The University Of Sheffield.

Network Design for Low Energy Cure

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Dedication

In dedication to my beautiful mam, my rock and always my inspiration. She was so proud when I was accepted to do a PhD, but sadly passed away before I completed it.

This is for you mam, love you always.

Abstract

The aim of this work was to design novel functional polymers which required a lower cure energy versus conventional systems in order to lower temperature cure or faster rates of cure in stoved coatings. This will help reduce global energy usage and curing costs. This project has been broken down into several phases, the first of which was to understand network design and polymer structure, and the characterisation of these polymers.

The chemistry chosen in this work was an alternating chain growth polyester synthesis in which cyclic species are subsequently polymerised by alternating ring opening. First, model reactions were used to give a deeper understanding of the chemistry and any side reactions or by-products which occurred. Six catalysts were screened throughout the progression of the model reactions. This provided an understanding of the optimum synthesis conditions and catalyst which minimised side reactions. Following the choice of catalyst, polymers of higher molecular weight were synthesised. The first investigation allowed a gain in understanding of the change in the functionality the initiating species had on the polymer and coating properties. The work undertaken showed difficulties in reaching the expected molecular weights. After investigations, purity of monomers was found to have a high impact on this, and in particular, it was found that water content was critical to retain the cyclic and reactive nature of the monomers. As the reaction included propagation by OH groups, water content was critical. However, drying monomers such as cyclic anhydrides to the required standard would be an industrial challenge. Therefore, alternative routes were explored.

Methods to formulate these polymers into coatings were investigated and the resulting films were tested. Various coating testing was carried out, including mechanical testing and surface appearance tests. In general, the coatings showed that increased functionality yielded an increase in Tg and produced more brittle coatings. This resulted in poor mechanical properties but provided excellent adhesion to the substrate.

Further work is to be carried out following this project, to further understand the relationship between this specific polymer chemistry, polymer functionality and the

impact on physical properties, and investigations into new catalysts to further increase the speed of the curing in fast or low bake coatings.

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List of Abbreviations

2MI	2-methyl imidazole
BTSFA	Bis-trimethylsilyl trifluoro acetamide
DER431	Dow Epoxy Resin 431
DMA	Dynamic mechanical analysis
DMAP	4- (dimethyl amino) pyridine
DSC	Differential scanning calorimetry
EEW	Epoxy Equivalent weight
ETPPB	Ethyltriphenylphosphonium bromide
GC-MS	Gas chromatography – mass spectrometry
GPC	Gel permeation chromatography
HHPA	Hexahydrophthalic anhydride
IR	Infrared
Mn	Number Average molecular weight
Mw	Weight Average molecular weight
NMR	Nuclear Magnetic Resonance
OMTS	Octamethyl tetra siloxane
PA	Phthalic Anhydride
PGE	Phenyl glycidyl ether
SA	Succinic Anhydride
GPC-MS	Gel permeation chromatography – mass spectrometry
TBAB	Tetrabutylammonium bromide
Tg	Glass transition temperature
TGA	Thermogravimetric analysis

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Chapter 1 - Introduction

1 Introduction

1.1 Overview

The coatings industry is in constant demand to develop improved coating systems to offset increased customer demands and ever-changing environmental legislation. At present such product development relies on a time consuming, trial-and-error approach to paint formulation rather than one based on true understanding the properties that a given material can deliver. Therefore, a novel approach to fundamental research of polymer design and the impact on coating performance is required to deliver the 'low energy cure' coatings of the future.

To understand how to modify a polymers structure, an understanding into polymer science, in relation to coatings is required. A polymer structure is often described as falling into one of three categories: 'thermoset', 'thermoplastic' or 'elastomer', Examples of thermoplastics include polyethylene, polystyrene and nylon. The molecules in thermoplastics upon heating will melt and flow. This work however focusses on systems that are able to undergo a thermosetting reaction and the properties these offer. Elastomers are crosslinked polymers which can be stretched easily to high extensions, which when the stress is released, they revert back to the original shape[1]. They are Thermosets, are a class of polymer which do not flow upon heating, due to the bonds present between polymer chains[2]. When transforming from an uncured polymer formulation to a cured coating, reactive polymers contained within the formulation form new covalent (or sometimes non-covalent) bonds between polymer strands, a process either directly between two polymer chains or sometimes between a polymer and a crosslinker. This thermosetting reaction is also known as 'cure'. This can be facilitated by heating the coating to accelerate the reaction kinetics, and this process will ultimately form a continuous molecular network around the substrate. In liquid paints, solvents are added to supress the Tg of the formulation, to help the flow of the coating, and to allow the reaction to occur at lower temperatures. If the solvent evaporates too quickly, a full cure may not be possible due to the polymers reaching a glassy state as the solvent evaporates. This process is called vitrification[3]. The crosslinked network in both types of coating (liquid and powder types) acts as a barrier to aid in the protection of the substrate from the environment

but also provide mechanical properties such as flexibility and resistance to impact in order to prevent deformations to the substrate.

It is well known that the design of reactive polymers and their cross-linker counter parts (i.e. molecules that link the polymers together during the cure process) is critical to deliver a coating that performs in the desired way for long term substrate protection under aggressive environmental conditions. However, due to their complexity, a true understanding of the relationship between the coating formulation and the properties that coating provides is often lacking, and this can prevent the effective development of new coating systems. The aim of this work is to develop a deeper understanding of the relationships between polymer and cross-linker properties and structure to then relate this to the impact they have on the application, network formation and performance for the final coating.

A key aspect of this project is to understand how the tailored design of polymers and polymer networks can allow the development of low energy cure coatings, which means coatings that can deliver the same high performance as high temperature cure coatings, but at reduced temperature. For example, the curing of a coating on large steel objects such as truck chaises is conducted at temperatures in excess of 200°C[4], requiring a huge amount of energy to effectively heat up the coating but also the subsequent mass of metallic substrate. Reducing these energy requirements and associated carbon footprint will have a huge impact on the application costs of this industry in addition to highly significant environment benefits. This project will aim to deliver this, without compromising the performance of the coating, through intelligent polymer, cross-linker and network design.

After an introduction to industrial organic coatings, we will develop the concepts of a change in functionality of the binder and how this affects a coatings properties overall, explaining if an increased functionality to the overall polymer improves coating properties in this chemistry,

1.2 Coatings

1.2.1 Types of coatings

A coating is a thin continuous layer of an organic or inorganic material applied on a surface[5]. Coatings are designed to form a continuous film which adheres to a surface

and can be applied in a single or multiple layers[6]. Coatings are used for either decorative purposes or protective purposes, such as protection from corrosion or UV radiation, for example[7,8]. Therefore, only few materials used in our everyday lives are left un-coated. Corrosion protection coatings, for example, will slow the oxidation metals including iron (converting into iron oxide or rust), for an extended period of time, which prevents damages to exposed assets and the need for early replacement whilst also improving the aesthetics of the substrate. Decorative coatings fulfil aesthetic purposes such as colour, texture, and gloss. Decorative paints are used to personalise the surfaces in our surroundings via the selection of various colours but also textures and gloss levels. They are found in many aspects of everyday life from large infrastructures and transport – aeroplanes, cars, ships, to plastic toys and office furniture[9,10,11].

One way of categorising coatings types is based on the medium in which the polymeric components are delivered to the substrate. The three main categories are: solvent based, water-based, and solvent- free coatings. All coatings types essentially contain the same key ingredients which are the polymer (also known as resin or binder), pigments and various additives to tailor the coating to specific applications. However, the delivery mechanism and details of the polymer type differ. For solvent based coatings, the resin and additives are usually dissolved and the pigments are dispersed into a solvent. This technique is also applied to waterborne coatings; however, the materials are dispersed into water[12]. One class of coatings, particularly relevant to this project, is powder coatings[13]. They are not dissolved nor dispersed into any liquids - all ingredients are co-extruded with a polymer solid at ambient temperature[14].

Thermoset coatings always contain polymeric materials which often can undergo cross-linking, producing a network structure. The combination of the functional polymer and the reactive cross-linker is referred to as the resin or binder in a coating[5], and is the major component in a coating which primarily determines flexibility and mechanical strength of a coating [15].

Resins in coatings can be either thermoplastic or thermosetting[11]. Thermoplastic coatings usually contain a high Mwt polymer which provides mechanical strength without further polymerisation and higher molecular weight increase the

entanglement of the polymer strands creating a resilience similar to polymer networks. Thermosetting coatings typically contain lower Mwt polymers which undergo a crosslinking reaction after application to achieve the desired film properties, such as mechanical or chemical resistant properties[11,13,16]. This process can be accelerated by heating, triggered by light irradiation, or delayed by solvent evaporation[17] (or a combination of these) to alter the reaction kinetics. This process forms a continuous molecular network over the substrate that, once complete, delivers a chemical barrier to protect the substrate from the environment[18].

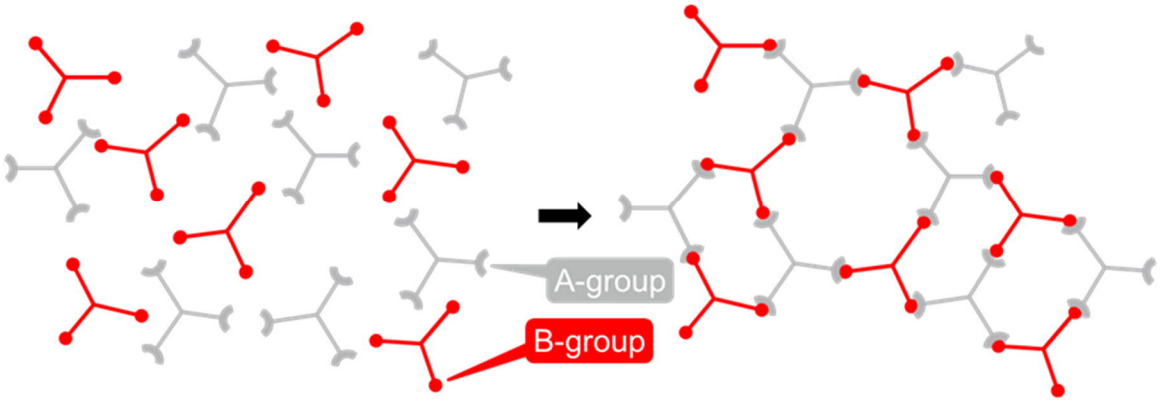

Figure 1-1 - Crosslinking schematic between polymer and crosslinker

The Tg is defined by Young and Lovell as the temperature at which the polymer transforms abruptly from a glassy state (hard) to a rubbery state (soft)[1]. It can be influenced by the chemical structure of the monomers from which it is made. For example, if the monomers have flexible structures with free rotation and unrestricted degrees of freedom, then the Tg of the polymer will be lower than if the polymer was built by monomers based on rigid structure. For example, monomers with higher number of sp^3 hybridised C-C bonds with free rotation this will give low Tg polymers whilst monomers with sp^2 C=C bonds will result in more rigid structures (e.g. benzyl rings) which will give higher molecular weights. For polyesters this would be noted by the difference between Adipic acid (AA) and Terephthalic acid (TPA) (Figure 1-2).

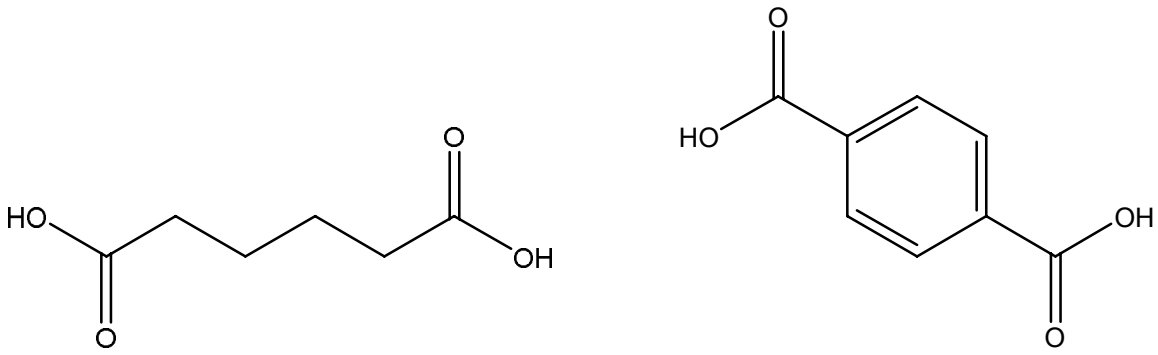

Figure 1-2 - Adipic acid (left) and Terephthalic acid (right)

1.2.2 Formulating a binder for a coating

When formulating a polyester polymer for a standard powder coating, calculations are based on the theories of Flory and Stockmayer which can be used to calculate the expected properties of the polymer. These are given based on statistical distributions of reaction products. This is due to most powder coatings containing mainly polyesters formed through a step growth process. The properties predicted are used to determine whether the binder will be suitable for the intended use. For polymers based on the reaction of diacids and diols, these could include; acid value, hydroxyl value, end group functionality, Mw, Mn, r (stoichiometry) and gelation point (P_{gel}). The gelation point (or extent of functional group conversion required for form a gel) is calculated through the Flory – Stockmayer equation[19] (Equation 1-1) and corresponds to the extent of conversion required to create a network. It is therefore a critical tool of the chemist and any $P_{gel} < 1$ (100% conversion of reactive groups) gives rise to the risk of gelling the polymer during synthesis taking place in a reaction vessel but not in a thermoset coating. This process is accompanied with an exponential increase in fluid viscosity of a polymer.

$$p_{gel} = \frac{1}{\sqrt{r(f_1-1)(f_2-1)}}$$

Equation 1-1 -Flory - Stockmayer equation which describes the extent of reaction at the gel point (Pgel) of an A + B polymerisation, where r is the stoichiometry ([MA]/[MB]), f_1 and f_2 are the effective functionality of species A and B

1.2.3 Low energy cure coatings

Investigations into lower energy cure, either via lower temperature cure or faster cure rate are of high interest due to reduction in energy usage, carbon footprint and subsequent cost reduction in the production of coated articles. The lower energy cure requirement affects all types of coatings: solvent-borne, water-borne, 100% solids, regardless of the curing temperature regimes utilized over the various coating areas.

In developing the next generation of coatings, focus must be on the design of the polymer networks by the informed selection of appropriate building blocks to provide, not only the application and curing properties, but to also meet environmental regulations. A detailed understanding and appreciation of network and polymer design should facilitate the development of breakthrough products and establish the basis of coating technologies for the future.

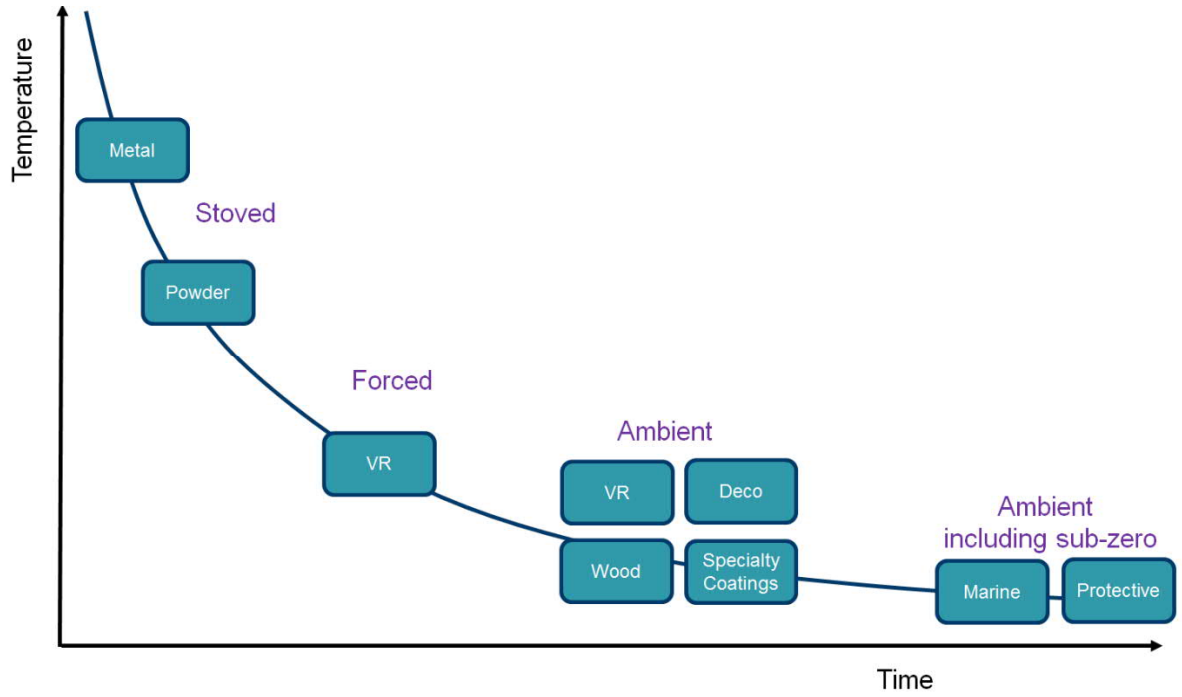

Figure 1-3- Conceptual cure time vs. cure temperature of various coating markets

Coatings used for the metal, powder and vehicle refinishes industry, all use elevated temperatures to cure the coatings as shown in Figure 1-3. All other coatings require solvent evaporation at ambient and sub-ambient temperatures to cure. All

thermosetting coating types could benefit from a lower energy cure either by reducing the cure temperature or the cure time (which equates to less energy consumption conceptually). For example; powder and metal coatings from a lower stove temperature, protective and marine coatings from a lower sub ambient cure temperature to adapt to application conditions which can vary greatly from one location to another.

As mentioned before there are two main reasons for coating a substrate – decoration and protection. Decoration is to improve the appearance. Protection is to maximise the life of the substrate or increase resistance to a variety of agressions[20].

The coatings performance is determined by how much protection can be offered from chemical damage or mechanical ageing. Mechanical performance covers a wide range of properties specific to the application, and ranges from impact resistance to weathering resistance or corrosion resistance, but also heat or frost insulation to stain resistance and so on. Ageing from weathering can be related to exposure to sunlight (UV), oxygen and heat among many others. How a coating maintains its properties over time is also crucial[21], and so it is often important to measure these properties as a function of time. Chemical resistance performance describes the resistance of a coating to a variety of substances such as household cleaning products[22], fuels and automatic fluids, alcohols and other industrial cleaning liquids.

1.3 Polymers and control

1.3.1 Polymer structures

The term polymer was derived from Greek ‘poly’ meaning many and ‘meros’ meaning part[23]. In the 1920’s it was believed that molecules could not have a molecular weight higher than a few thousand. This was challenged by Hermann Staudinger, a German chemist who proposed that polymers did exist and went on to make hydrogenated rubber, showing it was made up of over 10000 atoms and showing that these were, in fact, macromolecules[24] (or in this case polymers). He went on to win the Nobel Prize for his contribution to chemistry in 1953. Since his invaluable contributions in the 1920s, a great volume of research has resulted in an ever-increasing diversity of polymeric materials and a wealth of associated applications. Millions of tons of polymeric materials are synthesised each year and the discovery and development of new synthetic polymers continues to grow at a rapid pace [25,26].

Polymers are long chain molecules (macromolecule) made up by covalently bonding smaller molecules (monomers) repetitively, which exist in a wide variety of forms ranging from food (protein, starch) to everyday items (coatings, plastic bags, automotive parts, clothes)[15] to in the human body (poly(nucleic acids), proteins)[27].

Polymers can have a diverse range of structures from being homopolymers, containing all of the same monomer continuously, to copolymers containing different molecules in a chain which also includes block copolymers in which blocks of monomer are connected (Figure 1-4). These can also have structural differences from being linear, branched, with more or less degree of ordering (e.g. regular branches, star shaped polymers, hyperbranched polymers and so on). These polymers can also be subject to different stereochemistries such as isotacticity (groups on the same side of the backbone), syndiotacticity (groups on alternating sides) or atacticity (random).

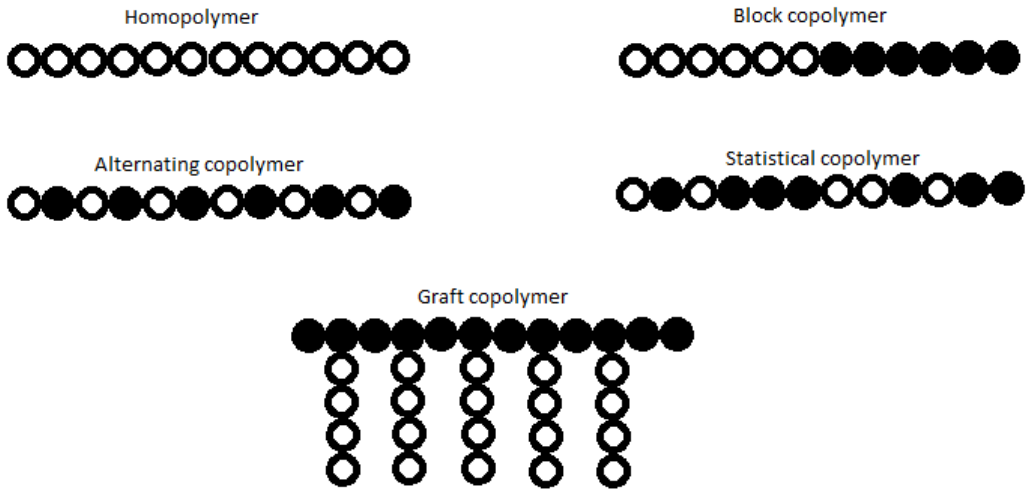

Figure 1-4 - Visual explanation of different types of copolymer structures

Copolymers are polymers which have been derived from 2 or more structurally different monomers (Figure 1-4) Copolymerisation allows for the alteration or random arrangement of monomers on the overall polymer backbone resulting in the possibility of the intra- and intermolecular forces of the polymer to be altered. Therefore, properties such as glass transition temperature, melting point, elasticity and chemical reactivity can be manipulated leading to a wide variety of polymers being produced.

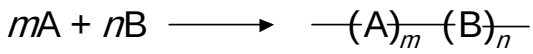

Figure 1-5 - Formation of copolymers

Polymers also have different classifications and will fit into one of the three classification groups;

- Thermoplastic – these are linear or branched polymers and can be melted and reformed on heating and can be further split into two categories; crystalline and amorphous. Crystalline polymers have very closely packed chains which have repeating units able to align to the repeating units on the adjacent polymers, amorphous polymers are polymers which will not naturally exhibit this alignment[28,29].
- Elastomers – these are moderately cross-linked amorphous polymers which can be stretched and rapidly recover their original dimension[30],
- Thermosets – these are normally rigid polymers, with a high degree of crosslinking and once formed, will degrade with heat rather than become fluid like elastomers[1].

1.4 Controlling polymerisations

1.4.1 Step growth

Step-growth polymerisation usually uses two or more monomers that have two or more reactive functionalities. Oligomers are formed which will retain some of the functional groups which in turn provide sites for further reaction, either with other oligomers or monomers. Step-growth often generates a by-product, water in the case of polyesters, (hence why it was originally called condensation polymerisation as a molecule of water would be generated with each bond formation[31]) but other examples include hydrochloric acid[32] (for instance reaction diacyl chlorides with dihydroxyls). An industrial example is the formation of the polyester known as PET (polyethylene terephthalate) synthesised from terephthalic acid and ethylene glycol where hydroxyl groups on the ethylene glycol esterify with the acid groups on terephthalic acid (TPA). In this case the esterification produces a molecule of water which is distilled out of the reaction. However, there are polymers such as polyurethanes as, that will polymerise by step-growth but do not eliminate a small molecule by-product.

Predictive calculations for step-growth processes such as the Carothers equations[33,34] and the further developments by Flory[35], Stockmayer[36], Miller and Macosko[19] to allow relationships between extent of reaction and resulting polymer structure to be predicted. However, these calculations assume there is ideal reactivity of the functional groups during the polymerisation process as it is this control that allows prediction of degree of polymerisation (DP) and associated polymeric descriptors such as Mn, Mw and polydispersity in both linear and non-linear polymers to be modelled.

$$\bar{X}_n = \frac{1}{1-p}$$

Equation 1-2: The Carothers equation for predicting DP for equimolar polymerisations. Xn is the number average degree of polymerization, and p is the conversion of reactive groups of the minor component

Without high levels of control on the reaction of functional groups, standard measurable and quantifiable descriptors of polymers used to predict parameters such as degree of polymerisation and molecular weight distributions at a given monomer conversion cannot be applied.

1.4.2 Chain growth

Chain growth polymerisation follows three steps; Initiation, propagation & then termination (in most cases) (Figure 1-6). For anionic and cationic polymerisations, initiation will generate an ion, which can be generated by a chemical reaction or by a source of irradiation[37]. Once this active centre is generated, it produces chains by the consecutive addition of monomers through the propagation step of the reaction. As active centres are present at the end of the chains, the propagation reaction continues until it becomes interrupted by a chain transfer or a termination event[3]. An example of chain growth polymerisation is below.

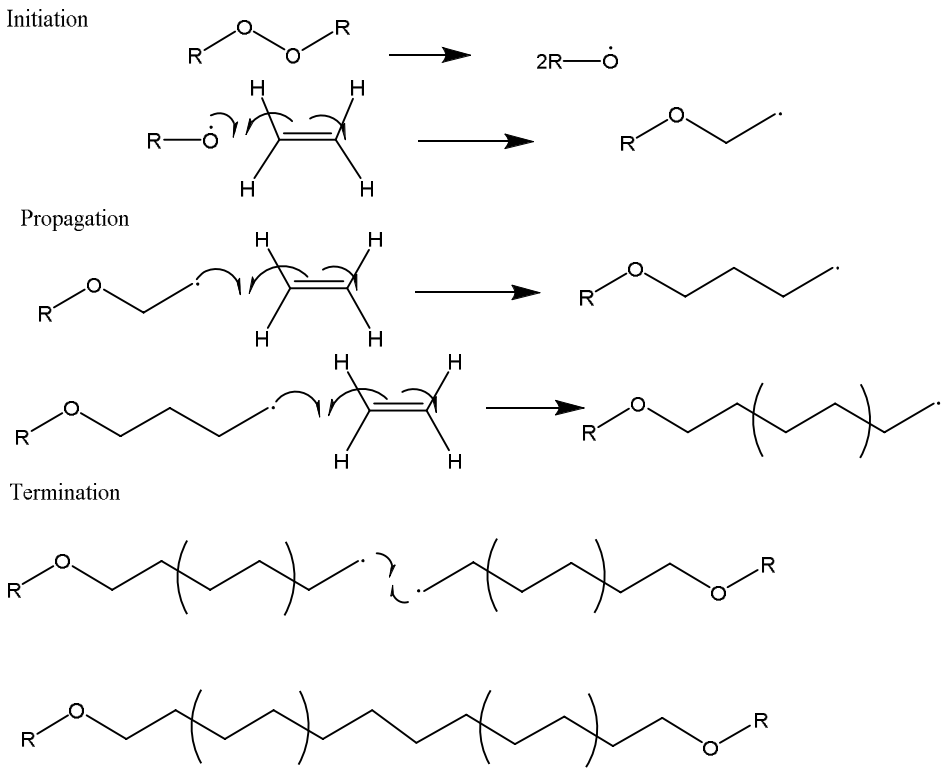

Figure 1-6 - Example of chain growth polymerisation terminated by two free radical species reacting together to produce a non-radical adduct

Chain growth polymerisations of epoxy resins into polyethers can be anionic or cationic and both types of reaction are of important in epoxy resin technologies[3]. Other systems commonly use radical polymerisation in the case of, for instance the polymerisation of unsaturated monomers (e.g. acrylics or vinylic).

The main parameters controlling the molecular weight of the polymer are the functionality of monomers, the molar ratio between initiator and monomers, the concentration of species that are involved in chain transfer steps, and temperature that affects the relative rates of the different steps. As the rate of initiation, propagation, chain transfer and termination are linked to the specific initiator(s), monomer(s) and process conditions, it is difficult to devise a uniformed, simple equation for prediction of molecular weight in chain growth polymers like there is for step growth polymerisation[38].

1.4.3 Living polymerisation

The concept of living polymerisation was originally proposed by Ziegler in 1936[39], however it was not until 1956 that Szwarc first experimentally demonstrated the living polymerisation of styrene using anionic polymerisation[23,40]. The official IUPAC definition of a living polymerisation is 'a chain growth polymerisation from which chain transfer and chain termination reactions are absent' which indicates once monomer conversion is complete, active functional ends remain allowing continued polymerisation if a further addition of monomer occurred[41]. The continued polymerisation must occur from the chain ends of the original polymer, thus resulting in a chain extension, and without any new chains being formed.

Anionic living polymerisation is often employed to produce synthetic polydiene rubbers, styrene-butadiene rubbers (SBR), and thermoplastic styrenic elastomers[42]. This polymerisation does not have a chain termination step as there is charge repulsion between reactive chain ends so no reaction can occur to terminate by disproportionation or combination[43]. The rate of initiation needs to be comparable or faster than the propagation step and the rates of exchange between various forms of the living species, such as free ions and ion pairs are much faster than the rate of polymerisation[44]. Consequently, the number of polymer chains is equivalent to the number of initiating species and so the number-average degree of polymerisation (DP_n) can be described by the equation (Equation 1-3) below, where $[M]_0$ and $[I]_0$ are the initial monomer and initiator concentrations, respectively.

$$DP = \left(\frac{[M]_0}{[I]_0} \right) \text{x conversion}$$

Equation 1-3 - Degree of polymerisation for anionic chain growth polymerisation

If this occurs, the chain will continue to grow from a single point until all monomers have reacted during the propagation step and should produce a polydispersity index value close to 1 [45]. A polydispersity index close to 1 indicates all chains are of similar molecular weight with minimal side reactions and unreacted monomers[46] and that the

rate of initiation was considerably faster than the rate of propagation. As a result, the molecular weight distribution would be narrow and a near mono-disperse molecular weight distribution which would be described as a Poisson type distribution[47]. The polydispersity (*Đ*) (PDI) of the distribution is described as the ratio of the weight-average molecular weight, M_w, to the number-average molecular weight (M_w/M_n).

$$\text{PDI} = \left(\frac{[\boldsymbol{Mw}]}{[\boldsymbol{Mn}]}\right)$$

Equation 1-4 - Equation for calculating polydispersity index (PDI)

Many desirable properties of polymers, such as thermal behaviour (i.e. Tg) and mechanical strength are to an extent dependent on their molecular weight[48]. Great strides have been made in the field of controlling molecular weight, especially in the area of controlled and living polymerizations. Over the past decade, techniques known to control molecular weight and structure, such as living anionic techniques, several new methods such for ring-opening metathesis polymerization for cyclic hydrocarbons (ROMP), group transfer polymerization (GTP) for polymerization of (meth)acrylates, Lewis base-mediated cationic polymerization for vinyl ethers and Ziegler Natta polymerisations have been developed or improved[49 50 51 52]. GTP is a chain growth mechanism producing low PDI acrylic polymers. The process uses initiators but the catalysts used are sensitive to moisture and therefore renders the initiator inactive and produces a lower Mn if purification of all materials is not carried out beforehand[53]. ROMP is carried out due to ring strain of the monomers, with stereochemistry highly dependent on the catalyst used, most commonly the 'Grubbs' indicator, named after the inventor of the catalyst and one of the inventors of the chemistry itself[54]. Ziegler Natter catalysts are usually metal compounds involving a transition metal from IV-VIII. They're shown to produce ethylene in a rapid polymerisation which can occur at low temperature and atmospheric pressure. They're used with this method to produce high density polyethylene, which in time, was found to also be very effective for production of polypropylene[50].

All these methods have been found to be capable of controlling both the average chain length and the molecular weight distribution[55,56].

1.4.3.1 Reversible Deactivation radical polymerisations

For over 50 years, radical polymerisation has been one of the most commercially important polymerisation techniques[57]. Recently, an increased understanding of equilibrium radical concentrations has allowed highly controlled/living free radical polymerisation techniques to be developed, known as RDRP (reversible deactivation radical polymerisation)[58,59]. Techniques such as stable free radical polymerisation (SFRP)[60], atom-transfer radical polymerisation (ATRP)[61] and reversible addition-fragmentation chain transfer (RAFT)[40] are commonly applied to prepare vinylic or acrylic copolymers[62].

Reversible deactivation radical polymerisations can produce very well-defined polymers[43]. Polymer chains will continuously grow until all monomers have been consumed. The presence of a chain transfer agent considerably reduces the rate of termination, making the polymer chain apparently living. Terminations are however still present which is why these polymerisations cannot be classed as living polymerisations, but as controlled polymerisations. To produce a very low polydispersity index (PDI), the rate of initiation needs to be larger than the rate of propagation, resulting in $K_I \gg K_p$ (K_I – Rate of initiation, K_P, Rate of propagation)[63,30].

Using such type of polymerisations, it is possible to achieve a good control over the polymer definition and obtain PDIs as low as 1.10 with radical polymerisation techniques[64]. This is because the reaction proceeds with radicals that can be reversibly activated and de-activated to be able to control and define the reaction, rather than radicals only existing for a very short time which results in a reaction which cannot be controlled and in return produce a well-defined polymer[65]. There are different types of RDRP such as; Atom transfer radical polymerisation, nitroxide mediated polymerisation and radical addition fragmentation transfer polymerisation, among others[66 67].

Atom transfer radical polymerisation (ATRP) was discovered in 1995 by Sawamoto's group[68] and by Matyjaszewski's group[69] and can produce well-defined polymers. ATRP

uses an alkyl halide (mono or multifunctional) and a copper complex to initiate the propagation, which undergoes a single electron transfer and will abstract a halogen[70]. This results in a radical carbon produced, which is able to propagate and re- abstract the halogen. This generates polymers which are possible to end functionalise and are controlled, so are able produce low polydispersities[71]. ATRP however suffers from the toxicity (and cost) of Copper so that an important area of academic research focusses on reducing the amount of copper used or finding alternative metals.

Reversible addition fragmentation chain transfer polymerisation (RAFT) uses mainly dithio-compounds such as dithiocarbonates, dithiocarbamates and trithiocarbonates[23] as chain transfer agents. Xanthates are also used in the case of a similar technique called MADIX (macromolecular design via the interchange of xanthate)[40].

Nitroxide mediated polymerisation (NMP) is also a radical transfer polymerisation technique which can produce well defined polymer structures. This commonly uses a nitroxide initiator radical known as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)[60].

Other polymerisations which are controlled which use radicals are iodine degenerative transfer polymerisation (IDT)[67], single electron transfer-degenerative chain transfer living radical polymerization (SET-DTLRP)[72], single electron transfer-living radical polymerization (SET- LRP), copper-mediated azide–alkyne cycloaddition (CuAAc)[73], initiator transfer agent terminator[74] and cobalt mediated radical polymerisation (CMRP)[75].

1.5 Alternating polymerisation reactions

This project will investigate an alternating copolymerisation, involving an OH initiator, an anhydride and an epoxy. Firstly, reactions involving an epoxy are explained below, to understand the propagation step of this reaction in further detail. The reaction is then investigated in further detail in 1.5.2 in which the history of this chemistry is investigated and to recognise what has already been discovered with this reaction to further the understanding and advance the project.

1.5.1 Polymerisation reactions involving epoxy Groups

Epoxy functional polymers are very commonly used in coatings and are commercially available[76]. They are one of the most important thermosetting polymers and have been used worldwide since their introduction into the coatings industry in 1946[77]. They can undergo many different polymerisations depending on the process conditions due to the electrophilic nature of the carbons and the ring tension on the 3 membered ring. They are most commonly used for step growth reactions with amines, acids, anhydrides and phenols but can also undergo both chain growth anionic and cationic homopolymerisations[78].

An example of epoxy polymerisation is Anionic chain growth. This requires the use of an anion (negatively charged ion) to initiate the reaction[79]. For example, in the initiation step, a nucleophile adds on the oxirane ring, opening the ring into an alkoxide, which in turn attacks another ring and this is the propagation step[76]. This step will continue and produce a polymer until it reaches a termination step[76]. This reaction usually uses a tertiary amine (or other non-protic nucleophile) as an initiator (often referred to as catalyst).

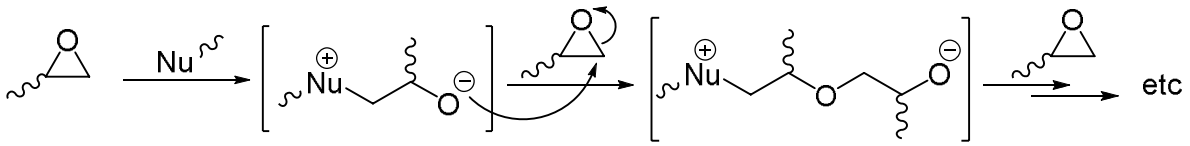

Figure 1-7 - Schematic reaction of epoxy anionic chain growth polymerisation

Due to their low steric hindrance, epoxies are used commonly with nucleophiles in reactions such as an S_N2 reaction of nucleophilic substitution to the unhindered carbon (in most cases this reaction preferentially reacts with the unhindered alpha carbon, but as shown in this thesis, beta opening is also possible) resulting in the formation of an –OH group. When multi-functional epoxies and multi-functional protic nucleophiles are used, this process leads to a step-growth polymerisation an exchangeable atom (Figure 1-8).

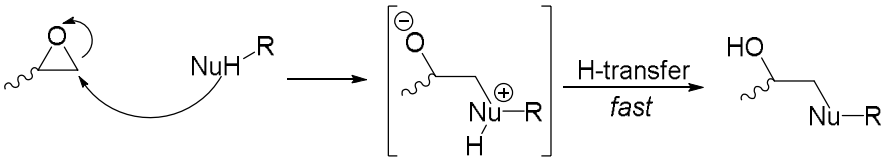

Figure 1-8 - Overall schematic reaction of step- growth epoxy polymerisation

Using this understanding, the acid produced from the anhydride used this chemistry, should also follow the reaction set out in Figure 1-8, with the acid acting as a nucleophile, therefore explaining one of the 2 parts to the chemistry used in this project.

1.5.2 Alcohol - anhydride – epoxy polymerisations

A reaction between an alcohol and an anhydride produces an acid functional product. The oxygen of the alcohol will attack the C=O of the anhydride, breaking the C-O bond and producing an acid (Figure 1-9). This acid is very crucial to the alternating reaction as this will further the reaction and react with an epoxy, as explained above.

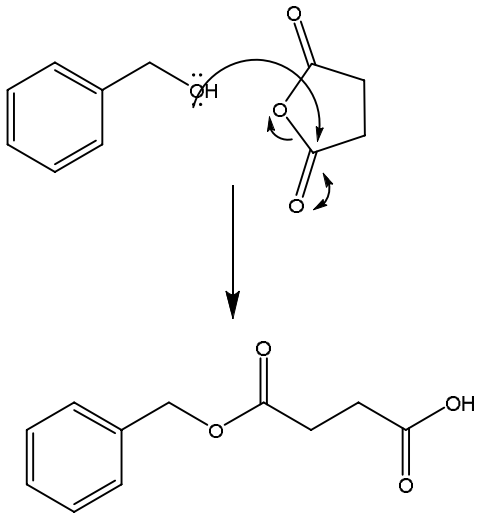

Figure 1-9 - Mechanism of alcohol - anhydride reaction – the initiation step in the alternating process

Processing of the alcohol - anhydride - epoxy reaction follows steps in which each addition requires its own new activation and therefore resembles the idealised alternating co-polymerisation[80].

An alternative chain-growth route to both aliphatic and semi aromatic polyesters is the alternating copolymerization of epoxides and cyclic anhydrides shown in Figure 1-10. The use of two distinct monomer sets allows for tuning of properties and post-polymerization modification[81]. Alternating ring opening polymerisations had not attracted much attention of researchers for many years due to the difficulties in obtaining high molecular weight polyesters and eliminating the side reactions such as homopolymerisation of epoxides[82].

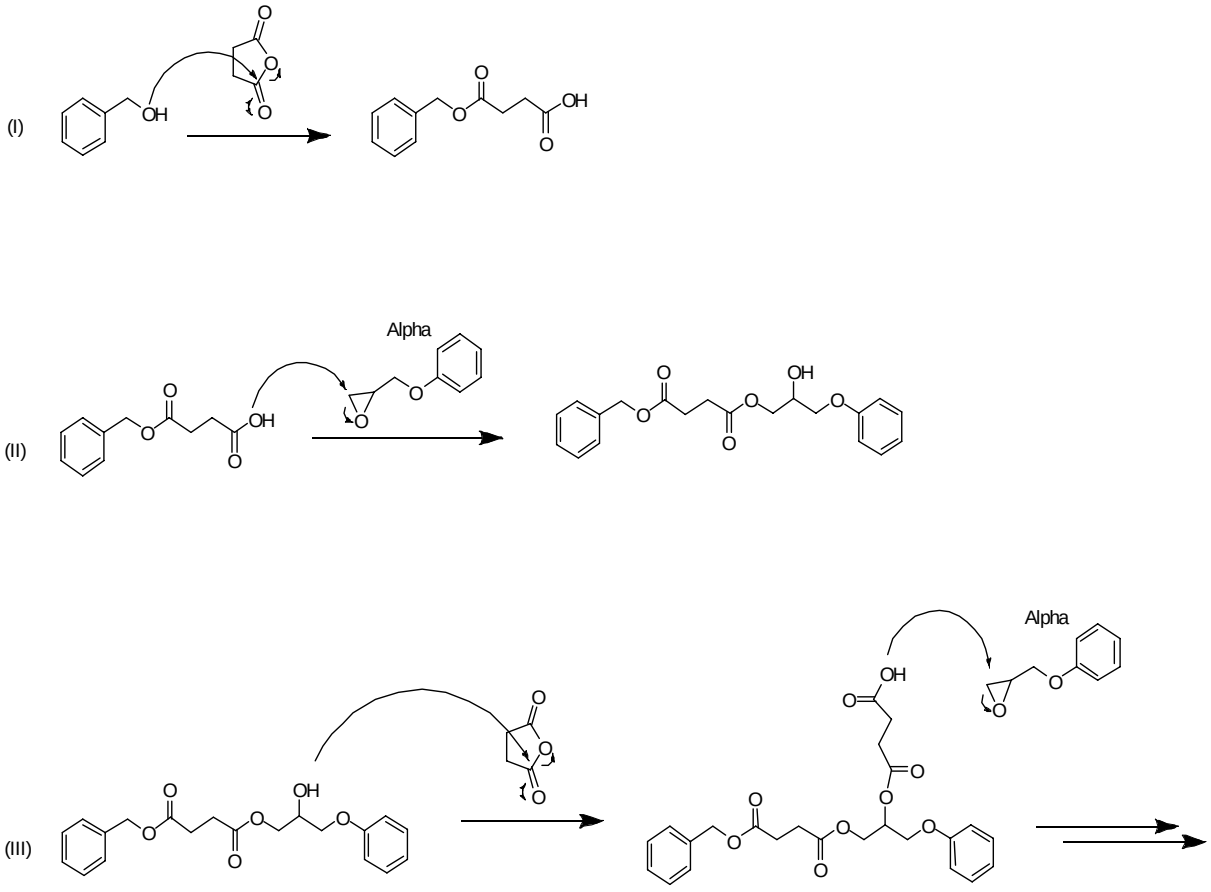

Figure 1-10 – Alternating chain growth polymerisation of Alcohol, anhydride and epoxy reaction

The first alternating copolymerization of epoxide with anhydrides to linear polyesters was reported by Fischer in 1960 using tertiary amines as catalysts[83]. He discovered that a 1:1 ratio of the epoxy: anhydride provided the highest yielding products, which would be understandable as no reactants would be left in excess. Many different epoxy and anhydride monomers were tried and found when using unsymmetrical epoxy molecules with a range of different molecular weights such as allyl glycidyl ether to

epichlorohydrin and cyclohexene oxide, the resulting polymers showed to be amorphous and provide a range of Tg from 35°C – 125°C. He found when using ethylene oxide, as this is a symmetrical molecule, he had produced crystalline structures which had a melting point of 108°C. He tried a range of anhydrides but used phthalic anhydride the most often due to cost and the colour and satisfactory results of the products. Other anhydrides such as succinic anhydride were tried but appeared to give dark coloured products and a very slow reaction time.

Almost 10 years later in 1969, Tsuruta and colleagues[84] reported using organometallic catalysts such as $ZnEt_2$ for the copolymerization of epoxides/anhydrides. In 1985, Takuzo and Inoue showed an alternating co-polymerisation between phthalic anhydride and epoxypropane, occurring simultaneously on either side of a metal complex plane (Figure 1-11), but revealed that they have very low catalytic activity[85].

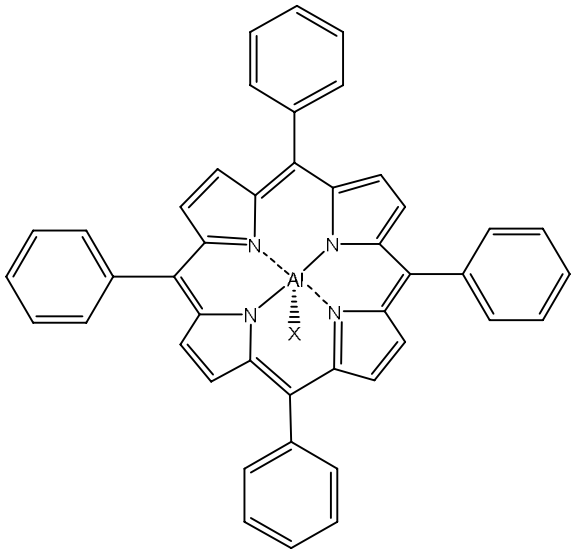

Figure 1-11 - Structure of metal complex used in Takuzo and Inoue's research in 1985. (X= -Et, -Cl, various -O(-CH/CH_2/CH_3-)Cl complexes)

In 2007 subsequent progress was achieved with the development of new well-defined metal catalysts. Coates and his team published work on cyclic aliphatic anhydride with various epoxies, using zinc complexes[86]. This paper showed that a narrow molecular weight distribution of 1.2 could be achieved for the first time. Furthermore, in 2010 a paper was published by Williams and her colleagues explaining how ring opening copolymerisation (ROCOP) had very little attention but the properties of the resulting materials when using ROCOP can have great advantages. They described that ROCOP

polymers can be easily manipulated by a simple substitution of just one monomer. For example, switching the epoxide from propylene oxide to cyclohexene oxide, using the same ROCOP catalysts, demonstrates it is possible for the glass transition temperature to range from 33–123°C[87].

Since then, academic interest increased in subsequent years regarding alternating low molar mass polyesters which were achieved with various metal complexes as catalysts. In 2011, Coates and colleagues reported a salen chromium complex catalyst (Figure 1-12) for the ring opening copolymerisation (ROCOP) of maleic anhydride (MA) with variety of epoxides producing alternating polyesters, giving very low PDI polyesters down to 1.1[88].

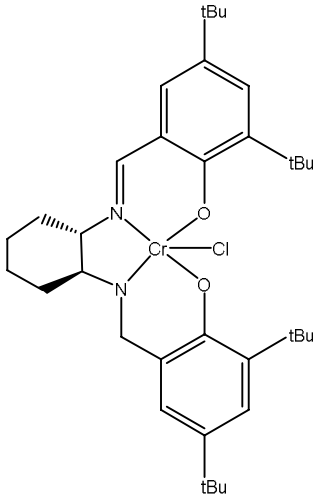

Figure 1-12 - Chromium salen complex used as a catalyst in ROCOP reported by Coates in 2011

These polymers had Mn values up to 25kgmol$^{-1,}$ with low PDI, indicating a very controlled reaction had taken place. Similar findings were discovered by Huijser and team in the same year[89]. They explained the polymerisation of cyclohexene oxide and various alicyclic anhydrides using a metal chromium complex (Figure 1-13) and 4-dimethylaminopyridine (DMAP) as a cocatalyst. They found that using CO_2 during reaction minimised the epoxy homopolymerisation which took place.

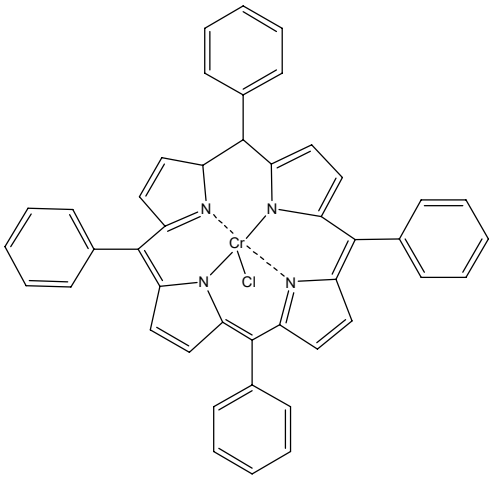

Figure 1-13- Metal chromium complex used as a catalyst in ROCOP reported by Hujser in 2011

Following on from that, in 2013, Chisholm and colleagues investigated other metals for use as catalysts in this reaction. They tested aluminium, chromium and Cobalt complexes[90]. Propylene oxide and various anhydrides were used, but the highest molecular weight was found using phthalic anhydride. They found that the rate of reaction in the metal-carboxylate was faster than the metal-alkoxide, resulting in the reaction between the anhydride and epoxy being faster the than epoxy-epoxy homopolymerisation. In 2014, Williams and colleagues reported a copolymerisation of phthalic anhydride and cyclohexene oxide using di-magnesium and zinc catalysts, which showed good polymerisation control, with PDIs reported as low as 1.06[91].

Work similar to Chisolm in 2013 was reported by Coates in 2016[92], in which large cobalt complexes were investigated catalysts. They used a Co(III) complex with propylene oxide and a range of anhydrides, but found they produced semi crystalline polymers with PDIs ranging from 1.13 – 1.29 - higher values than found in the past.

All these reactions reported used the metal complex to activate (open) the epoxy ring to initiate the reaction, which once activated, reacted with the anhydride ring and an alternating reaction was propagated. It is also worth noting, all the polymers produced that are explained in this chapter, all had low PDI values (down to 1.1), however were linear difunctional polymers.

More recently, in 2017, Zhao and co-workers, describe the first paper using an initiator for the reaction. An alternating reaction of phthalic anhydride and ethylene oxide used BDM (1,4-benzenedimethanol) as an initiator. They showed it could be controlled

whilst using a phosphazene base (t-BuP) (Figure 1-14) as a catalyst, producing PDIs as low as 1.06[93].

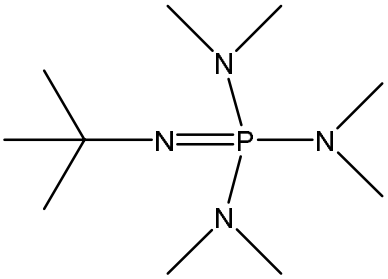

Figure 1-14 - Phosphazene base (t-BuP) used in reactions by Zhao et al.

In the same year, further developments were made in this chemistry using less toxic Lewis acid catalysts, developed by Li and colleagues[94]. They explained using metal ligands containing cobalt and chromium, gave toxic contaminants to the final polymer. They also showed whilst small organic compounds such as t-BuP (phosphazene base) as mentioned in the work by Zhao[93], showed lower catalytic activity and a lack of structural variation. This enabled a work in Lewis acids and bases such as $ZnEt_2$ and DMAP, with the Lewis acid used to catalyse the polymerisation.

To explore further the use of the metal free catalysts, Merna and colleagues reported initiating the reaction with organic bases, in 2017[95]. They used a PPNCl (bis(triphenylphosphine imi- nium)chloride), with a range of anhydrides and epoxies. They found selectivity was not as high as the metal complexes and showed PDI values ranging from 1.07- 5.39. They discovered the polymerisation of maleic anhydride with propylene oxide produced dark brown solids insoluble in solvents due to crosslinking. They also found that copolymerisation of the tetrachlorophthalic anhydride (TClPA) with varying epoxies showed to give lower Mn values than expected and broader PDI values. When reacting TlCPA with styrene oxide, they found only oligomeric product, showing catalytic activity was very poor with these monomers. Phthalic anhydride showed to give polymers with molecular weights closest to the expected values, with high conversion and the lower PDI values averaging 1.3 suggesting a higher degree of control over the synthesis. Overall, they showed they could produce difunctional alternating reactions using these catalysts, but the conversions and broad PDIs compared to metallic catalyst were not as effective.

It was found only a small amount of academic research had been focussing on this type of polymerisation and was found that none investigated the use of these polymers in coatings.

This chemistry appears to be very interesting as it has the possibility to obtain very well controlled polymers in terms of Mn and PDI values. In turn, this also gives the possibility to obtain well controlled functionality. Currently, powder polyesters used for powder coatings don't have a good control over functionality, due to losses in glycol during synthesis creating a mismatch with expected values. Expected functionality in the current powder polyesters is equally limited, with current formulations resulting in lower functionality when processed to the same acid values compare to the alternating chemistry. The alternating reaction is also more time efficient, with literature showing reaction time in under 4 hours, whereas a current powder polyester is synthesised in 4 days.

Therefore, the alternating anhydride – epoxy polyesterification initiated by hydroxyls had been chosen for this project to understand the properties and benefit that may arise for these new systems applied as coatings, and to understand the effect of low PDI and exact functionalities over coatings properties. Polyesters are of industrial relevance and can provide important coating properties, such as mechanical resistance and UV resistance. The polyester structure can be manipulated in terms of molecular weight and number/type of end groups using this chemistry which is useful for this project to understand how changing a polymer property affects the coating property and this reaction has been found to give high conversion rates and high yields in a previous 'in-house' AkzoNobel research project which however was not aiming at using these as main polymeric binders but as formulation additives.

This project aims, by using an alternating copolymerisation chemistry, to modify and optimize binder technologies to achieve the required ultimate film performance whilst using significantly less energy curing systems to deliver these targets. It is anticipated that in better understanding the structure, reactivity and general polymer design criteria, a high film performance can be delivered. This knowledge can be applied to design and synthesise an optimal polymer-cross-linker combination to allow performance criteria to be achieved at lower cure temperatures.

Chapter 2 demonstrates how model reactions are used to gain understanding of the chemistry, and how to minimise any possible side reactions, mentioned above. Using the literature review, it was noticed all polymers made were difunctional, and only very minimal using an alcohol to initiate the reaction. This is the first understanding – to evaluate how effective using an alcohol is in this reaction to initiate. Furthermore, as it would be beneficial to change the properties of the polymer to see how a change in the coating occurs, altering the functionality will be the next desired learning. Building on this knowledge, chapter 4 explains how this chemistry is scaled up to make polymers which can be used in coatings and the difficulties found with that. As literature explains only di functional, an understanding into how possible it is to make a higher functionality polymer is very interesting.

Finally, an understanding in how the properties of a coating change when changing the functionality of the polymer, is investigated to provide basis for coatings optimisation. This chemistry can be tailored far easier than a step growth polyester which is the current technology for powder coatings. To be able to change and manipulate a polymer very easily to change the property desired will be a tool which has fascinating possibilities in the coating's world. Therefore, chapter 6 investigates the use of these well-defined polymers in coatings and their change in chemical and physical properties.

Chapter 2 - Investigation of the reaction scheme and starting materials using model reactions

2 Investigation of the reaction scheme and starting materials using model reactions

As the overall alternating copolymerisation scheme involves several reactions, it was thought that these should be best investigated in simpler, model reactions using monofunctional reagents. This will allow a deeper understanding of the reactions involved in the ROCOP, its kinetics and the role of various catalysts in this scheme.

An 'alternating epoxy-anhydride' polyesterification (Figure 2-1) involving the repeat and sequential reactions of anhydride and epoxide functional monomers, had been chosen for this project for a number of advantageous reason such as; the raw materials required to make this polymer are easily accessible, a polyester can be easily manipulated in terms of molecular weight and number/type of end groups and this reaction has been found to be reproducible with consistent results in terms of molecular weight and acid functionality in a previous 'in-house' AkzoNobel research project[96].

To gain initial insight into the chemistry used, model reactions were carried out before making any polymers to understand and control the chemo-selectivity of the reactions, to understand the side reactions which could occur, to prevent these side reactions and to give greater understanding on optimum processing conditions.

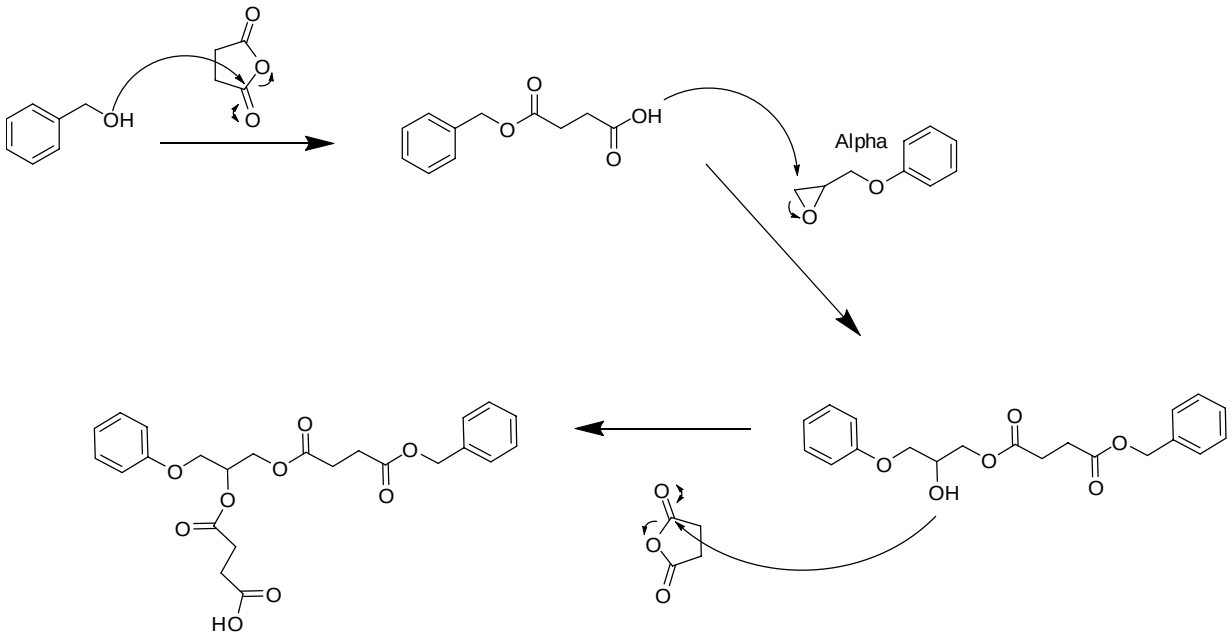

Figure 2-1 - Alternating copolymerisation of phthalic anhydride with phenyl glycidyl ether, initiated by benzyl alcohol

2.1 Monomer selection

The monomers are a vital choice required for this project to give high yield, controlled and predictable molecular weights, polymer structures and end group functionalities. If these have high levels of impurities or the impurity level is not known, side reactions or unwanted by-products may occur. As impurities are frequently present in most chemicals, investigation and possible purification was necessary to give a better understanding of the exact structure of the final polymer.

This polymerisation requires four types of starting materials, a hydroxyl functional material to initiate the polymerisation, an anhydride and an epoxy to advance the polymer chain, and an appropriate catalyst. Interestingly as a hydroxyl group is required to initiate the reaction by opening an anhydride, this polymerisation could be regarded as a chain growth polymerisation that will grow from the original hydroxide. This does mean that any other hydroxide present in the system could also act as an initiator with uncontrollable quantities and functionalities. As model reactions were the first part of this experiment, molecules containing each functional group required were used.

Benzyl alcohol, and phenyl glycidyl ether (Figure 2-2) are both molecules with the desired functional groups and a supplier purity of 99+%.

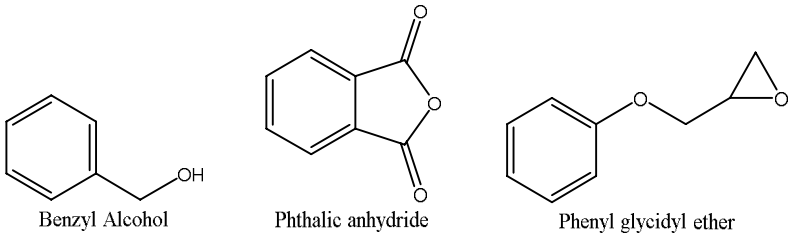

Figure 2-2- Structures of monomers used in model reactions

2.1.1 Anhydride selection

Initial attempts at selecting an anhydride proved difficult. Hexahydrophthalic anhydride (HHPA, Figure 2-3) was initially tested and showed to process well in the alternating reaction. However, it is possible to have cis and trans isomers of HHPA which added extra possible structures to the end product and therefore the anhydride was changed to prevent more complex mixtures of polymeric products being formed (Figure 2-3).

Figure 2-3 – cis- (left) and trans- (right) hexahydrophthalic anhydride

Succinic anhydride (Figure 2-4) was also tested but was found to crystallise out of solution as would be expected as process temperature is considerably higher than sublimation temperature (35°C). However high purity levels (99+%) could be purchased.

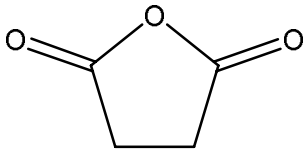

Figure 2-4 - Structure of Succinic Anhydride

FTIR was carried out on reactions with both succinic anhydride and HHPA to understand the reaction further, using DMAP (Figure 2-5) as a catalyst.

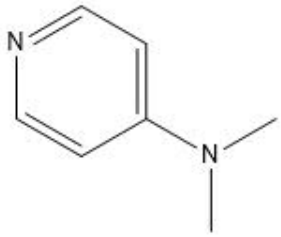

Figure 2-5 - Structure of 4-(Dimethylamino) pyridine

FTIR showed that succinic anhydride reacted considerably quicker, which may be due to the succinic anhydride having no bulky groups[97], as succinic anhydride seemed to allow faster kinetics with a reaction time of less than 4 minutes compared to around 30 minutes for HHPA to show full disappearance of the anhydride peak, whilst an acid peak appeared to show. However succinic anhydride could not be processed efficiently in practice due to sublimation, therefore it was decided to use another anhydride. Throughout the FTIR run, no sublimation was observed. Figure 2-6 shows the ratio of anhydride (~1783cm^{-1}) reacted over the C=O ester carbonyl acid (~1733 cm^{-1}) formed.

Formulation 1	Benzyl alcohol	HHPA	PGE	DMAP
Mole ratio	1	10	9	0.1
Formulation 2	Benzyl alcohol	Succinic Anhydride	PGE	DMAP
Mole ratio	1	10	9	0.1

Table 2-1 - Formulations used in IR experiment shown in Figure 2-6

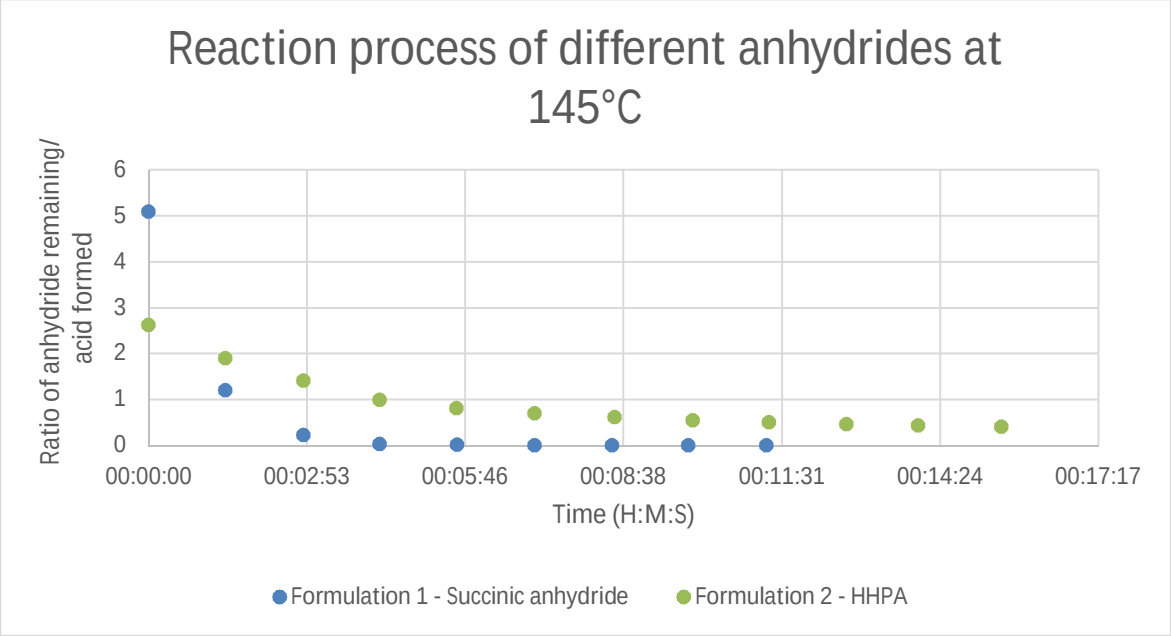

Figure 2-6 – Ratio of reactants/ products vs time showing reaction process at 145°C (formulation: benzyl alcohol/HHPA or SA/ PGE/DMAP). Calculated by = peak height anhydride peak/ peak height C =O acid carbonyl peak

Phthalic anhydride (Figure 2-7) is an aromatic anhydride, which had 99+% purity but did not sublime out of the reaction during processing as much as the succinic anhydride. This is due to phthalic anhydride having a higher enthalpy of sublimation temperature to succinic anhydride (88°C and 35°C respectively).

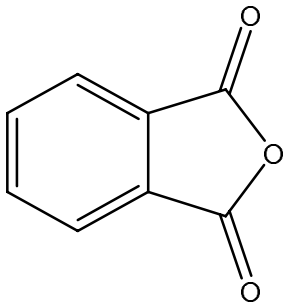

Figure 2-7 - Structure of Phthalic anhydride

It was therefore decided to use phthalic anhydride in all subsequent polymerisations in this thesis.

2.1.2 Catalyst selection

An initial literature review was carried out to understand which catalysts were known for this type of polymerisations. Many catalysts were screened through literature

search, including choline chloride, benzyltrimethylammonium bromide[98] and benzyldimethylhexadecylammonium chloride[99]. A selection of six catalysts were tested and chosen based on performance in acid-epoxy polymerisations, ranging from Lewis acid catalysts to nucleophilic catalysts. Choline chloride and 2-methylimidazole showed very similar results in literature[98] and due to having many halide catalysts chosen already, choline chloride was removed as an option to be tested. Benzyltrimethylammonium bromide would provide a very similar chemistry to Tetrabutylammonium bromide and therefore was the only one of this class was selected in order to get a varied range of catalysts[98]. Benzyldimethylhexadecylammonium chloride was shown to catalyse the reactions, but slower than some other catalysts in literature[99]. Therefore, the six catalysts taken forward for this study were:

- Zinc stearate (Lewis acid) which gave excellent cure rates with no yellowing[79]
- Ethyltriphenylphosphonium bromide (quaternary halide salt) which showed to provide a high conversion and was used on similar reactions previously in literature[100]
- Tetrabutylammonium bromide (quaternary halide salt) which showed high conversions with low PDI for epoxy-anhydride reactions[81]
- 2-methyl imidazole (nucleophilic catalysis) which indicated to provide short cure times at low temperatures[101]
- 4-dimethylamino pyridine (nucleophilic catalysis) which also proved successful as a catalyst in epoxy-anhydride reactions[81]
- Triethylamine (base catalysis) which showed to be successful as a catalyst in star armed epoxy- anhydride polymerisations[102].

It is believed that Lewis acids catalyse the reaction through complexing with the oxygen of the epoxy and results in the carbons being more electrophilic and susceptible to nucleophilic attack[103] (Figure 2-8). However, many of this class of catalysts are very hygroscopic and therefore need to be used in anhydrous conditions[104] to avoid ring opening the anhydrides.

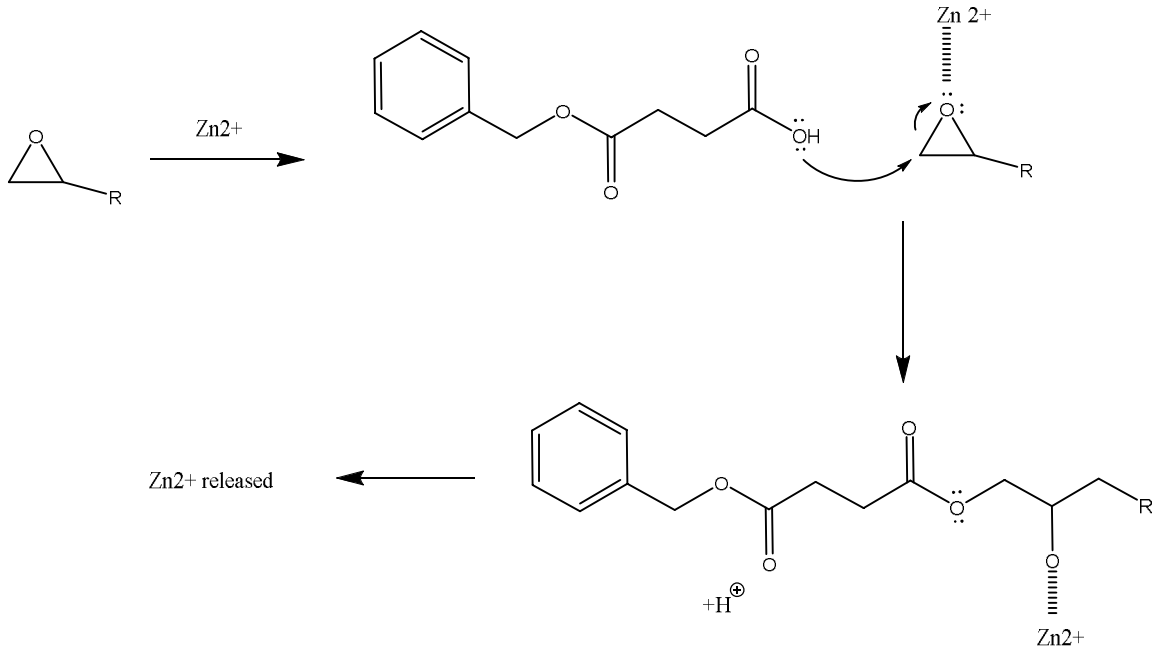

Figure 2-8 - Schematic of Lewis acids as catalysts

Catalysts containing halides generally work through an S_N2 nucleophilic substitution reaction as the halide is a very susceptible leaving group[105,106] due to its electronegativity (Figure 2-9)[107].

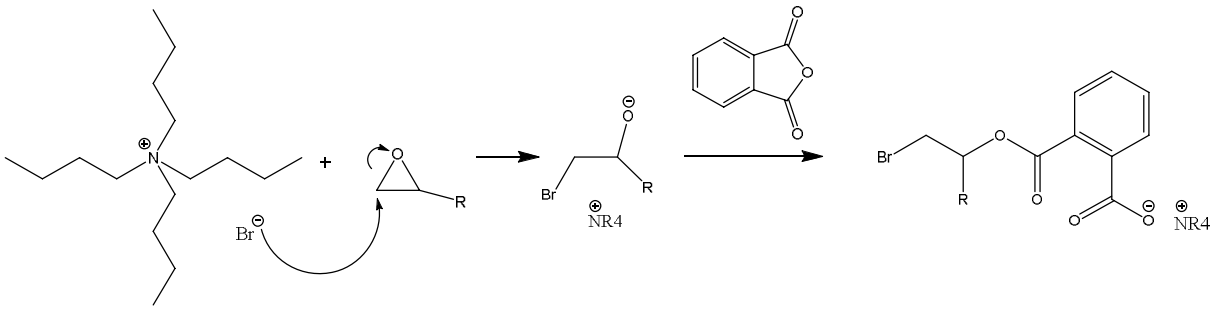

Figure 2-9 - Schematic of catalysis using halides

Catalysts containing heteroatoms such as Nitrogen or Phosphorous, react by opening the epoxide group producing an alkoxide[3], and generally remain bound to the alkoxide during the reaction (Figure 2-10). As the catalyst remains bound, this results in reducing the number of functional groups available to react and affecting stoichiometry which therefore needs to be taken into consideration when formulating or concluding results.

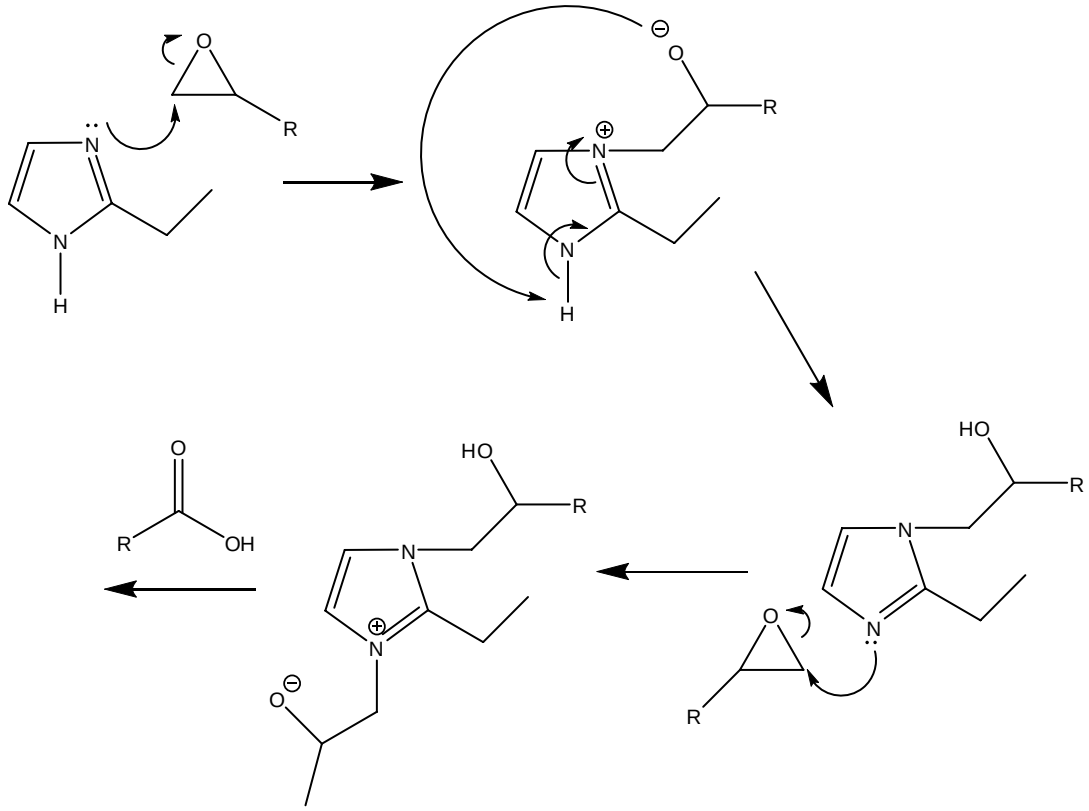

Figure 2-10 - Schematic of amines as catalysts

2.2 Raw materials in processing model reactions

Further model reactions were then undertaken using the monomers shown in Figure 2-2. They were made in a 1:1:1 molar ratio of alcohol:anhydride:epoxy to give a clear analysis of all undesired reaction products.

Monomer	Mwt (g/mol)	Moles (mol)	M/R		Mass (g)
Benzyl alcohol	108.14	0.07382	1	108.14	7.98
Phthalic Anhydride	148.1	0.07382	1	148.1	10.93
1,2-Epoxy-3-phenoxypropane (PGE)	150.17	0.07382	1	150.17	11.09
TBAB (0.1mol%)	322.37				0.03
Total		0.2214		406.41	30.00

Table 2-2 - Formulation of LW1 - model reaction using benzyl alcohol, phthalic anhydride and phenyl glycidyl ether in a 1:1:1 ratio, with TBAB catalyst

	% AV reacted	% epoxy reacted	Expected Mn (g/mol)	Actual Mn (g/mol)
LW1	94.6	99.29	406	494

Table 2-3 - Results of LW1 – model adduct using benzyl alcohol, phthalic anhydride, PGE and TBAB

Once synthesised and tested, it was found that the products which were being produced were not reaching the theoretical acid conversion (100%) which was the cause of further investigation. It was believed the purity of phthalic anhydride could be a possible cause. By ^{1}H NMR, an acid impurity level of 2.6% was recorded (2 peaks showing from the acid at 7.77ppm and 7.62ppm were ratioed against the protons from the anhydride to calculate a % impurity – (0.0553+0.0490)/4 *100 = 2.6075%) which is higher than the manufacturer's quoted purity of 99% (Sigma Aldrich). It is believed however that more than 99% of the mass of reagent was made of phthalic anhydride and phthalic acid, however the anhydride being unstable in the presence of moisture a proportion of it could have opened into a diacid, explaining the discrepancies between manufacturer's and measured purity levels.

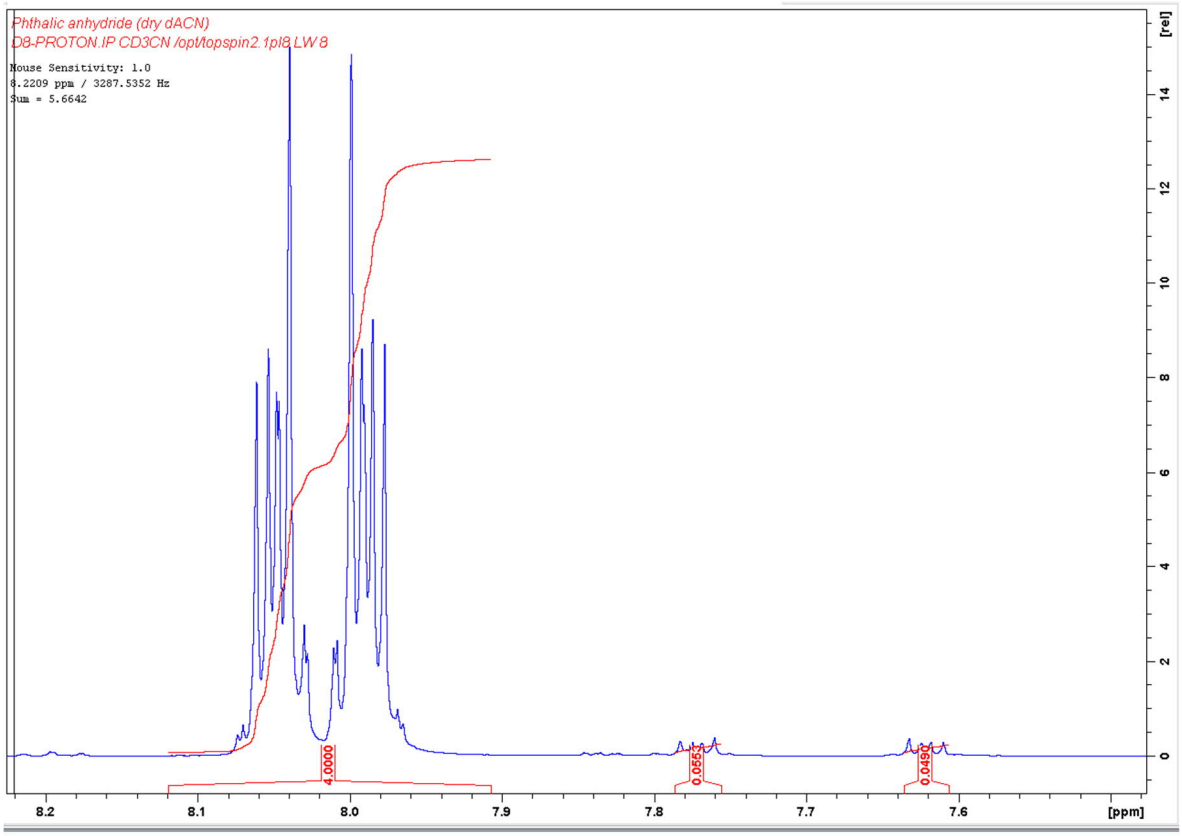

Figure 2-11 – ^{1}H NMR spectra of phthalic anhydride showing peaks of phthalic acid found in the anhydride (solvent: dry deuterated acetonitrile)

An experiment was then carried out to understand whether at higher temperature, phthalic acid could dehydrate and reform the anhydride. Literature suggested that the dehydration reaction is possible at elevated temperatures, in this case as high as 340°C, indicating this is unlikely to occur during synthesis[108]. This was tested to confirm as no literature could be found specifically for phthalic acid and explained below.

An adduct with the same stoichiometry as the 1:1:1 adduct in Table 2-4 was produced, substituting the phthalic anhydride for phthalic acid, and the process conditions were kept identical apart from the reaction time which, due to the reactivity of the acid group being significantly lower than the reactivity of an anhydride group, had to be increased. The reason for this, is that phthalic anhydride is cyclic and therefore liberates ring strain upon esterifying with the hydroxyl. However, for the phthalic acid, no ring strain is liberated, reducing significantly the reaction rates. Due to the acid functionality on the phthalic acid, for the reaction to push the equilibrium forwards and the reaction to occur, water is required to be liberated. This doesn't occur when using anhydride functionality, which also results in a slower reaction with the acid compared to the anhydride.

Monomer		Mwt (g/mol)	Moles (mol)	M/R		Mass (g)
Benzyl alcohol		108.14	0.07382	1	108.14	7.98
Phthalic Anhydride		148.1	0.07382	1	148.1	10.93
1,2-Epoxy-3-phenoxypropane		150.17	0.07382	1	150.17	11.09
2MI (0.1mol%)						0.3
Total			0.2214		406.41	30.00

Table 2-4 - Formulation of LW2 - model adduct using phthalic anhydride

Monomer		Mwt (g/mol)	Moles (mol)	M/R		Mass (g)
Benzyl alcohol		108.14	0.07068	1	108.14	7.64
Phthalic Acid		166.14	0.07068	1	166.14	11.74
1,2-Epoxy-3-phenoxypropane		150.17	0.07068	1	150.17	10.61
2MI (0.1mol%)						0.3
Total			0.212039		424.45	30.00

Table 2-5 - Formulation of LW3 - model adduct using phthalic acid

The reaction mixture using phthalic acid (LW2) was processed for double the amount of time compared to that of the anhydride mixture (LW1) (~2 hours after the epoxy was added, compared to 1 hour for anhydride containing polymer LW1).

	% AV reacted
LW2	96.5
LW3	67.8

Table 2-6 - Results for % acid reacted comparing LW2 and LW3

Analysis of LW3 by titration showed that 67.8% of the acid groups had reacted in this time, which suggests the acid does not close and react as an anhydride at higher temperatures (140°C) as initially discussed as a possibility. It should not however produce a different structure if acid was present as it should only affect the reaction rates resulting in a significantly slower reaction (see Figure 2-12). This had to be carefully considered when formulating future polymers, especially if the polymers were not reaching the expected acid conversion values.

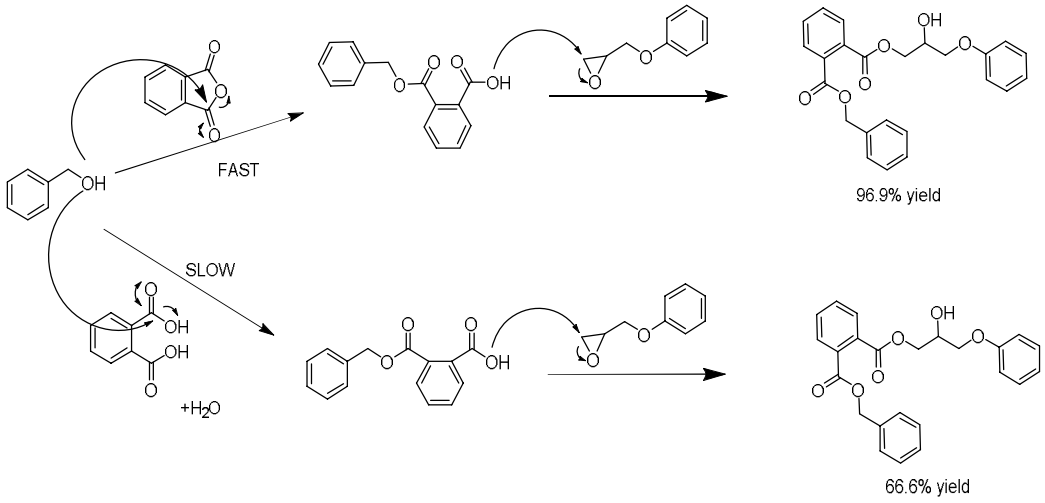

Figure 2-12 – Schematic showing both anhydride and acid will produce the same reaction but when in acid form will possess a slower reaction rate

The Figure above (Figure 2-12) also shows water is liberated when reacting an acid with an alcohol, following an esterification reaction. This could act as an initiator and new chains could propagate from the water, lowering the average polymer molecular weight value, due to more initiation than expected, resulting in an increase of shorter chains.

2.3 Possible reactions & catalyst screening

. A considerable number of reaction routes may occur when using this chemistry, several of which will lead to undesired products and needed to be investigated. A comprehensive list of theoretical reaction pathways is shown below in Figure 2-13.

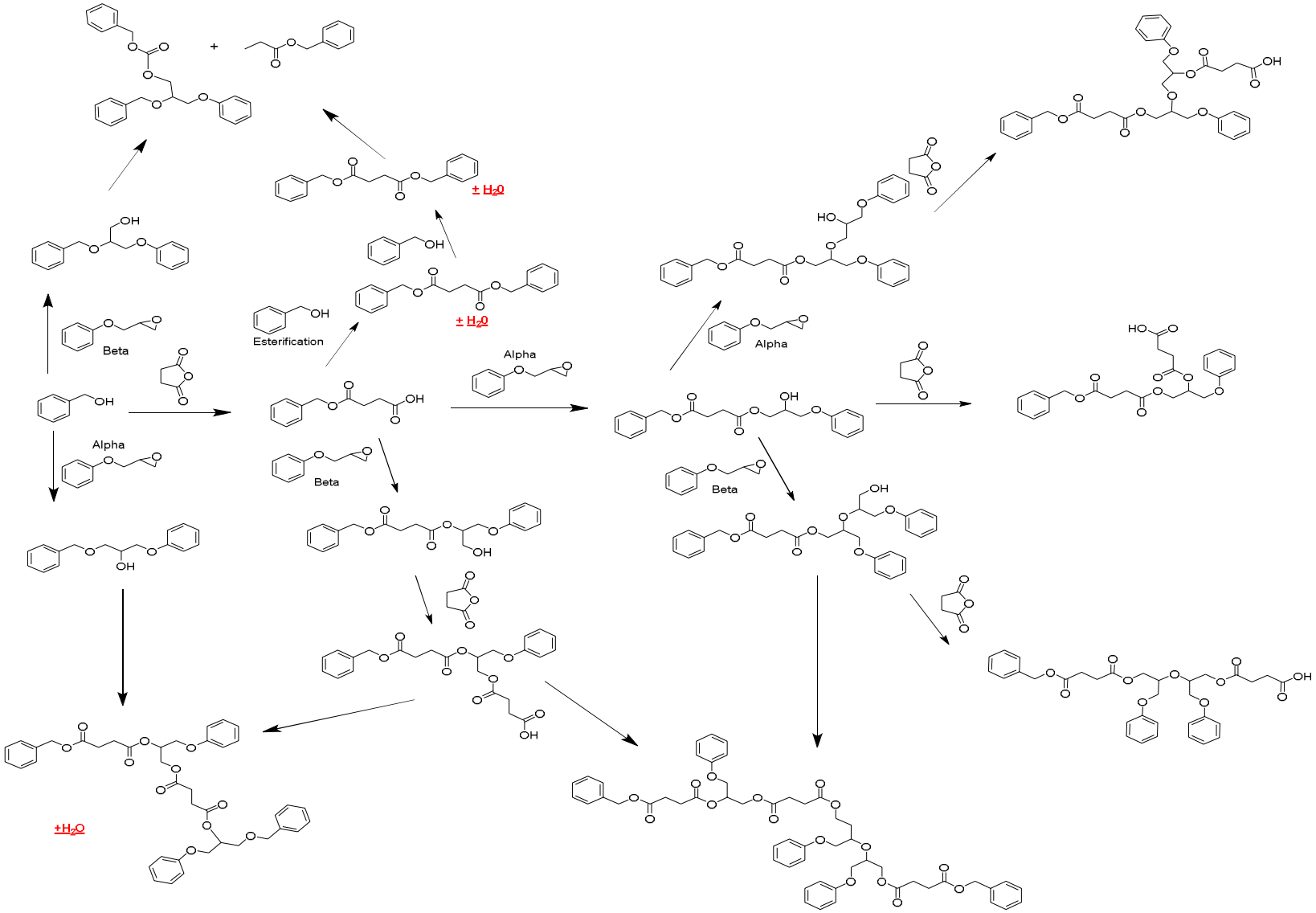

Figure 2-13- Possible reactions pathways which may occur

Ten possible reactions were identified from the same set of monomers. This can have a negative impact on the control over the functionality of a polymer and in turn could affect coating performance. As this project was to explore the relationships between the network structure and the coating performance, this was crucial information to understand and could further impact future work. Reactions which could occur were discussed and are listed below;

1) Primary hydroxyl + Anhydride – Desired (Figure 2-14)

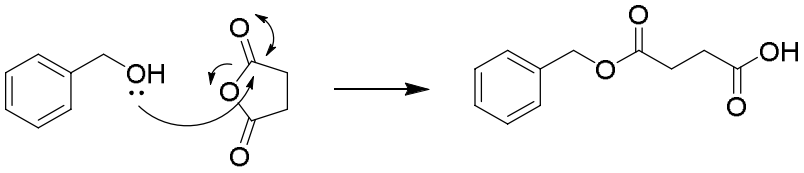

Figure 2-14 - Primary hydroxyl + Anhydride

2) Esterification of acid + alcohol - Undesired (Figure 2-15)

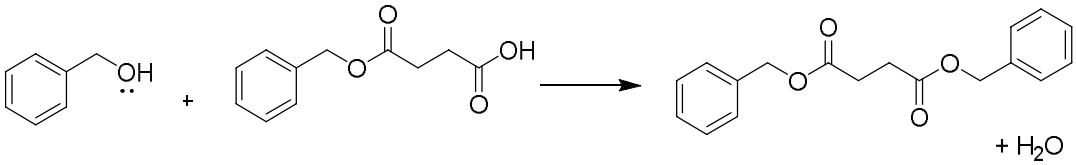

Figure 2-15 - Esterification of acid + alcohol

3) Acid + Epoxy – Desired (Figure 2-16)

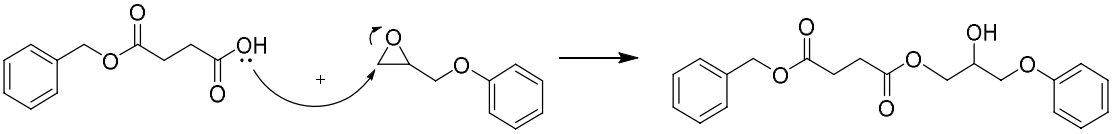

Figure 2-16 - Acid + epoxy

4) Secondary OH + anhydride – Desired (Figure 2-17)

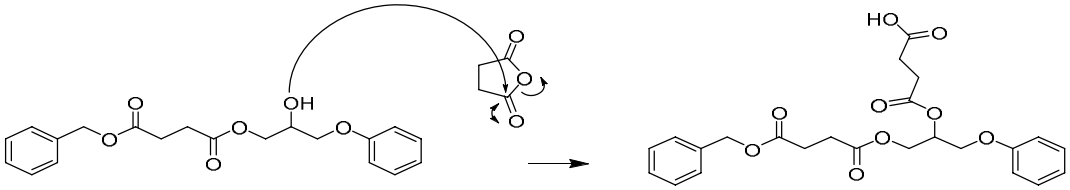

Figure 2-17 - Secondary OH + Anhydride

5) Secondary OH + epoxy (epoxy homopolymerisation)– Undesired (Figure 2-18)

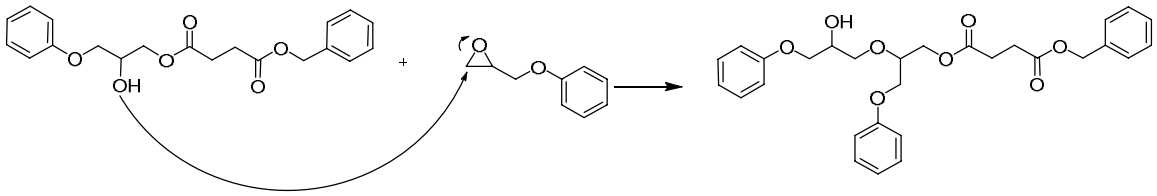

Figure 2-18 - Secondary OH + epoxy

6) Primary OH + Epoxy – Undesired (Figure 2-19)

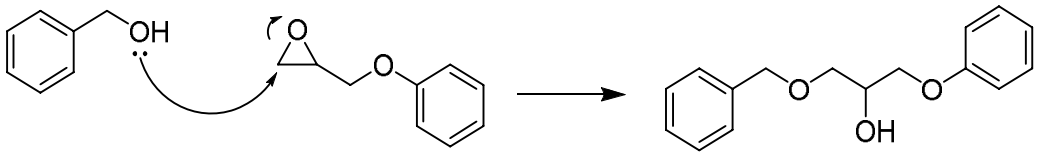

Figure 2-19 - Primary OH + Epoxy

7) Secondary OH + ester (transesterification) – Undesired (Figure 2-20)

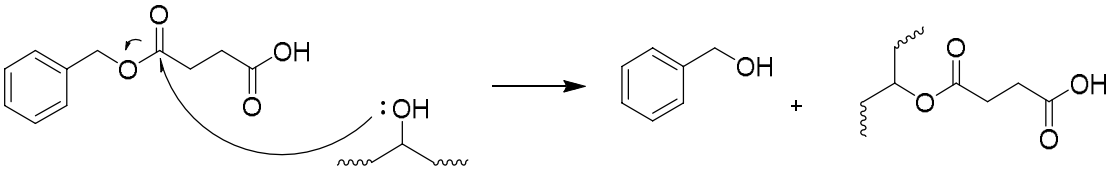

Figure 2-20 - Secondary OH + ester

8) Primary OH + ester – Undesired (Figure 2-21)

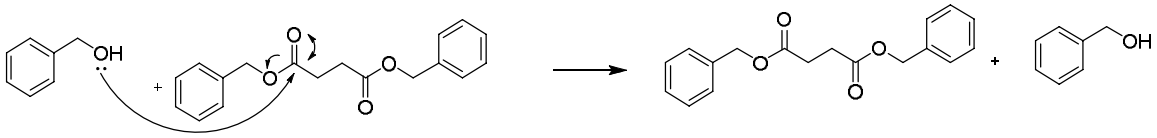

Figure 2-21 - Primary OH + Ester

9) Polyanhydride formation – Undesired (Figure 2-22)

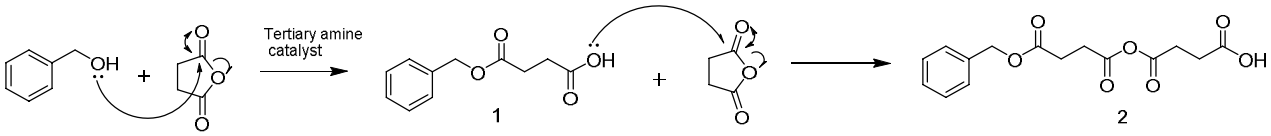

Figure 2-22 - Polyanhydride formation

10) Water + anhydride – Undesired (Figure 2-23)

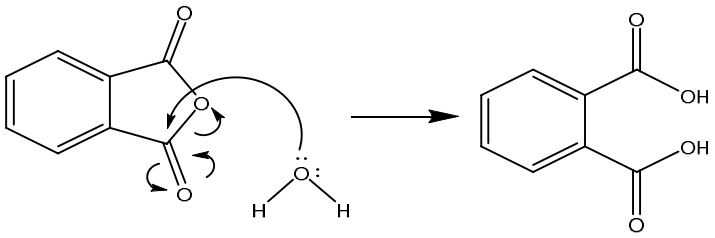

Figure 2-23 - Water reacting with an anhydride to form an acid

A blend was formulated to a 1:1:1 mole ratio (benzyl alcohol: phthalic anhydride: phenyl glycidyl ether) which at high levels of conversion (>99%) should have given a hydroxyl functional oligomer, with negligible residual carboxylic acid functional groups remaining. Initially, a formulation using Zn stearate as catalyst was trialled. This gave further insight, as the reaction did not progress further than 80.2% acid conversion. Initial thoughts were that the oligomer needed further processing in order for the residual OH groups to complete reaction with anhydride, or a higher temperature to increase the reaction speed. However, with a higher temperature, this still did not progress the reaction further so we assume that the reaction stopped. An epoxy equivalent weight (EEW) analysis was then carried out showing there was no epoxy left to react. This indicated a different reaction was competing with the expected reaction when using this catalyst, most likely possibility was an epoxy homopolymerisation, which would result in a lower conversion of acid or anhydride groups but no unreacted epoxy groups.

Further catalysts were evaluated with success as acid functional group consumption was improved, showing much higher acid conversions up to 96.99% (Table 2-14). There were still acid groups present however as the epoxy had processed to completion

(based on EEW results), this indicated that undesired reactions may be occurring, such as epoxy homopolymerisation.

Polymer code	Catalyst	% acid reacted	% Epoxy reacted
LW1	Tetrabutylammonium Bromide	94.60%	99.29
LW2	2- Methyl Imidazole	96.99%	100
LW4	Zinc Stearate	84.21%	99.15
LW5	4- Dimethylaminopyridine	96.42%	98.27
LW6	Ethyltriphenyl phosphonium bromide	95.57%	98.44
LW7	Triethylamine	91.70%	98.25

Table 2-7 - Table showing % acid conversion when using different catalysts. Formulation: Benzyl alcohol + Phthalic Anhydride + PGE (0.1mol% catalyst)

The formation of undesired products from side reactions was investigated and found that they did not occur. However, it was also just as important to confirm that desired reactions were occurring and this will be described in the following sub sections.

2.3.1 Primary alcohol + anhydride reaction

The type of reactions occurring can be confirmed in numerous analytical ways. The primary hydroxyl + anhydride reaction can be confirmed via titration of acid groups. This measurement can be carried out via two different methods; namely Partial acid value (PAV) and Total acid value (TAV) in which the former measures the carboxylic acids content only whilst the later measures the sum of the carboxylic acids and anhydrides present[109]. The difference between the two titration values will therefore give an idea of how many anhydride groups are present in the reaction mixture.

The total acid value method uses an addition of water at the beginning of the process, which will ring open the anhydride groups and subsequently allow the titrant (KOH) to salt these functional groups as shown in Figure 2-24 below.

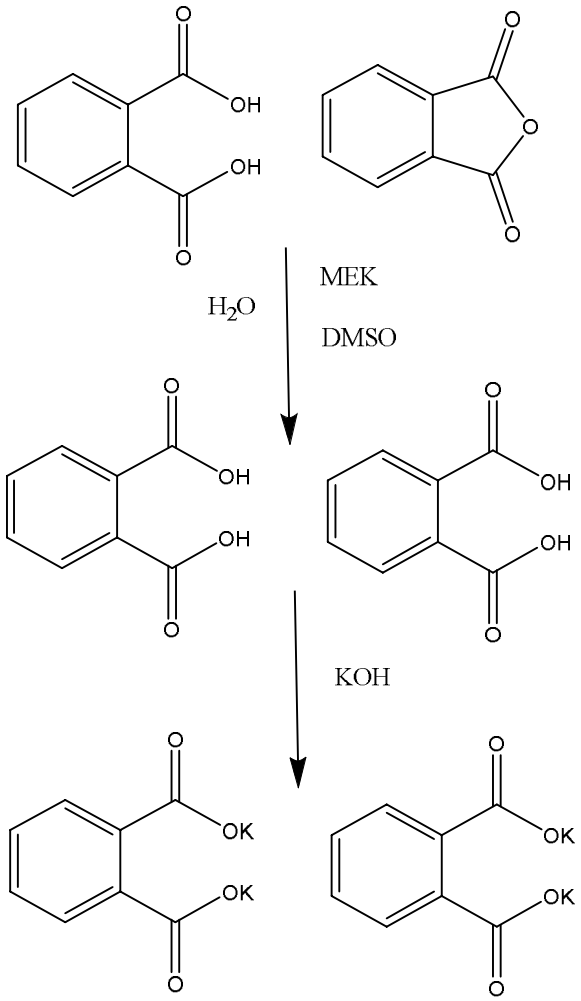

Figure 2-24 - Figure showing a schematic of the total acid value method

The partial acid value method (Figure 2-25) is a similar method and is carried out in anhydrous conditions, in which a functional hydroxyl group is added to the solvent blend. This is in the form of 1-methoxy-2-propanol, which contains a secondary hydroxyl group. It is believed the OH from the 1-methoxy-2-propanol is reacting and ring opening the anhydride producing an ester.

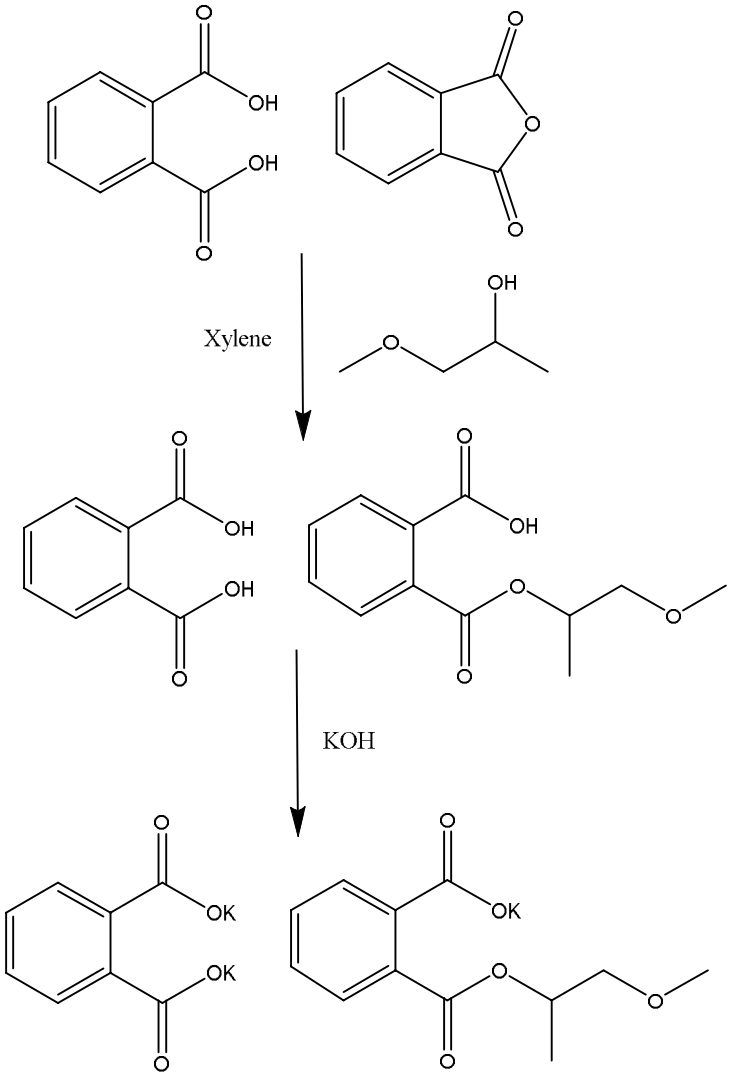

Figure 2-25 - Schematic of the partial acid value method

This theoretical schematic can be proven by titrating trimellitic anhydride with both methods. Trimellitic anhydride (TMA) is a monofunctional anhydride derived from the trifunctional acid molecule which contains one anhydride and one acid functionality.

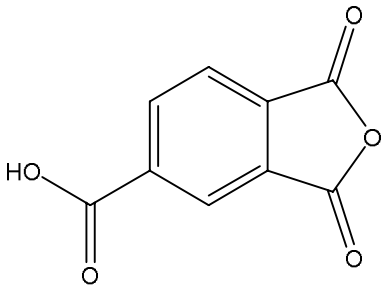

Figure 2-26 - Structure of trimellitic anhydride (TMA)

The expected acid values from the reaction of 1, 2 or 3 acid groups were as shown in the table below:

Number of carboxylic groups titrated	Expected Acid value (mgKOH/g)
1	292.2
2	584.4
3	876.5

Table 2-8 - Table showing predicted acid values dependant of the number of functional groups titrated

TMA was then titrated using both methods and the results are shown below;

	Partial AV method(mgKOH/g)	Total AV method (mgKOH/g)
TMA	590.9 +/- 4.8	838.4 +/- 5.4

Table 2-9 - Results of TMA using both partial and total methods

This shows that during a partial measurement, two of the three possible groups are measured, indicating the schematic above in Figure 2-25 is plausible. Total method indicated that trimellitic anhydride is opened and both acid groups from the anhydride are titrated as well as the acid group attached to the ring.

This work confirmed that a partial acid value will measure all acid groups and half the anhydride groups in the sample, and that the quantification of carboxylic acid groups can be done by subtracting the difference between TAV and PAV to the PAV.

Once the partial acid value method had been fully understood, further model reactions could be made.

Model products were produced using a 1:1:1 ratio, producing hydroxyl functional oligomers, following the formulation below:

Monomer	Mwt	Moles	M/R		Mass (g)
Benzyl alcohol	108.14	0.073817	1	108.14	7.98
Phthalic Anhydride	148.1	0.073817	1	148.1	10.93
1,2-Epoxy-3-phenoxypropane	150.17	0.073817	1	150.17	11.09
Total		0.2214512		406.41	30.00

Table 2-10 - Formulation of all model reactions used following a 1:1:1 ratio producing hydroxyl functional oligomers

Polymer code	Catalyst	Predicted PAV (and TAV) (mgKOH/g)	Measured PAV (mgKOH/g)	Measured PAV (mol/g)	Measured TAV (mgKOH/g)	Measured TAV (mol/g)
LW4	ZnS	0	46.9	0.00084	51.1	0.000911
LW1	TBAB	0	18.7	0.00033	19.1	0.000340
LW5	DMAP	0	14.0	0.00025	12.1	0.000216
LW6	ETPPB	0	16.1	0.00029	17.4	0.000310
LW7	TEA	0	26.96	0.00048	27.6	0.000492
LW2	2MI	0	13.32	0.00024	13.3	0.000237

Table 2-11 - Table showing differences in total and partial acid values for the range of catalysts screened (Formulation: Benzyl alcohol + Phthalic Anhydride + PGE + Catalyst – 1:1:1 mole ratio with 0.1mol% catalyst)

The results above in Table 2-11 shows that all model products did not reach a full conversion as the acid value was expected to be 0mgKOH/g and as can be shown from the results, 2MI and DMAP processed acid lower than all other catalysts. Further discussion of these polymers is continued throughout this chapter to understand these results in more depth.

2.3.2 Secondary alcohol + anhydride reaction

However slower, the secondary OH + anhydride reaction can also be investigated the same way as the primary OH and anhydride reaction. A typical method to measure the amount of hydroxyls present is via the back titration of remaining acid groups after reacting the hydroxyls with acetic anhydride. This measurement would indicate that, not only has the correct amount of acid functionality have been formed, but also had the correct alcohol functionality. However, it was concluded that the hydroxyl value titration could not accurately measure the polymers produced, as values measured were very widespread with no relationships between triplicates, so this method was not accepted to be used. The problems and discussion surrounding this are discussed in the experimental section. Other methods involving derivatisation using a chlorophospholane functional molecule then quantification via ^{31}P NMR may be investigated in future as a possible way to measure the OH value of the polymer.

2.3.3 Polyanhydride formation

Formation of polyanhydride is a possible reaction which may occur. Polyanhydrides can be formed when an anhydride group is opened, by i.e. alcohol, and then the opened anhydride reacting with a second anhydride instead of the desired epoxy molecule. As these anhydrides are cyclic, the resulting product would be polymeric. This was tested in a reaction using benzyl alcohol and excess anhydride, heated to process temperature (140°C), and left to process for 4 hours.

To prove whether this was a possible undesired reaction, NMR was carried out on the product. As shown in the results below (Figure 2-28), polyanhydrides were not formed under process conditions as the corresponding peaks in ^{1}H NMR were not found. This was most likely due to a reduced nucleophilicity of an acid group compared to a hydroxyl group and was therefore ruled out as a potential undesired side reaction with this chemistry.

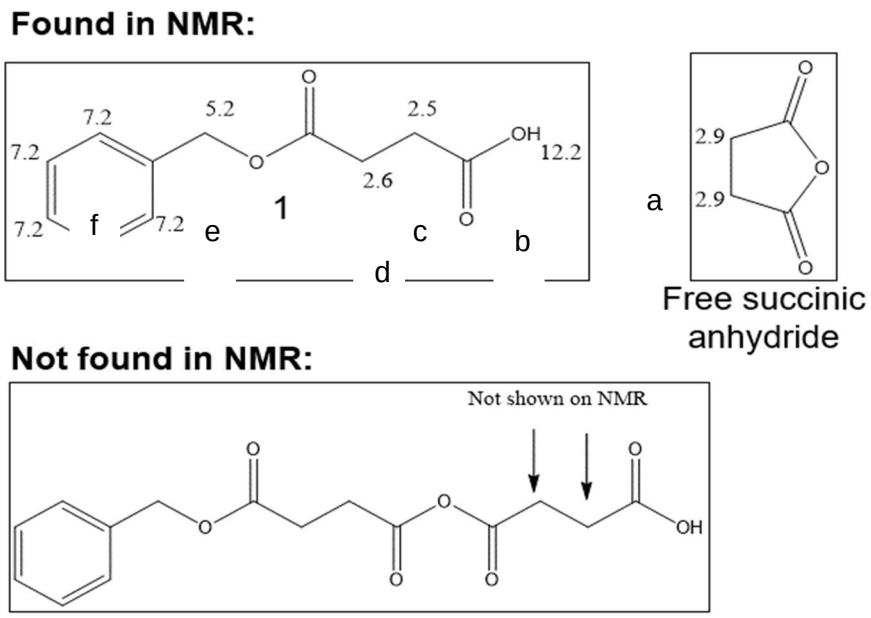

Figure 2-27 - Structures of products which confirm polyanhydrides do not form during a polymerisation at process temperature

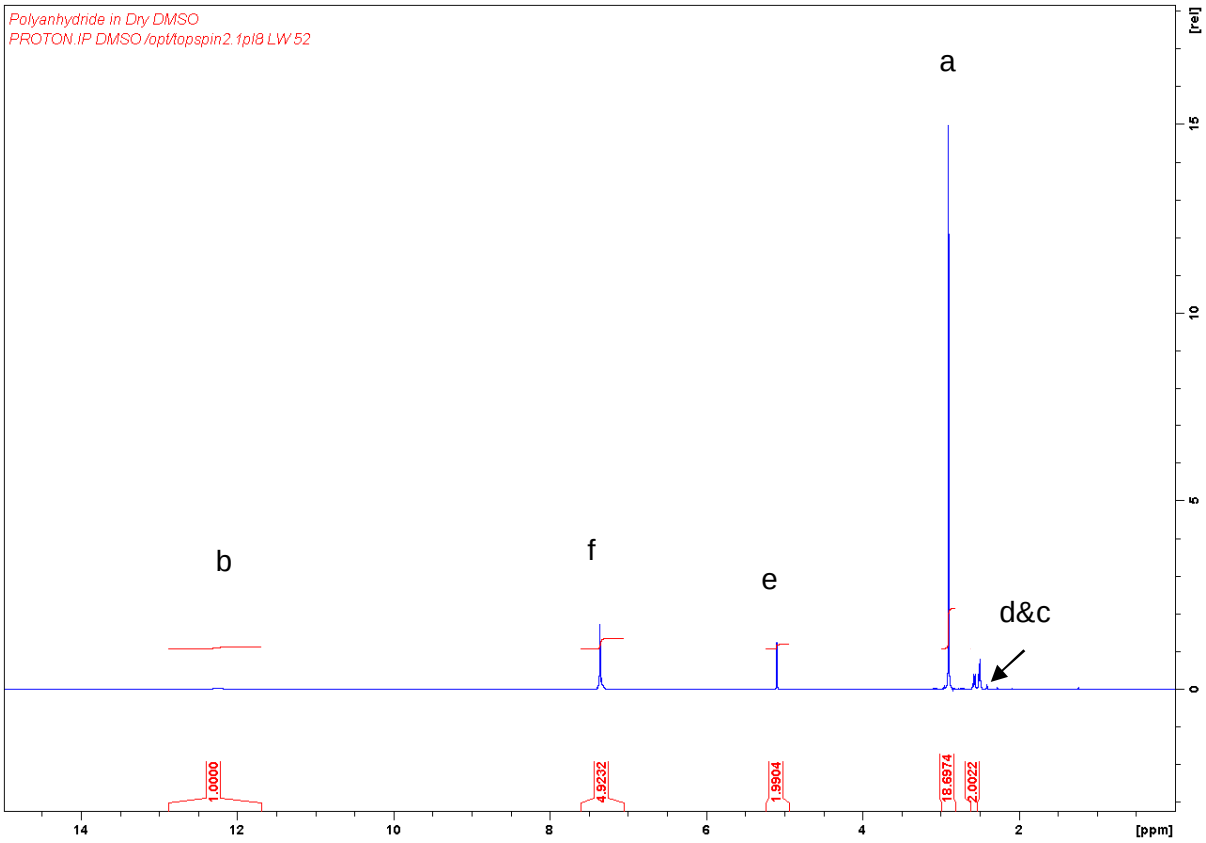

Figure 2-28 - Figure showing protons observed in NMR results for polyanhydride formation proof

2.3.4 Acid - epoxy reaction

Quantification of residual epoxy groups is also important to understand the advancement of the reaction. Furthermore, nucleophiles could react on either carbon of the epoxy ring, with potentially a preference for the least hindered carbon. GC-MS can be used to confirm whether the epoxy undergoes alpha or beta ring opening (explained further below in chapter 2.3.4.1). Undesired reactions can also be confirmed such as the esterification of an acid and alcohol group reaction which may occur. GPC-MS can also be used to confirm whether this reaction takes place, as a peak for an esterification product can be seen in Chapter 2.3.7 (Figure 2-2-39).

2.3.4.1 Epoxy ring opening

Epoxy groups can undergo nucleophilic attack and subsequent ring opening at the alpha position (secondary carbon) or the beta position (tertiary / substituted carbon) on the epoxy ring (Figure 2-29). Analysis of experimental reactions were required to understand at which position ring-opening was initiated, and therefore an indication as to which type (primary or secondary OH) polymers would result. The type of hydroxyls created may have an impact as to how reactive these are towards the opening of further anhydrides, or in the case of hydroxy-functional polymers this may have an impact on their curing kinetics.

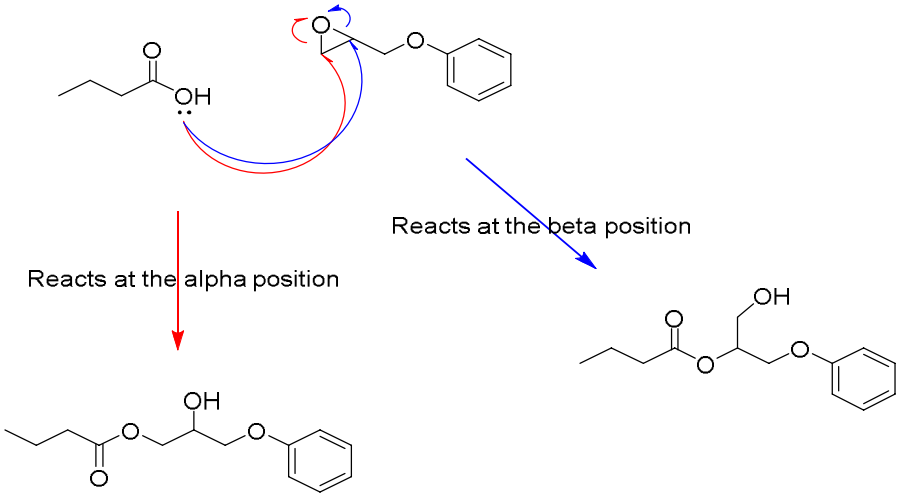

Figure 2-29 - Epoxy ring opening in alpha (red) or beta (blue)

Mixtures of butanoic acid and phenyl glycidyl ether (1:1 mol ratio) were prepared, and reacted at a temperature of 140°C, with 6 different catalysts (0.01 mol%), and the

resulting reaction mixtures were analysed by GC-MS and NMR. Butanoic acid was used to mimic the reaction of a polymer chain terminated with an acid group, e.g. opened anhydride, with an epoxy whilst not allowing any polymerisation and simplifying the analysis.

The six catalysts selected and the observations from these are below;

LW8 – Triphenylphosphine – dark orange colour appeared.

LW9 – Ethyltriphenylphosphonium bromide – clear liquid

LW10 – 4-(Dimethylamino) pyridine – clear liquid

LW11 – Tetra –n- butyl ammonium bromide- clear liquid

LW12 – Choline chloride – clear liquid

LW13 – Benzyl trimethyl ammonium chloride- clear liquid

0.003g of each catalyst were added to 1g of butanoic acid and phenyl glycidyl ether in a 1:1 molar ratio. Subsequently they were stirred on a 140°C hotplate for 1 hour.

^{1}H NMR results showed three peaks at around 5.3ppm. This was expected to be the protons required to determine the stereoselectivity of the opening mechanism. However, as these molecules were very similar, it could not be confirmed whether these three environments had come from the epoxy opening in the different positions (alpha or beta), or whether these were all signals corresponding to the same protons.

GC-MS did not, initially, indicate anything other than one peak for the final product; however, after derivatising the samples in BTSFA (Bis-trimethylsilyl trifluoro acetamide)[110] two peaks were shown, giving the same molecular weight but with different fragmentation patterns. The experimental discussion for this method can be found in chapter 5.3.2.

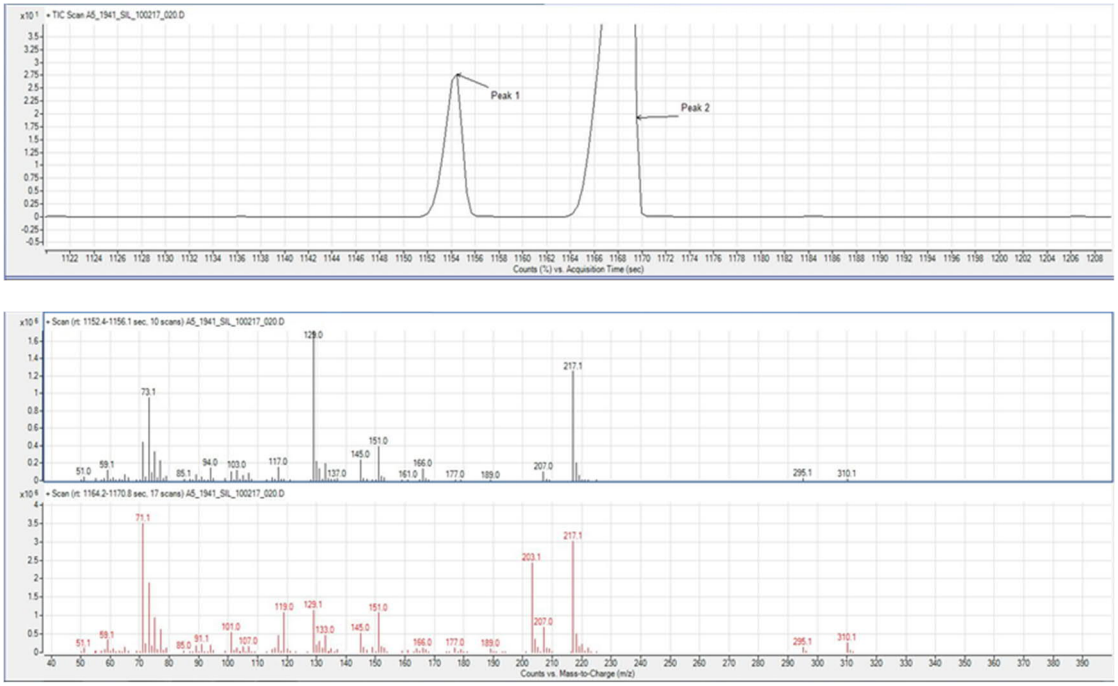

Figure 2-30 - Gas chromatogram(above) and corresponding Mass spectrums (below) showing two peaks indicating alpha or beta epoxy ring opening

A mass peak of m/z = 202AMU can be seen in one fragmentation pattern but not in the other and it was believed this peak was the key to identifying which peak indicated which opening. Figure 2-31 explains this and gives a possible explanation to why the difference in the openings can be observed through GC-MS when the molecules had been silanised.

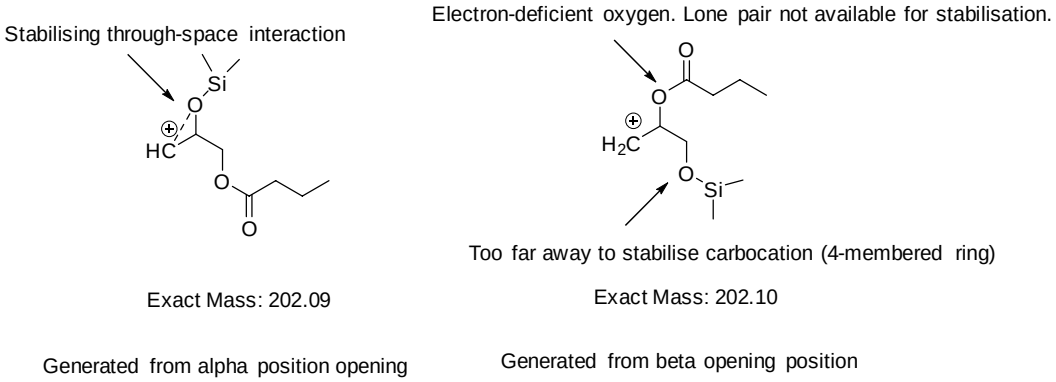

Figure 2-31 – Possible structures to indicate why epoxy ring opening differences can be seen once silanised.

This could also indicate that peak 2 is the alpha opening position as this molecule is stable from the interactions between the oxygen and carbon. As the other fragment is less stable, it is unlikely to be present as a stable fragment in the GCMS, and therefore could be the explanation as to why one peak does not show the m/z=202 fragment.

Formulation	Ratio on GC-MS for alpha/beta opening from GC peak intensity
Butanoic acid + PGE + ETTPB (LW9)	72.0:28.0
Butanoic acid + PGE + TBAB (LW11)	83.0:17.0
Butanoic acid + PGE + 2MI (LW14)	76.2:23.8
Butanoic acid + PGE + ZnS (LW15)	52.9:47:1
Butanoic acid + PGE + DMAP (LW10)	76.0:24.0
Butanoic acid + PGE + TEA (LW16)	80.5:19.5

Table 2-12 - Ratios of GC peak intensities of alpha to beta openings for different catalysts

Results in Table 2-12 show that all nucleophilic catalysts open in the same ratios, whereas the metal based catalyst (Lewis acid) Zinc stearate open in approximately a 50:50 ratio. This was believed to be due to Lewis acids favoring an SN1 mechanism, whereas nucleophiles will favor an SN2 mechanism, distributing the products of epoxy ring opening differently.

In the case of nucleophilic catalysts, it is found the majority of openings are at the alpha position, thus creating a majority of secondary hydroxyls rather than primary hydroxyls. As the steric hindrance of the former is higher, it is believed that this may slow the overall reaction kinetics down to a degree.

2.3.5 Transesterification reaction

The transesterification of secondary hydroxyls on existing esters is also an interesting and possible side reaction. (Figure 2-32).

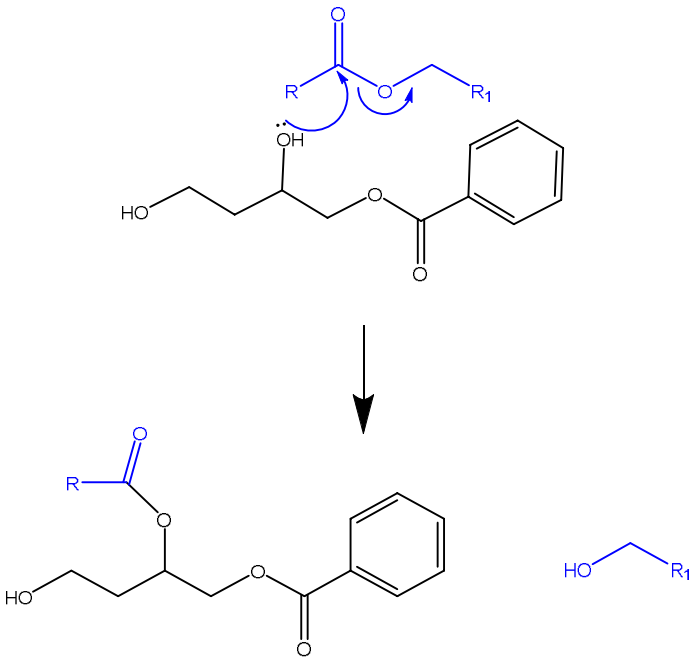

Figure 2-32 – Schematic of transesterification applied to the monomers used in this work

Transesterification is a reaction which may occur during this reaction. This could result in structures which are undesired and therefore this reaction's occurrence needed to be proved. Transesterification is a process in which an organic group, usually from an ester, is exchanged with an organic group from an alcohol. The reaction in this polymerisation could result in shorter chained polymers if the acid and alcohol groups are in different positions. The resulting polymer is shown in Figure 2-32.

Transesterification occurring in this polymerisation would result in polymers which have higher polydispersity index values[111]. This is because the hydroxyls can trans-esterify with esters present in the backbone of the polymer randomly cutting and reforming chain at various positions, thus increasing the polydispersity of the polymer. and could result in higher polydispersity indexes because this reaction would affect weight average molecular weight more considerably than affect the number average molecular weight (Figure 2-32).

Transesterification can be confirmed by an experiment designed by Paul Flory[112,113]. The procedure was to produce a large acid functional polymer and a short hydroxyl functional polymer. A mixture of these polymers should exhibit 2 distinct peaks by GPC. However, if the 2 polymers were then blended with an appropriate catalyst, heated at sufficient temperature so that transesterification can take place and stirred

for a sufficiently long time, then the GPC trace could show evidence of transesterification. If it had occurred, the 2 peaks from the initial polymers would shift gradually towards a single, broad peak of average molecular weight. However, if esterification had occurred between the two polymers, the resulting polymer mass would increase to a value possibly close to the sum of the masses of the parent polymers.

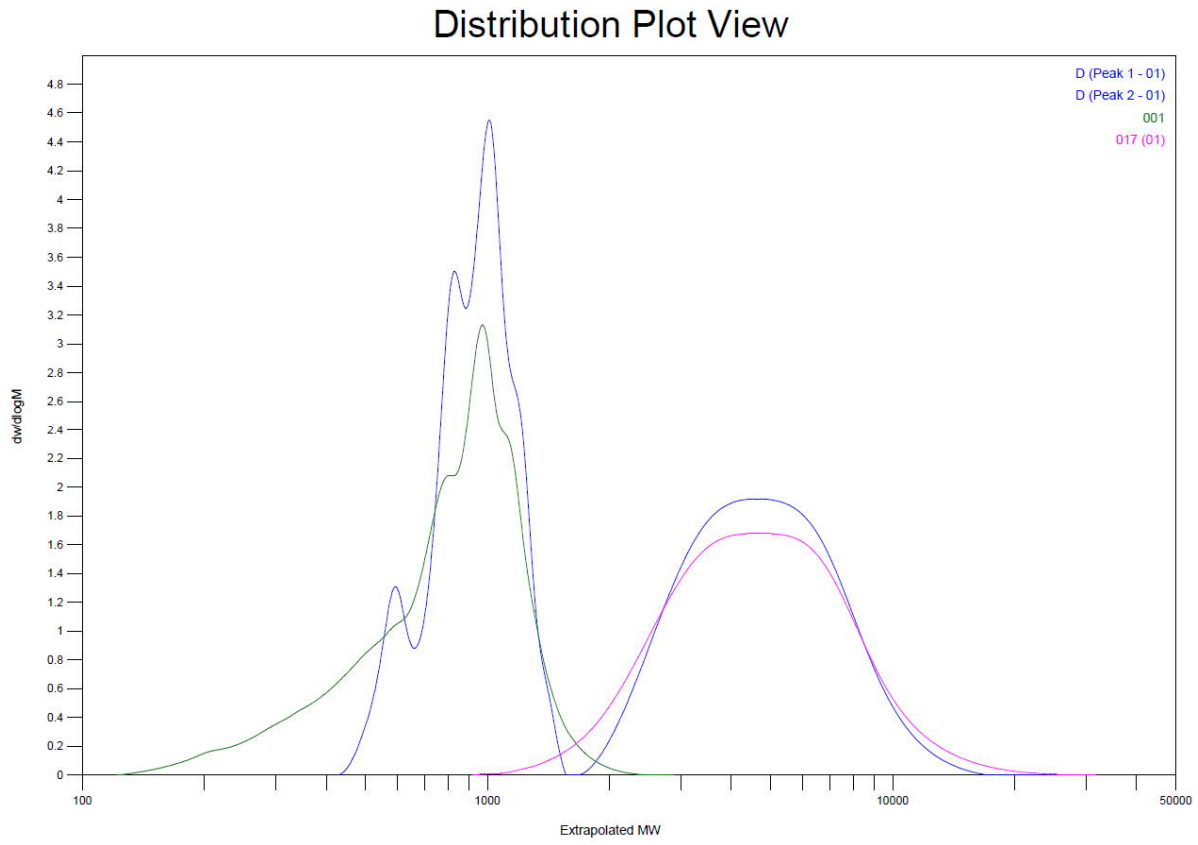

Figure 2-33 - GPC chromatogram showing results from transesterification study with high molecular weight polymer (pink), low molecular weight polymer (green), blend after processing the mixture (blue)

As can be seen through GPC the low molecular weight polymer, and the higher molecular weight polymer retained their molecular weights distributions processing at 140°C and with ETTPB catalyst added to mimic process conditions (Figure 2-33). This indicated that transesterification did not occur.

Sample	Mn (g/mol)	Mw (g/mol)	PDI
Blend peak 1	4192	4966	1.185
Blend peak 2	876	927	1.058
Low Mw OH functional	662	824	1.245
High Mw Acid functional	3865	4937	1.277

Table 2-13 - GPC results confirming transesterification does not occur under process conditions

As can be seen from the GPC overlay, and the table above, no transesterification had occurred, and both polymers did not react. It could be concluded that the low molecular weight shoulder that was present in the low Mn OH functional polymer, has processed further into the polymer, as the molecular weight does increase. However, it is believed to be under expected chain growth esterification, not transesterification, as it can be seen in the original polymer, but not the blend.

2.3.6 Epoxy homopolymerisation reaction

Epoxy homopolymerisation is a reaction in which a previously opened epoxy (e.g. by an appropriate catalyst) reacts onto another epoxy and so on. In the case of the ROCOP this would cause lower conversion rates as less epoxies would be available for the ROCOP, and free epoxy homopolymer chains.

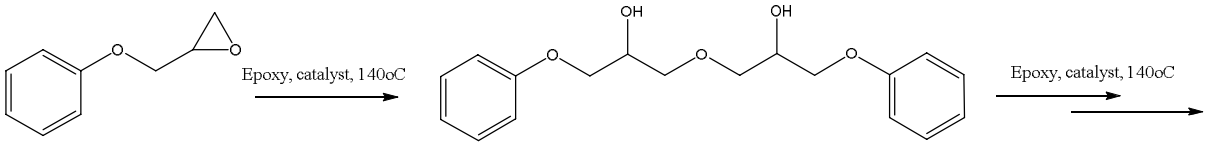

Figure 2-34 - Simple reaction of epoxy homopolymerisation

This reaction[114] was believed to occur when processing a 1:1:1 ratio oligomer as the epoxy was reaching almost full conversion in all hydroxyl functional polymers but the acid was not reaching full conversion. This indicated the epoxy could be reacting with something other than the acid functional groups forming ether linkages, i.e. epoxy was reacting with other epoxy groups or hydroxyl groups (Figure 2-19).

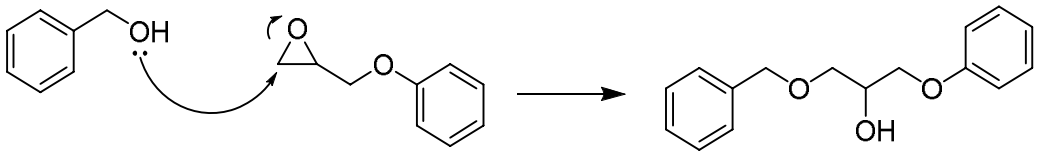

Figure 2-35 - Primary OH + Epoxy

This was tested through a catalyst study to understand the affects different catalysts have on the extent of epoxy homopolymerisation which occurred. This also gave insight into which catalysts to use in further studies and ultimately in the final polymer processing conditions. Results are shown below in Table 2-14.

Polymer Code	Catalyst	EEW (g/eq.)	% epoxy reacted	% acid reacted
LW4	ZnS	47500	99.15%	84.21%
LW1	TBAB	57000	99.29%	94.60%
LW5	DMAP	23500	98.27%	96.42%
LW6	ETPPB	26000	98.44%	95.57%
LW7	TEA	23244	98.25%	91.70%
LW2	2MI	No free epoxy peaks present	100.00%	96.99%

Table 2-14 - % epoxy and acid reacted using different catalysts. Formulation: Benzyl alcohol + Phthalic Anhydride + PGE in a 1:1:1 ratio producing hydroxyl functional oligomers (0.1mol% catalyst)

The reactions which were predicted to be occurring are shown in Figure 2-36 below;

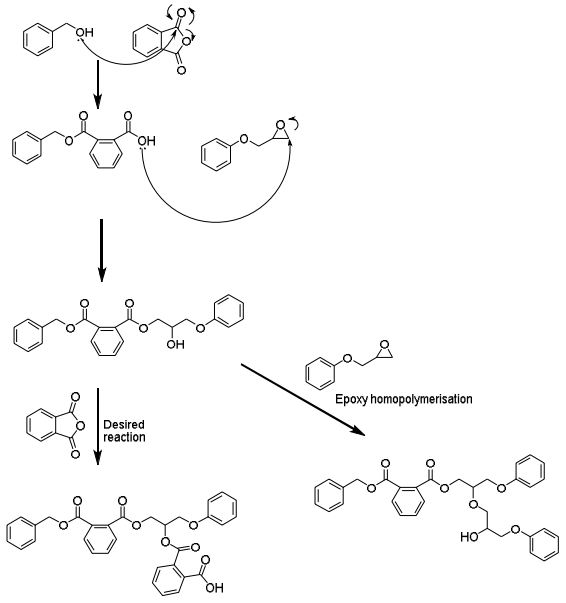

Figure 2-36 – Reaction pathways of desired reaction vs epoxy homopolymerisation

To understand this reaction, epoxy was added with catalyst and heated to process temperature. This was left to process for 2 hours.

Epoxy homopolymerisation can be confirmed using a number of methods[115], but ^{1}H NMR gave a good indication from the clear proton signal in the 3.4ppm region of the spectra, whether it had occurred and to what extent (Table 2-14). The % epoxy homopolymerisation was calculated by measuring ratios of the unreacted epoxy proton peak at 3.4ppm to one of the aromatic proton peaks from the PGE at 7.0 ppm.

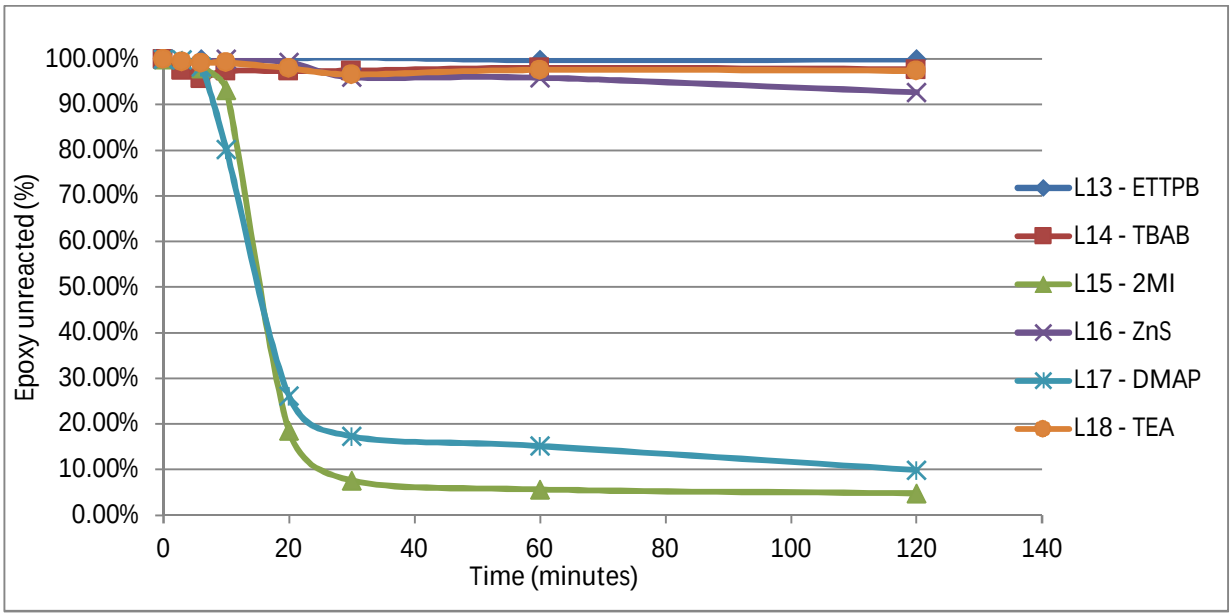

Figure 2-37 - Epoxy homopolymerisation extent when using different catalysts (determined by proton NMR). Epoxy was added solely with catalyst to determine these results.

As shown in Figure 2-37, 2 methyl imidazole (2MI) and 4-dimethyl amino pyridine (DMAP) gave rise to extensive epoxy homopolymerisation under identical processing conditions meaning that these are not suitable catalysts for the ROCOP due to their poor selectivity as catalyst for this reaction. The other 4 catalysts all showed good results but TBAB and ETPPB stood out the most showing the best results with almost no epoxy homopolymerisation. The values observed indicated no homopolymerisation occurred at all under these conditions.

2.3.7 Esterification reaction

The esterification reaction, acid – epoxy – acid, was a reaction which is desired in the polymer synthesis, however, was undesired in this experiment due to stoichiometry. This experiment was designed to understand if the epoxy could react with the acid and not produce any other undesired reactions. Butanoic acid + PGE + catalyst samples were produced in a 1:1 stoichiometry and tested on GPC (Figure 2-38). It was believed it should be possible to see by GPC as it would produce a different molecular weight to reacting in a 1:1 ratio with epoxy molecule. Further reaction should be observed in the higher molecular weight region, if undesired reaction occurred.

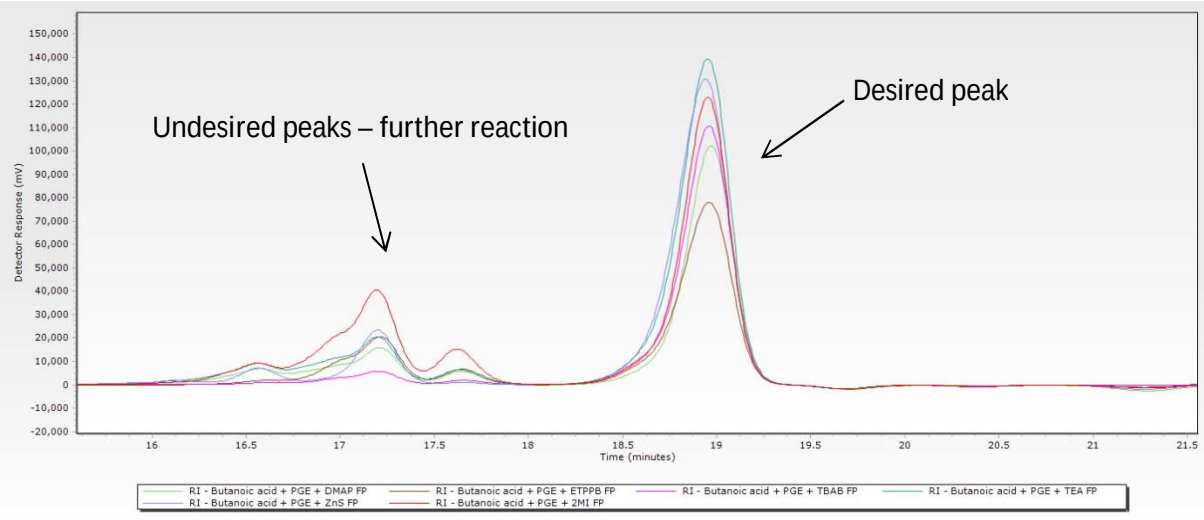

Figure 2-38 - GPC overlay identifying undesired reactions with different catalysts. (Formulation: Butanoic acid:PGE 1:1 stoichiometry with varying catalysts)

As the GPC showed that not only could the desired peak to be seen, and the esterification, it could show many undesired reactions occurring but is not very specific with molecular weights. To understand this further, three samples were initially sent for Gel permeation chromatography – Mass spectrometry (GPC-MS) at the AkzoNobel Deventer site, Netherlands to test and understand if specific molecular weights for each of these peaks could be confirmed. These samples were prepared using the monofunctional model acid butanoic acid and PGE in a 1:1 molar ratio as the Acid-epoxy reaction was used as a simple way to see how the reaction can be affected by a catalyst. These results gave great insight into how each catalyst works and what reactions each of them promotes.

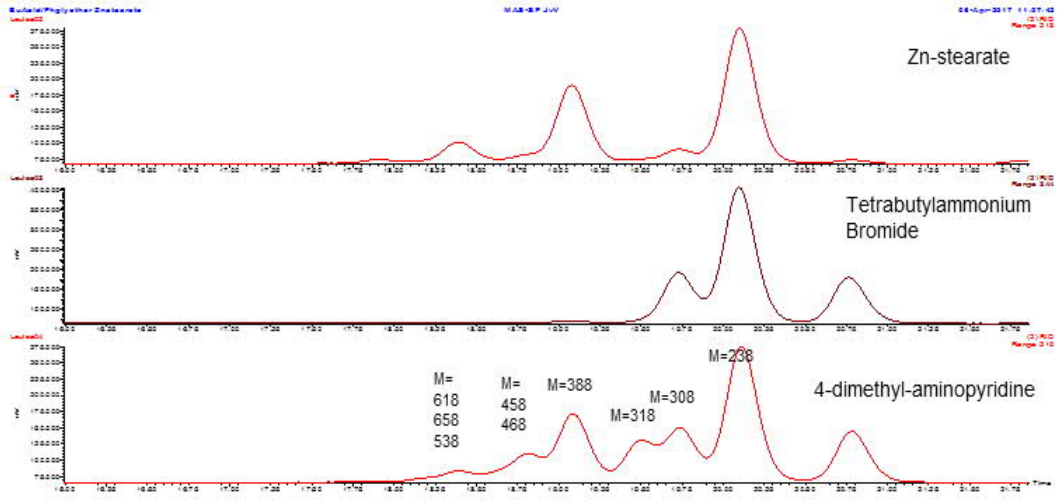

Figure 2-2-39 - GPC-MS traces of butanoic acid PGE adduct with Zn stearate, TBAB and DMAP

The expected reaction product had a mass of 238g/mol, indicating all other peaks shown in Figure 2-2-39 are undesirable and represent a number of different identifiable side reactions. A selection of peaks identified are shown in the table below (Table 2-15), with all molecules identified and shown by mechanism in the figures below (Figure 2-40&Figure 2-41);

M/Z	Breakdown	Chemistry	Reaction
238	150+88	Acid-epoxy	Nucleophilic substitution - Desired
308	238+88-18	Acid-epoxy-acid	Esterification
388	238+150	Acid-epoxy-epoxy	Epoxy homopolymerisation
458	238+150+88-18	Acid-epoxy-epoxy-acid	Epoxy homopolymerisation and Esterification

Table 2-15 - GPC-MS results breakdown

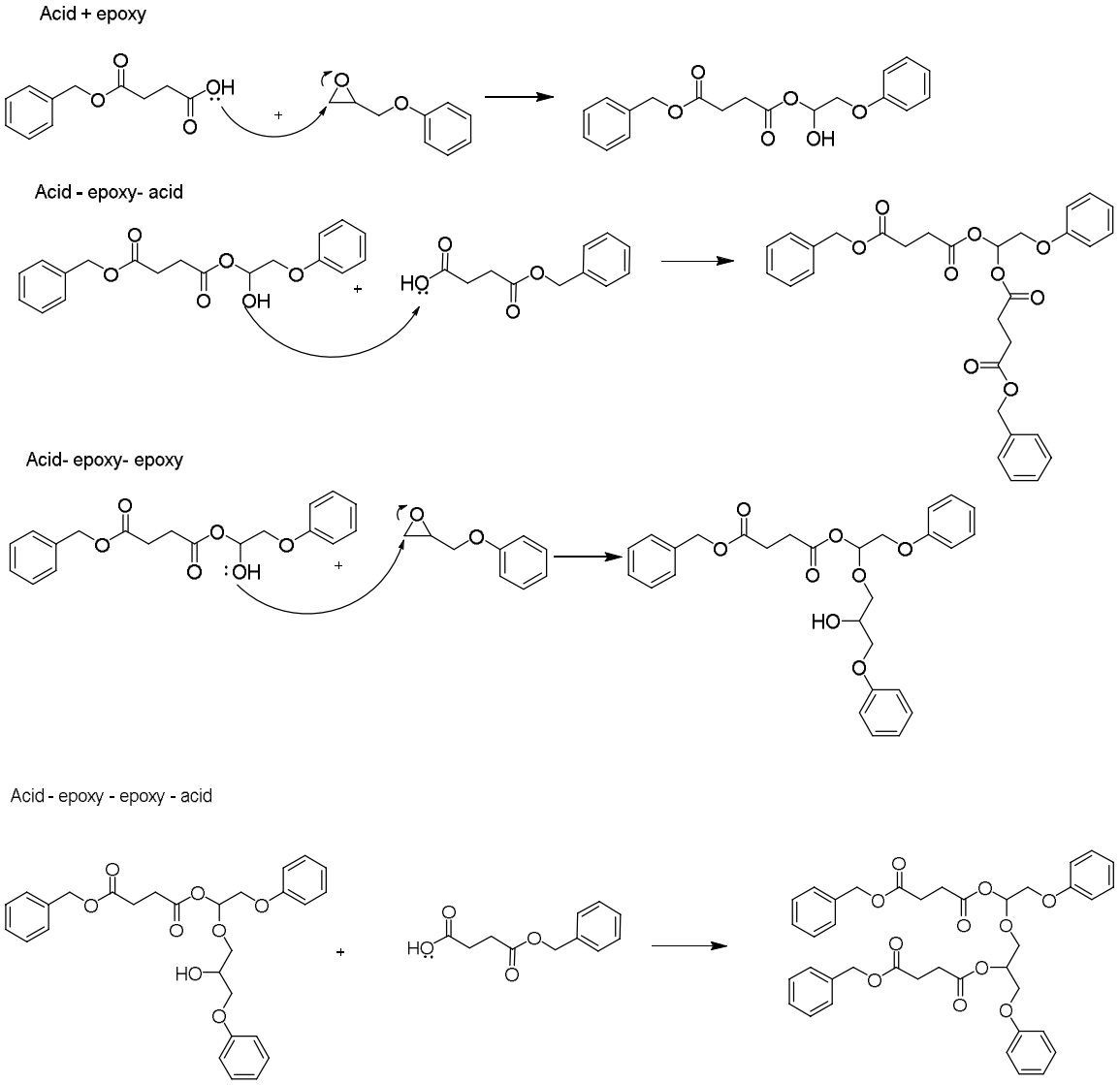

Figure 2-40 - Schematic reactions of the lower Mwt GPC-MS results of the butanoic acid PGE (1:1) adduct

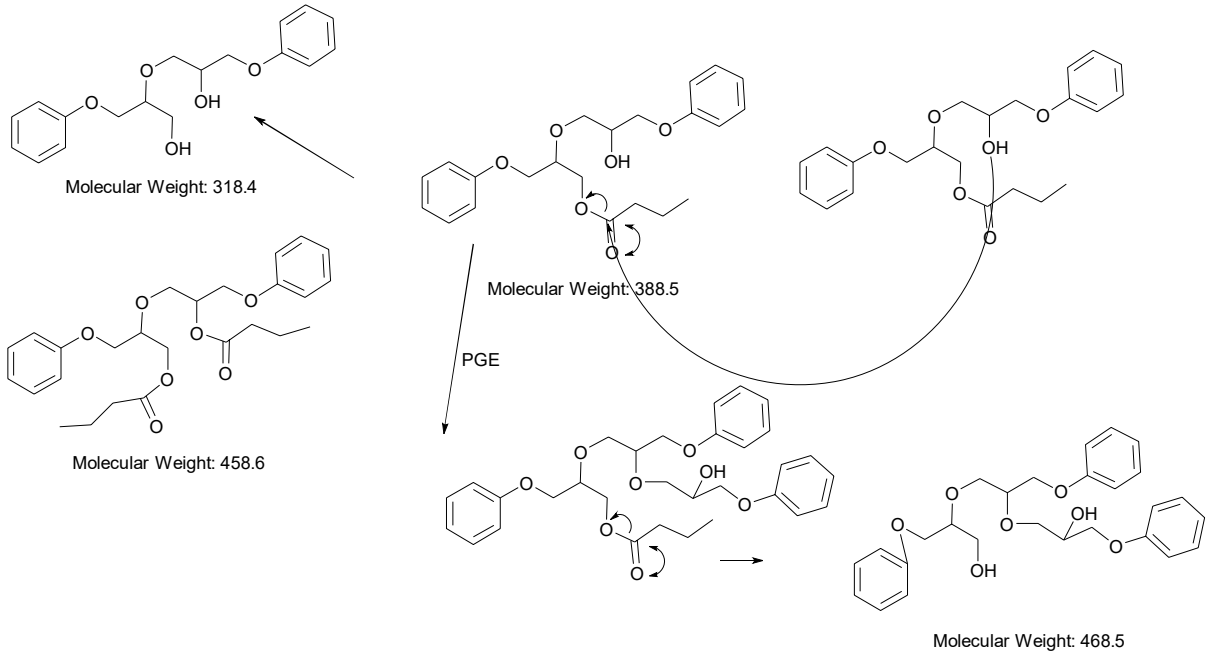

Figure 2-41 - Mechanisms showing formation of higher Mwt molecules found on the GPC-MS of the butanoic acid PGE (1:1) adduct

This indicated that DMAP and Zn-stearate promoted epoxy homopolymerisation as well as esterification and the desired nucleophilic substitution which confirmed the loss in epoxy in chapter 2.3.6 explaining epoxy homopolymerisation. From these results it was also shown TBAB did not promote epoxy homopolymerisation. This allowed conclusions of indicating DMAP and zinc stearate are less selective catalysts for this reaction and using TBAB from these results should lead to a better controlled, more selective polymerisation reaction.

As this gave a great insight into the reaction and what undesired reactions had occurred, samples prepared from the different catalysts in screening including a sample without any catalyst were processed under the same conditions as the previous tests (140°C for 1 hour) analysed by GPC-MS. This was to give an overall conclusion on all types of catalysts that had been tested in the catalyst screening process (Figure 2-42).

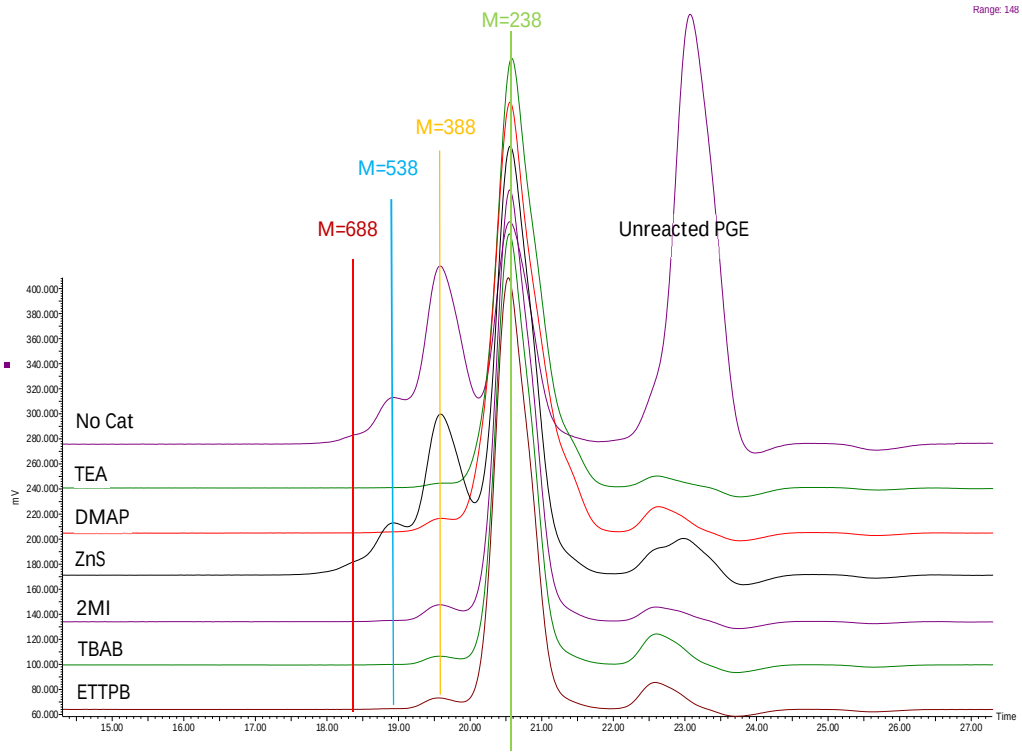

Figure 2-42 - Overlay of GPC-MS spectra for all catalysts. Butanoic acid:PGE 1:1 ratio, with various catalysts

These results showed that when the mixture contains no catalyst, a large amount of reaction does not occur, as understood from the unreacted PGE peak. All reactions appeared to show the desired peak, but other undesired reactions occurred depending on the catalyst used. ZnS showed a large amount of undesired reaction, as it did in the previous test shown above. ZnS was the only lewis acid tested and some lewis acids are known to be hygroscopic[116], which would be undesired in this reaction as moisture could initiate side reactions so this may explain the poor results found with this catalyst. DMAP and 2MI are also observed to show epoxy homopolymerisation in these results, confirming the previous results in Chapter 2.3.6. DMAP and 2MI both follow nucleophilic substitution reactions, indicating nucleophilic substitution catalysis allows epoxy homopolymerisation[114]. From this graph, it could be concluded that TBAB, ETTPB and TEA are the most suitable catalysts for this reaction, showing no undesired side reactions in this experiment.

2.4 Thermal stability of catalysts

DSC and TGA analysis were carried out on all catalysts to understand how they degrade at process conditions (Table 2-2-16).

Catalyst	Mass lost by 250°C (%)	Degradation temperature (°C)
ZnS	0.13	250
TBAB	94.64	135
DMAP	100.00	137
ETPPB	0.82	232
TEA	-*	450**
2MI	99.89	130

Table 2-2-16 - Degradation results of all catalysts tested. *Not carried out due to the nature of the chemical and H&S issues surrounding this. ** From literature.

This study showed which catalysts would be stable at process temperatures and therefore optimum for this chemistry. From results it could be seen that TBAB, 2MI and DMAP decompose around process temperature (140°C) whereas ETTPB, ZnS and TEA can be processed up to above 200°C. As the reaction is exothermic and exotherms have been observed when processing, this was crucial information as the catalyst may not be effective if an exotherm at or above the degradation temperature was to occur.

2.5 Catalyst summary

The graph below shows all 6 catalysts (Figure 2-43), compared against one another. This shows that TBAB is the overall highest yielding and most selective catalyst to move forward with when making higher molecular weight polymers.

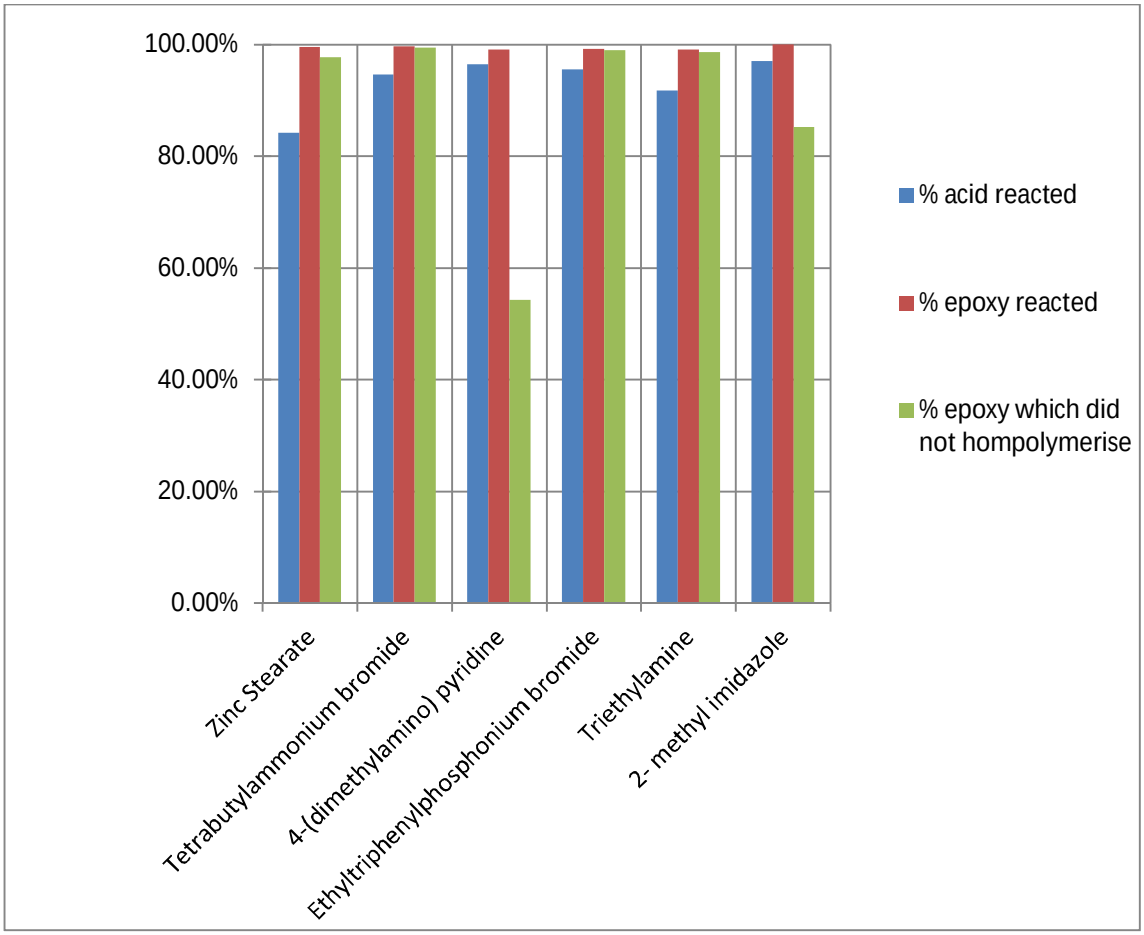

Figure 2-43 - Figure showing summary of 6 catalysts screened, showing % of acid reacted (blue), % of epoxy reacted (red) and % epoxy which didn't hompolymerise (green). Chart designed so highest peaks are desired

The graph was designed as a benchmark comparison and so that the values are normalised to 100% so that the highest value corresponds to the highest selectivity towards the ROCOP. From this graph, it could be concluded that ETTPB, TBAB and TEA are the best candidates. Taking into consideration, from the GPC, that TEA gives rise to esterification, and confirmed in literature that base catalysts give rise to this type of undesired reaction[117], this was ruled out as a potential catalyst. It was also showed that TBAB was degrading around the process temperature, and therefore ETTPB would be used for the next stage of the project, in which higher molecular weight polymers are to be synthesised using the knowledge gained.

Chapter 3 - Relationship between polymer structure and polymer properties using higher molecular weight polymers

3 Relationship between polymer structure and polymer properties using higher molecular weight polymers

3.1 Aim

So far this project has focused on model reactions, creating either non-polymeric model compounds or very low molecular weight polymers, which could be classed as oligomers due to size[1], in order to develop a deeper understanding of the reactions involved in the ring opening copolymerisation This allowed to understand how the alternating chemistry worked and how to synthesise such polymers using said chemistry efficiently. Once understood, higher molecular weight polymers could be synthesised. Structural changes to the polymers would then give an understanding of how the properties of a coating can be affected by such changes. The primary focus of this work was to develop new polymer for use in Powder Coatings, for which a polymer should have a Tg in excess of 50°C to provide a formulated powder mixture which is stable on storage[13]. Higher molecular weight polymers, with appropriate structural modifications, were therefore targeted to ensure adequately high Tgs. These polymers could also be used for liquid coatings, the requirement for higher Tgs would not necessarily be required.

The polymers were formulated to have a target number average molecular weight of approximately 6000g/mol which is similar the Mn of the commercial polyester resins used in Powder Coatings providing a Tg above 50°C .

The polymers initially made in this section were initiated with hydroxyl function initiators with functionalities ranging from 1 to 6, whilst keeping a target Mn of 6000g/mol. This should result in structures that have shorter arms from the central branch point as the functionality increases (Figure 3-1).

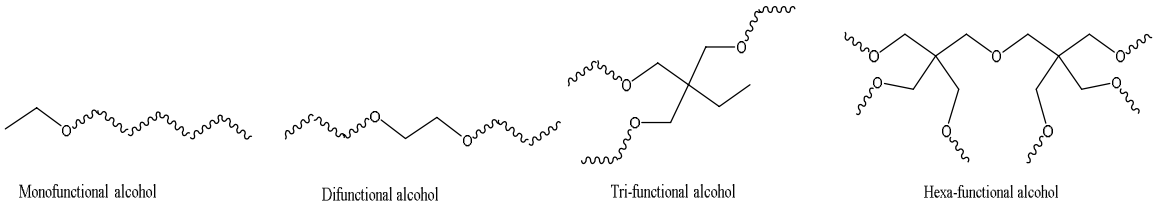

Figure 3-1 - Figure showing examples of the theoretical desired multifunctional polymer structures using the alternating chemistry

All compounds illustrated in Figure 3-1 have the same target Mn but have different chain lengths from the central branch point, thus the distance between functional groups will vary when the functionality of hydroxyl groups in the initiating alcohol varies; this is the first investigation into structural change.

This work should give insight into how varying the functionality of a polymer, can affect a coating's properties, From the model work in section 2, it appeared this reaction is synthesised efficiently and as theoretical set points predict. This work should allow understanding of ideal process conditions for this reaction, any complications when producing higher molecular weight polymers, and if they show any differences between each other when added to a coating.

3.2 Formulation and theoretical characteristics of the polymers

In the case of polymers synthesised via step growth, such as standard polyesters, the theoretical work out carried out before synthesis relies on the theories of Miller and Macosko[19] to predict results of polymer properties. These theories can be used to derive expressions for pre-gel and post-gel properties of multi-functional mixtures able to react with each other, including both synthesis of polymers and the curing of these with cross-linkers[19]. These however only allow for a single type of reaction (for instance in the case of polyesters, the reaction of carboxylic acids with hydroxyls) whereas the ROCOP requires two. Therefore, a different formulating technique was required.

The reaction was worked out step by step, to understand which functional groups would provide the end functionality when adding different mole ratios. A spreadsheet was produced to do this, which showed a step by step reaction with end functionality calculated. An example of a polymer using a trifunctional initiator is given below in Table 3-1.

				Step Number												
				1	2	3	4	5	6	7	8	9	10	11	12	13
Trifunctional system	MW (g/mol)	Moles	Effective moles	2	1	2	1	2	1	2	1	2	1	2	1	2
Trimethylol propane	134.17	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Phthalic anhydride	148.10	20	20	17	17	14	14	11	11	8	8	5	5	2	2	0
1,2-epoxy-3-phenoxypropane (PGE)	150.17	17	17	17	14	14	11	11	8	8	5	5	2	2	0	0
COOH functional groups present			0	3	0	3	0	3	0	3	0	3	0	3	1	3
OH functional groups present			3	0	3	0	3	0	3	0	3	0	3	0	2	0

Table 3-1 - Evolution of reactive groups during processing following the alternating chemistry, using a TMP:PA:PGE formulation in a 1:20:17 ratio

In the initial step, one mole of hydroxyl groups from the initiator (in this case, TMP), which is equivalent to 3 hydroxyl groups reacts with 3 different anhydrides (in this case Phthalic anhydride), thus using all hydroxyls present and creating 3 carboxylic acids. In turn the 3 acid groups are then able to react with 3 epoxy molecules, which will form 3 hydroxyl groups when reacted. These will go on to react with another 3 anhydride groups, and so the reaction continues until at least one of the monomers is fully consumed. As an acid functional polymer was desired, it was necessary to create a formulation in which an excess of acid groups was used, in the form of phthalic anhydride (each bearing 2 acid groups), compared to hydroxyls, in the form of epoxy groups (each bearing 2 hydroxyls) and hydroxyl initiator.

Using this technique, polymer theoretical data can be calculated such as the theoretical Mn, acid value (to indicate the polymer functionality and reaction advancement), epoxy equivalent weights and hydroxyl values (to confirm the reaction advancement). However as mentioned previously the hydroxyl value titration did not

give reliable values so this has not been measured in the subsequent work. Acid value, EEW and Mn were the values relied upon.

3.2.1 Experimental Hydroxyl determination

Hydroxyl values (OHV) of polyesters are commonly determined, alongside acid values, to confirm that a monomer formulation has not drifted during synthesis, as it is common to lose monomers during synthesis if these have boiling points close or below the process temperature. The hydroxyl value is measured via a solution back-titration method as shown in Figure 3-2. This method will give an OHV value, which with an acid value, can provide a total hydroxyl number (OHN), given no free diol present.

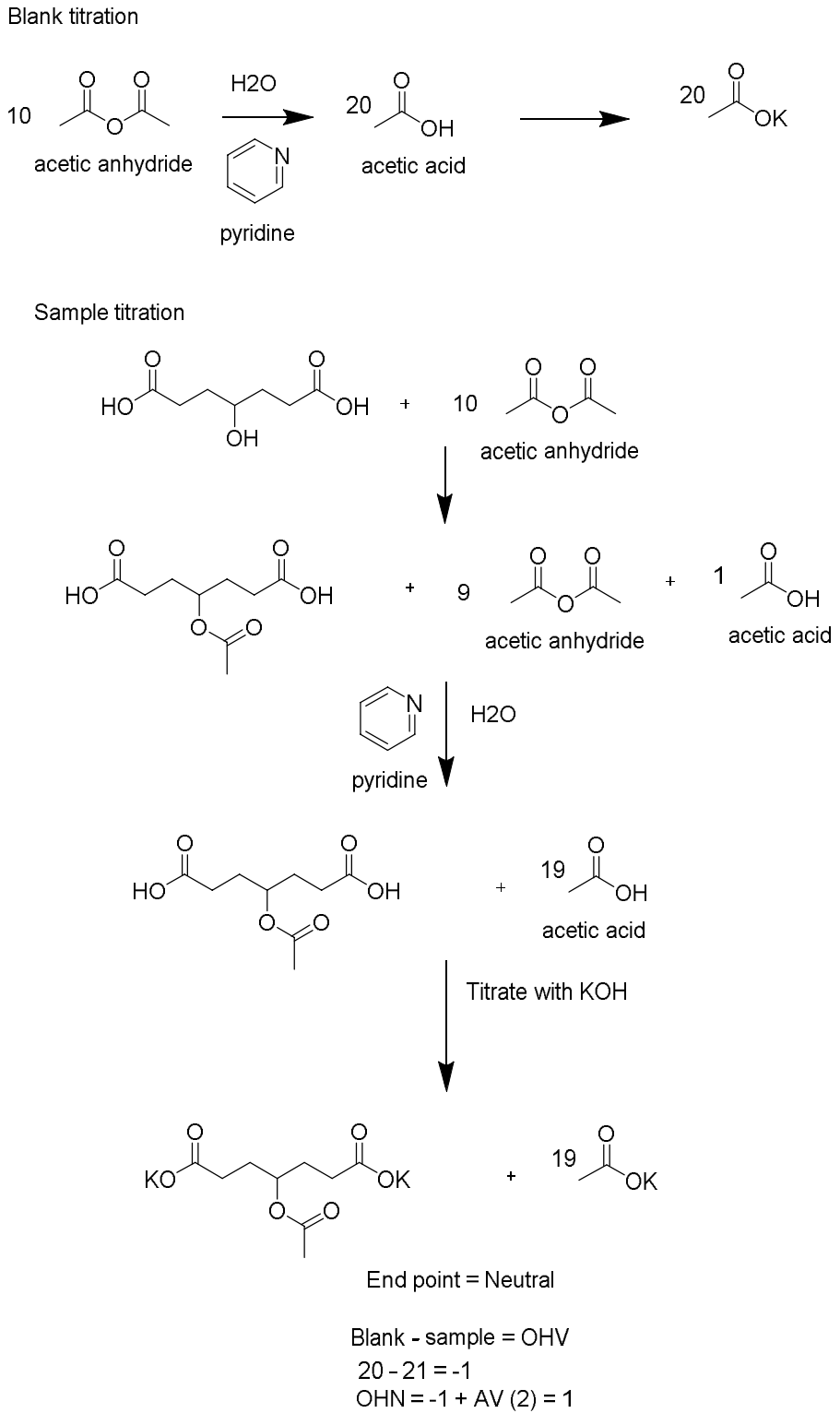

Figure 3-2 - Schematic of the OHV titration

For polyesters made by ROCOP, the wet titration method could not accurately measure the hydroxyl value, as shown in (Table 3-2) below. The expected value for the resin below was -9.52 mgKOH/g. The table shows 3 samples of the same polymer, ran

in the same conditions in triplicate on the same equipment, same solvents and using very similar sample weights (all samples within 0.1g – sample weight ~2.5g) but producing significantly different results.

	Run 1 (mgKOH/g)	Run 2 (mgKOH/g)	Run 3 (mgKOH/g)
First sample in triplicate	1.1	32.20	19.00
Second sample in triplicate	3.96	16.45	19.78
Third sample in triplicate	7.26	14.43	20.10

Table 3-2 - Variation in hydroxyl measurements on the same polymer sample

As this data suggests, a value cannot be reliably determined. It was believed to be due to the majority of hydroxyl groups in this chemistry are secondary hydroxyls, which are reacting slower than primary hydroxyls usually measured by this method.

From literature, it seems however it is possible to measure hydroxyl values through ^{31}P NMR– this would be a technique to investigate in future, if OHV is deemed a necessary measure[118].

3.2.2 Predicting polymer setpoints for synthesis

Using predicted data, an estimate of Mn can be obtained. This prediction is important as it allows to compare with the polymers synthesised and assess any possible deviations. The Mn is described as the number average molecular weight and is calculated by multiplying the molecular weight of the monomers by the mole ratio in which it is added (Equation 3-1).

$$\text{Predicted Mn (g/mol)} = \text{Mw(g)} \times \text{Moles}$$

Equation 3-1 - Predicted Mn equation

An acid value (AV) is a value which is more commonly used in industry instead of an acid equivalent weight (calculated by Equation 3-2), however are directly related as per equation 3.3. The acid value indicates the amount of carboxylic acid groups the polymer.

$$Acid\ equivalent\ weight\ (AEW)(g/mol) = \frac{Total\ weight\ of\ the\ polymer\ (g/mol)}{Acid\ Functionality}$$

Equation 3-2 - Acid equivalent weight, the mass per acidic unit equation

$$Acid\ value\ (mgKOH/g) = \frac{56100\ (mgKOH/mol)}{AEW\ (g/mol)}$$

Equation 3-3 - Equation showing relationship between acid value and Acid equivalent weight

This helps predicting values which indicate whether a reaction has proceeded as expected or not, and if so, is the extent of reaction. Total acid values give a value of how many acid groups and unreacted anhydride groups are present. Partial acid values will measure acid groups and count unreacted anhydride as 1 acid. Acid values are described in more detail in chapter 2.3.1

$$TAV = \frac{(56100(mgKOH/mol)\ x\ (Acid\ groups(mol)\ +\ 2x\ anhydride\ groups(mol)))}{Total\ weight\ (g)} = mgKOH/g$$

Equation 3-4 - Equation for calculating total acid value

Following the reaction sequence as explained above, partial and total acid value decreases as the reaction proceeds. It also shows that the hydroxyl value should not change, but the OHN will due to a secondary OH being created at every other step, so OHV still needs to be measured to be able to calculate OHN. As OHV cannot be measured accurately for these polymers, this value is not taken into consideration however is shown here for completion.

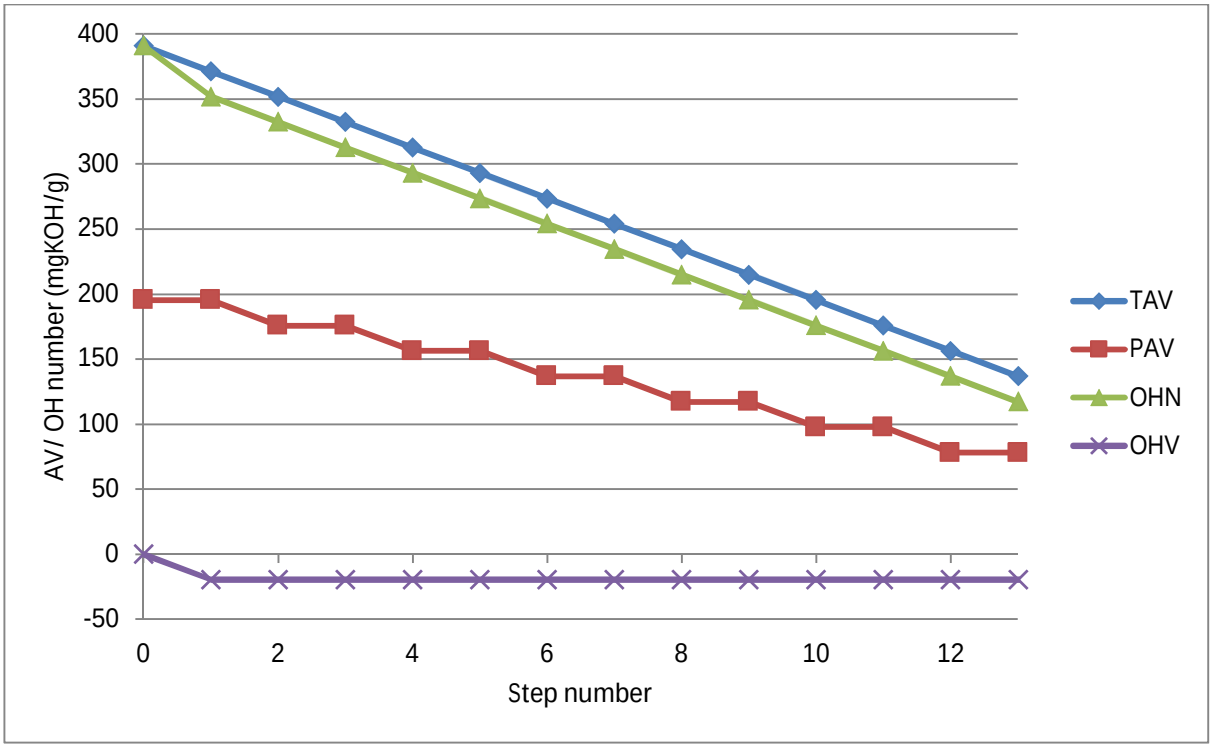

Figure 3-3 - Graph showing the modelled data indicating the importance of each property measured in polymer synthesis

This polymerisation model will allow a general understanding of the addition sequence on individual polymer branches, however in reality these various steps will happen at different times for different polymer chains and so the measured values during the synthesis may differ. End values however should give a good correspondence with the predicted ones.

These predicted results (TAV/PAV/OHV) can be used to calculate the extent of reaction. This is predicted by calculating the initial amount of potential acid groups (based on the anhydride) added initially, the calculated AV at the end of the reaction both in mgKOH/g and working what the percentage of acid is left based on the acid value at the present step (Equation 3-5).

$$\%\ acid\ reacted\ (\%) = \frac{100 - (Acid\ value\ (mgKOH/g) - final\ expected\ acid\ value(mgKOH/g))}{(initial\ acid\ value - final\ expected\ acid\ value(mgKOH/g))}$$

Equation 3-5 - Equation calculating % acid reacted using acid values

The predicted values of AV and OHV can be used give a Mn and % conversion at each step. The Mn is calculated by subtracting the mole ratio multiplied by the molecular weight of the starting monomers from the predicted final Mn (Equation 3-6).

$$In-process\ Mn(g/mol) = Final\ theoretical\ Mn(g/mol) - (Moles\ of\ monomer(mol)\ x\ Mw\ of\ monomer(g))$$

Equation 3-6 - Equation showing how to calculate in-process Mn

The in-process Mn value can then be used to give % conversion at each step of the process identified in the model. The Mn is to be divided by the end Mn weight and multiplied by 100 (Equation 3-7).

$$In\ process\ \%\ conversion\ at\ specific\ steps\ (\%) = \frac{Mn\ (g/mol)}{Final\ Mn\ (g/mol)} \times 100$$

Equation 3-7 - Equation showing how to calculate % conversion using Mn

This process of calculations gives an excellent indication of how the reaction has progressed and allows control over process times, to prevent over-processing giving possible undesired reactions, or under-processing and resulting in unreacted monomers still present.

This work showed that predictions for Mn and acid value can be calculated to indicate the reaction progression. OHV could be predicted as shown in Figure 3-3, however as proved in section 3.2.1, this value cannot be measured accurately and will not be used when determining the conversion of the reaction. These calculations will be used during synthesis to confirm the conversion of the polymer, to help forward the reaction and understand if the polymer is forming as expected.

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Chapter 4 - Application of model work in polymerisation and control of polymer properties

4 Application of model work in polymerisation and control of polymer properties

The results from the work described in chapter 2 – model reactions were applied to the synthesis of higher molecular weight polymers. To initially understand if the model was valid, small polymers/oligomers were produced, with an n value (number of repeating units) of 1.

Furthermore, it was found that dipentaerythritol was insoluble in most solvents that could have been used for the polymer synthesis, and so will not be used. The subsequent therefore focussed on the synthesis of polymers with initiators functionality of 1 to 4.

This chapter will apply the knowledge gathered in chapter 2 and apply to larger molecules, producing polymers rather than oligomers as previous experiments have. The initial tests are carried out on small polymers, explained in section 4.1. If the chemistry can be used for larger polymers, these can be used in coatings, and the properties understood.

4.1 Formulation and monomer selection

The first polymer was synthesized using trimethylol propane (TMP) (Figure 4-1) and was formulated to contain only one repeating group on each hydroxyl present on TMP. A repeating unit being deemed as the adjunction of a phthalic anhydride and a PGE, the polymer formulation meant that for every TMP, 3 PA and 3 PGE were used. (Table 4-1). To make these polymers acid functional a final 3 PA were required.

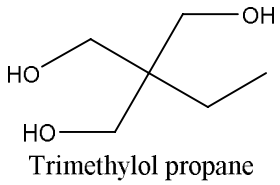


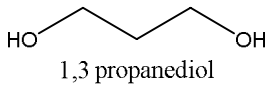
Figure 4-1 - Structure of TMP

Polymer Code: LW17					
Monomer	Molecular mass (g/mol)	Moles	Mole Ratio	Formula weight (g/mol)	Mass (g)
Trimethylol propane	134.18	0.0203	1	134.18	2.73
Phthalic Anhydride	148.1	0.1221	6	888.6	18.09
1,2-Epoxy-3-phenoxypropane	150.17	0.0676	3	450.51	9.17
Total		0.210162		1473.29	30.00

Table 4-1 - Formulation of LW17 - a low molecular weight trifunctional polymer. Synthesised at 140**ºC in toluene.**

LW17 reached 100.4% conversion based on the acid value (Table 4-4). As all polymers were synthesised in toluene and then dried in a vacuum oven, it could be possible this polymer was not fully dry, hence showing a higher conversion. As the acid value is measured through titration (see section 5.1.6), an experimental error could also affect the percentage conversion and read above 100%. Moreover, as the theoretical Mn was reached (within error), it was thought that the conversion was quantitative.

The second polymer was synthesised using a difunctional initiator (Figure 4-2) and the same epoxy and anhydride raw materials (Table 4-2). Formulation was however adapted to cater for a difunctional initiator rather than three-functional initiator.



1,3 propanediol

Figure 4-2 - Structure of 1,3 PDO

Polymer code: LW18					
Monomer	Molecular mass (g/mol)	Moles	M/R	Formula weight (g/mol)	Mass (g)
1,3 propane diol	76.09	0.030965	1	76.09	2.36
Phthalic Anhydride	148.1	0.123861	4	592.4	18.34
1,2-Epoxy-3-phenoxypropane	150.17	0.068557	2	300.34	9.30
Total		0.223383		968.83	30.00

Table 4-2 - Table showing formulation of low molecular weight difunctional polymer. Synthesised at 140**ºC in toluene.**

LW18 reached 99.95% reaction based on the acid value, which was expected as the theoretical Mn was attained (Table 4-4).

LW19 using pentaerythritol (Figure 4-3) was then produced (Table 4-3). This resulted in a 96.01% conversion based on acid value, and only 88% of the expected Mn. It was anticipated that this polymerization would be more difficult to control due to the molecular weight and functionality of the initiator. It is likely that as the reaction of the primary hydroxyls progresses, the steric hindrance on the remaining hydroxyls increase, reducing their reactivity and the degree of control[119]. Pentaerythritol is also hygroscopic, and therefore water could also be used to initiate the reaction. Both explanations could lead to obtaining shorter chains, or lack of reaction leading to lower polymer functionality.

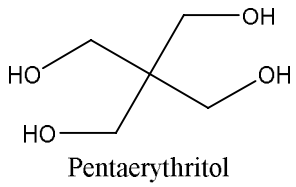


Figure 4-3 - Structure of pentaerythritol

Polymer code: LW19					
Monomer	Molecular Mass (g/mol)	Moles	M/R	Formula weight (g/mol)	Mass (g)
Pentaerythritol	136.15	0.015612	1	136.15	2.13
Phthalic Anhydride	148.1	0.124894	8	1184.8	18.50
1,2-Epoxy-3-phenoxypropane	150.17	0.069129	4	600.68	9.38
Total		0.209635		1921.63	30.00

Table 4-3 - Table showing formulation of LW19 - low molecular weight four functional polymer. Synthesised at 140°C in toluene.

Formulation	% acid reacted	Theoretical Mn (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI
LW17 (TMP/PA/PGE 1:6:3)	100.40%	1500	1400	1600	1.10
LW18 (PDO/PA/PGE 1:4:2)	99.95%	1000	1000	1100	1.09
LW19 (Penta/PA/PGE 1:8:4)	96.01%	1900	1700	2000	1.16

Table 4-4 - Table showing theoretical vs actual results for lower Mw polymers (accurate to the nearest 100)

The increasing difficulty to initiate the polymerisation using pentaerythritol was observed through the inability to reach the expected molecular weight values, under the same process conditions as the di and tri functional initiators.

These results show that the findings from model reactions can be successfully transferred and applied to larger molecules, as the results show that the predicted Mn and actual Mn are similar. However, the difference in reactivity of primary and secondary hydroxyls would provide the same polymer molecular weights and

therefore cannot be observed via Mn values. These polymers produced are also able to produce low polydispersity values, indicating a good degree of control over the reaction[62].

4.2 Higher molecular weight polymers

4.2.1 Initial polymer property results

Small polymers shown in the previous chapter showed a low PDI and 2 and 3 functional initiators indicated the expected polymers produced based on Mn and AV conversion. To make larger polymers, the first polymer was synthesised using benzyl alcohol as mono-functional initiator (Table 4-5). This polymer was designed as a starting point, owing to the presence of a single, relatively unhindered hydroxyl group, which would not boil off due to its high boiling point of 205°C being above reaction temperature, whereas other monofunctional alcohols such as ethanol would. As there is a single hydroxyl group, this would allow propagation of the chain though secondary hydroxyls but the resulting polymer is expected to be linear (single initiation point) with a functionality of 1 (Figure 4-4). Therefore, reacting this polymer with crosslinkers would not result in a crosslinked network due to the singular functionality.

Monomer	Mwt (g/mol)	Moles	M/R	Formula weight (g/mol)	Mass (g)
Benzyl Alcohol	108.14	0.01688	1	108.14	1.83
Phthalic Anhydride	148.1	0.33764	20	2962	50.01
1,2-Epoxy-3-phenoxypropane	150.17	0.32076	19	2853.23	48.17
Total		0.67529		5923.37	100.00

Table 4-5 - Formulation of LW20 – a monofunctional high Mn polymer (BA:PA:PGE in 1:20:19 ratio). Synthesised at 140°C in toluene.

The resulting polymer (LW20) (Figure 4-4) possessed a Tg of 35°C which would be too low for use in Powder coatings, due to storage stability issues of polyesters with a Tg below 50°C. However, this would help in understanding the impact on the Tg of polymers with increased functionality, without increasing the molecular weight.

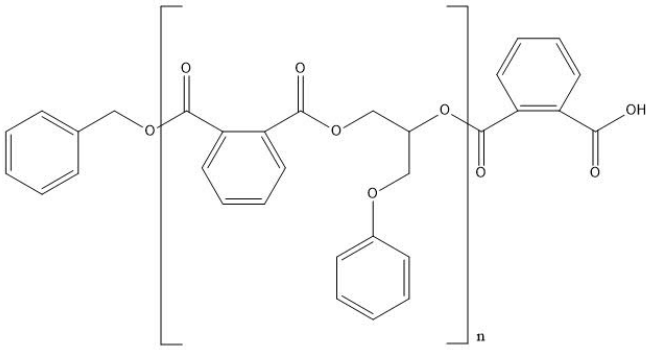


Figure 4-4 - Desired structure of LW20

Conversion of Acid and epoxy groups was measured to understand the progress of the reaction. Acid conversion was calculated from TAV as a percentage of the predicted value. Epoxy conversation was calculated the same way but using the epoxy equivalent weight calculated from NMR.

LW20 reached an acid conversion of 99.4% and an epoxy conversion of 100% therefore it can be assumed that the reaction went to completion.

Further analysis was carried out in AkzoNobel, Holland in which they ran this sample through a SEC-MS, and using a TIC (total ion chromatography) to understand the intensity of the peaks, a breakdown could be understood of the reaction and how the polymer had formed, which showed that the initial part of the reaction had proceeded effectively, as can be seen below (Figure 4-5 & Figure 4-6).

The first spectrum is generated from a SEC, measured by a refractive index detector. This shows one very large broad peak starting around 10 minutes, showing the higher molecular weight material, and then a smaller peak around 20minutes. The sample is then passed through to a mass spec which is the green graph below. This is ran through a TIC-MS (Total ion chromatography – mass spec) using a time of flight TOF detector which is used to give very accurate masses compared to a standard quadrupole mass spectrometer.

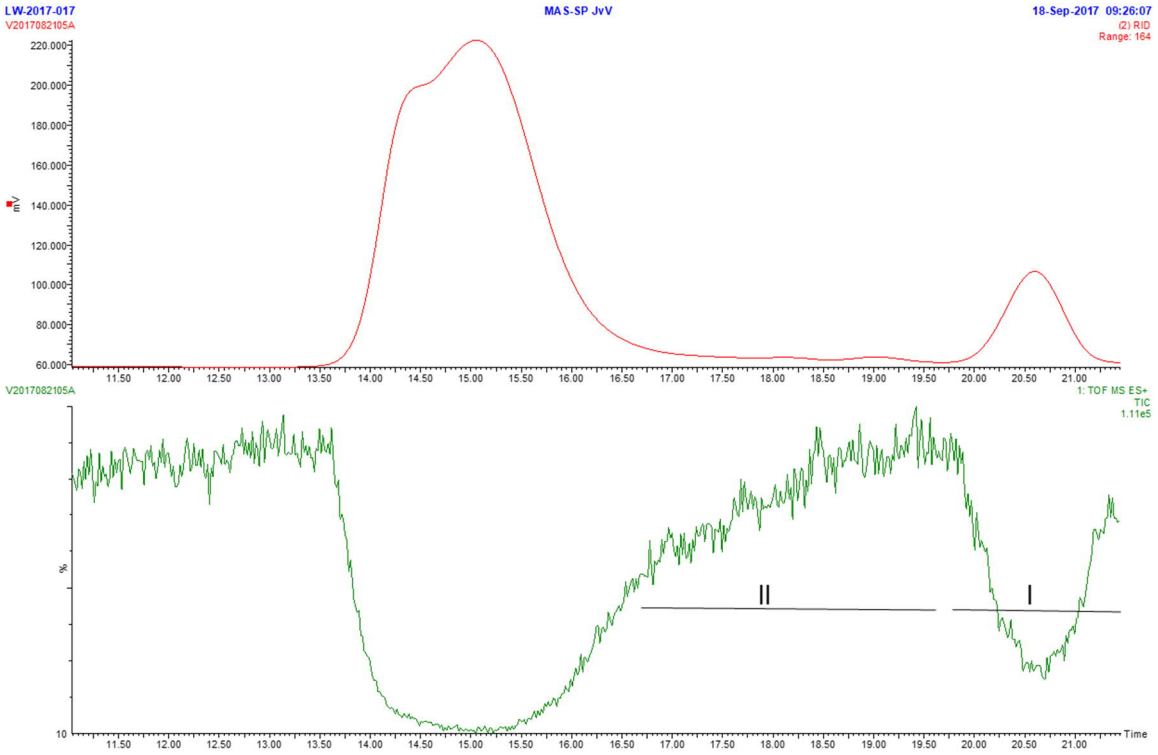


Figure 4-5 – Trace from SEC-MS on LW20 – BA:PA:PGE 1:20:19 ratio

On the green spectrum, 2 areas have been highlighted (area I and II). These are the lower molecular weight areas and as averages of peaks can be analysed on a TOF-MS, these areas have been analysed in further detail in the graphs below (Figure 4-6).

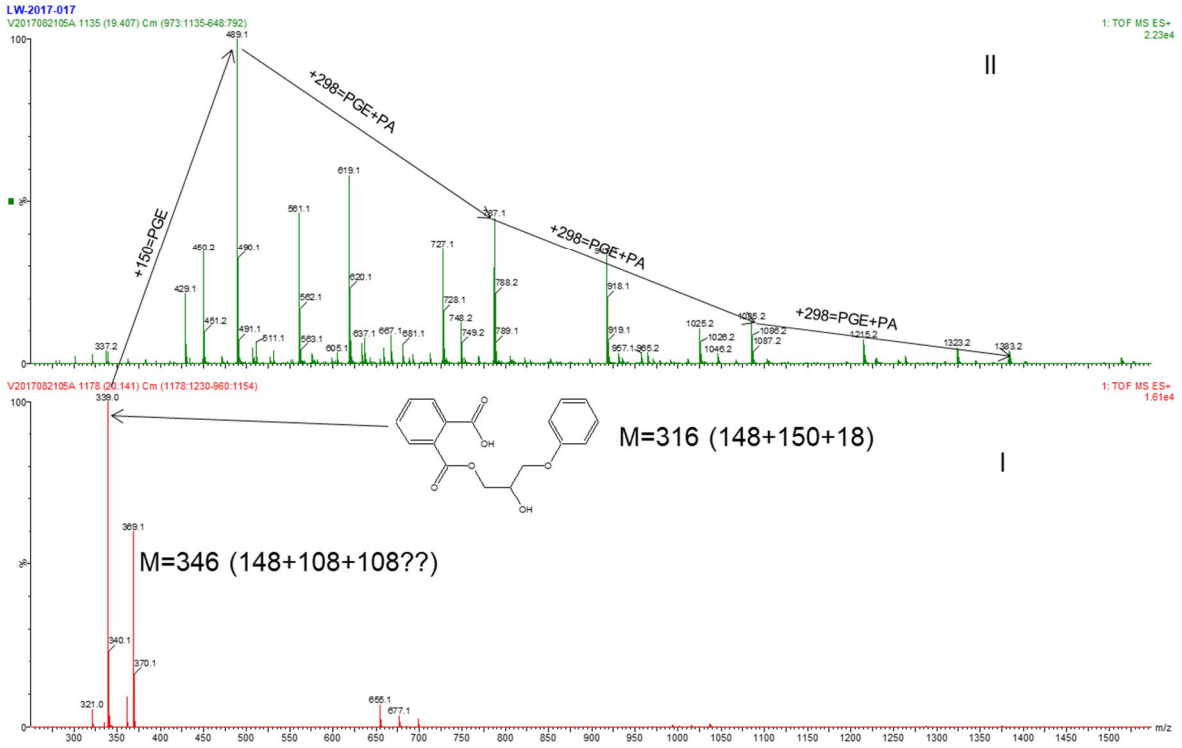


Figure 4-6 – MS spectra from SEC-MS specific time selects (top from 16.75min to 19.75 min, bottom from 19.8 min to 21.5min), showing how the oligomers have been formed correctly

This graph shows the SEC-MS results broken down further within the 2 areas highlighted. The green spectrum at the top of the figure shows area II which is the lowest molecular weight material within the sample. This shows that the polymer has been formed as expected, with peaks showing each set (anhydride and epoxy) of monomers added.

The second spectrum in red shows the area highlighted as I in Figure 4-5. This shows 2 weights in which the structures have been predicted.

The peak at m/z = 346AMU is likely to be the result of the reaction of benzyl alcohol (BA) with phthalic anhydride (PA), which in the presence of additional BA, will esterify with BA and create a dead chain with a mass of 346 g/mol (Figure 4-7). This reaction may be predominant at the early stages of the synthesis where a larger amount of BA is present and will compete with the reaction of PA with secondary hydroxyls from the epoxy. The BA primary hydroxyls will react faster than the secondary hydroxyls therefore creating the BA-PA-BA trimer. However, despite the high peak intensity from the GC-MS, the quantity of the trimer was considered to be negligible owing to the good correlation between the theoretical and actual polymer molecular weights. It may also be that the presence of this trimer in larger proportions has affected the polymer formulation, and effectively reduced the concentration of BA (which is the initiator of the polymerisation), thus creating longer chains than obtained previously (e.g. around 3000g/mol) and bringing the molecular weight of the polymer closer to the theoretical values.

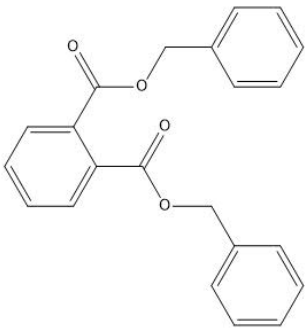


Figure 4-7 - Structure of BA-PA-BA found at 346AMU in the GC-MS

A second polymer was synthesised using the di-functional alcohol, 1,3 propanediol (LW21). This polymer reached an acid conversion of 98.0%, and an epoxy conversion of 100%. Data shown in Table 4-6 below.

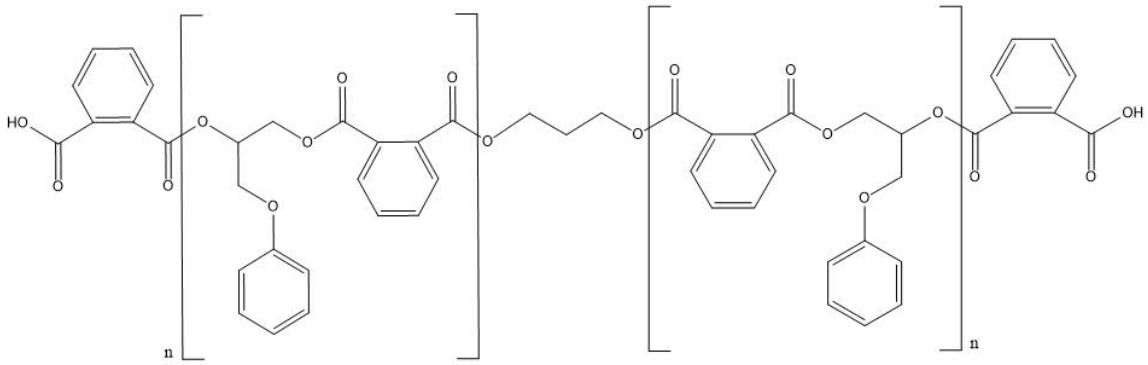


Figure 4-8 - Structure of theoretical LW21 - 1,3PDO initiated polymer

A polymer with similar predicted Mn was produced using a tri-functional alcohol (LW22), and this also reached full epoxy conversion and a 98.2% acid conversion.

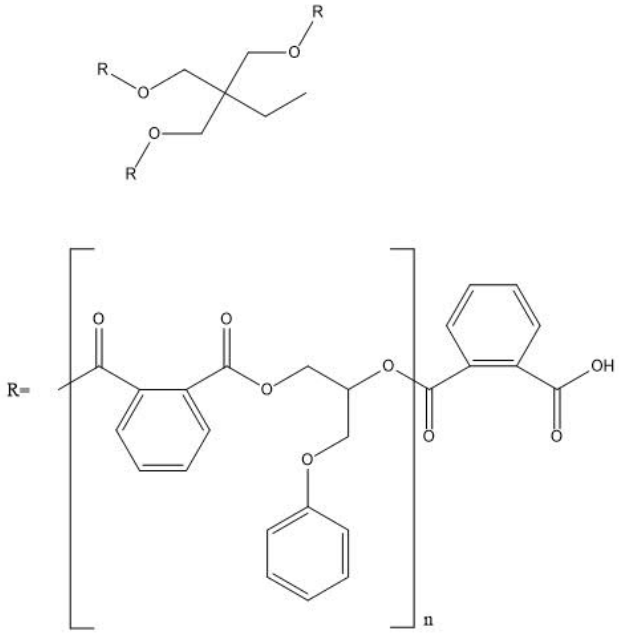


Figure 4-9 - Structure of theoretical LW22 - TMP initiated polymer

All three polymers were analysed and compared and it was noticed the polymers were only producing a small percentage of the expected Mn. The analysis is shown in the table below;

Formulation: Phthalic Anhydride + PGE	Mole ratio	% acid reacted	% epoxy reacted	Tg(°C)	Theoretical Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI
LW20 (Benzyl alcohol)	01:20:19	99.39%	100%	36.47	5923	5107	6405	1.2542
LW21 (1,3 propane diol)	01:20:19	98.00%	100%	39.7	5741	3340	3705	1.1093
LW22 (Trimethylol propane)	01:20:19	98.18%	100%	43.06	5949	3669	4421	1.2050

Table 4-6 - Characterisation of mono/di/tri functional polymers

As the molecular weights were not as predicted, this was further investigated in the next section (Section 4.3).

4.3 Synthesis development

Analysis by GPC showed that the polymer molecular weights were lower than expected based on the model experiments and model calculations. As such, further investigation was required on the polymer synthesis process, to explore the cause of this deviation and to optimise reaction conditions to solve this problem and achieve the desired molecular weights.

4.3.1 Understanding the polymerisation process

To understand the process further, confirmation was required as to what type of polymerisation reaction this polymer followed. It was noticed the PDI of each of the polymers was close to 1, which initially indicated the polymerisation was chain growth[120]. The experiment below (Table 4-7) shows aliquots of epoxy added at regular time intervals, and the Mn measured at each point.

Step growth polymerisation produces many small oligomers which, over time, react together[35]. Chain growth reacts from one single point from the chain end and will continue to grow until all raw materials have reacted. This can produce a low PDI, if controlled, as there are no unreacted oligomers[121]. This compares to step growth which produces a higher PDI and contains many small oligomer molecules.

Time (min)	Overall % of epoxy added	Mn (g/mol)	Mw (g/mol)	PDI
0	0	251	254	1.01
7	11.29	405	406	1.00
37	33.887	1192	1253	1.05
52	45.182	1374	1450	1.05
63	56.478	1642	1720	1.02
74	67.774	2037	2156	1.05
92	79.07	2315	2466	1.06
107	90.365	2514	2658	1.05
117	100	3277	3472	1.05
267	100	6114	6579	1.07

Table 4-7 - Mn and Mw as aliquots of epoxy are added to phthalic anhydride and initiator

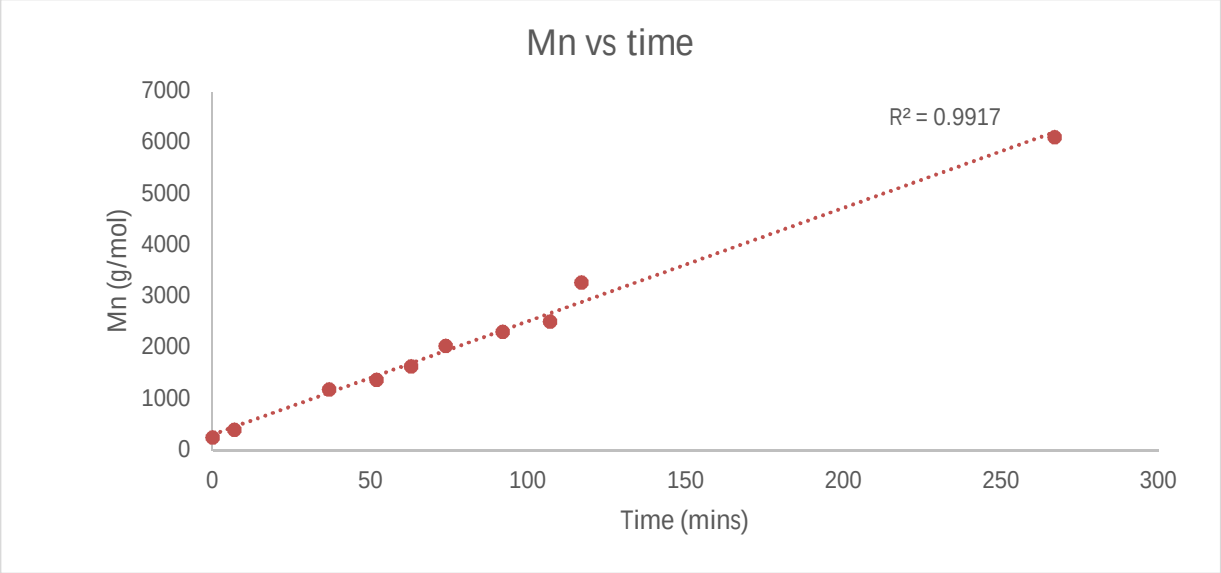


Figure 4-10 - Mn vs time when aliquots of epoxy are added to phthalic anhydride and initiator

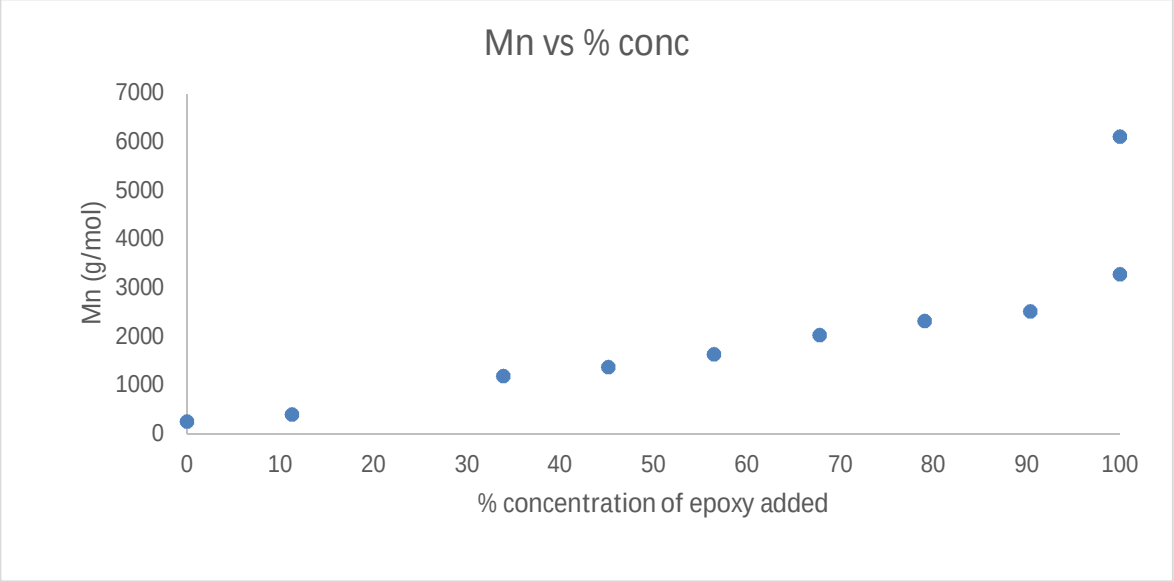


Figure 4-11 - % concentration of epoxy added to phthalic anhydride and initiator against Mn (NB two points are shown at 100% as the sample was left to process over time for 1 hour, the second sample is an hour after all epoxy had been added)

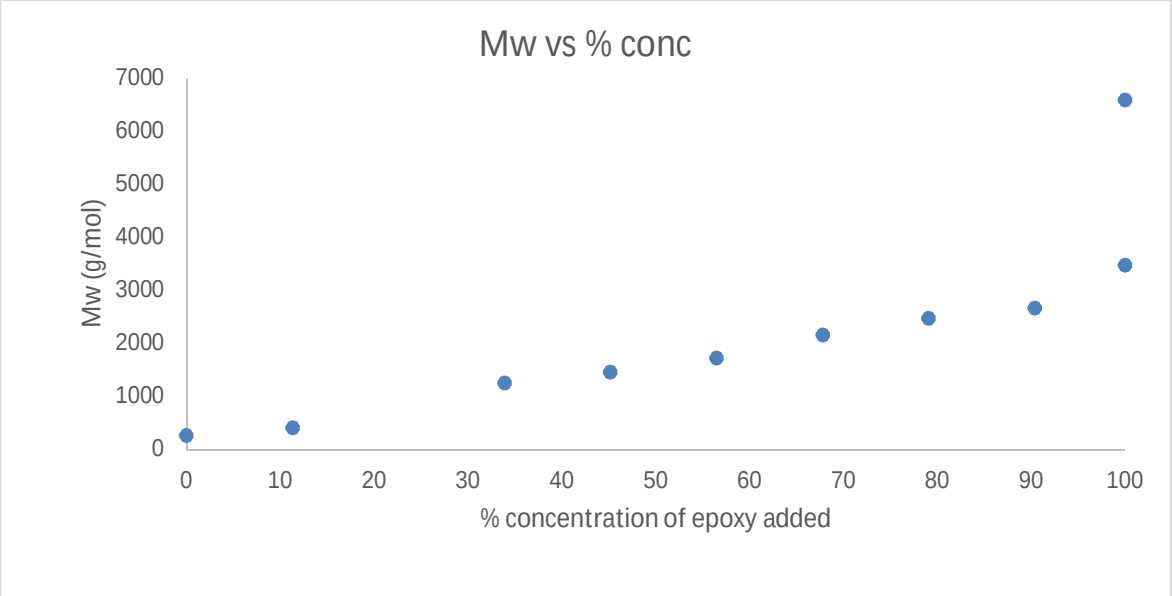


Figure 4-12 - % concentration of epoxy added to phthalic anhydride and initiator vs Mw

Figure 4-10 shows a straight line, however, as this reaction was added in aliquots (as shown in Figure 4-11 & Figure 4-12), it could not be sufficiently concluded from this data that this is a living polymerisation. As the PDI data shows low values, this confirms it is a controlled reaction. PDI values are low in controlled reactions as all polymer chains grow at the same rate [43].

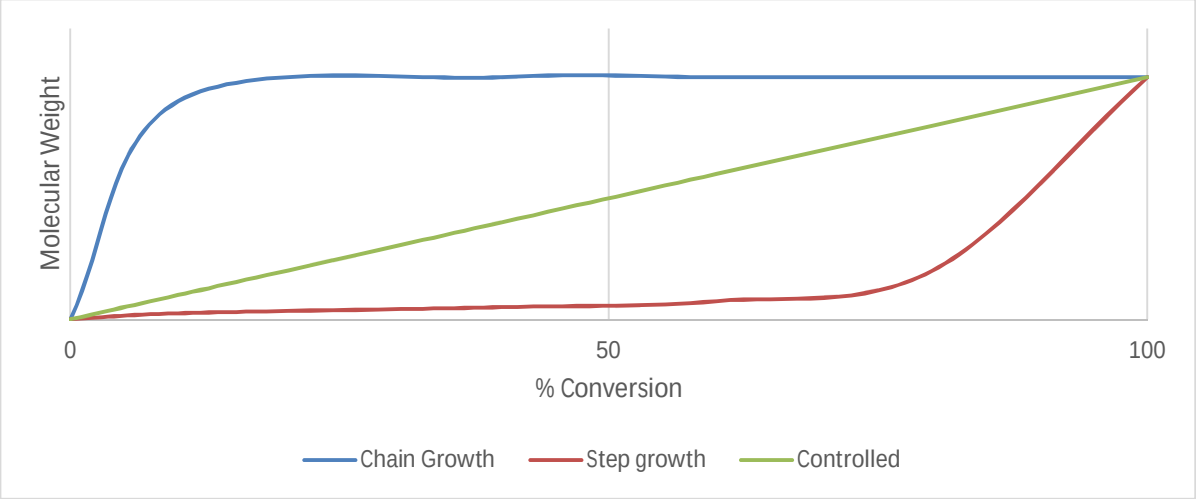


Figure 4-13 - Comparison of step growth, chain growth and controlled polymerisations molecular weight growth over time

4.3.2 Process conditions modification

A series of four polymers were then synthesised initiated with trimethylolpropane (3 functional alcohol) formulation (LW22). All had different processing conditions to determine which process conditions were optimum.

Formulation: Trimethylolpropane+ Phthalic Anhydride + PGE + Cat	Mole ratio	% acid reacted (using PAV)	% acid reacted (using TAV)	% epoxy reacted	Tg (°C)	Theoretical Mn	Measured Mn (g/mol)	Measured Mw (g/mol)	PDI	Colour
High feed rate, Low heat (140°C)	01:20 :19	98.4	97.7	100	44.8	5949	3056	3605	1.180	Slight Yellowing
High feed rate, High heat (190°C)	01:20 :19	99.5	98.4	100	41.6	5949	3111	5544	1.782	Very dark brown
Low feed rate, Low heat (140°C)	01:20 :19	96.8	95.5	100	39	5949	2622	3134	1.195	Slight yellowing
Low feed rate, High heat (190°C)	01:20 :19	100.6	99.3	100	30.91	5949	2404	4479	1.863	Very dark brown

Table 4-8 - Process optimisation of trifunctional polymer

Clearly, all of these polymer Mn values were significantly below the target molecular weight. Further work would be required to understand the cause of this problem.

In addition to this, based on the data above, the high feed rate, low heat combination was concluded to be the most effective of the four conditions trialled. This was because the low feed, low heat combination had a high acid conversion; and the low feed, high heat had given a broad PDI. This could be caused by many reasons for example; unknown side reactions at higher temperatures, or possible competing reactions at higher temperatures i.e. transesterification may also be a cause in these process conditions. The high heat, high feed rate combination also gave rise to a broad PDI and discoloration due to the oxidation of the polymer under high heat (Figure 4-14). Broad PDI values show the polymerisation to be less controlled, with other possible reactions occurring, which is highly undesired and against the aim for the polymer synthesis of this project.

Figure 4-14 - Colour difference between polymers. From left to right high feed low heat, high feed high heat, low feed low heat, low feed high heat

The high heat high feed graph below in Figure 4-15 shows that exposure of the polymer to high heat over time gradually increases the Mw but not the Mn, broadening the PDI. This indicates that the polymer is producing longer chains over time through heat, forcing possibly undesired reactions, such as transesterification. When low heat is applied, this does not occur, and the PDI stays the same.

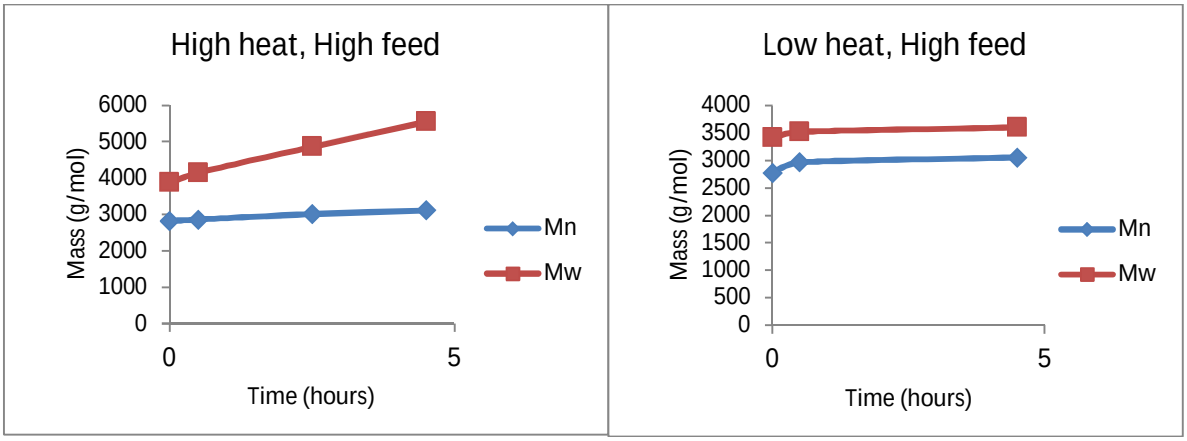


Figure 4-15 - Process optimisation in process samples Mn & Mw changes over time showing changes when high and low heat are applied to the polymer process

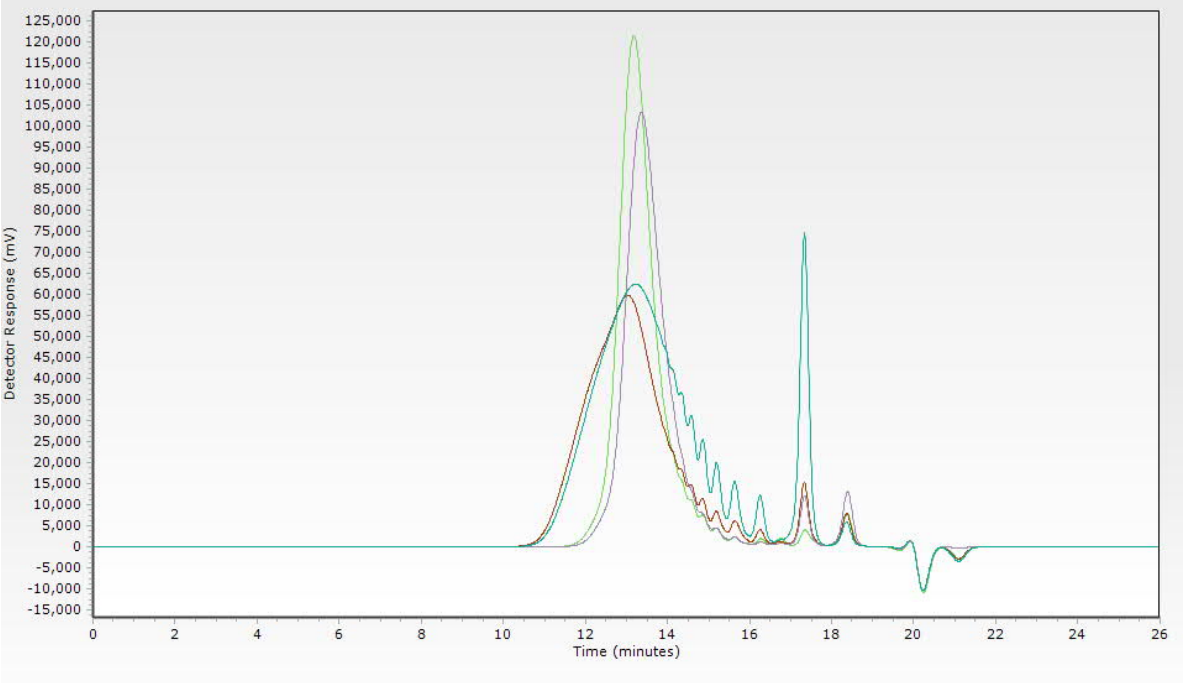


Figure 4-16 - Differences in GPC traces between high heat and low heat. Light green – High feed, low heat, Red – High feed, High heat, Purple – Low feed, Low heat, Blue – Low feed, High heat

In the GPC traces in Figure 4-16, the peak corresponding to the polymer exposed to high heat conditions show very well defined low molecular weight peaks at regular intervals in the build up to the high molecular weight peak, which may be due to poor processing technique, but due to the high heat could also be degradation fragments. As can be seen from the lower heat traces (purple and light green), these oligomer peaks are very minimal in comparison.

4.4 Polymers synthesised with new process conditions

Once a set of process conditions was devised from the previous section, polymers were then scaled up, using the low heat, high feed conditions of the first one. This was to understand how they would react on a larger scale (400g). This was processed for 2 days with the polymer cooled to 70°C which below process temperature but kept above room temperature to prevent solidifying overnight. This was to give a greater insight into how far these polymers can react with time. It appeared to give insight into several issues.

	Mole ratio	% acid reacted (using PAV)	% epoxy reacted	Tg1 (°C)	Tg2(°C)	Mn	Mw	Theoretical Mn	PDI	Colour
1,3 propane diol (LW21)	01:20:19	98.00	100	37.3	39.0	2485	2795	5891	1.12	Clear
Trimethylol propane (LW22)	01:20:19	98.18	100	42.0	42.3	2585	2932	5949	1.13	Clear
Pentaerythritol (LW23)	01:20:19	98.29	100	43.4	44.2	2914	3535	5951	1.21	Slightly yellow

Table 4-9- Characterisation of scale up multifunctional polymers. Formulation: Phthalic Anhydride + PGE

Figure 4-17 - Photos of colour change with process time of LW23

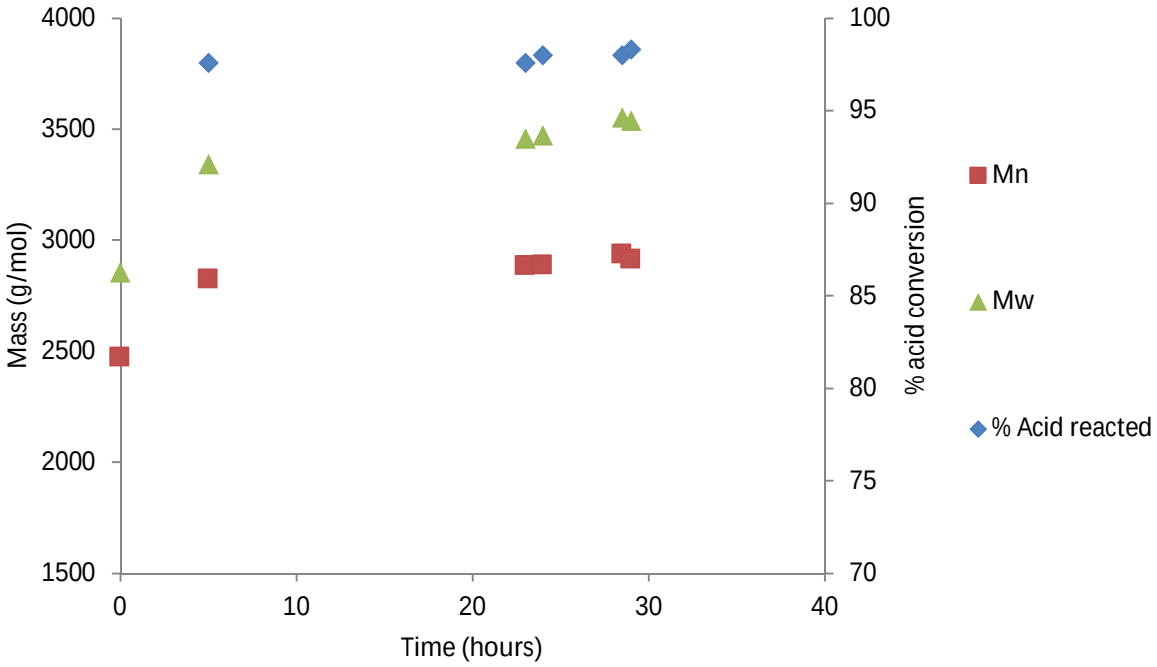


Figure 4-18 - Acid conversion and molecular weight change over time during processing OF LW23 – Penta:PA:PGE in 1:20:19 ratio

The results also showed that leaving the polymer overnight and continuing synthesis for a second day does not improve conversion but does impact the discolouration of the polymer indicating undesired degradation or oxidation pathways[122] (Figure 4-17). It was also observed that the Mn of all 3 polymers produced was significantly below what was targeted (Table 4-9).

4.4.1 Unexpected peak investigation in GC-MS from high molecular weight polymers

GC-MS had been carried out on the polymers made in the section above and showed all expected peaks in mass spectrometry apart from single peak which was unexpected at 298g/mol (Figure 4-19 & Figure 4-20). No free starting materials were found in the GC-MS traces, but a peak with an m/z of 298.0g/mol was found in every polymer at a retention time of 24.5 minutes, which could have possibly been an 8 membered ring, which could be formed from depolymerisation of an OH terminal polymer (Figure 4-21). This problem could be expected to be greater at the end of reaction when anhydride concentrations are low and OH terminal polymer are present at high temperatures.

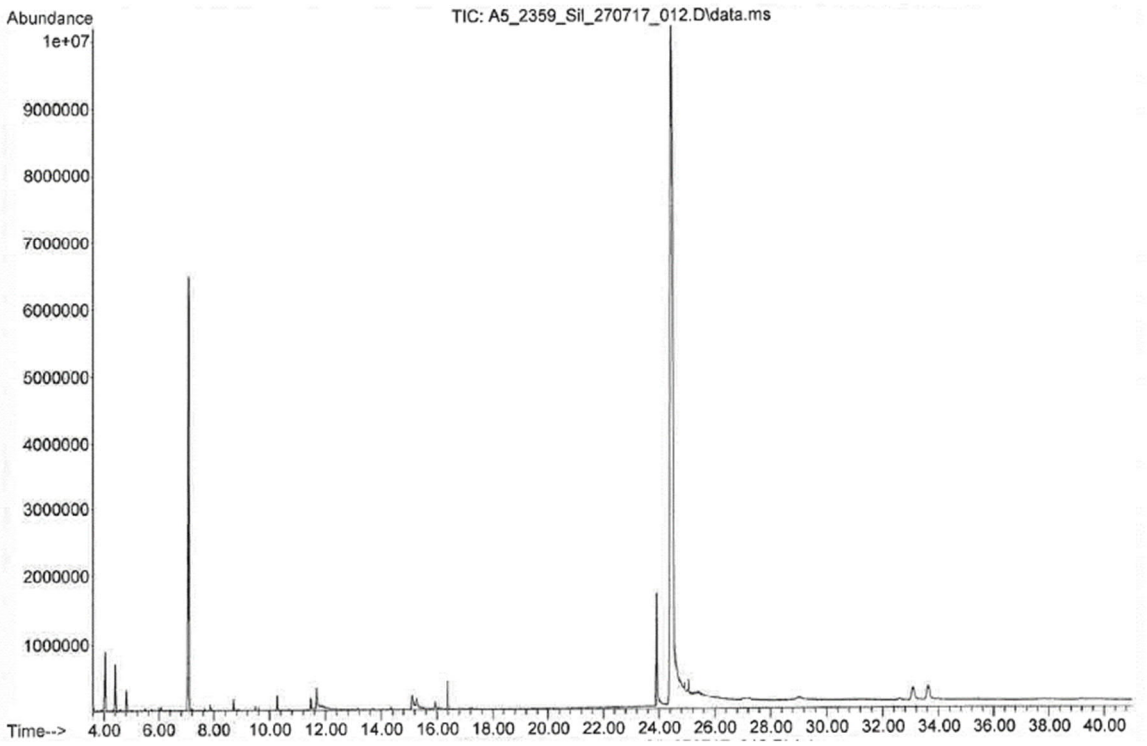


Figure 4-19 - GC showing peak at 24.5 minutes of unidentified material in polymer found in all polymers produced with phthalic anhydride and PGE and different functionality initiators

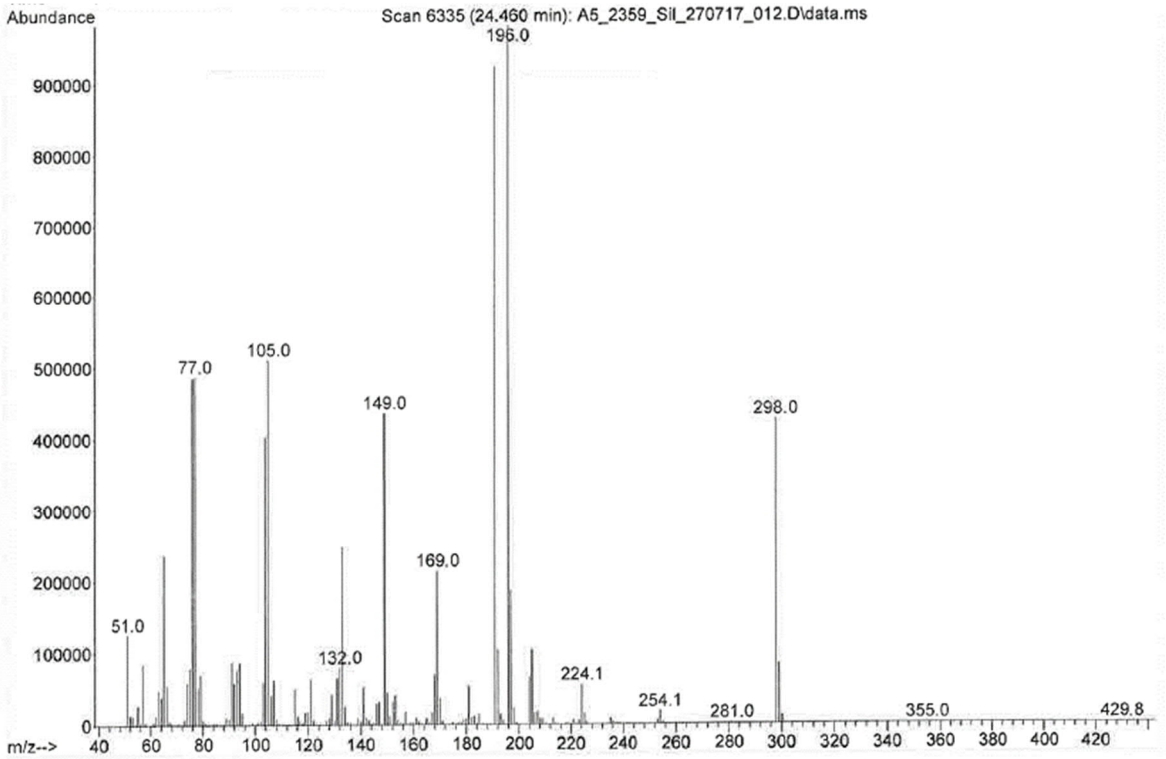


Figure 4-20 - Mass chromatogram of unexpected peak at 24.6minutes, showing a mass of 298g/ m/z peak

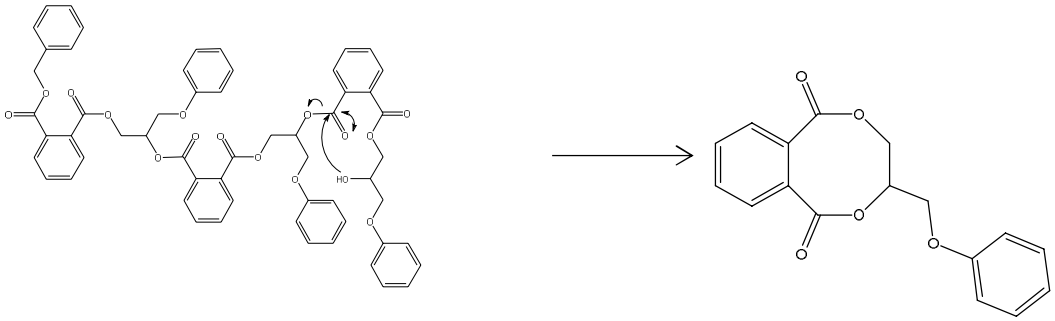


Figure 4-21 – Possible schematic of the formation of an 8 membered ring formed during polymerisation of phthalic anhydride and PGE found with all functionality initiators

However, it was also possible that this structure could have been formed in the GC-MS therefore analysis of another type was required. The GPC data (Figure 4-22) showed that a peak of approximately the same mass can be observed. This suggests that this molecule is formed in the polymerisation. The GPC is calibrated against polystyrene standards and may not give an accurate molecular weight data. This may also be a possible explanation why the Mn and Mw are low.

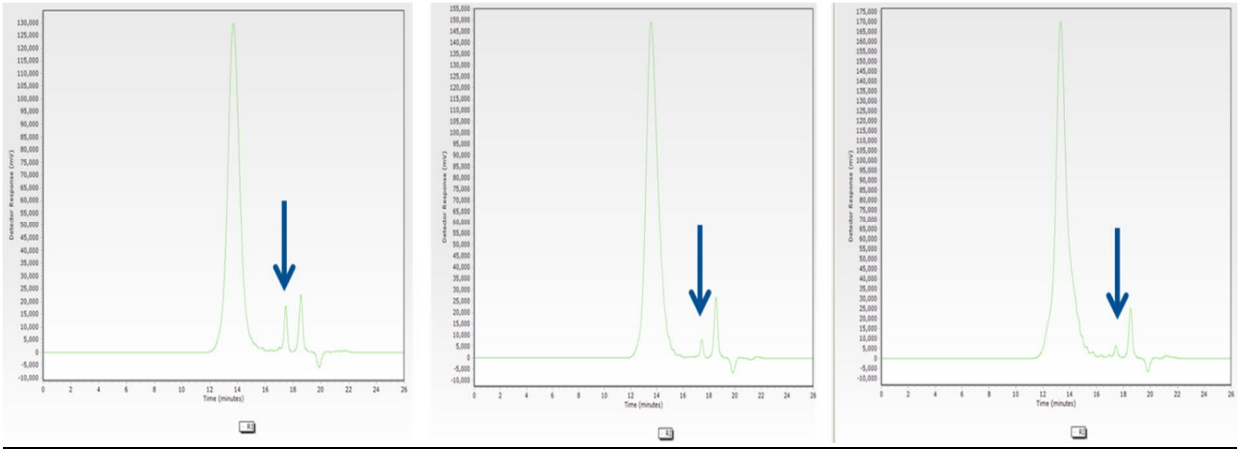


Figure 4-22 - GPC chromatograph showing peak of 298g/mol in each polymer at retention time 17.5 minutes. From left to right, polymer made from PDO, TMP and pentaerythritol

	Mn (g/mol)	Mw (g/mol)
Chromatogram 1 (2 functional initiator)	288	291
Chromatogram 2 (3 functional initiator)	286	287
Chromatogram 3 (4 functional initiator)	293	298

Table 4-10 - Molecular weights of peak highlighted in GPC chromatograms above showing an unidentified peak of ~298g/mol formed during polymer synthesis in all three polymers from different functionality initiating species

Samples were further analysed in GPC-MS to give more accurate molecular weights by coupling 2 techniques together.

4.4.2 Analysis of polymers by GPC-MS

The GPC-MS showed that the cyclic molecule above (Figure 4-21) does not exist, as the smaller molecules could be analysed accurately. The molecular weight was in fact 316g/mol rather than the 298g/mol as originally thought. This indicates that the cyclic molecule was formed in the GC-MS possibly due to the electron impact ionisation via the loss of water (Mwt = 18g/mol). The molecule which was believed to be seen in the GPC-MS could possibly have the structure as shown below;

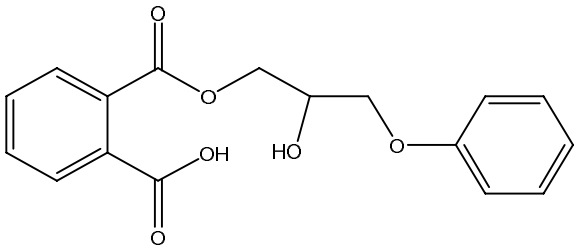


Figure 4-23 - Possible structure of molecule formed in the polymer synthesis of phthalic anhydride and phenyl glycidyl ether, which has a theoretical MW of 316g/mol – the peak found in the GC-MS

This molecule could have been formed from phthalic anhydride and phenyl glycidyl ether, which could explain the lower molecular weight, if parts of the synthesis were producing small oligomers such as the one above (Figure 4-23) rather than reacting with the end of the chain.

4.4.3 Triple detection GPC results

As the molecular weight of the overall polymer couldn't be confirmed by GPC-MS due to restrictions on the MS, the samples were analysed by triple detection GPC, which can provide absolute molecular weights. This was a more reliable value to have due to the structures of these polymers varying significantly from polystyrene.

As standard GPC runs were calibrated against polystyrene standards, the values were an indication, rather than an accurate value, of the molecular weights of the polymers. Therefore, a GPC fitted with triple detectors including refractive index, Viscosity and light scattering detectors, was used to carry out analysis on the polymers to confirm the polymers were not reaching the expected Mn,

The triple detection GPC results were taken direct from the light scattering signal. The results of these tests are shown below (Table 4-11):

	GPC results		Triple detection GPC results		Mn difference between PS standard GPC and Triple detection GPC (%)	Mw difference between PS standard GPC and Triple detection GPC (%)	% Conversion using triple detection GPC (%)
	Mn (g/mol)	Mw (g/mol)	Mn (g/mol)	Mw (g/mol)			
LW20 B1 (BA:PA: PGE – 1:20:19)	5107	6405	5600	7900	8.8	18.9	93.3
LW21 B1 (PDO:PA: PGE – 1:20:19)	3340	3705	3700	4000	9.7	7.3	61.6
LW21 B2 (PDO:PA: PGE – 1:20:19)	2485	2795	3600	4000	30.9	30.1	60.0
LW22 B1 (TMP:PA: PGE – 1:20:19)	3669	4421	4300	4900	14.6	9.7	71.6
LW22 B2 (TMP:PA: PGE – 1:20:19)	2585	2932	3500	4100	26.1	28.4	58.3
LW23 B1 (Penta: PA: PGE – 1:20:19)	2914	3535	4300	5100	32.2	30.6	71.6
LW22 B3 (TMP:PA: PGE – 95% cat in epoxy feed)	2782	3323	4100	4800	32.1	30.7	68.3

Table 4-11 - Results and differences between GPC against polystyrene standards and GPC measuring absolute molecular weight. % showing difference between the values rather than % deviation from expected.

As can be shown in Table 4-11 above, the results from GPC against polystyrene standards compared to the results from triple detection GPC, indicate that the results gave a considerable difference ranging from ~500g/mol – 1300g/mol. However, the molecular weight increase didn't reach the expected molecular weights. Therefore, it could be concluded that the polymers are not building molecular weight as expected and further investigation is required. It can also be concluded that even though a difference is shown between the two different GPC methods, the triple detection GPC instrument is not readily accessible in our lab (used at a different location) and there is not a large enough difference to justify sending samples to it each time for analysis, so the standard polystyrene method on site will suffice to give adequate indication. If

raw data can be obtained, a Mark-Houwink plot could be drawn to give further understanding between the polymer structure and the molecular weight. By plotting molecular weight vs intrinsic viscosity graph, a difference in density between polymers could be observed, indicating different levels of branching.

4.5 Formulating discrepancies

During the investigation into the polymers in section 4.4.3 it was noticed that the formulations adapter for different initiator functionalities resulted in hydroxyl functional polymers rather than acid functional polymers. The mole ratio used for each polymer above was 1:20:19, 1 alcohol: 20 anhydride: 19 epoxy, which would in fact be correct when formulating a monofunctional polymer. However, as the aim was to produce the same length chains in each polymer and each polymer resulting having acid end group functionality, the ratio required less epoxy when the functionality increased. This was noticed through working the polymer reaction out by hand as shown in Table 4-12.

Trifunctional system	MW (g/mol)	Moles	Effective moles	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Trimethylol propane	134.17	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Phthalic anhydride	148.10	20	20	17	17	14	14	11	11	8	8	5	5	2	2	0	0
Phenyl glycidyl ether	150.17	19	19	19	16	16	13	13	10	10	7	7	4	4	1	1	0
COOH groups to react			0	3	0	3	0	3	0	3	0	3	0	3	0	2	1
OH groups to react			3	0	3	0	3	0	3	0	3	0	3	0	3	1	2

Table 4-12 - Step by Step reaction scheme of polymer initiated by TMP

Trifunctional system	MW (g/mol)	Moles	Effective Moles	1	2	3	4	5	6	7	8	9	10	11	12	13
Trimethylol propane	134.17	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Phthalic anhydride	148.10	20	20	17	17	14	14	11	11	8	8	5	5	2	2	0
Phenyl glycidyl ether	150.17	17	17	17	14	14	11	11	8	8	5	5	2	2	0	0
COOH groups to react			0	3	0	3	0	3	0	3	0	3	0	3	1	3
OH groups to react			3	0	3	0	3	0	3	0	3	0	3	0	2	0

Table 4-13 - Corrected step by step reaction of trifunctional polymer

As can be seen from the tables above (Table 4-12 & Table 4-13), the polymer formulated in the case of the trifunctional material, was hydroxyl functional. This would alter the molecular weight, but if polymerised correctly, this should have produced a higher Mn rather than a lower Mn as more moles of epoxy were added rather than less. The polymer with 19 moles of epoxy added would have an expected Mn of 6041g/mol, the one with 17 moles would have an expected Mn of 5741g/mol. The table above shows the formulation worked out step by step, the first step shows 3 hydroxyl groups (from TMP) have reacted with 3 anhydride group to produce 3 acid groups (See section 4.8 Hydroxyl – anhydride reaction investigation). The following step shows an acid-epoxy reaction, in which the 3 acid groups formed from the previous step, react with 3 epoxy groups producing 3 less epoxy groups and forming 3 alcohol groups, which are the 3 secondary hydroxyl groups formed when opening the epoxy. This continues throughout the process until there is no epoxy left to react. This model gives the chain end functional groups expected, in this case, 3 acid ends shown in the final box highlighted in blue.

This did not solve the issue with molecular weight but did shed light on new of formulating techniques, by looking deeper into what each step entailed and concluding what functional groups theoretically should be present.

These polymers were remade with the correct mole ratios to produce acid functional polymers but still did not reach the expected Mn as seen in Table 4-14.

	Mole ratio	% acid reacted	% epoxy reacted	Predicted Mn (g/mol)	Predicted Mw (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI
1,3 propane diol (LW24)	01:20:18	96.8	100	5649	5649	3257	3494	1.07
Trimethylol propane (LW25)	01:20:17	100.07	100	5741	5741	3417	4249	1.24

Table 4-14 - Analysis of polymers with corrected mole ratios values. Formulation: Initatitor + Phthalic Anhydride + PGE + Cat. Synthesised at 140**°C in toluene.**

As can be seen in Table 4-14 the values measured still do not reach the expected values, once formulated to the correct mole ratios, concluding the formulation issue was not

the cause of the molecular weight problems. As a result, further investigation is required into how the measured values can reach the expected values as this project requires very controlled polymers, with a high level of confidence and accuracy.

4.6 New processing approaches to improve molecular weight control

4.6.1 Process optimisation

The processing of this polymer involves the catalyst being added with reactants at the start of the process. The epoxy is gradually fed in due to the large exotherm when added quickly. As this was the case and it was yellowing the polymer, it was believed the high temperatures created by the exotherms could be causing the issue to the molecular weight and degrading the polymer when it reached a higher temperature due to exotherm. Temperatures as high as 200°C have been observed in some instances whereas the process temperature was 140°C. An idea to solve this problem was to add 95% of the catalyst to the epoxy feed before adding and only 5% to the mixture of initiator and anhydride in the flask, to help catalyse the alcohol anhydride reaction. Theoretically the exotherms should be reduced as the amount of catalyst inside the flask is reduced.

Formulation	Mole ratio	% acid reacted (using PAV)	% epoxy reacted	Predicted Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI	Colour
Trimethylol propane+ Phthalic Anhydride + PGE + Catalyst	01:20:17	97.35	100	5741	2782	3323	1.19	Slightly yellow

Table 4-15 - Results from new processing techniques trifunctional polymer synthesis (1:20:17 ratio). Synthesised at 140**°C in toluene.**

Figure 4-24 - Photograph of the yellowing observed from the polymer with new processing conditions

As can be seen from the results above in Table 4-15, the molecular weight did not reach the expected molecular weight yet again. A smaller exotherm was still observed, and this was believed to have caused the yellowing of the polymer (Figure 4-24). It was also interesting to note, that with this new processing technique, the polymer still produced an oligomer peak in the GPC (Figure 4-25), confirming an exotherm is not the issue, but should be avoided if possible to help with the yellowing of the polymer.

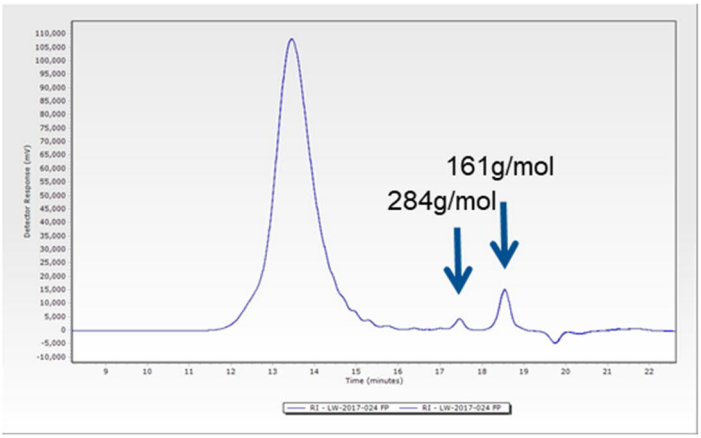


Figure 4-25 - GPC chromatogram of polymer with new processing conditions, showing a small oligomer peak is still produced

As the oligomer peak was still observed and the molecular weights did not reach the expected values, the new processing conditions did not solve the issue. As this process did not improve the issues, this will not be used as the more desired process conditions, and the original conditions in which the catalyst is added to the flask will be continued.

4.6.2 Further investigation into yellowing

In the model reactions stage of this project, catalysts were screened to understand how they performed when used in this chemistry. The catalyst decided upon was TBAB as it prevented all undesired reactions, as did ETTPB and TEA. It was later discovered that TBAB has a very low degradation temperature (from 140˚C), which was a possible cause of the yellowing due to exotherms occurring, raising the temperatures well above 140°C. These values were confirmed through TGA analysis.

The initial TGA analysis of the polymers were carried out at process temperature to understand to what extent the catalyst was degrading at that temperature. These printouts are shown below in Figure 4-26 & Figure 4-27.

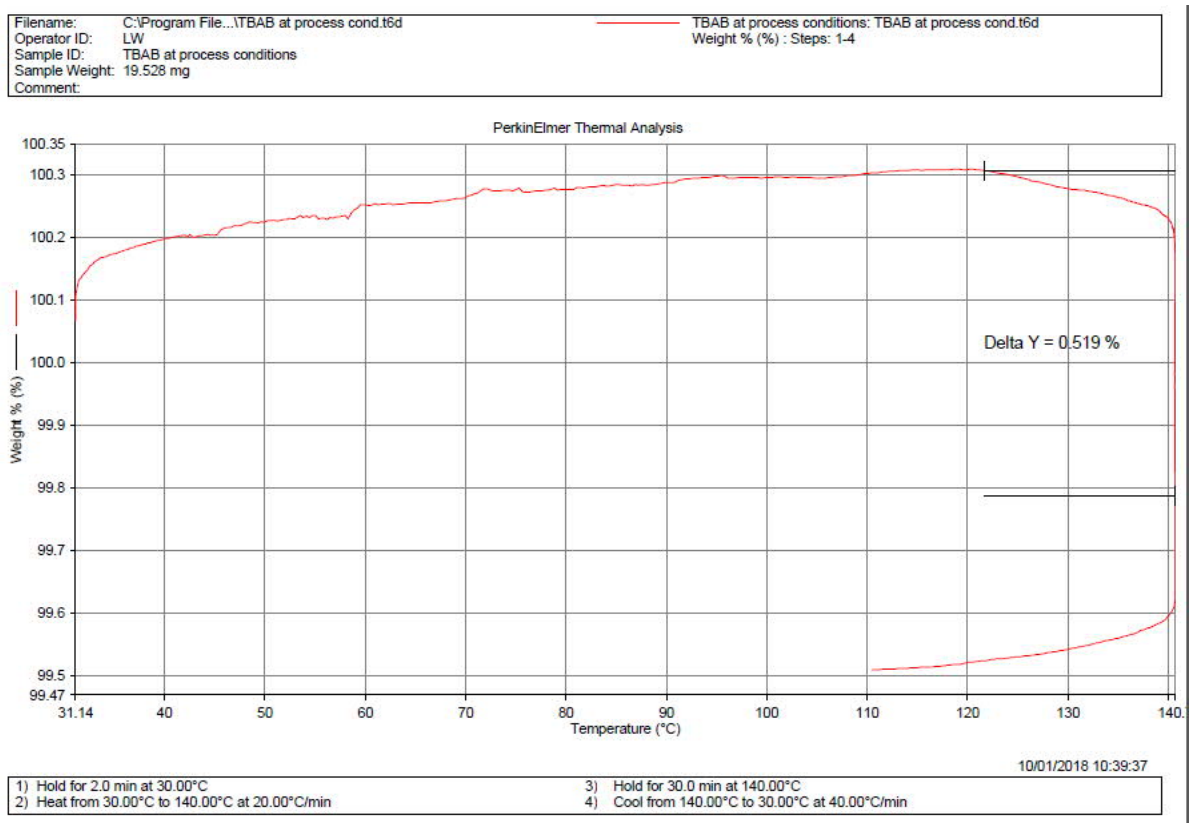


Figure 4-26 - TGA print out from TBAB at process conditions

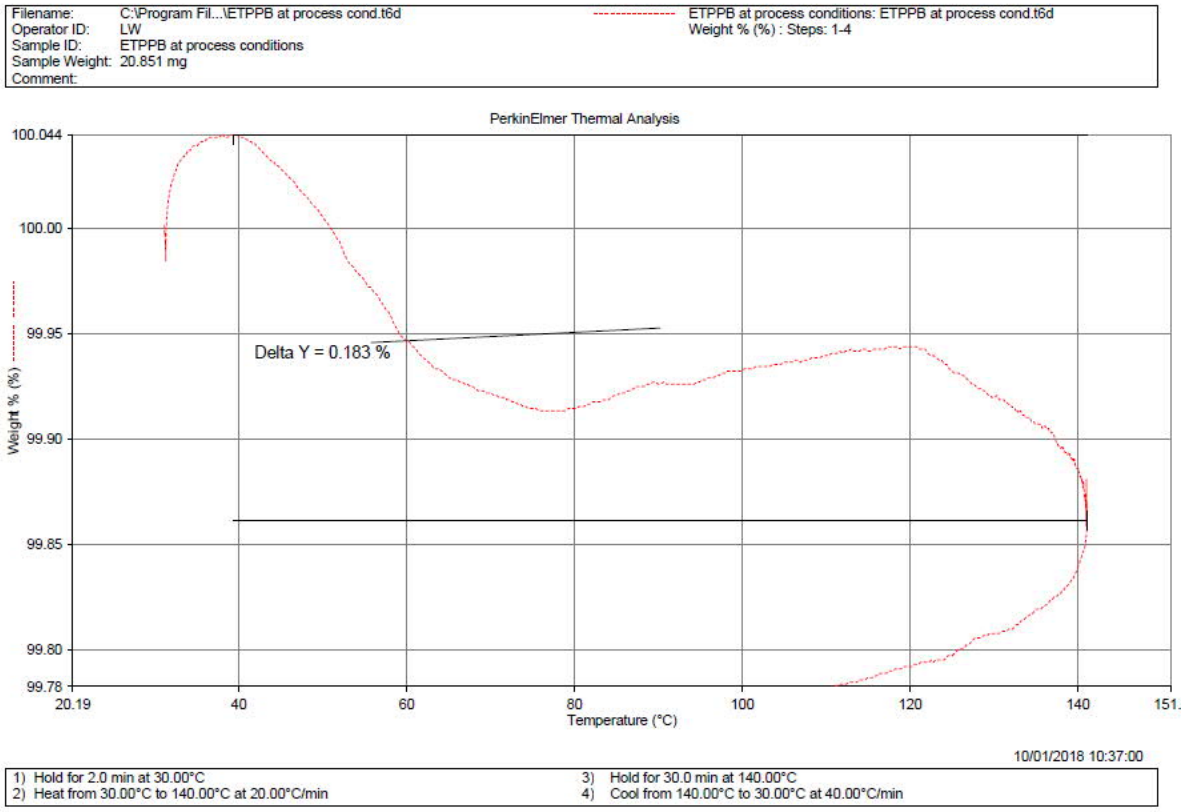


Figure 4-27 - TGA print out of ETTPB at process conditions

It can be seen from Figure 4-26 that TBAB starts to degrade ~122°C, losing 0.5% weight when reaching 140°C. ETPPB however shows it does not degrade to the same extent at process temperature, showing a loss of only 0.1% when 140°C is reached. To give further understanding on catalyst stability at high heat, TGA was ran on all catalysts, up to 250°C, giving an indication into the degradation temperature, and how much catalyst would be remaining in the reaction, if an exotherm were to occur during synthesis.

Catalyst	Mass lost by 250°C (%)	Degradation temperature (°C)
ZnS	0.13	250
TBAB	94.64	135
DMAP	100.00	-
ETPPB	0.82	232
TEA	-*	-*
2MI	99.89	130

Table 4-16 - Table showing Degradation temperatures of catalysts tested

*Not carried out due to the nature of the chemical and H&S issues surrounding this.

An example of the degradation TGA graphs is shown below (Figure 4-28). This shows 100% of the DMAP added, was gone by 248°C. Initially this was believed to be degradation, however on further investigation of DMAP, it has a boiling point of 162°C, so it is believed the DMAP weight loss is due to evaporation.

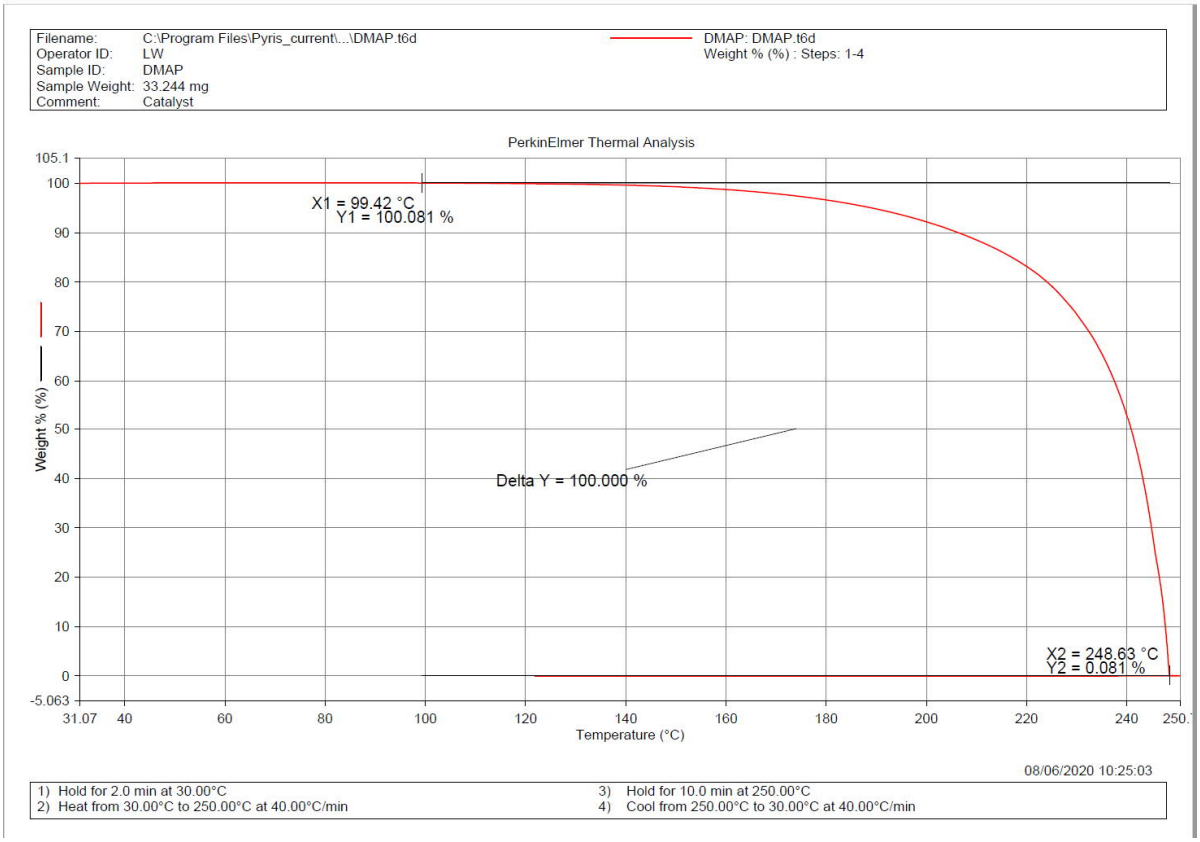


Figure 4-28 - TGA graph of DMAP evaporating by 248°C

4.7 Remelting polymers for further processing

As the new polymers produced (Table 4-14 – LW24 & LW25) were still below the expected Mn and Mw and given the living nature of this polymerisation scheme it was thought that the polymers a further feed of monomers could be added to continue the processing. So that polymers were remelted into a reactor and further monomers were added. As it was believed that unreacted epoxies were still present but all anhydrides were either consumed or had sublimed during synthesis, an amount of anhydride was added. The amount added was calculated through measuring the acid value through wet titration and back calculating the theoretical amount of acid functional monomer that should be added to achieve the desired result. Effectively, the amount was calculated by the difference between expected and measured "total" acid value (Section 2.3.1).

Initially the polymer was remelted dry, with no solvent added, once melted, the anhydride was added and allowed to process in at process temperature. This reaction showed sublimation on the top of the flask believed to be from the anhydride, and this can be observed in the results as the acid value measurement, does not change and therefore it shows no acid has reacted in. See Table 4-17.

In g/mol	Original	Remelt	Difference
Total acid	7.49×10^{-4}	8.56×10^{-4}	1.07×10^{-4}
Partial acid	6.24×10^{-4}	6.24×10^{-4}	0
Anhydride added		1.07×10^{-4}	
% conversion based on TAV	96.49	94.76	
Mn(g/mol)	3417	3365	
Mw(g/mol)	4249	4213	
PDI	1.243	1.252	

Table 4-17 - Extra addition of anhydride to LW24 polymer after cooling and remelting

As sublimation took place, and as shown from Table 4-17, the values do differ, but not significantly and not as expected. The TAV increased as expected, however this did not increase the Mn or Mw as it should have if the anhydride had reacted onto the chain, confirming this reaction was not successful. This experiment was repeated however the second time, toluene was added to reduce sublimation and processed the same way. As can be shown below in Table 4-18, the values do differ, but not as much as expected. They appeared to increase by half what was added. This indicated either the anhydride was not able to react with the hydroxyl groups present, possibly due to steric reasons due to the nature of the secondary hydroxyls, or because not as many are present as the OH value indicated. This would lower the concentration of the reactive groups and lead to slower kinetics. Another possibility could be to also add further epoxy, to see how the reaction occurs, and to give a possible insight into whether block copolymers could be produced using this chemistry.

In g/mol	Original	Remelt	Difference
Total acid	7.49×10^{-4}	7.95×10^{-4}	4.68×10^{-5}
Partial acid	6.24×10^{-4}	6.93×10^{-4}	6.95×10^{-5}
Anhydride added		1.07×10^{-4}	
% conversion based on TAV	96.49	95.73	
Mn(g/mol)	3417	3277	
Mw(g/mol)	4249	4093	
PDI	1.243	1.249	

Table 4-18 - Extra addition of anhydride to LW24 after cooling and remelting (in solvent). Synthesised at 140°C in toluene.

4.8 Hydroxyl – anhydride reaction investigation

As remelting the polymer did not successfully reach the correct expected acid values, an investigation into the anhydride – hydroxyl initiation reaction was carried out. This is the initial reaction into the polymer synthesis in which a primary hydroxyl opens the

anhydride, and it is crucial this occurs correctly and produces an acid functional molecule in near quantitative yield. A blend of TMP with 3 equivalents of phthalic anhydride was processed under standard reaction conditions (140°C, N_2). The resulting sample (LW30) was then analysed through GC-MS. As there was a possibility OH groups could be present, the sample was required to be silanised before analysis[123]. The mass spectra of the main GC peak at 28.4min is as below in Figure 4-29.

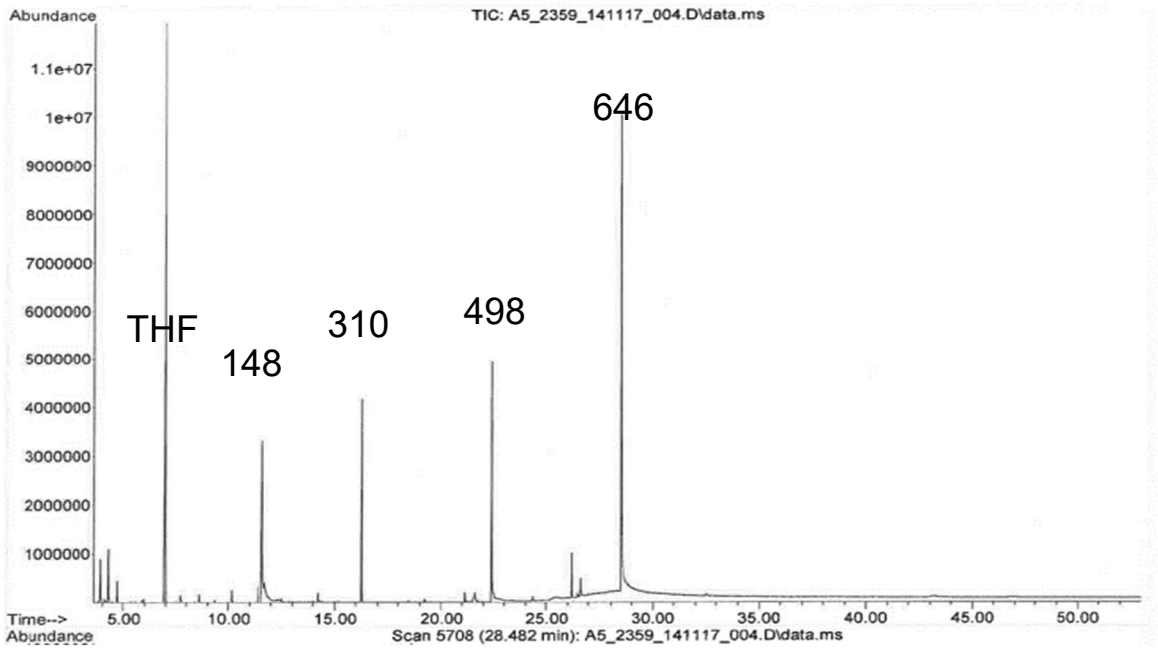


Figure 4-29 - MS spectra for alcohol anhydride investigation of LW30 – TMP:PA in 1:3 ratio

	No Si (g/mol)	With 3 x Si (g/mol)
TMP + 1 PA	282	498
TMP + 2 PA	430	646
TMP + 3 PA	578	794

Table 4-19 - Theoretical molecular weights for an ideal reaction of LW30 – TMP:PA in 1:3 ratio

Table 4-19 shows the expected values if the reaction carried out was as expected. Any values shown on the spectra which are not on the right-hand side of the table indicate

the ideal reaction has not occurred. The spectra also shows no peak for a m/z of 166 (phthalic anhydride + water) or 238 (silanised phthalic anhydride + water), which indicates water/ moisture was not a cause for concern in this experiment.

M/Z	Structure
148	PA
310	Silanised PA
498	TMP – PA
646	PA - TMP - PA

Table 4-20 - Peak identification of MS spectra

The table above shows the predicted molecules for each value given. There is free phthalic anhydride present and therefore it has not fully reacted with all 3 possible sites on the trifunctional TMP molecule. The 794 peak is not observed; however, it was inconclusive as to whether this was due to the 3 functional not being synthesised, or whether the molecular weight limit of the instrument had been reached (the specification of the instrument allows up to 800 m/z[124]). As this oligomer was approaching the theoretical limit, the samples were analysed on GPC as confirmation and to understand whether the reaction adduct of 1 TMP and 3 PA was either not detected due to instrument limitations or was simply not synthesised. However, the GPC did not show a great distinction of peaks at low levels, so this work is inconclusive and would possibly require the use of GPC-MS, as the mass spectrometer attached this equipment was able to reach higher MW (up to m/z= 800).

4.9 Step by step processing

Another thought of processing was to add the monomers sequentially in the reaction. Therefore, the formulation below was carried out adding 1 mol of alcohol initiator, with 3 moles of anhydride and left to react at 140°C for 1 hour. A sample was then taken and 3 mol epoxy added. Once exotherm had taken place, a sample was taken and the final 3 mol of anhydride was added. This can be seen in Figure 4-30 below.

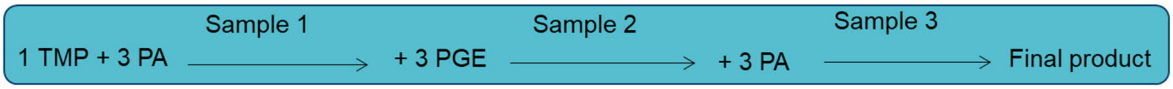


Figure 4-30 - Schematic of step by step reaction processing

Monomer	MWt (g/mol)	Moles	M/R	Formula weight (g/mol)	Mass (g)
Trimethylol propane	134.18	0.033938	1	134.18	4.55
Phthalic Anhydride	148.1	0.203626	6	888.6	30.16
1,2-Epoxy-3-phenoxypropane	150.17	0.112707	3	450.51	15.29
Total		0.35027		1473.29	50.00

Table 4-21 – Formulation of LW17 used in step by step processing. Synthesised at 140**ºC in toluene.**

	Expected Mn (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI
Sample 1	578	715	738	1.03
Sample 2	1028	1234	1327	1.07
Sample 3	1473	1278	1391	1.08
Final product	1473	1454	1554	1.09

Table 4-22 - Results of molecular weights from step by step processing using LW17 formulation (TMP:PA:PGE in 1:6:3 ratio)

The results above (Table 4-22) showed that the expected Mn and predicted Mn were very similar and therefore indicated that this type of synthesis was very effective. It indicated that the reaction does occur as predicted when using lower molecular weight polymers, and that molecular weight can be controlled this way.

For the higher molecular weight polymers that are trying to be produced however, this would be a very long reaction synthesis and would not be sustainable in industry. For this reason, this type of synthesis could not be used, but is very useful to confirm the reaction occurs as expected.

4.10 Change in difunctional initiator to aromatic difunctional alcohol

As the aromatic monofunctional alcohol initiator was able to reach the expected Mn, it was decided to investigate a difunctional initiator of similar structure. Even though it is believed that benzyl alcohol reached the expected Mn due to only growing from a single chain, instead of numerous sites, it may also be due to the presence of a bulkier core such as a benzyl ring. Its presence will increase steric hindrance and the rigidity in the growing polymer chain at the early stages of the propagation and reduce the chances of the polymer cyclising thus losing functionality.

It was hypothesised that conformations in which the polymer is able react on other functional group on another end of the same polymer chain will result in increased creation of cyclic species. These cyclic species can reduce Mn, by producing shorter chains but also loose functionality on the polymer chains.

The polymers produced in this investigation are small, and therefore coiling is unlikely to occur, however, reducing the chance of cyclics being formed, could be very advantageous in larger polymers.

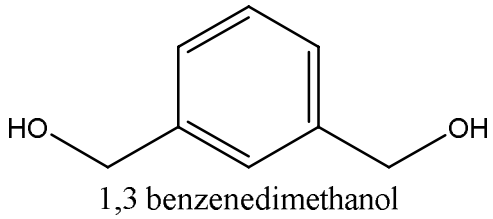


Figure 4-31 - Structure of 1,3 benzenedimethanol

1,3 benzenedimethanol (Figure 4-31) is a molecule with a very similar structure to benzyl alcohol, which could help reduce cyclic species being formed. As this project is understanding how changing polymer structure can affect the network design and coatings properties, it would also benefit increasing understanding into how cyclics can change the properties.

Monomer	Mwt	moles	M/R	Formula weight (g/mol)	Mass (g)
1,3 benzenedimethanol	138.166	0.025848	1	138.166	3.57
Phthalic Anhydride	148.1	0.516954	20	2962	76.56
1,2-Epoxy-3-phenoxypropane	150.17	0.465258	18	2703.06	69.87
Total		1.00806		5803.226	150.00

Table 4-23 - Formulation of LW29 polymer synthesised using aromatic difunctional alcohol. Synthesised at 140**°C in toluene.**

The LW29 polymer produced followed the formulation in Table 4-23 above. It was made with an excess of phthalic anhydride into an acid functional polymer and theoretically should produce an Mn of 5803g/mol if synthesised correctly.

	Predicted Mn (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI	% conversion based on acid value
LW29 (1,3BDM/PA/PGE/ETTPB 0.1mol%)	5803	4174	4674	1.12	98.6%
LW24 (1,3PDO/PA/.PGE/ETTPB 0.1mol%)	5649	3257	3494	1.07	96.8%

Table 4-24 - Table comparing polymer properties of polymer containing difunctional aromatic alcohol initiator against PDO initiated polymer

As can be seen in Table 4-24, LW29 did produce a higher molecular weight and an increased acid conversion. It indicated that the reaction was more controlled than when using 1,3 PDO.

This monomer could also help increasing the Tg, although the contribution will be low due to the low mass ratio of this in the polymer.

After further discussions on this molecule being used as a monomer, even though a more efficient reaction was observed, as this project was to understand relationships, it was agreed a linear initiator would give more of a difference in coating results over

an aromatic monomer. However, as the preliminary work has been carried out, this could be used in the case of failures in the 1,3 PDO, such as poor crosslinking, should that occur. Also, with the preliminary work carried out, this could also be used in further work, if PDO does not occur any problems.

4.11 Varying initiator concentrations

A possible idea to understand how the chain could growth effectively was to reduce the initiator concentration. This should result in a higher molecular weight, as the initiator concentration has reduced but the number of monomers would be the same. If this produced the correct Mn, it would confirm the initiation step may be the possible cause of the low molecular weight observed.

As shown in Table 4-25 below, the expected molecular weights were not reached, but had very low PDIs. This indicated the chain growth step of the reaction was possibly an issue and did not synthesise as expected.

Sample	Target Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI
LW24 (standard) PDO/PA/PGE/ETPPB (1/19/18/0.1mol)	5649	3257	3494	1.07
PDO/PA/PGE/ETPPB (0.5/19/18/0.1mol)	11298	6909	7294	1.05
PDO/PA/PGE/ETPPB (0.25/19/18/0.1mol)	22596	6776	7422	1.09
PDO/PA/PGE/ETPPB (0.125/19/18/0.1mol)	45192	7666	8519	1.11
PA/PGE/ETPPB (19/18/0.1mol)	5573	7717	8528	1.11

Table 4-25 - Results from varying the initiator concentration. Synthesised at 140°C in toluene.

Another test which was carried out, as seen in the bottom row of Table 4-25, which was to completely remove the initiator, and to see if the reaction would still process. As can be seen, it processed to considerably more than the molecular weight of LW24 and of the predicted molecular weight, with a higher PDI, but did process. This indicated that there was an issue with the purity of the materials, as if all anhydride was pure with no acid present, or the epoxy was pure with no diol present, there shouldn't have been anything to initiate these reactions. This indicated water may be present to initiate these reactions.

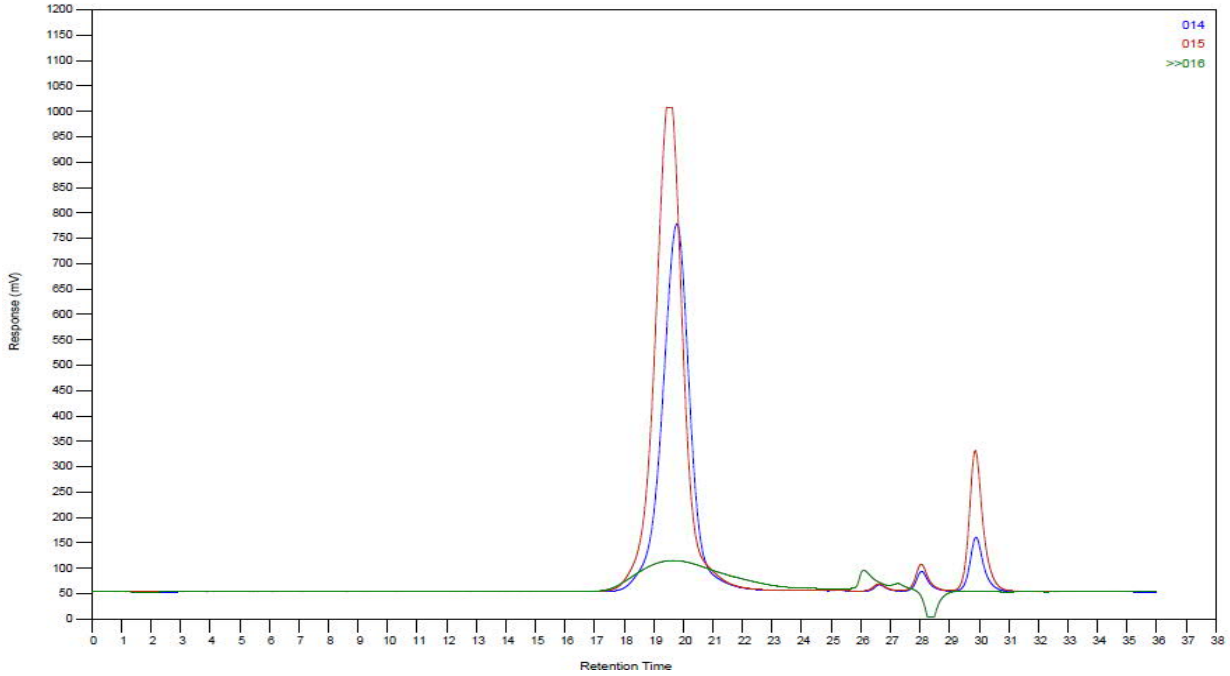


Figure 4-32 - GPC showing comparison of varying initiator concentration. Green = No initiator, Red= 0.125 M/R initiator, Blue = 0.25 M/R initiator

The GPC in Figure 4-32 shows the polymer made without catalyst (green line) widely spread in comparison, showing very little control over the polymerisation. The other two peaks show a slight shift as expected, but the PDI was still very low in comparison to the polymer made without initiator. Since understanding these results, it was clear the purity of the raw materials was required to be reinvestigated.

4.12 Purity issues

Raw materials were tested for purity at the beginning of this project but appeared very pure on testing (see section 2.1). As molecular weight wasn't reached, the moisture content was questioned and tested in the polymers.

If moisture was present, phthalic anhydride could open into phthalic acid, which could act as an initiator alongside the primary hydroxyls used to that effect. If this occurred, the amount of raw would be reduced and the chains would be considerably shorter than expected by having higher concentrations of initiators and lowering the amount of reactive monomer to propagate – i.e., reducing the Mn of the high molecular weight segment of the GPC spectra.

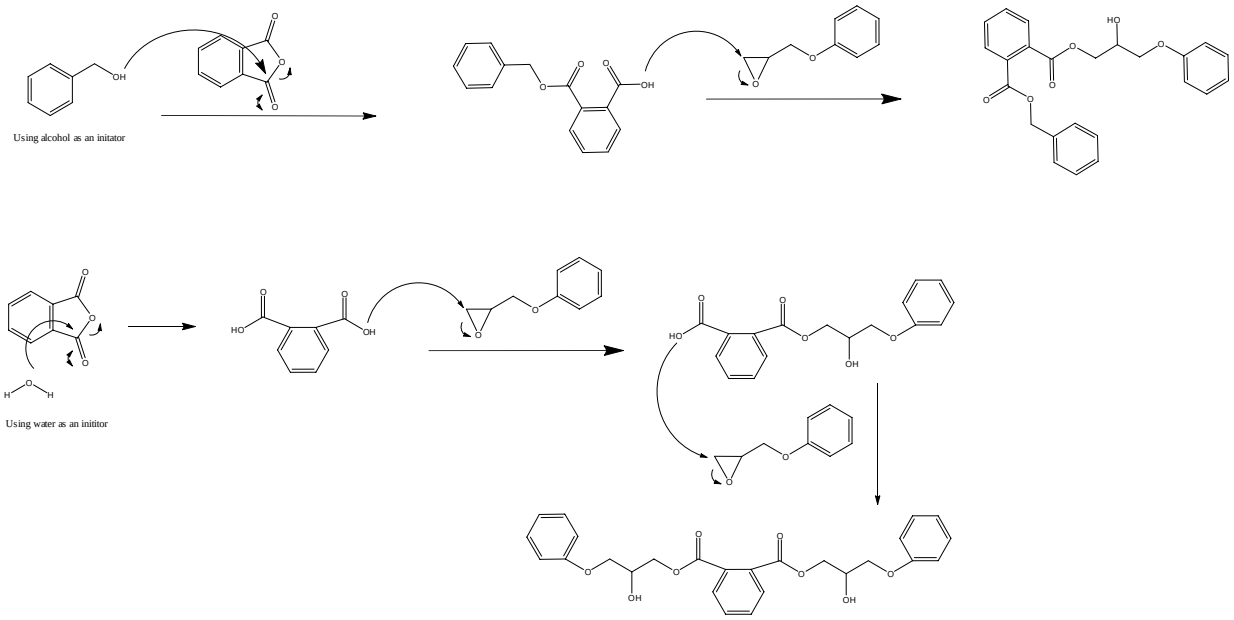


Figure 4-33 - Schematic showing possible reaction if moisture issues occurred. First reaction showing ideal reaction using alcohol as an initiator, second reaction showing if water was present and how that could be used as an initiator resulting in an undesired product and lower Mn

4.12.1 Investigation via Karl-Fischer titration into a possible presence of moisture

If moisture was present in the polymer sample, this could either promote the breaking of ester chains, or could react with anhydrides present, producing acids and therefore reducing the higher reactivity of the anhydride versus diacid (strain on the ring of anhydride) resulting in a reduced reactivity of reactants.

The four new polymers produced with the correct formulations were tested for moisture content as they now had the correct molar ratios but did not reach the expected molecular weights. The four polymers were tested by Karl-Fischer, titration which measures the moisture content through titration[125].

Sample	Water content (% w/w)	Relative Standard Deviation (%)
LW25 (TMP/PA/PGE/ETTPB – 1:20:17:0.1mol%)	0.10	20.12
LW25 RM	0.17	2.67
LW25 RM2	0.16	6.47
LW30 (TMP/PA – 1:3)	0.13	3.46

Table 4-26 - Karl Fischer results showing moisture content of LW25 (TMP:PA:PGE – 1:20:17), remelts of LW25 (extra anhydride added in remelt) and LW30 (1:3 TMP:PA).

As shown in Table 4-26, the results show a very small amount of water present, an amount which should not to be sufficient to affect the reaction. This was due to the error observed, the error is believed to be large due to the nature of the samples and due to there being very little water present. This was to be expected, as any moisture present would be very quickly reacted with anhydride, forming a diacid.

4.12.2 Purification of Phthalic Anhydride

Phthalic anhydride is very prone to reacting with water, due to the strain in the anhydride ring. This makes using anhydride a difficult task when attempting to make a pure polymer.

The anhydride used is phthalic anhydride, and as there was a possibility it would accept moisture, resulting in reacting as phthalic acid, so a purification of the anhydride was carried out. This can be done in several ways, and each was tried and analysed.

Phthalic Anhydride with a standard purity was purchased from Sigma (Expected purity level <99%) and used in each polymer up to this point. An 'extra pure' version of the anhydride was purchased from Fisher (expected purity level 99+%) and tested. Phthalic Anhydride was also purified through sublimation, and through recrystallisation using acetic acid, and using chloroform.

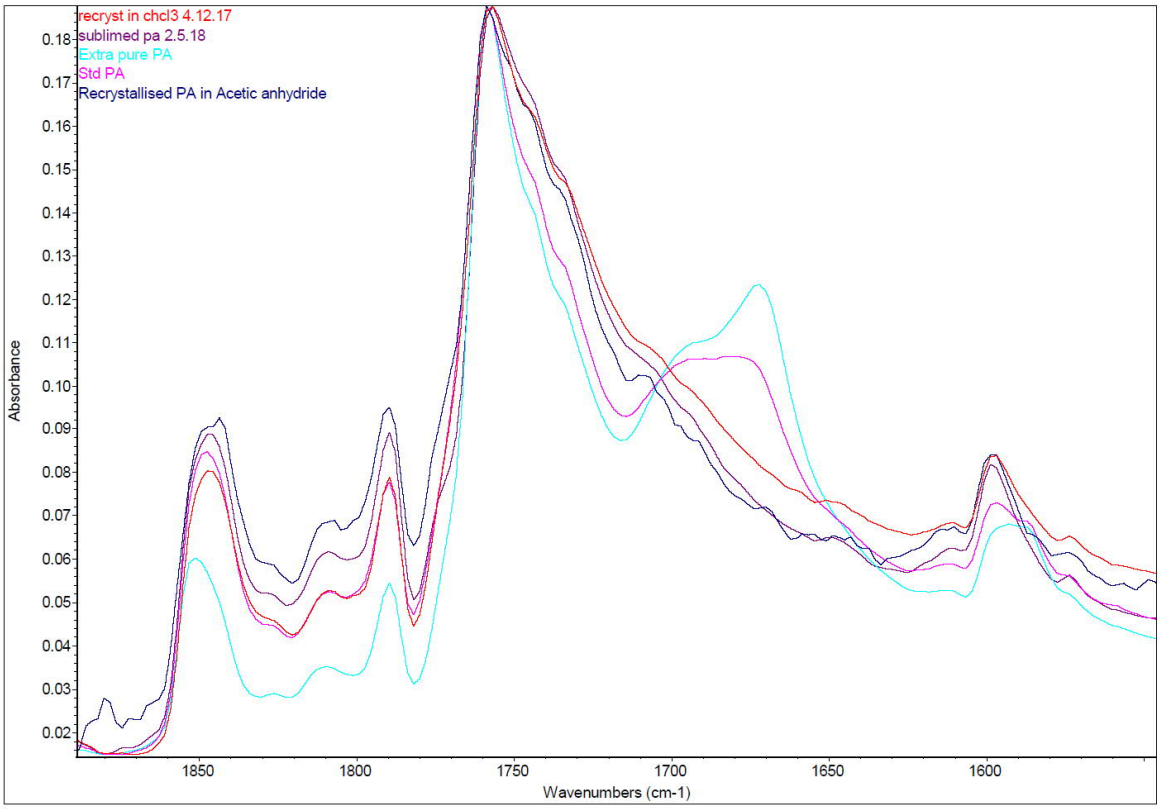


Figure 4-34 - IR spectrum highlighting acid presence in phthalic anhydride. Spectra zoomed into the 1800-1600cm^{-1} region (red – recrystallised in CHCl3, purple – sublimed PA, light blue – extra pure PA, pink – standard PA, dark blue – recrystalised in acetic anhydride)

Looking at the infrared spectra (Figure 4-34), it was identified that an acid peak at 1675cm^{-1} can be observed alongside the anhydride peak at 1750 cm-1. This gave excellent indication as to whether the anhydride had been purified[126]. It could also be seen that when purified - the acid peak (highlighted) has gone. The standard anhydride and the extra pure purchased anhydride, both contained a small amount of acid. However, it could not be quantified as a true 100% purity could not be given with confidence to calculate a quantity, but this was used an indication for all polymers from this point onwards, to test the anhydride in the IR before adding to a synthesis.

These anhydrides were used in the higher molecular weight polymers with a trifunctional initiator in a 1:20:17 ratio. As shown in Table 4-27 below, it could be observed that the molecular weights are increasing when purified anhydride has been used. The expected Mn was still 5741g/mol, but it is an improvement, and one to be further investigated.

Purity of phthalic anhydride	Mn (g/mol)	Mw (g/mol)	PDI
Standard	2636	3076	1.167
Extra pure	2859	3316	1.160
Recrystallized in $CHCl_3$	3515	4281	1.218
Sublimed	3484	4197	1.205

Table 4-27 - Polymers with purified and impurified anhydrides. These were tested in a trifunctional polymer using TMP:PA: PGE in a 1:20:17 ratio, the predicted Mn was 5741g/mol.

The GPC spectra below (Figure 4-35) shows the 4 polymers as explained above in the table. It can be seen that there are many more oligomer peaks for the standard and

extra pure anhydrides and can be seen to be a lower molecular weight as mirrored in Table 4-27 above.

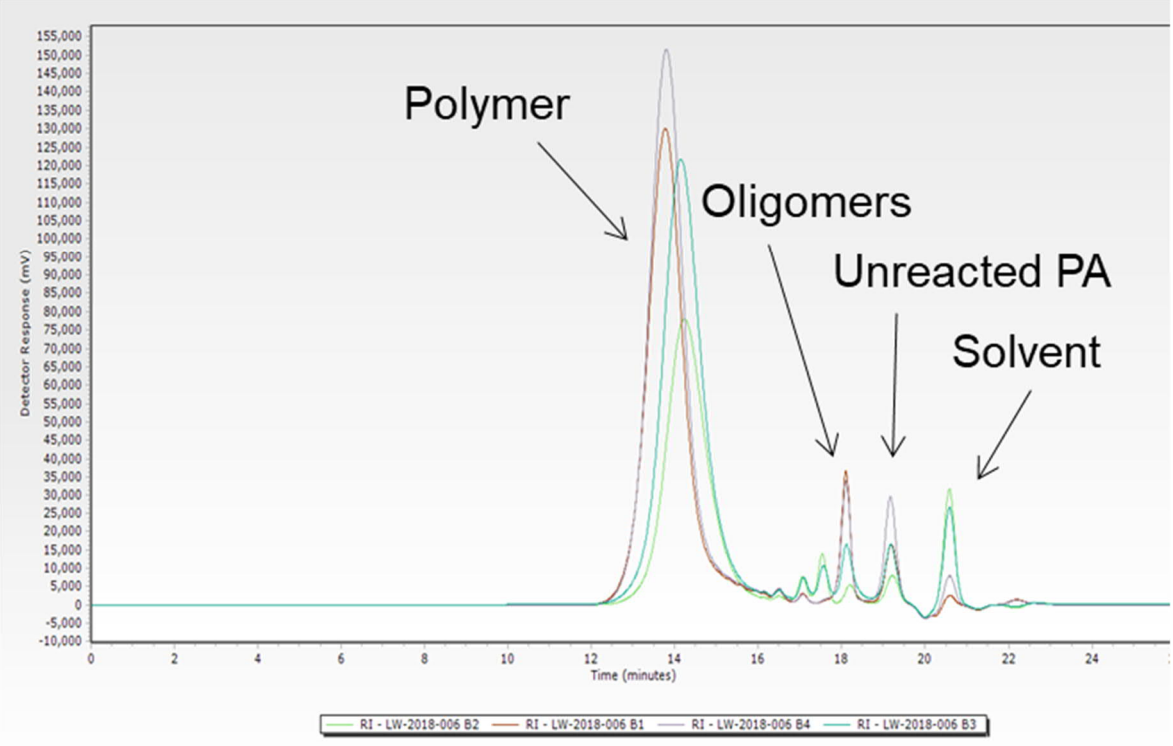


Figure 4-35 - GPC overlay of polymers produced with different purity anhydrides. Light green - $CHCl_3$ purified, Red - Standard, Purple - Sublimed, Blue - extra pure

As concluded above, an improvement can be seen when purifying the anhydride, the molecular weight is higher than without a purification and the oligomer levels appear lower in the GPC spectra. As this has shown to improve the properties of the polymer, this knowledge is to be used and expanded on to further benefit this synthesis.

4.12.3 Purification of all other raw materials

As it could be observed that purifying the anhydride was a benefit to the reaction, all other monomers were purified, to see if the molecular weight increased further. These were purified in advance, sealed against moisture and kept in a desiccator overnight in preparation for the following day. The 2 functional initiator - 1,3 PDO was used for this synthesis, which was purified by distillation before use. The epoxy was also distilled

and the EEW was confirmed to have dropped from 155.8 g/eq to 150.2 g/eq by ^{1}H NMR which is matches the theoretical equivalent weight. It was believed a possible amount of diol was the impurity in the epoxy. The catalyst (ETTPB) was dried over 4 hours at 110°C as it is hygroscopic, all materials were left in a desiccator overnight. These polymers followed the LW24 formulation (PDO/PA/PGE/ETTPB in a 1:20:18 ratio) but as monomers were purified, new codes were given as shown below in Table 4-28.

Polymer	Target Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI	Tg (°C)
Polymer with purified anhydride (LW26)	5649	3377	3684	1.090	41.8
Polymer with Standard anhydride from supplier (LW27)	5649	2380	2676	1.124	

Table 4-28 - Difference in Mn when anhydride monomers have been purified, when using purified monomers of the alcohol, epoxy and catalyst. Synthesised at 140°C in toluene.

To understand if the other monomers purification (PDO, PGE and ETTPB) would have an impact on the polymer, two polymers were synthesised, one with purified anhydride and one without. As can be seen from the table above (Table 4-28) and the trace below (Figure 4-36), the purity of the other reagents equally make a significant contribution to the control over this reaction.

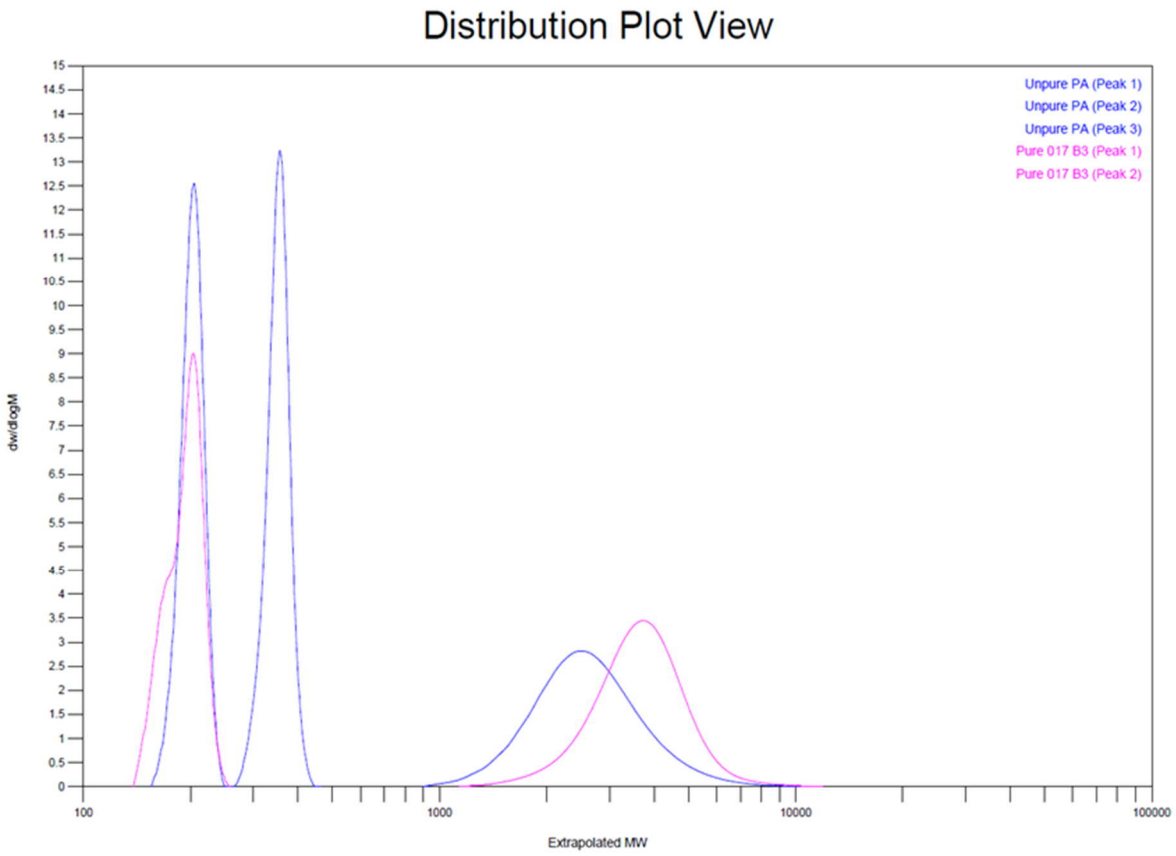


Figure 4-36 - GPC overlay comparing pure raw materials vs impure anhydride in pure raw materials (blue – pure polymer with standard PA (LW27), pink – pure polymer with purified anhydride (LW26))

The GPC shows 2 peaks, one low molecular weight peak, at 200g/mol which can be attributed to unreacted anhydride. The polymer containing the impurified anhydride, reacted less efficiently, or to a lesser extent as the molecular weight was lower, and showed a third peak at 350g/mol, which indicated longer oligomers, which have not reacted further. The high molecular weight portion can be seen to be considerably lower as well. This was expected with more oligomers present.

It could be concluded that purifying the reagents could lead to a significant difference in the advancement of the reaction, though it does not reach the theoretical Mn, so further investigation is required.

It was suggested that the anhydride could start opening under the effect of moisture quickly after the purification took place, and so to try and purify the anhydride on the same day as the synthesis. The reagents were all prepared the day before, except for the anhydride which was prepared on the same day, using the same formulation as

used previous LW26 but given a new code (LW28) due to new process conditions (Table 4-29);

Raw Material	M/R
1,3 PDO	1
Phthalic anhydride	20
PGE	18
ETPPB	0.1mol%

Table 4-29 - Formulation of LW28 polymer synthesised using purified materials, with the anhydride being purified on the day of synthesis

Sample	Target Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI	Predicted PAV (mgKOH/g)	PAV (mgKOH/g)
LW28	5649	4764	5359	1.12	19.54	17.05

Table 4-30 - Results of LW28 polymer synthesised

These results show a much-improved Mn towards the aim of 5649g/mol. This was the closest the polymer had been to the expected Mn using this ratio of monomers. As this had been successful, it gave indication the storage of the materials overnight was not sufficient, and also gave indication that the anhydride had most likely gained moisture despite precautions. This could be an explanation into the previous polymer's issues regarding the molecular weights. Therefore, the following step were to purify all materials the day of the synthesis to confirm. It must be noted, all glassware was dried overnight in the oven and not removed from the oven until the synthesis the following day. This was also the case with the catalyst, so the catalyst dried over 24 hours and was used hot from the oven to minimise chances of moisture ingress.

The polymer formulation as used previous in LW28 (Table 4-29) was used however new process conditions generate a new code – LW29.

Sample	Target Mn (g/mol)	Mn (g/mol)	Mw (g/mol)	PDI	Predicted PAV (mgKOH/g)	PAV (mgKOH/g)
S1 (1 hour after epoxy added)	5649	6085	6685	1.10	19.54	10.32
S2 (2 hours after epoxy added)	5649	5806	7707	1.15	19.54	8.85
FP (3 hours after epoxy added)	5649	6063	6861	1.13	19.54	13.00

Table 4-31 - Results of LW29 using a di-functional initiator. Synthesised at 140°C in toluene.

This polymer was synthesised so that detailed analysis could be undertaken by sampling at regular intervals. As can be seen from the results in Table 4-31, using purified monomers, dry glassware, and dry conditions, i.e. nitrogen, a polymer was produced at the expected Mn, with a very low PDI of only 1.1. It can also be observed that further processing time did not aid this polymer any further than the first sample taken as the Mn/Mw did not grow, confirming all monomer had been consumed.

4.13 Lower molecular weight polymers

After the success of producing the polymers desired and reaching a controlled reaction which can be confirmed to be as expected through GPC results, it was then looked at from a scale up perspective. In industry, manufacturing companies could not take on such a polymer to produce, they do not have the capabilities to purify monomers before use and it would not be economically viable. As a result of this, it was decided that, to produce a polymer that industry would use, the lower molecular weight polymers produced at the beginning of this chapter, were a much more sustainable option for industrial purposes.

New low molecular weight polymers were synthesised and were to be used in coatings going forward (Table 4-32). However, if these polymers were to be used in commercial

coatings, further investigation would be required into the storage stability, As new polymers were produced for this part of the project, the older polymers produced with the same formulation at the beginning of this chapter, could be retested and their storage stability (i.e. changes in acid value) could be understood,

Formulation	% acid reacted	Expected Mn (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI
LW17 B2 (TMP/PA/PGE – 1:6:3)	99.3%	1473	1390	1607	1.15
LW18 B2 (PDO/PA/PGE – 1:4:2)	104.6%	968	868	967	1.11
LW19 B2 (Penta/PA/PGE – 1:8:4)	102.5%	1921	1492	1682	1.12

Table 4-32 - New low molecular weight polymers produced for coatings testing. Synthesised at 140**°C in toluene. 2, 3 and 4 functional initiators used.**

These new polymers were made after a wealth of knowledge has been gained from this reaction and therefore these polymers have much higher acid conversions. Since processing conditions such as speed of addition, and temperature as well as purity of monomers was understood more sufficiently, these smaller polymers have shown more improved results in terms of the acid conversion. Molecular weights and PDI values are very comparable between the two sets of polymers but were very close to expected to begin with.

As these polymers do not have a Tg suitable for use as powder coatings, they will be required to be made into solvent borne paint formulations. This is something to investigate in the future, once the relationship between chemistry and physical properties of the current polymers is fully understood.

Overall, chapter 4 has given great insight into this reaction, giving understandings of many things, such as correct formulating of this polymer, along with the conclusion to what was causing the very low molecular weights in the higher molecular weight polymers. Understanding into how much purity affects this reaction was also a crucial

piece of information for how this reaction works most effectively but also for how to use this chemistry in industry. As purification isn't an option on a large scale, other avenues will need to be explored if higher molecular weights are required. For this project, lower molecular weight polymers with the expected values will be used in solvent to understand the polymers properties in coatings when varying functionality, in which the results of this are discussed in Chapter 6.

Chapter 5 – Experimental and Monomer Analysis

5 Experimental and Monomer Analysis

5.1 Analysis techniques

The following analytical techniques were employed in order to determine the successful syntheses of the polyesters and model reaction oligomers or to determine whether any un-desirable side reactions have taken place.

5.1.1 Gas chromatography – mass spectrometry (GC-MS)

GC-MS was used to detect residual monomers or oligomers in a polymer sample and to determine the purity of raw materials. The analysis was performed using an Agilent 5977A Mass Spectrometer with 7890A Gas Chromatograph. Injections of 1µL of diluted sample were made using a Gerstel MPS2 autosampler with the GC inlet in split mode. The GC was fitted with an Agilent DB-5MS column (30m x 250µm x 0.5µm) using Helium as the carrier gas. The temperature program consisted of an initial hold at 80 °C for 3.0 min, ramped up to 300 °C at a rate of 10 °C/min and held for 15 minutes. The 5977A MS is a single quadrupole Electron Impact (EI) model using 70eV for Ionisation. A solvent delay was utilised to prolong the life of the instrument's filament and a scanning range of 50 to 650 m/z was set.

5.1.2 Gel permeation chromatography (GPC)

GPC was used to determine mass distribution of the polymers, such as weight average (Mw) and number average (Mn) molecular weights. The molecular weight is the mass of one mole of polymer. As a polymer can contain monomers, oligomers, short and long polymer chains, it cannot be represented by a single molecular weight value and so at minima number average and weight average molecular weights are used to represent the average distribution of masses. The ratio of Mw/Mn also gives an indication of the breadth of the polymer peak and its polydispersity.

The analysis was performed on an Agilent 1260 Infinity series fitted with a refractive index detector and using the following parameters:

- Isocratic run using HPLC grade THF as mobile phase.
- Pump flow rate 0.3 ml/min.
- Column type: 1x Polymer Lab PLgel 3µm Minimix-D + 2 x Polymer Lab PLgel 3µm, 250x4.6mm Minimix-E at 40 °C.
- Elution time of 36 minutes

The samples were prepared by dissolving the polymers in THF at 2% w/v concentration Then filtered through a 0.45µm filter before adding to the run list. The polymer solutions were then injected in duplicate and all data were analysed relatively to polystyrene standards prior to the unknown polymers (Table 5-1 & Table 5-2).

Analysis was carried out using the Agilent GPC reprocessing software version A.02.01 after calibrating the response using the set of polystyrene standards to a cubic fit.

Point	Peak Max RT (mins)	Average Mw (g/mol)	Percent Error of Mw (%)
1	10.96667	45120	7.07
2	11.37500	27810	-1.13
3	11.68333	19500	-7.90
4	12.53333	9590	-3.44
5	13.06667	6320	-1.25
6	13 45833	4730	0.46
7	14.06667	3090	3.12
8	14.75833	1920	3.80
9	15.85833	945	3.60
10	16.65000	580	1.82
11	17.26667	370	-8.70
12	20.13333	92	1.33

Table 5-1 - Low Molecular weight routine columns calibration standards

Point	Peak Max RT (mins)	Peak molecular weight Mp (g/mol)	Percent Error of Mw (%)
1	11.24167	1074000	0.00
2	12.00000	482000	0.68
3	12.80833	202100	-1.32
4	13.83333	70500	0.14
5	15.05000	19920	0.65
6	15.75000	9590	1.35
7	16.38333	4730	-1.67
8	17.48333	1440	-0.20
9	18.29167	580	0.33

Table 5-2 - Routine column calibration standards

5.1.3 Nuclear magnetic resonance (NMR)

^{1}H NMR was used to characterise the synthesised polymers by identification of the main hydrogen chemical shifts in the samples. This helped to determine whether any un-desirable products have been formed. NMR was also be used to confirm epoxide equivalent weight and degree of polymerisation.

^{13}C NMR was used to characterise the synthesised polymers by identification of the main carbon chemical shifts in the samples. This also allowed the identification of un-desirable side reactions.

All nuclear magnetic resonance spectroscopy was completed using a Bruker Avance 400 MHz spectrometer. Samples were dissolved in an appropriate deuterated solvent depending on the sample's polarity (most samples dissolved in d-Chloroform, however some experiments, mentioned when used, required other solvents such as d-DMSO, or d-MeOH). TMS was not added to samples as a chemical shift reference.

Spectrum were analysed using Topspin version 3.5 by first adjusting the solvent signal to its reference value and then integrating peaks after identification[127].

5.1.3.1 Epoxide equivalent weight (EEW)

EEW is the weight in grams that contains 1 mole or 1 "equivalent" of epoxide groups giving units of g/mol. Epoxy equivalent weight is determined by ^{1}H NMR. An accurately weighed amount of 100mg of polymer was dissolved in $CdCl_3$, to which an accurate amount of 10mg of OMTS (octamethyltetrasiloxane used as internal standard) was added. 3 epoxy peaks are observed if epoxy is present at 2.6ppm, 2.8ppm and 3.2ppm. The epoxy equivalent weight can be calculated using the integration of these 3 peaks, the integration of the OMTS peak and the weight of the samples.

This method is used to calculate epoxy concentration vs target epoxy concentration, giving a percentage reacted.

5.1.4 Size Exclusion Chromatography – mass spectrometry

The analysis was performed on an GPCmax equipped withTDA305 triple detection array and used the following parameters;

- Column type: 2x Plgel Resipore7.8 x 300 mm
- Mobile phase: Tetrahydrofuran stabilized by 0.025% BHT; 0.5% Acetic Acid
- Flow rate: 0.6ml/min.
- Column temperature: 35 °C
- Detection: RI, Dual Angle Light Scattering, Viscometry
- Injection volume: 50 µl

5.1.5 Differential Scanning Calorimetry

DSC was used to measure the change in the heat absorption of the samples as function of time and/or temperature. This led to the measurement of glass transition temperature (Tg) which can be observed as a second order transition on the spectra whilst exotherms and melting events were observed as first order transitions (peaks). Tg is the temperature in which the polymer transitions from a glassy solid polymer to a rubbery polymer. Other properties of a polymer were elucidated from a DSC, such as melting point (endothermic peaks), crystallinity, presence of volatile materials, and exothermic curing reactions. DSC measurements were made on a PerkinElmer DSC 8500, and analysis performed on Pyris thermal analysis software version 8.0.0.0172. Samples of 10 ± 5 mg were weighed into an aluminium pan and placed into the DSC. Heating rate of 20 degrees per minute was applied and the samples were ran twice to eliminate possible thermal history observed in the first run.

5.1.6 Acid value titration

Acid value titrations are used to determine in-process, intermediate and final acid values on clear polymer samples. For partial acid value, the acid groups on the polymer react with the potassium hydroxide to form the polymer salt and water.

For the total acid value, the purpose is to give an indication of residual anhydride content in polyester resins. The anhydride group is hydrolysed with water to give two acid groups. The resulting acid groups and the acid groups on the polymer react with the potassium hydroxide to form the polymer salt and water.

This method is used to calculate acid concentration vs the target acid concentration

5.1.6.1 Partial acid value titration:

2.5g of polymer was accurately weighed in 250mL conical flask and dissolved in 50mL of a neutralised mixture of xylene and methoxy propanol (in a ratio of 3 to 1 by volume) with 1ml/L thymolphthalein indicator (2.5% thymolphthalein w/v in methanol) on a hot plate. The solution was then cooled down to room temperature and titrated using a 0.6M methanolic KOH solution until equivalence point was observed by the appearance of a persistent faint blue colouration. The volume of KOH solution was then used to determine the Acid Value of the polymer using the following equation (Equation 5-1):

$$AV = \frac{SampleTitre(ml) \times Factor(KOH)}{Sample(g)} = mgKOH\ /\ g$$

Equation 5-1- Equation to calculate partial acid value

Samples were analysed in triplicate.

5.1.6.2 Total acid value titration:

0.8g of polymer was accurately weighed in 250mL conical flask and dissolved in 50mL of a mixture of MEK and DMSO (in a ratio of 4 to 1 by volume) and 5ml deionised water added, on a hot plate. The solution was then cooled down to room temperature and 10 drops of mixed indicator solution (Cresol red: thymol blue in 1% methanol) titrated using a 0.1M methanolic KOH solution until equivalence point was observed by the appearance of a persistent blue colouration. A solvent blank titration is required in this titration as water is added and therefore ester formation can prematurely occur. A blank titration involves 50ml of the mixture solvent and 5ml water and then titrated to see an end point. The volume of KOH solution from both the sample and blank was

then used to determine the Total Acid Value of the polymer using the following equation (Equation 5-2):

$$TAVorPAV = \frac{(SampleTitre(ml) - BlankTitre(ml)) \times Factor(KOH)}{Sample(g)} = mgKOH\ /\ g$$

Equation 5-2 - Equation to calculate total acid value

Samples were analysed in triplicate.

5.1.7 Infrared spectroscopy (IR)

FT-IR (Fourier Transformed - InfraRed) can be used to understand the reaction kinetics, how the reaction occurs and observations of any obvious side reactions. The IR used is a Golden Gate Diamond ATR Infra-red Accessory with Heated Top Plate which comprises a 2mm square diamond brazed into Tungsten Carbide in a steel plate (approx. 14 x 12.5cm). The accessory is positioned in the sample compartment of the infra-red spectrometer and the optics (mirrors and lenses) within the accessory are fully enclosed and constantly purged with Nitrogen.

The accessory allows acquisition of attenuated total reflectance (ATR) infra-red spectra (in the range 4000 - 400cm-1 with KRS-5 lenses) of both solid and liquid samples. The active sampling area is approximately a 0.6mm diameter ellipse in the centre of the diamond. The top plate of the accessory can be heated between room temperature and 200°C if required. For testing of phthalic anhydride purity, the samples were tested at room temperature. When testing for reaction conditions, this was carried out at 140°C. There is a clamp bridge, with a screw-down sapphire anvil, attached to the top plate of the accessory. This anvil is used to apply pressure to obtain the essential contact required between solid samples and the diamond surface. The software which is used to record and analyse the spectra was Omnis version 9.9.

5.1.8 Thermogravimetric analysis (TGA)

TGA was used to determine the thermal degradation of polymers at set temperatures (isothermal runs), or a gradual increase of temperatures, by measuring the exact weight before/ during and after heat, providing a % weight loss. TGA analysis was

performed on a Pyris 6 TGA Thermogravimetric Analyser controlled by Pyris Thermal Analysis Software version 8.0.0.0172.

5.2 Raw material purity

On each raw material, gas chromatography - mass spectrometry (GC-MS) was carried out. ^{1}H NMR, ^{13}C NMR, COSY, HSQC were also carried out but proved to be less useful as peaks identification was more complex than with other methods. All samples which contained an OH group, whether that is from an alcohol or an acid, were silanised in BTSFA (Bis-trimethylsilyl trifluoro acetamide) before analysis on the GC-MS[110].

5.2.1 Benzyl alcohol

Mass spectrometry showed there to be predominantly benzyl alcohol in the sample, but also showed traces of benzaldehyde to be present (ab.0.29%). δH (400 MHz; $CDCl_3$): 7.4 (3H, t, ArCH), 7.3 (2H, dd, ArCH), 4.7 (2H,s, CH_2), 2.45 (1H,s,OH), 1.3 (2H, s, H_2O); δC(400 MHz; $CDCl_3$): 141 (ArCH), 129 (2 ArCH), 128 (1ArCH), 127(2ArCH), 65 (1 CH_2).

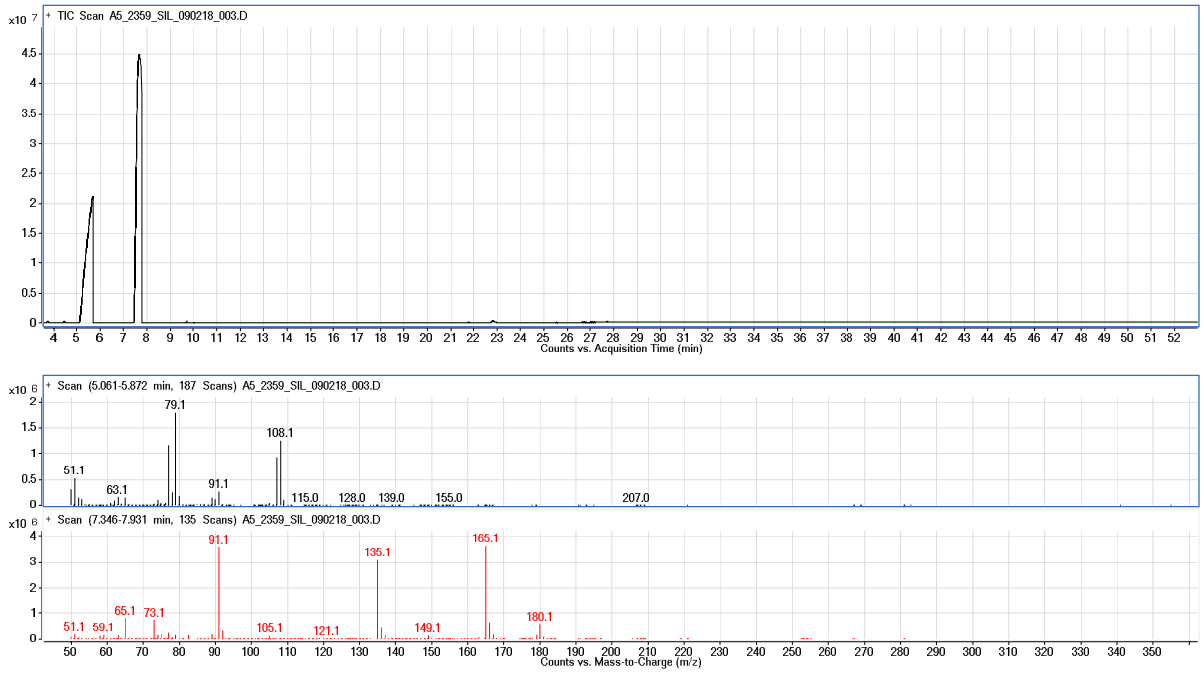


Figure 5-1 - GC-MS spectra of Benzyl alcohol

5.2.2 Phenyl glycidyl ether (PGE)

Gas chromatography showed that the sample contained very small baseline peaks which are shown in all runs when the sample is repeatedly measured. Due to the size

of the peaks, it cannot be confirmed with certainty if these peaks are an impurity to give rise to a concern currently. δH (400 MHz; $CDCl_3$): 7.3 (2H, t, ArCH), 7.0 (3H, td, CH), 4.3 (1H, dd,CH_3), 4.0 (1H, q, CH_3), 3.4 (1H, m, CH), 2.9 (1H, t, CH), 2.8 (1H, q, CH); δC(400 MHz; $CDCl_3$): 159 (ArC), 130 (2 ArCH), 121 (ArCH), 115 (2 ArCH), 69(CH_2), 50(CH), 45(CH_2).

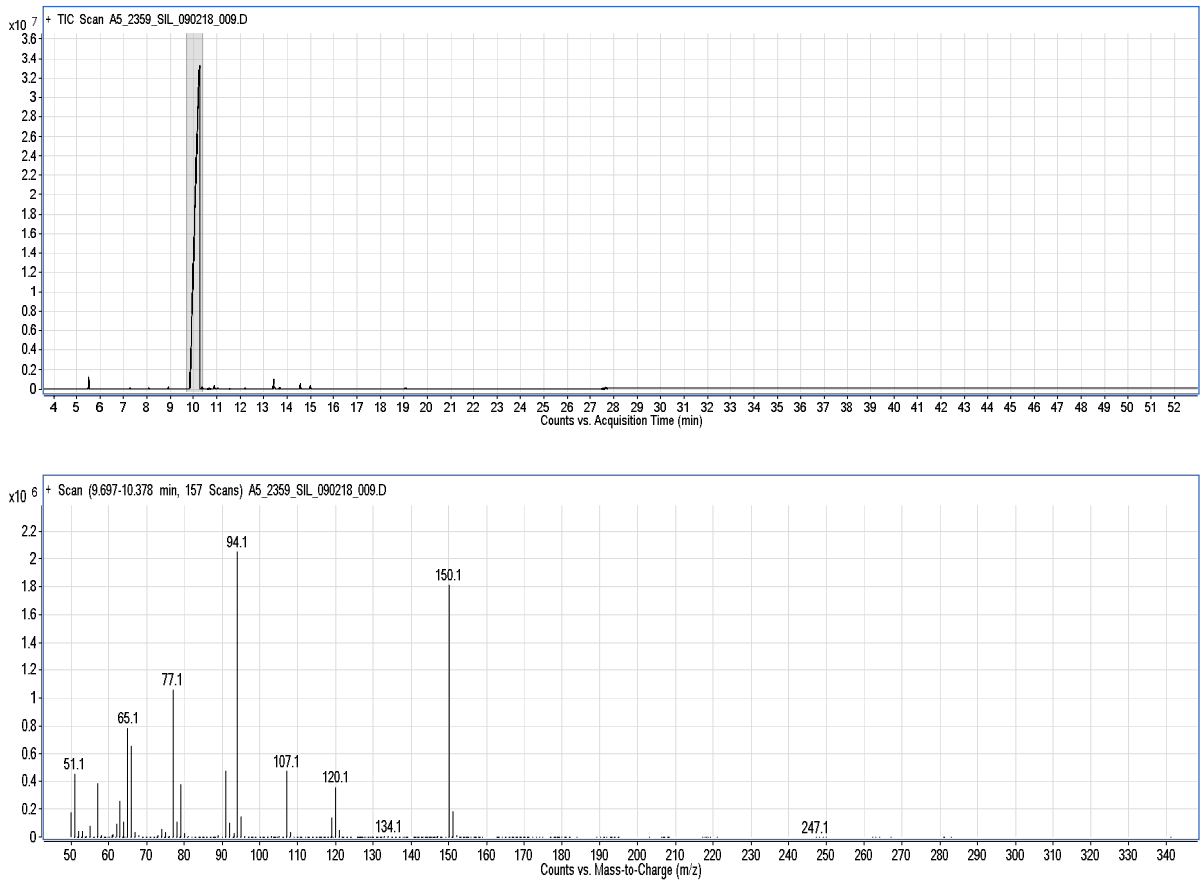


Figure 5-2 - GC-MS integration of 9.7 and 10.5 peaks of PGE spectra

5.2.3 Hexahydrophthalic anhydride (HHPA)

GC-MS showed that the sample contained both cis and trans isomers of HHPA. A very small peak at 11 mins, just before the 11.65-minute peak for the cis isomer was present which was believed to be the trans isomer. No other peaks were present (Figure 5-3).

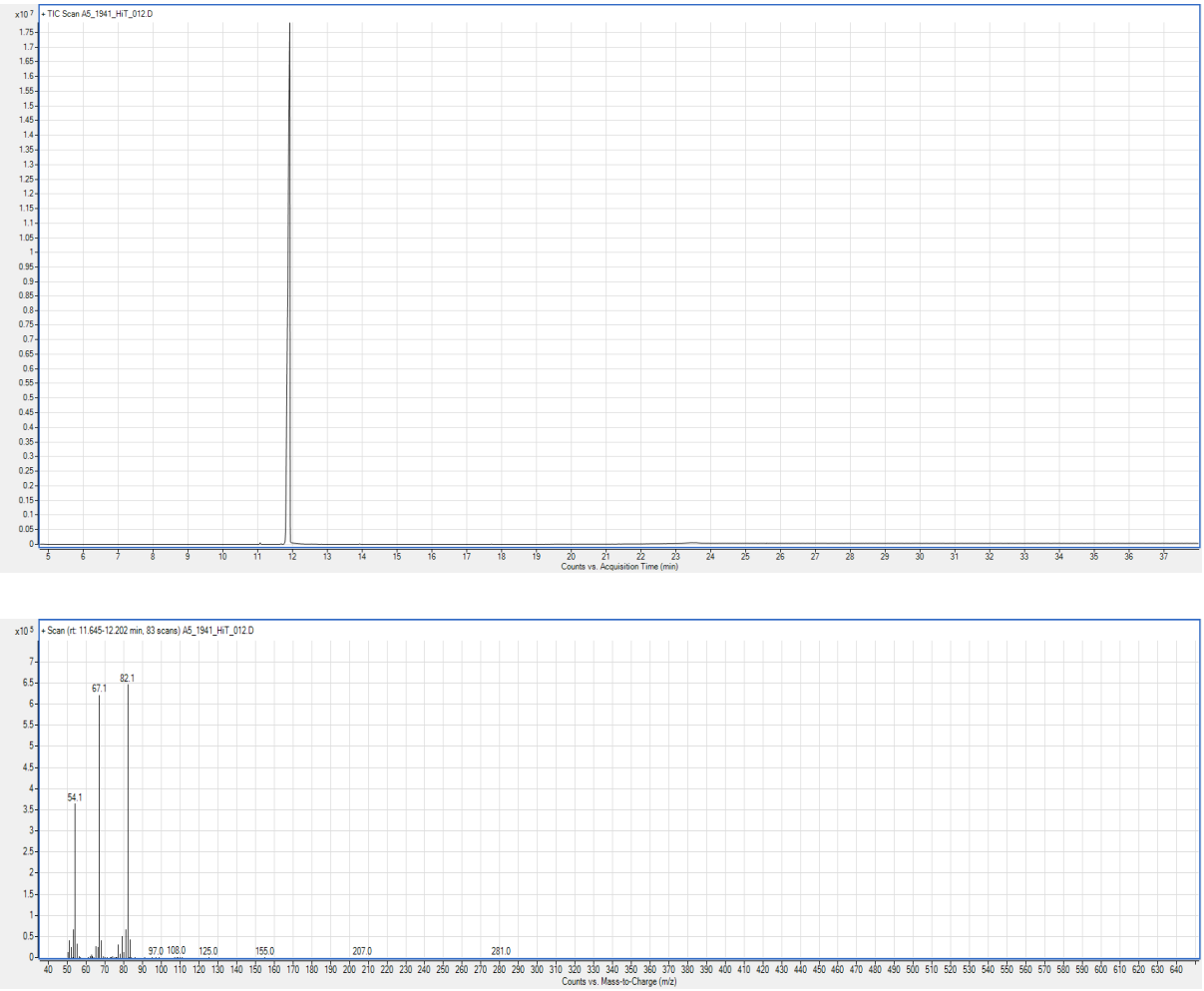


Figure 5-3 – Analysis of GC-MS Spectra of HHPA

The NMR showed ab. 98.5% of the sample was the cis isomer; peaks also confirmed a small amount of trans isomer. However, there were a few very low intensity peaks, all of which were very small so could not be identified. δH (400 MHz; $CDCl_3$): 3.2 (2H, m,CH_2), 1.9 (4H, dd, CH_2), 1.5 (4H, quin, CH_2); δC(400 MHz; $CDCl_3$): 173 (C=O), 40 (2 CH), 24 (2 CH_2), 22 (2 CH_2).

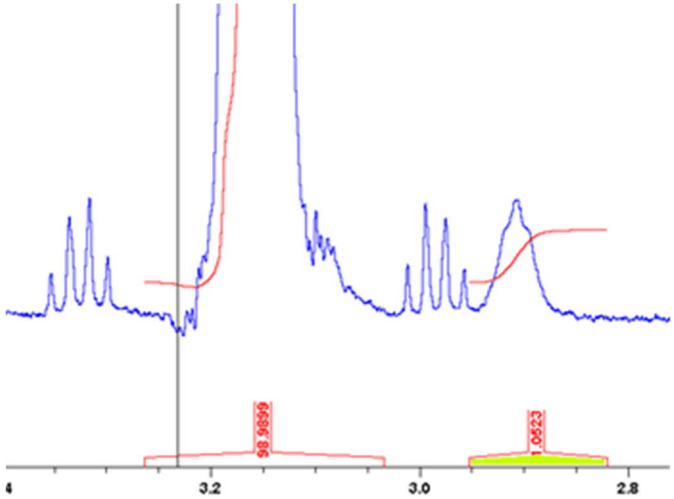


Figure 5-4 - 1H NMR showing peaks indicting a presence of cis HHPA is present in the sample

5.2.4 Phthalic anhydride

GC-Ms showed that there was a significant amount of phthalic acid impurity in the phthalic anhydride sample. This can be seen through 2 peaks showing on the GC-MS spectra, one at 16.12 minutes, showing the fragmentation pattern of the acid, and the other, at 11.54 minutes, of the anhydride.

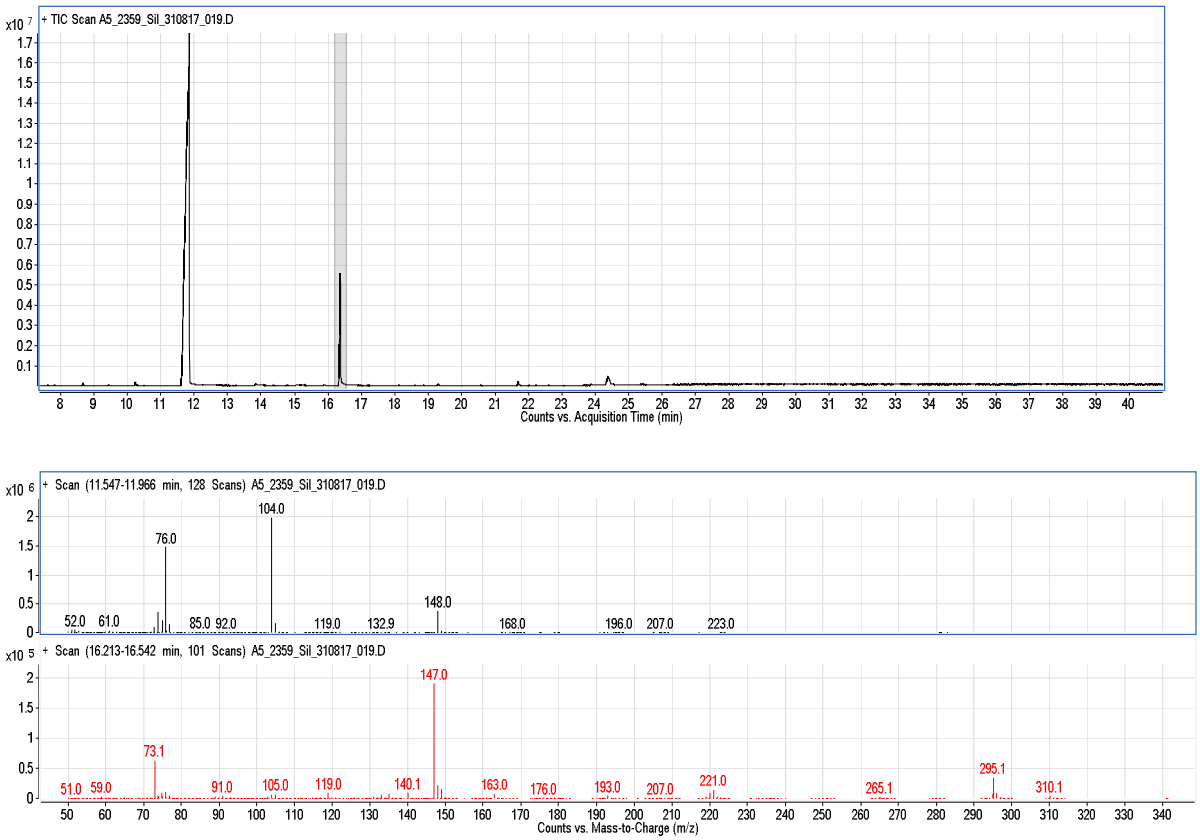


Figure 5-5 – GC-MS spectra of Phthalic anhydride

Phthalic anhydride was analysed by ^{1}H-NMR in d-chloroform and found to have 2.6% acid containing in the anhydride. This work can be found in Chapter 2 - 1.1.2. δH (400 MHz; dry ACN): 8.0 (2H, quintet 2CH), 8.1 (2H, pentet, 2CH).

5.2.5 Succinic Anhydride

Succinic anhydride was tested in the initial stages of the project, in chapter 2 – model reactions and therefore was tested for purity before using in synthesis. It was analysed through GC-MS and showed no impurities.

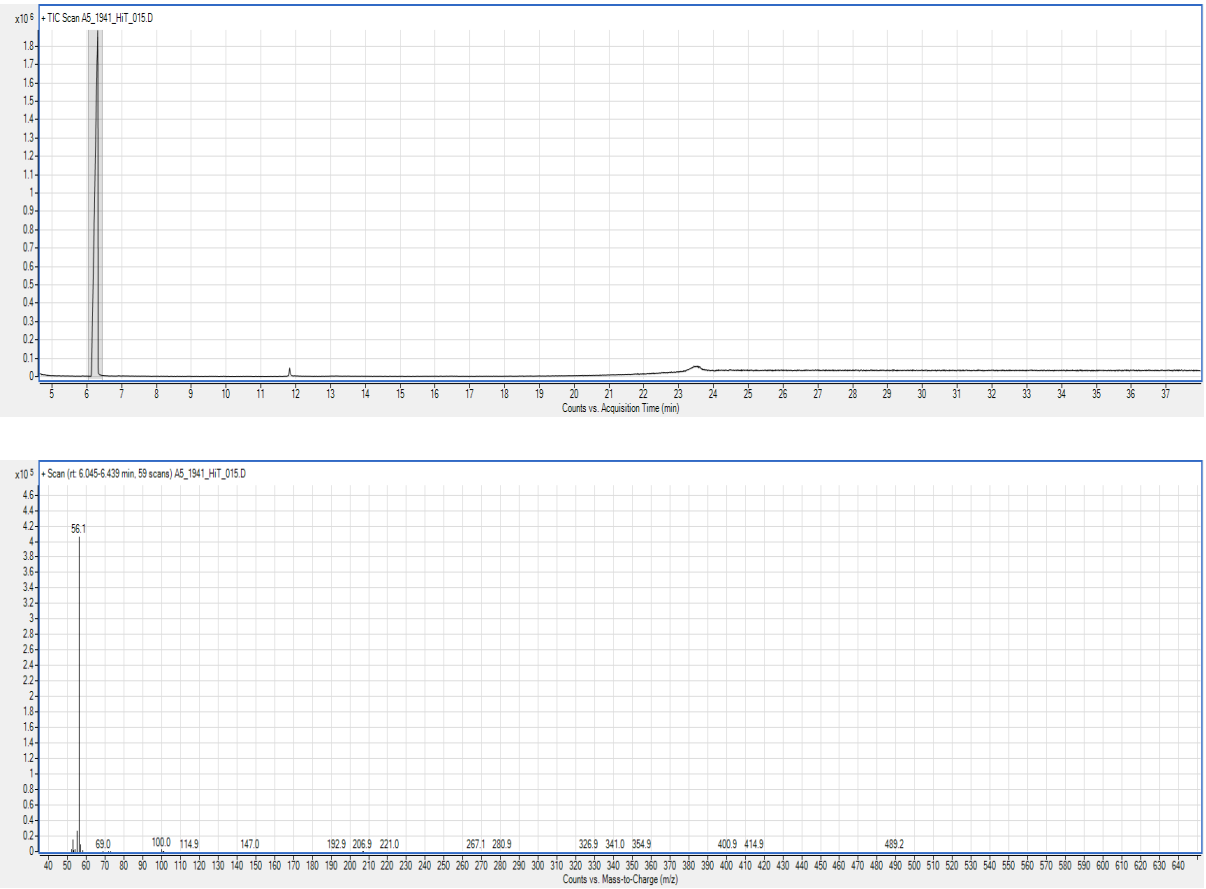


Figure 5-6 - GC-MS spectra of Succinic anhydride

5.2.6 4-(Dimethylamino)pyridine (DMAP)

GC-MS showed that the sample contained 100% DMAP with no impurities present. δH (400 MHz; $CDCl_3$): 8.2 (2H, d, 2 ArCH), 6.5 (2H, d, 2 ArCH), 3.0 (6H, s,2 CH_3); δC (400 MHz; $CDCl_3$): 154(C), 150 (2C), 107 (2C), 39 (2 CH_3).

5.2.7 Ethyltriphenylphosphonium bromide (ETTPB)

GC-MS showed that there were traces of small peaks which could not be identified but seemed to be very small so were assumed to not affect the overall efficiency of the catalyst. N.B for NMR - the sample had to be dissolved in a blend of deuterated THF & d-methanol.

δH (400MHz; THF/MeOH): 7.4 (15H,dm, ArCH), 3.8 (2H, sextet,CH_2), 2.2 (?H, s, ?), 1.3(3H,dt, CH_3); δC(400 MHz; $CDCl_3$): 135 (ArCH), 133 (ArCH), 131 (ArCH), 118 (ArCH), 17 (CH_2), 7 (CH_3).

5.2.8 Zinc stearate

It was not possible to analyse Zinc Stearate by GC-MS due to its low solubility in the solvents.

Zinc Stearate had to be dissolved in trifluoroacetic acid-d for NMR experiments. The 1H-NMR showed 52 protons present, indicting a 75:25 blend of zinc stearate: zinc palmitate.

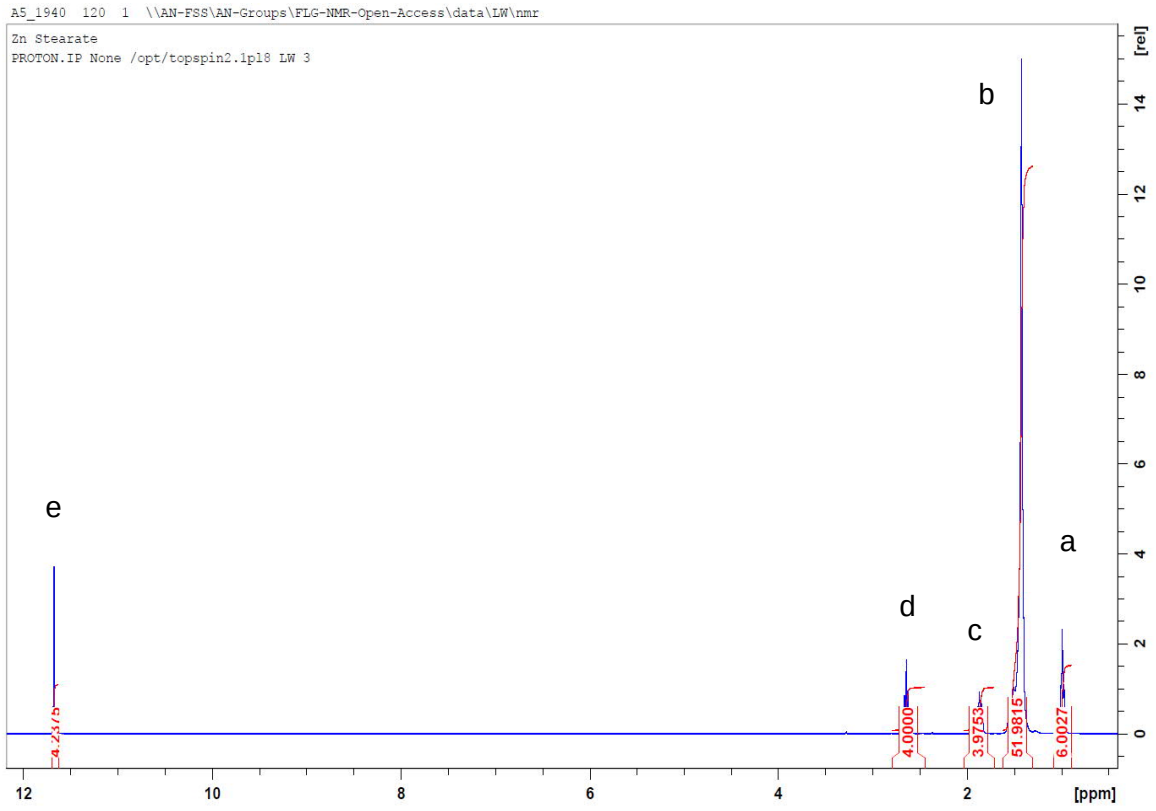


Figure 5-7 - 1H NMR of Zn Stearate sample

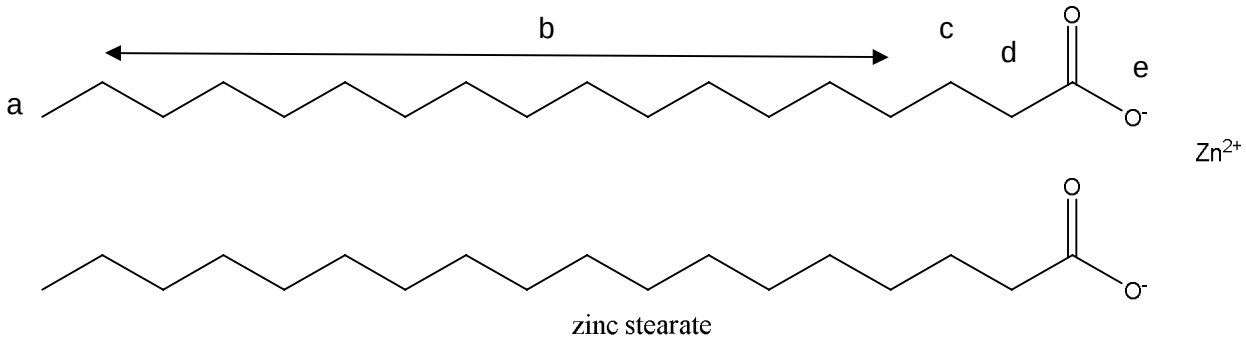


Figure 5-8 - Structure of Zn Stearate

5.2.9 TBAB

TBAB did not dissolve in any useful analytical solvents and therefore was not further analysed.

Alcohols used in multifunctional polymer synthesis:

5.2.10 1,3 propane diol

GC-MS showed propane diol to have no impurities, with showing only 1 peak on the spectra at 7 minutes (Figure 5-9).

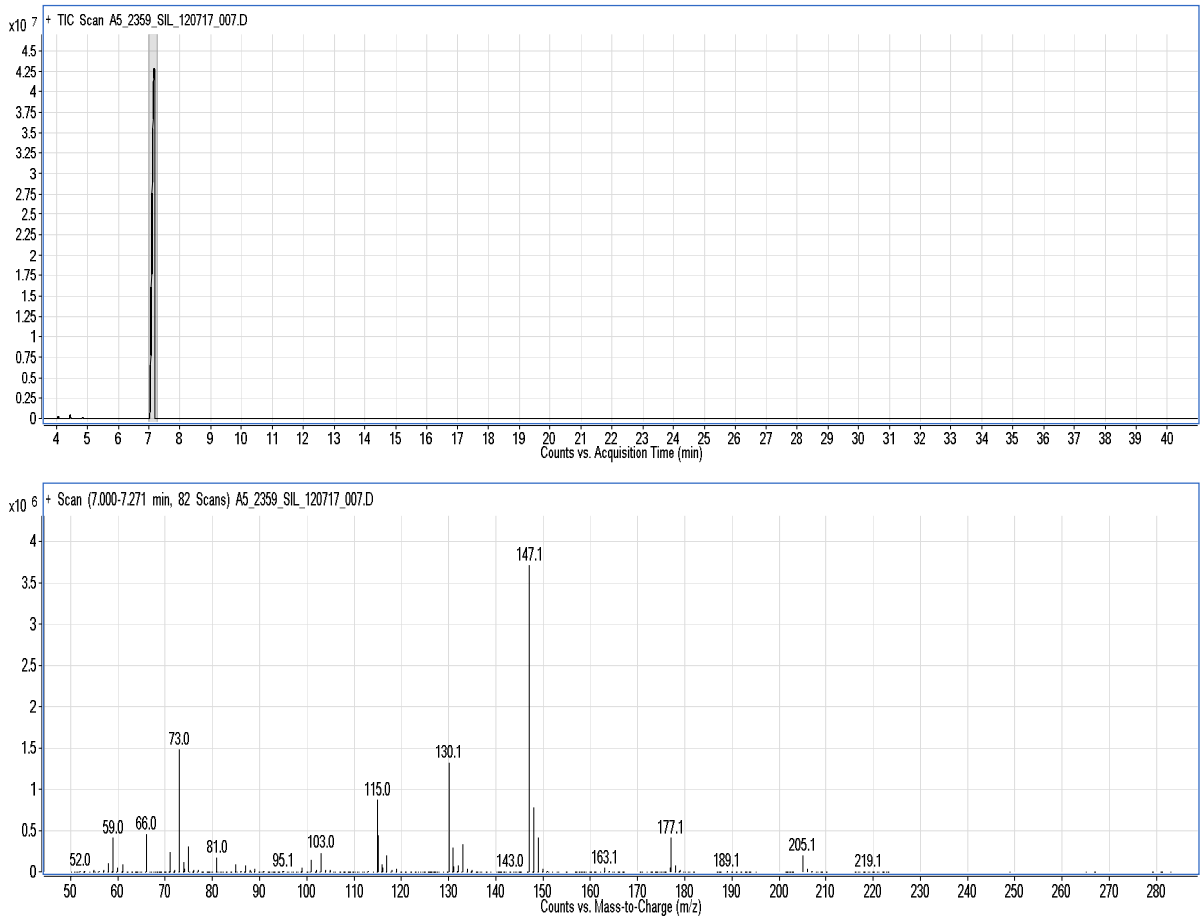


Figure 5-9 - GC-MS of 1,3 propane Diol (PDO)

5.2.11 Trimethylol propane

GC-MS showed TMP to have no impurities, and only showed a single peak at 12.6 minutes (Figure 5-10).

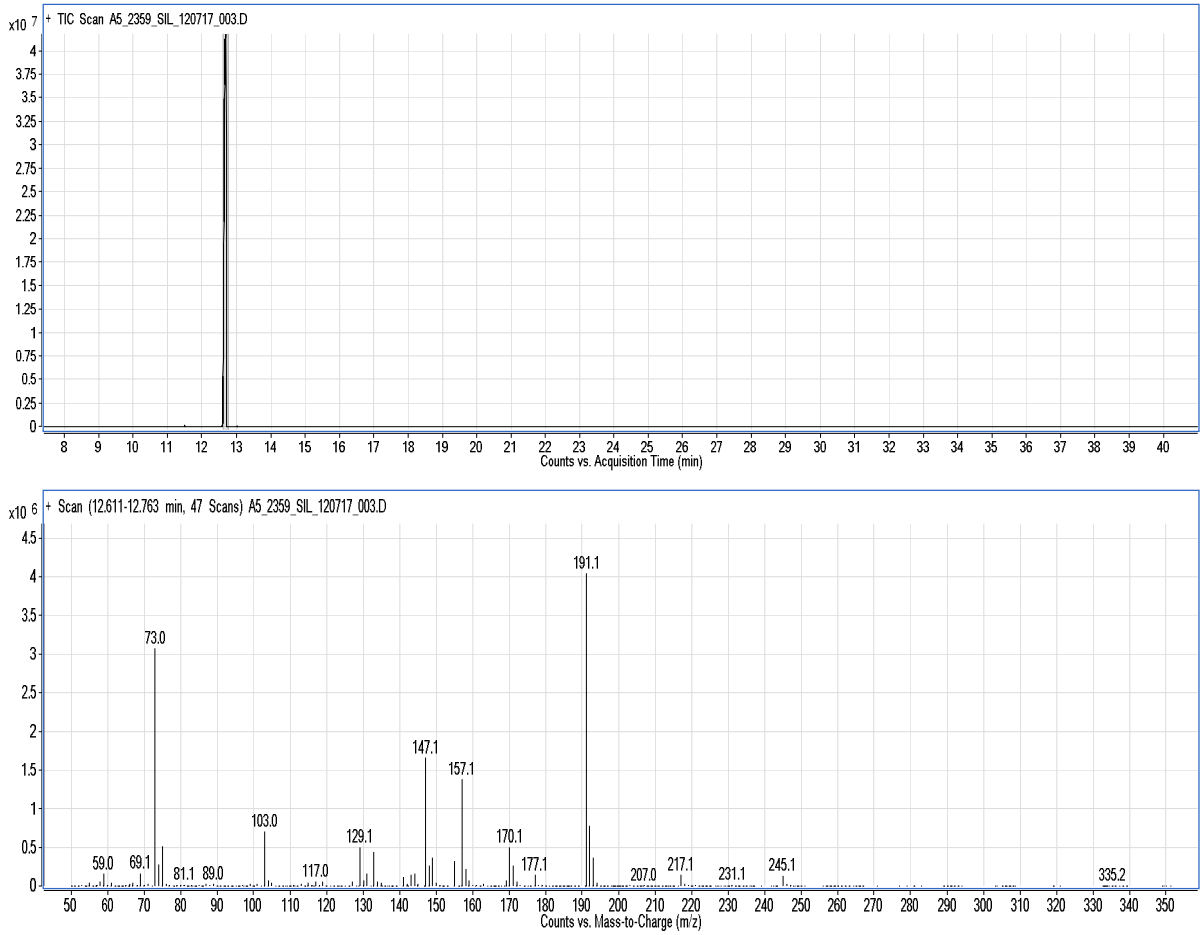


Figure 5-10 - GC-MS spectra of TMP (trimethylol propane)

5.2.12 Pentaerythritol and dipentaerythritol

Analysis by GC-MS showed that pentaerythritol had an impurity at 22 minutes (Figure 5-11).

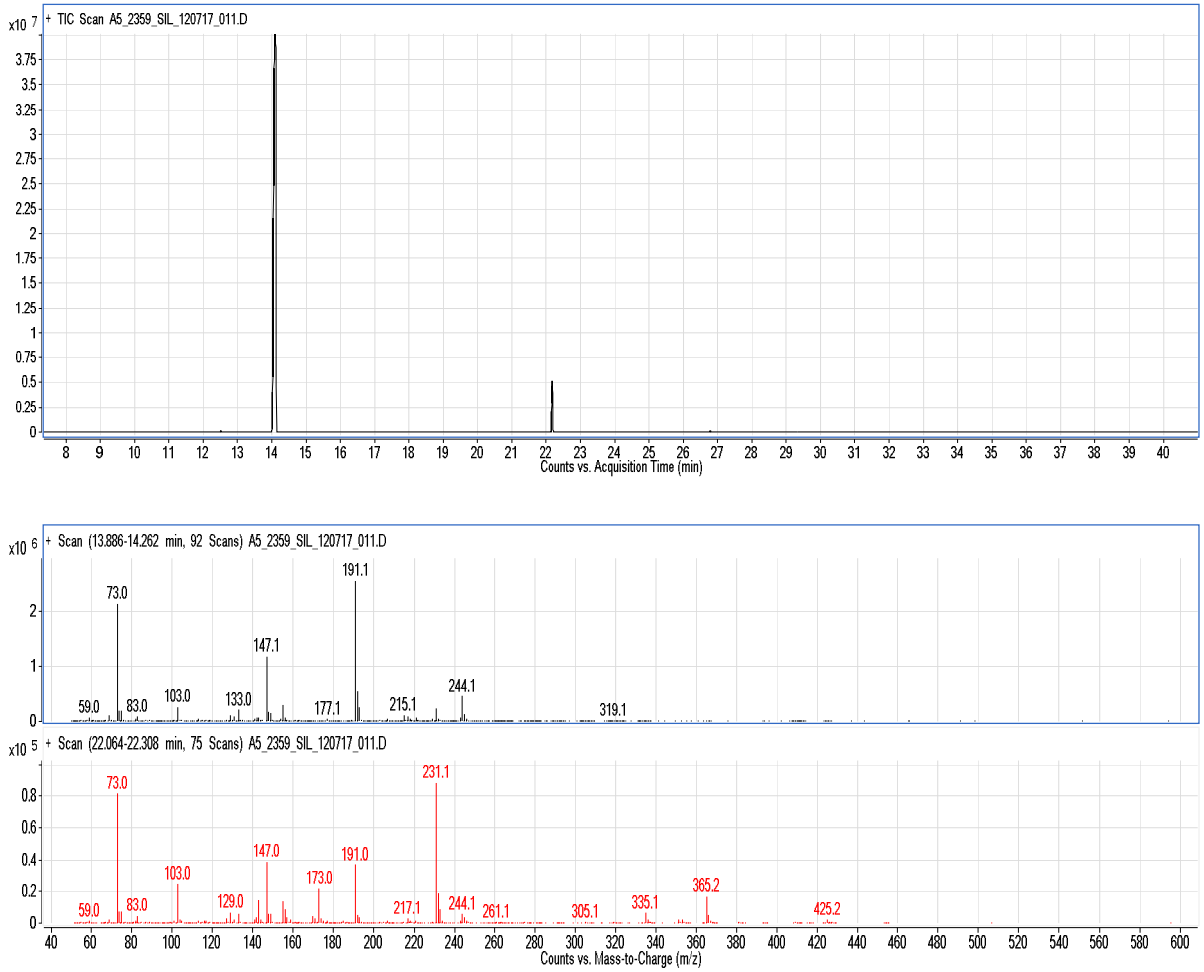


Figure 5-11 - GC-MS of pentaerythritol

Dipentaerythritol could not be dissolved in any solvents to determine purity, therefore was not taken forward within this research.

5.3 Model reactions

5.3.1 Synthesis

All model reactions synthesised in chapter 2 were carried under the same set of conditions; 140ºC heating (internal temperature), stirring, and under inert (N_2) gas. Typical synthesis procedure was carried as follows.

Benzyl alcohol (Sigma Aldrich, 7.98g, 0.073mol), Phthalic anhydride (Sigma Aldrich, 10.93g, 0.073mol) and 4-(Dimethylamino) pyridine (Sigma Aldrich, 0.03g, 0.1wt%) were heated to 140ºC in a 50mL round bottom flask fitted with a condenser and temperature probe and placed on a heating plate with magnetic stirrer. Phenyl glycidyl ether (VWR, 11.09g, 0.073mol) was added drop wise into the flask over 3 hours (0.55ml/min). An exotherm of around 12°C was observed initially with a maximum peak of 152°C. The reaction was then allowed to process for a further hour and discharged. Over time the process was optimised using a quick feed of epoxy, averaging 7ml/min. This was because it was found the same control on the exotherm could be achieved at this rate if the heating had been removed. It also resulted in polymers being produced more quickly, so the discoloration of the polymer was reduced. Therefore, when the reaction reached process temperature, the heating mantle was removed as the epoxy was added in order to anticipate and minimise the temperature rise due to the reaction exotherm.

NMR was carried out on all model reactions to obtain the epoxy content. Using NMR to characterise the polymeric products produced did not prove effective and was not used extensively. This was due to the polymers producing broad poorly resolved multiplets as shown in Figure 5-12.

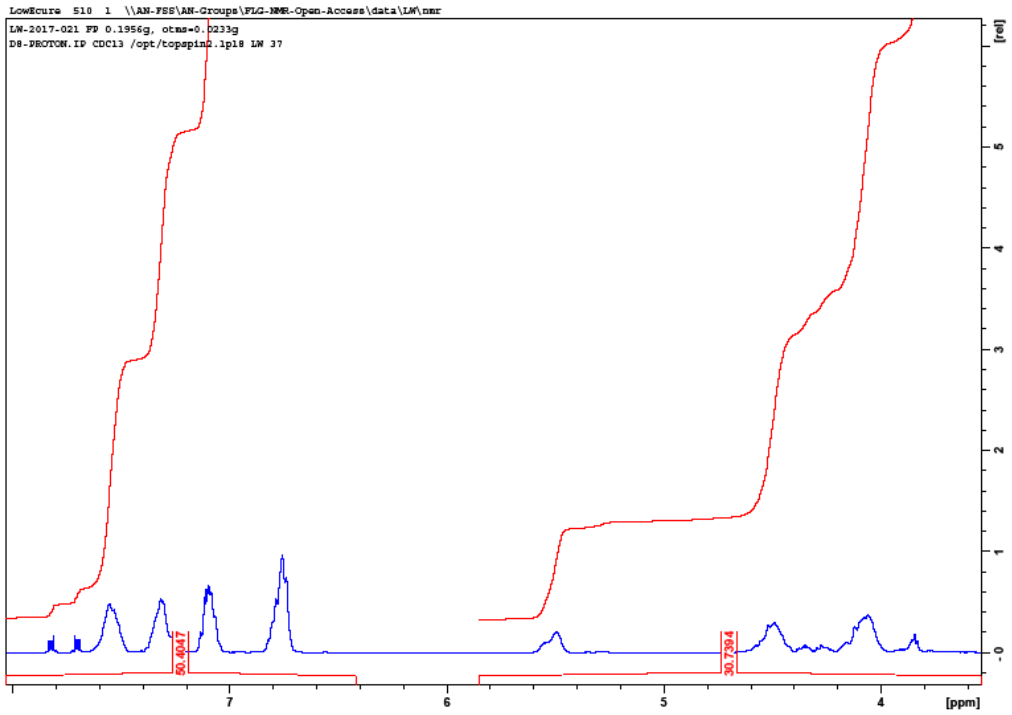


Figure 5-12 - 1H NMR of 3 functional high Mw polymer

Model polymers produced peaks with low resolution but still appeared as multiplets, making it difficult to accurately characterise using this method. Polymers in NMR generally appear poorly as the mobility of the hydrogens in restricted as it is polymerised, so gives poor peaks. An example of a model polymer produced (Benzyl alcohol: phthalic anhydride: phenyl glycidyl ether: DMAP 1:1:1) is as follows and in Figure 5-13; δH (400 MHz; $CDCl_3$): 7.8 (3H,m,3CH), 7.5 (2H,m,2CH), 7.4 (9H,m,9CH), 5.4(2H,s,CH_2), 4.5(1H,m,1CH), 4.4(1H,m,1CH), 4.1(2H,m,CH_2).

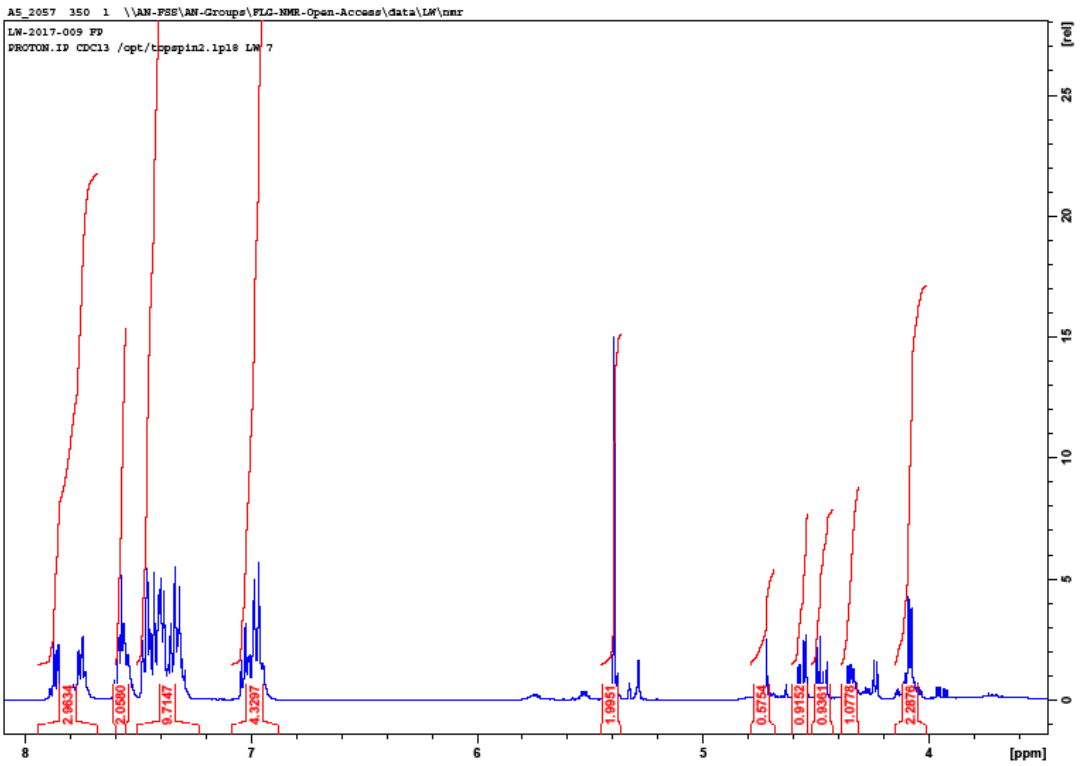


Figure 5-13 - 1H NMR of model polymer

5.3.2 Epoxy ring opening experiment

GC-MS samples were prepared in a mixture of THF (tetrahydrofuran) and BSTFA (bis-trimethylsilyl trifluoro acetamide). The BSTFA was used to silanise all alcohol groups to reduce the interaction with the GC column and increase the peaks resolution and symmetry. Using THF only, the polymer appeared as only one peak in the GCMS however after derivatisation using BSTFA, the polymer showed 2 peaks with the same mass, but different fragmentation patterns. This indicated 2 different isomers with the same mass, as expected, due to alpha and beta openings in oxirane rings producing different hydroxyls. This method was therefore used to analyse the ratio of alpha to beta opening obtained using the different catalysts used in this work. See Chapter 2 – 1.1.3.7. for the analysis.

5.4 Higher molecular weight polymers with varying functionality

5.4.1 Polymer synthesis

Polymers were processed under the same conditions however; adjustments were made depending on batch size. The epoxy was added through a dropping funnel when

in the small 5g-100g flasks, however when made on a larger scale, a peristaltic pump was used. A description of how the polymer based on trimethylolpropane was made on a 300g scale is as below.

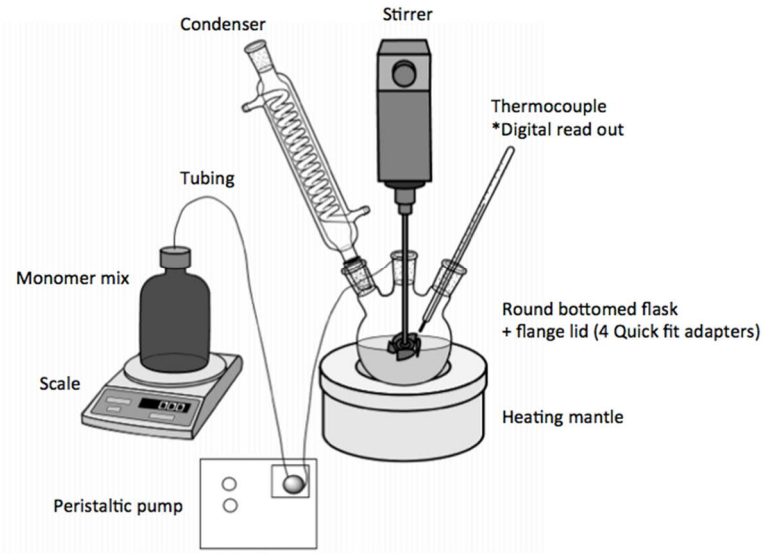


Figure 5-14 - Figure showing reaction set up for small scale polymer synthesis

For larger polymers, all monomers and catalyst were first purified using the methods described in Chapter 4.3 and kept under inert atmosphere in sealed vials.

Trimethylol propane (Lanxess, 0.0505mol, 6.77g) was added to a 100ml round bottom 3 neck reaction flask with phthalic anhydride (Sigma Aldrich, 1.008mol, 149.36g) and ETTPB catalyst (Fisher scientific, 0.1mol%, 0.6509g). They were heated to 140ºC, with overhead stirring and N_2 flow and once the desired temperature was reached, phenyl glycidyl ether (VWR, 1.062mol, 143.87ml) was fed into the reaction through a peristaltic pump (7ml/min, 3.2mm tube, 20min). The heating mantle was removed for the epoxy addition as this reaction was exothermic and it was found that the heat generated by the exotherm was enough to sustain the target process temperature of 140°C without further heating. The reaction was processed for 6 hours, sampling regularly. Samples were tested for acid value content and epoxy equivalent weight. Once the desired acid conversion had been reached, or the acid conversion had stopped increasing, the reaction was stopped, and the polymer was discharged.

5.5 Coatings

5.5.1 Panel preparation

5.5.1.1 Production of the coating

The epoxy functional crosslinker DER 431 was added to polymers of varying functionality for crosslinking. The epoxy was added in a 1:1 equivalence ratio, based on an acid value measurement. The formulations were as follows:

Polymer	Acid value (mgKOH/g)	Polymer weight (g)	DER431 (g)
LW18 (2 functional)	102.57	1.0	0.32
LW17 (3 functional)	110.96	1.0	0.35
LW19 (4 functional)	115.20	1.0	0.36

Table 5-3 - Table showing formulations of the three coating formulations produced

The above mixtures were added to a mixture of ethyl acetate and methyl n-amyl hexane (MnAK) in a 3:1 weight ratio, in a 1:1 mass ratio of solvents to resins (50% NVC or non-volatile content). The solutions were agitated 30 minutes to accelerate the dissolution of the polymers.

5.5.2 Drawdown procedure

Aluminium panels (purchased from Q-Lab, specifications — 3” x 6”, smooth mill finish, type A, alloy 3003 H14), PTFE panels and glass panels were used as substrates to make coatings for mechanical tests. All coatings applied to panels were applied using a drawdown bar of 150µm thickness. Since the solutions consisted of 50% NVC, the dry film thickness would be 50% of the “wet” film thickness and the resulting cured film thickness would be around 75µm.

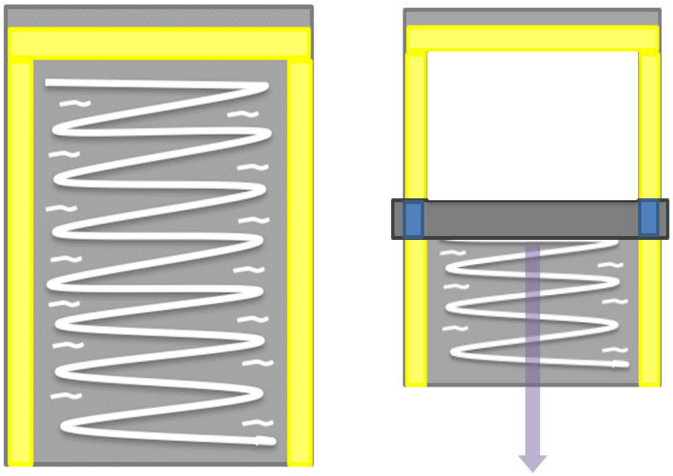


Figure 5-15 - Drawdown procedure

Uncured coatings were placed at the top of the panel and drawn down the panel using the drawdown bar. Excess was removed by pulling the bar off the end of the panel. Solvent evaporation from the uncured coatings on the panels was carried out using different times and different heats – these are explained in chapter 6.3. All panels were cured by leaving the coated panels in an oven set at 160°C for 20 minutes.

5.5.3 Coatings Testing

The cured coatings were characterized for their solvent resistance, adhesion, flexibility, and thermal properties.

5.5.3.1 Measuring Glass transition temperature

To determine glass transition temperature (Tg °C) of the cured films, a Perkin Elmer Differential Scanning Calorimeter (DSC) was used according to the description in section 5.1.5. 10 to 15 mg samples of each film were tested subject to a cycle involving a temperature range between -10°C to 210°C. Heating and cooling rates were maintained at 20°C/min. A heating cycle at the start of the run was required to remove any thermal history. A thermal history is commonly known in literature as an enthalpic relaxation. In polymers, an initial run above the Tg of the polymer, is carried out to allow the polymer to relax from mechanically induced stresses resulting from the production of the material. If this is not carried out, the Tg can be observed incorrectly due to the polymer chains possibly being in a unnatural orientation[128]. A further two

runs were carried out and Tg was determined as the onset of the transition in the third heating cycle. This can be found in detail in Table 5-4 below.

DSC Heat cycle for measuring Tg	
1) Heat from 30.00°C to 130.00°C at 20.00°C/min	Removing thermal history
2) Hold for 1.0 min at 130.00°C	
3) Cool from 130.00°C to -10.00°C at 20.00°C/min	
4) Hold for 5.0 min at -10.00°C	Tg1
5) Heat from -10.00°C to 210.00°C at 20.00°C/min	
6) Cool from 210.00°C to -10.00°C at 20.00°C/min	
7) Hold for 5.0 min at -10.00°C	Tg2
8) Heat from -10.00°C to 200.00°C at 20.00°C/min	
9) Cool from 200.00°C to -10.00°C at 20.00°C/min	

Table 5-4 - Table showing heating and cooling cycle for a DSC measurement of glass transition temperature (Tg)

5.5.3.2 Measuring Adhesion

Crosshatch adhesion test was conducted on the coatings according to ASTM D 3359[129]. Cross hatching is performed to assess the adhesion of the coating to the metal surface upon damage to the coating using a sharp edge. An appropriate cutter is selected, in accordance with the test surface, in this project a 2mm thick cutter was used. The cutter template contains 6 metal lines that contain gaps of 2mm for a cutting edge to be used along. The cutting-edge cuts in between the line, even pressure is used throughout the cut, taking place in one single motion. It is standard to cut lines approximately 4cm long. The cutting edge is then turned to the right by 90° and the procedure is repeated – producing a crosshatch pattern. Tape is then placed onto to the crosshatch pattern on the panel and removed. This allows any small pieces of coating which have been partially dislodged to be removed.

The results were reported as 5B (best) to 0B (worst), depending on the amount of film removed after the tape was removed (Figure 5-16).

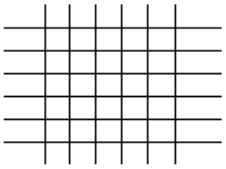
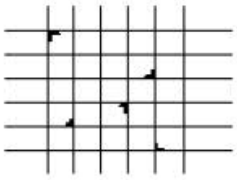
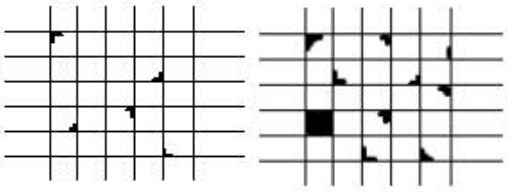
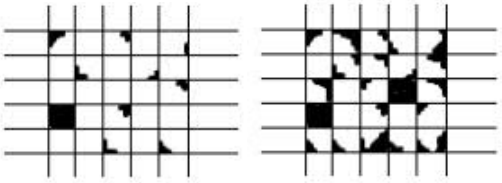
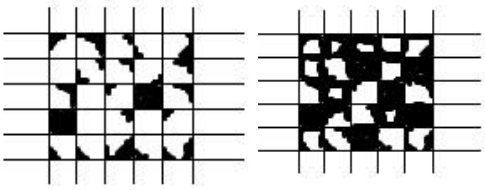
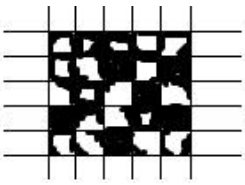
ISO Class:0/ ASTM Class: 5B The edges of the cuts are completely smooth; none of the squares of the lattice are detached.	
ISO Class:1/ ASTM Class: 4B Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5 % is affected.	
ISO Class:2/ ASTM Class: 3B The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5 %, but not greater than 15 %, is affected.	
ISO Class:3/ ASTM Class: 2B The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15 %, but not greater than 35 %, is affected.	
ISO Class:4/ ASTM Class: 1B The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35 %, but not greater than 65 %, is affected.	
ISO Class:5/ ASTM Class: 0B Any degree of flaking that cannot even be classified by classification 4.	

Figure 5-16 - ASTM standard showing the defect ratings

5.5.3.3 Solvent resistance

Methyl ethyl ketone (MEK) double rubs test was conducted per ASTM D 5402[130] to initially assess the extent of crosslinking in the coatings and its chemical resistance. As the solvent penetrates the film, the film will get gradually softer and will tear apart under the shear/rubbing action. A paper cloth was soaked in MEK. Coatings were rubbed using the soaked cloth, for 50 double rubs (100 single rubs) at a constant pace and pressure. The appearance of the coating after the rubs was noted and compared to a standard scale. If the film is removed by the solvent, loses gloss or is softened, the film is considered as not satisfactorily crosslinked. Films which are unaltered, are considered adequately crosslinked[131].

5 = No effect on surface.

4 = Burnished appearance.

3 = Some marring and apparent depression of the film.

2 = Heavy marring. Obvious depression of the film.

1 = Heavy depression in film but not actual penetration to the substrate.

0 = Penetration through the film, to the substrate.

Figure 5-17 - Solvent rub standard pass scale

5.5.3.4 Measuring flexibility

Flexibility of the coating was measured by bending the panels using a conical mandrel (Figure 5-18). Bend testing is a test in which the panel, with coating facing away from the cone, is bent around a specific sized cone and diameter, which is known as the conical mandrel test. The test follows the ASTM D522 method[132], in which the cone radius widens with length ranging from 3mm to 38mm wide, so when the panels are bent, it can provide good information on how much strain the coating can withstand before cracking. The results were reported on a scale of 'no failure', 'tear/stretching observed' and 'delamination of the film' caused during experimentation.

Figure 5-18 - Film undergoing a conical mandrel bend test

5.5.3.5 Measuring microhardness

Microhardness was carried out following the ASTM standard E384[133] using a Fischerscope H100C instrument which has a high accuracy containing a testing force resolution of 0.2uN and a penetration depth resolution of 0.1um. The machine operates by a measuring head, which contains a diamond pyramid indenter (Vickers indenter), gently indenting into the coating. The depth or the force the indenter required to complete the test is measured and analysed.

Measurement and analysis were carried out at room temperature on a WinHCU v4.4 software. A thick polymer film on aluminium slides was held on the indenter's stage and 5 indentations were made at 5 different positions of the slide location being 5 mm apart from each other. Indentation parameters used were a 15 µm deep indentation was performed in 20 s, a creep period of 5 s then the indenter tip was retracted of 15 µm at the same speed then another 5 s creep period was used to finish the experiment. The indenter was a Vickers type tip with a face angle of 136°, a young's modulus of 1.2 GPa and a Poisson's number of 0.07.

5.5.3.6 Measuring UVA resistance

Accelerated UV testing was carried out in an Accelerated Weathering Tester manufactured and supplied by ATLAS. Ultraviolet tubes emitting in the UV-A region of

the electromagnetic spectrum with peak emission at 340nm were used, which provides simulation of sunlight in the critical short wavelength region.

The cycle used was 4 hours of dry U.V. at 55° ± 3°C followed by 4 hours water condensation at 45° ± 3°C, with no UV emissions.

The testing Room are to be sufficiently ventilated and maintained within a temperature range of 20° to 30°C, as measured by thermometers mounted 1500mm above floor level and at least 300mm from any heated apparatus.

Panels were prepared on 6"x3" aluminium Q-panels as described before and placed in the UV panel holders. Panels are required to be placed in the same position when removed and replaced after testing as a specific section is exposed to the UV as shown in Figure 5-19.

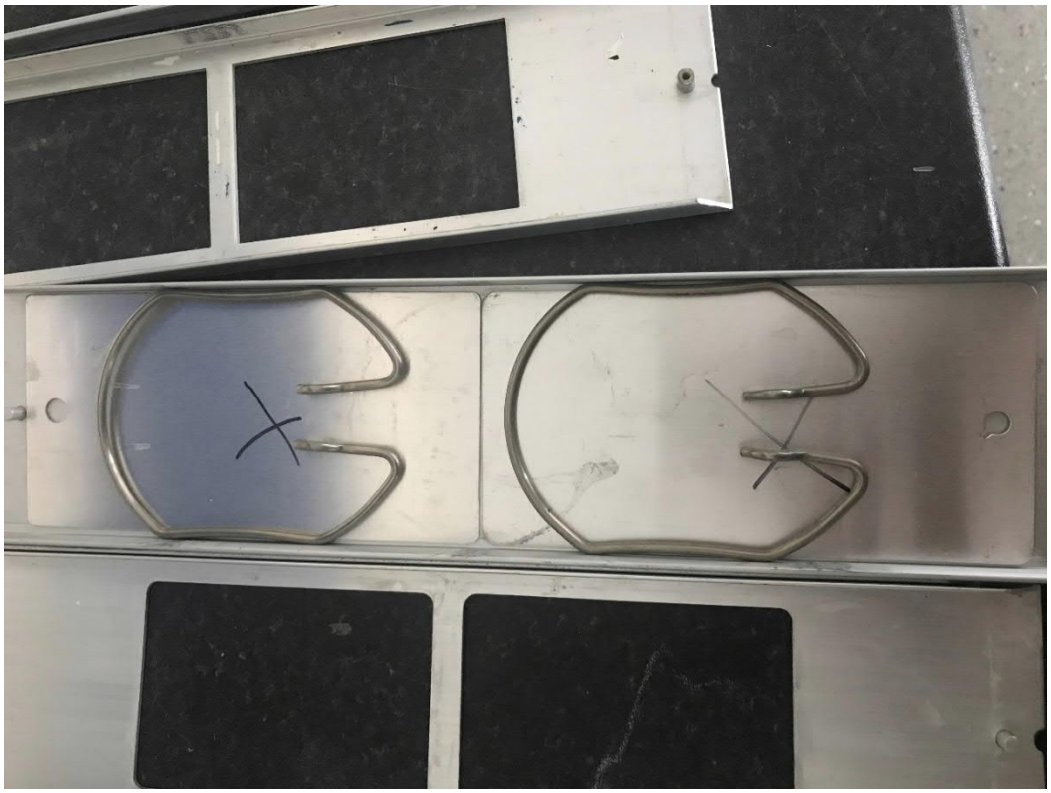


Figure 5-19 - UV panel preparation

To use the equipment, the panels are placed in the Q.U.V. cabinet at the midpoint of the UV cycle e.g. if the UV cycle is 4 hours, insert panels at the 2-hour point, this is to ensure that all panels are introduced at the same point in the cycle. Panels were taken out after specific intervals of time, and examine for chalking, fading, discolouration,

loss of gloss and other film defects before returning them to the UV chamber for further exposure, as necessary. Test panels should be examined towards the end of the dry phase of the test cycle, to prevent coatings being wet which may change coating properties during tests. This testing continues until gloss has significantly reduced, usually 50% reduction.

Once panels are removed from the test chamber at time intervals, the panels are tested for gloss and colour. Gloss was measured with a Rhopoint IQ glossmeter. Gloss was measured at three different angles - 20°/60°/85° angles along with a measure of Distinctiveness of image and haze.

Spectrophotometers are used to objectively measure and validate colours, removing the possibility of metamerism experienced by the person measuring. The spectrophotometer used was a Datacolor 800 Spectro and measurements were analysed using Datacolor Tools version 2.0.11.

The reflectance is measured for the full visible spectrum. This is done by dispersing the gathered light beam into spectral colours (using a prism or grating) and projecting the colours onto a photodiode array. Each part of the array measures a different wavelength of light.

Measurements are gathered and differences are measured between the samples if desired. The Datacolor software measures the differences in values such as DL which indicates how light or dark the coating has become to DH which indicates the change in shade of a colour. For understanding yellowing, the software can give a value for Db, which is the difference on the blue – yellow scale. They are also shown on a graph in the software, in which the Db value is the vertical y axis, with a more negative indicating more blue in colour and a more positive value indicating a more yellow colour, to give an indication of trends present.

Panels are placed in the clamp and the position circled in pen to be able to measure the same part of the panel for each measurement.

Chapter 6 –
Coating Relationships

6 Coating Relationships

6.1 Network crosslinking system

Initial testing on the crosslinking capabilities of the functional polymers was carried out on polymeric samples produced earlier in the project. These were formulated to contain the same molecular weights of the various chain growth monomers (i.e. anhydride and epoxide) to ensure consistency across the polymeric products. However, by the varying the functionality of the initiating multifunctional alcohol (i.e. di-ol, tri-ol and tetra-ol), number of terminal functional groups on the final polymer can also be varied. The final molecular weight of the resulting polymer also varies but in a predictable way (Figure 6-1).

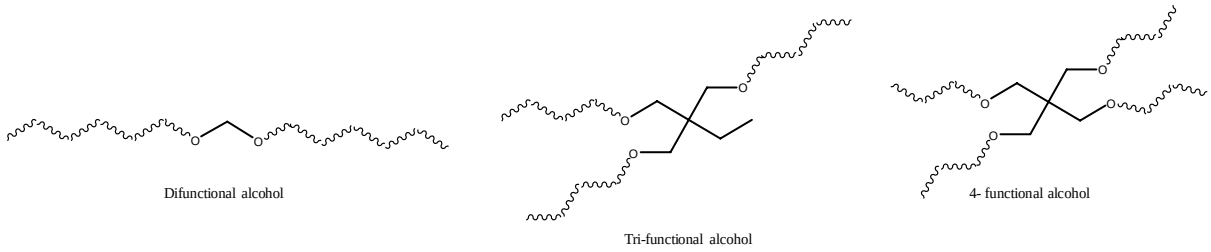


Figure 6-1 - Differences in functionalities of 2,3 and 4 functional initiators.

Formulation	Functionality	% acid reacted	Expected Mn (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI
LW17 - TMP/PA/PGE – 1:6:3	3	100.7%	1473	1440	1593	1.10
LW18 - PDO/PA/PGE – 1:4:2	2	95.4%	968	996	1091	1.09
LW19 - Penta/PA/PGE – 1:8:4	4	94.2%	1921	1691	1970	1.16

Table 6-1 - Analysis of low molecular weight polymers produced in Chapter 4 using 2,3 and 4 functional initiators

New polymers were synthesised using the optimised polymerisation process developed within this research project (see experimental chapter 5 for details). Upon analysis using established analytical techniques including GPC for molecular weight analysis and functional group titrations for end group analysis showed that polymers produced using these optimised processing conditions were consistent in their analytical result. This overcomes the lower than expected molecular weight concerns when using these new polymers for the testing section of this project. Polymers were analysed for confirmation as shown in Table 6-2.

Formulation	Functionality	% acid reacted	Expected Mn (g/mol)	Actual Mn (g/mol)	Actual Mw (g/mol)	PDI
LW17 B2 - TMP/PA/PGE – 1:6:3	3	99.3%	1473	1390	1607	1.15
LW18 B2 - PDO/PA/PGE – 1:4:2	2	104.6%	968	868	967	1.11
LW19 B2 - Penta/PA/PGE – 1:8:4	4	102.5%	1921	1492	1682	1.12

Table 6-2 - Analysis of newly synthesised low molecular weight polymers produced

The three polymers were synthesised using 2,3 and 4 functional initiators namely 1,3 propane diol, trimethyl propane and pentaerythritol respectively (Figure 6-1). This was to examine the influence that these initiators of varying functionality would have on the polymer properties and resulting film properties. The polymers shown in Table 6-2, also show low PDI measurements typical of the polymerisation developed within this project. It can be seen that, the LW17 (3-functional polymer), yielded a PDI of 1.15, with the 2 and 4 functional polymers showing lower PDI values at 1.11 and 1.12 respectively, which is low for a polyester polymer as most polyester polymers have a PDI in the

region of 2-3 due to following a step growth reaction[1]. Acid value measurements can be seen close to 100% suggesting completion or near completion of the synthesis.

In order to cure these polymers, several cross-linkers were considered, including an epoxy known as ARALDITE PT910 (Figure 6-2). This is a crosslinker commonly used in coatings applications[6], particularly for the use in thermoset coatings based on carboxylic acid functional polyesters. As can be seen from Figure 6-2 and Figure 6-3, this material is made from a di- and tri- functional epoxide, therefore an undisclosed amount of trimellitic acid triglycidylester is also in the sample (Figure 6-3)[134]. To test if this crosslinker was suitable as a crosslinker, an MEK (methyl ethyl ketone) resistance test was performed on the cured coating (see section 5.5.3.3 for more details)[130]. Thermoset coatings that have reacted beyond the gel point should have low solubility in organic solvents and be mechanically more robust and thus perform well in this test.

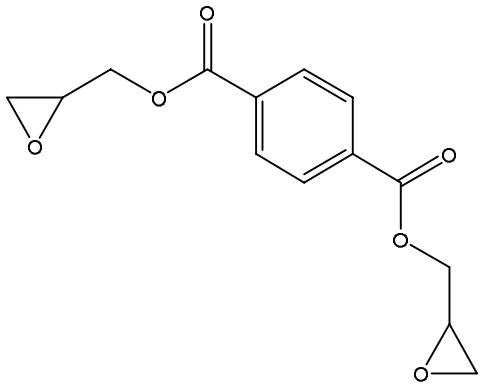


Figure 6-2 - Structure of terephthalic acid diglycidylester – main component in Araldrite PT910

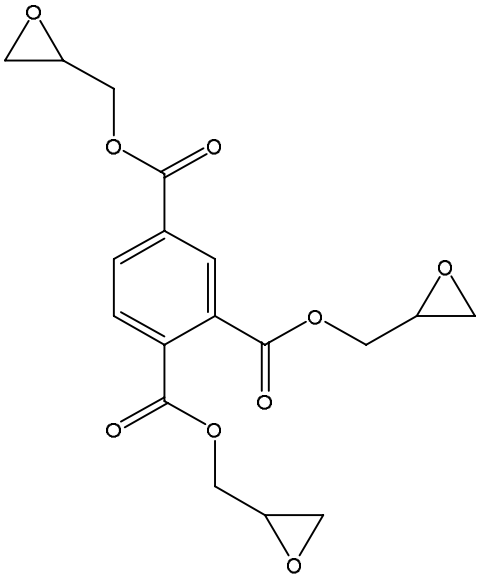


Figure 6-3 - Trimellitic acid triglycidylester – impurity in Araldrite PT910

Despite a theoretical conversion at gelation below 100% (according to the gelation theories by Flory and Stockmayer) in all 3 polymers It became apparent that this crosslinker did not provide enough functionality to give a sufficiently cross-linked network, which was tested with the 3 functional polymer system. This was confirmed through the MEK resistance test (as explained in 5.5.3.3). In this case, the coating was completely removed from the panel, indicating no cure had occurred. The panel shown below in Figure 6-4 is the panel discussed, once removed from the oven. It was found to be sticky to touch, therefore possibly not fully cured, with no defects observed.

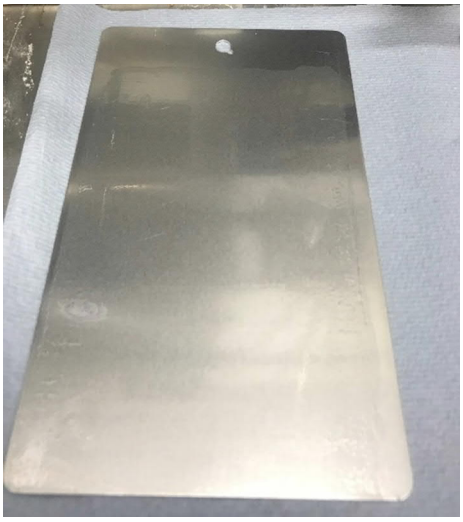


Figure 6-4 – Q-panel coated in LW17 B2 - 3 functional polymer + PT910 crosslinker after 'cure'. 1:1 ratio, stoved at 160˚C for 20 minutes.

As a result of this, DEN431 was used. This is a 3 functional novolac epoxy (Figure 6-5) and contained no solvent. This provided adequate crosslinking for the polymers tested, which is explained in the section 6.2.

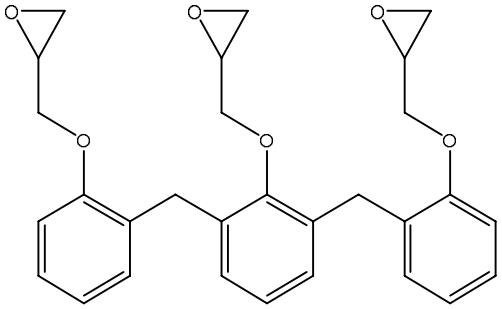


Figure 6-5 - Structure of DEN431

6.2 Curing schedule

To understand what curing schedule was required, a gel time test was carried out. This involves adding the test mixture to a heated plate at a set temperature and mixing until the sample has lost all fluidity (a gel). The time taken to gelation is measured, and the test repeated in triplicate for accuracy. Polyester resins tend to yellow, specifically carbonyl – epoxy reactions at 180°C[79], so the gel times were performed at 160°C. This test gives enough data to indicate whether the formulation will cure as a film, because if a gel occurs quickly, and under the planned oven curing time, this will indicate a full cure is possible in the oven.

Polymer + DEN431 + 0.03mol% ETTPB +50% MnAK at 160°C	Polymer functionality	Gel time (avg. seconds)	Gel time (avg. Minutes)
LW17 B2	3	310	5:10
LW19 B2	4	195	3:15

Table 6-3 - Table showing gel time of cured samples when catalyst is added

With catalyst added to the blend, a very fast gel time can be observed at 160°C (Table 6-3). To understand the curing schedule of the coatings without catalyst, based on the speed of curing with catalyst, and the issue that catalyst may induce yellowing, samples were tested without catalyst also.

Polymer + DEN431 + 50% MnAK at 160°C	Polymer functionality	Gel Time (avg. Seconds)	Gel time (avg. minutes)
LW18 B2	2	1120	18:40
LW17 B2	3	745	12:25
LW19 B2	4	645	10:45

Table 6-4 - Table showing Gel times for all functional systems at 160oC in MnAK with no catalyst

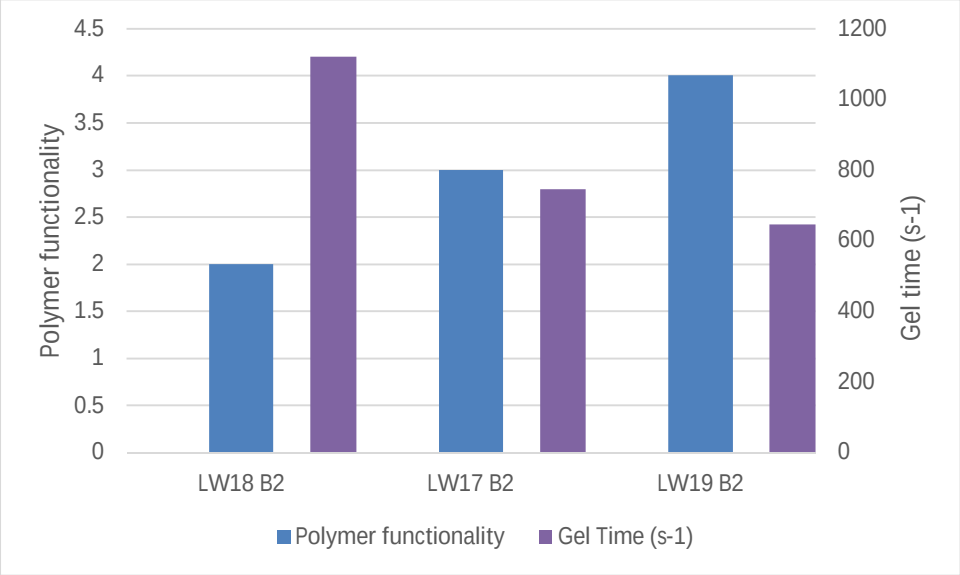


Figure 6-6 - Graph showing a change in gel time with a change in polymer functionality

The gel time test shows that the cure temperature of 160˚C is sufficient for all formulations as the final panels are stoved for 20 minutes when no catalyst is added. As these samples shown in Table 6-4 contain no catalyst, any yellowing of the resin film at temperature would not be confused with yellowing caused by the catalyst. However, as the curing was considerably quicker for samples containing catalyst, catalyst was added to the coatings for testing.

It is worth noting, that the gel times observed with catalyst, are extremely fast for coating curing times at lower than 200˚C. This is very interesting, and a possible route to low energy curing coatings. This is discussed further in the conclusion – chapter 7, Section 7.2

6.3 Film formation and method development

Paints and coatings can be applied to surfaces using many different methods. Standard paints for the home DIY use are applied using a brush or roller. They can also be applied using a spray gun in some circumstances[135]. In industry, when testing coatings these can also be applied with a brush if a wet paint is being applied. For this project, a binder, crosslinker and catalyst is all that is to be applied. This is because relationships between the polymer functionality and the coating properties can be more easily observed without introducing additives to the coating. If a binder with a particular functionality is giving inadequate flow to a coating, with no additives this can

be observed however if a flow aid had been added to the formulation, this would not be observed and possible significant information could be lost. Due to the nature of the materials used for this testing and quantities of materials available, the drawdown method was used. This requires a quantity of sample to be applied to the top of the panel, and a drawdown bar (of a specific micron depth) is then dragged through the sample, and down the panel to produce an even film[131]. This method is explained in further detail in chapter 5 section 5.5.2.

Initially it was decided to make a sample containing a 1:1 equivalence of acid: epoxy, with a 0.03mol% catalyst loading of ETTPB using the drawdown method. Liquid paints often contain a solvent or a reactive diluent which reduces viscosity, helps with mixing and allows for easier application. This could be a common organic solvent, such as xylene or butanol, or water for water-based coatings. If no solvent or additives are used, a better understanding of the chemistry could be acquired, therefore the first attempts of this method development were made using only the polymer, the crosslinker and the catalyst in bulk (i.e. without solvent).

As the binder and catalyst used were solid and the crosslinker is a viscous liquid, heat was applied to the panel to lower the viscosity and ease the application.

The first attempt was carried out using LW17 B2. It gave rise to many surface defects and the flow across the panel surface was poor. Once stoved, the flow was not improved, and the panel shown in Figure 6-7 as the resulting film. It was unclear as to whether the poor film appearance was due to some degree of pre-reaction between the polymer and crosslinker before the panel was stoved or whether this high viscosity was inherent to the polymer itself, it could also possibly mean that the flow is acceptable but air could be trapped under or in the film due to the application technique and the viscosity of the polymer was not low enough to release these.

Figure 6-7 – Q-panel coating in LW17 B2 + Novolac crosslinker using 1:1 equiv. of Acid: epoxy with 0.03mol% catalyst applied with heat and no solvent, oven heated at 160˚C for 20 minutes.

Due to the difficulty in application, and the poor appearance of the film, it became apparent that a solvent was required to help with flow and viscosity on application to produce a film which was more reliable for testing results, as any defects may affect any physical testing of the coating

Due to the issues with flow, an equal mass of solvent was added due to the nature of the sample, reducing the concentration of reagents to 50% of the applied sample. As the binder used is a solid and the crosslinker is a viscous liquid, therefore ideally if dissolved in a solvent, the application would be a much easier process as heat alone was not allowing a sufficient flow.

Several solvents were tested with the formulations but few successfully dissolved the mixture completely. Dichloromethane (DCM) dissolved all the formulation components well at room temperature (Figure 6-8), but due to the hazardous nature of the solvent a less hazardous solvent was sought. Xylene dissolved the components when heat was applied, but at least one of the components precipitated out of solution when it was cooled, so the mixture was heated just before the draw down was performed. Thus, formulations containing LW18 B2 polymer, DEN431 crosslinker and ETTPB catalyst were dissolved in xylene to give a 50:50 wt.% solution (Figure 6-9).

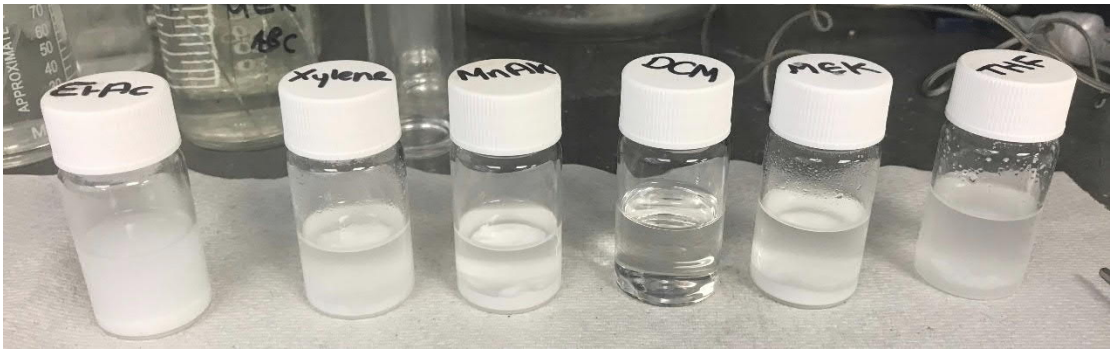


Figure 6-8 - Solubility of polymer crosslinker blend in varying solvents. Solvents from left to right: EtAc (Ethyl Acetate), Xylene, MnAK (Methyl n-iso amyl ketone), DCM (Dichloromethane), MEK (Methyl ethyl Ketone), THF (Tetrahydrofuran)

Figure 6-9- Q-Panel showing LW18 (2 functional binder) + DEN431 in a 1:1 mol ratio +0.03mol% ETTPB + 50% xylene, stoved at 160˚C for 20 minutes.

Figure 6-10 - Q-Panel showing LW19 (4 functional binder) + DEN431 in a 1:1 ratio +0.03mol% ETTPB + 50% xylene, stoved at 160˚C for 20 minutes.

Attempts using 2 (Figure 6-9) and 4 functional (Figure 6-10) binders are shown above in xylene. As can be observed, the films have a considerable amount of bubbling. It was

believed that because it was a heated draw down, the xylene could not evaporate quickly enough through the coating before the film hardened, thus causing the entrapped bubbles.

These panels were tested through a bend tester, which is a bend applied to the top corner of the panel by hand to assess the adhesion and flexibility of the coating. As can be seen in Figure 6-11, the film was not flexible and cracked easily. The adhesion however seemed very good, as no delamination of the film occurred.

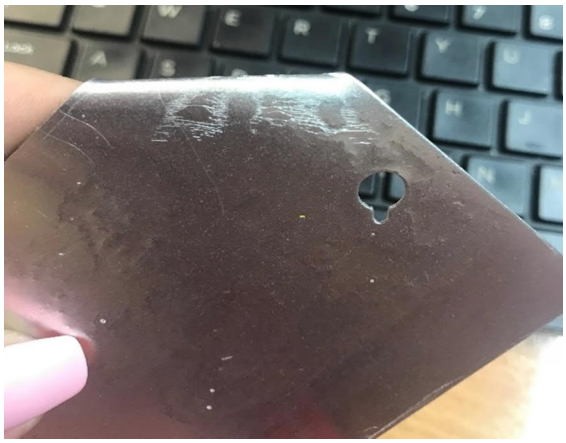


Figure 6-11 - Bend test of the Q-Panel showing LW19 (4 functional binder) + DEN431 in a 1:1 ratio +0.03mol% ETTPB + 50% xylene, stoved at 160˚C for 20 minutes.

As bubbling was repeatedly observed, all panels were left overnight before being oven heated to allow all the solvent to evaporate. As initial solvent investigations showed, the blend crashed out on cooling in xylene and the components would not be adequately mixed.

Other solvents which were initially tested as shown in Figure 6-8 which also precipitated during cooling, were also tested. This was due to the samples being soluble at high temperature and therefore if the mixture would remain clear and soluble hot before and during cure, the cured film may remain homogeneous and give rise to a uniform coating. Coatings were drawn down at elevated temperature and using a preheated sample to allow flow but it was concluded they were curing during drawdown which was producing defected films. It was also observed that the solvent

was still leaving the film when curing due to the holes in the film. This suggested incomplete solvent evaporation prior to the drawdown.

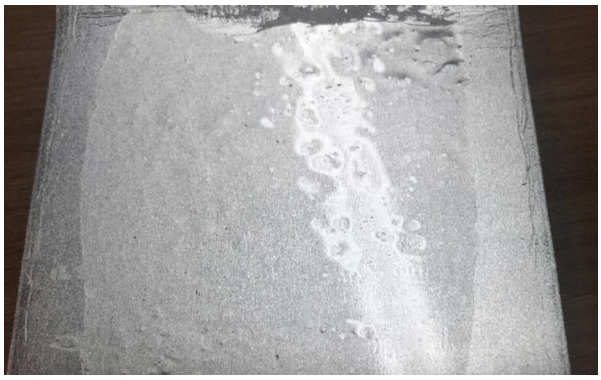


Figure 6-12 - Film of LW19 B2 (4 functional system) + DEN431 in a 1:1 ratio, with 0.03mol% ETTPB in 50% THF, stoved at 160˚C for 20 minutes.

Figure 6-13 - Film of LW19 B2 (4 functional system) + DEN431 in a 1:1 ratio, with 0.03mol% ETTPB in 50% MEK, stoved at 160˚C for 20 minutes.

As shown in Figure 6-12 and Figure 6-13, small particles of undissolved material could be seen. It was thought that this may be the catalyst if so, that an insufficient quantity of catalyst was available to facilitate the curing process due to solubility issues. As a result of this, and using knowledge gained from Table 6-4, this curing process can be carried out without a catalyst despite having longer curing times. On removing the catalyst, it can be seen in Figure 6-14 that the small undissolved particles on the coating surface, have disappeared.

Additionally, removing the catalyst would also allow for use of other solvents due to the catalyst not dissolving in some of the options. A mixture of ethyl acetate and methyl iso amyl ketone dissolved all binders and crosslinker and remained dissolved on cooling.

Figure 6-14 - Q-Panel showing LW19 (4 functional binder) + DEN431 in a 1:1 ratio + 50% blend of EtAc/ MnAK, stoved at 160°C for 20 minutes, after 24 hours of solvent evaporation

The panel (Figure 6-14), which was left for 24 hours before stoving to allow solvent evaporation, showed a small number of defects, but considerably less than observed in all films produced thus far. The defects observed were small holes in the coating. This could be due to solvent evaporation, indicating the panels were not left long enough to allow all solvent to evaporate. To understand if this was the cause, the panels were remade and left for longer to evaporate (Figure 6-15).

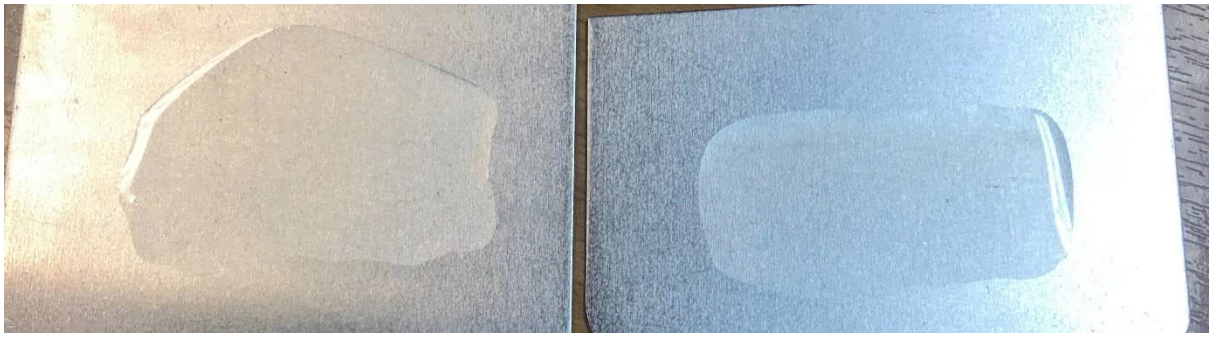


Figure 6-15 - Q-Panel showing LW17 B2 (left) and LW19 B2 (right) + DEN431 in a 1:1 ratio + 50% blend of EtAc/ MnAK, stoved at 160°C for 20 minutes, after 48 hours of solvent evaporation

The same formulations were then applied to panels and were left for 48 hours before stoving as shown in Figure 6-15. These panels produced films with minimal defects compared to those left for 24 hrs before stoving showing that the solvents required longer evaporation time before curing the coatings. The adhesion of these films appeared to be extremely good as the coating could not be removed from the panel to perform analysis.

6.4 Free films

Free films were required in order to perform DSC and DMA testing. As the adhesion of the coatings on metal panels was high, several methods were investigated to create un-supported samples of films made from the cured polymers. Small chips of film could be removed from bend tests on certain polymers but other polymers adhered so well to the panel that they could not be removed. For crosslink density testing, a free film of a certain dimension was required to be produced for the testing. Many coatings are flexible and once removed are easily cut for DMA testing. However, the coatings produced above in Figure 6-15 appeared too brittle so free films made separately were required.

6.4.1 Glass slides

Glass slides were initially tested as curing substrate, as it was thought that the coatings may not adhere as well to this surface. However, adhesion of the test polymers was as strong to the glass substrate as to the aluminium panels.

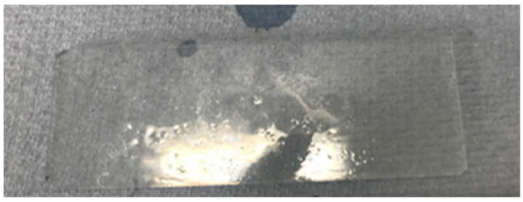


Figure 6-16 - Glass slide containing LW18 B2 + DEN431 in a 1:1 ratio + 50% blend of EtAc/ MnAK, stoved at 160˚C for 20 minutes.

Figure 6-17 - Glass slide containing LW18 B2 + DEN431 in a 1:1 ratio + 50% blend of EtAc/ MnAK, stoved at 160˚C for 20 minutes.

It was noted with these slides, the surface appearance was lower in comparison to aluminium, which may have been due to a difference in the film thickness. It was also observed, the coating had excellent adhesion, and therefore this method could not be used for free films.

6.4.2 PTFE slides

The second attempt at trying to remove the coating, was to use a PTFE slide as PTFE provides a different surface tension to aluminium. Fluorinated surfaces provide a lower surface energy and a lower adhesion[136]. As is shown in Figure 6-18 below, the film had a very large dewetting. The adhesion was low as expected but as the film did not fill the dimensions of the slide, it could not be used.

Figure 6-18 - PTFE slide containing LW17 B2 + DEN431 in a 1:1 ratio + 50% blend of EtAc/ MnAK, stoved at 160˚C for 20 minutes.

6.4.3 Release agents

The third attempt at removing the film was by using a pre-treatment called marbocote 227CEE. Marbocote 227CEE is an advanced polymeric resin in a non-chlorinated organic solvent blend and is used as a release agent for films.

Figure 6-19 – LW17 B2 + DEN431 in a 1:1 ratio + 50% blend of EtAc/ MnAK, stoved at 160˚C for 20 minutes coating on a panel containing Marbocote release agent

As shown in Figure 6-19, a considerable wettability issue can be observed when the droplets which are on the panel have cured. These droplets can be peeled off easily, however film of the necessary dimensions could not be produced via this method.

6.4.4 Silicone moulds

As silicone is known to have low adhesion to materials, they are regularly used to cast free films for testing requirements. Therefore, silicone moulds were made to produce films with the correct dimensions required for DMA analysis (1cm width).

Figure 6-20 - Process of making silicone moulds to be used for making free films

A blend of LW17 B2 polymer and DEN431 crosslinker were added to the moulds without solvent, as adding solvent to a free film could result in cracking inside the film. As shown in Figure 6-21 below, bubbling throughout the film after cure (160°C for 20 minutes) was an issue. As the films produced are to be used for DMA testing, it must be free of bubbles or any other defects.

Figure 6-21 - Free film of LW17 B2 + DEN431 in a 1:1 ratio with no solvent, stoved at 160°C for 20 minutes cast in a silicone mould showing a bubbling defect

Light vacuum was added to remove bubbles. As shown in the moulds below (Figure 6-22), this was a success in removing bubbles but it also removed the coating partially. As it cannot be confirmed if this was both polymer and crosslinker removed equally, or whether one has been more removed than the other affecting the stoichiometry, this could not be used as a method. It may equally just be a dewetting problem, in which no coating has been removed it has just moved to the edges of the mould.

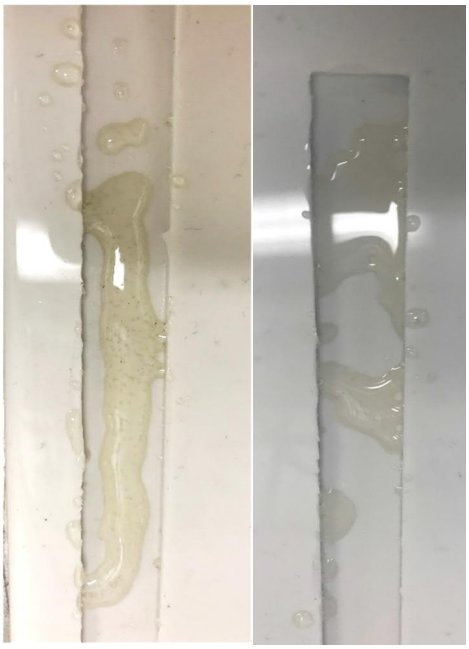


Figure 6-22 - Moulds after light vacuum showing LW18 B2 (left) and LW17 B2 (right) + DEN431 in a 1:1 ratio with no solvent stoved at 160˚C for 20 minutes

As these moulds were larger than what was required for a DMA measurement, smaller moulds were made. It was thought that if the film was thinner, the bubbles could leave the film more easily.

Figure 6-23 - Smaller moulds before cure showing LW18 B2 (left) and LW17 B2 (middle and right) + DEN431 in a 1:1 ratio

The moulds were left for 48 hours under ambient laboratory conditions to allow the solvent to evaporate, to allow for any solvent to evaporate. As can be seen in Figure 6-23, the films looked smooth and bubble free after 48 hours, so were placed in the oven to cure. Figure 6-24 below shows the film appearance after cure.

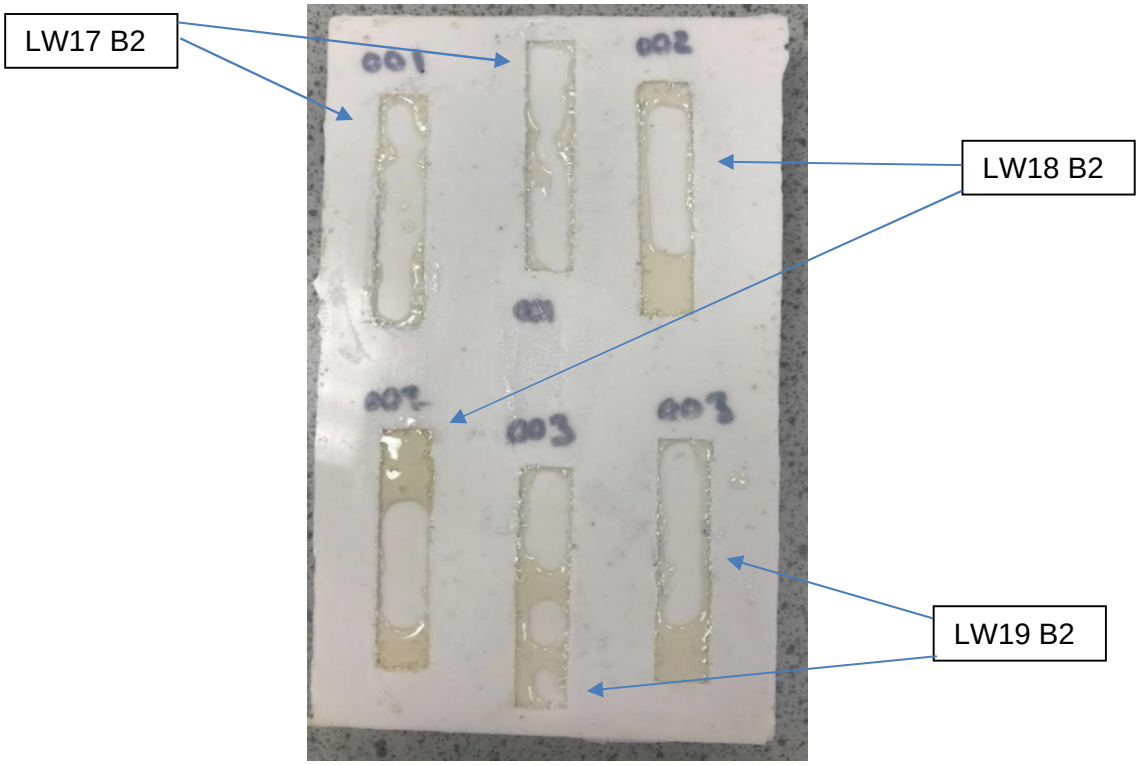


Figure 6-24 - Small moulds after cure Moulds after light vacuum showing LW17 B2 (top left and top middle), LW18 B2 (top right and bottom left) LW19 B2 (bottom middle and bottom right) + DEN431 in a 1:1 ratio in 1cm wide moulds

As can be seen from Figure 6-24 the films have reduced considerably. A possible conclusion from this was the solvent does not release sufficiently when left to evaporate, or it may be a dewetting issue when stoved as films look thinner before stoving. These samples are considerably smaller and were left for 48 hours as previous samples were, so dewetting is the more likely option. A slight yellowing can also be observed, which is expected with polyesters due to chromophores present.

As the blends of polymer and crosslinker were free flowing when preheated at 100°C but were not curing (confirmed earlier by DSC), a possible option was to mix the blend under heat once all solvent had evaporated to attempt to remove the residual defects (bubbles) manually. The 2 and 3 functional polymers (LW002 B2 and LW003 B2 respectively) were very easily mixed with the crosslinker. Figure 6-26 below shows the majority of bubbles were no longer present after stoving at 160°C temperature. The 4 functional resin was more difficult to mix, presumably as the Tg of the resin was higher. As this is expected to have a higher crosslink density it was tested by DSC to confirm it was not curing and the difficulties in mixing observed were due to the melting point being higher than the others due to the more branched structure. From the DSC

(Figure 6-25) an exotherm can be observed and therefore can be concluded that the coating was able to react, therefore not fully cured, so that the higher melting point was the most probable explanation for the behaviour observed.

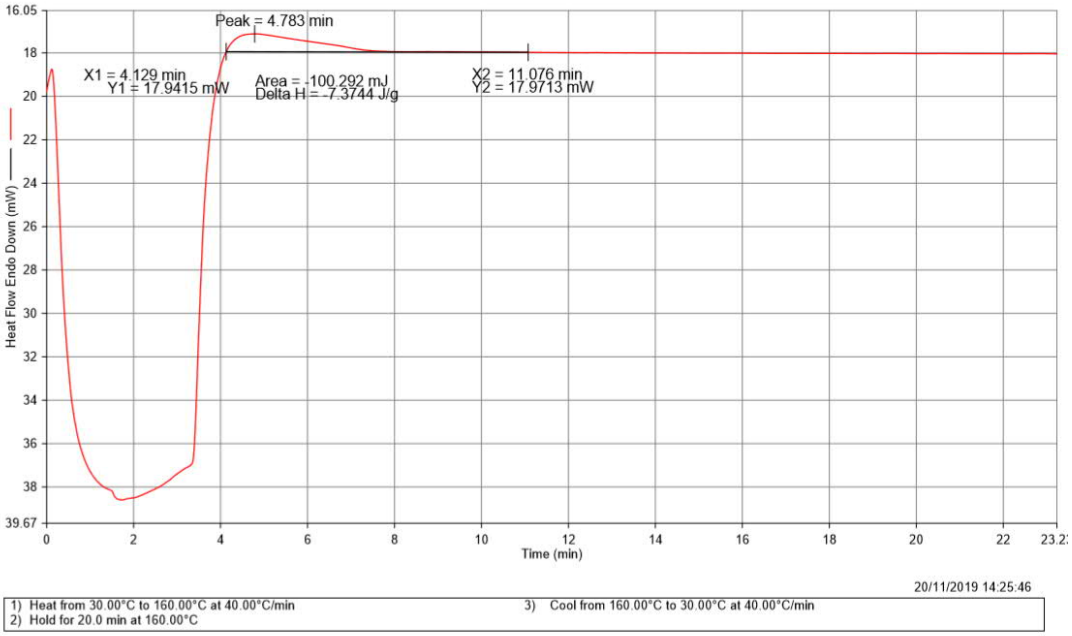


Figure 6-25 – DSC trace showing LW19 B2 producing an exotherm after being drawdown by heat, confirming a curing reaction had not occurred. The large dip is due to rapid heating from 30°C to 160°C at 40°C/min. At 4 minutes, it is held at 160°C for 20°C, at which point an exotherm is observed, with a peak of 4.783 minutes, and ending at 11.076 minutes

The blend of polymer (LW19 B2) and crosslinker still mixed sufficiently to remove most of the bubbles. Unfortunately, as observed in Figure 6-26 some bubbles are still present, generally around the edges of the free film. As these samples are to be used in DMA, the results from this testing would be inaccurate, as defects are present.

Figure 6-26 - Larger moulds after cure and sufficient mixing when hot. LW18 B2 (left) and LW17 B2 (right) + DEN431 in a 1:1 ratio

An idea of trying to add a sample of the blend to a piece of heatproof tape applied to a panel was tested. This was because the bubbles seemed to appear of the sides of the silicone moulds, so on tape no deep side edges would be present.

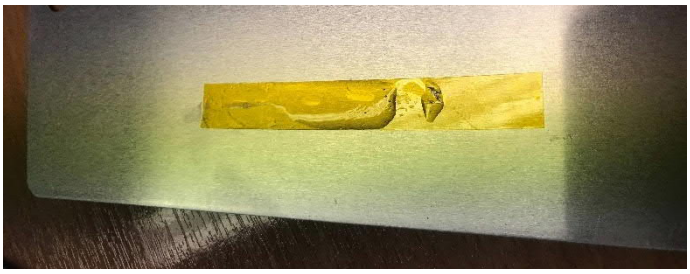


Figure 6-27 – LW17 B2 + DEN431 in a 1:1 ratio on heat proof tape placed on an aluminium Q-Panel before cure.

The coating was applied to the tape at 150micron thickness and then the tape moved to a different position on the panel. This was to remove any excess overlaying the edges of the tape, to prevent it sealing to the panel.

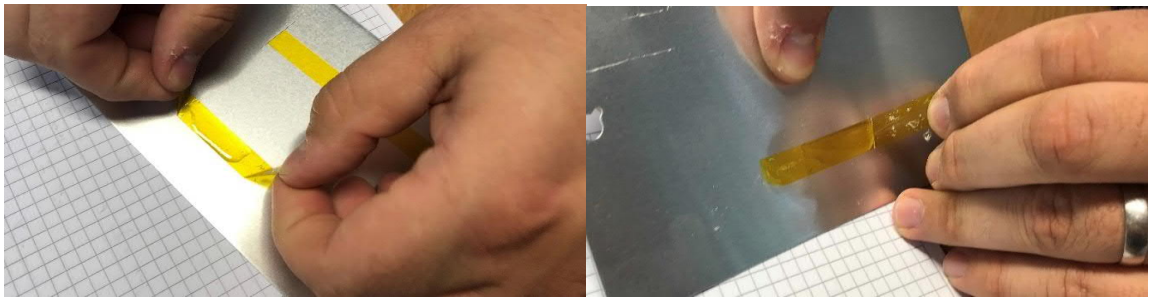


Figure 6-28 – LW17 B2 + DEN431 in a 1:1 ratio on heat proof tape placed on an aluminium Q-Panel after cure showing how brittle the coating was during tape pull off

As can be seen in Figure 6-28, the coating was very brittle and started to crack as soon as the tape was removed.

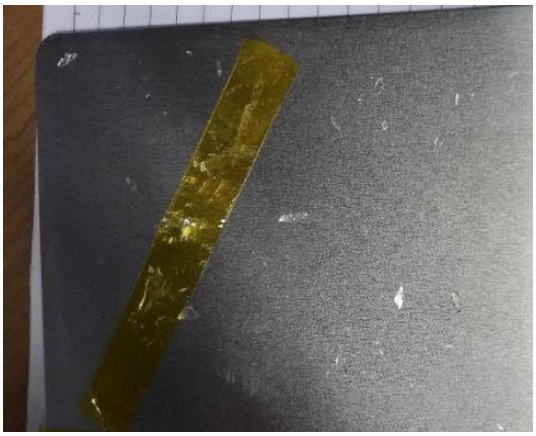


Figure 6-29 – LW17 B2 + DEN431 in a 1:1 ratio on heat proof tape placed on an aluminium Q-Panel after cure showing film cracking on removal of the tape

As the coating is very brittle, using the same technique as with the previous test, heatproof tape was added onto the top of a silicone mould. This was using the idea; the mould is very flexible and the coating may possibly be able to be taken off with considerably less cracking.

Figure 6-30 - LW17 B2 + DEN431 in a 1:1 ratio coating on heat proof tape placed on heatproof tape on a silicone mould before cure

Figure 6-31 – LW17 B2 + DEN431 in a 1:1 ratio cured coating on heatproof tape

Once cured, the tape lifted from the silicon mould, as can be observed in Figure 6-31. This made it very easy to remove from the mould, however the coating was still very brittle.

Figure 6-32 – Heat proof tape + coating removed after cure

The coating was removed very slowly and carefully from the tape, however the coating cracked very easily. The photos shown in Figure 6-33 are the resulting crosslinked coating. There are no defects, and shows a very clear coating. Unfortunately these pieces of sample were approximately 1cm in size and are too small to be tested in DMA as strips of 4 cm in length were required.

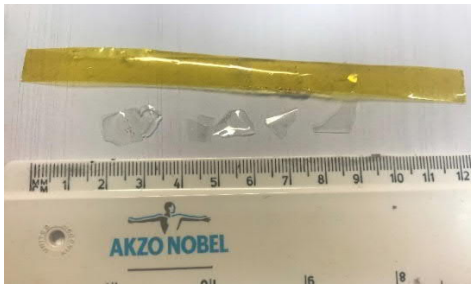


Figure 6-33 – LW17 B2 + DEN431 in a 1:1 ratio coating once removed from tape

Overall, no suitable solutions were found to obtain a free film of any of the coatings, due to bubble defects and cracking.

6.5 Testing

6.5.1 Tests performed

In the coatings industry, many testing methods are required to understand how the coating will perform in-service. Coatings can be made specifically for different purposes; however, all coatings must pass a number of tests to be able to withstand the stresses under which they will be exposed. These tests are also very useful to understand the relationships between the polymer structure, network structure and the overall performance of the coating.

For this project, several tests were to be performed in order to understand how changing the functionality of the binder can affect the coating. Changing the functionality of the initiators and so of the polymers would change the network crosslink density. Therefore, what is being measured ultimately is the difference between the network structure and the coating performance in each test carried out.

The majority of coatings will experience a force of some sort applied to them in their lifetime. There are many different mechanical tests which can test different types of stresses such as compression, elongation or bending. Some tests to measure these are direct (compression) and reverse impact testing (elongation), conical mandrel testing and simple bend tests (bending). If a coating applied to steel is damaged, this results in the bare substrate exposed to the atmosphere. If this occurs, this will leave a rapid pathway for materials responsible for the corrosion (water, oxygen, and various chemicals) to the substrate, and if the coating has a poor corrosion resistance, either could result in the coating having a short lifespan[137]. Therefore, in many cases, dependant on end use, corrosion resistance testing is another test which is carried out regularly.

Adhesion testing measures the strength of the bond between the coating and the substrate. This can be measured via a crosshatch test in which the panel is damaged through scribing and then the adhesion is measured by application of a tape, which is pulled off and any displaced coating removed.

Chemical resistance testing can be made specific to the end use. For example, coatings used for the inside of cargo holds on ships (tank linings) need to be resistant to many types of potentially aggressive and corrosive substances, such as crude oils, food products and solvents. Coatings for household use, are less likely to be in long term contact with such corrosive chemicals, and therefore less intensive testing needs to be applied to this type of coating. Tests carried out can include simple solvent rub tests[130], or more aggressive tests such as swelling experiments[138].

Other testing on coatings are looking at the surface aesthetics which can be important to many markets of the coating industry. Testing of this type can include gloss measurements[139], colour measurements, DOI and thickness measurements[140]. These tests are generally carried out at the beginning and end of many other test methods such as UV testing and humidity testing. UV testing is used for coatings which will be placed in any sunlight, direct or indirect, and will undergo different levels of UV testing depending on the final use[141].

Finally testing the network of the coating is critical for any polymer research. This is usually tested through DSC (Tg) measurements and DMA testing to give the Crosslinking density. These tests are heavily relied upon in R&D to understand the coating on a molecular level.

6.6 Understanding influence of polymer functionality on coating properties

Testing was carried out to understand the relationships between coating properties and the change in functionality of the polymer. Theoretically, the polymer functionalities investigated were 2,3 and 4 based upon the initiators used. Acid value is a good indicator of the extent of a reaction, and from the acid values previously given in Table 6-2 (section 6.1) it can be observed, they are not reaching completion. This may be due to measurement error due to acid values being obtained through titration, but it could also give indication the acid functionality of the polymer is not precisely 2,3 and 4. If it was lower functional than expected, some strands would be 2 functional and some strands would be 1 functional, which would reduce the chances of complete crosslinking, producing a gel.

A more relatable measurement to estimate the polymer functionality and the absence or presence of a network is to measure a gel time on the sample and apply relationships of the gel time and the coating property through this, as this is a measure of reactivity which is inversely related to the site average functionality. Gelation time is an important measure to have when understanding the polymers network formation. A gel time gives the time in which it takes the network to form and reach its 'gelation point' at which, a covalent network has been formed, also known as a p_{gel} which can be calculated through the Flory - Stockmayer equation[142].

$$p_{gel} = \frac{1}{\sqrt{(r(F_a - 1) * (F_b - 1))}}$$

Equation 6-1 - Flory - Stockmayer equation used to calculate 'Pgel' which provides the extent of reaction the polymer will reach a gelation point (r = stoichometry, f1 = functionality of reactant 1, f2=functionality of reactant 2)

The p_{gel} as described in the equation will give a % conversion value, in which the resin will reach gelation. When crosslinking starts between the polymer and the crosslinker, the viscosity starts to increase. At some point, the viscosity rapidly increases, the mixture becomes elastic and rubbery and this is classed as 'gelled'[143]. Crosslinking can continue beyond this point and the polymer will become insoluble. The length of time it takes to reach the gel point will differ depending upon the functionality of the polymer and the density of the crosslinks required to form the network. The gel times were measured for each formulation and reported in Table 6-4. These gel times indicated a large increase in time between the formulations containing 2 and 3 functional polymers, but a smaller increase in time between the formulations containing 3 and 4 functional polymers, which could indicate the 4 functional is not exactly 4 functional. Because of this, it is a more relevant test, if relationships between gel time and coating property are formed with these gel times instead of a theoretical functionality.

The reference used for this testing, was a standard commercial powder formulation called OZ014GF. It is a clear coat with a polyester base, which is crosslinked with PT910, which is a mixture of 2 and 3 functional epoxy (glycidyl esters) molecules discussed and shown in Figure 6-2 above. It is required to note that the formulation does contain UV inhibitors and other additives as it is a commercial powder coating, however

powder polyester resins have poor solubility in many common solvents and therefore, could not be tested in the same way as the samples produced in this project.

	LW18	LW17	LW19
Polymer functionality	2	3	4
Crosslinker functionality	3	3	3
Stoichiometry used (polymer: crosslinker)	1	1	1
Theoretical pgel	0.71	0.50	0.33
Gelation time (in seconds - at 160oC)	1124	746	644

Table 6-5 - Summary of properties from all 3 polymers

As Table 6-5 is showing above, it can be observed a higher functionality gives a faster gel time. As reaction order is second order, it is highly dependent on the concentration of the functional groups. Higher functionality means pgel will be lower, and in turn it will reach a gelation point quicker with having more sites to react with.

6.6.1 Influence of polymer functionality on Glass transition Temperature

At room temperature, the polyester resins used in this project range from semi solid to solid, dependant on functionality.

Cross-linking of these polymers should decrease the molecular motion of the polymer, resulting in the need for higher energy or temperature to realise that motion and result in a higher Tg value. Reduction of van der Waal's forces between polymer chains and the increase of stronger covalent bonds during crosslinking in turn reduces the mobility of polymer segment by holding the chains more rigidly together and therefore increasing temperature resistance[144,142].

To understand the thermal properties when increasing the functionality of the binder, Tg measurements were carried out (Table 6-6). A difference in Tg was expected to be observed between the polymeric binder Tg and the crosslinked polymer network

coating Tg, due to the curing of the coating which results in large increase in polymer molecular weight (towards infinite molecular weight) and therefore substantially reduces the mobility of chains and resulting free volume[145].

	LW18 B2 (2 Functional binder) (°C)	LW17 B2 (3 Functional binder) (°C)	LW19 B2 (4 functional binder) (°C)	Polyester standard (OZ014GF)
Resin	17.9	21.8	35.7	67.0*
Crosslinked coating	33.3	44.8	52.4	62.6

Table 6-6 - Table showing Tg values of LW17 B2, LW18 B2 and LW19 B2 in a 1:1 ratio with DEN431 for resin Tg and Coating Tg. *Tg taken from technical data sheet[146]

Figure 6-34 shows the relationship between the theoretical functionality of the (based upon the initiator monomer used) and the Tgs of the resin and the cured formulation. These theoretical functionalities show a correlation, indicating an increase in functionality results in an increase in Tg.

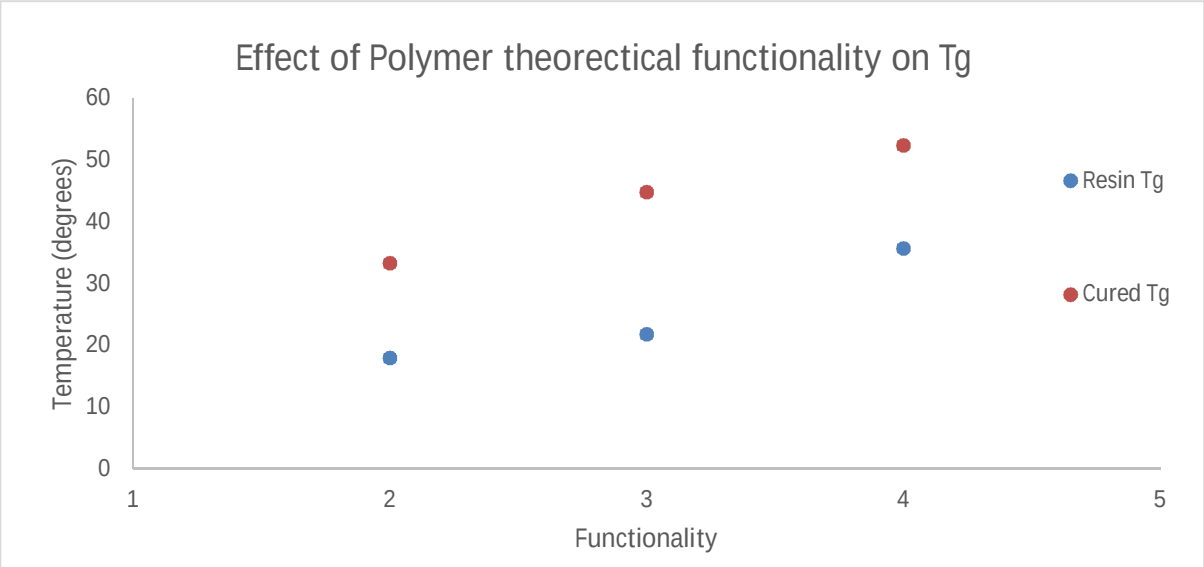


Figure 6-34 - Effect of Polymer theoretical functionality and Tg. Error bars are within the width the points.

As can be observed from the graph (Figure 6-34), the increase in functionality of the binder, increases the resin Tg and the crosslinked coating Tg, by an average of 20°C in each sample. This is a considerable jump in Tg and one that is interesting in the coatings business. Powder coatings use mainly polyesters or acrylic resins in their coatings, but when used in a powder coating, the cure Tg usually only increases by ~5-10°C for a polyester coating in comparison to the resin Tg when cured. This could be due to these polyesters having been cured with a rigid aromatic epoxy whereas most powder coatings are cured with a hydroxyalkylamide crosslinker, which could result in Tg differences. This could result in less possible confirmations, when using a rigid epoxy, whereas the hydroxyalkylamide contains an aliphatic core and contributes to a lower Tg. IT is more likely due to these polymers having higher functionalities. Acrylic polymers contain a higher functionality and observe this jump in Tg. This is due to having more functional groups to react with, increasing the crosslink density and in turn, increasing the Tg between polymer and coating. However, this large increase may be useful for the powder coatings business as it gives possibilities of producing lower Tg polyester resins with a resulting acceptable coating Tg, allowing more variations on resins which originally the business could not do, due to restrictions on the final powder having a Tg higher than 50°C for stability purposes. Using this crosslinker will increase the hazard rating of the final powder, due to an epoxy being used instead of an ester-amide, however once additives for colour, flow and fillers are added, the concentration of this will be low. Please note; error bars are added to both Figure 6-34 & Figure 6-35, but error is low.

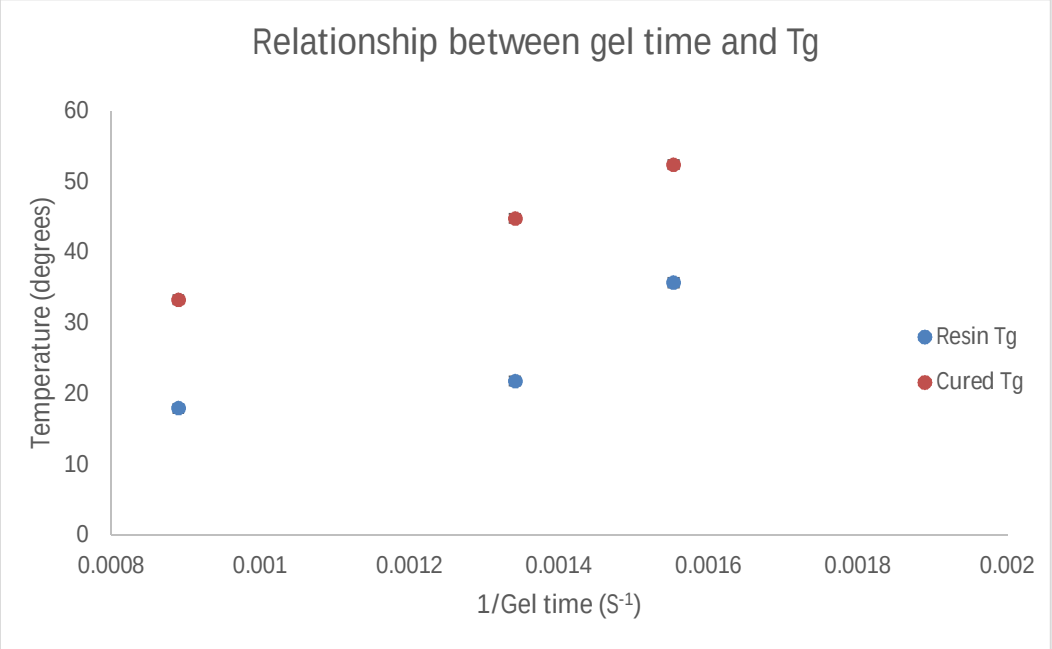


Figure 6-35 - Relationship between Tg of resin and cured film VS 1/gel time. Error bars are within the width the points.

By measuring gel time, Figure 6-35 indicates a similar pattern as seen in Figure 6-34. Gel time is quoted as 1/gel time, as otherwise the graph would show a negative correlation as the lowest functionality has the longest gel time due to a lower reactivity.

As can be seen in the graph above, the Tg increases with functionality, because the free volume around the polymer decreases at the point of branching.

However, as explained previously (section 6.6), there is a link between functionality and gel time (the higher the functionality, the lower the gel time) because Pgel is lower (lower conversion required to reach gelation from the flory-stockmayer equation). Therefore, it is expected that there is a relationship between Tg and gel time, as there is a relationship between Tg and functionality and gel time and functionality, in this specific chemistry.

6.6.2 Influence of functionality on coatings adhesion

Adhesion to a substrate is a fundamentally important requirement when producing a coating. In some cases, such as laminates, free films are required in which the adhesion is required to be extremely poor so a film can be removed. Due to this being such an

important property for a coating testing was carried out to understand if a relationship could be found between adhesion and functionality.

Many tests can be carried to understand adhesion in the coatings industry, however the a widely accepted test is the crosshatch test which is found in ASTM standard D3359[129].

It involves a very sharp blade drawn down in 6 parallel lines, and then turned 90°C and another 6 lines drawn down. The scored area then has tape applied and pulled off to remove any coating which has detached (this is explained in further detail in experimental chapter 5 section 5.5.3.2). All crosshatch testing follows an ASTM standard (Figure 6-36), which gives a grading on crosshatch results. It allows differentiation between results, to show which have a better adhesion than others.

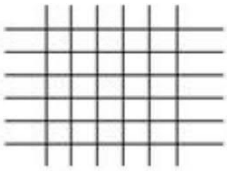
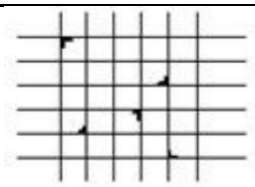
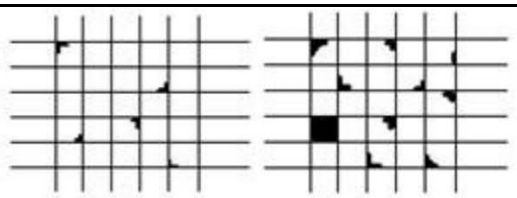
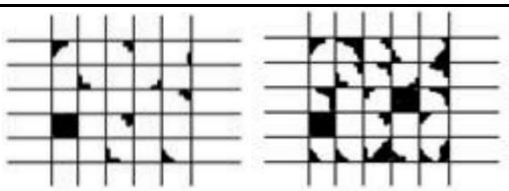
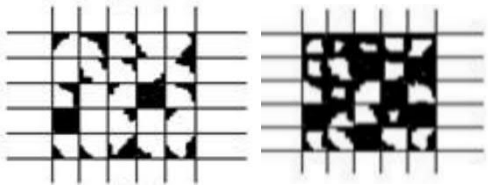
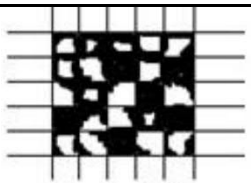
ISO Class:0/ ASTM Class: 5B The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	
ISO Class:1/ ASTM Class: 4B Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut area not greater than 5 % is affected.	
ISO Class:2/ ASTM Class: 3B The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5 %, but not greater than 15 %, is affected.	
ISO Class:3/ ASTM Class: 2B The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area greater than 15 %, but not greater than 35 %, is affected.	
ISO Class:4/ ASTM Class: 1B The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area greater than 35 %, but not greater than 65 %, is affected.	
ISO Class:5/ ASTM Class: 0B Any degree of flaking that cannot even be classified by classification 4.	

Figure 6-36 - ASTM standard showing the defect ratings

Using the method explained above and the ASTM D3359 standard defect rating table (Figure 6-36) to understand results, panels were tested and the results of this are below (

Figure 6-37)[129].

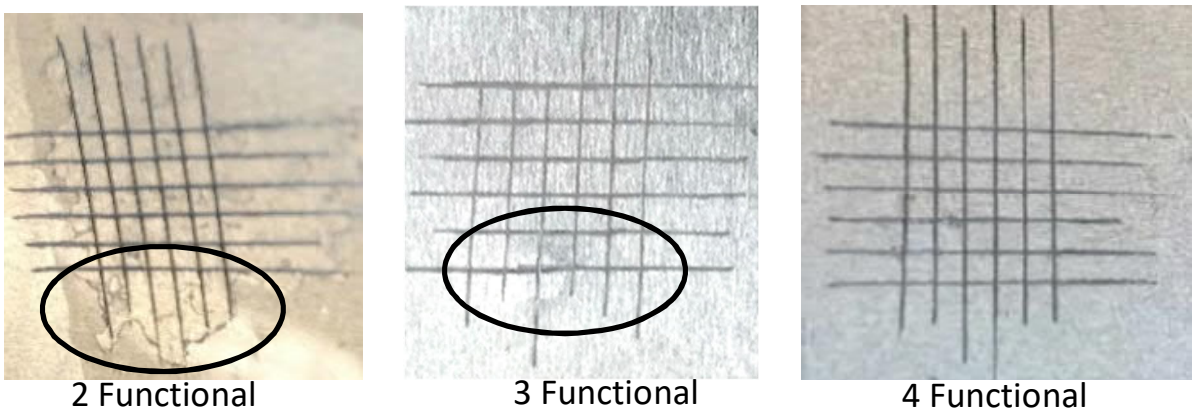


Figure 6-37 - Crosshatch testing on LW18 B2, LW17 B2 and LW19 B2 respectively

As can be seen in

Figure 6-37, the adhesion of the 2 functional polymer is poor as considerable delamination of the film occurs. This photo was taken at an angle to give the best view of the delamination, the most prominent delamination is circled. The 3 functional shows a small amount of delamination, mainly at the intersections, one has been circled above. The 4 functional polymer formulation shows no delamination at all and would be classed as having excellent adhesion to the substrate.

The relationship between the expected functionality of the polymers and adhesion grade is shown in Figure 6-38.

These measurements were made 3 times for each sample but reproduced the same results each time and given the categorical nature of the data, no error bars are shown.

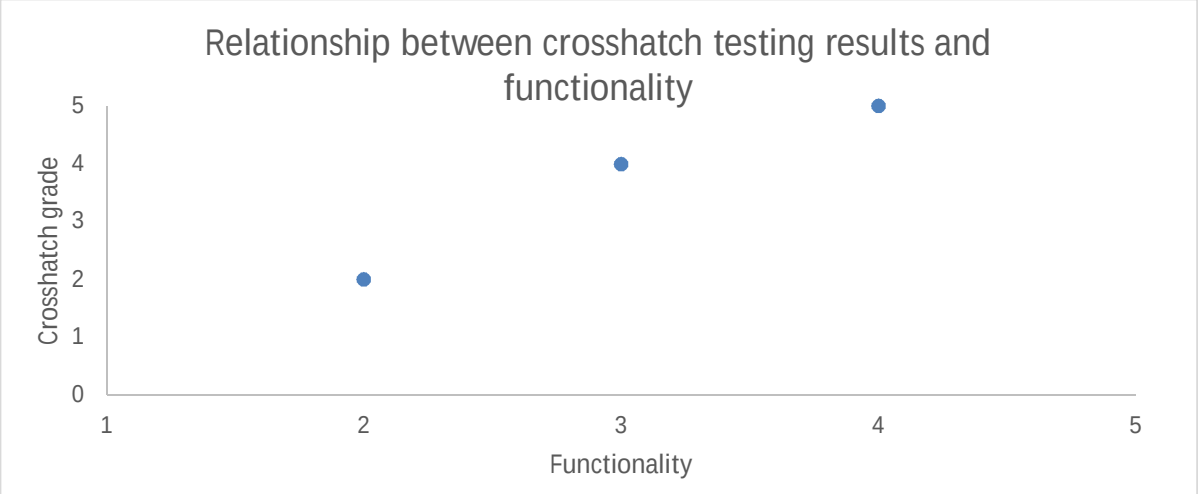


Figure 6-38 - Relationship between crosshatch adhesion grade and functionality

However, as functionality being a theoretical value and gel time being a measured value, Figure 6-39 also shows an interesting correlation.

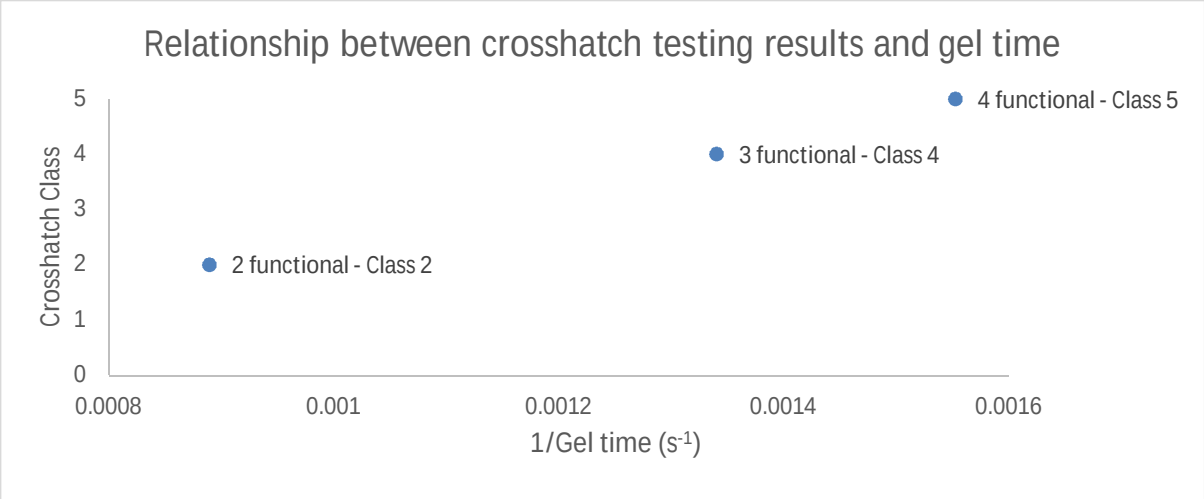


Figure 6-39 - Relationship between gel time and crosshatch (error bars too small to be observed for gel time)

There is a clear trend that increasing the polymer functionality (and shortening gel time) also increases the coating's adhesion. It could be concluded that a higher functionality results in an increased adhesion. This is expected to be due to the increase in hydrogen bonding to the surface as more sites will be available for bonding with a higher functionality. A higher functionality produces a higher crosslink density which will result in more OH groups at the interface between the coating and the substrate formed from the crosslinking reaction increasing adhesion resistance.

6.6.3 Influence of functionality on solvent resistance

Methyl ethyl ketone (MEK) double rubs test was conducted per ASTM D 5402 to initially assess the extent of crosslinking in the coatings and chemical resistance. A solvent rub is the initial test to confirm a coating has crosslinked. This is explained further in (5.5.3.3 Solvent).

The photographs below in Figure 6-40 show that coating has been damaged by the solvent rub, but not removed, indicating they are crosslinked but some have a poor solvent resistance.

The 2 functional showed a partial loss of film, the solvent resistance was very poor. As functionality increased, the solvent resistance improved, up to 4 functional which had no loss of film, but a circle was formed around the solvent rub.

These measurements were made 3 times for each sample, but reproduced the same results each time so therefore no error bars are shown in the graphs in Figure 6-41 and Figure 6-42.

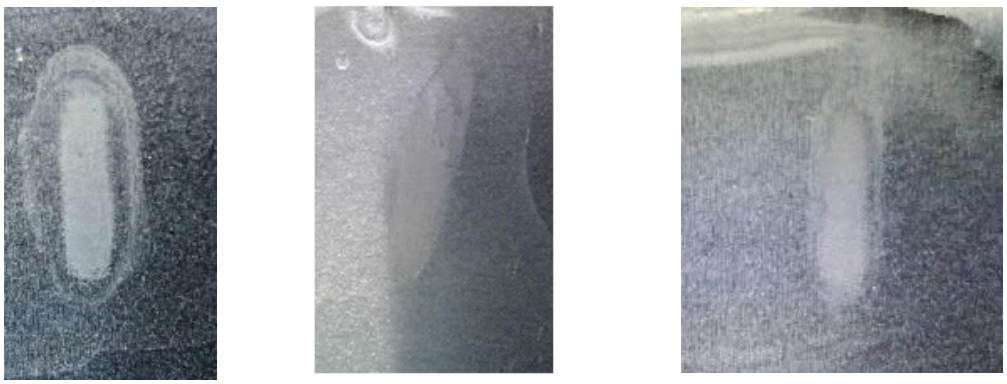


Figure 6-40 - MEK rub showing 2 (left), 3 (middle) and 4 (right) functional systems

To measure the resistance to MEK, a scale is used from official guidelines, also mentioned in section 5.5.3.3;

5 = No effect on surface.

4 = Burnished appearance.

3 = Some marring and apparent depression of the film.

2 = Heavy marring. Obvious depression of the film.

1 = Heavy depression in film but not actual penetration to the substrate.

0 = Penetration through the film, to the substrate.

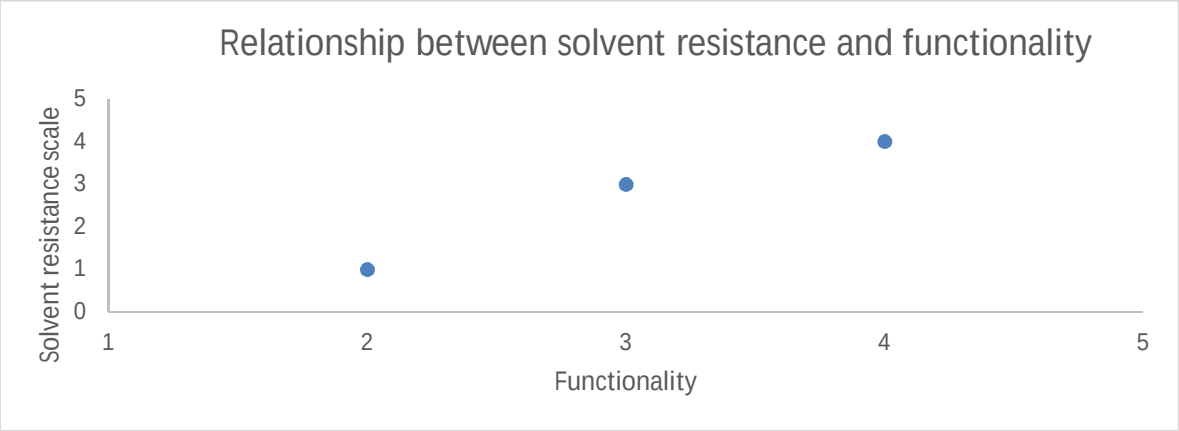


Figure 6-41 - Relationship between MEK resistance and theoretical functionality

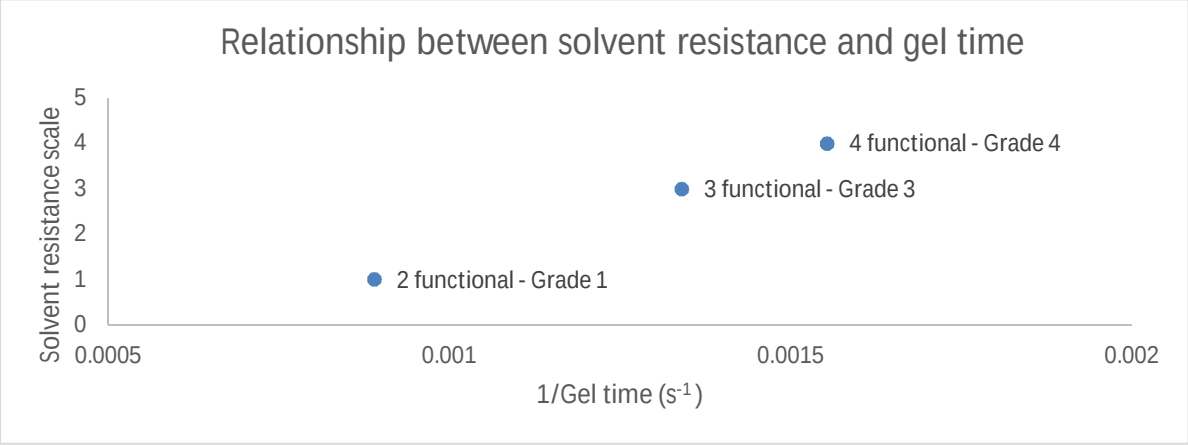


Figure 6-42 - Relationship between solvent resistance and gel time (error bars too small to be observed)

Figure 6-41 indicates that the shorter the gel time, the better the solvent resistance is. This would result in the conclusion that a higher functionality results in a greater solvent resistance, which is the same conclusion as many authors in the coatings industry[147]. This is expected to be due to the higher crosslink density, which would

require more the breaking of more bonds due to the swelling of the network by the solvent, and therefore provide a higher solvent resistance with the higher functionality.

6.6.4 Influence of functionality on mechanical properties

During the lifetime of a coating, it will usually experience some mechanical stresses. In industry, mechanical tests can be carried out through impact testing or bend testing. Bend testing is a simple test in which the panel is bent around a specific sized cone and diameter, which is known as the conical mandrel test (as shown in Figure 6-43). The test follows the ASTM D522 method, in which the cone radius widens with length ranging from 3mm to 38mm wide, so when bent, it can provide good information on how much bend strain the coating can withstand before cracking.

Figure 6-43 – Film undergoing a conical mandrel bend test

As can be seen in Figure 6-44 below the 2 functional polymer is showing good bend resistance. There is no flaking, and only minor fracture lines. However, as the functionality increases, the cracking resistance reduces, resulting in the 4 functional coating delaminating considerably. This is possible to be due to the 2 functional having a lower Tg and is a therefore a softer coating as shown in section 6.6.5.

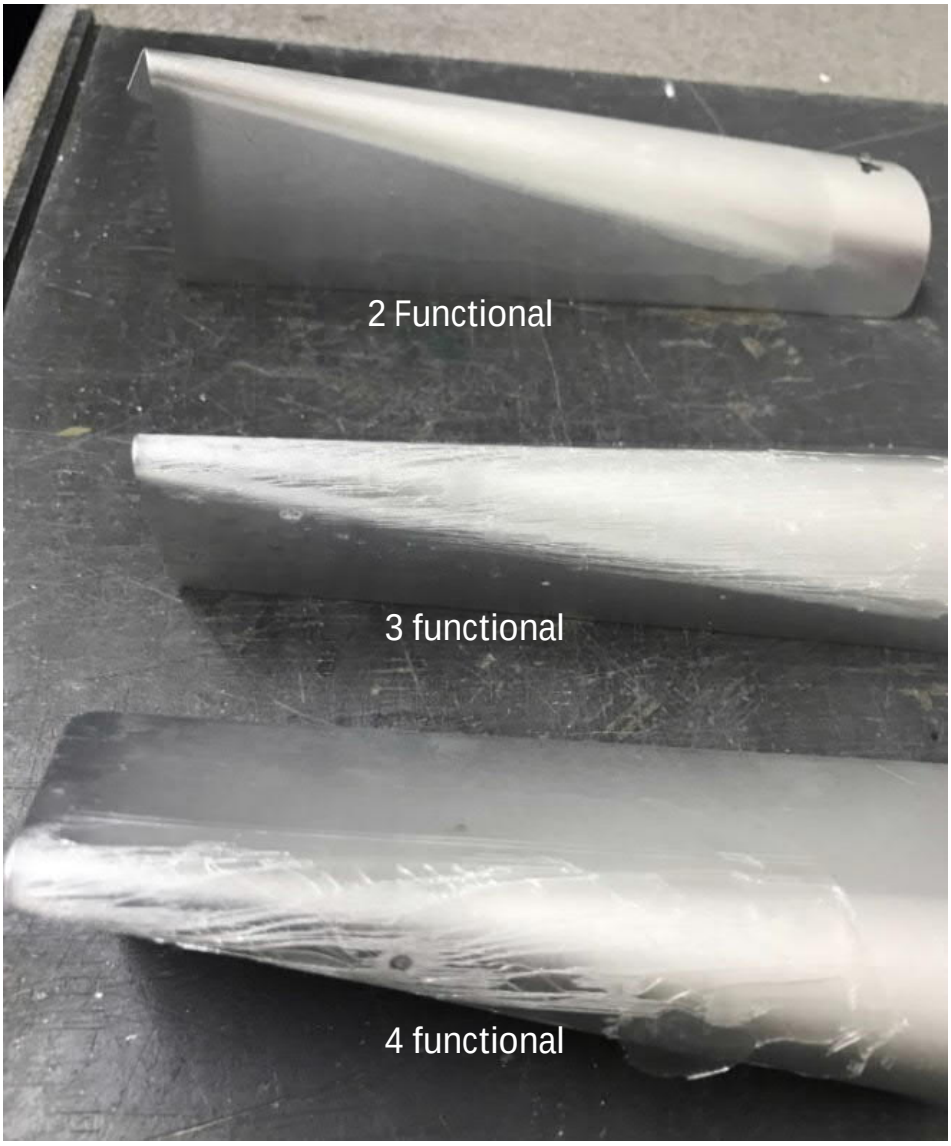


Figure 6-44 - Results of conical mandrel testing on the 3 different initator functionalities

Figure 6-45 - Result of standard after conical bend testing

Figure 6-45 shows the result of the standard powder coating. As can be seen there is also no cracking as shown in the 2 functional, however it can be seen a stretch has been applied to the coating as it has acquired a white colouring to the bent part of the panel as highlighted in the circle in the figure. It could be expected that the higher functionality coating will be a more brittle coating as it has a higher crosslink density, whereas the lower functionality has a lower crosslink density so will make the coating a lot softer and easier to bend without breaks.

6.6.5 Influence of functionality on hardness

Hardness measurements can give information on the changes in hardness and brittleness during humidity or UV testing. Other uses are scratch resistance, and durability[148].

Microhardness is defined as the resistance to permanent surface indentation or penetration[149]. However, the term may also refer to stiffness or the resistance to scratching. This property when tested in coatings gives an indication into the ability to resist being permanently deformed when a load is applied[150].

This technique is used in industry to understand how a coating can withstand pressure applied. Panels were tested on the 3 different polymer types. Each sample was tested 5 times and an average was taken. Below shows 2 graphs (Figure 6-46 & Figure 6-47) comparing properties measured when measuring microhardness. Hardness is defined as the resistance of a material against local surface deformation[150]. Elastic deformation measures the % of coating, which is reformed once penetrated, plastic deformation gives the % which does not recover from the penetration.

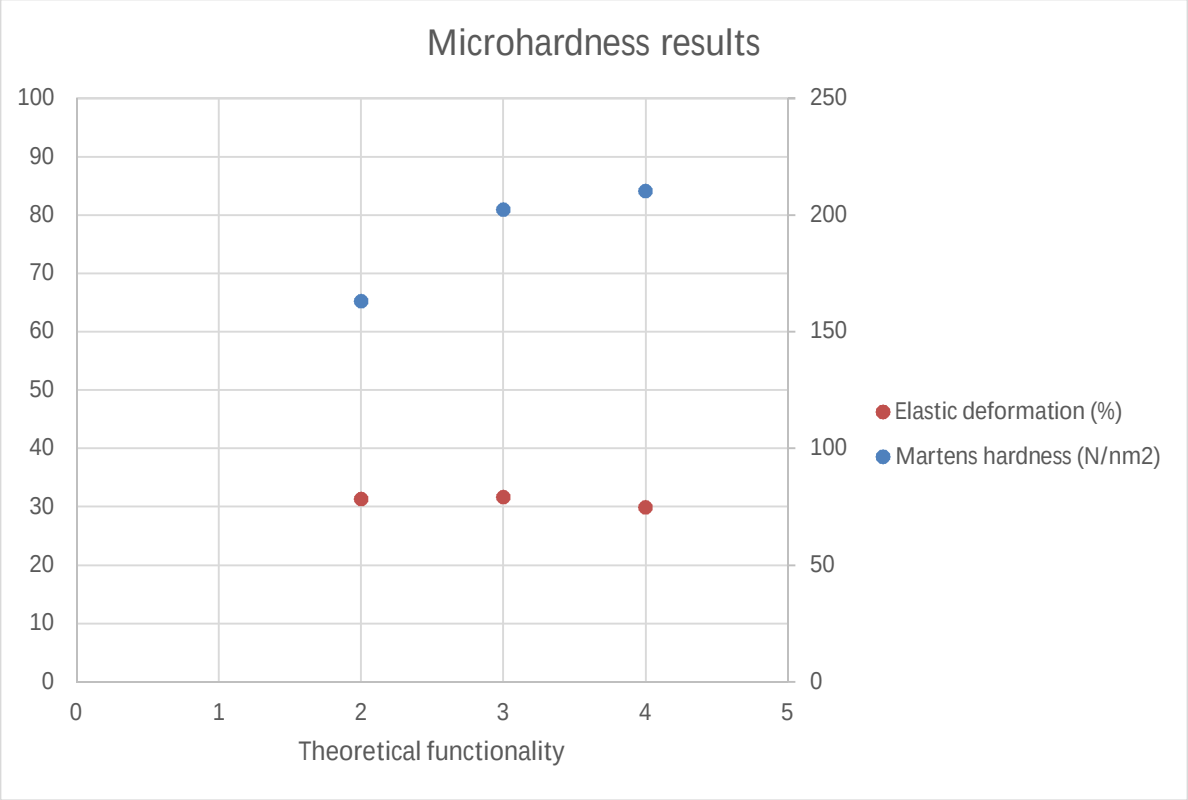


Figure 6-46 - Microhardness results vs functionality of the polymer

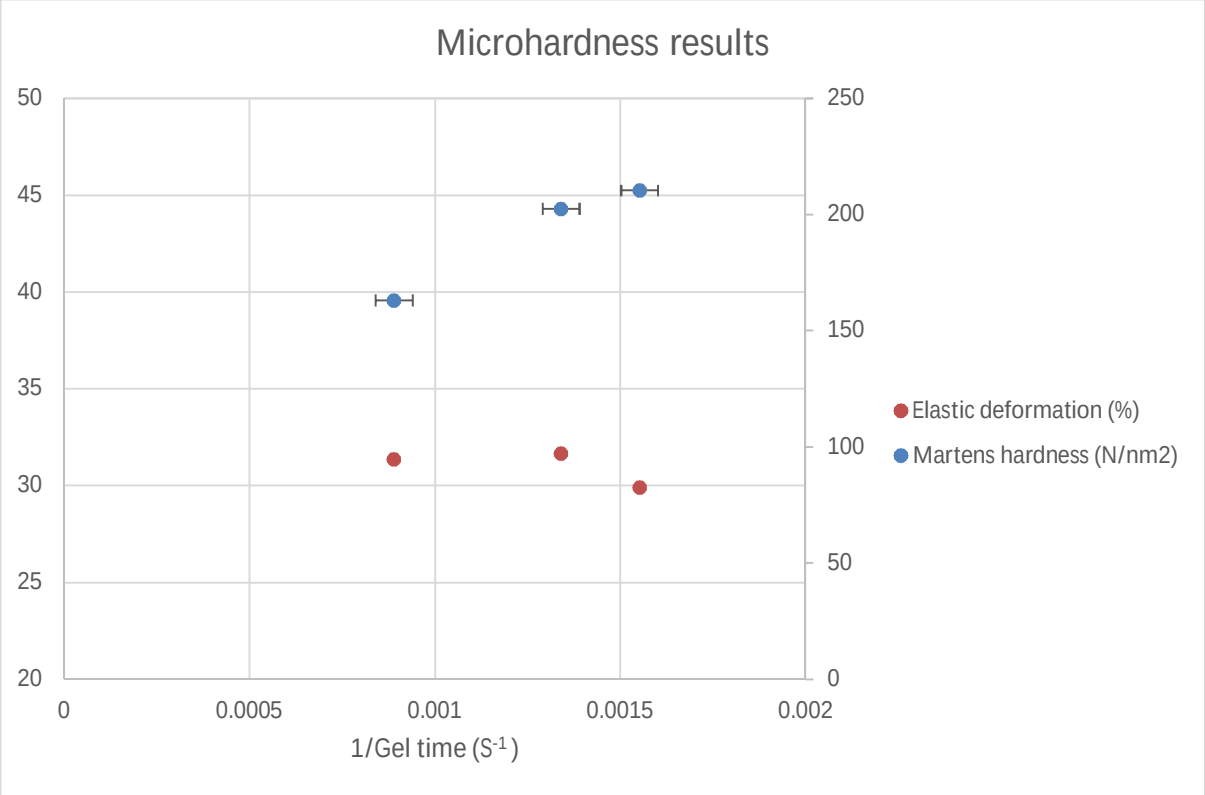


Figure 6-47 - Microhardness results vs inverse gel time

From the graphs in Figure 6-46 & Figure 6-47, Elastic deformation appears which indicates a change in functionality/ size of polymer, does not affect these properties. However, the Martens hardness appears to increase as functionality increases. This could be due to a higher functionality with theoretically higher crosslink density, providing a harder coating.

As the crosslink density could not be measured due to issues in producing a free film, other conclusions could be made such as in a higher functionality polymer, there are more covalent bonds holding the junctions together, which could also harden the coating.

Overall, even though the 4-functional coating showed a harder coating through microhardness testing, this showed brittleness in the coating resulting in a poor bend test result and major flaking of the coating observed. 2 and 3 functional appeared to perform better than the 4 in the bend test, most likely due to a softer coating confirmed by microhardness, and therefore a less brittle and more stretching within the coating is obtained.

6.6.6 Influence of functionality on UV resistance

6.6.6.1 Weathering testing

All coatings degrade when exposed to natural weathering although this can happen at different time scale, the normal degrading elements being ultraviolet light, water and oxygen. The natural weathering of coatings is a long-term process and it would be extremely useful to be able to accelerate this by exposing the coatings in a suitable apparatus with the degrading elements controlled to give reproducible results[151].

Much work on this has been carried out, over several decades, in the coatings and allied industries but, to date, acceptable acceleration has not proved universally possible since there is no one light source or cycling conditions which can simulate exactly the effects of outdoor exposure, with or without water. Moreover, natural exposure conditions vary substantially from one location to another and from one

season to another, therefore an exact correlation between in-service exposure and accelerated weathering is impossible. Despite this, various types of equipment have been developed and have been widely used for the testing of coatings over the years, each incorporating different light sources, panel/spray geometry, wet/dry and light/dark cycles and temperature of operation[140].

The U.V. Accelerated Weathering Tester is the standard equipment for rapid assessment of likely weathering properties, provided a link has been established between the test conditions and the expected natural weathering conditions[122]. UV test equipment uses UV-A light sources and condensed water in the form of a vapour, in alternating cycles. It utilises those UV wavelengths present in sunlight which are most destructive of polymer chemical bonds, associated to the softening, solubilising of the bonds. Alongside osmotic effects of the condensed pure water invariably shown to be present for long periods on paint films in the form of dew. Further acceleration is obtained by using elevated temperatures[141]. The operation and use of the U.V. tester and similar equipment are given in ASTM standard G 154. The cycle used was 4 hours of dry U.V. at 55°C ± 3°C followed by 4 hours water condensation at 45°C ± 3°C, with no UV emissions. The Accelerated Weathering Tester manufactured and supplied by ATLAS using ultraviolet tubes emitting in the UV-A region of the electromagnetic spectrum with peak emission at 340nm.

6.6.6.2 Colour testing

Colour testing is required to be carried out on all samples that endure an accelerated weathering experiment as a mean to assess the changes in the coating with time. Gloss and colour values are measured for every panel and all panels are produced in triplicate.

The coatings produced in this project were all clear coats and therefore had no pigments added, which allowed any yellowing observed to be concluded as the polymer/crosslinker blend as the cause.

Figure 6-48 shows one of the triplicate panels for each sample before going into to UV accelerated test. It can be observed these coatings are clear, almost completely free of defects and have no yellowing.

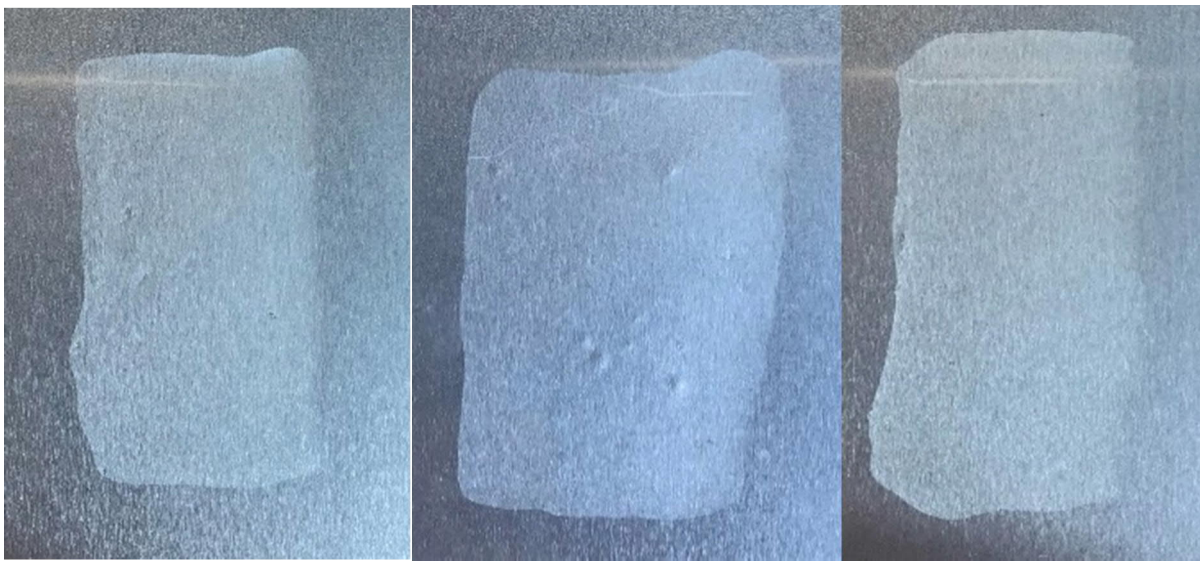


Figure 6-48 - Panels coated for UV testing - initial panels; LW17 (3 functional), LW18 (2 functional), LW19 (4 functional) respectively

Once panel had been in the UV tester for 7 days, Figure 6-49 shows that yellowing has occurred significantly already. LW18 (the middle photo) shows significant defects to the panel, producing a very rough textured surface.

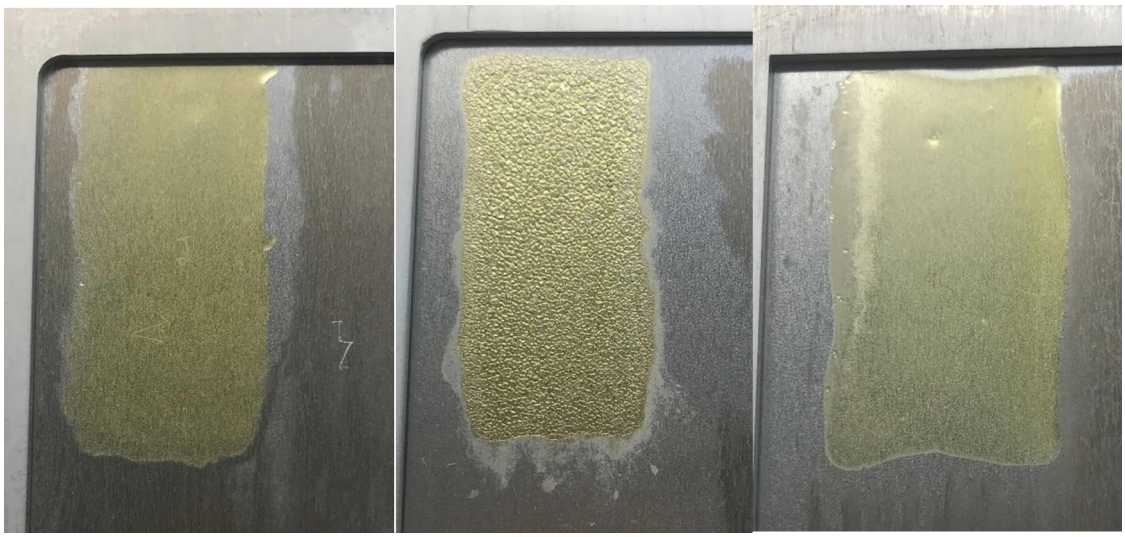


Figure 6-49 - 7 Days UV panels; LW17 (3 functional), LW18 (2 functional), LW19 (4 functional) respectively

As UV testing continued, the panels appear to the eye to not yellow a significant amount more. However it can be observed that a haze appears over all panels over time which can be observed in Figure 6-50, Figure 6-51, Figure 6-52 and Figure 6-53.

It is worth noting that panels have a small part at the top of each of the coatings which has not been exposed to UV due to the test set up, so a clear coating at the top of each panel can be observed.

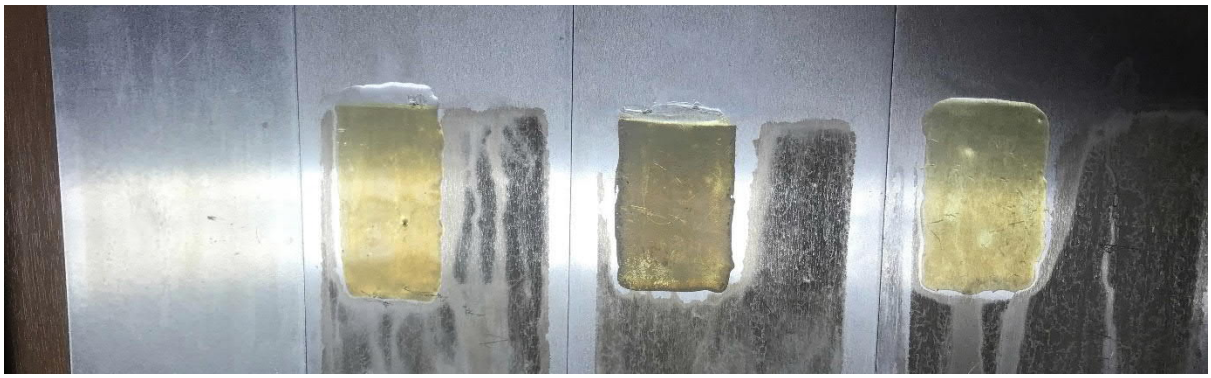


Figure 6-50- 15 days UV panels; Standard, LW17 (3 functional), LW18 (2 functional), LW19 (4 functional) respectively

Figure 6-51 - 22 Days UV panels; Standard, LW17 (3 functional), LW18 (2 functional), LW19 (4 functional) respectively

Figure 6-52 - 43 days UV panels; Standard, LW17 (3 functional), LW18 (2 functional), LW19 (4 functional) respectively

Figure 6-53 - 84 days UV panels; Standard, LW17 (3 functional), LW18 (2 functional), LW19 (4 functional) respectively

As can be seen from the panels in the figures above (Figure 6-49 to Figure 6-53), the aluminium appears hazy. It is believed that the aluminium is oxidising, as aluminium oxide is white[152]. It was also observed that leaching may be occurring in the LW19 B2 (right hand side of photo) panel throughout including the final testing panel in Figure 6-53. This can be concluded due to the aluminium oxidation not occurring below the coating on this panel, where white oxidation is absent from directly below the coating. This could be caused by residual solvent if a small amount of solvent were to still be present. However, as the LW17 and LW19 coatings are not hazy, this could also indicate they are protecting the panel from this oxidation.

It also seems that as all coatings appear cloudy, it may appear to have absorbed water and the haziness on the coating is due to different phase layers of a water layer and an organic layer.

To the naked eye, these coatings show a degree of yellowing, however using a spectrophotometer, this can be quantified into values and trends.

All samples were run on a Datacolor 800 spectrophotometer and analysed in a Datacolor Tools version 2.0.11 software. This software calculates differences between samples and gives an indication of the change in colour visually from start to finish. The Datacolor software uses a 'Lab' colour scale. 'Lab' is now more often used as an informal abbreviation for the CIE 1976 colour space which is also called CIELAB, whose coordinates are L*, a*, and b* (Figure 6-54)[153]. The L* value is a measure of the lightness of an object and is quantified on a scale such that a perfect black has an L* value of zero and a perfect reflecting diffuser an L* value of 100. The a* value is a measure of redness (positive a*) or greenness (negative a*). The b* value is a measure of yellowness (positive b*) or blueness (negative b*)[154]. The asterisk (*) after L, a and b are part of the full name, since they represent L*, a* and b*, to distinguish them from Hunter's L, a, and b. The Datacolor software can measure the changes in properties such as changes in L (DL) and changes in b (Db).

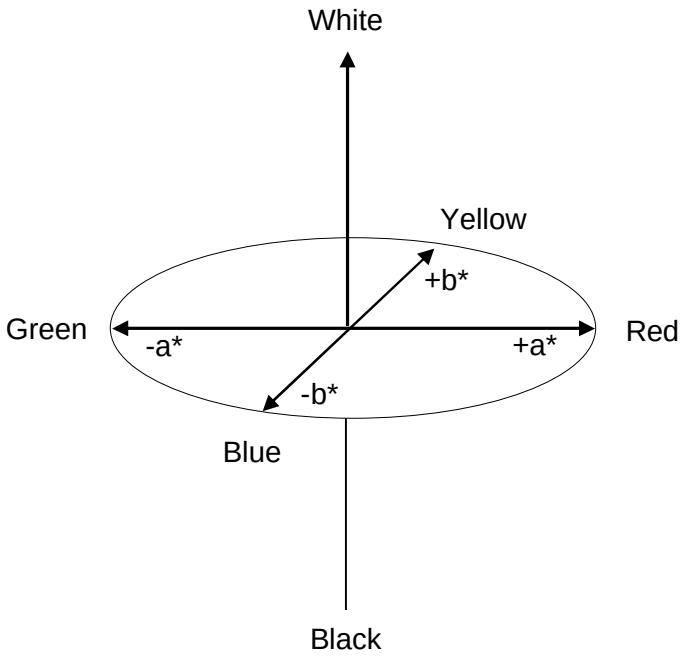


Figure 6-54 - CIE colour Lab scale

All results shown above, measured on the colour lab scale, are shown below (Figure 6-55) as differences from the original panel.

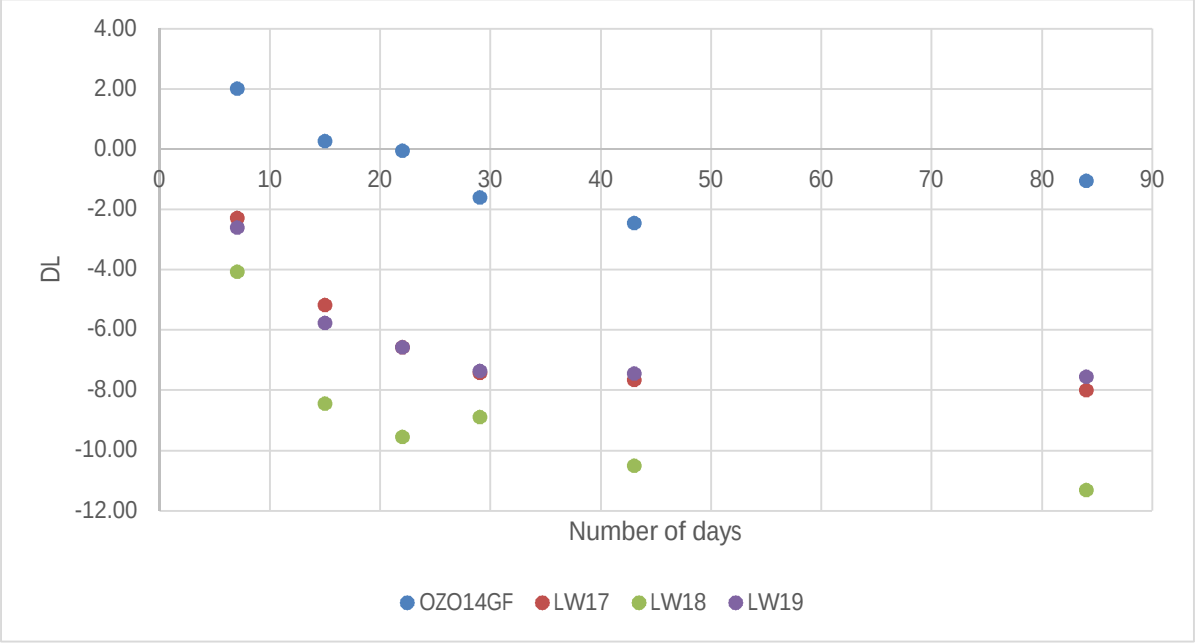


Figure 6-55 - Differences in DL over an increasing number of days in UV testing

From Figure 6-55 a trend over time can be observed. As time exposed to UVa increases, the panels become darker. It could also be concluded, that LW18 (2 functional) darkens the most, with LW17 and LW19 showing similar results, but all samples show they become darker over time than the standard. This is expected to be due to chromophores, on either phthalic anhydride, the PGE phenyl ring or the phenolic crosslinker. This is caused by the double bonds in the aromatic ring. 2, 3 and 4 functional having a similar number of phenyl rings in the structures and therefore, the similar number of chromophores, so as 2 functional yellows quicker this may be due to the lower functionality. A lower functionality gives a lower crosslink density. Therefore the 2 functional has less network, resulting in an easier degradation, and in turn, yellowing more significantly than the higher crosslinked coatings. The standard polyester coating also contains aromatic rings, however as this is a commercial powder coating, this formulation also contains UV inhibitors so therefore will not yellow at the same rate.

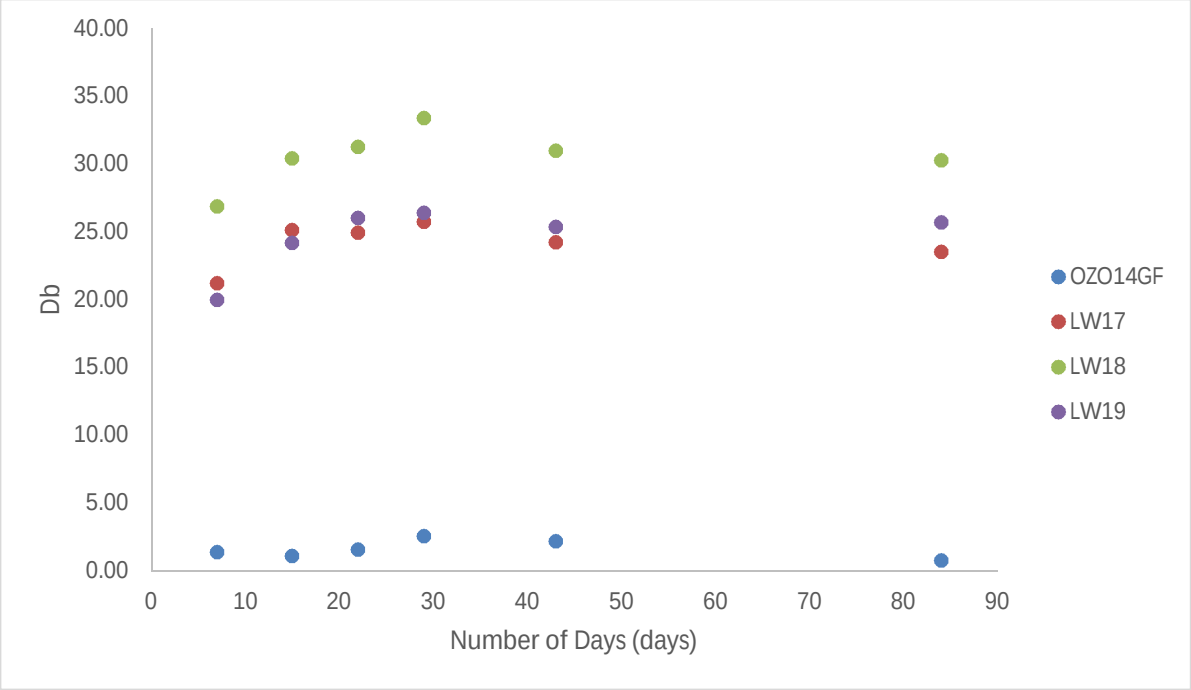


Figure 6-56 - Differences in Db over an increasing number of days in UV testing

Figure 6-56 gives similar trends as the trends observed with the DL values in Figure 6-55, in which LW18 performs the more poorly than all other samples tested, whereas the standard showed almost no yellowing. This could conclude, the samples require a UV inhibitor, to be considered a pass for testing.

Overall, all 3 polymers prepared in this project show significant yellowing, with the LW18 giving the worst yellowing results, and all samples not reaching the same level of UV resistance as the standard. However, as the standard contained UV inhibitors, if these polymers were to be put in a standard formulation and had additives included, a more accurate comparison could be made on the UV performance of these polymers.

6.6.6.3 Polymer functionality influence on gloss

Gloss can be measured at different angles - a measurement proportional to the amount of light reflected from a surface measured at 20° (high gloss finishes), 60° (mid gloss finishes) and 85° (matt finishes). This is used for coatings which use pigments. When a coating is a clearcoat (no pigment), the reflection behaviour changes. This is because a clearcoat does not hide the substrate below, and therefore if on a metal, the

gloss of the metal will also be reflected, increasing the gloss measurement. This may happen for all angles, but it is the most likely at higher angles.

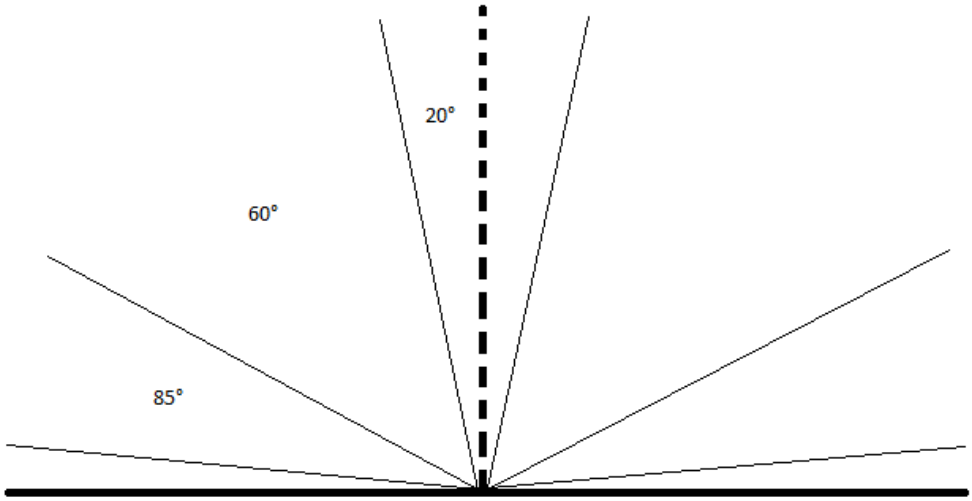


Figure 6-57 - Gloss measurements at 3 different angles to give different types of gloss

Gloss is defined by the American Society for Testing and Materials (ASTM) to be "the angular selectivity of reflectance, involving surface-reflected light, responsible for the degree to which reflected highlights or images of objects may be seen as superimposed on a surface"[155]. Several types of gloss can be differentiated by being measured at specific angles as illustrated in Figure 6-57. Specular gloss is the exact mirror direction. Sheen measures the shininess at grazing angles. Distinctness-of-image gloss measures the sharpness of mirror images, relevant for high-gloss surfaces[156].

The test for Specular Gloss, measures the light reflected in the specular direction off the sample surface, 60 degrees down from surface normal. A high gloss surface will reflect most light in the specular direction while a surface with low gloss will reflect most of its light in directions other than specular. Part of the standard are two more angles, 85 degrees from normal, which measures specular gloss at grazing angles (called sheen) and is therefore used generally for low gloss samples. The other angle measured is 20 degrees which measures specular gloss at near normal angles and used for high gloss samples[155]. ASTM E430 Test Method A defines the distinctness-of-image gloss measurements. These measurements compare the light reflected directly in the specular direction to that reflected in the slightly off-specular direction. The

angle of offset is essentially a mere 0.3 degrees. This is to mimic the keen discrimination of the human visual system for detecting the sharpness of the reflection of an object in a highly reflective surface[156].

The coatings produced, were formulated as clear coats - containing no pigment. This caused an issue for gloss measurements as it can take in the gloss given from the substrate below. Therefore, gloss was measured at all 3 angles, and the Distinction of image (DOI) (See 6.6.6.4) was measured, to give a more conclusive result when looking at the gloss. The graph below (Figure 6-58) has been defined as percentage of the original gloss value described as the retention of gloss.

The measurements at 20° are expected to be the most reliable as they are used for high gloss systems, which these panels appeared to be. Using an angle of 20° will also considerably remove any concern surrounding measuring a clear coat. Measuring gloss in clear coatings can be difficult as the gloss of the coating can be taken into consideration when using certain angles. As 20° is a very shallow angle, the reflection will give a truer measurement of the actual coating, with less influence of the underlying substrate. However, to make sure this does not affect the results, they have been shown as a percentage retention, rather than as a gloss value. As can be seen from the results, it shows all coatings are becoming depleted by the UV weathering, with the standard and the 2 functional showing the worst retention in gloss. As the standard contains additives, this is a positive result.

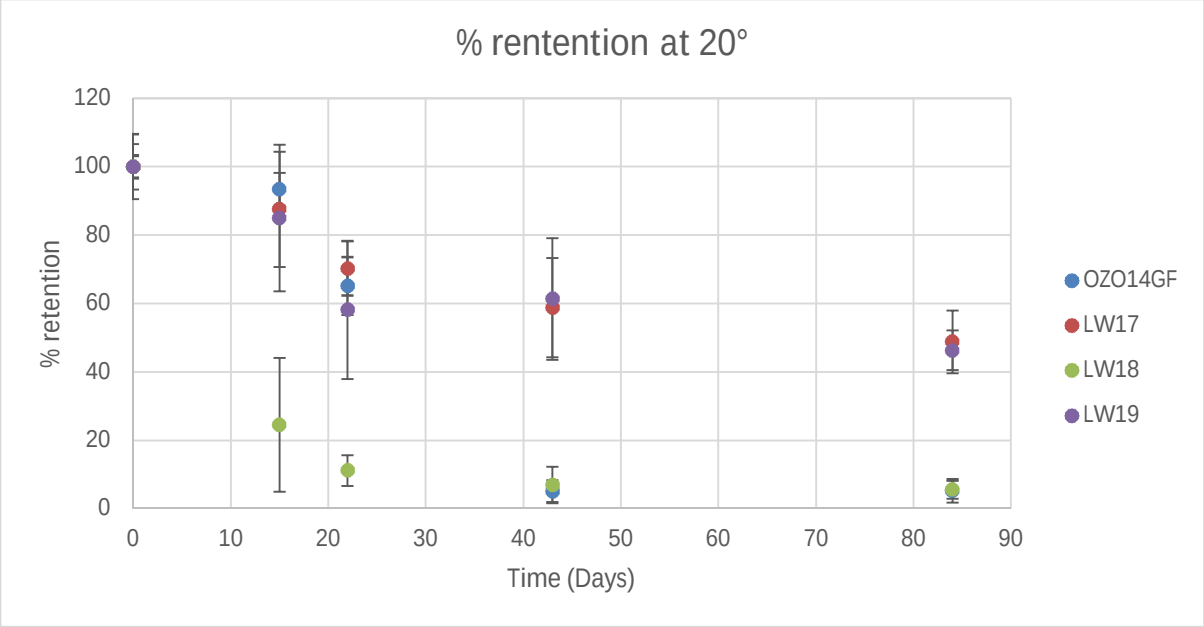


Figure 6-58 - Gloss retention after 84 days of UV weathering testing measured at an 20° angle. LW17 - 3 Functional, LW18 - 2 functional, LW19 - 4 functional, OZO14GF is the standard polyester powder coating

6.6.6.4 Influence of polymer functionality on Distinction of Image (DOI)

Distinction of image was measured as an extra insight into how the gloss could change. This is an indication into how sharp a reflection into the coating is. It is used in industry for coatings as it better mimics human perception to a surface texture. DOI is measured using the same Q point gloss meter. When a gloss measurement is taken, a DOI value for that gloss measurement will also be given. When a DOI value is low, or can be observed to decrease over time, it indicates reflective images from the coating are distorted. This could be a for a number of reasons such as haze, orange peel or brush marks[157].

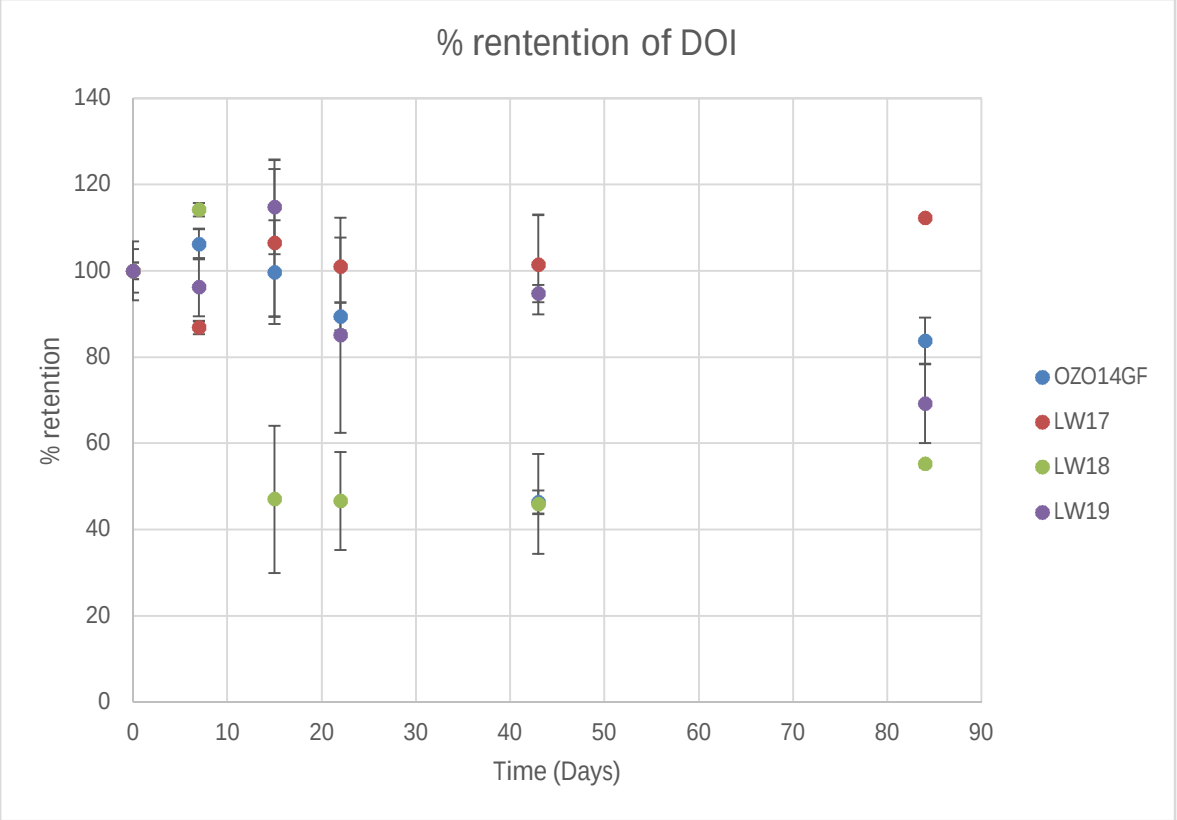


Figure 6-59 - DOI gloss retention after 84 days of UV weathering testing. LW17 - 3 Functional, LW18 - 2 functional, LW19 - 4 functional, OZO14GF is the standard polyester powder coating

As can be seen in Figure 6-59, the 3 functional coating appears to give a higher DOI than all others tested, with the 2 functional coating performing the worst, indicating a relationship cannot be made between DOI and functionality. It could be concluded that the 2 functional polymer coating performed the worst due to containing a lower crosslink density which would result in allowing more water uptake, which would produce a more textured surface. It could also be concluded the 3 functional polymer coating performed better in this test than the standard powder coating, whilst the 4 functional polymer coating performed very similar to the standard.

Overall, from a change in functionality, observable changes could be seen in the results of the coating testing. The 4-functional coating showed a higher Tg, but it also showed a higher solvent resistance and a higher crosshatch resistance. An increased hardness compared to the other 2 coatings tested was also observed. Good results in weathering was found with retaining the gloss to a similar rate as the other better performing panels, and a lower yellowing than other coatings tested. This looked to be

a promising coating, however, bend tests on the panel showed very poor results with flaking of the whole coating very observed. This meant that the 4 functional coating had very poor adhesion to the panel. This may be something that could be improved using appropriate additives (such as organofunctional silane based additives), however with the damage to the coating shown, a larger amount of additive would be needed to help with this issue for this coating in comparison to the other 2 coatings, which could damage other properties this polymer provides, and also could increase the overall cost of the coating which would be undesired to industry.

The brittleness observed by the 4 functional coating, was however not seen by the 2 functional coating. This was most likely due to a softer coating with a lower Tg so more internal stretch was possible. The 2 functional coating did appear poor in weathering testing, yellowing the most of all and losing the majority of the gloss, retaining only 5% gloss after the UV cycle. It also appeared to perform the worst in the solvent resistance testing and the crosshatch testing, concluding that 2 functional in this chemistry was not the ideal coating system and higher functionalities gave more promising coating results.

Increasing the functionality has shown that this indirectly increases Tg which is explained by a reduction in free volume around the polymer at the point of branching. This reduction in free volume, can also help to explain the poor bend test results, which indicates less flexibility in the polymer. Increasing the functionality, also results in a higher crosslink density, which will result in more OH on the surface and therefore will increase the adhesion. This explains the improved crosshatch testing result. With higher crosslink density, will also explain how a higher functionality improves the solvent resistance, as more solvent will be required to break more bonds, and why the hardness of the coating increases with a higher crosslink density. In terms of the UV resistance, testing showed that the lowest functionality, yellowed the most, with higher functionalities showing similar results. As all functionalities has the same chromophores, the severe yellowing of the 2 functional coating, would most likely be explained by functionality. A lower functionality would result in lower crosslink density, which could allow degradation of the coating more easily than a higher density. This result was also observed when testing gloss and distinction of image, which could be explained by the same reasoning.

Concluding these results, it appears a higher functionality brings many advantageous qualities to a coating, and if coatings are experiencing issues in these areas of testing, an increase of functionality could be an option, after these findings, to help improve that issue. If flexibility of a coating is an issue however, these results show, adding linear material, whether that be a blend of polymers in the coating or a linear section added into a 4 functional polymer, should improve that problem.

Chapter 7 – Conclusions

7 Conclusions and next steps

7.1 Overview

This work was undertaken to improve our understanding of network properties of stoved systems, with the aim to reduce the curing temperature whilst retaining appropriate coatings properties. This was done through the synthesis of novel, well-defined polymers and then the understanding of the relationship between polymer structure, network structure and coatings properties.

To make the basis of this project, polymers with controlled synthesis conditions was required to produce a very well-defined polymer structure. It was thought that carboxylic acid functional polyesters would be suitable candidates due to the ability to cross-link with epoxies and β-hydroxylalkylamines as widely used in Powder Coatings[107]. Ease of manipulation of the structure and of the functionality of the polymer were the main reasons for this choice of polymer type. Other reasons included the ease of access to raw materials, based upon which materials are already readily available in the coatings industry. Polyesters however are normally made from poly-carboxylic acid and polyol monomers, in presence of (trans-)esterification catalysts which can create dispersity in terms of polymer chain length but also functionality. Therefore, the work undertaken in this thesis investigated an alternative way to synthesise polyesters from anhydrides and epoxies, their curing properties and the resulting coating properties.

Chapter 2 gave insight into ideal reaction conditions, by investigating the cause of induced side reactions and how they could be minimised. Undesired reactions such as homopolymerisation of the epoxies were observed when trialling a variety of catalysts, and it was shown that certain types of catalysts were more selective towards the desired reaction, rather than epoxy homopolymerisation. Experiments using butanoic acid and phenyl glycidyl ether gave great insight into how epoxies were opened, explaining the ratio in which they opened in the alpha beta position when using different catalysts. Model work on the reaction of hydroxyls and anhydrides, and later carboxylic acids with epoxies was complete, concluding a controlled model reaction

oligomer could be produced to reach expected values. Only then it was possible to start the synthesis of well-defined polymers.

Chapter 3 and 4 then investigated the development of well-defined polymers of different molecular weights and functionalities. Higher molecular weight polymers were attempted with an aim of a number average molecular weight (Mn) of around 6000g/mol dependent upon functionality of the initiator. These polymers proved difficult to synthesise as the Mn was not reaching the expected values. Once the key issues were understood and all monomers were purified before use, along with all equipment required to be dried and the reaction to be carried out under nitrogen – it was possible to reach our expected molecular weights however it seemed clear that purifying all reagents was not an industrially acceptable process to be used. Industry require minimal purification, as many tonnes are used at a time to produce polymers in bulk, therefore a more economically viable solution was required. Polymers of lower molecular weights were then made. Based on the work carried out on model reactions in chapter 2, which has yielded well defined products, these were produced closer to the theoretical polymer.

These polymers were then formulated based upon adding a set number of molecules to the chain, rather than a target molecular weight. This proved successful and these polymers reached the expected molecular weights or close to, within measurement error.

Once polymers were made and tested to confirm the structure, Subsequent chapters investigated their curing behaviour and properties in coatings. They were blended with a well-defined phenol-formaldehyde (Novolac) epoxy crosslinker in a 1:1 equivalence ratio and drawn down onto test panels. Coatings were tested for their physical properties in chapter 6. Correlations of these properties were acquired and analysed and showed certain properties such as Tg, gloss and microhardness gave were influenced by changes in initiator functionality, which in turn changed the polymer functionality. All properties showed a change when increasing functionality. Trends were observed in most testing, showing an improvement in the coating property, with an increase of functionality. The majority of these trends could be explained by an increase in crosslink density or reduced free volume around the branches of the

polymer when increasing the functionality. The UV resistance showed less of a trend but did show that the 2 functional coating had significantly reduced resistance in comparison to the higher functionalities, which could be explained by a lower crosslink density and therefore easier to degrade. The experimental for all work described is explained in chapter 5.

This chemistry showed possible benefits to the coatings industry, which were not expected when the project began. These coatings show a potential for fast cure coatings[158] when catalysed and as a significant increase in Tg values from resin to cured coating were observed, this is also something worth a further investigation. These ideas are explained further below in section 7.2.

These coatings were all cured at 160°C, which was decided upon due to a gel time study explained in chapter 6, As these coatings were able to be produced at this temperature, that's a 40°C decrease in oven temperature compared to the standard powder polyester coatings. Due to the fast cure observed with catalyst, a gel time study, alongside a viscosity study at lower temperatures, is required to understand the full potential of this chemistry used regarding reducing energy consumption by using lower temperatures.

7.2 Further work

The polymers synthesised showed interesting results which will be of relevance for the coatings industry. Firstly, this chemistry shows potential for fast cure when catalysed. Catalysts are often added to coatings formulations but were not in this project due to solely investigating the polymer crosslinker relationship. Other benefits included a significant increase in Tg values from resin to cured coating. This is not something usually seen in polyester coatings and a possible route for investigation as it allows a lower Tg resin to be used initially. As this project has sparked some interesting knowledge, this project will be continued within AkzoNobel in the future.

It is believed that further investigations will bring valuable knowledge on this chemistry and application in the coatings industry, example of these are detailed below.

Catalysts as mentioned may lead to yellowing of the coating although an appropriate catalyst could increase the curing kinetics drastically as seen in chapter 6.2. Tests were carried out by means of measuring the gelation time and measuring exotherms by DSC to give a full understanding of the catalysis. The tests showed a fast cure time at 160°C with catalyst.

This gives a great insight into a fast cure opportunity in the coatings industry. The regular coating is cured for 15 to 20 minutes at 160°C to 200°C. With the appropriate catalysts, this coating can cure in less than 4 minutes at 160°C, suggesting even faster cure times at higher temperatures. Only a small amount of catalyst was added and this was tested with a single catalyst, other catalysts may increase this cure time even further. This may also allow for a low temperature cure, which was the aim of this project initially. Understanding cure at below 140°C would be interesting for future project prospects. With a change or an increase in catalyst, this may induce some great possibilities for low or fast cure. As the coating cured in less than 4 minutes, this is a great success for this project as fast cure is also an excellent route into a lower energy cure coating.

Industrially, the process by which a polymer is made is important and needs to be cost effective as well as involving as low chemical hazard as possible. If higher molecular weight polymers were to be made, they would require to be synthesised without purification for cost and time restrictions, which, as shown in results in chapter 3, is not currently possible. Therefore, if the coatings industry does require the benefits this chemistry could provide such as low cure or fast cure, it is possible that screening further catalysts for polymer synthesis could be beneficial. Other catalysts may aid reaction, furthering the reaction process, to allow the polymer molecular weight to reach the theoretical molecular weight. Only a selection of catalysts were screened and they only presented the catalysis opportunities for a small amount of catalyst types.

Other aspects when using these polymers in to powder coatings; it would be required to be produced ideally with no solvent to prevent the extra step of stripping the polymer. As this would not be possible with phthalic anhydride as it easily sublimes during synthesis without solvent, a different anhydride may be advantageous to

investigate. From testing, it is known that Hexahydrophthalic anhydride (HHPA) does not sublime during synthesis and may be useful to understand how efficiently it synthesises a higher molecular weight polymer. Other monomers could be tested for other reasons also, such as increasing Tg. As the polymer needs purification when using phthalic anhydride, ideas into increasing aromatics on the backbone, or increased crosslinks through higher functionalities may be a possibility to increase the Tg higher to an acceptable temperature for powder coatings.

Polyesters for powder coatings are often synthesised in 2 steps during in which a polyol is synthesised in the first step and is then reacted with further diacids to yield a polyester with carboxylic acid end groups. This two-step process which allows corrections to be made, in the event of deviations in stoichiometry of monomers (e.g. low boiling point monomers may distil out before reacting). Once added, the monomers used for correction are processed into the polymer and then the synthesis continues to the next step. The same concept may also be possible in the case of the chemistry described in thesis as theoretically shouldn't terminate, the reaction stops when all monomers have been consumed and reacted. If impurities are causing issues or deficiencies lowering the molecular weight, this may be a solution to the higher molecular weight polymers.

An initial and crucial development for this project was to understand why the measurement of residual hydroxyl groups were not able to be measured accurately using the standard titration method used for usual polyesters. Alternative methods have been reported in literature[118] and it is believed that the polymer could be derivatised in a solution of 2-chloro-4,4,5,5-tetramethyldiox-aphospholane, which will react with the hydroxyl and carboxylic acid groups on the polymer. The polymer could then be analysed by ^{31}P NMR against an internal standard to accurately work out hydroxyl and carboxylic acid equivalent weights.

Another crucial analysis which requires further understanding is confirming the functionality of the polymers produced. It can be predicted through calculation based upon the acid value and an indication can be given with gel time values, but an accurate method has yet to be developed.

Overall, there are many next steps which will further understanding, but could also provide possible routes into products for the coatings industry. With the knowledge discovered already and knowledge to be discovered in the future, this project could provide some truly interesting information for the industry and push the performance of a wide range of coatings ahead.

Chapter 8 - Bibliography

8 Bibliography

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