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Determination of zinc glutarate complexes synthesis factors affecting production of propylene carbonate from carbon dioxide and propylene oxide

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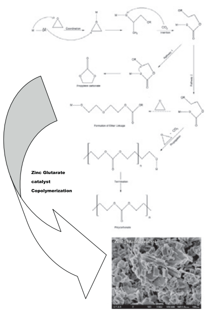
HIGHLIGHTS

- Zinc glutarate (ZnGA) catalyst copolymerize carbon dioxide and propylene oxide.
- High crystallinity ZnGA produce higher yield and selectivity of polypropylene carbonate (PPC).
- Producing PPC with high molecular weight (97,100 Da) and narrow polydispersity index (1.28).

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this research was to investigate 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. Various ZnGA catalysts were synthesized at several combinations of temperature (40 °C, 50 °C, 60 °C and 70 °C) and time (3 h, 6 h and 9 h). The ZnGA were then used to copolymerize propylene oxide and carbon dioxide to produce PPC. It is 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 to produce higher yield and selectivity PPC. However, the incorporation of glutaric acid into the catalyst is vital as well. Although some of the ZnGA exhibit high crystallinity, their low intensity of characteristic peaks of zinc-carboxylate bond (COO−) may causes low yield of PPC with byproducts. This is especially found on the catalysts synthesized at lower temperature (40 °C). Among the all the combinations of temperature and time, the ZnGA prepared using 9 h at 70 °C possess 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 (97,100 Da) and narrow PDI (1.28), high crystallinity (23.44%), high and narrow T_m at 244 °C with excellent mechanical properties (tensile strength of 8.48 MPa, tensile elongation >400%, and Young's modulus of 748.7 MPa).

1. Introduction

Carbon dioxide (CO_2) is one of the infamous greenhouse gases which plays a major role in causing global warming. However, it

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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 [1]. 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 [2]. 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 [3]. 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 to fulfil the 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 [4]. Examples of the compounds with two active hydrogens are water, aromatic dicarboxylic acids, primary amines, di- or trihydroxybenzenes, polymers, etc [5]. The copolymerization reaction requires a long reaction time and only produces PCs with low yield and selectivity [6].

Table 1
Different Sets of Experiment with Different Reaction Temperature and Time.

Reaction Temperature (°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

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 [7].

Several heterogeneous catalyst mixtures and homogenous discrete metal complex catalyst such as zinc dicarboxylates, metal prophyrin derivatives, zinc phenoxide derivatives, salen chromium chlorides have been shown to improve reactivity of carbon dioxide in reaction with epoxy function group [8]. Hence, investigation of the methods to synthesize these polymers is very advantageous to the implementation of more environmentally friendly industrial processes. Therefore in this study, the physical and mechanical properties of PPC synthesized from copolymerization of PO and CO_2 corresponded to the preparation temperature and time of zinc glutarate (ZnGA) catalyst was reported. The purpose of the study was to determine 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.

2. Methodology

2.1. Materials

Zinc Oxide (ZnO) was obtained from Rank Synergy Sdn. Bhd., Malaysia while Glutaric Acid (GA) was supplied by Merck Sdn. Bhd., Malaysia. Propylene oxide (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

2.2. Catalyst preparation

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

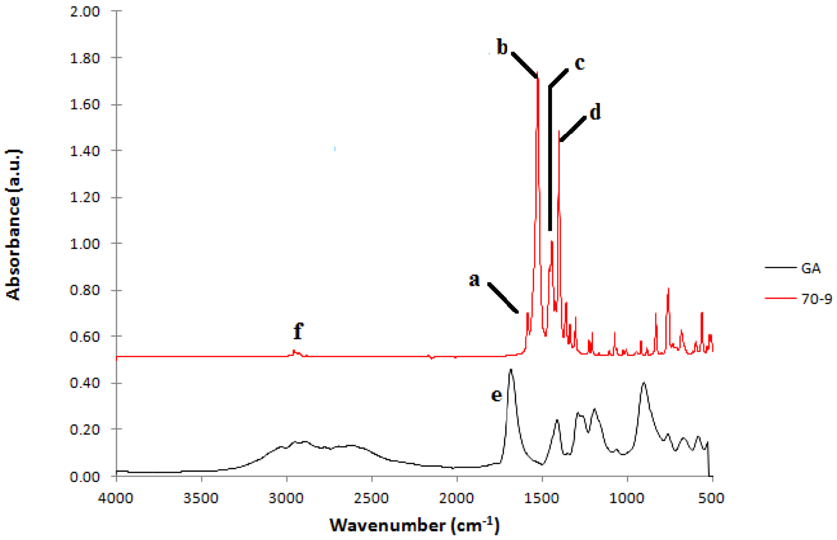

Fig. 1. FTIR spectra of ZnGA synthesized at 70 °C for 9 h and FTIR spectra of pure GA.