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H2020 Work Programme

D4.1 - Reclaimed monomers from WP2 and WP3 used for preparation of new polymers

Lead Contractor: DTU

Authors: ACIB, RWTH, DTU

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This document is the UPLIFT project D4.1 titled: Reclaimed monomers from WP2 and WP3 used for preparation of new polymers (M28) lead by DTU and supported by the partners ACIB and RWTH. This document provides a short and comprehensive description of the different tasks undertaken as part of fulfilling the deliverable. Additional advice and support can be requested from the coordinator.

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1 Executive summary

The concept of UPLIFT is to introduce biological depolymerization technology as an addition and integration to established recycling practices, by converting persistent plastic waste into more easily recyclable and/or degradable polymers.

Deliverable 4.1 – "Reclaimed monomers from WP2 and WP3 used for preparation of new polymers" relates to the conversion of monomers produced in the earlier WPs 2 and 3. In these WPs, monomers have been produced using biological methods and isolated for testing and evaluation in WP4. All the received monomers at their respective purities have been tested and evaluated in WP4 and we here have supplied an overview of the results from these proof-of-concept polymerizations, which serve to confirm polymerizability and tolerance to residual impurities from the different processes applied in WP2-3.

The main findings relate to the conversion of the specific monomers (terephthalic acid, hydroxyphenyl acetic acid, furandicarboxylic acid, lactic acid, lactide). Here D4.1 confirms that we are able to produce polymers from the various monomers identified as primary output materials from WP2-3. This has been conducted with an emphasis also on greener polymerization methods using both, more benign chemicals, as well as processes with higher efficiency or faster polymerization rates.

Acronyms:

BHET	bis(hydroxyethyl terephthalate)
COET	cyclooligoethylene terephthalate
DMSO	dimethylsulfoxide
DSC	differential scanning calorimetry
EG	ethylene glycol
FDCA	2,5-furanedicarboxylic acid
LA	L-lactic acid
^{1}H-NMR	proton nuclear magnetic resonance spectroscopy
HPA	4-hydroxyphenylacetic acid
OEF	cyclooligoethylene furanoate
PBAT	poly(butylene adipate-co-terephthalate)
PET	poly(ethylene terephthalate)
PHA	poly(hydroxyalkanoate)
pMeBnOH	*para*-methyl benzyl alcohol
SEC	size exclusion chromatography
TA	terephthalic acid
TGA	thermogravimetric analysis

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2 Introduction

This document is the UPLIFT deliverable D4.1 "Reclaimed monomers from WP2 and WP3 used for preparation of new polymers" (M24) lead by DTU in collaboration with the partners of WP4, Task 4.1 (ACIB, RWTH and DTU). The main objective of Task 4.1 in WP4 has been the polymerization of monomers produced by partners in WP2 and WP3. This encompasses the assessment of polymerizability, purity requirements of monomers as well as evaluation of the output of different processes in WP2/WP3 and how these affect the potential to polymerize the final monomer products. In addition to assessing the possibility to produce polymers from the prepared monomers, there is also a strong desire to establish green and more efficient methods of polymerization, which essentially will lead to greener and more sustainable polymers.
In the following, we will report on the polymerization of the prepared monomers, as well as the outcome of more efficient synthesis of using more benign catalyst and polymerization methods. This report is intended as public and will be substantiated by multiple publications that are currently being prepared and would be expected to become public during autumn 2023, which will further act to support D4.1 and extend the dissemination of the achieved results to the public.

3 Prepared polymers – Synthesis and methods development

The monomers that have been received from WP2/WP3 for evaluation in polymerization covers terephthalic acid, aromatic hydroxy-acids, furane dicarboxylic acid, lactic acid and lactide. The different monomers are still expected in both, different purities and quantities, during the remaining part of the project, and there is an expectancy to evaluate the impacts of particularly purity and evaluate this against the processes being developed in WP3 throughout the project. In addition, additional monomers for the remaining tasks in WP4 will be evaluated in the upcoming period of the project.

3.1. Aromatic polyesters

A number of bio-based aromatic hydroxy-acids (hydrophenylacetic acid, coumaric acid, and 4-hydroxybenzoic acid) were presented as possible monomers (supplied by fermentation from WP3). Initial assessment of the relatively scarce literature on polymers based on these, led to the recommendation that 4-hydroxyphenylacetic acid (HPA) could be a promising candidate for scale-up, because homopolyesters of this hydroxy-acid were reported to have a glass transition temperature (Tg) of around 60 °C and to show liquid crystallinity above approximately 200 °C.[1] The combination of a

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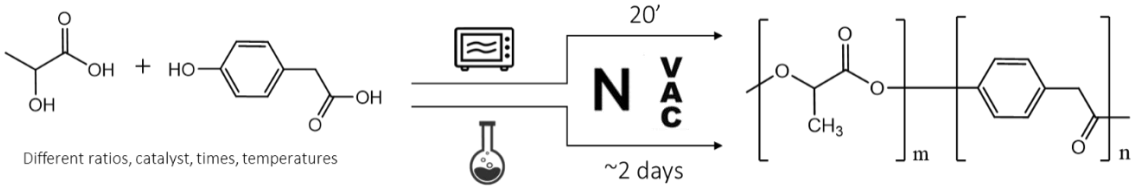
glass transition temperature not too far from that of PET and liquid crystallinity at relatively low temperatures was attractive in terms of preparing a PET-like polymer that could be processed at low-temperature. Literature was not helpful in providing information on what mechanical properties such polymers would have or whether it would be possible to make high-molecular weight polymers that could be processed at all.

Initial reproduction of the literature methods indicated that polymerisation of HPA was possible, but that the resulting polymers were almost impossible to dissolve completely. In addition, it was found that colouration of the resulting polymers and even of copolymers (with lactic acid) were very difficult to avoid, presumably due to the ease of oxidation of the phenol acid.

In order to overcome the solubility issues, the HPA was copolymerised with lactic acid (see Scheme 1). Interestingly, it was found that when conducted in a microwave oven, copolymers could be formed in 20 minutes, which had similar characteristics to copolymers prepared conventionally over several days.



Scheme 1: *Copolymerisation of lactic acid and 4-hydroxyphenyl acetic acid in microwave oven and using conventional heating and vacuum methods (detailed procedures and methods will be included in the scientific papers currenlty being prepared)*

During copolymerisation, colouration remained an issue, especially during microwave synthesis, while a variety of different esterification catalysts were tested. It was found that less active catalysts, like zinc acetate, generally gave less colouration and insoluble material than more active catalysts, like titanium(IV) tetrabutoxide or zinc triflate.

Further suppression of colouration could be achieved through addition of an antioxidant, where it was found that 1 mol percentage of 2,6-di-tert-butyl-4-methylphenol (BHT) worked well.

This process gave relatively short copolymers with molecular weights of a few thousand g/mol and compositions close to those targeted.

In order to prepare copolymers with larger molecular weight, the short copolymer was prepared in the presence of small amounts of ethylene glycol (various ratios were studied), which ensured that both ends of the final copolymer had an alcohol terminus. An example of such a copolymer is given in Table 1, entry 1. Following this first step, the resulting copolymer was mixed with cyclic lactide monomer (as also described below for lactide in general) in an extruder, which led to ring-opening polymerisation and significantly larger molecular weights (see Table 1, entry 2).

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Table 1: *Polymers prepared from lactic acid (LA)or lactide and 4-hydroxyphenylacetic acid. Entry 2 is based on combining the polymer from entry 1 with lactide in an extruder in the presence of 1 mol percent tin(II) ethyl hexanoate*

Entry	Polymerization Method	Feed Composition (molar)	Product Composition (molar)	Mw (g/mol)	Đ
1	Microwave heating	(HPA: LA) +EG 50:50	(HPA : LA) 40:60	2000	1.2
2	Reactive extrusion	(HPA : LA) 50:50 With lactide (50:50) to the copolymer	(HPA : LA) 25:75	>60000	1.7

Work is currently undergoing towards investigating the mechanical properties of these copolymers compared to polylactide (PLLA) prepared without aromatic groups. Furthermore, it is currently under investigation how polymerisation parameters affects the conversion and aromatic content of the copolymers, in order to minimise any monomer loss.

3.2. Reclaimed acids

3.2.1. Analysis of reclaimed acids

Reclaimed terephthalic acid from different sources were received from WP2. All samples were analysed by IR spectroscopy, thermogravimetric analysis and quantitative NMR (using maleic acid as an internal standard). Figure 1 shows ATR-FTIR spectra and thermogravimetric analyses (TGA) of selected terephtalic acid samples received from ACIB. The IR spectra of all samples are consistent with terephthalic acid, as expected. However, the TGA reveals that the samples also consist of various amounts of incombustible material, as indicated by the significant residue for all received samples above 350 °C. In contrast, the commercially available terephthalic acid completely combusts. These results are consistent with the observations done during the preparation of NMR samples that the reclaimed acids were only partly soluble in dimethyl sulfoxide, a good solvent for the high-purity terephthalic acid. The nature of these impurities were not investigated further, but it is likely that they consist of inorganic salts, and possibly terephthalate salts.

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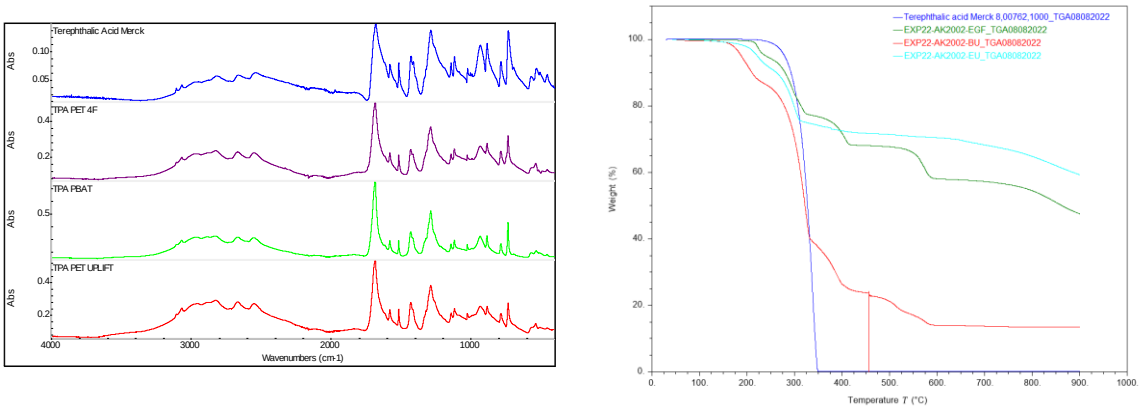

Figure 1: *ATR-FTIR spectra (left) and TGA curves (right) of commercial terephtalic acid (Merck) and reclaimed terepthalic acids from PET (ACIB) and PBAT (ACIB).*

The purity of received reclaimed terephtalic acids as well a reclaimed furandicarboxylic acid, based on Q-NMR using maleic acid as standard, are given in Table 4.
Rather than pursuing cleaner starting materials, efforts have focused on preparing polymers directly from the acids as-received.

3.2.2. Preparation of cyclic aromatic oligoesters from terephthalic acid and ethylene glycol

One route to polymers from reclaimed monomers (specifically terephtalic- or furandicarboxylic acid) is through an intermediate formation of cyclic oligoesters as detailed in Scheme 2 for terephthalic acid. This strategy was chosen in order to prepare polymers through ring-opening polymerisation of cyclic oligomers rather than through the more commonly used step-growth polymerisation of bifunctional monomers via condensation of volatiles.
The ring-opening polymerisation is attractive because the molecular weight increases rapidly with conversion and the reaction is reported to be very fast (<30 min at 280 °C)[2,3]. This minimizes monomer evaporation during polymerisation and reduces overall energy consumption.
Traditionally, the preparation of cyclic monomers has been the limiting step, because they are typically prepared at very low concentration. Thus, for the process to be feasible, it is necessary to develop methods that allow easy isolation of the product and ideally re-use of the solvent. The authors of reference 2 describes a procedure, where the cyclisation of the bis(hydroxyethyl) terephthalate is accomplished in a high-boiling solvent mixture (Scheme 2, I reaction C), where the cyclic product precipitates in high purity upon cooling.

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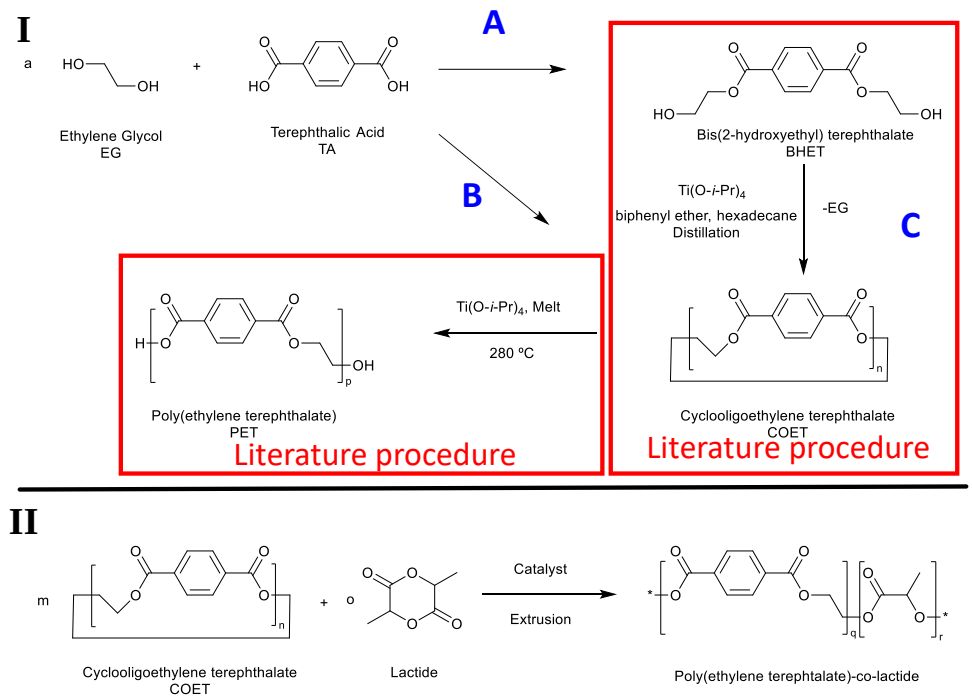

Scheme 2: *Preparation of polymers from reclaimed terephthalic acid. I: Preparation of poly(ethylene terephthalate). A: Preparation of intermediate bis(hydroxyethyl terephthalate) (BHET) from ethylene glycol and terephthalic acid. B: Preparation of cyclic oligomers of ethylene terephthalate (COET) from BHET following a literature procedure[2]. C: Preparation of poly(ethylene terephthalate)(PET) from COET following a literature procedure[2]. II Copolymerisation of COET and lactide in bulk.*

Provided that the majority of the impurities are insoluble, a procedure including a filtration step for impurity removal prior to cyclisation, could be a means to use starting materials of lower purity. The main issue is that the crude starting product is predominantly terephthalic (or furandicarboxylic) *acid* (*vide supra*) and not the bis(2-hydroxyethyl) ester described in literature.[2]

Therefore, initial efforts were focused on examining whether the esterification of terephthalic acid and subsequent cyclisation of the resulting BHET could be accomplished either in one step (Scheme 2, B) or in a concerted 2-step reaction (Scheme 2, I, A and C). This initial exploratory work was carried out using commercially available terephthalic acid and ethylene glycol.

Initially, the reaction was carried out in the solvent used in reference 2 (Scheme 2, I, reaction C), where around 30 % rings were formed as identified by ^{1}H NMR (see Table 2, entry 1) at the reflux temperature of the solvent (in excess of 250 °C). The relatively low yield is believed to be a combination of low solubility of terephthalic acid as well as removal of volatile ethylene glycol from the reaction mixture before the ester is formed (EG BP 197 °C). In addition, early tests on crude terephthalic acids indicated that the high temperature led to significant discolouration of the reaction mixture due to degradation of organic material, which could not entirely be removed during work-up.

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Table 2: *Formation of cyclic oligo(ethylene terephthalates) from terephthalic acid and ethylene glycol in a variety of solvents and mixtures. Entry 1-8 conditions: [terephthalic acid] = 20 mg/mL. [terephthalic acid]:[ethylene glycol] = 0.5. [terepthalic acid]:[titanium tetrabutanoxide](catalyst) = 1000. Reaction time: 6 h. Entry 9: No solvent was used, but the [terephthalic acid]:[ethylene glycol] ratio was varied between 0.5 and 0.25. [terepthalic acid]:[titanium tetrabutoxide](catalyst) = 1000.*

Entry	Solvent	Temperature (°C)	Results
1	Diphenyl ether:hexadecane 3:1	Reflux (>250)	Ring formation (~30 %) and low yield
2	Dimethyl sulfoxide	200	Ring formation + side-product (dominating, not separable)
3	Anisole (azeotrope EG)	Reflux (~155)	Not soluble – no product
4	Acetonitrile	Reflux (~80)	Not soluble – no product
5	Gamma valerolactone	200	Not soluble – no product
6	DMSO:Anisole mixtures (various composition)	Reflux (155-200)	Ring formation + side-product (dominating, not separable)
7	Cyrene	150-180	Ring formation + highly coloured side-product, not separable)
8	Cygnet 2.0 [4]	150-180	Ring formation + highly coloured side-product, not separable)
9	Ethylene Glycol	150 (3 h)	*~90 % BHET* formation

As a consequence, the reaction was screened in a variety of solvents and solvent mixtures (see Table 2), where focus was to substitute with greener, renewable solvents that could dissolve the acid and allow the reaction to proceed at lower temperatures. As is apparent from Table 2, entries 1-8, rings do form in a variety of high-boiling polar solvents, like dimethyl sulfoxide, cyrene and cygnet 2.0 (prepared by ACIB). However, in general, the formation of side-products is dominant, making the isolation of cyclic monomers difficult. These results indicate that the 1-step ring formation from terephthalic acid and ethylene glycol (Scheme 1, I, reaction B) is difficult to effectuate in a feasible manner.

Instead, the bulk reaction between ethylene glycol and terephthalic acid was explored. It was found that even at [TA]:[EG] ratio of 1:2, the formation of BHET was significant (Table 2, entry 9). These results suggest that a concerted pathway through initial formation of BHET followed by cyclisation may be feasible (Scheme 2, I, A and C), especially since the same catalyst (titanium tetrabutoxide) is used in both steps. A further advantage of this approach is that BHET is significantly more soluble in common solvents than terephthalic acid, which should expand the possible solvent choices. The reaction is

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somewhat heterogenous at the ratio given in Table 2, which is why some consideration should be given to maximise the surface area of the terephthalic acid, e.g. by milling the acid prior to reaction. This is currently under investigation.

The ring formation of BHET was tested in anisole and dimethyl isosorbide. Anisole forms an azeotrope with ethylene glycol, which should allow removal of the excedent reactant. On the other hand, dimethyl isosorbide is miscible with water, which could allow easy isolation of the product through precipitation. These particular solvents both are considered to have low toxicity,[5,6] being commonly used in perfumes and cosmetics. In addition, at least dimethyl isosorbide is currently biorenewable. These experiments were conducted using commercially available BHET of high purity (> 98 % according to the manufacturer). The initial results are listed in Table 3.

Table 3: *Formation of cyclic oligo(ethylene terephthalates) from BHET in various solvents. Conditions: [BHET] = 25 mg/mL. [BHET]:[titanium tetrabutoxide] = 1000. Reaction time: Ref [2]: up to 4 h. Anisole: 24 h. Dimethylisosorbide : 9 h.*

Entry	Solvent	Temperature (°C(	Yield of cyclics (%)	Results
1	Diphenyl ether:hexadecane 3:1	Reflux (>250)	> 90[2]	Ring formation.[2] Yields according to literature. Varies depending on concentration.
2	Anisole (Azeotrope)	Reflux (~155)	20	Ring formation, relatively slow, clean reaction, lower temperature.
3	Dimethyl isosorbide	200	50	Ring formation, precipitates by addition of water. Slight colouration.

In general, yields are seen to be somewhat lower than what was reported when using high-boiling solvents,[2] which is probably to a large extent related to the lower reaction temperature. However, for both, anisole and dimethyl isosorbide, ring formation was evident and few side-products were detected. It should be noted that the catalyst concentration is relatively low and current efforts are focused on investigating the effect of increasing the catalyst concentration. In addition, it is of course possible to increase the reaction time. When using dimethyl isosorbide, the product mixture of BHET and rings could be isolated by addition of water, which led to precipitation.
In case of anisole, the products can be isolated by evaporation of the relatively volatile solvent (which may be collected and reused) or through precipitation with a saturated hydrocarbon.

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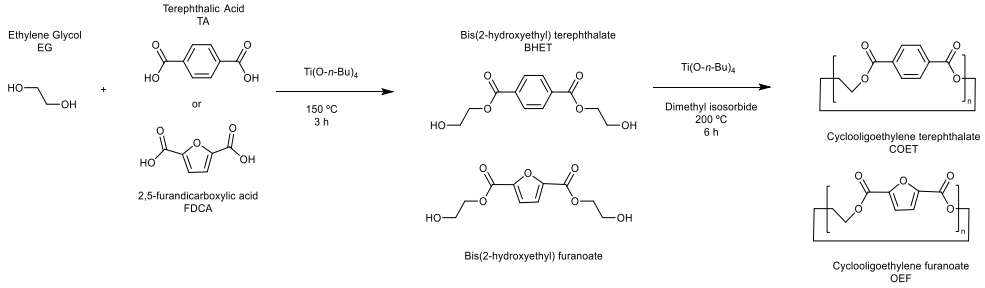
3.2.3. Use of acids reclaimed from depolymerized polyesters to prepare cyclic esters

Having demonstrated successful formation of cyclic esters in dimethyl isosorbide (Table 2) from the commercially available terephthalic acid of high purity, the reclaimed acids from WP2 were used as substrates (*as-received*, i.e. with no further purification steps), following the procedure shown in Scheme 3. Thus, the bis(2-hydroxyethyl) ester was first prepared in bulk, following the addition of dimethyl isosorbide for ring formation. Although the purity of these acids in principle was known (see Table 4) and it would be possible to add the equivalent amount of ethylene glycol, initially ethylene glycol was added by assuming 100 % purity, i.e., added in excess.



Scheme 3: *Preparation of cyclic monomers from reclaimed aromatic acids and ethylene glycol in a 2-step, 1-pot procedure*

The results from analysis of the crude reaction mixtures are shown in Table 4. Ring formation was detected in all cases, although the relative yield does not appear to follow the measured purity of the acid starting material, but to a larger degree the efficiency of the BHET formation in the initial step. This may reflect possible issues with the heterogeneity of the first reaction step, although the exact nature of the impurities may also have an influence.

For these samples, addition of water did not lead to substantial precipitation of the terephthalic-based samples but rather to the formation of an emulsion, which probably reflects the presence of residual carboxylate anions detected above. Thus, an optimized process will probably need to address this, e.g., by adding additional acid to the reaction mixture. This is currently under investigation.

The FDCA sample did not precipitate, neither upon addition of water, which may reflect the increased solubility of the acid and polyester in polar solvents.[7,8]

Table 4 : *Ring formation from reclaimed acids. Conditions : 1) [terephthalic acid] :[ethylene glycol] = 0.5 [terephthalic acid]:[titanium tetrabutoxide](catalyst) = 1000, no solvent, 150 °C [2]) Dimethyl isosorbide, 200 °C, 6 h.*

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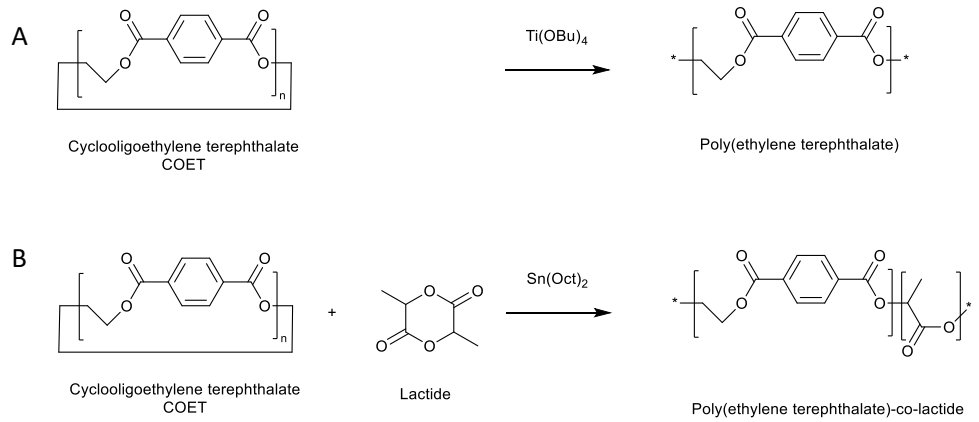
Sample designation / source	Acid	Q-NMR purity starting material (mass %)	BHET formation (approx. BHET:Acid, ^{1}H NMR)	Ring formation (approx. COET:Other aromatics, ^{1}H NMR)	Comments
TPA from PET 4F	TA	36 %	Yes (40:60)	Yes (20:80)	Non-soluble brown/black residue.
TPA from PBAT	TA	65 %	Yes (10:90)	Yes (15:85)	Non-soluble brown/black residue
TPA from PET UPLIFT	TA	19 %	Yes (40:60)	Yes (20:80)	Non-soluble brown/black residue
TPA ULund	TA	70 %	Yes (10:90)	Not detected	Non-soluble brown/black residue
FDCA ULund	FDCA	100 %	Yes (bis(2-hydroxyethyl) furandicarboxylate) (15:85)	Await purification (solvent signals overlap possible ring signals).	Non-soluble brown/black residue

3.2.4. Ring opening polymerization and copolymerization with lactide

The homopolymerisation of the cyclic oligoethylene terephthalate (see Scheme 4 A) was tested in bulk, following a procedure from reference 2, and rapid formation of PET was found, with a molecular weight that was mostly limited by the residual BHET content of the starting material. Thus, a sample of COET containing approximately 10 % residual BHET gave a polymer with a molecular weight determined by ^{1}H NMR of around 6000 g/mol, based on end-group analysis. Thus, for bottle-grade PET (M~30000 g/mol), it will likely be necessary to optimize the ring-closure process further or to introduce a purification step (e.g., recrystallization). Since the BHET impurity is itself a common precursor to PET synthesis, it is possible that this can be reclaimed and reused in the process.



Scheme 4: *Ring opening polymerisation of cyclic oligoethylene terephthalate. A: Bulk homopolymerisation of COET using 200 ppm titanium (IV) tetrabutoxide, 45 min at 265 °C. B: Copolymerisation of COET and lactide 1:9 in extruder at 150 °C using 1% tin(II) 2-ethyl hexanoate catalyst.*

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In addition, the copolymerization of COET with cyclic lactide was tested (see Scheme 4 B). Here, a common ring-opening catalyst, tin (II) 2-ethyl hexanoate was used and the reagents were mixed directly in an extruder. The resulting copolymer remained opaque, indicating phase separation and / or crystallization. DSC showed a glass transition temperature (Tg) not too different from that of polylactic acid (see Table 5) and indicated a melting point above 250 °C. However, it was not possible to determine this exactly, presumably since the polylactide part of the copolymer starts degrading around 300 °C.
The copolymer was soluble in tetrahydrofuran, which allowed easy analysis by size exclusion chromatography (SEC). These measurements revealed formation of a relatively polydisperse polymer (see Table 5). Inspection of the absorption signal at 254 nm for the size exclusion chromatogram confirmed that aromatic groups had been incorporated into the copolymer, i.e., the material was to a large extent a copolymer rather than a dispersion of cyclic oligomers in a polylactide matrix.

Table 5: *Measured properties of copolymer of COET and lactide*

Target [Lactide]:[COET]	M_w (Da) (PS)	Đ	Tg (°C)
10 :1	16,200	1.74	42.6

These early results indicate that it is possible to copolymerise COET and lactide rapidly under relatively mild conditions.
Work is undergoing to optimise molecular weight and determine mechanical properties of these novel copolymers. In addition, cyclic oligomers based on reclaimed acids will be used for the polymerisation.

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3.3. Synthesis of polyesters using enzymatic methods and green solvents

There is a need for thermoplastics materials to be made more sustainable across their entire lifecycle. Although improved recycling of these materials is currently the focus of WP2, their synthesis is also problematic, due to use of fossil-based feedstocks. Ideally, thermoplastics would be synthesised from bio-based or recycled feedstocks in a sustainable way. One such sustainable method for synthesising polyesters is the use of enzymes, which are innately green due to their bio-based origin and low temperature (<100℃) requirements.

In enzymatic syntheses, solvent is often necessary as increasing molecular weight is always accompanied by an increase in viscosity and eventual solidification of the reaction product at the used operational temperature. The use of an appropriate reaction solvent will also reduce or eliminate any compatibility issues between the enzyme and the monomers. Many solvents have been tested in enzymatic polycondensations, such as ionic liquids[9], and various bio-based organic solvents[10-11] with varying results. One class of solvents that shows promise is Cyrene and its derivatives (Cygnets)[12], which can be produced from Cyrene and a diol in a one-step reaction and using a workup that involves only the use of ethyl acetate as the organic solvent[12]. Different diol reagents can be used, allowing tailoring of the solvent properties. Here, several Cygnets were synthesised and tested in the polycondensation of a wide range of aliphatic and aromatic monomers.

Polyesters were synthesised using an equimolar ratio of diester and diol, which were reacted at 85 °C in the presence of a biocatalyst (immobilized *Candida antarctica* lipase B) for 96 hours. After 6h, a vacuum of 20mbar was applied to remove the alcohol by-product. At this point a solvent was added to the reaction mixture, a cellulose filter was applied to remove the immobilized biocatalyst, and the polyesters were precipitated into cold antisolvent. The final products were recovered through centrifugation and characterised via ^{1}H-NMR, SEC, TGA and DSC once dry. Non-toxic and bio-based solvents were used at every stage of this process.

These bio-based solvents have been used to polymerize both aliphatic and aromatic (bio-based) monomers, showing their versatility. In the polycondensation of aliphatic monomers, weight average molecular weights of up to 38 kDa were achieved. In all cases, use of these solvents managed to match or exceed the results obtained with less sustainable conventional organic solvents. These can be applied in future enzymatic polycondensations with monomers obtained by WP2 and WP3.

The developed methodology was also applied for preparation of oligomeric polyester additives as part of Task 4.2 for evaluation as polymer additives in PHAs. This will be reported in D4.2. and is expected to be submitted as a scientific publication during autumn 2023.

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3.4. Lactide ROP with the new catalysts

Polylactide is one of the materials covered by the UPLIFT project. In order to synthesize this polymer from lactide via a ring-opening polymerization, catalysts are required. In one of our previous works on benign iron (II) guanidine catalysts, it could be shown that these compounds have the potential to replace conventional tin-based catalysts because of their robustness and high activity.[13] Based on these findings, new iron (II) guanidine catalysts were developed in order to investigate their polymerization behavior and understand the connection between the complexes' structure and their activity (see Figure 2). The complexes were synthesized from iron (II) chloride and simple literature-known guanidine ligands[14-18] to allow a straightforward preparation. Complexes **C1**–**C4** contain bisguanidine ligands, which are equipped with an aromatic backbone in **C1**–**C2** and an aliphatic backbone in **C3**–**C4**. Complexes **C5** and **C6** contain ligands that combine one guanidine donor unit with one pyridine donor unit. The six complexes were fully characterized by infrared spectroscopy, mass spectrometry, elemental analysis and single-crystal X-ray diffraction.

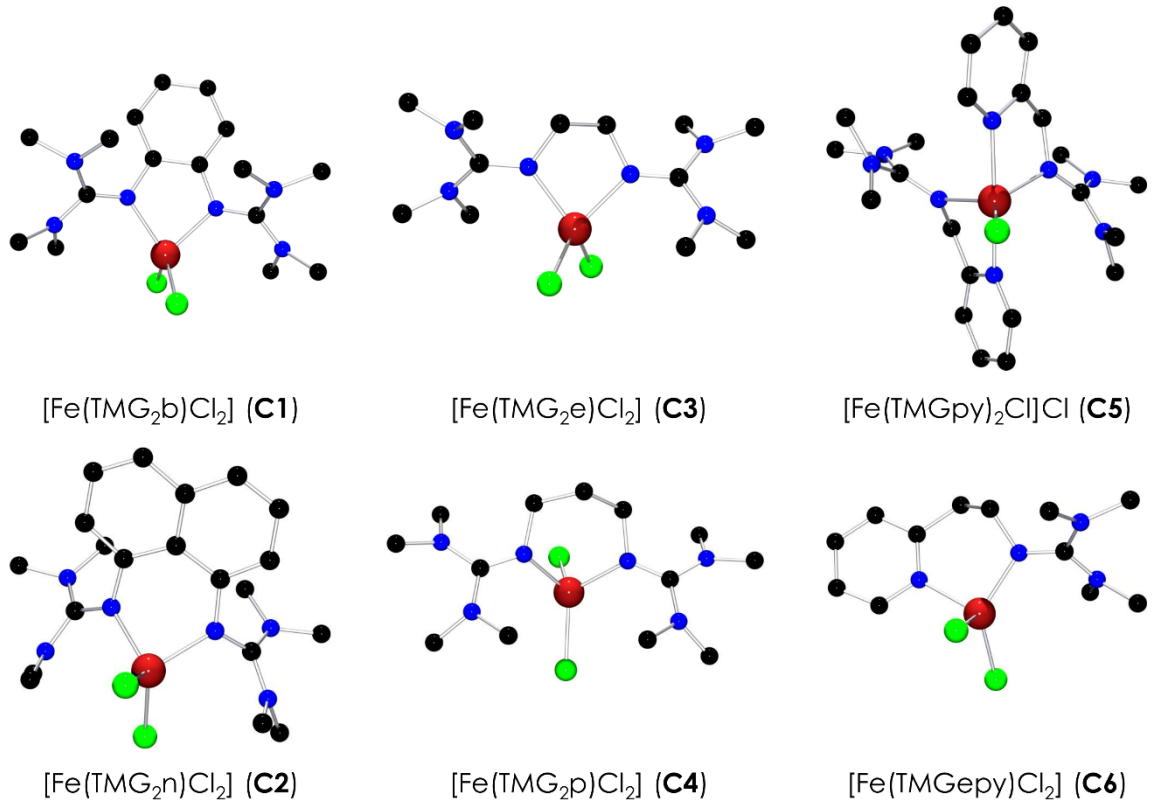

Figure 2: *Molecular structures of the investigated iron (II) guanidine complexes determined by single-crystal X-ray diffraction.*

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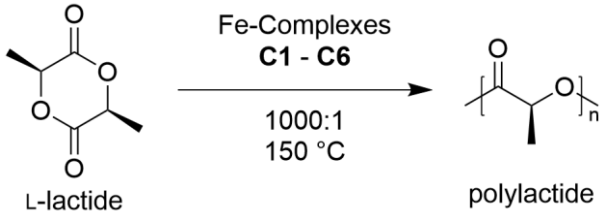
Polymerization experiments were carried out on an 8 g-batch scale applying a low catalyst loading with a monomer-to-initiator ratio ([M]/[I]) of 1000:1 (see Scheme 5). The experiments were conducted at 150 °C in bulk without additional solvent and were monitored by in-situ Raman spectroscopy. The respective semilogarithmic plots for a pseudo-first order reaction are depicted in Figure 3. For each experiment, the initial apparent rate constant k_{app}, the conversion as well as the molar masses and dispersities of the resulting polymers were determined (see Table 6).



Scheme 5: *Reaction equation of the ring-opening polymerization of L-lactide to polylactide.*

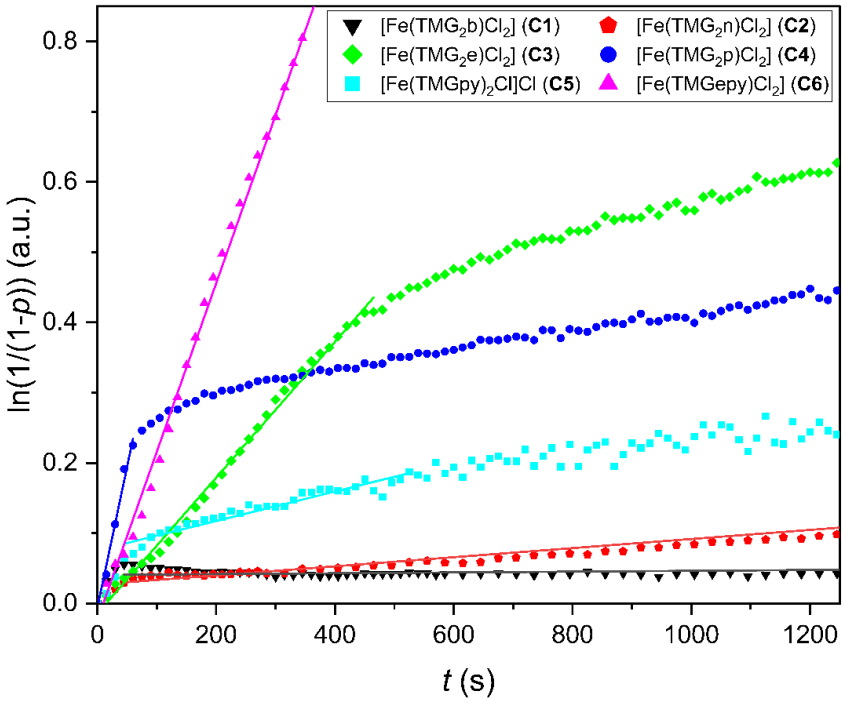


Figure 3: *Semilogarithmic plots for the polymerization with complexes* ***C1–C6*** *(Conditions: recrystallized L-lactide, [M]/[I] = 1000:1, 150 °C, 260 rpm). Shown are the first 1250 s for clarity.*

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Table 6: *Results of the polymerization of L-lactide with iron guanidine complexes* ***C1–C6****.*[a]

complex	t (min)	conv. [%][b]	k_{app} (10^{-4} 1/s)	M_n (kg/mol)[c]	M_w/M_n[c]
C1	300	11	0.0629±0.0047	n.d.[d]	n.d.[d]
C2	300	65	0.575±0.073	25.0	1.5
C3	60	56	9.63±0.05	25.3	1.5
C4	60	42	54.2±14.1	14.1	1.5
C5	60	41	2.35±0.27	11.0	1.4
C6	10	59	24.1±0.2	47.3	1.4

[a] Conditions: recrystallized L-lactide, 150 °C, [M]/[I] = 1000:1, reaction times were adjusted depending on catalyst activity. Polymerizations were performed in duplicate. Conversion, molar masses and dispersities are only given for one experiment per catalyst. [b] Determined by ^{1}H NMR. [c] Determined by SEC in THF. [d] Polymer did not precipitate from ethanol.

As can be seen from the plots in Figure 3, the catalysts **C1**–**C6** exhibit strongly different activities and also stabilities. While catalysts **C1** and **C2** only exhibit a low activity and are therefore not suitable as catalysts under the chosen conditions, the catalysts **C3** and **C4** containing an aliphatic ligand backbone as well as the hybrid guanidine-containing complex **C6** show very high initial k_{app} values. However, **C3**, **C4** and **C6** maintain their high initial activity for very different durations. While complex **C4** is highly active in the first minute of the polymerization only, complex **C6** maintains its activity and yields a polymeric material with a number average molar mass of 47.3 kg/mol after merely 10 min. Overall the activity of **C6** is comparable to the until now most active iron(II) guanidine catalyst [Fe(TMG5NMe$_2$asme)][13] with the benefit of a two-step synthesis compared to a five-step synthesis for [Fe(TMG5NMe$_2$asme)]. Further experiments with **C6** and *para*-methyl benzyl alcohol as a co-initiator allowed to even lower the catalyst loading while still achieving a high M_n of 68.3 kg/mol ([M]/[I]/[pMeBnOH] = 2000/1/1, 150 °C, 1 h, M_w/M_n = 1.4).

A research article manuscript dealing with a comprehensive study on the new iron (II) guanidine catalysts including computational studies is in preparation.

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