THERMAL CHARACTERISATION OF XB2-CA4: CYCLIC POLY(BUTYLENE TEREPHTHALATE) WITH STANNOXANE CATALYST

by

ALICE VICTORIA MARY MATTHEWS

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ABSTRACT

Thermal Characterisation of XB2-CA4: Cyclic Poly(Butylene Terephthalate) with Stannoxane Catalyst

The following investigation presents the melting, polymerisation and crystallisation kinetics of XB2-CA4, an oligomer powder of cyclic butylene terephthalate with a stannoxane catalyst, which polymerises into cyclic poly(butylene terephthalate) (cPBT).

When heated this material undergoes very rapid concurrent polymerisation and crystallisation. These processes were separated using a combination of two different techniques in the DSC, and Avrami analyses on the data produced.

As reported in previous literature it was thought that Stannoxane catalyst degradation above 220^{o}C caused production of linear polymer[1]. However, FTIR and GPC experiments on samples heated to 230^{o}C and 250^{o}C, do not show production of linear polymer, but rather an increased production of cylcic polymer, but of a slightly lower molecular weight than that produced at 170^{o}C and 190^{o}C.

It was initially thought that XB2-CA4 did not melt below 170^{o}C, however, GPC experiments showed that some heavier molecules were produced in samples that were held at 150^{o}C for more than 5 minutes.

The molecular weight distributions from the GPC showed some significant findings with regard to the potential degradation of the samples above 220^{o}C.

TABLE OF CONTENTS

LIST OF FIGURES

Chapter 1 : Introduction

Chapter 2 : Materials and Methods

Chapter 3 : Results and Discussion

LIST OF TABLES

Chapter 2 : Materials and Methods

Chapter 3 : Results and Discussion

CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 Development of thermoplastic oligomers

Polymers have been a massive part of product manufacturing over the past century; almost everything we touch has polymer material within it, or coating it! Manufacturers have very successfully taken advantage of the low viscosity and malleability of many polymers, developing complex machinery and moulding techniques capable of producing products in virtually every shape and size. Thermosetting polymers have been used in every area of every industry due to their low viscosity in melt allowing easy formability, and then high stiffness, but keeping a low molecular weight, and good heat resistance when formed into a final product. However, a recurring issue with these thermosetting polymers, is that the heavy cross-linking that occurs during processing, which gives the products their final properties, means no second generation usage for the material i.e. the products cannot be recycled.

There are of course thermoplastic polymers, with the necessary heat resistance for high temperature applications, which would be capable of producing second and third generation products due to recycling capabilities. However, these materials cannot be processed using traditional manufacturing techniques as they have very high melt viscosities. One solution would be to revolutionise our manufacturing techniques to allow these engineering resins to be used in all areas of manufacture. A less costly route would be to develop a material that has a low melt viscosity, good stiffness to weight ratio and heat resistant, but with the added capacity to be recycled.

PBT is such a material (Figure 1.1). It has been available commercially since the late 1960's, and has been utilised by some manufacturers for its unique thermoplastic processing capabilities [1]. Oligomer Butylene Terephthalate , which has an extremely low viscosity at reasonably low processing temperatures, can be easily processed using traditional techniques [2]. In addition to this, with the use of specific catalysts, PBT can undergo rapid polymerisation and crystallisation as soon as it is injected into a composite matrix; creating products of a high stiffness, and high molecular weight, with the additional possibility of recycling [1]

Linear PBT consists of four flexible methylene groups, and a rigid terephthalate group segment:

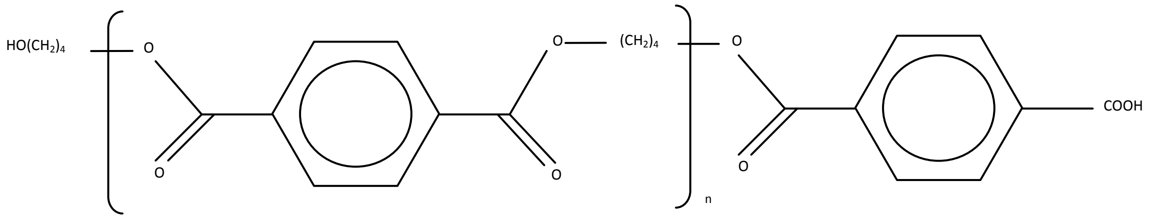

Figure 1.1 Structure of linear poly(butylene terephthalate)

1.1.2 Cyclic Oligomers

Traditionally, polymers, such as plastics and rubbers, consist of long chains of molecules covalently bonded to one another. Cyclic describes a polymer with no end groups. Rather than a long chain of repeat units, with two end groups, one on either end, this polymer chain comes right round and reattaches itself, literally forming a loop. Cyclic polymers are still able to branch and form networks between other rings, but this basic structure of a loop, rather than a long chain, results in differing material properties to its linear creator [1].

Cyclic oligomer structures are a known by-product of most condensation polymer reactions. Present at levels between 0.25-2.0% in commercial polyesters and polycarbonates [3]. During the polymerisation of linear PBT, 1.5-2% of the chains are found to be cyclic [1]. Carothers [4] was the first to highlight this phenomenon, of cyclic polymers forming as a by-product during polymerisation, while Jacobsen and Stockmeyer [5] went on to hypothesise that each polymer had a critical monomer concentration, whereby an optimum ratio of linear to cyclic structure could be produced within a material during polymerisation.

1.2 Overview of Research

Since its introduction into industry, PBT has been the focus of much research; developing the understanding of it properties and capabilities for different applications and blending. The research conducted for this project focused on developing the understanding of cyclic poly(butylene terephthalate) (cPBT) (Figure 1.2). Rather than the traditional step growth polymerisation as occurs with linear PBT, a cyclic oligomer, CBT, will be used with a cyclic catalyst, 1,1,6,6-Tetrabutyl-1,6-di-stanna-2,5,7,10-tetraoxacyclodecane (stannoxane) (see Figure 1.3), to allow a process similar to ring expansion polymerisation preserving the cyclic structure of both polymer and catalyst. The product being tested in this work is a premixed powder of cyclic PBT monomer and stannoxane catalyst. The oligomer powder contains molecules of 2 to 7 repeat units in length [6]. After the polymerisation process has occurred, the polymer chains will be approximately 600 repeat units in length [7]. A mechanism similar to ring opening expansion occurs as the powder is heated and the polymerisation process occurs, both initiation and propagation stages are known to occur. However, due to the structure of the material, there is no ring strain or exothermic reaction during polymerisation [6][8][9].

The material c-PBT has provided a particular interest for this research, as the polymerisation and crystallisation processes occur concurrently. Depending on the speed that these reactions occur, the final characteristics of the sample will differ. Also, the work done here raises issues over the suitability of Stannoxane as a catalyst for this material, as it could degrade at temperatures before the polymer has fully melted. However, this particular catalyst is unique due to its cyclic structure. This means that negligible by-products, and no end groups, will be created during the polymerisation process. Where linear catalysts are used, the catalyst end groups control the molecular weight of the final product, and therefore need to be specifically controlled to produce a specific molecular weight in the final material [8].

Various thermal characterisation techniques will be used to investigate the unique properties of cPBT, and to further understand the polymerisation and crystallisation process from CBT oligomer to cPBT polymer. These will be discussed further in the following chapters.

Investigations into the thermal kinetics of polymer materials, particularly the crystallisation, are fundamental for future utilisation of that polymer in processing and industry. The reason this area is of such importance is that the crystal structures within a material dictates the physical properties of the material, and thus denotes what applications it could be fulfilling.

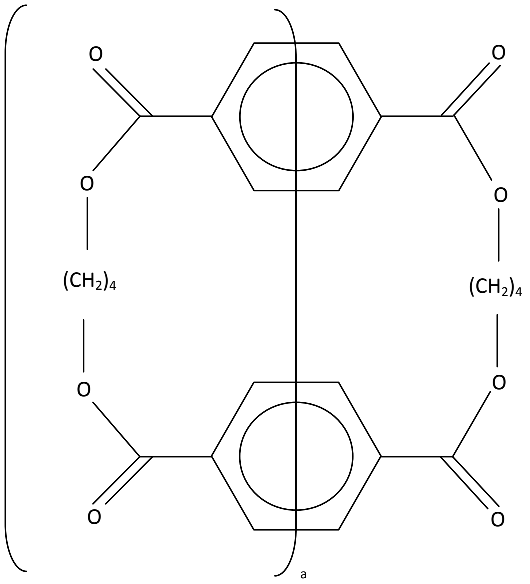

Figure 1.2 Structure of cyclic poly(butylene terephthalate)

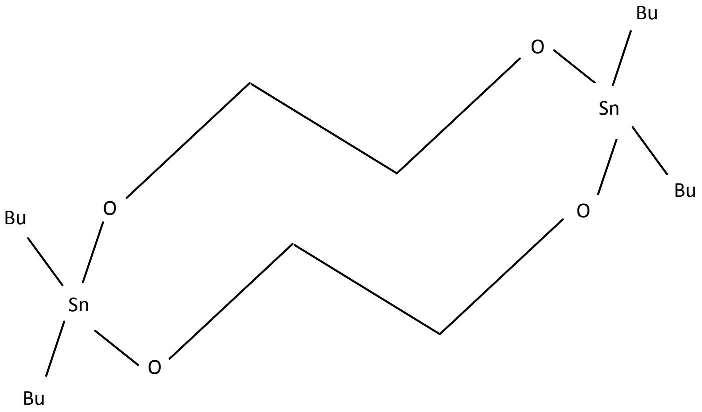

Figure 1.3 Structure of stannoxane catalyst

1.2.1 Cyclic Poly(Butylene Terephthalate)

The vast majority of research on PBT has investigated the linear polymer; characterisation, crystallinity, processing techniques, blending, and more recently, recycling. It is a thermoplastic polyester, created via polycondensation reactions of terephthalic acid and 1,4-butanediol. Investigations into the blending of PBT have often happened alongside other aromatic polyesters such as polyethylene terephthalate (PET) and polytrimethylene terephthalate (PTT) [2]. Similar physical and chemical recycling techniques can be used with PBT as they are with PET. However, the recycling possibilities investigated for linear PBT, such as methanolysis [10] hydrolysis [11] and degradation [12] are not ecological and still create by-products.

Cyclic polymers are strands of linear polymer, with the same molecular composition, apart from they have no end groups (Figure 1.4). Rather than growing from a monomer into a long winding, branching chain, as many traditional polymers do, cyclic polymers grow from oligomers, which are only a few repeat units long, and in a loop rather than a chain. When the small chains are exposed to some sort of initiator, like a catalyst and/or heat, rather than propagation or condensation reactions, which are the processes that describe the growth of linear polymers, cyclic polymers commonly grow by ring opening expansion (ROE) and the loops and cycles of polymer get larger and larger [7][8][13].

Cyclic polymers were discovered many years ago as a by-product during condensation polymerisation. When it was first discovered that commercial polymer products contained small percentages of cyclic material, research in the area boomed. In 1962, Schnell and Bottenbruch [14] attempted to isolate the cyclic material that was formed during the processing of a bisphenol A, reporting a 21% yield. However, the techniques used were expensive, extremely time consuming and required extensive purification techniques not making them viable for introduction into industry. In fact, it is not until quite recently that any cyclic materials have been fully utilised for commercial processing in industry. This is due to the highly expensive processes of purification that have needed to occur before a pure cyclic polymer is produced, considerably reducing the positive environmental and ecological implications of using them [8]. In 1984, Brunelle [8], along with a team working at GE Global Research, set about trying to develop a cyclic polymer, culminating in the commercialisation of cyclic polyester oligomer technology by Cyclics Corporation.

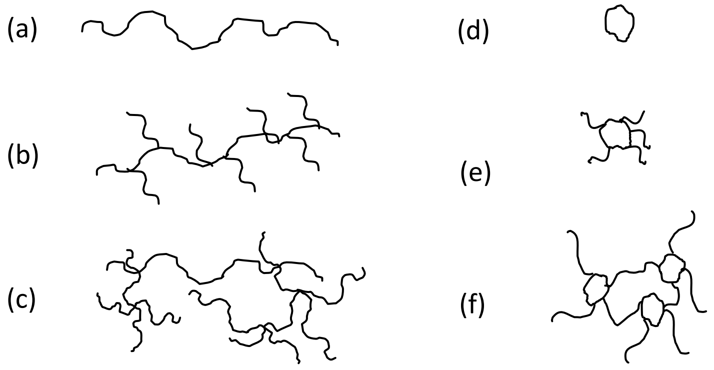

Figure 1.4 Three types of linear polymer: (a) linear, (b) branched, (c) network, and three types of cyclic polymer: (d) cyclic, (e) network, (f) network [3]

1.2.2 Stannoxane

In order for ring expansion to occur efficiently in CBT, a catalyst such as stannoxane is needed [8][15]. The ring structures of the CBT cannot open themselves and attach onto the next chain, a process of ligand exchange occurs where the active site on the catalyst attaches to a specific structure in the CBT molecule [1][8]. Stannoxane is particularly reactive as it has four active sites, where insertion polymerisation can take place [16]. The polymerisation mechanism that occurs between stannoxane and CBT is shown in Figure 1.5.

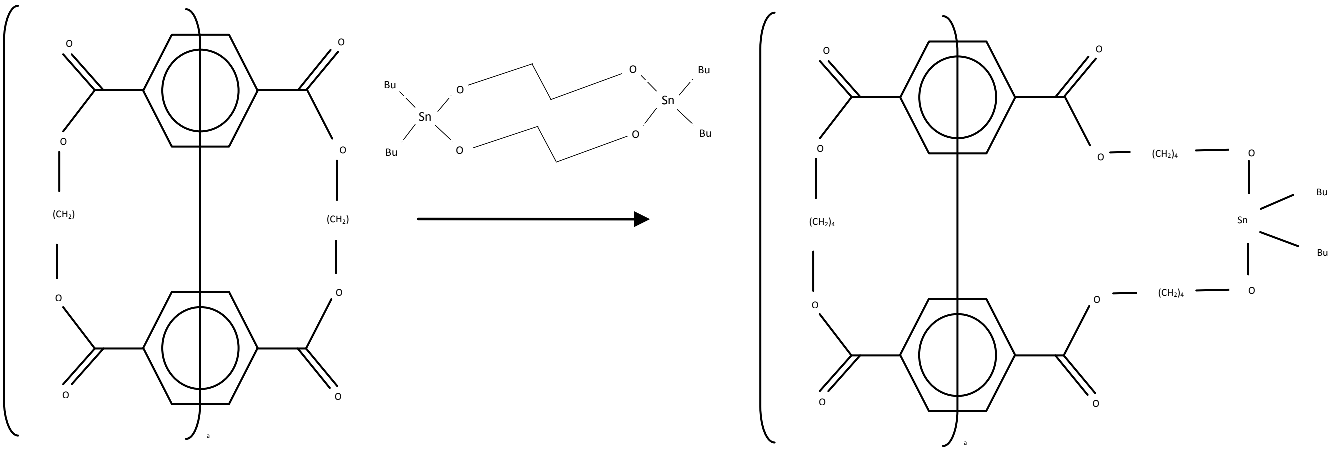

Figure 1.5: Ring growth mechanism of CBT with Stannoxane catalyst.

There is a breaking and reforming of a Sn-O bond from a stannoxane molecule, and a C-O bond from a CBT molecule. The remaining three Sn-O polymerisation sites are still capable of attaching to other CBT molecules, including those that have already undergone polymerisation, creating large macrocyclic molecules. Particularly interesting with this combination of cyclic oligomer and cyclic catalyst, is that the ring opening and ring exchange processes appear to occur concurrently, producing virtually no polymerisation exotherm [8]. This process of continuously expanding chains, and the lack of any by-product, results in the final polymer being of a comparatively high molecular weight compared to a material that has undergone normal step polymerisation [1]. The size and number of macrocyclic chains produced is dependent on the number of active sites available for polymerisation to occur. Thus the molecular weight is dependent on the ratio of catalyst to oligomer [1].

Miller [1] found during his research of PBT, that stannoxane held at 220˚C loses 12% of its weight within 30 minutes. It was assumed that any weight loss below 100˚C was due to loss of residual moisture in the sample, however, the weight of the catalyst continued to decrease above 100˚C. It was therefore assumed that stannoxane was undergoing some form of degradation below its melting temperature of 230˚C. Miller also found an anomalous low temperature endotherm on DSC traces of stannoxane, which could not be accredited to moisture loss, as it occurred on both first and second run tests in a crimped DSC pan. It was then assumed that there could be some monomer present in the catalyst, but this does not explain the low temperature weight loss.

The research done by GE Global Research found CBT to be completely molten at 190˚C, whereas Parton et al [6] later found the oligomer to melt between 130˚C and 160˚C, and polymer melting to occur at around 225˚C. However,) difficulty arose when trying to complete polymerisation before polymer melting began. Further testing showed that moisture in the samples had a detrimental effect on the yield of cyclic material, and in fact resulted in the production of linear oligomer [17] (Figure 1.6).

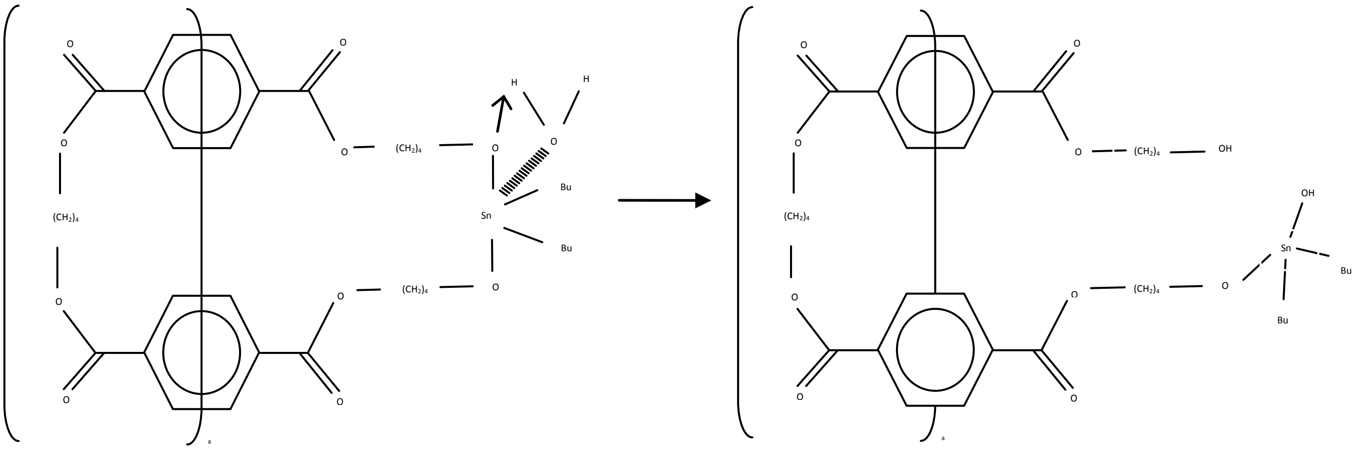

Figure 1.6: Mechanism of water degradation causing the formation of end groups with stannoxane catalyst

The melting point of CBT being below that of PBT allows isothermal processing to occur, depending on the rate of heating and cooling, the process may result in simultaneous polymerisation and crystallisation [1][6][8]. Brunelle et al [17], and also Youk et al. [18] found that the three most important factors in successfully polymerising cyclic oligomer into cyclic polymer is to ensure the monomer is void of impurities, the initiator and monomer are well mixed, and finally that the polymerisation occurs rapidly, so as not to overlap with the crystallisation.

CHAPTER 2

MATERIALS AND METHODS

2.1 Selecting Cyclic Butylene Terephthalate (CBT)

The material being used in this research is supplied by Cyclics Corporation. Cyclics Corporation, alongside GE Global Research has developed a range of cPBT resins and composite materials from the traditional linear PBT. The material has been developed for its thermal stability, compatibility with other polymers for blending, and negligible volatile organic compounds [29]. A range of CBT oligomer materials exist, with various catalysts pre mixed into the material. The catalysts are present to initiate the polymerisation process. XBO-CA4 is the name given to virgin CBT oligomer, whilst XB3-CA4 contains a butylin chloride dihydroxide catalyst [29]. The material being used for this investigation into the crystallisation kinetics of cPBT, is a pre-mixed powder of CBT with a stannoxane catalyst; XB2-CA4.

This grade of CBT was chosen after preliminary DSC tests on various cPBT powders, with XB2-CA4 giving the clearest and most consistent results. XB2-CA4 is a 50:50 mixture of the virgin CBT oligomer, XBO-CA4, and a mixture of oligomer and catalyst, XB2HC-CA4. The stannoxane catalyst is present at 0.25% in the powder mixture.

To put together a full material characterisation, and attempt to complete the story of concurrent polymerisation and crystallisation that appears to occur on heating CBT, a grade of the oligomer had to be chosen. Preliminary research into the thermal properties of the different grades of CBT that Cyclics Corporation produced found that XB2-CA4, illustrated the different processes of oligomer melting, polymerisation, crystallisation and polymer melting the most clearly.

2.2 Apparatus and Experimental Techniques

A series of techniques will be used in order to produce a thorough characterisation of the material. The techniques used complement one another to give a thorough set of comparable results, each demonstrate a different aspect of the materials character. By repeating studies of the reactions of the material when exposed to specific environments, a consistent picture can be established of the materials structures and composition, and the intermolecular reactions that may be occurring.

The object of this study was to develop the understanding of cyclic Poly(Butylene Terephthalate) (cPBT), specifically the crystallisation kinetics. Therefore, the techniques chosen for this research focused on the thermal behaviour of cPBT. By varying either the amount time the material was exposed to a specific heat, or allowing the sample to react to varying temperatures. The traces from these tests can then be analysed to describe the behaviour and physical transformations of the material over a range of temperatures. Any differences in molecular weight and structure, and images of the samples can then be linked with specific processes involved in the polymerisation and crystallisation of the material. Lastly, the involvement of the stannoxane catalyst, and its potential degradation at higher temperatures can be investigated.

2.2.1 Differential Scanning Calorimetry

The differential scanning calorimeter (DSC) compares the thermodynamics of a material compared to a controlled environment, or reference sample. The reference has a well defined heat capacity over the range of temperatures scanned, which is normally linear. When the sample, or test material, undergoes physical transformation i.e. phase transitions, either an increase or decrease of heat flow will need to occur (exothermic or endothermic). For example, when a polymer crystallises, it will require a decrease in heat flow (exothermic) to raise the sample temperature. The difference between the heat flows to the material sample, compared to the reference should show clear transitions; in affect the DSC measures the amount or heat absorbed and released by a sample.

The DSC can be set up to simulate dynamic or isothermal conditions on a sample. A dynamic condition would be a constantly changing condition, i.e. heating or cooling the sample, while an isothermal condition would impose a specific temperature on the sample, for a particular length of time. These two processes can be used together to produce thermal biographies of the material in question. DSC is the most commonly used technique to measure Tg and Tm.

A traditional DSC trace for a polymer is illustrated in Figure 2.1. The glass transition temperature (Tg), crystallisation temperature (Tc) and melting temperature (Tm) are labelled. The CBT powder that will be used for the DSC experiments in this project is an oligomer, so there will be an additional exothermic trough before the Tc, when polymerisation occurs.

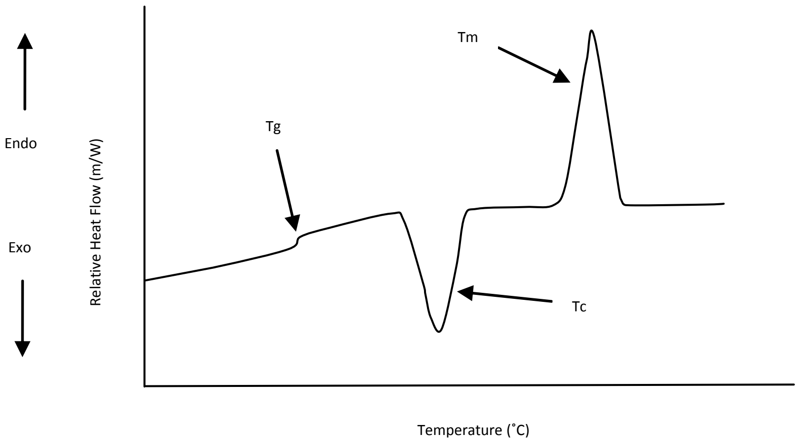

Figure 2.1: Traditional polymer DSC trace showing Tg, Tc, and Tm

DSC polymerisation and crystallisation studies were carried out on cPBT under both dynamic and isothermal conditions. Initial dynamic analysis created a clear picture of the temperatures at which each phase transition was occurring, and that indeed the polymerisation and crystallisation processes were occurring concurrently as the temperature was increased. These dynamic traces allowed appropriate isothermal temperatures to be chosen to better illustrate the physical changes that were occurring.

In order to collect results with ecological validity, every DSC sample was 20mg, weighed to the nearest 0.5mg on a microbalance. The same aluminium DSC pans and lids were used for all samples, and no samples were loaded into the DSC before the argon cooling system had been turned on for at least 45 minutes. The DSC was calibrated by processing separate samples of Indium and Tin, both with known melting temperatures.

The first dynamic scan was preset to heat the sample from room temperature at a rate of 10˚C/min to 250˚C, the temperature suggested by Miller [1], to allow full polymer melting, without cPBT degradation. The sample was held at 250˚C for 10 min, and allowed to cool back to room temperature at the same rate as heating; 10˚C/min.

The first set of DSC experiments investigated the effect of holding time on the crystallisation half life of cPBT; this is half the amount of time it would take for complete crystallisation to occur. By heating the sample to 240˚C, crystallisation will be occuring, as illustrated by Figure 3.1. The holding time was varied from 5 to 25 minutes in 5 minute increments. The purpose of the varying holding times is to establish whether complete crystallisation can occur in 5 minutes, or a more substantial amount of time is required for complete crystallisation to occur. The samples were then held at 196˚C, this was considered an optimum temperature to illustrate the crystallisation mechanism from Figure 3.1.

These experiments may also prove useful in understanding the degredation process that may be occuring in the catalyst at temperatures over 220˚C. Miller highlighted in his thesis that there are questions over the stability of the Stannoxane catalyst. Miller interpreted thermogravametirc (TGA) studies on the stannoxane initiator to suggest a loss of weight in the initiator at 220˚C [1]. However, this weight loss could be attributed to loss of residual moisture in the samples, as there is a constant decrease in weight as soon as heat is applied to the sample.

The second set of DSC experiments involved heating the samples to various crystallisation temperatures and holding them there for 60 minutes. This method was used to investigate the optimum temperature for complete crystallisation to occur. By heating directly to the crystallisation temperature, without first heating to 240˚C, there is no suggestion that the stannoxane catalyst will undergo any sort of degradation, and cyclic polymer should be produced.

However, because the polymerisation and crystallisation processes are occurring concurrently, it is necessary to perform another set of experiments, ensuring only crystallisation is occurring. Therefore, the third set of experiments heated the samples firstly to 240˚C and held there for 20 minutes; this was to allow the oligomer to fully melt and polymerise, and for the polymer to then undergo crystallisation and polymer melting. By allowing these processes to occur, and then reducing the temperature back down to the crystallisation temperatures investigated previously, only crystallisation will be occurring, without polymerisation.

The data is collected from the DSC using Pyrus software. In order to investigate the crytallisation of the samples, an Avrami software was employed. The Avrami equation is used to calculate the crystallisation kinetics of a material, and has been specifically developed for use with polymer materials. By adopting this analysis technique for the above experiments, the difference in the crystallisation processes occuring in the samples that have been previously heated to 240˚C, and those that were taken straight to the crystallisation temperatures without any pretreatment, can be directly compared. This will illustrate the concurrent polymerisation and crystallisation, and may also demonstrate whether any degradation is occuring to the polymer or the catalyst at 240˚C.

Avrami took a theory intended for metallurgy, and adapted it for use with polymers [30]. The theory has been used for many years, and has been adapted, rearranged, and simplified for its application to polymer crystallisation. Avrami described the relative crystallinity as a funtcion of time, and expressed it like so:

$$1 - X_r = \exp (- k t^n)$$

Equation 2.1: The Avrami equation

X_r referred to the maximum degree of crystallinity, with t, the crystallisation time, calculated according to the induction time, and the kinetic constant, k, and exponent, n, are the parameters characterising the crystallisation process [30][31].

The particular software used in this research, Origin, helps to calculate the crystallisation half life. From this it is then possible to manipulate the data to produce graphs for various crystallisation characteristics.

The final set of DSC experiments involed heating samples to a range of crystallisation temperatures, ranging from 196˚C to 204˚C, held for one hour and cooled to room temperature. The samples were then heated and cooled at 10˚C/min from room temperature to 240˚C, and back to room temperature.

2.2.2 Fourier Transform Infrared Spectroscopy ((Nicolet 860 FTV) ATR attachment (specac) (golden gate))

The Fourier Transform Infrared Spectroscopy (FTIR) technique is used to identify the molecular composition and structure of a material. Techniques such as nuclear magnetic resonance (NMR) spectrometry, or X-ray diffraction would often take precedence over infrared spectrometry, unless using polymers [22].

As with other absorption techniques, molecules will only absorb specific wavelengths of radiation, dependent on the bonds present within the molecule. When the infrared radiation matches the frequency of the vibration of a bond within the molecule it will be absorbed, and cause an increase in amplitude of that bonds vibration. Most molecular vibrations sit within the infrared range, therefore by using the infrared spectrum, individual bonds and functional groups can be detected, it is important to note here that only bonds that have dipole moment, are capable of absorbing infrared radiation [23].

An infrared spectrum presents the absorption peaks of a sample, which correspond to the vibrations between the bonds of the atoms making up the material. The spectrum produced for a material is the wavelengths of the light against the amount of infrared radiation that passes through the sample [24].

FTIR can positively identify any material, as no two compounds have completely identical bonds. Although the samples tested for this project are the same material, FTIR could identify possible degradation, and also the peak intensity indicates the quantity/concentration of that bond within the sample i.e. may be able to help identify when polymerisation and then crystallisation occur and complete, or even if there are end groups present in the sample i.e. linear PBT.

The FTIR spectrometer works by producing a beam of infrared light; this is then split by a series of mirrors into two beams. One beam is directed at the sample, and the other is used as a reference for comparison. The beams are then alternately passed through a rotating prism, which varies the radiation reaching the detector. The information from the detector is then collected via a computer and the difference between the beam intensity coming from the sample beam and the reference beam is recorded [23][24].

The Nicolet spectrometer used in these experiments has the capacity to heat the sample in-situ using a variable temperature cell. The sample started as powder oligomer, and was slowly heated at 10˚C/min. The sample was scanned 100 times at 5 predetermined temperatures, at a resolution of 4cm^{-1}. For each spectra, the average of the 100 scans was recorded. The temperatures, at which the spectra were taken, were at 20˚C intervals, from 150˚C to 230˚C. These temperatures coincide with those used in the other characterisation techniques, covering oligomer melting, polymerisation, crystallisation and polymer melting.

The purpose of these experiments was to discover whether it would be possible to distinguish from a breakdown of the molecular structures within the sample if the material was indeed cyclic, or if linear polymer was also present, and also, if structures changed above 210˚C, if that was due to catalyst degradation.

2.2.3 Gel Permeation Chromatography

The molar mass distribution of a polymer is fundamental to its physical properties, and thus a vital characteristic to research when developing a material. Gel permeation chromatography (GPC), a form of size exclusion chromatography (SEC), was the final technique used to characterise cPBT. GPC is a separation technique, used mainly for the separation of polymer samples, sometimes referred to as molecular sieving [25][26]. Traditionally, the Polydispersity Index (PDI) and viscosity molecular weight (M_v) of a material are interpreted from the results of GPC analysis, however more frequently the technique is used to investigate other properties such as copolymer composition [27]. The aim for this project is that the GPC results can help identify how the molecular weight of cPBT develops as it progresses from oligomer powder, to polymer. Also, if there is any degradation in the samples prepared at higher temperatures, it may be possible to identify this from a decrease in molecular weight.

GPC works by dissolving the material sample in a solvent, once the sample is fully dissolved; the whole solution is injected into the top of the chromatographic columns, and carried by a stream, of the same solvent, at a constant flow rate. In the case of GPC the chromatographic columns are filled with a cross-linked gel, which the mixture of solvent and sample then has to flow through (other SEC techniques may use a porous material such as glass, or even gas) [28]. The larger molecules will need to travel through fewer pores than the smaller molecules, and thus will exit the columns first. Therefore, in this case, if any monomer is left in the sample after DSC processing, it will exit the column last, after any polymer that is present [27]. The chromatograph instrument allows for automated solution injection, polymer fraction detection via refractive index, or ultraviolet and infrared spectroscopy, flow-through by pump and computer software data analysis [25].

The particular GPC instrument used in these experiments is calibrated with polymethylmethacrylate (PMMA), with the same solvent, and at the same processing temperature, as will be used for the samples. Thus the results are expressed as ‘PMMA equivalent’ molecular weights. The final chromatogram, which will be produced by analysis software connected to the detector on the machine, will be a ‘PMMA equivalent’ so it should be appreciated that the true values of the samples molecular weights could be considerably different. However, this still allows comparison of the samples against one another.

Samples were selected from different stages of the materials development from oligomer to polymer, particularly around temperatures where there was the possibility of catalyst degradation, during the polymer melting phase. The samples that were chosen for GPC are described in tables 3.1 and 3.2.

Sample	Sample weight / mg	Sample Description
1	39.90	CBT in powder form.
2	29.46	CBT heat up to 150^{o}C (melting temperature of cyclic oligomer is 142^{o}C)
3	43.68	CBT heat up to 170^{o}C (crystallization and polymerisation may occur at this temperature)
4	39.42	CBT heat up to 190^{o}C (rapid (less than 1 min) crystallisation and polymerisation may occur at this temperature)
5	31.45	CBT heat up to 210^{o}C (crystallisation may complete at this temperature)
6	35.69	CBT heat up to 230^{o}C (cyclic oligomer now cyclic polymer. Tm of cPBT is 225 ^{o}C)
7	45.83	cPBT produced from ring expansion polymerization
8	44.72	Catalyst (1,1,6,6-Tetrabutyl-1,6-di-stanna-2,5,7,10-tetraoxacyclodecane)

Table 2.1: Samples prepared and tested for GPC

Further testing was later carried out on the following samples:

Sample	Temperature held (˚C)	Holding Time (mins)	Sample Description
1	190	0	Polymerisation not yet complete
2	190	3	Some polymerisation occurs
3	190	5	Some polymerisation occurs
4	190	10	Optimum holding time for production of cyclic PBT
5	190	30	Polymerisation complete but causes double melting peak on second run
6	190	60	Polymerisation complete but double melting peak on second run shifts
7	240	20	Effect of degradation
8	150	5	To see if any polymerisation can occur
9	150	30	To see if any polymerisation can occur

Table 2.2: Samples prepared and tested for GPC

The samples were analysed by “Smithers Rapra”, using an in-house procedure for gel permeation chromatography using 1,1,1,3,3,3-hexaflouro-2-propanol (HFIP) as the solvent, with 25mM NaTFac. A single solution of each sample was prepared by adding 5ml of solvent to 10mg of sample and leaving for four hours to dissolve. The solutions were well mixed and transferred to autosampler vials, without filtration. The conditions were kept the same for all samples; PL HFIPgel guard plus two 300 x 7.7mm, 9μm columns were used, at 40˚C, with a nominal flow rate of 0.8ml/min, and using a refractive index detector.

2.2.4 Scanning Electron Microscopy (Jeol 6060)

Scanning electron microscopy was chosen for the imaging process in this project for its large depth of field; up to 400 times greater than that of a light microscope. The instrument works by producing a beam of electrons which is directed through a condenser lens, and then focused as a very small point on the sample by the objective lens. Coils of wire (scan coils), located within the objective lens generate a magnetic field, deflecting the beam of electrons to and fro. The SEM image is produce via a cathode ray tube (CRT). Coils of wire around the neck of this tube also create a magnetic field from the same scan generator as is varying the voltage to the scan coils. The magnetic field around the CRT causes the deflection of a spot of light onto the CRT matching the pattern of deflection of the beam of electrons. The spot of light on the CRT varies in intensity depending on where on the sample the electrons are hitting i.e. a projection or a depression, secondary electrons are produced during these interactions and the information is collected by a detector. Depending on whether the electrons are hitting a depression of a projection, the detector signals the relevant intensity of the beam of light; this gives the topography of the sample [19][20][21].

Microscopy studies have been done to evidence the physical changes within the cPBT samples. The selections of samples were at various stages of oligomer melting, polymerisation, crystallisation, and polymer melting. The samples were extracted from DSC pans, and put through an etching process before imaging occurred, in order to expose any cyclic structures or spherulites that may be present at different development stages of cPBT from its cyclic oligomer.

Samples were prepared in the DSC; they were heated from room temperature to temperatures of 150˚C, 170˚C, 190˚C, 210˚C and 230˚C, and held for 30 minutes, and then cooled to room temperature. The samples were then extracted from the DSC pans, resulting in small disc shaped samples. Inside a fume cupboard, these samples were then placed in separate petri dishes and covered in 50ml of Dichloroethane. The etching process is important, as the samples form a smooth film around the outside as they heat, and the true structure of the material can only be found within the sample. Etching in this instance is used instead of fracturing the samples to see the internal structures. Fracturing was not favoured, as there were concerns that the extreme cold temperatures that the sample would be exposed to prior to fracture i.e. liquid nitrogen -196˚C, would alter the structures that had formed during heating. Three sets of samples were put through this process, each being exposed to the Dichloroethane for differing lengths of time.

Sample 1, prepared at 150˚C, completely dissolved in the 20 minute etching time, and could not be prepared for SEM. The remaining samples were carefully removed from the dishes and cleaned with distilled water. The samples were then mounted onto stubs using black carbon stickers and silver paint. The samples were then taken down to the SEM laboratory and covered in gold.

Once the samples were mounted inside the SEM, the machine is locked and a vacuum is used to pressurise the chamber inside. The different samples were imaged at various samples and the clearest images were chosen to compare.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Crystallisation kinetics of XB2-CA4

3.1.1 DSC

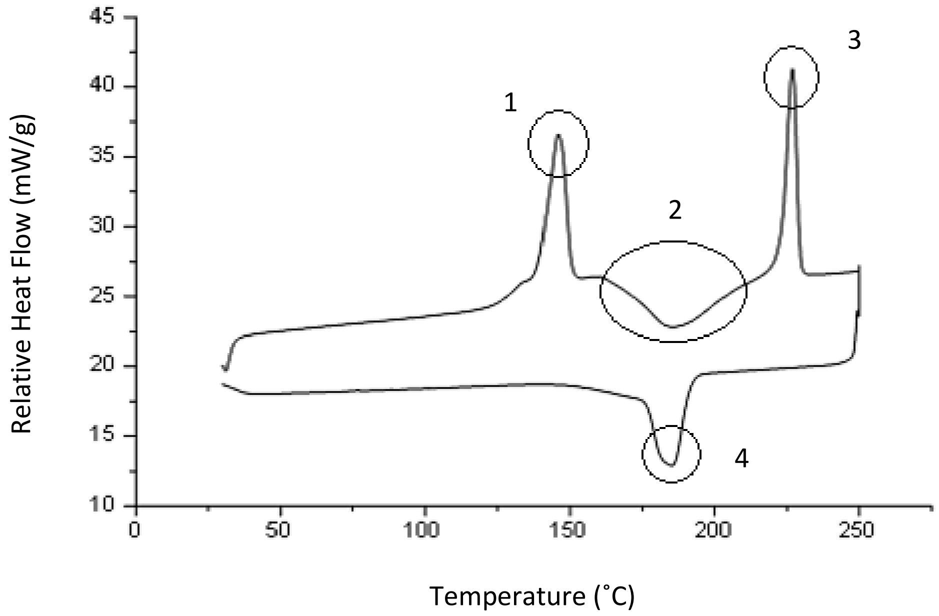

Figure 3.1: First dynamic run to illustrate oligomer melting (1), polymerisation and crystallisation (2), polymer melting (3), and re-crystallisation (4) (10 deg/min)

The initial DSC scan of XB2-CA4 (Figure 3.1) shows the temperatures at which the oligomer melting, polymerisation, crystallisation, polymer melting and re-crystallisation occur. The oligomer melting occurs at 146˚C, shown by the first endothermic peak. The first exothermic trough illustrates the temperature at which polymerisation, and crystallisation are occuring, this is between the temperatures of 160˚C and 215˚C. The second larger endotherm illustrates the temperature at which melting of the polymer occurs; 227˚C. The trace shows that the sample is then heated to 250˚C, before being allowed to cool at 10˚C/min. During cooling, a second exothermic trough is seen at 185˚C; this is assumed to be the polymer re-crystallising.

From this information the following experiments were used to investigate the polymerisation and crystallisation processes.

The first set of experiments (Figure 3.2) investigated the effect of holding time on the crytsallisation exotherm. To ensure there was no cPBT degradation, the samples were heated to 240˚C. This is well below the 250˚C at which degradation is thought to start [1], but a high enough temperature for polymer melting to have occured, as is clear from the initial dynamic run (Figure 3.1). These experiments aim to discover an optimum holding temperature, at which full crystallisation can occur in the minimum amount of time. The figures below show the DSC trace after the sample has been held at 240˚C, and the sample temperature has been reduced to 196˚C, the optimum temperature for crystallisation to occur as deduced from Figure 3.1. The figures have been produced from the raw data, using Origin software, giving relative heat flow (mW/g) against time (min).

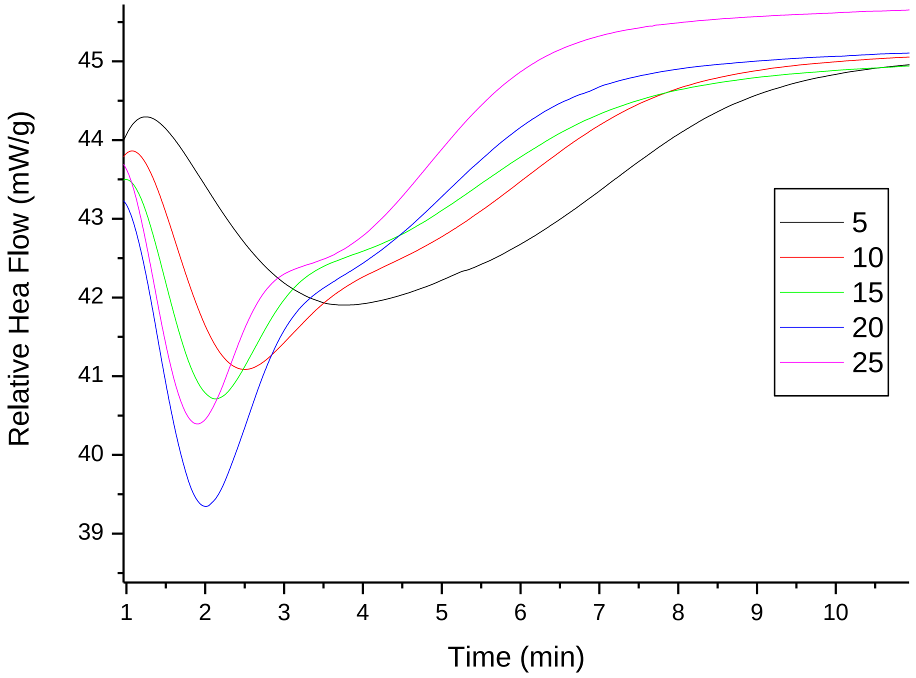

Figure 3.2: Comparing the effect of holding time on crystallisation half life for 20mg of XB2-CA4

In order to acurately compare all the results from this first experiment, the data from all five holding times are placed on top of one another in a single figure , as seen in Figure 3.2. The shorter the amount of time that the samples are held at 240°C, the longer it takes for crystallisation to complete once they are reduced to crystallisation temperature. The first sample was held for 5 minutes at 240°C before being reduced to crystallisation temperature. The sample was left to crystallise for an hour, but never appeared to complete i.e. the trace did not become completely horizontal. The samples held for 10 and 15 minutes at 240°C before being reduced to crystallisation temperature, completed crystallisation within the hour holding time at 196°C, but the first sample to complete crystallisation within 10 minutes at 198°C, was then held for 20 minutes at 240°C. Therefore, 20 minutes is the shortest amount of time the sample should be held at in order for crystallisation to complete within 10 minutes. For the remaining experiments conducted using the DSC, this seems an appropriate time to be holding the samples.

The following experiments were conducted to find the crystallisation half life of cPBT. That is the temperature at which half of the material has crystallised. Before these next experiments were undertaken on the DSC, the instrument was recalibrated using indium and tin. This led to the dicovery of the machine being out by -4°C i.e. in the previous experiment the crystallisation temperture was infact 200°C. Therefore the temperatures to investigate were adjusted accordingly. The temperatures decided were 198°C, 199°C, 200°C, 201°C, 202°C and 203°C.

The first set of crystallisation half life experiments involved the samples being heated straight to the six predetermined crystallisation temperatures, and held there for 60 minutes. Origin software was then used to analyse the raw data, and create the following representations of the crystallisation exotherms of XB2-CA4 (Figure 3.3). Due to the uncertainty of the precise temperature at which polymerisation starts and ends, and when crystallisation begins, the following exotherms are likely to be due to a combination of both processes.

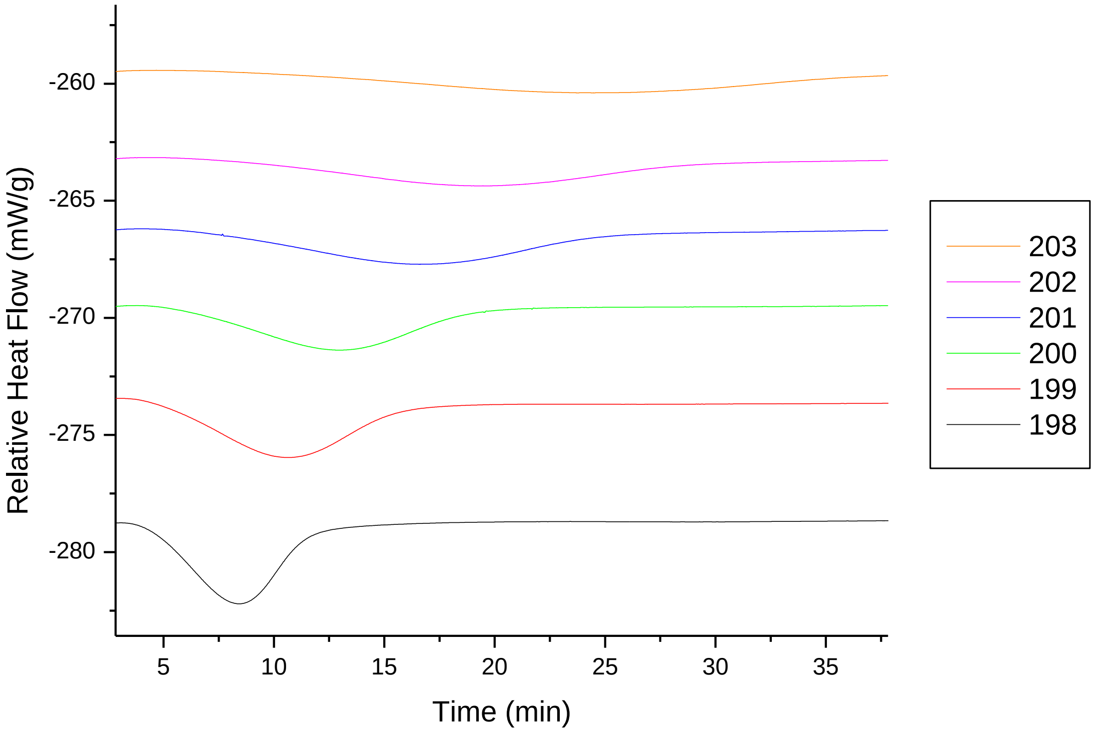

Figure 3.3: Comparison of holding XB2-CA4 for 60 minutes at various temperatures (198-203°C) on crystallisation time

Avrami analysis software was then employed to calculate the different crystallisation half life of each sample (t1/2). Due to the exothermic troughs, illustrated in Figure 3.3, not being symmetrical, it is not possible to simply follow the bottom of the trace down to the x axis to discover the time it takes for crystallisation. Therefore, in order to compare the results obtained from this experiment, the data need to be accurately interpreted using a relevant mathematical equation that will give a numerical value to the crystallisation half life of each sample. The equation being used in this project is the Avrami equation, which was briefly explained in chapter 2 (Equation 2.1). The software used in this project was developed to calculate the crystallisation according to the area of the exothermic trough produced during heating. The following parameters were calculated by the software for each sample; n is the

Avrami exponent; Xp is the degree of crystallinity at time t; t1/2 is crystallisation half life; the area is that for the whole crystallisation process; Z is the rate constant i.e. the rate at which crystallisation occurs [32] (Table 3.1).

Crystallisation Temperature [˚C]	**N [± 0.1]**	**Half life, t1/2**	**Degree of crystallinity, Xp**	**Rate Constant, Z [min-1]**
198	3.143971	4.783	1	0.005057
199	2.988727	6.900	1	0.002156
200	3.030692	8.546	1	0.001040
201	2.969877	11.600	1	0.000478
202	2.976548	13.547	1	0.000296
203	2.922862	18.266	1	0.000142

Table 3.1: Avrami parameters for 20mg of XB2-CA4 held at a range of temperatures for one hour (198-203°C)

The data from the DSC has been interpreted by the Avrami software using the above parameters from the Avrami equation. Data collected via the Avrami software, can be manipulated by Origin software into qualitative images. Figure 3.4 below, shows the relative crystallinity (Xp from Table 3.1) of all six samples, against time, and a clear trend has occurred. As the holding temperature increases, so does the amount of time required for crystallisation to occur. Looking at Table 3.1, all six samples reach full crystallisation of 1, but Figure 3.4 illustrates the differing amounts of time it takes each sample to reach this level of crystallisation.

In Figure 3.5, the rate constant, Z, and the crystallization temperature are compared for each sample. As the crystallisation temperature is increased, Z decreases i.e. the rate of crystallisation per minute lessens as the crystallisation temperature is increased. This corresponds with Figure 3.4, which shows that the sample held at 198°C has the fastest crystallisation time, i.e. the rate of crystallisation occurs at a higher rate per minute. That is, sample 1, held at 198°C has a rate constant of 0.005057/min^{-1}, while sample 6, held at 203°C has a rate constant of 0.000142/min^{-1}.

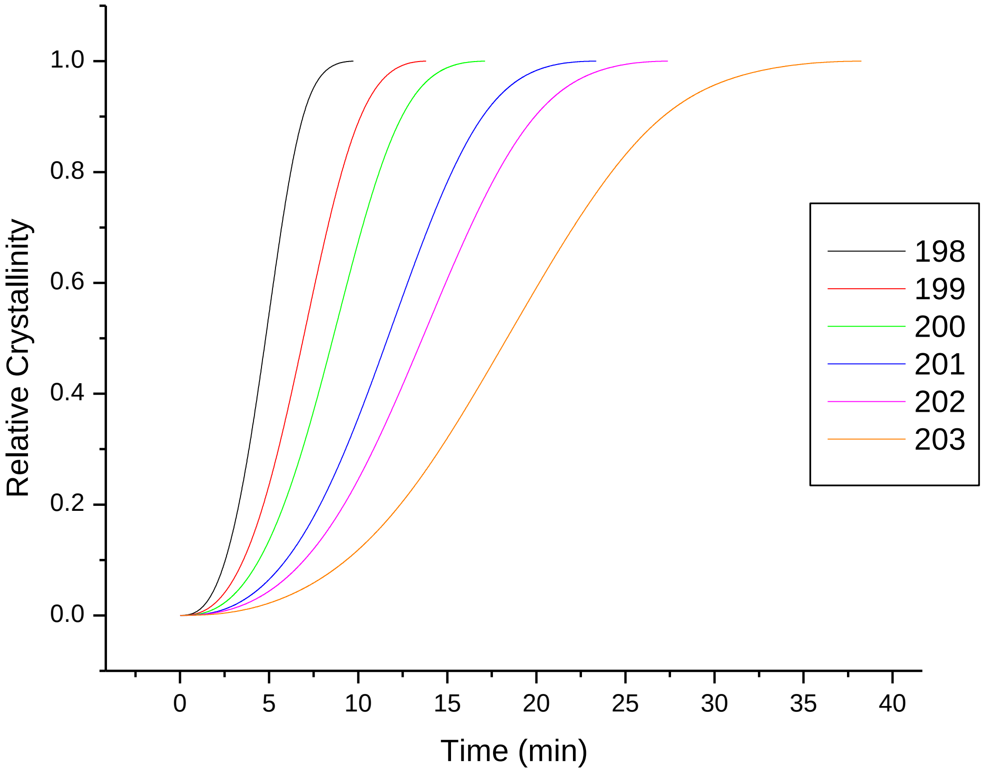

Figure 3.4: Development of crystallinity with time for XB2-CA4 held at a range of temperatures for one hour (198-203˚C)

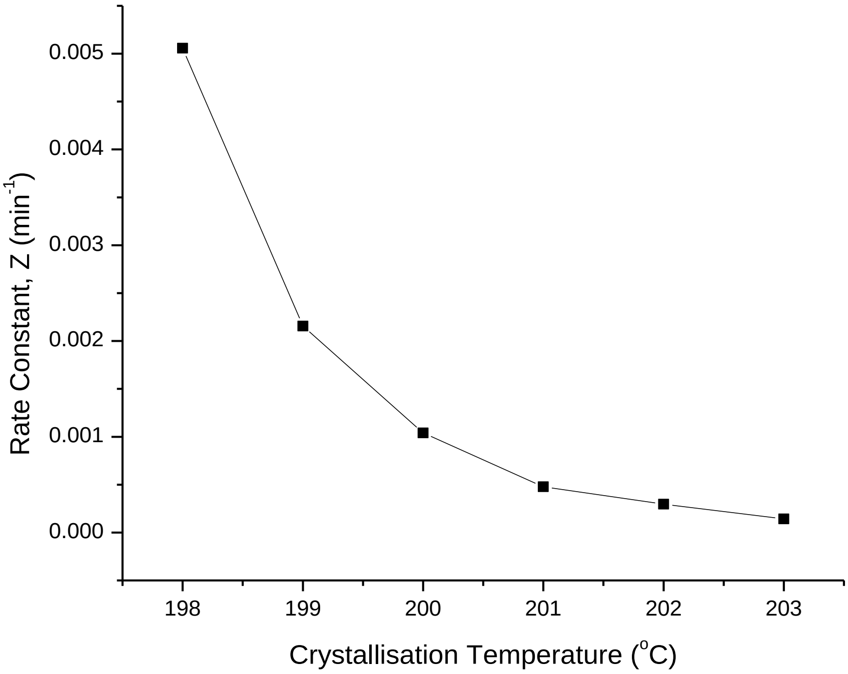

Figure 3.5: Variation of rate constant (Z) as a function of crystallisation temperature (Tc) for 20 mg of XB2-CA4 held for one hour at a range of temperatures (198-203˚C)

The same trend is seen again in Figure 3.6. The crystallization half life, t1/2, and the crystallization temperatures at which each sample was held are compared. As the crystallization temperature is increased from 198°C to 203°C, the t1/2 also increases. Table 3.2 illustrates this in quantitative terms, i.e. the crystallisation half life of the samples (t1/2) increases from 4.783 for the sample held at 198˚C, to 18.266 for the sample held at 203˚C.

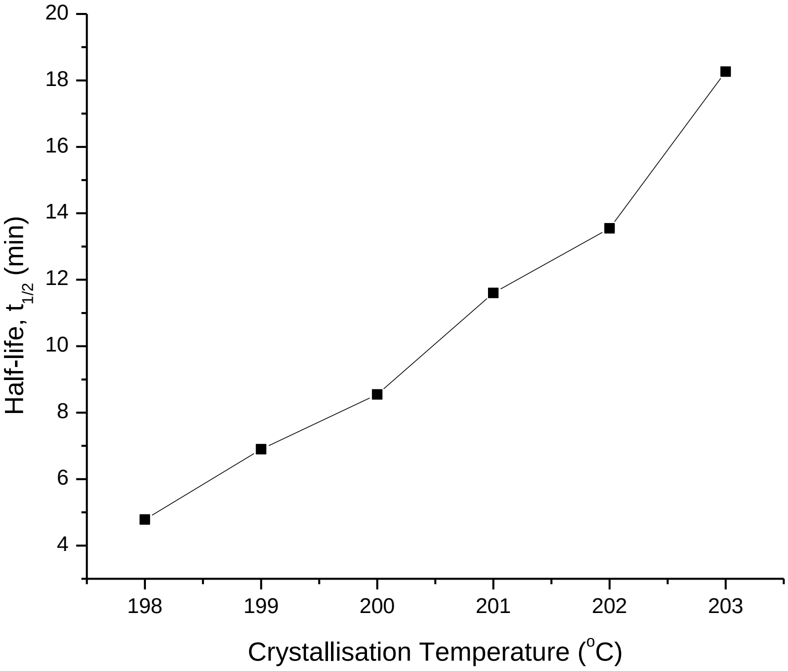

Figure 3.6: Variation of half-life ($t_{1/2}$) as a function of crystallisation temperature (Tc) for 20mg of XB2-CA4 held for one hour at a range of temperatures (198-203˚C)

The first set of crystallisation half life experiments involved the samples being heated straight to a predetermined crystallisation temperature, and held for 60 minutes. In order to separate the polymerisation and crystallisation processes, the following experiments involved heating the sample to 240˚C, and held for the previously decided optimum holing time of 20 minutes. This allows the polymerisation and crystallisation processes to occur before polymer melting. The samples were then cooled back down to one of the six crystallisation temperatures used in the previous experiment. This should ensure that only crystallisation is occuring once the temperature is reduced to crystallisation temperature. Origin software was then used to analyse the raw data, and create the following representations of the crystallisation exotherms of XB2-CA4 (Figure 3.7).

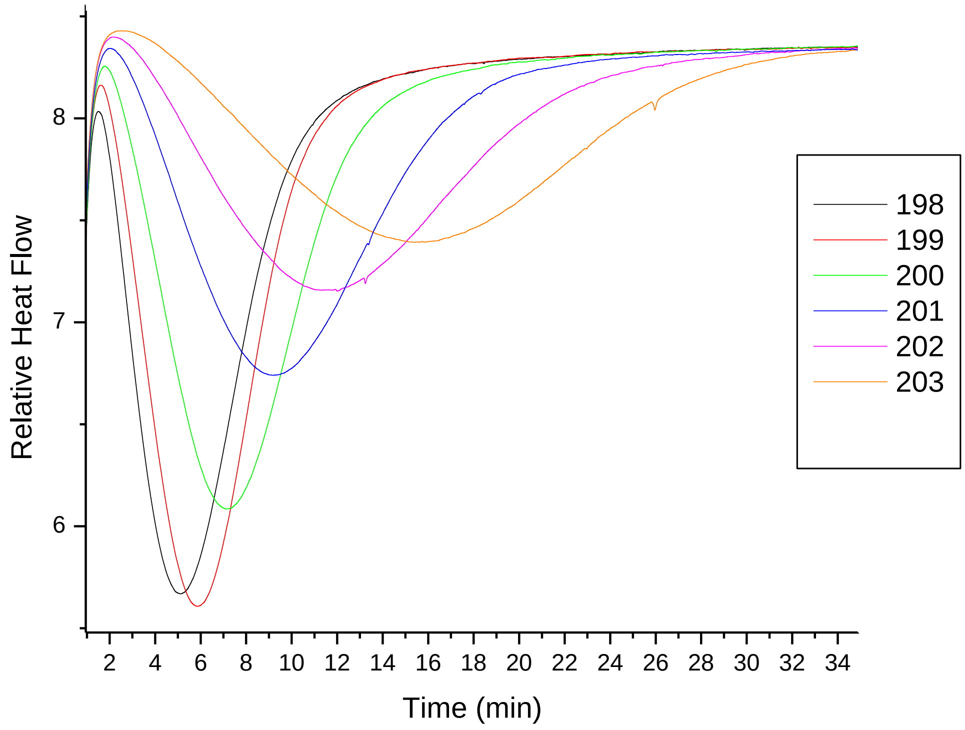

Figure 3.7: Comparison of crystallisation half life of XB2-CA4, after holding at 240°C, and then reducing to various holding temperatures

As with the previous experiment, the exothermic troughs are not symmetrical, and so Avrami analysis software is used to determine accurate values for the Avrami parameters, and crystallisation half life can be calculated.

Crystallisation Temperature [˚C]	**N [± 0.1]**	**Half life, t1/2**	**Degree of crystallinity, Xp**	**Rate Constant, Z [min-1]**
198	2.2401	3.837	0.96	0.034089
199	2.4053	4.390	0.98	0.019746
200	2.4257	5.413	0.97	0.011527
201	2.4405	7.510	0.93	0.005106
202	2.3941	9.903	0.90	0.002864
203	2.4301	13.480	0.96	0.001246

Table 3.2: Avrami parameters for 20mg of XB2-CA4 held at a range of temperatures (198-203°C) for one hour after a 20 minutes holding period at 240°C

The data from the DSC has been interpreted by the Avrami software using the above parameters from the Avrami equation. Data collected via the Avrami software, can be manipulated by Origin software into qualitative images. Figure 3.8 below, shows the relative crystallinity (Xp from Table 3.2) of all six samples, against time, and a clear trend has occurred. As the holding temperature increases, so too does the amount of time required for crystallisation to occur. Looking at Table 3.2, all six samples reach a similar degree of crystallinity (between 0.90 and 0.98), but Figure 3.8 illustrates the differing amounts of time it takes each sample to reach this level of crystallisation.

In Figure 3.9, the rate constant, Z, and the crystallization temperature are compared for each sample. As the crystallisation temperature is increased, Z decreases i.e. the rate of crystallisation per minute lessens as the crystallisation temperature is increased. This corresponds with Figure 3.8, which shows that the sample held at 198°C has the fastest crystallisation time, i.e. the rate of crystallisation occurs at a higher rate per minute. That is, sample 1, held at 198°C has a rate constant of 0.34089/min^{-1}, while sample 6, held at 203°C has a rate constant of 0.001246/min^{-1}.

The same trend is seen again in Figure 3.10. The crystallization half life, t1/2, and the crystallization temperatures at which each sample was held are compared. As the crystallization temperature is increased from 198°C to 203°C, the t1/2 also increases. Table 3.2 illustrates this in quantitative terms, i.e. the crystallisation half life of the samples (t1/2) increases from 3.837 for the sample held at 198˚C, to 13.480 for the sample held at 203˚C.

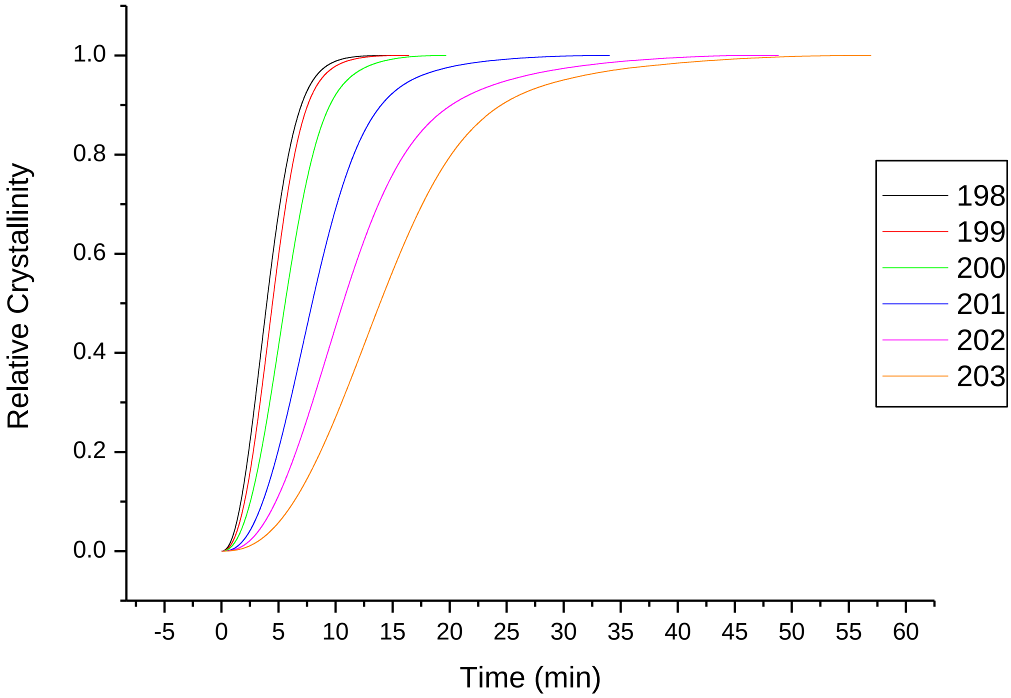

Figure 3.8: Development of crystallinity with time for XB2-CA4 held at a range of temperatures for one hour (198-203˚C) after a 20 minutes holding period at 240˚C

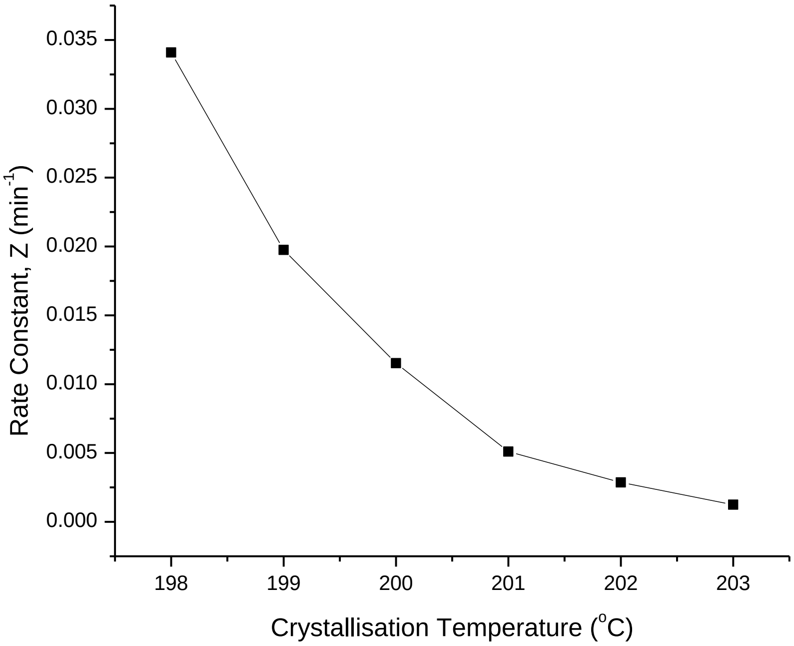

Figure 3.9: Variation of rate constant (Z) as a function of crystallisation temperature (Tc) for 20 mg of XB2-CA4 held for one hour at a range of temperatures (198-203˚C)after a 20 minutes holding period at 240˚C

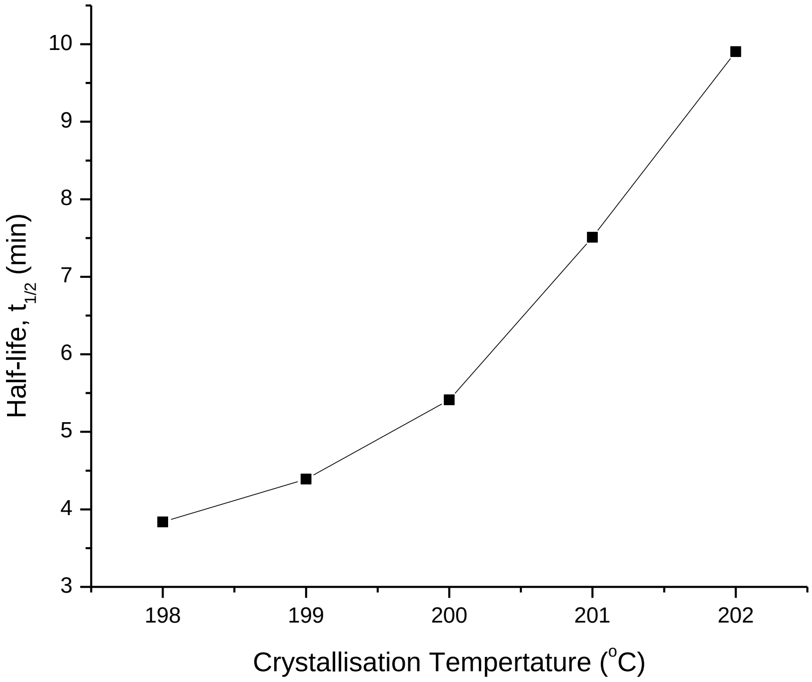

Figure 3.10: Variation of half-life ($t_{1/2}$) as a function of crystallisation temperature (Tc) for 20 mg of XB2-CA4 held for one hour at a range of temperatures (198-203˚C) after a 20 minutes holding period at 240˚C

3.1.2 F.T.I.R

Figure 3.11 shows the different structures that correlate to the different peaks that appeared on the FTIR spectrometer for the oligomer powder at room temperature. The structure of CBT is inset in the top left hand corner of the scan to illustrate the different structures present in the material.

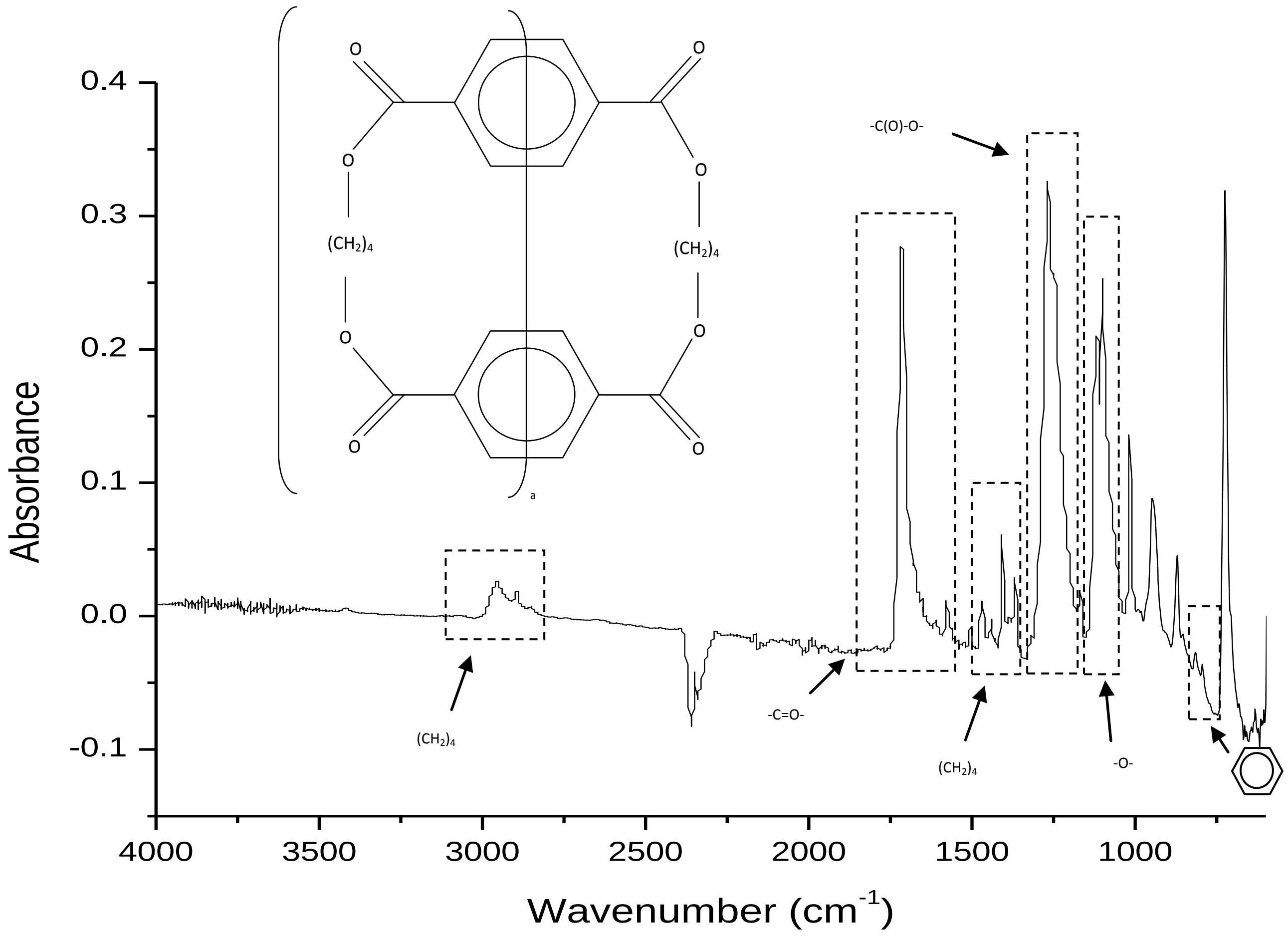

Figure 3.11: FTIR showing the structures present in CBT oligomer powder

The following figures (Figure 3.12 and 3.13) show all six of the different temperatures at which FTIR scans were taken. The exact values for the absorbance are not important, so all six scans have been off-set along the y-axis for comparison purposes. The peaks correlate almost exactly, which shows that the chemical structures within the cyclic material are not changing, and that cyclic polymer is being produced.

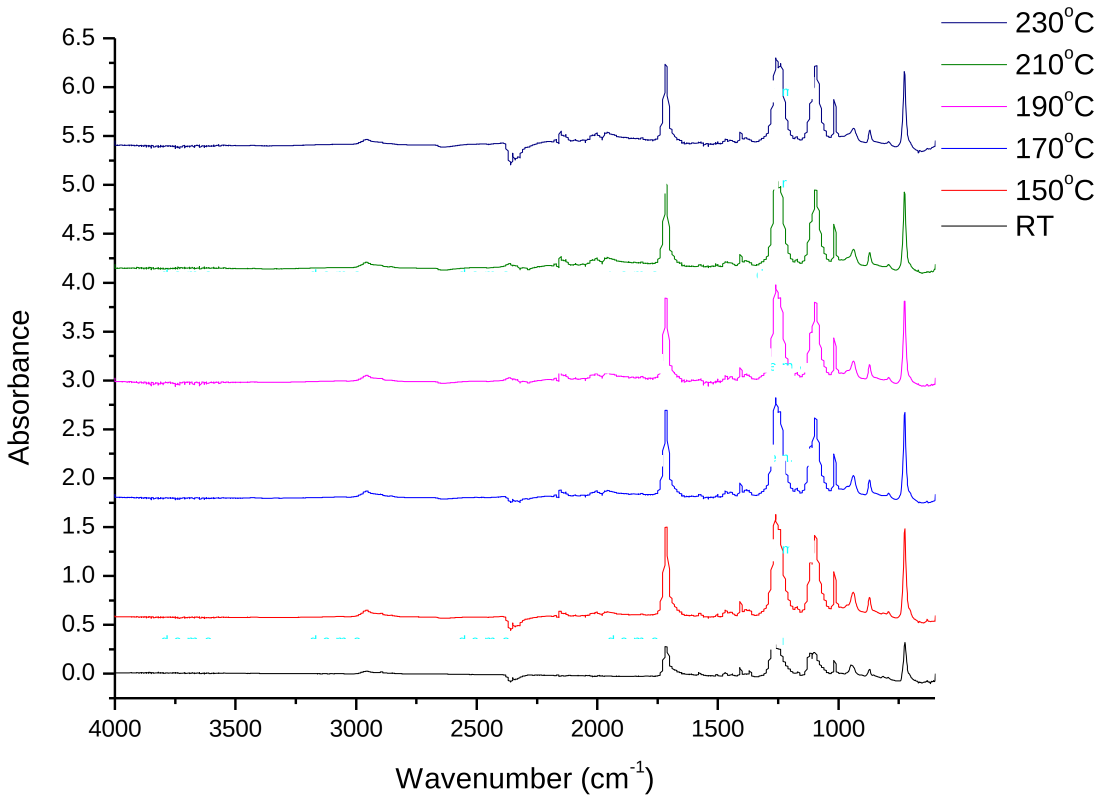

Figure 3.12: Comparison of structural characteristics of XB2-CA4 at room temperature, 150˚C, 170˚C, 190˚C, 210˚C and 230˚C using FTIR

Figure 3.12 illustrates the almost identical absorbencies seen for all 6 samples. Had there been dramatic differences in the scans it would have shown that different structures were forming i.e. non cyclic material. Therefore this figure illustrates that any differences found between samples using the DSC, GPC and SEM, are not the result of structural abnormalities caused during heating.

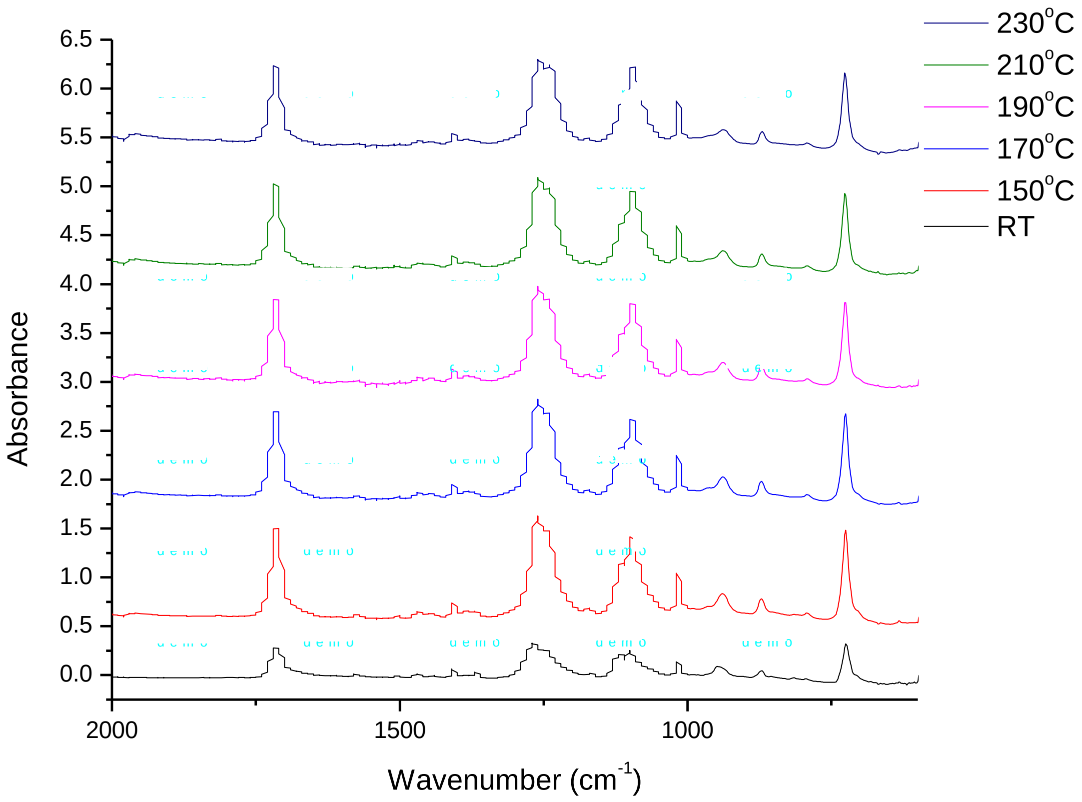

Figure 3.13: Comparison of structural characteristics, isolating the absorbencies between 2000 and 500 cm^{-1}, of XB2-CA4 at room temperature, 150˚C, 170˚C, 190˚C, 210˚C and 230˚C using FTIR

Isolating the area of the FTIR scan in Figure 3.13 shows that there are definitely no remarkable differences between the structures found in the samples. Therefore, any degradation that may take place in the sample at higher temperatures is not causing changes to the molecular composition of the sample.

3.1.3 GPC

All the samples fully dissolved and there were no problems with the chromatography of the solutions. The following figures show the GPC chromatograms for the first set of samples tested. The first sample was the oligomer powder, and the other samples were prepared in the DSC by rapidly heating and cooling to 150˚C, 170˚C, 190˚C, 210˚C, 230˚C and 250˚C.

The results have been shown using refractive index chromatograms; these show the retention time and response of the GPC machine. As the molecules leave the gel columns, they are detected by a differential refractometer. The heavier the molecules, the faster they will travel through the gel, and exit the column; thus the faster a molecule is detected, the shorter the retention time, the heavier the molecule is.

The computed molecular weight distributions have also been calculated from the data gathered; these show the concentration of molecules at each molecular weight, from the lowest to the highest. Both the molecular weight and the polydispersity have been shown using a log scale.

The figures below show computed molecular weight distributions, and refractive index chromatograms for samples 1 to 7 from the first set of samples tested using GPC. The first figure, Figure 3.14, shows the computed molecular weight distribution of the whole samples. The peaks at the beginning of the trace have the lowest molecular weight, and the peaks further along the trace have higher molecular weights. The height of each peak illustrates the concentration of the molecule at that particular molecular weight.

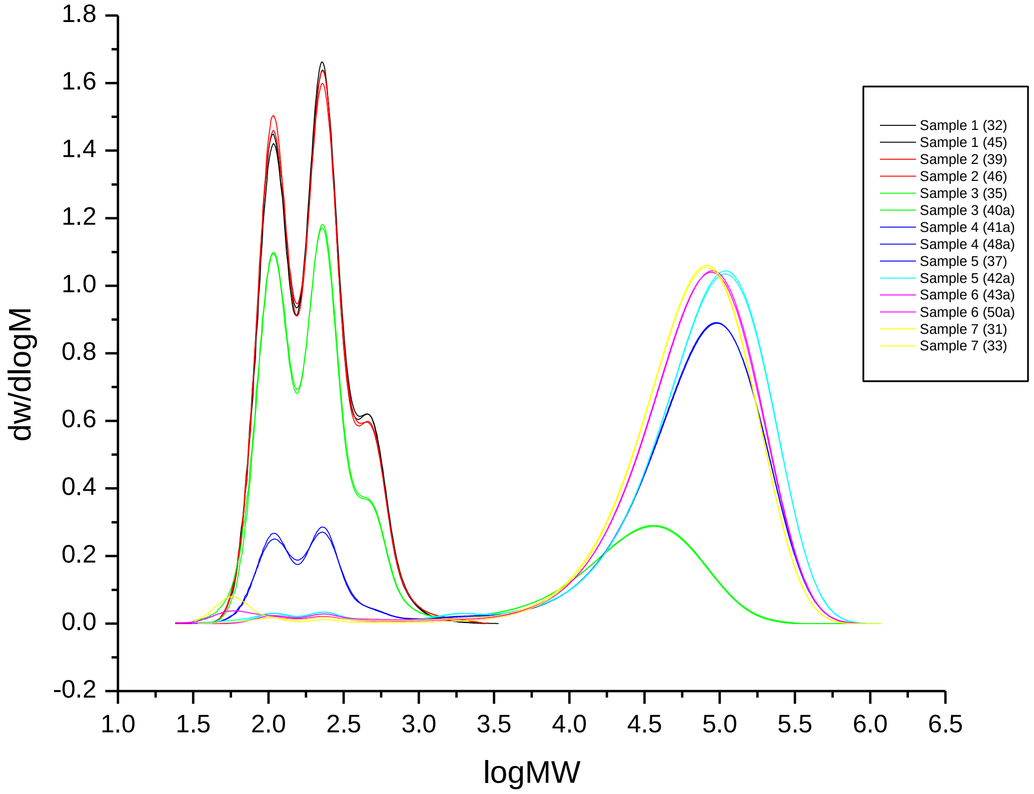

Figure 3.14: Computed molecular weight distribution for first set of samples tested using GPC; showing whole sample

In order to investigate the relationships between the samples more closely, the above trace (Figure 3.14) has been divided into two halves; the first showing the oligomer content of each sample (figure 3.15), and the second showing the polymer content of each sample (Firgure 3.16). From Figure 3.15 we can see that only sample 1 to 4 contain the oligomer components within cPBT, therefore once heated above 210˚C (samples 5 to 7) the majority of oligomer is converted into polymer. There is also a clear correlation between the quantity of oligomer molecules present, and the temperature each sample has been subjected to. For samples 1 (oligomer powder) and 2 (heated to 150˚C), only oligomer molecules are present. The quantity of oligomer present in sample 3 (heated to 170˚C) and sample 4 (heated to 190˚C) decreases respectively, as the temperature the samples are heated to increases. There are two very clear peaks present, showing two different molecular weights in the oligomer, and a third peak, or shoulder, on the second peak also insinuation a different molecular weight present. This may be attributed to different size oligomers, as they can vary from 4 to 7 repeat units in length.

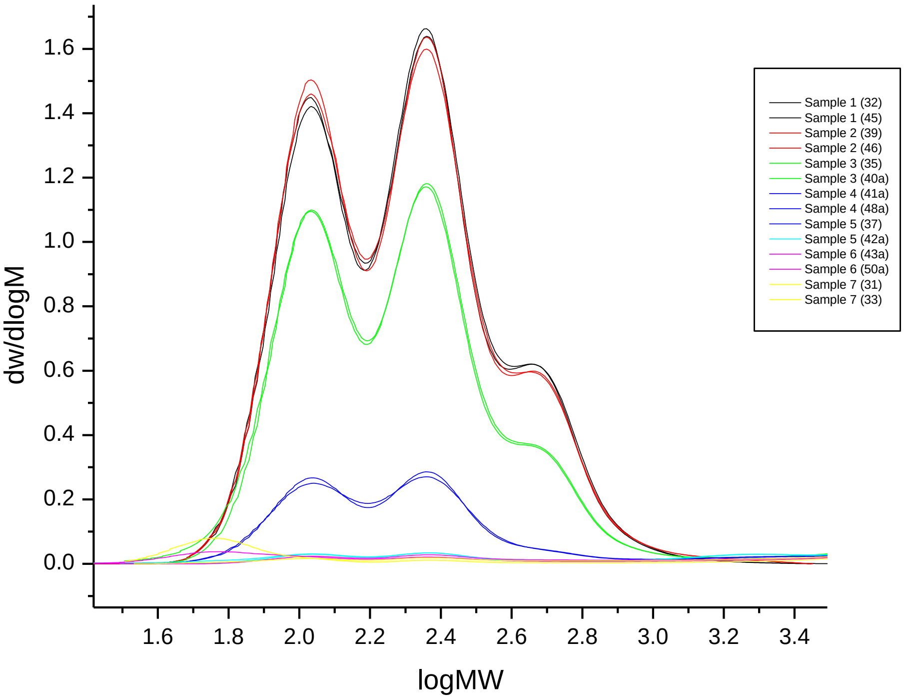

Figure 3.15: The molecular weight distribution for the first set of sample tested using GPC; only showing oligomer present

Figure 3.16 supports the claim that there is no polymer present in sample 1 or 2 as neither continues into the higher molecular weight regions of the trace. The trace also correlates with the amount of oligomer present in sample 3 and 4; as the temperature at which the sample is subjected increases, so too does the quantity of heavier polymer molecules present in the sample. Sample 5 (heated to 210˚C), sample 6 (heated to 230˚C) and sample 7 (heated to 250˚C) show only the presence of the heavier polymer molecules. However, there is a slight shift to the left for sample 6 and sample 7, compared with sample 5. This may be attributed to the degradation of the stannoxane catalyst above 220˚C.

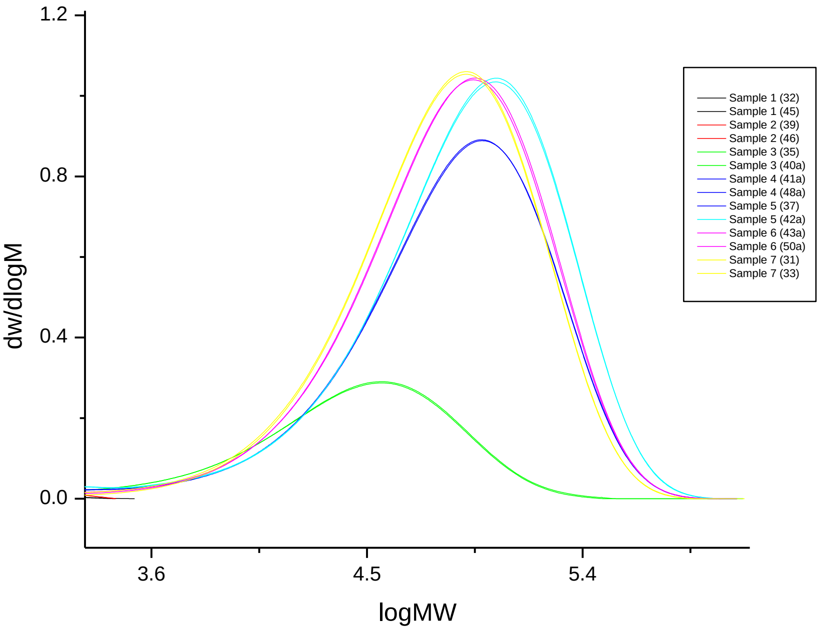

Figure 3.16: The molecular weight distribution for the first set of sample tested using GPC; only showing polymer present in samples

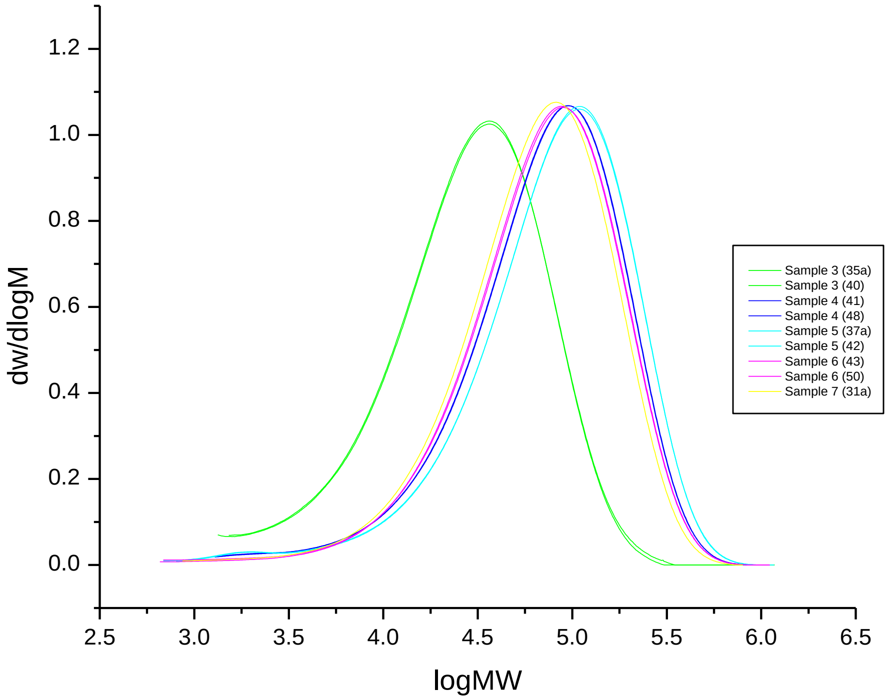

Figure 3.17: The molecular weight distribution of the duplicate run of polymer component in sample 3 to 7

Figure 3.17 shows a duplicate run of the polymer components present in samples 3 to 7. This illustrates the same shift seen in Figure 3.16 of sample 6 and 7 to the left. Sample 3 produces polymer at the lowest molecular weight, and this increases for sample 4 and 5 respectively, however, sample 6 and 7 give lower molecular weights than sample 4 and 5. This supports the claim that some degradation occurs above 220˚C.

The following three figures demonstrate the refractive index chromatogram of the first set of samples that were tested using GPC. They show the whole sample, Figure 3.18, just the polymer in the samples, Figure 3.19, a duplicate re-run of the polymer component, Figure 3.20, and the oligomer present in the samples, Figure 3.21. The traces appear to be the reverse of the computed molecular weight distribution, this is because the heaviest molecules will move through the gel the fastest, thus be detected first before the smaller molecules which will take longer to travel through the columns.

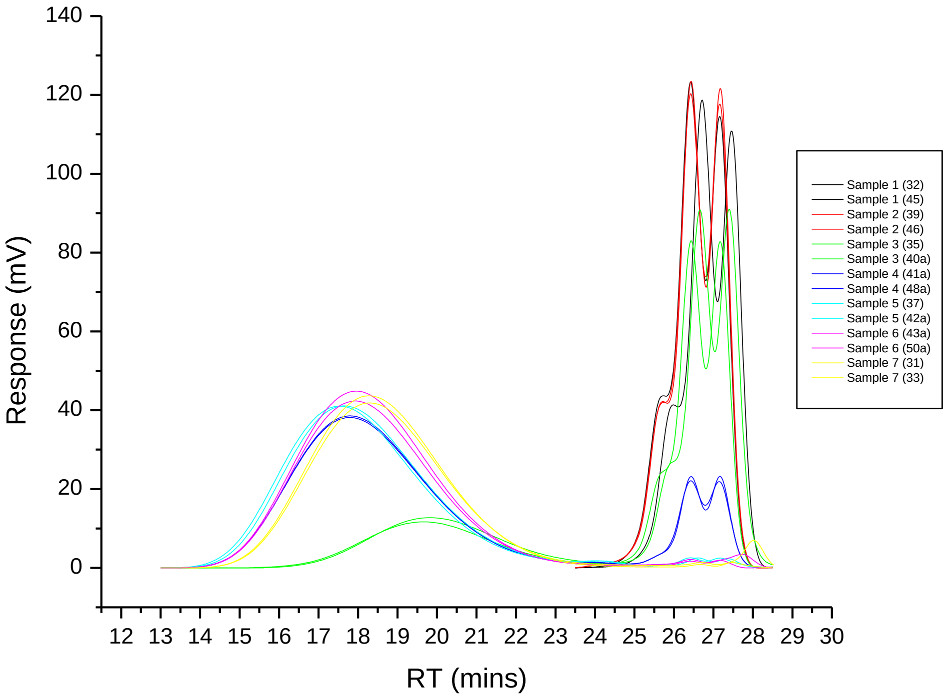

Figure 3.18: Refractive index chromatogram of the first set of samples tested using GPC; showing whole sample

As with the previous figures the GPC detect none of the higher molecular weight molecules exiting the gel columns for sample 1 or 2. Both figures of the polymer component, Figure 3.19 and Figure 3.20 show that the heaviest molecules are found in sample 5. This is shown by the trace for sample 5 starting first, i.e. molecules are detected exiting the gel columns in the fastest time. Sample 4 and sample 6 appear to have molecules of the same molecular weight, but a larger quantity are found in sample 6, this is due to sample 4 not been heated to a sufficient temperature for all oligomer to be converted into polymer. Sample 7 has the next heaviest molecules present, but at a lower quantity than sample 6. These findings support the claim that the stannoxane catalyst begins to degrade above 220˚C. Sample 3 contains polymer of the lowest molecular weight, which is supported by the quantity of oligomer present in this sample, suggesting that only a small amount of oligomer is able to be converted into polymer at or below 170˚C.

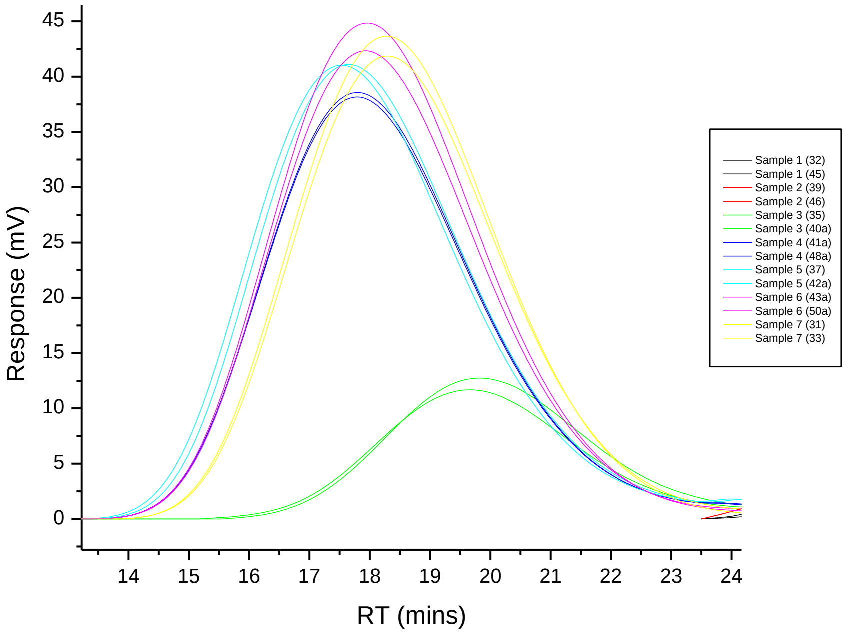

Figure 3.19: Refractive index chromatogram of the first set of samples tested using GPC; showing only polymer

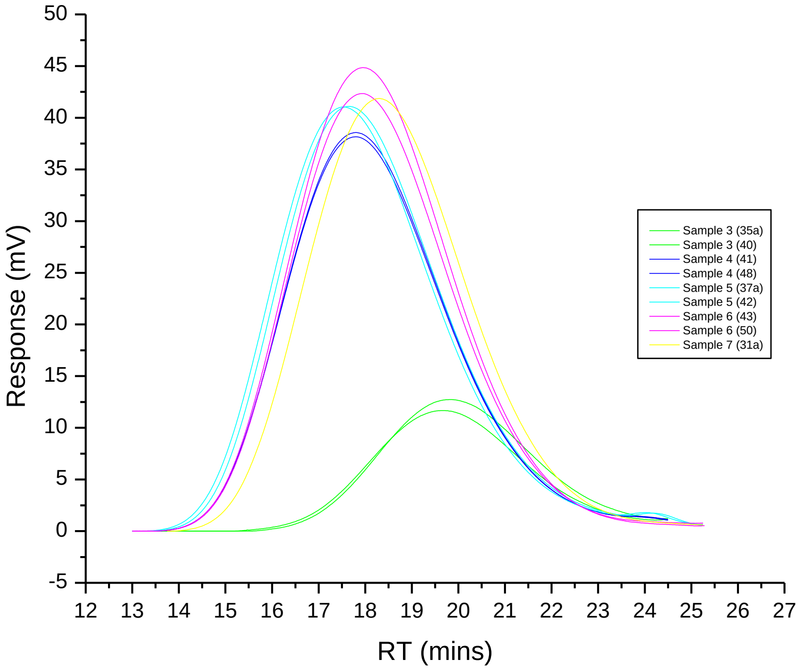

Figure 3.20: Refractive index chromatogram of the first set of samples tested using GPC; showing duplicate run of polymer component

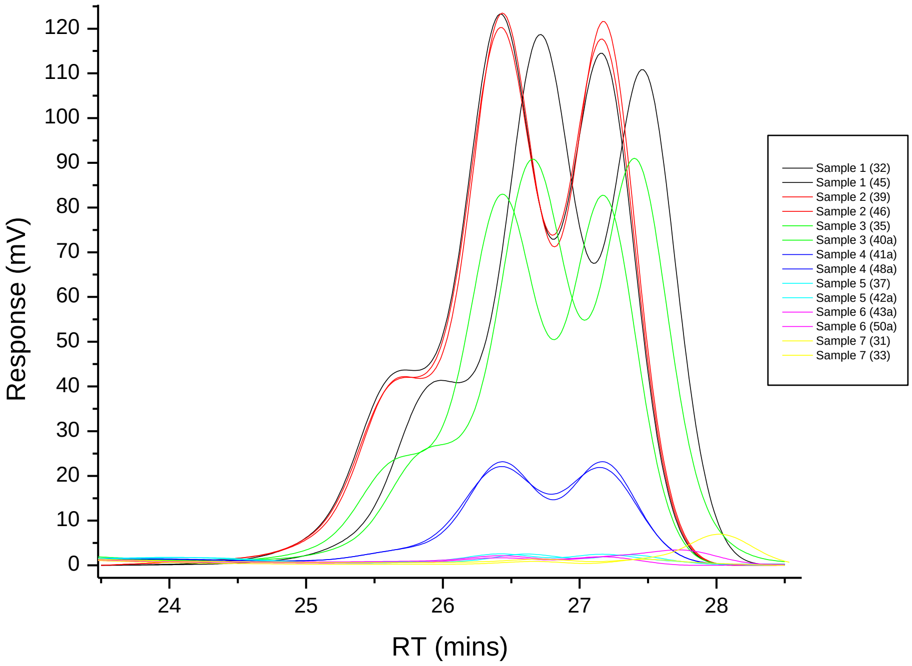

Figure 3.21: Refractive index chromatogram of the first set of samples tested using GPC; showing oligomer

We can decipher from Figure 3.21 that samples one and two show only late retention time peaks, suggesting they consist solely of molecules of a lower molecular weight than any of the other samples; this would be attributed to the oligomer molecules. For sample 3, and to a lesser extent 4, the chromatograms show earlier retention time peaks due to polymer as well as the earlier peaks due to oligomer, and samples 5 to 7 just show early retention time peaks, suggesting the consist wholly of polymer.

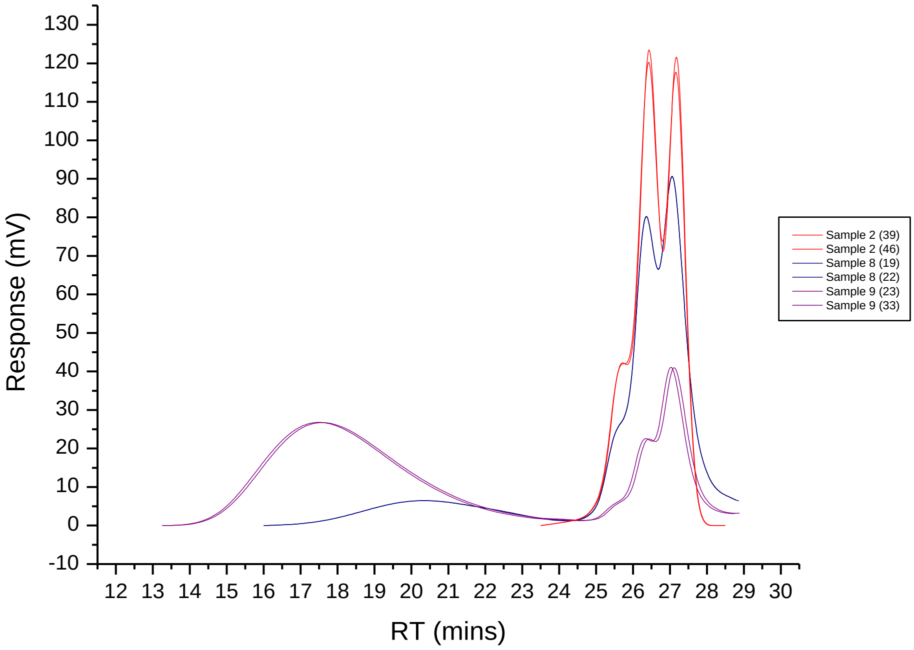

Figure 3.22: Refractive index chromatogram comparing samples 8 and 9 (held at 150˚C) with sample 2 (heated to 150˚C and cooled straight back to room temperature)

In order to clarify if it is possible for any polymerisation to occur at 150˚C, two more samples were processed and tested using GPC. Both samples were heated to 150˚C, with sample 8 being held there for 5 minutes, and sample 9 being held there for 30 minutes. Figure 3.22 shows sample 8 and 9 compared with the original sample heated to 150˚C, sample 2, which was not held. It is clear from this graph that the samples definitely produce heavy polymer molecules when held for a period of time at 150˚C. Both sample 8 and sample 9 produce polymer molecules, with sample 9, having been held for a considerably longer time than sample 8, producing much heavier and a larger quantity of polymer molecules. The amount of oligomer present in the sample correlates with the quantity of polymer molecules detected; sample 9 having the fewest and sample 2 having the most oligomer molecules present.

The second set of samples that were tested using GPC is shown in the following figures. These samples concentrated on the effect of holding time on the molecular weight of the molecules produced in each sample, they were held from 0 to 60 minutes at 190˚C. As with the previous samples, the figures have been broken down into the whole samples, the polymer present in the samples, and the oligomer present in the samples.

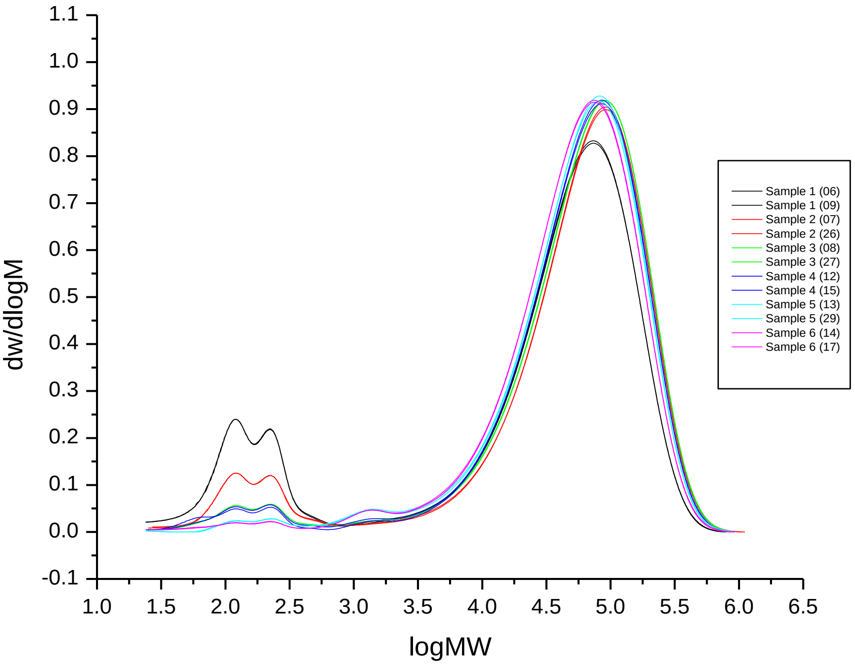

Figure 3.23: Computed molecular weight distribution for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; for whole sample.

It is clear from figures 4.40 and 4.41 that the quantity of oligomer present in the sample reduces as the holding time is increased. Sample 1 (held for 0 minutes) clearly shows the highest quantity of low molecular weight oligomer molecules. The amount of oligomer present in each sample then reduces respectively as the holding time increases, with sample 6 (held for 60 minutes) having the least amount of oligomer present.

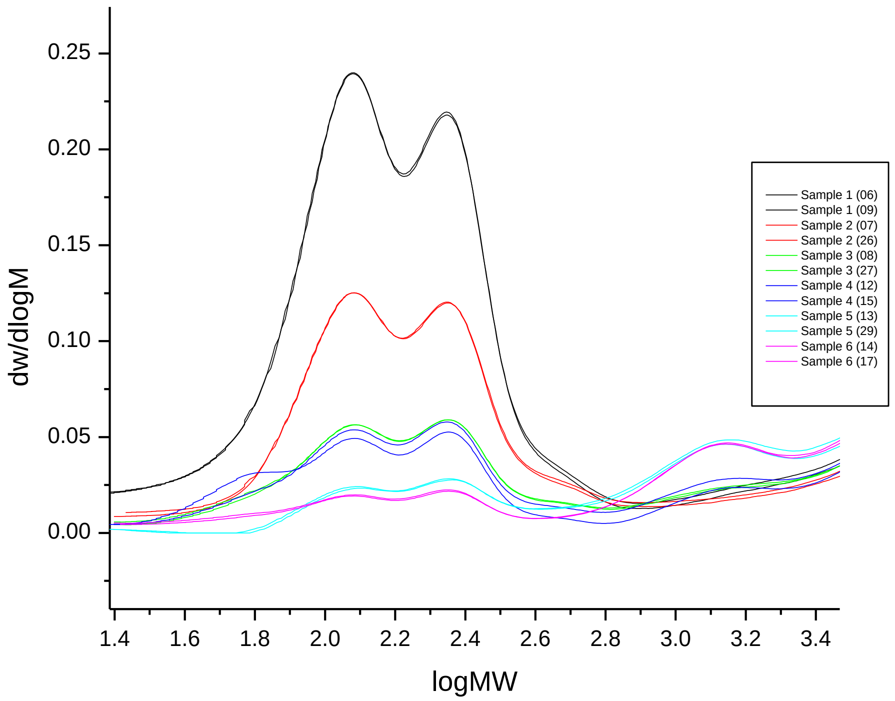

Figure 3.24: Computed molecular weight distribution for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; for oligomer in samples

Figures 4.42 and 4.43 shows the polymer content of each sample. Each sample appears to contain molecules of around the same weight, with sample 1 (held for 0 minutes) having the smallest quantity of heavier polymer molecules present. Sample 2 does appear to have a slightly higher quantity of the heavier polymer molecules present than the other samples, with a slight depreciation in the amount of polymer molecules as the holding time increases. A small peak appears before the larger peak for samples 5 and 6. This may be attributed to an optimum holding time of less than 10 minutes to produce the highest quantity of heavier polymer molecules. After 10 minutes holding it may be possible that some degradation is occurring in either the oligomer, polymer of catalyst in the samples.

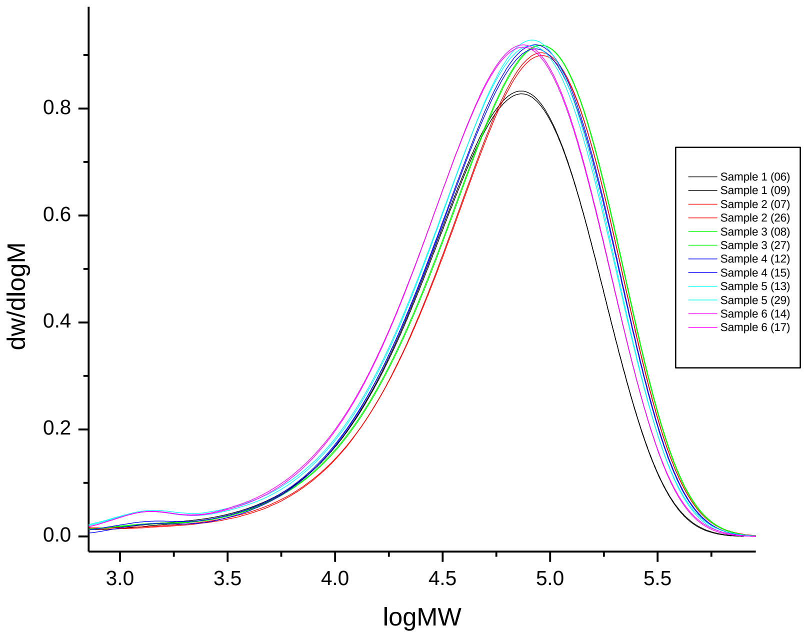

Figure 3.25: Computed molecular weight distribution for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; for polymer in sample.

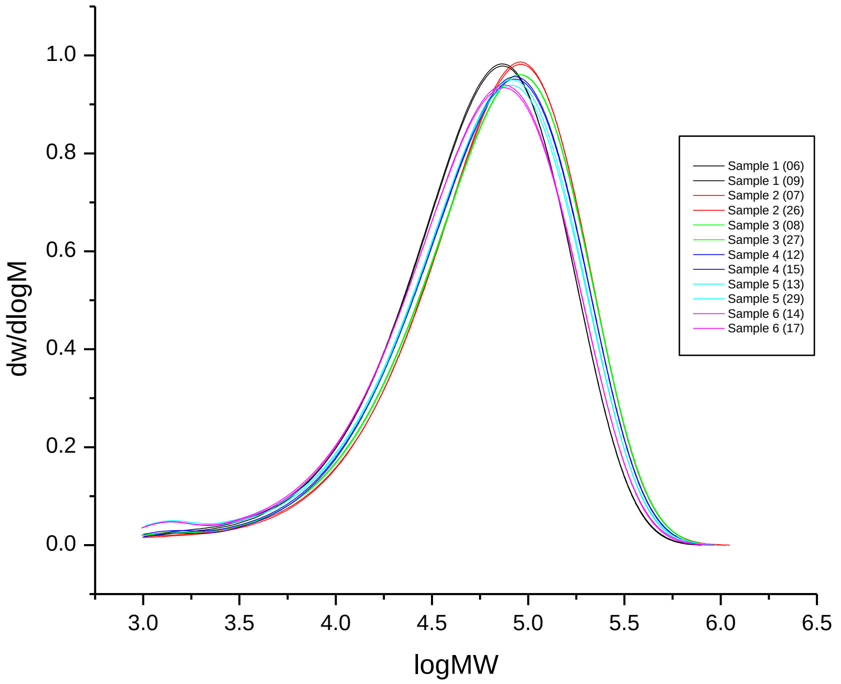

Figure 3.26: Computed molecular weight distribution for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; for duplicate run of polymer component

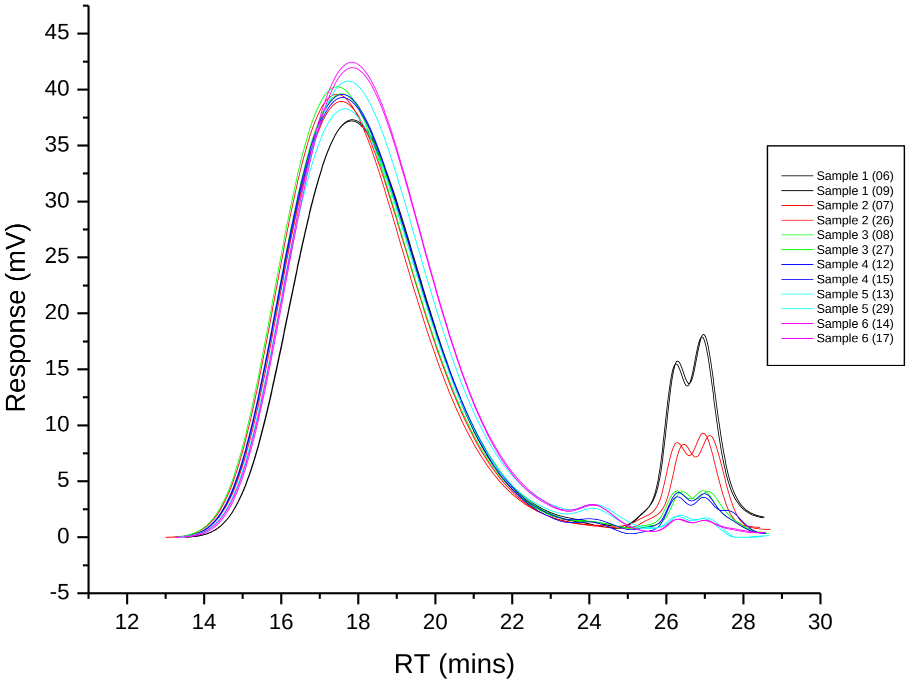

Figure 3.27: Refractive index chromatogram for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; for whole sample

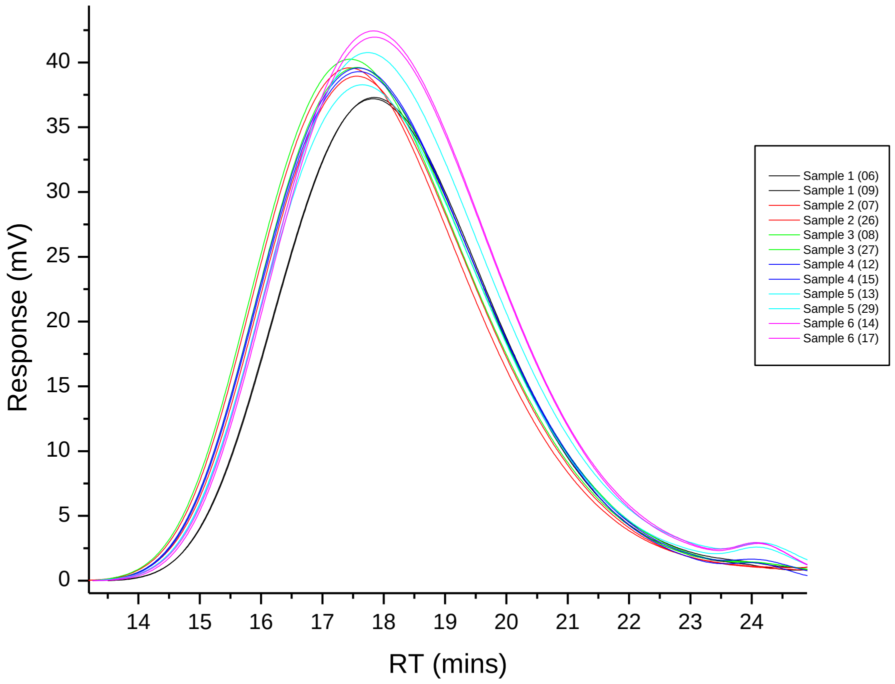

Figure 3.28: Refractive index chromatogram for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; showing only polymer

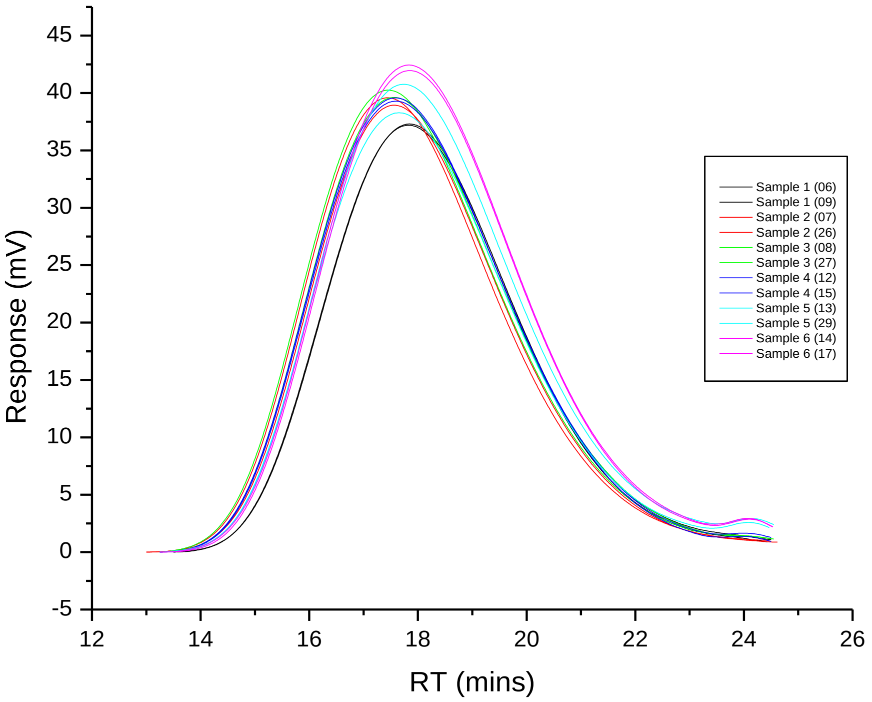

Figure 3.29: Refractive index chromatogram for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC: duplicate run of polymer component

Figures 3.28 and 3.29 show the heavier polymer molecules present in the samples. Sample one show the latest retention time, suggesting the presence of molecules of lower molecular weight than the other samples. Sample 6 has the highest quantity of polymer molecules present, but the heaviest molecules are not as heavy as in samples 2 and 3. Sample 5 and 6 also appear to have a second peak, after the initial peak present for all samples, indicating a breakdown of polymer, or possible presence of linear polymer. This second peak is clearer in Figure 3.30, and also appears to occur in sample 4, and to a lesser extent sample 3.

Figure 3.30 shows the content of lower molecular weight oligomer molecules in each sample. The two separate peaks are attributed to different length oligomers present in the material. This figure reiterates the findings from Figure 3.24, with sample 1 having the greatest quantity of oligomer molecules present. The quantity of oligomer present in each sample then decreases with increased holding time, with sample 6 having the least amount of oligomer present.

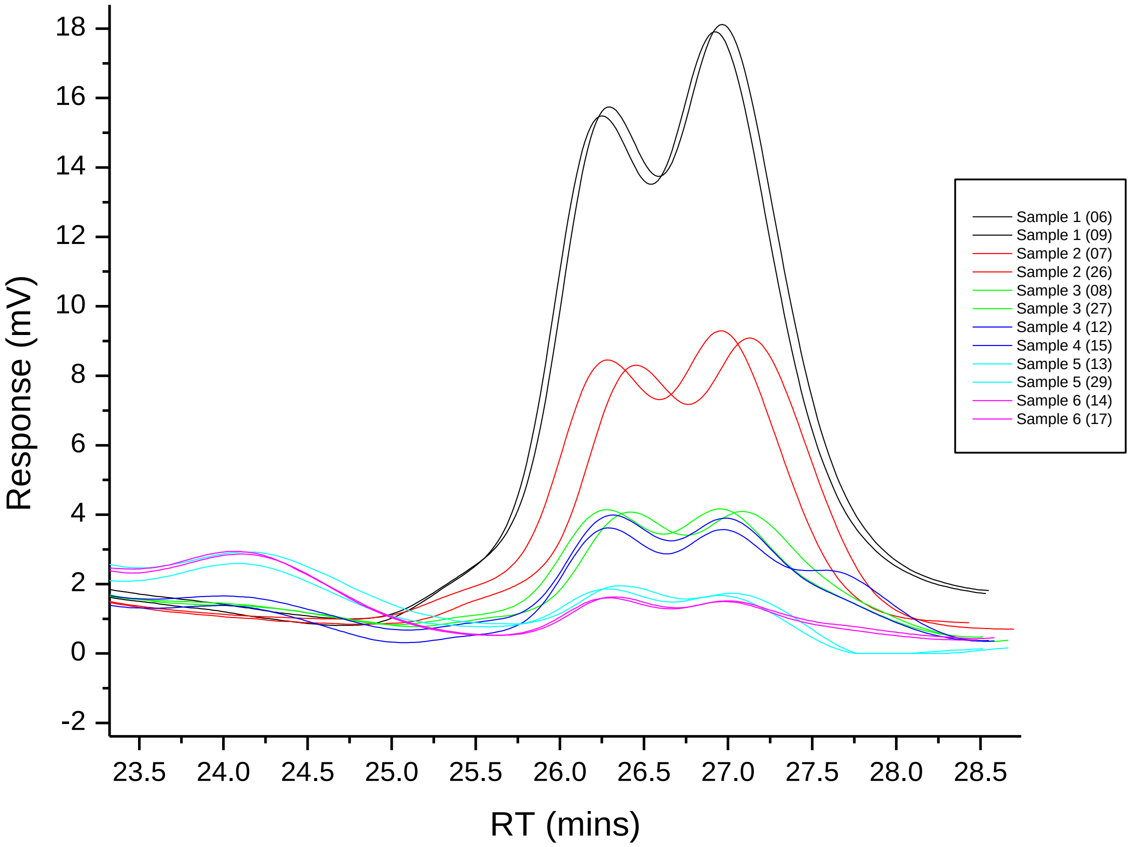

Figure 3.30: Refractive index chromatogram for the second set of samples, sample 1 to 6, each held at 190˚C for varying lengths of time, tested using GPC; showing oligomer in sample

To try and better understand the extent of catalyst degradation that may be occurring, another sample was tested using GPC that had been processed up to a temperature of 240˚C, and held for 20 minutes. At this temperature it would be expected that any peaks or shifts in peaks could be attributed to some sort of degradation. Figure 3.31 shows this sample (sample 7) compared with sample 6 (held at 190˚C for 60 minutes).

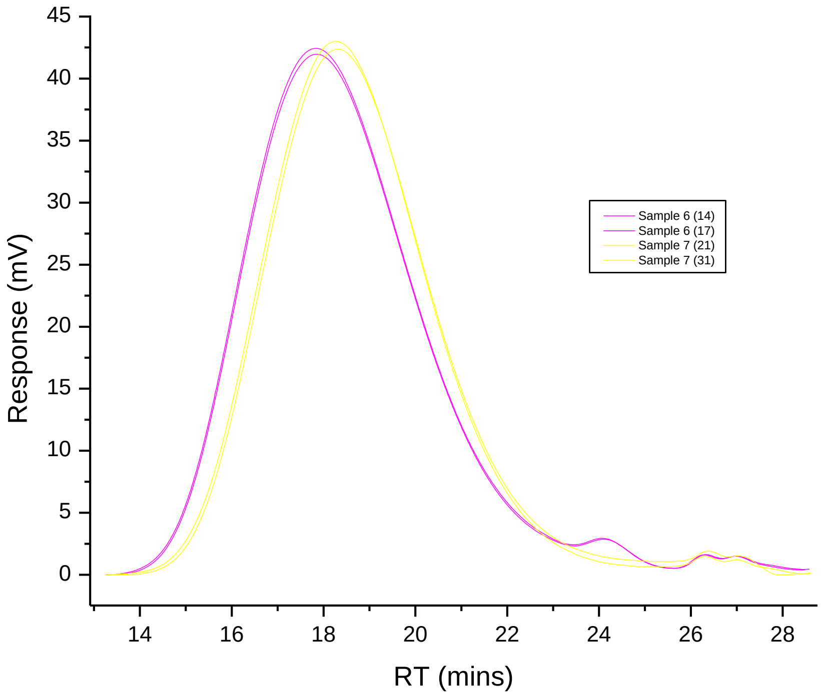

Figure 3.31: Refractive index chromatogram: comparison of sample 7 (held at 240˚C) and sample 6 (held at 190˚C)

Figure 3.31 shows that sample 6 has a slightly shorter retention time than sample 7, but sample 7 has no second peak, as is seen in sample 6. If the second peak was due to degradation due to high temperature then it would definitely be present in the trace for sample 7. Therefore it is more likely that the second peak is due to another molecule present in sample 6, linear PBT for example.

Figure 3.32 shows the difference in molecular weight between sample 6 and sample 7. Sample 6 contains more heavy molecules, suggesting larger polymer molecules present in the sample. Sample 7 contains slightly less heavy molecules, but a larger quantity of them. This suggests that more of sample 7 has polymerised than sample 6, but the molecules produced are of a lesser molecular weight.

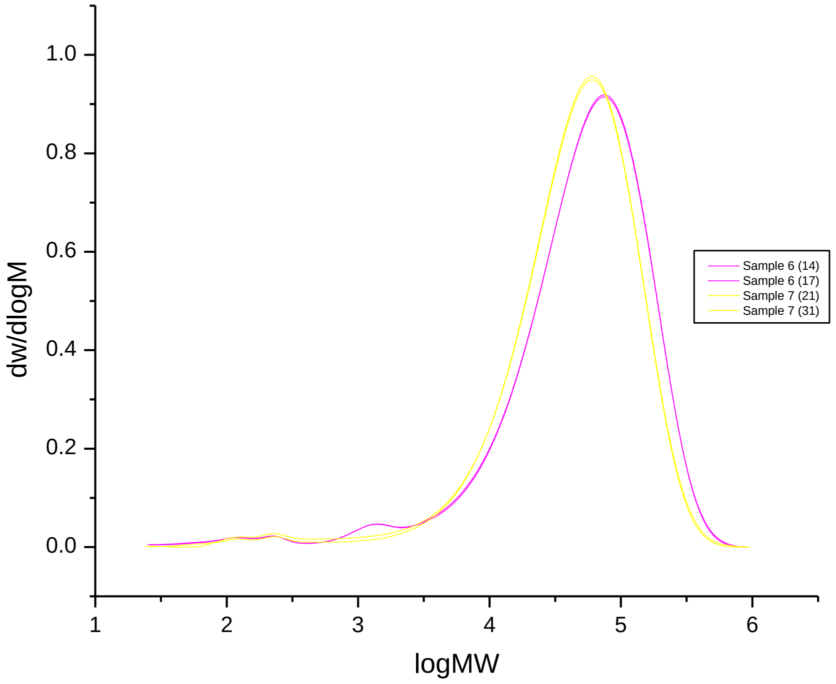

Figure 3.32: Computed molecular weight distribution: comparison of sample 7 (held at 240˚C) and sample 6 (held at 190˚C)

3.1.4 SEM

SEM images were taken of the samples used for the first GPC experiment to try and correlate the molecular weight of the samples with the structures present.

The samples for the SEM were prepared using the DSC. Samples were heated to 5 separate temperatures; 150˚C, 170˚C, 190˚C, 210˚C and 230˚C. The first figure shown below is of the sample that was heated to 150˚C in the DSC (Figures 4.50, 4.51 and 4.52). Three different magnifications are shown for this sample, 1000x, 2500x and 5000x. These images illustrate the beginning stage of oligomer melting.

The second set of samples were heated to 170˚C, it is expected at this temperature for some oligomer melting to have occurred (Figures 3.36, 3.37, 3.38). The three SEM images used to illustrate the physical structures within the sample at 190˚C are shown in Figures 3.39 and 3.40. Only two figures have been included to illustrate the physical characteristics of this sample, as it became very difficult to produce clear images however the contrast between these images and those shown for the second sample are clear. These images show the structure of the sample during concurrent polymerisation and crystallisation.

The next sample to be imaged had been heated to 210˚C (figures 3.41 and 3.42). This sample should have undergone completed polymerisation and crystallisation according to the initial DSC trace, Figure 3.1. The fifth set of samples imaged using the DSC were heated to 230˚C (Figure 3.43 and 3.44), it is thought that some degradation may be occurring at this point, as there is a loss in molecular weight, as shown by the GPC results. The final sample was heated to 250˚C (Figure 3.45 and 3.46), where it is also assumed there is some degradation occurring due to a loss in mass.

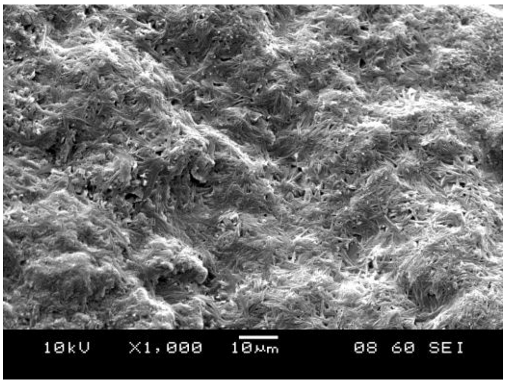

Figure 3.33: SEM image of XB2-CA4 heated to 150˚C at magnification 1000x

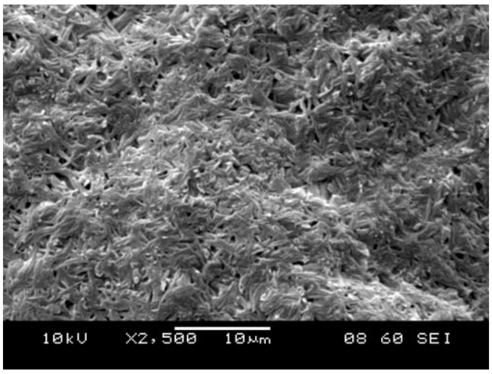

Figure 3.34: SEM image of XB2-CA4 heated to 150˚C at magnification 2500x

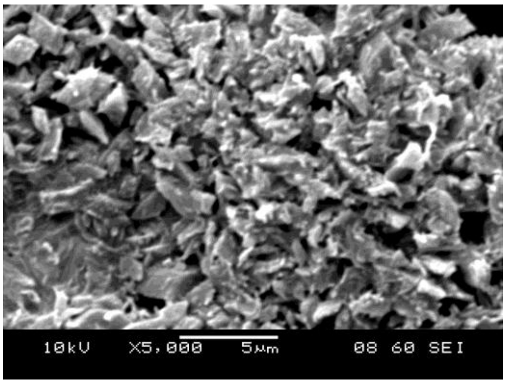

Figure 3.35: SEM image of XB2-CA4 heated to 150˚C at magnification 5000x

As was shown in the GPC results, no melting occurs when XB2-CA4 is heated to 150˚C, without holding. The sample therefore contains only oligomer powder molecules, the individual crystal structures of the oligomer are visible in the figures above, particularly Figure 3.35.

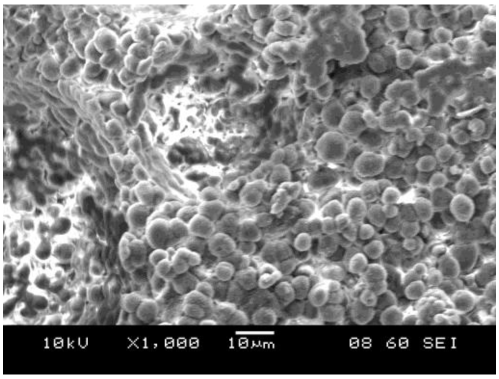

Figure 3.36: SEM image of XB2-CA4 heated to 170˚C at magnification 1000x

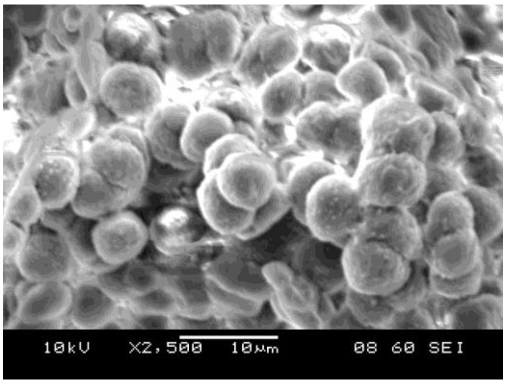

Figure 3.37: SEM image of XB2-CA4 heated to 170˚C at magnification 2500x

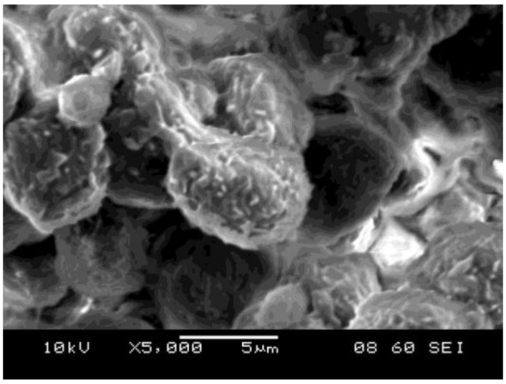

Figure 3.38: SEM image of XB2-CA4 heated to 170˚C at magnification 5000x

At 170˚C the DSC (Figure 3.1) showed that oligomer melting is occurring. The less rigid crystal structure seen here compared with the sample heated to 150˚C supports this claim. As the oligomer powder melts, the structure becomes more amorphous, and a less crystalline structure is seen.

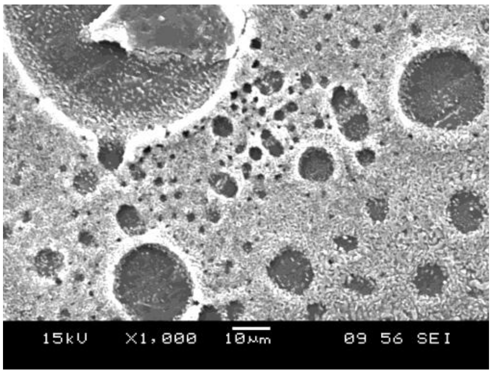

Figure 3.39: SEM image of XB2-CA4 heated to 190˚C at magnification 1000x

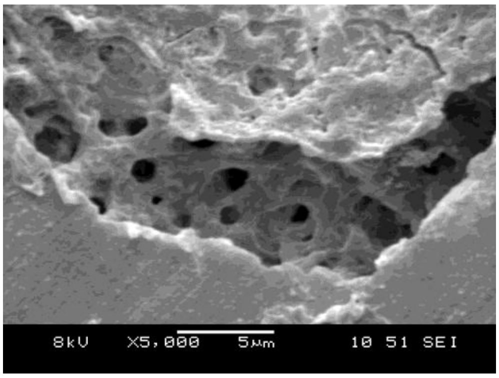

Figure 3.40: SEM image of XB2-CA4 heated to 190˚C at magnification 5000x

Imaging got more difficult as the samples were heated to higher temperatures. At 190˚C we would expect to see the production of polymer molecules, and a more amorphous structure. This image shows that there are less defined crystal structures, and therefore more amorphous material present.

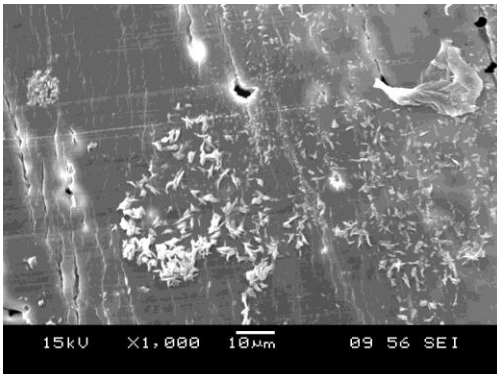

Figure 3.41: SEM image of XB2-CA4 heated to 210˚C at magnification 1000x

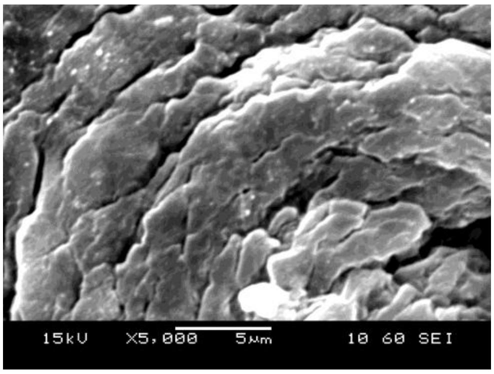

Figure 3.42: SEM image of XB2-CA4 heated to 210˚C at magnification 5000x

It is very difficult to identify any crystal structures in these images (Figures 3.41 and 3.42), this correlates with the lack of oligomer molecules present in the samples when heated to 210˚C.

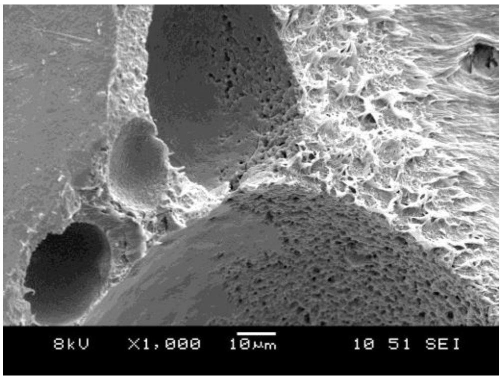

Figure 3.43: SEM image of XB2-CA4 heated to 230˚C at magnification 1000x

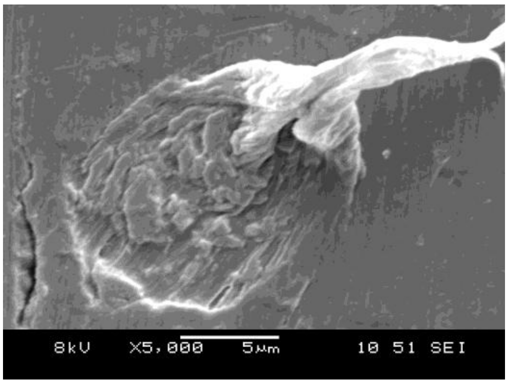

Figure 3.44: SEM image of XB2-CA4 heated to 230˚C at magnification 5000x

The images of the sample heated to 230˚C show mainly a smooth uniform structure with occasional deformation on the surface. This could have occurred during the sample extraction from the DSC pan before imaging (Figure 3.44).

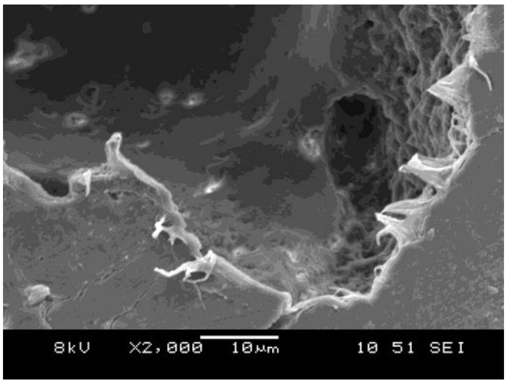

Figure 3.45: SEM image of XB2-CA4 heated to 250˚C at magnification 1000x

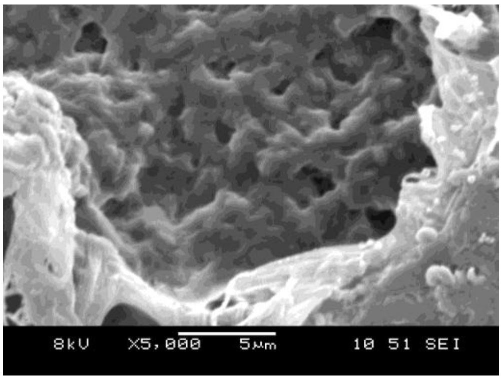

Figure 3.46: SEM image of XB2-CA4 heated to 250˚C at magnification 5000x

As with the sample heated to 230˚C, this sample, heated to 250˚C, was more difficult to extract from the DSC pan so it is difficult to attribute the structures seen here solely to the heating of the material, and therefore production of polymer material. However, it appears that an amorphous polymer is produced (Figures 3.45 and 3.46).

CHAPTER 5

CONCLUSIONS

4.1 Conclusions from DSC results

From Figure 3.1 it can be concluded that isothermal heating and cooling results in the concurrent polymerisation and crystallisation of XB2-CA4. This is shown by the large exothermic trough seen between 160˚C and 215˚C.

Comparing the Avrami analysis for the DSC results for samples of XB2-CA4 that have been held at polymer melting temperature, and those that were heated straight to crystallisation temperature confirms the conclusion that the processes of polymerisation and crystallisation occur concurrently. The samples that were heated to 240˚C (Figures 3.8 to 3.10), at which melting of cPBT occurs, will only show crystallisation, whereas the sample that were heated to crystallisation temperatures will also show some polymerisation if the processes occur together. The discrepancies between the Avrami analyses for these two experiments show that crystallisation is not the only process occurring in the samples heated straight to crystallisation temperatures (Figures 3.4 to 3.6). Therefore concurrent polymerisation and crystallisation will occur on primary heating of cPBT.

4.2 Conclusions from FTIR results

The same chemical structures are present in XB2-CA4, regardless of the temperature to which it is heated. However the quantity of certain structures alters slightly, related to the amount of polymerisation and crystallisation that has occurred by that temperature.

4.3 Conclusions from GPC results

The GPC traces show multiple peaks around the molecular weight of the oligomer. This is due to varying chain lengths present in the oligomer powder.

The molecular weight of XB2-CA4 is dependent on the temperature to which it is heated, and the amount of time it is held at that temperature.

When XB2-CA4 is heated to 150˚C there are no polymer molecules created, therefore no polymerisation or crystallisation can occur when the material is heated straight to 150˚C, and cooled straight back down to room temperature. However, with just 5 minutes holding time at 150˚C there are some heavier molecules created, and after 30 minutes holding time, a considerable amount of polymer is produced. Therefore oligomer melting occurs as low as 150˚C, and stannoxane catalyst initiation is also able to occur at this low temperature.

As the temperature to which XB2-CA4 is heated increases, the oligomer content decreases, and the amount of heavier polymer molecules increases. By 210˚C there is negligible oligomer produced, therefore the material is able to fully polymerise at 210˚C without holding at that temperature.

As the holding temperature is increased from 210˚C to 230˚C, and then 250˚C, the polymer molecules get less heavy. The quantity of heavier polymer molecules is higher, but the actual molecular weight of those molecules slightly decreases. This infers smaller cyclic molecules are being produced in the samples heated to 230˚C and 250˚C, but more of the oligomer is converted to polymer. Rather than catalyst degradation, this could show that the optimum temperatures to produce the highest quantity of cyclic material are those nearer the polymer melting temperature of XB2-CA4.

4.4 Conclusions from SEM results

The results for the DSC and GPC are supported by the SEM imaging results. The images produced of the sample heated to 150˚C support the claim that only oligomer chains are present when XB2-CA4 is not held for any length of time at 150˚C. The powder may have begun to melt, but the crystal structure present, visible in Figure 3.35, demonstrate that no polymer is produced.

As the samples are heated from 150˚C up to 250˚C the images show more amorphous material is being produced. There is nothing from these imaging results to support the decrease in molecular weight for the samples heated to 230˚C and 250˚C.

4.5 Overall conclusions

The decrease in molecular weight of the XB2-CA4 samples heated above 230˚C, compared to those heated to 190˚C and 170˚C cannot be attributed to catalyst instability and therefore polymer degradation, as suggested by Miller [1]. The FTIR images show that the same chemical structures are present in the samples regardless of the temperature to which they had been heated, also the fact that the quantity of polymer produced, as shown by the molecular weight, is greater for the samples heated to 210˚C and 250˚C than 170˚C and 190˚C shows that more oligomer is being converted into polymer. As the temperature is increased from 190˚C to 210˚C, the polymerisation and crystallisation processes occur more quickly, and thus the stannoxane catalyst is able to convert more oligomer, because these processes occur more rapidly could explain the lower molecular weight molecules that are produced i.e. higher conversion of oligomer to polymer, but at a faster rate results in less cross-linking and smaller cyclic molecules.

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