at [M]:[C]=400:1: the reaction rate increased as temperature elevated from 50 to 100 °C, followed by a drop as temperature raised to 125 and 150 °C.

Again, both EMH methods showed greater initial conversion at 5 min than CH; this could again as a result of initial high power input as found from the previous section. A detailed study of short reactions focusing on the initial conversion will be presented later in this section.

The kinetics of the ROP was then investigated at different temperature values. This allowed for the identification of the polymerisation rate constant and helped for identifying the activation energy of the reaction. Figure 4.20 detailed the kinetic plots of the CH experiments at various temperature and Table 4.9 summarised rate constant (k_{app}) obtained from these kinetic plots.



Figure 4.20 Kinetic plots of $ln(M_0/M)$ versus time at different temperature using CH with best fit line (BFL). Condition: $[CL]:[FeCl_3]=800:1$.

Inspection of kinetic plots using different heating methods shown in Figure 4.20, the plots exhibited similar behavior as which found in [M]:[C] = 400:1 results.

A Linear relationship between $\ln(M_0)/(M)$ and time from 50 °C to 100 °C indicates the polymerisation follows a first order reaction for all heating methods. The R^2 value (shown in Table 4.9) for these lines were between 0.91-0.99 for CH suggests that the reaction was well controlled. However, after 100°C, the plots started to deviate from the linear relationship, i.e. R² value for all results was in a range of 0.78-0.86. It was noticed that the variation from the fitted regression line became greater (lower R² value) as reaction temperature increased. Higher temperature intensifies the transesterification reaction bringing as a result the broadening of regression distribution. Among these kinetic results, lower R² values were found for both EMH than CH even at high temperatures, for example, the R^2 values were typically between 0.87-0.89 for EH and 0.84-0.93 for HH at 125 and 150 °C. This observation again indicates that reactions in EMH potentially possessed a higher site temperature that intensified side reactions and caused lower R² values. From the data in Table 4.9, it was found that rate constant reaches a peak value at 100 °C followed by a drop at 125 and 150 °C in both CH and EMH.

	СН		Ε	EH		НН	
Temperature (°C)	R ²	k_{app} (min ⁻¹)	\mathbb{R}^2	k_{app} (min ⁻¹)	R ²	k_{app} (min ⁻¹)	
50	0.9989	0.0045	0.9599	0.0086	0.9396	0.0083	
75	0.983	0.0119	0.9857	0.0177	0.9905	0.0162	
100	0.9139	0.0194	0.9254	0.0358	0.8928	0.0354	
125	0.861	0.0151	0.8927	0.0213	0.9303	0.0216	
150	0.7868	0.0122	0.8709	0.0201	0.8424	0.0208	

Table 4.9 Summary of rate constant (k_{app}) and R^2 values at different temperatures using CH, EH, and HH. Condition $[CL]:[FeCl_3]=800:1$.

This again suggested that higher reaction temperature may have a detrimental effect in reaction because it promotes side reactions. Comparing k_{app} values between CH and EMH, greater k_{app} values were found in EMH,

e.g. 1.41-1.91 times greater for EH, and 1.36-1.84 times greater for HH at each temperature.

Interestingly, similar k_{app} values were obtained between EH and HH at this catalyst level. Reminding that the k_{app} values were found to be up to 50% higher in EH experiments at [M]:[C] ratio of 400:1 when compared to the HH experiments as shown in Table 4.9. This result suggested that reducing the concentration of the species that were experiencing selective heating could reduce the significance of the selective heating effects, as reflected by a reduced difference in the k_{app} values during the propagation period.

The observed higher propagation rates in EMH than CH could potentially be attributed to a higher effective temperature than the bulk temperature in EMH. Therefore, the activation energy was investigated next to calculate the effective temperature.

Based on the k_{app} values found in kinetic studies, the activation energy of the reaction can be determined. Again, the rate constant from 50 to 100 °C were used in this study because, at 125 and 150 °C, the side reaction started to compete with polymerisation reactions and affected the polymerisation rate. The Arrhenius plot was shown in Figure 4.21.



Figure 4.21 The relationship between lnk_{app} versus the reciprocal of absolute temperature with best fit line (BFL). Condition: $[CL]:[FeCl_3]=800:1$.

The Arrhenius plot of ln k_{app} versus the reciprocal of absolute temperature shows a linear trend in the range of temperature studied. The activation energy for three heating methods was found similar to each other typically 29.6, 28.7, and 29.1 kJ/mol for CH, EH, and HH, respectively. These results suggested that the mechanism of the reaction was same no matter which heating methods were used. The potential differences in conversion and Mwt should be due to greater local temperature on reaction site than measured bulk temperature. Follow the same methodology as the previous section; the potential effective temperature were calculated and summarised in Table 4.10.

Table 4.10 Estimation of effective temperature of the reaction for EH and HH heating methods at $[CL]:[FeCl_3]=800:1$ (T_b : the bulk temperature the reaction is conducted at; T_{eff} : the effective temperature of the reaction estimated based on Arrhenius plot).

	Ε	H	HH		
T _b (°C)	$T_{eff}(^{o}C)$	ΔT (°C)	$T_{eff}(^{o}C)$	ΔT (°C)	
50	68.48	18.48	67.32	17.32	
75	93.99	18.99	90.66	15.66	
100	122.84	22.84	122.34	22.34	

Analysis of the data in Table 4.10, both EH and HH showed a calculated reaction temperature that was greater than the measured bulk temperature, i.e., at least 18 °C and 15 °C greater than CH in EH and HH, respectively. From this study, it was able to estimate the potential local temperature differences within the bulk which were not able to be measured. Comparing ΔT results between [M]:[C]=400:1 and [M]:[C]=800:1, it was noticed a greater ΔT value was obtained at a lower concentration. This could suggest that reduction in catalyst concentration improved selective EMH because less competition in absorbing EM energy and this may indicate potential penetration depth issues with the higher concentration levels.

It was mentioned earlier in this section that greater initial conversion was observed in EMH could be due to initial high input power. Therefore, studies of short time scale reactions with different input power were also conducted to investigate the effects of initial input power. Again, five different input power, namely 25, 50, 75, 100, 125, and 150 W, were used. Two series of short reactions were conducted: the first series stopped after set temperature was reached, and the second was continued for 240 s (see below). Results for the first series were summarised in Table 4.11 and Table 4.12. Typical GPC results were shown in Figure 4.22.

			EH		
input power	Time ^a (s)	M_n^b (gmol ⁻¹)	M_p^{b} (gmol ⁻¹)	D^{b}	Conversion ^c (%)
25W	127	1260	1030	1.306	13.0
50W	74	1200	820	1.231	9.1
75W	55	1070	820	1.224	9.9
100W	39	1110	810	1.208	10.7
125W	29	1030	930	1.109	5.7
150W	26	1140	800	1.372	6.5

Table 4.11 Average results of ROP of CL with FeCl₃ and BzOH using various input power to reach 100 °C at [M]: [C] ratio of 800:1 with EH.

^a time required to reach 100 °C

^b determined by GPC, measured in THF at 35 °C

^c determined by ¹H-NMR

Table 4.12 Average results of ROP of CL with FeCl₃ and BzOH using various input power to reach 100 °C at [M]: [C] ratio of 800:1 with HH.

			HH		
input power	Time ^a (s)	M_n^b (gmol ⁻¹)	M ^b (gmol ⁻¹)	D^{b}	Conversion ^c (%)
25W	321	1460	2040	1.215	17.4
50W	117	1260	1000	1.215	12.3
75W	64	1190	1000	1.225	14.5
100W	44	1310	1030	1.335	9.1
125W	38	1160	1140	1.23	10.7
150W	30	1240	940	1.126	11.5

^a time required to reach 100 °C

^b determined by GPC, measured in THF at 35 °C

^c determined by ¹H-NMR

From inspection of Table 4.11 data, it was noticed again that EH required less time to elevate the bulk temperature to set temperature than HH. This was more significant at low input power e.g. 127 s and 321 s at 25 W for EH and HH, respectively, and 26 s and 30 s at 150 W for EH and HH, respectively, the difference in time required reduced from 152% to 15% as input power increased. This identified that HH was more efficient at higher input power because of the combined effect of dominant HH with substantial effective low EH as discussed earlier.

Comparing the Mwt results between EH and HH, it was found that Mwt obtained from HH was better than EH in both M_n and M_p . At 25W, the M_n and M_p were found to be 15% and 98% greater in HH than EH, respectively. However, it should be noticed that the reaction time was 152% longer in HH, and the polymerisation could take place during this heating time as the reaction was still effective at lowered temperatures such as 50 °C and 75 °C. Comparing results from 50W to 150W, 5-15% greater in M_n and 18-26% greater in M_p were found for HH than EH. A typical GPC graph was shown in Figure 4.22.



Figure 4.22 Comparison of the GPC traces of the product polymer synthesised using FeCl₃ with (a) EH (solid lines) and (b) HH (dot lines).

It can be seen that PCL has a peak at around 12-14 min and another peak at around 14-16 min for HH whereas most peaks for EH located around 13-16 min. This again showed that PCL Mwt in HH was grown substantially more than with EH, but it should be noted that an additional reaction time of 12-58% was required in HH to achieve this higher molecular weight material.. Therefore, the second series of experiments were conducted with identical reaction times of 240 s. The results were shown in Table 4.13 and Table 4.14, and a typical GPC results were shown in Figure 4.23.

	ЕН									
input	Mn ^a	Mp ^a	\mathbf{D}^{a}	Conversion ^b						
power	(gmol ⁻¹)	(gmol ⁻¹)		(%)						
25W	1000	1200	1.14	11.5						
50W	1250	1660	1.34	14.5						
75W	1400	1660	1.20	19.3						
100W	1420	1840	1.27	15.9						
125W	1350	1960	1.21	16.7						
150W	1390	2000	1.35	24.8						

Table 4.13 Average results of ROP of CL with $FeCl_3$ and BzOH using various input power at [M]: [C] ratio of 800:1 for 240 s using EH.

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

Table 4.14 Average results of ROP of CL with FeCl₃ and BzOH using various input power at [M]:[C] ratio of 800:1 for 240 s using HH.

	НН									
input power	M _n ^a (gmol ⁻¹)	M_p^a (gmol ⁻¹)	${ m D}^{ m a}$	Conversion ^b (%)						
25W	960	1180	1.21	14.5						
50W	1240	1740	1.14	18.6						
75W	1430	1750	1.19	21.2						
100W	1400	1870	1.19	20.6						
125W	1310	1960	1.15	18.6						
150W	1220	1940	1.24	21.8						

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

Analysing results from Table 4.13 and Table 4.14, the Mwt results between EH and HH were found similar with identical reaction time. For example, the differences were within 12% and 10% for M_n and M_p , respectively. Comparing these results against those were done at higher catalyst level (in Table 4.6 and Table 4.7), the differences in Mwt between EH and HH diminished as the catalyst level was reduced.



Figure 4.23 Comparison of the GPC traces of the product polymer synthesised using FeCl₃ with (a) EH (solid lines) and (b) HH (dot lines).

Moreover, as can be seen in Figure 4.23, the Mwt peak obtained from EH and HH almost overlay with each other, indicating similar Mwt were achieved in both heating methods. Unlike the observed significant differences in Mwt in [M]:[C]=400:1 (shown in Figure 4.17), the PCL product Mwt were similar in EH and HH as the catalyst concentration was halved.

This study showed that the effects of the selective heating of the catalyst in both EH and HH could be reduced as its concentration was lowered. In the meantime, although HH could not outperform EH in the produced PCL Mwt as observed in high catalyst load, PCL produced in HH and EH could still have comparable results. This suggests that HH could still be an alternative to EH that offers similar product quality, but with additional beneficial advantages like ease of scale up and set up as mentioned in the introduction.

Furthermore, as the longer time scale EH experiment has also produced higher Mwt materials. These results may also suggests that here may be differences in how the mechanism was conducted when the reaction was exposed to different levels of input power. The generation of low molecular weight materials in the early stages of the polymerisation may suggest that initiation was being favoured over propagation. This difference in initiation between the different heating methods at different catalyst concentrations may therefore explain the different Mwt observed for different heating strategies. It may also point to there being optimum catalyst concentrations regions to get the best results from particular heating methods.

4.3.1.3 ROP of CL with FeCl₃ at [M]:[C] ratio of 1600:1

The next step was to reduce that catalyst concentration to [M]:[C]=1600:1 to further investigate the how different heating methods could potentially affect the PCL quality as the catalyst concentration was changed. The conversion and characteristics of PCL produced at a catalyst concentration of [M]:[C]=1600:1 were summarised in Table 4.15.

Entry	Temperature (°C)	time (min)	heating method	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	50	90	СН	2100	2400	1.08	16.0
2	50	90	EH	4400	4700	1.09	30.8
3	50	90	HH	4400	4500	1.09	21.8
4	75	90	СН	4400	4800	1.06	24.2
5	75	90	EH	5300	5700	1.08	41.2
6	75	90	HH	5400	6000	1.10	44.2
7	100	90	СН	6400	8200	1.29	46.7
8	100	90	EH	7300	8900	1.15	62.1
9	100	90	HH	7300	9100	1.18	65.9
10	125	90	СН	5400	8100	1.28	46.5
11	125	90	EH	7100	9500	1.19	60.6
12	125	90	HH	6800	10400	1.26	62.9
13	150	90	СН	5000	7300	1.30	48.2
14	150	90	EH	6900	10400	1.35	70.2
15	150	90	HH	6600	10000	1.31	62.8

Table 4.15 Average results of ROP of CL with $FeCl_3$ and BzOH at various temperature at [M]: [C] ratio of 1600:1.

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

Inspecting PCL conversions achieved with CH, the conversion to polymer decreased sharply by reducing the amount of catalyst used in the polymerisation, e.g. 3 h into the reaction, and only 29% conversion was achieved at 50 °C which took less than 5 min to achieve at [M]:[C]=400:1. This could be attributed to the reduction in the polymerisation rate due to the low concentration of catalyst, potentially supporting the conclusion that the catalyst participates at the active chain end.

Elevating the reaction temperature to 75 °C and 100 °C resulted in improvement in polymer yield and higher PCL Mwt. However, the dispersity of the polymer raised at the same time (i.e. D = 1.29 at 46% conversion at 100 °C), indicating promotion in the side reaction. Further increasing temperature to 125 °C and 150 °C, the dispersity further increased to 1.28 and 1.30 at around 50% conversion, respectively. Cross-referencing the results with that done at higher catalyst loadings, it was found that the decreasing of the amount of catalyst used seems to be favoring a better control over the polymerisation, such as it was reflected by the mass distribution, i.e. the D decreases with increasing in the [M]:[C] ratio.

The comparative EMH reactions carried out using the same catalyst concentration again showed improvement in polymer conversion and Mwt at each temperature point (an average of 20% greater conversion were achieved for EMH than CH at each temperature point). Additionally, both EMH still was capable of maintaining the control of the reaction and resulted in lower D comparing to which obtained at high catalyst loadings (i.e. D = 1.35 at 70% conversion at [M]:[C] = 1600:1 at 150°C, whereas D = 1.87 at 70% conversion

at [M]:[C] = 400:1 at 150 °C in EH). Increasing reaction temperature again resulted in faster reaction rate, but also caused broadening in D of the polymer.

Further comparing PCL Mwt results between EH and HH, it was found that similar Mwt were achieved in both heating methods (less than 5% differences in M_n and M_p). This was unlike which observed at high catalyst load, i.e. M_p obtained in HH was at least 16% and 10% greater than EH at [M]:[C] ratio of 400:1 and 800:1, respectively. The enhancement in Mwt obtained from HH was reduced as catalyst loading was reduced. This was suggesting that the reduction in catalyst could have a more significant effect in PCL product in HH than EH because FeCl₃ was primarily experiencing selective heating in HH whereas both monomer and FeCl₃ were selectively heated by EH. The improvement in Mwt obtained from HH may be reduced when the species that can be heated by HH were reduced. This could suggested that if a species that undergoes magnetic selective heating was too small in quantity, the predominant heating method remains as electric heating due to the presence of weak electric field. As a result, comparable results between EH and HH were still obtainable. From these results, it suggested that there was a critical concentration level for the species that can undergo selective heating, below this "tipping point", the effect of selective heating would be diminished.

Further kinetic studies of the experiments were conducted to define the conversion achieved with time adopting the temperature change. A typical conversion versus time plots for such reaction with CH at various temperatures were shown in Figure 4.24.



Figure 4.24 Conversion versus time plots for ROP of CL at different temperatures with CH. Condition: [CL]: [FeCl₃] = 1600:1.

Inspecting the kinetic studies of the ROP experiments at [M]:[C] ratio of 1600:1, similar behavior was observed to high catalyst load. The elevating in temperature enhances the polymerisation rate. However, at 125 °C and 150 °C, after the high initial conversion (first 30min of the reaction), the gradient of the plot started to decrease. This again could be due to the increased rate of side reactions at high temperature that started in competing with propagation reactions. It should also indicate of the reduced catalyst level resulting in a different growth rate as a result.

Comparing the conversion between EH and HH, the differences in conversion were below 5% for all points. This suggesting that although HH was not outperforming EH in PCL product characteristics, HH could still offer comparable ROP results as obtained in EH even at low catalyst concentration.

The next step was to identify the rate constant at each temperature from kinetic plots, and therefore, calculate the kinetic energy of the reaction. The kinetic plots for CH experiments were shown in Figure 4.25.



Figure 4.25 kinetic plots for ROP of CL catalysed by $FeCl_3$ at various temperatures using CH as the heating method with best fit line (BFL). Condition: $[CL]:[FeCl_3]=1600:1$.

From the above graph, a linear relationship between $ln(M_0/M)$ and reaction time was observed for the reaction below 100°C. This result indicate that the polymerisation was accurately first-order concerning monomer concentration. The $ln(M_0/M)$ value started to deviate from the linear relationship as the temperature went up to 125 °C and 150 °C, as a result, the deviation from the regression fit line became greater and larger R² values were obtained for all heating methods as shown in Table 4.16. for example, the R² values reduced from 0.93 at 100 °C to 0.59 and 0.38 at 125 and 150 °C in CH. This again indicates the change in the reaction rate and the significant presence of side transesterification / depolymerisation reactions. The calculated k_{app} values were summarised in Table 4.16.

Table 4.16 Summary of rate constant (k_{app}) and R^2 values at different temperatures using CH, EH, and HH. Condition $[CL]:[FeCl_3]=1600:1$.

		СН		EH		HH
Temperature (°C)	R ²	k _{app} (min ⁻¹)	R ²	k _{app} (min ⁻¹)	R ²	k _{app} (min ⁻¹)
50	0.925	0.0021	0.9317	0.0033	0.9503	0.0028
75	0.9957	0.0029	0.9851	0.0063	0.9663	0.0061
100	0.9384	0.0087	0.9923	0.012	0.9531	0.0105
125	0.5906	0.0051	0.5834	0.0093	0.7754	0.009
150	0.3886	0.0061	0.6863	0.0097	0.6223	0.0091

Inspecting the k_{app} results in Table 4.16, again the peak value for k_{app} was found at 100°C. This again suggested that the best polymerisation temperature for ROP of PCL using FeCl₃ was at around 100 °C to achieve high conversion rate without significant side reactions. Comparing k_{app} obtained in EH and HH, similar values were obtained as similar conversion was achieved at each sample point. Based on these results, the activation energy could be determined using the Arrhenius plot as shown in Figure 4.26.



Figure 4.26 The relationship between lnk_{app} versus the reciprocal of absolute temperature with best fit line (BFL). Condition: [CL]:[FeCl₃] ratio of 1600:1.

In the inspection of the plot of lnk_{app} versus the reciprocal of absolute temperature shown in Figure 4.26, a linear trend in the range of temperature

studied was found for all heating methods. The activation energy was found to be 28.2, 26, and 26.5 kJ/mol for CH, EH, and HH, respectively. Again, very similar activation energy was found among three heating methods.

After identifying the activation energy, the potential effective temperature in EH and HH was calculated using the same methodology as previous sections. Inspecting results shown in Table 4.17, higher potential temperatures than CH were obtained in EH and HH (at least 18 and 13 °C higher than the bulk temperature in EH and HH). Again, higher or similar effective temperature was found for EH than/to HH. This could be explained by that both monomer and catalyst were heated in EH and resulted in a greater effective temperature, whereas the only catalyst was mainly heated by HH and ended up with lower effective temperature.

Table 4.17 Estimation of effective temperature of the reaction for EH and HH heating methods (T_b : the bulk temperature the reaction is conducted at; T_{eff} : the effective temperature of the reaction estimated based on Arrhenius plot).

	Ε	Н	HH		
Т _b (°С)	Teff (°C)	ΔT (°C)	T _{eff} (°C)	ΔT (°C)	
50	69.40	19.40	63.79	13.79	
75	93.42	18.41	92.14	17.14	
100	120.94	20.94	114.91	14.91	

4.3.2 Synthesis of PCL using CoCl₂ as Catalyst

After identifying and comparing the differences in PCL yield and Mwt using FeCl₃ as catalyst with CH, EH, and HH, the next step was to investigate if the obtained trend remains the same when the catalyst was replaced by CoCl₂. Unlike the ferromagnetic FeCl₃ that interacts with the magnetic field and retains the magnetism even after the magnetic field was removed, CoCl₂ was paramagnetic which can interact with the magnetic field but doesn't preserve the

magnetism after the magnetic field was removed, therefore, it may have less ability in interacting with the alternating magnetic field.

Identical reactions were conducted using BzOH as initiator and CoCl₂ as the catalyst with [M]:[C] ratio of 200:1 400:1 and 800:1. The [M]:[C] ratio of 1600:1 was not used because the reaction was slower than the iron comparative reactions reaching only 10% yield after 5h at 150 °C. ROP at different temperatures was also conducted, however, because the CoCl₂ provides no/negligible conversions at a temperature below 130 °C (after 8h reaction). Therefore, experiments were conducted at 140, 150, and 160 °C.

Before conducting the ROP reactions, a heating experiment of CoCl₂ mixed with CL was carried out first to identify its heating behavior when exposed to EMF. Similar to FeCl₃, an [M]:[C] ratio of 800:1 was used as the catalyst concentration. The sample was heated using MiniFlow at a maximum power of 150W in both E-field dominated, and H-field dominated regions. The temperature and power profile of EH and HH experiments were shown in Figure 4.27 and Figure 4.28, respectively.



Figure 4.27 Example of typical temperature profile and power profile of CL and CL+CoCl₂ mixture using EH at 150W input power where PA is Power Absorbed.

The temperature profile of CL containing CoCl₂ showed a measurable temperature difference compared to CL on its own. In particular, a maximum temperature difference of 9 °C was identified from the temperature profile, which identified that the catalyst must experience significant selective heating to provide such a significant temperature increment in the bulk temperature. Further inspecting the power profile, an average of 8 W more power was found to be absorbed by the CL+CoCl₂ sample compared to CL alone. Comparing this result against that of FeCl₃, the absorbed power found for CoCl₂ was about 10 W less than FeCl₃, and indeed a greater temperature difference was observed for FeCl₃. Thus this result suggested that CoCl₂ could be benefited from E-field selective heating, but it would not be at similar level to that of FeCl₃.



Figure 4.28 Example of typical temperature profile and power profile of CL and $CL+CoCl_2$ mixture using HH at 150W input power at [M]:[C] ratio of 800:1 where PA is Power Absorbed.

Inspecting Figure 4.28, insignificant temperature differences between CL itself and that containing CoCl₂, indicating that the magnetic selective heating on CoCl₂ was not significant enough to induce a temperature difference of the bulk temperature. Compared this heating profile to that of FeCl₃, it was found that FeCl₃ was able to induce more significant temperature differences than CoCl₂. This was due to that the heating of the catalyst was induced by the resonance of unpaired electron spin in the metal centre. The number of unpaired electrons in the metal centre determines its ability in interacting with the H-field and converting the absorbed energy into heat. In this case, both FeCl₃ and CoCl₂ stay in the high spin state and thus have spin configurations as shown in Figure 4.29.



Figure 4.29 Spin configuration of cobalt metal centre in $CoCl_2$ (left) and iron metal centre in $FeCl_3$ (right) at high spin state.

From the figure above, it was found that both FeCl₃ and CoCl₂ should be susceptible to the HH due to the presence of unpaired spins in their metal centre. However, it was noticed that there were only three unpaired spins present in CoCl₂ whereas five unpaired spins were located in FeCl₃. The more unpaired spin present in the metal centre, the metal would have better ability in interacting with the H-field and converting the absorbed energy into heat. Therefore, the FeCl₃ was found to have a higher heating rate with HH than CoCl₂.

From these heating experiments, it was clear that the selective heating of the CoCl₂ was significant with EH. Whereas, by using HH, it was not able to observe any measurable temperature difference between CL and CL with CoCl₂. Therefore, experiments were conducted to define was this different heating behavior with EH and HH was also reflected in the results for the ROP polymerisations conducted using CH, EH, and HH.

Initial ROP experiments were conducted at [M]:[C] molar ratio of 200:1 at 150 °C using CH, EH, and HH. Again, the MiniFlow was used for EH and HH experiments operated at 2.45 GHz with a maximum input power of 150 W. The results of ROP of CL were shown in Table 4.18 and a typical conversion versus time plot was shown in Figure 4.30.

Table 4.18 Average results of ROP of CL with $CoCl_2$ and BzOH at 150 °C at [M]:[C] ratio of 200:1.

Fntry	Heating	Time	Mn ^a	Mp ^a	Da	Conversion ^b
Entry	methods	(min)	(gmol ⁻¹)	(gmol ⁻¹)	D	(%)
1	CH ^c	180	150	160	N/A	<5%
2	СН	180	2900	2900	1.26	90.7
3	CH	240	4100	4600	1.51	96.4
4	EH	180	3400	3600	1.25	93.4
5	HH	180	3700	4100	1.33	93.8

^a determined by GPC, measured in THF at 35 °C

^b determined by ¹H-NMR

^c conducted without the use of CoCl₂



Figure 4.30 Kinetic study of ROP of CL using different heating methods at 150° C. Condition: [CL]:[CoCl₂]=200:1.

When the ROP of CL was carried out without $CoCl_2$ (Table 4.18, Entry 1). There was no polymerisation obtained after 180 min, indicating the necessity of using of $CoCl_2$ as the catalyst. When $CoCl_2$ was used as the catalyst, the conversion was able to reach 90% after 180 min (Table 4.18, Entry 2). However, an

induction period of 30 min was observed as can be seen in Figure 4.30. Extending the reaction time to 240 min, the reaction reached higher conversion and Mwt as a result of longer reaction period (Table 4.18, Entry 3). Similar results were obtained by Rajashekhar; they managed to synthesise PCL with M_n of 4500 gmol⁻¹ in 4.6 hours using CoCl₂ and BzOH as the catalyst and initiator.^[18]

In comparison, when EH was applied to the system, significant enhancement in Mwt and conversion was observed (Table 4.18, Entry 4). The obtained M_n value was about 21% greater using EH compared to CH. This indicated that EH has beneficial effects on ROP of CL. However, improvement in Mwt and conversion was also obtained when HH was used as the heating method. Additionally, the induction period was also reduced in EH and HH as shown in Figure 4.30. For example, around 10% of conversion was obtained at 30 min mark for both EH and HH (compared to 0% in CH). Part of this reduction in initiation period was due to the fast heat up time in EH and HH. In EH and HH, time required to heat the bulk to set temperature was around 150-160 s, whereas around 240 s was required in CH. However, after taking this into account, a 30 min difference in the on-set of initiation and propagation between two methods still required explanation. This could be attributed to the selective heating of individual components affecting the polymerisation mechanism.

The ROP of CL using $CoCl_2$ was proposed to proceed through the activated monomer mechanism. In this mechanism, the $CoCl_2$ first activates the monomer which facilitates BzOH attack on the electron-deficient carbon centre in the C=O group within the CL monomer, followed by the acyl-oxygen bond cleavage. As a result, the propagation of CL starts following the same route. In this case, if the catalyst was selectively heated, the ROP reaction site could also potentially possess a higher temperature than the bulk temperature, as a result, the activation of the monomer was potentially accelerated during the initiation period. Therefore, reduction in the initiation period were observed in EH and HH.

Inspecting Figure 4.30, a constant increase in conversion was observed after the initiation period for all heating methods, indicating that the polymerisation exhibited controlled/pseudo living characteristics no matter what heating methods were used.

However, from the previous heating experiment, insignificant temperature differences were noticed when $CoCl_2$ was added to CL. It was realised that the [M]:[C] ratio used in heating experiments was 800:1, whereas the [M]:[C] ratio used in the reaction was 200:1. Therefore, additional heating experiment using [M]:[C] ratio of 200:1 were conducted as shown in Figure 4.31. The reproducibility of the temperature profile was less than ± 2 °C, and less than ± 5 W in the power profiles.



Figure 4.31 Example of typical temperature profile and power profile of CL and $CL+CoCl_2$ mixture using HH at 150W input power at [M]:[C] ratio of 200:1 where PA is Power Absorbed.

Interestingly, it was found that when the catalyst load was increased, it was able to observe measurable temperature difference between CL and CL containing $CoCl_2$ (up to 7 °C). This clearly demonstrated that the concentration of species that were susceptible to HH was a critical factor. Additionally, in the low catalyst load heating experiment ([M]:[C]=800:1), the level of the catalyst may be below the critical concentration needed to deliver differentiated magnetic selective heating effects. Similarly, Horikoshi *et al.* also found that the heating of the sample with the H-field was more significant as the concentration of the solute was increased. ^[29]

Inspecting the power profile in HH, it was found low input power (below 20 W) were detected in the samples. This was again because MiniFlow was not able to detect the input and output of the magnetic power. Therefore, to identify if the observed temperature difference was originated from low power EH, identical EH experiment at 50 W was conducted, and the results were shown in Figure 4.32.



Figure 4.32 Example of typical temperature profile and power profile of CL and $CL+CoCl_2$ mixture using EH at 50W input power at [M]:[C] ratio of 200:1 where PA is Power Absorbed.

From the low power heating experiments, both samples reach 120 °C at around 130 s, which was similar to the period required in the HH experiments (120 s for CL). But, insignificant temperature differences were noticed between two

samples, indicating the observed differences in temperature with HH should be originated from the selective heating of CoCl₂ from the H-field. Additionally, compared the temperature profiles between EH with high and low input power, it proved that the selective heating of the catalyst with EH was more significant at high input power than that at low input power.

Therefore, combining the fact that measurable temperature difference was able to be observed when CoCl₂ was added to CL in HH at high catalyst load, it suggested that the selective heating on the catalyst could have significant effects on either/both the initiation and/or the propagation processes. To further investigate how catalyst concentration affects the ROP of the reaction and to identify if the observed beneficial effects remained when the catalyst concentration was reduced, lowered [M]:[C] ratios were used for the identical reaction. The [M]:[C] ratios used were 400:1 and 800:1. The summary of the ROP results were shown in Table 4.19, and the conversion versus time plot for all heating methods at [M]:[C] ratio of 400:1 was shown in Figure 4.33.

Table 4.19 Average results of ROP of CL with $CoCl_2$ and BzOH at 150 °C at [M]: [C] ratio of 400:1 and 800:1.

Entry	Heating methods	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	CH	400:1	180	2000	2200	1.203	34.2
2	EH	400:1	180	2700	3000	1.15	43.5
3	HH	400:1	180	3300	3600	1.18	51.4
4	CH	800:1	180	1500	1700	1.24	20.8
5	EH	800:1	180	2100	2500	1.189	29.4
6	HH	800:1	180	1700	2000	1.19	22.9

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR



Figure 4.33 Conversion versus time plots for ROP of CL using different heating methods at 150° C. Condition: [CL]:[CoCl₂]=400:1.

Inspecting Figure 4.33, again an initiation period of 60 min was obtained for CH. Conversely, the initiation period was reduced when EH and HH were applied. This was again due to the combination of fast heat up and selective heating on the catalyst as discussed previously. After the initiation period, the conversion was found to increase constantly indicating the control of the polymerisation was still maintained after the catalyst concentration was reduced.

From Table 4.19, inspecting the results obtained using [M]:[C] ratio of 400:1, the conversation rate was found to be reduced significantly, i.e. only 34% was reached after 180 min compared to 90% within 180 min at [M]:[C] ratio of 200:1. Conversely, the Mwt results were improved after the catalyst load was reduced. For example, the M_n value was around 2000 gmol⁻¹ at 34% at [M]:[C] ratio of 400:1, whereas M_n of 2800 gmol⁻¹ was obtained at 90% when [M]:[C] ratio was 200:1. Comparing results obtained among all three heating methods, a similar trend to that of [M]:[C] ratio of 200:1 was obtained, and HH was found to show the most improvement in Mwt and conversion. In particular, the M_n value was improved by 65% compared to CH, and conversion was 17% higher than that in CH. Results obtained from EH also showed improvement, but was less significant than HH, suggesting at [M]:[C] ratio of 400:1, HH was still able to provide more beneficial effects to ROP than EH.

Further, reducing the catalyst concentration to [M]:[C] ratio of 800:1, it was again found that the reaction time was prolonged, and Mwt obtained at identical conversion was increased. But interestingly, it was noticed that EH showed the highest Mwt results and conversion among all three heating methods, and similar Mwt and conversion were obtained between HH and CH. Combining the fact that undifferentiated temperature profile between CL and CL+CoCl₂ when using HH, suggesting that the concentration of the catalyst may be below the critical concentration needed to deliver significant magnetic selective heating effects.

To identify how temperature affects the ROP of CL, another two temperature, namely 140 °C and 160°C, were used to compare the results against that at 150°C. The [M]:[C] molar ratio used was 800:1. The kinetic studies at each temperature using different heating methods were shown in Figure 4.34, Figure 4.35, and Figure 4.36.



Figure 4.34 Conversion versus time plots for ROP of CL at different temperatures with CH. Condition: [CL]:[CoCl₂]=800:1.

Inspecting the conversion versus time plot using CH, it was found that at 140 °C, an induction period of 60min was required before the propagation process started. Raising the temperature to 150 °C and 160 °C, the initiation time was further reduced to below 60 min. In particular, at 160 °C, the conversion was able to reach 6% after only 30 min. During the propagation period, the constant increment in conversion was observed for all temperatures, suggesting the control over the polymerisation were still maintained. Additionally, increasing the temperature was found to accelerate reaction rate and allow to reach higher conversion, indicating that conducting reactions at elevated temperature could provide beneficial effects in the reaction.



Figure 4.35 Conversion versus time plots for ROP of CL at different temperatures with EH. Condition: [CL]:[CoCl₂]=800:1.

Similarly, when the reaction was conducted using EH, the initiation period was again found to be reduced significantly as the temperature was elevated. Moreover, the higher conversion was able to be reached as the temperature was increased, i.e. 45% conversion was reached after 120 min at 160°C, whereas only 7% was achieved at 140 °C. Again, a constant increase in conversion was noticed at all temperature indicating CoCl₂ remained good control over the polymerisation. Comparing the results against that done in CH, it was found that higher conversion was achieved by EH at the identical temperature. This again proved that applying EH to the reaction could accelerate both/either the initiation and / or propagation period.



Figure 4.36 Conversion versus time plots for ROP of CL at different temperatures with HH. Condition: [CL]:[CoCl₂]=800:1.

Inspecting Figure 4.36, when HH was used, the reaction again proceeded in two steps: an initiation period with no conversion, followed by a constantly increase in conversion during the propagation period. Good control over the conversion was again observed. However, the similar conversion was achieved compared to CH (i.e. only 6% conversion was achieved after 30 min at 160 °C). This was again indicating at this catalyst level, there was no significant selective heating on the catalyst, and so the outcomes of the HH and CH reactions were very similar.

Now that the time-conversion curves were plotted, it was possible to investigate to the kinetics of the ROP of CL using CoCl₂. In order to do this, kinetic plots of $\ln([M_0]/[M])$ versus reaction time were studied, and so allowed for the calculation of the apparent k_{app} for the polymerisation at the temperature used. The summary of k_{app} at various temperature using all three heating methods were shown in Table 4.20, and an example of such kinetic plot was shown in Figure 4.37.

Table 4.20 Summary of rate constant (k_{app}) at different temperatures using CH, EH, and HH. Condition [CL]:[CoCl₂]=800:1.

	СН	EH	HH
Temperature	k _{app}	k _{app}	k _{app}
(°C)	(\min^{-1})	(\min^{-1})	(min^{-1})
140	0.0005	0.0007	0.0005
150	0.0016	0.0023	0.0017
160	0.0044	0.0059	0.0042



Figure 4.37 Kinetic plots of $ln(M_0/M)$ versus time at different temperature using CH with best fit line (BFL). Condition: $[CL]:[CoCl_2]=800:1$.

Inspecting Figure 4.37, a straight line relationship holds for $\ln([M_0]/[M])$ as a function of reaction time. This indicated that the polymerisation was accurately first-order concerning monomer concentration. Additionally, k_{app} values were found to increase with temperature. This holds true for all three heating methods. Therefore, this indicated that if the selective heating on the catalyst elevated its temperature to a higher degree, it could potentially accelerate the propagation rate. As a result, higher conversion and Mwt was achieved when EH was applied to the polymerisation. Indeed, a higher k_{app} value was obtained in EH compared to CH and HH at each temperature set point, because the catalyst was found to experience electric selective heating in EH heating experiments.

Conversely, similar k_{app} values for CH and HH at each temperature suggested that the propagation rate was not improved when HH was applied to the ROP. Combining the fact that there was no significant magnetic selective heating were observed when heating experiments were conducted at [M]:[C]=800:1 using HH, the results suggested that the concentration of the catalyst below the "tipping point" where significant magnetic selective heating effect could be observed, and so the predominant heating method remains as CH.

As the reactions were first order reactions, the activation energy can be identified by using the Arrhenius plot. The Arrhenius plot of lnk_{app} versus the reciprocal of absolute temperature was shown in Figure 4.38.



Figure 4.38 The relationship between lnk_{app} versus the reciprocal of absolute temperature with best fit line (BFL). Condition: $[CL]:[CoCl_2]=800:1$.

It was observed that the Arrhenius plot showed a linear trend in the range of temperature studied. Based on the plot, the activation energy of the ROP of CL were found to be: 162, 159, and 159 kJmol⁻¹, for CH, EH, and HH, respectively. The insignificant differences in activation energy among three heating methods

indicating the observed differences in ROP results should be purely thermal effects.

4.3.3 Synthesis of PCL using SnCl₂ as Catalyst

Now that the ROP of CL using FeCl₃ and CoCl₂ were investigated, the next step was to identify how the ROP results between CH, EH and HH would be changed if the catalyst was not able to interact with the H-field. In this case, a diamagnetic material SnCl₂ was used as the catalyst. In diamagnetic materials, there were no unpaired spins present in the d-orbital of the metal centre, and thus no magnetic heating of the material should be observed. Therefore, to identify how SnCl₂ was heated with EH and HH, heating experiments of SnCl₂ were conducted first. The temperature and power profile of EH and HH experiments were shown in Figure 4.39, Figure 4.40 and Figure 4.41.



Figure 4.39 Example of typical temperature profile and power profile of CL and CL+SnCl₂ mixture using EH at 150W input power where PA is Power Absorbed.

The heating experiment was first conducted using EH at a high input power of 150 W, a measurable temperature difference between CL and CL containing SnCl₂ was observed. A maximum temperature difference up to 12 °C was obtained from the temperature profile, indicating that the SnCl₂ was

experiencing significant selective heating from the E-field. Inspecting the power profile shown in Figure 4.39, additional 14W were absorbed by the CL+SnCl₂ sample compared to the CL itself.



Figure 4.40 Example of typical temperature profile and power profile of CL and CL+CoCl₂ mixture using EH at 50W input power where PA is Power Absorbed.

Interestingly, when the input power was reduced to 50 W as shown in Figure 4.40, it was found that the temperature and power profiles between CL and CL+SnCl₂ were almost identical, indicating that the selective heating of the sample was more significant at high input power. This could be because CL was a good MW absorber, so that competition in absorbing the E-field energy occurred at low input power. As a result, there was insufficient energy for SnCl₂ to deliver a differentiated bulk temperature. Conversely, at high input power, the energy was sufficient for both species to absorb and convert into heat. Therefore, the selective heating effect on the catalyst was able to be observed at high input power.


Figure 4.41 Example of typical temperature profile and power profile of CL and CL+CoCl₂ mixture using HH at 150W input power where PA is Power Absorbed.

By comparison, when heating experiments were conducted using HH at high input power as shown in Figure 4.41, identical temperature profiles between CL and CL containing SnCl₂ were observed, identified that there was no significant selective heating on SnCl₂ with HH. This was due to the fact that there were no unpaired electrons present in the d-orbital of the SnCl₂ metal centre as shown in Figure 4.42, thus it was not susceptible to the alternating H-field.



Figure 4.42 Spin configuration of the tin metal centre in SnCl₂.

Therefore, from the heating experiments, it was found that the selective heating effects on SnCl₂ were only observable when in EH. Thus, series of ROP experiments using SnCl₂ were conducted using identical conditions as FeCl₃ and CoCl₂. Results of initial experiments using [M]:[C] ratio of 400:1 were summarised in Table 4.21 and a typical conversion versus time plot for different heating methods was shown in Figure 4.43.

Table 4.21 Summary of ROP of CL with SnCl₂ at 150 °C using different heating methods at [M]:[C] ratio of 400:1.

Entry	Heating methods	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Ъ	Conversion ^b (%)
1	СН	10	3300	3600	1.11	93.5
2	СН	20	4300	4700	1.33	98.6
3	EH	10	3500	3800	1.19	98.7
4	EH	20	4600	5100	1.27	98.1
5	HH	10	3200	3600	1.21	95.8
6	HH	20	4200	4600	1.31	97.9

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR



Figure 4.43 Conversion versus time plots for ROP of CL using different heating methods at 150°C. Condition: [CL]:[SnCl₂]=400:1.

Figure 4.43 showed that a constant increment in conversion against time was observed for all heating methods, indicating the catalyst was able to provide control to the polymerisation. Comparing the conversion achieved by different heating methods, an average of 6% higher conversion was achieved by EH than CH and HH. Additionally, very similar conversion was achieved between CH and HH. Combined the fact that selective heating effects of SnCl₂ were only observed when using EH, this suggested that the improvement in conversion should be due to the existence of the selective heating effect.

At [M]:[C] ratio of 400:1, the ROP of CL were able to reach over 90% within 10 min for all heating methods. Entries 1, 3, and 5 in Table 4.21 compared the data from the reactions between different heating methods, the PCL produced *via* EH showed an average of 10% higher values in both M_n and M_p compared to CH and HH. Conversely, similar Mwt results were obtained between CH and HH. Again, this could potentially be attributed to the fact that selective heating effects were only observed when SnCl₂ was performed in EH.

Extending the reaction time by an additional 10 min, higher Mwt results were able to obtain, i.e. an approximately 30% increment in M_n values was observed for all heating methods. In the meantime, the D of the product were found to expanded, indicating the existence of transesterification reactions. Among all three heating methods, the EH was again found to produce PCL with the highest Mwt, whereas products obtained using CH and HH were very similar.

To extend the applicability of this catalyst system, the polymerisation was conducted at reduced catalyst levels, in this case [M]:[C] ratio of 800:1 and 1600:1 were used to be the catalyst concentration. The summary of the results was shown in Table 4.22, and Figure 4.44 demonstrated the typical conversion versus time plot of such polymerisation at [M]:[C] ratio of 800:1.

Table 4.22 Summary of ROP of CL with SnCl₂ at 150 °C using different heating methods at [M]:[C] ratio of 800:1 and 1600:1.

Entry	Heating methods	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	СН	800:1	30	6100	6400	1.25	99.3
2	EH	800:1	30	6600	6900	1.19	98.6
3	НН	800:1	30	6100	6000	1.12	96.4
4	СН	1600:1	45	7200	7500	1.22	99.0
5	EH	1600:1	45	7800	8100	1.11	98.5
6	НН	1600:1	45	7400	7500	1.14	97.7

^a determined by GPC, measured in THF at 35 °C

^b determined by ¹H-NMR



Figure 4.44 Conversion versus time plots for ROP of CL using different heating methods at 150 °C. Condition: [CL]:[SnCl₂] =800:1.

The Figure above showed that the polymerisation exhibited a constant increase in conversion as the reaction proceeded, indicating the control of the polymerisation still remained. Very similar trends in conversion between all three heating methods were observed from the kinetic study. The only difference was a measurable increase conversion in the EH case throughout the course of the reaction (typically 10-15% greater at each point than that of CH and HH). This was again should be due to the selective heating effects on the catalyst.

Inspecting the results from Table 4.22, at both [M]:[C] ratios, it was again found that reducing the catalyst load extended the reaction time, but provided an improvement in the Mwt. Among all three heating methods, again higher Mwt results were obtained by EH compared to CH and HH. This showed that the selective heating effects on the catalyst from EH could still affect the polymerisation even at reduced catalyst load. Additionally, low D (<1.5) were obtained for all samples, indicating the catalyst have good control over the polymerisation even at reduced catalyst level.

After identifying how catalyst concentration affected the polymerisation with different heating methods, the next step was to identify how the reaction temperature affects the polymerisation. To do this, two additional sets of identical experiments but at 140 and 160 °C were conducted using all three heating methods at [M]:[C] ratio of 800:1. Evaluating the rate constant from kinetic studies, a summary of k_{app} at different temperature of all three heating methods were shown in Table 4.23, and a typical ln([M₀]/[M]) versus time plot at 150 °C using all three heating methods was shown in Figure 4.45.

Table 4.23 Summary of rate constant (k_{app}) at different temperatures using CH, EH, and HH. Condition [CL]:[SnCl₂]=800:1.



Figure 4.45 Kinetic plots of $ln(M_0/M)$ versus time at 150 °C using different heating methods with best fit line (BFL). Condition: $[CL]:[SnCl_2]=800:1$.

From Figure 4.45, it was obvious that the k_{app} value obtained from EH was significantly greater than CH and HH, this was again due to the selective heating effect with EH. Additionally, this trend was also found when the reaction

temperature was changed to 140 and 160 °C. Comparing the k_{app} values at different temperatures, it was found that the rate constant was comparably greater at a higher temperature. This was indicating that elevating the reaction temperature improves the propagation process significantly, and thus resulted in the higher rate constant. Moreover, this was again suggesting that selectively heating the catalyst to a higher temperature could accelerate the propagation rate and allow for enhancement in propagation process and Mwt results. Calculating the activation energy (E_a) based on the obtained k_{app} values using Arrhenius plot as shown in Figure 4.46, very similar E_a values were obtained among all heating methods, namely, 34.2, 34.1, and 35.2 kJmol⁻¹, for CH, EH, and HH, respectively. This again suggested that the observed enhancement in PCL product with EH should be purely thermal effects.



Figure 4.46 The relationship between lnkapp versus the reciprocal of absolute temperature with best fit line (BFL). Condition: [CL]:[SnCl₂]=800:1.

4.4 Conclusion

ROP of CL has been conducted using FeCl₃ at various temperatures. In this study, it has demonstrated that temperature has a significant effect on PCL product and the optimum temperature for FeCl₃ catalyst was around 100°C. Exceeding the

temperature may result in an enhancement in side transesterification reactions, and causing detrimental results in both conversion and PCL Mwt, such as expanding the polydispersity and reducing the average Mwt. Reducing the catalyst concentration has a significant improvement in the control of the reaction which was reflected by reductions in product polydispersity. In comparison between CH and EMH, the EMH was capable of delivering significant enhancement in PCL conversion and characteristics than CH. This was potentially delivered by the selective heating in monomer and catalyst in EH, and selective heating in the catalyst in HH. Further investigation in kinetic studies, it was found the rate constant for EH and HH was significantly higher than CH. This leaded to the identification of the activation energy which were found to be similar between all three heating methods at each concentration. But a potential "heat concentration" around/at the catalyst was found for EH and HH when determining the effective temperature from activation energy. Additionally, the effective temperature was found to have be greater or similar in EH than HH, this could be due to both monomer and catalyst were selectively heated in EH. This again supported that the selective heating of the catalyst in EH and HH was the potential origin for the enhancement in PCL conversion and Mwt observed in the ROP reactions. The effects of input power were also studied in short reaction experiments. It was found that increasing in input power had a more significant effect in HH than EH. Additionally, it was found that at higher catalyst load, the PCL produced in HH possesses greater Mwt than EH at identical reaction time, but this difference diminishes as the catalyst load was reduced. This indicated the HH could potentially provide more beneficial effects at high catalyst load. However, comparable results to EH were still achievable in HH at low catalyst load, suggesting that HH could still be a potential alternative heating method to EH.

Conversely, when CoCl₂ was used as the catalyst for the ROP reactions, it was found that the reaction involved two stages: the initiation stage and the propagation stage. The initiation stage was able to be reduced by either raising the reaction temperature or applying EMH. During the propagation step, the catalyst was able to control the polymerisation with a constant increase in conversion for all three heating methods. It was found that using EMH was able to accelerate either/both the initiation and/or the propagation process via the selective heating on the catalyst, and as a result shorter reaction times were achieved. Reducing the catalyst concentration was found to prolong the reaction time, but allowed for the produced PCL to reach significant higher Mwt. Additionally, the concentration of the species that was susceptible to microwave electric and magnetic selective heating was found to be a critical factor to deliver differentiated selective heating effects. If the catalyst undergoes selective heating was at a concentration higher than the "tipping point", the outcomes of the EMH and CH reactions would be different in favour of the former one. In contrast, if the catalyst was present in too small quantity, there would be no significant selective heating effects, and similar results to CH was then observed. The reaction temperature was also found to have significant effects on the ROP of the CL, such as reducing initiation period and accelerate the reaction rate. Therefore, this indicated that if the catalyst undergoes selective heating, it was likely to deliver differentiated reaction/product properties. Indeed, from the Arrhenius plot, similar activation energy among all three heating methods was

found, indicating the observed difference between each heating methods were purely thermal effects.

A rapid synthesis of PCL using SnCl₂ with CH, EH, and HH was also successfully performed at various catalyst concentration. A controlled/pseudo living characteristic was exhibited by the polymerisation without notification of significant initiation period. Comparison between the heating of the catalyst in EH and HH demonstrated different heating mechanism between the two heating methods. Significant selective heating effects were observed in EH, whereas identical temperature profile to CL was obtained in HH due to its magnetism. This selective heating effect later was found to provide acceleration in reaction rate and improvement in the product Mwt. Conversely, very similar results were obtained between CH and HH. Reducing the catalyst concentration, the control of the polymerisation was still able to be maintained, and the beneficial effects of selective heating were still obtainable. Elevating the reaction temperature was found to accelerate the polymerisation reaction, and this potentially suggests that the beneficial selective heating effects were due to a higher temperature of the catalyst. Indeed, from the activation energy studies, very similar E_a values were obtained among all heating methods, suggesting that the observed selective heating effects should be purely thermal effects.

4.5 Future Work

Future work to be investigated in this area is to see if these observed beneficial selective heating effects are still obtainable when other cyclic esters are used for the ROP reactions. Also, to investigate if the combination of HH and FeCl₃ can be successfully applied to other ROP reaction. More work needs to be done on

the HH to identify how to maximise the beneficial magnetic selective heating effects and to investigate the possible scale up of the reaction using HH.

4.6 References

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Chapter 5. Investigation into the Comparison of the Effect of Electromagnetic Field Has on the Organometallic Catalyst in Ring Opening Polymerisation of ε -caprolactone

5.1 Aim and Objective

This chapter outlines the application of iron octanoate for use in the control of Ring Opening Polymerisation (ROP) process of ε -caprolactone (CL). This complex was used as an alternative for the current benchmark catalyst tin octanoate. Another complex which is cobalt octanoate was also studied to compare how the metal centre affect the control of the ROP reaction. We have rigorously investigated the effect that conventional heating (CH), microwave electric heating (EH), and microwave magnetic heating (HH) has upon the polymerisation process based on these catalysts. The catalytic activity of these catalysts were also investigated by comparing the polymer yield and control over the molecular weight (Mwt) and polydispersity of the product. Additionally, detailed investigation in assessing the effect of (a) catalyst concentration and (b) reaction temperature has upon the efficiency of the ROP process. Once the polymerisation process was optimised, it opens the possibilities to replace the current tin octanoate with catalysts based on metals that are cheap like iron and cobalt.

5.2 Introduction

The unique properties of polycaprolactone, such as good biodegradability, solubility with many other polymers, and also mechanically compatible with other different polymers, have drawn increasing attention in both industrial and academic fields.

A large number of catalysts and catalytic systems have been investigated. Consequently, achieving the efficient and rapid ROP of CL has been a popular topic in academia. Most of these studies focused on the control characteristics achieved by adopting particular catalytic mechanisms/species. However, few of these new catalytic systems are available for commercial exploitation due to most have not met the regulatory clearance required for industrial exploitation and/or are not commercially available. ^[1-3]

Subsequently, development of processing techniques including microwave heating (MWH), have been investigated to identify if they could deliver improvement in poly-caprolactone (PCL) production. MWH provides volumetric heating to replace conventional conductive/convective heating. Several reports have proved the method of microwave (MW) assisted ROP of CL to prepare PCL rapidly and efficiently in lab scale (monomer<10 g). ^[4-9] A variety of catalysts were tested in MW assisted ROP reactions. But among them, the current most widely used catalyst is tin ethylhexanoate also known as tin octanoate (Sn(Oct)₂). It is efficient, commercially available, easy to handle, and soluble in most commonly used solvents. Typically, it has proved to provide good control to the ROP reaction of cyclic esters via the coordination-insertion process. Additionally, with MWH when in the presence of an alcohol initiator, increased rates have also been reported.

Fang *et al.* studied the MW-assisted ROP reaction for PCL at a temperature of 120, 150, 180 and 200 °C using Sn(Oct)₂ at a forward power of 90-135 W at 2.45 GHz. ^[10] The reaction temperature was kept constant with MW energy been pulsed into the bulk. No obvious reactions were observed at 120 °C, but above 90% conversion was achieved at the other temperatures in a period of 2 h. They

demonstrated that the ROP of CL could be performed efficiently and effectively with MW irradiation without the aid of conventional heating.

In 2002, Liao and coworkers performed the same ROP of PCL with Sn(Oct)₂ but at a greater power at 170, 340, 510, and 680 W. ^[6] An increment in Mwt was observed as input power was increased at an identical reaction time of 30 min. The reaction temperature was not constant at each input power, ranging from 80 to 220 °C depending on the input power. The increment in the concentration of Sn(Oct)₂ was also noticed to lead to lower Mwt.

Liao further studied the same experiment at two different monomer scales (1 and 10 g). ^[11] They found that increasing the amount of monomer from 1 to 10 g induced an increase in the bulk temperature of the sample at 680 W (from 200 to 300 °C), and thus resulted in higher conversion and greater Mwt in PCL product. Additionally, they noticed exothermal peaks in these MW experiments, and the temperature overshoot was proportional to the input power, i.e. the overshoot was 43 °C at 680 W and was 29 °C at 170 W. They concluded that the observed high conversion and Mwt resulted from the temperature overshoot.

Later in 2006, the same group compared the MW assisted Sn(Oct)₂ catalysed ROP of CL conducted at 2.45 GHz (700 W input power) with 'flash' CH (i.e. introduction into a hot salt bath to achieve fast heating of the bulk). ^[12] The typical heating time in 'flash' CH was half of that in MW heating. It was concluded that the rate observed in 'flash' CH was superior to that achieved by MW heating in both rates of chain propagation and molar mass of the resulting PCL.

The same author then further investigation into the kinetics of ROP conducted using MW and 'flash' CH at various temperatures. ^[13] The study led to the conclusion that the 'flash' CH rate enhancement was purely thermal effect as it obeyed Arrhenius law. But, the increase in the MW heating rate constant was claimed not to fit this law, suggesting the presence of non-thermal MW effect in the reaction.

To identify the possibility of industrialise the MW-assisted process, the same group then developed a large scale MW assisted ROP system at 2.45 GHz with IR temperature sensor in 2010. ^[14] The system was able to perform with monomer mass from 750 to 2450 g at various MW power levels (850, 1700, and 2550 W). An inter dependency between the input power and/or monomer mass with the reaction temperature was reported. The higher the power and mass, the higher the temperature achieved.

Meanwhile, Sinnwell and co-workers conducted ROP with Sn(Oct)₂ using methacrylic and acrylic acid as initiators, fibre optic thermocouple was used to access the temperature. ^[15] They reported no significant rate acceleration between CH and MW heating.

Nguyen *et al.* carried out a detailed study focusing on the influence that MW heating has upon mechanic steps involved in ROP of CL using Sn(Oct)₂. ^[16] Direct comparison between CH and MWH showed the reduction in reaction time in MWH was due to elimination /reduction of the induction time. Further investigating the dielectric property and heating behaviour of the sample, observations of significant temperature overshoot in MWH were obtained when the catalyst was introduced into the monomer, it was concluded that selective

heating on the organometallic species contributes directly to the differences in the reaction conditions.

From this short literature survey, beneficial effects can be seen when conducting ROP reactions with MWH compared to CH. But the major hurdle regarding the commercialization of such processes is the difficulty in removing catalyst residues and the cytotoxicity associated with such residues, which limits the use of these polymers in biomedical applications. ^[17, 18] Even though tin-based catalysts are FDA-approved, studies with long-term liberation and physiological effects of tin-ions from large tissue-embedded scaffold-matrices have not yet been conducted and may impose a different level of risk. ^[17] The accessible data on biological tin ion effects allow driving potential risks and possible adverse effects of tin catalysts remaining in the biopolymers used and composted in agriculture or biomedical applications. These risks impact terrestrial and aquatic microorganisms for agricultural uses and mammalian cells in tissue engineering. ^[17] Due to potential side effects and unknown long-term effects of Sn²⁺ in tissue, the application of other metal salts as catalysts for the ROP of biopolymers used in regenerative medicine and tissue engineering is of great interest. ^[17-20]

An attractive process is envisioned to be engineered upon new catalysts that have environmentally benign metals that are constituents in the mammalian anatomy so that the residues are potentially harmless. ^[21] In this study, alternative catalysts with identical ligands based on iron and cobalt, namely iron octanoate (Fe(Oct)₃)and cobalt octanoate (Co(Oct)₂), were compared to Sn(Oct)₂ regarding control of polymerisation in terms of the reaction conversion and the product molecular weight. The Co(Oct)₂ was found to be used as a catalyst for the anionic living polymerisation of conjugated dienes ^[22], whereas a magnetic susceptible bimetallic Fe-Ni octanoate nanoparticles were used as column pack for high gradient magnetic separation in water treatment. ^[23] However, none of this catalyst have been applied to be the catalyst for ROP reactions. This would be the first time these catalysts were used as a catalyst in ROP of CL.

As described in Chapter 4, it was found that metal halides based on cobalt and iron were able to interact with magnetic field (H-field). Additionally, the microwave magnetic heating (HH) provided sufficient energy to the reactions to produce PCL similar to which produced with microwave electric heating (EH). The metal centre could affect the catalyst's ability in interacting with the H-field. Therefore, in this study, three heating methods (CH, EH, and HH) were applied to the reaction to study and compare the characteristic and conversion of PCL produced when using various heating methods. Eventually, comparing the performance of each catalyst with different heating methods to identify if the iron or cobalt alternatives could be the replacement for Sn(Oct)₂. Therefore, this section of the study has focussed upon developing a environmentally benigned catalyst with a potential of simple scaling up of the process.

5.3 Results and Discussion

5.3.1 Investigation of ROP with the Application of Conventional Heating (CH)

Before conducting any MW-assisted reactions, it is important to understand the mechanism and catalytic efficiency of each catalyst. Therefore, initial reactions were conducted using conventional heating (CH) method, with all three catalysts at a range of [M]:[C] ratios. By doing so, it is possible to establish a

comprehensive comparison between the alternative catalysts and the benchmarking catalyst Sn(Oct)₂.

ROP reaction of PCL was carried out at 150 °C using Sn(Oct)₂, Fe(Oct)₃, and Co(Oct)₂. Three catalyst concentration namely [Monomer]:[Catalyst] ([M]:[C]) ratio of 400:1, 800:1, and 1600:1 were used. BzOH at [Catalyst]:[Initiator] ([C]:[I]) ratio of 1:10 was used for all reactions. Results of these experiments can be seen in Table 5.1, and a typical Mn versus conversion plot was shown in Figure 5.1.

Table 5.1 Average results of ROP of CL with different catalysts and BzOH at [M]:[C] ratio of 400:1 using CH. The target Mwt was 4500 gmol⁻¹ at 100% conversion.

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Ъ	Conversion ^b (%)
1	-	-	60	160	170	1.05	<1
2	Sn(Oct) ₂	400:1°	60	200	200	-	<1
3		400:1	10	5200	5200	1.06	92
4		400:1	15	5500	5500	1.32	96
5	Fe(Oct) ₃	400:1	55	3500	3500	1.13	80
6		400:1	75	4100	4300	1.16	91
7	Co(Oct) ₂	400:1	55	2800	2800	1.12	69
8		400:1	75	3600	3700	1.16	80

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

^c Reaction was conducted without any initiator

The ROP was first carried out in the absence of any catalyst (Table 5.1, Entry 1), low conversion (<5%) was obtained. Similarly, when no initiator was used in the reaction, no polymerisation of the product was observed (Table 5.1, Entry 2). This suggested that both the catalyst and the initiator were essential to initiate ROP. When the ROP reaction was carried with Sn(Oct)₂, the reaction was able to reach above 90% in 10 min (Table 5.1 Entry 3). Further extending the reaction time to 15 min, increase in the Mwt of the product was observed, but with a broadened Đ value which increased from 1.06 to 1.32 (Table 5.1 Entry 4), suggesting the presence of significant transesterification side reactions at high conversion. As a result, the Mwt results were found to deviate from the theoretical Mwt at high conversion as shown in Figure 5.1.

When Fe(Oct)₃ was used as the catalyst (Table 5.1 Entry 5), it required 55 min to reach 80% conversion. Low Đ values (typically 1.14) was found for the product suggesting the Fe(Oct)₃ has good control of the reaction. Further, extend the reaction time by 20min, the conversion was able to reach 92%, but took 5.5 times longer than Sn(Oct)₂. This longer reaction time indicated there was a reduced level of catalytic activity, suggesting that the iron catalyst was less active than the tin based catalyst.

Similarly, when the ROP reaction was conducted using Co(Oct)₂ as the catalyst, it was noted that the polymerisation showed the slowest conversion (Table 5.1, entry 6 and 7) among all three catalysts. It took 75 min to reach 81% which was 36% longer in time than Fe(Oct)₃. The Mwt result was found to be close to the theoretical Mwt which was 3700 gmol⁻¹, suggesting the catalyst exhibited good control over the polymerisation.

Comparing the catalytic efficiency of each catalyst in ROP of CL, it was found that the catalytic efficiency followed an order of Sn > Fe > Co. This difference in catalytic efficiency was hypothesised to be due to the Lewis acidity of the metal centre. ^[2, 24-27] In C+I process, the coordination between the monomer to the metal centre depends on the Lewis acidity of the metal centre. It was found that with stronger Lewis acidity in the metal centre, it was more likely to start the coordination process with the CL monomer through the ether oxygen. ^[1, 28, 29] Therefore, $Sn(Oct)_2$ was found to be the most efficient catalyst among the three.

To further investigate the control over the polymerisation for each catalyst, a Mwt versus conversion plot was showed in Figure 5.1 which demonstrated how the Mwt of the produced polymer increase as the reaction progress.



Figure 5.1 Evolution of Mwt depending on the reaction conversion in ROP of CL for different catalysts at [M]:[C] ratio of 400:1.

Inspecting Figure 5.1, it was found that all Mwt results were close to the theoretical Mwt line except for the polymers produced with $Sn(Oct)_2$ at high conversion. This suggested that all catalysts have a similar level of control over the polymerisation at conversion below 90%. Conversely, the Mwt result produced with $Sn(Oct)_2$ at above 90% showed deviation from the theoretical Mwt, suggesting the control over the Mwt was lost at high conversion due to the transesterification/depolymerisation reactions.

A series of identical reactions but at lower catalyst load [M]:[C] ratio of 800:1 was then conducted to identify the effect of catalyst concentration has on the ROP reaction. The results of these experiments were detailed in Table 5.2, and

a typical Mwt versus conversion plots were shown in Figure 5.2.

Table 5.2 Average results of ROP of CL with different catalysts and BzOH at [M]:[C] ratio of 800:1 using CH.

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1		800:1	10	2100	2200	1.071	30
2	Sn(Oct) ₂	800:1	20	5400	5500	1.103	79
3		800:1	30	6400	6600	1.16	93
4		800:1	120	4200	4100	1.159	74
5	Fe(Oct) ₃	800:1	180	5400	5200	1.198	88
6	Co(Oct) ₂	800:1	120	3400	3200	1.214	61
7		800:1	180	4400	4100	1.252	80

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

From the table above, it was found that reducing the catalyst concentration, longer reaction time was required to reach high conversion (over 80%) for all three catalysts. i.e. for Sn(Oct)₂, when the [M]:[C] ratio was reduced from 400:1 to 800:1, the reaction time prolonged from 10 min to 30 min to reach above 90% conversion. But at the same time, the Mwt of the produced PCL with Sn(Oct)₂ was 23% higher at this reduced catalyst level. This was because fewer catalysts were presented in the reaction. Therefore, it requires longer time for the initiation and propagation process, but in the meantime, allows for more monomers to be attached to a single polymer chain. Low D for the product was also noticed, suggesting good control of the polymerisation (i.e. all D values were found to be below 1.3). Inspecting results for Fe(Oct)₃, higher Mwt were found when catalyst load was reduced (i.e. Mn=4100 gmol⁻¹ at 91% conversion at 400:1 ratio compared to Mn=5400 gmol⁻¹ at 88% conversion at 800:1 ratio). Similarly, reducing the Co(Oct)₂ load resulted in prolonging reaction time but improving Mwt in the meantime, for example, the reaction time extended from 75 min to

180 min to reach 80% conversion when the catalyst load was reduced from 400:1 to 800:1.

Comparing the reaction time required for the ROP to reach high conversion, ROP using $Sn(Oct)_2$ catalyst required the shortest time followed by $Fe(Oct)_3$, and $Co(Oct)_2$ needed the longest time. This trend was identical to that found in previous results suggested that the tin metal centre has the highest efficient than iron followed by cobalt.



Figure 5.2 Evolution of Mwt depending on the reaction conversion in ROP of CL for different catalysts at [M]:[C] ratio of 800:1 using CH.

Inspecting Figure 5.2, it was found that the Mwt versus conversion plot for $Fe(Oct)_3$ and $Co(Oct)_2$ were close to the theoretical Mwt, suggesting that there was no retardation of these catalysts. However, PCL produced using $Sn(Oct)_2$ showed a higher Mwt than the theoretical Mwt again suggested the presence of transesterification/depolymerisation reactions at higher conversion when using $Sn(Oct)_2$ as the catalyst.

Finally, the [M]:[C] ratio was further reduced to 1600:1, this concentration was close to the catalytic load used for ROP of CL in industry. By doing this, it allowed direct comparison of the PCL produced to which produced via an industrial process using the benchmarking catalyst. The results of different catalysts were shown in Table 5.3.

Table 5.3 Average results of ROP of CL with different catalysts and BzOH at [*M*]:[*C*] *ratio of 1600:1 using CH.*

Entry	Catalyst	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	Sn(Oct) ₂	60	7100	7500	1.239	96
2	Fe(Oct) ₃	150	4900	4700	1.141	72
3	Co(Oct) ₂	240	4000	4200	1.21	63

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

When the reaction was carried out at low catalyst load typically [M]:[C] ratio of 1600:1, it was observed that an even longer reaction time was required to achieve high conversion (above 90% conversion) (Table 3 entry 1). This was again due to the slower rate of initiation and propagation process. Using $Fe(Oct)_3$ and $Co(Oct)_2$ followed the same trend as which at high catalyst load and resulted in slower reaction rate and longer reaction time. i.e. 150 min was required to reach 72% for $Fe(Oct)_3$ whereas only 63% was reached for $Co(Oct)_2$ for 240 min. The D values were found to be above 1.2 for $Sn(Oct)_2$ and $Co(Oct)_2$, suggested that the presence of side reactions and resulted in expanding the polydispersity of the polymer.

Thus the conclusion of the first experimental series was that, whilist all catalysts did actively participate in the ROP reactions, the benchmark catalyst Sn(Oct)₂ outperformed the iron and cobalt alternatives in CH. The next parameter that was investigated was the temperature of the reaction. A series of kinetic studies

conducted at 140, 150, and 160 °C were carried out using three catalysts in CH. The [M]:[C] ratio of 800:1 was chosen for this study because it allows sufficient time to follow the reaction without reaching high conversion where transesterification reactions occurred.



Figure 5.3 Comparison of kinetic experiments between different temperatures using Sn(Oct)₂ at [M]:[C] ratio of 800:1 using CH.

The time-conversion curve in Figure 5.3 shows that the reaction rate increases with the temperature and it can be observed that the conversion of CL to PCL increase with reaction time. For all temperatures, the reaction proceeds in two steps: an initiation period of 'inactive' catalyst with no conversion, followed by a constant increase in conversion with a linear relationship between conversion and time during the propagation period. The initiation period was found to be reduced as the reaction time increased. For example, a conversion of 9% was able to be achieved in 5 min at 160°C, whereas no conversion was observed at 5 min mark at 140°C. Comparing the effect of temperature, the rate of polymerisation was at least 60% and 170% greater at 150 and 160 °C than which at 140 °C. This suggests that increasing the reaction temperature provides a significant acceleration in both the initiation and propagation process.

It can also be noted that regardless of the temperature, the reaction always has initiation period. At 140°C, the initiation period was over 5 min. The previous study at the University of Nottingham has identified that the induction period has been linked to the need to form the 'true' catalyst species from the initiator and Sn(Oct)₂ pre-catalyst via the process shown in Figure 5.4.



Figure 5.4 Mechanism of formation of (a) monoalkoxide, (b) dialkoxide, (c) the first species of ring opening process

The first active monoalkoxide Figure 5.4 (a) is formed rapidly followed by a second equilibrium to form the actual catalyst, which is a tin dialkoxide Figure 5.4 (b). This initiator would then start the ring opening the monomers via the coordination-insertion process to form the first chain component of the polymerisation (Figure 5.4 (c)), which would subsequently continue to ring-open the remaining monomer during propagation until the monomer is exhausted. ^[30] Literatures studies on induction period when using different diols as initiators showed that slow initiation process was because they act as a bidentate ligand exhibiting strong interactions between the diol and Sn(Oct)₂. ^[30] Additionally, when BzOH and Sn(Oct)₂ initiator system was studied, the strong complex formation has been reported between Sn(Oct)₂ and BzOH even at ambient temperature using ¹H, ¹³C, and ¹¹⁹Sn NMR. Therefore, the induction period observed in this practical data can be rationalised as a result of (a) slow formation of the equilibrium to generate the 'true' catalyst, (b) strong complexation of the

BzOH which leads to a slow rate for the initial C+I process. These factors contribute to the slow initiation process. Additionally, the controlled polymerisation characteristics after induction period suggested that the C+I process did not start until the formation of the 'true' catalyst had been fully completed. This suggested that these initial initiation stages were the rate determining step (RDS).

In order to identify if similar mechanism was obtained by the other two alternatives, identical kinetic studies were done for the iron and cobalt alternatives as shown in Figure 5.5 and Figure 5.6.



Figure 5.5 Comparison of kinetic experiments between different temperatures using Fe(Oct)₃ at [M]:[C] ratio of 800:1 using CH.

From Figure 5.5, the reaction rate versus time plots at 140, 150, and 160 °C were presented. Similar to the trend found from Sn(Oct)₂, an initiation period of 5 min without any conversion, followed by steady increasing in conversion in a linear relationship with time were observed. An induction period of 5 min was noticed for all temperatures; this could again be due to the slow formation of the 'true' catalyst, and/or strong interactions between Fe(Oct)₃ and BzOH. Because, the Fe(Oct)₃ has 3 organic ligands that can exchange with BzOH compared to

2 ligands in $Sn(Oct)_2$, this could add additional time for the formation of the "true" catalyst. Additionally, it was noticed that about 2-3 min was required for $Fe(Oct)_3$ to be dissolved in CL monomer due to the $Fe(Oct)_3$ was in solid form. As a result, this could also add up the initiation time.

However, unlike Sn(Oct)₂, the temperature has more significant impact on reaction rate at a higher temperature, i.e. the enhancement in reaction rate at 150 °C was only up to 40% greater than which at 140 °C, but the differences increased up to 170% at 160 °C. Obviously, this denotes that greater reaction temperature has a more significant enhancement in reaction rate. However, a linear relationship between conversion and time was still obtainable at 160 °C, suggesting the polymerisation was still in controlled behaviour at elevated temperature. This significant improvement in conversion at elevated temperature could be related to the higher temperature that allowed for the catalyst to overcome the energy barrier and steric hindrance when involving in the C+I process.

Cross referencing results obtained from $Fe(Oct)_3$ to that of $Sn(Oct)_2$; it was again found that reaction with $Fe(Oct)_3$ required a longer time to achieve high conversion (about four times longer at 160 °C). But increasing in temperature could reduce the differences in catalytic efficiency between $Fe(Oct)_3$ and $Sn(Oct)_2$. For example, when using $Fe(Oct)_3$ only 42% was achieved at 150 °C after 60 min, but 82% conversion was achieved at the 60 min mark when the temperature was raised to 160 °C.



Figure 5.6 Comparison of kinetic experiments between different temperatures using $Co(Oct)_2$ at [M]: [C] ratio of 800:1 using CH.

The time-conversion plot of Co(Oct)₂ at 140, 150, and 160 °C (showed in Figure 5.6) showed that the reaction rate. It was noticed that again an induction period of 5 min was required before any conversion started. Similar to Fe(Oct)₃, around 2-3 min was required for Co(Oct)₂ to be dissolved into CL monomer. After the initiation stage, the reaction rate increases with reaction time, and it can be observed that conversion of CL to PCL increased with temperature. At 140 and 150 °C, the difference between conversion rates was not significant within the temperature range studied (only up to 23% greater at 150 °C). Further increasing temperature to 160 °C, a greater degree of enhancement in reaction rate was again observed, i.e. the reaction conversion was up to 80% greater than 140 °C. This again suggests that conducting reactions at a higher temperature would accelerate both the initiation and propagation rate.

Comparing the results obtained using $Co(Oct)_2$ with the other two catalysts, it was observed that the cobalt catalyst possesses the slowest propagation rate against time. The result followed the same trend as previous results showed in Table 1, Table 5.2, and Table 5.3.

The kinetics of the ROP with different catalyst was further investigated by the quantifying the propagation rate at a different temperature. The propagation rate was defined as the slope of the kinetic plot after the induction period. Therefore, the determined rate constant represents the propagation rate constant. By calculating the propagation rate during the polymerisation, it was possible to quantitatively assess how the polymerisation reaction was affected by different heating methods. The Figure 5.7, Figure 5.8, and Figure 5.9 showed the kinetic plots of ROP of PCL using Sn(Oct)₂, Fe(Oct)₃, and Co(Oct)₂, respectively.



Figure 5.7 Temperature dependence of the reaction apparent rate constant (kapp) using CH with best fit line (BFL). Condition: $[Sn(Oct)_2]$: [CL] = 800:1.

Figure 5.7 showed a straight-line relationship which holds for $ln(M_0/M)$ as a function of reaction time for all set temperatures. This result indicated that the polymerisation was a first-order reaction, which proceeded at a rate depended only on the monomer concentration. Thus the calculation of the apparent rate constant (k_{app}) can be conducted for the ROP initiated by Sn(Oct)₂ at the temperature used, and the results were as follow: k_{app} =0.095 min⁻¹ at 140 °C, k_{app} =0.1089 min⁻¹ at 150 °C, and k_{app} =0.1838 min⁻¹ at 160 °C. The intercept
between the best-fit line and x-axis indicated the approximate induction period for the reaction, which was around 10min, 6min, and 5min for 140, 150, and 160 °C, respectively. These time marks were the estimated time for the initiation period, which were again found to be reduced as the reaction temperature increased. Inspecting the k_{app} values, it can be seen that the polymerisation rate at 150 °C was only 15% higher than that 140 °C, but at 160 °C, the rate was 94% higher than that at 140 °C. These results showed that increasing temperature from 140 °C to 150 °C (15% increment in the rate constant) did not have as significant impacts on conversion rate as that when the temperature was elevated from 150 °C to 160°C (69% increment in the rate cponstant). But significant reduction in the induction period were observed as temperature increased. This suggested that increasing temperature has a beneficial effect in both reduction in induction time and acceleration in polymerisation rate, and the latter one was more significant at higher temperature.



Figure 5.8 Temperature dependence of the reaction apparent rate constant (k_{app}) using CH with best fit line (BFL). Condition: $[Fe(Oct)_3]$:[CL]=800:1.

Inspecting Figure 5.8, Fe(Oct)₃ exhibited similar trend as Sn(Oct)₂. All ln(M₀/M) versus time plots showed a linear relationship, indicating the reaction was first order controlled polymerisation. This allowed for the calculation of k_{app} values for Fe(Oct)₃: k_{app} =0.0066 min⁻¹ at 140 °C, k_{app} =0.0117 min⁻¹ at 150 °C, and k_{app} =0.0316 min⁻¹ at 160 °C. Increasing reaction temperature from 140 °C to 150 °C showed an increment of 77% in k_{app} value. Further increasing the reaction temperature to 160 °C, the k_{app} value increased by 4.8 times compared to which at 140 °C. The increment in k_{app} values at different temperatures again suggested that the reaction temperature has a critical impact on reaction rate, i.e. the polymerisation rate could be 4.8 times faster with a temperature increment of 20 °C.



Figure 5.9 Temperature dependence of the reaction apparent rate constant (k_{app}) using CH with best fit line (BFL). Condition: $[Co(Oct)_2]:[CL]=800:1$.

From Figure 5.9, linear relationship between $ln(M_0/M)$ and reaction time was observed for all temperature, indicating the reaction was first order with controlled behaviour. The k_{app} values were then calculated to be 0.0055, 0.0077, and 0.0134 min⁻¹ at 140, 150, and 160 °C, respectively. Again, it was found that the increment in k_{app} values between 140 °C and 150 °C (40% greater at 150 °C compared to that at 140 °C) was not as significant as that between 150 and 160 °C (74% greater at 160 °C compared to that at 150°C). The rate constant increased by about 2.44 times from 140 °C to 160 °C. Comparing this result with that for Sn(Oct)₂ and Fe(Oct)₃, the reaction temperature has the most significant effects on Fe(Oct)₃ (k_{app} differences up to 4.8 time), followed by Co(Oct)₂ (k_{app} differences up to 2.4 time), and Sn(Oct)₂ has the least impact from reaction temperature change (only 1.94 times). This differences in the result could potentially provide significant differences in catalyst performance when MWH was applied due to the existence of selective heating on the catalyst.

Despite the differences in the impact of reaction temperature on each catalyst, it could be noticed that the k_{app} value for Fe(Oct)₃ and Co(Oct)₂ was approximately an order of magnitude less than the Sn(Oct)₂. This demonstrates that the Sn(Oct)₂ was a superior catalyst for ROP of caprolactone in CH system.

After identified the k_{app} values at different temperature for each catalyst, it was possible to determine the activation energy of the reaction using the Arrhenius plot of lnk_{app} versus the reciprocal of absolute temperature as shown in Figure 5.10.



Figure 5.10 The dependence of apparent rate constant (k_{app}) of polymerisation with best fit line (BFL) when using different catalysts in CH

Inspecting the Arrhenius plots showed in Figure 5.10, a linear trend in the range of temperature studied was found for all catalysts. The activation energy was found to be 50, 117, and 75 kJmol⁻¹ for Sn(Oct)₂, Fe(Oct)₃, and Co(Oct)₂, respectively. The lower activation energy required for Sn(Oct)₂ could be rationalised as that Sn has the highest electron density compared to the Fe and Co alternatives. The nucleophilicity of the Sn metal centre makes it require less energy to initiate the C+I process. Conversely, Fe and Co have similar electron density, but because Fe(Oct)₃ has three organic ligands attached to the metal centre which required more energy to overcome the steric hindrance within molecules when catalysing the reaction.

5.3.2 Investigation of ROP with the Application of E-field Heating (EH)

After identifying the catalyst performance of different catalysts in CH, the next series of experiments was to using electric heating (EH) as the heating method. And thus the effect of EH upon the catalysts can be identified. Before investigating the performance of different catalysts in EH, studies in the dielectric property of these catalyst when mixed with a solvent were performed, and heating experiments of the catalysts were also conducted to predict and assess the extent of selective heating on the catalyst when using EH.

Before conducting the heating experiments, a series of dielectric property measurements were carried out for all three catalysts dissolving in cyclohexanone. By doing so, it was possible to predict the heating behaviour of these catalysts. The plots of the loss tangent of the neat solvent and solvent containing each catalyst were shown in Figure 5.11.



Figure 5.11 Plots of loss tangent of cyclohexanone (cyclo) and cyclohexanone containing $Fe(Oct)_3$, $Co(Oct)_2$, and $Sn(Oct)_2$.

In Figure 5.11, the plots of loss tangent (tan δ) for neat cyclohexanone solution and solution containing each catalysts were shown to follow similar trend: the tan δ value for all samples decreased as the temperature increased. At temperature range from 20 to 60 °C, the solution containing Fe(Oct)₃ and Co(Oct)₂ showed similar tan δ values as cyclohexanone, while the tan δ for Sn(Oct)₂ solution was about 25% higher than the others. The result identified that Sn(Oct)₂ solution could potentially possess faster heating rate compared to others samples when the temperature was below 60 °C. However, at this temperature range, Fe(Oct)₃ was not dissolved in the cyclohexanone, therefore the dielectric property measurement for the solution containing $Fe(Oct)_3$ was only measuring the solvent. Once the $Fe(Oct)_3$ started to dissolved in the solvent at around 65 °C, the difference between the tan δ of $Fe(Oct)_3$ solution and that of the solvent became more significant as the temperature rose. Additionally, the tan δ value for $Fe(Oct)_3$ sample was around 10-15% higher than that of the Sn(Oct)_2 sample at temperature between 80 and 120 °C. This data suggested that after Fe(Oct)_3 was dissolved in the solvent, its solution could potentially experience better MW heating than Sn(Oct)_2 solution.

Now that the prediction for heating of various catalysts in cyclohexanone using EH were done, heating experiments for these catalysts dissolved in CL monomers were then carried out using a MiniFlow with a maximum power of 150 W operating at 2.45 GHz. From previous CH experiments, it was found that no polymerisation would take place without the presence of the initiator, so there were no additional components competed in interacting with the electromagnetic field (EMF), i.e. no dimer nor initiator were presented in these experiments. Therefore, any differences in heating performance were solely originated from the selective heating of the monomer and/or the catalyst in EH.

Identical molar concentration of [M]:[C] ratio of 800:1 were used for all catalysts. 10 mL of CL monomer was used as the solvent. Both high input power (150 W) and low input power (50 W) were used in these experiments, to identify how input power affected the selective heating of the catalysts. The temperature profile and power profile of high input power were shown in Figure 5.12 and Figure 5.13, whereas those with low input power were showed in Figure 5.14 and Figure 5.15. The errors were around ± 3 °C for heating profiles, and ± 7 W for power profiles.



Figure 5.12 Example of the typical temperature profile of CL containing different organometallic catalysts using EH at 150 W input power. Condition: [M]:[C] ratio of 800:1.

In Figure 5.12, the temperature profiles of CL on its own and mixing with each catalyst were shown. The temperature profiles for all solutions followed the same trend as the solvent. In particular, the solution containing Co(Oct)₂ had almost the identical heating profile as the solvent (temperature differences were less than 1 °C), suggesting that the cobalt catalyst did not experience significant selective heating. This was similar to the predications from the dielectric property study. This could be due to the cobalt catalyst was not able to compete with CL in absorbing MW energy.

Conversely, solutions containing $Fe(Oct)_3$ or $Sn(Oct)_2$ showed significant temperature differences against the neat solvent. A maximum temperature difference of 15 °C and 8 °C were noticed for the solution of $Fe(Oct)_3$ and $Sn(Oct)_2$, respectively. This could be due to the selective heating on the catalysts that reflected by such significant increase in the bulk temperature. Identical heating profile was found for both catalyst for the first 25 s, after this point, $Fe(Oct)_3$ showed greater enhancement in heating of the solution. It should be noticed that Fe(Oct)₃ was not dissolved in CL at room temperature. During the heating experiment, it was found that after 10 s, the Fe(Oct)₃ started to dissolve in CL, and at around 25 s the Fe(Oct)₃ was fully dissolve in CL by visual confirmation, and the colour of the solution became brown. Indeed, it was found that the heating profile of CL+Fe(Oct)₃ started to deviate from that of CL after 10s into the heating experiment, and after Fe(Oct)₃ was fully dissolved in CL, it showed greater increment in the temperature profile than that of $Sn(Oct)_2$. This suggested that Fe(Oct)₃ could potentially experience stronger selective heating than Sn(Oct)₂. It should be noted that the Sn metal centre has more electrons to interact with the electromagnetic field than Fe. But, in Fe(Oct)₃, three organic ligands were attached to the metal centre rather than two in Sn(Oct)₂, this additional ligand increased the size of the molecule, and magnified the friction with the surrounding molecules (as discussed in Chapter 3). As a result, more significant temperature differences were observed for the CL+Fe(Oct)₃ sample. The power profile of the heating experiment was also studied as shown in Figure 5.13.



Figure 5.13 Example of typical power profile of CL containing different organometallic catalysts using EH at 150 W input power

It was observed that there were insignificant differences in power profiles between each solution. In comparison to CL power profile, the additional absorbed power was less than 11W for solutions containing organometallic catalysts. Conversely, the power profile for $Sn(Oct)_2$, $Fe(Oct)_3$, and $Co(Oct)_2$ were found to be identical (less than 3W difference). Reminding the significant differences in temperature profiles found in Figure 5.13, it suggested that $Sn(Oct)_2$ and $Fe(Oct)_3$ could potentially have higher efficiency in converting the absorbed power into heat. This was identical to the dielectric property results found in Figure 5.11.

The series of heating experiments at high input power had clearly demonstrated that the MW selective heating on catalysts had a significant impact on the heating of the bulk depending on the choice of catalyst. To further investigate the effect that input power had upon the selective heating of catalysts, identical heating experiments with low input power (50W) were also conducted and were shown

in Figure 5.14 and Figure 5.15. The errors were around ± 3 °C for heating profiles, and ± 7 W for power profiles.



Figure 5.14 Example of typical temperature profile of CL containing different organometallic catalysts using HH at 50 W input power

It was observed that there were no significant differences in temperature profiles for CL, CL+Co(Oct)₂, and CL+Sn(Oct)₂ samples. Approximately 150 s were required for the bulk to reach 120 °C. In comparison, for CL+Fe(Oct)₃ sample, during the section where the bulk was being heated from ambient to 45 °C, the temperature profiles were identical with other samples. However, as the temperature of the media entered the region where most of the Fe(Oct)₃ were dissolved in bulk (after around 30s), the profiles were noted to diverge. This indicated that the dissolved Fe(Oct)₃ started to convert the incident electromagnetic (EM) energy into heat even at low input power. The Sn and Co catalysts did not show any significant temperature differences suggesting that these catalyst was not efficient in converting the absorbed electromagnetic energy into heat at this power level. These results suggested that the Fe(Oct)₃ has the highest potential to be selectively heated and able to dissipate absorbed EM energy to surroundings. Figure 5.15 shows the corresponding power profiles of the heating experiment. Comparing the power profiles of each sample confirms that all solutions absorbed a similar amount of EM energy (differences were less than 5W). However, with identical power profile, the differences in temperature profile suggests that Fe(Oct)₃ has the best efficiency in converting absorbed EM energy into heat.



Figure 5.15 Example of typical power profile of CL containing different organometallic catalysts using HH at 50 W input power

Now that the heating behaviour of this catalyst in EH had been demonstrated via these heating experiments, ROP of CL using EH was then conducted. This would produce comparable results to CH and so investigate the effect of applying EH to the ROP reaction which involved organometallic catalysts that experienced E-field selective heating. Identical preparation procedures to CH were conducted. The prepared sample tube was then transferred into single-mode MiniFlow operating at 2.45 GHz with an input power of 150 W. The results of [M]:[C] ratio of 400:1 can be seen in Table 5.4, and a typical Mwt versus conversion plot was shown in Figure 5.16.

Table 5.4 Average results of ROP of CL with different catalysts and BzOH at [*M*]:[*C*] *ratio of 400:1 using EH.*

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Ъ	Conversion ^b (%)
1	-	-	60	160	170	1.05	<1
2	Sn(Oat)	400:1	10	5600	6000	1.17	93
3		400:1	15	5800	6500	1.51	97
4	Fe(Oct) ₃	400:1	40	4300	4200	1.168	89
5	Co(Oct) ₂	400:1	60	3900	4100	1.213	92

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR



Figure 5.16 Evolution of Mwt depending on the reaction conversion in ROP of CL for different catalysts at [M]:[C] ratio of 400:1 using EH.

Figure 5.16 showed the relationship between Mwt and conversion as the reaction proceed. All three plots show a linear behaviour close to the theoretical Mwt. Such results showed that the ROP reactions were controlled with all catalysts using EH. However, inspecting the Mwt results obtained from $Sn(Oct)_2$, deviation from the theoretical Mwt were observed. This indicated the control over the polymerisation was lost, and this could be related to the presence of transesterification/depolymerisation reactions as greater D values were observed at high conversion (i.e. D>1.5 at 97% as shown in Table 5.4 Entry 3).

When the ROP was carried out in the absence of catalysts (Table 5.4, Entry 1) a low conversion (less than 1%) was obtained. This was attributed to the fact that

no ring opening agent present in the bulk to initiate the ROP process. A low Mwt around 200 gmol⁻¹ was obtained also suggested that there was no propagation of monomers occurred.

When the ROP was carried out with $Sn(Oct)_2$, the polymerisation was able to reach above 90% conversion within 10 min (Table 5.4, Entry 2). Crossreferencing the results with CH, the Mn value for PCL using EH was 5% higher than in CH, but the peak molecular weight (M_p) was 15% higher in EH. This improvement in Mwt results, combined with the fact Sn(Oct)₂ experience selective heating observed in heating experiments, suggested that EH could potentially promoted the imitation process and/or the propagation process and thus resulted in a development in Mwt. Further extend the reaction time to 15 min, no significant increment in Mwt were noted, but the D expanded from 1.51. 1.17 to This was ิล clear indication that the transesterification/depolymerisation reaction participated at high conversion.

In comparison, when $Fe(Oct)_3$ was used as the catalyst instead of $Sn(Oct)_2$ (Table 5.4, Entry 4), it was again found that longer reaction time was required for $Fe(Oct)_3$ to achieve 90% yield. However, inspecting the Mwt versus conversion plots in Figure 5.16, showed that the obtained Mwt were close to theoretical Mwt, suggesting that the $Fe(Oct)_3$ had better control over polymerisations than $Sn(Oct)_2$. Comparing the results obtained from CH, it was noticed that the reaction time was reduced by 47% to achieve 90%, and the Mwt was approximately 10% higher in EH. This result showed that using the EH resulted a significant enhancement in both conversion and Mwt compared to CH. These observations, combined with the fact that $Fe(Oct)_3$ experienced significant selective heating, suggested that the selective heating on catalyst could

potentially improve its catalytic efficiency while maintaining its control over the reaction. These experiments showed that the EH selective heating on catalysts could potentially provide beneficial effects to the ROP reaction.

Similarly, when the ROP was conducted using Co(Oct)₂ as the catalyst, it was noted that the polymerisation was accelerated when EH was used (Table 5.4, Entry 5). The reaction time was reduced by 35% and the final conversion was 12% higher than CH. Inspecting Figure 5.16, the Mwt results were close to theoretical Mwt suggested Co(Oct)₂ provides good control over polymerisation. However, in previous heating experiments, it was noticed that CL monomer containing Co(Oct)₂ did not show significant temperature difference to CL, but the obtained improved results in ROP indicated that EH still provided beneficial effects. This could be due to the fast heating of the bulk using EH as discussed previously. It was also postulated that this could be because: (a) the volumetric heating of CL promoted the reaction; and/or (b) the selective heating on Co(Oct)₂ was not significant enough to show the substantial temperature difference but enough to promote the initation and propagation process. It has been demonstrated by the authors that as low as 5W was enough to promote synthesis of an *in situ* catalysts. ^[31]

Thus, the conclusion from the first set of EH experimental was that, while all ROP experienced improvement in product yield and Mwt when using EH instead of CH, the Fe(Oct)₃ showed the most significant improvement which could potentially be due to the EH selective heating. The variables that were investigated next were the influence of catalyst concentration.

Identical ROP reactions with reduced catalyst concentration were investigated to identify if the selective heating on catalyst were affected when the level of catalyst was reduced. In the previous study from the group, it was found that if the concentration of the species that undergoes selective heating was not sufficient to surpass the 'tipping point', the predominant heating methods remain as convection/conduction. [32, 33]

The identical ROP reaction with reduced catalyst concentration, namely [M]:[C] ratio of 800:1 and 1600:1 were investigated, so that the results could be directly compared to those obtained in CH. The results of these experiments were detailed in Table 5.5, and a typical Mn vs. conversion plot was shown in Figure 5.17.

Table 5.5 Average results of ROP of CL with different catalysts and BzOH using EH

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	Sn(Oct) ₂	20	800:1	6100	6300	1.15	96
2		60	1600:1	7500	7700	1.21	96
3	Fe(Oct) ₃	120	800:1	6300	6800	1.167	99
4		240	800:1	3300	8500	2.427	99
5		120	1600:1	6500	7000	1.291	84
6	Co(Oct) ₂	120	800:1	5000	5400	1.277	87
7		240	1600:1	6300	6600	1.19	77

^a determined by GPC, measured in THF at 35°C ^b determined by ¹H-NMR



Figure 5.17 Evolution of Mwt depending on the reaction conversion in ROP of CL for different catalysts at [M]:[C] ratio of 800:1 using EH.

Reducing the Sn(Oct)₂ concentration extended the reaction time to reach high conversion (>90%).For example, the reaction time was prolonged to 20 min and 60 min to reach over 90% conversion for [M]:[C] ratio of 800:1 and 1600:1 (Table 5.5, Entry 1 and 2). Furthermore, the Mwt of PCL had increased significantly at identical conversion. Hence, if high Mwt PCL was targeted, low catalyst concentration was required, and longer polymerisation time was also needed.

Similarly, it was observed that the reaction time for ROP using $Fe(Oct)_3$ was prolonged to 120 min to reach above 90% conversion at 800:1 monomer:catalyst ratio. When the reaction was carried out for an additional 120 min, the product Mn was noted to be reduced significantly and a broadened D was found (Table 5.5, Entry 4). This again identified the existence of transesterification reaction at high conversion. Thus, the reaction time was a critical factor to be considered in order to terminate the reaction before side reactions become dominant in the polymerisation. Further reducing the catalyst by half, the reaction was only able to reach 84% after 120 min. But a higher Mwt was obtained at equivalent conversion than that at [M]:[C]=800:1.

When Co(Oct)₂ was used as the catalyst, the polymerisation was again found to be the slowest among three catalysts. The reaction was carried out for 120 min and 240 min, but the conversion was not able to achieve over 90% and 80% for [M]:[C] ratio of 800:1 and 1600:1 (Table 5.5, Entry 6 and 7). But inspecting Figure 5.17, it was found that the Mwt obtained were close to the theoretical Mwt. Therefore, this identified that there was not retardation of Co(Oct)₂ during the reaction, but its catalytic efficiency was not high enough for the polymerisation process to match the other two catalysts.

From the experimental studies of the reduced catalyst load, it was found that although longer reaction time was required to achieve high conversion, no retardation of the catalyst during the reaction were found. Additionally, the reaction time was found to be critical to the PCL product, extending the reaction time when high conversion was reached could have a detrimental effect on the PCL Mwt results. Using EH at a reduced catalyst load was still found to be promising, and control of the polymerisation was still maintained.

Now that the effect of catalyst concentration on ROP had been demonstrated, the next series of experiments which studied the effect of reaction temperature were conducted at 140, 150, and 160 °C. The [M]:[C] ratio used in these experiments was 800:1, which was identical to that had done in CH. This would produce equivalent results to CH, and so investigate if the observed acceleration in ROP using EH was originated from the selective heating on the catalyst which was

postulated to elevate the reaction site temperature. The kinetic study of these experiments was detailed in Figure 5.18, Figure 5.19, and Figure 5.21.



Figure 5.18 Comparison of kinetic experiments between different temperatures using Sn(Oct)₂ at [M]:[C] ratio of 800:1 using EH.

With the application of EH, it was found that the reaction reached at least 15% after the first 5 min. The reduction in initiation period was found to be significant when using EH compared to CH, which showed an approximately 3-5 min induction period for all temperatures. The period of 'inactivity' was severely reduced in EH experiments could be related to (a) fast heat up time exhibited by the different heating methods, and (b) the selective EH of individual components affecting the formation of the 'true' catalyst which was then involved in the C+I process.

The typical heat up time for EH was around 60-90 s (depending on the set reaction temperature), conversely, the time required to heat up samples in CH was at least 180 s in a preheated oil bath. Therefore, in EH, the reaction reaches to set temperature around 90 s earlier than CH. However, after taking this into account, there was still a 5 min difference in the on-set of initiation and propagation between the two heating methods, i.e. at 140° C, the CH required

10 min to reach 15% conversion, whereas in EH only 5 min was required. This reduction in reaction time was linked to the fast synthesis of the tin dialkoxide which was then participated in the C+I process. In the previous study from the group, it was found that the selective EH of the tin catalyst and CL in the reaction mixture resulted in a significant increase in the rate of the first C+I of the monomer to form the first species. ^[16] Similarly, Deng *et al.* found that significantly reduced reaction time when MWH was applied to synthesis 3- and 4-arm star branched polymers were also due to increasing rate of 'in-situ' catalyst formation. ^[34] Therefore, this reduction in induction period observed in this study should be attributed to both fast system heat up time and the acceleration in the synthesis of the 'true' catalyst which participated in the C+I process.

Inspecting Figure 5.18, it was found that the difference in conversion between 140 and 150 °C were less than 10%. This could be related to the insignificant difference in propagation rate at 140 and 150 °C. In the CH study, it was found that the rate constant (k_{app}) were similar at 140 °C and 150 °C (k_{app} =0.945 min⁻¹ at 140 °C, and k_{app} =0.1077 min⁻¹ at 150 °C), and the difference in conversion rate was mainly attributed to the initial "waiting" time. However, the induction period was significantly reduced in EH, and because the rate constant at both temperatures were close (as previously found in CH study), therefore, the conversion between 140°C and 150°C were found to be close.

Similar to CH, further increasing the temperature to 160 °C, the enhancement in conversion was found to be significant. This identified that in EH when $Sn(Oct)_2$ was used as the catalyst, increasing the reaction temperature from 140 to 150 °C

would have an insignificant impact on conversion rate, but further raise the temperature to 160 °C would significantly improve the conversion rate.

Next, the kinetic study of ROP using Fe(Oct)₃ was studied at various temperature and the results were shown in Figure 5.19.



Figure 5.19 Comparison of kinetic experiments between different temperatures using $Fe(Oct)_3$ at [M]:[C] ratio of 800:1 using EH.

Inspecting Figure 5.19, the first set of experiments was found that at 140 °C, an induction time of 5 min was required before the propagation step started. But at 150 and 160 °C, around 8% of conversion was achieved in 5 min. However, inspecting the plots for 150 °C and 160 °C, it was noticed that no significant difference in conversion was found, which was contradicted to the observed trend in CH. Close inspecting temperature profile of the experiment as shown in Figure 5.20, it was noticed that the reaction temperature was not well controlled and the sample was overheated to up to 168 °C after the first sample point. Around 120 s was required for the sample to cool back to 150 °C. Therefore, another run at 150 °C was conducted with good temperature control (as shown in Figure 5.20, EH 150°C controlled). Interestingly, it was found that similar trend to CH was obtained in this run. This suggested that temperature had a

critical impact in conversion, and well control over temperature was needed to establish accurate comparisons. Additionally, it was again found that increasing the reaction temperature can improve the conversion rate of the reaction significantly.



Figure 5.20 Example of temperature overshoot during the EH experiment. PA: power absorbed.

Now that the kinetic studies for $Sn(Oct)_2$ and $Fe(Oct)_3$ at various temperatures were done, identical studies for $Co(Oct)_2$ were then conducted in order to direct compare the results against the other two catalysts. The kinetic study results for $Co(Oct)_2$ were shown in Figure 5.21.



Figure 5.21 Comparison of kinetic experiments between different temperatures using Co(Oct)₂ at [M]:[C] ratio of 800:1 using EH.

The kinetic study showed in Figure 5.21 followed the same trend as obtained in CH and the other two catalysts. At 140 and 150 °C, the difference between conversions was insignificant, whereas, at 160 °C, this difference became significant. Again, the induction period was noticed to be reduced dramatically when EH was applied (i.e. at least 5% was reached in 5 min using EH).

From these kinetic studies at different temperatures using EH, it was found that applying EH to ROP of CL could significantly reduce the induction period. Additionally, increasing temperature from 140 to 160 °C would result in a significant enhancement in the initiation and propagation rate, identifying that increasing reaction temperature would have a beneficial effect on conversions. Additionally, it should be concerned that well temperature monitoring and control was required in EH to obtain accurate experimental results when comparing to CH results.

Now that the kinetic study of the ROP of CL using different catalysts had been demonstrated, the next series of the experiments was to identify the rate constant

 (k_{app}) based on these kinetic studies *via* the ln(M₀/M) versus time plots. By doing this, it was possible to establish a quantitative comparison against CH, and also allow for determination of the activation energy using the Arrhenius plot. The summary of k_{app} was shown in Table 5.6, and a typical kinetic plot using Sn(Oct)₂ as shown in Figure 5.22.

Table 5.6 Summary of rate constant k_{app} of each catalyst at a different temperature using EH.



Figure 5.22 An example of a kinetic plot of ROP of CL using $Sn(Oct)_2$ at a different temperature using EH with best fit line (BFL).

This example plot showed that the relationship between $ln(M_0:M)$ versus time was similar to the trend obtained in kinetic studies. The increment in k_{app} was not significant between 140 and 150 °C but became significant when temperature was raised to 160 °C. Closer inspection of the table, quantitative comparisons were able to establish. Comparing k_{app} among all catalyst at the identical temperature, the Sn catalyst was found to have approximately an order of magnitude more than the Fe and Co alternatives. This demonstrated that in EH, the $Sn(Oct)_2$ was still a superior catalyst regarding reaction rate and catalytic efficiency.

Comparing k_{app} between each temperature for the same catalyst, it was found that the increment between two temperature set point was close to which obtained in CH. i.e. between 140 and 150 °C, the increment in k_{app} for Co(Oct)₂ were 40% and 44% for CH and EH, respectively. This result could potentially suggest that although there was the presence of selective heating in EH, the potential temperature difference between each temperature set point was close.

Now that the rate constant at each temperature were identified, it was able to determine the activation energy of the reaction using EH. The Arrhenius plot of lnk_{app} versus the reciprocal of absolute temperature shows a linear trend in the range of study, see Figure 5.23. The activation energy was found to be 50, 110, and 75 kJmol⁻¹ for Sn(Oct)₂, Fe(Oct)₃, and Co(Oct)₂, respectively. These results were found to be close to which obtained in CH, suggesting that the mechanism of the reaction was not affected by different heating methods. Again, the plot for Fe(Oct)3 showed different trend compared to the other two catalyst, this could be due to that Fe(Oct)3 had three ligands attached to the metal centre whereas only two ligands were presented on the other two catalysts. This additional ligand induced steric hindrance and thus required more energy to overcome the barrel to follow the C+I mechanism.



Figure 5.23 The dependence of apparent rate constant (k_{app}) of polymerisation with best fit line (BFL) using different catalysts in EH.

From these EH experiments, it could be concluded that the organometallic catalysts were able to experience EH selective heating when mixed with CL, and this observed selective heating could potentially be the origin of the acceleration in initiation and propagation process. Comparing the kinetic study results with CH, a similar trend to CH were obtained suggesting that using EH did not affect the mechanism of the reaction, but rather promote the reaction through elevated reaction site temperature (pure thermal effect).

5.3.3 Investigation of ROP with the Application of H-field Heating (HH)

The results from the EH experiments have shown that it was possible to apply EH to achieve rate enhancements in both initiation and propagation process, and thus significantly reduce reaction time. The next step was to investigate if the application of H-field heating (HH) could also have beneficial effects to the polymerisation. In the previous chapter, it was found that if the catalyst was susceptible to HH, the catalyst could show similar or improved performance than EH depending on the magnetism of the catalyst. Therefore, identical ROP experiments using HH with all three catalysts were conducted. However, before the investigation of different catalyst performance using HH, heating experiments of the catalysts need to be conducted to assess the extent that the catalyst would experience the selective heating from HH. Initial heating experiments were conducted with identical conditions as EH but using HH. A maximum input power of 150 W was applied to the sample. The molar ratio between [monomer]:[catalyst] ([M]:[C]) was 800:1. The temperature profile and power profile as shown in Figure 5.24 and Figure 5.28.



Figure 5.24 Example of typical temperature profile of CL containing different organometallic catalysts using HH at 150 W input power.

The Figure 5.24 demonstrated that the temperature profile of the CL and CL containing Sn(Oct)₂ were very similar when using HH, indicating that a limited level of system heating resulted from the presence CL and Sn(Oct)₂. By comparison, the solution containing the Fe(Oct)₃ and Co(Oct)₂ were noted to produce a measurable increase in the heating rate and achieved higher bulk temperature than neat CL (around 9 and 3 °C higher than CL). In HH, the magnetic interactions between a metal centre and an alternating magnetic field (H-field) depend on the rotation of the unpaired spins in the metal. ^[35, 36] The number of unpaired spins present in a metal centre determines its ability in

interacting with the H-field. If there were no unpaired spin in the metal centre like Sn as shown in Figure 5.25, the metal complex was recognised as a diamagnetic complex which does not interact with the H-field. Similarly, CL does not possess any magnetism, so would not interact with the H-field as well. Therefore, insignificant differences between the heating profile of CL and CL-Sn mixture were noticed.



Figure 5.25. Example of spin state of Sn centre in Sn(Oct)₂

Conversely, the Fe and Co catalysts were able to be heated by the H-field indicating they were susceptible to the magnetic loss heating mechanism. Such magnetic loss was induced by electron-spin resonance. ^[37] The Co and Fe metal centre are recognised as paramagnetic which means they possess unpaired spins that can interact with the H-field. However, different heating behaviour between these two catalysts was obtained. This different performance could be related to the spin state of the metal centre. The spin state refers to the potential spin configurations of electrons in d-orbital of the metal centre. The spin states vary between high-spin and low-spin configurations. These configurations were determined based on the ligands that were attached to the metal centre. Both the Fe and Co catalyst was found to be in the octahedral state, and therefore an e_g , (refers to three lower-energy orbitals) to t_{2g} (refers to two high-energy orbitals) distribution in d-orbital was used in the following studies as shown in Figure 5.26.



Figure 5.26 Example of spin state distribution in d-orbital of metal in octahedral state.

In Fe(Oct)₃ and Co(Oct)₂, the organic ligand that was attached to the metal centre was carboxylate octanoate (also known as 2-ethylhexanoate). It is recognised as weak ligands in spectrochemical series, which has the small splitting of the e_g, and t_{2g} orbitals. ^[38-41] The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting (Δ_0) that they produced. ^[42-44] In crystal field stabilisation energy (CFSE), when placing e-s into d-orbitals, there is a choice of high spin and low spin. ^[45, 46] Depending on Δ_0 and energy needed to pair 2e⁻ (P). If P> Δ_0 , less energy is required to place e- from e.g., to t_{2g} orbitals than pairing two e- together, and thus high spin state is obtained (as shown in Figure 5.27 a). Conversely, if the pairing energy is less than splitting energy, then low spin state is obtained because it requires less energy to pair two e- than transfer an e⁻ to t_{2g} orbital (as shown in Figure 5.27 b). In this case, the octanoate ligands has low splitting energy, therefore, the metal centre that it attached to stays at high spin state.



Figure 5.27 Example of different spin state of Fe metal centre. (a): High spin $P > \Delta_0$ (weak field). (b): Low spin $P < \Delta_0$ (strong field). ^[47]

When the organometallic catalyst forms a dialkoxide intermediate that participates in C+I process, the dialkoxide is also recognised as weak ligands, because it is a π -donor ligand which has low splitting energy in the spectrochemical series. ^[48, 49] Therefore, when the intermediate metal dialkoxide is formed in the reaction, the metal centre remains at high spin state.

Therefore, the spin configuration of the $Co(Oct)_2$ and $Fe(Oct)_3$, and their dialkoxide intermediates should be in the high spin state as shown in Figure 5.28.

It can be seen that in $Co(Oct)_2$, there are only three unpaired spins that are able to interact with the H-field, whereas five unpaired spins are presented in Fe(Oct)₃. Thus, the empirically observed temperature differences in temperature profile can be linked with the presence of the unpaired spins in the metal centre.



Figure 5.28 Example of spin configuration of cobalt metal centre in $Co(Oct)_2$ (a) and iron metal centre in $Fe(Oct)_3$ (b) at high spin state.

Inspecting the power profile shown in Figure 5.29, it was found that a maximum input power of only 25 W was obtained for all samples. Again, this was because the equipment was only capable of recording the input and reflected power from E-field, and was not able to quantify the power from H-field.



Figure 5.29 Example of typical power profile of CL containing different organometallic catalysts using HH at 150 W input power.

To establish a comprehensive understanding of the heating behaviour of the catalyst using HH, identical heating experiments but at low input power (50 W) were then conducted. By doing this, it was possible to identify how the input power affects the heating behaviour of the catalysts using HH. The heating

profiles using 50 W input power for all catalysts using HH were shown in Figure 5.30.



Figure 5.30 Example of typical temperature profile of CL containing different organometallic catalysts using HH at 50 W input power.

From the temperature profile above, it was found that insignificant temperature differences were obtained for all samples. This identifies that there was no significant magnetic selective heating on catalysts to induce temperature differences that were obtainable as in high input power experiments. Additionally, this also suggested that using EH, the observed heating performance should be purely originated from EH, because weak HH did not induce significant magnetic selective heating on the catalysts.

However, the fact that both CL and CL+Sn(Oct)₂ mixture were able to be heated using HH was still unclear. It was postulated that this was resulted from either induction heating by the alternating H-field or weak EH from weak E-field. To investigate this, a series of heating experiments with two optical fiber thermometers located at the centre and outskirt (wall of the tube) of the solution were conducted. This allows for identification of the heat distribution of the solution and thus identify how the non-magnetic materials (CL and $Sn(Oct)_2$) were heated using HH.



Figure 5.31 Demonstration of temperature difference between centre and outskirt of CL sample in heating experiment using HH at high input power (150 W).

Inspecting Figure 5.31, clearly, there was a temperature gradient inside the sample between the outskirt and the centre of the sample. The temperature measured at the outskirt was found to be up to 6 °C higher than that at the centre. This heating experiment demonstrated that there was a temperature gradient within the sample. Only the outskirt of the sample was heated. Such a phenomenon is reminiscent of the skin effect showed by MWH. ^[50] However, when the identical heating experiment was conducted in EH, there was no such effect observed as shown in Figure 5.32. The outskirt and centre temperature reading were identical to each other. This clearly showed that at high input power, the E-field energy was able to penetrate through the whole sample to achieve volumetric heating. Therefore, this observed 'skin effect' in HH was postulated to be (a) induction heating from the H-field and/or (b) weak EH which was only able to heat the outskirt of the sample.



Figure 5.32 Demonstration of temperature difference between centre and outskirt of CL sample in heating experiment using EH at high input power (150 W).

Horikoshi and coworkers studied the heating of electrolyte solution with MW by adding electrolyte into the water. ^[37] They found that at high electrolyte load (above 1 Molar solute concentration), the HH efficiency was higher than EH. This was hypothesised to be that the alternating H-field was able to penetrate through the sample and induced ring currents that were perpendicular to the H-field. Since the H-field was distributed throughout the sample, these currents were generated within the whole sample and the resistance leaded to Joule heating of the system. They concluded that the observed phenomena were regarded as indirect conduction loss heating by the alternating H-field. However, this was not the case in CL heating experiment studied here because there were no ions present in the solution, so there was no Joule heating involved. Therefore, this observed temperature gradient should be generated from the weak EH that was not able to penetrate throughout the sample. Therefore, identical experiment with low input power (30 W) using EH was then conducted as shown in Figure 5.33.



Figure 5.33 Demonstration of temperature difference between centre and outskirt of CL sample in heating experiment using EH at low input power (30 W).

Interestingly, it was found that when low input power was used in EH, there was a temperature gradient between the centre and the outskirt of the sample. This suggested that the input power was too low to heat the sample thoroughly, and thus resulting in higher 'wall' temperature. The heat energy was then transferred to the centre of the sample *via* conduction/convection similar to CH. Therefore, this empirical observation supported the previous discussion that the observed temperature gradient in CL using HH was originated from weak EH. Additionally, the results also indicated that if there were no material that was susceptible to HH present in a sample, the heating behaviour of the sample using HH would be similar to CH (heat energy was transferred from outside to the centre of the sample).

To identify if the $Fe(Oct)_3$ also possess the temperature gradient between the centre and outskirt of the sample, identical HH experiment using 150 W input power was conducted, and the temperature profile was shown in Figure 5.34.



Figure 5.34 Demonstration of temperature difference between centre and outskirt of CL containing $Fe(Oct)_3$ sample in heating experiment using HH.

From the temperature profile above, very similar heating behaviour between the centre and the 'wall' of the sample were observed. It was clear that the $Fe(Oct)_3$ experienced volumetric HH throughout the sample. This also indicated that adding $Fe(Oct)_3$ to CL would improve the heat distribution using HH, because $Fe(Oct)_3$ was able to interact with the H-field.

From these heating experiments, it could be concluded that $Fe(Oct)_3$ and $Co(Oct)_2$ were susceptible to HH, whereas CL and $Sn(Oct)_2$ were not. Moreover, adding $Fe(Oct)_3$ to CL would improve its ability to be heated by HH. It was also found that although CL and $Sn(Oct)_2$ were not able to interact with the H-field, they still experienced heating using HH, this was due to the presence of weak E-field that heats the sample *via* EH.

Now that the heating mechanism of these catalysts using HH was identified, the next step was to investigate how these differences in heating performance could affect the conversion and characteristics of the PCL produced *via* the ROP of CL. Identical experimental preparation procedures were used as CH and EH, but the reaction was carried out in single-mode MiniFlow using TM cavity operated

at 2.45 Ghz with a maximum input power of 150 W. By doing this, a systematic comparison among CH, EH and HH was able to be established. The results of ROP of CL at [M]:[C] ratio of 400:1 can be seen in Table 5.7, and a typical Mwt versus conversion plot was shown in *Figure 5.35*.

Table 5.7 Average results of ROP of CL with different catalysts and BzOH using HH

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	N:A	N:A	60	160	170	1.05	<1
2	Sn(Oct) ₂	400:1	10	5100	5200	1.23	94
3		400:1	15	5200	5300	1.56	98
4	Fe(Oct) ₃	400:1	40	4600	4800	1.14	92
5	Co(Oct) ₂	400:1	60	4300	4600	1.24	97

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR



Figure 5.35 Evolution of Mwt depending on the reaction conversion in ROP of CL for different catalysts at [M]:[C] ratio of 400:1 using HH.

Inspecting Table 5.7, when the ROP reaction was carried out without any catalysts (Table 5.7, Entry 1), there was no polymerisation were obtained after 60 min. This again proved that the catalyst was essential for the ROP to be successfully conducted no matter which heating method was used.

When $Sn(Oct)_2$ was used as the catalyst, again the conversion was able to reach above 90% within 10 min (Table 5.7, Entry 2). Extending the reaction time for an additional 5 min, the conversion was able to reach 98%, but the D value was broadened to 1.56 (Table 5.7, Entry 3) indicating the existence of significant side reaction. Cross-referencing the Mwt results with that of CH, it was found that there were no significant differences between these two heating methods, the Mwt of PCL produced *via* these two heating methods were rather very close $(M_{n CH}=5200 \text{ gmol}^{-1}, M_{n HH}=5100 \text{ gmol}^{-1})$. Moreover, from Figure 5.35, the Mwt results obtained using $Sn(Oct)_2$ were close to theoretical Mwt results, indicating there was no retardation of the catalysts. These observation, combined with the fact that the HH was only able to heat the CL+Sn(Oct)₂ solution from outskirt of the sample similar to CH, suggested that there was no significant difference in reaction between HH and CH when there were no material susceptible to HH.

In comparison, when $Fe(Oct)_3$ was used as the catalyst, it was noted that the reaction was able to reach 90% within 40 min which took about 47% less time than CH. Inspecting Figure 5.35, the obtained Mwt were close to the theoretical Mwt, indicating there was no retardation in the catalyst. Combining the fact that significant improvement in heating rate using HH for CL+Fe(Oct)₃, it could be concluded that the observed differences between CH and HH were potentially originated from the selective heating of $Fe(Oct)_3$ by the alternating H-field. Additionally, the Mwt of PCL produced with $Fe(Oct)_3$ was comparable with which done with $Sn(Oct)_2$ (Mwt difference was less than 10%), indicating that $Fe(Oct)_3$ could be a replacement for the benchmark catalyst $Sn(Oct)_2$.

Similarly, inspecting results obtained from Co(Oct)₂, significant improvement in Mwt and reduction in reaction time was also observed when using HH instead
of CH. Compared to the other two catalysts, ROP using Co(Oct)₂ still required the longest reaction time. But from the Mwt versus conversion plot, it could be seen that it has similar control over the reaction as the other two catalysts in terms of Mwt. Interestingly, it was noticed that the Mwt and conversion obtained using HH were improved comparing to which done with EH. In fact, in heating experiments, it was observed that Co(Oct)₂ show insignificant improvement in heating when added to CL using EH, whereas a measurable difference was observed using HH. This suggested that the improved results using HH compared to EH was potentially originated from the difference in the extent of the selective heating on the catalyst. This would be discussed in more details in a later section.

From these ROP experiments using HH, it could be concluded that if no material was susceptible to HH (i.e. $Sn(Oct)_2$ and CL), then the obtained ROP results using HH should be close to which obtained with CH. However, if the catalyst was able to be heated by HH, significant improvement in conversion and characteristic of the product compared to CH were able to be obtained.

The variable that was investigated next was the influence of the catalyst concentration. In the previous chapter, it was found that the HH was more significant at high catalyst load (i.e. improvement in ROP results using FeCl₃ using HH was more significant at [M]:[C] ratio=400:1 than [M]:[C] ratio=1600:1 when compared to EH). Therefore, reduced catalyst concentration namely, [M]:[C] ratio of 800:1 and 1600:1, were then studied using all three catalysts. The results of the ROP were shown below in Table 5.8, and a typical Mwt versus conversion plot was shown in Figure 5.36.

Table 5.8 Average results of ROP of CL with different catalysts using HH

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	Sm(Oat)	800:1	20	5400	5700	1.18	84
2	Sn(Oct) ₂	1600:1	60	7100	7200	1.28	96
3	E ₂ (O ₂ t)	800:1	120	6600	7100	1.40	98
4	re(Oct)3	1600:1	120	7300	7400	1.26	92
5	$C_{\alpha}(0_{\alpha}t)$	800:1	120	5300	5600	1.23	84
6		1600:1	240	6000	6400	1.22	75

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR



Figure 5.36 Evolution of Mwt depending on the reaction conversion in ROP of CL for different catalysts at [M]:[C] ratio of 800:1 using HH.

When Sn(Oct)₂ was used at reduced concentration, the reaction time was found to be extended similarly to CH and EH (Table 5.8, Entry 1 and 2). For example, 10 min was required to reach 90% when [M]:[C] ratio was 400:1, whereas the reaction only reaches 85% after 20 min when [M]:[C] ratio was reduced to 800:1. Further reducing the [M]:[C] ratio to 1600:1, 60 min was required to reach similar conversion that was done in 10 min when [M]:[C] ratio was 400:1. The final Mwt achieved was increased as the catalyst concentration was reduced. The D value for the obtained PCL was below 1.5 suggesting the catalyst have a good control over the Mwt. This was also supported by the fact that obtained Mwt was close to the theoretical Mwt as shown in Figure 5.36. When compared the obtained results with CH and EH, it was found that the EH has the highest Mwt achieved, whereas the Mwt obtained *via* CH and HH were rather similar. This again supported the previous finding that when no material was able to interact with the H-field, the heating of the bulk in HH was to that in CH, and thus similar results in Mwt and conversion were observed.

When the reaction was conducted with $Fe(Oct)_3$ at reduced catalyst load, it was again found that extended reaction time was required to achieve similar conversion to which was done at [M]:[C] ratio of 400:1. Conversely, the obtained Mwt was significantly higher at lower catalyst load when compared at similar conversion (Table 5.8, Entry 3 and 4). Comparing these results against that of CH and EH, it was found that a higher Mwt and conversion was achieved when HH was applied. Unlike Sn(Oct)₂ which was not able to be heated by HH, the Fe(Oct)₃ showed significant heating improvement when using HH. Therefore, this potentially suggests that when Fe(Oct)₃ was used as the catalyst, HH could provide more beneficial effects than EH. This could be potentially attributed to the fact that the both Fe catalyst and CL was experiencing selective heating and competing in absorbing the energy from the E-field in EH, whereas only Fe catalyst was able to be selectively heated by HH. The catalyst temperature could be potentially higher in HH than EH and therefore promoted the propagation process. However, in the previous chapter, it was found that when FeCl₃ was used at lowered catalyst load, the difference in obtained Mwt and conversion between EH and HH became insignificant. This could be because higher temperature (>100 °C) has a detrimental effect in Mwt in ROP using FeCl₃ where side reactions became significant. However, this was not the case in Fe(Oct)₃ because higher temperature provided significant beneficial effects on the

reaction. Therefore, a significant higher Mwt was obtained for $Fe(Oct)_3$ when using HH than EH (Mn was around 12% higher in HH at [M]:[C] ratio of 1600:1).

Similarly, inspecting results of Co(Oct)₂, higher Mwt was achieved at reduced catalyst level (Table 5.8, Entry 5 and 6). Comparing the obtained results with that using CH, significant improvement in Mwt and conversion was observed. Combined the fact that Co(Oct)₂ showed improved heating of the bulk using HH, this observed improvement using HH should be due to the selective heating on Co(Oct)₂. However, the improvement in heating when using EH (temperature difference <1 °C) and HH (temperature difference <4 °C) was not as significant as Fe(Oct)₃, and thus the conversion and Mwt results were not significantly different between EH and HH.

Thus, the conclusion from these experiments was that, while all catalysts were able to initiate and control the ROP of CL, the Fe(Oct)₃ showed the most significant improvement in PCL products when using HH. The Sn(Oct)₂ showed close results between CH and HH which was due to the similar heating mechanism of the bulk between HH and CH. The variable that was investigated next was the influence of temperature. Three temperatures namely 140, 150, and 160 °C were used for ROP of CL at [M]:[C] ratio of 800:1 using all three catalysts. Thus, an equivalent study to CH and EH could be established. The kinetic study of these experiments was detailed in Figure 5.37, Figure 5.38, and Figure 5.40.



Figure 5.37 Comparison of kinetic experiments between different temperatures using Sn(Oct)₂ at [M]:[C] ratio of 800:1 using HH.

When conducting ROP of CL with Sn(Oct)₂ at 140 °C, an induction time of at least 5 min was required before any conversion was noticed. This inactive period was followed by a constant increase in conversion during the propagation stage. Increasing the reaction time to 150 and 160 °C, the induction time was significantly reduced to below 5 min. i.e. at the reaction was able to reach 11% at 6 min mark at 150 °C, whereas 30% conversion was reached in 5 min at 160 °C. Comparing the obtained kinetic plots with CH, a similar trend was found between two graphs, but the induction period was noticed to be different. This should be attributed to the fast heat up time of the bulk (around 250 s in CH and around 160 s in HH). Additionally, the linear relationship between conversion and time during propagation period indicated the reaction was well controlled.



Figure 5.38 Comparison of kinetic experiments between different temperatures using $Fe(Oct)_3$ at [M]:[C] ratio of 800:1 using HH.

Inspecting the conversion versus time plot for Fe(Oct)₃, an induction period of 5 min was also noticed when the reaction was conducted at 140 °C. Again, this induction period was reduced by increasing the reaction time to 150 and 160 °C. It was found that the conversion reached 150 °C were close to which at 160 °C. This could be similar to the observed error in EH which was due to lost control of the temperature during heating up. However, inspecting the temperature profile as shown in Figure 5.39, the temperature was well controlled (no overshooting over 2 °C), indicating this observed improvement in conversion should be due to the selective heating on the catalyst which could potentially elevate the catalyst temperature close to 160 °C.



Figure 5.39 Example of temperature and power profile of a typical ROP of CL experiment using HH. PA: power absorbed.



Figure 5.40 Comparison of kinetic experiments between different temperatures using $Co(Oct)_2$ at [M]: [C] ratio of 800:1 using HH.

When the identical experiments were carried out using Co(Oct)₂, it was found that similar to CH and EH, the induction period for all temperatures were less than 5 min. During the propagation period, a constant increase in conversion was observed indicating good control over the polymerisation. Again, the higher conversion was reached at each time mark at elevated temperature. This suggested that higher temperature provided beneficial effects to the polymerisation. From these kinetic studies at various temperatures using HH, it was found that increasing reaction temperature provided beneficial effects to the reaction. Additionally, the control over the polymerisation was still maintained. Increasing temperature was found to reduce induction time significantly for Sn(Oct)₂ and Fe(Oct)₃. But it was found that the conversion achieved for Sn(Oct)₂ were similar to that achieved in CH due to its similar heating mechanism between CH and HH. The difference between conversion was mainly originated from faster heat up time in HH.

The next series of experiments was to identify the rate constant (k_{app}) for all the reactions done at different temperatures based on the kinetic studies above. By doing this, it was able to quantitatively compare the reaction rate between CH, EH, and HH. Additionally, this allows for the determination of the activation energy of the reaction for each catalyst. The summary of k_{app} was shown in Table 5.9, and a typical kinetic plot using Sn(Oct)₂ as shown in Figure 5.41.

	Sn	Fe	Co
Temperature	k	k	k
(°C)	(min^{-1})	(\min^{-1})	(\min^{-1})
140	0.0974	0.0096	0.007
150	0.1016	0.0236	0.0121

0.0454

0.0189

0.189

160

Table 5.9 Summary of rate constant of ROP of CL conducted using different catalyst using HH



Figure 5.41 An example of a kinetic plot of ROP of CL using $Sn(Oct)_2$ at a different temperature using HH with best fit line (BFL).

The example showed that a linear relationship holded between $ln(M_0:M)$ and time when $Sn(Oct)_2$ was used for the ROP using HH. This result indicated that the polymerisation was first order controlled polymerisation. Increasing the temperature from 140 to 150 °C, increment in k_{app} was noticed, but the shift of intercept between the best fit line and x-axis was rather more significant, indicating a significant reduction of the induction period. Further increasing the temperature to 160 °C, reduction in induction time and increment in k_{app} was identified, suggesting conducting ROP of CL at 160 °C should be more beneficial for faster conversion. However, comparing the k_{app} values obtained in HH with CH, insignificant differences between these values were found (i.e. 0.095, 0.109, and 0.184 min⁻¹ at 140, 150, and 160 °C in CH, compared to 0.97, 0.102, and 0.189 min⁻¹ at 140, 150, and 160 °C in HH). This again supported the conclusion that the observed similar conversion and PCL characteristic results between CH and HH for Sn(Oct)₂ was due to its similar heating mechanism when using CH and HH. In comparison, for $Fe(Oct)_3$ and $Co(Oct)_2$, the increment of k_{app} was significant when the temperature was elevated. This obtained trend was different to that in CH due to different heating mechanisms between CH and HH for these two catalysts. Thus the improvement in k_{app} values could potentially be originated from the selective heating of the catalyst using HH.

Inspecting the k_{app} values between each catalyst at the identical reaction temperature, it was found that the Sn(Oct)₂ has an order of magnitude more than the Fe(Oct)₃ and Co(Oct)₂. Alrough, the improvement between CH and HH, was not significant for Sn(Oct)₂ compared to the Fe and Co alternatives, but the nature of catalyst was still having dominant effects on its performance.

To determine the activation energy of this reaction using HH, Arrhenius graphs were plotted based on the obtained k_{app} values and its corresponding temperature. The plots of lnk_{app} versus the reciprocal of absolute temperature show a linear trend in the range of study for all catalysts, as shown in Figure 5.42. The activation energy was found to be 49, 116, and 74 kJmol⁻¹, for Sn(Oct)₂, Fe(Oct)₃, and Co(Oct)₂, respectively. Comparing these results to that of CH and EH, it was found that for the same catalyst, there were insignificant differences in activation energy between all heating methods, indicating the observed differences in reaction rate and product quality should be purely thermal effects.



Figure 5.42 The dependence of apparent rate constant (k_{app}) of polymerisation with best fit line (BFL) using different catalysts in HH.

From previous experiments, it could be concluded that the observed improvement when EH was applied to the ROP for $Sn(Oct)_2$ should be purely originated from EH because it did not have significant interactions with the H-field from HH experiments. Whereas for Fe(Oct)₃, there might be a combination of strong EH and weak HH or *vice versa*. Therefore, additional ROP studies using Fe(Oct)₃ at low input power were then investigated to identify how input power has upon the reaction conversion and product quality. The results of low input power experiments were summarised in Table 5.10. The reaction was conducted with Fe(Oct)₃ at [M]:[C] ratio of 800:1 using a maximum input power of 50 W.

*Table 5.10 Average results of ROP of CL with Fe(Oct)*³ *and BzOH using EH and HH at 50 W input power*

Entry	Catalyst	[M]:[C] ratio	Time (min)	Mn ^a (gmol ⁻¹)	Mp ^a (gmol ⁻¹)	Đª	Conversion ^b (%)
1	CH	800:1	60	2300	2300	1.111	42
2	EH	800:1	60	3200	3300	1.08	46
3	HH	800:1	60	2800	2800	1.1	45

^a determined by GPC, measured in THF at 35°C

^b determined by ¹H-NMR

Table 5.10 demonstrated that using EH and HH at low input power still showed improvement in Mwt and conversion. The Mn value increased from 2400 to 3200 gmol^{-1} (increased by 33%) and 2800 gmol^{-1} (increased by 16%) for EH and HH, respectively, whereas the conversion between all three heating methods was similar. These results demonstrated that even at low input power, there was still improvement in Mwt when EH and HH were applied. However, differences in Mwt results between EH and HH was also noticed. This result, combined with the fact that Fe(Oct)₃ showed more significant temperature difference in weak EH than HH, indicated that Fe(Oct)₃ experienced stronger selective heating with weak EH than weak HH, and thus resulting in a more significant difference in the Mwt results. From this experiment, it was also identified that weak EH would provide more improvement in the product quality than weak HH. Therefore, it would be more beneficial when Fe(Oct)₃ was used in HH because there would be a combined effect of strong HH and weak EH.

From these HH experiments, it was able to conclude that Fe(Oct)₃ was more promising when used using HH due to a combination of strong HH and weak EH. Indeed, from the ROP results, the Mwt and conversion achieved with Fe(Oct)₃ was superior with HH. Similarly, Co(Oct)₂ also showed measurable temperature differences in magnetic heating experiments and thus improved Mwt and yield were achieved compared to CH. Conversely, Sn(Oct)₂ did not experience any magnetic selective heating due to its magnetism and resulted in the similar heating mechanism as in CH. As a result, very similar results between CH and HH were obtained.

Now that the reaction rate constant for ROP reactions using all three catalysts using CH, EH, and HH were obtained, it was possible to quantitatively compare these results to identify how the heating methods affect the propagation process. The summary of k_{app} values for all catalysts using three heating methods was shown in Table 5.11.

Table 5.11 summary of the rate constant of the different catalyst using CH, EH, and HH at 150 °C. Condition: [M]:[C] ratio of 800:1

	Sn	Fe	Со
Heating methods	k _{app} (min ⁻¹)	k _{app} (min ⁻¹)	k _{app} (min ⁻¹)
СН	0.1089	0.0117	0.0077
EH	0.1557	0.0156	0.0088
HH	0.1016	0.0236	0.0121

Comparing the results between CH, EH and HH for $Sn(Oct)_2$, very similar k_{app} values were found between CH and HH, whereas an increment of 43% in k_{app} value was found for EH. These results, combined with the fact that $Sn(Oct)_2$ only showed significant different temperature profile to CL when using EH, indicated that the observed enhancement in propagation rate was due to the selective heating on the catalyst. The selective heating on $Sn(Oct)_2$ could potentially elevate the catalyst temperature, and this in turn accelerated the initiation process. Additionally, because the ROP reaction took place on the catalyst, therefore this selective heating could also potentially promote the propagation process, as a result improvement in the k_{app} values were identified. Conversely, if no selective heating was observed like in HH, similar results to CH was then obtained.

When the k_{app} values for Fe(Oct)₃ were compared between each heating methods, improvement in k_{app} value was found when EH or HH was applied. This was again due to the selective heating of the catalyst as measurable differences in temperature profiles compared to that of CL were identified. However, Fe(Oct)₃ was found to provide a more significant improvement in the k_{app} value when using HH compared to EH. Although $Fe(Oct)_3$ showed the most heating improvement when using both EH and HH, the higher k_{app} results obtained in HH suggested that the selective heating of $Fe(Oct)_3$ was more significant when HH was applied. This could be because in EH, both CL and $Fe(Oct)_3$ were selectively heated, and thus competitions in absorbing the EM energy between two substances took place. Whereas in HH, the catalyst was selectively heated by the alternating H-field, but CL was heated by the weak E-field at the outskirt of the sample. In this case, $Fe(Oct)_3$ possessed significant higher temperature than CL and PCL in HH compared to that in EH. Therefore, this potentially promoted the propagation process when using HH. Additionally, the combination of strong HH and weak EH when using HH could also enhance the propagation process as found in low power experiments.

In comparison, when $Co(Oct)_2$ was used as the catalyst, it was found that the improvement in k_{app} value was not significant in EH compared to HH. This difference was attributed to the fact that the temperature differences were found to be more significant in HH than in EH. Therefore, the selective heating of the $Co(Oct)_2$ in EH was not significant enough to promote the propagation process compared to that in HH. The fact that k_{app} value was found to be higher using HH than EH also suggest that HH could be a comparable alternative heating method to CH and EH if the material were able to interact with the H-field, i.e. Fe and Co.

Comparing the k_{app} values between each catalyst, it was found that $Sn(Oct)_2$ has an approximate order of magnitude more than Fe and Co alternatives, indicating it has superior catalytic efficiency than the other two catalysts. However, it should be noticed that the k_{app} value for Fe(Oct)₃ when using HH was only four times less efficiency than Sn(Oct)₂ using CH. The catalytic efficiency was significantly improved compared to that in CH and EH which was ten times less efficient compared to Sn(Oct)₂ using CH. Such results indicate that the Fe(Oct)₃ was most efficiency using HH. However its catalytic efficiency was still limited by the natural of the metal centre (Lewis acidity). Although Sn(Oct)₂ was still the best catalyst especially using EH, if EH were applied to these reactions, the major limitation would be the penetration depth of the EMF. This limitation was normally overcome by reducing the frequency (increase the penetration depth) or transfer to continuous processes with small reactor size. But the high viscosity of the product could cause blockage of such continuous process. As previously discussed that HH was easy to scale up without concern of the penetration depth because only the catalyst absorbs the magnetic energy. Therefore, with the application of Fe(Oct)₃ to ROP reactions using HH, it was possible to provide an alternative route for scaling up the process with advantages such as simple and environmentally benign. Such development could potentially bring a revolution to the current industries.

5.4 Conclusion

This study has clearly demonstrated that PCL could be successfully synthesised by the use of $Sn(Oct)_2$, $Fe(Oct)_3$, and $Co(Oct)_2$ in CH, EH, and HH. For the first time, $Fe(Oct)_3$ and $Co(Oct)_2$ were applied to ROP of CL as a catalyst, and the product was compared to the benchmarking catalyst $Sn(Oct)_2$. When CH was used as the heating method, all ROP reactions showed an induction period followed by a constant increase in conversion during the propagation period. All catalysts showed good control over the polymerisation, but the $Sn(Oct)_2$ showed the highest catalytic efficiency among three catalysts. Reducing the catalyst load showed an increase in achieved Mwt and longer reaction time, but the control of the polymerisation was still maintained with Mwt close to theoretical Mwt. Increasing the reaction temperature was found to provide beneficial effects, such as significantly reduce the initiation period and improve reaction rate. The kinetic study showed that the propagation rate constant for $Sn(Oct)_2$ was at least ten times faster than the other two catalysts.

After identifying the mechanism of the reaction using CH, EH experiments were then conducted. In EH heating experiments, it was found that Sn(Oct)₂ and Fe(Oct)₃ showed significant improvement in heating rate when added into CL. It should be reminded that the catalyst concentration was at [M]:[C] ratio of 800:1, therefore, the catalyst must possess a significantly higher temperature in order to show such difference in the temperature profile. This was later found to be the potential reason for the improved Mwt and reaction rate when compared to CH. Conversely, Co(Oct)₂ had similar temperature profile as CL and showed less improvement in product quality compared to the other two. This was postulated to be resulted from the selective heating on CL and/or the selective heating on Co(Oct)₂ was masked by CL. Among all three catalysts, it was found that the initiation period was significantly reduced when EH was applied. This was found to be due to fast heat up of the bulk and accelerated synthesis of the 'true' catalyst. Later in the kinetic studies, it was found that all three catalysts exhibited good control over the polymerisation. The activation energy was found to be close to that when using CH, suggesting that all the observed improvement in EH should be purely thermal effects.

The identical reactions using HH was also conducted for systematic comparison against CH and EH. It was found that $Sn(Oct)_2$ exhibited similar heating

behaviour in HH compared to CH, whereas $Fe(Oct)_3$ and $Co(Oct)_2$ exhibited substantial selective heating in HH. This was found to be due to their magnetism and the presence of the unpaired spin in the metal centre. During the ROP experiments, it was found that similar results between CH and HH were obtained for Sn(Oct)₂, suggesting the heating method did not affect the product yield and quality of the polymerisation, due to the similar heating mechanism in CH and HH. Conversely, Fe(Oct)₃ and Co(Oct)₂ showed improved yield and Mwt when using HH than CH. Compared these results against that of EH, it was found that Fe(Oct)₃ and Co(Oct)₂ have better catalytic efficiency in HH than EH, suggested that the HH could also be an alternative heating method for materials that were able to interact with the H-field. Additionally, the Fe(Oct)₃ was found to be the best alternative when used using HH. Although Sn(Oct)₂ still has the highest catalytic efficiency, the non-toxic Fe(Oct)₃ combined with HH which has advantages like easy to scale up and set up, and environmentally benign could potentially provide an alternative route for scaling up the process.

5.5 Future Work

Future work regarding to this area is to see if the observed beneficial effects from HH can still be obtainable when the scale of the experiment is magnified. Thus, the potential of scaling up such HH process can be identified. Additionally, the application of Fe(Oct)3 and HH to other polymerisation reactions can also be investigated to broaden the application of the process. Eventually, batch or continuous process with HH can be designed as an alternative route for ROP processes.

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6.1 Conclusions

This work aimed to identify the differences between different heating methods in the ring opening polymerisation of ε -caprolactone, including conventional heating (CH), microwave E-field heating (EH), and microwave H-field heating (HH), and highlight how these heating methods affect the produced polymer in terms of conversion and molecular weight when catalysts with various dielectric and magnetic properties are used. This thesis started with the investigation of microwave selective heating, with the use of dielectric property measurements and heating experiments. Then, experiments in identifying how such selective heating can affect the reaction conversion and polymerisation quality were carried out. Throughout the work, direct comparisons were made between different heating sources, which has not been shown by any other researcher. By doing so, it opens an alternative route for replacing the current benchmark catalyst by using a catalyst that is specifically designed to work efficiently when using microwave electromagnetic heating.

From Chapter 3, it was found that the addition of metal halides and organometallics to a solvent could induce differences in the dielectric properties of the solution to a different extent. Additionally, the use of different organic ligands and the choice of the various metal centre were found to be critical in affecting the dielectric properties of the solution. This was due to the use of different ligands, or metal centres which would result in (a) differences in overall molecular size, (b) the flexibility of the overall molecule structure, (c) number of electrons available to interact with the EM field. Therefore, organometallics were found to show greater differences in the dielectric properties when

dissolved in the solvent. In addition, from the heating experiments, it was found that the addition of metal halides and organometallics improved the heating performance of the solution as predicted from the dielectric property measurements. Such observation was also reflected by the power profiles in which additional power was found to be absorbed by metal halides and organometallics. This additional power allowed solutes to be selectively heated by the microwave and contributed to the overall heating of the solution. This work has shown that the complexes could experience microwave selective heating and this could be enhanced by alternating the metal centre or the attached organic ligands. Additionally, such selective heating effect could be reflected by the improvement in the heating of overall solution.

In Chapter 4, it has been clearly shown that significant differences in conversion and molecular weight (Mwt) of polymers were found when using different heating methods to conduct ring opening polymerisation (ROP) of ε -caprolactone (CL). It was shown that the temperature has significant effects on the overall conversion and polymer quality, and an optimum temperature was found for FeCl₃ catalyst. Beyond this temperature may result in enhancement of side transesterification reactions which could cause detrimental results to polymer products, such as broadening the polydispersity and reducing the average Mwt. Direct comparisons among CH, EH, and HH were carried out with different catalysts. It has been shown that catalyst that has stronger abilities in interacting with the microwave E- or H-field could show significant improvement in reaction conversion and polymer Mwt compared to results obtained from CH. However, the calculation of activation energy suggested the mechanics of the polymerisation remaine the same among all heating methods. Further investigation in this work, it was found that the concentration of the catalyst was a critical factor to deliver differentiated selective heating effects between CH, EH, and HH. If a catalyst undergoes selective heating is at a concentration higher than the "tipping point", the outcomes of the EMH and CH reactions would be different in favour of the former one. In contrast, if the catalyst is present in too small quantity, there would be no significant selective heating effects, and similar results compared to CH are then observed. In addition, the results suggested that HH could potentially be more beneficial at high catalyst load. This work has demonstrated that for the first time, that the ROP of CL can be carried out with the use of HH. It was shown that HH could potentially show improved, or comparable results compared to EH.

From Chapter 5, the ROP of CL was successfully carried out using two novel catalysts (Fe(Oct)₃ and Co(Oct)₂) as alternatives for the benchmarking catalyst (Sn(Oct)₂) with various heating methods. The presence of induction time was noticed for all ROP reactions that conducted using CH. However, this was diminished or reduced when using EH or HH. This was found to be due to (a) the fast heat up of the bulk and (b) the accelerated synthesis of the 'true' catalyst. In HH experiments, results obtained for Sn(Oct)₂ were found similar to that obtained in CH; this was due to the diamagnetic natural of the Sn metal centre. However, both Fe(Oct)₃ and Co(Oct)₂ showed higher catalytic efficiency when using HH compared to EH. This suggested that HH could be an alternative heating method for materials that are able to interact with the H-field. Additionally, this work has shown that it is possible to combine magnetic catalysts with HH as an alternative method to replace the expensive and toxic catalysts.

6.2 Future work

The main aim of this work was the development of understandings in ROP of CL when using different heating methods. From this work, some key areas for further investigation have been highlighted.

It was found that the actual dielectric property of complexes, when dissolved in a solvent, or involved in ROP reaction, was not able to be identified. Quantification of this is important as it is critical in the process to prevent thermal runaway from happening. A method to identify the actual temperature of a catalyst when heated with MW would also be essential to identify the extent of selective heating on the catalyst. Further experiments with pulsed MW system should also be investigated to identify if the selective heating effect can be improved.

For ROP of CL with metal halides, other types of cyclic esters could also be investigated to broaden the library. Additionally, more work needs to be done to identify how to maximise the beneficial effects of HH.

In addition to ROP of CL using organometallics, the potential of scaling up an HH process could be studied to investigate if the beneficial effects from HH can still be obtainable when the process is scaled up. Additionally, the application of Fe(Oct)₃ to other polymerisation reactions could also be studied to broaden the application of the catalyst. Ultimately, a continuous or batch process with HH can be designed as an alternative ROP processes.