Synthesis of Bio-based Polyesters and Polycarbonates from Lipid Derived Monomers

by

Liejiang Jin

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Bioresource Technology

Department of Agricultural, Food and Nutritional Science
University of Alberta

Abstract

Petroleum-derived polymers have applications in various industrial sectors including packaging, aerospace, automotive, adhesives, cosmetics, construction, medical and other industrial fields. Recently, due to dwindling fossil fuel resources and environmental concerns, both academia and industry has focused their attention on the development of biopolymers from renewable resources which could be eco-friendly and potentially biodegradable. Lipids are regarded as potential renewable resources for the synthesis of such biopolymeric materials. This thesis firstly reports a rapid and efficient route to convert lipids into a desired diester monomer and synthesis of polyesters from the monomer under microwave irradiation conditions. The plant oils were transferred into diester using microwave-assisted metathesis chemistry in solvent free conditions within few minutes at low temperature (50°C). The diester monomer was further modified to produce polyesters using conventional heating, microwave irradiation and conventional heating coupled with microwaves. The biopolyesters with number average molecular weight (M_n) as high as 30 kDa were synthesized. The biopolymer with desired molecular weight could be synthesized in less than half time using microwaves and coupled method compared to conventional heating method.

Secondly, microwave-induced syntheses of lipids derived α-olefin to polyesters and polycarboantes were carried out. An α-olefin was converted to epoxide with >90% yield. Using ring opening polymerizations, this monomer was copolymerized with carbon dioxide (CO_2) and different cyclic anhydrides including maleic, succinic, itaconic, phthalic and tetrahydrophthalic anhydrides to develop biopolymers under microwave conditions. The biopolymers were rapidly synthesized (3-30mins for CO_2 and 10-60mins for anhydrides) with high conversions (up to 99%) and molecular masses (M_w) as high as 17 kDa. The synthesized monomers were characterized using different techniques including nuclear magnetic resonance (^{1}H NMR & ^{13}C NMR), fourier transform infrared spectroscopy (FT-IR) and gas chromatography- mass spectroscopy (GC-MS). The biopolymers were characterized using ^{1}H NMR, ^{13}C NMR, FT-IR, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile tests. The semi-solid to solid biopolymers with highest degradation temperature ~400°C, tensile strength ~ 5 MPa, and melting temperature ~ 50°C were synthesized with great potential to be used in different applications.

Acknowledgements

First and foremost, I would like to express my sincere gratitude to my supervisor, Dr. Aman Ullah for giving me this opportunity to work and study in this group, and his kind guidance, instructions, advices and financial supporting throughout the whole program. The knowledge and experiences I have obtained from him in University of Alberta will be beneficial in my following life.

I would also like to thank my supervisory committee member, Dr. Hongbo Zeng for his interesting course, devoted time and effect into my study. I’m also thankful to Dr. Muhammad Arshad (our group) and Ereddad Kharraz (Dr. Curtis group) for their guidance and help in using different pieces of equipment.

My group members, Muhammad Arshad, Muhammad Safder, Muhammad Zubair, Reza Ahmadi, Manpreet Kaur, Yanet Rodriguez Herrero have helped me a lot in my work throughout the program. Without them, it’s impossible to complete all the work by myself.

In addition, a thank you to AFNS staff, including Urmila Basu, Robin Miles and others for their kindness of supplying materials, suggestions and convenience during my whole program.

Finally, I would like to thank my parents and my girlfriend for their unconditional support, encouragement and love during my studies. I’m so appreciative of their understanding they show that I’m always busy engaged in the research and cannot accompany them in those years.

Table of Contents

List of Figures

List of Tables

Chapter 1 Introduction & Objectives

1.1. Synthetic Polymers and their Limitation

From the first synthetic polymer invented in last century, the polymer industry keeps flourishing on this planet, tremendously influencing the human's daily life and environment. From navigation to aerospace, painting to medical equipment, polymers have their wide applications in each aspect. However, in contrast to the concordant compliments since the invention appeared in the market, the polymer industry is receiving more and more criticism with the world's gradually improving consciousness of environment protection and health care.

In other words, synthetic polymers are unable to meet the new environmental pollution restrictions and the problems associated with their expanded use, are grabbing more intensive attraction than ever. A primary concern the humans are anxious about is the source of polymer, whose majority is fossil oils (Feldman & Barbalata, 1996), and only small percentage is from natural products (Belgacem & Gandini, 2011). Mainly depending on non-renewable petroleum resources, the polymer production accelerates the consumption of fossil fuels. It has been predicted that, over time, the cost of polymer will eventually rise up depending upon the decline of oil reserves. Therefore, development of natural resource-derived polymers to substitute petroleum based polymers is gaining more attention from all over the world.

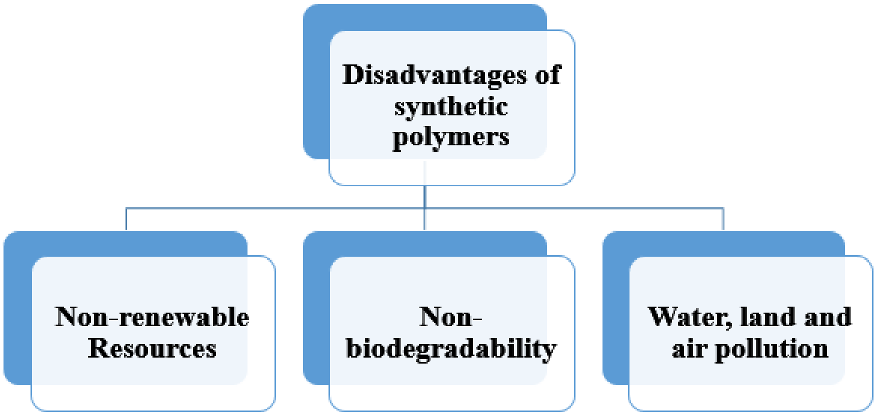


Figure 1.1. Disadvantages of synthetic polymers

The poor degradability of synthetic polymers is another main issue. It is estimated that 86% of plastic packaging (Neufeld, Stassen, Sheppard, & Gilman, 2016) is used only once in its life time before being disposed. Over the past decades, the discarded polymers are continuously accumulating on the planet including in some developing areas leading to a major environmental danger. As an example, in the case of polyethylene terephthalate (PET), fifty or more years (Webb, Arnott, Crawford, & Ivanova, 2012) are needed for its complete decomposition in natural circumstance. Though in many countries, now polymers are well classified, collected and recycled, it is still difficult to dispose abandoned polymers. Currently, landfills and incineration are two major but imperfect methods to tangle with huge amount of polymer waste. Landfills (Swift, 2004) occupy large areas of lands and there is a potential risk of polluting the surrounding soil (Yaron, Calvet, & Prost, 1996) and with toxic substances penetrating into the associated underground water (DeWalle & Chian, 1981). In addition, greenhouse gases (Swift, 2004) such as methane are also emitted during polymer decomposition which impact air quality and causes health problems. The problem of detrimental emission (C.-T. Li, Zhuang, Hsieh, Lee, & Tsao, 2001) also occurs with incineration. Consequently, biodegradable polymers (C.-T. Li et al., 2001), which could be broken down by microorganism, are becoming increasingly popular to help decrease the negative impact of synthetic polymer on the environment.

Apart from these expectations, energy consumption (Gervet, 2007), product efficiency and exhaust emission (Henneuse & Pacary, 2003; Patel & Xanthos, 2001) are the constant concern for most industries. However, polymer manufacturing generally involves long reaction time and high temperature. In addition, decreasing the reaction time and moderating the reaction conditions could generate more profit for chemical companies, and it would decrease the use of non-renewable fuels such as fossil coal, oil and natural gas and reduce the greenhouse gas emission.

1.2. Bio-based Resources for Polymers

Though synthetic polymers currently dominate the global market, human being has a long history using natural polymer in their life. From the end of 20th century, a renaissance of renewable resources for polymer industry is experienced and is expected to fully or partially provide solutions to the disadvantages of fossil resource-based polymers listed above (Figure 1.1). Two strategies have been adopted for transforming biomass into biopolymers: (i) naturally produced or modified biopolymers; (ii) polymerization of biomass derived monomers.

Therefore, the manufacturing of bio-based polymers could be divided into several categories, including:

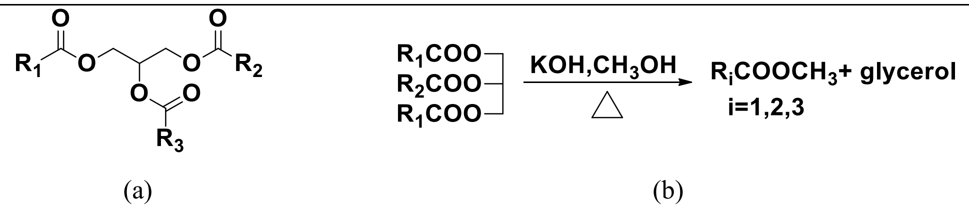
(i) Animal proteins (Cuq, Gontard, & Guilbert, 1998), starch (Vilaseca et al., 2007) and carbohydrate based biomass like cellulose (Saheb & Jog, 1999), chitosan are the most abundant biopolymers available from natural sources. Human used cotton, silk, plant fiber to make clothes from ancient time. A wide range of applications, including textiles, adhesives, food packaging has been found for biopolymers with or without modification.

(ii) Valuable monomers and polymers from bacterial fermentation. With the development of new technologies, various types of monomers and polymers were developed using industry process. For instance, the monomer of poly(lactic acid) (PLA), lactic acid is mainly produced from starch, glucose, cellulose using anaerobic fermentation by *lactobacillus* (John, Nampoothiri, & Pandey, 2007). Other examples, such as 1,3-propanediol, succinic acid and ethanol could be obtained from the fermentation of saccharides. Polymers, such as poly(hydroxyalkanoates) (PHAs) can also be produced directly by this method as well. Till now, more than 100 types of PHAs have been generated by adjusting bacterial types, fermentation substrates and conditions(Steinbuchel & Doi, 2002). Four types of PHAs have been industrialized, namely, poly[(*R*)-3-hydroxybutyrate] (PHB), poly[(*R*)-3-hydroxybutyrate-*co*-(R)-3-hydroxyvalerate](PHBV), poly[(*R*)-3-hydroxybutyrate-*co*-4-hydroxybutyrate] (P3HB4HB), and poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyhexanoate] (PHBHHx) (G.-Q. Chen, 2010). Among the dozens of companies who manufacture PHAs, only a few have a production scale of more than 10,000 tons, including Meredian (USA), Bio-on(Italy), ADM (USA) and Tianjin Green Bioscience (G.-Q. Chen, 2009). It appears that there’s a great potential to industrialize more types of PHAs for practical applications.

(iii) Synthetic polymers from bio-based monomers, such as poly(lactic acid) (PLA), (butylene succinate) (PBS), Nylon1010, Nylon11 and poly(ε-caprolactone) (ε-PCL). The monomers of these materials, ε-caprolactone, lactic acid, succinic acid, C10 diol and diamine can be produced by a fully bio-based process via chemical or biological pathways.

1.3. Plant Oil as Bio-resource for Polymers

In variation from polysaccharides and proteins, plant oil is composed of small and simple molecules that cannot be directly used as a polymer. However, recent work in this area has shown that it is possible to produce useful monomers from vegetable oils (Meier, Metzger, & Schubert, 2007) employing a variety of synthetic routes. By comparison to other bio-renewable resources, large sources and easy access are significant advantages of plant oils. According to statistics ("United States Department of Agriculture Foreign Agricultural Service,"), in Canada, 360,000 tons soybean oil and 3.9 million tons canola oil were produced in 2016. The oil components are simple triglycerides (Figure 1.2a), that have varying fatty acid compositions. The multi-functional groups in these fatty acids provide multiple possibilities and simple routes for the creation of monomers or polymers. Since three chains exists in triglyceride, direct polymerization always leads to the generation of thermosetting polymer (F. Li, Hanson, & Larock, 2001), which is not under control. Therefore, the triglycerides are hydrolyzed in methanol to obtain fatty acid methyl esters (FAMEs), which is also known as biodiesel (Figure 1.2b). This technology has been developed by a number of countries to produce alternative fuels.



R(x:y)	14:0	16:0	18:0	18:1	18:2	18:3	20:0
Sun flower	-	6	4	28	61	-	-
Linseed	-	5	4	22	15	52	-
Rapeseed	0.5	4	1	60	20	9	2
Soybean	-	10	5	21	53	8	0.5

(c)

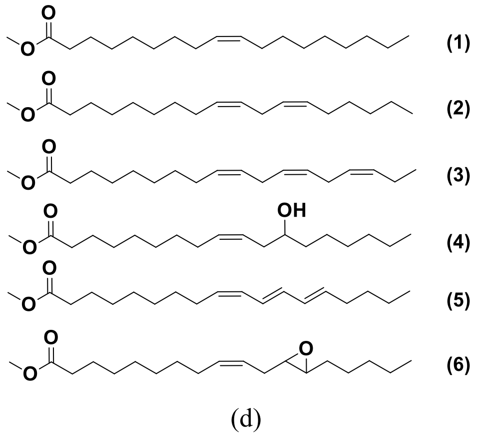


Figure 1.2. (a) plant oil structure (triglyceride). (b) plant oil transesterification. (c) plant oil compositions (data was from the reference (Meier et al., 2007)). (R(x:y) = compositions of different fatty acids, while x means the number of carbon atoms and y represents number of double bonds). (d) Some common fatty acid methyl esters (FAMEs).

Several common types of fatty acid chains arise frequently in various vegetable oils, as depicted by Figure 1.2d. Generally, plant oils contain several types of fatty acids of different percentages, depending upon plant species and environmental conditions. Figure 1.2c shows the components of common industrial oils. It's apparent that the listed oils are comprised of a relatively large proportion of unsaturated fatty acids. Consequently, utilization of carbon-carbon double bonds present in these unsaturated fatty acids is a key for preparation of polymers. Unfortunately, the internal carbon-carbon double bonds are not highly active to be directly polymerized into polyolefins of high performance. Moreover, fatty acid molecules contain only single ester group, which is impossible to proceed for condensation polymerization. The strategies of converting FAMEs to valuable monomers will be introduced later in this Chapter.

1.4. Microwave Techniques

Other than developing renewable biopolymers, this study also focuses on development of rapid and environment friendly reactions. Microwave irradiation provides a feasible solution for this purpose. Technically, microwaves are invisible electromagnetic waves whose wavelengths are among one millimeter to one meter (Sorrentino & Bianchi, 2010). Inspired by their application of quick food heating, microwaves have recently been applied in organic reactions, and are being recognized as clear energy for rapid synthesis.

Richard Gedye, Frank Smith, Kenneth Westway and their colleagues reported a few different types of organic reactions carried out in microwave oven (Gedye et al., 1986). The reactions included hydrolysis of benzamide, permanganate oxidation of toluene, esterification of benzoic acid and S_N2 reaction between sodium 4-cyanophenoxide and benzyl chloride. In all four cases, high yields, comparable to conventional heating, were achieved within a few minutes. The reaction rates were increased to 6-240 folds. The results suggested that microwave play a positive role for several reaction types. Almost at the same time, Giguere's group studied the Diels-Alder and Claisen reaction under microwave irradiation (Giguere, Bray, Duncan, & Majetich, 1986). Likewise, the time was shortened to a few seconds or minutes. The effect of solvent system was also studied, which indicated that the high polar solvents were heated rapidly compared to less polar solvents which needs longer time to reach desired temperature.

1.4.1. Thermal Effect of Microwave Induced Reaction

Over the past decades, microwave induced reactions have become a hotspot in the field of organic chemistry. Microwave has been widely applied for reactions, including substitution, addition, reduction and alkylation, etc (Lidström, Tierney, Wathey, & Westman, 2001). To understand the role that microwaves play on reactants, people are trying to illustrate it from different perspectives.

For a traditional organic reaction, collision theory is classic to explain the reaction kinetics. It is hypothesized that the reaction rate is directly related to the molecular motion rate. Macroscopically, temperature is the index which directly reflects average molecular motion condition. During reactions, high temperature is applied in order to increase the effective molecular collision. By comparison to classic heating, where energy is only transferred on contacted surfaces, microwave directly affects each accessible polar molecule. For polar molecules, the centers of positive and negative charges are not superimposed. In electric field, the dipoles try to align themselves by rotation, oscillation and movement. By swift changing (0.3-300 GHz) of electric field via microwave, the dipoles oscillate and conflict at super high frequencies and their kinetic energy soars in short time. Hence, the temperature and the possibility of effective molecular collision is increased remarkably, which is recognized as thermal effect of microwave (Hayes, 2002). It is now accepted as a main reason for accelerated reactions.

1.4.2. Non-Thermal Effect of Microwave Induced Reaction

Apart from rapid heating, other phenomena are also observed from microwave-induced reactions. Such as, the structure of product, the selectivity, byproduct and yield of some reactions are totally different under microwave irradiation from conventional heating at same temperature. Huang et al. discovered that during the oxidation of potassium iodide by hydrogen peroxide, irradiated by microwave, the activation energy and pre-exponential factor of reaction were changed (Huang, Liu, Tang, Zhao, & Wang, 1996). Luo has studied the fluorination of *p*-nitrochlorobenzene by heating and microwave (LUO, CAI, & Lü, 2003). Under microwave radiations, the reaction was not following the first-order kinetics as it was using conventional heating.

The non-thermal effects of microwave are illustrated from the following aspects: (1) The high frequencies of microwave are possibly close to inherent frequencies of molecules, which causes the breakup of chemical bonds. It may lead to acceleration and undesired side reactions. (2) The polarity of reaction system would be increased due to a strong interaction between the molecules and microwave, and the energy level of transition state is decreased. Therefore, activation energy is reduced, which facilitates the occurrence of the reaction.

1.5. Aliphatic Polyesters from Plant Oil Resources

Aliphatic polyesters increasingly attracting the attention from institutions and industry due to their potential of providing environmental benefits which include renewable sources, lower toxicity, good biodegradability and biocompatibility (U Edlund et al., 2003). These polyesters have so far displayed advantages in ecological and biomedical field, being used as tissue engineering scaffold, commodity materials, drug delivery systems (Albertsson & Varma, 2002; Ulrica Edlund & Albertsson, 2002). Aliphatic polyesters from renewable resources, which are also biodegraded after disposal, are ideal products to not only satisfy the human demands but also meet environmental requirements (Scholz & Gross). The development of aliphatic polyesters involves diverse polymerization approaches from biomass into polymers (Bakare, Pavithran, Okieimen, & Pillai, 2006; Zia, Noreen, Zuber, Tabasum, & Mujahid, 2016). Unlike polysaccharides and cellulose, natural polyesters rarely exist. PHAs are the only polyesters that we could obtained from fermentation. By contrast, chemical synthesis route is more common to acquire polyesters for its controllability, stability of process and diversity of applicable monomers. Carbohydrate and lipids (Thakur & Thakur, 2016) are two categories of organic compounds from bio-resource. However, modifying monomeric sugars to desiring monomers, generally diacids, diols, diesters and hydroxyl acids, takes multi-steps and increases complexity.

1.5.1. Polyester Monomers from Plant Oil Resources

On the other hand, lipids, especially plant oils are better resource for desired monomers. As mentioned above, the majority of fatty acids in plant oil are unsaturated, which afford sites for functional group modification. Moreover, few functional groups other than carbon-carbon double bonds emerge in fatty acid chains, which helps to avoids side reactions and byproducts as much as possible, during the modification of plant oil. Herein, several modification methods from fatty acids or their esters to polyester monomers have been developed.

1.5.1.1. Ozonolysis of Oleic Acid to Dicarboxylic Acids.

The amount of dicarboxylic acids from oleochemistry reached 100,000 tons annually from the beginning of 21st century (Hill, 2000), and is continuously increasing afterwards. Among them, the manufacturing of pelargonic and azeleic acid via oleic acid ozonolyzsis is significantly important in oleochemistry.

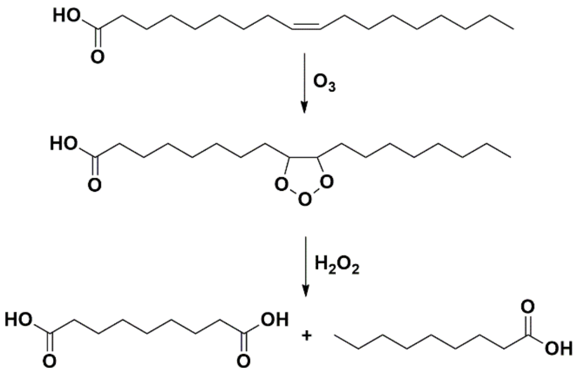
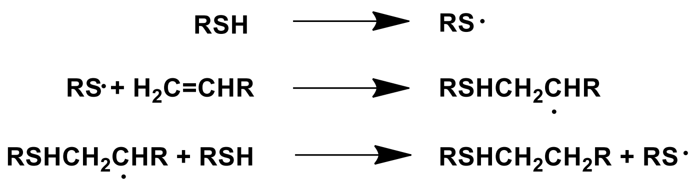


Figure 1.3. Ozonolysis of oleic acid (Meier et al., 2007).

The oxidation reaction involves the rupturing of double bond and carboxylic acids are generated for each segment. Via 1,3-dipolar cycloaddition, an intermediate, in which the ozone molecule connects to both sides of double bonds, comes into being. By oxidative workup, such as addition of hydrogen peroxide, the 5-membered ring was cleaved, carboxylic acids are generated, as shown in Figure 1.3 (Meier et al., 2007). The cleavage of double bond into dicarboxylic acid can also be achieved with high yield, in the presence of acidic potassium permanganate (Wiberg & Saegebarth, 1957) and hydrogen peroxide/catalyst system (Santacesaria, Sorrentino, Rainone, Di Serio, & Speranza, 2000). Due to the long alkyl chain segments in diacids, from the resulted polyesters, certain properties, such as hydrophobicity, flexibility and elasticity, can be found.

1.5.1.2. Thiol-ene Click Chemistry

The thiol-ene click reaction (Griesbaum, 1970) is recognized as a feasible and effective pathway to attach needed functional groups onto the fatty acid chains of plant oil. The reaction is stereoselective in nature and provides high yield with fast reaction rate. Thiol-ene reaction could be initialized by UV radiation or radical initiator. Once initialized, the thiol radical adds to a double bond and the free radical is transferred to carbon, sequentially shifted to another thiol by capturing a hydrogen atom. The procedure will continuously repeat until the free radical is terminated. It is widely used for simple modification of organic compounds.



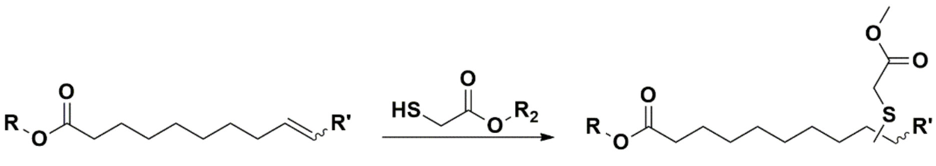
$$\mathrm{RSH} \longrightarrow \mathrm{RS}\cdot$$

$$\mathrm{RS}\cdot + \mathrm{H_2C{=}CHR} \longrightarrow \mathrm{RSHCH_2\underset{\cdot}{C}HR}$$

$$\mathrm{RSHCH_2\underset{\cdot}{C}HR} + \mathrm{RSH} \longrightarrow \mathrm{RSHCH_2CH_2R} + \mathrm{RS}\cdot$$

Figure 1.4. The mechanism of thiol-ene free radical reaction (Oĝuz Türünç & Meier, 2010).

The thiol-ene modification of fatty acid methyl esters has been widely reported by research groups over the world. Early in 1950s, Koenig and his coworkers already have thorough investigation on this topic (Koenig & Swern, 1957a). Several common FAMEs, such as elaidate, oleate, ricinoleate and undecenoate, in the presence of ester or acid form, were reacted with mercaptoacetate or its acid, to yield various dicarboxylic acids or diesters (Oğuz Türünç & Meier, 2013).



R: H or alkyl
R_2: H or alkyl
R': H (10-undecenoic acid or ester)
cis-$(CH_2)_8CH_3$ (oleic acid or ester)
trans-$(CH_2)_8CH_3$ (elaidic acid or ester)
$(CH_2)_2CH(OH)(CH_2)_5CH_3$ (ricinoleic acid or ester)

Figure 1.5. Modification of fatty acids (or esters) with mercaptoacetic acid (or acetate).

Dicarboxylic acids and diesters can also be obtained by connecting two acid/ester molecules via thiol-ene click reaction. Koenig tried the addition of thioacetic acid to undecenoate later in the same year (Koenig & Swern, 1957b). The product was further reduced to thiol and diester was obtained via oxidation by iodine to generate disulfide bonds (Koenig, SASIN, & Swern, 1958).

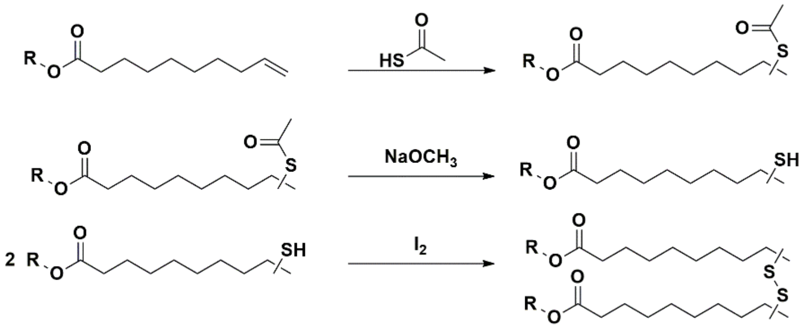


Figure 1.6. Modification of fatty acids with thioacetate (Oğuz Türünç & Meier, 2013).

However, the multiple steps (Figure 1.6) increased the complexity of reactions and consequently, reduced the yield. A more direct and effective approach is to connect two fatty acid (or their ester) molecules through dithiol. Meier and his coworker have investigated the thiol-ene reaction of tetramethylenedithiol with undecenoate and undecen-1-ol (Oĝuz Türünç & Meier, 2010). Due to the high reactivity of external double bonds, linear products were produced, which afford good crystallinity for the resulted polyester.

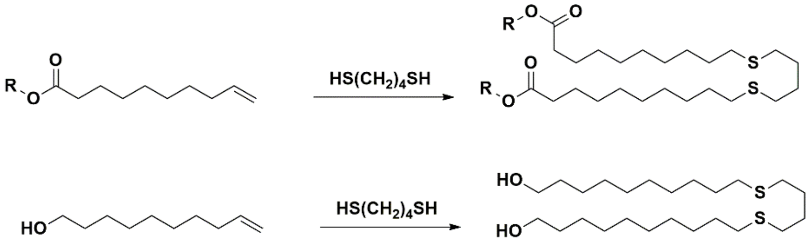


Figure 1.7. Diester & diol through the modification of C10 ester & alcohol with dithiol (Oĝuz Türünç & Meier, 2010).

Not only polyester, the thiol-ene click reaction is also convenient for the preparation of monomers for polyamides, polyurethanes via similar strategies. The natural abundance of double bonds from plant oil, affords much possibility to be derived to biopolymers.

1.5.1.3. Olefin Metathesis Approach

Like thiol-ene addition reaction, metathesis is another type of reaction which involves specifically double bonds. Olefin metathesis was initially observed in the middle of 20th century (Truett, Johnson, Robinson, & Montague, 1960) and have been developed as a powerful tool for the cleavage of carbon-carbon double bonds and its regeneration allows the exchange of substituents in between two different olefins, as depicted in Figure 1.8. The approach of olefin metathesis provides sustainable routes for the preparation of polymer and value-added chemicals from renewable resources. In addition, the formation of toxic byproducts and waste can be avoided if reasonable pathways are designed.

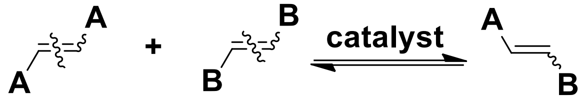


Figure 1.8. An example of olefin self-metathesis.

The metathesis of vegetable oil didn't attract much attention at first due to the catalysts' poor tolerance to air and moisture and their low activities. Recently, the development and commercialization of several catalysts with good performance has renewed human's interests in plant oil metathesis (Burdett et al., 2004). Grubbs et al. (Grubbs, Nguyen, Johnson, Hillmyer, & Fu, 1996) proved effective self-metathesis of methyl oleate and its cross-metathesis with ethylene by using a novel catalyst. High turnover number of 960 was achieved for its self-metathesis. Hong et al. (Mol, 1994) evaluated several ruthenium based metathesis catalysts, and achieved TONs > 20,000 with specific catalyst.

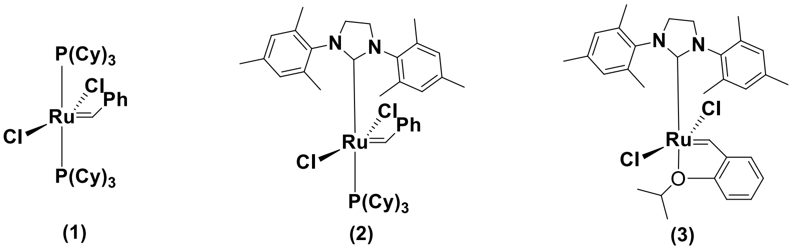


Figure 1.9. Structures of several commonly used olefin metathesis catalysts: (1) Grubbs catalyst 1st generation (**G1**); (2) Grubbs catalyst 2nd generation (**G2**); (3) Hoveyda Grubbs catalyst 2nd generation (**HG2**).

The approaches to yield polyester monomers from FAMEs are various, including cross-metathesis and self-metathesis. Cross-metathesis with unsaturated esters, such as methyl acrylate and methyl crotonate (Vignon et al., 2015), is a possible route to generate diester. Rybak et al. reported the cross-metathesis of methyl oleate with methyl acrylate. With 5mol% **HG2** (Figure 1.9-3) loading, 99% conversion and 99% yield of cross-metathesis products was observed (Figure 1.10). Cross-metathesis of methyl 10-undecenoate with methyl acrylate was also performed, and same conversion and yiel of cross-metathesis products were achieved using 0.1mol% **HG2** (Rybak & Meier, 2007).

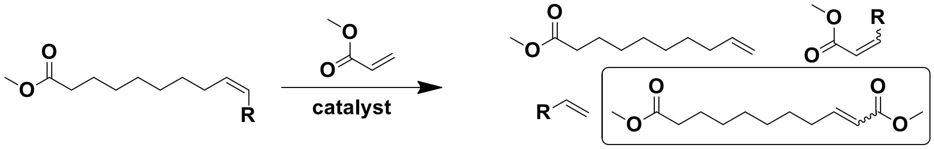


Figure 1.10. Cross metathesis of FAME/methyl acrylate (Rybak & Meier, 2007).

Moreover, self-metathesis is a simple approach to obtain diester without additional reactants. Meier and his colleagues have reported the self-metathesis of FAME mixtures from different vegetable oil sources (Mutlu, Hofsäß, Montenegro, & Meier, 2013). **G1**, **G2**, **HG2** and indenyliene catalysts were investigated at low loading. For methyl linolenate (technical grade), 92.5% conversion and 86.8% selectivity towards diesters were obtained by the catalysis of **G2** catalyst under vacuum. The small molecular weight olefins were extracted and therefore, equilibrium state of reaction shifted to increase the conversion.

Though the diester yield is not high as it was in case of thiol-ene reaction but in the meantime it provided other valuable components, such as olefins with different chain lengths. These compounds could be further modified by pyrolysis to obtain raw materials used for the preparation of other chemical products. (Sunggyu Lee & Shah, 2012). To get benefit of these advantages, self-metathesis method was selected in this work for the preparation of diester.

1.5.2. Olefin Metathesis Induced by Microwave Irradiation

The olefin metathesis is intensively studied by both conventional and unconventional means. Microwave synthesis has great performance as an unconventional method. Murray and his group members have studied the cross-metathesis between ethyl acrylate and β-ketophosphonate in dichloromethane under classic heating and microwave conditions (Bargiggia & Murray, 2005). The reaction was carried out for 15 min using microwave radiations at 100 ºC. Up to 81% yield of desired ketophosphonate was obtained, while for conventional heating, 6 hours of refluxing was required to achieve similar yield.

Solvent-free ring-closing metathesis was studied by Thanh and his coworkers. A reaction was performed on a series of compounds, which have terminal double bonds on both ends. Corresponding cyclenes were generated within 3 min with high yields (> 70%). The reaction was also performed in the absence of solvent, though its yield was bit lower, a greener and convenient method was introduced (Thanh & Loupy, 2003).

However, few studies on microwave induced metathesis of plant oil derivatives have been published. In this study, solvent free microwave assisted self-metathesis will be investigated to meet the requirement of green chemistry. Different vegetable oil sources, such as canola oil, soybean oil were introduced as starting materials, for the preparation of diester.

1.5.3. Polycondensation Reaction under Microwave Condition

Polycondensation is one of the most common method to produce polyamide, polyimde and polyester in industry. It involves step-growth condensation (Flory, 1953) between reactive bifunctional groups until desired molecular weight is achieved. In this chapter, the polycondensation of diester and diol, as shown in the following scheme is one of our major objective of study.

$$nCH_3COO{-}R{-}COOCH_3 + nHO{-}R'{-}OH \rightarrow H{-}[OOC{-}R{-}COO{-}R']_n{-}OH + (2n-1)CH_3OH$$

Polycondensation is usually conducted using vacuum and at high temperature to continuous remove byproducts of small molecules. Long reaction time is also necessary to achieve high molecular weight. These disadvantages make traditional polycondensation approach inefficient and energy intensive. In recent years, microwave-assisted polycondensation was intensively studied as a fast, facile and green method (Komorowska-Durka, Dimitrakis, Bogdał, Stankiewicz, & Stefanidis, 2015).

The microwave-accelerated polycondensation of lactic acid was a focus of interest in this field. Nagahata tried to polymerize lactic acid using different catalysts under microwave irradiation at a reduced pressure of 30 mmHg at 200 ºC for 30 min. Poly(lactic acid) (PLA) with a weight average molecular weight (Mw) of 1.6×10^4 g/mol was obtained in the presence of $SnCl_2$/*p*-TsOH (Nagahata, Sano, Suzuki, & Takeuchi, 2007). It suggested that obtained PLA has great strength to be made into pellet and films. An attempt was also tried to make aliphatic polyester under microwave condition. Poly(butylene succinate) (PBS) was synthesized using 0.5 mol% $SnCl_2$ as a catalyst at 260 ºC using a pressure of 4000 Pa. Polyester with a Mw of 2.90×10^4 g/mol was obtained within 10 min (Velmathi, Nagahata, & Takeuchi, 2007).

Although great progress has been made till now, there are still some limitation for obtaining polymer with higher molecular weight and better performance. Factors such as reaction time (Keki, Bodnar, Borda, Deák, & Zsuga, 2001), pressure (Nagahata et al., 2007) and temperature

(Velmathi et al., 2007) are difficult to handle for microwave induced reactions. Long reaction time and high temperature under microwave radiation may result in degradation of polymer and formation of oligomers, while short reaction time and low temperature cannot provide polymers with required molecular weight. Pressure is also a key role in the process. For step growth polymerization by conventional heating, vacuum is fully controlled. Contrast to it, in microwave polycondensations, if high vacuum is applied, strong plasma will occur which possibly burns reactants and destroys reaction vessel (Nagahata et al., 2007). However, using low vacuum, byproducts cannot be entirely removed and high molecular weight cannot be achieved (Velmathi, Nagahata, Sugiyama, & Takeuchi, 2005).

1.6. Polyester & Polycarbonate Polyol from Plant Oil Resources

1.6.1. α-olefins from Plant Oil Resources

Other than self-metathesis, olefin metathesis of unsaturated FAMEs with ethylene, which is also called ethenolysis, has also been receiving intensive attentions in recent years. It provides various α-olefins, which can be used for the preparation of surfactants, polyolefins and epoxides. Consider canola oil methyl ester (COME) as an example, its ethenolysis process produces more than five kinds of α-olefins with different chain length, as shown by Figure 1.11. Apart from academia, ethenolysis also draws the attention of commercial giant like Du Pont. Maughon et al. (Burdett et al., 2004) have done some fundamental studies to figure out specific factors related to catalyst performance. Some suggestions are provided to achieve commercial process.

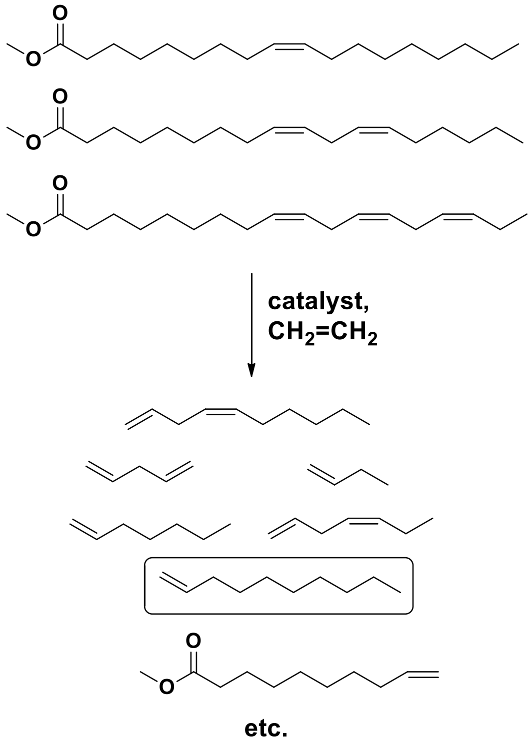


Figure 1.11. Ethenolysis of canola oil FAMEs.

1.6.2. Polyester & Polycarbonate from Epoxide with CO_2/anhydride Copolymerization

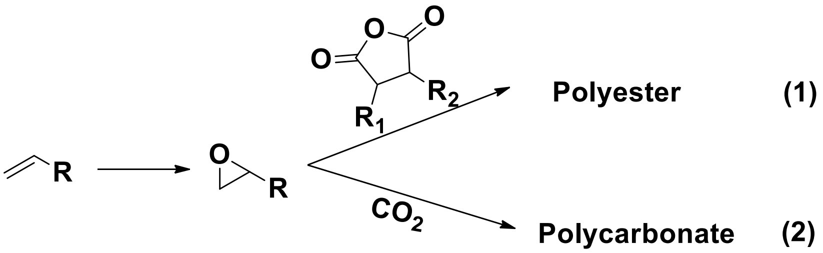
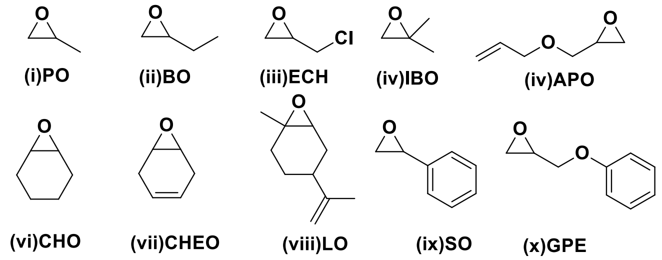
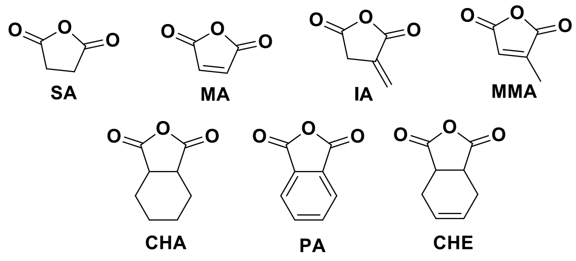


Figure 1.12. Routes from monomers to polyester (1) & polycarbonate (2).

In Section 1.5, we have introduced the preparation of polyester from plant oil self-metathesis products. However, the traditional condensation polymerization of diester/diol has its own limitations, such as high energy consumption, long reaction time and extra cost for vacuum equipment installation and maintenance. Ring opening polymerization (ROP) to prepare polyester is an alternative route to avoid these disadvantages. Large amount of research work related to ROP has been reported, especially the ROP of cyclic esters. A few examples have already been industrialized. Poly(lactic acid) (PLA) is among those examples, which is produced by ROP of lactide catalyzed by tin octoate (Drumright, Gruber, & Henton, 2000). Like regular polyester, its products, such as wires, packaging and furniture materials, have wide applications in our daily life. In addition, due to its biodegradability and biocompatibility, it's widely used in medical fields as drug encapsulation, implants, osteone, surgical sutures (Avérous, 2008). PLA sutures or osteons will be gradually degraded in human bodies. Consequently, secondary operation is no more necessary and its damage are avoided. In addition to ROP of cyclic esters, polyesters can also be prepared from ring opening copolymerization of epoxy and cyclic anhydride to prepare polyester, which gains attentions recently. Initially, the copolymerization of epoxy and anhydride suffered from low activity, yield and molecular weight (W_ Kuran & Niestochowski, 1980; Takenouchi, Takasu, Inai, & Hirabayashi, 2002). Ground-breaking improvement has been made at the end of 20th century with the development of novel catalyst systems. Compared to cyclic ester monomer, wide selection of epoxides and anhydrides monomers helps to obtain polymers with adjustable glass transition temperature (Tg) and mechanical strength and other properties. For instance, Darensbourg et al. copolymerized cyclohexene oxide (CHO) with maleic anhydride(MA) and cyclohexene anhydride (CHA) respectively (D. J. Darensbourg, Poland, & Escobedo, 2012). Eventually, the Tg of corresponding polyester increased from 53 ºC (MA) to 95 ºC (CHA).



(a) Epoxides



(b)cyclic anhydrides

Figure 1.13. Common epoxides and anhydrides used for copolymerization.

If anhydride is replaced by carbon dioxide, corresponding polycarbonate can be produced from copolymerization of epoxy and CO_2. Similar to polyesters, polycarbonates are mainly manufactured from the polycondensation (Serini, 2000) of diols and phosgene. In addition to the disadvantages of traditional polyester manufacturing, phosgene is a highly toxic substance (Schneider & Diller, 2000), which exposes potential risks to the operators during its preparation, transportation and storage. Moreover, hydrogen chloride is generated as byproduct from polycondensation of diols and phosgene, which is corrosive to the reactor and environmentally unfriendly. Hence, new method for polycarbonate preparation is in need of industry.

Carbon dioxide, a major contributor to the so-called greenhouse effect, keeps increasing in the atmosphere (Schmalensee, Stoker, & Judson, 1998) since the world's first industrial revolution. The global warming is accelerating, sea level is rising and abnormal climate occurs frequently in recent years (Barth & Titus, 1984). These phenomena are always associated with the CO_2 release. It not only changes the natural environment, but also affects crop yield (Mendelsohn, Nordhaus, & Shaw, 1994), animal behavior (Koneswaran & Nierenberg, 2008) and human health (Patz, Campbell-Lendrum, Holloway, & Foley, 2005).

Carbon dioxide capture (Gibbins & Chalmers, 2008) and utilization (Langanke et al., 2014) is a hot topic for environmentalists and chemists. While the environmentalists are focusing on CO_2 storage underground or deep in the sea, chemists are trying to utilize it as chemical feedstock. Although the low reactivity of CO_2 hinders its application in manufacturing, the copolymerization of CO_2 with epoxide (Coates & Moore, 2004) a promising research field of CO_2 utilization. In contrast to phosgene, CO_2 is non-toxic, and it can be easy obtained, safely transported and stored.

1.6.3. Early History of Epoxide with CO_2/anhydride ROP

Carbon dioxide was never a direct feedstock for polymer synthesis until Inoue discovered its activity to copolymerize with epoxides alternatively. In the initial study (Inoue, Koinuma, & Tsuruta, 1969), simple organometallic compounds, such as $ZnEt_2$, $AlEt_3$ were used as catalysts, and equal molar of alcohol or water was added as co-catalyst. The copolymerization of propylene oxide (PO) with CO_2 was then tried under atmospheric pressure at room temperature catalyzed by $ZnEt_2/H_2O$. After 5.5 hours, a methanol insoluble part was found with a strong absorbance at $1745cm^{-1}$. Since the poly(propylene oxide) was insoluble in methanol and the specific signal of carbonyl group occurred, it was speculated that carbon dioxide took part in in the copolymerization and this viewpoint was confirmed further by proton NMR. According to the calculation, the ratio of carbonate/ether groups was 0.88/0.12. Though the ratio of carbonate linkage was high, the polymer yield was quite low (0.16 g polymer from 23.2 g propylene oxide).

After the discovery, a series of catalyst systems of $ZnEt_2$ with simple organic compounds were investigated. Instead of atmosphere pressure, >20 atm of carbon dioxide was sealed in the vessel to expect high alternative polycarbonate with high yield. The results from Table 1.1 were worked out mainly in 1970s. The activities of these systems were so low that it took several days for the completion of polymerization.

Catalyst	Time (h)	T (°C)	Pressure (atm)	TON	TOF (h^{-1})
$ZnEt_2/H_2O$	48	80	20-50	5.9	0.12
$ZnEt_2$/resorcinol	48	35	30	8.1	0.17
$ZnEt_2$/isophthalic acid	44	35	40	19.1	0.43
$ZnEt_2$/hydroxybenzoic acid	44	35	40	19.6	0.45
$ZnEt_2$/phenethylamine	68	40	40	3.9	0.06
$ZnEt_2$/pyrogallol	44	35	60	12.0	0.27
$ZnEt_2$/bromopyrogallol	45	35	60	13.8	0.31

Table 1.1. Selected cocatalyst with $ZnEt_2$ to copolymerize CO_2 with PO (The data were retrieved from the review (Coates & Moore, 2004)).

Similarly, the research regarding alternating copolymerization of epoxide/anhydride was also started by Inoue using dialkylzinc. The first selected monomers were propylene oxide/phthalic anhydride. Since the polycarbonate and polyester synthesis has numerous similarities during the early development, the history of anhydride/epoxide ROP was skipped here. In addition, other analogue features, such as mechanisms and catalyst systems are discovered for both types of reaction. Therefore, the mechanism and effective catalyst systems of these two reactions will be introduced together in the following parts.

1.6.4. The Mechanism of Epoxide and Anhydride/CO_2 Copolymerization

To fully understand the function of epoxy/CO_2 copolymerization, Inoue has discussed its polymerization mechanism early in 1969, which is widely accepted till now (Inoue, Koinuma, et al., 1969). In Figure 1.14, the catalyst is written as LnMX for simplicity, in which M represents metal center, L is the ancillary ligand (n stands for the ligand number) and X is generally a simple functional group, such as halogen, alkoxide or carboxylate. Herein, M-X bond is active as the insertion site for polymer initiating or propagation.

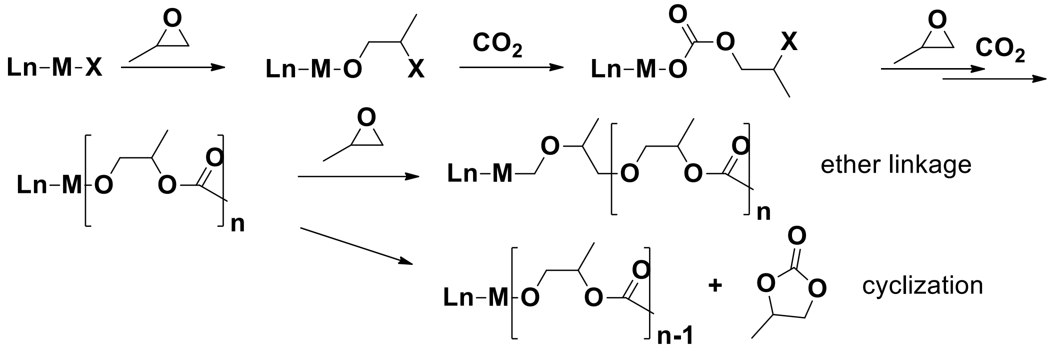


Figure 1.14. The catalysis mechanism of propylene oxide/CO_2 copolymerization.

The initiation starts from the insertion of a first epoxide molecule between M and X, and an alkoxide intermediate comes into formation. Further, CO_2 and epoxide alternatively enters into the active site, generates new carbonate linkage and prolongs polymer chain as propagation occurs. The C-O bonds breakup during the insertion of both CO_2 and epoxide. The oxygen atom forms a new linkage with metal center and the carbon atom connects to polycarbonate chain.

It's worth mentioning that copolymerization is not always completely alternative. Formation of ether linkage is possible by continuous insertion of epoxide. The percentage of carbonate linkage is decided by multiple factors, like reaction temperature, pressure and especially catalyst system. In addition to this, cyclic carbonate (D. J. Darensbourg & Holtcamp, 1996) will also be generated as a byproduct from cyclization reaction. Always an equilibrium exists between cyclic carbonate and polycarbonate, whose percentages are decided by catalyst, pressure and solvent systems. The cyclic carbonate forms by the backbiting of the metal-oxygen linkage to a neighboring carbonate group (Witold Kuran & Listoś, 1994).

Another phenomenon is always observed with a few catalysts that the molecular weight distribution of polycarbonate was narrower than that from polycondensation. Chain transfer reaction (X. K. Sun et al., 2012) is assumed to play an important role for narrow polydispersity. The exchange of living site between a terminated polyester chain and a living chain will help to get polymer chain length controlled. The termination step could simply be carried out by adding additional terminator (alcohol, water) or changing reaction conditions (monomer removal, temperature decrement).

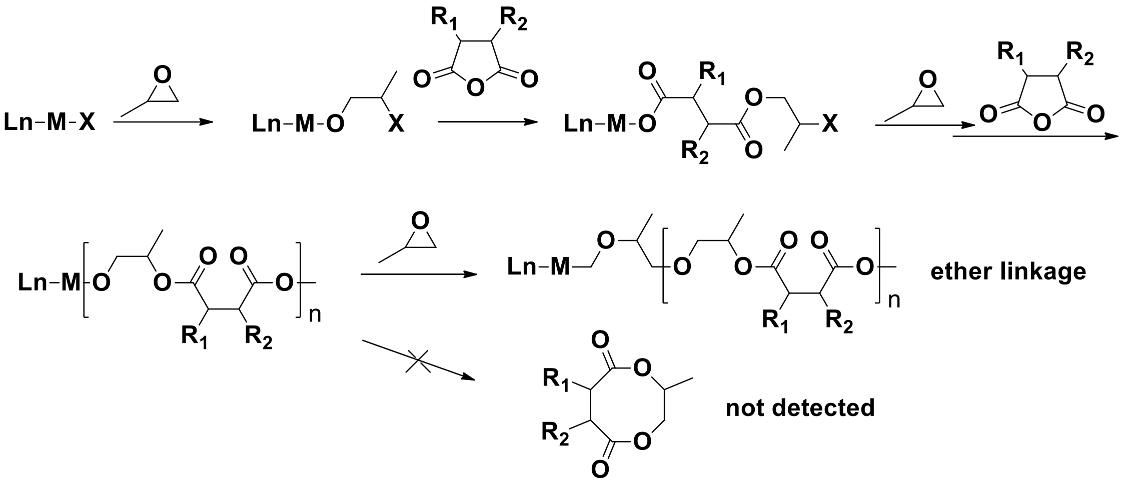


Figure 1.15. The catalysis mechanism of epoxy/cyclic anhydride copolymerization.

The initiation and propagation steps of epoxide/anhydride copolymerization are described in Figure 1.15. During the copolymerization of epoxide/anhydride, the anhydrides do not take part in the initiation step. This point has been demonstrated by Inoue in 1969 (Inoue, Kitamura, & Tsuruta, 1969). Anhydride could only insert into active site after epoxide insertion. The growth of polyester was also accomplished by the alternative insertion of anhydride and epoxide. Ether linkage will come into formation when epoxy molecules insert into polymer chain continuously. It's noticeable that unlike polycarbonate, cyclic ester is not discovered from the products. The cyclization phenomenon only occurs in case of copolymerization of epoxide/CO_2. Proper explanation was not given in publications. Probable high energy barrier from epoxy, anhydride to cyclic ester may be a reasonable interpretation.

1.6.5. Novel Catalyst Systems for Epoxide and CO_2/anhydrides ROP

Due to the low activity of early catalyst, new catalysts are designed based on proposed mechanism to achieve high reactivity, polymer yield, molecular weight and low ether linkage percentage. Herein, several main catalysts would be introduced for a comprehensive understanding of research progress nowadays.

1.6.5.1. Zinc Dicarboxylate

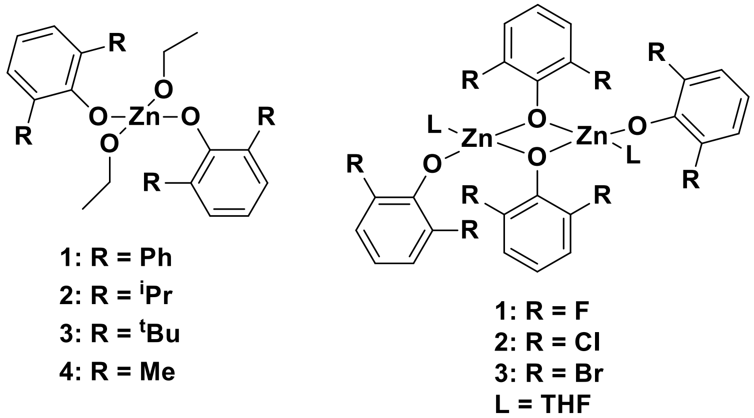
Zinc dicarboxylate is an early developed heterogeneous catalyst for polycarbonate preparation. In early stage, the zinc organometallic compounds were intensively studied, and it was found that the mixture of $Zn(OH)_2$ and glutaric acid (Soga, Imai, & Hattori, 1981) was able to catalyze the copolymerization and yield polymers with higher molecular weight. Though the exact active site still remains unknown nowadays, its advantages of easy preparation, providing high molecular weighted polymer, make it to be a competitive catalyst (Motika, Pickering, Rokicki, & Stein, 1991).

Zinc glutarate catalyst could be obtained from different zinc source with glutaric acid. Interestingly, the source of zinc will affect the polymer yield and molecular weight greatly. Shin et al. prepared zinc glutarates from ZnO, $Zn(OH)_2$, $Zn(NO_3)_2 \cdot 6H_2O$ and $ZnEt_2$, respectively (M Ree, Bae, Jung, & Shin, 1999). Bulk polymerization of PO with CO_2 under the catalysis of those four catalysts indicates that catalyst made from ZnO possesses the highest yield (64 g polymer/g catalyst) and molecular weight (Mw = 343 kDa).

However, the yield and catalytic activities are still not as high as other studied catalysts nowadays. Investigation on its structure (Zheng, Lin, & Zhang, 2000) revealed that its activity was limited to surface area. Its high crystallization structure hampers the monomer diffusion inside the crystal (Moonhor Ree et al., 2006). Several methods were focused on to increase its surface area (Klaus, Lehenmeier, Anderson, & Rieger, 2011; Meng, Du, Tiong, Zhu, & Hay, 2002): (1) ball-milling and ultrasonic treatment to decrease crystal size; (2) the introduction of substrates with high surface area. (3) to add growth controllers to keep small crystal size. These methods have been verified by a few groups. Though higher activities were occasionally observed (S. Wang, Du, Zhao, Meng, & Tjong, 2002), they are still not comparable to novel homogeneous catalysts.

1.6.5.2. Zinc Phenoxide System

Zinc phenoxide was initially developed by Darensbourg in 1995 as a homogeneous catalyst for copolymerization of epoxy and CO_2 (D. J. Darensbourg & Holtcamp, 1995). Because the substitution of zinc center by other metals will lead to the lower activity (D. Darensbourg, Niezgoda, Draper, & Reibenspies, 1998), zinc centered phenoxide catalysts were the most commonly used. The first developed zinc phenoxide was depicted by Figure 1.16a-1. It was demonstrated that copolymerization of CHO/CO_2 and terpolymerization of CHO/PO/CO_2 were feasible at 80 °C at pressure of 51 atm. The carbonate content could reach above 90% and high molar mass (Mn = 38000 g/mol) was achieved.



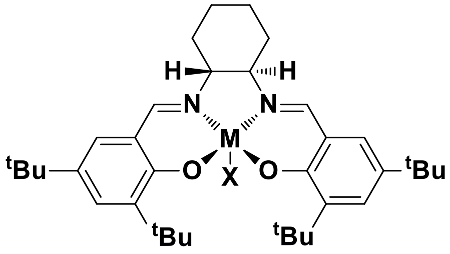
(a) (b)

Figure 1.16. Structure of phenoxide systems.

However, it had low activity was low (TOF=2.5h^{-1}) that after long reaction time (69h), conversion of only 65% was achieved. In addition to this, the copolymerization of PO/CO_2 cannot be activated by catalyst 1 (Figure 1.16a). It resulted in the formation of propylene carbonate instead (Inoue, Koinuma, et al., 1969). Further studies discovered that ligand structure plays the key role for higher activity and efficiency. The size of R groups (Figure 1.16a) hugely affects the yield(D. J. Darensbourg et al., 1999). The corresponding yield increases when the steric hindrance decreases (efficiency: 1441 g polymer/g catalyst (Figure 1.16a-4), 677 g polymer/g catalyst (Figure 1.16a-3), 602 g polymer/g catalyst (Figure 1.16a-1), 477 g polymer/g catalyst (Figure 1.16a-2)) (Klaus et al., 2011). Zinc phenoxide dimers (Figure 1.16b) also have activities for copolymerization. In dimeric phenoxide systems, halides were introduced in ortho-position, the activity of phenoxide system increased in the order of F > Cl > Br (D. J. Darensbourg, Wildeson, Yarbrough, & Reibenspies, 2000). The sequence was consistent with electronegativity of the halogens. A feasible explanation was that halides contributed to decrease the electron density of zinc center. Therefore, the increased electrophilicity lowered the activation energy to bind with epoxide. Nevertheless, the catalyst activity and efficiency are still not comparable to other homogeneous catalyst systems.

1.6.5.3. Salen System

In 2000, as the very first work, Jacobsen's group has reported a patent on salen catalyst used for the copolymerization of 1,2-epoxyhexane and CO_2 (Jacobsen, Tokunaga, & Larrow, 2000). In the same year, Darensbourg's group also started their work to employ salen catalyst for the coupling of CO_2 and epoxides. Complex 4 (Figure 1.17) was used as the catalyst to copolymerize cyclohexene oxide and CO_2 in the presence of N-methylimidazole as co-catalyst. In addition to copolymerization, cyclization of epoxy and CO_2 can be performed with salen system. Nguyen and Paddock reported another product, cyclic carbonate synthesis using a series of salen catalysts with DMAP as the cocatalyst (Paddock & Nguyen, 2001). At 75-100 °C for a few hours, high yields (>90%) were achieved for various types of epoxides, such as propylene oxide, epichlorohydrin and styrene oxide. The discovery indicates that both cyclic carbonate and polycarbonate could be obtained (D. J. Darensbourg, Yarbrough, Ortiz, & Fang, 2003) and only under proper conditions, polycarbonate would be the dominated species.



1. M = Cr, X = Cl
2. M = Co, X = OAc
3. M = Co, X = $OBzF_5$
4. M = Co, X = Cl
5. M = Co, X = Br

Figure 1.17. The presentative structure of salen catalysts.

In 2003, Coates and his coworkers reported the (salen)MX, where M=Co and X=OAc (Figure 1.17-2). Poly(propylene carbonate) with 99% carbonate linkage was produced with TOF around $70h^{-1}$ (Qin, Thomas, Lee, & Coates, 2003). Further studies revealed that the type of X and cocatalyst will drastically affect the selectivity of polycarboante/cyclic carbonate (Cohen, Chu, & Coates, 2005). In their investigation, complex 3 or 4 (Figure 1.17) with equivalent bis(triphenylphosphine)iminium chloride, provides >99% selectivity towards poly(propylene carbonate) in 2 h at 22 °C. If reaction time is prolonged, the percentage of poly(propylene carbonate) starts to decrease. A high TOF (1100 h^{-1}) and molecular weight (Mn = 49 kDa) were achieved in their experiments. Darensbourg discovered that the increasing temperature leads to higher portion of propylene carbonate (D. J. Darensbourg & Yarbrough, 2002). Overall, though multiple steps and complex synthesis is involved for the preparation of salen catalysts giving well molecular weight, selectivity, carbonate linkage and activity could be achieved.

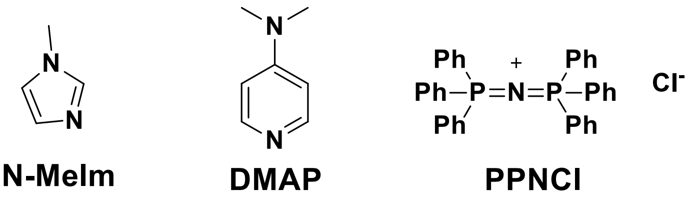


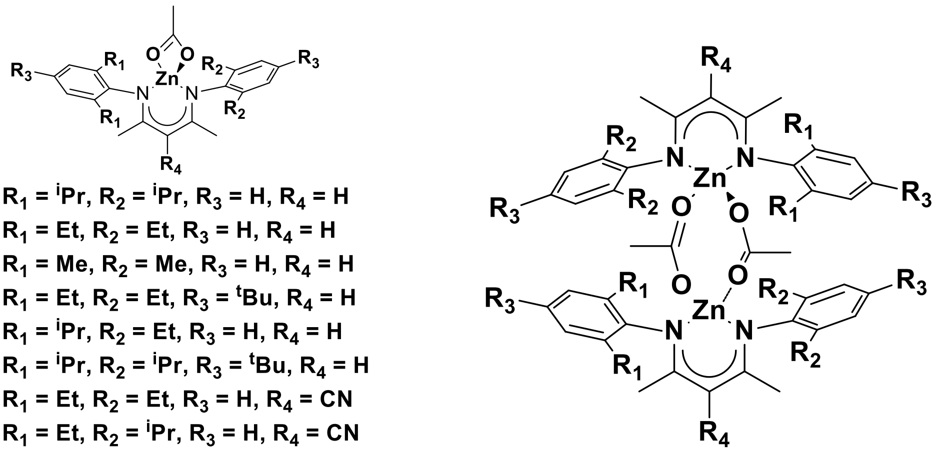
Figure 1.18. The presentative co-catalysts used together with salen catalyst.

The (salen)CrCl drawn in Figure 1.17-1 was also reported as an effective system by several research groups for anhydride/epoxide copolymerization. Diciccio and Coates have reported the ROP of maleic anhydride with different epoxides at 45 ^{o}C catalyzed by (salen)CrCl without using any co-catalyst (DiCiccio & Coates, 2011). The molar mass (Mn) of these polyesters were among 21-33 kDa. Glass transition temperature (Tg) varied depending upon the rigidity of epoxide structure. It could reach 41 ^{o}C from the copolymer of maleic anhydride with glycidyl phenyl ether. Darensbourg also explored epoxide/anhydride copolymerization using (salen)CrCl/PPNCl as catalyst system. Higher temperature was applied to explore the kinetics. In situ ATR-FTIR was used to monitor reaction, which indicated that more than 10h was necessary for the complete copolymerization of phthalic anhydride and cyclohexene oxide (D. J. Darensbourg et al., 2012). The molecular weight of polyesters depends on monomer types, varying from 5.7-14 kDa (Mn data). Rob Duchateau investigated the effect of cocatalyst types in copolymerization of SO/anhydrides (Nejad, Paoniasari, Koning, & Duchateau, 2012). It was discovered that (salen)CrCl with phosphines presented high activities and the molecular weight was slightly higher than polyester with cocatalyst PPNCl or DMAP.

1.6.5.4. Zinc β-diiminate System

Similar to salen system, the zinc β-diiminate catalysts are able to copolymerize epoxide/CO_2 at moderate temperature and low pressure. Coates' group has deep investigation on zinc β-diiminate catalysts. Different from salen catalyst, most of these zinc β-diiminate catalysts exist in dimeric form in solid state, while in solution they are presented in monomeric/dimeric equilibrium (Cheng, Lobkovsky, & Coates, 1998). In Coates' research, a variety of zinc β-diiminate (Figure 1.19a, complex 1-7) were synthesized with varying zinc-zinc distance (in the range of 0.3~0.5 nm) in microstructure. Their influence on polymerization of CHO/CO_2 was investigated (Moore, Cheng, Lobkovsky, & Coates, 2003). It was found that the species with larger zinc-zinc distance generally had better activity. It offered enough space and weaker metal alkoxide bonding for CHO or CO_2 insertion to propagate the polymer chain. However, the catalyst monomer incapable of dimerization impeded the catalytical reactivity. In others' work, it was observed that catalyst activity had a downward trend when the monomeric state predominated over dimer by decreasing the catalyst concentration (B. Y. Lee et al., 2005; van Meerendonk, Duchateau, Koning, & Gruter, 2004).

High activity (TOF = 729) was achieved by $[(BDI\text{-}5)ZnOAc]_2$ (Figure 1.19a-5). The polymer was almost completely alternative (carbonate linkage = 99%), and its number average molecular weight reached 23.3 kDa with narrow distribution (Đ = 1.15). The adjustability of catalyst electronics and steric using different ligands if a great advantage of zinc β-diiminate catalysts to optimize the polycarbonate properties. Nevertheless, the complicated synthesis and instability of intermediates and catalysts in the air and moisture creates problems for mass production and product storage (Cheng et al., 2001).



(a) zinc β-diiminate with different ligands (b) dimer structure

Figure 1.19. The structure of several zinc β-diiminate systems.

Most of zinc β-diiminate (complex 1-6, Figure 1.19a) were proven to be inactive for the copolymerization of epoxide/anhydride (Jeske, DiCiccio, & Coates, 2007). With the assistance of NMR study, Coates discovered that β-diiminate catalyst completely decomposed during the copolymerization. It was hypothesized that anhydride reacted with β-diiminate complex at the site of carbon bearing R_4 (Figure 1.19b) due to its high electronegativity. The substitution of nitrile group on this carbon makes the BDI complex stable with anhydride and therefore keeps its activity for the epoxide/anhydride copolymerization. (BDI)ZnOAc complex 8, Figure 1.19a) was able to copolymerize epoxides/cyclic anhydride. Polyesters with molecular weight (Mn) ranging from 10-55 kDa and narrow distribution (D = 1.1 - 1.5) were harvested. From ^{1}H NMR, ether linkage was invisible and it was almost completely alternative copolymerization. High decomposition temperature (~290 ºC) and moderate Tg (50-62 ºC) were observed, which strongly support their potential applications at low temperature. However, the activity of copolymerization was still low (TOF = 79 h^{-1}).

1.6.5.5. Double Metal Cyanide (DMC) Catalyst

DMC catalyst was initially developed in 1960s for ring opening polymerization of epoxy. Till 1980s, DMC was utilized as an extremely effective catalyst for industrial manufacturing of polyether polyols by numerous companies, like Bayer, BASF and DOW. Recently it was found that DMC catalyst was also valuable in many other types of reactions.

Apart from ROP of epoxy, these reactions include copolymerization of epoxy/cyclic anhydride (D. Wang et al., 2007), epoxy/CX_2 (X = O, S) (S. Chen, Hua, Fang, & Qi, 2004; D. J. Darensbourg, Adams, Yarbrough, & Phelps, 2003) and cyclization of epoxy/CO_2 (Dharman, Yu, Ahn, & Park, 2009). Simple preparation, stable in water and air, together with its high efficiency, DMC is regarded as a competitive catalyst for the copolymerization of CO_2/epoxy. With these advantages, DMC attracts more attention in recent years.

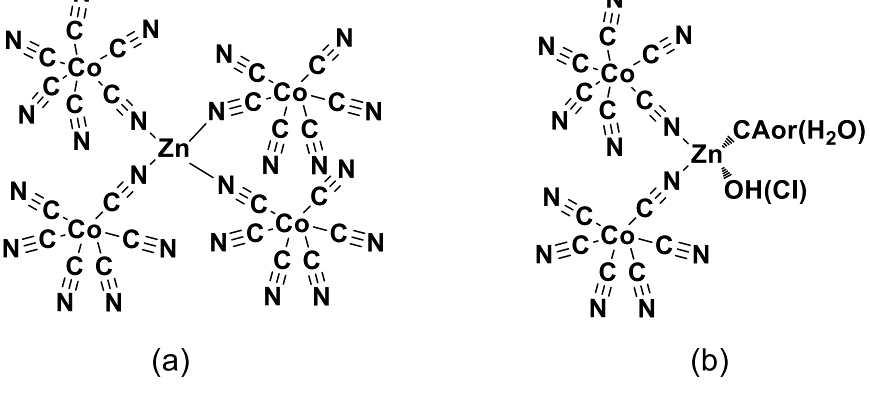


Figure 1.20. (a) Highly crystallized inside structure of DMC. (b) possible active site of DMC.

DMC catalyst is usually prepared from zinc salt, multi-cyanate metal salt and complexing agent (CA), which is generally alcohols and cyclic ethers. Generally, equivalent zinc salt with multi-cyanate metal salt results to a highly crystallized structure (Figure 1.20a), it has no activity for the polymerization. Only when excessive zinc salt is added, the obtained DMC is able to catalyze the copolymerization (Xinghong & Guorong, 2012). It's believed that the unique surface structure generated by excess zinc salt plays the key role for its activity. Although precise characterization of the surface structure is difficult, after investigations from massive experiments, the possible active site of DMC (Figure 1.20b) was proposed (Wei et al., 2013). Given in Figure 1.21, the halogen ions firstly departs and leaves a coordination site for the insertion of epoxy. Sequentially, the complexing agent leaves the metal center and will attach to the far-end of epoxy (X.-K. Sun et al., 2010). After the initiation step, the following steps are similar to those described in Figure 1.14.

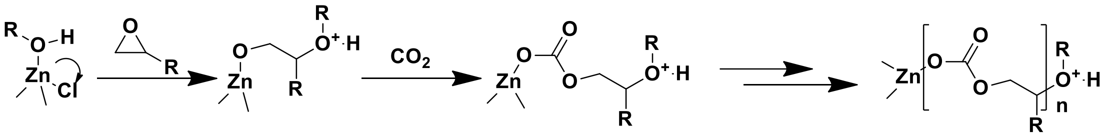


Figure 1.21. Possible catalytic mechanism of DMC for the copolymerization of epoxy/CO_2 (Dharman et al., 2008a).

Qi et al. selectively tried numerous complexing agents, finally concluded t-BuOH was the best option for the copolymerization of CO_2/CHO (S. Chen, Qi, Hua, & Yan, 2004). Polymer was obtained with Mn=17 kDa at 70 °C for 2 h. High activity of DMC was observed as the TOF reached to 1670 h^{-1}. The DMC catalyst loading could be reduced to several ppm (parts per million) without loss of activity. 1.8 - 2.3 kg polymer can be yielded from 1g catalyst. To further increase the polymer yield, nano-sized DMC was developed to enhance its surface area. By adopting 40 - 60 nm sheeted DMC catalyst, TOF could reach to 3815 h^{-1} (X. K. Sun et al., 2008).

Like copolymerization of epoxide/CO_2, the epoxide/anhydride copolymerization yield can reach to 10 kg polymer/ g catalyst (Hua, Qi, & Chen, 2004). Qi's group has deeply studied the copolymerization of MA/PO (Hua et al., 2004). Almost alternative copolymer (maximum 99.6%) was obtained when monomer ratio MA/PO > 1 was used. Different solvent systems are studied and it was concluded that THF helps to improve the conversion and molar mass of polymer. The obtained polyester has Mn about 3000 ~ 4000 g/mol . Kim and his colleagues later investigated the copolymerization of PO with SA/MA/PA (Suh et al., 2010). Polyester was obtained with Mw around 2300 ~ 10600 g/mol and molecular weight distribution among 1.1 ~ 1.5.

Due to the advantages of high activity, easy preparation of DMC, good properties of the resulted polymer, DMC was selected and used as a catalyst in this research work for the copolymerization of renewable epoxide with CO_2/anhydride. Though the induction period for DMC catalyst always predominate the polymerization process and it takes a few hours before the viscosity increment, which hampers the development of rapid polymerization method. Reducing the polymerization time will bring great benefits to industry. DMC was selected for catalyst system and microwave irradiation served as energy source for rapid synthesis.

1.6.6. Microwave-assisted Copolymerization of Epoxide/CO_2

The copolymerization of epoxy/CO_2 assisted by microwave radiation was rarely reported from articles. Kim's group attempted to add quaternary ammonium salt (QAS)/DMC as catalyst system for the ring opening polymerization of PO (Sanghyun Lee et al., 2007). It indicated that the addition of QAS effectively reduced the induced period. The time to reach to maximum polymerization rate decreased from 321 minutes to 10 minutes. It was explained that nucleophilic QAS changed the polarity of epoxide, lowered the energy of activation, led to epoxide ring-opening and bonding to DMC center rapidly.

Since the polarity of polar species could also be altered by absorbing microwave irradiation, Kim tried microwave-induced polymerization of CHO/CO_2 using DMC later (Dharman et al., 2008a). Polycarbonate was obtained within 30 minutes with Mn = 19.3 kDa and 75% carbonate linkage. Among the trials, highest TOF could reach 2.5×10^4 h^{-1}. Compared to the polycarbonate from conventional heating, reaction time was cut down to less than 25%, without affecting polymer properties. In this study, microwave was selected as the energy source for the polymerization of 1,2-epoxydecane/CO_2. Microwave-induced ROP of epoxide/anhydride was not published according to our knowledge, but its mechanism is similar to ROP of epoxide/CO_2. The polymerization of 1,2-epoxydecane/various anhydrides will also be tried in this thesis.

1.6.7. Usage of Polycarbonate/Polyester

The polyester and polycarbonate from ROP can be used for several materials: (1) Unsaturated polyester resin using epoxide/unsaturated anhydride as monomers. (2) Adhesives (3)

Polyurethane made from polycarbonate and polyester polyols, which probably enhanced tensile strength, impact strength and heat resistance. Further effort can be made for polyurethane manufacturing.

1.7. Hypotheses and objectives of the study

Hypotheses:

1. The copolymerization of 1,2-epoxydecane with cyclic anhydrides or CO_2 are not reported in literature. However, the copolymerization of similar epoxides, such as 1,2-epoxybutane, have been reported. We hypothesized that 1,2-epoxydecane should also be active for these reactions.
2. We hypothesized that microwaves can accelerate reactions, such as self-metathesis of FAMEs, polycondensation and ring opening polymerizations of plant oil derived monomers.
3. In addition, we assumed that microwave irradiations enhance the reaction rates without affecting product properties.

Objectives:

The main objective of this thesis was to develop a rapid and effective method to convert plant oil resources to diester monomer and use the diester and other lipid metathesis products such as 1-decene for the synthesis of biopolyesters and biopolycarbonates.

The specific objectives were;

1. To investigate microwave induced FAMEs self-metathesis from different oil sources and to prepare diols by reduction of diester.
2. To perform condensation polymerization of diol and diester into polyester by conventional heating, microwave irradiation, and conventional heating coupled with microwaves respectively.
3. To characterize the obtained aliphatic polyesters by NMR, FTIR, DSC, TGA, DMA and tensile tests.
4. To transform 1-decene to corresponding epoxide and characterize it by different spectral techniques (NMR, FTIR, etc).
5. To prepare copolymers of synthesized epoxy with CO_2 under microwave irradiation and

evaluate properties of these biopolymers.

6. To prepare copolymers of synthesized epoxy with cyclic anhydrides using microwave-induced ring-opening polymerizations.

1.8. References

Albertsson, A.-C., & Varma, I. K. (2002). Aliphatic polyesters: synthesis, properties and applications *Degradable Aliphatic Polyesters* (pp. 1-40): Springer.

Avérous, L. (2008). *Polylactic acid: synthesis, properties and applications*: Elsevier: Oxford, UK.

Bakare, I., Pavithran, C., Okieimen, F., & Pillai, C. (2006). Polyesters from renewable resources: preparation and characterization. *Journal of Applied Polymer Science, 100*(5), 3748-3755.

Bargiggia, F. C., & Murray, W. V. (2005). Cross-metathesis assisted by microwave irradiation. *the Journal of Organic Chemistry, 70*(23), 9636-9639.

Barth, M. C., & Titus, J. G. (1984). Greenhouse effect and sea level rise: A challenge for this generation.

Belgacem, M. N., & Gandini, A. (2011). *Monomers, polymers and composites from renewable resources*: Elsevier.

Burdett, K. A., Harris, L. D., Margl, P., Maughon, B. R., Mokhtar-Zadeh, T., Saucier, P. C., & Wasserman, E. P. (2004). Renewable monomer feedstocks via olefin metathesis: Fundamental mechanistic studies of methyl oleate ethenolysis with the first-generation Grubbs catalyst. *Organometallics, 23*(9), 2027-2047.

Chen, G.-Q. (2009). A microbial polyhydroxyalkanoates (PHA) based bio-and materials industry. *Chemical Society Reviews, 38*(8), 2434-2446.

Chen, G.-Q. (2010). Industrial production of PHA *Plastics from bacteria* (pp. 121-132): Springer.

Chen, S., Hua, Z., Fang, Z., & Qi, G. (2004). Copolymerization of carbon dioxide and propylene oxide with highly effective zinc hexacyanocobaltate (III)-based coordination catalyst. *Polymer, 45*(19), 6519-6524.

Chen, S., Qi, G. R., Hua, Z. J., & Yan, H. Q. (2004). Double metal cyanide complex based on Zn3 [Co (CN) 6] 2 as highly active catalyst for copolymerization of carbon dioxide and cyclohexene oxide. *Journal of Polymer Science Part A: Polymer Chemistry, 42*(20), 5284-5291.

Cheng, M., Lobkovsky, E. B., & Coates, G. W. (1998). Catalytic reactions involving C1 feedstocks: new high-activity Zn (II)-based catalysts for the alternating copolymerization of carbon dioxide and epoxides. *Journal of the American Chemical Society, 120*(42), 11018-11019.

Cheng, M., Moore, D. R., Reczek, J. J., Chamberlain, B. M., Lobkovsky, E. B., & Coates, G. W. (2001). Single-site β-diiminate zinc catalysts for the alternating copolymerization of CO2 and epoxides: catalyst synthesis and unprecedented polymerization activity. *Journal of the American Chemical Society, 123*(36), 8738-8749.

Coates, G. W., & Moore, D. R. (2004). Discrete Metal‐Based Catalysts for the Copolymerization of CO2 and Epoxides: Discovery, Reactivity, Optimization, and Mechanism. *Angewandte Chemie International Edition, 43*(48), 6618-6639.

Cohen, C. T., Chu, T., & Coates, G. W. (2005). Cobalt catalysts for the alternating copolymerization of propylene oxide and carbon dioxide: combining high activity and selectivity. *Journal of the American Chemical Society, 127*(31), 10869-10878.

Cuq, B., Gontard, N., & Guilbert, S. (1998). Proteins as agricultural polymers for packaging production. *Cereal Chemistry, 75*(1), 1-9.

Darensbourg, D., Niezgoda, S., Draper, J., & Reibenspies, J. (1998). Mechanistic aspects of the copolymerization of CO2 and epoxides by soluble zinc bis (phenoxide) catalysts as revealed by their cadmium analogues. *Journal of the American Chemical Society, 120*(19), 4690-4698.

Darensbourg, D. J., Adams, M. J., Yarbrough, J. C., & Phelps, A. L. (2003). Synthesis and structural characterization of double metal cyanides of iron and zinc: catalyst precursors for the copolymerization of carbon dioxide and epoxides. *Inorganic Chemistry, 42*(24), 7809-7818.

Darensbourg, D. J., & Holtcamp, M. W. (1995). Catalytic activity of zinc (II) phenoxides which possess readily accessible coordination sites. Copolymerization and terpolymerization of epoxides and carbon dioxide. *Macromolecules, 28*(22), 7577-7579.

Darensbourg, D. J., & Holtcamp, M. W. (1996). Catalysts for the reactions of epoxides and carbon dioxide. *Coordination Chemistry Reviews, 153*, 155-174.

Darensbourg, D. J., Holtcamp, M. W., Struck, G. E., Zimmer, M. S., Niezgoda, S. A., Rainey, P., . . . Reibenspies, J. H. (1999). Catalytic activity of a series of Zn (II) phenoxides for the copolymerization of epoxides and carbon dioxide. *Journal of the American Chemical Society, 121*(1), 107-116.

Darensbourg, D. J., Poland, R. R., & Escobedo, C. (2012). Kinetic studies of the alternating copolymerization of cyclic acid anhydrides and epoxides, and the terpolymerization of cyclic acid anhydrides, epoxides, and CO2 catalyzed by (salen) CrIIICl. *Macromolecules, 45*(5), 2242-2248.

Darensbourg, D. J., Wildeson, J. R., Yarbrough, J. C., & Reibenspies, J. H. (2000). Bis 2, 6-difluorophenoxide dimeric complexes of zinc and cadmium and their phosphine adducts:

lessons learned relative to carbon dioxide/cyclohexene oxide alternating copolymerization processes catalyzed by zinc phenoxides. *Journal of the American Chemical Society, 122*(50), 12487-12496.

Darensbourg, D. J., & Yarbrough, J. C. (2002). Mechanistic aspects of the copolymerization reaction of carbon dioxide and epoxides, using a chiral salen chromium chloride catalyst. *Journal of the American Chemical Society, 124*(22), 6335-6342.

Darensbourg, D. J., Yarbrough, J. C., Ortiz, C., & Fang, C. C. (2003). Comparative kinetic studies of the copolymerization of cyclohexene oxide and propylene oxide with carbon dioxide in the presence of chromium salen derivatives. In situ FTIR measurements of copolymer vs cyclic carbonate production. *Journal of the American Chemical Society, 125*(25), 7586-7591.

DeWalle, F. B., & Chian, E. S. (1981). Detection of trace organics in well water near a solid waste landfill. *Journal (American Water Works Association)*, 206-211.

Dharman, M. M., Ahn, J.-Y., Lee, M.-K., Shim, H.-L., Kim, K.-H., Kim, I., & Park, D.-W. (2008a). Moderate route for the utilization of CO 2-microwave induced copolymerization with cyclohexene oxide using highly efficient double metal cyanide complex catalysts based on Zn 3 [Co (CN) 6]. *Green Chemistry, 10*(6), 678-684.

Dharman, M. M., Yu, J.-I., Ahn, J.-Y., & Park, D.-W. (2009). Selective production of cyclic carbonate over polycarbonate using a double metal cyanide–quaternary ammonium salt catalyst system. *Green Chemistry, 11*(11), 1754-1757.

DiCiccio, A. M., & Coates, G. W. (2011). Ring-opening copolymerization of maleic anhydride with epoxides: a chain-growth approach to unsaturated polyesters. *Journal of the American Chemical Society, 133*(28), 10724-10727.

Drumright, R. E., Gruber, P. R., & Henton, D. E. (2000). Polylactic acid technology. *Advanced Materials, 12*(23), 1841-1846.

Edlund, U., & Albertsson, A.-C. (2002). Degradable polymer microspheres for controlled drug delivery *Degradable aliphatic polyesters* (pp. 67-112): Springer.

Edlund, U., Hakkarainen, M., Karlsson, S., Liu, Y., Ranucci, E., Ryner, M., . . . Albertsson, A.-C. (2003). *Degradable aliphatic polyesters* (Vol. 157): Springer.

Feldman, D., & Barbalata, A. (1996). *Synthetic polymers: technology, properties, applications*: Springer Science & Business Media.

Flory, P. J. (1953). *Principles of polymer chemistry*: Cornell University Press.

Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L., & Rousell, J. (1986). The use of microwave ovens for rapid organic synthesis. *Tetrahedron Letters, 27*(3), 279-282.

Gervet, B. (2007). The use of crude oil in plastic making contributes to global warming.

Renewable Energy Research Group, Division of Architecture and Infrastructure, Luleå University of Technology, SE-97187 Luleå, Sweden. www. ltu. se/cms_fs/1.5035.

Gibbins, J., & Chalmers, H. (2008). Carbon capture and storage. *Energy Policy, 36*(12), 4317-4322.

Giguere, R. J., Bray, T. L., Duncan, S. M., & Majetich, G. (1986). Application of commercial microwave ovens to organic synthesis. *Tetrahedron Letters, 27*(41), 4945-4948.

Griesbaum, K. (1970). Problems and possibilities of the free‐radical addition of thiols to unsaturated compounds. *Angewandte Chemie International Edition in English, 9*(4), 273-287.

Grubbs, R. H., Nguyen, S. T., Johnson, L. K., Hillmyer, M. A., & Fu, G. C. (1996). High activity ruthenium or osmium metal carbene complexes for olefin metathesis reactions and synthesis thereof: Google Patents.

Hayes, B. L. (2002). *Microwave synthesis: chemistry at the speed of light*: Cem Corporation.

Henneuse, C., & Pacary, T. (2003). *Emissions from plastics* (Vol. 14): iSmithers Rapra Publishing.

Hill, K. (2000). Fats and oils as oleochemical raw materials. *Pure and Applied Chemistry, 72*(7), 1255-1264.

Hua, Z., Qi, G., & Chen, S. (2004). Ring‐opening copolymerization of maleic anhydride with propylene oxide by double‐metal cyanide. *Journal of Applied Polymer Science, 93*(4), 1788-1792.

Huang, K.-M., Liu, Y.-Q., Tang, J.-X., Zhao, J., & Wang, B.-Y. (1996). A study of athermal action of electromagnetic waves on chemical reaction. *CHEMICAL JOURNAL OF CHINESE UNIVERSITIES-CHINESE EDITION-, 17*, 768-771.

Inoue, S., Kitamura, K., & Tsuruta, T. (1969). Alternating copolymerization of phthalic anhydride and propylene oxide by dialkylzinc. *Die Makromolekulare Chemie, 126*(1), 250-265.

Inoue, S., Koinuma, H., & Tsuruta, T. (1969). Copolymerization of carbon dioxide and epoxide. *Journal of Polymer Science Part B: Polymer Letters, 7*(4), 287-292.

Jacobsen, E. N., Tokunaga, M., & Larrow, J. F. (2000). Stereoselective ring opening reactions: Google Patents.

Jeske, R. C., DiCiccio, A. M., & Coates, G. W. (2007). Alternating copolymerization of epoxides and cyclic anhydrides: an improved route to aliphatic polyesters. *Journal of the American Chemical Society, 129*(37), 11330-11331.

John, R. P., Nampoothiri, K. M., & Pandey, A. (2007). Fermentative production of lactic acid from biomass: an overview on process developments and future perspectives. *Applied Microbiology and Biotechnology, 74*(3), 524-534.

Keki, S., Bodnar, I., Borda, J., Deák, G., & Zsuga, M. (2001). Fast Microwave‐Mediated Bulk Polycondensation of d, l‐Lactic Acid. *Macromolecular Rapid Communications, 22*(13), 1063-1065.

Klaus, S., Lehenmeier, M. W., Anderson, C. E., & Rieger, B. (2011). Recent advances in CO 2/epoxide copolymerization—new strategies and cooperative mechanisms. *Coordination Chemistry Reviews, 255*(13), 1460-1479.

Koenig, N., SASIN, G. S., & Swern, D. (1958). Organic Sulfur Derivatives. V. 2 Preparation and Properties of Some Long-Chain Mercapto Acids and Related Compounds3. *the Journal of Organic Chemistry, 23*(10), 1525-1530.

Koenig, N., & Swern, D. (1957a). Organic sulfur derivatives. I. Addition of mercaptoacetic acid to long-chain monounsaturated compounds. *Journal of the American Chemical Society, 79*(2), 362-365.

Koenig, N., & Swern, D. (1957b). Organic Sulfur Derivatives. II. 2 Sulfides, Sulfoxides and Sulfones from Thiols and 10-Undecenoic Acid. *Journal of the American Chemical Society, 79*(15), 4235-4237.

Komorowska-Durka, M., Dimitrakis, G., Bogdał, D., Stankiewicz, A. I., & Stefanidis, G. D. (2015). A concise review on microwave-assisted polycondensation reactions and curing of polycondensation polymers with focus on the effect of process conditions. *Chemical Engineering Journal, 264*, 633-644.

Koneswaran, G., & Nierenberg, D. (2008). Global farm animal production and global warming: impacting and mitigating climate change. *Environmental Health Perspectives, 116*(5), 578.

Kuran, W., & Listoś, T. (1994). Degradation of poly (propylene carbonate) by coordination catalysts containing phenolatozinc and alcoholatozinc species. *Macromolecular Chemistry and Physics, 195*(3), 1011-1015.

Kuran, W., & Niestochowski, A. (1980). Investigations on organic catalysts for the maleic anhydride-propylene oxide copolymerization. *Polymer Bulletin, 2*(6), 411-416.

Langanke, J., Wolf, A., Hofmann, J., Böhm, K., Subhani, M., Müller, T., . . . Gürtler, C. (2014). Carbon dioxide (CO 2) as sustainable feedstock for polyurethane production. *Green Chemistry, 16*(4), 1865-1870.

Lee, B. Y., Kwon, H. Y., Lee, S. Y., Na, S. J., Han, S.-i., Yun, H., . . . Park, Y.-W. (2005). Bimetallic anilido-aldimine zinc complexes for epoxide/CO2 copolymerization. *Journal of the American Chemical Society, 127*(9), 3031-3037.

Lee, S., Baek, S. T., Anas, K., Ha, C.-S., Park, D.-W., Lee, J. W., & Kim, I. (2007). Tuning of activity, induction period and polymer properties of double metal cyanide catalyzed ring-opening polymerizations of propylene oxide by using quaternary ammonium salts. *Polymer, 48*(15), 4361-4367.

Lee, S., & Shah, Y. T. (2012). *Biofuels and bioenergy: processes and technologies*: CRC Press.

Li, C.-T., Zhuang, H.-K., Hsieh, L.-T., Lee, W.-J., & Tsao, M.-C. (2001). PAH emission from the incineration of three plastic wastes. *Environment International, 27*(1), 61-67.

Li, F., Hanson, M., & Larock, R. (2001). Soybean oil–divinylbenzene thermosetting polymers: synthesis, structure, properties and their relationships. *Polymer, 42*(4), 1567-1579.

Lidström, P., Tierney, J., Wathey, B., & Westman, J. (2001). Microwave assisted organic synthesis—a review. *Tetrahedron, 57*(45), 9225-9283.

LUO, J., CAI, C., & Lü, C.-x. (2003). Microwave-promoted Halogen-exchange Reaction for Preparation of Fluoronitrobenzenes: Selection of Solvents and Their Properties in Microwave Field [J]. *Fine Chemicals, 1*, 016.

Meier, M. A., Metzger, J. O., & Schubert, U. S. (2007). Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews, 36*(11), 1788-1802.

Mendelsohn, R., Nordhaus, W. D., & Shaw, D. (1994). The impact of global warming on agriculture: a Ricardian analysis. *The American economic review*, 753-771.

Meng, Y., Du, L., Tiong, S., Zhu, Q., & Hay, A. S. (2002). Effects of the structure and morphology of zinc glutarate on the fixation of carbon dioxide into polymer. *Journal of Polymer Science Part A: Polymer Chemistry, 40*(21), 3579-3591.

Mol, J. (1994). Metathesis of unsaturated fatty acid esters and fatty oils. *Journal of Molecular Catalysis, 90*(1-2), 185-199.

Moore, D. R., Cheng, M., Lobkovsky, E. B., & Coates, G. W. (2003). Mechanism of the alternating copolymerization of epoxides and CO2 using β-diiminate zinc catalysts: evidence for a bimetallic epoxide enchainment. *Journal of the American Chemical Society, 125*(39), 11911-11924.

Motika, S. A., Pickering, T. L., Rokicki, A., & Stein, B. K. (1991). Catalyst for the copolymerization of epoxides with CO2: Google Patents.

Mutlu, H., Hofsäß, R., Montenegro, R. E., & Meier, M. A. (2013). Self-metathesis of fatty acid methyl esters: full conversion by choosing the appropriate plant oil. *RSC Advances, 3*(15), 4927-4934.

Nagahata, R., Sano, D., Suzuki, H., & Takeuchi, K. (2007). Microwave‐Assisted Single‐Step Synthesis of Poly (lactic acid) by Direct Polycondensation of Lactic Acid. *Macromolecular Rapid Communications, 28*(4), 437-442.

Nejad, E. H., Paoniasari, A., Koning, C. E., & Duchateau, R. (2012). Semi-aromatic polyesters by alternating ring-opening copolymerisation of styrene oxide and anhydrides. *Polymer Chemistry, 3*(5), 1308-1313.

Neufeld, L., Stassen, F., Sheppard, R., & Gilman, T. (2016). *The new plastics economy: rethinking the future of plastics.* Paper presented at the World Economic Forum.

Paddock, R. L., & Nguyen, S. T. (2001). Chemical CO2 fixation: Cr (III) salen complexes as highly efficient catalysts for the coupling of CO2 and epoxides. *Journal of the American Chemical Society, 123*(46), 11498-11499.

Patel, S., & Xanthos, M. (2001). Environmental issues in polymer processing: A review on volatile emissions and material/energy recovery options. *Advances in Polymer Technology, 20*(1), 22-41.

Patz, J. A., Campbell-Lendrum, D., Holloway, T., & Foley, J. A. (2005). Impact of regional climate change on human health. *Nature, 438*(7066), 310-317.

Qin, Z., Thomas, C. M., Lee, S., & Coates, G. W. (2003). Cobalt ‐ Based Complexes for the Copolymerization of Propylene Oxide and CO2: Active and Selective Catalysts for Polycarbonate Synthesis. *Angewandte Chemie International Edition, 42*(44), 5484-5487.

Ree, M., Bae, J., Jung, J., & Shin, T. (1999). A new copolymerization process leading to poly (propylene carbonate) with a highly enhanced yield from carbon dioxide and propylene oxide. *Journal of Polymer Science Part A: Polymer Chemistry, 37*(12), 1863-1876.

Ree, M., Hwang, Y., Kim, J.-S., Kim, H., Kim, G., & Kim, H. (2006). New findings in the catalytic activity of zinc glutarate and its application in the chemical fixation of CO 2 into polycarbonates and their derivatives. *Catalysis Today, 115*(1), 134-145.

Rybak, A., & Meier, M. A. (2007). Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry. *Green Chemistry, 9*(12), 1356-1361.

Saheb, D. N., & Jog, J. (1999). Natural fiber polymer composites: a review. *Advances in Polymer Technology, 18*(4), 351-363.

Santacesaria, E., Sorrentino, A., Rainone, F., Di Serio, M., & Speranza, F. (2000). Oxidative cleavage of the double bond of monoenic fatty chains in two steps: a new promising route to azelaic acid and other industrial products. *Industrial & Engineering Chemistry Research, 39*(8), 2766-2771.

Schmalensee, R., Stoker, T. M., & Judson, R. A. (1998). World carbon dioxide emissions: 1950–2050. *Review of Economics and Statistics, 80*(1), 15-27.

Schneider, W., & Diller, W. (2000). Phosgene. *Ullmann's Encyclopedia of Industrial Chemistry*.

Scholz, C., & Gross, R. A. Biopolyesters and biocatalysis introduction.

Serini, V. (2000). Polycarbonates. *Ullmann's Encyclopedia of Industrial Chemistry*.

Soga, K., Imai, E., & Hattori, I. (1981). Alternating copolymerization of CO2 and propylene oxide with the catalysts prepared from Zn (OH) 2 and various dicarboxylic acids. *Polymer Journal, 13*(4), 407-410.

Sorrentino, R., & Bianchi, G. (2010). *Microwave and RF engineering* (Vol. 1): John Wiley & Sons.

Steinbuchel, A., & Doi, Y. (2002). Polyesters III–Applications and commercial products. *Biopolymers. Weinheim (Germany): Wiley-VCH, 398*.

Suh, H. S., Ha, J. Y., Yoon, J. H., Ha, C.-S., Suh, H., & Kim, I. (2010). Polyester polyol synthesis by alternating copolymerization of propylene oxide with cyclic acid anhydrides by using double metal cyanide catalyst. *Reactive and Functional Polymers, 70*(5), 288-293.

Sun, X.-K., Zhang, X.-H., Chen, S., Du, B.-Y., Wang, Q., Fan, Z.-Q., & Qi, G.-R. (2010). One-pot terpolymerization of CO 2, cyclohexene oxide and maleic anhydride using a highly active heterogeneous double metal cyanide complex catalyst. *Polymer, 51*(24), 5719-5725.

Sun, X. K., Zhang, X. H., Liu, F., Chen, S., Du, B. Y., Wang, Q., . . . Qi, G. R. (2008). Alternating copolymerization of carbon dioxide and cyclohexene oxide catalyzed by silicon dioxide/Zn□ CoIII double metal cyanide complex hybrid catalysts with a nanolamellar structure. *Journal of Polymer Science Part A: Polymer Chemistry, 46*(9), 3128-3139.

Sun, X. K., Zhang, X. H., Wei, R. J., Du, B. Y., Wang, Q., Fan, Z. Q., & Qi, G. R. (2012). Mechanistic insight into initiation and chain transfer reaction of CO2/cyclohexene oxide copolymerization catalyzed by zinc□ cobalt double metal cyanide complex catalysts. *Journal of Polymer Science Part A: Polymer Chemistry, 50*(14), 2924-2934.

Swift, G. (2004). Degradable polymers and plastics in landfill sites. *Encyclopedia of Polymer Science and Technology*.

Takenouchi, S., Takasu, A., Inai, Y., & Hirabayashi, T. (2002). Effects of geometrical difference of unsaturated aliphatic polyesters on their biodegradability II. Isomerization of poly (maleic anhydride-co-propylene oxide) in the presence of morpholine. *Polymer Journal, 34*(1), 36-42.

Thakur, V. K., & Thakur, M. K. (2016). *Handbook of sustainable polymers: Processing and applications*: CRC Press.

Thanh, G. V., & Loupy, A. (2003). Microwave-assisted ruthenium-catalyzed olefin metathesis under solvent-free conditions. *Tetrahedron Letters, 44*(51), 9091-9094.

Truett, W., Johnson, D., Robinson, I., & Montague, B. (1960). Polynorbornene by Coördination Polymerization1. *Journal of the American Chemical Society, 82*(9), 2337-2340.

Türünç, O., & Meier, M. A. (2010). Fatty Acid Derived Monomers and Related Polymers Via Thiol‐ene (Click) Additions. *Macromolecular Rapid Communications, 31*(20), 1822-1826.

Türünç, O., & Meier, M. A. (2013). The thiol‐ene (click) reaction for the synthesis of plant oil derived polymers. *European Journal of Lipid Science and Technology, 115*(1), 41-54.

United States Department of Agriculture Foreign Agricultural Service. from http://apps.fas.usda.gov/psdonline/psdQuery.aspx

van Meerendonk, W. J., Duchateau, R., Koning, C. E., & Gruter, G. J. M. (2004). High‐Throughput Automated Parallel Evaluation of Zinc‐Based Catalysts for the Copolymerization of CHO and CO2 to Polycarbonates. *Macromolecular Rapid Communications, 25*(1), 382-386.

Velmathi, S., Nagahata, R., Sugiyama, J. i., & Takeuchi, K. (2005). A Rapid Eco‐Friendly Synthesis of Poly (butylene succinate) by a Direct Polyesterification under Microwave Irradiation. *Macromolecular Rapid Communications, 26*(14), 1163-1167.

Velmathi, S., Nagahata, R., & Takeuchi, K. (2007). Extremely rapid synthesis of aliphatic polyesters by direct polycondensation of 1: 1 mixtures of dicarboxylic acids and diols using microwaves. *Polymer Journal, 39*(8), 841-844.

Vignon, P., Vancompernolle, T., Couturier, J. L., Dubois, J. L., Mortreux, A., & Gauvin, R. M. (2015). Cross‐Metathesis of Biosourced Fatty Acid Derivatives: A Step Further Toward Improved Reactivity. *ChemSusChem, 8*(7), 1143-1146.

Vilaseca, F., Mendez, J., Pelach, A., Llop, M., Canigueral, N., Girones, J., . . . Mutje, P. (2007). Composite materials derived from biodegradable starch polymer and jute strands. *Process Biochemistry, 42*(3), 329-334.

Wang, D., Zhang, G., Zhang, Y., Gao, Y., Zhao, Y., Zhou, C., . . . Wang, X. (2007). Synthesis, characterization, and properties of novel polyetherester polyols and developed polyurethanes. *Journal of Applied Polymer Science, 103*(1), 417-424.

Wang, S., Du, L., Zhao, X., Meng, Y., & Tjong, S. (2002). Synthesis and characterization of alternating copolymer from carbon dioxide and propylene oxide. *Journal of Applied Polymer Science, 85*(11), 2327-2334.

Webb, H. K., Arnott, J., Crawford, R. J., & Ivanova, E. P. (2012). Plastic degradation and its environmental implications with special reference to poly (ethylene terephthalate). *Polymers, 5*(1), 1-18.

Wei, R.-J., Zhang, X.-H., Du, B.-Y., Sun, X.-K., Fan, Z.-Q., & Qi, G.-R. (2013). Highly Regioselective and Alternating Copolymerization of Racemic Styrene Oxide and Carbon Dioxide via Heterogeneous Double Metal Cyanide Complex Catalyst. *Macromolecules, 46*(9), 3693-3697.

Wiberg, K. B., & Saegebarth, K. A. (1957). The mechanisms of permanganate oxidation. IV. Hydroxylation of olefins and related reactions. *Journal of the American Chemical Society, 79*(11), 2822-2824.

Xinghong, S. X. C. S. Z., & Guorong, Q. (2012). Double Metal Cyanide Complex Catalyst and Its Catalysis for Epoxides-Involved Polymerization. *Progress in Chemistry, 9*, 017.

Yaron, B., Calvet, R., & Prost, R. (1996). *Soil pollution: processes and dynamics*: Springer Science & Business Media.

Zheng, Y.-Q., Lin, J.-L., & Zhang, H.-L. (2000). Crystal structure of zinc glutarate, Zn (C5H6O4). *Zeitschrift für Kristallographie-New Crystal Structures, 215*(4), 535-536.

Zia, K. M., Noreen, A., Zuber, M., Tabasum, S., & Mujahid, M. (2016). Recent developments and future prospects on bio-based polyesters derived from renewable resources: A review. *International Journal of Biological Macromolecules, 82*, 1028-1040.

Chapter 2 Aliphatic Polyester from Plant Oil Derived Diester/diol

2.1. Introduction

Fossil feedstocks, which are abundant and cheap, have been supplying the vast majority raw materials for polymer production. However, fossil oil is gradually depleting as non-renewable resource, and its exploitation and combustion have negative impact on environment. As an alternative to avoid these disadvantages, using renewable resources as building blocks for preparation of polymer materials, which meets the requirements of environment protection and sustainable development, has attracted a growing interest from academia and industry.

The largely available and easily accessible renewable resources are taken into consideration, such as plant oils. In Canada, more than million tons of plant oils are being produced every year, providing renewable feedstocks used for the production of fine chemicals and polymers. These plant oils, including canola oil and soybean oil have abundant unsaturated hydrocarbon chains. They are generally converted to fatty acids (FAs) or fatty acid methyl esters (FAMEs) for the simplicity of modification. Many reactions have been developed to modify FAs and FAMEs into α, ω-functionalized compounds as valuable monomers of polyesters, polycarbonates and polyamides. For instance, isomerizing alkoxycarbonylation (Quinzler & Mecking, 2010; Roesle et al., 2014) is effective to convert unsaturated FAMEs to compounds with esters on both ends. Other reactions, such as ozonolysis (Meier et al., 2007; Santacesaria et al., 2000) and thiol-ene click reaction (Oĝuz Türünç & Meier, 2010; Oğuz Türünç & Meier, 2013) have also been used to provide additional carboxyl acid or ester or amine groups to fatty acids.

Moreover, olefin self-metathesis (Rybak, Fokou, & Meier, 2008), a type of reaction allow the exchange of substitutes on olefinic double bonds, is also a powerful tool for the preparation of bifunctionalized monomers. By comparison to the reactions mentioned above, olefin metathesis is an easily operational and environmentally friendly method without using flammable gases or odorous reactants. The self-metathesis of unsaturated FAMEs was initially investigated by Boelhouwer's group. Using WCl_6 and Me_4Sn as catalytical system in chlorobenzene solution, methyl oleate and methyl elaidate were transformed to desired alkene and diesters with ~50% conversion in 24 h (Van Dam, Mittelmeijer, & Boelhouwer, 1972). Solvent free self-metathesis was successfully carried out in a later stage and commonly used. For instance, Mecking et al. obtained C20 diester with 33% yield from self-metathesis of 10-undecenoic acid at 48ºC within

4h (Trzaskowski, Quinzler, Bährle, & Mecking, 2011). Recently, Meier et al. has reported 98% conversion of FAMEs from linseed oil into desired products in the presence of 0.15 mol% Grubbs 1st generation catalyst (Mutlu et al., 2013). With the advantages of low catalyst loading, solvent free and moderate conditions, olefin self-metathesis has extraordinary performance to build α, ω-functionalized acids or esters from plant oil.

Microwaves, whose wavelengths is in the range between infrared and radio regions, have been widely used as an unconventional technique for the acceleration of various organic reactions from late 20th century (Gedye et al., 1986; Lidström et al., 2001). Microwave characteristics of rapid heating and non-thermal effect (de la Hoz, Diaz-Ortiz, & Moreno, 2005; LUO et al., 2003; Wroe & Rowley, 1996) are considered as major contributing factors that change the kinetics of reactions. The olefin metathesis reactions under microwave irradiation have ever been studied. More than 70% yield was achieved in 3 mins, and the reaction rate was >1000 fold than traditional heating (Thanh & Loupy, 2003). Recently, Ullah et al. reported metathesis of FAMEs with ethylene using microwave energy, which was completed within 1 min (Ullah & Arshad, 2017). In addition to olefin metathesis, research work regarding polycondensation of monomers using microwave technology has attracted the attention all over the world (Cao, Wang, & Yuan, 2009; Nagahata et al., 2007). Takeuchi et al. obtained poly(butylene succinate) (PBS) with Mw of 23,500 g/mol using microwave synthesis in a short time of 20 mins (Velmathi et al., 2005), which tremendously enhanced production efficiency.

In this study, Hoveyda Grubbs 2nd (**HG2**) was selected as a catalyst for microwave-assisted self-metathesis of FAMEs due to its high activity. FAMEs are prepared from canola oil, high oleic soybean oil and chemical source. Factors such as reaction time, catalyst loading are studied in order to optimize reaction conditions. Moreover, fully renewable biopolyester is prepared by polycondensation of diester from metathesis products and diol obtained from the reduction of diester via conventional heating and microwave methods.

2.2. Experiment Section

2.2.1. Materials

High oleic soybean oil was purchased from DuPont. Oleic acid (technical grade) was supplied by Anachemie. Canola oil, Hoveyda-Grubbs catalyst 2nd generation, lithium aluminum hydride, tin(II) chloride, titanium butoxide, silica gel (technical grade, 63-200 μm), 1,1,2,2-

tetrachloroethane-d_2, chloroform-d were purchased from Sigma Aldrich. Thin layer chromatography plates (TLC silica gel 60 F_{254}) were from Merck Group. Hexanes were gained from Caledon chemicals.

Organic solvents, including tetrahydrofuran (THF), dichloromethane (DCM), methanol, acetone, ethyl acetate and inorganic materials, such as potassium hydroxide, sodium sulfate, sodium hydroxide, sodium sulphate were purchased from Sigma Aldrich. Otherwise mentioned, these chemicals were used as received.

2.2.2. General Consideration

Fourier Transform Infrared- Attenuated Total Reflectance (FTIR-ATR) spectroscopic analyses were carried out on a Nicolet 8700 spectrometer *(Madison, WI, USA)*. For FTIR analysis, the dissolved solid or liquid samples were placed directly onto the surface of the ATR crystal and analyzed. ^{1}H NMR and ^{13}C NMR was carried out at room temperature by a Varian INOVA at the frequencies of 400 MHz and 100 MHz, respectively. The shifts of non-deuterated solvent residues, including chloroform and 1,1,2,2-tetrachloroethane, were considered as references. Perkin Elmer GC-FID Clarus 500 instrument equipped with flame ionization detector (FID) was used to identify and quantify FAMEs and products from olefin metathesis. Temperature of 280^{o}C was set for detector and 240^{o}C for injector. Hydrogen and air gases were used as flow phase at a rate of 450mL/min and 45mL/min respectively. A fused silica capillary column SP2560 (100 m × 0.25 mm × 0.2 μm film thickness) and detector 5975B inert XL MSD. 2 μL sample was injected and 20:1 ratio of split mode was selected. Oven temperature was held at 45 ^{o}C for 4min and then increased to 175 ^{o}C at an increase rate of 13 ^{o}C/min. After holding for 27 mins, it was eventually increased to 215 ^{o}C at a rate of 4 ^{o}C/min and kept for 35 min. GC-MS analysis was conducted on Agilent 6890N *(USA)* equipment. The used column and other conditions were set the same as GC-FID. The molecular structures were identified by MS with scanning range of 50 - 600 amu at a rate of 2.66/second. The microwave assisted reactions were carried out in open vessel mode microwave reactor *(CEM Discover Labmate)* equipped with infrared temperature sensor (Maximum pressure = 250 psi, maximum power = 200 W).

Figure 2.1. Microwave-assisted reactions of self-metathesis and polycondensation.

2.2.3. Esterification of Oleic Acid (Technical Grade)

The esterification synthesis was performed following the procedure reported by Jala's work (Srikanth et al., 2016). Oleic acid (10 g) was slowly added into a solution of 2% sulfuric acid in methanol (100 mL) The reaction mixture was refluxed for 6 hours and monitored by thin layer chromatography. After the reaction completed, the volatiles were evaporated under reduced pressure. The residuals were dissolved in ethyl acetate, and washed with distilled water until the acid residues were removed. The organic layer was dried using anhydrous sodium sulfate and the organic solvent was evaporated under vacuum. Products were further purified with silica gel column chromatography using hexane/ethyl acetate (97:3) as an eluent to obtain FAMEs (9.4 g, 90% yield).

2.2.4. Synthesis of High Oleic Oil (Soybean or Canola) Methyl Ester

100g plant oil was added into a round-bottom flask equipped with a stirring bar. 1 g KOH was dissolved in 25 mL methanol and the mixture was added into oil slowly. The reaction mixture was kept at 40 ^{o}C for 1.5 hours and then stirring was stopped. The bottom layer (containing glycerol) was removed by pasteur pipette. The above procedure was repeated for a second time to ensure complete transesterification. The reaction mixtures were dissolved in 150 mL dichloromethane and washed with distilled water twice and then by saturated NaCl solution. The organic layer was dried over anhydrous sodium sulfate and solvent was evaporated. The crude product was purified with column chromatography as described in section 2.2.3 to give 85 g FAMEs.

2.2.5. Self-metathesis of FAMEs Assisted by Microwave irradiation

FAMEs (2 g) were placed into a 10mL microwave tube equipped with a stirring bar. **HG2** (0.05 mol%) catalyst was added into the reaction vessel in an inert atmospheric glovebox. The tube was placed in the cavity of microwave reactor and reaction was carried out at set temperature for required time period in the presence of nitrogen flow. Product mixtures were passed through silica in order to remove catalyst. A sample of 0.5 mg/ml DCM solution was prepared, which was used for the characterization of products by GC-MS and GC-FID analysis. Dimethyl-9-octadecene-1,18-dioate (**diester**) was separated with silica gel column chromatography using 2% ethyl acetate in hexane as an eluent.

Dimethyl-9-octadecene-1,18-dioate (**diester**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 – 5.20 (m, 2H), 3.65 (s, 6H), 2.29 (t, *J* = 7.6 Hz, 4H), 2.27 – 1.81 (m, 4H), 1.68 – 1.50 (m, 4H), 1.45 – 1.22 (m, 16H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.23 (s), 130.28 (s), 129.80 (s), 51.37 (s), 34.07 (s), 32.52 (s), 29.58 (d, *J* = 12.8 Hz), 29.00 (d, *J* = 17.9 Hz), 27.14 (s), 24.92 (s). IR: 2924cm^{-1}, 2853cm^{-1}, *1737cm^{-1} (C=O)*, 1435cm^{-1}, 1360cm^{-1}, *1244cm^{-1} (C-O-C ester)*, 1195cm^{-1}, *1168cm^{-1} (C-O-C ester)*, 968cm^{-1}, 880cm^{-1}, 725cm^{-1}.

2.2.6. Synthesis of 9-octadecene-1,18-diol

The synthesis for 9-octadecene-1,18-diol (**diol**) was performed following a literature procedure reported by Mecking (Quinzler & Mecking, 2010). THF was stirred over CaH_2 for 3 days and then filtered in nitrogen atmosphere. 470 mg $LiAlH_4$ was suspended in 40 mL dry THF and vigorously stirred. 2.00 g dimethyl-9-octadecene-1,18-dioate was dissolved by 20 mL dry THF and added into the suspension dropwise. Additional 10 mL THF was added. The slurry was refluxed for 1 hour and then stirred overnight at room temperature. Sequentially, 0.5 mL water, 0.5 mL 15% aqueous NaOH solution and 0.5 mL water were slowly added to quench the reaction. The white precipitate was filtered out at 40 °C and the solvent was removed under reduced pressure. The crude product (white powder) was dissolved in DCM and washed with distillated water, dried over anhydrous sodium sulphate. Solvent was evaporated under vacuum and the product was collected with 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 – 5.22 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 4H), 2.00 (dt, *J* = 10.9, 5.6 Hz, 4H), 1.70 – 1.48 (m, 6H), 1.33 (dd, *J* =

16.8, 12.3 Hz, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.34 (s), 129.87 (s), 62.98 (s), 32.78 (s), 32.55 (s), 29.54 (dd, *J* = 21.7, 8.5 Hz), 29.12 (d, *J* = 15.9 Hz), 27.16 (s), 25.73 (s). IR: *3340cm^{-1}(-OH)*, 2924cm^{-1}, 2853cm^{-1}, 1461 cm^{-1}, 1055cm^{-1}, 968cm^{-1}.

2.2.7. Polycondensation of 9-octadecene-1,18-diol and Dimethyl-9-octadecene-1,18-dioate by heating method

0.5 mmol diol and equivalent diester were added into a 10mL tube, followed by 2.0 mol% $SnCl_2$ or $Ti(OBu)_4$ catalyst. Reduced pressure was applied at 100 ºC and reaction temperature was gradually raised from 100 ºC to 200 ºC at a rate of 10 ºC/20 min and the reaction was stopped after 16 h to obtain yellow solid with quantitative yield. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ 5.37 (d, *J* = 14.4 Hz, 4H), 4.03 (t, *J* = 6.6 Hz, 4H), 2.28 (t, *J* = 7.4 Hz, 4H), 2.04 (d, *J* = 62.5 Hz, 8H), 1.56 (t, *J* = 23.9 Hz, 8H), 1.29 (s, 36H). ^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ 173.86 (s), 130.16 (s), 129.78 (s), 64.27 (s), 34.23 (s), 32.47 (s), 29.20 (dt, *J* = 23.2, 7.6 Hz), 28.51 (s), 27.08 (s), 25.80 (s), 24.87 (s). IR: 2918cm^{-1}, 2850cm^{-1}, *1733cm^{-1} (C=O)*, 1466cm^{-1}, *1242cm^{-1} (C-O-C ester), 1169cm^{-1} (C-O-C ester)*, 963cm^{-1}, 722cm^{-1}.

2.2.8. Polycondensation of 9-octadecene-1,18-diol and Dimethyl-9-octadecene-1,18-dioate Assisted by Microwave Radiation

The starting materials were added into the vessel, and then it was placed into microwave reactor. The microwave assisted reaction was performed at 200 ºC in nitrogen atmosphere for 15 min. And then it was carried out under reduced pressure (~0.1 bar) for certain time at same temperature.

2.2.9. Calibration of Standards by GC-FID

Highly pure methyl oleate and diester were dissolved in DCM for the preparation of standard solutions with different concentration. Values of their peak areas were used for plotting standard curves and mass response factors were calculated. The concentrations of corresponding FAMEs and diester in self-metathesis product are calculated using their mass response factors.

2.2.10. Differential Scanning Calorimetry (DSC) Analysis

DSC experiments were performed on a TA Instrument *(2920 Modulated DSC, USA)* in nitrogen atmosphere. 4.0-7.0 mg sample sealed in a pan was placed into DSC cell and equilibrated at -30 ºC. The temperature was programmed to 150 ºC at a rate of 3 ºC/min and the cell was cooled down naturally. DSC data was recorded from 2nd heating cycle to eliminate the thermal history of the materials.

2.2.11. Thermogravimetric Analysis(TGA)

TGA was performed on a TGA Q50 instrument in nitrogen flow at a rate of 60 ml/min. 5.0 - 20.0 mg sample was placed in TGA pan and heated from room temperature to 600 °C at a rate of 10 °C/min.

2.2.12. Film Preparation

Polyesters are prepared at an amplified scale of several grams using the procedures described in section 2.2.7 and 2.2.8. Polyester (1.5 - 2 g) was placed inside a mortar and crushed. Films of polyester was compressing moulded at 80 °C using a carver presser at a pressure of 100 psi for 8 min.

2.2.13. Tensile Testing

The mechanical properties of polyester films were measured by a universal testing machine *(autograph AGSX Shimadzu)* at room temperature. Both ends of the film were fixed to 50 N load cell. The film was stretched at a rate of 0.90 mm/s until raptured.

2.2.14. Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of polyester film were measured using a TA Instrument *(DMA Q800)*. At an oscillatory frequency of 1 Hz with applied deformation of 0.2% during heating, the measurement was carried out in a tensile mode where temperature was programmed from -90 °C to 60 °C at a rate of 2 °C/min.

2.3. Result and Discussion

2.3.1. FAME Compositions from Different Sources

The self-metathesis of FAMEs by conventional heating has been investigated by a few research groups. Studies showed that the degree of unsaturation of FAMEs has significant influence on metathesis products. Self-metathesis of polyunsaturated FAMEs generated several volatile olefins, including cyclohexa-1,4-diene and hex-3-ene, which may lead to inaccuracy of identifying and measuring products. In addition to this, several types of diesters were distinguished from the products, which was adverse for further polymerization. Renewable sources with high content of monounsaturated fatty acids were selected for the study of microwave induced metathesis. Firstly, FAME compositions are identified by GC-MS and their percentages are calculated using GC-FID, as shown in Table 2.1. The polyunsaturated FAMEs (c18:2 and c18:3) from all three sources are less than 17%, while the monounsaturated FAMEs (c16:1 and c18:1) are more than 75%. Saturated FAMEs, which do not participate in metathesis reaction, are the minors.

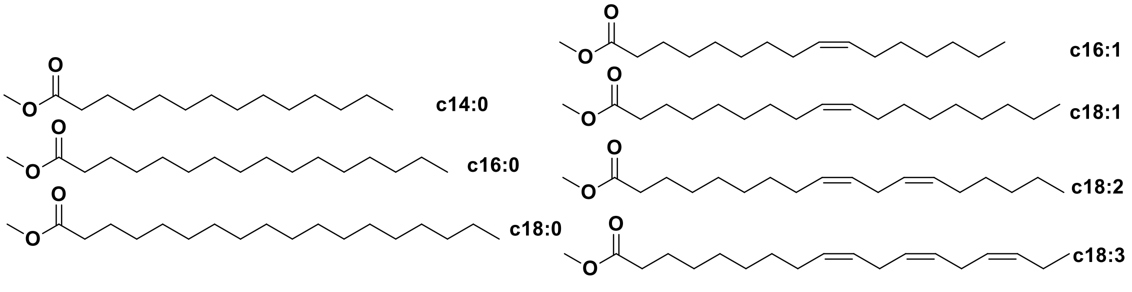


Figure 2.2. Fatty acid methyl esters from different sources.

FAMEs	c14:0	c16:0	c18:0	c16:1	c18:1	c18:2	c18:3
A	-	6.7%	-	-	77.0%	13.3%	3.0%
B	-	7.4%	5.6%	-	82.5%	4.4%	-
C	3.4%	5.8%	-	5.8%	79.2%	5.8%	-

Table 2.1. The components of different FAMEs (A: canola oil methyl ester, B: high oleic soybean oil methyl ester, C: technical grade methyl oleate) from three kind of oil sources determined by GC-FID. It was assumed that all FAMEs have same mass response factor in GC-FID analysis.

2.3.2. Self-metathesis Reactions and Products

Hoveyda Grubbs 2nd catalyst (**HG2**) was particularly employed in this study for its high activity and good tolerance of polar and protic environments. Literature review (Doll, 2014) of pure methyl oleate self-metathesis provides evidence that high reaction temperature will lead to drop of conversion rate. Therefore, moderate temperature of 50 ºC was chosen for this study.

FAME Self-metathesis products were identified by GC-MS spectra (Figure 2.4). The structures of products are deduced by their elution time, peak areas and MS spectra. Typically, canola oil methyl esters and their products after self-metathesis are depicted in Figure 2.3 regardless of saturated FAMEs. The products can be classified into three types: (1) olefins with internal double bonds, (2) unsaturated FAMEs and (3) unsaturated diester. In accordance with the fact that methyl oleate accounts for the majority of starting materials, big peak areas were afforded by GC: (**c**) 9-octadecene, (**f**) methyl 9-octadecenoate, (**g**) dimethyl-9-octadecene-1,18-dioate (C18 diester), which were from the self-metathesis of methyl oleate. Cis- and trans- isomers were identified for compounds **e**, **f** and **g** from GC-MS, where isomers earlier eluted were more favored by ~5:1 ratio. Commonly the cis- compound has larger dipole moment and higher polarity, so trans- isomer are suggested to be eluted ahead of cis- isomer based on the separation principles of GC. This point of view is confirmed by comparing the elution time of c18:1t in products and c18:1c in FAMEs.

Olefin isomerization was an annoying side reaction that sometimes occurred in olefin metathesis. During the isomerization, carbon-carbon double bonds shift to adjacent positions and it will increase the complexity of metathesis products. Diesters with shorter or longer chain lengths will be generated, which are difficult to separate and create troubles for polymerization. In this case, only peaks of C18 diester was found after 40mins of elution time. Failure of searching C17 or C19 diesters in GC-MS spectrum strongly proved that olefin isomerization did not take place during microwave reaction.

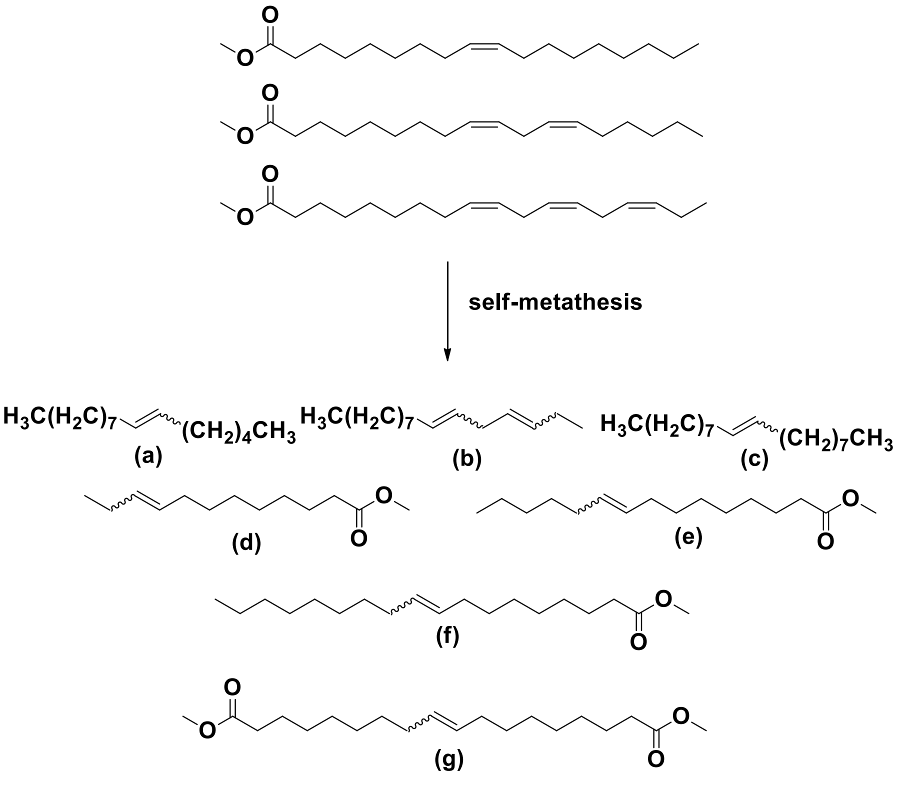


Figure 2.3. Self-metathesis of canola oil methyl ester. Conditions: 50°C, 0.05% HG2 loading, 2 min reaction time.

However, the existence of compound **f** indicated that the reactants were not fully converted due to equilibrium state of alkene self-metathesis. Conversion rate of ~50% was widely observed from publications. For instance, Thomas A. FoGlia observed exactly 50.0% conversion rate from olefin-metathesis of methyl oleate using $Re_2O_3 \cdot Al_2O_3 \cdot Me_4Sn$ catalyst (Kohashi & Foglia, 1985).

Roland Winde reported conversion rate of 49.6% for methyl oleate self-metathesis using a phoban-indenylidene ruthenium catalyst (Forman et al., 2006).

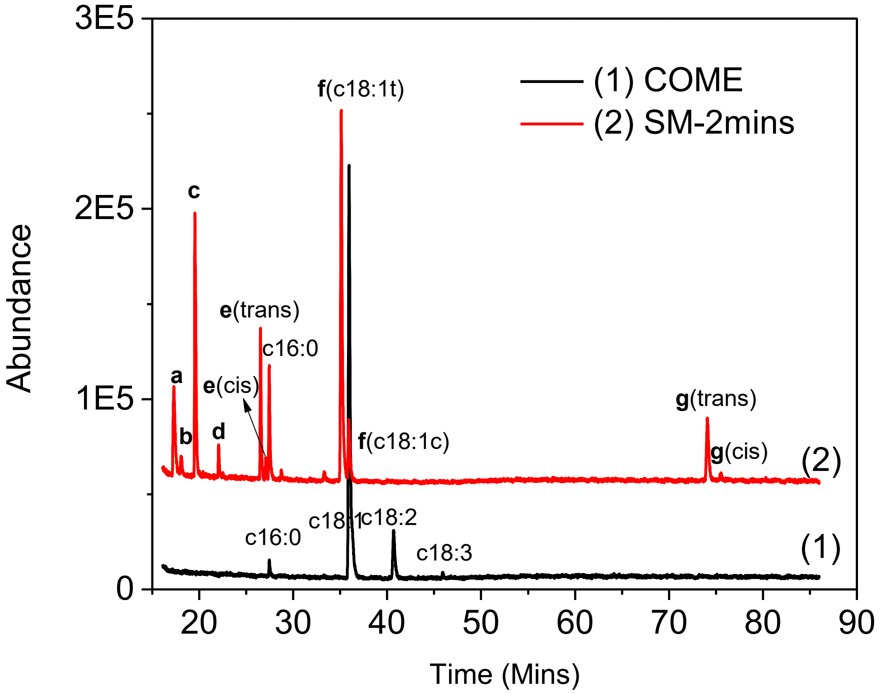


Figure 2.4. GC-MS spectra of (1) canola oil methyl esters and (2) self-metathesis products after 2min.

2.3.3. Calibration & Calculation of Conversion Rate

In Section 2.3.2, the generated compounds of self-metathesis are identified. However, the conversion of FAME self-metathesis has not been figured out. This section is to introduce the calculations used to measure the conversion rate based on GC-FID calibrations.

2.3.3.1. Calibration of Standards

GC-FID spectra give us information of peaks and their corresponding areas. However, for equal amounts of different compounds, their peak areas are not the same. Herein, the term, mass response factor (MRF) was introduced, which refers to the peak area of standard at concentration of 1 mg/mL. To identify the concentration of self-metathesis products, calibration of standards is necessary. However, it will be huge work if each type of reactants or products is calibrated. It is difficult to either separate each pure component from products or obtain from commercial sources. Therefore, methyl oleate and diester were selected as representative standards for approximate calculation based on three principles: (i) MRF of double-bond isomers, such as c18:1t and c18:1c, were considered the same; (ii) FAMEs were assumed to have same MRF values depending upon their analogous structures; (iii) the amount of generated olefins equals to that of diester.

The purities of standards were verified by GC-MS initially. A single peak was observed for pure methyl oleate from commercial resource, and two signals were observed for purified dimethyl-9-octadecene-1,18-dioate Z/E isomers.

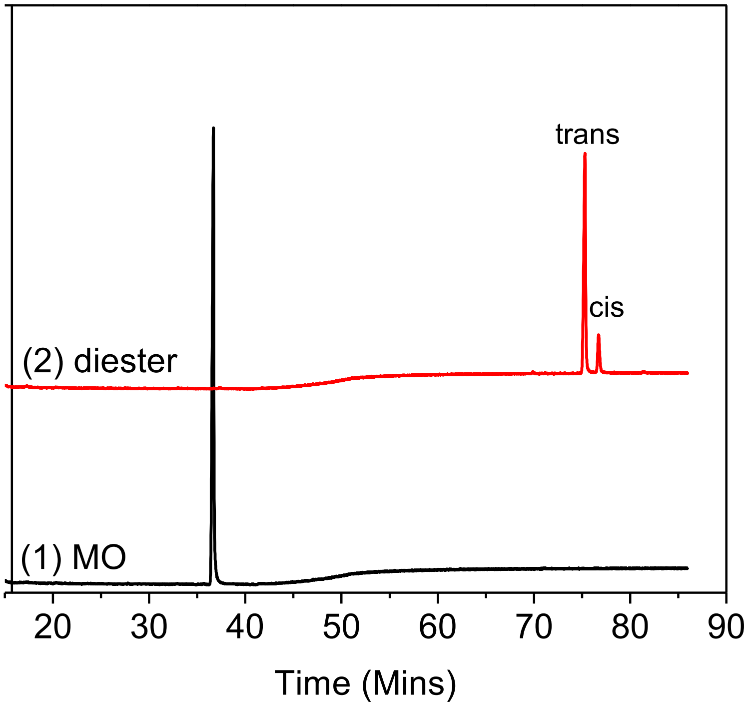


Figure 2.5. GC-MS spectra of standards: (1) methyl oleate and (2) diester.

According to our assumption, the peak areas of diester Z/E isomers were simply summed. The peak areas of standards of different concentrations were recorded for the calculation of MRFs and verification of linearity. Linearity is the precondition to assure that MRFs are applicable for GC-FID samples in certain concentration ranges.

c[diester](mg/ml)	Area Sum(Uv*sec)	c[MO](mg/ml)	Area(Uv*sec)
0.50	27077.34	0.50	37756.82
0.25	13988.23	0.40	29113.42
0.15	8775.03	0.30	22160.25
0.10	6015.59	0.20	14169.54
0.05	3067.77	0.10	7687.70

Table 2.2. The GC-FID peak areas of diester and methyl oleate standards.

According to the peak areas recorded in Table 2.2, both standard curves were plotted in Figure 2.6. The point of 0.5 mg/mL diester was excluded for linear fitting due to its deviation from standard curve. It showed that the linearity of methyl oleate standards keeps well below 0.5 mg/mL, and the linearity of diester is also good under 0.25 mg/mL, depending upon their R^2 values, which are more than 0.99. Their corresponding MRFs are 74136 /unit and 57110 /unit, respectively, which means 1mg/mL methyl oleate solution will present a peak of 74136 uv*sec area and so does the diester.

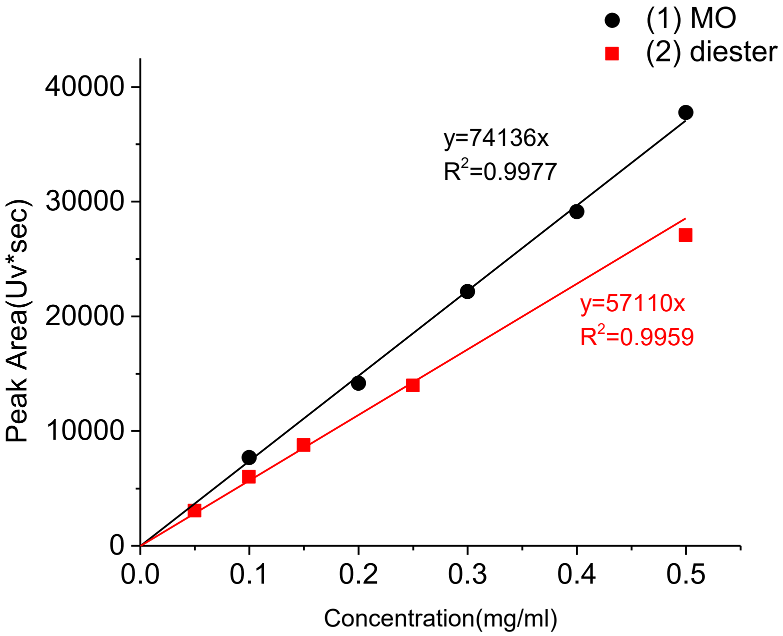


Figure 2.6. Linear fitting curves of methyl oleate (1) and diester (2) standards determined by GC-FID method.

2.3.3.2. The Calculation of Conversion Rate and Selectivity

On the basis of calibration, the conversion and selectivity of self-metathesis are calculable by the Formulas 2.1 and 2.2. Hereon, to exhibit chemical equilibrium state directly, real conversion (Conv(R)) was defined as the conversion rate of FAMEs to olefins and diester (Formula 2.3). In the case of canola oil methyl ester (Figure 2.4), the Conv(R) was 50.6%. The calculation was coincident with the yield from an amplified reaction. 14.5 g diester was separated after the self-metathsis reaction of 63 g FAMEs. Without concerning to product loss during purification, 43% Conv(R) was observed in an amplified reaction.

$$\text{Conv} = \frac{n(new\ compounds)}{n(total\ compounds)} = \frac{n(a+b+c+d+e+g)}{n(a+b+c+d+e+f+g)} = \frac{2n(g)+n(d+e)}{2n(g)+n(d+e+f)} \times 100\% \quad (2.1)$$

$$\text{Selectivity} = \frac{n(olefins+diesters)}{n(new\ compounds)} = \frac{n(a+b+c+g)}{n(a+b+c+d+e+g)} = \frac{2n(g)}{2n(g)+n(d+e)} \times 100\% \quad (2.2)$$

$$\mathrm{Conv(R)} = \mathrm{Conv} \times \mathrm{Selectivity} \qquad (2.3)$$

2.3.4. FAME Self-Metathesis from Plant Oil Sources

Entry	FAMEs	Reaction Time (min)	Conv(R)%
1	A	2	50.6
2	B	2	39.2
3	C	2	51.3

Table 2.3. The real conversion of FAMEs self-metathesis from FAMEs (A: canola oil methyl ester, B: high oleic soybean oil methyl ester, C: technical grade methyl oleate). Conditions: 50 ºC under microwave radiation at 0.05% HG2 loading.

Further, FAME mixtures from two other oil sources were investigated for microwave-induced self-metathesis. Both of technical grade methyl oleate and high oleic soybean oil methyl esters were converted successfully. The Conv(R) of entry 3 was approximate 50% and was in line with previous work. However, in entry 2, only 39.2% of FAMEs were converted into diester and olefins. Several reasons might be accounted for the low conversion. The remains of minor glycerol in FAMEs might be a conceivable cause. Analyzed by thin layer chromatography, high polar impurity was detected, which was possibly glycerol. The study showed that, self-metathesis of crude FAMEs does not occur even after 20 min if the component was not removed with column chromatography. Less purification of high oleic soybean oil methyl esters might be reason of lower conversion. In summary, microwave-induced FAME self-metathesis was proven to be an extreme rapid and effective method to obtain diester monomer from different oil or fatty acid sources.

2.3.5. Kinetic Studies of FAME Self-metathesis

Although ~50% conv(R) of FAME self-metathesis was achieved within 2min. it is not sure whether the reaction has reached to the chemical equilibrium state or not. Herein, reaction was studied for longer time to figure out its equilibrium point. To avoid the negative effect from glycerol contents in FAMEs, the self-metathesis of technical grade methyl oleate, which was prepared from technical grade oleic acid, was conducted for 2, 6, 10, 20, 30 and 60 min. From 2 min to 1 h, conv(R) vibrated around ~50%, which indicated that the equilibrium was established within 2 min.

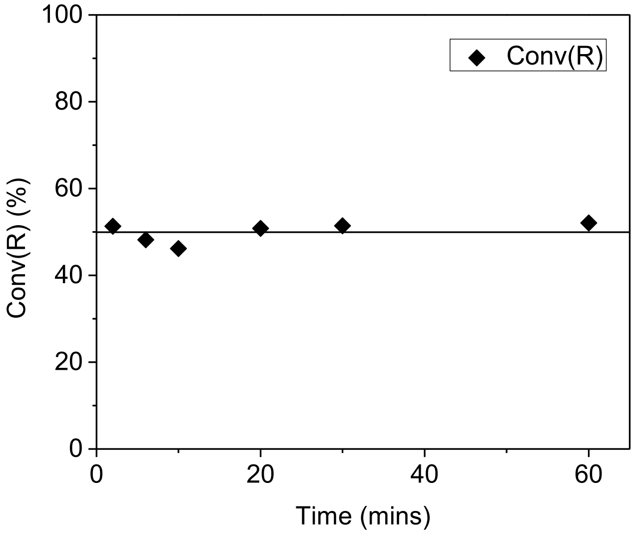


Figure 2.7. Conv(R) of FAMEs at different time points. Conditions: the reaction temperature was set at 50 ºC, HG2 loading was 0.05%.

2.3.6. Effect of Catalyst Loading on Conversion

Some other publications reported olefin metathesis at lower catalyst loading. Although **HG2** is commercially available, its price is as high as gold. Cutting down its usage is significantly important for cost effective reaction. In this work, the **HG2** loading was gradually reduced from 0.05% to 0.005%. Once the **HG2** was decreased to 0.01%, the required reaction time was prolonged from 2 to 6 min. A further **HG2** loading decrement to 0.005% led to a sharp drop of conv(R) (Entry 3, Table 2.4). Even with extended reaction time, the conversion was not promoted. We hypothesized that **HG2** completely degraded before the reaction was completed. 0.01 mol% was the optimized catalyst concentration for self-metathesis comprehensively considering reaction time and catalyst cost.

Entry	HG2 Loading (%)	Reaction Time (min)	Conv(R)%
1	0.05	2	51.3
2	0.01	2	40.9
3	0.01	6	50.8
4	0.005	2	8.5

Table 2.4. The real conversion of FAMEs self-metathesis from methyl oleate (technical grade). Conditions: 50 ºC under microwave radiation.

2.3.7. Characterization of Monomers & Polyester

The diester and diol were firstly characterized by ATR-FTIR, as shown in Figure 2.8. After reduction of diester, the characteristic absorptions at 1737 cm^{-1} (C=O vibration), 1197 cm^{-1} (C-O-

C ester) and 1168 cm^{-1} (C-O-C ester) disappears. Instead, diol exhibits a broad peak at 3340cm^{-1}, which is a typical absorption of hydroxyl group.

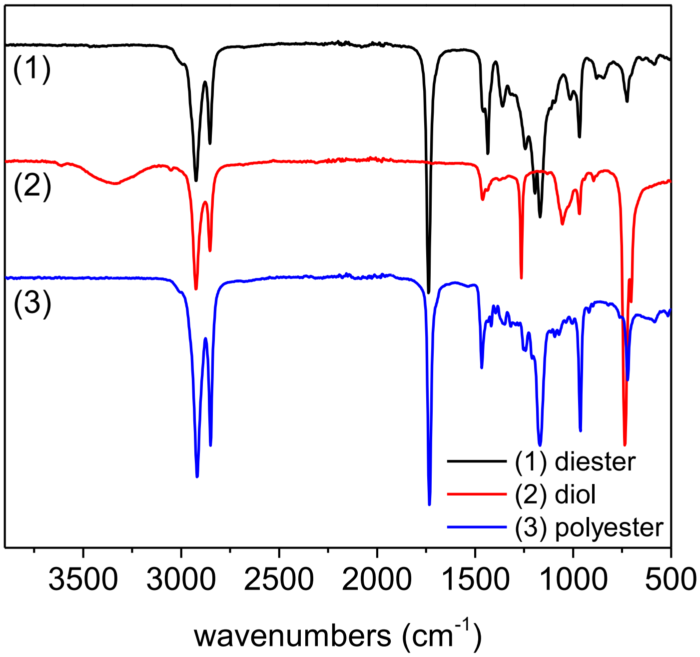


Figure 2.8. FTIR-ATR spectrum of (1) dimethyl-9-nonadecene-1,18-dioate, (2) 9-octadecene-1,18-diol (solution in DCM), (3) poly(1,18-9-nonadecendiyl-1,18-9-nonadecenedioate).

For polycondensation of several monomers, the ratio of each components is a critical factor that directly influences the molecular weight of ultimate polymers and it should be exactly controlled. Therefore, highly pure monomers are the prerequisite to obtain high molecular weighted polymer. Monomers were characterized by ^{1}H NMR and ^{13}C NMR. The purities of diester and diol were confirmed by ^{1}H NMR. ^{1}H NMR spectra clearly indicate the complete conversion from diester (Figure 2.9X) to diol (Figure 2.9Y). Diester peak (c) at 2.29ppm fully disappeared and the singlet at 3.65 ppm (b) turns to a triplet.

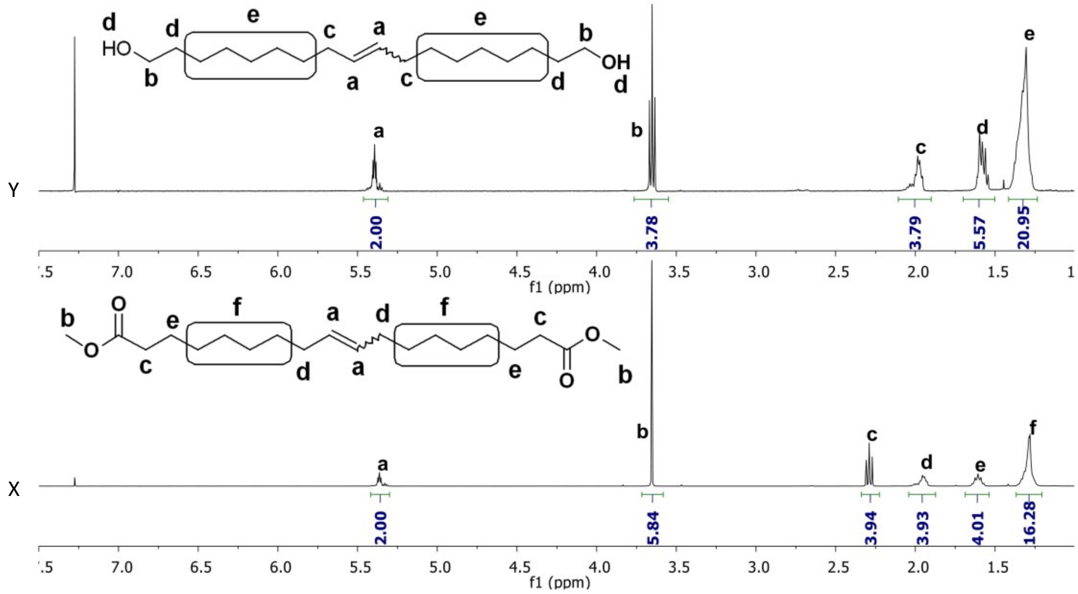


Figure 2.9. ^{1}H NMR spectra of dimethyl-9-nonadecene-1,18-dioate and 9-nonadecene-1,18-diol.

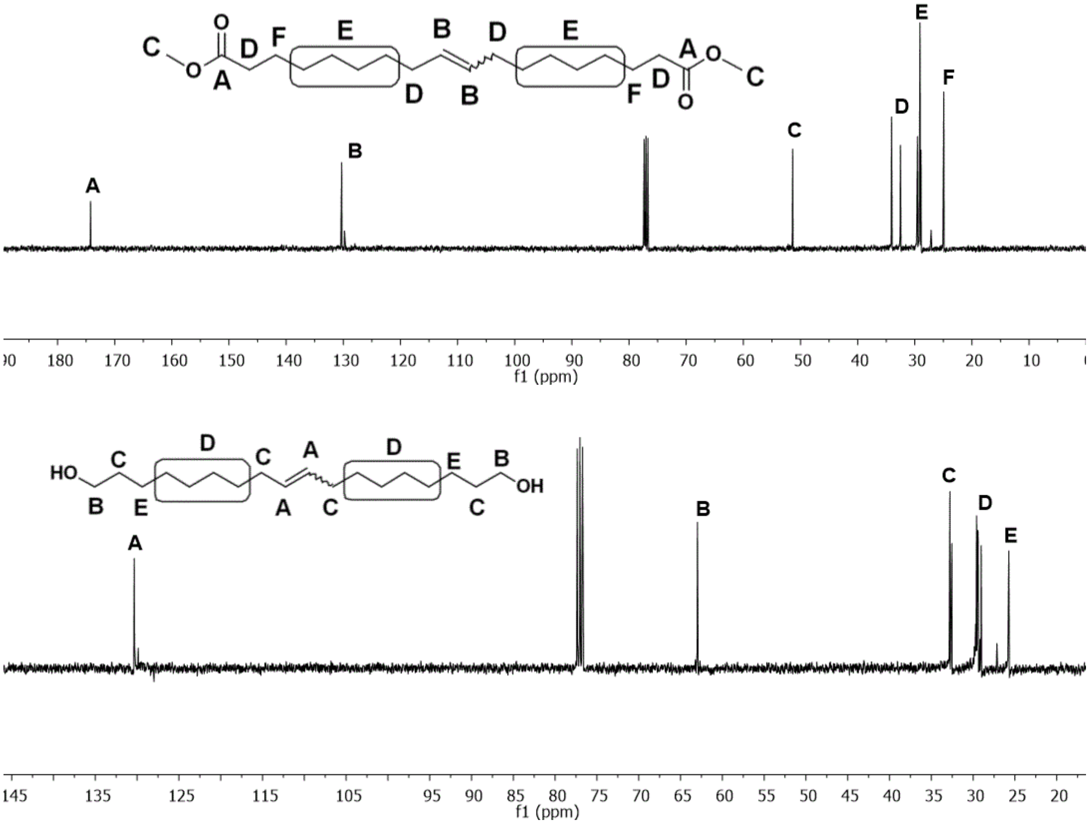


Figure 2.10. ^{13}C NMR spectra of dimethyl-9-nonadecene-1,18-dioate and 9-nonadecene-1,18-diol.

The obtained polyester was yellow solid at room temperature. It was insoluble in most of solvents, such as THF, hexane, ethyl acetate. Polyester ATR-FTIR spectrum was presented in

Figure 2.8. Peaks at 1733 cm^{-1} (C=O) and 1169 cm^{-1} (C-O-C) confirmed the existence of ester group. The polyester was also characterized by ^{1}H NMR. After attribution of peaks to corresponding protons (Figure 2.11), two small peaks were observed at 3.66 ppm (singlet), 3.65 ppm (triplet). By comparison to ^{1}H NMR spectra of diol and diester, these two peaks are attributed as $-CH_2OH$ and $-OCH_3$, the residuals of ester and hydroxyl terminal groups. The terminal groups are helpful for the determination of number average molecular weight(Mn) of polyester. Using the integration of typical peaks, degree of polymerization (DP), which means the average number of repeated units in the polymer, can be calculated. Herein, (b/4)×2 ("b" represent peak area of $-OCH_3$) was the amount of original functional groups. After polycondensation, only (h/3)+(g/2) functional groups left in both ends. Therefore, DP equals to (b/4)×2/[(h/3)+(g/2)]. Mn was calculated by multiplying DP with molar mass of repeated unit (560.87 g/mol), whose estimated value was 28763 g/mol in this case.

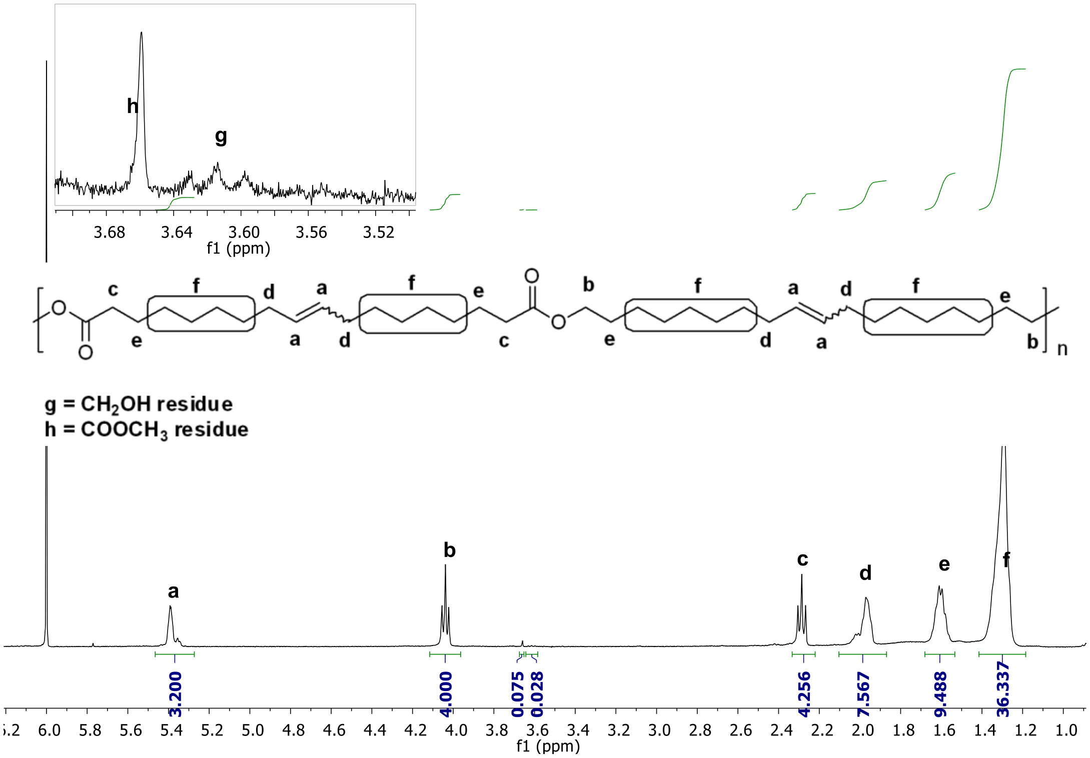


Figure 2.11. ^{1}H NMR spectrum of polyester.

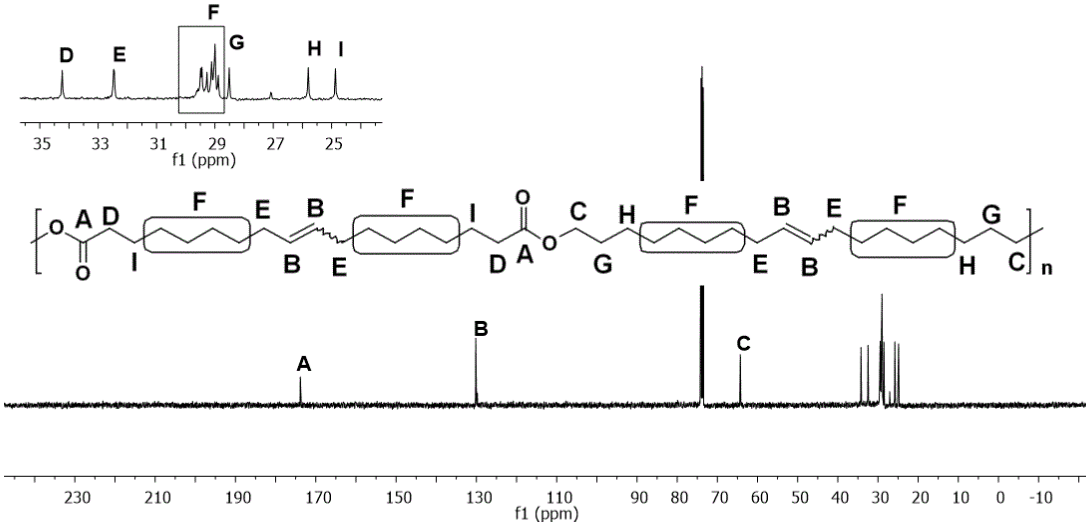


Figure 2.12. ^{13}C NMR spectrum of polyester.

2.3.8. Polycondensation by Conventional Heating

To explore optimum conditions for polyester preparation, experiments of different catalysts with different time intervals were recorded as shown in Table 2.5. Theoretically, with extended reaction time, the molecular weight of polyester increased correspondingly. The comparison of Mn data of entries 1 & 2 and entries 3 & 4 from Table 2.5 agreed with this cognition. Using 2% $SnCl_2$ as catalyst, Mn reached to 30 kDa after 16h reaction.

Entry	Catalyst	Time (h)	Tm (ºC)	ΔHm (J/g)	Mn (kDa)
1	2% $Ti(OBu)_4$	8	50.6	87.5	20.0
2	2% $Ti(OBu)_4$	16	49.8	78.9	28.8
3	2% $SnCl_2$	8	51.6	85.4	25.3
4	2% $SnCl_2$	16	50.0	78.8	30.2

Table 2.5. Polycondensation of diester/diol using 2 kinds of catalyst for 8 and 16 hours, respectively.

The polyesters were characterized by DSC. Melting temperature (Tm, recorded values of melting peak summit) of the four entries in Table 2.5 was between 50 – 52 ºC, which was not affected by molar mass. However, the melting point of polyester prepared unsaturated long-chain monomers are lower than saturated polyesters. Mecking and his colleagues have prepared aliphatic saturated long-chain C19 (Quinzler & Mecking, 2010) and C20 (Trzaskowski et al., 2011) polyesters. Their corresponding Tm are both 103ºC and ΔHm are 144 J/g and 178 J/g, respectively, which are comparable to low density polyethylene (LDPE). The reported high ΔHm values indicate that these saturated polyesters possess higher degree of crystallization. In our cases, ΔHm is only 78-88 J/g. The double bonds in unsaturated polyester restrict the free motion of hydrocarbon chain in our cases, and therefore, the arrangement of unsaturated long-chain in microstructure is less organized than saturated polyester, which leads to lower degree of crystallization and melting point.

2.3.9. Microwave Assisted Polycondensation

Microwave-induced polycondensation of diester/diol was carried out in a microwave tube using open vessel mode. Trials under high vacuum using 2% $Ti(OBu)_4$ and $SnCl_2$ were attempted initially. Nevertheless, irradiated by microwaves for only few seconds, blue plasma occurred. The starting materials were charred and glassware was destroyed immediately (Figure 2.13a). It was explained that the microwave energy was mostly absorbed by the polymer debris attached on the vessel wall and caused a sharp temperature rise of glassware under high vacuum (Nagahata et al., 2007). Furthermore, the vacuity was decreased to ~0.1 bar, and condensation polymerization was carried out again. Unfortunately, experiment using $Ti(OBu)_4$ as catalyst failed again with the occurrence of plasma.

Entry	Atmosphere	Time (min)	Tm (°C)	ΔHm (J/g)
1	N_2	15	50.9	111.4
2	N_2	60	50.6	97.2
3	0.1bar vacuo	60	51.0	108.6

Table 2.6. Polycondensation of diester/diol using 2% $SnCl_2$ under microwave conditions at 200 °C.

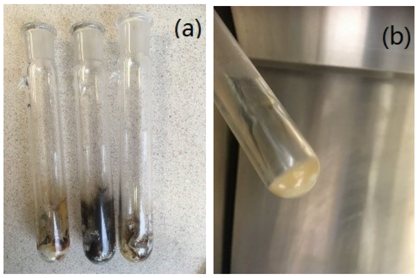


Figure 2.13. (a) The charred starting material and broken vessel by microwave under high vacuum. (b) polyester prepared by microwave assisted method.

$Ti(OBu)_4$ was replaced by $SnCl_2$, and microwave assisted reactions were attempted under nitrogen atmosphere and 0.1 bar vacuum, separately. Plasma was not observed anymore. The formation of polymer was accomplished within 15min (entry 1, Table 2.6), while by conventional polymerization, the required time was much longer. In addition, melting point of polyesters from microwave induced method also falls in the range of 50 - 51°C, as compared to the polyesters obtained by heating method.

However, melting enthalpy (ΔHm) of polyesters (Table 2.6) from microwave assisted method are much higher than those from heating method (Table 2.5). As we discussed above, ΔHm is a valuable index of degree of crystallization. Generally, for polymer with same structure, the increase of molecular length, will results in more difficulty of crystallization. Though quantitative relation could not be determined, ΔHm will generally decrease with the rise of molecular weight. This point of view was confirmed by comparing polyesters prepared by both heating and microwave methods. The molecular weight of polyester from conventional method is obviously higher than that by microwave irradiation, which will be discussed next.

With the assistance of vacuum, molar mass of entry 3 ought to be higher than entry 2 (Table 2.6). However, ΔHm of entry 3 was obviously higher than entry 2 by 11.4 J/g. The evaporation of diol and diester monomers under vacuum may be a possible reason for the higher ΔHm. In microwave reactor, temperature was raised to 200 °C so rapid that some monomers got evaporated under vacuum before they were converted to oligomers. The ratio of two different functional groups cannot be kept exactly at 1:1, which leads to a lower molecular weight. In consideration of monomer evaporation, the polycondensation was carried out under nitrogen atmosphere for 15min initially and then vacuum was applied.

Entry	T (°C)	Time (min)	Tm (°C)	ΔHm (J/g)
1	200	15	51.2	100.0
2	200	30	51.4	96.5
3	200	60	50.1	94.2
4	200	90	51.1	94.6
5	220	15	50.8	103.9
6	220	30	50.9	97.0
7	220	60	50.4	106.5

Table 2.7. Polycondensation of diester/diol using 2% $SnCl_2$ under 0.1bar under microwave conditions. Initially it was implemented in N_2 atmosphere for 15mins.

The conditions were optimized and results were recorded in Table 2.7. ΔHm decreased slowly at 200 °C with increase of reaction time, which can be observed from entry 1-3. After 1h, ΔHm did not distinctly change any more. Once temperature was increased to 220 °C, a rise of ΔHm occurred from 30 min to 1 h (entry 6, 7), which might be the result of polymer degradation. Molar mass of entry 3 was measured by ^{1}H NMR and it was determined that Mn was equal to 16.1 kDa. It confirms that the microwave induced method helps to achieve polycondensation process in short time. However, due to limitations of high vacuum utilization, molecular weight of polyester cannot be improved to the level achieved by conventional method. In addition, the hardness and strength of polyesters in Table 2.7 at room temperature were obviously lower than polyesters from conventional heating.

2.3.10. Coupled Microwave and Heating Energy for Polycondensation

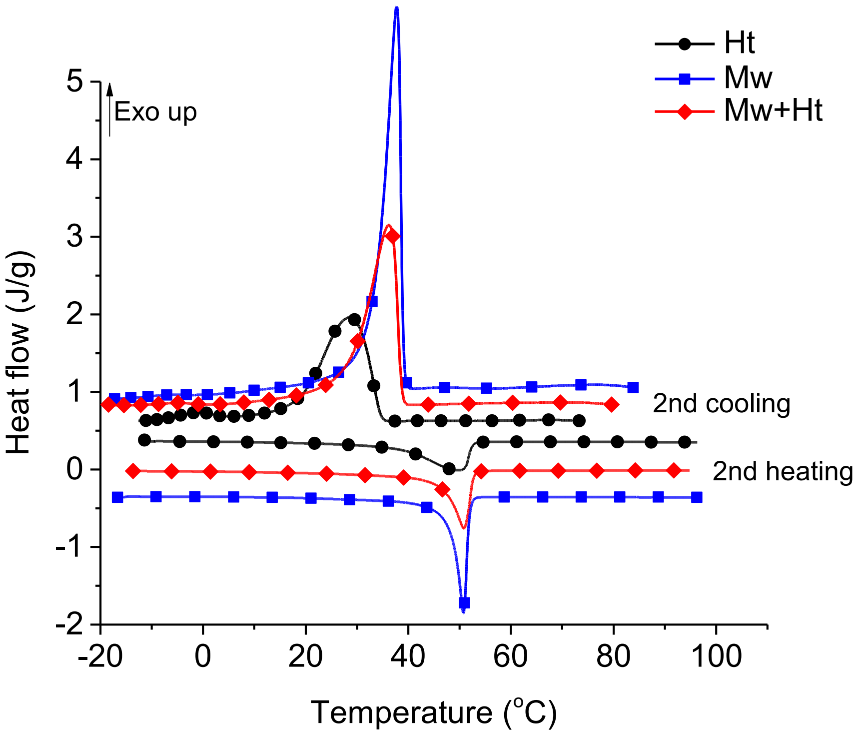


Figure 2.14. DSC curves of polyesters using (1) conventional heating (entry 4, Table 2.5), (2) microwave irradiation (entry 3, Table 2.7) and (3) coupled methods.

Considering the worse mechanical property of microwave-assisted polyester, a coupled method for polycondesation was established. These polyesters were then heated to 200 °C on a hot plate under high vacuum by oil pump for further polymerization. The heat source was removed after 2.5 h to obtain much stronger and harder polyester. Molar mass determined by ^{1}H NMR reached to 22.7 kDa, approximately equivalent to the polyester from conventional heating in 8 h (Entry 1 & 3, Table 2.5). Using coupled method, total reaction time was cut to less than 4 h. DSC curve of polyester from coupled method is presented in Figure 2.14, whose melting peak and crystallization peak are medium by comparison to the polyesters from heating or microwave irradiation. A distinct increment of ΔHm to 86.75 J/g was observed, which is also close to those of entries 1 & 3 in Table 2.5.

2.3.11. Thermal Properties of Polyester

Polyesters obtained by both heating and microwave method displayed similar TGA curves. Therefore, only the curves of polyester from heating method were plotted in Figure 2.15. Weight loss started at ~350 °C and ended before 500 °C. Two peaks were observed in between 400 - 500 ºC region of the derived weight loss curve. From literature review, the decomposition temperature of polyethylene terephthalate is in the range of 283 - 306 ºC (Bawn, 1987), which is much lower than the observed range of polyester in this case. The high boiling points of two C18 residuals after the breakdown of ester groups (with or without carbonyl group) might be the reason for delayed weight loss derivative signal of TGA. Though the polyester might already be degraded to monomers before 400 ºC, the monomer debris were prone to remain in TGA pan until the temperature was close to their boiling points.

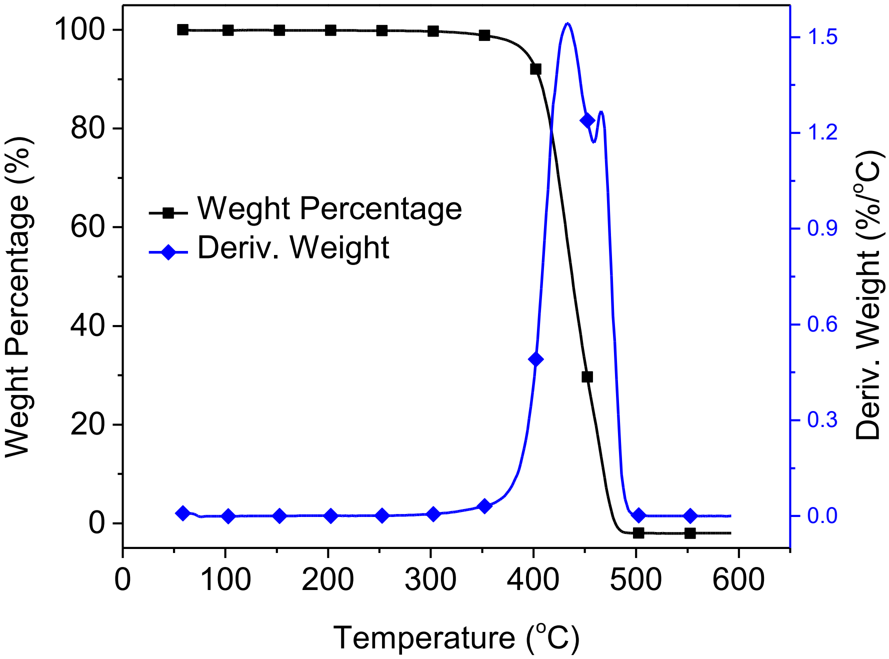


Figure 2.15. TGA and DTGA curves of polyester.

2.3.12. Mechanical Strength of Polyester

Figure 2.16. Films of polyester from conventional heating (left) and coupled methods (right).

For the preparation of polyesters films (Figure 2.16), the polymer powder was hot pressed using a Carver Press. The mechanical strength of polyesters was determined by tensile test. For polymer from microwave and heating coupled method, break stress of 2.3 MPa was observed, while for polymer from classic heating, maximum break stress could reach 5.5 MPa. However, the elongation at break of polyester from coupled method is up to 11%, twice as much as of polyesters from heating. The molar mass of polyester from coupled method is still lower than polyesters obtained by conventional heating for 16 h, which is the reason why its hardness and strength are lower. To further improve its mechanical properties, reaction time should be extended.

Entry	**Stress (MPa)**	**Elongation at break (%)**	**Elasticity (MPa)**
Ht1	5.47	7.0	239
Ht2	4.91	4.5	293
Mw+Ht1	2.34	11.0	110
Mw+Ht2	2.33	11.3	104

Table 2.8. Stress, strain and elasticity of polyester prepared from different methods.

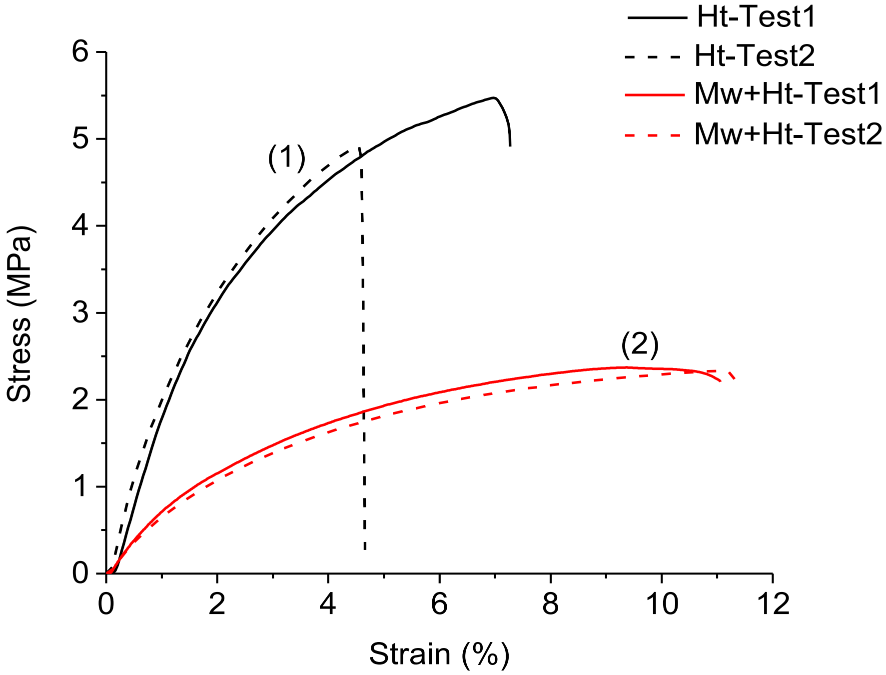


Figure 2.17. Mechanical tests of polyesters from heating (polymer 1, entry 4, table 2.5) and coupled methods (polymer 2).

2.3.13. Viscoelastic Properties

The dynamic mechanical properties of polymers from two methods were analyzed, as shown by Figure 2.18. Due to higher rigidity of polymer 1, it broke down below -50 ºC, so the temperature range was set above -50 ºC. A peak at -60 ºC occurred in tan delta curve of polymer 2, which might indicate glass transition temperature of polyester. Another peak at 13ºC in tan delta curve was observed for polymer 1, which did not appear in the tan delta curve of polymer 2. Considering the molecular weight and thermal history of polymer 1 and 2, recrystallization of polymer 1 might take place at such temperature, which led to the increment of tan delta. The molecular weight of polymer 2 was relatively lower, so its crystallization was complete and no recrystallization occurred during temperature rise. Once the temperature was above 50 ºC, storage modulus went down rapidly to 0 while the tan delta soared to higher value for both polymer 1 and 2. The polymers turned to viscous state after 50 ºC, which was coincident with Tm values from DSC measurements.

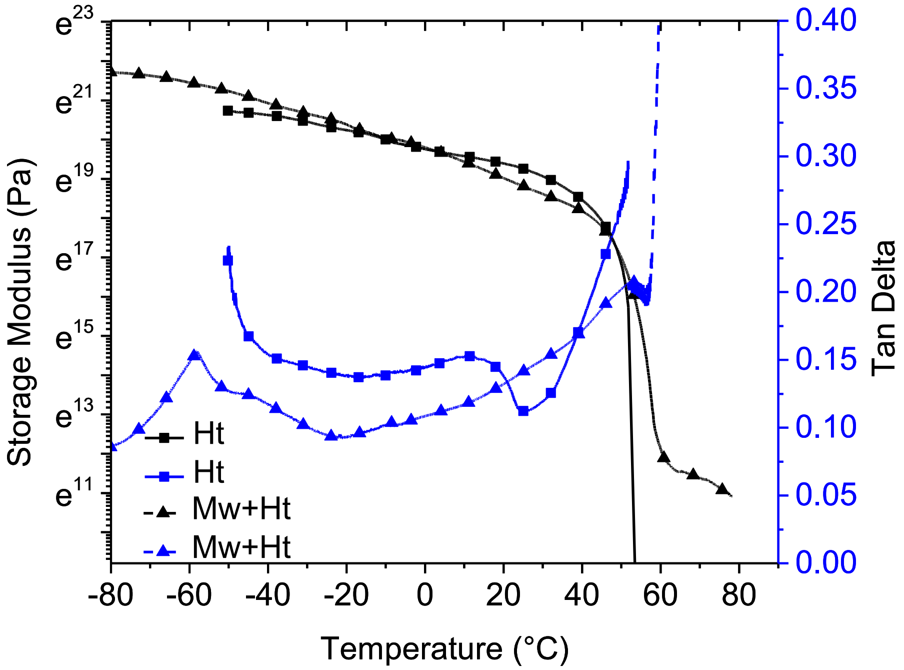


Figure 2.18. DMA curves of polyesters from heating (polymer 1, entry 4, Table 2.5) and coupled methods (polymer 2).

2.4. Conclusion

Self-metathesis of FAMEs from different sources was completed within 2 min providing ~50% conversion using microwave technique. The products of self-metathesis were identified and quantified by GC-MS and GC-FID analysis. The same conversion was achieved in 6 mins, once HG2 catalyst loading was decreased from 0.05% to 0.01%. Diester was separated from self-metathesis products of FAME. Diol with high purity and yield was obtained by reduction of diester. Polycondensation of diester and diol was carried out using both conventional heating and microwave irradiation. The polyesters were characterized by various analytical techniques including NMR, ATR-FTIR, DSC, TGA and DMA. From the results, the melting temperature of polyesters were among 50 – 52 °C showing that molecular weight variations have no effect on Tm. Using microwave energy, rapid polymerization was achieved, giving polyester with molar mass (Mn = 16,100 g/mol). Its Mn value is half as compared to the polyester (Mn = 30,200 g/mol) obtained by classic heating due to limitation of high vacuum utilization. Combining microwave and traditional heating, strong and hard polyester was produced with higher molecular weight (Mn = 22,700g/mol) within 4 hours. Polyester of such molecular weight takes 8 hours by conventional heating. Its break stress was 2.3 MPa with 11% elongation.

2.5. References

Bawn, C. (1987). Encyclopedia of polymer science and engineering: JI Kroschwitz, HF Mark, N. Bikales, CG Overberger and G. Menges (eds.) John Wiley and Sons, New York, 1985, 906 pages, US $240,£ 170, ISBN 0-471-89540-7: Elsevier.

Cao, H. L., Wang, P., & Yuan, W. B. (2009). Microwave‐Assisted Synthesis of Poly (L‐lactic acid) via Direct Melt Polycondensation Using Solid Super‐Acids. *Macromolecular Chemistry and Physics, 210*(23), 2058-2062.

de la Hoz, A., Diaz-Ortiz, A., & Moreno, A. (2005). Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chemical Society Reviews, 34*(2), 164-178.

Doll, K. M. (2014). Increased functionality of methyl oleate using alkene metathesis. *International Journal of Sustainable Engineering, 7*(4), 322-329.

Forman, G. S., Bellabarba, R. M., Tooze, R. P., Slawin, A. M., Karch, R., & Winde, R. (2006). Metathesis of renewable unsaturated fatty acid esters catalysed by a phoban-indenylidene ruthenium catalyst. *Journal of Organometallic Chemistry, 691*(24), 5513-5516.

Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L., & Rousell, J. (1986). The use of microwave ovens for rapid organic synthesis. *Tetrahedron Letters, 27*(3), 279-282.

Kohashi, H., & Foglia, T. A. (1985). Metathesis of methyl oleate with a homogeneous and a heterogeneous catalyst. *Journal of the American Oil Chemists Society, 62*(3), 549-554.

Lidström, P., Tierney, J., Wathey, B., & Westman, J. (2001). Microwave assisted organic synthesis—a review. *Tetrahedron, 57*(45), 9225-9283.

LUO, J., CAI, C., & Lü, C.-x. (2003). Microwave-promoted Halogen-exchange Reaction for Preparation of Fluoronitrobenzenes: Selection of Solvents and Their Properties in Microwave Field [J]. *Fine Chemicals, 1*, 016.

Meier, M. A., Metzger, J. O., & Schubert, U. S. (2007). Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews, 36*(11), 1788-1802.

Mutlu, H., Hofsäß, R., Montenegro, R. E., & Meier, M. A. (2013). Self-metathesis of fatty acid methyl esters: full conversion by choosing the appropriate plant oil. *RSC Advances, 3*(15), 4927-4934.

Nagahata, R., Sano, D., Suzuki, H., & Takeuchi, K. (2007). Microwave‐Assisted Single‐Step Synthesis of Poly (lactic acid) by Direct Polycondensation of Lactic Acid. *Macromolecular Rapid Communications, 28*(4), 437-442.

Quinzler, D., & Mecking, S. (2010). Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angewandte Chemie International Edition, 49*(25), 4306-4308.

Roesle, P., Stempfle, F., Hess, S. K., Zimmerer, J., Río Bártulos, C., Lepetit, B., . . . Mecking, S. (2014). Synthetic polyester from algae oil. *Angewandte Chemie International Edition, 53*(26), 6800-6804.

Rybak, A., Fokou, P. A., & Meier, M. A. (2008). Metathesis as a versatile tool in oleochemistry. *European Journal of Lipid Science and Technology, 110*(9), 797-804.

Santacesaria, E., Sorrentino, A., Rainone, F., Di Serio, M., & Speranza, F. (2000). Oxidative cleavage of the double bond of monoenic fatty chains in two steps: a new promising route to azelaic acid and other industrial products. *Industrial & Engineering Chemistry Research, 39*(8), 2766-2771.

Srikanth, V., Prasad, R., Poornachandra, Y., Babu, V. P., Kumar, C. G., Jagadeesh, B., & Jala, R. C. R. (2016). Synthesis of dihydrosterculic acid-based monoglucosyl diacylglycerol and its analogues and their biological evaluation. *European Journal of Medicinal Chemistry, 109*, 134-145.

Thanh, G. V., & Loupy, A. (2003). Microwave-assisted ruthenium-catalyzed olefin metathesis under solvent-free conditions. *Tetrahedron Letters, 44*(51), 9091-9094.

Trzaskowski, J., Quinzler, D., Bährle, C., & Mecking, S. (2011). Aliphatic Long‐Chain C20 Polyesters from Olefin Metathesis. *Macromolecular Rapid Communications, 32*(17), 1352-1356.

Türünç, O., & Meier, M. A. (2010). Fatty Acid Derived Monomers and Related Polymers Via Thiol‐ene (Click) Additions. *Macromolecular Rapid Communications, 31*(20), 1822-1826.

Türünç, O., & Meier, M. A. (2013). The thiol‐ene (click) reaction for the synthesis of plant oil derived polymers. *European Journal of Lipid Science and Technology, 115*(1), 41-54.

Ullah, A., & Arshad, M. (2017). Remarkably Efficient Microvawe‐Assisted Cross‐Metathesis of Lipids in Solvent Free Conditions. *ChemSusChem*.

Van Dam, P., Mittelmeijer, M., & Boelhouwer, C. (1972). Metathesis of unsaturated fatty acid esters by a homogeneous tungsten hexachloride–tetramethyltin catalyst. *Journal of the Chemical Society, Chemical Communications*(22), 1221-1222.

Velmathi, S., Nagahata, R., Sugiyama, J. i., & Takeuchi, K. (2005). A Rapid Eco‐Friendly Synthesis of Poly (butylene succinate) by a Direct Polyesterification under Microwave Irradiation. *Macromolecular Rapid Communications, 26*(14), 1163-1167.

Wroe, R., & Rowley, A. (1996). Evidence for a non-thermal microwave effect in the sintering of partially stabilized zirconia. *Journal of Materials Science, 31*(8), 2019-2026.

Chapter 3 Rapid Copolymerization of Canola Oil Derived Epoxy Monomer with CO_2/Anhydride

3.1. Introduction

Petroleum-derived polyesters and polycarbonates find applications in various industrial sectors including packaging, automotive, adhesives, construction and other industrial fields. Currently, the majority of polyesters and polycarbonates are produced through polycondensation of diols with diacids or phosgene, respectively. Nevertheless, the current method is energy intensive, requires high temperature, high vacuum and long reaction times to achieve appropriate molecular weight. In order to replace the unfriendly and health detrimental chemicals, particularly phosgene, a novel route of coupling CO_2 with epoxides to yield polycarbonates is attracting academic and industrial attention (Inoue, Koinuma, et al., 1969; Schneider & Diller, 2000; Soga et al., 1981; X. K. Sun et al., 2008). Indeed, substituting phosgene by CO_2 not only reduces risk for its transportation, manufacturing and storage, but also aids to recycle the greenhouse gas and retards its negative impact on global warming (Schmalensee et al., 1998). Moreover, utilization of such an abundant resource will bring substantial benefits to both polymer and chemical industries. The synthesis of different CO_2-based polycarbonates has already been reported. As an example, poly (propylene carbonate) finds applications in food packaging and disposable tableware (Luinstra & Borchardt, 2011; Seo, Jeon, Jang, Bahadar Khan, & Han, 2011).

Likewise, the ring-opening copolymerization of epoxides with cyclic anhydrides to prepare polyesters is now being investigated as an alternative route to avoid some of the disadvantages of polycondensation process mentioned above. The polyesters of different properties could be prepared using different combinations of anhydrides and epoxides. The copolymerization of maleic anhydride with synthetic epoxides, such as epoxybutane and phenyl glycidyl ether, catalyzed by (salen)CrCl has recently been reported (DiCiccio & Coates, 2011).

The most commonly investigated epoxides for the preparation of polyesters and polycarbonates include propylene oxide (S. Chen, Hua, et al., 2004; Qin et al., 2003; M Ree et al., 1999) and cyclohexene oxide (Bok, Yun, & Lee, 2006; D. J. Darensbourg et al., 2004; Mang, Cooper, Colclough, Chauhan, & Holmes, 2000), which are mainly derived from petroleum resources.

Various catalytic systems have been designed for the copolymerization of epoxides with anhydrides or CO_2, such as metal salen system(Paddock & Nguyen, 2001), zinc β-diiminate system (Cheng et al., 2001) and zinc dicarboxylates (Moonhor Ree et al., 2006). Due to the complex synthesis, low activity and high cost of these catalysts, the double metal cyanide (DMC) catalyst has recently emerged as an active and stable for ring-opening polymerization of aliphatic and aromatic epoxides (Zhang, Wei, Zhang, Du, & Fan, 2015).

More recently, due to dwindling fossil fuel resources and environmental concerns, both academia and industry have focused their attention on the development of biopolymers from renewable resources which could be eco-friendly and potentially biodegradable.

Plant oils are abundant resources to satisfy industrial demands besides food utilization. The presence of double bonds in fatty acid chains provides multiple choices to convert them into various products, such as epoxides (Chua, Xu, & Guo, 2012), fuels (Liu, He, Wang, Zhu, & Piao, 2008), detergents (Ohlrogge, 1994) and other fine chemicals (Warwel, 1999). Canada is among the largest producers of canola oil. Canola oil comprises of ~94% unsaturated fatty acids and especially oleic acid is accounted for high proportion ~60% (Przybylski, 2001). Ethenolysis, a term specially referring to olefin metathesis with ethylene, is a versatile and green reaction to prepare α-olefins from plant oil methyl esters (Schrodi et al., 2008; Ullah & Arshad, 2017). The terminal double bond of α-olefins offers great activity for further modification and polymerization. We used 1-decene as a model olefinic starting material which is main product from the ethenolysis of canola oil methyl esters (Thurier, Fischmeister, Bruneau, Olivier‐Bourbigou, & Dixneuf, 2008).

Microwave is clean energy widely used for rapid domestic food heating. The microwaves are not only applied for food warming but various organic synthesis reactions have also been carried out successfully utilizing microwave energy in shorter times (de la Hoz et al., 2005; Giguere et al., 1986). However, to the best of our knowledge, there is only few report on microwave induced copolymerization of cyclic epoxides with CO_2 (Dharman et al., 2008a, 2008b) and no report on copolymerization of epoxy with anhydride. Herein, for the first time, we report the ring-opening polymerization of 1-decene derived epoxy with CO_2, aliphatic and aromatic anhydrides under microwave irradiation conditions.

3.2. Experiments

3.2.1. Materials and General Consideration

Unless mentioned, all chemicals were used directly for the reactions and workups without further purification. M-chloroperbenzoic acid (≤77%), 1-decene (>94%), potassium hexacyanocobaltate(III) ($K_3Co(CN)_6$) (≥95%), phthalic anhydride(PA) (≥99%), itaconic anhydride(IA) (≥95%), cis-1,2,3,6-tetrahydrophthalic anhydride(THPA) (≥95%), succinic anhydride(SA) (≥97%), and diethyl amine (≥99.5%) were purchased from Sigma Aldrich. Zinc chloride anhydrous (>97.2%), maleic anhydride (MA) (≥99%) was purchased from Fisher Scientific. Dry ice (>99%) was obtained from Praxair (Edmonton, AB, Canada). Organic solvents like tetrahydrofuran (THF), dichloromethane (DCM), methanol, acetone, ethyl acetate and inorganic compounds, such as zinc chloride, potassium hydroxide, sodium sulfate, sodium hydroxide, sodium sulphate were all obtained from Sigma Aldrich. For solution polymerizations, solvents were stirred over CaH_2 for more than 3 days, and filtered in nitrogen atmosphere. $K_3Co(CN)_6$ was recrystallized from distilled water and dried overnight before usage.

^1H NMR (400MHz) and ^{13}C NMR (101MHz) spectrum of samples in deuterated chloroform were recorded on a Varian INOVA instrument at room temperature, using non-deuterated solvent residue shift as reference. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Nicolet 8700 spectrometer (Madison, WI, USA). For FTIR analysis, the dissolved solid or liquid samples were placed directly onto the surface of the ATR crystal and analyzed. The thermal degradation behaviors were investigated using Thermal Gravimetric Analysis (TGA) on Q50 TGA instrument in nitrogen atmosphere. Procedural temperature was increased from room temperature to 600 °C at a rate of 10 °C/min. DSC experiments were recorded on a TA instrument (2920 Modulated DSC, USA). Temperature was set to increase from -50 to 100 °C at a rate of 3 °C/min. DSC profiles of 2nd heating cycle were selected to eliminate material thermal history. Gel permeation chromatography (GPC) was performed on Agilent 1200 series using a Waters Styragel HR 4E THF 4.6×300 mm Column calibrated with polystyrene standards. We used reported procedures of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction spectroscopy (XRD) (Arshad, Kaur, & Ullah, 2016) to study catalyst surface. XPS analysis was carried out on ULTRA spectrometer (Kratos Analytical) with monochromatic Al Kα source ($h\nu = 1486.6$ eV) at a power of 140 W. Pressure of less than 3×10^{-8} Pa was applied in the analytical chamber. The data was collected for binding energy spanning from 1000 eV to 0 with analyzer pass energy of 160 eV and a step of 0.4 eV. XRD measurement was recorded on a Rigaku Ultima IV unit operated at 38 mA (current) and 38 kV (voltage) from 5 − 80° at a rate of 1° 2θ per minute with a step size of 0.02°.

3.2.2. Epoxidation of 1-decene

Epoxidation was carried out using reported procedure (Baylon, Heck, & Mioskowski, 1999) with some modifications. Briefly, in a 250 mL round bottom flask, 18.5 g meta-chloroperbenzoic acid was dispersed in 50 mL dichloromethane. The slurry was cooled on ice bath to 0 °C and then 10.0 g 1-decene was added slowly. After complete addition of decene, the contents were further diluted with 20 mL dichloromethane and stirred at room temperature overnight. The reaction was quenched by adding 50 mL of 20% Na_2SO_3 solution twice. The organic layer was separated, washed with 50 mL of 20% Na_2CO_3 solution three times, dried over Na_2SO_4 anhydrous, filtered and solvent removed by vacuum. Further purification was done by silica gel column chromatography using hexane/ethyl acetate (90:10) as mobile phase. The purified epoxy (10.1 g, 89.7% yield) was stirred over CaH_2 for about 3 days and filtered under nitrogen atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.95 – 2.82 (m, 1H), 2.73 (dd, *J* = 5.0, 4.0 Hz, 1H), 2.44 (dd, *J* = 5.1, 2.7 Hz, 1H), 1.64 – 1.16 (m, 14H), 0.89 (dt, *J* = 9.7, 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 52.32 (s), 47.03 (s), 32.48 (s), 31.83 (s), 29.46 (d, *J* = 6.5 Hz), 29.19 (s), 25.95 (s), 22.63 (s), 14.04 (s). IR: 2956 cm^{-1}, 2923 cm^{-1}, 2854 cm^{-1}, 1464 cm^{-1}, *1260 cm^{-1}*, 1129 cm^{-1}*, 916 cm^{-1}, 833 cm^{-1}(epoxy groups).*

3.2.3. DMC catalyst synthesis

DMC catalyst was synthesized using modified procedure reported by Yan and his co-workers(S. Chen, Qi, et al., 2004). Briefly, 2 g $ZnCl_2$ was dissolved in aquous solution of tert-butanol (2.5 ml H_2O + 2.5 ml tert-butanol) in a 20ml vial and then solution of $K_3Co(CN)_6$ (0.43 g in 5 ml water) was added dropwise into $ZnCl_2$ solution at 75 °C under vigorous stirring. The white precipitates appeared were centrifuged and washed with 50% aqueous tertiary butanol 6 times and then with pure tertiary butanol 3 times. The product was then dried in an oven at 70 °C overnight.

3.2.4. Representative microwave-induced copolymerization of 1,2-epoxydecane with CO_2

The microwave assisted copolymerizations were carried out in a single-mode microwave reactor (CEM Discover Labmate) equipped with infrared temperature sensor (Maximum pressure = 250 psi, maximum power = 200 W). An example copolymerization of epoxy with CO_2 under microwave heating conditions was as follows. For solution polymerizations, 0.3 mg DMC catalyst was added in a microwave reaction vessel equipped with a stir bar and purged with nitrogen for several minutes, then 1mmol 1,2-epoxydecane in 0.1 ml solvent (THF or hexane) and 0.3-0.4 g dry ice were added into the vial. The reaction vial was placed in the cavity of the microwave instrument and reaction conducted at specified temperature for required time. The bulk polymerizations were carried under similar conditions without solvent. The polymerization was quenched and obtained copolymer was dissolved in minimum amount of DCM and precipitated in excess methanol. Copolymer was filtered, washed with methanol for several times and dried in an oven at 60 ºC overnight. ^1H NMR (400 MHz, $CDCl_3$) δ 5.05 – 4.66 (m), 4.60 – 3.84 (m), 3.77 – 3.23 (m), 1.76 – 1.01 (m, 13H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.11 – 150.75 (m), 79.48 (s), 76.17 – 75.15 (m), 73.29 – 71.06 (m), 68.76 – 67.27 (m), 31.89 (d, *J* = 11.3 Hz), 30.50 (s), 29.55 (dd, *J* = 51.1, 18.0 Hz), 25.21 (d, *J* = 49.9 Hz), 22.68 (d, *J* = 5.4 Hz), 14.10 (s). IR: 2927cm^{-1}, 2855cm^{-1}, *1743cm^{-1} (C=O)*, *1113cm^{-1} (C-O-C ether).*

3.2.5. Representative microwave-induced copolymerization of 1,2-epoxydecane with anhydrides

The procedure was similar to the copolymerizations with CO_2 as described above. Briefly, 0.6 mg DMC catalyst was added in a microwave reaction vessel equipped with a stir bar and purged with nitrogen for several minutes, then 2 mmol 1,2-epoxydecane and 2 mmol anhydride were added into the vial. 0.2 mL THF was added except for the copolymerization of epoxy with maleic anhydride. The reaction vial was placed in the cavity of the microwave instrument, and copolymerizations were performed under programmed conditions. The polymerization was quenched and obtained copolymer was dissolved in minimum amount of DCM and precipitated in excess methanol. Copolymer was filtered, washed with methanol for several times and dried in oven at 60 ºC overnight. (**1**) Poly(1-decene-co-maleate): ^1H NMR (400 MHz, $CDCl_3$) δ 6.60 – 5.82 (m, 1.45H), 5.13 (d, *J* = 61.1 Hz, 0.74H), 4.61 – 4.06 (m, 1.56H), 3.98 – 3.21 (m, 0.50H), 2.03 – 1.08 (m, 14H), 0.90 (t, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16 – 163.94 (m), 130.29 – 128.87 (m), 73.09 – 71.67 (m), 65.63 – 64.47 (m), 31.84 (s), 30.54 (s), 29.31 (d, *J* = 19.8 Hz), 25.00 (s), 22.65 (s), 14.10 (s). IR: 2926 cm^{-1}, 2856 cm^{-1}, *1727 cm^{-1} (C=O), 1644 cm^{-1}(C=C)*, 1207 cm^{-1}, *1157 cm^{-1} (C-O-C ester).* (**2**) Poly(1-decene-co-succinate): ^1H NMR (400

MHz, $CDCl_3$) δ 5.07 (dt, *J* = 41.9, 20.9 Hz, 0.87H), 4.36 – 4.01 (m, 1.75H), 3.88 – 3.17 (m, 0.37H), 2.84 – 2.48 (m, 3.62H), 1.75 – 1.10 (m, 14H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.85 (d, *J* = 21.1 Hz), 71.91 (s), 65.21 (s), 31.83 (s), 30.68 (s), 29.13 (dd, *J* = 34.1, 19.9 Hz), 28.78 – 28.76 (m), 25.07 (s), 22.65 (s), 14.09 (s). IR: 2927 cm^{-1}, 2856 cm^{-1}, *1734* cm^{-1} *(C=O), 1154* cm^{-1} *(C-O-C ester)*. (**3**) Poly(1-decene-co-itaconate): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 0.05H), 5.85 (s, 0.23H), 5.77 (s, 0.05H), 5.09 (s, 0.47H), 4.20 (s, 1.10H), 3.42 (d, *J* = 46.8 Hz, 1.29H), 2.09 (d, *J* = 21.9 Hz, 1.05H), 1.80 – 0.99 (m, 14H), 0.90 (t, *J* = 6.3 Hz, 3H). IR: 2923 cm^{-1}, 2854 cm^{-1}, *1768* cm^{-1} *(C=O), 1728* cm^{-1} *(C=O), 1653* cm^{-1} *(C=C), 1163* cm^{-1} *(C-O-C ester), 1123* cm^{-1} *(C-O-C ether)*. (**4**) Poly(1-decene-co-phthalate): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.35 (m, 3.89H), 5.32 (d, *J* = 84.4 Hz, 1.46H), 4.45 (dd, *J* = 77.3, 30.7 Hz, 2.50H), 3.90 – 3.20 (m, 1.49H), 1.95 – 1.01 (m, 14H), 0.98 – 0.72 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.83 – 165.93 (m), 131.10 – 129.66 (m), 128.93 (d, *J* = 25.0 Hz), 128.56 – 128.28 (m), 73.67 – 71.97 (m), 66.32 – 65.37 (m), 31.85 (s), 30.74 (s), 29.34 (d, *J* = 21.0 Hz), 25.10 (s), 22.65 (s), 14.09 (s). IR: 2925 cm^{-1}, 2855 cm^{-1}, *1723* cm^{-1} *(C=O), 1599* cm^{-1}*, 1580* cm^{-1}*, 1492* cm^{-1}*, 1459* cm^{-1} *(phenyl)*, 1121 cm^{-1}, *1066* cm^{-1} *(C-O-C ester)*. (**5**) Poly(1-decene-co-tetrahydrophthalate): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (d, *J* = 9.3 Hz, 1.19H), 5.04 (d, *J* = 39.7 Hz, 0.76H), 4.08 (t, *J* = 84.6 Hz, 1.6H), 3.52 (d, *J* = 54.7 Hz, 0.98H), 2.96 (d, *J* = 59.6 Hz, 1.35H), 2.38 (dd, *J* = 84.5, 68.5 Hz, 2.61H), 1.42 (d, *J* = 114.9 Hz, 14H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.25 – 172.00 (m), 125.13 (s), 72.50 – 71.00 (m), 65.50 – 64.50 (s), 39.57 (s), 31.86 (s), 30.69 (s), 29.78 (t, *J* = 73.9 Hz), 27.00 – 24.50 (m), 22.66 (s), 14.10 (s). IR: 2924 cm^{-1}, 2855 cm^{-1}, *1730* cm^{-1} *(C=O), 1656* cm^{-1} *(C=C), 1181* cm^{-1} *(C-O-C ester), 1112* cm^{-1} *(C-O-C ether).*

3.2.6. Isomerization of poly(1-decene-co-maleate)

Post polymerization modification has several advantages including availability of more reactive groups for further reactions. Therefore, conversion of *cis* (less reactive form) to *trans* isomer which is more reactive was carried out as follows. The synthesized and purified poly(1-decene-co-maleate) was dissolved in chloroform and 0.1 equivalent of diethyl amine was added dropwise into the solution. The solution was kept at room temperature overnight. The volatiles were removed under vacuum.

3.3. Results & Discussion

3.3.1. Characterization of DMC catalyst

DMC catalyst was prepared using $ZnCl_2$, $K_3Co(CN)_6$ and tert-butanol as starting materials. Initially it was characterized by FT-IR and the spectrum was presented in Figure 3.1a. The υ(CN) shifts from 2126 cm^{-1} to a higher frequency (2197 cm^{-1}), which suggests the chelating of nitrile with the new metal (Zn^{2+}) center.

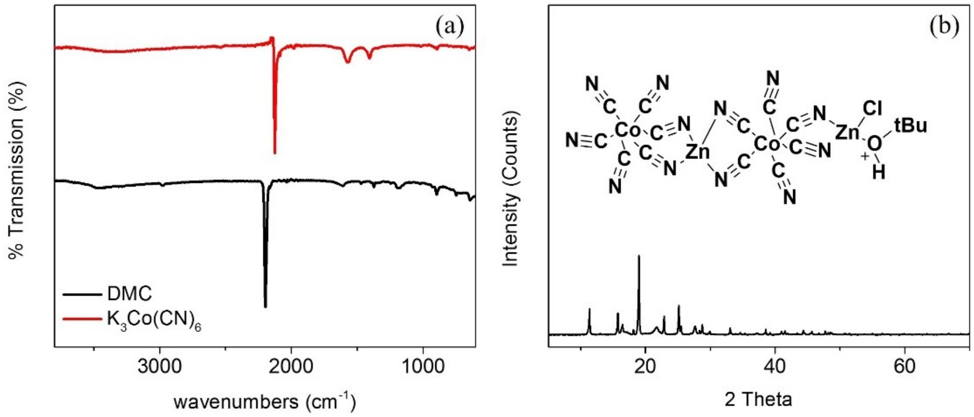
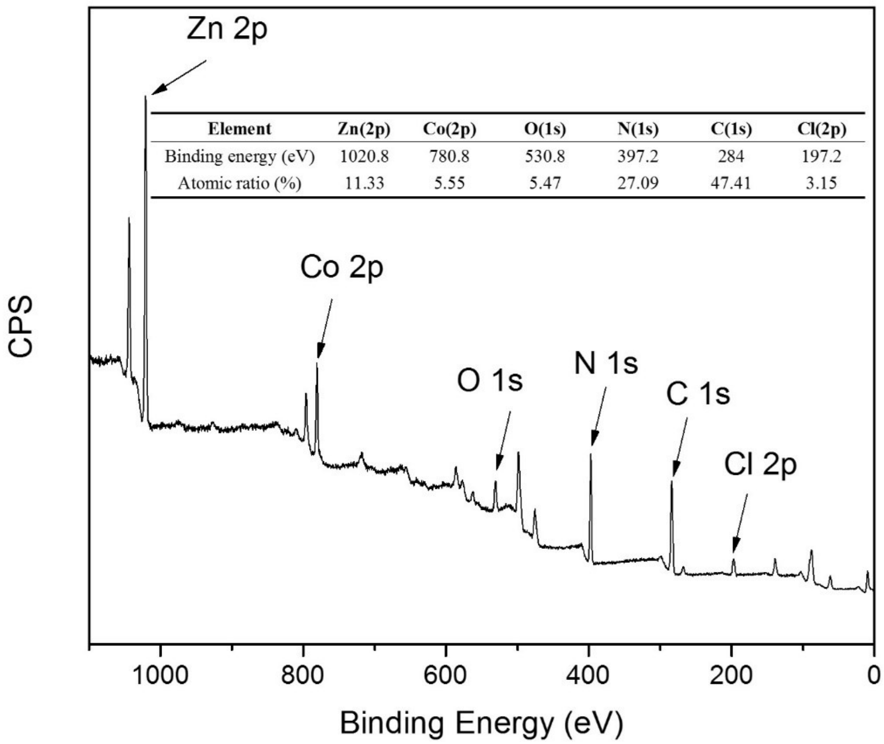


Figure 3.1. (a) ATR-FTIR spectra of DMC catalyst and $K_3Co(CN)_6$. (b) XRD patterns and proposed structure of DMC catalyst.

However, $Zn_3[Co(CN)_6]_2$, which is resulted from equivalent $ZnCl_2$ with $K_3Co(CN)_6$ has a highly crystallized structure, and is proven to be inactive for copolymerization of epoxy with CO_2 or anhydrides. It is believed that the introduction of excess $ZnCl_2$ and tert-butanol changes the surface structure and affords active sites for copolymerization. XRD pattern of DMC (Figure 3.1b) confirmed the change of crystal characteristics compared to XRD profile of $Zn_3[Co(CN)_6]_2$, which could be observed from the literature (Lawniczak - Jablonska et al., 2015). DMC was further characterized by XPS to figure out its elemental compositions on the surface. The existence of binding energy for Cl (2p) demostrated the incorporation of $ZnCl_2$. In addition, the characteristic absorption of O (1s) and the larger atomic ratio of carbon over nitrogen atom strongly indicated the chelating of catalyst metal with tert-butanol. Therefore, a proposal structure of DMC was given (Figure 3.1b).



Element	Zn(2p)	Co(2p)	O(1s)	N(1s)	C(1s)	Cl(2p)
Binding energy (eV)	1020.8	780.8	530.8	397.2	284	197.2
Atomic ratio (%)	11.33	5.55	5.47	27.09	47.41	3.15

Figure 3.2. XPS results of DMC catalyst.

3.3.2. Characterization of CO_2/epoxide Copolymer

The copolymerization of 1,2-epoxydecane with CO_2 was carried out under microwave conditions for 12 min at 70 ºC and 99 psi pressure. A purified copolymer with 91% conversion (65% yield) was obtained. The obtained viscos semi-solid copolymer having molecular weight of 11.3 kDa (Mw) was soluble in THF, DCM, chloroform, toluene and some other solvents, but not in methanol or ethanol.

The obtained molecular weight for copolymer under 12 minutes heating condition was lower than that of previously reported conventional copolymerization of CO_2 with epoxies including cyclohexene epoxide(Zhang et al., 2015). Nevertheless, the polymerization in this case was 74 times faster than that used for conventional heating methods reported above.

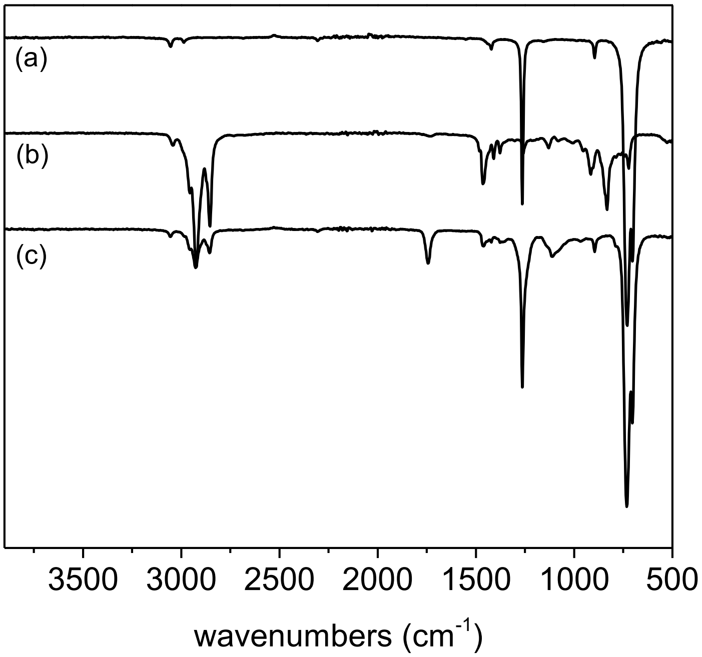


Figure 3.3. FTIR-ATR spectrum of solvent DCM (a), 1,2-epoxydecane (b), and poly(1-decene-co-carbonate) (c).

The synthesized epoxy monomer and copolymer were characterized by spectroscopic techniques. During copolymerization, the epoxies can homopolymerize to create ether linkages in addition to copolymerization with CO_2 leading to ester linkages. The ATR-FTIR spectra of the solvent DCM, monomer 1,2-epoxydecane, and copolymer poly(1-decene-co-carbonate) are presented in Figure 3.3. As can be seen from Figure 3.3b & 3.3c, the copolymer exhibits a peak at 1744 cm^{-1} which corresponds to the characteristic absorption of carbonate group, confirming the formation of polycarbonate. Nevertheless, in addition to carbonate absorption, a peak at 1113 cm^{-1} confirms the presence of ether linkage ν(C-O-C), suggesting that homopolymer part of epoxide also exists in addition to copolymer. Epoxy and copolymer were also characterized by ^1H NMR (Figure 3.4) and ^{13}C NMR (Figure 3.4 and 3.5). The existence of homopolymer were reconfirmed by ^1H NMR. The disappearance of distinctive epoxide peaks at chemical shifts of 2.95 - 2.82, 2.73 and 2.44 ppm (Figure 3.4X) confirms the conversion of epoxide into polymer. In addition, as evident from Figure 3.4Y, three broad peaks appearing in the range of δ 5.05-4.75 ppm, 4.60-3.84 ppm and 3.77-3.23 ppm further confirm the presence of both ether and ester linkages. The percentage of carbonate and ether linkage was calculated using integrations of ^1H NMR peaks as follows;

Carbonate linkage% = $(\text{-OCH-} + \text{-OCH}_2\text{-})/(\text{-OCH}_2\text{-} + \text{-OCH}_2\text{-} + \text{-OCHCH}_2\text{O-})\times 100\%$.

These calculations revealed that carbonate linkage was only 37.9%.

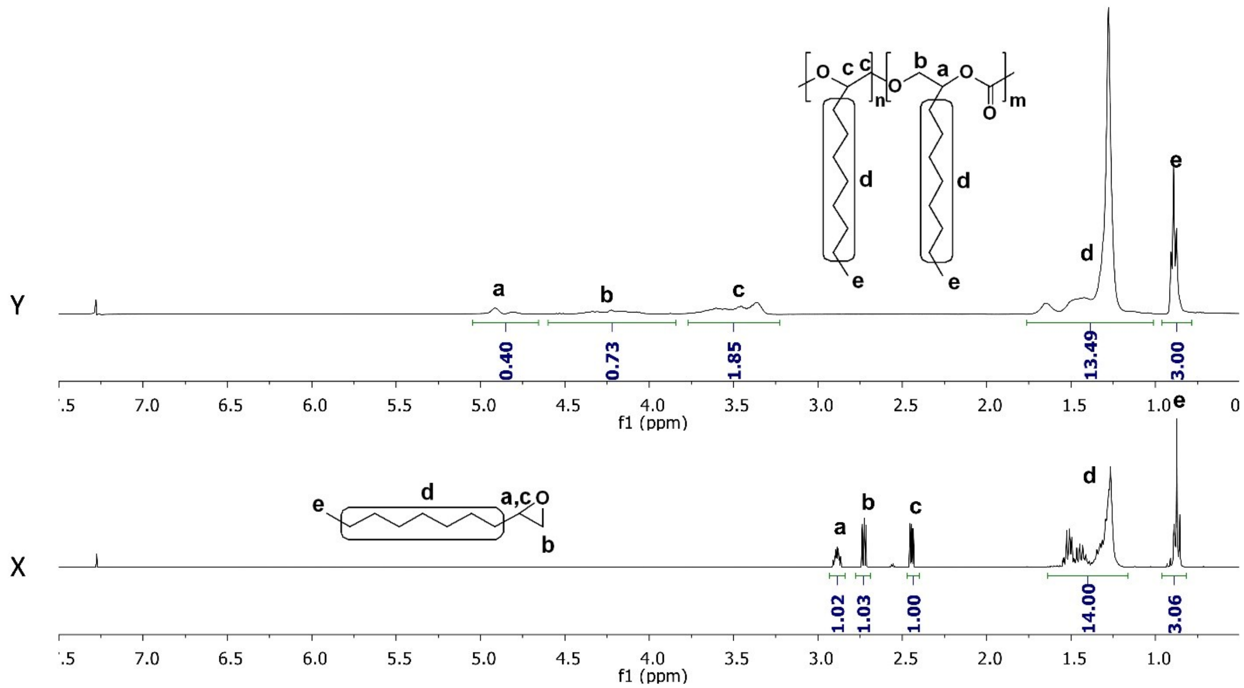


Figure 3.4. ^{1}H NMR spectra of 1,2-epoxydecane (X) and poly(1-decene-co-carboante) (Y).

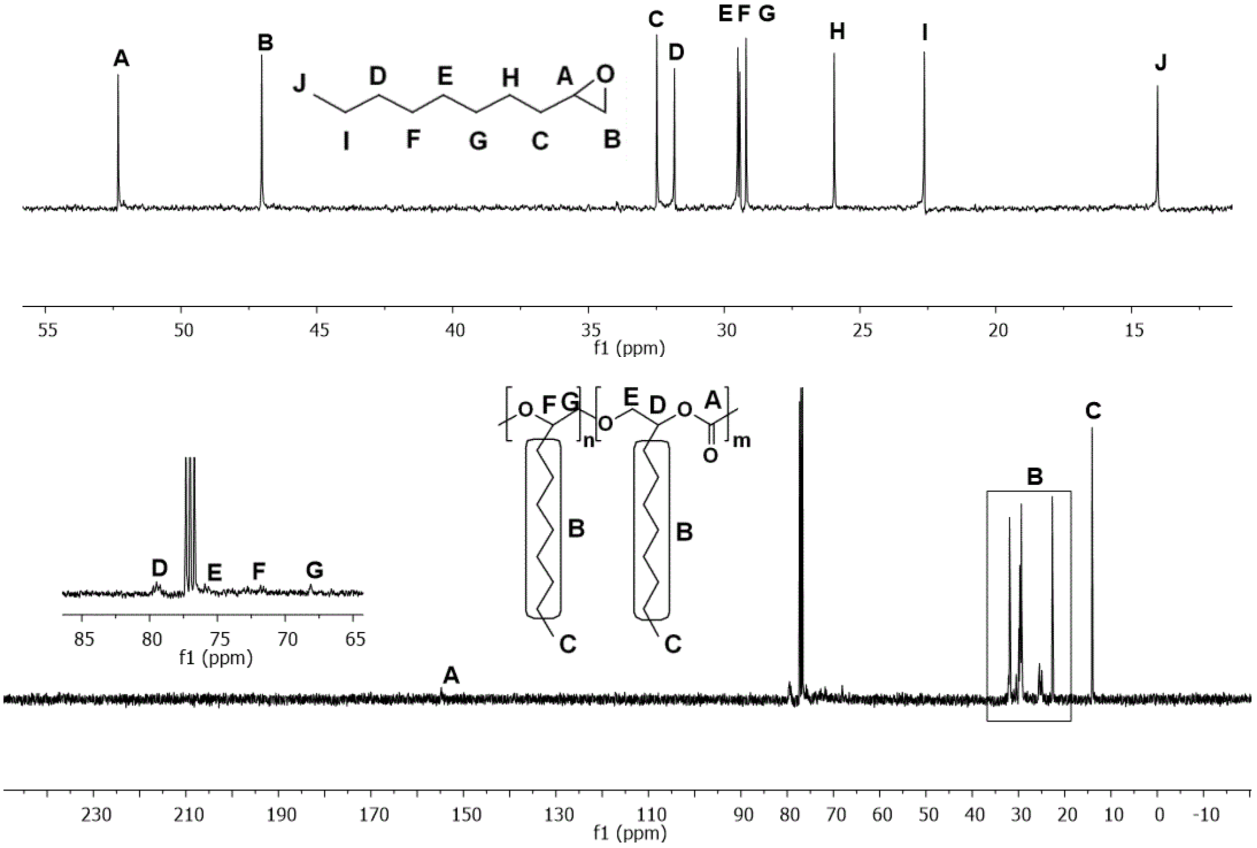


Figure 3.5. ^{13}C NMR spectra of 1,2-epoxydecane and poly(1-decene-co-carboante).

3.3.3. Characterization of Anhydride/epoxide Copolymer

The copolymerization of 1, 2-epoxydecane was also carried out with maleic anhydride (MA), succinic Anhydride (SA), phthalic anhydride (TA), itaconic anhydride (IA) and tetrahydrophthalic anhyride (THPA) under microwave conditions. The ATR-FTIR spectra of all copolymers are presented in Figure 3.3 and the characteristic absorptions listed in Table 3.1.

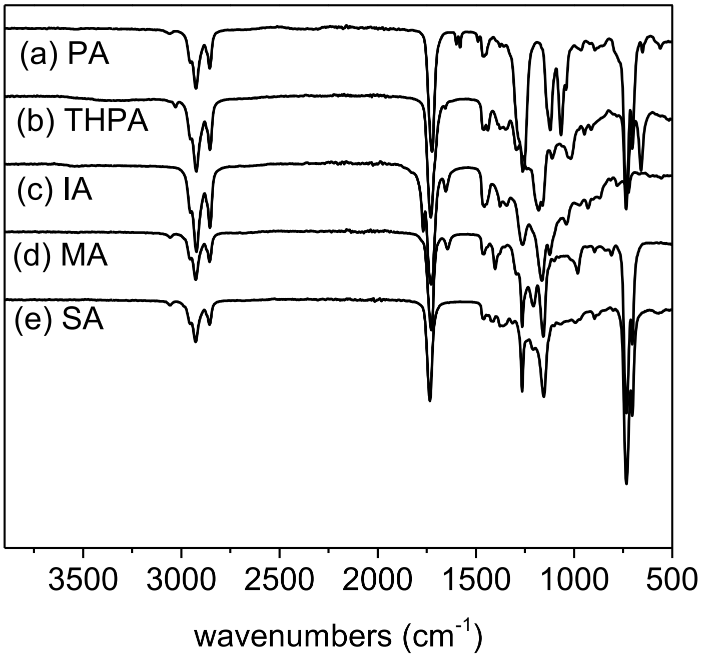


Figure 3.6. FTIR-ATR spectra of copolymers of epoxy with PA (a), THPA (b), IA (c), MA (d) and SA (e).

All copolymers exhibited peaks at approximate 1730 cm^{-1}, which are typical absorption peaks of ester group(Hua et al., 2004). The existence of ester group confirms that epoxide and listed anhydrides copolymerize to form polyesters. In addition, the -C-O-C- stretching vibrations for ester group can be identified at ~1200 cm^{-1} for all copolymers which are different from the copolymer of epoxide with CO$_2$. Furthermore, the characteristic absorptions for -C-O-C- stretching vibration of ether did not appear in some polyester particularly polyesters with low ether linkages (Table 3.1, entry 1, 2, 5).

Entry	**Anhydride**	**-COO-(cm^{-1})**	**-C=C-(cm^{-1})**	**C-O-C(cm^{-1}) [ester]**	**C-O-C(cm^{-1}) [ether]**
1	MA	1727	1644	1207, 1157	-
2	SA	1734	-	1154	-
3	IA	1768, 1728	1653	1163	1123
4	THPA	1730	1656(weak)	1181	1112
5	PA	1723	1599, 1580, 1492,1459 (phenyl)	1121,1066	-

Table 3.1. Characteristic IR absorption of epoxide/anhydride copolymer.

The synthesized copolymers were further characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. The proton NMR spectra are presented in Figure 3.4 and relevant peaks are summarized in Table

3.2. The peaks for ether, ester linkage and specific protons from anhydrides are all identified. The presence of -OCH- and $-OCH_2-$ peaks and exceptionally low intensity of the $CHCH_2O-$ peaks confirms that the ester linkages are dominant. The percentage of ester linkages was further calculated from ^1H NMR based on their peak integrations using below formula;

Ester linkage% = $(-OCH- + -OCH_2-)/(-OCH- + -OCH_2- + -OCHCH_2O-)\times100\%$.

The percent of ester linkages are presented in Table 3.3. Some additional peaks in the region of 6.5-5.5 ppm appeared for the copolymer of IA with epoxide [Figure 3.7(3)]. It is hypothesized that these peaks could be due to isomerization of double bonds under microwave irradiations. The isomerization under conventional heating has also been reported in the literature (Takasu, Ito, Inai, Hirabayashi, & Nishimura, 1999).

Entry	Anhydride	-OCH-(ppm)	$-OCH_2$-(ppm)	$-OCHCH_2O$-(ppm)
1	MA	5.13	4.61-4.06	3.98-3.21
2	SA	5.07	4.36-4.01	3.88-3.17
3	IA	5.09	4.20	3.42
4	THPA	5.04	4.08	3.62
5	PA	5.32	4.45	3.90-3.20

Table 3.2. ^1H NMR Ester/ether peaks of epoxide/anhydride copolymer.

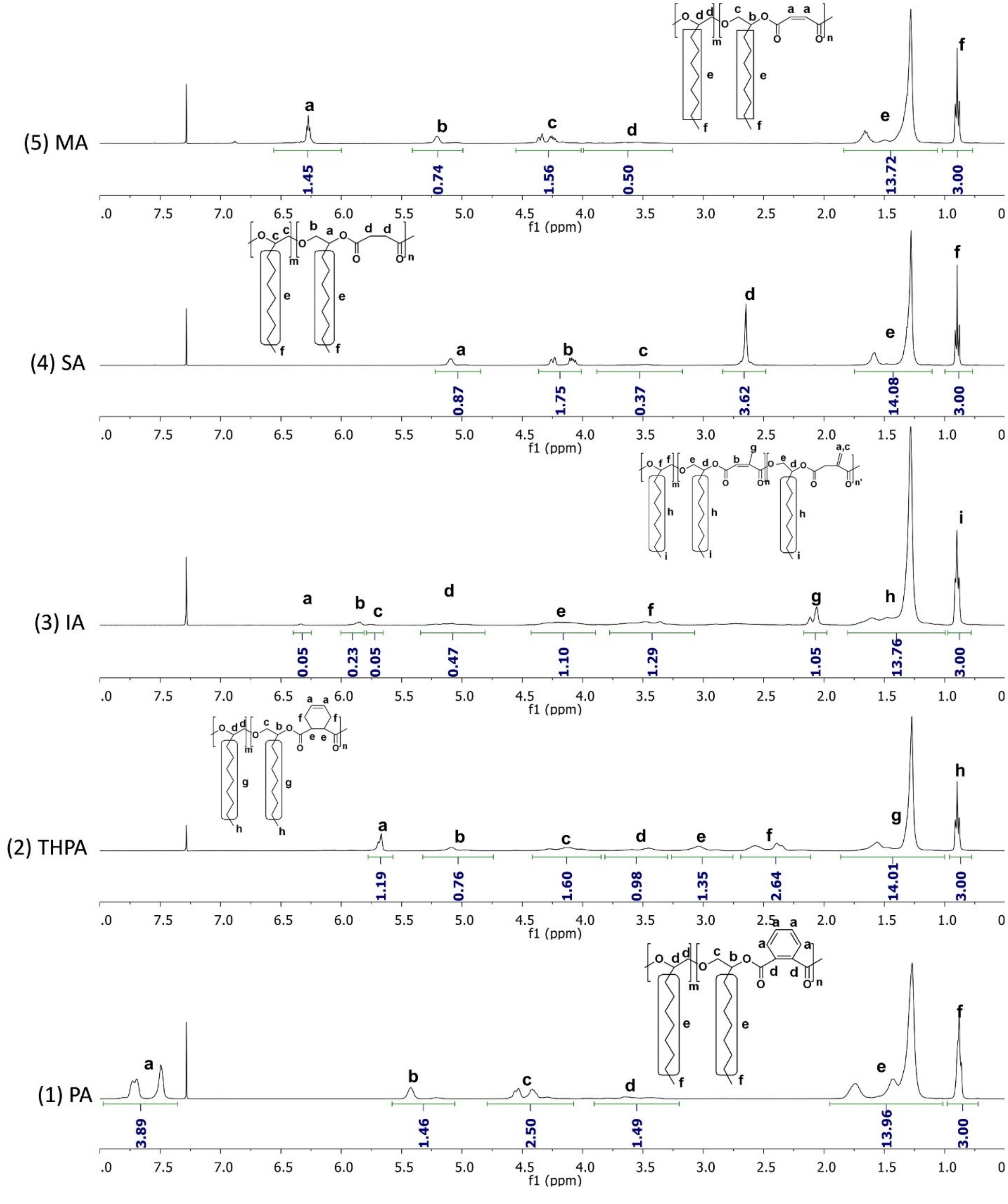
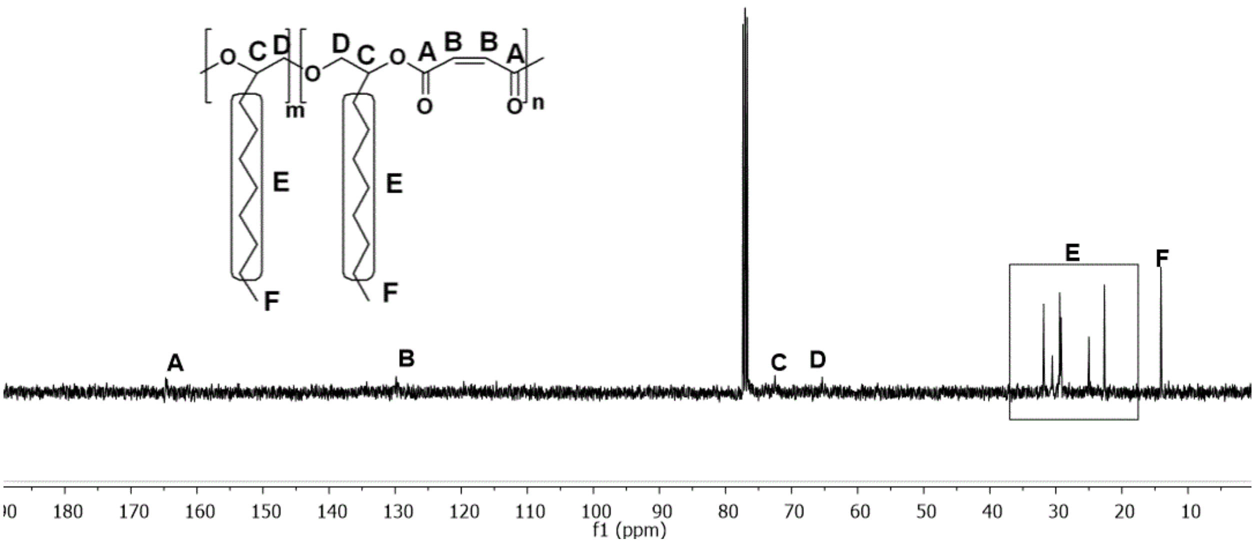
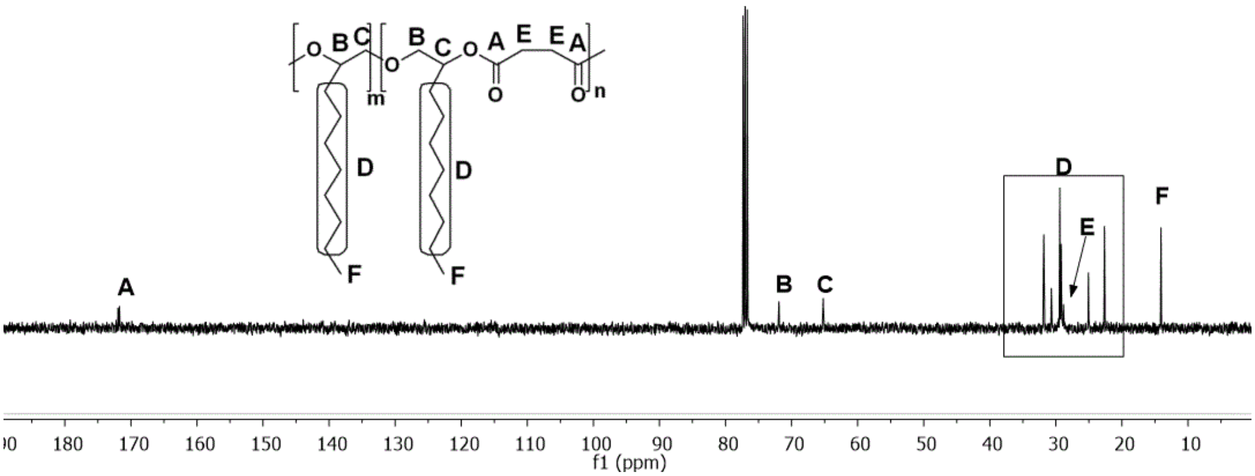
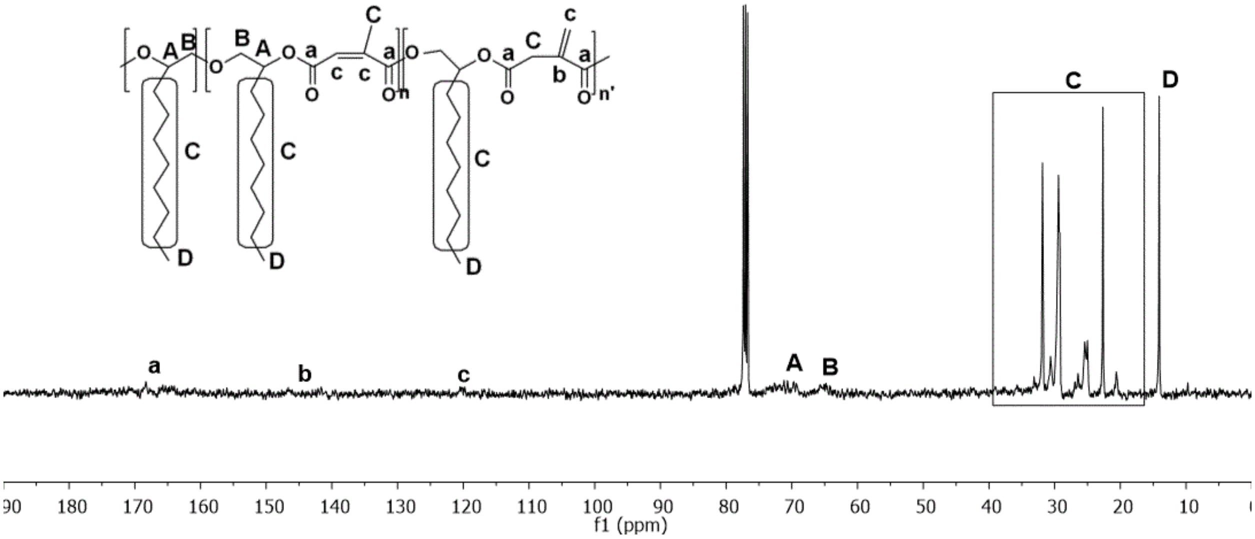


Figure 3.7. ^{1}H NMR spectra of copolymers from epoxide and anhydrides: (1) PA, (2) THPA, (3) IA, (4) SA, (5) MA.


C
D
D
C
A
B
B
A
m
n
E
E
F
F
A
B
C
D
E
F
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


B
C
B
C
A
E
E
A
m
n
D
D
F
F
A
B
C
D
E
F
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


A
B
B
A
a
c
c
a
C
n
a
C
b
c
a
n'
C
C
C
D
D
D
a
b
c
A
B
C
D
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

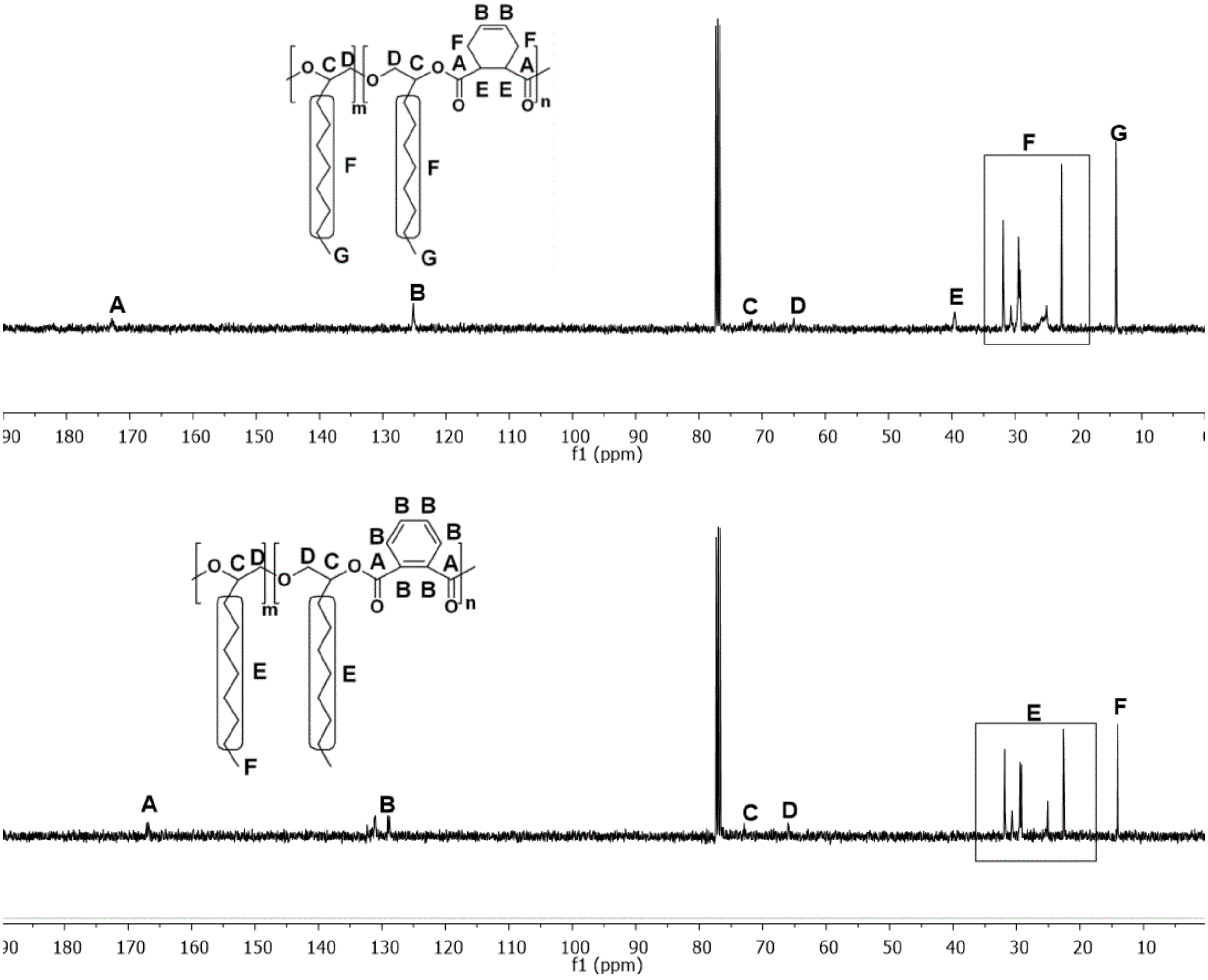


Figure 3.8. ^{13}C NMR spectra of copolymers from epoxide and anhydrides: PA, THPA, IA, SA and MA.

Table 3.3 presents the optimized reaction times at 100 °C for copolymerization of epoxy with different anhydrides. It is evident from Table 3.3 that rates of copolymerizations depend on anhydride types. The copolymerization of epoxide with anhydrides is completed in maximum 1h. By contrast, a reported copolymerization of MA with propylene oxide under conventional heating takes ~16h(Hua et al., 2004). Minimum 16 folds reduction in polymerization time under microwave conditions was observed as compared to conventional heating.

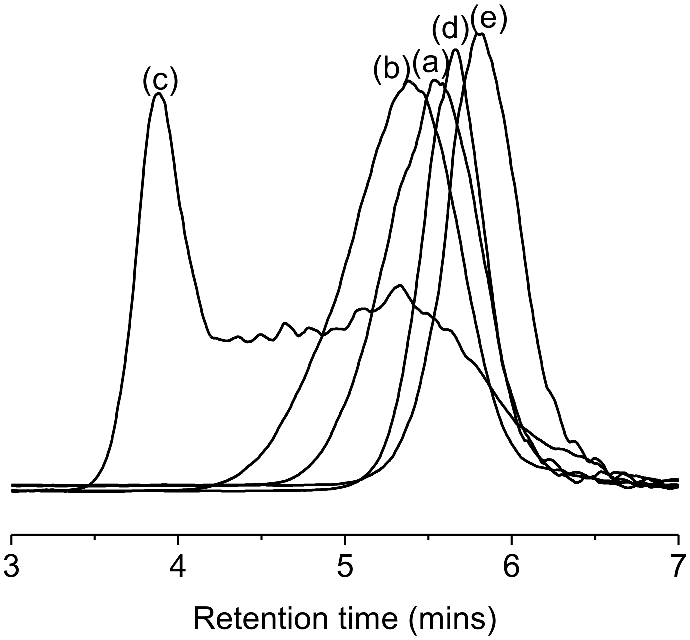


Figure 3.9. GPC traces of copolymers resulted from epoxy with SA (a), MA (b), IA (c), PA (d), THPA (e).

The representative gel permeation chromatography (GPC) traces of different copolymers are presented in Figure 3.9. Relatively sharper peaks and narrow PDI values can be observed in case of all other copolymers except copolymer of epoxy with IA (Figure 3.9c) indicating that in addition to longer polymer chains with high molecular mass, several smaller polymer units with shorter chain lengths are present leading to broad molecular weight distribution. This is due to the fact that itaconic anhydride exists in two isomeric forms (itaconic and citraconic) and both isomers take part in the copolymerization with epoxy leading to polymer chains with different molecular masses. The moderate molecular weights were observed for copolymers with MA/SA/PA. However, THPA had the lowest molecular weight probably due to steric hindrance of THPA which leads to low molecular weight, broader dispersity and long reaction time compared to MA/SA/PA copolymers. Overall, the molecular weights of copolymers prepared under microwave irradiation are comparable to those synthesized using conventional heating. Therefore, it was concluded that the microwave irradiation enhances polymerization rates without negative effect on polymerization. All these copolymers are highly viscous semi-solid, which are promising to be applied as adhesives.

Entry	Anhydride	Mins	Solv	Yield(%)	Tg^a	Ester%	Mw^c(kDa)	PDI^c
1	MA	10	-	48.5%	-27	91.1	8.212	1.28
2	SA	30	THF	68.4%	-41	87.6	6.277	1.28
3	IA	60	THF	49.0%	-23	54.9^b	17.18	2.78
4	THPA	60	THF	47.9%	-25	70.7	3.331	1.70
5	PA	20	THF	80.3%	-17	82.3	5.030	1.23

Table 3.3. Copolymerization of 1,2-epoxydecane/anhydrides at 100 °C. a: Tg was determined by DSC. b: unreliable calculated result considering integration of other peaks. c: Molecular weight was identified by GPC.

3.3.4. Heating and Pressure Profiles of Microwave-assisted Epoxide/CO_2/anhydride Copolymerization

The reactions were conducted in sealed reaction vessels at specified temperatures. The power is usually adapted by the instrument to reach and maintain the set temperature. The heating rate of reaction mixture was monitored and plotted by software automatically. Initially the dry ice absorbed more heat until sublimation. After sublimation, the microwave power reduced leading to low increase in temperature. It only took less than 2 mins to achieve 60 °C, but more than 8.5 mins to reach 90 °C (Figure 3.10a).

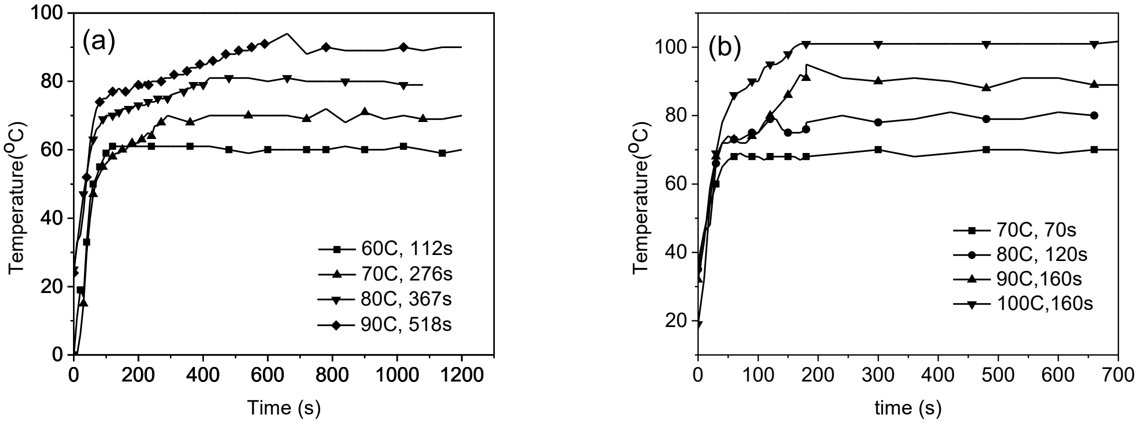


Figure 3.10. (a) Heat effect of microwave energy on epoxide/CO_2 reaction. 112 s, 276 s, 367 s and 518 s was necessary to achieve 60 °C, 70 °C, 80 °C, 90°C, respectively. (b) The temperature variation during microwave irradiated bulk polymerization of epoxide/MA.

In case of MA, due to its polar nature, the temperature rapidly increased. It took only 160 s to reach 100 °C from ambient temperature (Figure 3.10b) compared much longer time required for epoxide copolymerization with CO_2.

The pressure during copolymerization of epoxide with CO_2 rapidly increased within initial few seconds and then slightly decreased with the consumption of CO_2. Minumum 50 psi pressure was supplied to start copolymerization of CO_2 with epoxide and the highest points were recorded as the starting pressure of reaction. The pressure profile of epoxide reaction with CO_2 is presented in Figure 3.11.

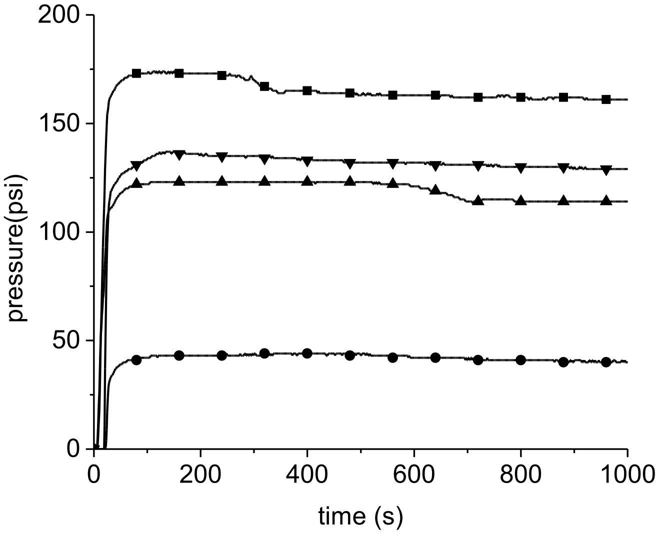


Figure 3.11. The pressure variation during microwave irradiated copolymerization of epoxide/CO_2.

3.3.5. Influential Factors on CO_2/epoxide Copolymer Properties

In addition to polycarbonate, polyether and cyclic carbonate can also be formed during copolymerization of epoxy with CO_2. The polyether is formed through homopolymerization of epoxy and cyclic carbonate is formed via cyclization of epoxy and CO_2 which is a byproduct during polymerization. Therefore, different parameters were studied to figure out their influence on %age of different monomer linkages and copolymer properties.

3.3.5.1. Pressure

Pressure was the first investigated parameter and the results are presented in Table 3.4. The percent of carbonate linkage linearly increased from 18.3% to 47.9% with increasing CO_2 pressure (from 76 to 130 psi) without any significant effect on monomer conversion or molecular weights obtained. Considering the pressure limitation of microwave instrument, higher pressure was not applied to the experiments. Overall, the percent carbonate linkage was lower than ether linkage for all copolymers synthesized (Table 3.4). The low carbonate linkage is in fact due to insertion of CO_2 into the propagating polymer chains. The main reason being the rapid reaction rate during microwave copolymerizations, reactions were completed so rapidly under microwave that the diffusion of CO_2 into the reaction mixture could not catch up with its consumption. The high ether linkage primarily results due to the quick exhaustion of CO_2. Therefore, higher pressure of CO_2 or reduced reaction rate may aid to increase carbonate linkage in polymer structure. The carbonate linkage as high as 75% was achieved by microwave-assisted copolymerization of cyclohexene oxide with CO_2 using ~140psi pressure(Dharman et al., 2008a). Nevertheless, the steric repulsion of cyclohexane ring to form epoxide-epoxide bonding is more than linear epoxy therefore greater CO_2 insertion was achieved in case of cyclohexene oxide compared to linear epoxy in our case.

Entry	Pressure(psi)	Conv (%)	Carbonate (%)	Mw^a (kda)	PDI^a
1	76	91	18.3	10.381	1.38
2	78	93	18.8	11.902	1.43
3	82	88	34.7	11.249	1.87
4	130	92	47.9	11.185	1.47

Table 3.4. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 at 70°C for 12 mins. a: Molecular weight and polydispersity index (PDI) was identified by GPC.

3.3.5.2. Reaction time

The effect of time on conversion and extent of cyclic carbonate was investigated using different time intervals for copolymerization. More than 90% conversions were generally achieved for different time intervals (6-30 min) under microwave irradiation Table 3.5. Although only little epoxide (2%) turned to cyclic carbonate at low irradiation times (up to 12 min) but cyclic carbonate %age increased with longer irradiation time particularly 30 min. Although, CO_2 pressure had little impact on molecular weight (Table 3.4), the reaction time could be considered as influencing variable for experiments as shown in Table 3.5. The molecular weight increased slightly from 6 min to 12 min and then declined after 15 mins. It can be concluded that longer exposure to microwave irradiation might have resulted in degradation of polymer.

Entry	Time(mins)	Conv (%)	Mw (kDa)	PDI
1	6	92	10.1	1.69
2	9	94	9.0	1.61
3	12	93	11.9	1.43
4	15	91	10.5	1.91
5	27	98	8.8	1.54
6	30	100	7.3	1.75

Table 3.5. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 at 70°C for different time.

3.3.5.3. Temperature

The influence of temperature on polycarbonate property was investigated sequentially. Overall, a minimum temperature of 60 °C was required to initiate the polymerization reaction and trend of decline in % carbonate linkage was observed with increasing temperature (60 to 100 ºC, Table 3.6). At 60 ºC, only 55% conversion was observed but the percentage of carbonate linkage was the highest (80%) among all the trials. This is probably due to the fact that at low temperature, the activity of DMC was not very high and therefore the supply of CO_2 into reaction mixture could keep in line with its consumption.

Entry	T(ºC)	Conv (%)	Carbonate (%)	CC^a (%)	Mw (kDa)	PDI
1	60	55	80.6	<1	14.2	1.44
2	70	100	35.3	11	7.3	1.75
3	80	97	32.3	6	7.8	1.84
4	90	95	18.6	3	8.5	1.74
5	100	94	22.3	1	9.2	1.68

Table 3.6. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 for 30 min. a: percentages of cyclic carbonate (CC%) were estimated by ^{1}H NMR of crude products.

In addition, the molar mass of polymer obtained at 60 °C was more than that of the polymers obtained at higher temperatures. Although its yield was lower, it seems that the rate of chain transfer or termination might have also decreased at lower temperature leading to higher molecular weight. By increasing temperature (from 70 ºC to 100 ºC), the mass of obtained copolymer increased from 7.3 to 9.2 kDa indicating that higher temperature might have suppressed polymer degradation. The decline of cyclic carbonate% reconfirmed that higher temperature is beneficial for polymerization over cyclization reaction. The GPC curves of three typical polymers are plotted in Figure 3.12.

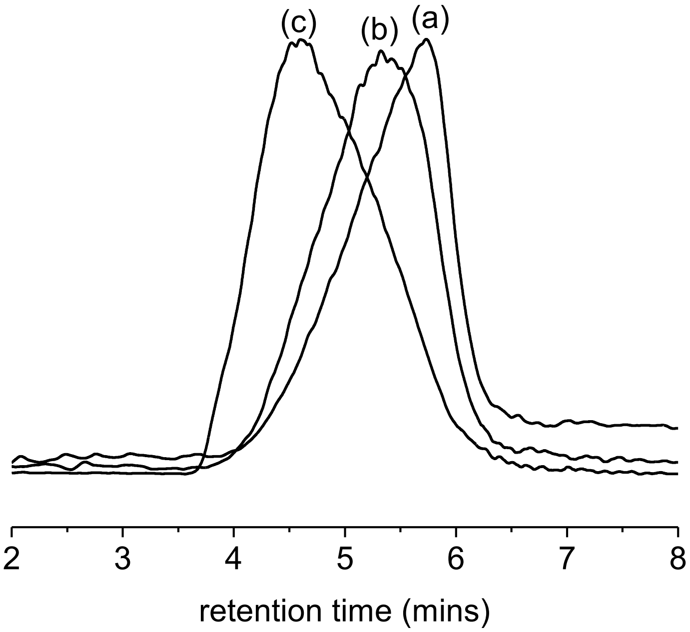


Figure 3.12. GPC traces of poly(1-decene-co-carbonate) under microwave conditions: (a) 70°C, 30mins (Entry 2, ***Table 3.6***), (b) 70°C, 9mins (Entry 2, ***Table 3.5***), (c) 60°C, 30mins (Entry 1, ***Table 3.6***).

3.3.5.4. Solvent

Further, the copolymerization of epoxide with CO_2 in two different solvents was studied, as shown in Table 3.7. The adding of hexane created similar results as decreasing reaction temperature. Despite low conversion, the polymerization in hexane lead to increased molecular weight and carbonate linkage compared to polymerizations in THF. However, in THF, the conversion was 97% but the ether linkage was more than 80%. The polarity of THF is much higher than epoxides and therefore it prefers dissolution of epoxy compared to non-polar CO_2 leading to promotion of homopolymerization.

Entry	**Solv**	**Conv (%)**	**Carbonate (%)**	**Mw (kDa)**	**PDI**
1	Hexane	52	87.7	15.2	1.30
2	THF	97	19.4	9.3	1.53

Table 3.7. Microwave assisted copolymerization of 1,2-epoxydecane/CO_2 at 70°C for 30 mins in different solvent.

3.3.6. Influential Factors on Epoxide/anhydrides Copolymer Properties

Highly alternative unsaturated polyester could be obtained from copolymerization of epoxide/MA, and is promising to form strong thermosetting polymer by further crosslinking. Hence, the exploration of optimized condition will be meaningful to obtain quality thermosetting polymer.

3.3.6.1. Temperature

The initialization of DMC with the first epoxide molecule is crucial for the copolymerization. Under 90 ºC, the copolymerization could not be initialized using less than 10 mins (entry 1, Table 3.8) while the copolymerization of 1, 2-epoxydecane/CO_2 could achieve 90% conversion within 6mins at such temperature. The plausible explanation could be that anhydride might have negative effect on the activation of DMC catalyst. However, by using longer reaction time of 20 mins, 100% conversion was achieved at 80 ºC and 90 ºC compared to at least 5 h required for the completion of copolymerization using conventional heating. In addition, the molecular weight of polyester from microwave method was higher than that from heating method.

Increasing reaction temperature from 80 ºC to 110 ºC, the required time could be reduced from 20 to 10 mins. However, the PDI became broader from 100 ºC to 110 ºC. Slight crosslinking may have occurred at 110 °C. Once the reaction time was extended to 20 mins at 110 ºC, insoluble polymer was generated. At high temperatures, the activity of double bonds in MA increases which leads to crosslinking. Therefore, 80-100 ºC was considered suitable temperature range for the copolymerization of 1,2-epoxydecane with MA. Compared to the copolymerization of epoxy and CO_2, the ether linkages in polyesters prepared by copolymerization of epoxy with anhydrides are much lower due to abundance of anhydrides in reaction solution.

Entry	T(ºC)	Time (mins)	Conv[b] (%)	Ester (%)	Mw (kDa)	PDI
1	90	10	-	-	-	-
2	80	20	100	82.3	8.151	1.23
3	90	20	100	92.3	8.692	1.27
4	100	10	100	91.1	8.212	1.28
5	110	10	100	85.9	10.659	1.57
6[a]	110	20	-	-	-	-
7	90	5h	100	75.0	6.013	1.52

Table 3.8. Copolymerization of 1,2-epoxydecane/MA. a: insoluble polymer was obtained. b: the conversion was determined by the epoxide residue measured by ^{1}H NMR.

3.3.6.2. DMC loading

DMC was reported as a highly effective catalyst. We attempted to adjust the catalyst loading to figure out its influence on microwave-induced copolymerization. The increase in catalyst loading from 0.3 mg to 0.6 mg led to shorter reaction time and high molecular weight (Table 3.9). However, further increase in loading does not have significant effect on conversion, yield or molecular mass.

Entry	DMC loading	Time (mins)	Conv (%)	Ester (%)	Mw (kDa)	PDI
1	0.3mg	20	100	87.7	6.311	1.32
2	0.6mg	10	100	91.1	8.212	1.28
3	0.9mg	10	100	90.5	8.421	1.25

Table 3.9. Copolymerization of 1,2-epoxydecane/MA at 100°C.

3.3.6.3. Solvent

THF and hexane were selected to carry out the solution polymerization for 1,2-epoxydecane with MA (Table 3.10). In both solvents, the reaction could not be finished in 10 min. In hexane, although percentage of ester linkage doesn't significantly change, the PDI was broader than bulk polymerization. The broadened PDI was also observed by Hua et al(Hua et al., 2004) while conducting the copolymerization of PO with MA in non-polar solvent. In THF, the incorporation of MA in the polymer declined distinctly and molecular weight also decreased suggesting that THF reduces the reactivity of MA in copolymerization. THF and MA are both 5-membered rings with higher polarity. Therefore, the interaction of THF with MA could be more than interaction of THF with epoxide. In addition, the MA has to conquer additional dipole-dipole force to participate in copolymerization.

Entry	Solv	Ester (%)	Mw (kDa)	PDI
1	Hexane	91.2	8.171	1.43
2	THF	69.3	7.336	1.17

Table 3.10. Copolymerization of 1,2-epoxydecane/MA for 20mins at 100°C in different solvents.

3.3.6.4. Monomer Ratios

To obtain completely alternative polyester, excess maleic anhydride was added to reaction mixture. The results opposite to our expectation and also opposite to reported data using conventional heating appeared leading to decrease in ester linkage from 90% to ~70% Table 3.11. Although it was not very much clear but the influence of microwave irradiation could be the plausible reason for these odd results. In addition, the molecular weight decreased slightly, which could be the result of traces of maleic acid remaining in MA. With the increase of MA ratio, more maleic acid was introduced in the reaction mixture which may act as a chain transfer agent or terminator.

Entry	Epoxy: MA	Ester (%)	Mw (kDa)	PDI
1	1.0:1.4	70.8	6.922	1.31
2	1.0:1.8	67.5	6.731	1.28

Table 3.11. Copolymerization of 1,2-epoxydecane/MA for 10mins at 100°C.

3.3.7. Isomerization of poly(1-decene-co-maleate)

Previous studies suggest that compounds with cis- double bonds have lower activities than trans-isomers(Jasinska & Koning, 2010). Isomerization of double bond configuration will bring benefits for further modifications, such as crosslinking. The isomerization of double bonds was detected by ^{1}H NMR. After isomerization, the signal of cis- double bonds presented at 6.24ppm disappeared; instead, a new peak at 6.87ppm corresponding to cis- alkene appeared.

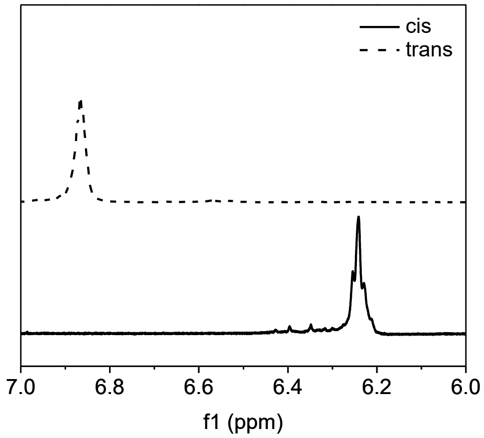


Figure 3.13. the region of C=C double bonds in ^{1}H NMR spectra before and after isomerization.

The isomerization catalyzed by diethyl amine was extremely rapid. Once the amine was added into poly(1-decene-co-maleate) solution, it turned from yellow to dark brown immediately, as presented in Figure 3.14. In the meantime, the viscosity of new polyester increased substantially.

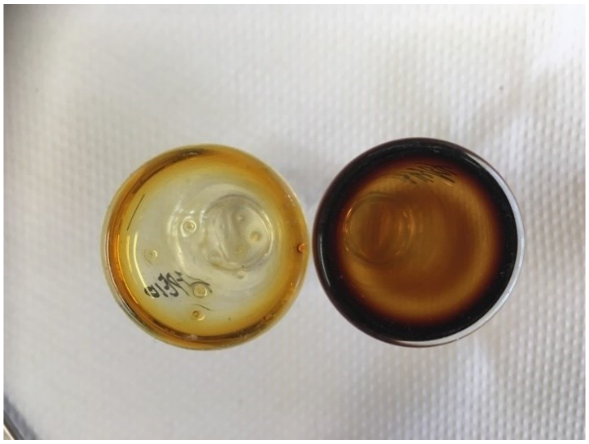


Figure 3.14. the appearance of polyester before(left) and after isomerization (right).

3.3.8. Thermal Properties of Copolymers

The thermal properties of copolymers were characterized by both TGA and DSC analysis. In DSC curves of copolymers of epoxy with CO_2 the peaks at around -30 ºC were observed as Figure 3.15. With the decrease in carbonate linkage, the peak intensity increased. It was hypothesized that this increase in peak intensity could be due to increase of the polyether segment in microstructure.

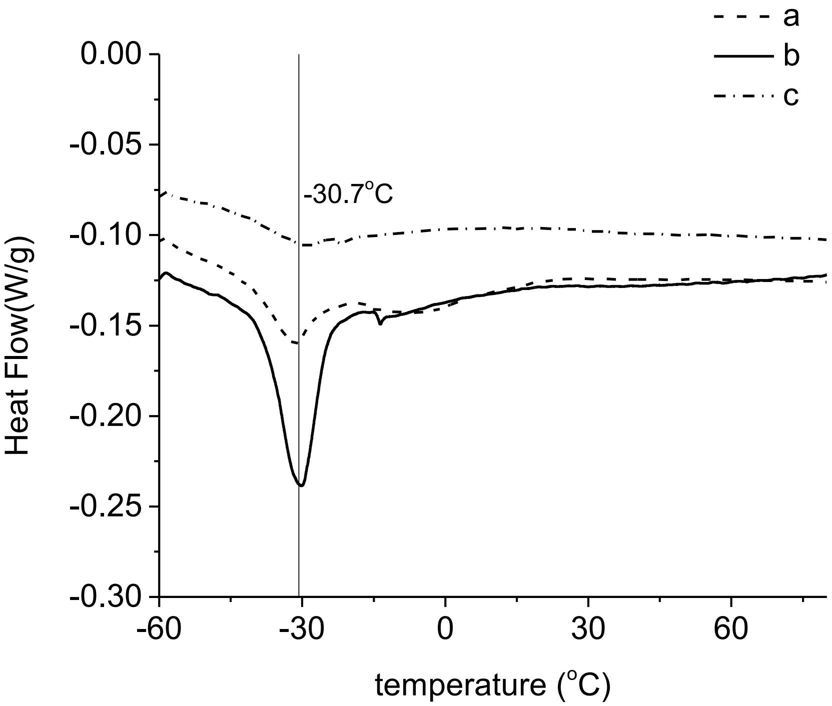


Figure 3.15. DSC curves(Exo up) of polymer contains different percentage of carbonate linkage. (a) Carbonate% = 35.3% (Entry 2, Table 3.6). (b) Carbonate% = 19.4% (Entry 2, Table 3.7). (c) Carbonate% = 87.7% (Entry 1, Table 3.7).

DSC analyses were also performed for the polyesters with various anhydrides Figure 3.16. T_g varied with anhydride type tremendously. Generally, T_g was greatly influenced by the flexibility of polymer chain. Once succinic anhydride was substituted by maleic anhydride, T_g increased from -41ºC to -27ºC suggesting that higher T_g could be achieved by enhancing the anhydride rigidity. Poly(1-decene-co-phthlate) shows almost highest glass transition temperature due to its aromatic structure. It's noticeable that after isomerization of double bonds in poly(1-decene-co-maleate), there was an increment of T_g from -27 ºC to -16 ºC. Most probably, the trans isomer increases hindrance by reducing chain mobility leading to increase in T_g.

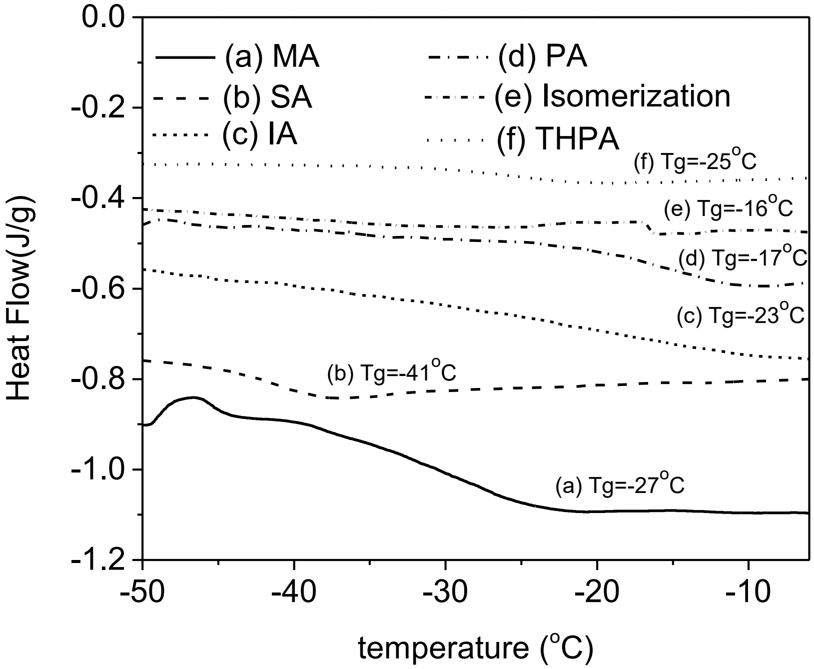


Figure 3.16. DSC curves(Exo up) of polyester using different anhydrides. The Tg were determined by Universal Analysis 2000 Software automatically.

The degradation behaviours of copolymers of epoxy with CO_2 were investigated using TGA instrument, the TG and DTG curves are shown in Figure 3.17. According to TG and DTG curves, the copolymers with high carbonate linkage started to decompose at approximate 200 ºC. A broad weight loss peak with minor shoulder was observed between 250-300 °C for copolymer with highest carbonate linkage (~88%), clearly two weight loss peaks were observed as carbonate linkage decreased from 88 to 35 % with high peak intensity at higher temperature ~ 360°C compared to lower temperature ~240 °C. With further decrease of carbonate linkage (~19%) the peak at lower temperature almost disappeared and peak intensity at higher tempearture ~ 360 °C substantially increased. Associated with the internal linkages of copolymer, the initial peak at lower temperature is due to the breakup of carbonate bonding and the later peak at higher temperature was due to decomposition of ether linkages.

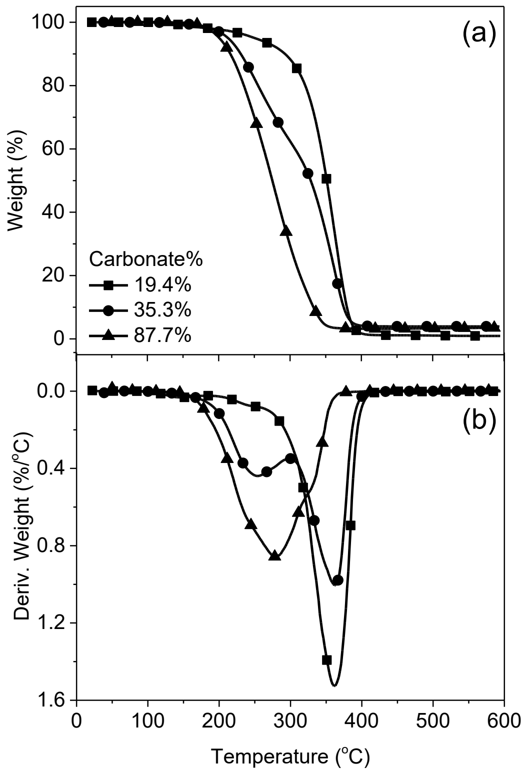


Figure 3.17. TG (a) and DTG (b) curves of copolymers of epoxy with CO_2.

The degradation of polyesters was also investigated by TGA analysis. From Figure 3.18, we concluded that most of the polyesters started decomposition at around 280ºC except initial copolymer of epoxy with MA and same copolymer after isomerization as well as copolymer of THPA with epoxy. Almost all copolymers fully decomposed before 500ºC. The low molar masses of copolymers of epoxide with THPA and PA was assumed to be the main reason for their early onset of decomposition and maximum weight loss peaks at lower temperature ~ 350°C compared to all other copolymers. The highest thermal stability was observed for copolymer of epoxy with MA before isomerization. Almost similar degradation behaviour was observed after isomerization except some minor weight loss below 350ºC which could be due to traces of Et_2NH present in the copolymer which was used for isomerization. Only single peak was observed for the derivative weight loss curve for all polyesters. From the TGA curves of copolymer of epoxide with CO_2, we know the breakup of ether linkage is between 300-400ºC. Therefore, the peak is possibly due to the disintegration of ester and ether bonds together.

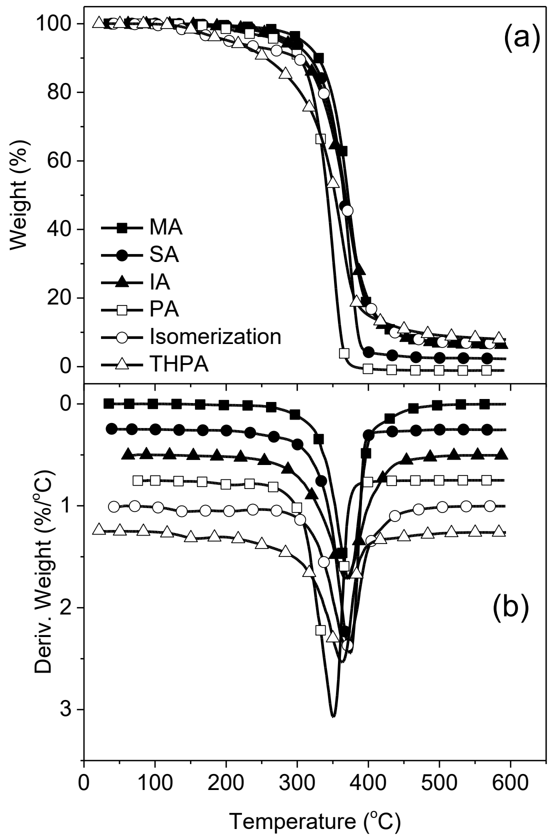


Figure 3.18. TG (a) and DTG (b) curves of copolymers of epoxy with several anhydrides. DTG curves have been offset for clarity.

Entry	**Anhydride**	**$T_{5\%}$(°C)**	**$T_{10\%}$(°C)**	**$T_{20\%}$(°C)**	**$T_{50\%}$(°C)**
(a)	MA	308	330	348	372
(b)	SA	289	318	342	365
(c)	IA	282	308	334	367
(d)	PA	276	304	321	342
(e)	Isomerization of (a)	204	301	337	369
(f)	THPA	205	257	305	353

Table 3.12. Decomposition temperatures (5%, 10%, 20%, 50% weight loss) for polyesters.

3.4. Conclusion

In summary, copolymers of epoxide with CO_2 and anhydrides have been successfully synthesized using DMC catalyst and characterized by ATR-FTIR, NMR, GPC, TGA and DSC instruments. Compared to conventional heating method, microwave-assisted polymerization is an extremely efficient method and can be completed within minutes.

Nevertheless, for copolymers of epoxide with CO_2, the lower pressure and faster reaction rate could result in low carbonate linkage in the polymers. Factors such as solvents, temperature, pressure, time were systematically investigated to optimize the polymer properties (molecular weight, % cyclic carbonate and % carbonates linkage). It was concluded that lower temperature (60ºC), higher CO_2 pressure and non-polar solvent such as hexane were beneficial to enhance the %age carbonate linkage and increase molecular weight. Longer time would probably lead to polymer degradation.

The microwave-assisted copolymerization of epoxide with anhydride were significantly quicker compared to classical heating method. Polymers of high ester content (up to 91%) were obtained with molecular weights as high as ~17 kDa. Factors such as temperature, solvent, catalyst loading and monomer ratios were investigated to establish their influence on molecular weight and ester linkage. The bulk polymerizations using temperatures between 90 and 100 ºC, and equal comonomer ratios were found to be more suitable. Poly(1-decene-co-meleate) was completely isomerized to poly(1-decene-co-fumarate) through post polymerization modification catalyzed by amine. These copolymers have great potential to be further crosslinked into thermosetting materials or can be used in different applications such as adhesives.

3.5. References

Arshad, M., Kaur, M., & Ullah, A. (2016). Green Biocomposites from Nanoengineered Hybrid Natural Fiber and Biopolymer. *ACS Sustainable Chemistry & Engineering, 4*(3), 1785-1793.

Baylon, C., Heck, M.-P., & Mioskowski, C. (1999). Bis Ring Closing Olefin Metathesis for the Synthesis of Unsaturated Polycyclic Ethers. O-Membered Ring Cyclization in Favor of C-Membered Ring Cyclization. *the Journal of Organic Chemistry, 64*(9), 3354.

Bok, T., Yun, H., & Lee, B. Y. (2006). Bimetallic Fluorine-Substituted Anilido− Aldimine Zinc Complexes for CO2/(Cyclohexene Oxide) Copolymerization. *Inorganic Chemistry, 45*(10), 4228-4237.

Chen, S., Hua, Z., Fang, Z., & Qi, G. (2004). Copolymerization of carbon dioxide and propylene oxide with highly effective zinc hexacyanocobaltate (III)-based coordination catalyst. *Polymer, 45*(19), 6519-6524.

Chen, S., Qi, G. R., Hua, Z. J., & Yan, H. Q. (2004). Double metal cyanide complex based on Zn3 [Co (CN) 6] 2 as highly active catalyst for copolymerization of carbon dioxide and cyclohexene oxide. *Journal of Polymer Science Part A: Polymer Chemistry, 42*(20), 5284-5291.

Cheng, M., Moore, D. R., Reczek, J. J., Chamberlain, B. M., Lobkovsky, E. B., & Coates, G. W. (2001). Single-site β-diiminate zinc catalysts for the alternating copolymerization of CO2 and epoxides: catalyst synthesis and unprecedented polymerization activity. *Journal of the American Chemical Society, 123*(36), 8738-8749.

Chua, S.-C., Xu, X., & Guo, Z. (2012). Emerging sustainable technology for epoxidation directed toward plant oil-based plasticizers. *Process Biochemistry, 47*(10), 1439-1451.

Darensbourg, D. J., Mackiewicz, R. M., Rodgers, J. L., Fang, C. C., Billodeaux, D. R., & Reibenspies, J. H. (2004). Cyclohexene oxide/CO2 copolymerization catalyzed by chromium (III) salen complexes and N-methylimidazole: Effects of varying salen ligand substituents and relative cocatalyst loading. *Inorganic Chemistry, 43*(19), 6024-6034.

de la Hoz, A., Diaz-Ortiz, A., & Moreno, A. (2005). Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chemical Society Reviews, 34*(2), 164-178.

Dharman, M. M., Ahn, J.-Y., Lee, M.-K., Shim, H.-L., Kim, K.-H., Kim, I., & Park, D.-W. (2008a). Moderate route for the utilization of CO 2-microwave induced copolymerization with cyclohexene oxide using highly efficient double metal cyanide complex catalysts based on Zn 3 [Co (CN) 6]. *Green Chemistry, 10*(6), 678-684.

Dharman, M. M., Ahn, J.-Y., Lee, M.-K., Shim, H.-L., Kim, K.-H., Kim, I., & Park, D.-W. (2008b). A novel and faster route for the synthesis of polyether–polycarbonate from carbon dioxide and epoxide through microwave irradiation. *Research on Chemical Intermediates, 34*(8), 835-844.

DiCiccio, A. M., & Coates, G. W. (2011). Ring-opening copolymerization of maleic anhydride with epoxides: a chain-growth approach to unsaturated polyesters. *Journal of the American Chemical Society, 133*(28), 10724-10727.

Giguere, R. J., Bray, T. L., Duncan, S. M., & Majetich, G. (1986). Application of commercial microwave ovens to organic synthesis. *Tetrahedron Letters, 27*(41), 4945-4948.

Hua, Z., Qi, G., & Chen, S. (2004). Ring‐opening copolymerization of maleic anhydride with propylene oxide by double‐metal cyanide. *Journal of Applied Polymer Science, 93*(4), 1788-1792.

Inoue, S., Koinuma, H., & Tsuruta, T. (1969). Copolymerization of carbon dioxide and epoxide. *Journal of Polymer Science Part B: Polymer Letters, 7*(4), 287-292.

Jasinska, L., & Koning, C. E. (2010). Unsaturated, biobased polyesters and their cross‐linking via radical copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry, 48*(13), 2885-2895.

Lawniczak‐Jablonska, K., Dynowska, E., Lisowski, W., Sobczak, J., Chruściel, A., Hreczuch, W., . . . Reszka, A. (2015). Structural properties and chemical bonds in double metal cyanide catalysts. *X‐Ray Spectrometry, 44*(5), 330-338.

Liu, X., He, H., Wang, Y., Zhu, S., & Piao, X. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel, 87*(2), 216-221.

Luinstra, G. A., & Borchardt, E. (2011). Material properties of poly (propylene carbonates) *Synthetic Biodegradable Polymers* (pp. 29-48): Springer.

Mang, S., Cooper, A. I., Colclough, M. E., Chauhan, N., & Holmes, A. B. (2000). Copolymerization of CO2 and 1, 2-cyclohexene oxide using a CO2-soluble chromium porphyrin catalyst. *Macromolecules, 33*(2), 303-308.

Ohlrogge, J. B. (1994). Design of new plant products: engineering of fatty acid metabolism. *Plant Physiology, 104*(3), 821.

Paddock, R. L., & Nguyen, S. T. (2001). Chemical CO2 fixation: Cr (III) salen complexes as highly efficient catalysts for the coupling of CO2 and epoxides. *Journal of the American Chemical Society, 123*(46), 11498-11499.

Przybylski, R. (2001). Canola oil: physical and chemical properties. *Canola Council of Canada, 1*.

Qin, Z., Thomas, C. M., Lee, S., & Coates, G. W. (2003). Cobalt‐Based Complexes for the Copolymerization of Propylene Oxide and CO2: Active and Selective Catalysts for Polycarbonate Synthesis. *Angewandte Chemie International Edition, 42*(44), 5484-5487.

Ree, M., Bae, J., Jung, J., & Shin, T. (1999). A new copolymerization process leading to poly (propylene carbonate) with a highly enhanced yield from carbon dioxide and propylene oxide. *Journal of Polymer Science Part A: Polymer Chemistry, 37*(12), 1863-1876.

Ree, M., Hwang, Y., Kim, J.-S., Kim, H., Kim, G., & Kim, H. (2006). New findings in the catalytic activity of zinc glutarate and its application in the chemical fixation of CO 2 into polycarbonates and their derivatives. *Catalysis Today, 115*(1), 134-145.

Schmalensee, R., Stoker, T. M., & Judson, R. A. (1998). World carbon dioxide emissions: 1950–2050. *Review of Economics and Statistics, 80*(1), 15-27.

Schneider, W., & Diller, W. (2000). Phosgene. *Ullmann's Encyclopedia of Industrial Chemistry*.

Schrodi, Y., Ung, T., Vargas, A., Mkrtumyan, G., Lee, C. W., Champagne, T. M., . . . Hong, S. H. (2008). Ruthenium olefin metathesis catalysts for the ethenolysis of renewable feedstocks. *CLEAN–Soil, Air, Water, 36*(8), 669-673.

Seo, J., Jeon, G., Jang, E. S., Bahadar Khan, S., & Han, H. (2011). Preparation and properties of poly (propylene carbonate) and nanosized ZnO composite films for packaging applications. *Journal of Applied Polymer Science, 122*(2), 1101-1108.

Soga, K., Imai, E., & Hattori, I. (1981). Alternating copolymerization of CO2 and propylene oxide with the catalysts prepared from Zn (OH) 2 and various dicarboxylic acids. *Polymer Journal, 13*(4), 407-410.

Sun, X. K., Zhang, X. H., Liu, F., Chen, S., Du, B. Y., Wang, Q., . . . Qi, G. R. (2008). Alternating copolymerization of carbon dioxide and cyclohexene oxide catalyzed by silicon dioxide/Zn□ CoIII double metal cyanide complex hybrid catalysts with a nanolamellar structure. *Journal of Polymer Science Part A: Polymer Chemistry, 46*(9), 3128-3139.

Takasu, A., Ito, M., Inai, Y., Hirabayashi, T., & Nishimura, Y. (1999). Synthesis of biodegradable polyesters by ring-opening copolymerization of cyclic anhydrides containing a double bond with 1, 2-epoxybutane and one-pot preparation of the itaconic acid-based polymeric network. *Polymer Journal, 31*, 961-969.

Thurier, C., Fischmeister, C., Bruneau, C., Olivier‐Bourbigou, H., & Dixneuf, P. H. (2008). Ethenolysis of methyl oleate in room‐temperature ionic liquids. *ChemSusChem, 1*(1‐2), 118-122.

Ullah, A., & Arshad, M. (2017). Remarkably Efficient Microvawe‐Assisted Cross‐Metathesis of Lipids in Solvent Free Conditions. *ChemSusChem*.

Warwel, S. (1999). Complete and partial epoxidation of plant oils by lipase-catalyzed perhydrolysis. *Industrial Crops and Products, 9*(2), 125-132.

Zhang, X.-H., Wei, R.-J., Zhang, Y. Y., Du, B.-Y., & Fan, Z.-Q. (2015). Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc–Cobalt (III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures. *Macromolecules, 48*(3), 536-544.

Bibliography

Albertsson, A.-C., & Varma, I. K. (2002). Aliphatic polyesters: synthesis, properties and applications *Degradable Aliphatic Polyesters* (pp. 1-40): Springer.

Arshad, M., Kaur, M., & Ullah, A. (2016). Green Biocomposites from Nanoengineered Hybrid Natural Fiber and Biopolymer. *ACS Sustainable Chemistry & Engineering, 4*(3), 1785-1793.

Avérous, L. (2008). *Polylactic acid: synthesis, properties and applications*: Elsevier: Oxford, UK.

Bakare, I., Pavithran, C., Okieimen, F., & Pillai, C. (2006). Polyesters from renewable resources: preparation and characterization. *Journal of Applied Polymer Science, 100*(5), 3748-3755.

Bargiggia, F. C., & Murray, W. V. (2005). Cross-metathesis assisted by microwave irradiation. *the Journal of Organic Chemistry, 70*(23), 9636-9639.

Barth, M. C., & Titus, J. G. (1984). Greenhouse effect and sea level rise: A challenge for this generation.

Bawn, C. (1987). Encyclopedia of polymer science and engineering: JI Kroschwitz, HF Mark, N. Bikales, CG Overberger and G. Menges (eds.) John Wiley and Sons, New York, 1985, 906 pages, US $240,£ 170, ISBN 0-471-89540-7: Elsevier.

Baylon, C., Heck, M.-P., & Mioskowski, C. (1999). Bis Ring Closing Olefin Metathesis for the Synthesis of Unsaturated Polycyclic Ethers. O-Membered Ring Cyclization in Favor of C-Membered Ring Cyclization. *the Journal of Organic Chemistry, 64*(9), 3354.

Belgacem, M. N., & Gandini, A. (2011). *Monomers, polymers and composites from renewable resources*: Elsevier.

Bok, T., Yun, H., & Lee, B. Y. (2006). Bimetallic Fluorine-Substituted Anilido− Aldimine Zinc Complexes for CO2/(Cyclohexene Oxide) Copolymerization. *Inorganic Chemistry, 45*(10), 4228-4237.

Burdett, K. A., Harris, L. D., Margl, P., Maughon, B. R., Mokhtar-Zadeh, T., Saucier, P. C., & Wasserman, E. P. (2004). Renewable monomer feedstocks via olefin metathesis: Fundamental mechanistic studies of methyl oleate ethenolysis with the first-generation Grubbs catalyst. *Organometallics, 23*(9), 2027-2047.

Cao, H. L., Wang, P., & Yuan, W. B. (2009). Microwave ‐ Assisted Synthesis of Poly (L ‐ lactic acid) via Direct Melt Polycondensation Using Solid Super ‐ Acids. *Macromolecular Chemistry and Physics, 210*(23), 2058-2062.

Chen, G.-Q. (2009). A microbial polyhydroxyalkanoates (PHA) based bio-and materials industry. *Chemical Society Reviews, 38*(8), 2434-2446.

Chen, G.-Q. (2010). Industrial production of PHA *Plastics from bacteria* (pp. 121-132): Springer.

Chen, S., Hua, Z., Fang, Z., & Qi, G. (2004). Copolymerization of carbon dioxide and propylene oxide with highly effective zinc hexacyanocobaltate (III)-based coordination catalyst. *Polymer, 45*(19), 6519-6524.

Chen, S., Qi, G. R., Hua, Z. J., & Yan, H. Q. (2004). Double metal cyanide complex based on Zn3 [Co (CN) 6] 2 as highly active catalyst for copolymerization of carbon dioxide and cyclohexene oxide. *Journal of Polymer Science Part A: Polymer Chemistry, 42*(20), 5284-5291.

Cheng, M., Lobkovsky, E. B., & Coates, G. W. (1998). Catalytic reactions involving C1 feedstocks: new high-activity Zn (II)-based catalysts for the alternating copolymerization of carbon dioxide and epoxides. *Journal of the American Chemical Society, 120*(42), 11018-11019.

Cheng, M., Moore, D. R., Reczek, J. J., Chamberlain, B. M., Lobkovsky, E. B., & Coates, G. W. (2001). Single-site β-diiminate zinc catalysts for the alternating copolymerization of CO2 and epoxides: catalyst synthesis and unprecedented polymerization activity. *Journal of the American Chemical Society, 123*(36), 8738-8749.

Chua, S.-C., Xu, X., & Guo, Z. (2012). Emerging sustainable technology for epoxidation directed toward plant oil-based plasticizers. *Process Biochemistry, 47*(10), 1439-1451.

Coates, G. W., & Moore, D. R. (2004). Discrete Metal‐Based Catalysts for the Copolymerization of CO2 and Epoxides: Discovery, Reactivity, Optimization, and Mechanism. *Angewandte Chemie International Edition, 43*(48), 6618-6639.

Cohen, C. T., Chu, T., & Coates, G. W. (2005). Cobalt catalysts for the alternating copolymerization of propylene oxide and carbon dioxide: combining high activity and selectivity. *Journal of the American Chemical Society, 127*(31), 10869-10878.

Cuq, B., Gontard, N., & Guilbert, S. (1998). Proteins as agricultural polymers for packaging production. *Cereal Chemistry, 75*(1), 1-9.

Darensbourg, D., Niezgoda, S., Draper, J., & Reibenspies, J. (1998). Mechanistic aspects of the copolymerization of CO2 and epoxides by soluble zinc bis (phenoxide) catalysts as revealed by their cadmium analogues. *Journal of the American Chemical Society, 120*(19), 4690-4698.

Darensbourg, D. J., Adams, M. J., Yarbrough, J. C., & Phelps, A. L. (2003). Synthesis and structural characterization of double metal cyanides of iron and zinc: catalyst precursors for the copolymerization of carbon dioxide and epoxides. *Inorganic Chemistry, 42*(24), 7809-7818.

Darensbourg, D. J., & Holtcamp, M. W. (1995). Catalytic activity of zinc (II) phenoxides which possess readily accessible coordination sites. Copolymerization and terpolymerization of epoxides and carbon dioxide. *Macromolecules, 28*(22), 7577-7579.

Darensbourg, D. J., & Holtcamp, M. W. (1996). Catalysts for the reactions of epoxides and carbon dioxide. *Coordination Chemistry Reviews, 153*, 155-174.

Darensbourg, D. J., Holtcamp, M. W., Struck, G. E., Zimmer, M. S., Niezgoda, S. A., Rainey, P., . . . Reibenspies, J. H. (1999). Catalytic activity of a series of Zn (II) phenoxides for the copolymerization of epoxides and carbon dioxide. *Journal of the American Chemical Society, 121*(1), 107-116.

Darensbourg, D. J., Mackiewicz, R. M., Rodgers, J. L., Fang, C. C., Billodeaux, D. R., & Reibenspies, J. H. (2004). Cyclohexene oxide/CO2 copolymerization catalyzed by chromium (III) salen complexes and N-methylimidazole: Effects of varying salen ligand substituents and relative cocatalyst loading. *Inorganic Chemistry, 43*(19), 6024-6034.

Darensbourg, D. J., Poland, R. R., & Escobedo, C. (2012). Kinetic studies of the alternating copolymerization of cyclic acid anhydrides and epoxides, and the terpolymerization of cyclic acid anhydrides, epoxides, and CO2 catalyzed by (salen) CrIIICl. *Macromolecules, 45*(5), 2242-2248.

Darensbourg, D. J., Wildeson, J. R., Yarbrough, J. C., & Reibenspies, J. H. (2000). Bis 2, 6-difluorophenoxide dimeric complexes of zinc and cadmium and their phosphine adducts: lessons learned relative to carbon dioxide/cyclohexene oxide alternating copolymerization processes catalyzed by zinc phenoxides. *Journal of the American Chemical Society, 122*(50), 12487-12496.

Darensbourg, D. J., & Yarbrough, J. C. (2002). Mechanistic aspects of the copolymerization reaction of carbon dioxide and epoxides, using a chiral salen chromium chloride catalyst. *Journal of the American Chemical Society, 124*(22), 6335-6342.

Darensbourg, D. J., Yarbrough, J. C., Ortiz, C., & Fang, C. C. (2003). Comparative kinetic studies of the copolymerization of cyclohexene oxide and propylene oxide with carbon dioxide in the presence of chromium salen derivatives. In situ FTIR measurements of copolymer vs cyclic carbonate production. *Journal of the American Chemical Society, 125*(25), 7586-7591.

de la Hoz, A., Diaz-Ortiz, A., & Moreno, A. (2005). Microwaves in organic synthesis. Thermal and non-thermal microwave effects. *Chemical Society Reviews, 34*(2), 164-178.

DeWalle, F. B., & Chian, E. S. (1981). Detection of trace organics in well water near a solid waste landfill. *Journal (American Water Works Association)*, 206-211.

Dharman, M. M., Ahn, J.-Y., Lee, M.-K., Shim, H.-L., Kim, K.-H., Kim, I., & Park, D.-W. (2008a). Moderate route for the utilization of CO 2-microwave induced copolymerization with cyclohexene oxide using highly efficient double metal cyanide complex catalysts based on Zn 3 [Co (CN) 6]. *Green Chemistry, 10*(6), 678-684.

Dharman, M. M., Ahn, J.-Y., Lee, M.-K., Shim, H.-L., Kim, K.-H., Kim, I., & Park, D.-W.

(2008b). A novel and faster route for the synthesis of polyether–polycarbonate from carbon dioxide and epoxide through microwave irradiation. *Research on Chemical Intermediates, 34*(8), 835-844.

Dharman, M. M., Yu, J.-I., Ahn, J.-Y., & Park, D.-W. (2009). Selective production of cyclic carbonate over polycarbonate using a double metal cyanide–quaternary ammonium salt catalyst system. *Green Chemistry, 11*(11), 1754-1757.

DiCiccio, A. M., & Coates, G. W. (2011). Ring-opening copolymerization of maleic anhydride with epoxides: a chain-growth approach to unsaturated polyesters. *Journal of the American Chemical Society, 133*(28), 10724-10727.

Doll, K. M. (2014). Increased functionality of methyl oleate using alkene metathesis. *International Journal of Sustainable Engineering, 7*(4), 322-329.

Drumright, R. E., Gruber, P. R., & Henton, D. E. (2000). Polylactic acid technology. *Advanced Materials, 12*(23), 1841-1846.

Edlund, U., & Albertsson, A.-C. (2002). Degradable polymer microspheres for controlled drug delivery *Degradable aliphatic polyesters* (pp. 67-112): Springer.

Edlund, U., Hakkarainen, M., Karlsson, S., Liu, Y., Ranucci, E., Ryner, M., . . . Albertsson, A.-C. (2003). *Degradable aliphatic polyesters* (Vol. 157): Springer.

Feldman, D., & Barbalata, A. (1996). *Synthetic polymers: technology, properties, applications*: Springer Science & Business Media.

Flory, P. J. (1953). *Principles of polymer chemistry*: Cornell University Press.

Forman, G. S., Bellabarba, R. M., Tooze, R. P., Slawin, A. M., Karch, R., & Winde, R. (2006). Metathesis of renewable unsaturated fatty acid esters catalysed by a phoban-indenylidene ruthenium catalyst. *Journal of Organometallic Chemistry, 691*(24), 5513-5516.

Gedye, R., Smith, F., Westaway, K., Ali, H., Baldisera, L., Laberge, L., & Rousell, J. (1986). The use of microwave ovens for rapid organic synthesis. *Tetrahedron Letters, 27*(3), 279-282.

Gervet, B. (2007). The use of crude oil in plastic making contributes to global warming. *Renewable Energy Research Group, Division of Architecture and Infrastructure, Luleå University of Technology, SE-97187 Luleå, Sweden. www. ltu. se/cms_fs/1.5035*.

Gibbins, J., & Chalmers, H. (2008). Carbon capture and storage. *Energy Policy, 36*(12), 4317-4322.

Giguere, R. J., Bray, T. L., Duncan, S. M., & Majetich, G. (1986). Application of commercial microwave ovens to organic synthesis. *Tetrahedron Letters, 27*(41), 4945-4948.

Griesbaum, K. (1970). Problems and possibilities of the free ‐ radical addition of thiols to unsaturated compounds. *Angewandte Chemie International Edition in English, 9*(4), 273-

287.

Grubbs, R. H., Nguyen, S. T., Johnson, L. K., Hillmyer, M. A., & Fu, G. C. (1996). High activity ruthenium or osmium metal carbene complexes for olefin metathesis reactions and synthesis thereof: Google Patents.

Hayes, B. L. (2002). *Microwave synthesis: chemistry at the speed of light*: Cem Corporation.

Henneuse, C., & Pacary, T. (2003). *Emissions from plastics* (Vol. 14): iSmithers Rapra Publishing.

Hill, K. (2000). Fats and oils as oleochemical raw materials. *Pure and Applied Chemistry, 72*(7), 1255-1264.

Hua, Z., Qi, G., & Chen, S. (2004). Ring‐opening copolymerization of maleic anhydride with propylene oxide by double‐metal cyanide. *Journal of Applied Polymer Science, 93*(4), 1788-1792.

Huang, K.-M., Liu, Y.-Q., Tang, J.-X., Zhao, J., & Wang, B.-Y. (1996). A study of athermal action of electromagnetic waves on chemical reaction. *CHEMICAL JOURNAL OF CHINESE UNIVERSITIES-CHINESE EDITION-, 17*, 768-771.

Inoue, S., Kitamura, K., & Tsuruta, T. (1969). Alternating copolymerization of phthalic anhydride and propylene oxide by dialkylzinc. *Die Makromolekulare Chemie, 126*(1), 250-265.

Inoue, S., Koinuma, H., & Tsuruta, T. (1969). Copolymerization of carbon dioxide and epoxide. *Journal of Polymer Science Part B: Polymer Letters, 7*(4), 287-292.

Jacobsen, E. N., Tokunaga, M., & Larrow, J. F. (2000). Stereoselective ring opening reactions: Google Patents.

Jasinska, L., & Koning, C. E. (2010). Unsaturated, biobased polyesters and their cross‐linking via radical copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry, 48*(13), 2885-2895.

Jeske, R. C., DiCiccio, A. M., & Coates, G. W. (2007). Alternating copolymerization of epoxides and cyclic anhydrides: an improved route to aliphatic polyesters. *Journal of the American Chemical Society, 129*(37), 11330-11331.

John, R. P., Nampoothiri, K. M., & Pandey, A. (2007). Fermentative production of lactic acid from biomass: an overview on process developments and future perspectives. *Applied Microbiology and Biotechnology, 74*(3), 524-534.

Keki, S., Bodnar, I., Borda, J., Deák, G., & Zsuga, M. (2001). Fast Microwave‐Mediated Bulk Polycondensation of d, l‐Lactic Acid. *Macromolecular Rapid Communications, 22*(13), 1063-1065.

Klaus, S., Lehenmeier, M. W., Anderson, C. E., & Rieger, B. (2011). Recent advances in CO 2/epoxide copolymerization—new strategies and cooperative mechanisms. *Coordination Chemistry Reviews, 255*(13), 1460-1479.

Koenig, N., SASIN, G. S., & Swern, D. (1958). Organic Sulfur Derivatives. V. 2 Preparation and Properties of Some Long-Chain Mercapto Acids and Related Compounds3. *the Journal of Organic Chemistry, 23*(10), 1525-1530.

Koenig, N., & Swern, D. (1957a). Organic sulfur derivatives. I. Addition of mercaptoacetic acid to long-chain monounsaturated compounds. *Journal of the American Chemical Society, 79*(2), 362-365.

Koenig, N., & Swern, D. (1957b). Organic Sulfur Derivatives. II. 2 Sulfides, Sulfoxides and Sulfones from Thiols and 10-Undecenoic Acid. *Journal of the American Chemical Society, 79*(15), 4235-4237.

Kohashi, H., & Foglia, T. A. (1985). Metathesis of methyl oleate with a homogeneous and a heterogeneous catalyst. *Journal of the American Oil Chemists Society, 62*(3), 549-554.

Komorowska-Durka, M., Dimitrakis, G., Bogdał, D., Stankiewicz, A. I., & Stefanidis, G. D. (2015). A concise review on microwave-assisted polycondensation reactions and curing of polycondensation polymers with focus on the effect of process conditions. *Chemical Engineering Journal, 264*, 633-644.

Koneswaran, G., & Nierenberg, D. (2008). Global farm animal production and global warming: impacting and mitigating climate change. *Environmental Health Perspectives, 116*(5), 578.

Kuran, W., & Listoś, T. (1994). Degradation of poly (propylene carbonate) by coordination catalysts containing phenolatozinc and alcoholatozinc species. *Macromolecular Chemistry and Physics, 195*(3), 1011-1015.

Kuran, W., & Niestochowski, A. (1980). Investigations on organic catalysts for the maleic anhydride-propylene oxide copolymerization. *Polymer Bulletin, 2*(6), 411-416.

Langanke, J., Wolf, A., Hofmann, J., Böhm, K., Subhani, M., Müller, T., . . . Gürtler, C. (2014). Carbon dioxide (CO 2) as sustainable feedstock for polyurethane production. *Green Chemistry, 16*(4), 1865-1870.

Lawniczak ‐ Jablonska, K., Dynowska, E., Lisowski, W., Sobczak, J., Chruściel, A., Hreczuch, W., . . . Reszka, A. (2015). Structural properties and chemical bonds in double metal cyanide catalysts. *X ‐ Ray Spectrometry, 44*(5), 330-338.

Lee, B. Y., Kwon, H. Y., Lee, S. Y., Na, S. J., Han, S.-i., Yun, H., . . . Park, Y.-W. (2005). Bimetallic anilido-aldimine zinc complexes for epoxide/CO2 copolymerization. *Journal of the American Chemical Society, 127*(9), 3031-3037.

Lee, S., Baek, S. T., Anas, K., Ha, C.-S., Park, D.-W., Lee, J. W., & Kim, I. (2007). Tuning of activity, induction period and polymer properties of double metal cyanide catalyzed ring-opening polymerizations of propylene oxide by using quaternary ammonium salts. *Polymer, 48*(15), 4361-4367.

Lee, S., & Shah, Y. T. (2012). *Biofuels and bioenergy: processes and technologies*: CRC Press.

Li, C.-T., Zhuang, H.-K., Hsieh, L.-T., Lee, W.-J., & Tsao, M.-C. (2001). PAH emission from the incineration of three plastic wastes. *Environment International, 27*(1), 61-67.

Li, F., Hanson, M., & Larock, R. (2001). Soybean oil–divinylbenzene thermosetting polymers: synthesis, structure, properties and their relationships. *Polymer, 42*(4), 1567-1579.

Lidström, P., Tierney, J., Wathey, B., & Westman, J. (2001). Microwave assisted organic synthesis—a review. *Tetrahedron, 57*(45), 9225-9283.

Liu, X., He, H., Wang, Y., Zhu, S., & Piao, X. (2008). Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst. *Fuel, 87*(2), 216-221.

Luinstra, G. A., & Borchardt, E. (2011). Material properties of poly (propylene carbonates) *Synthetic Biodegradable Polymers* (pp. 29-48): Springer.

LUO, J., CAI, C., & Lü, C.-x. (2003). Microwave-promoted Halogen-exchange Reaction for Preparation of Fluoronitrobenzenes: Selection of Solvents and Their Properties in Microwave Field [J]. *Fine Chemicals, 1*, 016.

Mang, S., Cooper, A. I., Colclough, M. E., Chauhan, N., & Holmes, A. B. (2000). Copolymerization of CO2 and 1, 2-cyclohexene oxide using a CO2-soluble chromium porphyrin catalyst. *Macromolecules, 33*(2), 303-308.

Meier, M. A., Metzger, J. O., & Schubert, U. S. (2007). Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews, 36*(11), 1788-1802.

Mendelsohn, R., Nordhaus, W. D., & Shaw, D. (1994). The impact of global warming on agriculture: a Ricardian analysis. *The American economic review*, 753-771.

Meng, Y., Du, L., Tiong, S., Zhu, Q., & Hay, A. S. (2002). Effects of the structure and morphology of zinc glutarate on the fixation of carbon dioxide into polymer. *Journal of Polymer Science Part A: Polymer Chemistry, 40*(21), 3579-3591.

Mol, J. (1994). Metathesis of unsaturated fatty acid esters and fatty oils. *Journal of Molecular Catalysis, 90*(1-2), 185-199.

Moore, D. R., Cheng, M., Lobkovsky, E. B., & Coates, G. W. (2003). Mechanism of the alternating copolymerization of epoxides and CO2 using β-diiminate zinc catalysts: evidence for a bimetallic epoxide enchainment. *Journal of the American Chemical Society, 125*(39), 11911-11924.

Motika, S. A., Pickering, T. L., Rokicki, A., & Stein, B. K. (1991). Catalyst for the copolymerization of epoxides with CO2: Google Patents.

Mutlu, H., Hofsäß, R., Montenegro, R. E., & Meier, M. A. (2013). Self-metathesis of fatty acid methyl esters: full conversion by choosing the appropriate plant oil. *RSC Advances, 3*(15), 4927-4934.

Nagahata, R., Sano, D., Suzuki, H., & Takeuchi, K. (2007). Microwave‐Assisted Single‐Step Synthesis of Poly (lactic acid) by Direct Polycondensation of Lactic Acid. *Macromolecular Rapid Communications, 28*(4), 437-442.

Nejad, E. H., Paoniasari, A., Koning, C. E., & Duchateau, R. (2012). Semi-aromatic polyesters by alternating ring-opening copolymerisation of styrene oxide and anhydrides. *Polymer Chemistry, 3*(5), 1308-1313.

Neufeld, L., Stassen, F., Sheppard, R., & Gilman, T. (2016). *The new plastics economy: rethinking the future of plastics.* Paper presented at the World Economic Forum.

Ohlrogge, J. B. (1994). Design of new plant products: engineering of fatty acid metabolism. *Plant Physiology, 104*(3), 821.

Paddock, R. L., & Nguyen, S. T. (2001). Chemical CO2 fixation: Cr (III) salen complexes as highly efficient catalysts for the coupling of CO2 and epoxides. *Journal of the American Chemical Society, 123*(46), 11498-11499.

Patel, S., & Xanthos, M. (2001). Environmental issues in polymer processing: A review on volatile emissions and material/energy recovery options. *Advances in Polymer Technology, 20*(1), 22-41.

Patz, J. A., Campbell-Lendrum, D., Holloway, T., & Foley, J. A. (2005). Impact of regional climate change on human health. *Nature, 438*(7066), 310-317.

Przybylski, R. (2001). Canola oil: physical and chemical properties. *Canola Council of Canada, 1.*

Qin, Z., Thomas, C. M., Lee, S., & Coates, G. W. (2003). Cobalt‐Based Complexes for the Copolymerization of Propylene Oxide and CO2: Active and Selective Catalysts for Polycarbonate Synthesis. *Angewandte Chemie International Edition, 42*(44), 5484-5487.

Quinzler, D., & Mecking, S. (2010). Linear semicrystalline polyesters from fatty acids by complete feedstock molecule utilization. *Angewandte Chemie International Edition, 49*(25), 4306-4308.

Ree, M., Bae, J., Jung, J., & Shin, T. (1999). A new copolymerization process leading to poly (propylene carbonate) with a highly enhanced yield from carbon dioxide and propylene oxide. *Journal of Polymer Science Part A: Polymer Chemistry, 37*(12), 1863-1876.

Ree, M., Hwang, Y., Kim, J.-S., Kim, H., Kim, G., & Kim, H. (2006). New findings in the catalytic activity of zinc glutarate and its application in the chemical fixation of CO 2 into polycarbonates and their derivatives. *Catalysis Today, 115*(1), 134-145.

Roesle, P., Stempfle, F., Hess, S. K., Zimmerer, J., Río Bártulos, C., Lepetit, B., . . . Mecking, S. (2014). Synthetic polyester from algae oil. *Angewandte Chemie International Edition, 53*(26), 6800-6804.

Rybak, A., Fokou, P. A., & Meier, M. A. (2008). Metathesis as a versatile tool in oleochemistry. *European Journal of Lipid Science and Technology, 110*(9), 797-804.

Rybak, A., & Meier, M. A. (2007). Cross-metathesis of fatty acid derivatives with methyl acrylate: renewable raw materials for the chemical industry. *Green Chemistry, 9*(12), 1356-1361.

Saheb, D. N., & Jog, J. (1999). Natural fiber polymer composites: a review. *Advances in Polymer Technology, 18*(4), 351-363.

Santacesaria, E., Sorrentino, A., Rainone, F., Di Serio, M., & Speranza, F. (2000). Oxidative cleavage of the double bond of monoenic fatty chains in two steps: a new promising route to azelaic acid and other industrial products. *Industrial & Engineering Chemistry Research, 39*(8), 2766-2771.

Schmalensee, R., Stoker, T. M., & Judson, R. A. (1998). World carbon dioxide emissions: 1950–2050. *Review of Economics and Statistics, 80*(1), 15-27.

Schneider, W., & Diller, W. (2000). Phosgene. *Ullmann's Encyclopedia of Industrial Chemistry*.

Scholz, C., & Gross, R. A. Biopolyesters and biocatalysis introduction.

Schrodi, Y., Ung, T., Vargas, A., Mkrtumyan, G., Lee, C. W., Champagne, T. M., . . . Hong, S. H. (2008). Ruthenium olefin metathesis catalysts for the ethenolysis of renewable feedstocks. *CLEAN–Soil, Air, Water, 36*(8), 669-673.

Seo, J., Jeon, G., Jang, E. S., Bahadar Khan, S., & Han, H. (2011). Preparation and properties of poly (propylene carbonate) and nanosized ZnO composite films for packaging applications. *Journal of Applied Polymer Science, 122*(2), 1101-1108.

Serini, V. (2000). Polycarbonates. *Ullmann's Encyclopedia of Industrial Chemistry*.

Soga, K., Imai, E., & Hattori, I. (1981). Alternating copolymerization of CO2 and propylene oxide with the catalysts prepared from Zn (OH) 2 and various dicarboxylic acids. *Polymer Journal, 13*(4), 407-410.

Sorrentino, R., & Bianchi, G. (2010). *Microwave and RF engineering* (Vol. 1): John Wiley & Sons.

Srikanth, V., Prasad, R., Poornachandra, Y., Babu, V. P., Kumar, C. G., Jagadeesh, B., & Jala, R. C. R. (2016). Synthesis of dihydrosterculic acid-based monoglucosyl diacylglycerol and its analogues and their biological evaluation. *European Journal of Medicinal Chemistry,* *109*, 134-145.

Steinbuchel, A., & Doi, Y. (2002). Polyesters III–Applications and commercial products. *Biopolymers. Weinheim (Germany): Wiley-VCH, 398*.

Suh, H. S., Ha, J. Y., Yoon, J. H., Ha, C.-S., Suh, H., & Kim, I. (2010). Polyester polyol synthesis by alternating copolymerization of propylene oxide with cyclic acid anhydrides by using double metal cyanide catalyst. *Reactive and Functional Polymers, 70*(5), 288-293.

Sun, X.-K., Zhang, X.-H., Chen, S., Du, B.-Y., Wang, Q., Fan, Z.-Q., & Qi, G.-R. (2010). One-pot terpolymerization of CO 2, cyclohexene oxide and maleic anhydride using a highly active heterogeneous double metal cyanide complex catalyst. *Polymer, 51*(24), 5719-5725.

Sun, X. K., Zhang, X. H., Liu, F., Chen, S., Du, B. Y., Wang, Q., . . . Qi, G. R. (2008). Alternating copolymerization of carbon dioxide and cyclohexene oxide catalyzed by silicon dioxide/Zn□ CoIII double metal cyanide complex hybrid catalysts with a nanolamellar structure. *Journal of Polymer Science Part A: Polymer Chemistry, 46*(9), 3128-3139.

Sun, X. K., Zhang, X. H., Wei, R. J., Du, B. Y., Wang, Q., Fan, Z. Q., & Qi, G. R. (2012). Mechanistic insight into initiation and chain transfer reaction of CO2/cyclohexene oxide copolymerization catalyzed by zinc□ cobalt double metal cyanide complex catalysts. *Journal of Polymer Science Part A: Polymer Chemistry, 50*(14), 2924-2934.

Swift, G. (2004). Degradable polymers and plastics in landfill sites. *Encyclopedia of Polymer Science and Technology*.

Takasu, A., Ito, M., Inai, Y., Hirabayashi, T., & Nishimura, Y. (1999). Synthesis of biodegradable polyesters by ring-opening copolymerization of cyclic anhydrides containing a double bond with 1, 2-epoxybutane and one-pot preparation of the itaconic acid-based polymeric network. *Polymer Journal, 31*, 961-969.

Takenouchi, S., Takasu, A., Inai, Y., & Hirabayashi, T. (2002). Effects of geometrical difference of unsaturated aliphatic polyesters on their biodegradability II. Isomerization of poly (maleic anhydride-co-propylene oxide) in the presence of morpholine. *Polymer Journal, 34*(1), 36-42.

Thakur, V. K., & Thakur, M. K. (2016). *Handbook of sustainable polymers: Processing and applications*: CRC Press.

Thanh, G. V., & Loupy, A. (2003). Microwave-assisted ruthenium-catalyzed olefin metathesis under solvent-free conditions. *Tetrahedron Letters, 44*(51), 9091-9094.

Thurier, C., Fischmeister, C., Bruneau, C., Olivier‐Bourbigou, H., & Dixneuf, P. H. (2008). Ethenolysis of methyl oleate in room‐temperature ionic liquids. *ChemSusChem, 1*(1‐2), 118-122.

Truett, W., Johnson, D., Robinson, I., & Montague, B. (1960). Polynorbornene by Coördination Polymerization1. *Journal of the American Chemical Society, 82*(9), 2337-2340.

Trzaskowski, J., Quinzler, D., Bährle, C., & Mecking, S. (2011). Aliphatic Long‐Chain C20 Polyesters from Olefin Metathesis. *Macromolecular Rapid Communications, 32*(17), 1352-1356.

Türünç, O., & Meier, M. A. (2010). Fatty Acid Derived Monomers and Related Polymers Via Thiol‐ene (Click) Additions. *Macromolecular Rapid Communications, 31*(20), 1822-1826.

Türünç, O., & Meier, M. A. (2013). The thiol‐ene (click) reaction for the synthesis of plant oil derived polymers. *European Journal of Lipid Science and Technology, 115*(1), 41-54.

Ullah, A., & Arshad, M. (2017). Remarkably Efficient Microvawe‐Assisted Cross‐Metathesis of Lipids in Solvent Free Conditions. *ChemSusChem*.

United States Department of Agriculture Foreign Agricultural Service. from http://apps.fas.usda.gov/psdonline/psdQuery.aspx

Van Dam, P., Mittelmeijer, M., & Boelhouwer, C. (1972). Metathesis of unsaturated fatty acid esters by a homogeneous tungsten hexachloride–tetramethyltin catalyst. *Journal of the Chemical Society, Chemical Communications*(22), 1221-1222.

van Meerendonk, W. J., Duchateau, R., Koning, C. E., & Gruter, G. J. M. (2004). High‐Throughput Automated Parallel Evaluation of Zinc‐Based Catalysts for the Copolymerization of CHO and CO2 to Polycarbonates. *Macromolecular Rapid Communications, 25*(1), 382-386.

Velmathi, S., Nagahata, R., Sugiyama, J. i., & Takeuchi, K. (2005). A Rapid Eco‐Friendly Synthesis of Poly (butylene succinate) by a Direct Polyesterification under Microwave Irradiation. *Macromolecular Rapid Communications, 26*(14), 1163-1167.

Velmathi, S., Nagahata, R., & Takeuchi, K. (2007). Extremely rapid synthesis of aliphatic polyesters by direct polycondensation of 1: 1 mixtures of dicarboxylic acids and diols using microwaves. *Polymer Journal, 39*(8), 841-844.

Vignon, P., Vancompernolle, T., Couturier, J. L., Dubois, J. L., Mortreux, A., & Gauvin, R. M. (2015). Cross‐Metathesis of Biosourced Fatty Acid Derivatives: A Step Further Toward Improved Reactivity. *ChemSusChem, 8*(7), 1143-1146.

Vilaseca, F., Mendez, J., Pelach, A., Llop, M., Canigueral, N., Girones, J., . . . Mutje, P. (2007). Composite materials derived from biodegradable starch polymer and jute strands. *Process Biochemistry, 42*(3), 329-334.

Wang, D., Zhang, G., Zhang, Y., Gao, Y., Zhao, Y., Zhou, C., . . . Wang, X. (2007). Synthesis, characterization, and properties of novel polyetherester polyols and developed polyurethanes. *Journal of Applied Polymer Science, 103*(1), 417-424.

Wang, S., Du, L., Zhao, X., Meng, Y., & Tjong, S. (2002). Synthesis and characterization of alternating copolymer from carbon dioxide and propylene oxide. *Journal of Applied Polymer Science, 85*(11), 2327-2334.

Warwel, S. (1999). Complete and partial epoxidation of plant oils by lipase-catalyzed perhydrolysis. *Industrial Crops and Products, 9*(2), 125-132.

Webb, H. K., Arnott, J., Crawford, R. J., & Ivanova, E. P. (2012). Plastic degradation and its environmental implications with special reference to poly (ethylene terephthalate). *Polymers, 5*(1), 1-18.

Wei, R.-J., Zhang, X.-H., Du, B.-Y., Sun, X.-K., Fan, Z.-Q., & Qi, G.-R. (2013). Highly Regioselective and Alternating Copolymerization of Racemic Styrene Oxide and Carbon Dioxide via Heterogeneous Double Metal Cyanide Complex Catalyst. *Macromolecules, 46*(9), 3693-3697.

Wiberg, K. B., & Saegebarth, K. A. (1957). The mechanisms of permanganate oxidation. IV. Hydroxylation of olefins and related reactions. *Journal of the American Chemical Society, 79*(11), 2822-2824.

Wroe, R., & Rowley, A. (1996). Evidence for a non-thermal microwave effect in the sintering of partially stabilized zirconia. *Journal of Materials Science, 31*(8), 2019-2026.

Xinghong, S. X. C. S. Z., & Guorong, Q. (2012). Double Metal Cyanide Complex Catalyst and Its Catalysis for Epoxides-Involved Polymerization. *Progress in Chemistry, 9*, 017.

Yaron, B., Calvet, R., & Prost, R. (1996). *Soil pollution: processes and dynamics*: Springer Science & Business Media.

Zhang, X.-H., Wei, R.-J., Zhang, Y. Y., Du, B.-Y., & Fan, Z.-Q. (2015). Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc–Cobalt (III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures. *Macromolecules, 48*(3), 536-544.

Zheng, Y.-Q., Lin, J.-L., & Zhang, H.-L. (2000). Crystal structure of zinc glutarate, Zn (C5H6O4). *Zeitschrift für Kristallographie-New Crystal Structures, 215*(4), 535-536.

Zia, K. M., Noreen, A., Zuber, M., Tabasum, S., & Mujahid, M. (2016). Recent developments and future prospects on bio-based polyesters derived from renewable resources: A review. *International Journal of Biological Macromolecules, 82*, 1028-1040.