



LUND UNIVERSITY

Investigation of acidic chemical recycling of poly(acetal-ester)s

by

Saga Vesterbacka

Department of Chemistry,
Faculty of Engineering, LTH, Lund University

Supervisor: **Baozhong Zhang**

Examiner: **Patric Jannasch**

Abstract

Plastic recycling is a very relevant topic from both environmental and economic viewpoints. Chemical plastic recycling is a logical solution to the plastic problems, which shows the potential to reduce plastic waste and carbon emissions from burning the plastics.

One strategy of chemically recycling plastic is to incorporate sensitive bonds into polymer chains, which can be selectively degraded under specific conditions. In this study, selective acetal hydrolysis of two poly(acetal-esters)s containing spiroacetal linkage was performed under different conditions regarding temperature, concentrations of acid, and additional solvents. More specifically, polymers with spiroacetal groups have been hydrolyzed, which include: Akestra 90, Akestra 110, PHVT-5 and PHVT-20. The experiments have been mainly analyzed with NMR spectroscopy. The results show that both Akestra 90 and Akestra 110 are very resistant to hydrolysis. However, PHVT-5 and PHVT-20 could be completely hydrolyzed. There was then an attempt to re-polymerize the oligomer of PHVT-5 which led the polymer to be polymerized to 79 %.

Sammanfattning

Polymeråtervinning är ett väldigt relevant ämne från både en miljösynpunkt och ett ekonomiskt perspektiv. Kemisk plaståtervinning har potentialen att minska plastavfall och kolutsläpp från förbränning av plast. Ett sätt att kemiskt återvinna plast är att hydrolysera acetal-grupper i polymerer under sura förhållanden och sedan polymerisera om oligomererna, vilket har undersökts i detta arbete. Mer specifikt, så har polymerer med spiroacetal-grupper blivit hydrolyserade vilket inkluderar Akestra 90, Akestra 110, PHVT-5 och PHVT-20.

Experimenten har i huvudsak analyserats med NMR spektroskopi. Resultaten visar att både Akestra 90 och Akestra 110 är väldigt resistent mot hydrolys. Dock är det möjligt att hydrolysera PHVT-5 och PHVT-20 helt och hållet.

2022-05-19

Acknowledgement

I would like to express my sincere gratitude to Tam Nguyen for guiding me in the lab, training me on how to use the equipment and supporting me through the entire process. Then I would like to thank Smita Mankar for providing me with the polymer PHVT-5 and for discussing how to move my project forward. I would like to extend my gratitude to my supervisor Baozhong Zhang and examiner Patric Jannasch for giving feedback and for guiding me. Lastly but not least, I want to give my gratitude to Niels Meijer that provided mental support and encouragement throughout the project.

Without you all it would not have been possible to finish this project, thank you!

Abbreviations

^{13}C NMR	Carbon-13 Nuclear Magnetic Resonance
^1H NMR	Proton Nuclear Magnetic Resonance
DMSO	Dimethyl sulfoxide
DSC	Differential Scanning Calorimetry
H_2SO_4	Sulfuric acid
HMBC	Heteronuclear Multiple Bond Corelation
HMQC	Heteronuclear Multiple Quantum Corelation
HSQC	Heteronuclear Single Quantum Coherance
MeOH	Methanol
oHVT	Oligo(hexamethylene spirodiol V terephthalate)
PET	Poly(ethylene terephthalate)
PHVT	poly(hexamethylene spirodiol V terephthalate)
pTSA	p-Toluene sulfonic acid
THF	Tetrahydrofuran
T_g	Glass transition temperature
T_m	Melting temperature

Table of Contents

Abbreviations	4
1. Introduction.....	7
1.1. Plastic Recycling.....	7
1.2. Chemical Recycling and Upcycling.....	8
1.3. Acetal Hydrolysis	8
1.4. Acid Degradation Studies of Poly(acetal-ester)s	10
1.5. Polyesters	10
1.6. Phenolic resins.....	12
2. Aim.....	13
2.1. Main goals of the thesis	13
3. Experimental.....	14
3.1. Materials.....	14
3.2. Methods	15
3.2.1. Precipitation	15
3.2.2. Hydrolysis	15
3.2.3. Re-polymerization of oHVT-5	15
3.2.4. Resol synthesis of oHVT5	15
3.2.5. Characterization methods.....	16
4. Results and Discussion.....	17
4.1. Characterization of PHVT	17
4.2. Hydrolysis of PHVT-5	18
4.2.1. Characterization of oligomers	19
4.2.2. Optimization of temperature	20
4.2.3. Solvent and organic acid	22

2022-05-19

4.3. Hydrolysis of PHVT-20	23
4.4. Characterization of Akestra	23
4.5. Hydrolysis of Akestra 90	25
4.5.1. Optimization of temperature	25
4.5.2. Optimization of solvents and organic acids.....	25
4.5.3. Effect of SPG units	26
4.6. Re-polymerization of oligomers	26
4.7. Resol synthesis of oHVT5.....	28
5. Conclusion	29
6. References	30
7. Supporting Information.....	33

1. Introduction

1.1. Plastic Recycling

Plastics are hugely demanded over the globe and the production of plastic is predicted to exceed 500 million metric tons per year by 2050 (1). However, less than 10 % of all plastic waste is being recycled. Another 12% is incinerated, leaving the remaining 78 % to be discarded in landfills and the environment (2). Currently there are around 7.4 billion metric tons of plastic on Earth, which is expected to increase to 40 billion metric tons of plastic by 2050. In addition, around 10 million metric tons of plastic waste ends up in the sea every year (2).

The plastic left in the environment and in landfills poses a huge environmental concern since plastics may take centuries to decompose naturally (3). Even degradable plastics may last for quite some time depending on physical factors such as temperature and exposure to oxygen and ultraviolet light (4). Furthermore, the plastics that have been deposited in the environment also have economic value. In the United States alone, the value of plastic waste in landfills have been estimated to be worth \$8.3 billion (5).

While many countries choose to recover energy via incineration in order to save space in landfills, the energy recovery is inefficient and there is a risk to emit hazardous compounds and green house gases (6). Plastic recycling is an alternative for plastic waste disposal with many benefits. Foremost, plastic recycling uses less energy and natural resources than producing a new plastic from the raw materials, which is economically desirable (7). Recycling plastics also creates a circular materials economy which addresses the issue of finite raw materials (1).

Currently mechanical recycling is the most common method of recycling plastic. However, there are drawbacks to mechanical recycling. In general, recycled plastic has reduced mechanical properties in relation to virgin plastics produced directly from raw materials. This essentially means that plastic recycling often becomes plastic downcycling (7). Often 'virgin' (new) polymers of the same kind are mixed in with the recycled polymers to give structural characteristics similar to the original plastic (2). While mechanical plastic recycling

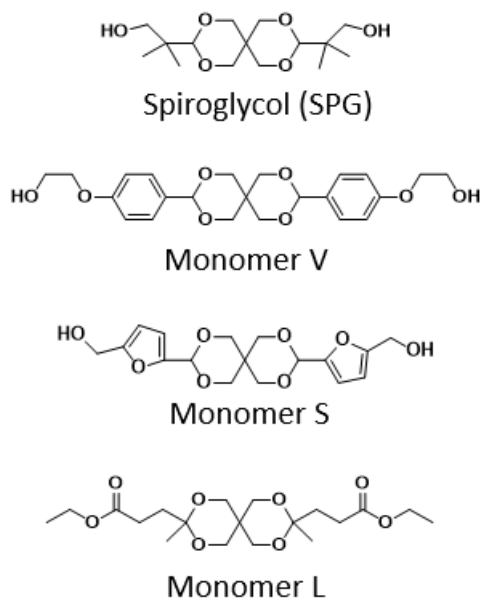
often reduces the value of the resulting plastic, chemical recycling and chemical upcycling appears to retain the quality of the plastic better (6).

1.2. Chemical Recycling and Upcycling

There are many different methods to chemically recycle and upcycle plastics: depolymerization of plastics into monomers, conversion of plastics into fine chemicals, degradation of plastics into crude oil, and conversion into new plastics with added value (6). A strategy to deal with the many polymers that are difficult to recycle chemically is to introduce a comonomer that can easily be broken, which makes it possible to chemically recycle the polymers. By incorporating cleavable comonomers in the backbone of polymers, the polymers can be chemically recycled or upcycled (8). Methods to chemically recycle poly(ethylene terephthalate) (PET) have been extensively studied during the recent decades. Different ways of depolymerizing the ester bonds in PET into original feedstock monomers that have been investigated include: hydrolysis, methanolysis, glycolysis and aminolysis. (9).

1.3. Acetal Hydrolysis

Acetal bonds have been shown to be prone to hydrolysis under acidic conditions (10). Spiroacetal comonomers that could be added to a polymer to increase the recyclability include SPG, Monomer V, Monomer S and Monomer L, see Scheme 1(11–14). The spiro diacetal group in the monomers is susceptible to acid-triggered degradation, which can facilitate the acid-catalyzed hydrolysis (11).



Scheme 1. The molecular structures of spiroacetal comonomers.

While the ester groups in poly(acetal-ester)s also can hydrolyze under acidic conditions the acetal bonds may have a higher degradation rate (11). Since the acetal group is prone to be hydrolyzed under acidic conditions, it is possible to get a controllable degradation where mainly only the acetal bonds have been broken. The controllable degradation could prove to be very helpful in reducing the amount of microplastics in the environment. (11). Hydrolysis is defined as breaking susceptible bonds by reacting with water. When susceptible polymeric bonds are hydrolyzed in solution the rate of the hydrolysis is proportional to the water concentration and number of hydrolysable bonds (15). Acetal hydrolysis is only possible in the presence of an acid and naturally water is required. Acetals are stable under basic conditions, therefore acidic degradation is required to break the acetal bonds in the polymer (16).

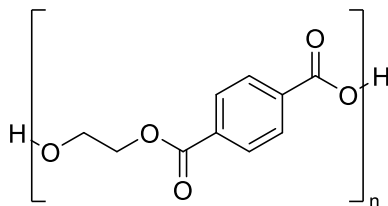
1.4. Acid Degradation Studies of Poly(acetal-ester)s

Several degradation studies have been done on polyesters containing a spirocyclic acetal monomer unit. Below is a short summary of some of them.

Firstly, there is a study done with SPG (Scheme 1) as a monomer where the polymer was degraded in 2M HCl solution (9:1, acetone:water, v/v) for 30 days. The finding from the study was 12.8, 40.1 %, 67,1 % and 79.5 % weight loss for respectively 10 %, 20 %, 30 % and 40 % SPG in polymer (11). A higher mol% of SPG seems to make the polymer degrade more. In another study on a different spirocyclic acetal, the hydrolysis was quicker despite having a lower acid content. The polymer degraded and dissolved after 182 minutes in a 0.1 M HCl solution (9:1, acetone:water, v/v) at 23 °C. If the temperature was increased to 50 °C the polymer was degraded and dissolved already after 19 minutes. If the concentration was increased to 1M the polymer degraded and dissolved after 9 minutes (17). One can conclude that a higher concentration of acid and a higher temperature likely increase the degradation rate.

1.5. Polyesters

Polyesters are an important class of polymers, where the most important polyester is poly(ethylene terephthalate) (PET), see Scheme 3. PET has aromatic units in the polymer backbone which gives PET good mechanical and thermal properties, suitable for bottles and textiles (18). Currently, PET is mostly synthesized from fossil-based materials but there are promising studies showing that PET can be synthesized with bio-based resources, such as the aromatic aldehyde precursors 4-hydroxybenzaldehyde, vanillin and syringaldehyde (19).

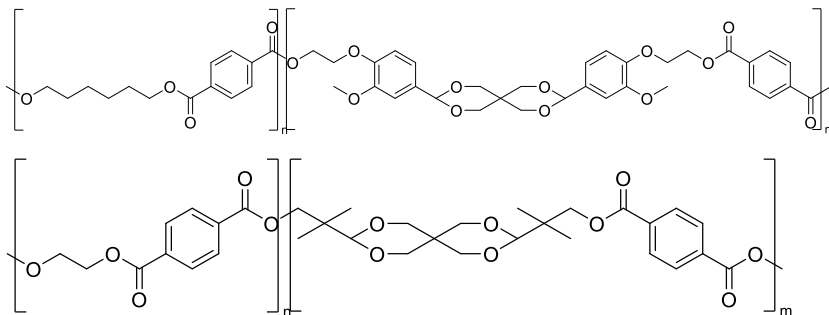


Scheme 2. The molecular structure of PET.

Conventional petrochemical-based plastics are not sustainable with problems such as carbon dioxide emissions and plastic waste littering (20). Sustainable bio-based plastics are needed to solve the problems that petrochemical plastics pose (20). Some of the sources for bio-based plastics are cellulose, starch, fatty acids, sugars and proteins and they can be used to make bio-based monomers that can be used to synthesize bio-based plastics (20). Ideally, the sources for bio-based plastics should come from waste that is inedible and bountiful (19).

PHVT (Scheme 3) is a partially biobased polymer that was synthesized in our lab from fossil-based terephthalic acid, hexanediol, and biobased monomer V (12). Monomer V was synthesized by acetalization between vanillin and pentaerythritol, followed by alkylation with ethylene carbonate. The number in PHVT-5 and PHVT-20 means the mol% of monomer V in the resulting polymer. The monomer V (Scheme 1) is similar to SPG, which has an acetal unit that could be degraded. The T_g increases with the mol% V and with the amount of the spirocyclic diol. The hydrolysis of PHVT-5 and PHVT-20 will be examined in this paper.

Akestra (Scheme 3) is a commercial copolyester of PET and SPG that is manufactured by Perstorp AB. The polymer is synthesized by copolymerization of three monomers, namely terephthalic acid, ethylene glycol and SPG. The name Akestra 90 has nothing to do with the mol% of the monomer parts but instead comes from the glass transition temperature close to 90 ($T_g=95$ °C). Another Akestra 110 is another polymer in the Akestra series with a possible higher mol% of SPG (12).



Scheme 3. The upper molecular structure is of PHVT where the left unit is identical to that of PHT and the right unit contains comonomer V. The lower molecular structure is of the commercial polymer Akestra, where the left unit is identical to that of PET and the right unit is a comonomer based on SPG.

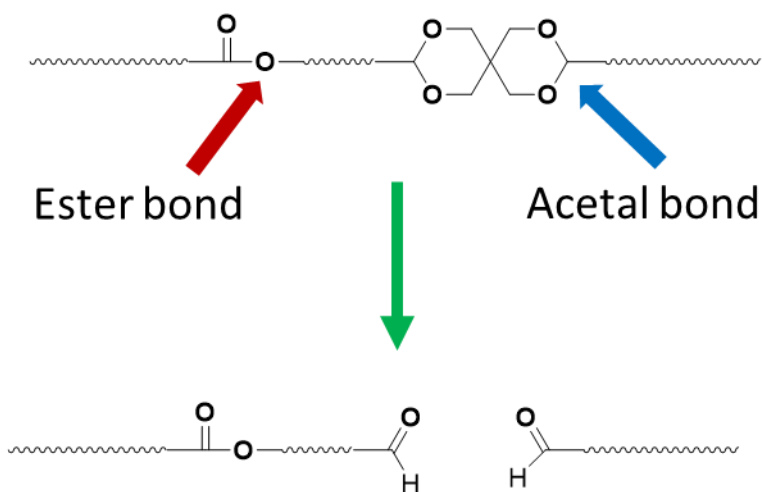
1.6. Phenolic resins

Phenolic resins were the first industrially synthesized polymer materials and have been produced for over a century now. (21) Today, 6 millions of tons are produced per year and some of the applications for phenolic resins are carbon foams, adhesives, molding compounds and fiber-resistant coatings (22). Phenolic resins are well-known to have high strength and long-term thermal, chemical and mechanically stability. The most common starting materials for phenolic resins are formaldehyde and phenol, which both are toxic and petrol based (22). Formaldehyde is particularly problematic, being both volatile and carcinogenic. Foyer et al. in 2016 have developed a method to synthesize formaldehyde-free phenolic resins from different bio-based aldehyde precursors (22). One of the product from the spiroacetal hydrolysis is a telechelic oligomer with aldehyde terminal groups that could be potentially used for polymerization to a phenolic resin, which could have a higher performance than the initial polyester. This could then be considered as upcycling.

2. Aim

2.1. Main goals of the thesis

Poly(spiroacetal-ester)s have two bonds that are prone to be hydrolyzed (Scheme 4). The main goal of this master thesis was to selectively hydrolyze the spirocyclic diacetal unit of the target polymers Akestra and PHVT (scheme 3) under acidic conditions while to keep the ester bonds largely unchanged.



Scheme 4. The desired reaction where the acetal bond is selectively hydrolyzed.

The conditions of the hydrolysis will be further examined, such as the temperature, the presence of a solvent, the concentration of acid and the type of acid could influence the hydrolysis of Akestra and PHVT.

In both the hydrolysis reaction of PHVT and Akestra, the spirocyclic acetal groups were hydrolyzed, which may result in the oligomers having aldehyde groups at the chain end. The oligomer can be used as an aldehyde pre-cursor for phenolic resins. Re-polymerization of the obtained telechelic oligomers by acetalization with pentaerythritol will also be preliminary investigated.

3. Experimental

3.1. Materials

Sulfuric acid (H_2SO_4 , 95 %), sodium bicarbonate (99.7 %), chloroform (99.1 %, stabilized with 0.6 % ethanol), Methanol (MeOH), acetone, xylene (a mixture of isomers, analytical grade), 1,4-dioxane and acetonitrile were purchased from VWR Chemicals. Chloroform-d (99.8 % atom D), p-toluenesulfonic acid monohydrate (p-TSA·H₂O) (reagent grade, 98 %), oxalic acid (99 %), phenol (99 %), sodium hydroxide (98 %, pellets) and dimethyl sulfoxide (DMSO, 99.9 %) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF) was purchased from Honeywell. Ethanol (99.7 %) was purchased from Solveco. HCl solution (37 %) was purchased from Scharlau. Acetic acid (99.8 %) was purchased from Acros Organics. Last but not least, bio-based pentaerythritol (Voxtar™, 99 %) was provided by Perstorp AB.

3.2. Methods

3.2.1. Precipitation

An amount of 5 g of Akestra 90 or 110 was dissolved in 50 ml chloroform. The solution, then was added dropwise into 400 ml methanol. The white powder of Akestra was precipitated and dried under vacuum for 2 days before further use.

3.2.2. Hydrolysis

The hydrolysis reaction of PHVT-5 in HCl (6M) at 60 °C for 4 hours with THF as second solvent is described as a typical example. Similar procedure was applied with Akestra. PHVT-5 (100mg) was add in 20 ml solution mixture of HCl (12M, 10 ml), THF (10 mL). The heterogenous mixture then was heated to 60 °C in a round-bottomed flask in the atmosphere. After 4 hours, the mixture was neutralized with sodium carbonate. The residue polymer sample was filtered, and the white solid powder was collected and dried in the vacuum oven.

3.2.3. Re-polymerization of oHVT-5

oHVT-5 (434 mg) was added in a 250 mL round bottom flask equipped with magnetic stirrer, and a vacuum outlet. To the flask, 11 mg of pentaerythritol and 2 mg of PTSA was added. The re-polymerizations flask were heated to 150°C under vacuum. After 3 hours the reaction was stopped.

3.2.4. Resol synthesis of oHVT5

An amount of 1 g Oligomer (oHVT-5), 250 mg phenol, 5 mg of solid NaOH and 5 ml of water were put in a round-bottom flask that was stirred under nitrogen. The mixture was heated to 130 °C for 1 hour.

3.2.5. Characterization methods

^1H and ^{13}C NMR measurements were performed in DMSO- d_6 and/or CDCl_3 at room temperature, utilizing a Bruker DR X400 spectrometer at 400.13 MHz and 100.61 MHz, respectively. Phase correction was applied for all spectra and the residual solvent signals (δH , DMSO- d_6 = 2.50 ppm, δC , DMSO- d_6 = 39.52 ppm, δH , CDCl_3 = 7.26 ppm, δC , CDCl_3 = 77.16 ppm) were used as internal reference. The data were processed by using the software TopSpin 4.2.0. The polymers were additionally analyzed with two-dimensional (2D) NMR analysis.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments DSC Q2000. The samples were studied with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen with a purge rate of 50 mL min^{-1} . The sequence consisted of a heating ramp from $0\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$, followed by a cooling ramp to $0\text{ }^\circ\text{C}$ and finally, a heating ramp to $250\text{ }^\circ\text{C}$ and the glass transition temperature (T_g) was determined from second heating cycle.

4. Results and Discussion

4.1. Characterization of PHVT

The target polymer PHVT-5 was first characterized by 1D and 2D NMR (Figure S5 and S6) in CDCl_3 . The ^1H NMR spectrum and full peak assignment are depicted below in Figure 1. As seen in the figure below, the singlet (H11) at 5.41 ppm and the multiple (H12) peaks at 4.86, and 3.65 ppm are attributed to the spiro acetal structure. The aromatic terephthalic protons in the PET unit (H4) can be found at 8.07 ppm and the aromatic protons in the V unit can be found at (H9) 7.05 ppm, at (H7) 7.01 ppm and at (H8) 6.86 ppm. The hydrogen in the methylene group can be found at (H10) 3.86 ppm. The hydrogen in the acetal at the end of the V unit can be found at (H6) 6.49 ppm. The hydrogen in the ester in the V unit (H5) at 4.39 ppm is overlapping with the proton in ester in the PHT unit (H1) at 4.35 ppm. The rest of the protons in the hexanediol part of the PHT unit were found at (H2), 1.82 ppm and (H3) 1.53 ppm.

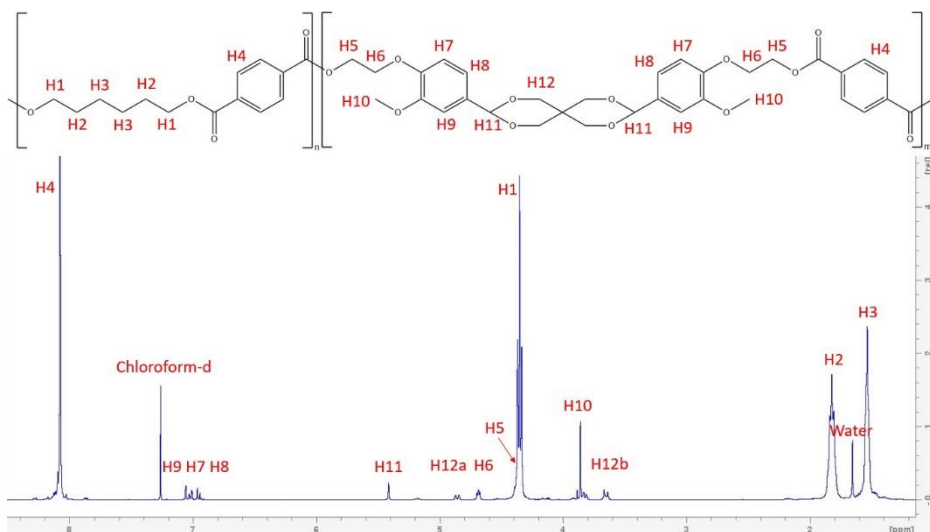


Figure 1. ^1H NMR categorization of PHVT.

The ^1H NMR spectrum of PHVT-5 is very similar to the one of PHVT-20 and the only difference is that the peaks attributed to the PET unit is bigger for PHVT-20 since the mol% of V is higher. With the full assignment of the signals of the ^1H NMR spectrum, mol% of V units in PHVT could be calculated by Equation 1:

$$\% V \text{ units} = \frac{I_{H11}}{I_{H4}} \quad (1)$$

According to Equation 1, PHVT-5 contains 5% of V units and PHVT-20 contains 20 % of V units. The conversion for PHVT could be calculated by comparing the integral of the H11 peak (Figure 1) with the integral of the aldehyde peak, H13 (Figure 3). The thermal properties of PHVT are reported in Table 1.

Table 1. Thermal properties of PHVT-5, PHVT-20 and oHVT-5 (the oligomer of the hydrolyzed PHVT-5).

	T_g ($^{\circ}\text{C}$) ^{a)}	T_m ($^{\circ}\text{C}$) ^{a)}
PHVT-5	28	139
oHVT-5	4	139
PHVT-20 ^{b)}	46	N/A

^{a)} Measured by DSC from the second heating cycle.

^{b)} Collected from the literature (ref. 12)

4.2. Hydrolysis of PHVT-5

The polymer came in powder form and could be used without further processing it. The hydrolysis of the spiroacetal units of PHVT-5 was optimized with respect to temperature, concentration of hydrochloric acid and by addition of a solvent. All the runs can be found in the supporting information (Table S1 and S2).

4.2.1. Characterization of oligomers

The ^1H NMR characterizations were done in order to determine which units of the polymer were hydrolyzed and which units remained intact. A ^1H NMR spectrum and full peak assignment of the oligomer from completely hydrolyzed PHVT-5 can be seen in Figure 3. As seen in Figure 3, acetal proton at 5.41 ppm has disappeared completely and instead there is an aldehyde peak at 9.86 ppm. This information was necessary in order to calculate conversion of spiroacetal units and evaluate the specificity of the hydrolysis. The conversion was calculated by comparing the acetal peak to the aldehyde peak. In addition, ^1H NMR was used to calculate an approximate molecular weight of the oligomers by taking into account the ratio of the aldehyde proton at 9.86 compared to the terephthalic aromatic protons at 8.07 ppm. The average molecular weight of 4 different samples, for the completely hydrolyzed oligomers calculated with NMR, was around 7100 g/mol (Table S8). The yield of the complete hydrolyses were around 94-99 %, which is reasonable since pentaerythritol and small oligomers were dissolved in the water phase.

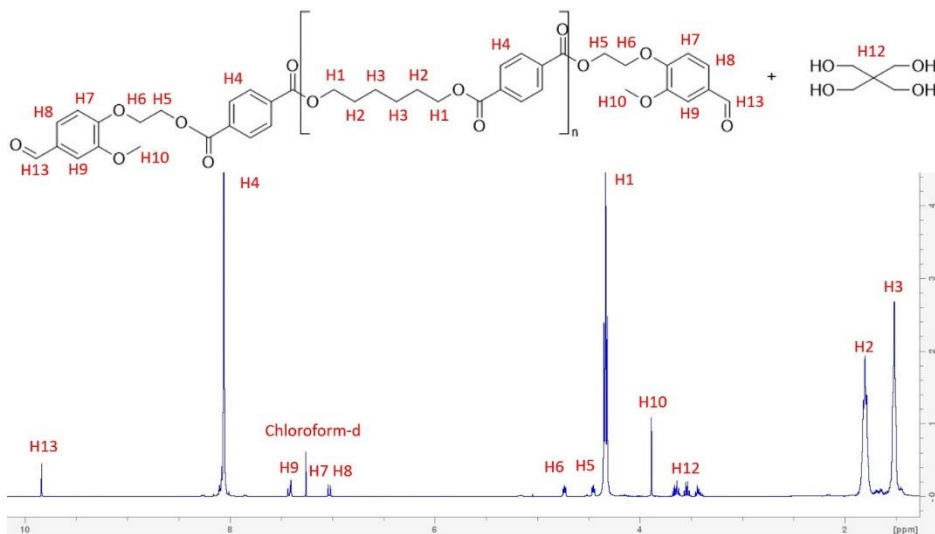


Figure 2. ^1H NMR spectra of the oligomer hydrolyzed from PHVT-5.

To investigate how T_g and T_m changed when PHVT-5 was hydrolyzed into oligomers, a DSC analysis was also done on the oligomer (Table 1, section 4.1). For the oligomer the T_g is 4 °C and T_m is 139 °C. While the T_m essentially remained unchanged, the T_g was drastically reduced when PHVT-5 was hydrolyzed. This can be attributed to the loss of the rigid spiroacetal unit in the polymer which is a group that facilitates high T_g . Furthermore, the T_g of the oligomer is lower than PHT (T_g of 20 °C), which could be explained by the high chain mobility of the low molecular weight oligomer after the hydrolysis (12).

4.2.2. Optimization of temperature

At first two hydrolyses of PHVT-5 with 12 M HCl was run for 4 hours at 30 °C and 40 °C, respectively. These temperatures was chosen due to the low T_g of PHVT-5, 28 °C. The conversion of the spiroacetal unit for the hydrolysis was calculated based on the peak of aldehyde bond at 9.86 ppm, which would be formed during the hydrolysis (Figure 2). The conversion for the hydrolysis ran at 30 °C was 73 % and for 40 °C 79 %. Then the same hydrolysis was repeated but at 60 °C which gave a conversion of 97 %. This shows a clear positive correlation between higher temperatures and higher conversion of spiroacetal units as seen in Figure 3 below.

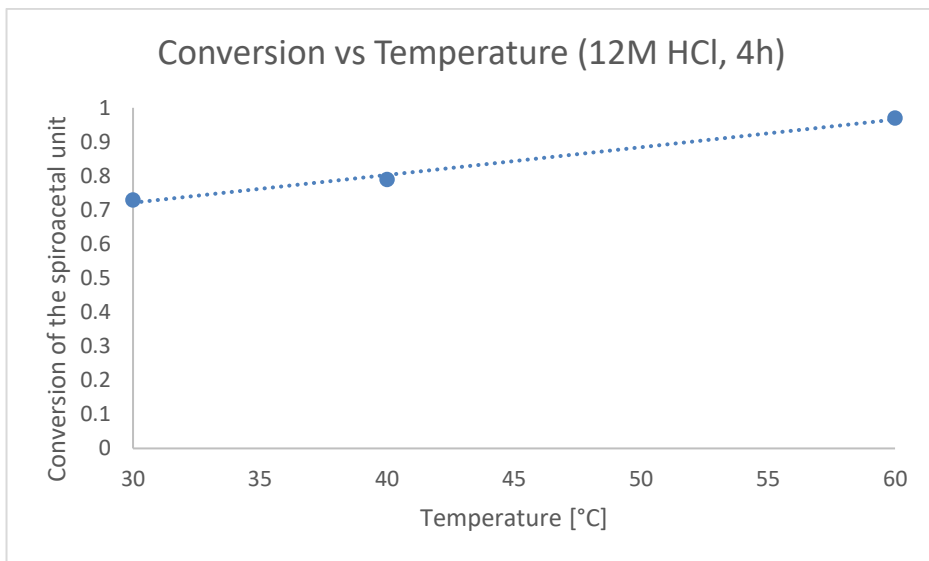


Figure 3. Conversion vs temperature for hydrolyzed PHVT-5 samples with 12 M HCl for 4 hours.

Next, it was examined if it was possible to reach complete hydrolysis of the spiroacetal unit in PHVT-5 at 40 °C if the time of the hydrolysis was extended. With 12 M HCl and no solvent added it did not prove possible, and the conversion plateaued after 24 h with 92 % conversion and remained at 92% conversion even after 72 hours. This means that at 40 °C the reaction reaches an equilibrium at 92 % conversion, and the temperature needs to be increased to reach higher conversion. This is illustrated below in Figure 4.

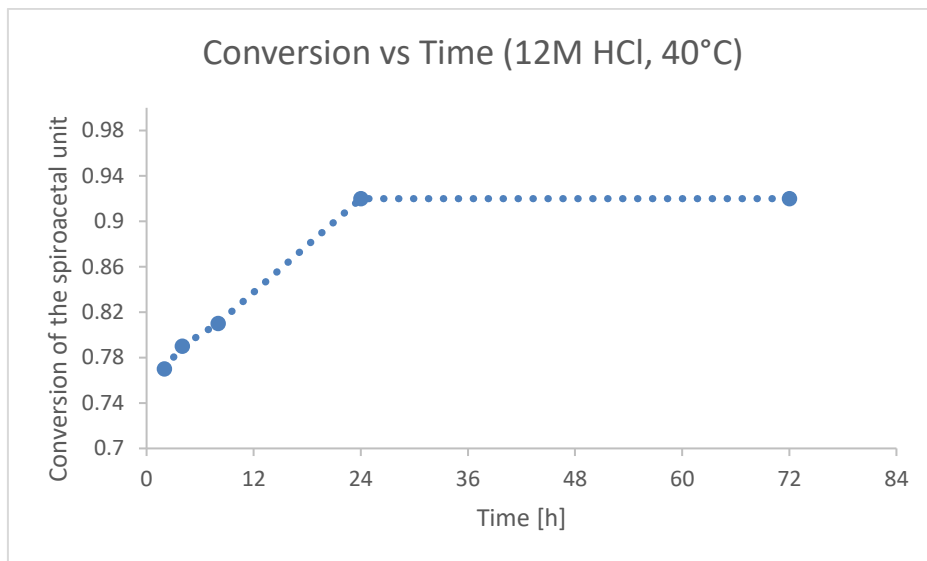


Figure 4. Conversion plotted against time for the PHVT-5 samples hydrolyzed in 12 M HCl at 40 °C.

4.2.3. Solvent and organic acid

Organic solvents, such as acetone, methanol, and THF have been proven to accelerate the hydrolysis of acetal groups (11,23). THF was chosen to be tested as a solvent since it is organic and has a boiling point above 60 °C. While it did not dissolve PHVT-5, it wetted the polymer in order to facilitate the hydrolysis. When THF was used in a 1:1 ratio to water at 40 °C in a hydrolysis with 6 M HCL, the conversion of spiroacetal units was 97 %. For comparison, a experiment with the same conditions, except it had no THF and 12 M HCl, reaches 79 % conversion. Also a 1:3 ratio of water:THF, with the lower 3 M HCl concentration, was examined. It gave the same conversion of 97%. It was proven that using THF as a solvent increased the hydrolysis rate of PHVT-5. A comparison between the presence and the absence of THF can be seen below in Figure 8 in hydrolyses that have been run for 4 hours.

It was thus decided to combine the presence of THF with increasing the temperature to 60 °C for a hydrolysis which proved successful with 100 % conversion of spiroacetal units. The complete hydrolysis condition was 100 mg PHVT-5 in 20 ml solvent with a 1:1 ratio to

water:THF with a concentration of 6 M HCl, that was run for 4 hours in 60 °C. The hydrolysis proved to be scalable where several more complete hydrolyses were run with 0.5 g, 2 g and 6 g. Furthermore, the hydrolysis of the acetal bond was selective and no other bond was broken to any significant degree. More specifically around 1 % of all ester bonds in the PET part and 1% of the non-spiroacetal were broken (Table S5).

Then it was examined if gentler conditions could be applied while still obtaining a complete hydrolysis. Acetic acid was tested instead of hydrochloric acid as a catalyst. A hydrolysis with 1 M acetic acid with 1:1 ratio of water:THF was run at 60 °C for 30 hours. However, the conversion was only 22 % when acetic acid was used under these conditions. This indicates that acetic acid is a too weak of an acid to use it for hydrolysis in chemical recycling of PHVT.

A lower concentration of HCl was also examined (Run 28, in Table S1). As in the table, lower concentrations of acid slow down the hydrolysis of the acetal groups, which led to prolonged time for complete conversion of spiroacetal units. It was shown that a lower concentration of 2M HCl could be used if the time was extended from 4 hours to 24 hours for full conversion.

4.3. Hydrolysis of PHVT-20

One hydrolysis of PHVT-20 was done with one of the procedures that had given complete conversion of spiroacetal units of PHVT-5: 100 mg PHVT-20 in 20 ml solvent with a 1:1 ratio to water:THF with a concentration of 2 M HCl, that was run for 24 h in 60 °C. The conversion for the hydrolysis of PHVT-20 was also 100 %, which indicates that the procedure could work for hydrolysis of all PHVT polymers regardless of the mol% V. The hydrolyzed PHVT-20 sample can be seen in the supporting information (Figure S7).

4.4. Characterization of Akestra

The target polymer Akestra 90 were first characterized by 1D- and 2D-NMR spectroscopy (Figure S1, S2, S3 and S4) in CDCl₃. The ¹H NMR spectrum and full peak assignment are depicted in Figure 5. As

seen in the below figure, the singlet H6 at 4.32 ppm and the doublets H7 at 3.57, 3.50, and 3.32 ppm are attributed to the spiroacetal structure. The methylene groups of SPG unit are observed at 4.18 (H4), 1.04 (H5) ppm. Furthermore, the PET units can be noted in the aromatic region at 8.10 (H2, H3) for the terephthalic protons, and the singlet peak around 4.69 ppm can be assigned to the methylene protons of the ethylene glycol-units (H1). The ^1H NMR spectrum of Akestra 110 is very similar to the one of Akestra 90 and the only difference is that the H1 peak's integral is smaller for Akestra 110 since the SPG mol% is higher. With the full assignment of ^1H NMR spectrum, mol% of SPG units in Akestra could be calculated by Equation 2:

$$\% \text{ SPG units} = \frac{2 * I_{H6}}{I_{H2} + I_{H3}} \quad (2)$$

According to Equation 2, Akestra 90 contains 20% of SPG units and Akestra 110 contains 45% of SPG units. Akestra 90 and 110 are completely amorphous with T_g of 95 °C and 110 °C respectively (12,24).

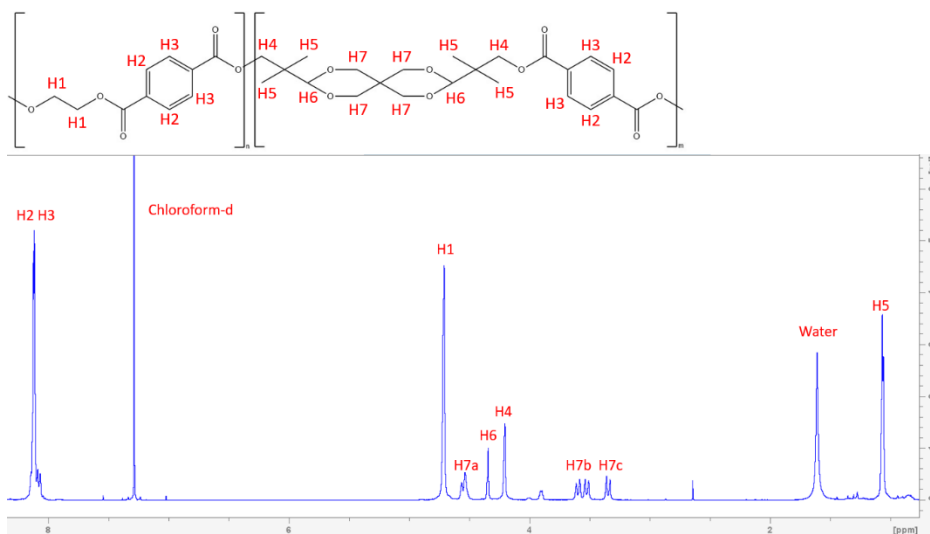


Figure 5. ^1H NMR categorization of peaks in Akestra.

4.5. Hydrolysis of Akestra 90

Akestra is a commercial polymer that came in pellet form that were precipitated to a powder. In order to have comparative results between Akestra and PHVT all polymer samples used for hydrolysis was in powder form. Powder has the advantage of a high surface area, which increases the rate of hydrolysis. The conversion was calculated for Akestra by comparing the integral of the H6 peak (figure 1) and the aldehyde peak. All experimental runs for Akestra 90 can be found in Table S3 in the supporting information.

4.5.1. Optimization of temperature

In order to find out the optimal temperature for hydrolysis of Akestra 90, one experiment was carried out at room temperature with 12 M hydrochloric acid with 100 mg polymer/20 ml water and an identical one at 100 °C. In room temperature, the polymer was not hydrolyzed at all, while at 100 °C the conversion of the spiroacetal unit was 35 %. The temperature could not be increased further since the boiling point of water is at 100 °C. Furthermore, since the acid concentration was already very high, the acid concentration could not be increased. The conditions are very harsh and still the polymer is not hydrolyzed. This could be explained by low chain mobility in Akestra 90 or steric hindrance of the SPG unit.

4.5.2. Optimization of solvents and organic acids

Different solvents and organic acids were tested in order to see if adding a solvent or changing the type of acid, a series of experiments was devised with the conditions of 50 °C, 1 M acid, 100 mg polymer/20 ml water and 72 hours. A temperature of 50 °C was chosen so that it was as high as possible while being below the boiling points of all the chosen solvents. The different solvents that were tested were acetone, ethanol, THF and dioxane with hydrochloric acid as a catalyst with a ratio of 1:1 of solvent to water. The different acids that were tested were acetic acid, oxalic acid, sulfuric acid and hydrochloric acid. Surprisingly, the conversion of spiroacetal units were 0% for all the experiments mentioned above.

It was concluded that the low conversion of spiroacetal units might be because of the low acid concentration and low temperature. Thus, the solvent with the highest boiling point of 101 °C, dioxane, was chosen to be tested again with a higher acid concentration and at a higher temperature. However, the temperature could not be increased all the way to 100 °C since it was observed that dioxane together with water created a low boiling azeotrope around 83 °C. Thus, the experiment was conducted at 80 °C, 6 M hydrochloric acid, 100 mg polymer/20 ml water, 24 hours, 1:1 dioxane:water. The results were, however, not too promising with a maximum of 15% conversion.

4.5.3. Effect of SPG units

Akestra 110 has a higher mol% of SPG than Akestra 90, more specifically 45 % compared to 20 %. Therefore, it would be possible that a higher mol% of SPG could increase the rate of hydrolysis. The first experiment with Akestra 110 was with done with same conditions of the most successful experiment with Akestra 90: 12 M hydrochloric acid with 100 mg polymer/20 ml water at 100°C. However, the conversion for Akestra 110 was even lower with 10 % conversion compared to the conversion of Akestra 90 of 35 %. Another series of experiments with solvents was done at 60 °C, 6 M hydrochloric acid, 100 mg polymer/20 ml water and 24 hours. The solvents used were dioxane and THF with 1:1 ratio to water. However, the conversion was 0 % in both cases. The results for Akestra 110 can be found in Table S4 in the supporting information.

4.6. Re-polymerization of oligomers

Oligomers obtained from the acetal hydrolysis of PHVT-5 were used for repolymerization since full conversion was obtained in those hydrolysis experiments. As discussed above, after acetal hydrolysis the oligomers are expected to have two reactive aldehyde terminal groups. This allows the oligomer to be repolymerized to virgin PHVT-5 by adding pentaerythritol with catalytic acid. The temperature for the repolymerization was around 150 °C which allowed the oligomer to be stirred without a solvent since the T_m was 139 °C.

All oligomers used for re-polymerization came from hydrolyzed PHVT-5 samples with 99-100 % conversion. The highest conversion for re-polymerizations reached 79 %. This is a reasonable conversion of acetalization reaction, and the oligomer possess decent molecular weight of 7100 g/mol which could restrict diffusion in repolymerization reactions. Also, only 5 mol% of V in the starting polymer indicates that the oligomer might not be completely telechelic, in other words, that not all chain ends consisted of an aldehyde unit. Some of the groups on the chain ends could be alcohols which would have made polymerization with pentaerythritol difficult.

It is also possible that, since PHVT-5 contains such a small amount of monomer V, the chance of the chain ends meeting each other is quite small and making it difficult for to polymerize the oligomer to full conversion. The re-polymerization might work better with a PHVT with a higher mol% of V such as PHVT-20.

One other possibility was that not enough pentaerythritol was used and therefore it was tested to add an excess amount of pentaerythritol. However, this caused the polymer to crosslink since pentaerythritol could easily link the polymer chains together in undesired ways since the molecule has four alcohol groups that can react. Instead of linking the aldehyde units link together with two each of the alcohol group in pentaerythritol, there is instead a possibility that pentaerythritol could connect four different oligomers, which would cause chain linkage. The result of the chain linkage was that the polymer could not be dissolved, and thus not analyzed by the NMR. Although the re-polymerization was not complete the molecules are still quite large. Since the oligomers have a molecular weight of 7100 g/mol, the molecular weight will rapidly increase with only a small amount of linkage between oligomers.

Further studies of re-polymerizing PHVT need to be conducted to see if it is possible to create a closed loop of chemical recycling with a high conversion and high yield. Another possibility would to examine different upscaling paths that the oligomers could be used for. Then it could be possible to develop the hydrolysis procedure further, to be a chemical recycling process used in an industrial scale.

4.7. Resol synthesis of oHVT5

To upscale the oligomer of PHVT-5, it was polymerized with phenol in order to create a phenol aldehyde resin. The pre-polymerization of the oligomer with phenol was carried out under basic conditions at 130 °C under nitrogen. However, the oligomer did not polymerize at all and it was concluded that it was not possible to create a phenol aldehyde resin under the tested conditions. One possible explanation for why it did not work is that the oligomers are quite large and there may be steric hindrance from the aromatic ring in phenol that prevents the phenol from being able to react with the chain ends.

5. Conclusion

The spiroacetal unit hydrolysis of Akestra 90 and Akestra 110 was not very efficient with very low conversion as the highest achieved conversion was 35 %. A high conversion was only reached for those hydrolyses where the temperature was around or above the T_g (95 °C for Akestra 90 and 110 °C for Akestra 110), or when a solvent was used. As both Akestra 90 and Akestra 110 are very resistant to hydrolysis, 1 month or longer under harsh conditions might be necessary to hydrolyze the polymers completely. However, then the ester bond might also break. Furthermore, hydrolysis worked better for Akestra 90 than Akestra 110.

The spiroacetal unit hydrolysis of PHVT-5 was selectively complete with the conditions at 60 °C for 24 hours with 2 M HCl and a 1:1 ratio of water:THF. These conditions could be applied in practical and industrial applications. These results suggest that a lower T_g facilitates hydrolysis since the conversion of the spiroacetal units increases when hydrolyzing polymers with lower T_g . Spiroacetal units in polymers increases the T_g and polymers with a higher T_g were harder to hydrolyze. Thus, the results suggest that polymers with a high mol% of spiroacetal units are harder to hydrolyze. A 79 % conversion in the re-polymerization was reached. However, further studies are needed to optimize the re-polymerization and the upscaling of the hydrolyzed oligomers.

5.1. Future research

- Investigating hydrolyzation of other poly(acetal-ester)s.
- Further study on increasing the conversion of PHVT re-polymerization.
- Studies of the properties of the re-polymerized PHVT.
- Investigation of the possible co-polymerizations and up-cycling that can be done with hydrolyzed PHVT oligomers.

6. References

1. Sardon H, Dove AP. Plastics recycling with a difference. *Science*. 27 april 2018;360(6387):380–1.
2. Korley LTJ, Epps TH, Helms BA, Ryan AJ. Toward polymer upcycling—adding value and tackling circularity. *Science*. 02 juli 2021;373(6550):66–9.
3. Chanda M. Chemical aspects of polymer recycling. *Adv Ind Eng Polym Res*. 01 juli 2021;4(3):133–50.
4. Hopewell J, Dvorak R, Kosior E. Plastics recycling: challenges and opportunities. *Philos Trans R Soc B Biol Sci*. 27 juli 2009;364(1526):2115–26.
5. Garcia JM, Robertson ML. The future of plastics recycling. *Science*. 17 november 2017;358(6365):870–2.
6. Chen H, Wan K, Zhang Y, Wang Y. Waste to Wealth: Chemical Recycling and Chemical Upcycling of Waste Plastics for a Great Future. *ChemSusChem*. 2021;14(19):4123–36.
7. Mantia FL. *Handbook of Plastics Recycling*. iSmithers Rapra Publishing; 2002. 460 s.
8. Kiel GR, Lundberg DJ, Prince E, Husted KEL, Johnson AM, Lensch V, m.fl. Cleavable Comonomers for Chemically Recyclable Polystyrene: A General Approach to Vinyl Polymer Circularity. *J Am Chem Soc*. 20 juli 2022;144(28):12979–88.
9. Guo Z, Lindqvist K, de la Motte H. An efficient recycling process of glycolysis of PET in the presence of a sustainable nanocatalyst. *J Appl Polym Sci*. 2018;135(21):46285.
10. Nguyen HTH, Qi P, Rostagno M, Feteha A, Miller SA. The quest for high glass transition temperature bioplastics. *J Mater Chem A*. 22 maj 2018;6(20):9298–331.
11. Tian Y, Li J, Hu H, Chen C, Li F, Ying WB, m.fl. Acid-triggered, degradable and high strength-toughness copolyesters: Comprehensive experimental and theoretical study. *J Hazard Mater*. 15 maj 2022;430:128392.

2022-05-19

12. Mankar SV, Garcia Gonzalez MN, Warlin N, Valsange NG, Rehnberg N, Lundmark S, m.fl. Synthesis, Life Cycle Assessment, and Polymerization of a Vanillin-Based Spirocyclic Diol toward Polyesters with Increased Glass-Transition Temperature. *ACS Sustain Chem Eng.* 02 december 2019;7(23):19090–103.
13. Warlin N, Nilsson E, Guo Z, Mankar SV, Valsange NG, Rehnberg N, m.fl. Synthesis and melt-spinning of partly bio-based thermoplastic poly(cycloacetal-urethane)s toward sustainable textiles. *Polym Chem.* 31 augusti 2021;12(34):4942–53.
14. G. Valsange N, Gonzalez MNG, Warlin N, V. Mankar S, Rehnberg N, Lundmark S, m.fl. Biobased aliphatic polyesters from a spirocyclic dicarboxylate monomer derived from levulinic acid. *Green Chem.* 2021;23(15):5706–23.
15. Brannigan RP, Dove AP. Synthesis, properties and biomedical applications of hydrolytically degradable materials based on aliphatic polyesters and polycarbonates. *Biomater Sci.* 20 december 2016;5(1):9–21.
16. Clayden J, Greeves N, Warren S. *Organic chemistry.* 2. ed. Oxford University Press; 2012.
17. Ma S, Wei J, Jia Z, Yu T, Yuan W, Li Q, m.fl. Readily recyclable, high-performance thermosetting materials based on a lignin-derived spiro diacetal trigger. *J Mater Chem A.* 2019;7(3):1233–43.
18. Mankar SV. Toward Biomass-Derived Recyclable Polyesters.
19. Tachibana Y, Kimura S, Kasuya K ichi. Synthesis and Verification of Biobased Terephthalic Acid from Furfural. *Sci Rep.* 04 februari 2015;5(1):8249.
20. Chen GQ, Patel MK. *Plastics Derived from Biological Sources: Present and Future: A Technical and Environmental Review.* *Chem Rev.* 11 april 2012;112(4):2082–99.
21. Hirano K, Asami M. Phenolic resins—100years of progress and their future. *React Funct Polym.* 01 februari 2013;73(2):256–69.

2022-05-19

22. Foyer G, Chanfi BH, Boutevin B, Caillol S, David G. New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors. *Eur Polym J.* 01 januari 2016;74:296–309.
23. Hu H, Tian Y, Kong Z, Ying WB, Chen C, Li F, m.fl. A High Performance Copolyester with “Locked” Biodegradability: Solid Stability and Controlled Degradation Enabled by Acid-Labile Acetal. *ACS Sustain Chem Eng.* 08 februari 2021;9(5):2280–90.
24. Perstorp Holding AB. Akestra™ Product Brochure [Internet]. Tillgänglig vid: <https://www.perstorp.com/-/media/files/perstorp/pb/akestra.pdf>

7. Supporting Information

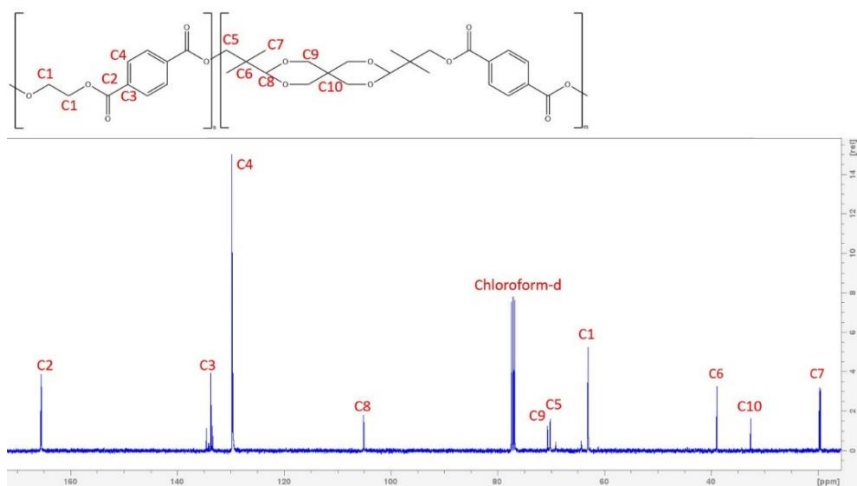


Figure S1. ^{13}C NMR spectra of Akestra 90

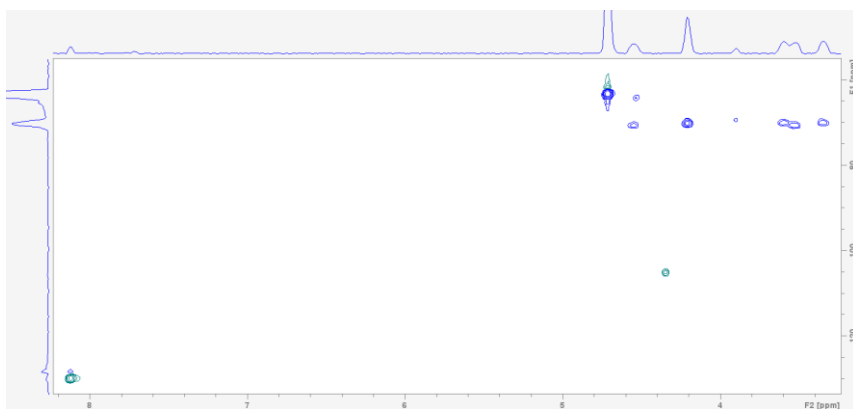


Figure S2. HSQC spectra of Akestra 90.

2022-05-19

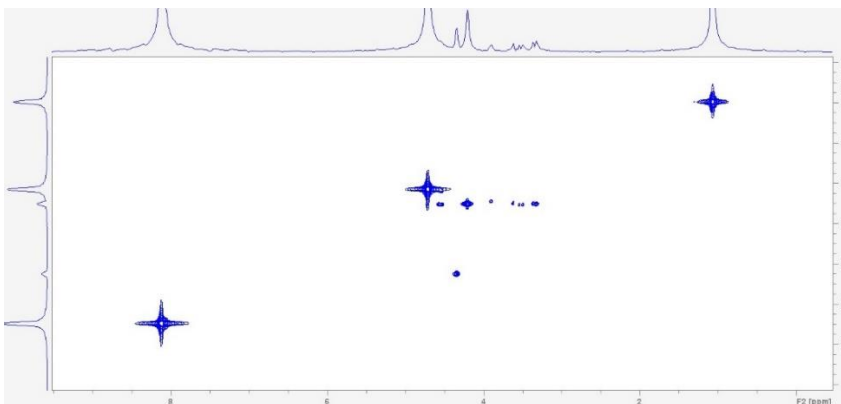


Figure S3. HMQC spectra of Akestra 90

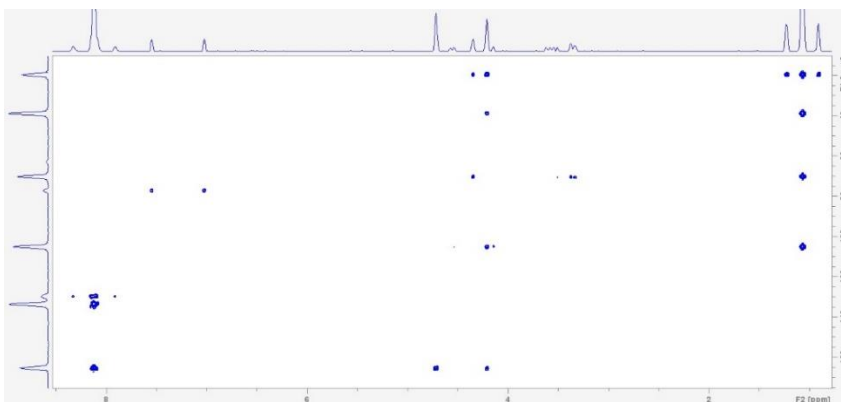


Figure S4. HMBC spectra of Akestra 90

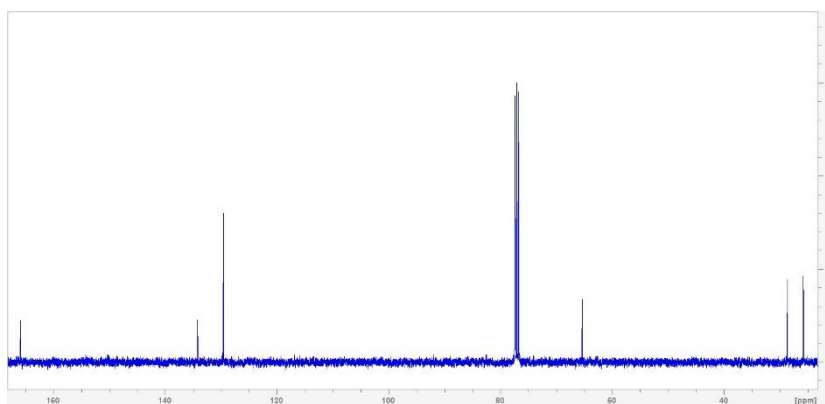


Figure S5. ^{13}C NMR spectra of PHVT-5

2022-05-19

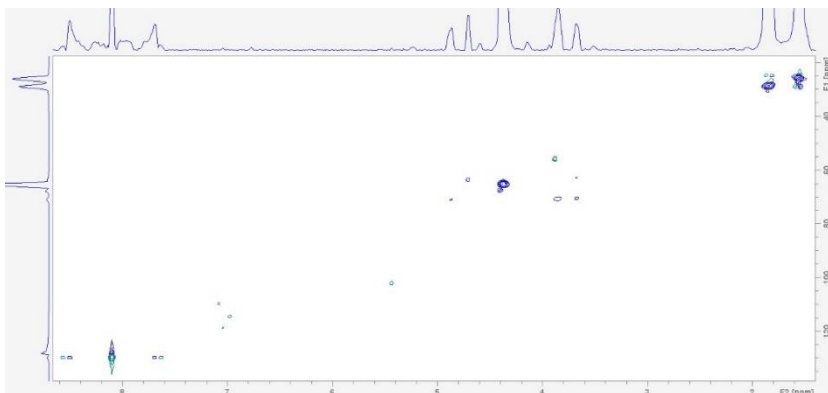


Figure S6. HSQC spectra of PHVT-5

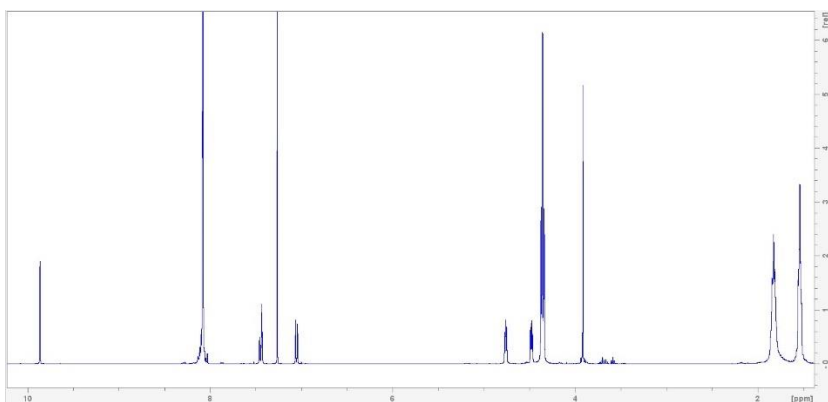


Figure S7. NMR spectra Completely hydrolyzed PHVT-20.

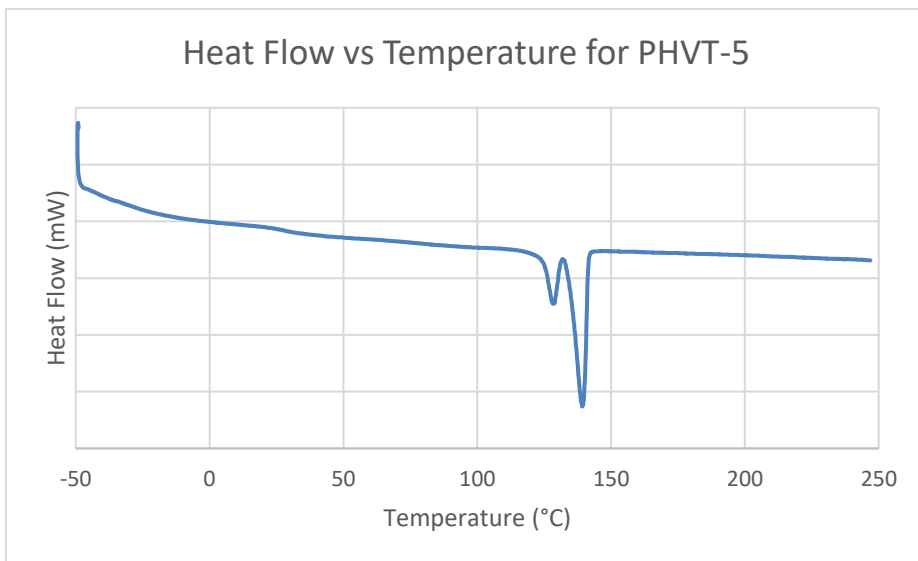


Figure S8. DSC analysis of PHVT-5. Exo up for the heat flow.

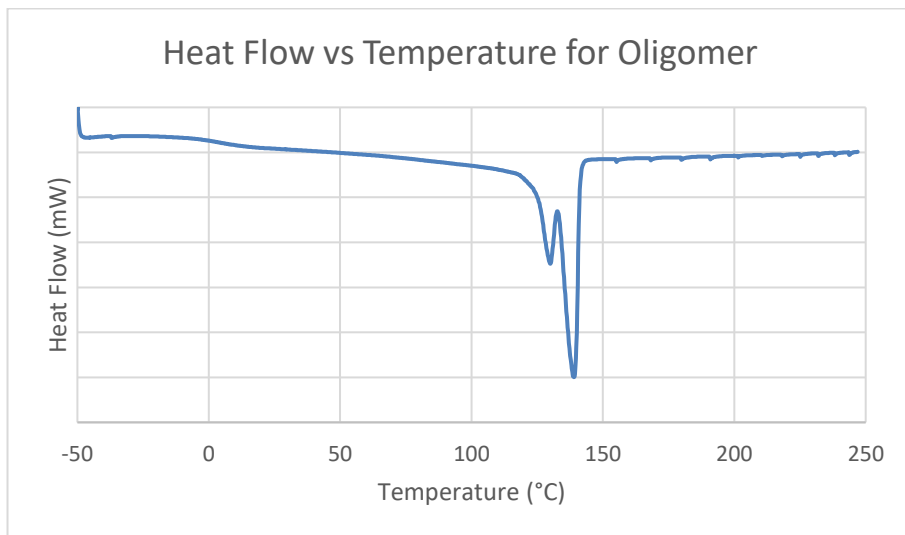


Figure S9. DSC analysis of the oligomer that had been hydrolyzed from PHVT-5. Exo up for the heat flow.

2022-05-19

Table S1. An overview of all the experiments with PHVT-5 containing 100mg. The volume is 20 ml in the following reactions.

Nr.	Concentration	Solvent ratio	Temperature (°C)	Time (h)	Yield (%)	Conversion (%)
13	12M HCl	-	30	4	56	73
14	12M HCl	-	40	4	76	79
15	2M HCl	-	40	24	97	45
16	12M HCl	-	40	8	100	81
17	6M HCl	1:1, Water: THF	40	4	90	97
18	12M HCl	-	40	24	91	92
19	12M HCL	-	60	4	94	97
20	12M HCl	-	40	2	95	77
21	12M HCl	-	40	72	84	92
22	3M HCl	1:3, Wat er:THF	40	4	88	97
23	6M HCl	1:1, Water: THF	60	4	94	100
27	1M Acetic acid	1:1, Water: THF	60	30	86	22
28	2M HCL	1:1, Water: THF	60	24	84	100

Table S2. An overview of the experiments with PHVT 5 with 100% conversion

Nr.	Mass (g)	HCl Concentration (M)	Solvent ratio	Temperature (°C)	Time (h)	Yield (%)	Conversion (%)
23	0.1	6	1:1 THF	60	4	94	100
24	0.5	6	1:1 THF	60	4	94	100
25	2	6	1:1 THF	60	4	99	99
26	6	6	1:1 THF	60	4	97	99

Table S3. An overview of all the experiments with Akestra 90. All reactions are with 100 mg Akestra 90 in 20 ml solvent.

Nr.	Concentration	Solvent ratio	Temperature (°C)	Time (h)	Conversion (%)
1	12M HCl		25	24	0
2	1.2M HCl		25	18	0
3	12M HCl		100	24	35
5	2M HCl	1:1, Water:Dioxane	83	24	9
6a	1M Acetic acid		50	72	0
6b	1M Oxalic acid		50	72	0
6c	1M HCl		50	72	0
6d	1M HCl	1:1, Water:Dioxane	50	72	0
6e	1M HCl	1:1, Water:Ethanol	50	72	0
6f	1M HCl	1:1, Water:THF	50	72	0
6g	1M Sulfuric Acid		50	72	0

6h	1M HCl	1:1, Water:Acetone	50	72	0
7	1M HCl		100	24	3
8	6M HCl	1:1, Water:Dioxane	80	24	15
9	6M HCl	1:1, Water:Dioxane	80	72	10

Table S4. An overview of all the experiments with Akestra 110. All reactions are with 100 mg Akestra 110 in 20 ml solvent.

Nr.	HCl Concentration (M)	Solvent ratio	Temperature (°C)	Time (h)	Conversion (%)
10	6		100	24	10
11a	6	1:1, Water:THF	60	23	0
11b	6	1:1, Water:Dioxane	60	23	0
12	6	1:9, Water:THF	25	24	1

Table S5. An overview of the integrals of the peaks in experiments that reacted using PHVT-5, the aromatic peak (H4) is used as a standard = 1.00.

Nr.	H13 (aldehyde)	H11 (acetal)	H6 (ester)	H1 (ester)
PHVT-5	0	0.025	0.042	0.98
23	0.0168	0	0.034	0.95
24	0.0177	0	0.037	0.94
25	0.0185	0	0.039	0.96
26	0.0177	0	0.035	0.94

Table S6. An overview of the integrals of the peaks in experiments that reacted using Akestra-90, the aromatic peak is used as a standard = 4.00.

Nr.	H8 (Aldehyde)	H1	H6	H4	H7c	H5
Akestra-90	0	2.95	0.41	0.84	0.42	2.50
3	0.090	2.91	0.17	0.30	0.14	1.08
5	0.036	2.90	0.35	0.71	0.35	2.31
7	0.010	2.90	0.39	0.81	0.38	2.38
8	0.063	2.56	0.37	0.76	0.41	2.37
9	0.039	2.80	0.35	0.47	0.23	1.10

Table S7. An overview of the integrals of the peaks in experiments using Akestra 110, the aromatic peak is used as a standard = 4.00.

Nr.	H8 (Aldehyde)	H1	H6	H4	H7c	H5
Akestra-110	0	2.06	0.85	1.77	0.89	5.25
10	0.089	1.89	0.78	1.65	0.79	4.64
11a	0.003	2.02	0.85	1.77	0.86	5.21
11b	0.004	2.02	0.85	1.76	0.87	5.22
12	0.007	1.98	0.83	1.78	0.85	5.04

Table S8. The DP and MW of completely hydrolyzed samples calculated by NMR.

Sample	DP	Molecular weight (g/mol)
23	29.7	7371 g/mol
24	28.3	7034 g/mol
25	27.0	6706 g/mol
26	28.2	6994 g/mol

Table S9. An overview of all re-polymerizations.

Nr.	Mass oligomer (mg)	Mass pentaerythritol (mg)	Temperature (°C)	Conversion (%)
RP2	434 (from 24)	11.2	150	76
RP3	163 (from RP2)	5	150	79
RP4	1000 (from 25)	40	155	16