

Synthesis of Bio-Based Polymers

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Abstract

With plastic polymer production at an all-time high and continuing to rise, there is a need for a sustainable alternative to the current petroleum-based plastics that dominate global markets. Bio-derived plastic polymers utilise renewable feedstocks and therefore are not reliant on fossil fuels that in future will suffer from increasingly unreliable supplies as reserves become depleted making this commodity more susceptible to economic and environmental issues that may disrupt supply. This project focuses on the synthesis of sustainably sourced highly cross-linked polyesters via the ring-opening copolymerization reaction between epoxides and cyclic anhydrides. Macaw oil and Baru oil, which can be obtained from Brazilian biomass, have been epoxidized prior to the start of this project. They were copolymerized with cyclic anhydrides that can be bio-derived, to produce eight different highly cross-linked polyester copolymers in a powder form, (yields ranging from 35-67%) four of which were then produced as polymer disks. These polyester powders were then used for end-of-life tests which showed that all powders testing completely decomposed in within 24hours of being soaked in 1M NaOH.

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Acknowledgements and Declaration

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I declare that this thesis is a presentation of original work, and I am the sole author. This work has not previously been presented for an award at this, or any other, University.

All sources are acknowledged as references.

1. Introduction

1.1. Global plastic usage

In 1950 global plastic production was 2 million tonnes a year. In 1985 that figure increased by 4400% as 90 million tonnes of plastic was produced¹. Another 30 years later in 2015, 381 million tons of plastic was produced which is a 76% increase from 1985 and an 18,950% increase from 1950¹. The amount of plastic we produce has continued to increase yearly and we now produce plastics in massive quantities, and we now rely on plastic more than ever. 48 million tons more plastic was produced in 2018² (396 million tons) than in 2017 (348 million tons). It is estimated that between 8% and 10% of the global oil supply annually is consumed in the production of synthetic polymers and that number is forecast to double over the next 20 years².

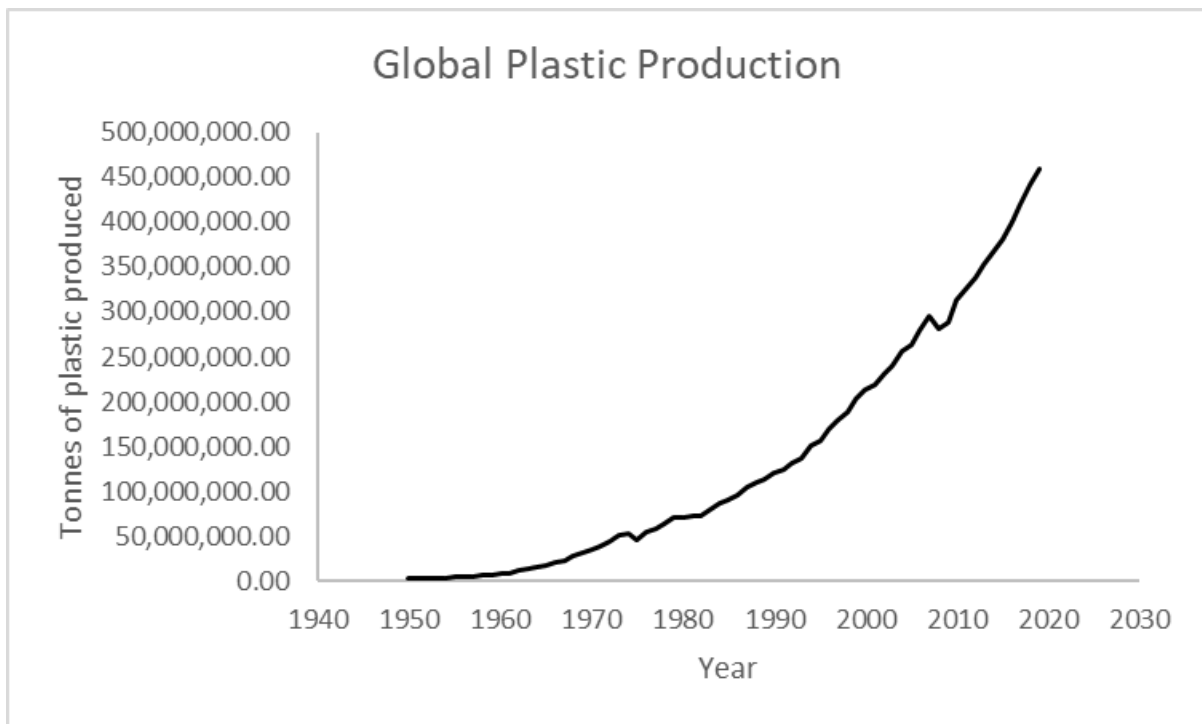


Figure 1- Global plastic production from 1950-2020²

As of 2019, it is estimated that since production began, over 9.5 billion tons of plastic has been produced. This equates to over one tonne for every person alive today².

Plastics continue to be produced in increasingly large quantities as they are economically viable³, (e.g., flexibility, availability, low production costs and lightweight), as well as having physical and chemical properties which allow for a wide variety of applications in household products and industrial sectors. Current plastic production and the life cycle of the most commonly used monomers involved in the production of plastics can be seen as unsustainable both in terms of production and waste management. Monomers such as ethylene, propylene and the large majority of monomers used to make plastics are derived from fossilised hydrocarbons which is a non-renewable source. Additionally, none of these commonly used plastics are biodegradable which ultimately results in these plastics accumulating in landfills or being released into the natural environment, predominately oceans.

1.2. Commonly used Polymers and their applications

Polyethylene (PE), polyurethane (PUR), polystyrene (PS), polyethylene terephthalate (PET), polyvinylchloride (PVC), and polypropylene (PP), are the most produced synthetic polymers and make up 90% of global plastic production.

The current method of producing plastics requires a petrochemical feedstock such as crude oil or natural gas. In the example of crude oil, naphtha which is a mixture of hydrocarbons consisting of five to ten carbon atoms is obtained from the distillation of crude oil³. These larger hydrocarbons such as decane are then broken down into compounds such as propylene, ethylene, and butylene which can then be polymerised to form plastics.

Major constituents in naphtha

Name of the constituents	Percentage by weight
<i>n</i> -Butane	2.85
2-Methylbutane	4.65
2-Methylpentane	2.71
<i>n</i> -Hexane	3.21
Benzene	2.33
<i>n</i> -Heptane	10.45
<i>n</i> -Methylcyclohexane	15.96
<i>n</i> -Methylbenzene	14.43
3-Methylheptane	3.11
3,5-Dimethylcycloheptane	2.13
<i>n</i> -Nonane	4.64
Sulphur	0.04

Table 1 - Major constituents in naphtha by weight³

There is a growing need for sustainable bio-based plastics to allow for a circularised bioeconomy. The currently globally accepted and adopted plastic production method is too reliant on fossil fuels. Not only are fossil fuels a limited resource which inhibits their long-term viability as a feedstock for plastic production, the act of removing fossil fuels from the ground has a significant negative impact on the natural environment and global eco-systems. As a result of this, the need for bio-derived plastic polymers has become more apparent. The

challenge is not only finding a bio-based alternative to plastics, but one that can be produced in massive quantities. This requires a large and sustainable feedstock. One method of synthesising bio-derived plastics is by performing a ring-opening copolymerisation (ROCOP), between epoxides and anhydrides to create polyesters. This project will involve attempting to synthesise highly cross-linked polyesters by reacting novel epoxidized oils obtained from Brazilian biomass with a variety of cyclic anhydrides that can be synthesised from biobased diacids. Once synthesised these cross-linked polymers will be characterised to find potential applications. The design and synthesis of high-performance and recyclable cross-linked polymers from bio-based sources has previously been reported²¹. The materials exhibit excellent properties with high stiffness, strength and toughness, and can be easily thermally reshaped and re-mended.

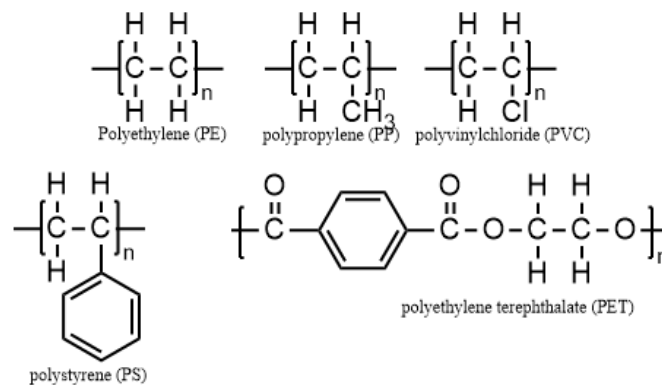


Figure 2 - Commonly used polymers in industry

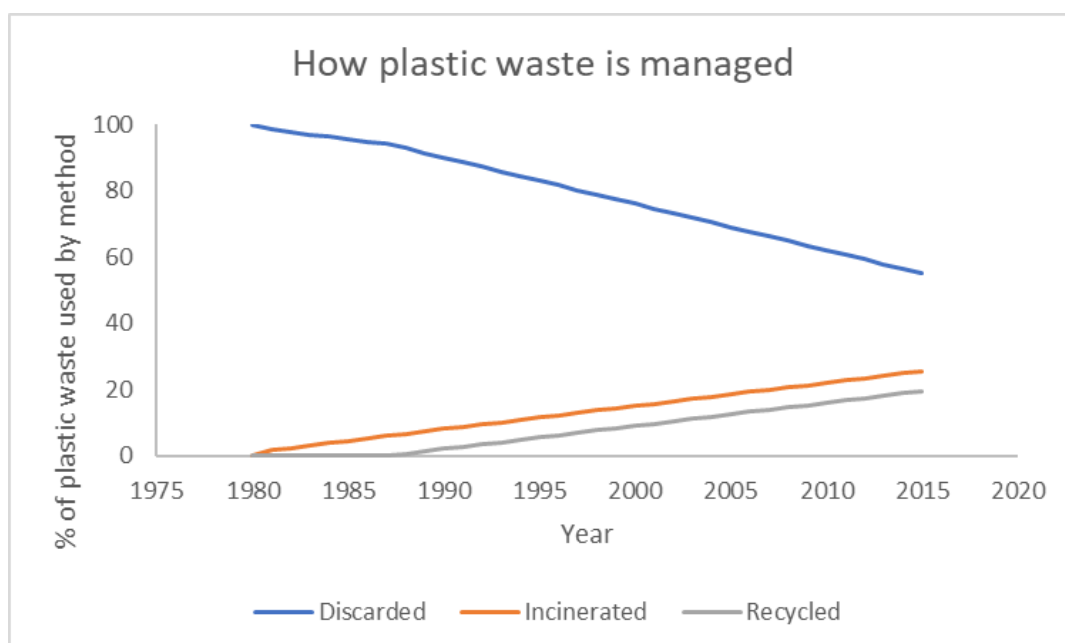
1.3. Issues with commonly used polymers

Commonly used polymers have issues with not just production, but with waste management and their end of life. Firstly, the obvious problem is that the feedstock used for the production of the most common polymers is crude oil. With a finite amount of crude oil being available, it is not possible for a polymer to be synthesised from this feedstock in any form of sustainable production. Whilst there is still a dispute regarding the quantity of crude oil still available for consumption in human activities, one truth is unavoidable. It will not be possible for us in the long term to continue to produce polymers and other goods in the quantities that are demanded without sourcing a viable, renewable feedstock.

Secondly, the quantity of plastic polymers derived from crude oil that is eventually disposed of in the world oceans is ever increasing. In excess of 10 million tonnes of plastic enter the oceans each year⁴, therefore it is no surprise that islands of waste plastic can be found with over a quarter million tons of discarded plastic. This number becomes easier to explain when the amounts are broken down. In 2010, 99.5 million tonnes⁴ of plastic waste was generated in the areas most at risk of having plastic entering the ocean, these are regions within 50 kilometres of the nearest coastline. Considering that over 2 billion people on our planet live within 50 kilometres of a coastline, it is no surprise that such a large quantity of plastic waste is produced so close to the planet's oceans. Not all 99.5 million tons of plastic waste produced within 50 kilometres of a coastline would enter the ocean⁴. However, the plastic waste that is mismanaged has a more significant risk of being leaked/released into the environment and

in 2010 that amounted to 31.9 million tons of plastic waste⁴. Of this mismanaged 31.9 million tons, eventually 8 million tons of plastic waste entered the oceans through a variety of outlets, including rivers. That means that in 2010, 3% of global annual plastic waste eventually made its way into the planet's oceans⁴.

Our methods of plastic waste disposal have changed over time with an ever-growing importance placed upon recycling. The three common current fates of plastic at a products end of life are, incineration, recycling and being discarded (including to landfill). Recycling and incineration made negligible contributions to the management of plastic waste before 1980 as 100% was discarded⁴. Since 1980 for incineration, and 1990 for recycling, contributions towards management of plastic waste have continuously increased on average by 0.7% per year⁴. In 2015 it is estimated that 20% of annual waste plastic was recycled with incineration accounting for 25% of waste plastic disposal. Despite continuous improvements for over 35 years, in 2015, 55% of plastic waste was discarded⁴. With such large quantities being discarded, the possibility of waste being mismanaged and finding its way into the planet's ocean is an ever present issue. However, if you extrapolate historical trends, it is plausible that by the year 2050, discarded waste would fall to just 6%. Recycling would account for 44% of plastic waste and incineration making up the remaining 50%⁴. It is worth noting that this is based on simple extrapolation of historical trends and governments all



around the globe aim to drastically reduce the amount of plastic waste discarded at much sooner dates.

1.4. Bio-derived polymers

Figure 3 - How plastic waste is managed⁴

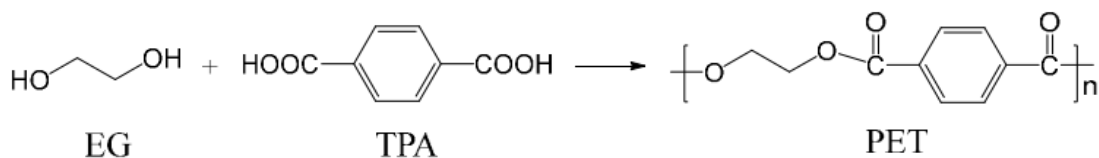
Historically, the vast majority of synthetic polymers are formulated with the use of fossil fuel feedstocks. Over the past 20 years there has been growing interest in the synthesis of bio-derived polymers as a promising and sustainable alternative to oil-based polymers⁵. Not only would these bio-derived polymers have the benefit of not relying on a limited source for their production. They could be extremely beneficial to the economies of countries that import most of their oil but have access to massive amounts of biomass e.g., Brazil.

When attempting to classify bio-based polymers it is important to note that although there are numerous sources and production methods, bio-based polymers can be sorted into three major groups⁵:

1. Polymers that are directly obtained from biomass source. E.g., Cellulose, starch, chitosan, and alginates.

2. Polymers that are structurally the same as their oil-based counterpart but have been synthesised using bio-derived monomers. E.g., Braskem's bio-based polyethylene (PE), which can be produced via the fermentation of sugar cane to ethanol, dehydration to ethene and then standard polymerisation to PE. Currently Braskem have a capacity of >200kT per annum for bio-based PE.
3. Polymers that have been bio-synthesized using plants and/or microorganisms or have been prepared directly from monomers that are typically bio-synthesized. E.g., polylactic acid (PLA) and polyhydroxyalkanoates (PHAs)⁶.

Bio-derived polymers can already be found in products that millions of people use every day. For example, in 2009, Coca-Cola started selling their soft drinks in plastic bottles that were produced with partially plant-based materials (via bio-based ethylene glycol, the terephthalate portion is still derived from petrochemical sources)⁶. Only 6 years later in 2015 the company announced they would be capable of producing bottles made up of plastic that was formulated using only renewable sources. In this example, the polymer was one of the most common globally. Coca-Cola was able to synthesis polyethylene terephthalate (PET), by polymerising ethylene glycol (EG) along with terephthalic acid (TPA), via an esterification reaction⁶.



Scheme 1 - Esterification reaction between ethylene glycol (EG) and terephthalic acid (TPA) to form polyethylene terephthalate (PET)

Bio-derived polymers have numerous advantages over their fossil fuel-based counterparts. The main advantage being that they are derived from a renewable source meaning in theory production could continue as long as the chosen feedstocks had the required availability to meet production demands. A further advantage of these polymers is that many tend to be biodegradable. This adds a lot of flexibility to the issue of waste management which is one of the main flaws of oil-based polymers, as discussed in the previous section. Although there are many advantages to bio-derived polymers when compared to those produced from fossil fuels. There are some disadvantages that must be discussed. The primary issue is the cost and time necessary in order for bio-derived polymers to become a viable marketable alternative to the current commonly used polymers. Further research is required for sustainable polymers to meet the polymer properties possessed by already established polymers such as PET or PVC⁵. Another issue is availability of feedstock. As discussed earlier we already produce over 400 million tonnes of plastic every year and with this number continuously growing, it is a massive challenge to find sustainable sourced polymers that can meet these demands year on year. Whilst research into and demand for bio-derived polymers is gradually increasing, they still only make up about 1% of all plastics on the global market⁵.

1.5. Polyesters

Polyesters, (general structure shown below), are extremely important and common polymers that vary widely in structure as well as function. Polyesters contain an ester function group in their backbone, they can be synthesized but also occur naturally⁷.

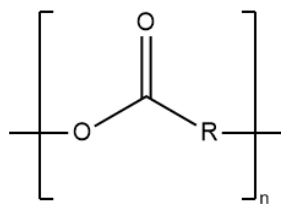


Figure 4 - General polyester structure

They can also be aliphatic, aromatic, or semi-aromatic depending on their backbone structure⁷, (below is an example of an aromatic polyester (PET) and an aliphatic polyester (polycaprolactone). In general, aromaticity in polyesters results in enhanced thermal stability, mechanical strength, chemical stability, and a more pronounced glass transition temperature (T_g)⁸.

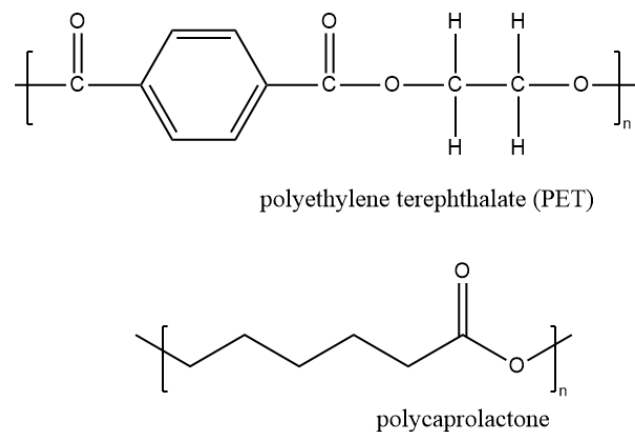


Figure 5 - Structures of an aromatic polyester (polyethylene terephthalate) and an aliphatic polyester (polycaprolactone)

One difference between natural and synthetic polyesters is that natural polyesters tend to be biodegradable, whereas synthetic polyesters are usually nonbiodegradable⁹. Although, this is not always the case. For example, bacteria are capable of producing poly(thioesters) that are non-degradable, whilst polycaprolactone is synthetic yet highly degradable.

One factor that makes polyesters so important as polymers is that they may be thermoplastic and thermoset polymers¹⁰. The key difference between a thermoplastic and thermoset polymer is in how the materials behave during the curing process. A thermoset polymer will form strong irreversible bonds during the curing process which results in thermoset polymers being set in a permanent physical and chemical composition once the first curing process is complete. The reason for this is that the polymers in the material will form strong bonds known as a 'cross-link'. This feature of thermoset polymers makes them ideal for applications that

require high stability, especially at elevated temperatures¹⁰. Thermoplastics on the other hand are re-mouldable and therefore recyclable due to the fact that they do not form strong chemical bonds between chains during synthesis and processing, allowing the polymer to melt and be moulded into new shapes¹⁰.

The most common polyester is polyethylene terephthalate (PET) with approximately 40 million tonnes produced annually worldwide⁴. Polyesters such as PET are typically produced using a dicarboxylic acid and a diol. PET can be synthesised by the step-growth polymerisation of the acid benzene-1,4-dicarboxylic acid, (more commonly known as terephthalic acid), and the alcohol ethane-1,2-diol (also referred to as ethylene glycol). Being an aromatic polyester, PET benefits from enhanced strength and stiffness due to the presence of benzene rings in the repeating units. The benefits relating to strength and stiffness are even greater when the polymer chains are aligned with one another in an orderly arrangement to give a semicrystalline form¹⁰ (i.e. containing both crystalline and amorphous regions to the polymer sample).

1.6. Bio-derived polyesters

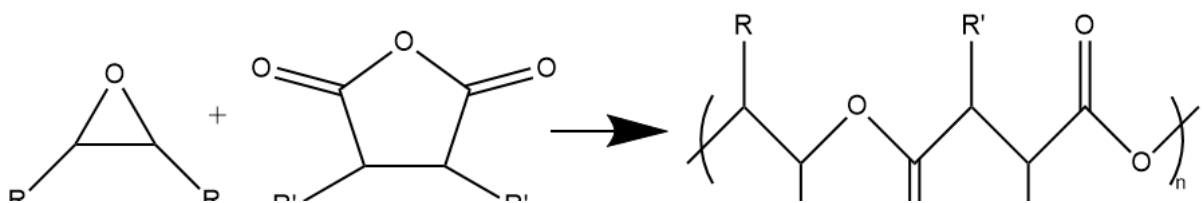
Synthesis of polymers from renewable feedstocks/resources has continued to become a major concern of academia as global resources, energy and the environment face huge challenges. Over recent years, bio-derived polymers have become an increasingly viable alternative to the conventional petroleum-based polymer industry¹¹. As polyesters are very versatile polymers with a wide range of applications including, plastics, fibres, coatings, elastomers, plasticizers, etc. It is no surprise that the desire for these crucial polymers to remain available for future use, has resulted in growing interest around the development of bio-derived polyesters¹². The continuous development in the synthesis of bio-derived

monomers is closely connected to the development of bio-derived polyesters. The development of bio-derived monomers used for producing bio-derived polyesters not only allows for the sustainable synthesis of conventional petroleum-based polyesters, including, PET, poly(butylene succinate (PBS), and poly(propylene terephthalate) (PTT or PPT), but also offer new insights into the production and development of new polyesters, such as poly(ethylene 2,5-furandicarboxylate) (PEF), and polylactic acid (PLA)¹³. Bio-derived monomers have also allowed for the production of a series of partly and fully bio-derived copolyesters prepared from bio-derived monomers by copolymerisation¹³.

Although there has been growing interest in the development and production of bio-derived polyesters, the market is still dominated by petroleum-based competitors. An example of this can be seen when looking at polyester in the textile industry. Polyesters, typically PET, make up a huge market share in the textile industry accounting for more than 75% of all synthetic fibres¹⁴. In order to reduce the industry's reliance on petroleum-based polyesters, bio-derived polyesters have been pushed and marketed as a more sustainable alternative. Despite this, bio-derived polyesters still only account for less than 1% of total polyester production¹⁴.

1.7. Ring-Opening Copolymerization (ROCOP)

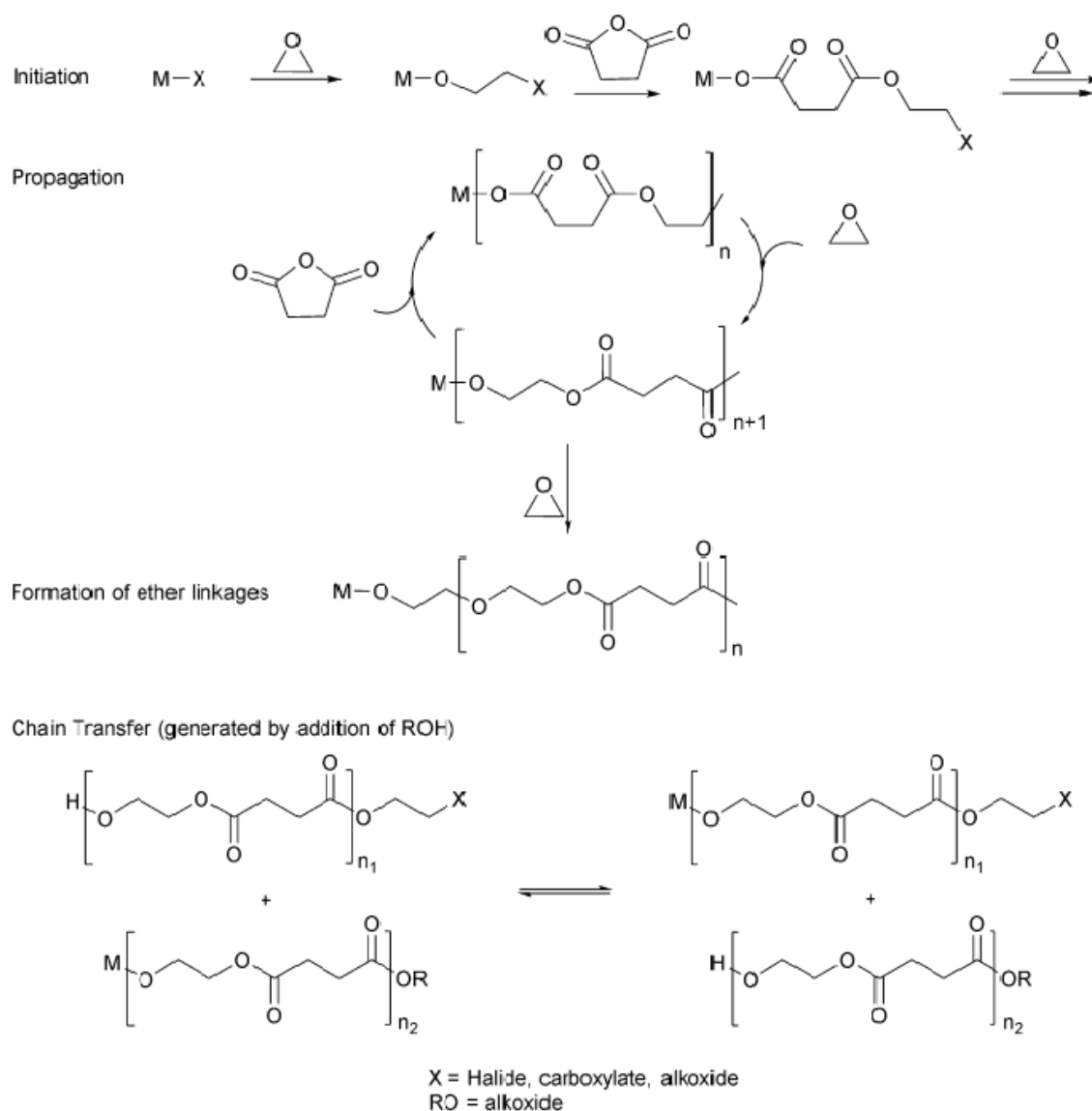
Polyesters and polycarbonates can be synthesised via a ring-opening copolymerization (ROCOP) reaction. For the purpose of this project, it is most relevant to consider a ring-opening copolymerisation of epoxides and cyclic anhydrides, yielding polyesters. These



reactions require the use of an initiator (also referred to as a catalyst), which is a species that is generally a single site metal complex of the form LMX, where L is an ancillary ligand, M is the metal site upon which catalysis occurs and, X is the initiating group and site at which propagation occurs¹⁵.

A reaction between the MX initiator and the monomers occurs during the initiation step of the reaction to generate a metal alkoxide-carboxylate intermediate. For these reactions, the initiating group tends to be an alkoxide, carboxylate, or halide group which becomes one of the chain end groups during controlled polymerization. The sequential formation of carboxylate and metal-alkoxide intermediates occurs as monomers are sequentially enchaind during the propagation of the reaction¹⁶. The resulting metal alkoxide intermediate then attacks the cyclic anhydride to generate a metal carboxylate intermediate which will then attack and ring-open the epoxide co-monomer, regenerating the metal alkoxide. For these polymerization reactions, an additional factor to consider is chain transfer, which are reactions in which the growing polymer chain can equilibrate due to the presence of added protic compounds, such as alcohols¹⁶. A beneficial consequence of chain transfer reactions is that they can be used to manipulate selectivity for a polymer end group. Finally, the termination of polymerization can be achieved in numerous ways. This is usually done by manipulating the reaction conditions, for example, reducing temperature, adding water or an acid, or removing the one of the co-monomers. Termination can also occur when the polymer chains reach a length that causes the reaction mixture to solidify therefore preventing any further collisions necessary for the reaction to continue. There are multiple catalysts that are viable options for this ROCOP reaction but there are some key parameters to consider. One is selectivity, this could be the case when attempting to control the molar mass by selecting the end groups resulting from chain transfer reactions or control of regio- and stereo-

chemistry during monomer enchainment¹⁶. Two more key parameters to consider are, the productivity of the catalyst (this can be measured by its turn-over number, TON), and the activity (determined as turn over frequency, TOF). TON and TOF are especially important factors to consider when selecting catalysts whilst attempting to optimise a reaction in context of sustainable chemistry¹⁷.



Scheme 3 - Formation of polyesters from the reaction between epoxides and cyclic anhydrides with the use of an MX initiator¹⁵

1.8. Sustainable Chemistry

Sustainable or green chemistry is a practise that is growing rapidly due to recognition that environmentally friendly products and processes will be economically desirable in the long term. The most crucial goals of sustainable chemistry are to reduce the adverse consequences of the substances that we use and generate as well as the processes used to make them¹⁸.

At the top of the list of fundamental changes that must occur as we pursue more sustainable practices is the necessity to shift from production that predominantly relies on the use of fossil fuels and petroleum-based compounds and towards more sustainable synthetic methods and processes that utilise renewable sources such as biomass¹⁸. Whilst predictions around the exact date that we will deplete our fossil fuels reserves are always met with scepticism, the ever changing political as well as economic landscape resulting in limited access and rising cost should only lead to an acceleration in the move towards renewable materials sooner rather than later. Use of renewable feedstocks is just one of the fundamental principles of green chemistry put forward by Paul Anastas and John Warner in 1998, when they headed the green chemistry programme at the EPA (US Environmental Protection Agency). Although these were not the first stirrings of green chemistry, they do present the coalescence of green chemistry as a defined discipline. By incorporating the twelve principles of green chemistry put forward by Paul Anastas and John Warner into research

practices, it is possible to move towards the creation of more sustainable synthetic methods and processes.

The twelve principles of green chemistry are:

1. Prevent waste – Prevention is better than cure and avoided waste doesn't need to be cleaned up.
2. Atom Economy – This is concerned with what percentage of the atoms that are put into a reaction eventually end up in the desired product.
3. Less hazardous chemical synthesis – Consider whether less toxic or environmentally hazardous reagents can be used when designing a reaction.
4. Design safer chemicals – Try to make the desired products you're attempting to synthesis as benign as possible.
5. Safer solvents and auxiliaries - Decide whether a solvent is completely necessary or if it's possible for the reaction to run dry and if a solvent is required, utilise the safest one possible.
6. Design for energy efficiency – Is it possible to use less energy by altering the reaction time, temperature, or pressure.
7. Use of renewable feedstocks – opt for bio-based substrates over petroleum-based.
8. Reduce derivatives – Minimise the number of steps required to reach the target molecule to reduce energy use and waste produced.
9. Catalysis – catalysts are often more efficient than a stoichiometric reagent that generates waste and re-usable catalysts are highly beneficial.

10. Design for degradation – Ideally products should be designed to break down into innocuous molecules that don't have negative effects on the environment
11. Real-time analysis for pollution prevention – Most relevant for industrial practises.
12. Safer chemistry for accident prevention – choose chemical routes to minimise risk.

These twelve principles can be further condensed into four groups:

1. (Atom) Efficiency – Minimise wasted atoms and extra steps. Consider, do you need a solvent? Can you do it without a protecting group? Can you avoid using solvents or silica for purification?
2. Safety – Make sure the processes, chemicals and products are as inherently safe as possible. This encompasses environmental hazards, toxicity (both to humans and otherwise) and physical hazards such as fires and explosions.
3. Climate Change and Resources – Renewable resources and feedstocks are always preferable as they avoid depletion of natural resources. Optimise energy use to reduce carbon footprint by considering reaction time, temperature, and pressure.
4. End-of-Life/ Pollution – Monitor industrial processes as they are occurring to prevent mishaps leading to pollution. Design chemical products to be benign in the environmental and to degrade into innocuous products.

At its core sustainable chemistry concerns the design and improvement of chemical processes and products to minimise their adverse impacts on health and the environment, as well as minimising the consumption of depleting resources.

1.9. This project

This project aims to make progress towards the development of sustainably sourced polymers by producing a series of highly cross-linked polyesters via a ring-opening copolymerization reaction. In prior work, two oils, (macaw oil **1** & baru oil **2**), which can be obtained from Brazilian biomass have been epoxidized. macaw oil and baru oil are similar in structure with the only difference being that macaw oil contains an average of four double bonds per molecule, whereas baru oil contains an average of three and a half double bonds per molecule. Subsequently, this means that the corresponding epoxidized oils have different numbers of epoxides, (MO=4, BO=3.5)¹⁹,

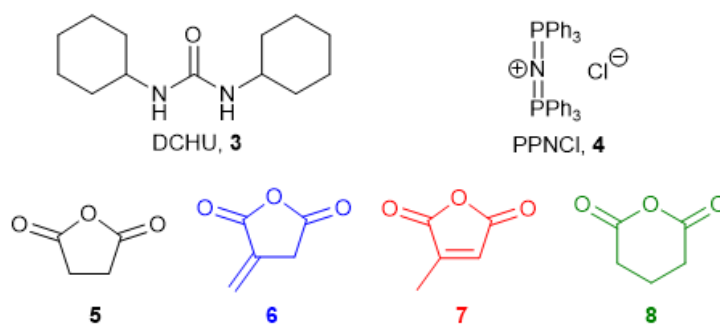


Figure 6 - structure of initiators, *N,N'*-dicyclohexylurea (**3**) and bis(triphenylphosphorylidene)ammoniumchloride (**4**), with bio-derived cyclic anhydrides, succinic anhydride (**5**), itaconic anhydride (**6**), citraconic anhydride (**7**), and glutaric anhydride (**8**)

which in turn means that the two oils are able to undergo different amounts of ROCOP reactions to form polyester chains when reacted with cyclic anhydrides using *N,N'*-dicyclohexylurea (DCHU) **3** and bis(triphenylphosphorylidene)ammoniumchloride (PPNCI) **4**

as catalysts. This project focuses on four cyclic anhydrides as the comonomer for the ROCOP reaction, succinic anhydride **5**, itaconic anhydride **6**, citraconic anhydride **7**, and glutaric anhydride **8**, all of which can be synthesised from renewable feedstocks.

2. Results and Discussion

2.1. Comparison of different anhydrides with macaw oil and baru oil

The focus of this project has been synthesising a series of highly cross-linked polyesters intended for potential applications in coatings. The method being followed is for a ring opening copolymerisation reaction between an epoxide and an anhydride. The epoxide being used has been either epoxidized macaw oil, which contains an average of four epoxides per molecule. As well as baru oil, which contains an average of 3.5 epoxides per molecule. For the anhydride, a variety of cyclic anhydrides that can be synthesised from bio-based sources have been used.

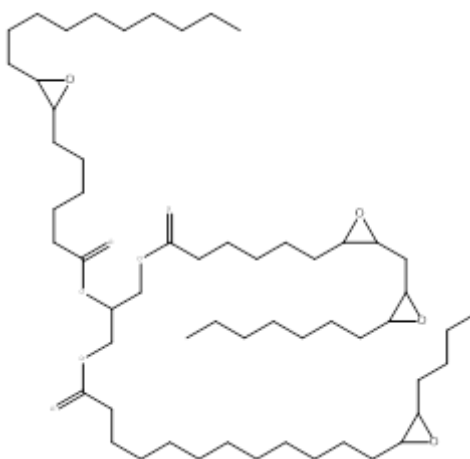


Figure 7 - Structure of epoxidised macaw oil

For each copolymer, an STA, IR, solid state NMR, and a DSC trace was collected for analysis and characterisation.

Oil (Epoxide)	Anhydride	Yield (%)
Macaw	Succinic	67
Macaw	Itaconic	61
Macaw	Citraconic	59
Macaw	Glutaric	46
Baru	Succinic	35
Baru	Itaconic	54
Baru	Citraconic	59
Baru	Glutaric	46

Table 2 - Reaction yields of various epoxidised oil and cyclic anhydride combinations. (Reaction conditions in section 3.1.)

The original reaction time of 18 hours, used for most of the syntheses with macaw oil was selected due to the viscosity of the reaction. Typically, after 18 hours the reaction mixture forms a single pellet, and the stirrer bar becomes unable to move. It was therefore believed that the yield of the reaction could be limited by its viscosity. However, it was also found that yields improved slightly when the reaction was left for an additional 4 hours despite the fact that the reaction mixture had now become a solid pellet. It is therefore more likely that viscosity is not what limits the yield. It is more likely that the yield of the reaction is limited by the accessibility of epoxide groups once the cross-linking process has begun and they become less accessible. This can be investigated using CHN analysis and comparing the results against a theoretical set which changes based on how many epoxides on average are opened during the reaction.

2.2 Macaw Oil w. Succinic Anhydride data: STA

During this project, STA was initially used as a way of estimating the purity of a compound which will be discussed in more detail in the purification section. One thing that has been shown by these traces is that changing the oil (and therefore the number of epoxides) does not seem to cause much of a difference to the properties of the polymer. This further suggests that the limiter of the reaction is indeed the accessibility with the epoxide groups once the cross-linking has begun. An overlay of all the epoxide + anhydride copolymers STAs, (which can be seen below), shows a very similar trace for all the synthesised polyesters which suggests that all samples contain minimum impurities which tends to be unreacted anhydride that gets trapped in the cross-linked polymer chains. This unreacted anhydride can later be removed by adding a purification step into the production of these polymers and this purification process will be discussed in a future section (2.4. Purification)

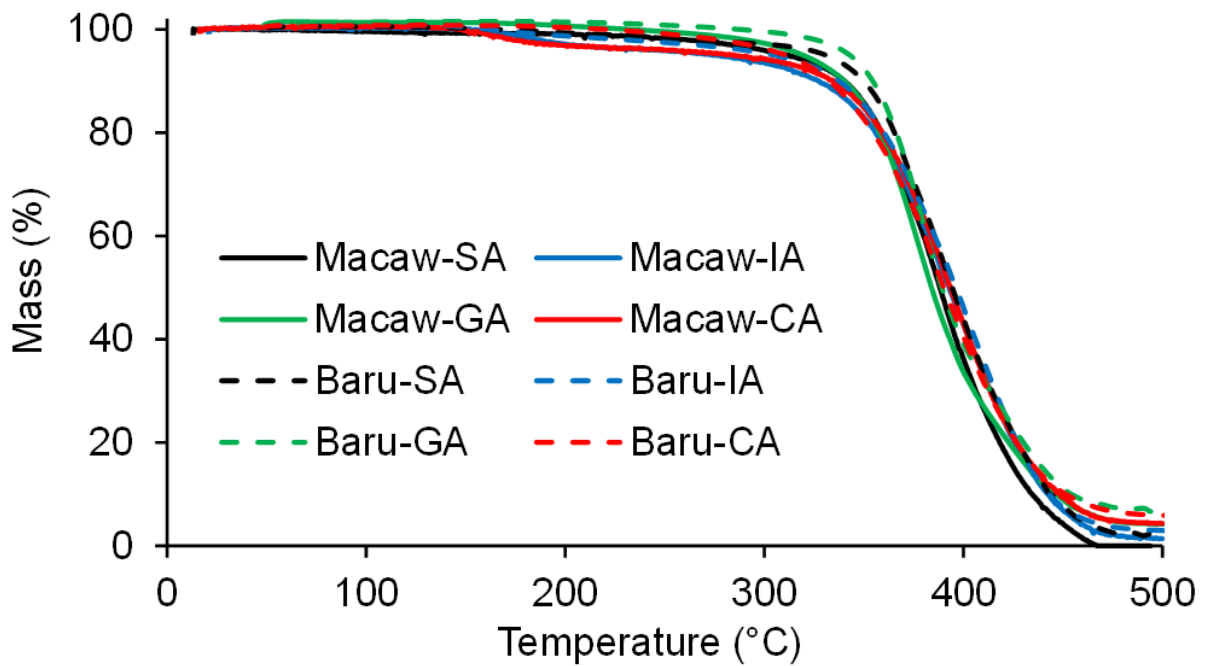


Figure 8 - Overlay of the 8 powdered polymers TGA traces

2.3. DSC

A DSC trace can be useful in finding or ruling out potential applications. In the example above, which is from a macaw oil w. succinic anhydride sample, the glass transition temperature (T_g) is -4.95°C . So far, all the samples tested have had a glass transition temperature that falls between -10°C and 0°C . This is useful information as it limits potential applications. For example, the glass transition temperature is too low for any of these polymers to have an application in food storage products that need to be frozen since if these compounds were in a freezer the low temperature would mean they would move below the T_g and would enter the glass phase meaning they would shatter if they were to be dropped.

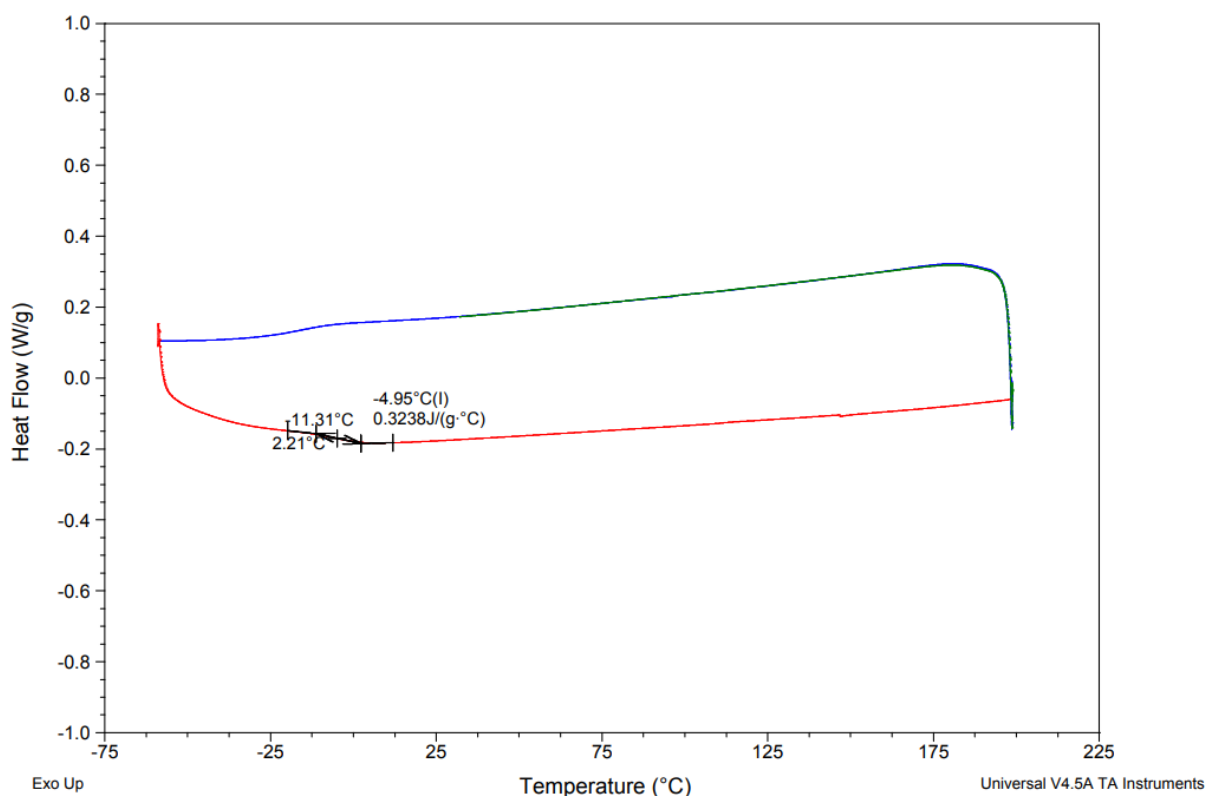


Figure 9 - DSC trace of MO-SA powdered polymer

The difference in glass transition temperature when using different anhydrides seems to be negligible which indicates that the physical properties are mainly determined by the oil (epoxide) which would be expected as it makes up the large majority of the overall mass.

2.4 Purification

One issue faced with when synthesising and characterising this group of bio-based copolymers was purity. When looking at the STA trace of these compounds initially it was clear to see that instead of having a smooth and continuous curve, there would be a small step where mass was lost before the thermal stability of the polymer should come into question. It was hypothesised that this small step could be due to excess anhydride remaining in the compound. To test this, hypothesise, STAs of the polymers were compared to the STAs of the corresponding anhydride.

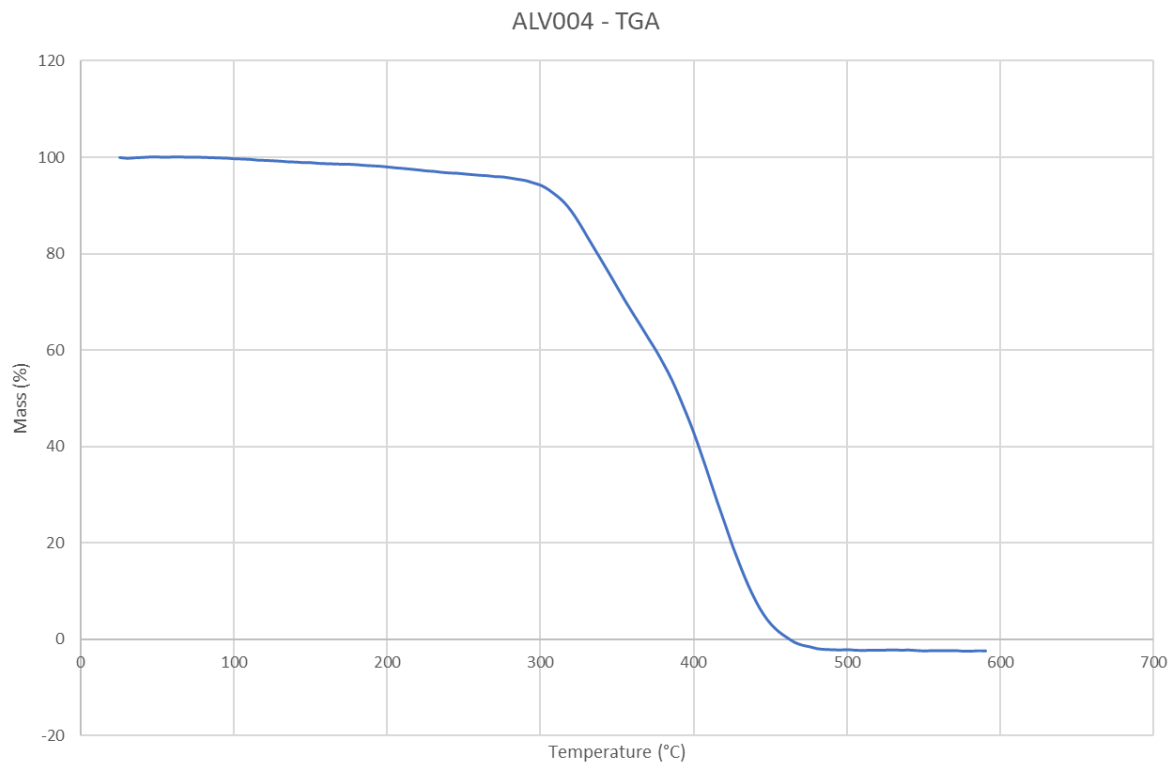


Figure 10 - TGA trace of MO-SA powdered polymer with remaining excess succinic anhydride

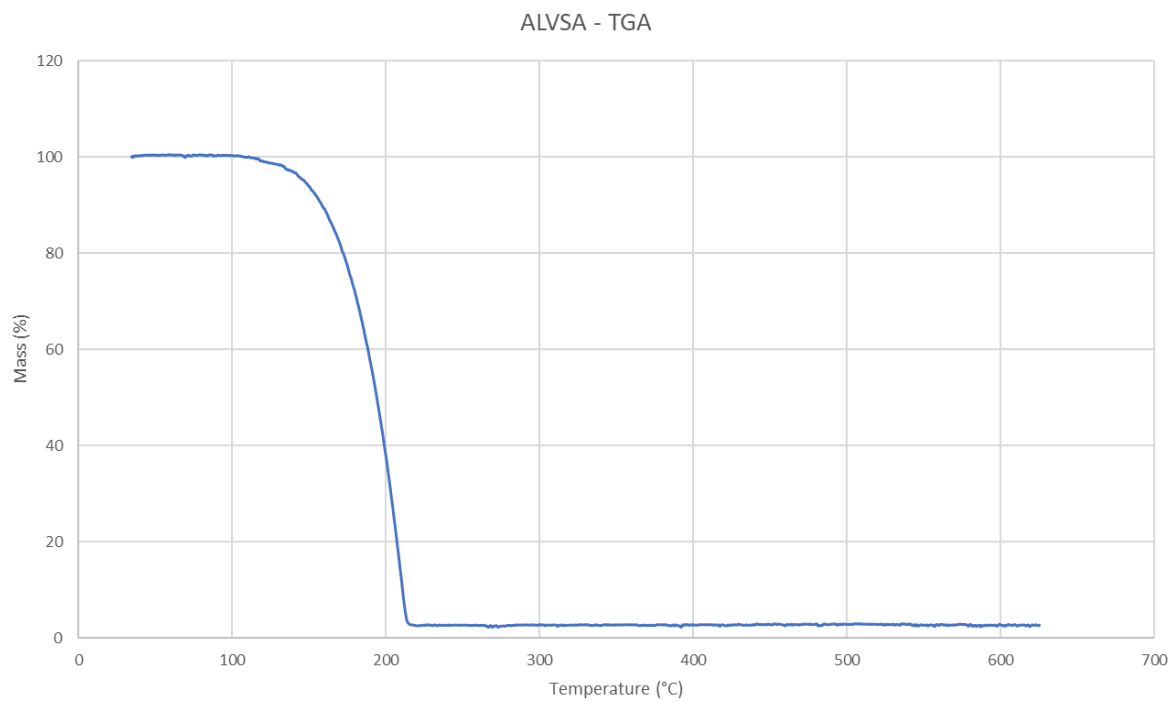


Figure 11 - TGA trace of succinic anhydride

As shown on the graph (ALV004 – TGA), which was synthesised using macaw oil and succinic anhydride as copolymers. An initial mass loss occurs just before the sample reached 200°C. This was believed to be due to excess anhydride and as shown in the second graph (ALVSA – TGA) which is the STA trace for succinic anhydride. Succinic anhydride loses around 60% of its mass at 200°C, predominantly by sublimation. The comparison of the two STA traces therefore suggests the hypothesis stating that the mass loss caused by an impurity could be excess anhydride was indeed correct.

The presence of excess anhydride was also confirmed by mass spectroscopy.

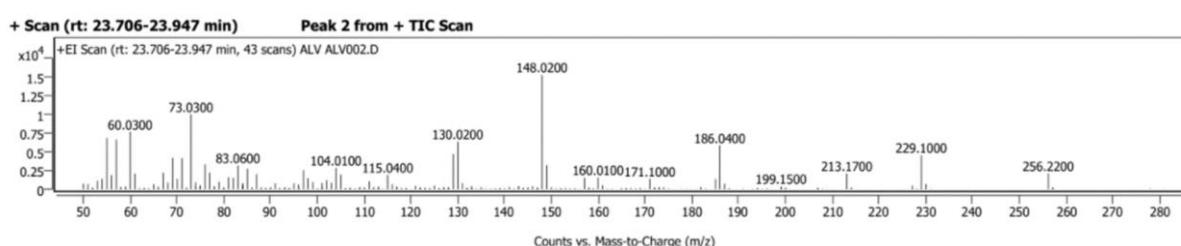


Figure 12 - Mass spectroscopy of MO-SA (ALV004) showing signs of excess succinic anhydride

The mass spectrum above was collected using a sample of macaw oil and phthalic anhydride as co-polymers. The STA trace of this sample showed a similar pattern to that of ALV004 (macaw oil + phthalic anhydride) which contained an excess of anhydride (succinic). As shown above, the most significant peak comes at 148 (m/z) which is also the relative molecular mass of phthalic anhydride. Therefore, the MS of this sample also suggests that mass loss seen before 200°C in STA traces of these co-polymers is a result of excess unreacted anhydride.

After concluding that the impurities in the compounds were from excess starting material (anhydride), the next step was to find a way to purify the copolymers. Due to the texture of

the compounds, it was clear that they would need to be insolvent for a prolonged period for the excess anhydride to be accessed and removed. From this, it was decided that a Soxhlet extraction may be the most appropriate method. To determine which solvent would be best suited for use in the Soxhlet extraction, a compound (MO-SA, ALV007) that was known to have excess anhydride remaining in it was separated into four 1g samples that would each undergo a Soxhlet extraction with a different solvent. The start and end mass were recorded to compare mass loss between compounds as a percentage difference.

Solvent	Start Mass	End Mass	% Difference	Time
DCM	1.0185g	0.8472g	-16.8%	18hrs
EtOAc	1.0145g	0.8968g	-11.6%	18hrs
EtOH	1.0131g	0.8804g	-13.1%	18hrs
THF	1.0251g	0.8969g	-12.5%	18hrs

Table 3 - Mass loss of sample ALV004 (MO-SA) in various solvents

As shown in the table above, DCM was the solvent that in 18 hours caused the biggest mass change due to excess anhydride being extracted and was therefore used for future Soxhlet extractions. Subsequent STAs of compounds that had been through a Soxhlet extraction still

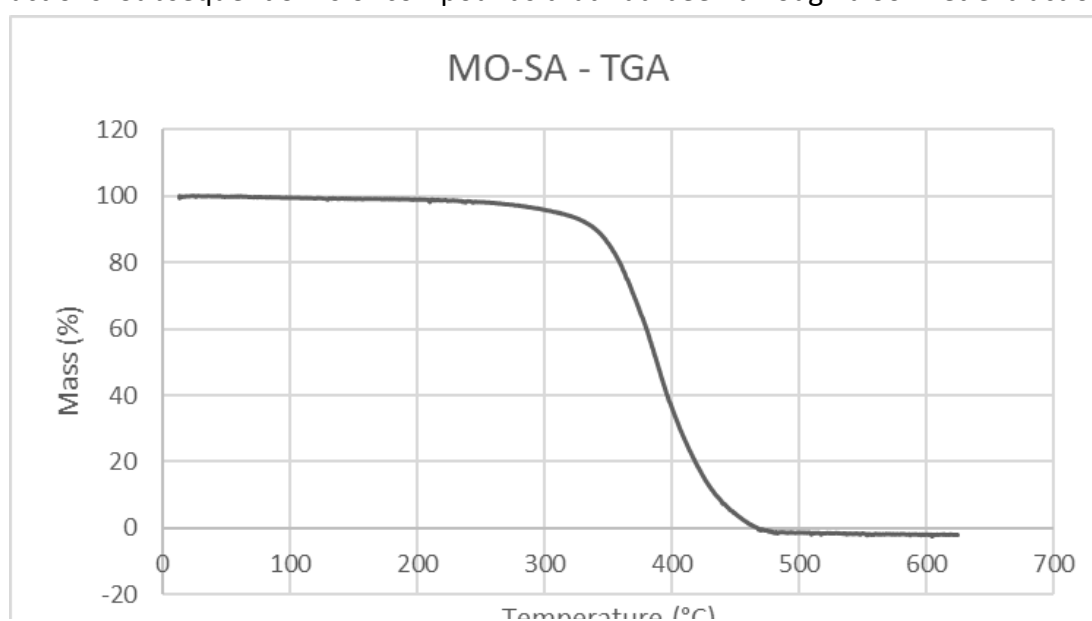


Figure 13 - TGA trace of MO-SA after removal of excess succinic anhydride

showed small amount of excess anhydride remaining. It was then decided to mash up the compound with a pestle and mortar after one Soxhlet extraction to free any trapped anhydride in the compound before starting a second extraction. By using this method of two consecutive Soxhlet extractions with DCM, STA traces were obtained which suggested that the excess anhydride was successfully removed.

The graph above was produced using the sample copolymers (macaw oil and succinic anhydride) as ALV004. The noticeable difference is that no significant mass loss occurs before 200°C as there is no longer enough anhydride remaining to cause the mass loss at 200°C.

2.5. Physical properties

A further thing to investigate would be exploring the possibility of synthesising a compound which is capable of being subjected to tensile strength tests. Although there have been polymer disks produced and had their hardest tested for all the macaw oil, anhydride combinations. So far it has not been possible to produce a polymer disk that is large enough for a sample to be cut out that is large enough for tensile strength testing. However, one physical property that has been measured is hardness. This test was done on polymer disks (3cm in diameter) that were produced using the method described in section 3.1 (general polymerisation procedure). All four epoxidized macaw oil, cyclic anhydride combinations had a Shore A hardness value of between 63 and 80 when used for impact testing. For reference, that means these disks has a medium hardness, similar to that of a tyre tread (70) or a shoe heel (80).

Epoxidized oil	Cyclic anhydride	Shore A hardness
Macaw	Succinic	63
Macaw	Itaconic	70
Macaw	Citraconic	72
Macaw	Glutaric	80

Table 4 - Shore A hardness results for different macaw oil + cyclic anhydride combinations

2.6. Comparison of solution state ^{13}C NMR and solid-state ^{13}C NMR

All eight polymer powders were also analysed by solid-state ^{13}C NMR spectroscopy. The two epoxidised oils were able to be analysed by solution state ^{13}C NMR. The polymer powders, however, were analysed using solid-state ^{13}C , as they are insoluble and are therefore not viable for solution state ^{13}C NMR. Figure 14 (shown below) shows a comparison of the solution state epoxidised macaw oil and the solid-state ^{13}C NMR spectrum of polymer MO-SA, (derived from macaw oil and succinic anhydride). The peaks between 10 and 35 ppm in both spectra correspond to the aliphatic chains of the epoxidised macaw oil and show that the oil has remained intact during the thermal polymerisation. Ester carbonyl peaks are also clearly visible at 170-180 ppm in both spectra. The most significant difference between the two spectra is in the 50-90 ppm range. In the spectrum of epoxidised macaw oil, a series of signals corresponding to C-O groups are present. Those in the range 50- 60 ppm can be assigned to carbons within epoxide rings, whilst the two signals between 60 and 70 ppm correspond to the esterified glycerol carbons. In the spectrum of polymer MO-SA, the epoxide carbons are clearly absent, showing that the polymerisation has gone to completion. Additionally, a broadened ester C-O signal is present at 70-90 ppm,

corresponding to both the glycerol esters and the newly formed esters arising from reaction of the epoxides with succinic anhydride.

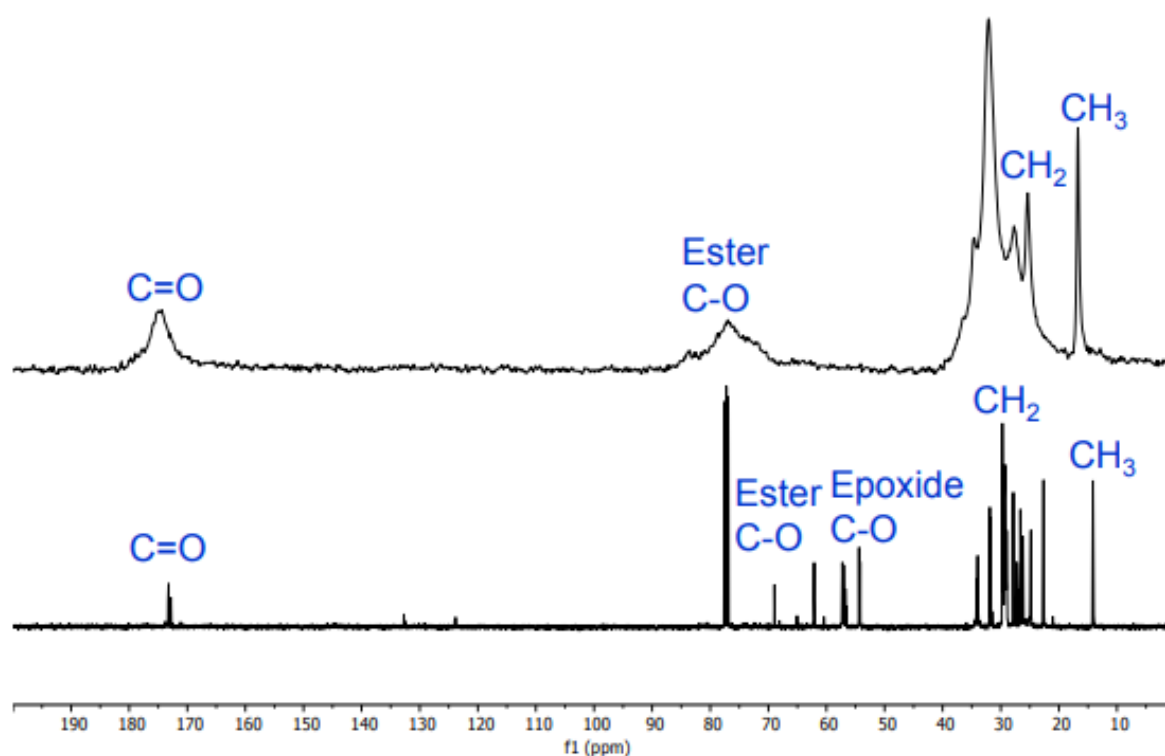


Figure 14 - Comparison of the ^{13}C NMR spectra of epoxidised macaw (bottom) and MO-SA polyester (top)

Whilst all eight polymer powders displayed very similar solid state ^{13}C NMR spectra (data appendices), there were subtle differences between the spectra. These subtle differences are illustrated in the 60–200 ppm expansions of the polymer powders produced using macaw oil (shown in Figure 15). Polymers MO-SA and MO-GA, derived from unfunctionalised anhydrides (succinic anhydride and glutaric anhydride), displayed almost identical spectra, however the C=O peak of polymer MO-GA was broader than that of polymer MO-SA. The spectra of polymers MO-IA and MO-CA derived from α,β -unsaturated anhydrides (itaconic and

citraconic), both showed an additional C=O peak at 165–170 ppm, corresponding to a conjugated carbonyl system. This was further supported by the presence of conjugated alkene signals between 120 and 155 ppm. It is known that itaconic and citraconic groups can equilibrate under thermal conditions, which accounts for both the complexity of the alkene region of the spectra of polymers MO-IA and MO-CA, and their similarity²⁰.

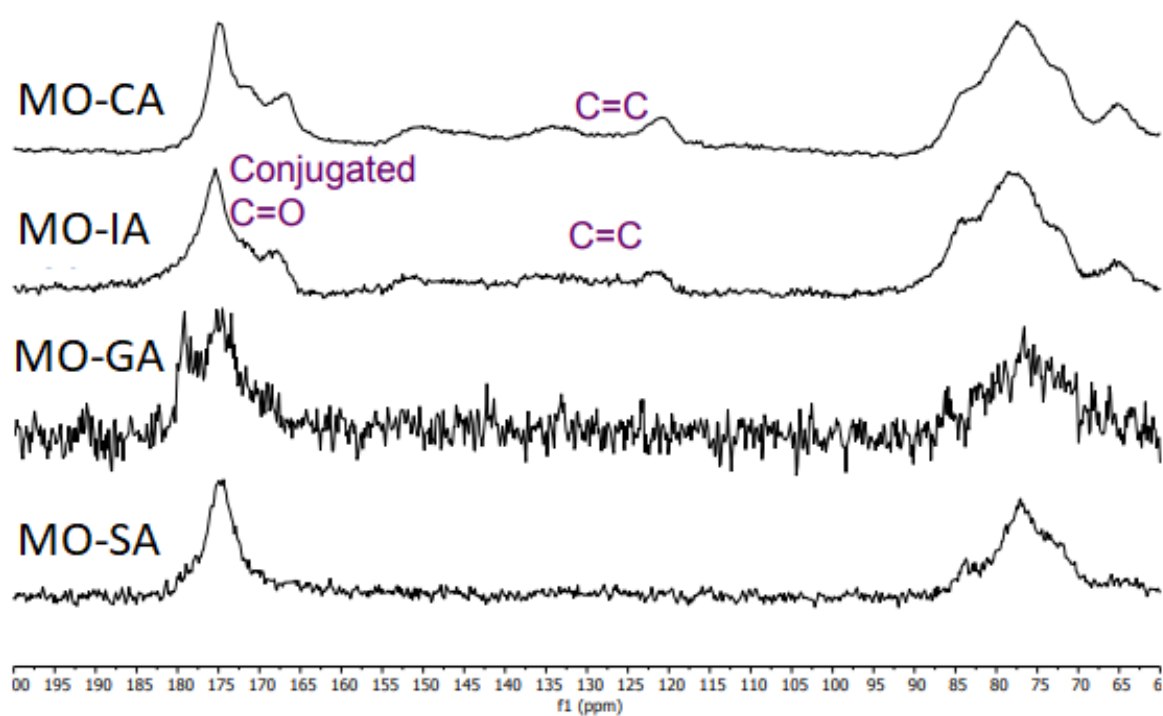


Figure 15 - Comparison of the 60–200 ppm region of the solid-state ¹³C NMR spectra of all eight polymer powders

2.7. Infrared analysis

Infrared analysis of all eight polymer powders revealed that in the functional group region (4000–1600 cm^{-1}), the spectra were very similar to those of the epoxidised vegetable oil from which they were prepared, but there were clear differences in the fingerprint region (1600–600 cm^{-1}) (data in appendices). However, detailed analysis of the 2000-1500 cm^{-1} region did show the presence of a weak alkene stretching band at 1653 cm^{-1} in polymers derived from macaw oil and the unsaturated anhydrides, (itaconic anhydride and citraconic anhydride), as shown in Figure 16. In the corresponding baru nut oil derived polymers, this alkene stretching band was weaker and only clearly visible in polymer MO-CA derived from citraconic anhydride (data in appendices). Carbonyl stretching at 1740 cm^{-1} provides evidence for ester bond formation and the successful synthesis of polyesters.

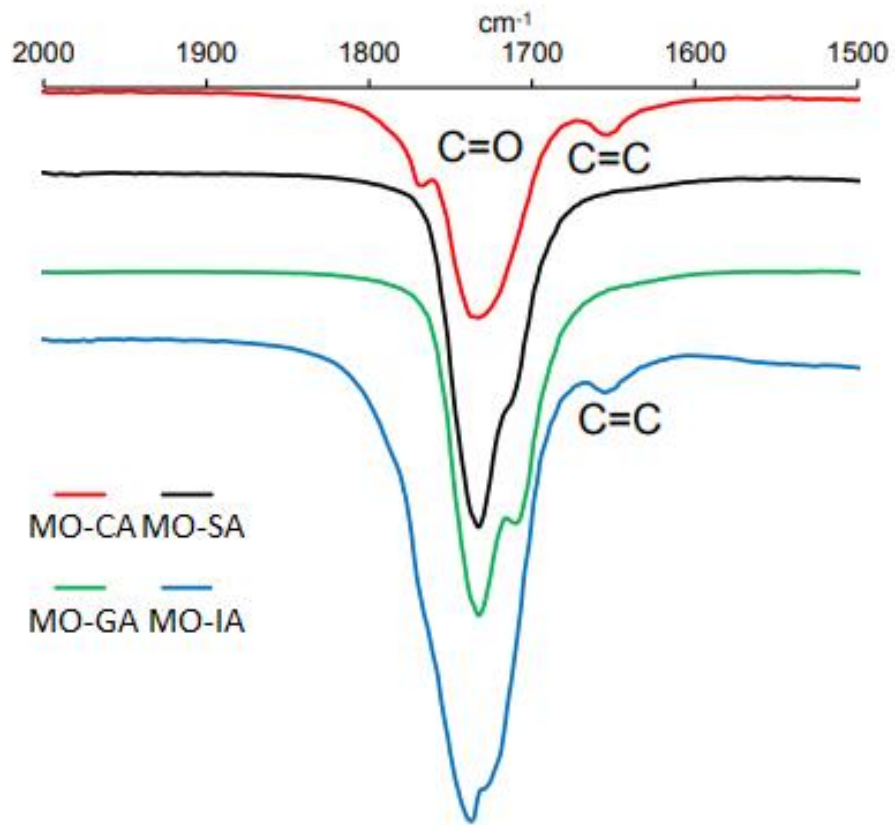


Figure 16 - Expansion of the IR spectra of macaw oil + cyclic anhydride polymers between 1500 and 2000 cm⁻¹

2.8. Polymer end-of-life hydrolysis

Another important aspect to consider when attempting to produce a sustainable polymer is the polymer end-of-life. In earlier section it was discussed that end-of-life management is one of the fundamental flaws of current polymer production and end-of-life consideration was also discussed as one of the key principles of green chemistry. Towards the end of this project, a key interest was placed into how these compounds may decompose. To test this, 100mg of MO-SA, MO-IA, MO-CA, and MO-GA was placed into individual vials and added to each was 1ml of 1M NaOH. All four vials were monitored using a GoPro with a photo being taken every four hours until complete degradation by hydrolysis was achieved which was determined to be the moment at which there was no visible solid material less suspended in solution. and it was found that complete degradation occurred for every sample within 8-24 hours. MO-SA, MO-IA, and MO-GA achieved complete degradation within 8 hours, whereas MO-CA took 24 hours to completely dissolve into the solution.

3. Experimental

3.1. General procedure for the synthesis of powdered polymers

To an oven-dried 15 mL sample vial were added DCHU **3** (2.24 mg, 0.01 mmol, 1 eq.), PPNCI **4** (5.7 mg, 0.01 mmol, 1 eq.), triglyceride **1** or **2** (2.5 mmol, 250 eq.) and anhydride **5–8** (10 mmol, 1000 eq.). The vial was sealed, purged with N₂, then heated to 100 °C for 18 hours. After cooling to room temperature, the polymerisation mixture was ground to a powder and placed in a Soxhlet extraction thimble. Extraction of initiators and unreacted monomers using CH₂Cl₂ until the polymer reached constant weight left polymers as white-yellow powders. EtOAc or EtOH could also be used as greener extraction solvents and were only marginally less effective than CH₂Cl₂ (4–5%, by weight, less material extracted after 18 hours). Yields determined using theoretical mass if a ROCOP reaction occurred at every epoxide site (4 for macaw oil compounds and 3 for baru oil compounds).

MO-SA. Obtained as a white powder (2.29 g, 2.42 mmol) in 67% yield. ν_{\max} 2926, 2855 and 1733 cm⁻¹; δ_{C} (100 MHz, solid) 174.9, 77.0, 34.8, 32.3, 27.8, 25.6 and 16.9 ppm; TGA (10% weight loss) 340 °C; DSC (glass transition temperature) -14.9 °C.

MO-IA. Obtained as a yellow powder (2.17 g, 2.29 mmol) in 61% yield. ν_{\max} 3000, 2970, 2926, 2855, 1737 and 1656 cm⁻¹; δ_{C} (100 MHz, solid) 175.4, 168.0, 151.0, 135.9, 120.8,

78.1, 65.4, 36.7, 34.8, 32.4, 27.9, 25.6, 23.5 and 16.9 ppm; TGA (10% weight loss) 325 °C; DSC (glass transition temperature) -5.5 °C.

MO-CA. Obtained as a yellow powder (2.11 g, 2.23 mmol) in 59% yield. ν_{\max} 2925, 2855, 1733 and 1653 cm^{-1} ; ν_{C} (100 MHz, solid) 174.8, 171.4, 166.8, 150.5, 134.1, 120.7, 77.2, 65.0, 36.1, 34.5, 32.3, 27.9, 25.5, 23.3 and 16.8 ppm; TGA (10% weight loss) 304 °C; DSC (glass transition temperature) none detected.

MO-GA. Obtained as a white powder (1.63 g, 1.72 mmol) in 46% yield. ν_{\max} 2926, 2855 and 1733 cm^{-1} ; ν_{C} (100 MHz, solid) 179.2, 174.8, 76.6, 34.6, 32.1, 27.9, 25.3, 22.8 and 16.6 ppm; TGA (10% weight loss) 341 °C; DSC (glass transition temperature) -14.9 °C.

BO-SA. Obtained as a white powder (1.26 g, 1.35 mmol) in 35% yield. ν_{\max} 2926, 2949, 2926, 2854 and 1738 cm^{-1} ; ν_{C} (100 MHz, solid) 174.9, 91.3, 84.6, 77.6, 75.2, 67.4, 59.0, 34.6, 32.2, 30.5, 27.3, 25.4 and 16.9 ppm; TGA (10% weight loss) 352 °C; DSC (glass transition temperature) none detected.

BO-IA. Obtained as a yellow powder (1.52 g, 1.63 mmol) in 54% yield. ν_{\max} 2976, 2926, 2855, 1737 and 1656 cm^{-1} ; ν_{C} (100 MHz, solid) 174.3, 91.4, 85.0, 77.4, 74.8, 74.1, 67.6, 32.3, 27.7, 25.3 and 16.8 ppm; TGA (10% weight loss) 339 °C; DSC (glass transition temperature) none detected.

BO-CA. Obtained as a yellow powder (1.67 g, 1.79 mmol) in 59% yield. ν_{\max} 2925, 2854, 1734 and 1655 cm^{-1} ; ν_{C} (100 MHz, solid) 175.2, 167.2, 134.5, 91.4, 84.6, 77.6, 75.0, 74.1, 71.9, 67.7, 64.8, 59.7, 36.6, 34.6, 32.1, 27.7, 25.3 and 16.6 ppm; TGA (10% weight loss) 334 °C; DSC (glass transition temperature) none detected.

BO-GA. Obtained as a white powder (1.31 g, 1.40 mmol) in 46% yield. ν_{\max} 2925, 2854 and 1733 cm^{-1} ; ν_{C} (100 MHz, solid) 175.0, 91.4, 84.4, 77.6, 74.8, 74.1, 67.6, 65.0, 60.1,

36.3, 34.6, 32.1, 27.7, 25.3, 23.2, 20.8 and 16.8 ppm; TGA (10% weight loss) 356 °C;
DSC (glass transition temperature) -13.6 °C.

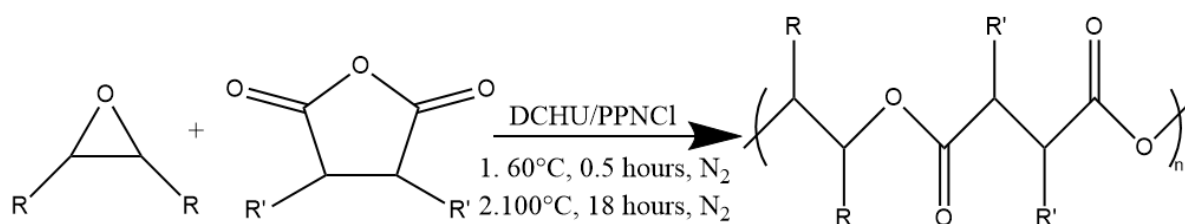
3.2. General polymerisation procedure for polymer disks

Forming the prepolymer:

To epoxidized macaw oil (2.44g, 2.5 mmol) or epoxidized baru oil (2 g, 2.5 mmol) was added dicyclohexylurea (2.24 mg, 0.01 mmol) and bis(triphenylphosphine)iminium chloride (5.7 mg, 0.01) and the solution stirred in a vial under nitrogen and heated to 50°C for 30 minutes.

Curing the polymer to form a disk:

After 30 minutes, the ground up cyclic anhydride was added. Succinic anhydride (1 g, 10 mmol), or itaconic anhydride (1.12 g, 10 mmol), or citraconic anhydride (1.12 g, 10 mmol), or glutaric anhydride (1.14 g, 10 mmol) and stirred in a vial under nitrogen and heated to 50°C for five minutes. Once mixture was the reaction homogenous, it was transferred to a dish and heated at 100°C, without stirring for 18 hours. The resulting light brown disk was then left over night at room temperature to set.



Scheme 4 - Reaction conditions for the synthesis of polymer disks

3.3. Reagents

Phthalic anhydride (Sigma-Aldrich), Itaconic anhydride (Sigma-Aldrich), Citraconic anhydride (Sigma-Aldrich), Glutaric anhydride (Sigma-Aldrich), Camphoric acid (Sigma-Aldrich), cyclohexeneoxide (Sigma-Aldrich), epichlorohydrin (Sigma-Aldrich), N,N'-dicyclohexylurea (Sigma-Aldrich), ethanol (Sigma-Aldrich), chloroform (SigmaAldrich), dichloromethane (Sigma-Aldrich), ammonium chloride (Sigma-Aldrich), succinic anhydride (Merck), bis(triphenylphosphorylidene)ammoniumchloride (Alfa Aesar) was used as received. Epoxidized Macaw palm oil and Baru oil were reused from a previous project.

3.4. Characterisation

. Infrared spectra were acquired on a Perkin-Elmer Spectrum 400 FTIR spectrometer. UV/visible absorption spectra were acquired on a Thermo Scientific GENESYS 180 UV-vis spectrophotometer. Mass spectrometry measurements were performed on a Bruker compact time-of-flight mass spectrometer (ESI) or a JEOL AccuTOF GCx plus time-of-flight mass spectrometer (LIFDI). DSC spectra were acquired using a TA Instruments Q2000 modulated Differential Scanning Calorimeter. TGA spectra were acquired using a Stanton Redcroft STA 625 instrument. Solid-state ^{13}C NMR spectra were acquired using a Bruker

AVIII 400 at 100MHz. Liquid state ^1H and ^{13}C NMR spectra were acquired on a Bruker AVIII 300 NB spectrometer or a JEOL ECS400 spectrometer at 300 MHz and 75 MHz or 400 MHz and 100 MHz respectively.

4. Conclusions

Using epoxidized Brazilian biomass (specifically baru oil and macaw oil) with cyclic anhydrides that can be obtained from bio-based sources to synthesise highly cross-linked polyesters has so far been effective. Multiple samples have already been produced with yields over 50% and it is possible that the current yields, (excluding the combination of succinic anhydride and Baru oil), are not far from being the maximum possible yields for this chemistry due to limiting factors such as accessibility of the third and fourth epoxide groups. Initial issues involving purity, resulting from remaining unreacted anhydride trapped away in the sample have been resolved and samples now show no signs of excess anhydride. These highly cross-linked polyesters have been produced as powders and polymer disks which has allowed for primary investigations into polymer properties, (such as hardness) to begin. The polymers were totally degraded to soluble components in 8–24 hours on treatment with 1M aqueous sodium hydroxide. Thus, the polymers are both sustainably sourced and at end of life can be treated to prevent their accumulation in the environment.

5. Future work

5.1. Behaviour in aqueous vs organic solutions

One thing to investigate going forward is looking into the possibility of using these copolymers to extract organic pollutants. During the process of developing a purification method it was noticed that the samples would swell in the presence of an organic solvent (specifically DCM). It was then theorized that it may be possible to extract organic pollutants from an aqueous solution. To test this, it was first necessary to ensure that the samples would not uptake an aqueous solution such as water. Three different samples of co-polymer, macaw oil w. itaconic anhydride, macaw oil w. succinic anhydride, and macaw oil w. phthalic anhydride, weighing roughly 320mg were left in 5ml of water for 24 hours at room temperature. The mass before and after was recorded.

Sample	Mass (before)	Mass (After)	Mass change
ALV006 (MO-PA)	320mg	305mg	-15mg
ALV012 (MO-IA)	321mg	301mg	-20mg
ALV013 (MO-SA)	321mg	317mg	-4mg

Table 5 - Mass change of three polymer powders in aqueous conditions

As expected, there was no mass increase, this shows that uptake of an aqueous solution doesn't occur, and the small mass loss can be attributed to loss of sample when transferring

for weighing. Some tests have been run and it is clear that these polyester compounds do uptake organic solvents, however it is not yet been possible to accurately determine the volume. The next step will be to measure uptake in an organic solution before investigation whether organic solvent can be extracted from a predominantly aqueous solvent.

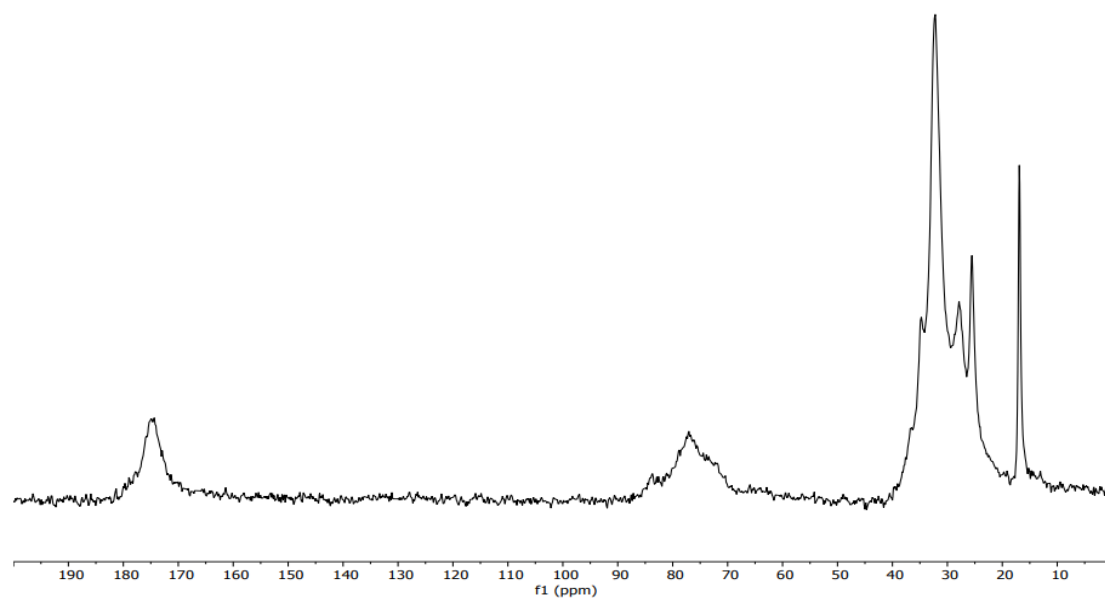
6. References

1. J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, *Science*, 2015, **347**, 768-771.
2. S. Mehnaz, A. Iftaykhairul, M. Shahriar, *Environmental Advances*, 2021, **5**, 100-119
3. A. Rajasekar et al., *Corrosion Science*, 2005, **47**, 257–271
4. R, Geyer, J.R. Jambeck, K.L. Law, *Science Advances*, 2017, **3**, 7
5. A.S. Mirabal, M. Carus, *Bio-based Polymers in the World: Capacities, Production and Applications: Status Quo and Trends towards 2020*, 2013
6. P. Cazón, G. Velazquez, J.A. Ramírez, M. Vázquez, *Food Hydrocolloids*, 2017, **68**, 136-148
7. B.H. Rehm, *Biochemistry*, 2003, **15**, 376
8. S.H. Aziz, M.P. Ansell, *Composite Science Technology*, 2004, **64**, 1219–1230
9. Z.N. Azwa, B.F. Yousif BF, A.C. Manalo, *Material & Design*, 2013, **47**, 424–442
10. O. Valerio, M. Misra, A.K. Mohanty, *ACS Sustainable Chemical Engineering*, 2018,**6**, 5681–5693
11. G. Alessandro, M. Talita, M. Lacerda, *Progress in Polymer Science*, 2015, **48**, 1-39
12. J. Derek, A. Saxon, M. Luke, S. Hussnain, W. B. Tolman, T. M. Reineke, *Progress in Polymer Science*, 2020, **101**, 101-196

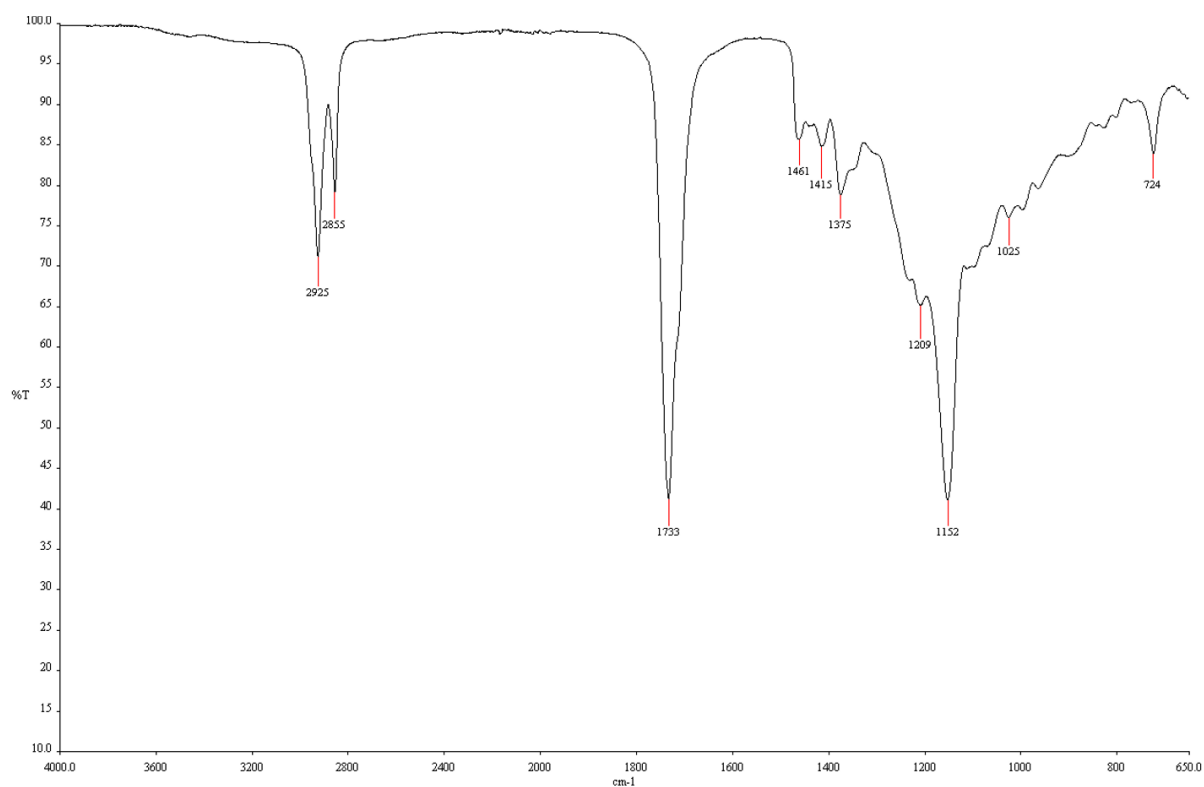
13. R. Chinthapalli, P. Skoczinski, M. Carus, W. Baltus, D. Guzman, H. Käb, A. Raschka, J. Ravenstijn, *Industrial Biotechnology*, 2018, **Aug. edition**, 237-241
14. S. Opperskalski, S. Siew, E. Tan, L. Truscott, Preferred fiber & materials market report, 2020
15. P. Shyeni, Z. Yunqing, C. Romain, R. Brooks, K. Prabhjot, K. Williams, *Chemistry Community*, 2015, **51**, 6459
16. T. Aida, S. Inoue, *J. Am. Journal of the American Chemical Society*, 1985, **107**, 1358–1364
17. M. I. Childers, J. M. Longo, N. J. Van Zee, A. M. LaPointe, G. W. Coates, *Chemical Reviews*, 2014, **114**, 8129–8152
18. Paul T. Anastas, *Chemical Reviews*, 2007, **107**, 2167–2168
19. R.T. Alarcona, C. Gaglieria, K.J. Lambb, M. North, G. Bannacha, *Industrial Crops and Products*, 2020, **154**
20. A. Takasu, M. Ito, Y. Inai, T. Hirabayashi, Y. Nishimura, *Polymer Journal* 1999, **31**, 961–969
21. S. Yu, R.Zhang, Q. Wu, T. Chen, P. Sun, *Advanced Materials*, 2013, **35**, 4912-4917

7. Appendices

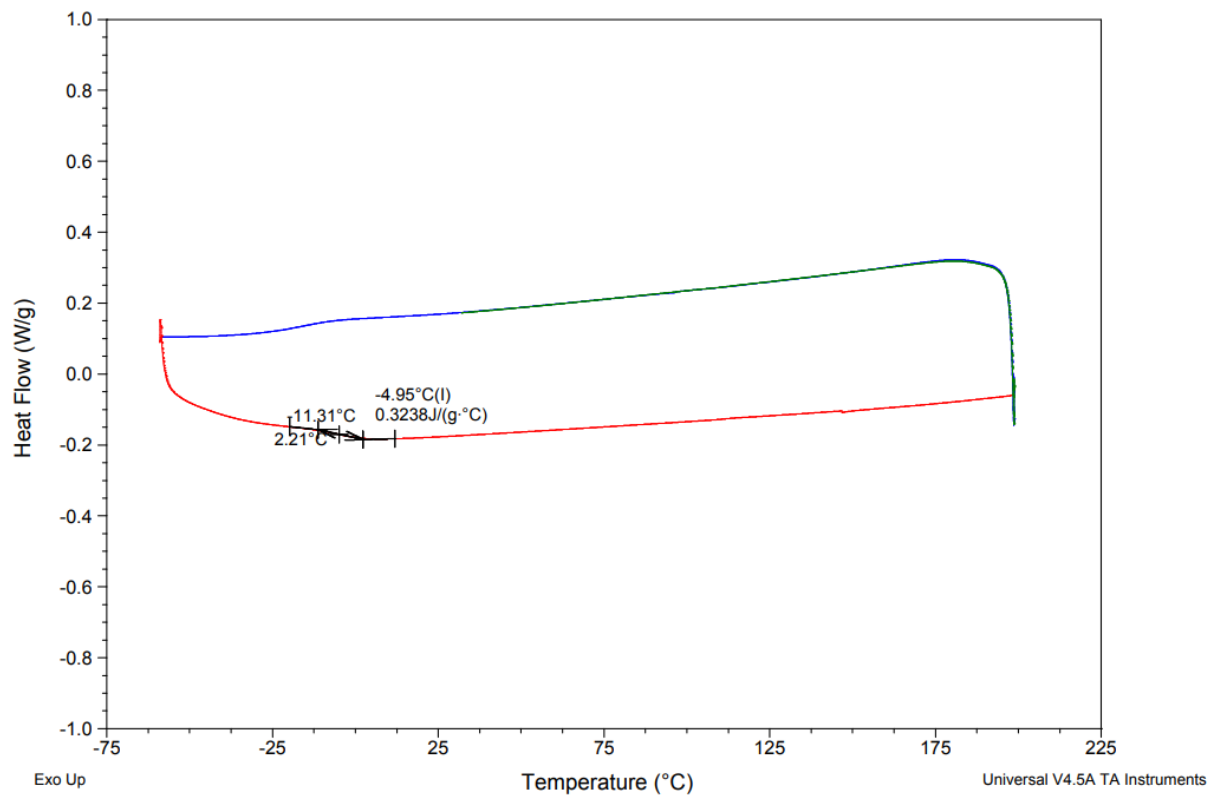
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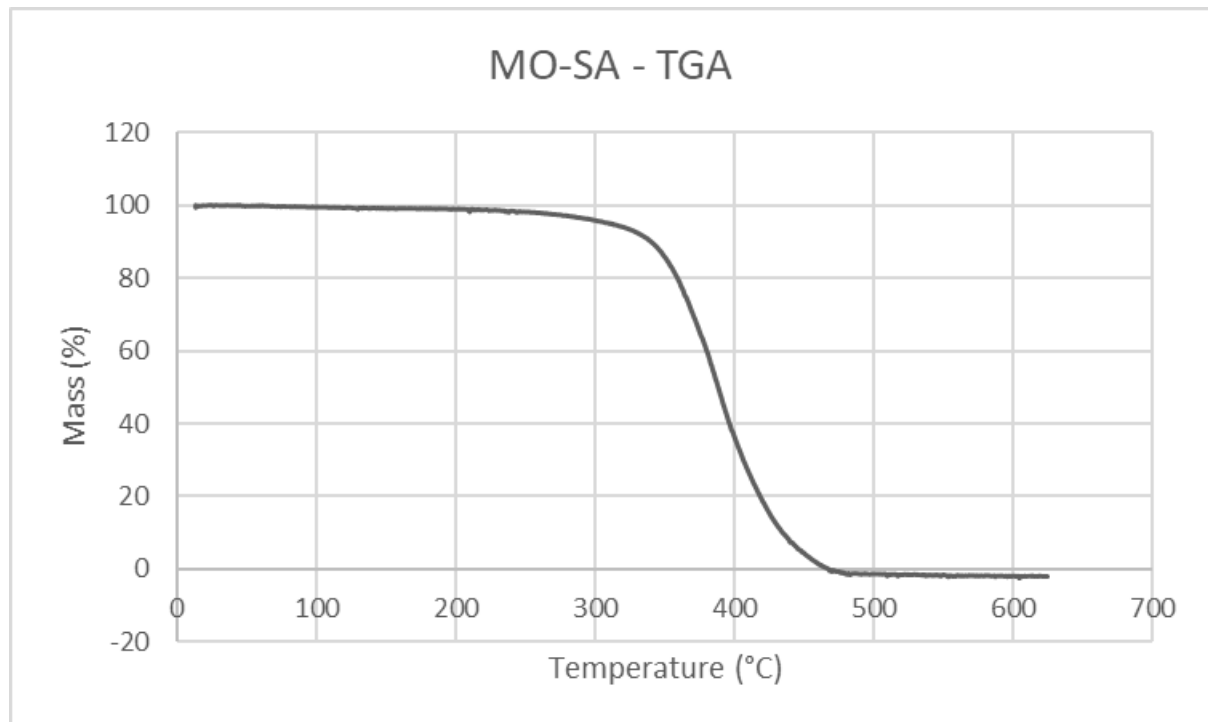
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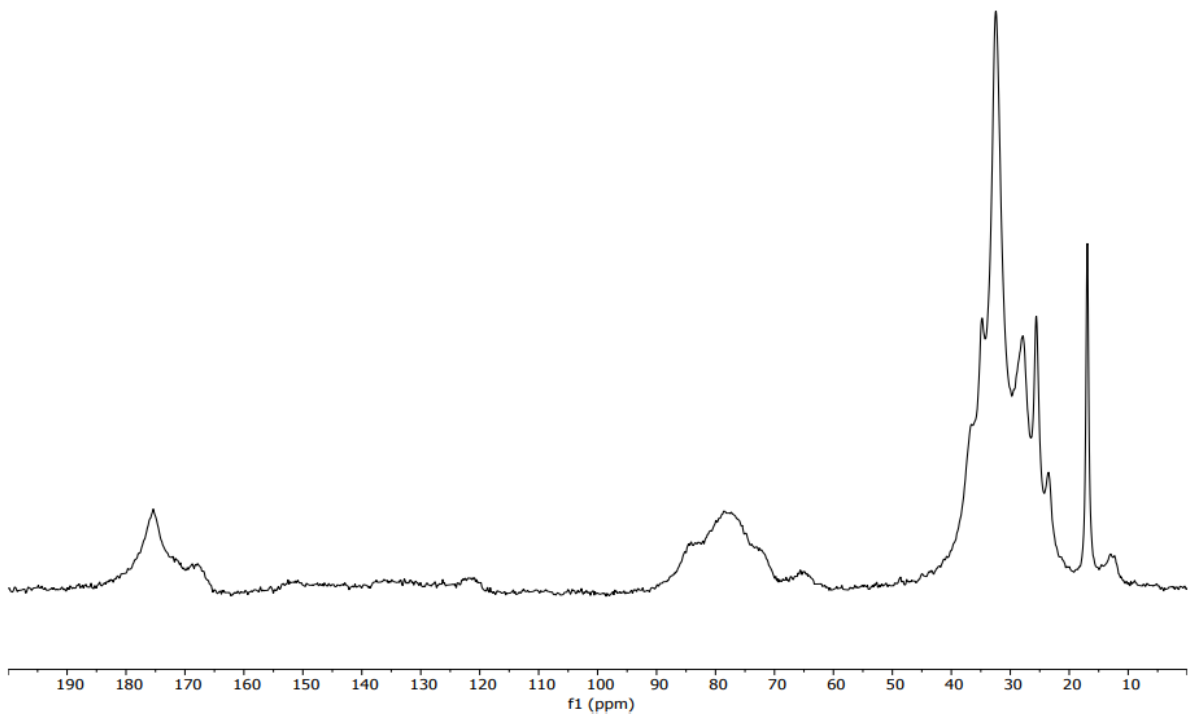
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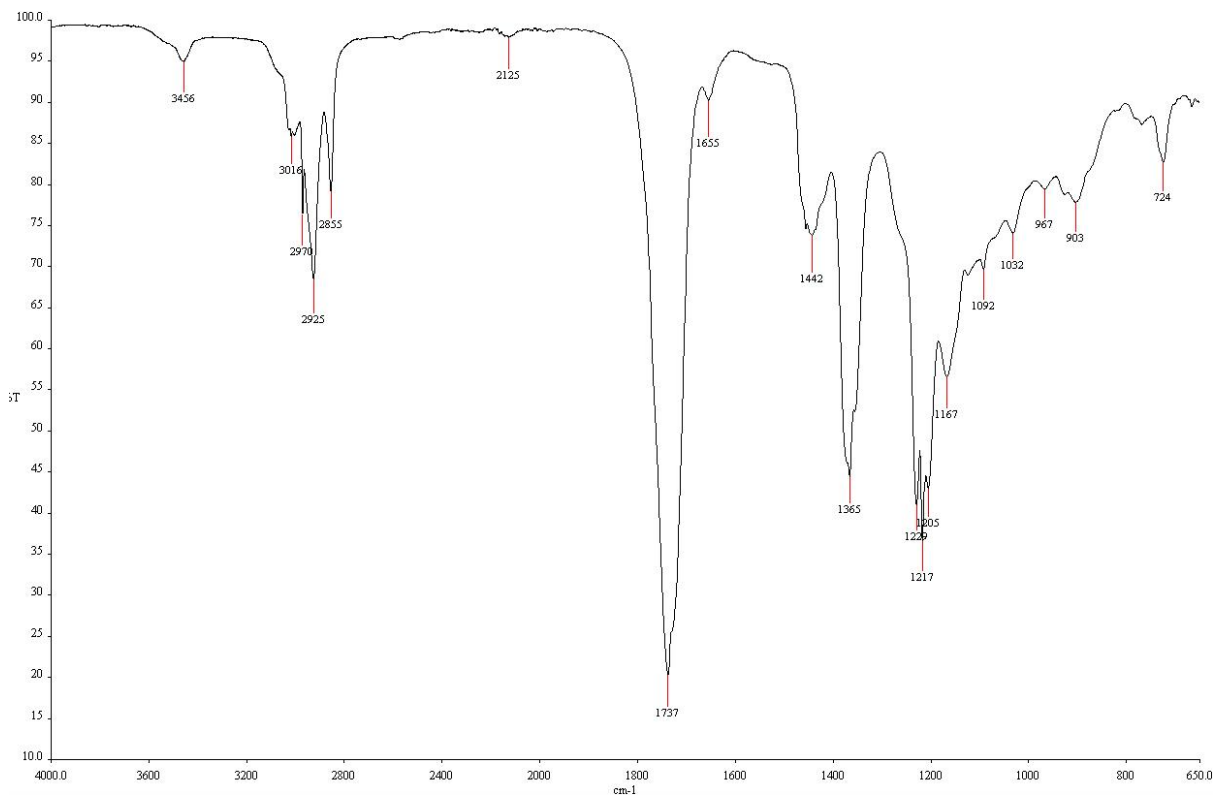
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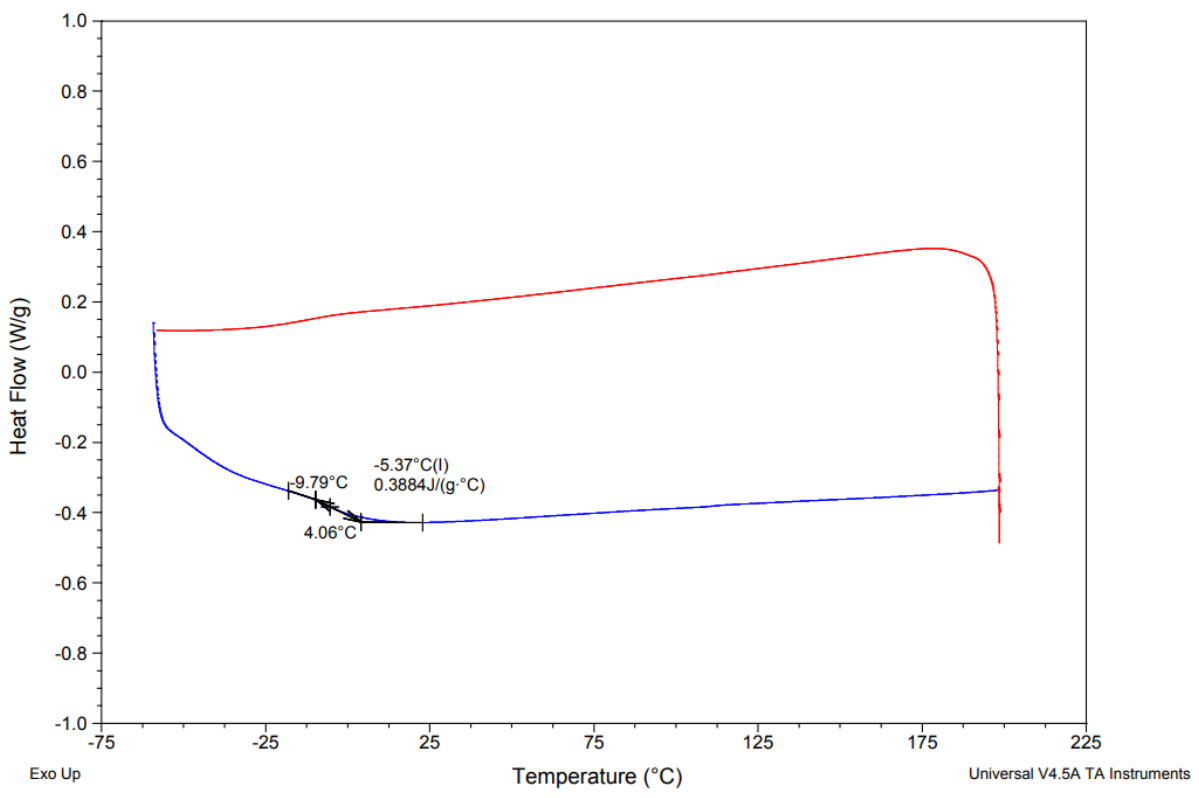
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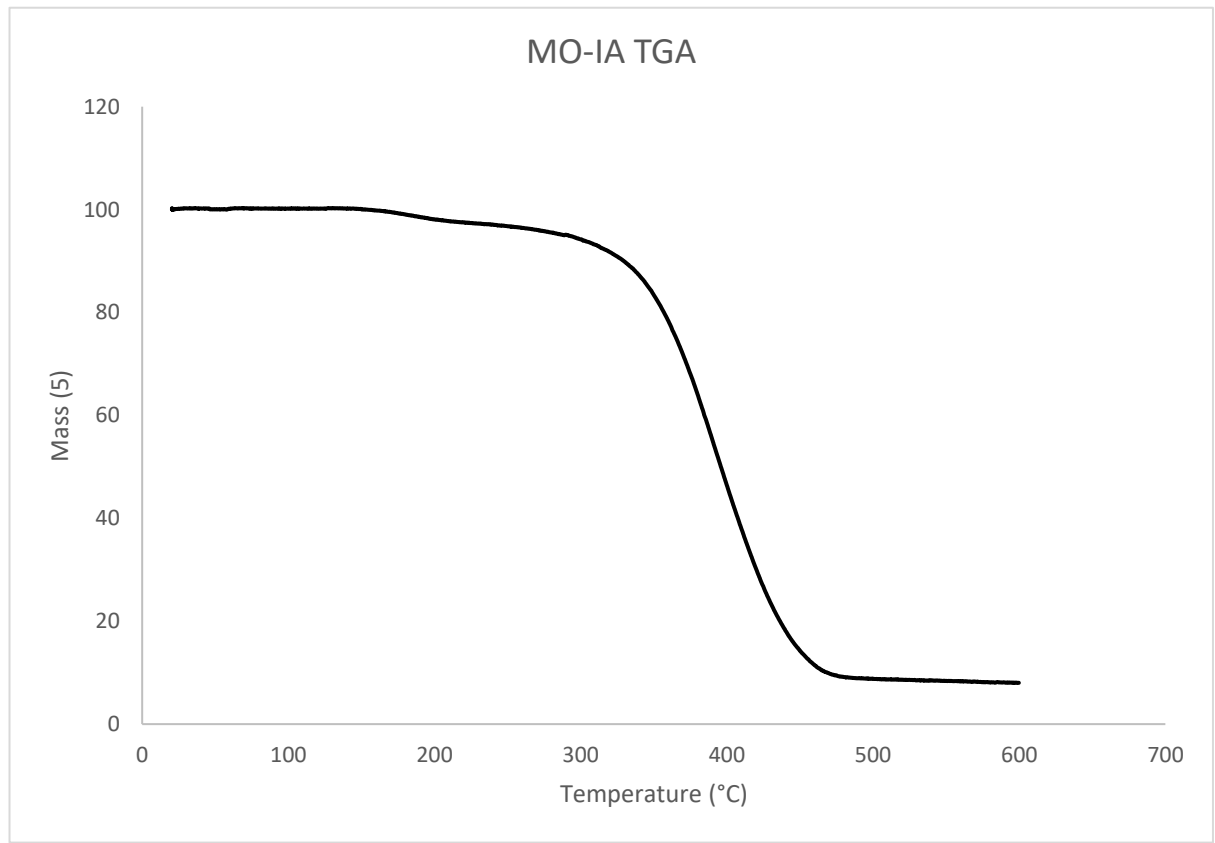
MO-IA IR



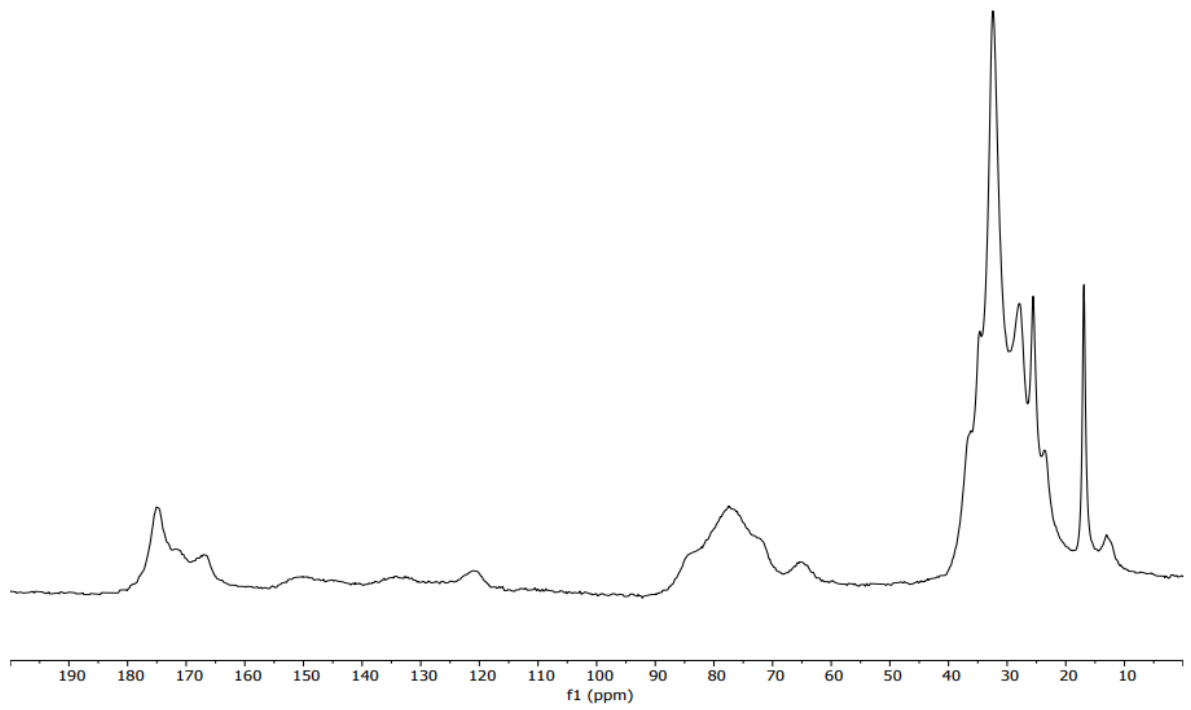
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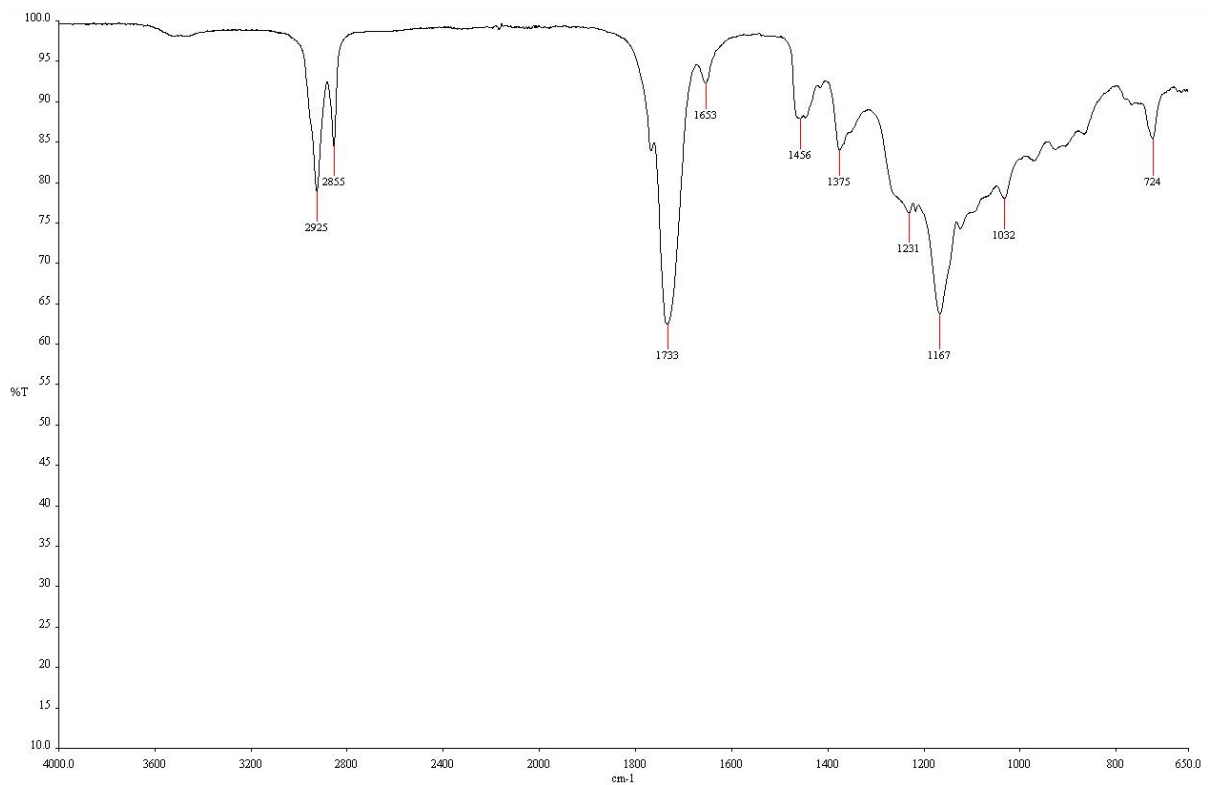
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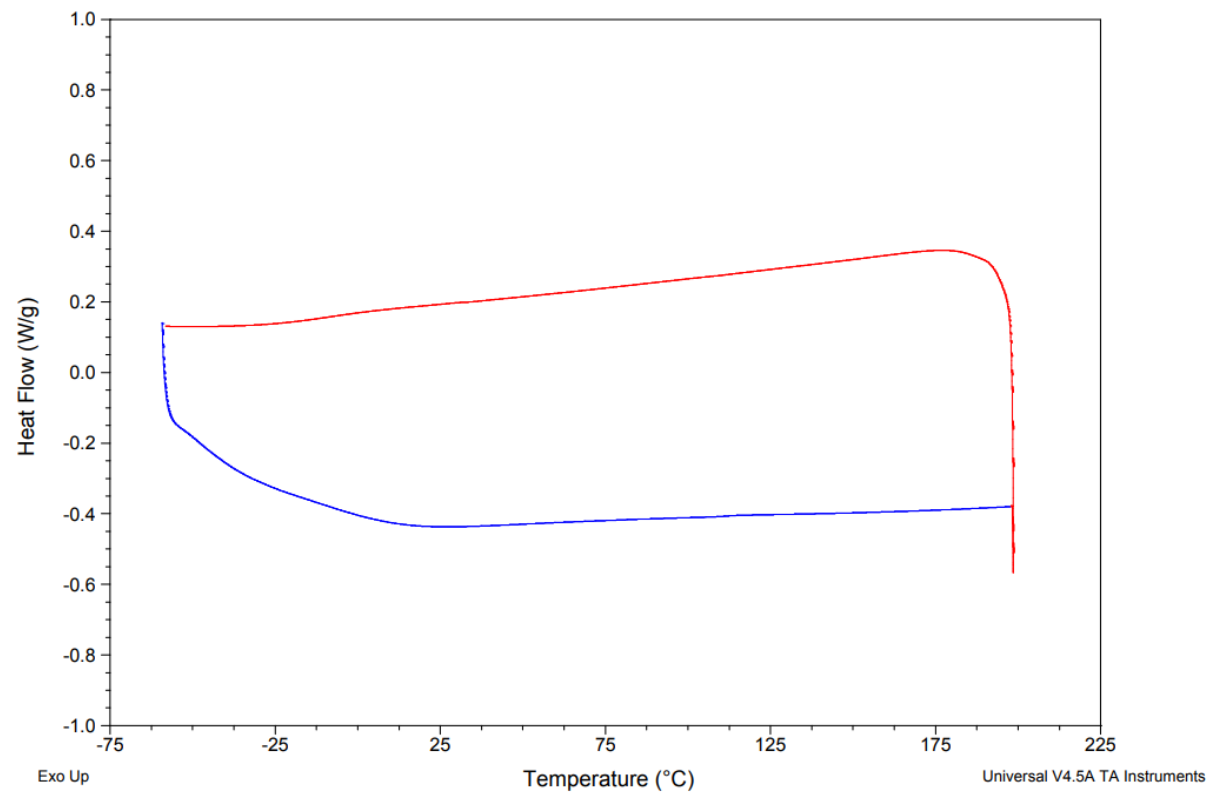
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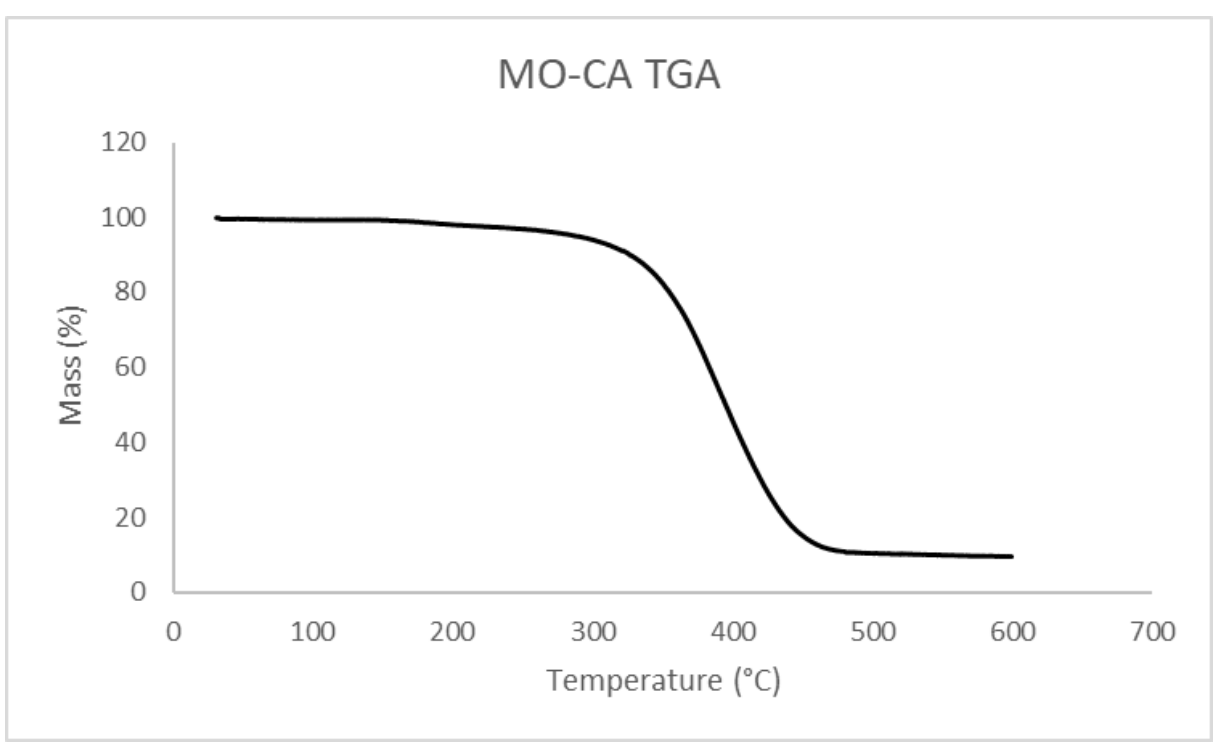
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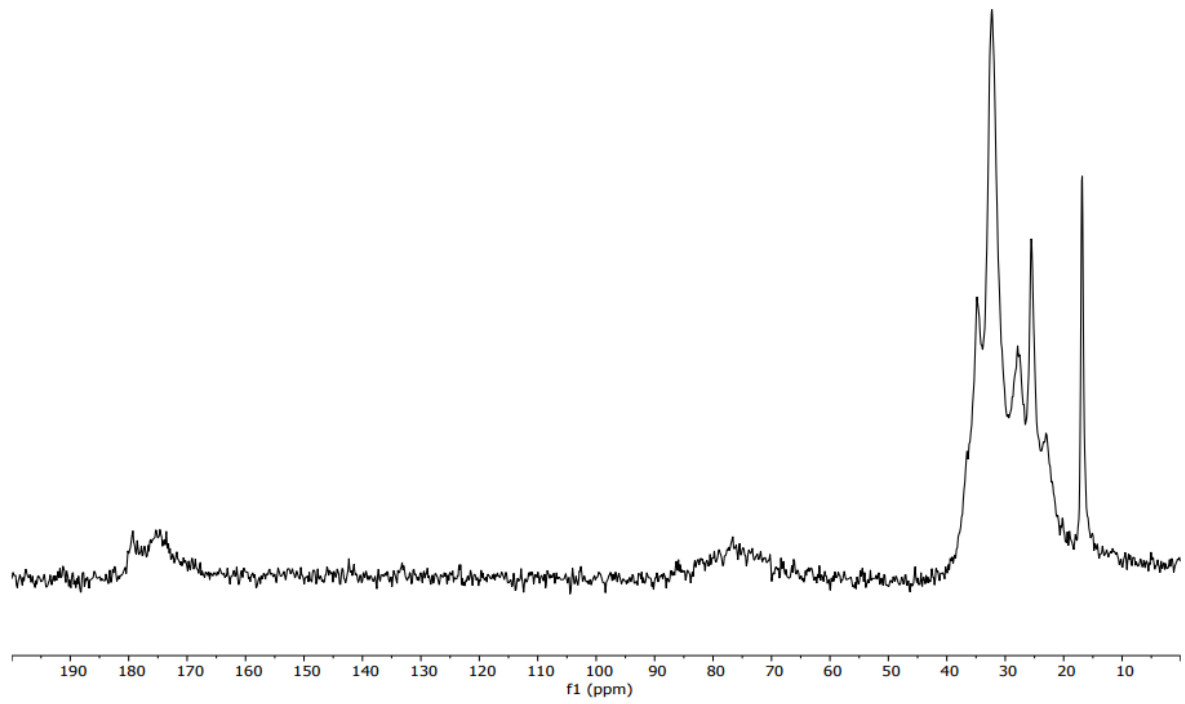
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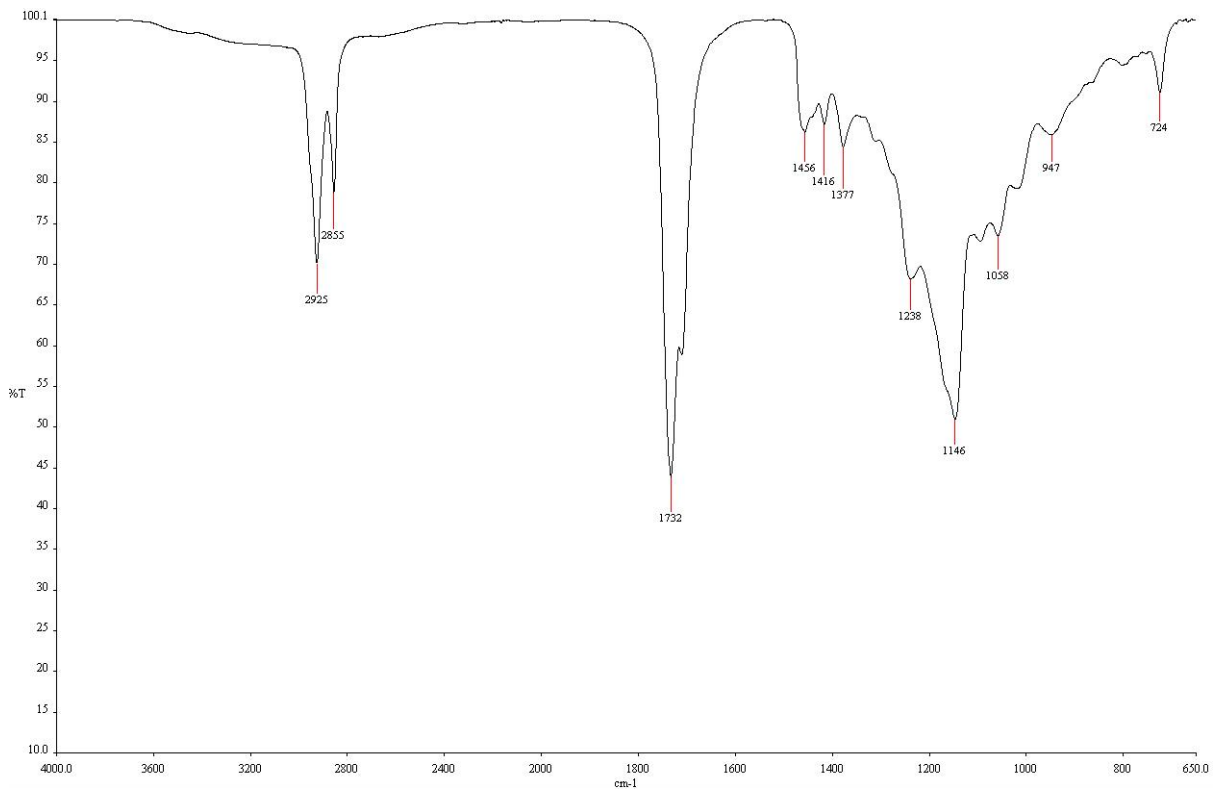
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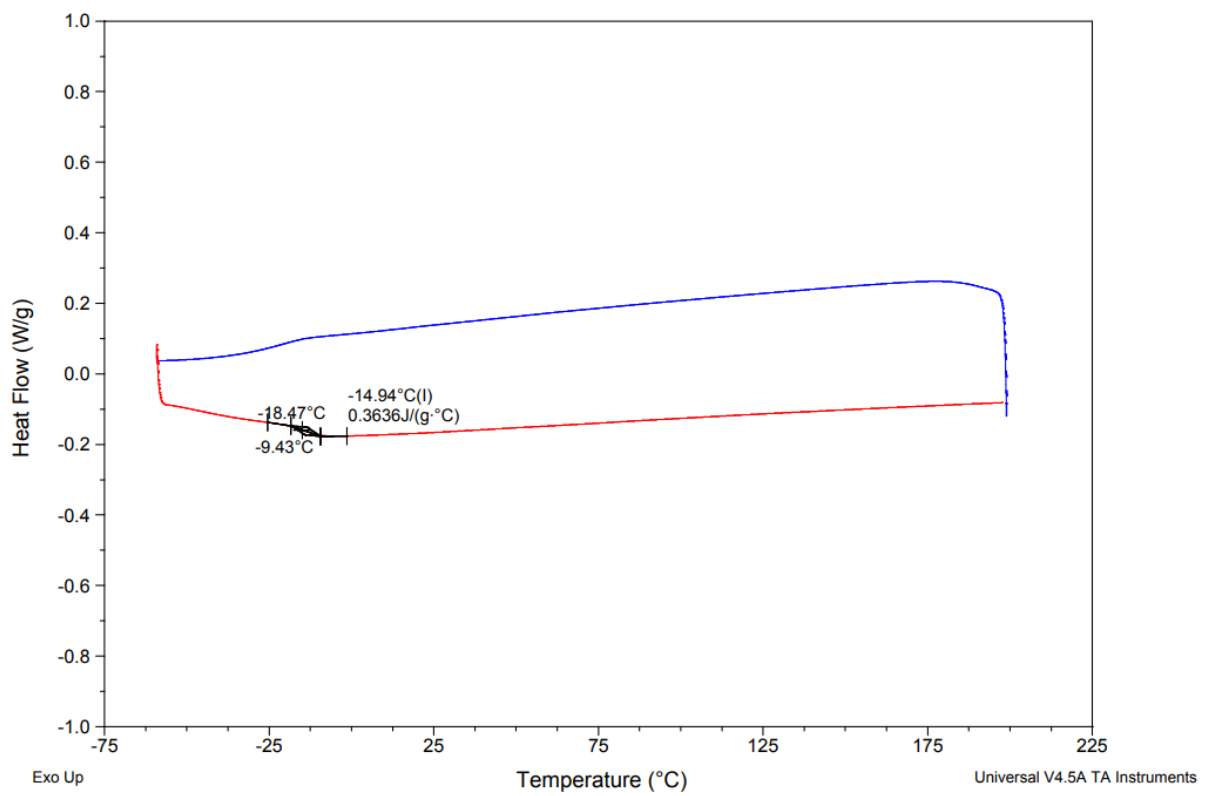
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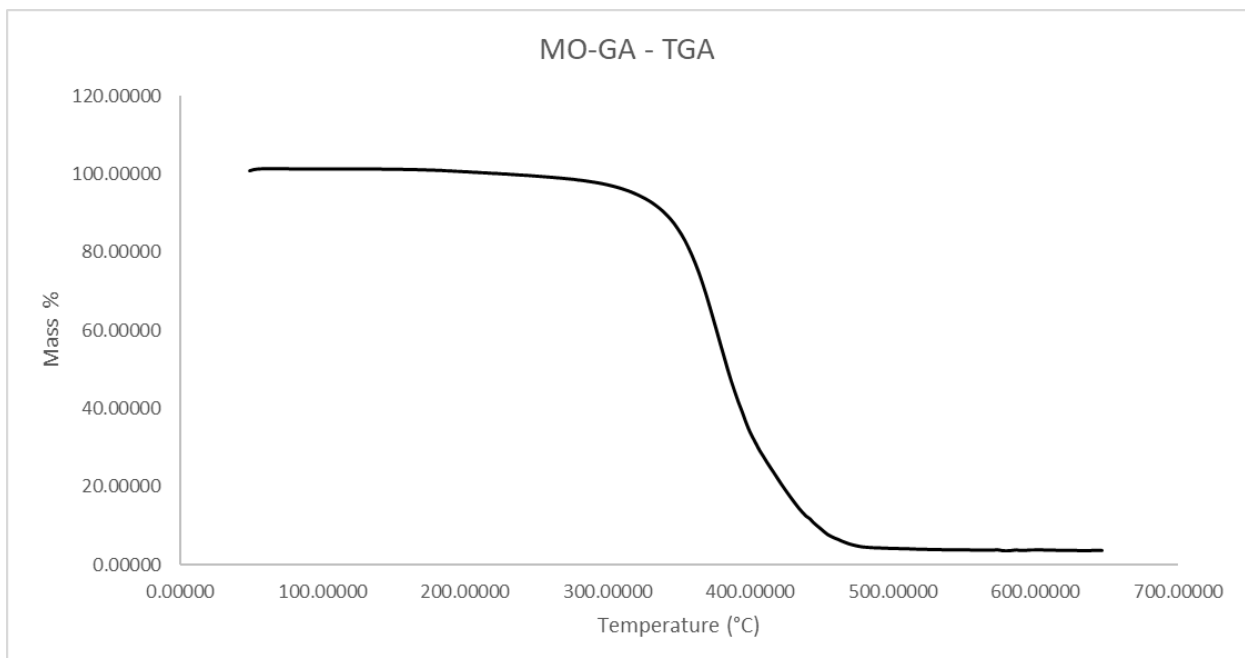
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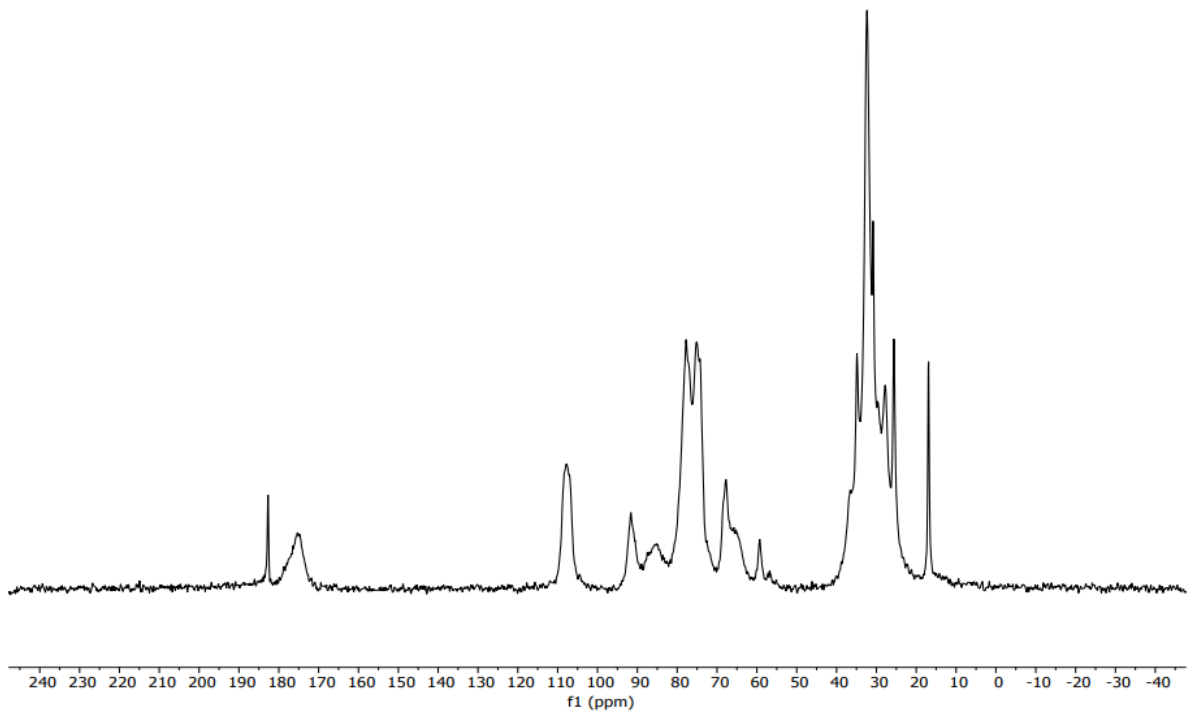
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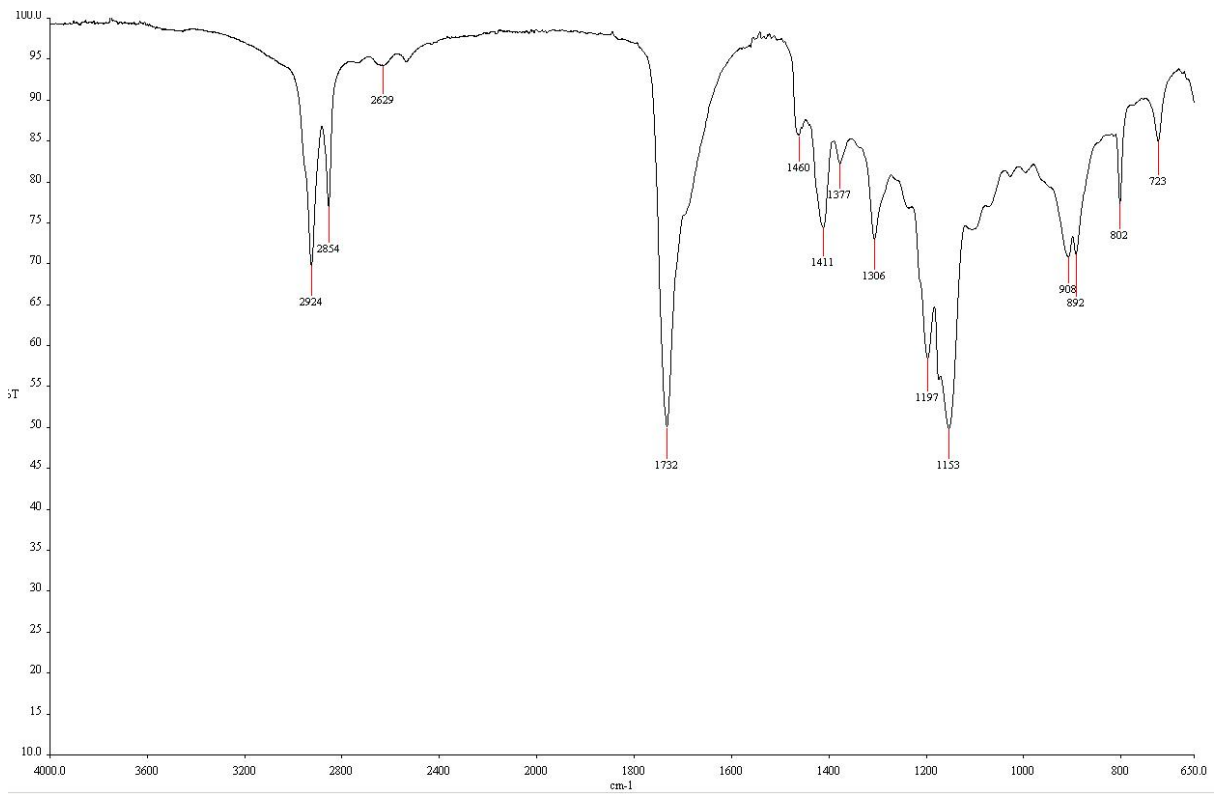
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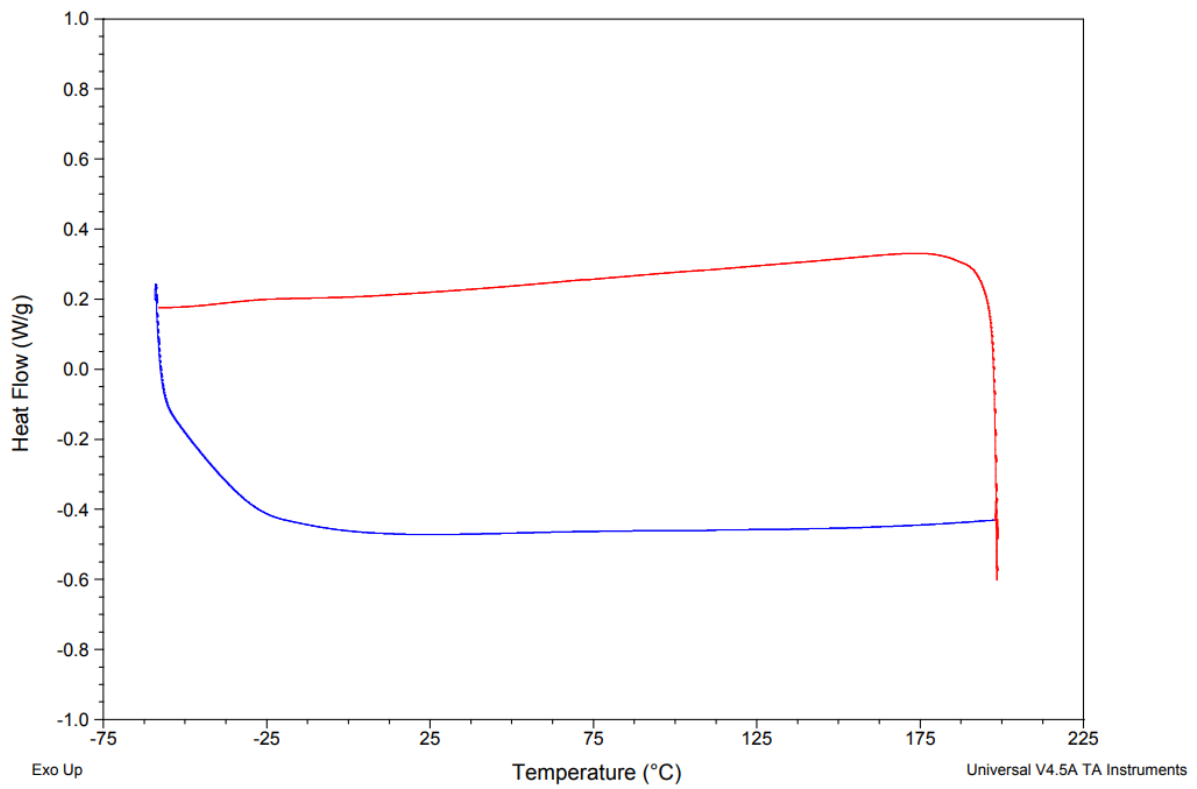
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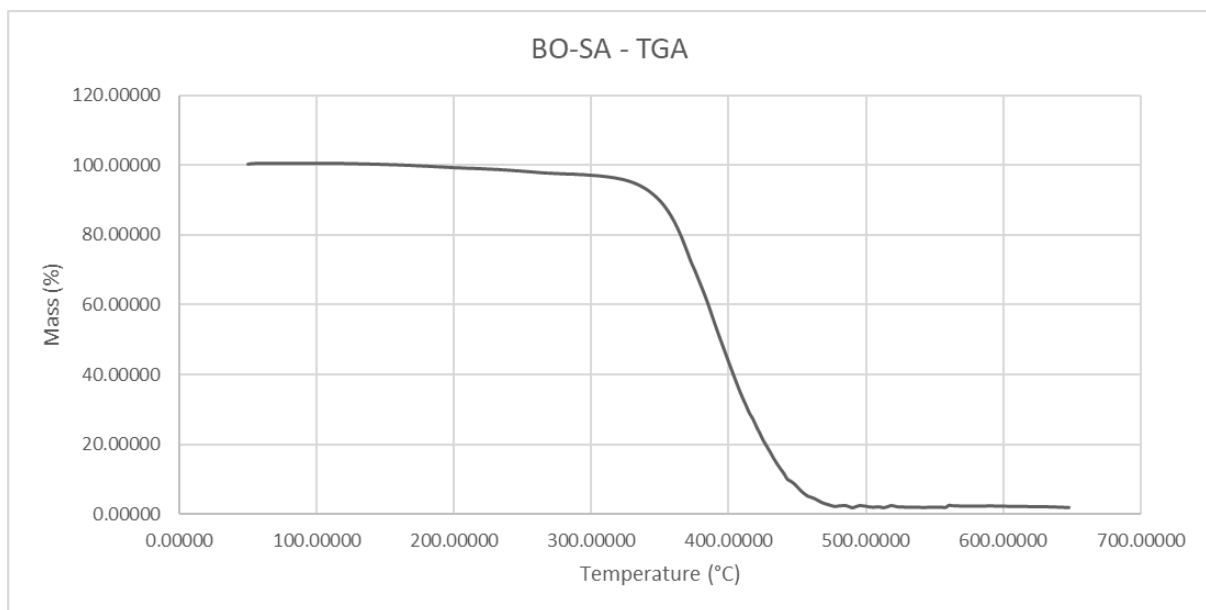
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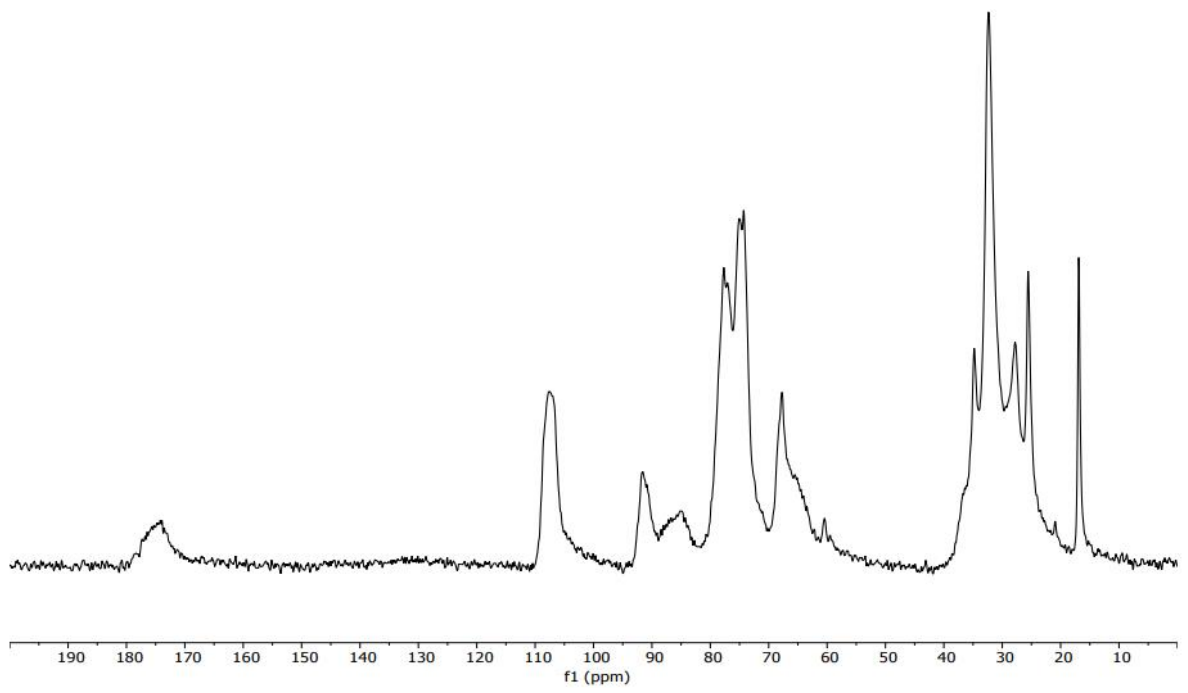
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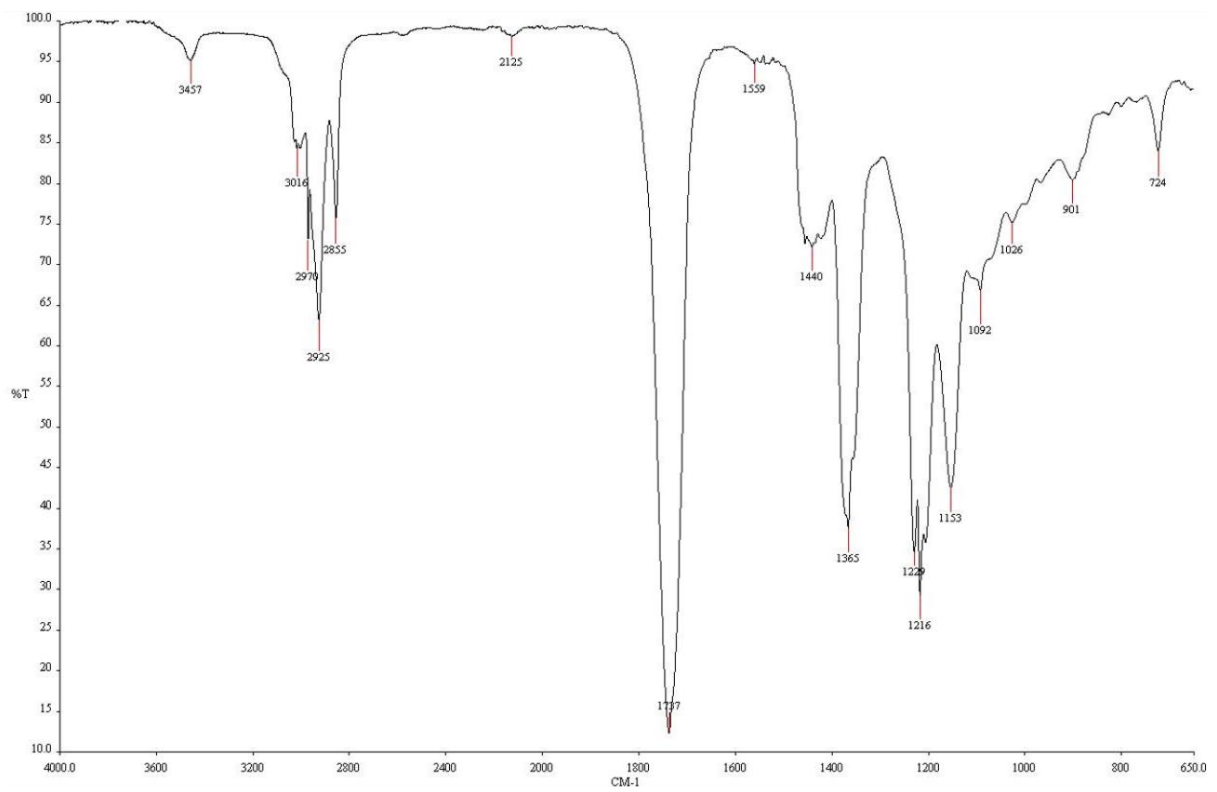
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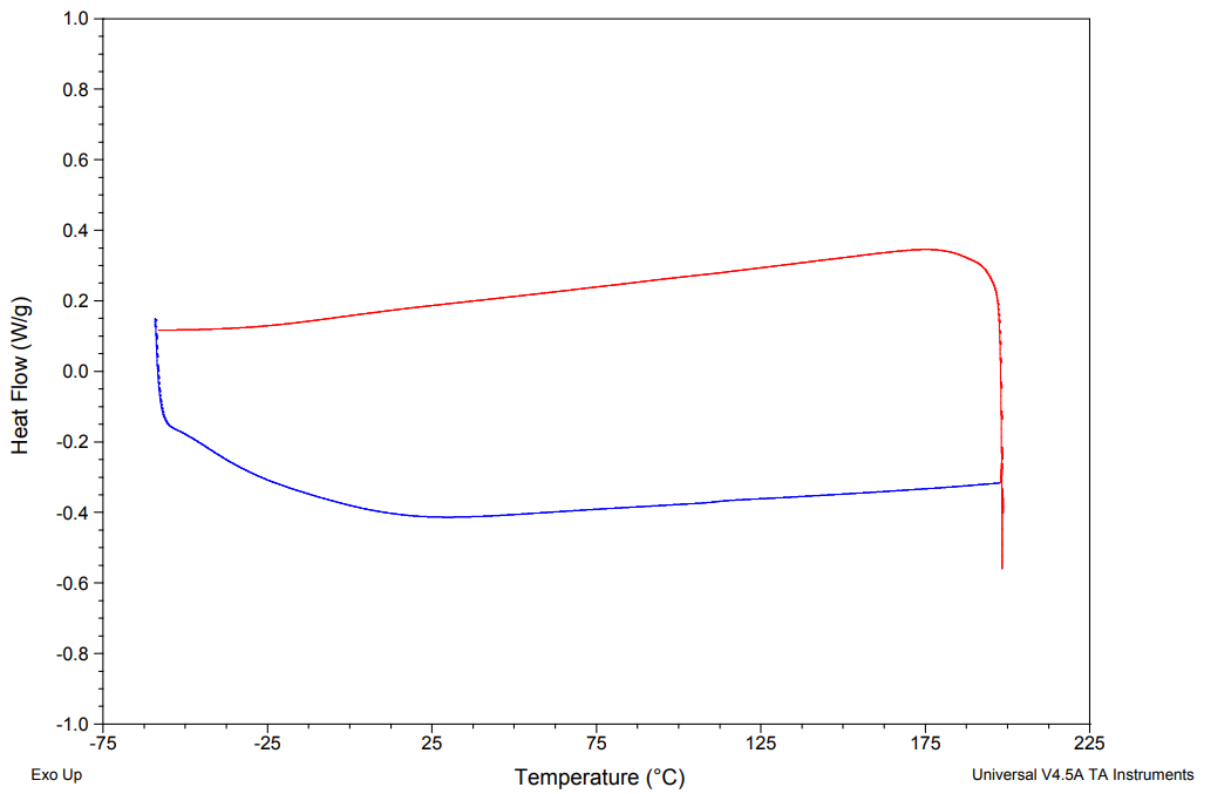
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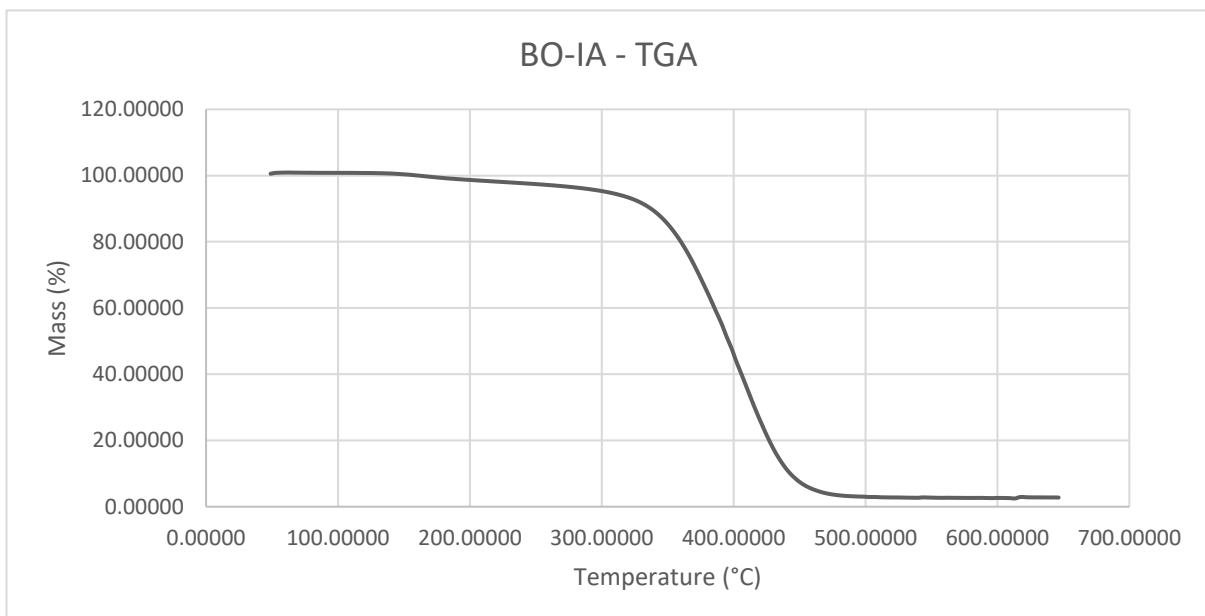
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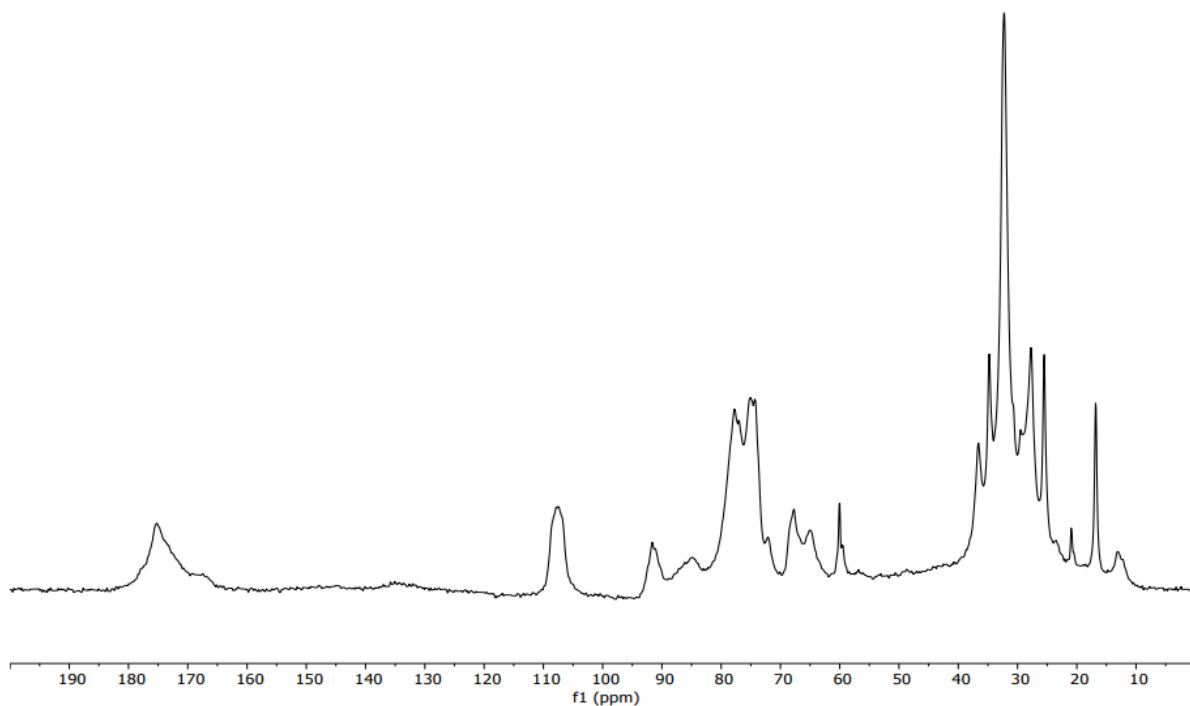
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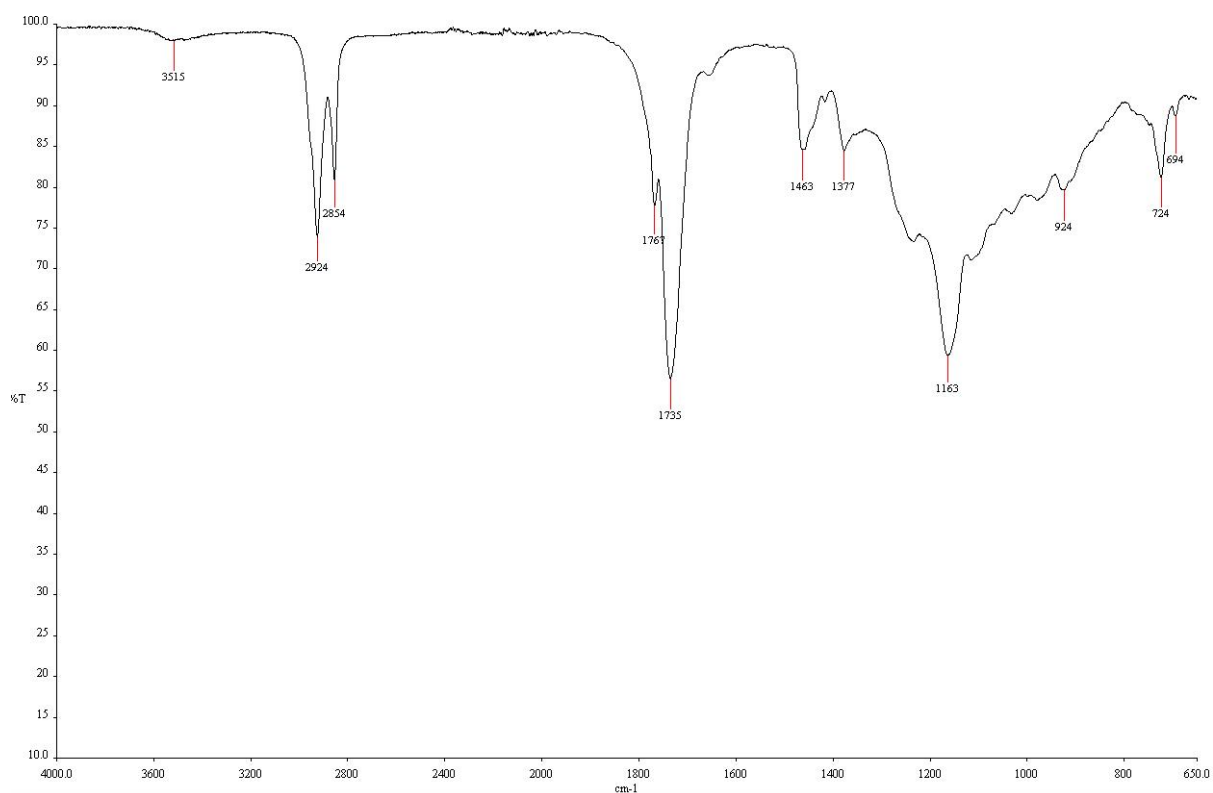
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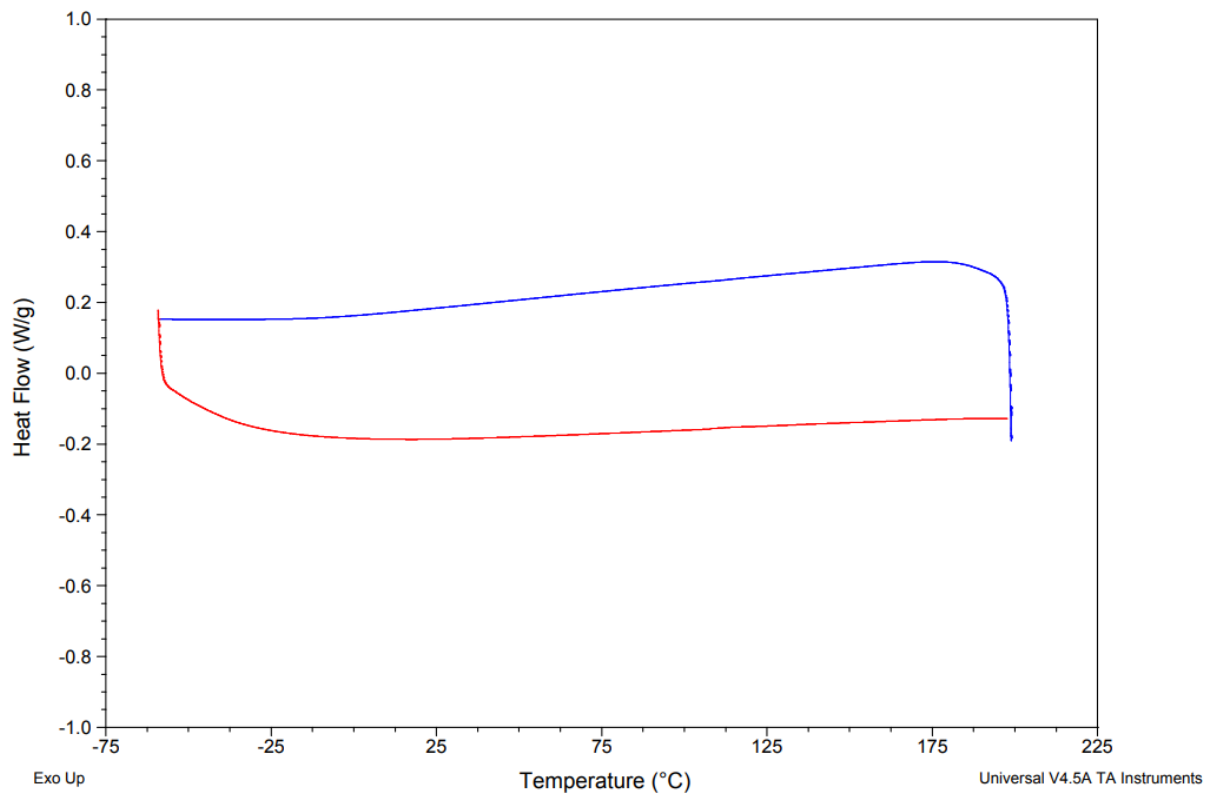
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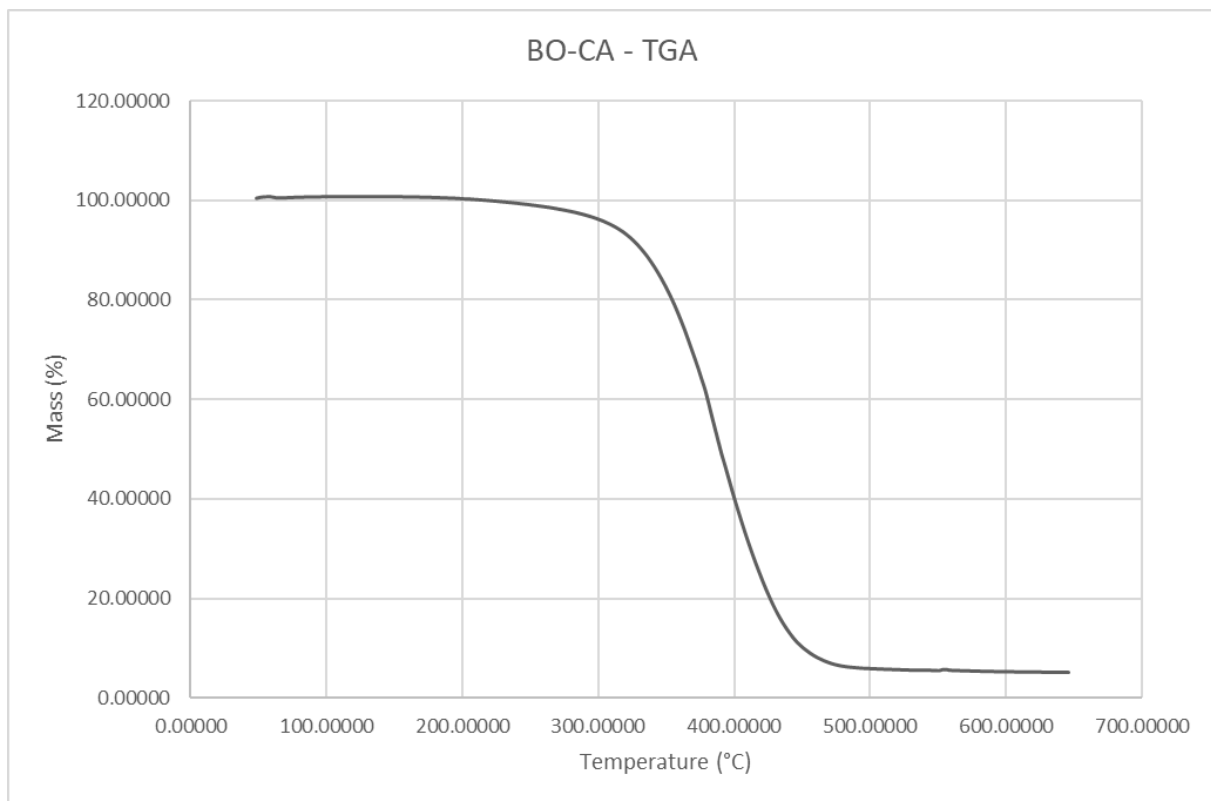
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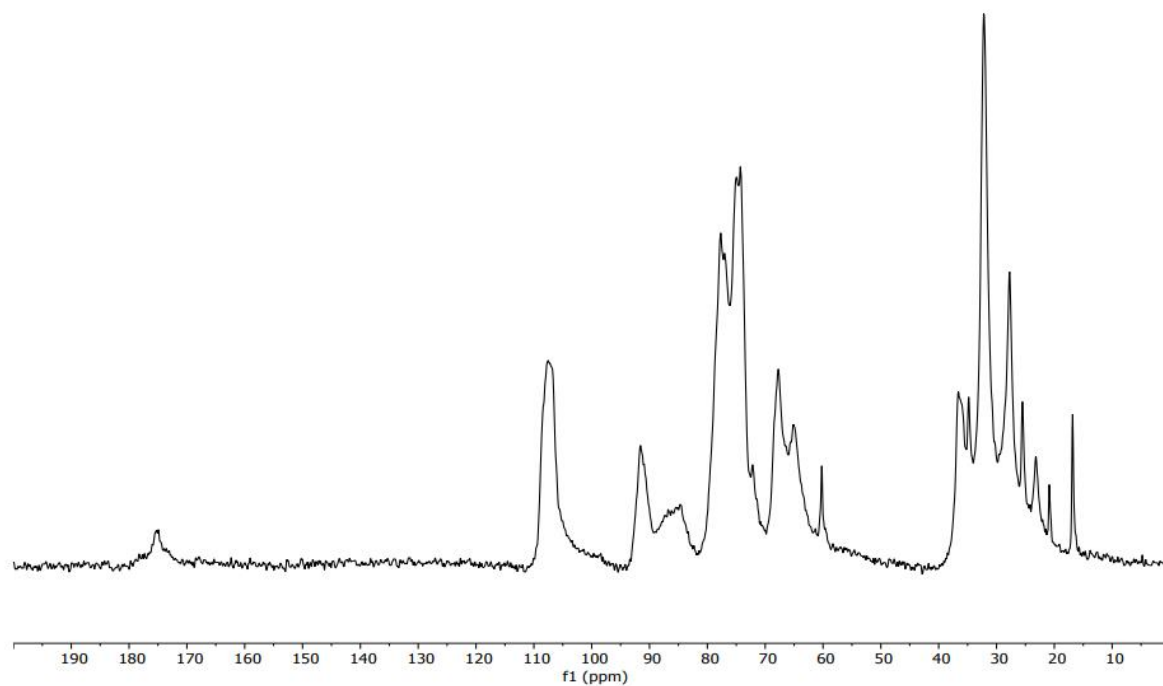
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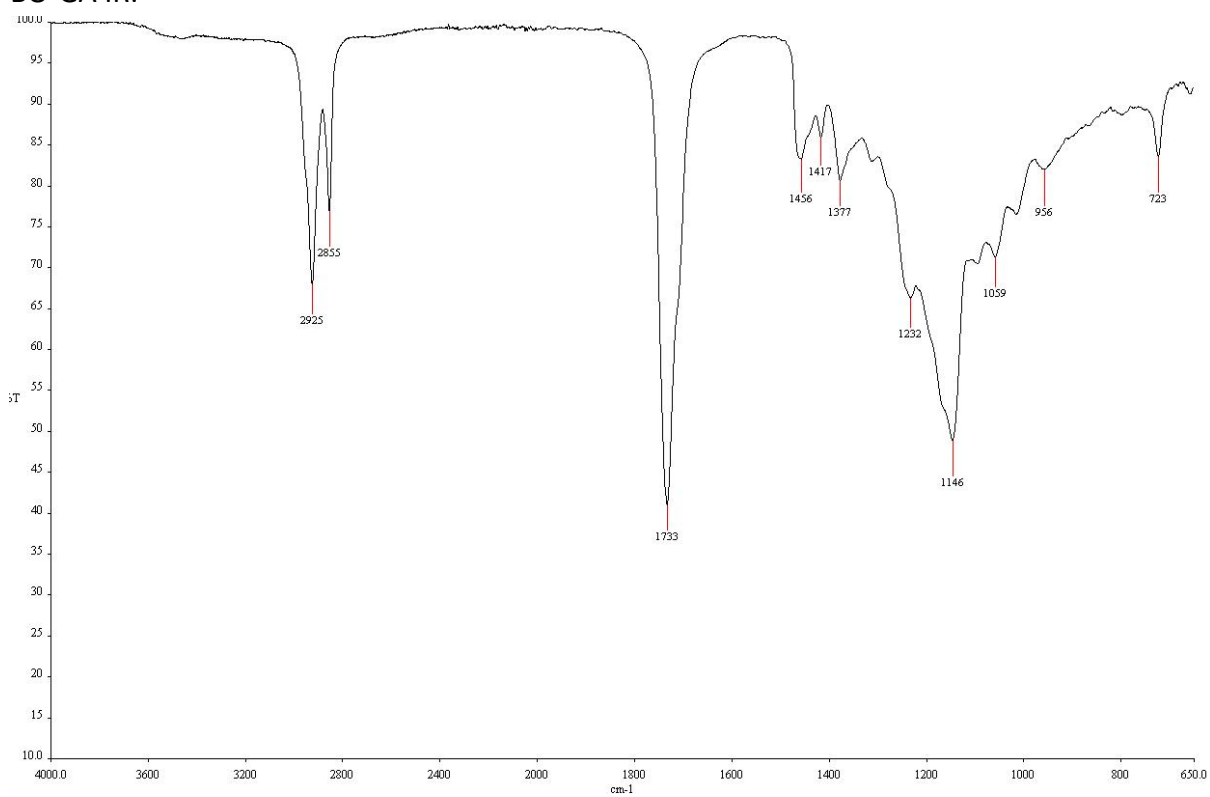
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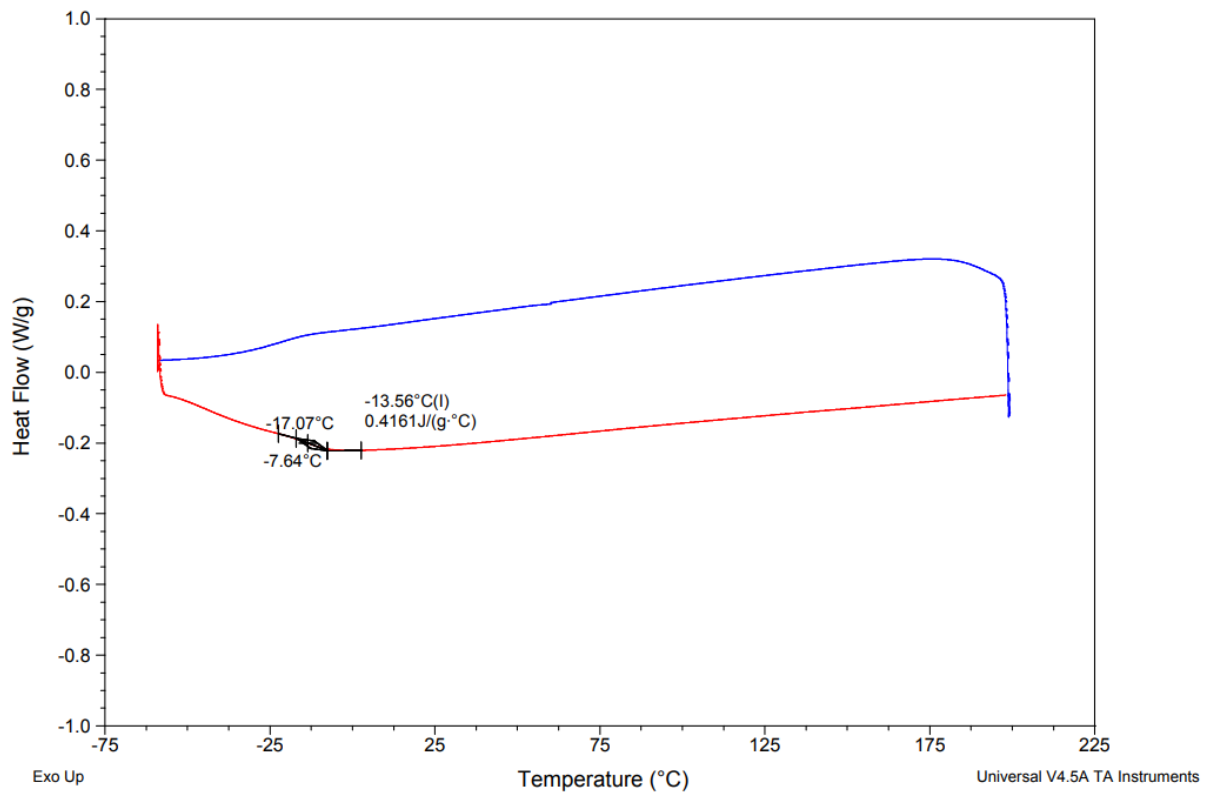
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BO-GA IR:



BO-GA DSC:



BO-GA TGA:

