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Synthesis of Poly(glycerol malonate) Oligomers from Bio-based Sources Utilizing $AlCl_3$ Catalyst

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Abstract: Due to the significant economic and environmental benefits, the demand for biomass-derived building blocks in polymer development has increased in recent years. Bio-based plastics, integral to advancing a circular economy, have consistently been a leading topic among emerging technologies. In this study, we aim to evaluate the effectiveness of different esterification catalysts. To achieve this, we synthesized a range of fully bio-based oligomers using glycerol and malonic acid as starting materials, along with three catalysts: tin(II) 2-ethylhexanoate (stannous octoate, $Sn(Oct)_2$), stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$), and aluminum chloride ($AlCl_3$). The chemical structures of the synthesized oligomers were confirmed using NMR and FTIR spectroscopy. Thermal properties were assessed using DSC and TGA. FTIR analysis verified successful oligomer synthesis, and a glass transition temperature (T_g) of approximately -56 °C was determined via DSC. Additionally, the oligomers exhibited maximum working temperatures at around 278 °C, corresponding to a 50 wt% loss.

Keywords: Bio-based oligomers, biopolymers and renewable polymers, polycondensation, catalyst.

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1. INTRODUCTION

Despite the advantages polymers offer in terms of energy savings, weight reduction, and durability, their appeal has diminished due to the rapid depletion of petroleum resources and increasing environmental concerns (Iwata, 2015). Bio-based polymers, derived from renewable resources, present a promising alternative to traditional petroleum-based polymers. The demand for biomass-derived building blocks for polymer development has surged in recent years, driven by both economic and environmental considerations. Bio-based plastics have consistently topped the list of emerging technologies, particularly within the framework of a circular economy. Recent research has led to the synthesis of various bio-based polymers, including poly(lactic acid) (PLA) (Balla et al., 2021), poly(glycolic acid) (PGA) (Jem & Tan, 2020), poly(butylene succinate) (PBS) (Wang et al., 2022), cellulosic plastics (Morinval & Averous, 2022), poly(hydroxyalkanoates) (PHA) (Ansari et al., 2021), poly(ε-caprolactone) (PCL) (Acik, 2020), and starch-based plastics (Zhang et al., 2021). These materials have garnered increasing interest from technical and industrial perspectives, with the potential to replace petroleum-based polymers in diverse applications such as clothing, sanitation, drug delivery, packaging, tissue engineering, agriculture, and toys (Tremblay-Parrado et al., 2021).

Two major challenges in the adoption of bio-based polymers have been their cost and performance. However, costs have decreased due to advancements in bioprocessing technologies and the establishment of global biorefineries that produce bio-based monomers and building blocks (Bozell & Petersen, 2010). For instance, succinic acid, a bio-based monomer, is now commercially produced by companies like BioAmber and Myriant. Over the past two decades, aliphatic polyesters derived from sebacic acid, itaconic acid, 1,4-butanediol, 1,3-propanediol, succinic acid, 2,5-furandicarboxylic acid, adipic acid, glycerol, and other compounds have been extensively studied, ranging from rigid plastics to soft elastomers (Fei et al., 2022; Kasmi et al., 2021; Zhang et al., 2021). These materials have attracted significant attention from both academic and industrial sectors. Malonic acid (MA), a dicarboxylic acid derived from glycerol, can function as either a monomer or a crosslinker

(Zhao et al., 2020). While some researchers have explored the use of MA in crosslinking polyvinyl alcohol (PVA) via esterification, its application in polymer synthesis remains relatively underexplored (Qiu & Netravali, 2013). Dogan and Kusefoglu reported some success in polymerizing MA with soybean oil, indicating potential for future studies in this area (Doğan & Küsefoğlu, 2008).

In this study, we aim to evaluate the performance of different esterification catalysts. To this end, we synthesized a variety of fully bio-based oligomers using glycerol and malonic acid as starting materials, in conjunction with three catalysts: $AlCl_3$, $Sn(Oct)_2$, and $SnCl_2{\cdot}2H_2O$. $AlCl_3$, in particular, is notable for its low environmental impact and cost-effectiveness compared to zeolites, transition metal catalysts, and rare earth catalysts. The chemical and thermal properties of the synthesized oligomers were characterized using NMR/FTIR and DSC/TGA techniques.

2. EXPERIMENTAL SECTION

2.1. Materials

Glycerol (GLY, ≥99.5%), malonic acid (MA, 99%), $AlCl_3$, $Sn(Oct)_2$, stannous chloride dehydrate ($SnCl_2.2H_2O$) and all solvents were purchased from Sigma-Aldrich. All reagents and solvents were used as received without further purification.

2.2. Synthesis of PGM Oligomers

Oligomers with various catalysts were produced by a two-step polycondensation method. First stage, esterification, led to the formation of oligomers with only low molecular weight compounds. Then, increasing the temperature and reducing the reaction pressure facilitated the coupling of the oligomer chains by either an esterification or a transesterification reaction. The experiments were run in 100 mL round-bottom flask equipped with a distillation setup and a nitrogen inlet to remove water and other by-products. All reactions of GLY with MA were carried out with a diol /diacid molar ratio of 1.1:1. At the first stage, the reaction mixture was continuously stirred under nitrogen to limit oxidation. The flask was immediately placed into an oil bath at 135 °C and allowed to react for 3 h. After oligomerization, at the second step of polycondensation, the reaction mixture was subsequently heated to final temperature 210 °C. A vacuum of 7 mbar was applied for another 3 h to remove water vapor. After polymerization, the reaction products were dissolved in chloroform and then precipitated in cold methanol (– 30 °C) to remove the unreacted monomers and catalyst. Precipitated polymer was then filtered and dried in a vacuum oven at room temperature for 24 h.

2.3. Characterization

^1H NMR spectra of oligomers were obtained on a Bruker (Ultrashield Plus Biospin Avance III) 400 MHz NMR spectrometer using tetramethylsilane as the internal standard. $CDCl_3$ was used as solvent to prepare solutions. The synthesized polymers were characterized by Fourier transform infrared spectroscopy (FTIR) with ATR using a Jasco 6800 at 450–4000 cm^{-1} wavelength range with 16 scans. The molecular weights were determined using Agilent 1200 gel permeation chromatograph (GPC). THF was used as eluent, and PMMA standards were used for calibration. The sample concentration was 1 mg/mL and eluent flow rate was 1 mL/min. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed under nitrogen on a Mettler Toledo (DSC 3) and Mettler Toledo (TGA/DSC 3+). For DSC, the samples were heated from room temperature to 160 °C at a rate of 10 °C/min and held for 3 min to eliminate the thermal history. Then, they were cooled to -60 °C and heated again from -60 to 160 °C at a rate of 10 °C/min. For TGA, samples were heated from 25 to 600 °C at 10 °C/min heating rate.

3.. RESULTS AND DISCUSSION

3.1. Chemical Structure of Synthesized Oligomers

Various bio-based oligomers were synthesized through a two-step melt polycondensation process using three different catalysts (Figure 1). The initial reactions were carried out at a temperature of 135 °C, selected based on the melting point (135 °C) and boiling point (140 °C) of malonic acid. Following synthesis, the number-average molecular weight (M_n) of the oligomers ranged from approximately 200 to 400 g/mol, indicating the formation of dimers or oligomers (Table 1). This suggests that the catalysts were not sufficiently effective during the second step, namely, transesterification. Among the catalysts, only the synthesis of PGM using $AlCl_3$ achieved the desired yield. Therefore, only its characterization was performed, and the results are presented in the following sections.

Figure 1: Image of the PGM oligomer samples produced using $AlCl_3$.

Table 1: Molecular weight and thermal properties of PGM oligomers with various catalysts.

Catalyst	**M_n (g/mol)**	**M_w (g/mol)**	**PDI**	**$T_{5\%}$ (°C)**	**T_{max} (°C)**	**Residue at 600 °C wt.%**	**T_g (°C)**
$AlCl_3$	247.7	326.4	1.32	178	268	1.7	-56.5
$Sn(Oct)_2$	423.5	434.0	1.02	-	-	-	-
$SnCl_2.2H_2O$	194.9	261.6	1.34	-	-	-	-

T_g glass transition temperature, $T_{5\%}$ temperature at 5 % weight loss, T_{max} temperature at 50 % weight loss.

The chemical structure of the synthesized poly(glycerol malonate) (PGM) oligomers was characterized using ^1H NMR spectroscopy. The ^1H NMR analysis revealed that the PGM oligomer backbone consisted of a mixture of alkane and ester bonds (Figure 2). In the ^1H NMR spectrum, the presence of ester bonds was confirmed by the signal at $\delta = 3.89$ ppm, which corresponds to the COO-CH_2- protons from the glycerol repeating units. The chemical shift at $\delta = 3.37$ ppm was attributed to the CO-CH_2-CO- protons from the malonate repeating units. Additionally, the hydroxyl terminal group (HO-CH_2-) signal was observed at $\delta = 3.71$ ppm, consistent with the relatively low molecular weight of the oligomeric samples.

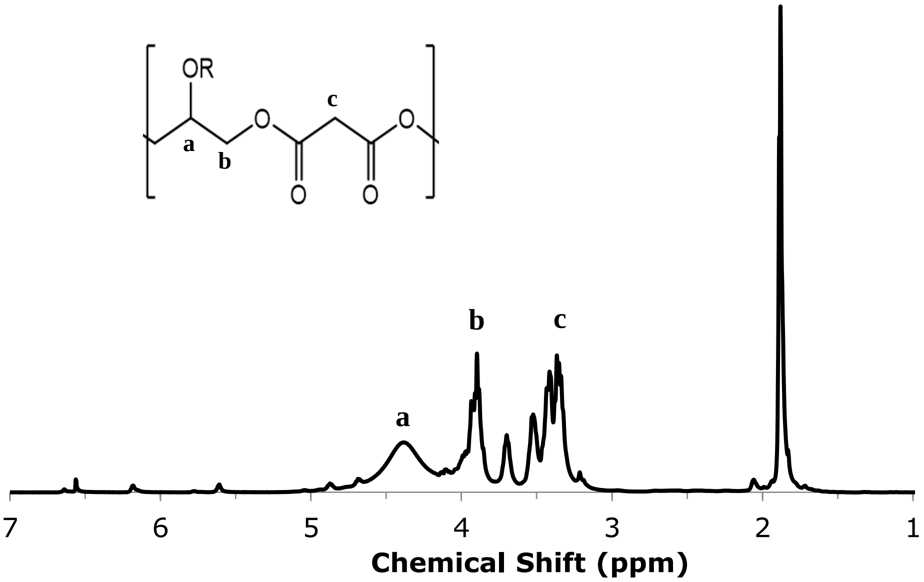

Figure 2: ^{1}H NMR spectrum of the PGM oligomers.

FTIR spectra were taken of the synthesized oligomers to evaluate their chemical composition and are shown in Figure 3. A broad O-H stretching peak can be seen around 3322 cm^{-1} indicating the presence of hydroxyl (–OH) from alcohols. Peaks around 2882 cm^{-1} correspond to C-H stretching. A strong absorption peak at approx. 1722 cm^{-1} is attributed to C=O stretching vibrations of ester group. Absorption peaks at 1240 and 1044 cm^{-1} indicate the presence of C-O stretching and O-CH_2 stretching, respectively.

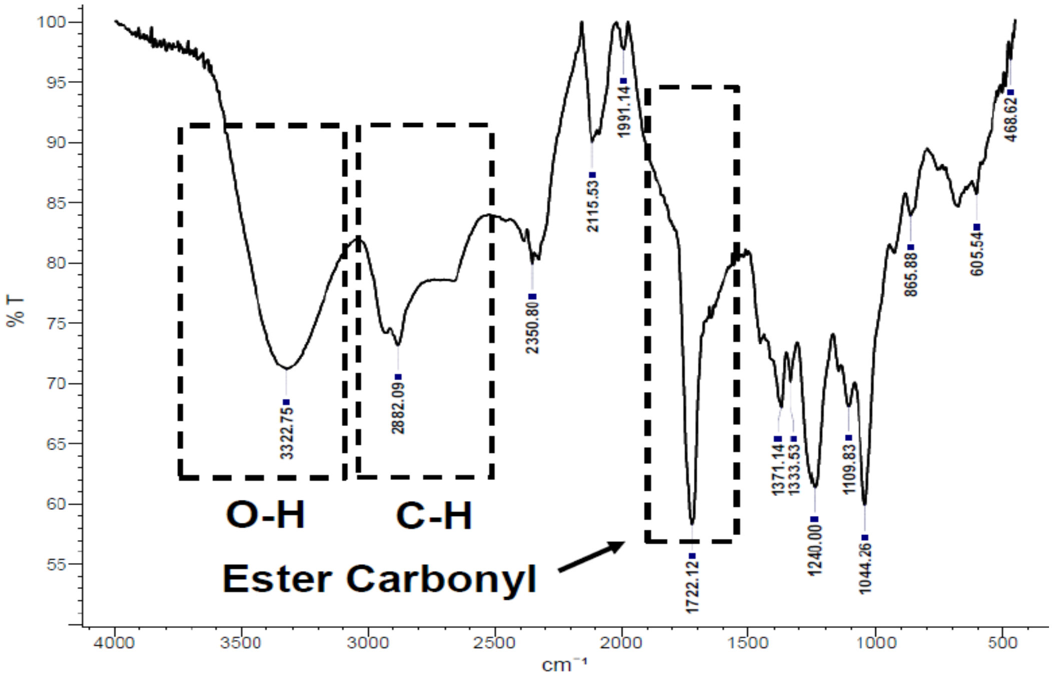

Figure 3: FTIR spectrum of PGM oligomers with $AlCl_3$.

3.2. Thermal Properties of Synthesized Oligomers

Differential scanning calorimetry (DSC) was utilized to investigate the thermal properties of the PGM oligomers. The DSC curve for the PGM oligomers synthesized with $AlCl_3$ is presented in Figure 4, with the glass transition temperature (T_g) summarized in Table 1. PGM, being an amorphous oligomer, displayed a glass transition temperature of approximately -56 °C. This low T_g suggests that PGM could serve as an effective plasticizer, offering advantages in mixing or blending processes.

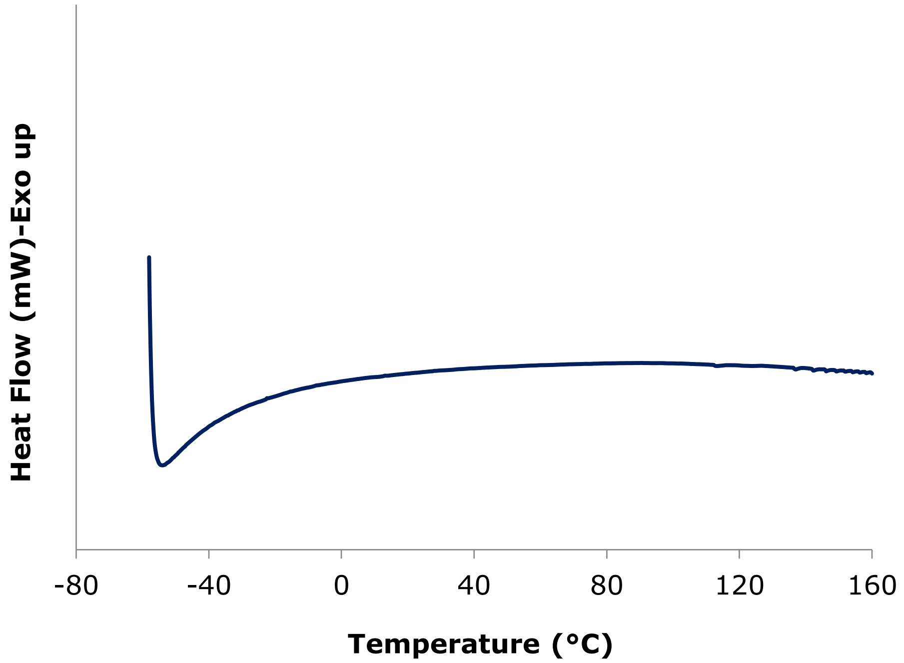

Figure 4: Second heating DSC curve of PGM oligomers with $AlCl_3$.

Thermogravimetric analysis (TGA) was performed on several samples of the synthesized oligomers, with the results summarized in Table 1. The TGA curve for PGM oligomers synthesized with $AlCl_3$ is shown in Figure 5. TGA analysis allows for the comparison of thermal stability among the samples. Thermal degradation of PGM oligomers occurred in a single degradation step, with an initial decomposition temperature ($T_{5\%}$) of 178 °C. Additionally, the maximum thermal degradation temperature ($T_{50\%}$) was observed at 268 °C. At the end, a small amount of residue (1.71 wt%) was recovered at 600 °C.

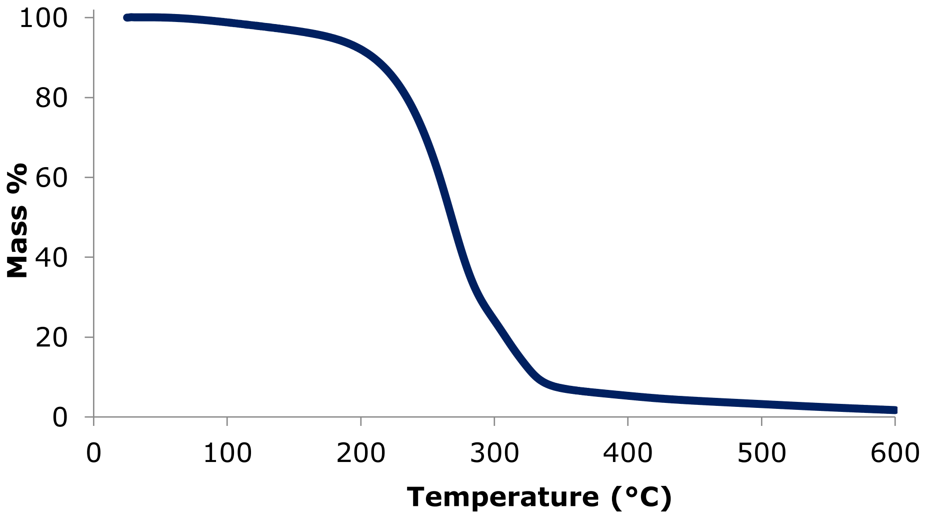

Figure 5: TGA curve of PGM oligomers with $AlCl_3$.

4. CONCLUSION

Bio-based oligomers were successfully synthesized via melt polycondensation using biomonomers glycerol (GLY) and malonic acid (MA), which are industrially produced through fermentation or extraction from biomass. The effects of three esterification catalysts on the chemical and thermal properties of the oligomers were evaluated. Among them, only the synthesis of PGM using $AlCl_3$ achieved the desired yield. The bio-based oligomers exhibited promising thermal stability, with a $T_{5\%}$ of 178 °C and a $T_{50\%}$ of 268 °C when synthesized with $AlCl_3$. Given its low cost and minimal environmental impact, $AlCl_3$ emerged as the most suitable catalyst for the synthesis of these oligomers.

5. CONFLICT OF INTEREST

The authors declare no conflict of interest.

6. ACKNOWLEDGMENTS

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