SYNTHESIS OF POLYPROPYLENE CARBONATE FROM PROPYLENE OXIDE AND CARBON DIOXIDE

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APPROVAL SHEET

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It is hereby certified that **ANG RUI REN** (ID No: **14UEM01372**) has completed this dissertation entitled **"SYNTHESIS OF POLYPROPYLENE CARBONATE FROM PROPYLENE OXIDE AND CARBON DIOXIDE"** under the supervision of Ir. Dr. Lee Tin Sin (Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, and Prof. Ir. Dr. Tee Tiam Ting (Co-Supervisor) from the Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science.

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(ANG RUI REN)

DECLARATION

I, **ANG RUI REN** hereby declare the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree at UTAR or other institutions.

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Date: 14 September 2016

SYNTHESIS OF POLYPROPYLENE CARBONATE FROM PROPYLENE OXIDE AND CARBON DIOXIDE

By

ANG RUI REN

A dissertation submitted to the Institute of Postgraduate Studies and Research,
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SYNTHESIS OF POLYMERIC MATERIAL FROM CARBON DIOXIDE

ABSTRACT

The effects of catalyst preparation temperature and time, and catalyst size in relation to the performance of the zinc glutarate (ZnGA) catalyst and the polypropylene carbonate (PPC) produced was investigated. Various ZnGA catalysts were synthesized at several combinations of temperature (40^{o}C, 50^{o}C, 60^{o}C and 70^{o}C) and time (3h, 6h and 9h). The ZnGA catalysts were then used to copolymerize propylene oxide and carbon dioxide to produce PPC. It was found that the catalyst preparation temperature plays a dominant role in affecting the catalytic activity of the ZnGA. The ZnGA catalyst produced at higher temperature were found to possess higher crystallinity and capable of producing higher yield and selectivity PPC. However, the incorporation of glutaric acid into the catalyst was vital as well. Although some of the ZnGA exhibit high crystallinity, the low intensity of characteristic peaks of zinc-carboxylate bond (COO-) may causes low yield of PPC with byproducts. This was especially found on the catalysts synthesized at lower temperature (40^{o}C). Among the all the combinations of temperature and time, the ZnGA prepared using 9 hours at 70^{o}C possessed the highest crystallinity (42.52%) and has the best incorporation of GA (1.24 a.u.). It is capable of producing PPC with high molecular weight (97,100Da) and narrow PDI (1.28), high crystallinity (23.44%), high and narrow T_m at 244^{o}C with excellent mechanical properties (tensile strength of 8.48MPa, tensile elongation >400%, and Young’s modulus of 748.7MPa).

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LIST OF ABBREVIATIONS

2,2-DMGA	2,2-dimethylglutaric acid
2-KetoGA	2-ketoglutaric acid
2-MGA	2-methylglutaric acid
3,3-DMGA	3,3-dimethylglutaric acid
3-KetoGA	3-ketoglutaric acid
3-MGA	3-methylglutaric acid
3-PhGA	3-phenylglutaric acid
3,3-TMGA	3,3-tetramethyleneglutaric acid
BA-PC	poly(bisphenol-A carbonate)
BDI	β-diiminate
BPA	bisphenol-A
CHO	cyclohexene oxide
CO_2	Carbon dioxide
Co	cobalt
DMC	double metal cyanide complexes
DGCA	diglycolic acid
DSC	differential scanning calorimetry
EO	ethylene oxide
Fe	iron
FESEM	Field Emission Scanning Electron Microscopy

FTIR	Fourier Transform Infrared
GA	glutaric acid
Gel Permeation Chromatography	GPC
MMT	montmorillonite
mono-MGA	mono-methylglutarate
NaCl	sodium chloride
NEXAFS	near X-ray adsorption fine structure
PC	polycarbonates
PDI	polydispersity index
PO	propylene oxide
PPC	polypropylene carbonate
PPO	propylene oxide
R&D	research and development
SO_2	sulphur dioxide
THF	tetrahydofuran
T_m	melting temperature
TOF	turnover frequency
TGA	thermogravimetric analysis
WAXD	wide-angle X-ray diffraction
XRD	X-Ray Diffraction Spectroscopy
$ZnEt_2$	zinc ethyl
ZnGA	zinc glutarate
ZnO	zinc oxide
$Zn(OAc)_2 \cdot 2H_2O$	zinc acetate dihydrate
$Zn(OH)_2$	zinc hydroxide

CHAPTER 1

INTRODUCTION

1.1 Background

Carbon dioxide (CO_2) is one of the infamous greenhouse gases which plays a major role in causing global warming. However, it is found that CO_2 can become an affordable and rich one-carbon chemical feedstock. Therefore, the CO_2 chemical fixation has become a very fascinating study subject. One of the effective utilization methods of CO_2 is the production of aliphatic polycarbonates (PC) from catalyzed copolymerization of CO_2 with oxiranes. Previously, propylene oxide (PO) and cyclohexene oxide (CHO) were used as an oxirane resource (Meerendonk et al., 2005). Although vast advancements have been achieved in the synthesizing high performance catalysts in copolymerizing CO_2 and CHO, their resulting product, poly(cyclohexene carbonate), are inferior in the restrictive world of commodity polymers. This is mainly because of its low biodegradability and the high cost of CHO (Wu et al., 2004). Generally, due to their low biodegradability, synthetic commodity polymers such as high density polyethylene need up to 100 years to degrade in landfill, causing ecological problems (Sivan, 2011). Therefore, there is a huge demand for polymers which able to degrade in nature without releasing any harmful substances yet possess excellent properties for various purposes.

In this aspect, lower molecular weight monomer PO is chosen to react with CO_2 where PO is an affordable and technically available comonomer which fullfill above demand. In the copolymerization reaction of CO_2 with oxiranes, organometallic catalysts which are made of diethylzinc and a compound with two active hydrogens were found capable to synthesize an alternating polycarbonate effectively (Lubczak and Cisek-Cicirko, 2002). Examples of the compounds with two active hydrogens are water, aromatic dicarboxylic acids, primary amines, di- or trihydroxybenzenes, polymers, etc (Zarzyka-Niemiec, 2007). Still, the copolymerization reaction requires a long reaction time and only produces PCs with low yield and selectivity (Zarzyka-Niemiec, 2008).

Due to their rapid and clean decomposition at elevated temperature, carbonate based polymer is widely used as binder for high performance industrial and commercial applications. It is known that carbonate based polymers such as PC are amorphous, transparent thermoplastics which decompose into environmental-friendly products at elevated temperature, thus making it the ideal candidate for broad applications in the industry fields of electronics, brazing and ceramics application. High molecular weight carbonate polymer can be used as biodegradable thermoplastic materials. It is naturally biodegradable by microorganisms (Joshi and Mebel, 2007).

Several heterogeneous catalyst mixtures and homogenous discrete metal complex catalyst such as zinc dicarboxylates, metal porhydin derivatives, zinc phenoxide derivateives, salen chromium chlorides have been shown to improve reactivity of carbon dioxide in reaction with epoxy function group (Pang et al., 2008). Hence, investigation of the methods to synthesize these polymers is very advantageous to the implementation of more environmentally friendly industrial processes.

Therefore, a study was conducted on the copolymerization of PO and CO_2 using zinc glutarate (ZnGA) catalyst. Various factors which affect the catalytic activity of the ZnGA catalyst were investigated. The factors investigated include catalyst preparation temperature, catalyst preparation time and catalyst size.

1.2 Problem Statements

The effects of catalyst preparation temperature and time on the copolymerization reaction of PO and CO_2 and the polypropylene carbonate (PPC) formed in the reaction were studied. During the study, several research questions were identified:

1. What is the effect(s) of the catalyst preparation temperature and time on the the ZnGA catalyst which affect its catalytic activity?
2. How the different combination of catalyst preparation temperature and time used to synthesize ZnGA influence the properties of the PPC produced?

1.3 Aims and Objectives

This study embarks on the following objectives:

1. To synthesis and characterize the ZnGA catalyst for polymerization of carbon dioxide and propylene oxide.
2. To study the relationship between the characteristic of synthesized ZnGA and the properties of copolymer produced.

1.4 Project Scope

In order to achieve the project objective, ZnGA catalysts were synthesized with different combinations of temperature and time. The ZnGA catalysts were then used to copolymerize PO and CO_2 to produce PPC. Both synthesized ZnGA catalysts and PPC were later subjected to various of analysis tests to study the effects of catalyst preparation temperature and time on the characteristics of the ZnGA and PPC produced.

CHAPTER 2

LITERATURE REVIEW

2.1 The monomers

Currently, one of the worldwide changes that have the highest impact on Earth is the global warming caused by greenhouse gases such as methane, ozone, nitrogen oxide and CO_2. Since the industrial evolution, the concentration of CO_2 in the Earth's atmosphere has increased tremendously to the latest data reported by United States National Oceanic and Atmospehric Administration that March 2014 at 399.47 ppm and this number still increasing (Mauna Loa Observatory: Scripps CO_2 Program, 2014)! Every year, human activities have added approximately 24 billion tons of CO_2 to the atmosphere, in which the burning of fossil fuels alone accounted for 22 billion tons. Although CO_2 can be removed by plants, soils and the oceans through photosynthesis, carbon storage method and absorption, there is still a net increment of 9 billion tons of CO_2 into the atmosphere per year. As a result, the average annual increase of CO_2 is 2.1 ppm (part per million) annually (Mauna Loo Observatory: Scripps CO_2 Program, 2014). Knowing the dangers which all living organisms facing, several national governments signed the Kyoto Protocol of the United Nations Framework Convention on Climate Change, developing and implementing every possible methods in decreasing the CO_2 gas emissions (David and Herzog, 2001; Gupta et al., 2003). Various drastic actions had been taken, includes capturing the CO_2 gas generated at major outlets such as thermal power plants and cement industries (Mandil, 2004). The captured CO_2 is being stored in safe place and/or then used as feedstock to produce value added chemicals and fuels.

CO_2 is recognized as the most fundamental carbon resource on Earth. Currently, many research and development (R&D) are being conducted to discover effective methods for reusing the captured CO_2 (Peters et al., 2009; Aresta, 2010; Areasta and Dibenedetto, 2007; Centi and Perathoner, 2009; Hoekman et al., 2010; Ma et al., 2009; Patil et al., 2010; Sakakura et al., 2007; Schaefer et al., 2010; Reddy and Thrimurthulu, 2009). In fact, many industrial methods have been developed to have an encouraging influence on atmospheric CO_2. For instance, application of CO_2 in manufacturing processes such as enhancement of oil and gas recovery, enhancement of agriculture production, as well as ponds of genetically modified algae to produce biodiesel using the captured CO_2 from the power plant (Reddy and Thrimurthulu, 2009; Arakawa et al., 2001.). In addition, they can be used as building block for the synthesis of chemicals and chemical intermediates, for example urea, salicylic acid and polycarbonate-based plastics. In this review, the development of CO_2-based PCs ever since it had been discovered is highlighted.

With a demand greater than 1.5 million tons worldwide every year, PC is an important class of commercial polymers (Gross et al., 1999). Because of their optical clarity and toughness, they are widely used in the manufacturing of various products such as food and drink containers, household appliance parts et cetera. (Bisphenol-A, 2013; Crivello et al., 2000). In the industry, the most widely used PC is made using bisphenol-A (BPA). The high molecular weight poly(bisphenol-A carbonate) (BA-PC) is commonly synthesized by using these two industrial approaches. The first approach consists of an interfacial reaction between phosgene and sodium salt of BPA in a heterogeneous system, while the second approach involves BPA and diphenyl carbonate in a melt-phase transesterification (Figure 2.1).

The first approach involves the usage of the hazardous dichloromethane and phosgene which are not environmentally friendly. In addition, it also produces huge quantity of sodium chloride (NaCl) as a side product. On the other hand, the second approach needs high temperature in order to eliminate phenol from the final products. Meanwhile, a different method to produce PC was reported by Inoue et al. in 1969 (Inoue et al., 1969). They had successfully copolymerized oxiranes with CO_2 and produced an alternating aliphatic PC (Figure 2.2). The method used has several pros and cons compared to the current industrial approaches. Firstly, the method reported by Inoue et al. (1969) is a chain growth process compared to BA-PC which involves step-growth mechanisms. Subsequently, it is capable of producing PC with better control of molecular weight and good selectivity. In addition, the oxiranes used in the copolymerization reaction do not possess the safety hazards like the phosgene used in the current industrial process. Besides that, the copolymerization reaction involving CO_2 can be considered as green chemistry as CO_2 is a renewable resource. The greenhouse gas CO_2 is also widely available, affordable, non-flammable and non-toxic (Beckman, 1999).

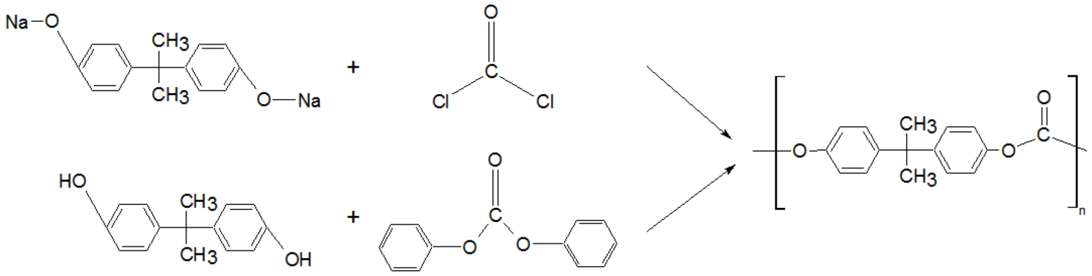


Figure 2.1: Industrial approaches to poly(bisphenol-A carbonate) (Gross et al., 1999)

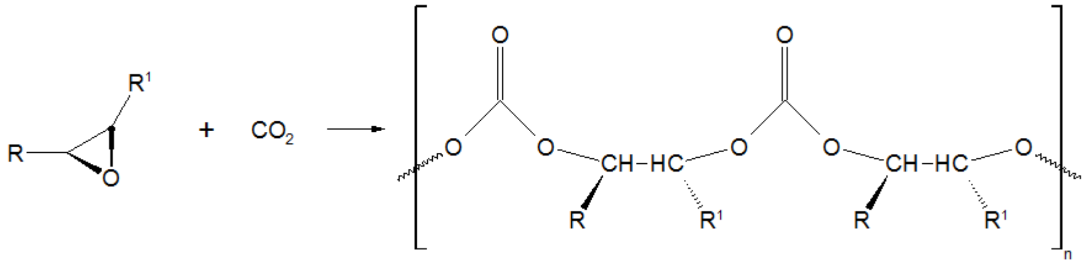


Figure 2.2: Alternating PC from the copolymerization of an oxirane with CO_2 (Inoue et al., 1969)

Nonetheless, the challenge of the copolymerization of CO_2 and oxirane is the polymer product is limited to an aliphatic C2 bridge. This caused the endeavor to improve the physical properties of the alternating PC to become comparable to the high impact strength, heat resistance and transparency of BA-PC becomes restricted within constraints. (Freitag et al., 1998). On the other hand, due to the lack of ring strain, large oxiranes such as oxetanes are not reactive enough to copolymerize with CO_2 to produce PC efficiently. Still, the advantages of copolymerization of CO_2 with cyclic ethers still outweigh the disadvantages. Therefore, such process has been triggered interest of many research groups, and many researches have been done to investigate possible new catalysts which can produce polycarbonate with higher yield and selectivity.

2.2 Copolymerization of CO_2 and epoxides

In year 1969, the first example of polymer synthesis from CO_2 was discovered (Inoue et al., 1969). The polymers were synthesized via reacting CO_2 and epoxides, also known as oxiranes, such as ethylene oxide (EO) and propylene oxide (PO). The copolymerization was done by using the equimolar reaction mixture of diethyl zinc and water as catalyst at room temperature with 30-50 atm CO_2 pressure. This has successfully produced an alternating copolymer of aliphatic PC with a high molecular weight of 50,000–150,000. Ever since then, the copolymerization of CO_2 with cyclic ethers has triggered the interest of several research groups. Due to high stability of CO_2, a highly active catalyst is needed in the copolymerization of CO_2 with cyclic ethers. Up to date, researchers have reported various catalyst systems mainly based on diethyl zinc; however more recently researches are focusing on other metals such as aluminium, chromium, cobalt, manganese and iron catalysts. In addition, there are several catalyst systems which is capable of copolymerizing oxiranes with other organic fragments such as CO_2 and sulphur dioxide, SO_2. Most of the works have been focused on the copolymerization reaction involving oxiranes and CO_2 using zinc based catalyst systems. The next section will be the summary of the promising catalysts for utilizing CO_2 to produce polycarbonate.

2.3 Zinc catalyst compound

Various transition and main group metals are capable of producing cyclic carbonates from oxiranes and CO_2. Besides the aluminium complexes, zinc is the only rare earth metal complexes and transition elements reported capable of copolymerizing oxirane and CO_2 to form alternating PC (Ang et al., 2015).

2.3.1 Diethylzinc

In year 1962, Inoue et al. discovered the copolymerization of carbon dioxide and epoxides by using dialkylzinc with optically active alcohol system as catalyst (Inoue et al., 1962). Later, heterogeneous catalyst was synthesized with equivalent amount of zinc ethyl ($ZnEt_2$) and water to be used in the copolymerization of PO and CO_2 to produce PPC with low molecular weight and turnover frequency (TOF) of about 0.12 mole of epoxide consumed per mole of zinc in an hour. The copolymerization was under the condition of 80 ^{o}C at 20-50 atm CO_2 pressure (Inoue et al., 1969). Therefore, a mixture of diethyzinc and compound having two or more labile hydrogen atoms such as water, primary amines or alcohols is considered as the pre-requisite to produce an effective catalyst system in the copolymerization (Sugimoto and Inoue, 2004).

In order to prepare the catalyst, a definite amount (frequently 0.5 equivalents) of an alcohol or water is added to a bis(alkyl) zinc precursor. It would further form a different multinuclear catalytic species ill-defined mixture. However, the copolymers produced by these catalysts were found to possess a very broad molecular weight distribution. In addition, these catalysts usually have low turnover frequencies. These disadvantages are mainly due to the multinuclear nature of these catalysts. Due to the fact that not every metal centre is accessible by the monomers equally, it is notable that different chemical sites produce different polymers. In year 1975, an interesting observation with these systems during copolymerization of styrene oxide and CO_2 was reported also (Hirano et al., 1975). The researchers found that when styrene oxide was used, the ring opening occurs at the methane oxygen bond, but not at the methylene oxygen bond, which is usually observed when PO and derivatives are used.

During the copolymerization, epoxide ring is believed to be opened by nucleophilic attack from the backside. On the other hand, the alternating characteristics of copolymer would imply that the epoxide insertion is the rate limiting step. Theoretically, if CO_2 insertion was slow and the epoxide ring opening was fast, the copolymer would not exhibit an alternating structure while high percentage of ether linkages will be observed. On the other hand, if the insertion of CO_2 was fast coupled with slow opening of the epoxide, the CO_2 insertion will almost exceed a following epoxide opening, exhibiting alternating copolymer structure. Although there have been numerous diethylzinc with active hydrogen compound catalysts developed, the exact nature of the active sites for the catalyst still remain unclear. Consequently, the structure and activity of the catalyst were hard to be studied, delaying the design process of the catalyst. Lastly, the low catalytic activity and high cost of the diethylzinc made the heterogeneous catalyst to be industrially not feasible.

2.3.2 Zinc glutarate

This is the group of zinc catalysts involve the usage of dicarboxylic acids as ligands. During the early 1990's, there were a few companies, including ARCO Co. and Mitsui Petrochem. Ind. filed patents on the application of some polycarboxylate zinc complexes in producing PPC with the presence of organic solvents. Today, several industrial processes have been done accordingly with these patents (U.S. Patent 4,783,445, 1987; U.S. Patents 5,026,676, 1990; U.S. Patents 4,943,677 1990, 1990). Indeed, the most active type of heterogeneous catalyst, zinc dicarboxylates, especially ZnGA which made up of zinc oxide and glutaric acid, is most widely used for the copolymerization of CO_2 and epoxides. Since the discovery by Inoue et al. in year 1969, several literatures have been published regarding the application of ZnGA as catalyst in the copolymerization process as it is easier to prepare, non-toxic and the ability to produce copolymer product in high productivity and high molecular weight (Inoue et al., 1969; Kember et al., 2011). In year 1995, the usage of heterogeneous ZnGA catalysts was reported by Darensbourg et al., where they synthesize these catalysts by addition of the corresponding dicarboxylic acids to the zinc oxide. A white precipitate was obtained after heating the solution in toluene. It was later used as such after drying (Darensbourg and Holtcamp, 1995). However, the exact structure of these catalysts has yet to be clarified, while its catalytic activity was found to be rather low (TOF = 6 h^{-1}) when propylene oxide is used as a monomer.

On the other hand, ZnGA had been used to terpolymerize CO_2 with polyproylene and caprolactone, attempting to synthesis biodegradable polyester carbonate (Hwang et al., 2003). It was found that dicarboxylic ligands with long fluorinated tails have better solubility in supercritical CO_2 (Figure 2.3). Under reaction conditions of 100-110^{o}C at 133 bar, a maximum TOFs of 8h^{-1} was achieved with these soluble carboxylate catalysts, producing polymers with about 90% carbonate content. Importantly, high molecular weight distributions were also obtained with these catalysts. Besides that, it was reported that the performance of the ZnGA catalysts can be enhanced by using ultrasonic stirring in the synthesis process in order to obtain higher interdispersion of the powdery starting materials (Wang et al., 2002). It is found that the catalyst's crystallinity possess a significant impact towards the activity of the copolymerization (Meng et al., 2002). Moreover, there was another effort made to improve activity which the catalyst is activated with sulphur dioxide (Eberhardt et al., 2004). When PO was used in the copolymerization reaction with CO_2, PPC was synthesized with TOF of 3-6 h^{-1}. In year 2002, Chisholm et al. performed a thorough investigation on the chain microstructure of PPC and PO obtained via these ZnGA catalyst (Chisholm et al., 2002). By using ^{13}C NMR, it was confirmed that there was a preference of head-to-tail coupling. In addition, zinc benzoate clusters were reported active in copolymerizing CHO and CO_2 as well as terpolymerizing PO, CHO and CO_2 (Darensbourg et al., 2002).

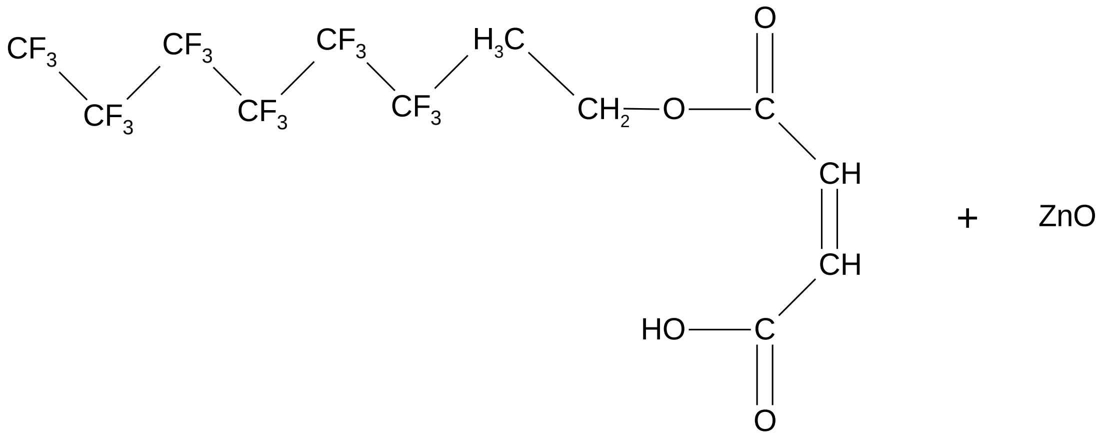


Figure 2.3: Carboxylate zinc catalysts with long fluorinated tail for the synthesis of PPC (Sun, 1987; Motika et al., 1990; Rockicki, 1990)

Over decades, the structure of ZnGA has been determined and confirmed (Kim et al., 2004; Luinstra et al., 2005). Moreover, the surface characteristics of ZnGA together with its catalytic mechanism in copolymerization of CO_2 and PO have been studied by employing near X-ray adsorption fine structure (NEXAFS) (Kim et al., 2003). From the study of Kim et al. concluded that more hydrocarbon units present in the outermost layer of the ZnGA catalyst as compared to its inner layers. Study on the catalytic mechanism further showed that there was adsorption of CO_2 and PO onto the ZnGA. It was found that PO has higher tendency to be adsorbed and inserted into the zinc oxide bond of the catalyst as compared to CO_2. Hence, this indicates that the catalyst surface could be modified by PO. Utilization of ZnGA in the copolymerization is initiated by propylene oxide rather than carbon dioxide.

2.3.2.1 Effects of zinc sources on ZnGA

Researches also have been done to investigate how different sources of zinc can affect the catalytic activity of ZnGA. Indeed, various of catalysts have been synthesized from the reactions of glutaric acid with zinc oxide (ZnO), zinc hydroxide ($Zn(OH)_2$) and $ZnEt_2$ by several groups of researchers (Ree et al., 1999; Motika et al., 1990). The condition of reaction and the reaction yield for the synthesis of catalysts are shown in Table 2.1. From the results shown in Table 2.1, it is clear that all the three types of ZnGA were able to be synthesized, with $Zn(OH)_2$/glutaric acid system having the lowest yield. The lowest yield in the $Zn(OH)_2$/glutaric acid system could be attributed to the types of solvent used, the reaction temperature and time employed, as well as the moles of glutaric acid used. All these would affect the reaction of $Zn(OH)_2$ and glutaric acid, hindering the bonding of the two compounds and results in a lower yield of ZnGA. When a lower yield of ZnGA is obtained, the catalytic activity in the copolymerization would be affected as well which further lowering the yield of the copolymer product.

Table 2.1: ZnGA synthesized from Different Zinc Sources (Ree et al., 1999)

Zinc Source (mmol)	GlutaricAcid Derivative (mmol)	Reaction Temperature (^oC)	Reaction Time (h)	Yield (%)
ZnO (100)	Glutaric Acid (98)	55	4	98
$Zn(OH)_2$ (50)	Glutaric Acid (50)	60	48	70
ZnEt2 (20)	Glutaric Acid (20)	25	12	100

The synthesized catalysts were tested by Brunauer-Emmet-Teller (BET) technique to determine the catalytic surface area. From the results, it is shown that $ZnEt_2$/glutaric acid system has the highest surface area of 34.09 m^2/g while the other two ZnGA are in the range of 19.78 to 22.43 m^2/g (Kim et al., 2004). Hence, this can conclude the increasing order of the ZnGA surface area is in the form of: ZnO/glutaric acid < $Zn(OH)_2$/glutaric acid < $ZnEt_2$/glutaric acid. In order to test the crystallinity of the catalysts, wide-angle X-ray diffraction (WAXD) was used. From the WAXD patterns, it is suggested that all the three ZnGA have almost the identical crystal structure despite of the different synthetic methods used. However, the overall crystallinity and crystal quality of the catalysts would vary accordingly based on the different synthetic methods. From the WAXD patterns, it is concluded that the overall crystallinity of the zinc glutarates with different zinc sources increase in the following order: $ZnEt_2$/glutaric acid < $Zn(OH)_2$/glutaric acid < ZnO/glutaric acid.

Based on 1 g of the respective ZnGA, copolymerization was performed with 100 mL PO in the reactor pressurized to 51.5 atm by CO_2. The copolymerization condition was 60°C and the reaction time was 40 h. The copolymerization yield which is determined by the methanol-insoluble alternating PPC, together with the molecular weight and polydispersity index (PDI) of the copolymer, were shown in Table 2.2. Different copolymer yield was obtained by using different type of zinc glutarates. This indicates that the copolymerization of CO_2 and PO is strongly dependent on the zinc glutarate catalyst, which happened to be synthesized from different zinc sources (Ree et al., 2006). Among the all the ZnGA catalysts, ZnO/glutaric acid was able to produce the highest yield of copolymer product with a relatively higher molecular weight and a narrow PDI. This result is said to be a higher copolymerization yield reported compared to the maximum yield of 34 g polymer/ g of catalyst described in the past literature (Ree et al., 1999; Jung et al., 1999). Although ZnO/glutaric acid system has the lowest catalytic surface area among the three zinc glutarates, the highest crystallinity in its catalyst structure has successfully produce copolymer in highest yield. Thus, it can be said that when it comes to the catalytic activity of zinc glutarates, crystallinity such as the morphology of the catalyst would be the key determining factor.

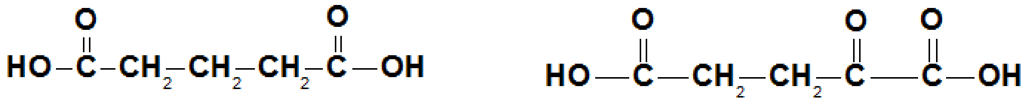
Table 2.2: Copolymerization of CO_2 and PO with zinc glutarates from different zinc sources (Ree et al., 2006)

Zinc Glutarate System	Copolymer Yield (g/g of catalyst)	PPC product		
		M_n	M_w	PDI
ZnO/glutaric acid	64.0	143k	343k	2.4
$Zn(OH)_2$/glutaric acid	8.8	22k	65k	3.0
$ZnEt_2$/glutaric acid	2.5	11k	124k	11.3

2.3.2.2 Effects of glutarate sources on ZnGA

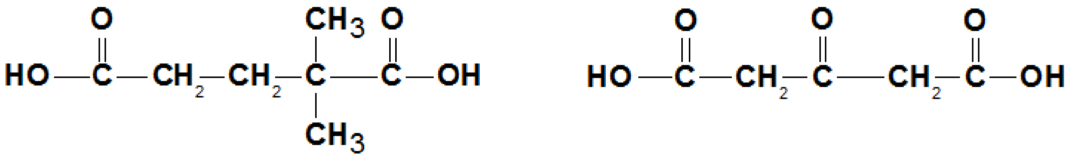
Generally, the zinc ion center constitutes the main active catalytic site in the ZnGA and it coordinates four carbonyl oxygen atoms from different glutarate ligands (Kim et al., 2003). The catalytic activity of the ZnGA in the copolymerization of carbon dioxide and epoxides is expected to be affected by the incorporation of other substituents into its glutarate ligand, which would change the characteristics of the Lewis acid represented by zinc ion center.

In order to investigate how the different sources of glutarate would affect the catalytic activity of ZnGA, several sets of ZnGA derivatives were prepared from the reactions of zinc oxide with various dicarboxylic acids: glutaric acid (GA), 2,2-dimethylglutaric acid (2,2-DMGA), 3,3-dimethylglutaric acid (3,3-DMGA), 2-methylglutaric acid (2-MGA), 3-methylglutaric acid (3-MGA), 3-phenylglutaric acid (3-PhGA), 2-ketoglutaric acid (2-KetoGA), 3-ketoglutaric acid (3-KetoGA), 3,3-tetramethyleneglutaric acid (3,3-TMGA), mono-methylglutarate (mono-MGA) and diglycolic acid (DGCA) (Ree et al., 2000). The chemical structure of various ZnGA derivatives and diglycolic acid are shown in Figure 2.4. Generally, all the ZnGA derivatives were synthesized via the standard method as described in the methodology part of this report. In addition, in order to obtain the reaction yield of the respective catalysts, the amount of reacted ZnO were determined by measuring the amount of unreacted dicarboxylic acids left after the removal of the used toluene and acetone from the filtrate (Ree et al., 2000). Table 2.3 shows the experimental yield of the ZnGA derivatives.



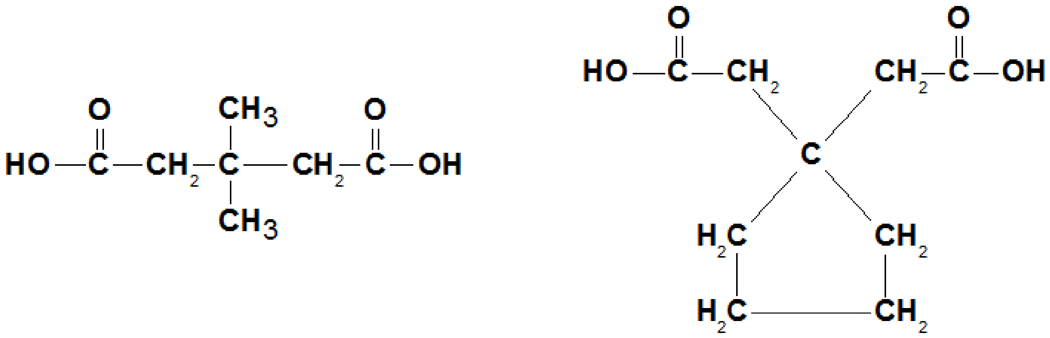
glutaric acid
(GA)

2-ketoglutaric acid
(2-KetoGA)



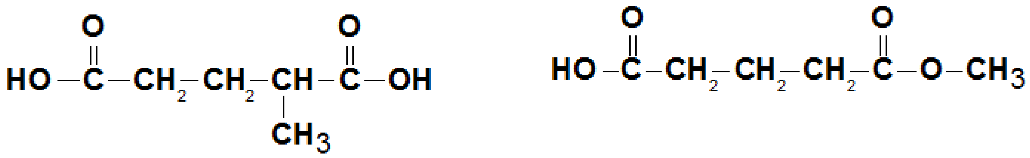
2,2-dimethylglutaric acid
(2.2-DMGA)

3-KetoGlutaric Acid
(3-KetoGA)



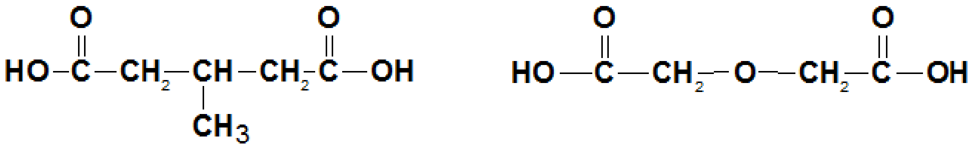
3,3-dimethylglutaric acid
(3,3-DMGA)

3,3-TetramethylGlutaric Acid
(3,3-TMGA)



2-methylglutaric acid
(2-MGA)

methylglutaric acid
(MGA)



3-methylglutaric acid
(3-MGA)

3,3-TetramethylGlutaric Acid
(3,3-TMGA)

Figure 2.4: The Chemical Structure of Various Glutaric Acid Derivatives and Diglycolic Acid (Ree et al., 2000)

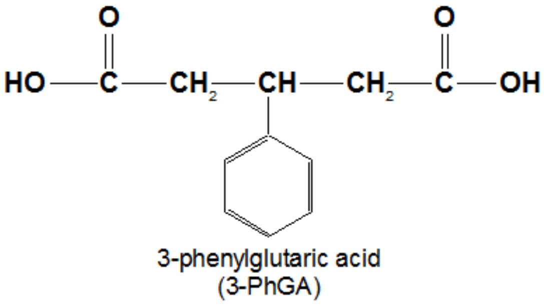


Figure 2.4 (cont'): The Chemical Structure of Various Glutaric Acid Derivatives and Diglycolic Acid (Ree et al., 2000)

Table 2.3: Catalyst Yield of ZnGA Derivatives from Zinc Oxide with Various Organic Dicarboxylic Acids (Ree et al., 2000)

Catalyst Product	Dicarboxylic Acid Used in the Reaction with ZnO	Yield (%)
ZnO/GA	glutaric acid	98
ZnO /2,2-DMGA	2,2-dimethylglutaric acid	66
ZnO /3,3-DMGA	3,3-dimethylglutaric acid	96
ZnO /2-MGA	2-methylglutaric acid	94
ZnO /3-MGA	3-methylglutaric acid	78
ZnO /3-PhGA	3-phenylglutaric acid	56
ZnO /2-KetoGA	2-ketoglutaric acid	15
ZnO /3-KetoGA	3-ketoglutaric acid	97
ZnO /3,3-TMGA	3,3-tetramethyleneglutaric acid	60
ZnO /mono-MGA	mono-methylglutarate	62
ZnO /DGCA	diglycolic acid	70

Based on the eleven type of glutarate acid derivatives obtained, several copolymerization processes (with 1.0 g of catalyst, propylene oxide of 100 mL, reaction time of 40 h, reaction temperature of 60^{o}C, and pressure of 51.5 atm) can be done to investigate their effects on the copolymer yields. The results of the copolymer yield together with other information such as the M_n, $M_w$and PDI are shown in Table 2.4. ZnO/GA is the only ZnGA system to contribute to the highest copolymer yield of 64.54 g per gram of catalyst, while others only able to give 0.02

to 9.66 g of copolymer per gram of catalyst. This can be explained by the lower reaction yield occurred during the preparation of ZnGA. In fact, smaller quantity of unreacted zinc oxide can be favored in order to result a higher catalyst yield, which further increases the yield of the copolymer.

Based on the investigation, several conclusions can be drawn. First, the incorporation of constituents into the glutarate ligand would affect the nucleophilicities of the carboxylic acids and change the Lewis acidity of the zinc ion center. Ultimately, this would suppress the activity of the ZnGA during the copolymerization process. Second, the side group constituents should not present in the ZnGA as they would generate electronic and stearic hindrance around the zinc ion center. This is because such side group would cause changes in the coordination of the carboxylates, and further lowering the activity of the catalyst. Lastly, most of the constituents are known to have additional bulk around the active zinc ion center which would affect the morphology of the catalyst, subsequently leading to changes in catalytic activity.

Table 2.4: Copolymerization of CO_2 and PO with ZnGA from different glutarate sources (Ree et al., 2000)

Zinc Glutarate System	Copolymer yield (g/g of catalyst)	PPC Product		
		M_n	M_w	PDI
ZnO /GA	64.54	143k	343k	2.4
ZnO /2,2-DMGA	0.02	-	-	-
ZnO /3,3-DMGA	0.61	14k	166k	11.7
ZnO /2-MGA	0.04	12k	62k	5.2
ZnO /3-MGA	1.30	37k	285k	7.7
ZnO /3-PhGA	0.02	22k	180k	8.2
ZnO /2-KetoGA	0.32	8k	48k	5.5
ZnO /3-KetoGA	0.02	11k	52k	4.4
ZnO /3,3-TMGA	0.13	15k	104k	6.6
ZnO /mono-MGA	9.66	23k	82k	3.5
ZnO /DGCA	3.41	32k	202k	6.1

2.3.2.3 Effect of structure and morphology on zinc glutarate

As discussed in the previous section regarding the impact of different sources of zinc towards the catalytic activity, ZnGA catalyst was found to be highly crystallized but with a rather low surface area (Ree et al., 1999; Jung et al., 1999). In fact, the factors affecting the performance of a heterogeneous catalyst include the crystallite size and size distribution, impurities present in the catalyst, the crystal structure of the catalyst and the content of polymorphous modification. As concluded in the previous section, high crystallinity is vital to ensure excellent performance of ZnGA catalyst in the copolymerization process (Meng et al., 2002). However, according to a technical report written by BASF Company in year 2000 (Technical Report of Pluronic, 2000), they found that crystallinity of about 77 % would be sufficient to provide high catalytic activity to the catalyst. Moreover, they have also examined and verified that for ZnGA catalyst with crystallinity of more than 77 %, larger surface area is more preferable to improve the activity of catalyst in the copolymerization. It was concluded that zinc source is not restricted to only ZnO when it sourced from the synthesis of ZnGA catalyst. Other zinc sources could be suitable as well whenever possess high crystallinity and large surface area.

2.3.2.4 Novel discoveries on zinc glutarates

From the previous section, it is clear that the catalytic activity of zinc glutarates in the copolymerization depends mainly on the surface area of the catalyst. Therefore, several approaches have been taken by researchers in the past few years in order to improve the surface area of the ZnGA. Recently, it has been known that organic templates can be used to change the external morphologies and the crystalline structure of inorganic particles such as calcium phosphate, ZnO and calcium carbonate during the synthesis process (Öner, 1998; Yang et al., 2002; Qi et al., 2000). Among the reported organic templates, amphiphilic block copolymer was selected due to its outstanding functionalities, well-controlled compositions, and lengths of its blocks. In this amphiphilic template, one block (anchor block) is adsorbed to the solid particle’s surface while another block (solution block or buoy block) forms a swollen layer bound to the same surface through the anchor block. As a result, the solution block is able to prevent particle agglomeration by forming a steric shield.

During the study pursued by Kim and coworkers, the surface of the ZnGA can be enhanced by the synthesis of ZnGA from zinc and glutarate sources in different reaction media with a triblock copolymer [Pluronic PE6400: poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)] (Technical report of Pluronic, 2000) as the amphiphilic template (Kim et al., 2005). In fact, ZnGA-T was synthesized by adding zinc oxide powder into the glutaric acid dissolved in toluene (Ree et al., 1999.). However, the other four types of ZnGA were prepared by using zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$) and glutaric acid. The reason of choosing these zinc and glutarate sources was due to the ionic or polar characteristics for both of the compounds would allow the interactions with the PE6400 template which is polar and having hydrophilic nature. In addition, several solvents were used for the synthesis of ZnGA-O, ZnGA-PE1, ZnGA-PE2 and ZnGA-PE3 rather than the conventional toluene as in the case of ZnGA-T. For ZnGA-O and ZnGA-PE3, the solvent used is an ethanol mixture that consists 5.5 wt% of water of the total solvent mixture weight. For ZnGA-PE1, only water was used instead. Meanwhile, ethanol was chosen as the reaction medium for ZnGA-PE2 (Kim et al., 2005). The synthesized ZnGA catalysts were then used to copolymerize PO and CO_2 where the results are shown in Table 2.5. It can be noticed that ZnGA-T has the smallest crystallite size of 5.7 µm with a surface area of only 19.8 m^2/g. This means that ZnGA-T is a dense zinc glutarate consists of small particles. For ZnGA-O, largest particle size of 15.5 µm and surface area of 38.0 m^2/g were resulted. This implied that the surface area of the catalyst is not proportional to the particle size of the catalyst. Particle size alone could not be used to determine the surface area of the catalyst (Kim et al., 2005).

Furthermore, for ZnGA synthesized with the aid of PE 6400 template, large surface areas (with the exception of ZnGA-PE1) in the range of 46.5 to 48.5 m^2/g can be seen with ZnGA-PE3 having the largest catalytic surface area (Kim et al., 2005). Hence, it can be concluded that the attempt of enhancing the surface area of ZnGA was successful. The surface area of the catalyst can be increased when a suitable polarity of solvent is used for the synthesis of ZnGA in the presence of block copolymer. By looking at the copolymerization result, it is observed that the highest yield of 83 g copolymer/g of catalyst can be obtained by using ZnGA-PE3 as catalyst. This result is higher than the conventional ZnGA-T which results copolymer yield of 64 g copolymer/g of catalyst. This is higher than the ZnGA-O which was synthesized with the same zinc source, glutarate source and reaction media as ZnGA-PE3, but without PE 6400 template (Kim et al., 2005). In fact, the high yield in the ZnGA-PE3 can be attributed to its high surface area obtained from the synthesis. This suggested that the synthetic history of ZnGA is important as it would affect the particle size, surface area, as well as the crystallinity of the catalyst, which would further affect the yield of the copolymerization and the characteristics of the copolymer (Meng et al., 2002). On the other hand, another conclusion can be drawn. The large surface area of the ZnGA-PE3 only produced PPC with relatively lower molecular which is a flaw in the copolymerization process. Perhaps in the near future, new ways can be discovered to increase the molecular weight of the copolymer (Kim et al., 2005).

Table 2.5: Details of the ZnGA synthesized under various conditions and their results in copolymerizing PO and CO_2 (Kim et al., 2005)

Catalyst	Template	Particle Size (μm)	Surface Area (m^2/g)	Copolymer Yield (g/g of catalyst)	PPC Product		
					M_n	M_w	PDI
ZnGA-T	-	5.7	19.8	64	343k	143k	2.4
ZnGA-O	-	15.5	38.0	35	335k	81k	4.2
ZnGA-PE1	PE6400	8.5	13.9	9.5	529k	51k	10.4
ZnGA-PE2	PE6400	13.3	46.5	67	238k	93k	2.6
ZnGA-PE3	PE6400	15.3	48.5	83	160k	60k	2.7

Apart from using amphiphilic template in the synthesis of ZnGA to increase the copolymerization yield, other methods have been adopted as well. ZnGA-MMT was prepared by the reaction of zinc oxide and glutarate acid, followed by the dispersion of catalyst on the acid-treated montmorillonite (MMT) surface in quinoline (Wang et al., 2005). This method has successfully produced PPC with high yield of 115.2 g copolymer/g of catalyst. Generally, the copolymerization of CO_2 and PO took place via an anionic coordination mechanism. Any presence of cations would influence the reaction of CO_2 with PO. In order to remove these cations, montmorillonite which is a kind of natural clay possess cation exchange ability was treated by acid according to the literatures (Rhodes and Brown, 1993; Clark et al., 1994). As a result, high yield of copolymer with complete alternating structure can be obtained. In addition, montmorillonite layers present within the copolymer has shown its ability to enhance the thermal properties of PPC after tested with differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). However, ZnGA-MMT in the copolymerization only produced low molecular weight of PPC, which is one of the problems encountered by the researchers.

2.3.3 Double metal cyanide complexes

Other than the catalysts mentioned above, another type of catalyst which can be employed in the copolymerization of CO_2 and oxiranes are the double metal cyanide complexes (DMC). As active catalysts, they are very useful for the ring-opening polymerization of heterocyclic monomers such as epoxides (Liu et al., 2003). Basically, DMC can be prepared by the reaction between a metal salt such as zinc chloride and an alkali metal hexacyanometallate such as potassium hexacyanocobaltate in aqueous form. The chemical formula is $Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yH_2O$. DMC has become a widely investigated heterogeneous catalyst as they have extensively been synthesized and applied in the industry. A more promising class of DMC includes the $Zn_3[M(CN)_6]_2$, where M could be the iron (Fe) or cobalt (Co) metal. According to the patent published by Kruper and Swart, $Zn_3[Fe(CN)_6]_2$ acts very mildly in the random copolymerization of CO_2 and PO to produce 2.8 g of propylene carbonate and about 0.53 g of polypropylene oxide. The total ratio of carbonate to ether was 4.8 with propylene oxide conversion of 71 % (U.S. Patent No. 4,500,704, 1985).

In year 2005, Kim et al. (2005) performed the copolymerization of CO_2 and epoxides by using DMC which was synthesized from zinc salt and $K_3Co(CN)_6$ by using tertiary butyl alcohol and poly(tetramethylene ether glycol) as the complexing reagents. This study has successfully showed that high reactivity of DMC in copolymerizing CHO and CO_2, where it achieve higher reactivity and yield compared to the homogeneous diethylzinc-based catalyst (Darensbourg et al., 1995; Darensbourg et al., 1999). From Table 2.6, it can observed that high activity and presence of carbonate content would be favored in the copolymerization of CO_2 and alicyclic oxide (such as cyclopentene oxide and CHO) as compared to CO_2/alkylene oxides copolymerizations. A recent advancement of the DMC could be traced back in year 2005, where high activity of 13 mole of PO/mmol cobalt in an hour was obtained through the copolymerization of CO_2 and PO by using $Zn_3[Co(CN)_6]_2$-based catalysts as described in the literature (U.S. Patent No. 6,921,737 B1, 2005; U.S. Patent No. 6,713,599, 2004).

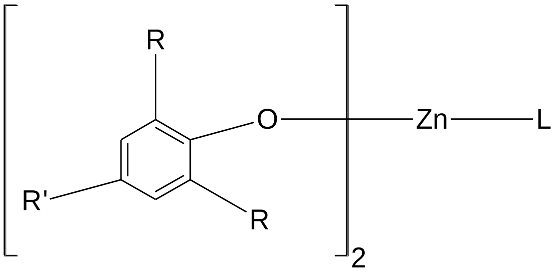
The copolymerization temperature employed was 100 ^oC and 6.2 MPa of CO_2 pressure was used. However, such reaction produces about 10 to 20 % of propylene carbonate which is the undesired by-product of the process (Chen, Hua, Fang and Qi, 2004). Furthermore, the incorporation of DMC in the copolymerization of epoxides and carbon dioxide have some disadvantages. One of the disadvantages is the low CO_2 insertion in the polymer chain. Besides that, the copolymerization conditions involving DMC catalyst were harsh, with temperatures in the range of about 80 to 130 ^oC and pressures from 50 to 100 atm. Importantly, the copolymer produced has only moderate molecular weight with wide polydispersity.

Table 2.6: Epoxides/CO_2 copolymerization results obtained by DMC catalyst (Kim et al., 2005)

Epoxides	T_p(^oC)	Time (h)	TON	TOF	M_n	M_n/M_w	f_{CO2}
Cyclohexene oxide	50	4	506.14	126.54	6800	1.81	0.50
	80	4	526.15	131.55	8900	1.67	0.53
Cyclopentene oxide	50	12	480.86	40.08	1900	1.83	0.32
	80	12	482.27	41.18	2300	1.55	0.36
4-vinyl-1-cyclohexene-1,2-epoxide	50	12	446.34	37.20	15500	2.66	0.63
	80	12	459.75	38.32	10100	2.22	0.73
Propylene oxide	50	24	506.80	21.11	4400	3.92	0.22
	80	24	535.58	22.32	6500	1.98	0.13
Butene oxide	50	24	404.12	16.84	9000	3.79	0.28
	80	24	419.73	17.48	2800	1.44	0.12
Hexene oxide	50	24	-	-	-	-	-
	80	24	413.14	17.22	6400	2.35	0
Octene oxide	50	24	397.09	16.49	9500	2.88	0
	80	24	404.56	16.86	12200	2.84	0
1-chloro-2,3-epoxypropane	50	24	520.87	21.70	2300	1.24	0.07
	80	24	545.94	22.76	3900	1.76	0
Phenyl glycidyl ether	50	36	467.66	12.99	9300	3.60	0.10
Alkyl glycidyl ether	50	36	448.31	12.44	6500	6.77	0.30

2.3.4 Bis(phenoxy) zinc complexes

In year 1986, Geerts et al. reported the first well-defined soluble aryloxide zinc complexes (Geerts et al., 1986). By reacting $Zn[N(SiMe_3)_2]_2$ with 2,6-di-*t*-butylphenol in tetrahydofuran (THF), the complex (2,6-di-*t*-butylphenoxide)$_2$Zn(THF)$_2$ was formed. This catalyst was found to be efficient in homopolymerizing oxiranes where it produced polyether with high molecular weight. However, it was found to be performed poorly in a copolymerization which involved incorporation of CO_2 (Darensbourg et al., 1999). For instance, the Bis(phenoxy) zinc complexes (refer Figure 2.5) which is usually binuclear can otherwise react differently when deployed by very bulky substituents of phenoxide ligands (e.g. *t*-butyl) (Darensbourg and Holtcamp, 1995). Generally, these catalysts have higher activities compared to aliphatic bis-alkyl zinc/alcohol based systems. They are usually in the form of agglomerates due to their lesser amount of steric hindrance as compared to phenoxy ligands,. Meanwhile Darensbourg et al. reported that the Lewis base binding affinity of the catalysts can be improved by replacing the electron withdrawing groups in the complexes with electron-donating *t*-butyl which consists of aryloxide ligands. Up to date, there is still lack of explanation on this unexpected behavior which has been a trend for many Lewis bases. Among the reported zinc complexes, the Lewis base binding affinity increases in the order of epoxides < THF< pyridine.



R = H,^{t}Bu, F, ^{i}Pr, Ph
R' = H, Me
L = Pyridine, THF, Et_2O

Figure 2.5: Bis(phenoxy) zinc complexes (Darensbourg et al., 1999)

A mononuclear (2,6-diphenylphenoxide)$_2$Zn(Et_2O)$_2$ catalyst which was capable of terpolymerizing PO, CHO and CO_2 was reported by Darensbourg as well (Darensbourg and Holtcamp, 1995). By introducing the third monomer (CHO), this terpolymerization reaction is capable of inhibiting cyclic carbonate formation which is undesirable by-product commonly formed during the copolymerization of PO and CO_2. On the other hand, fluoro substituted complexes is found to be a highly potential variations of the zinc phenoxides in term of performance. Darensbourg et al studied the dimeric complex $[Zn(O\text{-}2,6\text{-}F_2C_6H_3)_2.THF]_2$ thoroughly and found that it surpass all the other bis(phenoxy) zinc complexes as it has high TOF which can up to 7 h^{-1} (Darensbourg et al., 2000). The catalyst was found to be active in homopolymerizing CHO and forming copolymers exclusively in the presence of CO_2. This was mainly because there was one vacant coordination side for an oxirane. Indeed, there are two available free coordination sites in most systems, thus the tendency of two consecutive epoxide insertions is increased. Meanwhile, Koning et al. have physically characterized the polymers obtained with this catalyst system (Koning et al., 2001). It was found that these polymers have very broad molecular weight distribution, and thus their properties are inferior compared to commercially available BA-PC.

Darensbourg et al. also reported that the formation of polyethers requires two free coordination sites when bis(2,4,6-tri-*t*-butylphenoxy) zinc catalysts is used (Darensbourg et al., 2000). Upon the addition of tricyclohexyl phosphine PCy_3, the quantity of ether bonds of the polyethers was drastically reduced from more than 50 % to about 2 %, with about 6 h^{-1} TOFs. It seems that the phosphine block one of the coordination sites effectively. Meanwhile various experiments have been attempted on using polyhydric phenoxy zinc complexes in copolymerizing oxiranes and CO_2, but there were lack of enhancement in terms of catalytic activity and copolymer selectivity (Kobayashi et al., 1973; Rokicki, and Kuran, 1979; Kuran and Listos, 1994; Lukaszczyk et al., 2000). Recently a well-defined intramolecular dinuclear zinc catalyst was reported by Xiao, Wang and Ding (2005). Under the reaction conditions of $80^{o}C$ at 20 bar, this in situ generated catalyst was proved to be very dynamic in the copolymerizing CHO and CO_2 with TOF up to 142 h^{-1}. It was found that the copolymerization rate was enhanced by the intramolecular proximity of the second metal centrum, further indicating a binuclear mechanism (Xiao et al., 2005).

Besides that, Darensbourg made a few studies on several bulky bis(phenoxy) cadmium complexes, trying to reveal the mechanism and the coordination chemistry during the copolymerization reaction (Darensbourg et al., 1998). Cadmium complexes were normally less active compared with zinc complexes. In comparison to Zn(II), the relative softness of Cd(II) enable the segregation and characterization of some cadmium epoxide carboxylates (Darensbourg et al., 1995). Although various

Lewis bases, for example ether and THF exist in the solid-state zinc complexes, their base binding affinity in solution was strongly affected by various factors. The factors include temperature, solvent, type of Lewis base, as well as electronic and steric characteristics of the ligands.

Meanwhile for zinc complexes, oxirane adducts have yet to be isolated, which may due to either too low binding affinity or too fast ring opening. Based on the observation that with very bulky ligands, it can be concluded that oxirane was initially inserted into the Zn-aryloxide bond before CO_2 can be inserted (Darensbourg et al., 1997). This is mainly caused by the steric hindrance of the ligands. On the other hand, it can also be concluded that copolymerization reaction needs only one coordination site, while two sites are required for a consecutive oxirane insertion (Darensbourg et al., 2000). It was found that catalysts that perform well in oxiranes homopolymerization are usually not suitable to be applied in polymerizing completely alternating copolymers. Even if using excess amount of CO_2 as the solvent (such as supercritical carbon dioxide, it is still impossible to produce completely alternating copolymers with these catalysts..

2.3.5 β-diiminate (BDI) zinc complexes

The next important breakthrough in the homogeneous catalysts sourced from Coates and his co-workers' researches, who have discovered a series of β-diiminate (BDI) zinc complexes possess higher catalytic activity and even more active than the previous zinc bis(phenoxide) in copolymerization of CO_2 and epoxides (Cheng et al., 1998; Cheng et al., 2001; Moore et al., 2003). Basically, this single-site catalyst has organic ligands which remain in coordination with the zinc metal center during the copolymerization reaction by modifying the reactivity of the active zinc center. X-ray crystallographic analysis showed that the BDI complexes could form dimeric structure in solid state and monomeric structure in solution as proven by the ^1H NMR. Besides displaying active and high catalytic activity, BDI has advantage of copolymerizing CO_2 and epoxides rapidly under a mild condition, producing a narrow PDI of copolymer. The narrow polydispersity of the copolymer product suggested that quantitative and rapid initiation could be occurred during the polymerization process without a significant chain transfer or termination.

During a study by Allen et al., several BDI complexes were synthesized with different substituents (Allen et al., 2002). About 38 to 65 % yield of the BDI complexes were resulted from the reaction of zinc diethyl with the BDI ligand followed by addition of acetic acid at 0^oC. The catalysts were used in copolymerizing PO and CO_2 with the results shown in Table 2.7. In fact, BDI-2 in the copolymerization of PO and CO_2 at 50^oC produced almost 100% of propylene carbonate (PC). By reducing the reaction temperature to 25^oC (refer to the case of BDI-2a), formation of PC was suppressed and replaced by the formation of poly(propylene carbonate) (PPC) with almost 85 % (Allen et al., 2002).

From Table 2.7, several conclusions can be deduced. Firstly, the substitution of different components in the respectively R group of the BDI complexes would result in different TOF and PPC formation. Secondly as seen from BDI-3 and BDI-4, the shift of CF_3 group from the diethyl aniline side to the diisopropyl aniline side increased the TOF by nearly 10 times. In addition, incorporating both CN and CF_3 groups on the BDI-5 would cause complete deactivation of the ligand, yielding neither PC nor PPC. Numerous studies and researches need to be conducted to further investigate the sensitivity of the reaction to steric and electronic hindrance in the BDI complexes. Other than the effect of substituents, copolymerization conditions also played an important role in determining the yield of the copolymer. By comparing the results of BDI-4, BDI-4a and BDI-4b, it is clear that increasing the CO_2 pressure from 100 to 500 psi would decrease the TOF of the copolymer. However, the selectivity of PPC has increased from 75 % to 93 % (Allen et al., 2002). The percentage of cyclic carbonate decreased gradually, followed by the formation of PPC. On the other hand, by comparing the results of BDI-4, BDI-4c and BDI-4d, it can be seen that the catalytic activity of BDI-4 was optimum at 25^oC. Furthermore, higher selectivity of PPC can be obtained with gradual decrease of copolymerization temperature. Hence, it is concluded that BDI-4 is the superior catalyst among the BDI complexes reported above which gives an alternating structure of copolymer.

Table 2.7: Copolymerization of PO and CO_2 with different BDI complexes (*i*Pr = isopropyl group, Et = ethyl group) (Allen et al., 2002)

Catalyst	R_1	R_2	R_3	R_4	Time (h)	Temp (°C)	Pressure (psi)	TOF (mol PO/(mol Zn·h))
BDI-1	*i*Pr	*i*Pr	H	CH_3	8	25	300	3
BDI-2	*i*Pr	Et	CN	CH_3	8	50	300	50
BDI-2a	*i*Pr	Et	CN	CH_3	8	25	300	47
BDI-3	*i*Pr	Et	H	CF_3	8	25	300	26
BDI-4	Et	*i*Pr	H	CF_3	2	25	300	212
BDI-5	Et	*i*Pr	CN	CF_3	8	25	300	0
BDI-4a	Et	*i*Pr	H	CF_3	2	25	100	235
BDI-4b	Et	*i*Pr	H	CF_3	2	25	500	138
BDI-4c	Et	*i*Pr	H	CF_3	2	40	300	215
BDI-4d	Et	*i*Pr	H	CF_3	2	10	300	37

For the copolymerization of CHO and CO_2, it is shown that modifications on the N-aryl ligands (which are the R_1 and R_2 groups) would greatly affect the catalytic activity of BDI (Byrne et al., 2004). There is no TOF observed for the methyl-substituted BDI complexes, while TOF of 729 h^{-1} was seen for the copolymerization using isopropyl and ethyl substituted BDI (Moore et al., 2003). In an unsymmetrical ligand framework where electron-withdrawing group was substituted on the diimine parent chain (R_1 or R_2 = CN or CF_3), the catalytic activity was considered to be enhanced with TOF of about 424 h^{-1} (Moore et al., 2002; Kröger et al., 2005). Lastly, it is worth to mention that the incorporation of more electron-withdrawing groups would exhibit inactivity of the BDI catalyst, indicating no TOF similar to the copolymerization of propylene oxide and CO_2 above. The results are summarized as shown in Table 2.7.

2.3.6 Other zinc complexes

The synthesis of optically active PCs was also reported. The PCs were prepared by using an asymmetrical amide-alkoxide zinc catalyst and achieved a maximum enantiomeric excess of 73% (Nozaki et al., 1999). On the other hand, a bis-salicylamidinato zinc complex was reported (Darensbourg et al., 2001). This zinc complex produced was different when compared to most of the bis-phenoxide zinc catalysts, as it is in monomeric form. The catalytic activity was reported low (TOFs < 7.5 h^{-1}) with no ether linkages in the formed polymers as showed by ^1H NMR spectroscopy. This further affirms the theory that two consecutive oxirane insertions requires at least two vacant coordination sites.

2.4 Aluminium, chromium complexes and cobalt catalysts

Due to the capability of aluminum complexes in efficiently homopolymerizing epoxides, researchers have been investigating the potential of aluminium complexes as copolymerization catalysts since late 1970s. In year 1978, Takeda et al. explored the usage of porphyrinato aluminum complexes with the CO_2 incorporation was still below 40%. However, it was found possible to obtain completely alternating copolymers by incorporating cocatalysts such as quaternary ammonium salt or triphenylphosphine (Takeda and Inoue, 1978; Takeda and Inoue, 1978; Aida and Inoue, 1982). This was the first demonstration of a copolymerization of oxiranes and CO_2 in a living manner with PDI greater than 1.1. Under room temperature at 50 bar of CO_2, the reaction was reported to proceed slowly with reaction times between 12 and 23 day (Aida et al., 1986). In addition, these porphyrinato complexes were capable of copolymerizing CHO and CO_2, but with up to 40% of cyclic carbonate byproducts. Meanwhile, porphyrinato aluminum complexes were also reported capable of copolymerizing PO and CO_2. Detailed investigation has been made by Chisholm et al. on the the ring opening mechanism of PO in the copolymerization of PO and CO_2 (Chisholm and Zhou, 2004). It was revealed to be a first order dependence on concentration of [Al]. It was found that the ring opening of PO occurs via an interchange associate pathway when DMAP is used as cocatalyst. This is mainly due to the trans-activation of the cocatalyst which caused the the polymer-Al bond behaved almost ion-like. Besides that, the cocatalyst promotes the incorporation of CO_2 into the polymer alkoxide aluminum bond, as well as inhibiting the formation of polyether bonds.

1n year 1995, Kruper et al. reported the first usage of active porphyrinato chromium/DMAP catalysts (Kruper and Dellar, 1995), where they used the chromium catalyst to couple CO_2 with various oxiranes. Instead of producing the predicted cyclic carbonate, the copolymerization of CO_2 with CHO produced low molecular weight PC with TONs up to 10,000 while the catalyst itself was found recyclable. After that, it was reported that Cr(III) salen complexes are very active in coupling terminal oxiranes and CO_2 under 75 °C reaction temperature at 7 bar (Miller and Nguyen, 2004). In year 2000, chromium was used specifically as a copolymerization catalyst for the first time when Mang and his coworker reported some interesting porphyrinato chromium complexes (Mang et al., 2000.). After incorporation of some fluorinated substituents into the complexes, these systems $scCO_2$ became soluble when TOFs up to 72 h^{-1} were reached. Meanwhile, the polymers obtained possess about 3500 $gmol^{-1}$ of molecular weight with a PDI lower than 1.4 and 90-94% carbonate content. It was later reported by Stamp et al. that these porphyrinato chromium catalysts can be supported on Aerogel beads and to be successfully recycled (Stamp et al., 2001). Lately, the salen chromium/DMAP system was given attention. It was first used by Eberhardt et al. to synthesize cyclic carbonates (Eberhardt et al., 2003). They also found that it is possible to synthesize PC with the right amount of cocatalyst. When the concentration of cocatalyst (DMAP) concentration is increased from 0.5 to 2 equivalents, the formation of PPC becomes limited and propylene carbonate is produced as the major product instead.

In year 1978, Soga and co-workers reported the first usage of cobalt catalysts for copolymerization of PO and CO_2 (Soga et al., 1978). It was reported that a cobalt acetate catalyst can be used to couple PO and CO_2 but with awfully low product yield. Later, it was reported by Shi et al. that salen cobalt can synthesize propylene carbonate (Shen et al., 2003). In the same year, moderate activities in copolymerizing PO and CO_2 at room temperatures was reported by Coates and coworkers, where well-defined PPCs with more than 95% of CO_2 contents were synthesized (Qin et al., 2003). In opposition to the related chromium analogues, there was unnecessary additional of cocatalyst. Besides that, when PO is used as a monomer, there was hardly any cyclic carbonate formation. However, the drawback of this reaction is that it required high pressures (55 bar). It is possible to lower the reaction pressure to 10-20 bar by using *N*,*N*dimethylaminoquinoline as a cocatalyst without compromising the selectivity and activity of the reaction (Paddock and Nguyen, 2005). Meanwhile, it was reported that bis(triphenylphosphineiminium) chloride is the best candidate as the cocatalyst as it showed the most active combination in copolymerizing PO with CO_2 whereby a maximum TOF of 620 h^{-1} can be achieved (Cohen, Chu and Coates, 2005.). It was reported that higher reaction temperatures (> 100ºC) will favour the formation of cyclic carbonates. It was also found that even if the reaction occurred at lower temperature, the initiating group and cocatalyst will still be the determining factors in producing polycarbonates (Lu and Wang, 2004; Paddock and Nguyen, 2004; Lu et al., 2004; Paddock et al., 2004.).

2.5 Cadmium, manganese and rare earth metal coordination catalysts

There was investigation done on the catalytic activities of some cadmium complexes (Darensbourg et al., 1998; Darensbourg et al., 2000; Darensbourg et al., 2002). Compared to zinc complexes, cadmium complexes showed much lower activities. Even having the identical ligands with zinc bis(2,4,6-trimethylphenoxide), cadmium bis(2,4,6-trimethylphenoxide) is the most active species of the zinc bis(phenoxide) catalysts for the alternating copolymerization. It showed low activity in copolymerizing CO_2 with cyclohexene oxide and only produce copolymer with low molecular weight. It was found that cadmium bis(2,6-diphenylphenoxide) did not react with CO_2; instead it homopolymerized cyclohexene oxide and produced polyether in a very low yield, even under a CO_2 atmospheric pressure. While tris(pyrazolyl)borate and acetate was used as ligands, the cadmium complex catalyst produced only cyclic carbonate even under high CO_2 pressure (Darensbourg et al., 1995; Darensbourg et al., 1997).

Inoue and coworkers reported the first application of a porphyrinato manganese system in copolymerizing CHO and CO_2 at 80 °C and 1 bar of CO_2 pressures (Sugimoto et al., 2003). Even though the copolymerization reactions have a rather low TOF (3 h^{-1}), the exceptionally mild reaction conditions make these complexes worth-studying. Moreover, a high CO_2 contents (> 95%) and the low polydispersities (1.3 to 1.9) were obtained. When PO was used as a monomer, raising the pressure will enhance the catalytic activity to around 16 h^{-1}, which only produced propylene carbonate without any polyether bonds.

The copolymerization of PO and CO_2 using rare earth metal catalyst was first made possible by Chen, Shen and Zhang (1991). In the study, rare earth metal catalyst $Y(P_{204})_3$-$Al(i\text{-}But)_3$-glycerin was used to produce copolymer with molecular weight as high as 476 kg/mol (Chen et al., 1991). Although this copolymerization method was able to produce higher copolymer yield within shorter period of time, the copolymer obtained contain only about 10 to 30 % of carbonate linkages. Other than the rare earth metal catalyst discovered, rare earth metal catalyst system such as $Y(CF_3COO)_3$ or $Y(RC_6H_4COO)_3$ where (R = H, OH, Me, or NO_2) together with $ZnEt_2$ and glycerin were developed using yttrium carboxylates (Tan and Hsu,1997). Importantly, this ternary rare earth metal coordination catalyst was able to generate an alternating polycarbonate. The alternating copolymerization of PO and CO_2 produced PPC with relatively high molecular weight and carbonate linkages up to 98.5 %. From the two studies above, it can be seen that rare earth metal catalysts were beneficial in copolymerization process by shortening the induction periods, increasing the copolymer yield, improving the alternating ratios during copolymerization and raising the molecular weight of the copolymer (Qin and Wong, 2010). Further studies are required to investigate and enhance the catalytic activity of this type of heterogeneous catalyst so in order to improve the features of the copolymer product.

2.6 Copolymerization conditions

There are few factors that would influence the yield and molecular weight of the product produced from the copolymerization of PO and CO_2. These include the reaction time and temperature of the copolymerization, CO_2 pressure, amount of PO loading, amount of catalyst and the type of solvent used. In general, the copolymerization of PO and CO_2 yields PPC as the major product together with two minor by-products of propylene carbonate (PC) and poly(propylene oxide) (PPO) (Duan et al., 2010). In the study done by Duan et al., they examined the effect of CO_2 pressure on the copolymerization by using five sets of CO_2 pressures: 0.5 MPa, 1.2 MPa, 2.6 MPa, 3.5 MPa, and 5.2 MPa. Another control experiment was being conducted as well without the addition of CO_2. All six run of experiments were conducted with PO loading of 1000 g, supported catalyst of 42 g, reaction temperature of 60 °C and reaction time of 40 hours. The five results of the experiment (with exception of the control experiment with no CO_2 addition) are shown in Table 2.8. It can be seen that the second and third set of the experiment did not reach the reaction time of 40 hours due to the high viscosity happened during the copolymerization at the time of 16.5 hours and 17 hours. Despite the shorter reaction time, the PPC yields of the second and third set of the experiments were relatively high. This can be explained by the fast copolymerization (and cross-linking) rate happened in the second and third set of experiments.

By comparing the control experiment with no CO_2 addition to the first set of experiment above, Duan et al. has found out that the copolymerization process with no CO_2 addition generated a higher amount of PPOX with lower yield of PPC. When small amount of CO_2 at 0.5 MPa were added into the copolymerization, the copolymer yield increased tremendously. This shows that the insertion of CO_2 into the polymer chain is crucial to ensure a higher yield of PPC product. As shown in Table 2.8, the yield of the copolymer increased with the pressure when CO_2 pressure of 2.6 MPa below. The increment in CO_2 pressure indicates a rise in CO_2 concentration and thus accelerating the copolymerization, resulting in a higher PPC yield. However, above 2.6 MPa, the higher pressure leads to the expansion of CO_2 system volume. Consequently, dilution of the catalyst to PO ratio occurred which lowered the rate of copolymerization. All the copolymers produced under different sets of pressure exhibited high molecular weight with board distributions. Hence, it was concluded that the CO_2 pressure has no influence on the molecular weight and the distribution of the copolymer product.

Table 2.8: Effect of Pressure on PPC Yield, Molecular Weight and the Distribution (Duan et al., 2010)

Pressure (MPa)	Reaction Time (h)	PPC Yield (g/g of catalyst)	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)
0.5	40	53.7	65k	273k	4.2
1.2	17	51.0	93k	588k	6.3
2.6	16.5	60.2	75k	363k	4.8
3.5	40	61.2	104k	520k	5.0
5.2	40	58.8	78k	290k	3.8

Other than the CO_2 pressure, PO loading plays an important role in determining the yield of the copolymer and the molecular weight of the final product. Ree et al. has worked on examine the effect of PO loading on the copolymerization yield, whereby eight sets of experiment were designed with different volume of PO incorporated in the copolymerization process (Ree et al., 1999). However, all the eight experiments were conducted using 1 g of zinc glutarate catalyst under the identical condition of 40 hours at 60 ^oC, and CO_2 pressure of 51.5 atm. All the copolymerization processes were performed without the addition of organic solvents as excess propylene oxide was used. Table 2.9 illustrated the results of different PO loading on the yield of copolymer. From the results shown above, it can be seen that the copolymer yield has the highest value of 64.0 g per gram of catalyst with 100 ml of PO added. The copolymer yield increases together with the PO loading and then decreases above PO loading of 100 ml. Hence, it can be concluded that PO acts as a good solvent to the copolymer product as the product is highly soluble in it. The high solubility of PO in the product will enhance mixing of the reaction medium (which consists of PO and CO_2), producing a copolymer with high yield yet high molecular weight.

Table 2.9: Effect of PO Loading on the Copolymerization of Propylene Oxide and Carbon Dioxide (Ree et al., 1999)

Volume of PO (mL)	Yield (g/g of catalyst)	M_n	M_w	PDI
24	14.5	120k	355k	3.0
39	36.7	138k	363k	2.6
50	44.5	-	-	-
60	45.8	-	-	-
75	54.6	-	-	-
100	64.0	143k	343k	2.4
150	43.7	-	-	-
200	41.9	-	-	-

2.7 Future works

Nanocatalysis is a significant and promising field in catalysis science. Due to their minute size of particles (1–100 nm), nanocatalysts possess larger contact surface area and able to offer more active sites than the conventional one, and thus reducing the specific cost per function (Gawande et al., 2013.). Therefore, many researches have been done in trying to apply nanocatalyst in industrial processes, for instance Fischer-Tropsch synthesis where various metal nanocatalysts have been investigated, such as cobalt (Prieto et al., 2009) and iron (Pour et al., 2013). Other examples include investigation of iron(III) oxide nanocatalyst in decomposition of hydrogen peroxide (Gregor et al., 2010); investigation of silver nanocatalyst in selective hydrogenation of acrolein (Wei et al., 2013); investigation of nanocrystalline $MgAl_2O_4$ as an effective heterogeneous nanocatalyst in some important organic reactions (Ahmad et al., 2001). It is believed that nanocatalysts will be playing an important role in the future chemical industry. Thus, utilization of nanocatalysts in copolymerization of PO and CO_2 is a whole new field which is worth-investigating.

CHAPTER 3

METHODOLOGY

3.1 Materials

Zinc Oxide (ZnO) was obtained from Rank Synergy Sdn. Bhd., Malaysia while Glutaric Acid (GA) was supplied by Merck Sdn. Bhd., Malaysia. PO was obtained from Sigma Aldrich, Malaysia. All the three chemicals above are with 99% purity. Solvents used in this study are all analytical grade. Toluene was obtained from Rank Synergy Sdn. Bhd., Malaysia while acetone, dichloromethane, hydrochloric acid and ethanol were purchased from Labchem Sdn Bhd., Malaysia

3.2 Preparation of Catalyst

For synthesis of ZnGA catalyst, about 98 mmol of GA was dissolved in 150 mL of toluene in a round bottom flask (250 mL) equipped with a Dean-Stark trap and a reflux condenser with drying tube. Then, 100 mmol of fine powdery ZnO was added into the GA solution in toluene before the mixture was stirred vigorously for 3 hours at 40 ^{o}C. After being cooled down to room temperature, the reaction mixture was filtered and washed several times using acetone to remove any possible impurities or unreacted materials. The reaction mixture was then dried in vacuum pump oven at 60 ^{o}C overnight to give ZnGA catalyst in powder.

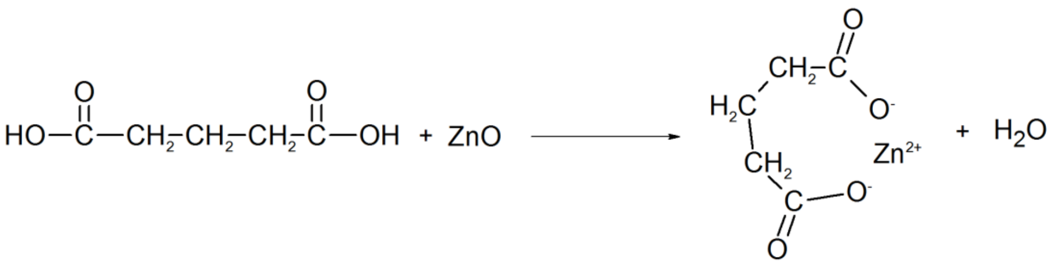


Figure 3.1: Reaction between Glutaric Acid and Zinc Oxide to synthesize Zinc Glutarate Catalyst.

After that, another five sets of experiment were done by using different reaction time and temperature. The sets of experiment can be shown in Table 3.1 below. It is important to notice that in order to obtain a more accurate and precise results, each set of experiment was repeated three times.

Table 3.1: Different Sets of Experiment with Different Reaction Temperature and Time.

Reaction Temperature (^{o}C)	Reaction Time (h)	ZnGA catalysts
40	3	ZnGA40-3
	6	ZnGA40-6
	9	ZnGA40-9
50	3	ZnGA50-3
	6	ZnGA50-6
	9	ZnGA50-9
60	3	ZnGA60-3
	6	ZnGA60-6
	9	ZnGA60-9

3.3 Copolymerization

The copolymerization of PO and CO_2 was conducted using a high pressure stainless steel reactor system with capacity of 100 ml with a programmable temperature controller. Both the ZnGA catalyst and the cleaned reactor body were dried in a vacuum oven for 3 days at 100 ^oC. After that, 1.00 g of dried ZnGA and 50 ml of PO was added into the reactor along with a magnetic stirrer. Next, the reactor was capped by the reactor head and sealed. The reactor was then been connected to CO_2 cylinders using a valve. Both the gas inlet and outlet were opened to allow CO_2 gas to flow continuously slowly for 5 minutes to remove all other possible gases in the reactor. Then, the reactor was pressurized to 50 bar with CO_2 gas in the reactor. The reaction then took place at 60 ^oC with stirring rate of 100 rpm for 40 hours.

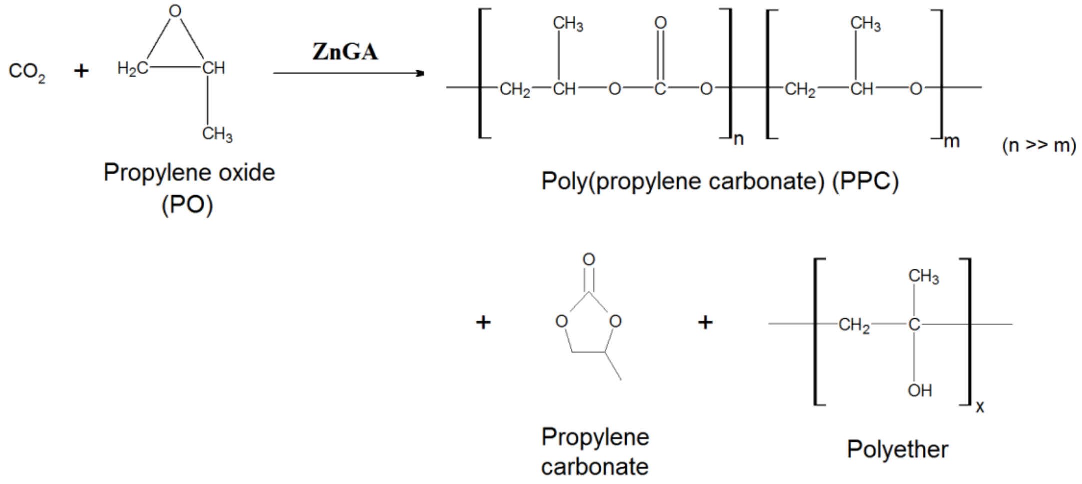


Figure 3.2: Copolymerisation of propylene oxide and carbon dioxide with zinc glutarate catalyst.

After 40 hours, the reactor was cooled down and depressurized. A small amount of the crude product (5 ml) was collected for gel permeation chromatography (GPC) test. The remaining crude product was dissolved in 50 mL of dichlormethane and ransferred to a separating funnel. Diluted hydrochloric acid (100ml) was added to the separating funnel and shaked vigorously to form 2 layers of solution. This extraction process was repeated three times to remove any catalyst residue from the crude product. Then, the bottom layer of the product solution was collected and concentrated to desired concentration using a rotary evaporator. The product solution was poured into excess ethanol to extract PPC which is insoluble in ethanol. The extracted PPC was then dried in vacuum oven.

3.4 Testing Methods and Characterization

In this section, the testing methods and the characterization of both the catalyst and the copolymer product are discussed.

3.4.1 Fourier Transform Infrared (FTIR)

Changes in functional group of the catalysts and copolymers were identified by using ThermoScientific Nicolet iS10 infrared spectrometer at frequency of wavelength ranged from 400-4000 cm^{-1}. The catalyst synthesized with different reaction parameters were tested in powder form while the copolymer products were tested in the form of thin film. After calibrated with a blank sample, the FTIR Spectra for both catalysts and copolymer products were obtained with automatic signal gain collected in 32 scans per sample with resolution of 4 cm^{-1}.

3.4.2 X-Ray Diffraction Spectroscopy (XRD)

The crystallinity of ZnGA catalysts and PPC was determined by using Shimadzu XRD-6000 with Cu K (1.54 Å) radiation operated at atmospheric conditions to analyse the structure of the catalysts and the copolymers. The catalysts were subjected to the XRD analysis in the form of powder with a scanning range from 2^{o} to 80^{o} and scanning rate of 1^{o}/min. On the other hand, the PPC thin film were analysed with a scanning range from 2^{o} to 40^{o} at 1.2^{o}/ min.

3.4.3 Field Emission Scanning Electron Microscopy (FESEM)

The morphologies of the surface of the catalyst were observed under Hitachi BS340 TESLA Scanning Electron Microscope. The ZnGA catalysts in the form of powder were coated with palladium-gold using a EMITECH SC7620 Sputter Coater and ready for scanning. The samples were scanned using magnifications of 10 000, 20 000 and 30 000 where the electron beam voltage was set at 15 kV.

3.4.4 Gel Permeation Chromatography (GPC)

The molecular weights and PDI of copolymers were measured by Viscotex multi-detector gel permeation chromatography with Tetrahydrofuran (THF) as eluent flowing at 1.0 mL/min at 40^{o}C. The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02.

3.4.5 Differential Scanning Calorimetry (DSC)

In order to determine the melting temperature T_m, all copolymer samples were subjected to differential scanning calorimetry (DSC) analysis by using a Mettler Toledo DSC821^{e} analyser. In each measurement, 5 – 8 mg of sample was heated from 30 to 280^{o}C at heating rate of 5 ^{o}C /min and then cooled down to 30 ^{o}C at same rate. The system was purged by dry nitrogen gas at constant volumetric flowrate of 20 ml/min throughout the entire measurement.

3.4.6 Mechanical Testing

Tensile strength, percentage of elongation and tensile modulus for each sample specimen were tested based on the standard of ASTM D1822 by using Instron Universal Testing Machine 5582 Series IX tensile tester. The test was carried out at room condition with 2 kN of load cell and 50 mm/min crosshead speed. The stress-strain curve and other tensile properties such as tensile stress as maximum load, tensile strain at maximum tensile stress and tensile extension at maximum tensile stress were projected on the tensile datasheet that generated by Bluehill software.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Zinc Glutarate (ZnGA) Catalyst

The copolymerization reaction between PO and CO_2 is initiated by the coordination of PO by the metal center of the catalyst (zinc metal). PO is then attacked by the nucleophilic site (glutarate ligands) and undergone ring opening to form a metal alkoxide intermediate (Bahramian and Dehghani, 2016; Ree et al., 2006; Trott, Saini and Williams, 2016). CO_2 molecule is then inserted into the metal-oxygen bond and to form a metal carbonate species. Depending on the selectivity of the ZnGA catalyst, the metal carbonate can either goes toward its ring closure and form five-membered ring cylic carbonate (propylene carbonate) or propagates by repeating coordination of PO and insertion of CO_2 and produces polycarbonate chain. If the second pathway is followed by the alternative coordination-insertion mechanism, a completely alternating polycarbonate is produced. However, if the reaction proceeds with the attack of metal alkoxide on PO without the insertion of CO_2, ether linkages are formed in the polymer chain (Bahramian and Dehghani, 2016;Ree et al., 2006; Trott, Saini and Williams, 2016). The reaction mechanism for the copolymerization of PO and CO_2 is illustrated in Figure 4.1. Therefore, ZnGA catalysts were synthesized with different combinations of reaction time and temperature to investigate the effects of the catalyst preparation temperature and time on the catalytic activity of the catalysts and the properties of the copolymers produced.

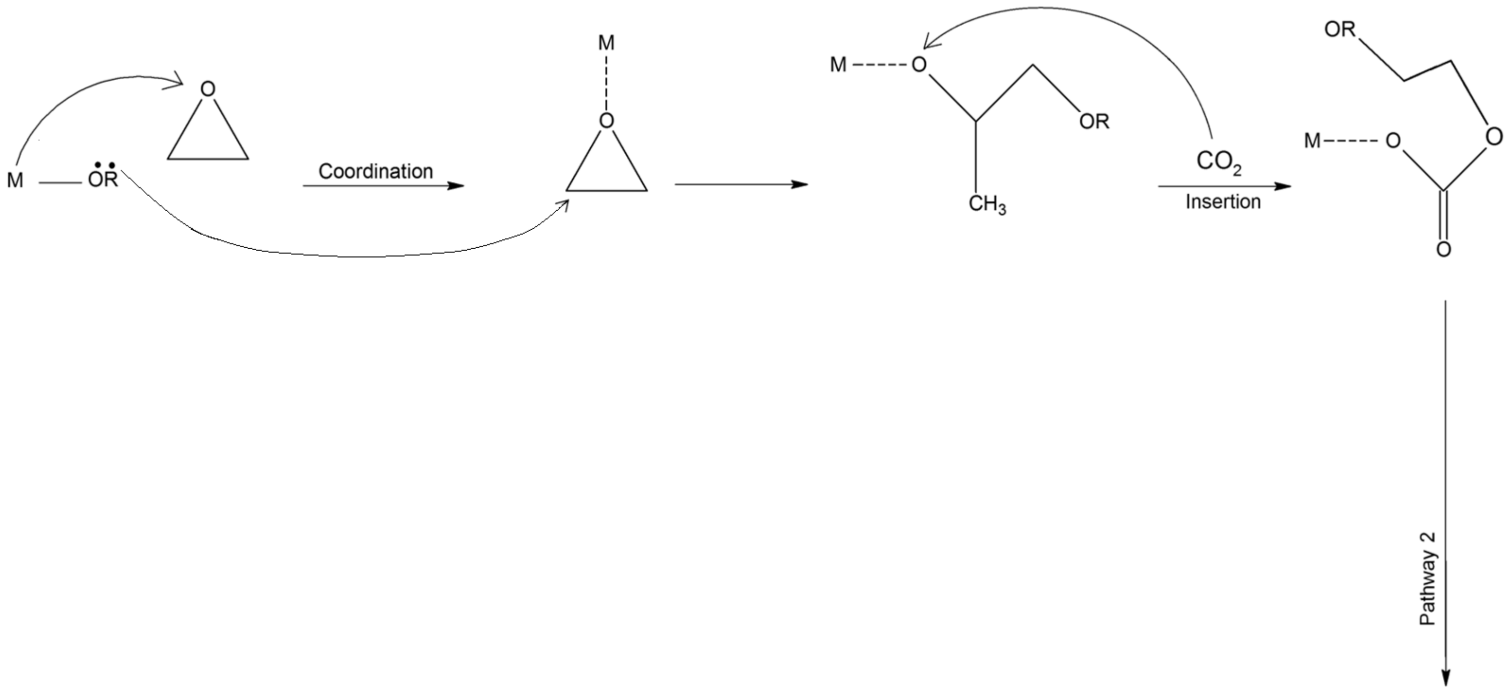


Figure 4.1: Reaction mechanism for the copolymerization of PO and CO_2 using ZnGA catalyst, where M refers Zinc metal at the center of the ZnGA catalyst while OR refers to the glutarate ligand which acts as the nucleophilic site.

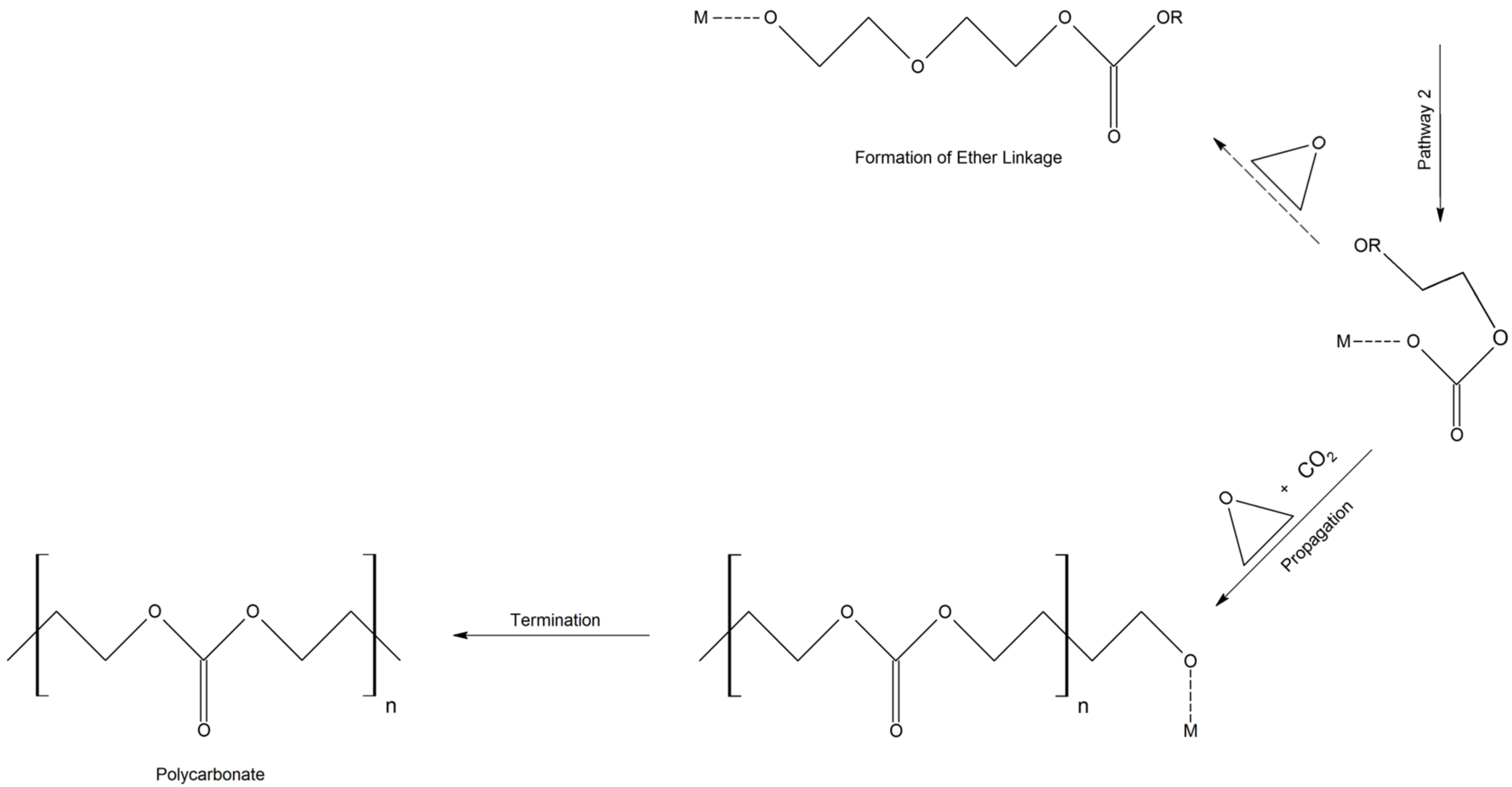


Figure 4.1 (cont'): Figure 4.1: Reaction mechanism for the copolymerization of PO and CO_2 using ZnGA catalyst, where M refers Zinc metal at the center of the ZnGA catalyst while OR refers to the glutarate ligand which acts as the nucleophilic site.

4.1.1 Fourier Transform Infrared (FTIR)

The formation of ZnGA catalysts was confirmed by using FTIR test. As shown in Figure 4.2, the absence of peak e (1697 cm^{-1}) and presence of peaks (peak a-c at 1585 cm^{-1}, 1536 cm^{-1} and 1405 cm^{-1}) shows that the carbonyl group (C=O) of GA transformed into zinc-carboxylate bond (COO-). In addition, the absorbance of CH_2 scissoring at peak d and CH stretching at 2952 cm^{-1} (peak f) was also detected. This indicates successful incorporation of GA to ZnO and produced ZnGA catalysts (Zhong and Dehghani, 2010).

The processing conditions (i.e. reaction temperature and time) have a significant impact on the characteristic of the catalyst. As observed from the Figures 4.3 - 4.5, peak a is absent in the FTIR spectrum for every ZnGA catalyst synthesized at different temperature with 3 h reaction time. However, as the reaction time slowly increases from 3 h to 6 h and 9 h, peak a is shown in the FTIR spectrum except for the ZnGA synthesized at 40 ^oC with 6 h reaction time. In addtion, it can be observed that as the reaction temperature increases, the intensity of the peak a, b and c increase qualitatively while the peak d also becomes sharper and taller. The intensity of the peaks also slowly increases as the reaction time increases. According to Arrhenius equation, the rate of reaction varies proportional with temperature and time. When the catalyst synthesis takes place at higher temperature, GA has higher tendency to form zinc carboxylate (COO-) bond with zinc oxide. This indicates formation of more active sites in the catalysts for the occurrence of copolymerization between PO and CO_2. In addition, the metal carbonate formed during the ring opening of PO has higher tendency to propagate to form PPC instead of cyclic carbonate. This results in higher yield and selectivity of PPC during the copolymerization reaction (Bahramian and Dehghani, 2016).

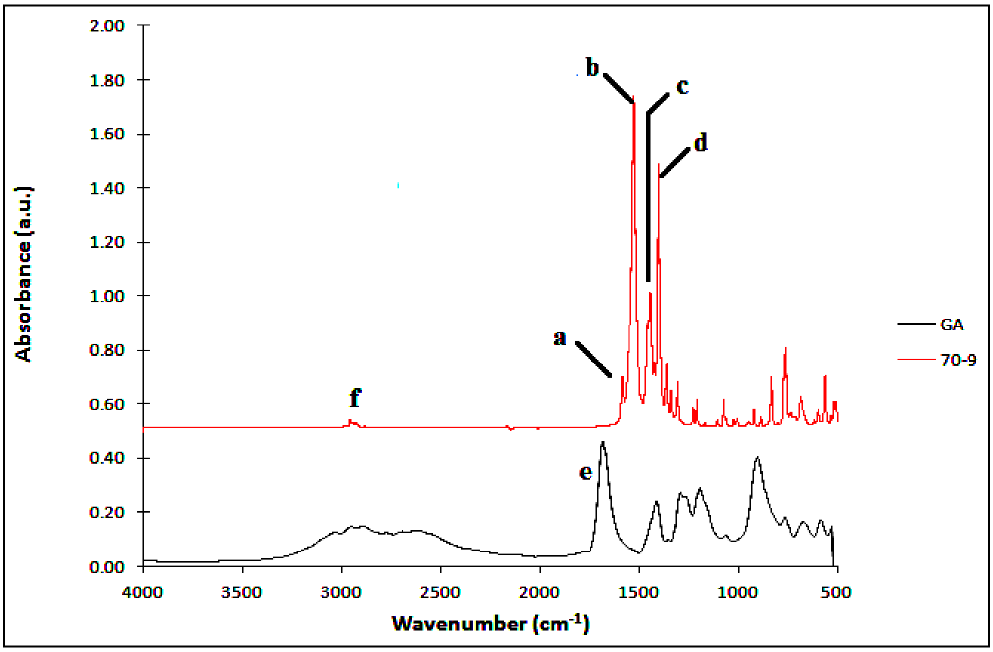


Figure 4.2: FTIR spectra of ZnGA synthesized at 70 ^{o}C for 9 hours and FTIR spectra of pure GA.

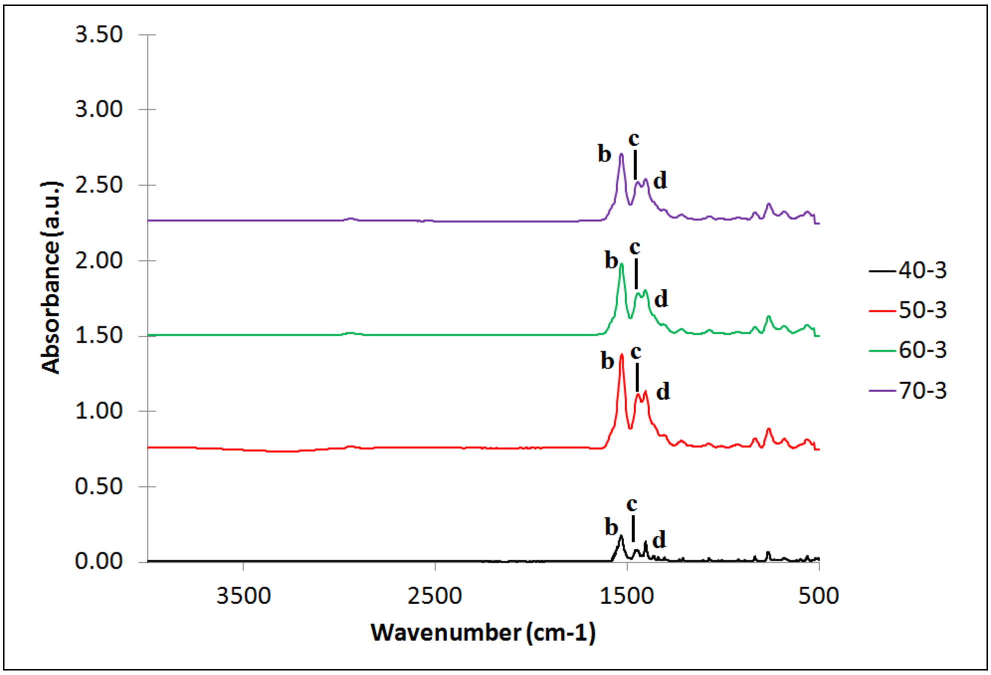


Figure 4.3: FTIR spectra of ZnGA synthesized at 40 ^{o}C, 50 ^{o}C, 60 ^{o}C and 70 ^{o}C for 3 hours.

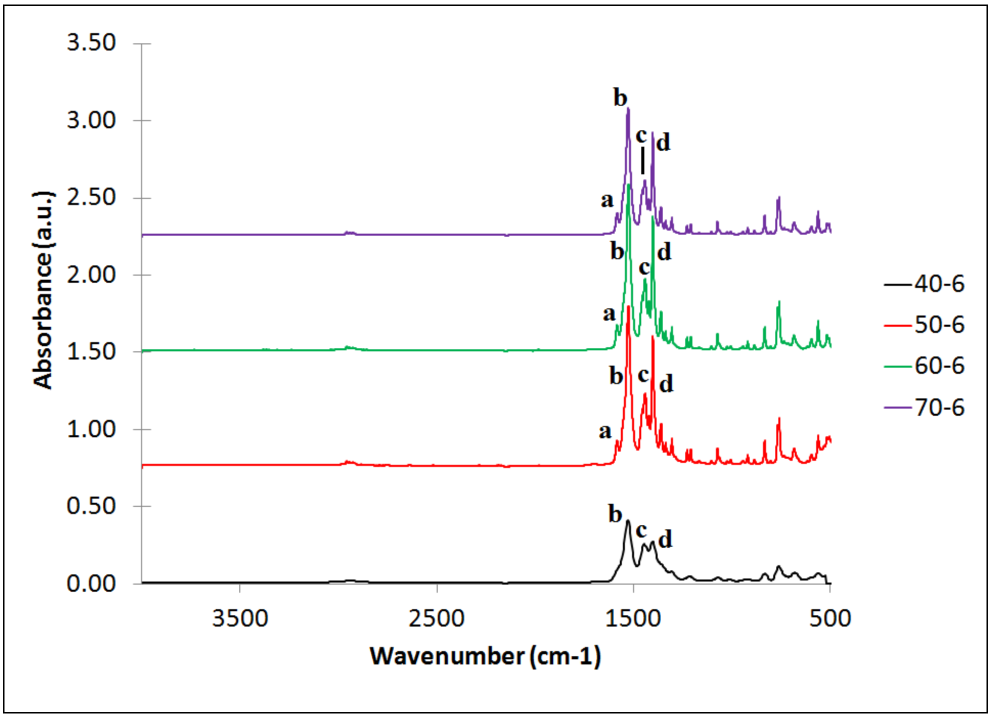


Figure 4.4: FTIR spectra of ZnGA synthesized at 40 °C, 50 °C, 60 °C and 70 °C for 6 hours.

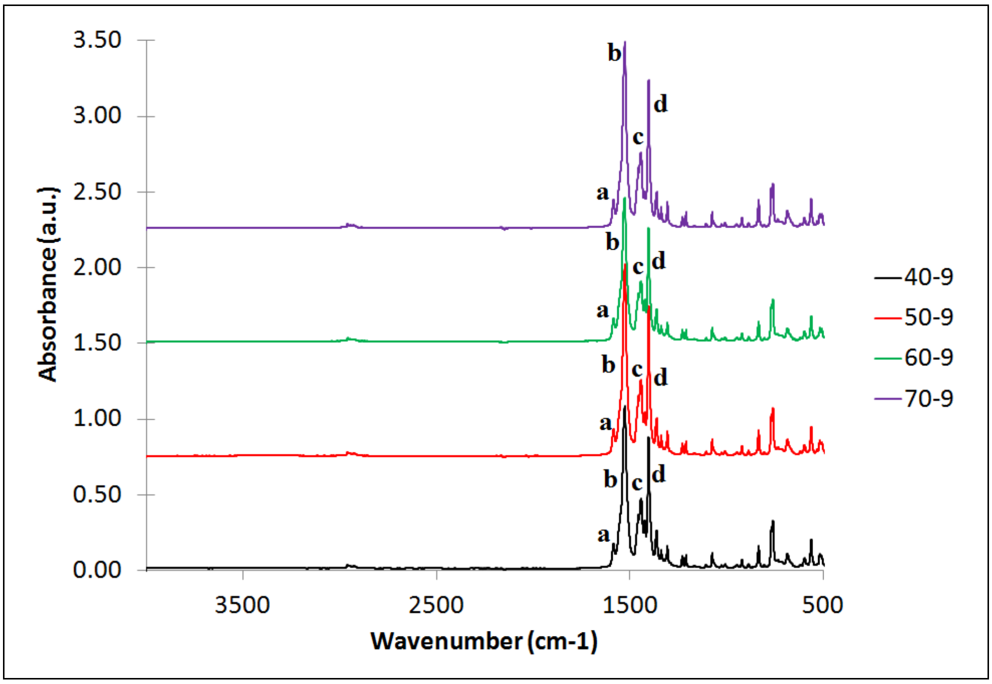


Figure 4.5: FTIR spectra of ZnGA synthesized at 40 °C, 50 °C, 60 °C and 70 °C for 9 hours.

4.1.2 X-Ray Diffraction Spectroscopy (XRD)

The degree of crystallinity of the ZnGA catalysts was determined by using XRD. The diffraction pattern of ZnGA catalysts and their crystallinity are shown as below. According to Scherrer equation (Eq 1), high crystallinity and excellent crystal quality including crystalline size and perfectness lead to formation of sharp peaks with high intensities. In other word, the peak intensities and broadness in XRD diffraction patterns directly reflect the crystallinity and crystal quality of ZnGA catalysts.

$$< L > = \frac{K\lambda}{\beta cos\theta} \qquad \text{(Eq 1)}$$

where < L > = mean crystallite dimension
K = Scherrer Constant
λ = Wavelength of radiation applied
θ = Angle between X-ray beam and the normal axis of the reflecting plane (in degree)
β = FWHM of the diffraction peak (rad)

As shown in the Figures 4.6 – 4.8, all of the ZnGA possessed three sharp peaks (Peak A, Peak B and Peak C) with high intensities (Peak A, Peak B and Peak C). This indicates all of the ZnGA catalysts have high degree of crystallinity. This is vital as the morphological structure of catalyst including the degree of crystallinity and shape affect the catalytic activity of the catalyst directly (Ang et al, 2015; Meng et al., 2002; Kim et al., 2003; Kim et al., 2004; Ree et al., 2000; Ree et al., 2006; Wang et al., 2002; Zhong and Dehghani, 2010). The higher the crystallinity of ZnGA, the higher the catalytic activity, and thus produce PPC with superior properties. However, the catalytic activity is also dependent on the incorporation of GA into the catalysts. From Figure 4.9, it is found that catalyst preparation temperature plays a dominant role; ZnGA catalysts produced at higher temperature were found to possess higher crystallinity and capable to produce PPC with better quality (Ang et al., 2015; Meng et al., 2002; Kim et al., 2003; Kim et al., 2004; Ree et al., 2000; Ree et al., 2006; Wang et al., 2002; Zhong and Dehghani, 2010).

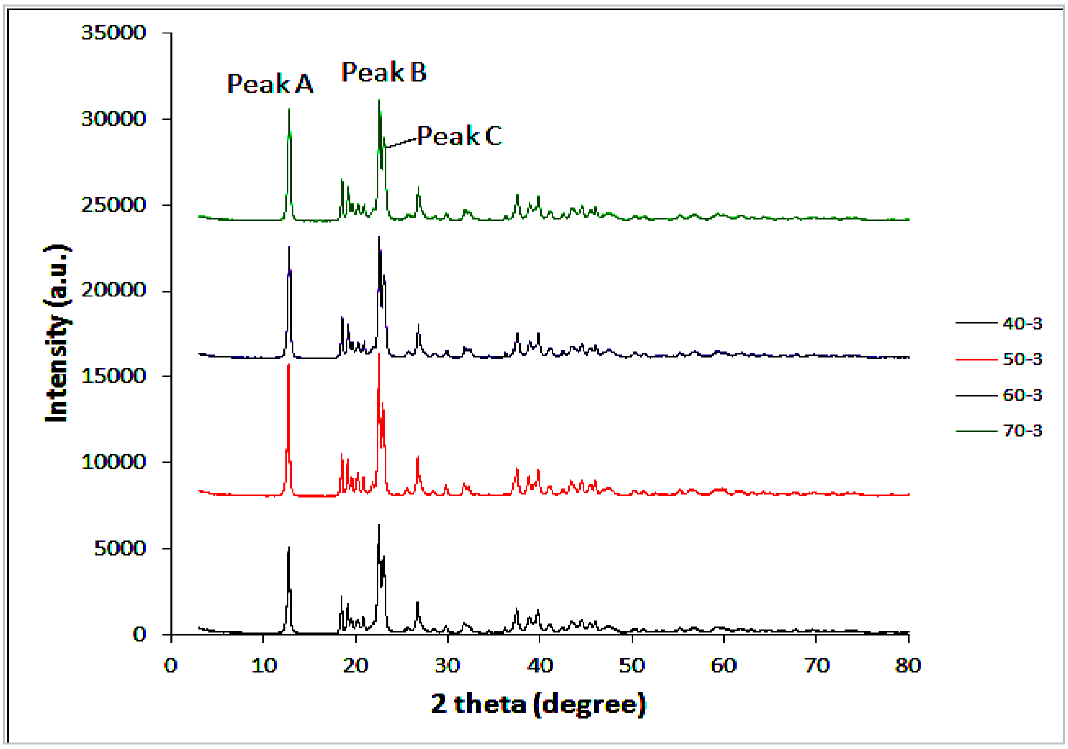


Figure 4.6: Diffraction pattern of ZnGA synthesized at 40 °C, 50 °C, 60 °C and 70 °C for 3 hours.

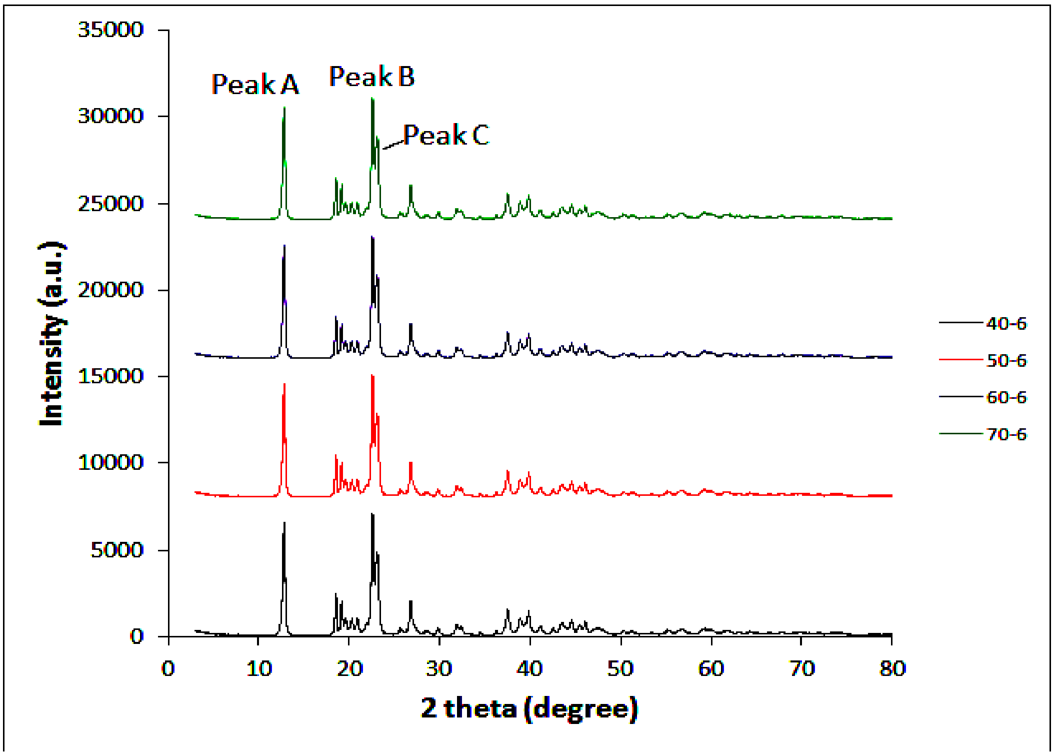


Figure 4.7: Diffraction pattern of ZnGA synthesized at 40 °C, 50 °C, 60 °C and 70 °C for 6 hours.

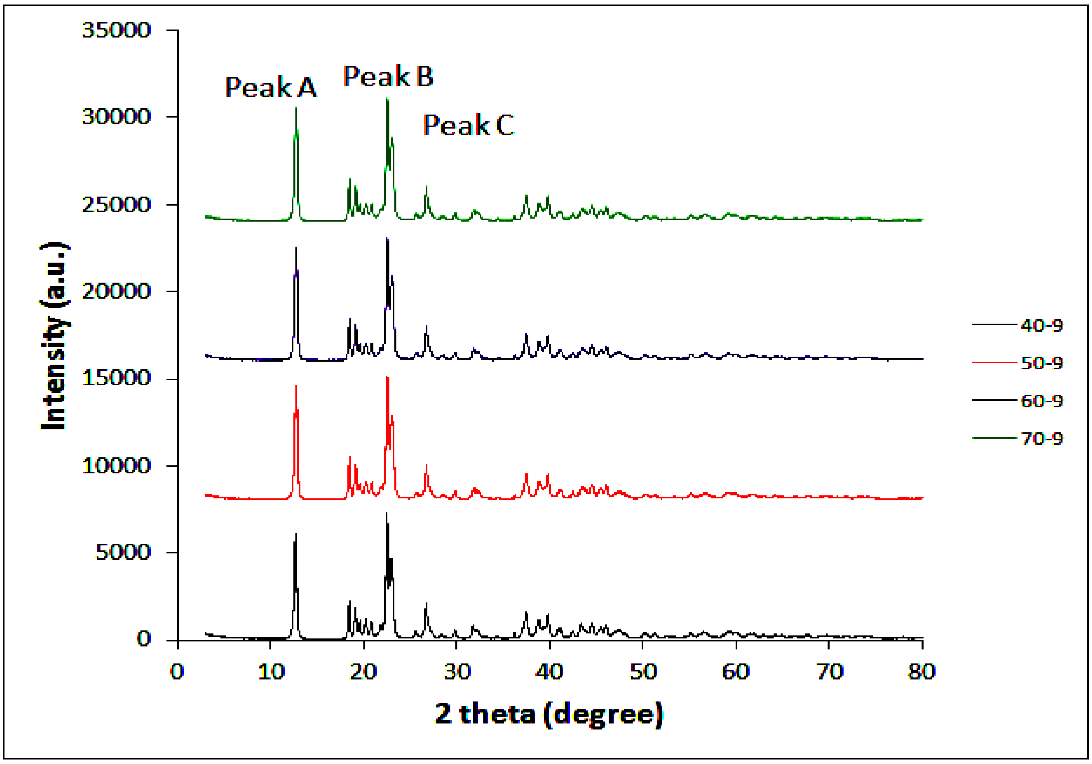


Figure 4.8: Diffraction pattern of ZnGA synthesized at 40 ^{o}C, 50 ^{o}C, 60 ^{o}C and 70 ^{o}C for 9 hours.

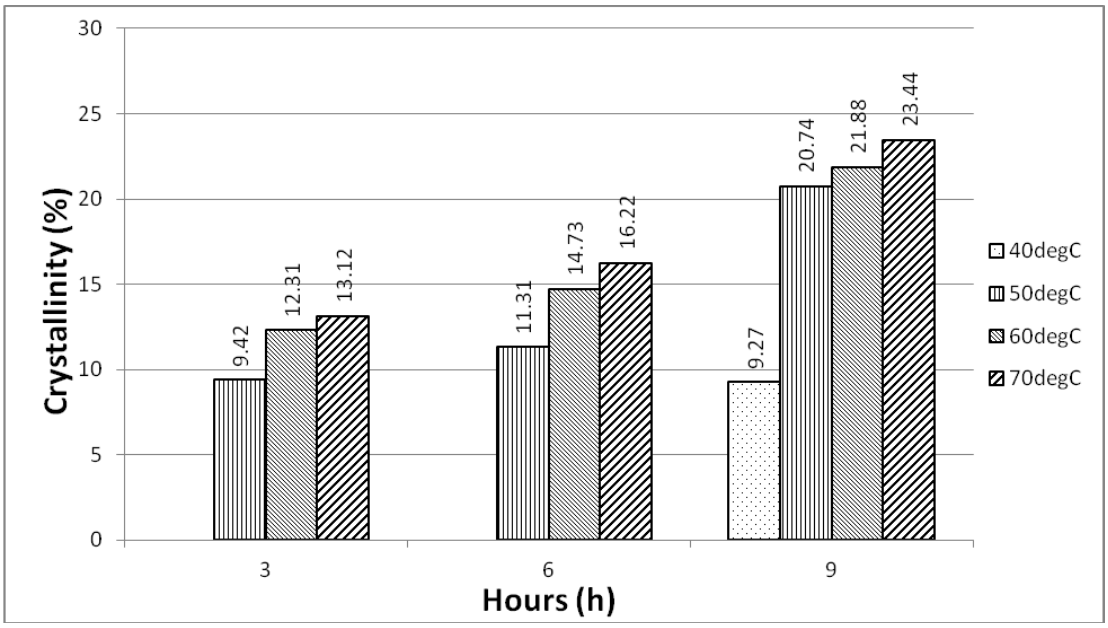
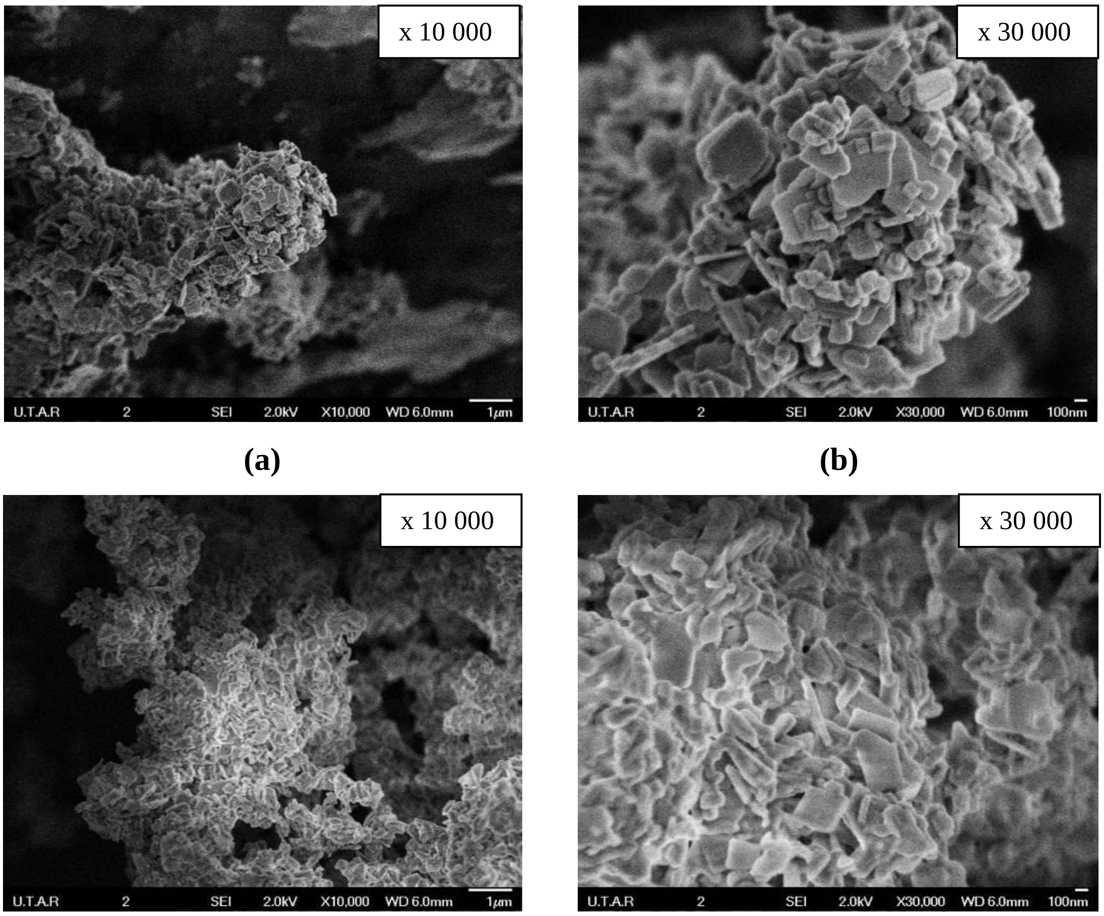


Figure 4.9: Crystallinity of the ZnGA synthesized with different combination of temperature and time.

4.1.3 Field Emission Scanning Electron Microscopy (FESEM)

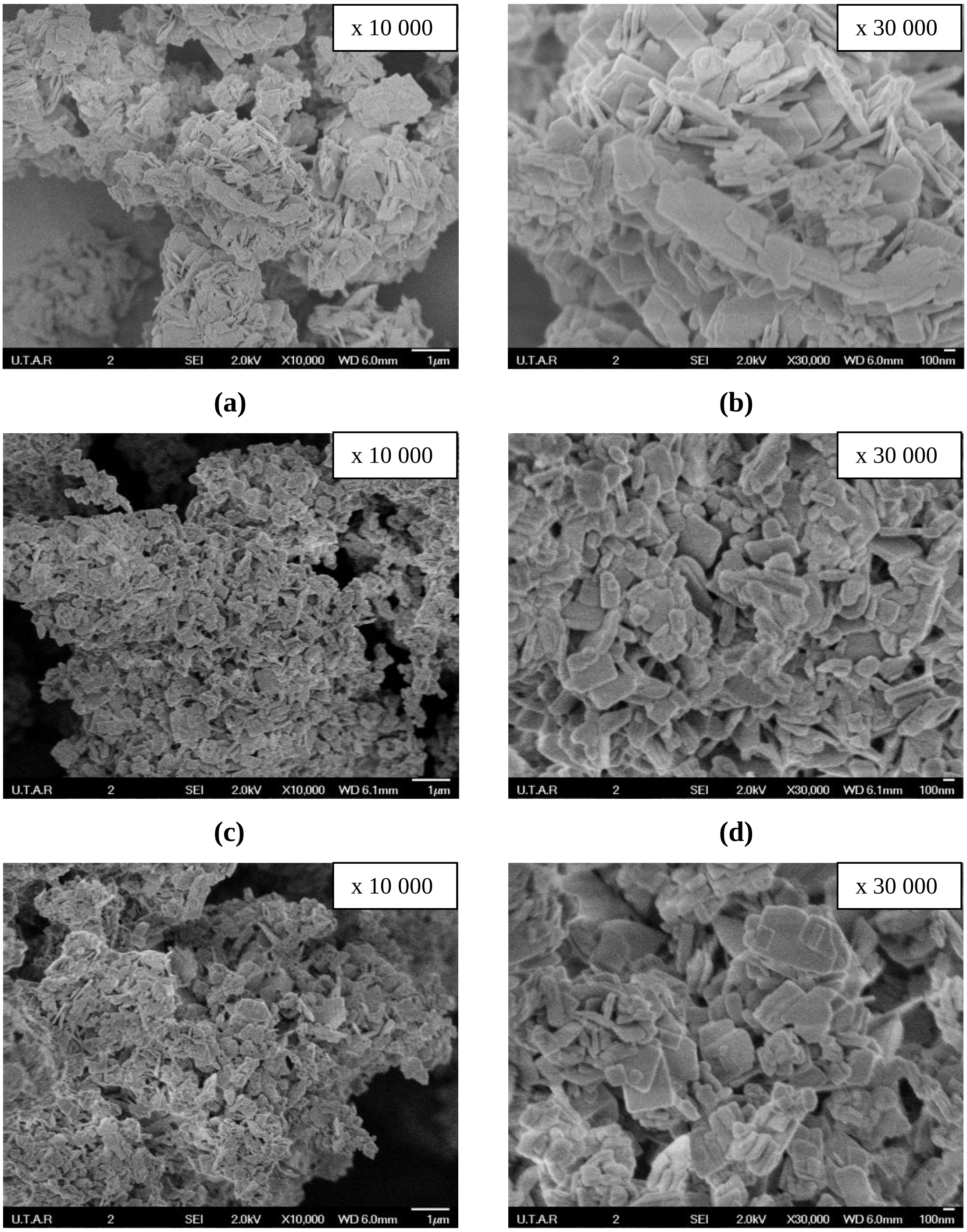
As observed from Figure 4.10 to Figure 4.12, the results demonstrate that ZnGA catalysts consist of aggregated small-rectangular plane crystals in all synthesis conditions. The rectangular morphology and the single-crystal ZnGA produced from the hydrothermal reactions of zinc perchlorate hexahydrate and glutaronitrile is very similar (Ree et al., 2006). It was found that the catalysts synthesized at higher temperature and longer reaction time presents more porous structure with more regular shape crystals. The crystalline size has significant effects on the overall crystallinity of ZnGA, where the high crystallinity of the catalyst can only achieved by having notably larger size and more uniform shape crystals.



(a) (b)

(c) (d)

Figure 4.10: FESEM Images of ZnGA catalysts prepared at (a & b) 40^{o}C for 3 hours and (c & d) 40^{o}C for 9 hours with magnification of 10,000 and 30,000.

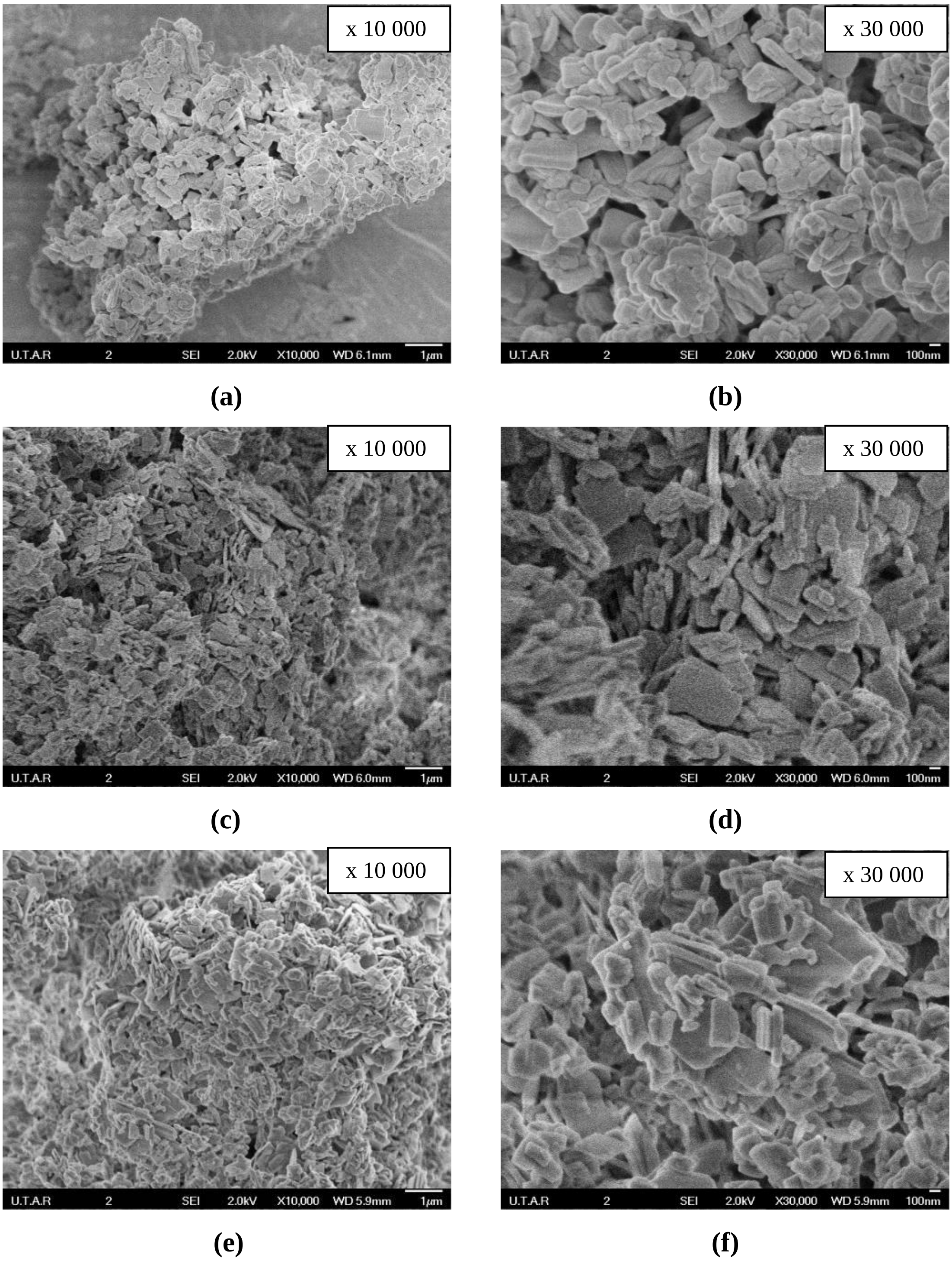


(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 4.11: FESEM Images of ZnGA catalysts prepared at (a & b) 50^{o}C for 3 hours, (c & d) 50^{o}C for 9 hours and (e &f) 60^{o}C for 3 hours with magnification of 10,000 and 30,000.



(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 4.12: FESEM Images of ZnGA catalysts prepared at (a & b) 60^{o}C for 6 hours, (c & d) 70^{o}C for 3 hours and (e &f) 70^{o}C for 9 hours with magnification of 10,000 and 30,000.

4.2 Polypropylene Carbonate (PPC) Copolymer

4.2.1 Fourier Transform Infrared (FTIR)

The copolymerization of PO and CO_2 with ZnGA as catalyst produces PPC along with cyclic propylene carbonate and polyether as byproducts (Ang et al, 2015; Bahramian and Dehghani, 2016; Ree et al., 2006; Trott, Saini and Williams, 2016). Due to high solubility of byproducts in ethanol and insolubility of PPC in the solvent, PPC can be extracted from the crude reaction products without minute trace of byproducts (Zhong and Dehghani, 2010). The FTIR spectrum of PPC (the ethanol insoluble polymer) is illustrated in the Figure 4.13. The peaks indicate the presence of C=O group (1749 cm^{-1}) and the C-O group (1236 cm^{-1}) vibration absorbance. This was to reaffirm the extracted polymer obtained for further investigation was PPC.

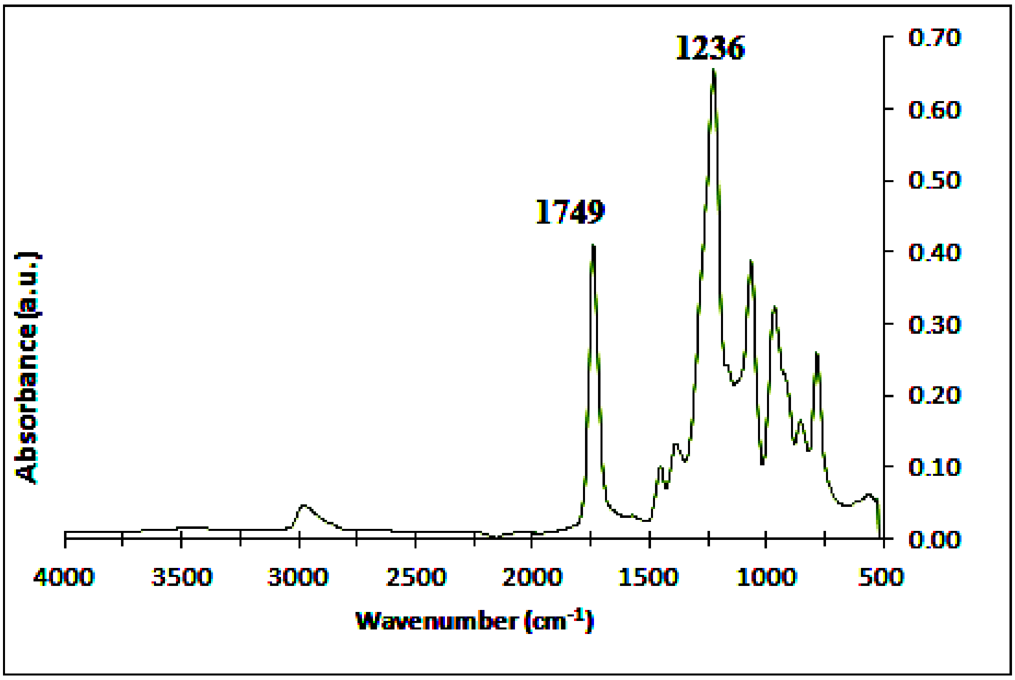


Figure 4.13: **FTIR Spectra of PPC obtained from the copolymerization reaction between CO_2 and PO**

4.2.2 Gel Permeation Chromotography (GPC)

GPC was used to determine the molecular weight of a polymer. In fact, similar polymers at different molecular weights exhibit different physical properties (Kato et al., 2015). Polymers with high molecular weight and low PDI possess excellent mechanical properties with narrow range of melting temperature. In this study, almost all the catalyst systems were able to produce PPC, except for ZnGA40-3 and ZnGA40-6. After the crude product obtained, it undergoes extraction process to obtain PPC. However the crude products of the mentioned catalyst contain no or little amount of ethanol- insoluble polymer (PPC).

From Figure 4.14, it was found that as the catalyst synthesis temperature increased, the molecular weight (Da) of the PPC obtained increased while the PDI of the PPC decreased as observed in Figure 4.15. As discussed earlier, catalyst synthesis temperature is the main factor which affects the ZnGA catalyst’s catalytic activity (Table 4.1). As catalyst synthesis temperature increases, the catalytic activity of ZnGA increases, thus improves the molecular weight and selectivity of the PPC.

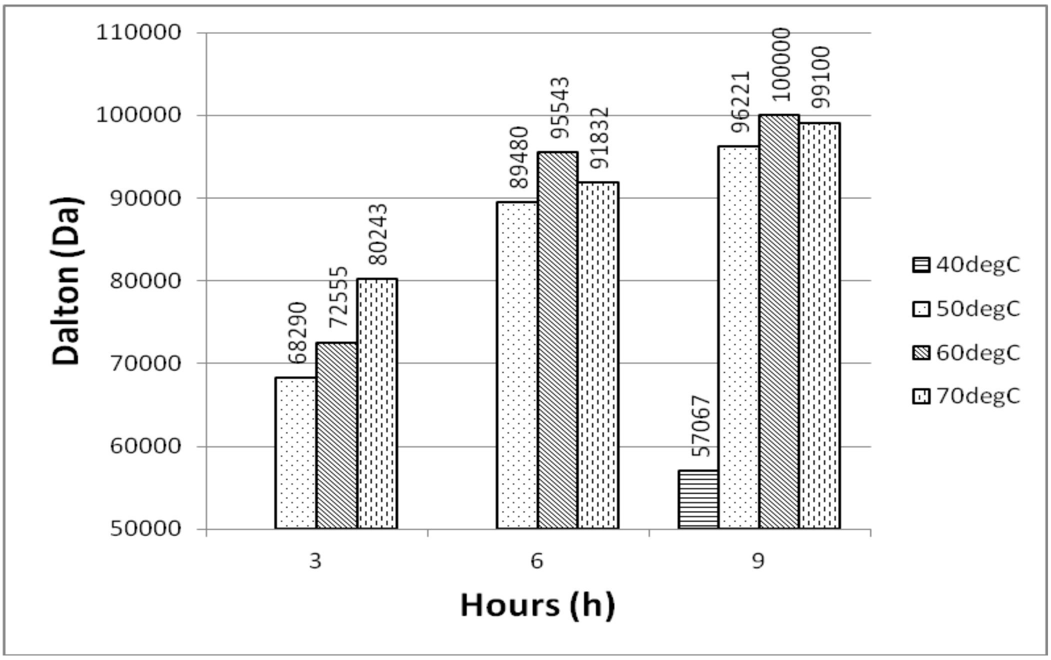


Figure 4.14: Molecular weight of all the PPC obtained using different catalysts synthesized with different combinations of catalyst preparation temperature and time.

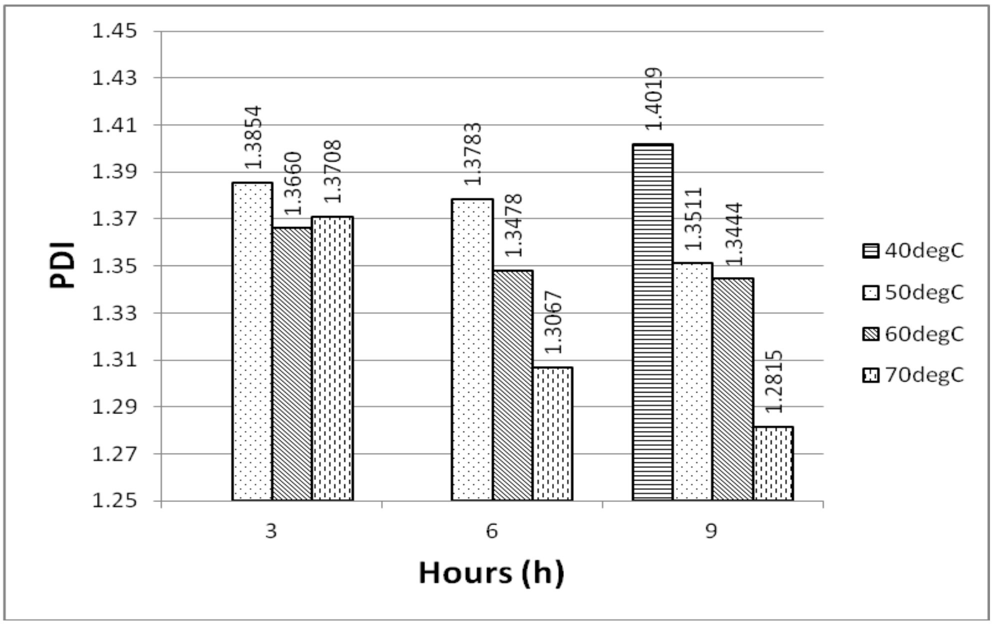


Figure 4.15: PDI of PPC obtained using different catalysts synthesized with different combinations of catalyst preparation temperature and time.

Table 4.1 Results of copolymerization of PO and CO_2 using ZnGA synthesized with different combinations of temperature and time.

Catalyst	Yield (g polymer/ g ZnGA)	M_n (Da)	PDI
ZnGA40-3	No yield		
ZnGA40-6			
ZnGA40-9	55.782	57067	1.4019
ZnGA50-3	58.238	68290	1.3854
ZnGA50-6	65.248	89480	1.3783
ZnGA50-9	65.826	96221	1.3511
ZnGA60-3	62.213	72555	1.3660
ZnGA60-6	64.924	95543	1.3478
ZnGA60-9	66.576	100000	1.3444
ZnGA70-3	64.822	80243	1.3708
ZnGA70-6	67.434	91832	1.3067
ZnGA70-9	68.257	99100	1.2815

4.2.2 Differential Scanning Calorimetry (DSC)

In this study, the values of melting temperature (T_m) for all synthesized PPC were extracted from DSC thermograms. As mentioned above, the physical properties of synthesized PPC are highly dependent on the catalytic activity of the ZnGA catalysts, while the T_m of the PPC is influenced greatly by the molecular weight and PDI of the polymers (Zhu et al., 2002; Peng et al., 2003; Xie et al., 2007; Luinstra and Borchardt, 2011; Kato et al., 2015). From the Figures 4.16 – 4.18, it showed that as the molecular weight increased, the T_m of the copolymer increased as well. However, at very high molecular weight, the changes on T_m were insignificant. On the other hand, it was also found that the narrower the PDI, the more the uniformity and microcrystallinity of the PPC, the sharper the DSC peak.

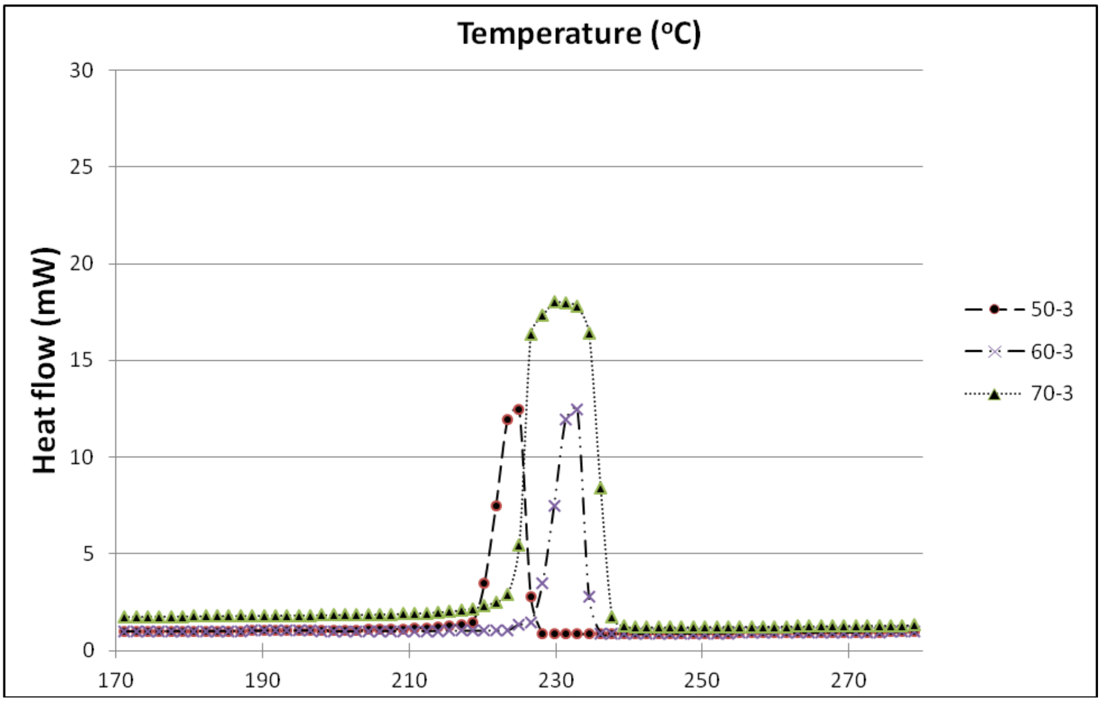


Figure 4.16: Differential Scanning Calorimetry Thermogram for PPC synthesized at different temperature for 3 hours.

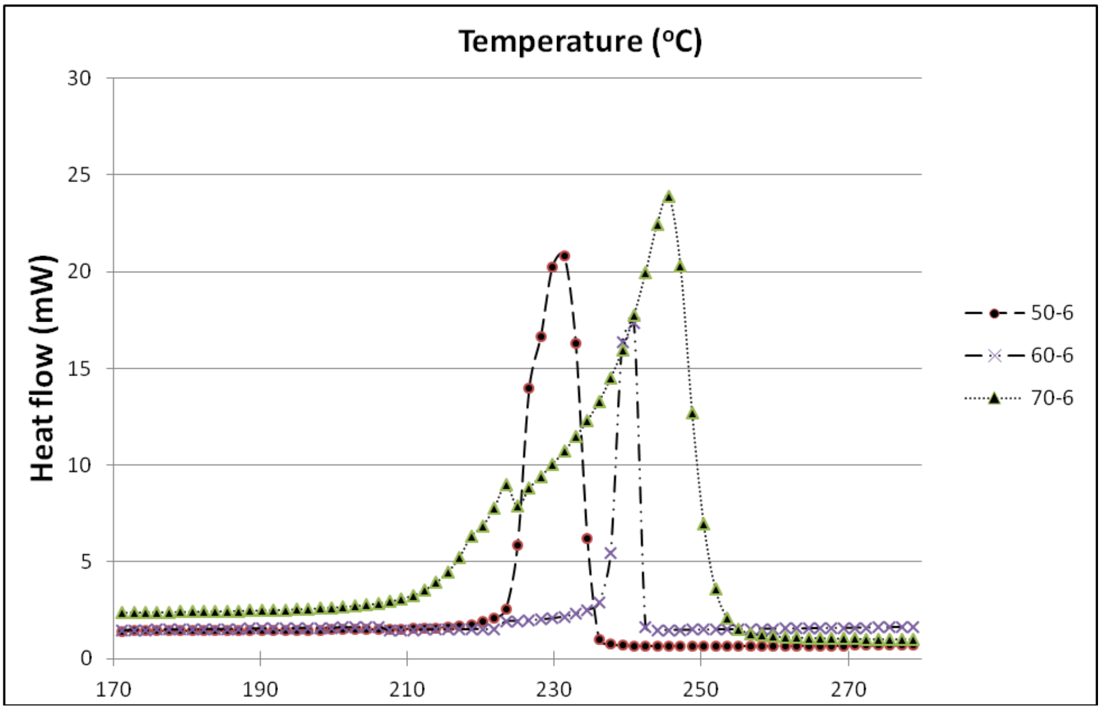


Figure 4.17: Differential Scanning Calorimetry Thermogram for PPC synthesized at different temperature for 6 hours.

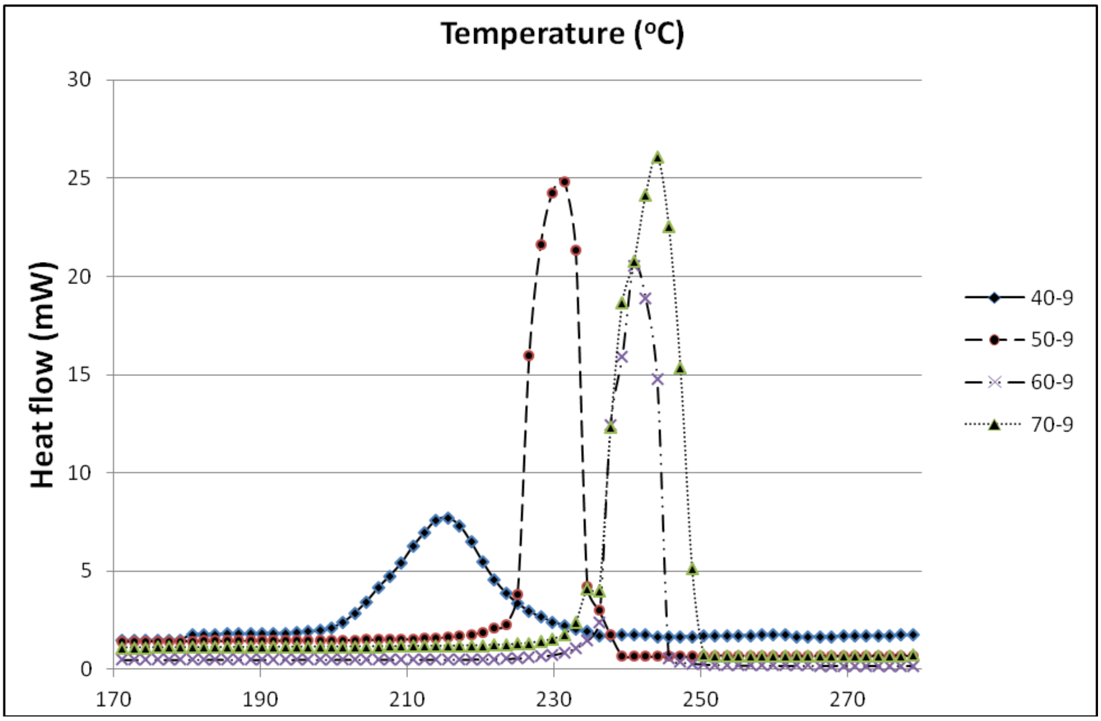


Figure 4.18: Differential Scanning Calorimetry Thermogram for PPC synthesized at different temperature for 9 hours.

4.2.3 Mechanical Properties and Crystallinity

Mechanical test was performed to investigate the mechanical properties of the PPC. As mentioned earlier, all the catalyst systems, except for ZnGA40-3 and ZnGA40-6, were able to produce PPC. All the PPC samples' tensile strength, tensile elongation and Young's Modulus are tabulated in the Table 4.1. It is noted that all the obtained PPC samples have tensile elongation more than 400%. As observed from Figure 4.19 and Figure 4.20, the tensile strength and the Young's modulus of the PPC polymers increases as the ZnGA catalysts used is synthesized at higher reaction temperature and longer reaction time. This is mainly due to improved catalytic activity of the catalysts, results in producing PPC with higher molecular weight and narrower PDI. As the molecular weight of a polymer increased, the effect of entanglement becomes more obvious (Yao et al., 2011). Besides that, the PPC samples produced by using ZnGA catalysts synthesized at higher reaction temperature and longer reaction time were also found to possess higher degree of crystallinity (Figure 4.21). The degree of crystallinity is important as it affects the mechanical properties of PPC to a great extent (Callister and Rethwisch, 2010). Subsequently, the high degree of crystallinity increased the tensile strength and Young's modulus of the copolymer.

Table 4.2: Tensile strength, Tensile Elongation and Young's Modulus for all the PPC samples undergone mechanical testing

	40^{o}C			50^{o}C			60^{o}C			70^{o}C		
	3h	6h	9h	3h	6h	9h	3h	6h	9h	3h	6h	9h
Tensile Strength (MPa)	No yield		3.44	2.77	3.21	6.40	3.20	5.67	8.45	4.05	7.05	8.48
Tensile Elongation (%)			More than 400% (Exact Value Can't Be Determined)									
Young's Modulus (MPa)			367.65	331.03	272.33	813.46	357.23	476.77	735.67	444.65	544.65	748.70

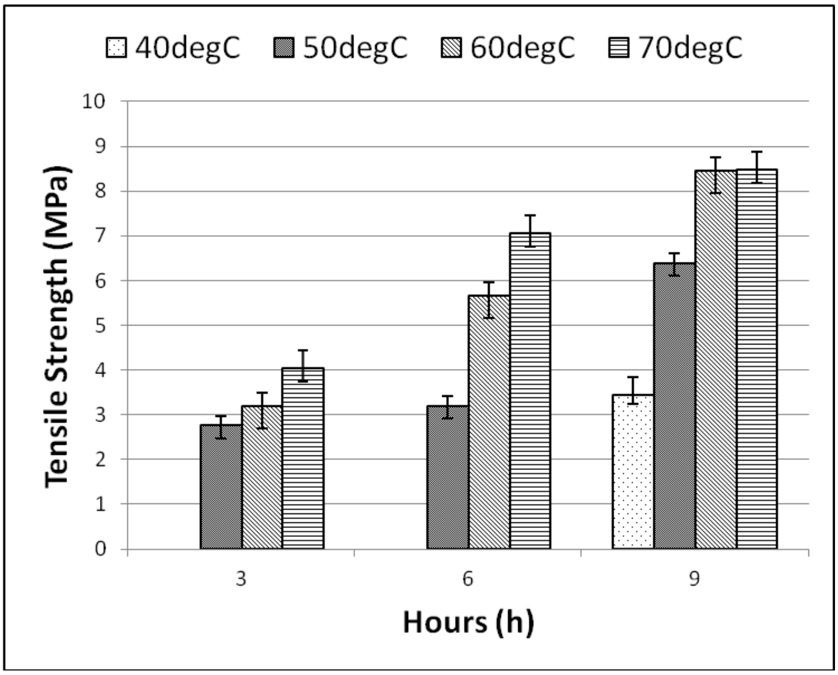


Figure 4.19: Tensile strength for all the PPC obtained using different catalysts synthesized with different combinations of catalyst preparation temperature and time.

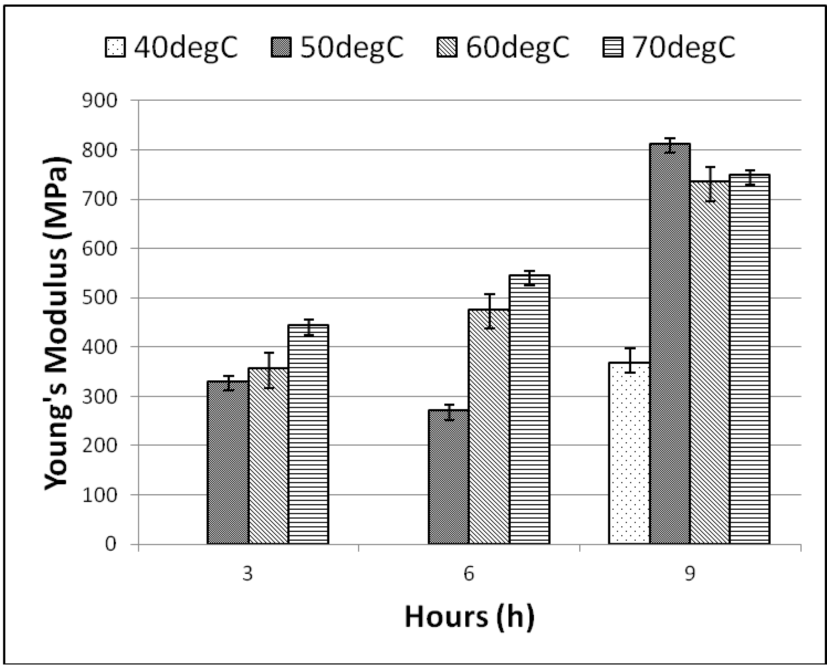


Figure 4.20: Young’s modulus for all the PPC obtained using different catalysts synthesized with different combinations of catalyst preparation temperature and time.

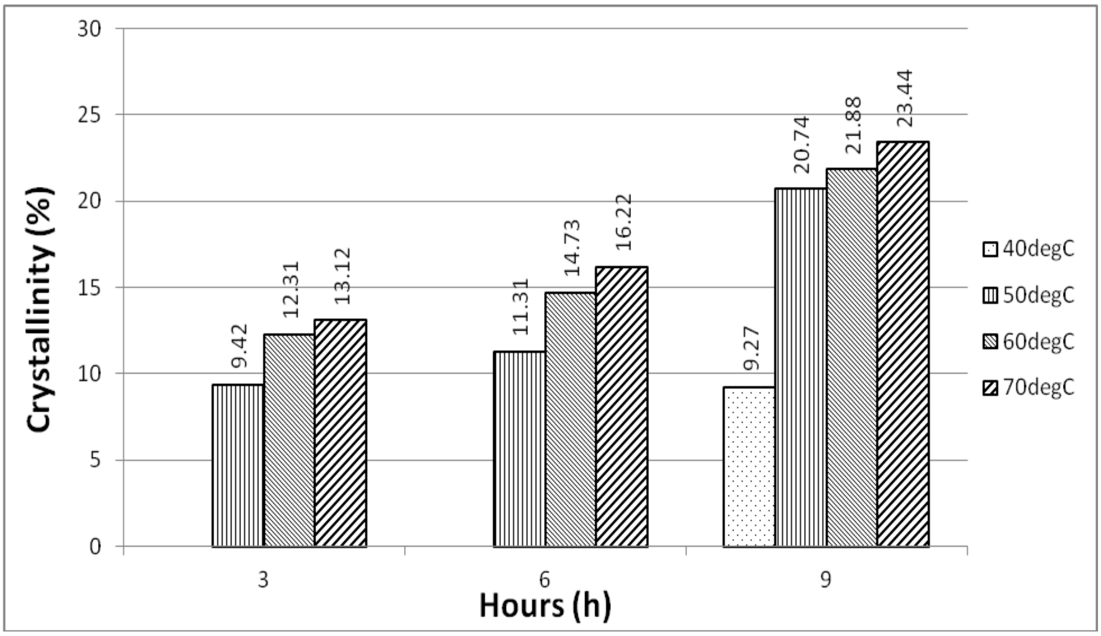


Figure 4.21: Crystallinity for all the PPC obtained using different catalysts synthesized with different combinations of catalyst preparation temperature and time.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The effects of catalyst preparation temperature and time on the copolymerization reaction of PO and CO_2 and the polypropylene carbonate (PPC) formed in the reaction were studied. During the study, various ZnGA catalysts were synthesized at several combinations of temperature (40 ^oC, 50 ^oC, 60 ^oC and 70 ^oC) and time (3 h, 6 h and 9 h). It was found that the catalyst preparation temperature plays a dominant role in affecting the catalytic activity of the ZnGA; the higher the temperature, the better the incorporation of GA into ZnO which will produce PPC with better quality. The ZnGA catalysts synthesized at higher temperature and longer reaction time were found to possess high degree of crystallinity as well. It was found that the degree of GA incorporation and degree of crystallinity of ZnGA possessed a significant impact towards the activity of the copolymerization. Among all the catalysts, ZnGA produced using 9 hours at 70^oC show the highest crystallinity (42.52%) and best incorporation of GA (1.24 a.u.). It produced PPC with high molecular weight (97,100 Da) with narrow PDI (1.28), high crystallinity (23.44%), high and narrow T_m at 244^oC. The produced PPC also exhibits excellent mechanical properties; tensile strength of 8.48MPa, tensile elongation more than 400% and Young’s modulus of 748.7MPa.

5.2 Recommendations

In order to further investigate the effects of catalyst preparation temperature and time on the catalytic activity of ZnGA catalysts and the properties of the PPC produced, additional analysis such as Brunauer-Emmett-Teller (BET) analysis, Carbon-13 Nuclear Magnetic Resonance (C-NMR) and Proton Nuclear Magnetic Resonance (H-NMR) can be conducted in the future.

In addition, as mentioned in section 2.7, nanocatalysis is an emerging field of study. Without doubt, due to their excellent catalytic activity and abundant active sites available for reaction, nanocatalysts will play vital role in the future industrial processes. Therefore, nano zinc oxide can be deployed to react with glutaric acid to form ZnGA catalysts. However, due to high surface area to volume ratio of nanoparticles, nano zinc oxide have high tendency to agglomerate in order to reduce its high surface energy (Fahlman, 2011). This may disrupt the reaction between zinc oxide and glutaric acid to form ZnGA catalysts. Further investigation on this field may able to synthesize nano ZnGA catalysts with far more superior catalytic activity which capable of producing PPC with better mechanical properties.

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