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# 1 Executive Summary

This comprehensive report details the synthesis process carried out using the selected organometallic catalyst titanium (IV) butoxide ($Ti(OBu)_4$) to produce three distinct types of polyesters on a gram scale. These polyesters were synthesized using diols and diacids of varying chain lengths, aligning with the objectives set forth in the ACTPAC project's Work Package 6 (WP6).

The polyesters synthesized in this study are referred to as 10,10-polyesters, 12,12-polyesters, and 14,14-polyesters. Each designation reflects the chain lengths of the diols and diacids used as monomers in the polymerization process. Specifically, 10,10-polyester was synthesized from a C10 diol and a C10 diacid, 12,12-polyester was derived from a C12 diol and a C12 diacid, and 14,14-polyester was obtained from a C14 diol and a C14 diacid.

Some characterization of the polyesters is also presented, encompassing a range of techniques such as nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), size exclusion chromatography (SEC) and thermogravimetric analysis (TGA). These analyses provide insights into the molecular structure, thermal properties, and molecular weight distribution of each polyester.

It is important to note, however, that SEC analysis could not be performed on the 14,14-polyester because of the lack of time encountered during the characterization process. The molecular weight distribution of this polyester remains undetermined, but alternative methods have been employed to assess its structure and thermal properties. The SEC will proceed in early 2025.

By varying the chain lengths of the diols and diacids, this study aims to explore the impact of the molecular architecture on the physical, thermal, and later mechanical properties of the resulting polyesters.

# Contents

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# Acronyms & Abbreviations

| Term | Description |
|---|---|
| D | Deliverable |
| Đ | Polydispersity index |
| DMA | Dynamic Mechanical Analysis |
| DSC | Differential Scanning Calorimetry |
| EC | European Commission |
| $M_n$ | Number average molar mass |
| NMR | Nuclear Magnetic Resonance |
| SEC | Size Exclusion Chromatography |
| TGA | Thermogravimetric analysis |
| $T_c$ | Crystallization temperature |
| $Ti(OBu)_4$ | Titanium (IV) butoxide |
| $T_m$ | Melting temperature |
| WP | Work Package |
| WT | Work Task |

# 2 Introduction

## 2.1 Overview

The most commonly used pathway to produce polyester today is the polycondensation of dicarboxylic acids and diols. To facilitate the process and yield high-molar-mass polyesters, a catalyst is needed. Many studies have shown that various catalysts are efficient for the synthesis of polyesters.[1] For the synthesis of the 3 polyesters, the catalyst used was titanium (IV) butoxide ($Ti(OBu)_4$) as it has already been reported to be one of the most efficient.[2]

## 2.2 Relation to other tasks and deliverables

As is an initial deliverable, this task does not rely on input from preceding tasks or deliverables. However, it provides essential output to the subsequent tasks and deliverables listed in Table 1.

**Provides outputs to:**

**Table 1.** D6.1 Output for other tasks and deliverables

| Deliverable | Due Date | Output from D6.1 |
|---|---|---|
| D11.1 | Month 45 | 3 target polyesters produced in 300-liter reactor by chemical polymerization (100 kg output per batch, per polyester) at TRL 6-7 with scalable protocol |
| D11.2 | Month 45 | Public report for scale-up production of 3 target polyesters by chemical polymerization at TRL 6-7 |

## 2.3 Structure of the deliverable

In this deliverable, the synthetic procedure, the purification process and the characterization of 3 polyesters are presented.

# 3 General information about the synthesis

All reagents were used without purification. $Ti(OBu)_4$, dodecanedioïc acid and 1,12-dodecanediol were purchased from Sigma-Aldrich, decanedioïc acid from Alfa, 1,10-decanediol and tetradecanedioïc acid from TCI; and 1,14-tetradecanediol from BLDpharma. TGA was run on a TA Instruments TGA Q550 unit using N2 purge gas at a flow rate of 20 mL/min and a platinum TGA pan. The postediting software used was Trios. DSC was performed on a TA Instruments DSC 250 unit using N2 purge gas. DSC analysis where performed using via 2 heating and cooling cycles with heating and cooling rates of 10°C/min. TA Trios software was used for the evaluation of the DSC data. For proton NMR, a Bruker Avance 400 spectrometer at room temperature (25°C) was used with Mestrenova software for data treatments and deuterated chloroform was used as the solvent. SEC was performed at 30°C in chloroform with polystyrene calibration.

# 4 Synthesis of a polyester (10,10-polyester) by polycondensing 1,10-decanediol with decanedioïc acid

## 4.1 Experimental part

### 4.1.1 Polymer synthesis

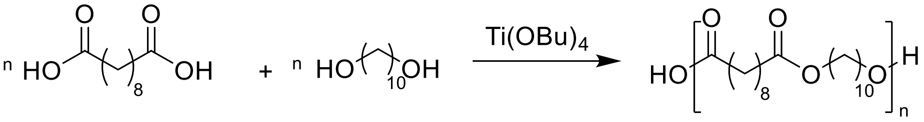


**Figure 1.** Synthetic pathway to obtain 10,10-polyester

In a three-necked round bottomed flask of 100 mL decanedioïc acid and 1,10-decanediol were added. The flask is equipped with a magnetic stirrer, and has an arm which is adapted for the argon inlet, a glass stopper and a Dean Stark connected to a reflux column. The reflux column was further connected to a bubbler to monitor argon flow, ensuring air exclusion while preventing overpressure. The reaction medium was set to 180°C under stirring (750 rpm) and after 2 hours, the catalyst, which was used at a 1:1000 molar ratio was dissolved in 2 mL of toluene and added. The oligomerization lasts 16 hours under an argon atmosphere. Then, the temperature was gradually increased to 200°C under static vacuum over 1 hour and the polymerization was run for another 7 hours. The obtained polymer is a white solid.

### 4.1.2 Purification

The polymer was dissolved in chloroform leading to a slightly viscous liquid. The polymer is reprecipitated in ethanol cooled with liquid nitrogen and then it is filtered through a paper filter. The polymer is air dried and vacuum dried for 8 h. A total of 2.43 g of polymer was obtained.

### 4.1.3 Characterization

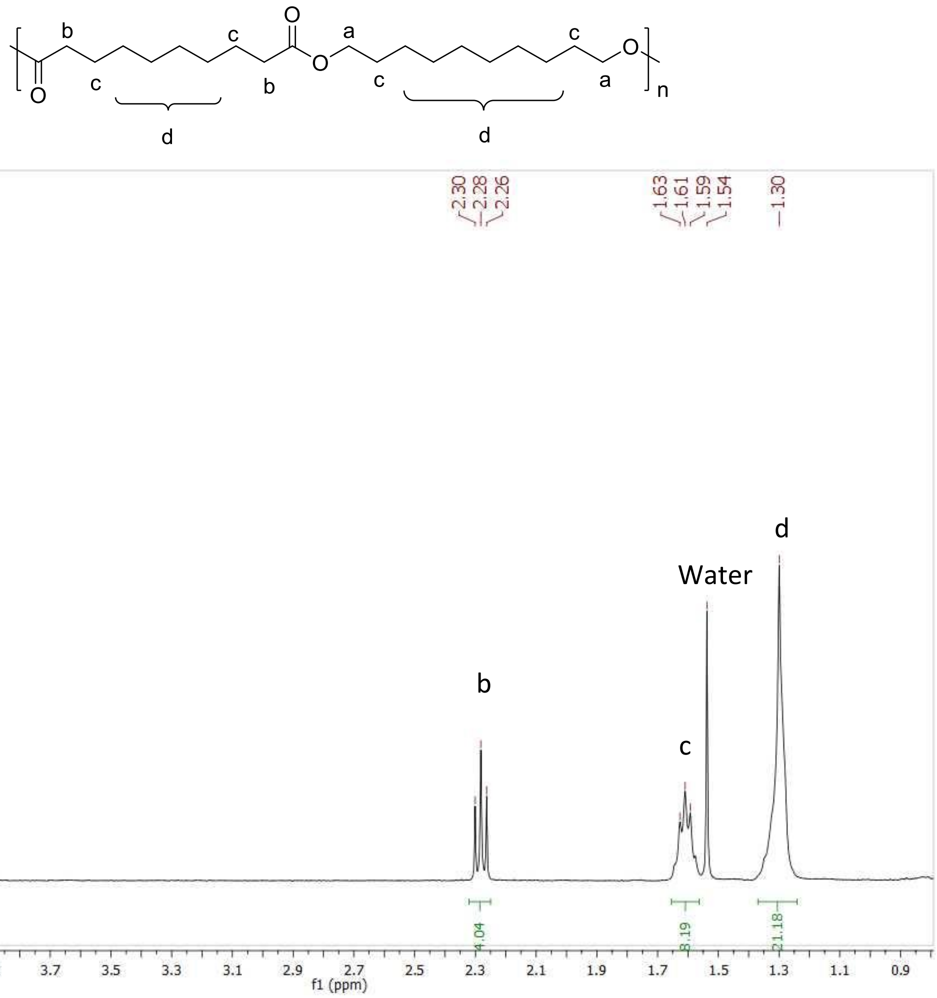


**Figure 2.** $^1$H NMR of 10,10-Polyester

The solid was then dried under vacuum for another 8 h to remove the remaining water and further characterization was performed.

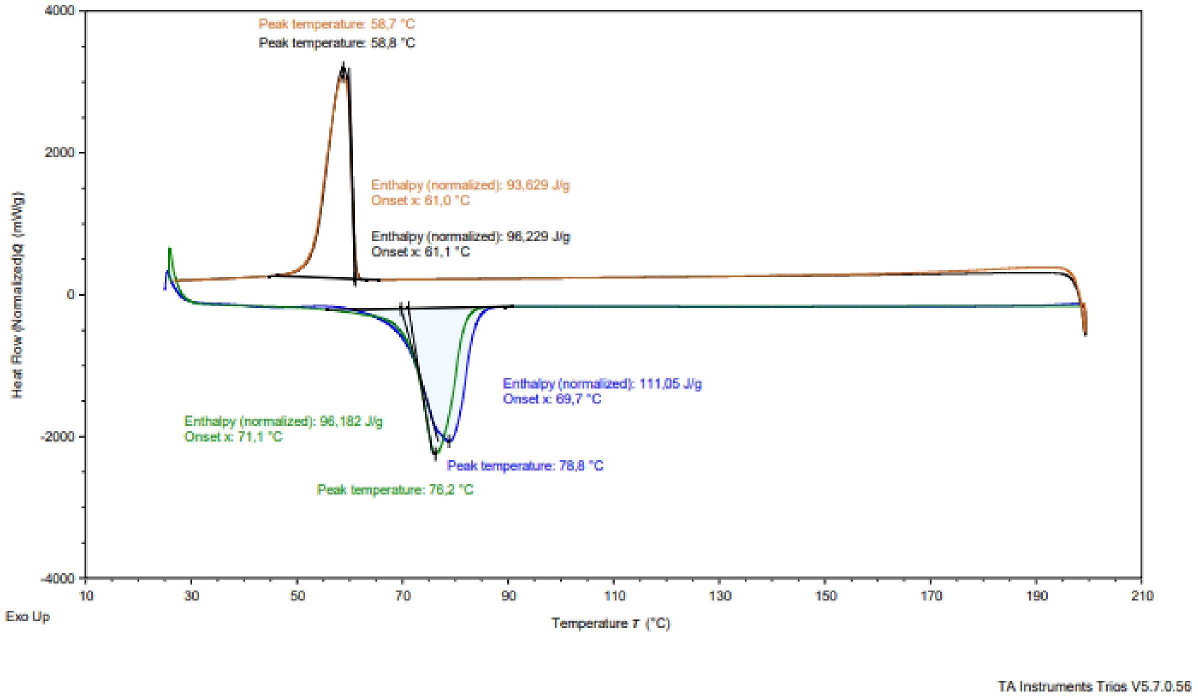


**Figure 3.** DSC of 10,10-polyester (blue represent the 1st heating ramp, green the 2nd heating ramp)

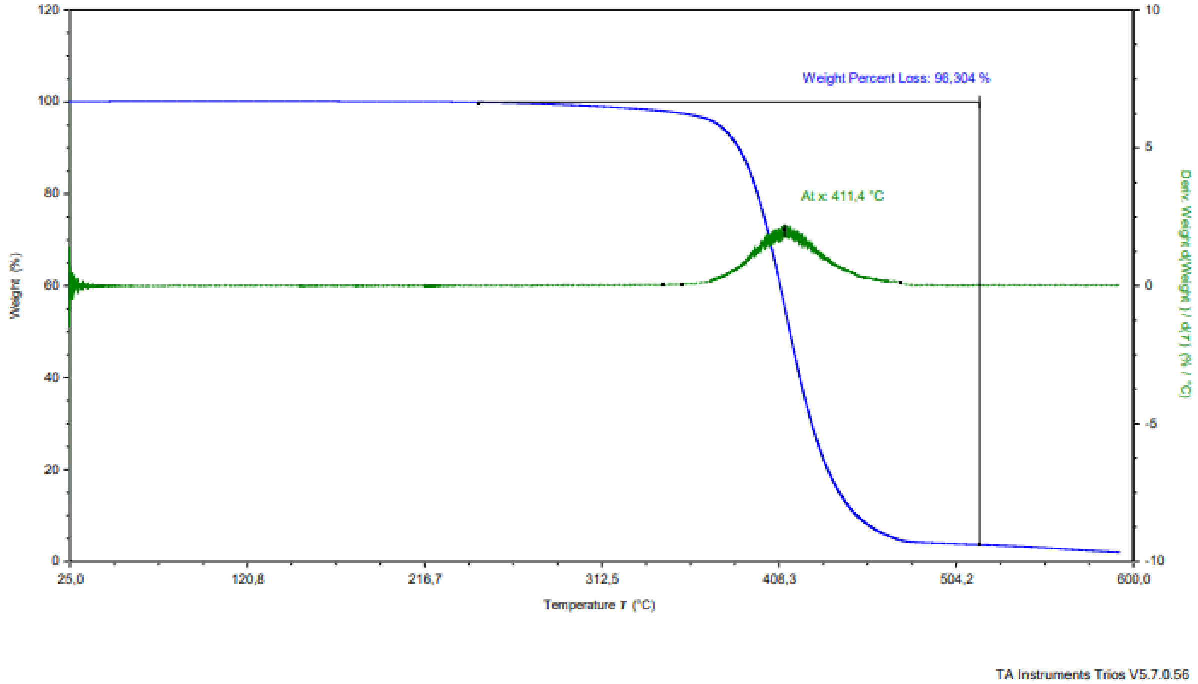
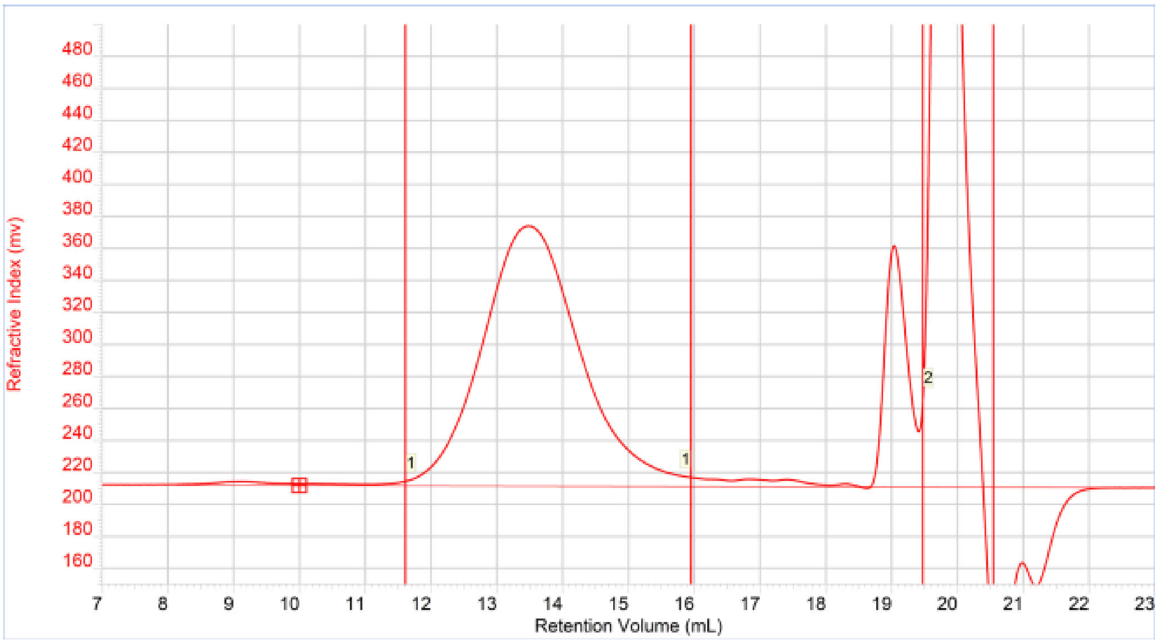


**Figure 4.** TGA of 10,10-polyester



| Peak | Mn | Mw | Mp | Mw/Mn | Ret Vol | RI Area |
|---|---|---|---|---|---|---|
| 1 | 30 425 | 69 001 | 53 227 | 2.268 | 13.477 | 280.27 |

**Figure 5.** SEC of 10,10-polyester

# 5 Synthesis of a polyester (12,12-polyester) by polycondensing 1,12-dodecanediol with dodecanedioic acid

## 5.1 Experimental part

### 5.1.1 Polymer synthesis

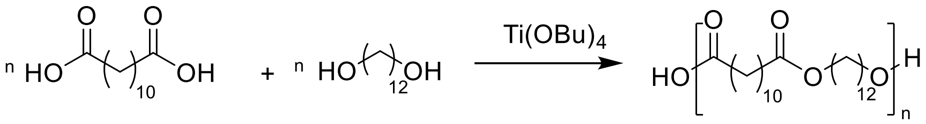


**Figure 6.** Synthetic pathway to obtain 12,12-polyester

The 1,12-dodecanediol and dodecanedioïc acid were used in a 1:1 molar ratio, with a catalyst loading of 1:1000. In a three-necked round bottomed flask of 100 mL the diacid and the diol were added. The flask was equipped with a magnetic stirrer and it has an arm which is adapted for the argon inlet, a glass stopper and a Dean Stark connected to a reflux column. The reflux column was further connected to a bubbler to monitor the argon flow, ensuring air exclusion while preventing overpressure. The reaction medium was set to 180°C with magnetic stirring (650-700 rpm) for 2 hours. The catalyst was dissolved in 2 mL of toluene. The mixture was allowed to oligomerize for 15h under argon. A slightly brownish viscous liquid was obtained. Then the temperature was gradually increased to 200°C under static vacuum over 1 hour, and the polymerization was run for another 8 hours. The solid obtained was slightly brown.

### 5.1.2 Purification

The polymer was dissolved in chloroform and reprecipitated in ethanol (previously cooled with liquid nitrogen). The mixture was then filtered through a paper filter and dried under air and vacuum for 8 h. The obtained polymer is white. A total of 2.6 g of polymer was obtained.

## 5.2 Characterization

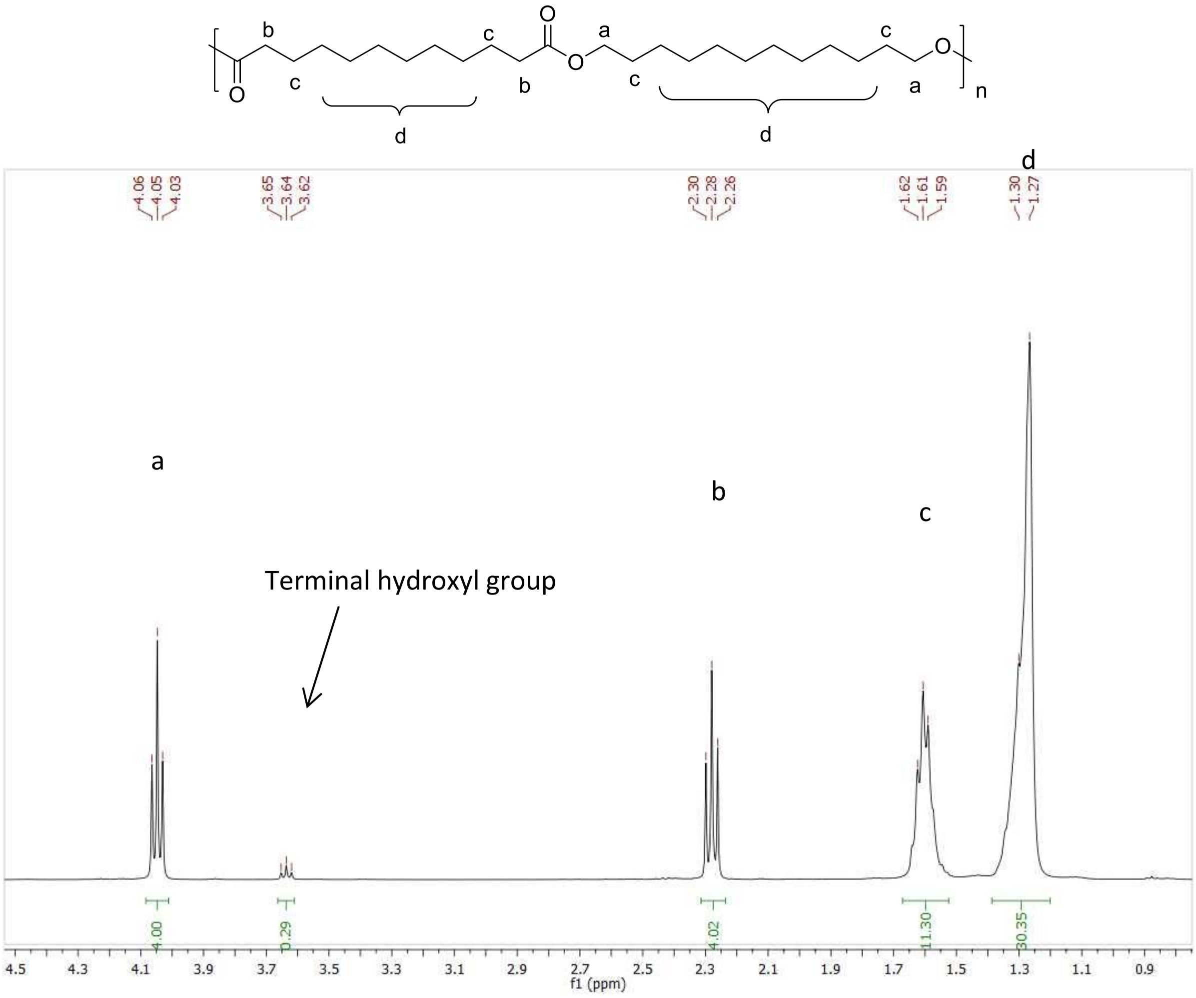
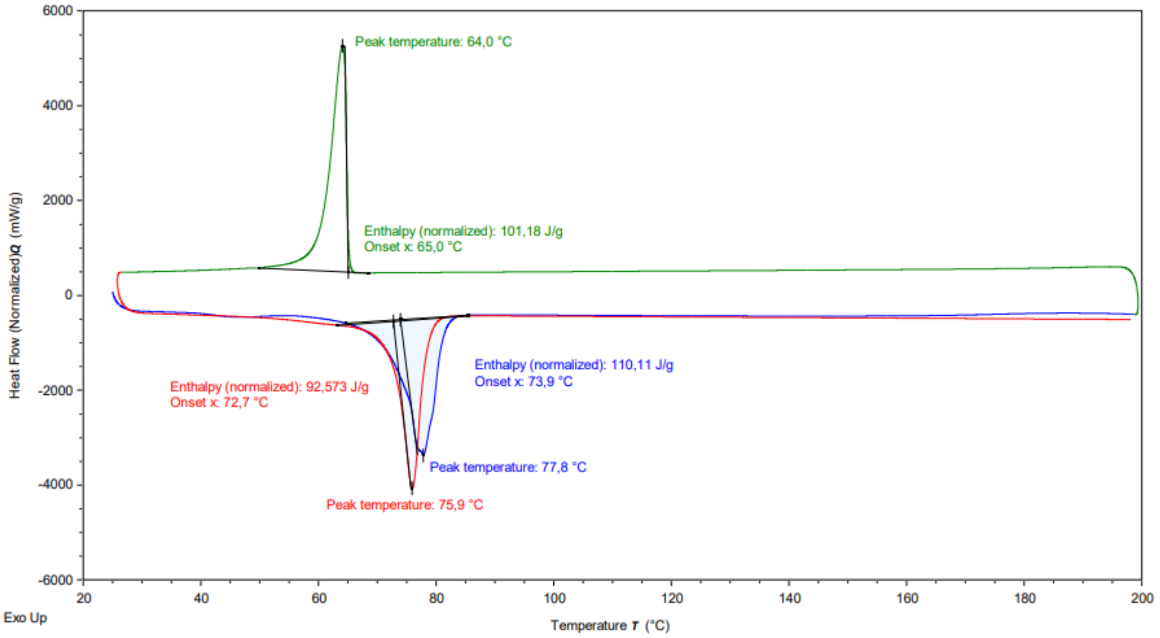
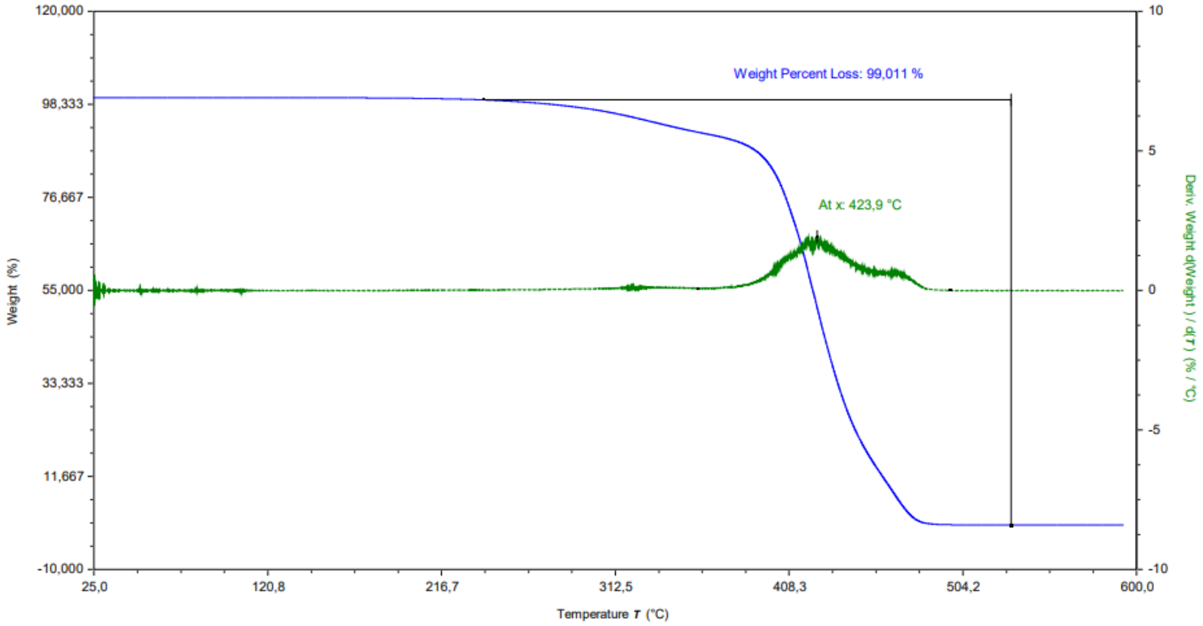


**Figure 7.** $^1$H NMR of 12,12-polyester



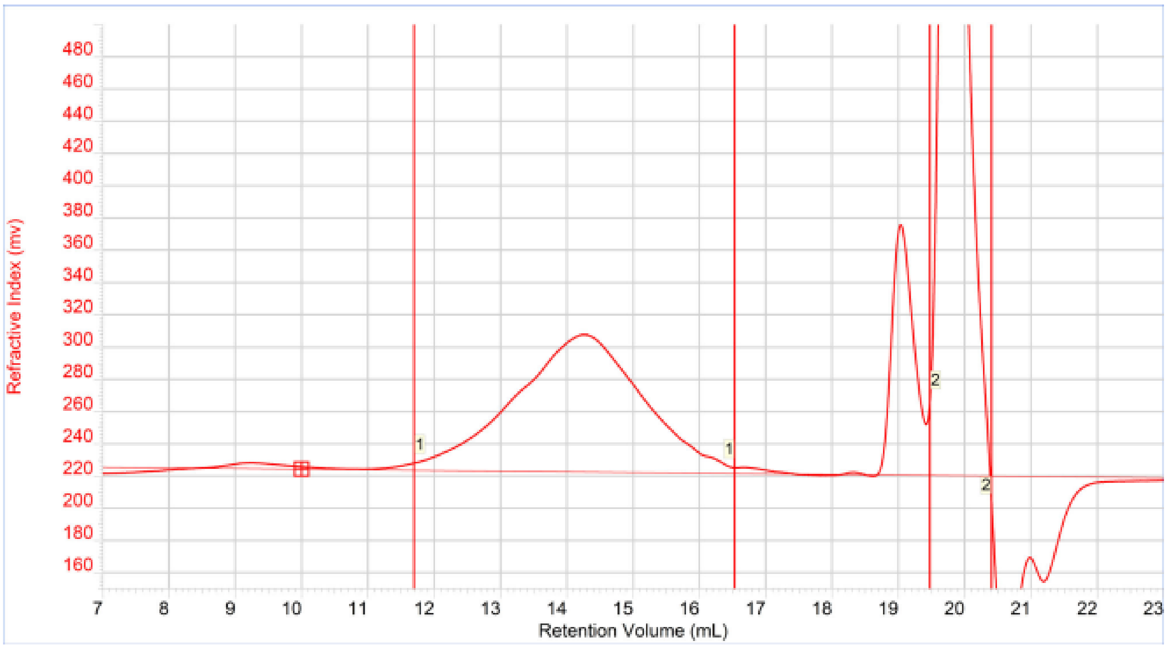
TA Instruments Trios V5.7.0.56

**Figure 8.** DSC of 12,12-polyester (blue represent the 1st heating ramp, and red the 2nd heating ramp)



TA Instruments Trios V5.7.0.56

**Figure 9.** TGA of 12,12-polyester



| Peak | Mn | Mw | Mp | Mw/Mn | Ret Vol | RI Area |
|---|---|---|---|---|---|---|
| 1 | 12 815 | 45 249 | 20 411 | 3.531 | 14.256 | 190.71 |

**Figure 10.** SEC of 12,12-polyester

# 6 Synthesis of 14,14-polyester by polycondensing 1,14-tetradecanediol with tetradecanedioïc acid

## 6.1 Experimental part

### 6.1.1 Polymer synthesis

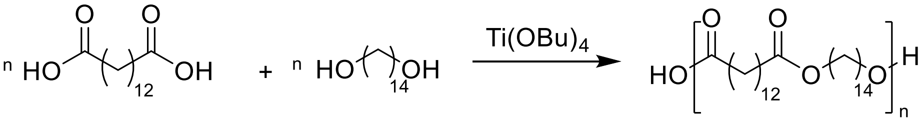


**Figure 11.** Synthetic pathway to obtain 14,14-polyester

In a three-necked round bottomed flask of 100 mL 1,14-tetradecanediol and tetradecanedioïc acid were added. The flask was equipped with a magnetic stirrer, adapter for the argon inlet, a glass stopper and a Dean Stark connected to a reflux column. The reflux column was further connected to a bubbler to monitor the argon flow, ensuring air exclusion while preventing overpressure. The reaction media was set to 180°C under stirring (650 rpm) and after 1 hour, the catalyst dissolved in 2 mL of toluene was added at a 1:1000 molar ratio. The mixture was allowed to oligomerize for 16 h under argon. Then, the polymerization was run for 8 hours under static vacuum.

### 6.1.2 Purification

The polymer was dissolved in chloroform. The polymer is reprecipitated in ethanol cooled with liquid nitrogen and then filtered. The polymer was air dried and vacuum dried for 8 hours. A total of 2.73g of polymer was obtained.

## 6.2 Characterization

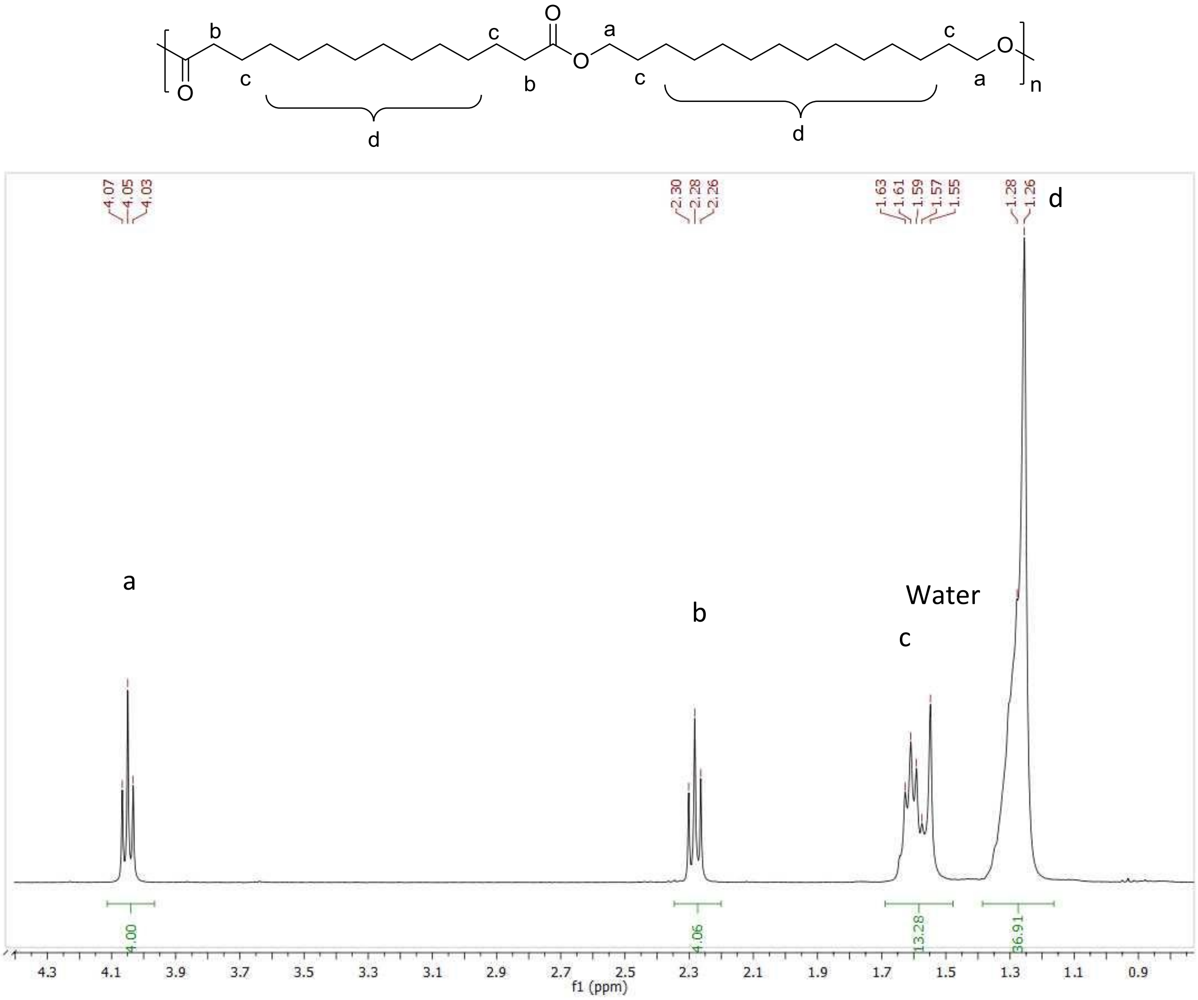


**Figure 12.** $^1$H NMR of 14,14-polyester

The polymer was dried for another 8 hours to remove the remaining water and further characterization was performed.

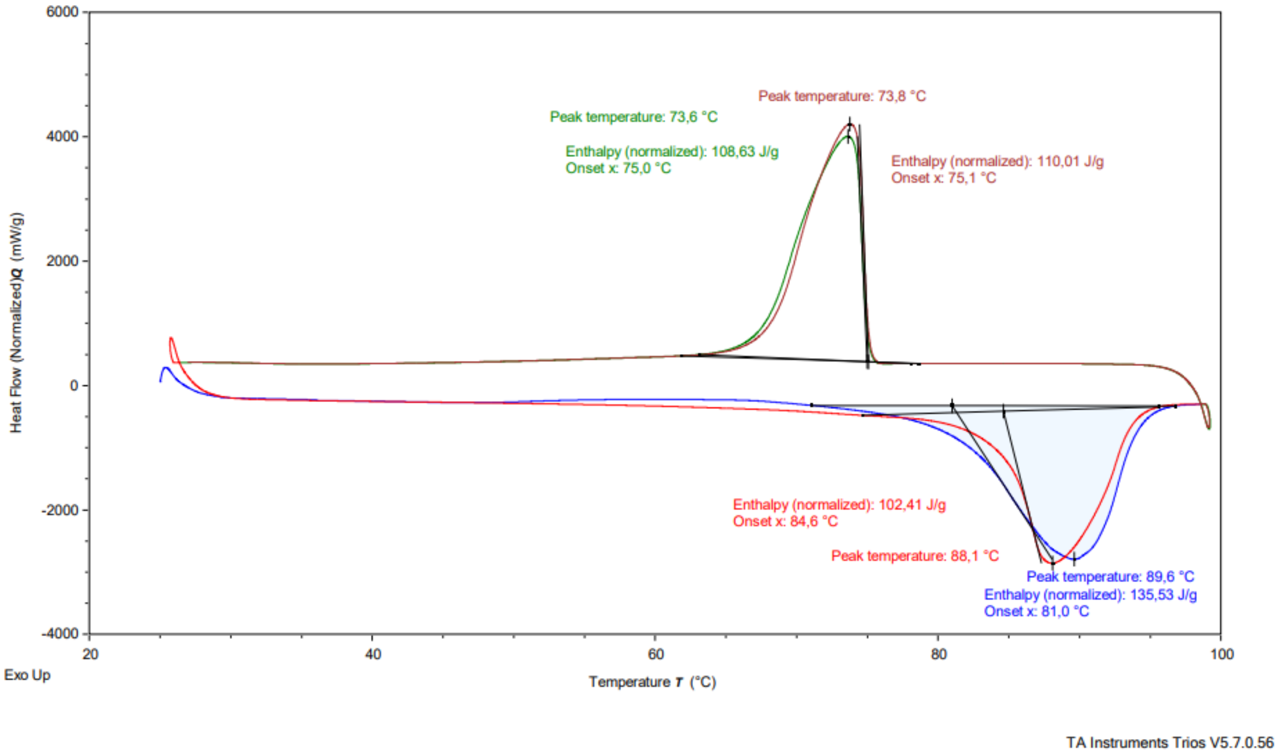


**Figure 13.** DSC of 14,14-polyester (blue represent the 1st heating ramp, and red the 2nd represents the second heating ramp)

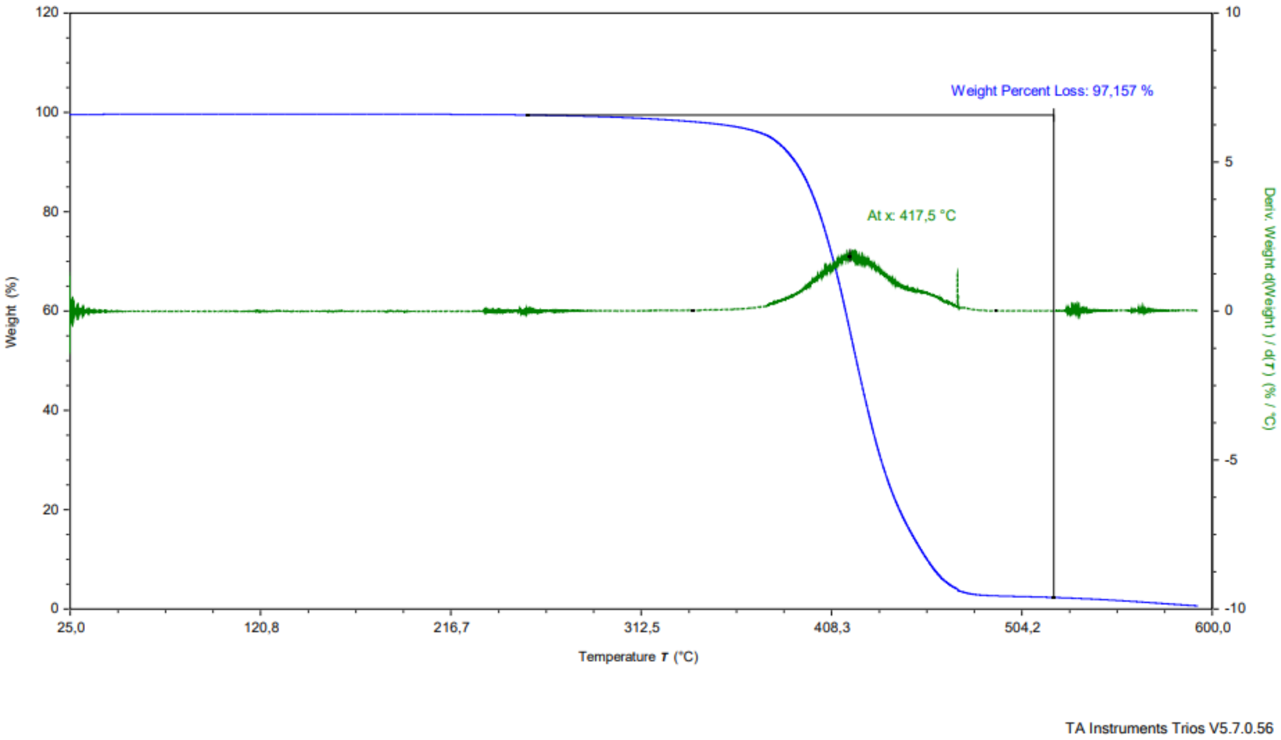


**Figure 14.** Figure 14. TGA of 14,14-polyester

# 7 Conclusions

We successfully synthesized three different polyesters at a gram scale and characterized them. SEC analysis of the 14.14-polyester will be conducted, along with additional analyses, such as infrared spectroscopy, DMA and tensile test for both the existing and newly synthesized polyesters.

**Table 2.** Summary of the polyester that was made for D6.1

| | Amount (g) | Mn (g.mol-1) |
|---|---|---|
| 10,10-Polyester | 2.6 | 30 400 |
| 12,12-Polyester | 2.43 | 12 800 |
| 14,14-Polyester | 2.73 | / |

# 8 References

[1] X. Fei *et al.*, “Efficient Catalytic Activity of Ti3C2Tx MXene for Polyester Synthesis,” *Ind. Eng. Chem. Res.*, vol. 63, no. 16, pp. 6868–6879, Apr. 2024, doi: 10.1021/acs.iecr.3c04485.

[2] S. M. Demyttenaere *et al.*, “Aliphatic polyesters based on 1,4-butanediol and even numbered C4 - C20 dicarboxylic acids - synthesis and properties including after surface treatment by VUV photo-oxidation,” *J. Polym. Res.*, vol. 30, no. 8, pp. 1–16, Aug. 2023, doi: 10.1007/s10965-023-03693-8.

## 8.1 Websites