

**THE EFFECT OF BRANCH DENSITY ON
POLYOXYMETHYLENE COPOLYMERS**

A Thesis

by

ANDREA DIANE ILG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2007

Major Subject: Chemistry

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ABSTRACT

The Effect of Branch Density on Polyoxymethylene Copolymers. (May 2007)

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Chair of Advisory Committee: Dr. Stephen A. Miller

Today, there is a great need for polymers made from biorenewable resources due to the increasing price and diminishing supplies of petroleum and the overabundance of plastic waste in landfills. Polyoxymethylene can be produced from biorenewable feedstocks, depolymerized to formaldehyde through chemical recycling, and may be a viable alternative to many polyolefins. However, there has been limited research on varying the thermomechanical properties of polyoxymethylene so that it can be used in a wider variety of applications. Our approach employs the cationic copolymerization of trioxane with various amounts of 1,2-epoxyalkanes and 4-alkyl-1,3-dioxolanes to arrive at polyoxymethylene derivatives with controlled branching and morphology.

Branching content has been measured by nuclear magnetic resonance (NMR) spectroscopy and correlates well with the comonomer feed fraction. The melting temperatures of the copolymers, determined from differential scanning calorimetry (DSC), are depressed predictably with increasing amounts of comonomer incorporation. The copolymerizations behaved the same regardless of whether the comonomer was an alkyldioxolane or epoxyalkane. 1,2-Epoxybutane/trioxane copolymers and 4-ethyl-1,3-dioxolane/trioxane copolymers gave the best melting

point and % crystallinity results using boron trifluoride diethyl etherate as the cationic initiator.

To My Family:

Mark

Lauren

Mom and Dick

Peter

Dad and Peg

Brian, Michael, and Patrick

Thanks for all the love and support!

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There are many people I would like to thank because without their help graduate school would not have been possible. I would like to start with my family because of their love and support I was able to reach this goal. To my husband, thank you for the time and patience you gave me throughout this ordeal. To my parents, thanks for all the guidance, encouragement, and support to achieve my goals I set many years ago.

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CHAPTER I

INTRODUCTION

Polymers are a widespread class of materials that have been under development since the early 1900's. They have become integrated into daily life in a wide array of materials. One concern with these materials is what they are derived from. Currently, the majority of synthetic polymers are produced from petroleum based materials and account for 4-5% of petroleum consumption, and as the oil crisis continues, the prices for these polymer products will increase as well.¹ The worldwide oil reserves have been estimated to be around 200 billion tons (1-1.5 trillion barrels) and are projected to last for about 40 years.^{1,2} Thus, there is a growing need for non-petroleum based materials to replace these materials to reduce the cost in the future. Also, there are rising environmental concerns with today's landfills due to the overabundance of plastic waste produced. Today there are currently 57.8 billion pounds of plastic being discarded out of 491.4 billion pounds of total waste (domestically), whereas in 1960 the plastic waste was only 780 million pounds out of 176.2 billion pounds.^{1,3} The amount of plastic waste over the last 45 years is tremendous, with most of that waste being derived from petroleum based materials that take tens or hundreds of years to decompose. Also, these petroleum

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based materials will eventually break down into chemicals that may seep into the groundwater table and affect the future's water supply. The majority of the plastic waste is not being recycled, as shown in Figure 1.1,³ which indicates that there needs to be a change in the manufacturing of plastics in order to protect the environment. Therefore, in the future, it will become more important to find starting materials that will be less harmful for the environment and can be found in great abundance, like petroleum. Biorenewable polymers are a class of materials that can fulfill these needs.

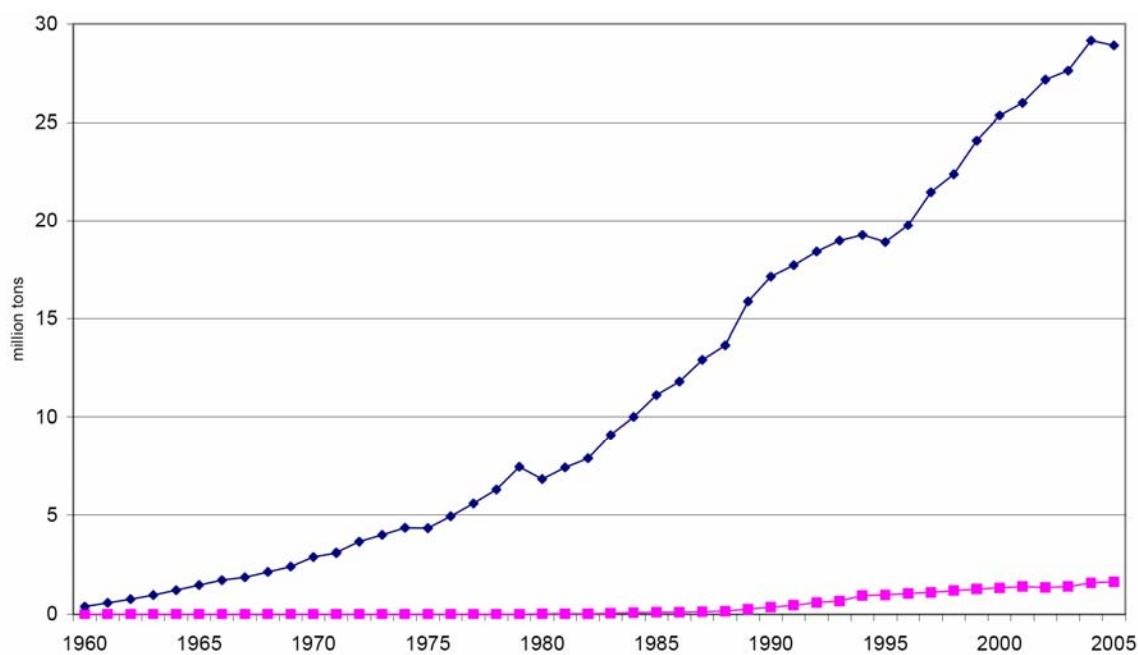


Figure 1.1. Comparison of plastics generation and recovery from 1960 to 2005 (blue line = generation, purple line = recovery).³

Biomass is a renewable source of matter derived from various human and natural activities, and can be obtained as byproducts from the timber industry, agricultural crops and crop residues, grassy and woody plants, forestry, and major parts of household waste and wood.⁴⁻⁸ These byproducts have become a major source of biorenewable monomers to produce polymers that are safer for the environment.⁸⁻¹⁰ Current estimates of biomass production range from 100 to 200 billion tons each year.¹ With such large amounts being produced each year, biomass is a likely source to replace many petroleum-based products.

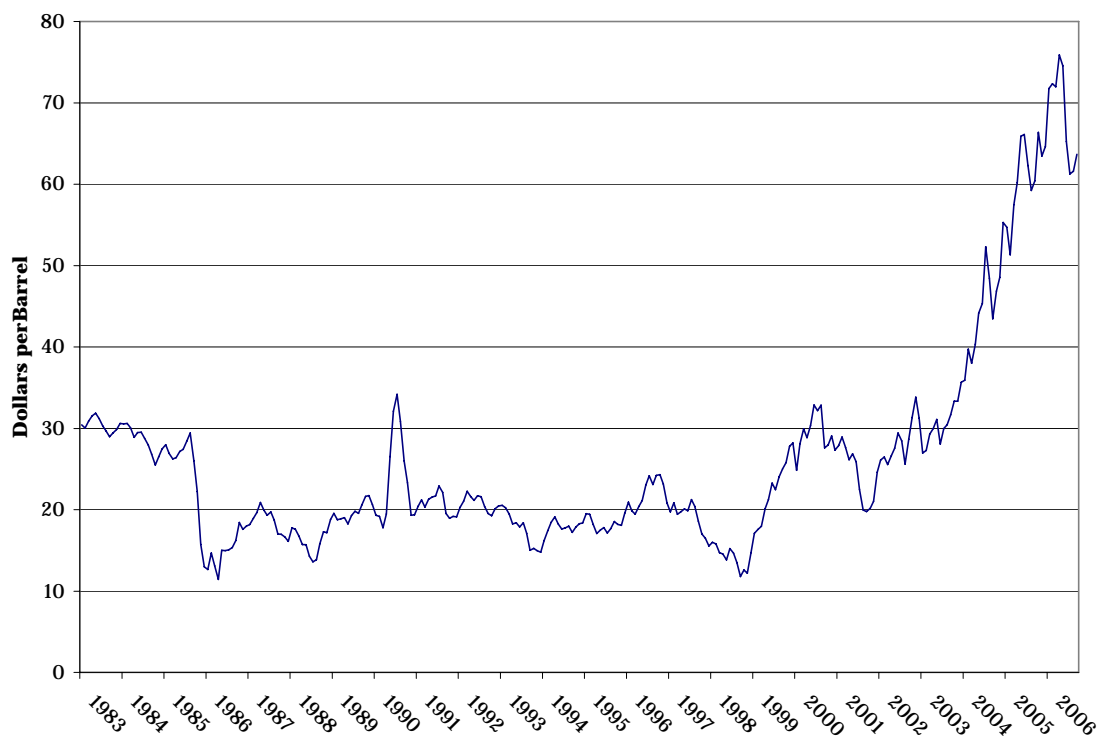


Figure 1.2. Crude oil prices from January 1, 1983-December 31, 2006 (dollars per barrel).¹¹

Eventually the production and pricing of biorenewable polymers will be less expensive than current petroleum-based polymers.¹² The price of oil has been increasing dramatically over the last several years (Figure 1.2) and with the petroleum feedstocks diminishing, we are beginning to face the possibility of another oil crisis due to current world events; so, it is becoming even more important to find alternatives.^{2,10,12}

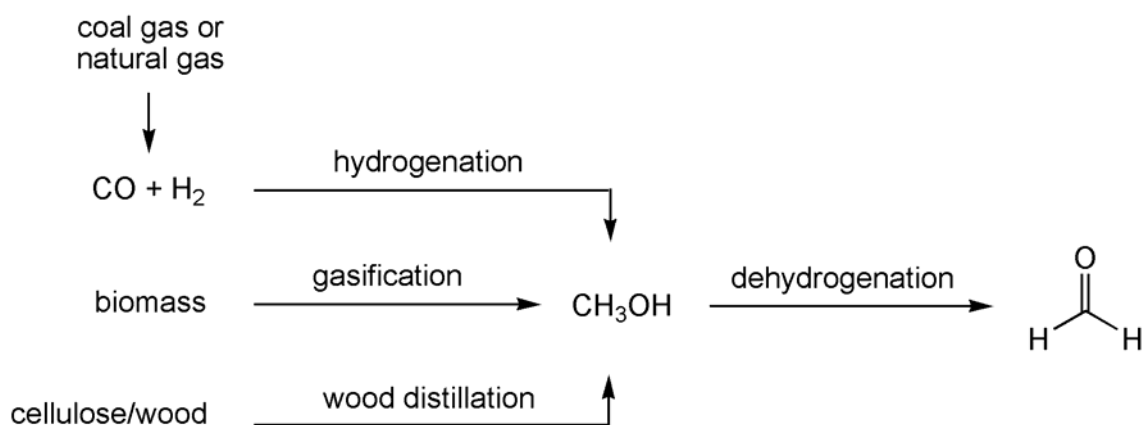


Figure 1.3. Biorenewable production of formaldehyde via production of methanol from wood distillation.

Polyoxymethylene (POM), also known as polyformaldehyde or acetal resin, can be produced from biorenewable feedstocks, depolymerized to formaldehyde through chemical recycling, and may be a viable alternative to many polyolefins. One method for POM synthesis is the cationic ring opening polymerization of trioxane. Trioxane is currently synthesized from formaldehyde, which is made from

methanol, which in turn, is mostly derived from petroleum based syn-gas.² However, methanol can also be isolated by the direct oxidation of methane,² the gasification of biomass,¹³⁻¹⁶ or from the distillation of wood products,^{13,14} thereby making homopolymers and copolymers of trioxane attractive alternatives to petroleum-based polymers (Figure 1.3).

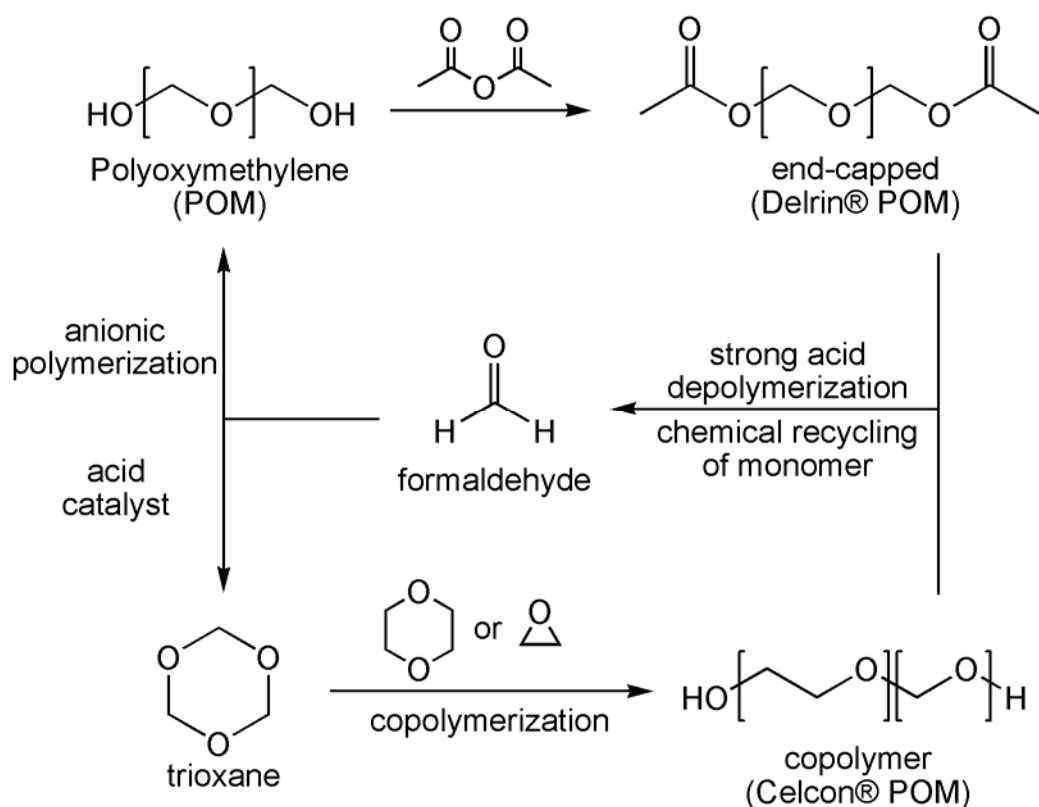


Figure 1.4. Thermally stable polyoxymethylene (POM) is typically prepared via one of two strategies: end-capping, and copolymerization/curing.

Polyoxymethylene is a semi-crystalline engineering thermoplastic that has been synthesized since the 1950s¹⁷⁻¹⁹ by DuPont as a substitute for metals. POM is of importance due to its good mechanical properties (high strength, hardness, and rigidity), high solvent resistance, and self lubrication properties.²⁰⁻²⁵ A downfall of the POM polymer is its lack of thermal stability and poor impact strength. One way to resolve the thermal instability problem focuses on the end groups. End capping is one method for addressing this issue and is most often accomplished by acetylating the end groups of the polymers.²⁶⁻²⁸ DuPont's Delrin® is an example of this type of polymer (Figure 1.4). An alternative method involves copolymerization of trioxane with a second monomer (usually a cyclic ether) via cationic ring-opening polymerization, a strategy which affords thermal stability once the polymer chain has depolymerized (via curing) to a non-acetal position.^{24,28-30} Celanese's Celcon® is a copolymer of trioxane and ethylene oxide (Figure 1.4). This copolymerization approach leads to a reduction in crystallinity and alters the thermomechanical properties relative to those of the homopolymer.

To date, extensive research efforts have focused on cyclic ethers, such as ethylene oxide,^{25,28,31,32} 1,3-dioxolane,^{24,25,31,32} diethylene glycol formal,²⁵ propene oxide,³¹ butadiene dioxide,^{31,32} ethylglycidylether,³² divinyl sulfone,³³ glycidic esters (ethyl and methyl glycidate),^{32,33} glycidonitrile,^{32,33} 1,3-dioxacycloheptane,²⁴ 1,3-dioxacyclooctane,²⁴ as comonomers for copolymerization with trioxane. The ones studied most often have been ethylene oxide and 1,3-dioxolane. Muck^{25,31} recently reported copolymers using various epoxides (including propene oxide and butene

oxide) and dioxolanes (1,3-dioxolane, diethylene glycol formal, and 1,4-butanediol formal). Braun²⁴ reported copolymers with varying lengths of the alkyl chain at the 4 position of dioxolane and 1,3-dioxacyclo-heptane and -octane. The cycloheptane and cyclooctane copolymers had moderate rates of incorporation, while the 4-alkyl-1,3-dioxolanes had considerably lower amounts of incorporation. However, neither studied the effects that these branches from the cyclic ethers had on the copolymers besides thermal stability, or made copolymers with higher epoxyalkanes. Varying

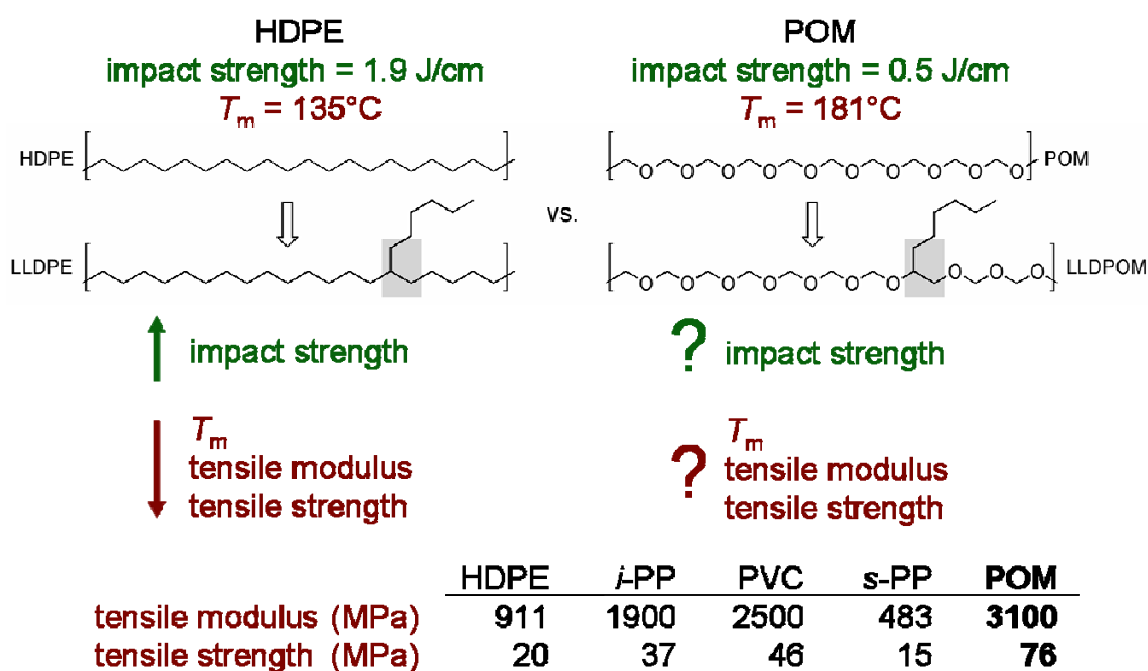


Figure 1.5. Comparison of polyoxymethylene (POM) to high density polyethylene (HDPE) and the effect of branching on the thermomechanical properties of the homopolymers.

the branch density of the comonomer (epoxide or dioxolane) is proposed to have an effect similar to what is seen for copolymerizing ethylene with small amounts of α -olefins (Figure 1.5).³⁴

In general, the same effects in physical and mechanical properties that are seen with the ethylene copolymers should be seen with POM copolymers. One goal is to increase the thermal stability of POM by copolymerizing with varying amounts of comonomer and as a result change the thermomechanical properties to create biorenewable copolymers for a wider range of applications. POM has a tensile modulus of 3100 MPa³⁵ while high density polyethylene has a tensile modulus of 911 MPa³⁶, and when POM is copolymerized, this value will likely decrease as it does for linear low density polyethylene. Because of such a large value of the tensile modulus, a decrease will not render the T_m of POM copolymers unsuitable. The impact strength for POM homopolymer is 0.5 J/cm²², which is one of the lowest values for commercial polymers; by copolymerizing with cyclic ethers, this property should improve.

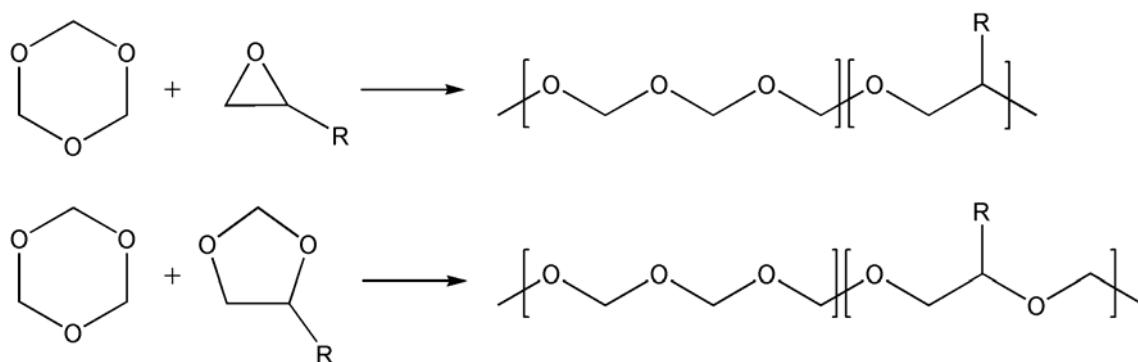


Figure 1.6. Branched copolymers based on trioxane and either 1,2-epoxyalkanes or 4-alkyl-1,3-dioxolanes.

This document focuses on three areas for the creation of a family of POM copolymers with prescribed amounts of branching in an otherwise linear chain. One area of study was the syntheses of biorenewable comonomers that can be derived from fatty acids, 1,2-epoxyalkanes and 4-alkyl-1,3-dioxolanes, and their copolymerization with trioxane (Figure 1.6). The second area focuses on the preliminary results for the epoxyalkane/trioxane copolymers and alkyldioxolane/trioxane copolymers. Finally, a comparison on the copolymerization activities of the epoxyalkane/trioxane copolymers versus the alkyldioxolane/trioxane copolymers will also be discussed.

CHAPTER II

COPOLYMERIZATIONS OF 1,2-EPOXYALKANES AND TRIOXANE *

Introduction

Copolymers of trioxane and 1,2-epoxyalkanes (more specifically 1,2-epoxyethane^{27-29,31-33,37} and 1,2-epoxypropane³¹⁻³³) have been well studied; however to date there has been no research on the effects of the branch of the epoxyalkanes in the copolymers except for the impact on thermal stability. Both trifluoromethanesulfonic acid^{25,31} and boron trifluoride diethyl etherate^{27,28,31-33,37,38} cationic initiators have been used for the homopolymerization of trioxane and copolymerizations of trioxane and cyclic ethers. A brief study was performed to determine which of these two initiators gives better copolymerization results. The effects of the branching on the copolymers was carried out and studied by copolymerizing 1,2-epoxypropane, 1,2-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyoctane, 1,2-epoxydecane, and 1,2-epoxydodecane with trioxane at various feed percentages. The copolymers were analyzed using ¹H NMR spectroscopy for determining percent incorporation of the 1,2-epoxyalkane comonomer and

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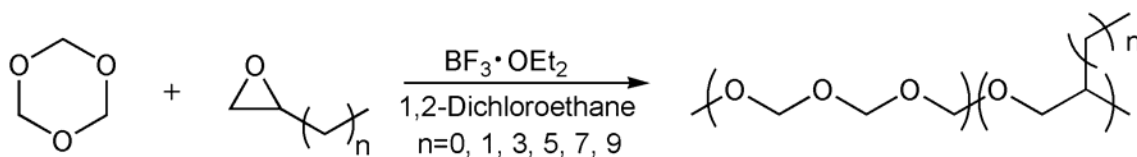
differential scanning calorimetry (DSC) for obtaining the melting temperatures and the percent crystallinity of the copolymers.

Results and Discussion

Two cationic initiators were employed: trifluoromethanesulfonic acid and boron trifluoride diethyl etherate. The trifluoromethanesulfonic acid initiator produced polymers with little or no incorporation of the epoxyalkane comonomer regardless of the type of 1,2-epoxyalkane or the percentage of comonomer feed. The boron trifluoride diethyl etherate initiator produced polymer up to certain percentages of comonomer, and resulted in decent yields and mol % incorporations for the 1,2-epoxyalkane/trioxane copolymers (Table 2.1). When the initiator employed was trifluoromethanesulfonic acid, the polymerizations were completed in 30 minutes, whereas for boron trifluoride diethyl etherate, the polymerization times needed to be longer with increasing percentages of comonomer feed. The polymerizations were faster with the trifluoromethanesulfonic acid initiator, probably because little to no incorporation of 1,2-epoxyalkane comonomer was obtained. So even though polymerization times are longer for the boron trifluoride diethyl etherate initiator it is a better initiator for incorporating the 1,2-epoxyalkane comonomer. The solvent in the reaction was also tested in order to find the optimum amount needed to produce polymer. The polymerizations were attempted with both 10 mL and 5 mL of dichloroethane (solvent in which trioxane was dissolved in) and the

lesser amount resulted in the greater amount of polymer produced with good incorporations of comonomer.

Table 2.1. 1,2-Epoxyalkanes/trioxane copolymerization results^a



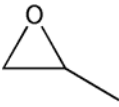
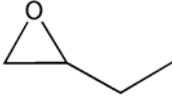
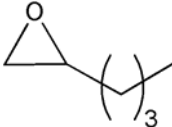
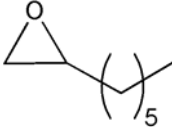
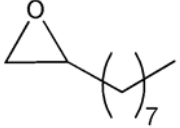
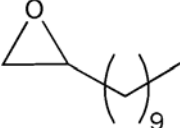
Comonomer	Feed (mol%)	Yield (g)	Incorporation (mol%) ^b	T_m (°C) ^c	% Crystallinity ^d	DB ^e
	3	3.227	5.49	165.81	68.51	9.41
	7.4	4.386	11.26	163.42	67.26	19.89
	10	4.791	12.34	163.04	66.31	21.92
	15	4.226	16.85	158.83	44.95	30.67
	20	4.084	17.98	156.55	47.76	32.93
	25	3.546	21.07	154.56	46.16	39.25
	3	3.890	6.66	167.11	79.74	11.48
	7.4	4.033	7.88	163.61	59.70	13.67
	10	4.221	9.86	163.45	49.57	17.29
	15	3.845	15.13	159.09	34.39	27.28
	20	2.438	20.37	152.42	22.84	37.80
	25	1.309	21.18	149.58	14.20	39.48
	3	4.502	6.86	169.77	62.82	11.84
	7.4	4.460	7.35	166.92	40.93	12.72
	10	3.812	12.12	162.23	41.33	21.50
	15	3.650	13.14	161.34	33.94	23.44
	20	2.248	19.38	157.57	21.99	35.77
	3	3.378	7.08	166.74	72.96	12.23
	7.4	4.188	9.03	164.06	44.05	15.76
	10	4.037	10.44	162.34	39.26	18.36
	15	2.797	18.48	159.01	24.47	33.94
	20	1.140	32.03	157.28	6.18	63.56

Table 2.1. Continued

Comonomer	Feed (mol%)	Yield (g)	Incorporation (mol%) ^b	T_m (°C) ^c	% Crystallinity ^d	DB ^e
	3	3.545	5.96	165.54	53.91	10.24
	7.4	4.656	10.48	163.50	56.75	18.43
	10	4.226	11.99	163.23	48.97	21.26
	15	3.465	14.33	161.03	27.04	25.73
	20	3.568	15.14	161.55	39.11	27.30
	3	3.684	5.93	169.19	64.13	10.19
	7.4	4.088	9.93	163.93	42.26	17.42
	10	2.454	11.47	162.24	57.86	20.28
	15	3.962	16.41	161.68	27.15	29.80
	20	2.911	22.29	161.99	17.84	41.81

^a Conditions: Epoxyalkane syringed into 5.00 g trioxane (55 mmol) in 5.0 mL 1,2-dichloroethane, then addition of 0.80 mol% solution of boron trifluoride diethyl etherate (0.074 g, 0.514 mmol) in cyclohexane (2.5 mL). Polymerization times: 3 mol%: 30 min, 7.4 mol%: 3 hours, 10 mol%: 12 hours, 15 mol%: 24 hours, 20 mol%: 48 hours, 25 mol%: 72 hours, 30 mol%: 96 hours. ^b Mol% incorporation first obtained by NMR integration then calculated after first run on DSC (differential scanning calorimetry) to account for the loss of formaldehyde through curing. ^c The melting temperature (T_m) determined from the second scan by differential scanning calorimetry (DSC). ^d % Crystallinity calculated by integrating the area under the melting endotherm from DSC trace and comparing to the POM standard melting endotherm of 190 J/g. ^e Degree of branching (DB) calculated as the number of branches per 1000 main chain atoms.

The results for the various epoxyalkane/trioxane copolymerizations can be seen in Table 2.1. As the feed of the epoxyalkane comonomer was increased the yields decreased with the 7.4 mol% feed producing the optimum yields. There appears to be a limiting factor with the amount of epoxyalkane comonomer present when reaching 25 or 30 mol%. Since there was no polymer being formed at these feed fractions, the polymerizations were also attempted with no dichloroethane present in the reaction in an attempt to produce polymer. The result of this approach still produced no polymer with the same reaction times. The poor solubility of

trioxane in the epoxyalkane seems to be preventing the polymerization from occurring and longer reaction times are needed. Regardless of the epoxyalkane comonomer, the melting temperature decreased in a roughly linear fashion relative to the mol% incorporation of the epoxyalkane comonomer, with the greatest depressed melting temperature being 149.6 °C from 1,2-epoxybutane with 21.18 mol% incorporation (Figure 2.1). The crystallinity also decreased in a relatively linear fashion, with the greatest depressed % crystallinity being 6.18% from 1,2-epoxyoctane with 32.03 mol% incorporation (Figure 2.2).

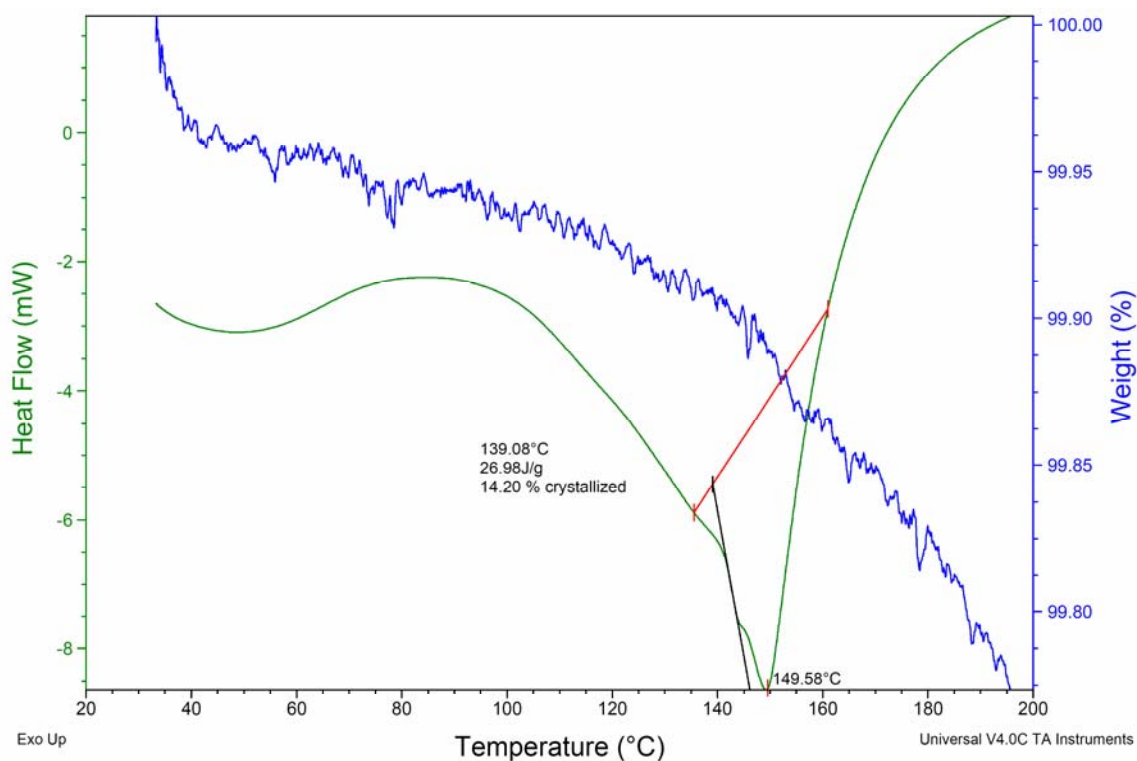


Figure 2.1. Melting endotherm for 21.18 mol% incorporation for 1,2-epoxybutane/trioxane copolymer from differential scanning calorimetry.

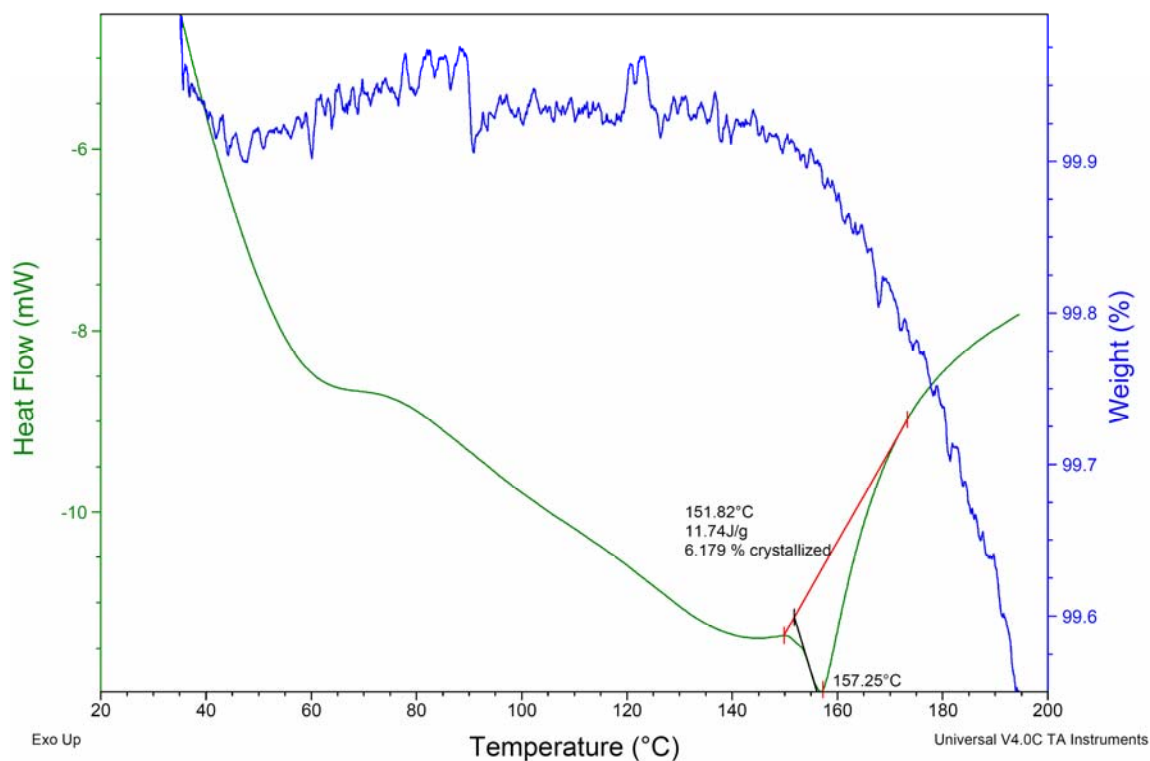


Figure 2.2. Melting endotherm for 32.03 mol% incorporation for 1,2-epoxyoctane/trioxane copolymer from differential scanning calorimetry.

The type of branching in the epoxyalkane/trioxane copolymerizations, whether there is a short or a long branch, does not have a significant effect on the copolymer's melting temperature and % crystallinity. Figure 2.3 shows a linear relationship of mol% incorporation versus the melting temperatures of the epoxyalkane/trioxane copolymers. When the branch from the epoxyalkane is methyl, ethyl, or butyl the trendlines appear to be about the same, whereas when the branch is hexyl, octyl, or decyl the trendlines follow a slightly different slope compared to the smaller groups. However, the 20 mol% feed for epoxyoctane/trioxane copolymer and epoxydodecane/trioxane copolymer are outliers, and when considered as

experimental error, the observed slope of the trendlines is a better fit to the shorter branched epoxyalkane/trioxane copolymers. A possible explanation for these outliers is that the alkyl branches are intermingling and crystallizing. When these considerations are made we observe the same effect of the branch on the POM copolymers as what is seen with ethylene/ α -olefin copolymerizations. That is, when ethylene is copolymerized with an α -olefin, the effects of the comonomer on the copolymer is about the same regardless of the branch length.³⁴ A comparison was

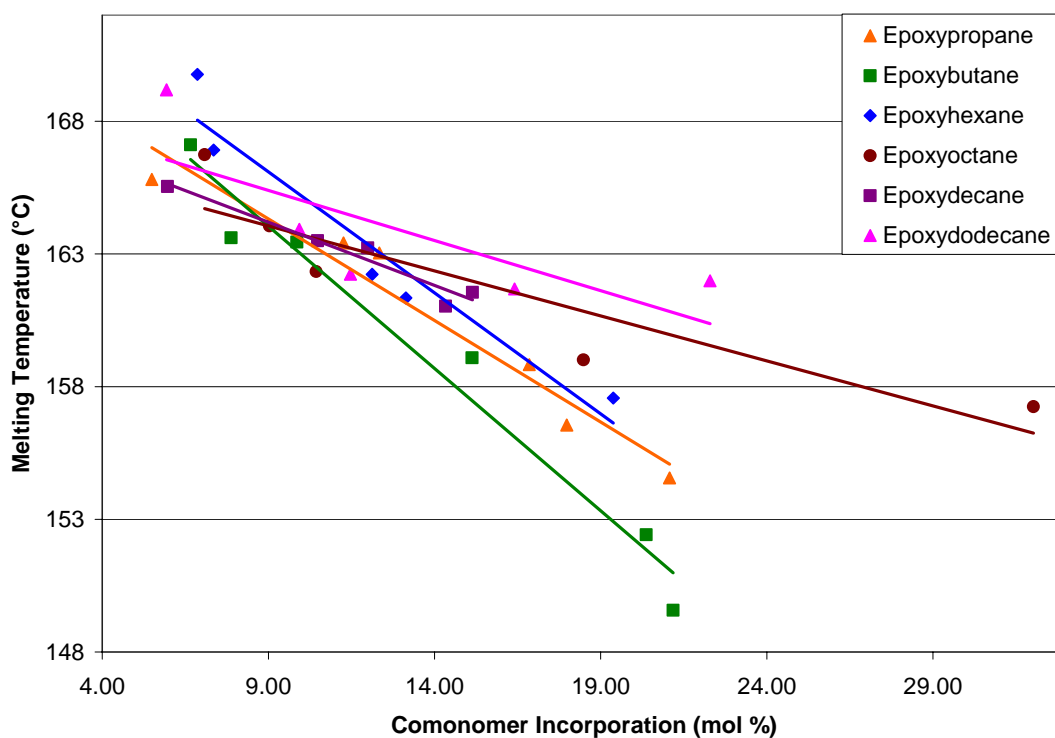


Figure 2.3. Copolymer melting temperatures versus mol% comonomer incorporation for various epoxyalkane/trioxane copolymers.

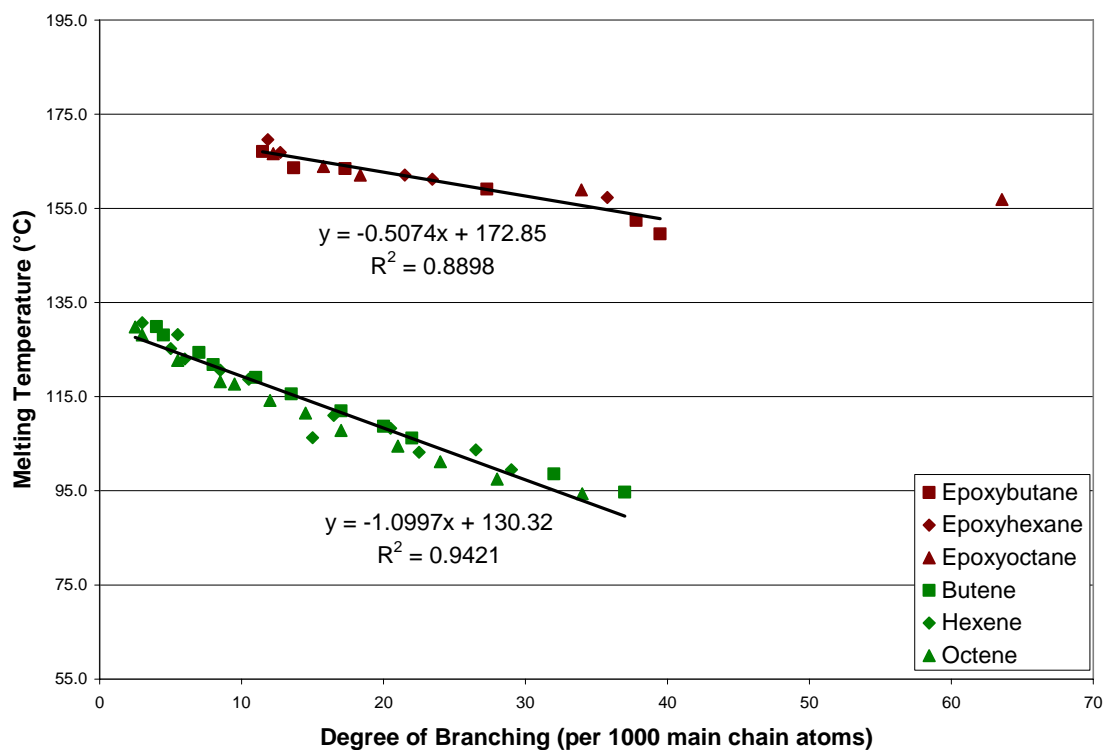


Figure 2.4. Comparison of degree of branching versus melting temperature for α -olefin/ethylene copolymers (green)³⁴ and epoxyalkane/trioxane copolymers (maroon).

made between epoxyalkane/trioxane copolymers and α -olefin/ethylene copolymers by looking at the degree of branching versus melting temperature and can be seen in Figure 2.4. Both types of copolymers follow a linear trend regardless of the type of branch; however, the slopes differ due to the main chain backbones. Also, there is an outlier around 64 DB (degree of branching) and is 20 mol% feed of epoxyoctane. More polymerizations will need to be conducted in order to determine if this is from experimental error or something else is occurring.

The epoxyalkane/trioxane copolymers have a carbon-oxygen main chain backbone, while α -olefin/ethylene copolymers have a carbon-carbon main chain backbone. The oxygen from polyoxymethylene gives the polymer a lower crystallinity and a significantly larger dipole moment compared to polyethylene. Polyethylene is able to form a lamellar crystallite by chain folding that allows the long chains to form strong bond connections, whereas polyoxymethylene has stronger dipole-dipole interactions. By introducing branches into polyethylene, there is a greater disturbance between the chains, and results in the melting temperature being depressed with a minimal amount of branch being incorporated, as compared to polyoxymethylene. It is possible that if the epoxyalkane/trioxane copolymerizations for 25 mol% comonomer and higher were left for longer reaction times (such as weeks) the melting points may be depressed even more, as suggested by the trendlines, especially for the longer branched epoxyalkane comonomers when more comonomer is incorporated. This may be of interest since 1,2-epoxydecane can be derived from natural sources and results in a different type of polymer than the epoxybutane.

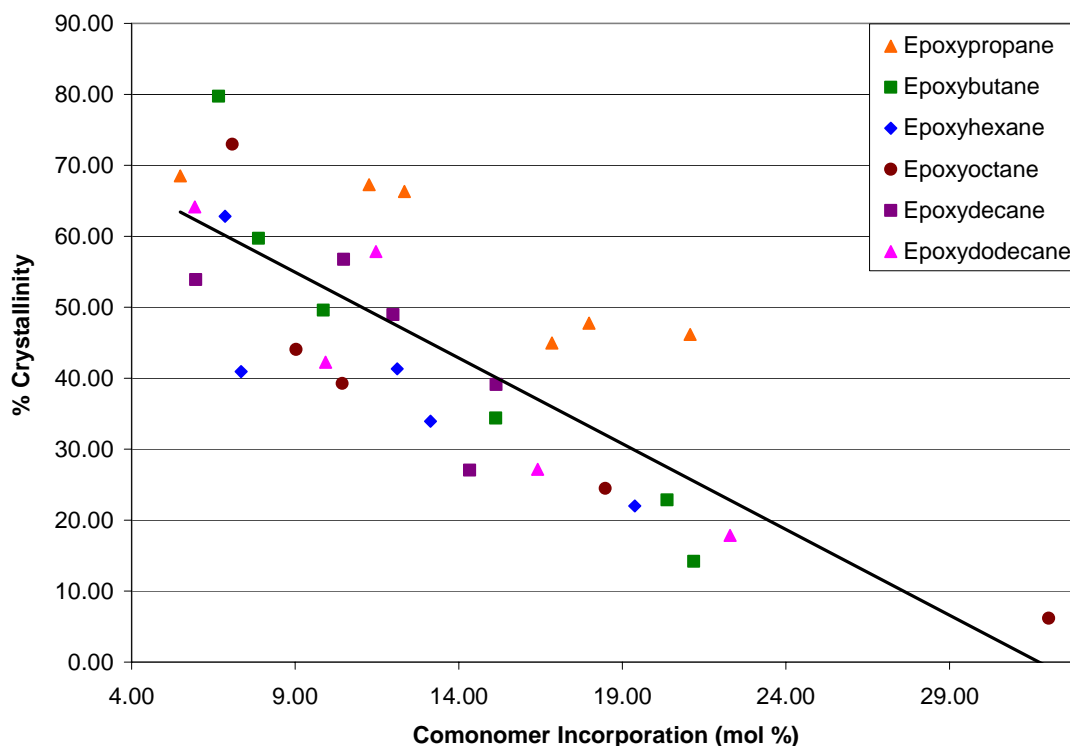


Figure 2.5. Copolymer % crystallinity versus mol% comonomer incorporation for various epoxyalkane/trioxane copolymers.

The crystallinity of the epoxyalkane/trioxane copolymers (Figure 2.5) shows a somewhat linear depression in relation to the mol% incorporation, regardless of the nature of the branch in the copolymer. However, 1,2-epoxypropane shows two depressions where there is an initial decrease in crystallinity followed by a second decreasing trend. Besides this odd trend, the rest of the copolymers seem to follow the same linear trend.

The 1,2-epoxybutane/trioxane copolymers give the most optimum results of all the epoxyalkane comonomers attempted, due to the greatest depression in melting

temperature from POM (180 °C - 181 °C) and the second greatest disruption in crystallinity. The 1,2-epoxybutane comonomer is also a good choice because the starting materials can be produced from biorenewable resources. The lower melting temperature is a benefit because the epoxyalkane/trioxane copolymer permits easier processing for industrial applications. The disruption to crystallinity is not much of a factor since POM already has an extremely high tensile modulus and tensile strength.

Experimental

Materials. All polymerizations were carried out using standard glove box and Schlenk line techniques under a dry nitrogen atmosphere. 1,2-Dichloroethane, cyclohexane, and all epoxyalkanes (1,2-epoxypropane, 1,2-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyoctane, 1,2-epoxydecane, 1,2-epoxydodecane) were distilled from calcium hydride before use. 1,3,5-Trioxane, trifluoromethanesulfonic acid and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) were used as received.

General Polymerization Procedure. The various feed fractions of epoxyalkane were syringed into a solution of trioxane (5.00 g, 56.0 mmol) and 1,2-dichloroethane (5.00 mL) at 42 °C under a dry-nitrogen atmosphere, followed by the addition of 0.074 g boron trifluoride diethyl etherate initiator (0.514 mmol) in 2.50 mL cyclohexane. The polymerization times were adjusted depending on the comonomer feed and corresponding activity. The polymerizations were quenched

with 5% aqueous Na_2CO_3 , washed with copious amounts of water and acetone, and air dried via vacuum filtration.

Instrumentation. Approximately 80.0 mg of polymer was dissolved in ~1.00 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and the ^1H NMR spectra of polymer samples were recorded on a Mercury 300 spectrometer at room temperature after obtaining a lock on deuterated chloroform. The thermal behavior of the copolymers was analyzed using a TA Instruments Q600 SDT differential scanning calorimeter under an argon atmosphere. The reported melting temperatures were for the cured copolymers and obtained during the second heating cycle. Using the software program with the instrument, the melting enthalpy and crystallinity were calculated by integrating the area under the melting endotherm of the DSC trace. The theoretical value for the melting enthalpy of 100% crystalline polyoxymethylene used was 190 J/g.³⁹

CHAPTER III

COPOLYMERIZATIONS OF 4-ALKYL-1,3-DIOXOLANES AND TRIOXANE*

Introduction

Copolymers of trioxane and alkyl-1,3-dioxolanes^{24,25,27,29-31,38,40,41} have been synthesized; however, to date there has been no research on the effects of the substituent of the alkyldioxolane in the copolymers (except for thermal stability) or on the comparison of the epoxyalkane/trioxane copolymers to alkyldioxolane/trioxane copolymers. Boron trifluoride diethyl etherate^{27,28,31-33,37,38} initiator was used for the alkyldioxolane/trioxane copolymerizations since the initiator was much more active at incorporating the comonomer for the 1,2-epoxyalkane/trioxane copolymerizations. These copolymerizations will be compared to the work of Braun et al.,²⁴ as he performed the copolymerizations using trifluoromethanesulfonic acid as the initiator. The effects of the branching on the copolymers was carried out and studied by copolymerizing 4-ethyl-1,3-dioxolane, 4-butyl-1,3-dioxolane, or 4-hexyl-1,3-dioxolane with trioxane and using various feed percentages of the 4-alkyl-1,3-dioxolane. The amount of incorporation of the alkyldioxolane/trioxane copolymers will be compared to the amount of incorporation

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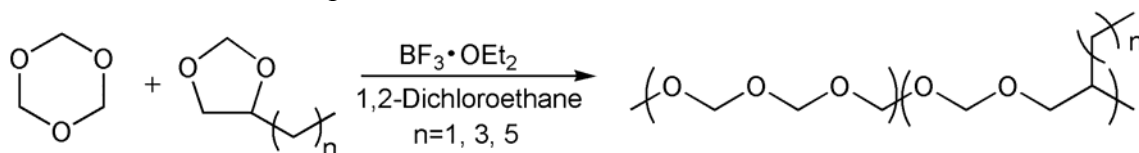
of the corresponding epoxyalkane/trioxane copolymers (1,2-epoxybutane, 1,2-epoxyhexane, and 1,2-epoxyoctane). The polymers were analyzed using ^1H NMR spectroscopy for determining percent incorporation of alkyldioxolane comonomer and using differential scanning calorimetry (DSC) for obtaining melting temperatures of copolymers and % crystallinity of copolymers.

Results and Discussion

The copolymerizations behaved rather the same whether the comonomer was an alkyldioxolane or epoxyalkane. The cationic polymerization initiator, boron trifluoride diethyl etherate, was the only one attempted due to the initiator results obtained from the epoxyalkane/trioxane copolymerizations and the results of Braun's²⁴ work. Braun reported copolymerizations of 4-alkyl-1,3-dioxolanes and trioxane with the linear alkyl branches being 1-4, 6, 8, 10, and 14 in length.²⁴ In his work, he used trifluoromethanesulfonic acid as the initiator and obtained very low incorporations of the alkyldioxolane comonomer for 1.3-4.0 mol% feed fractions.²⁴ The rates of incorporation results that were reported show that the shorter branched alkyldioxolanes (0.80-1.5 mol%) were better than the longer branched comonomer (0.40-0.80 mol%).²⁴ A comparison of Braun's²⁴ work and the research presented here is shown in Table 3.1. The boron trifluoride diethyl etherate initiator used for this project produced polymer up to certain percentages of comonomer, and resulted

in decent yields and mol % incorporations for the alkyldioxolane/trioxane copolymers (Table 3.2).

Table 3.1. Comparison of Braun's²⁴ 4-alkyl-1,3-dioxolane/trioxane copolymer results and our research presented in this document



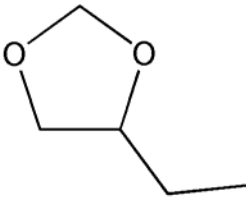
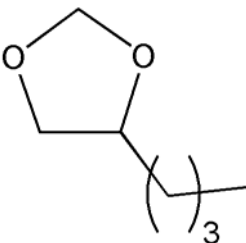
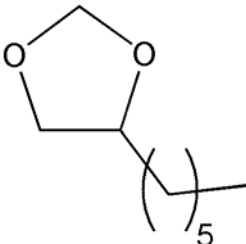
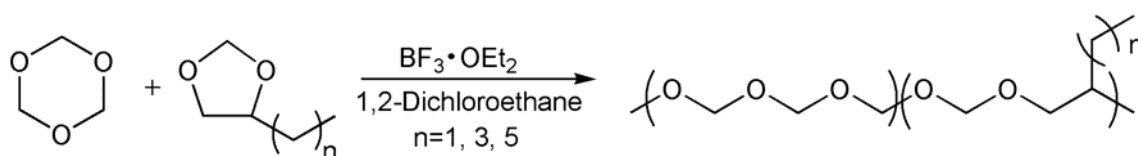
Comonomer	Our Research		Braun's ²⁴ Data	
	Feed (mol%)	Incorporation (mol%)	Feed (mol%)	Incorporation (mol%)
	3.0	5.32	1.3	0.80
	7.4	7.01	2.0	1.06
	10.0	9.14	2.5	1.21
	-	-	4.0	1.48
	3.0	3.46	1.3	0.44
	7.4	6.55	2.0	0.52
	10.0	8.06	2.5	0.62
	-	-	4.0	0.99
	3.0	5.89	1.3	0.44
	7.4	8.93	2.0	0.50
	10.0	6.44	2.5	0.57
	-	-	4.0	0.70

Table 3.2. 4-Alkyl-1,3-dioxolanes/trioxane copolymerization results^a

Comonomer	Feed (mol%)	Yield (g)	Incorporation (mol%) ^b	T_m (°C) ^c	% Crystallinity ^d	DB ^e
	3	3.573	5.32	167.86	59.16	9.11
	7.4	3.538	7.01	164.27	73.04	12.11
	10	3.691	9.14	162.93	69.02	15.96
	15	4.029	9.13	160.80	62.42	15.95
	20	5.289	11.81	160.72	63.40	20.92
	25	4.587	12.15	160.20	63.13	21.56
	30	3.579	12.25	158.08	50.44	21.75
	3	5.523	3.46	169.16	62.11	8.022
	7.4	3.719	6.55	167.68	64.99	15.76
	10	3.613	8.06	166.01	67.97	19.76
	15	5.116	8.71	163.12	59.60	21.67
	20	3.250	9.51	162.27	48.26	21.45
	25	1.750	12.03	160.08	54.05	31.32
	30	1.674	11.51	159.51	37.75	29.95
	3	3.802	5.89	167.86	70.48	5.87
	7.4	5.783	8.93	165.98	81.08	11.29
	10	3.525	6.44	165.26	56.75	14.00
	15	4.680	9.57	163.16	50.27	15.18
	20	2.316	10.01	160.96	50.03	16.64
	25	4.481	9.22	162.58	55.22	21.33
	30	0.639	12.30	160.74	45.74	20.36

^a Conditions: Alkyldioxolane syringed into 5.00 g trioxane (55 mmol) in 5.0 mL 1,2-dichloroethane, then addition of 0.80 mol% solution of boron trifluoride diethyl etherate (0.074 g, 0.514 mmol) in cyclohexane (2.5 mL). Polymerization times: 3 mol%-20 mol%: 30 min, 25 mol%: 1 hour, 30 mol%: 1.5 hours. ^b Mol% incorporation first obtained by NMR integration then calculated after first run on DSC (differential scanning calorimetry) to account for the loss of formaldehyde through curing. ^c The melting temperature (T_m) determined from the second scan by differential scanning calorimetry (DSC). ^d % Crystallinity calculated by integrating the area under the melting endotherm from DSC trace and comparing to the POM standard melting endotherm of 190 J/g. ^e Degree of branching (DB) calculated as the number of branches per 1000 main chain atoms.

The results for the various alkyldioxolanes/trioxane copolymerizations can be seen in Table 3.2. In general, the lower alkyldioxolane comonomer feeds produced low yields regardless of alkyl chain length, which is likely due to the fast polymerization times for feeds less than 10 mol%. The feed percentages could be increased greater than 30 mol% to get greater amounts of incorporation of the alkyldioxolane monomer since the percentages of incorporations are slightly low with fast reaction times. This is in contrast to the epoxyalkane/trioxane copolymerizations where we were unable to observe any polymers with 25-30 mol% feed for the epoxyalkane/trioxane copolymerizations in the given reaction time periods. This is ideal because the reaction times are particularly shorter for the alkyldioxolane/trioxane copolymers than for the epoxyalkane/trioxane copolymers. There seems to be slight solubility issues for these alkyldioxolane/trioxane copolymerizations since longer reaction times were needed for higher feed percentages (25-30 mol% feeds). However, the effect was not as pronounced as in the epoxyalkane/trioxane copolymerizations. Regardless of the alkyldioxolane comonomer, the melting temperature decreased in a roughly linear fashion to that of the mol% incorporation of the alkyldioxolane comonomer with the greatest depressed melting temperature being 158.08 °C from 4-ethyl-1,3-dioxolane with 12.25 mol% incorporation (Figure 3.1). The crystallinity shows no predictable trend, which may be a result of the lower % incorporation of the alkyldioxolane comonomer. The copolymer with the greatest depressed % crystallinity is 37.75% from 4-butyl-1,3-dioxolane with 11.51 mol% incorporation (Figure 3.2).

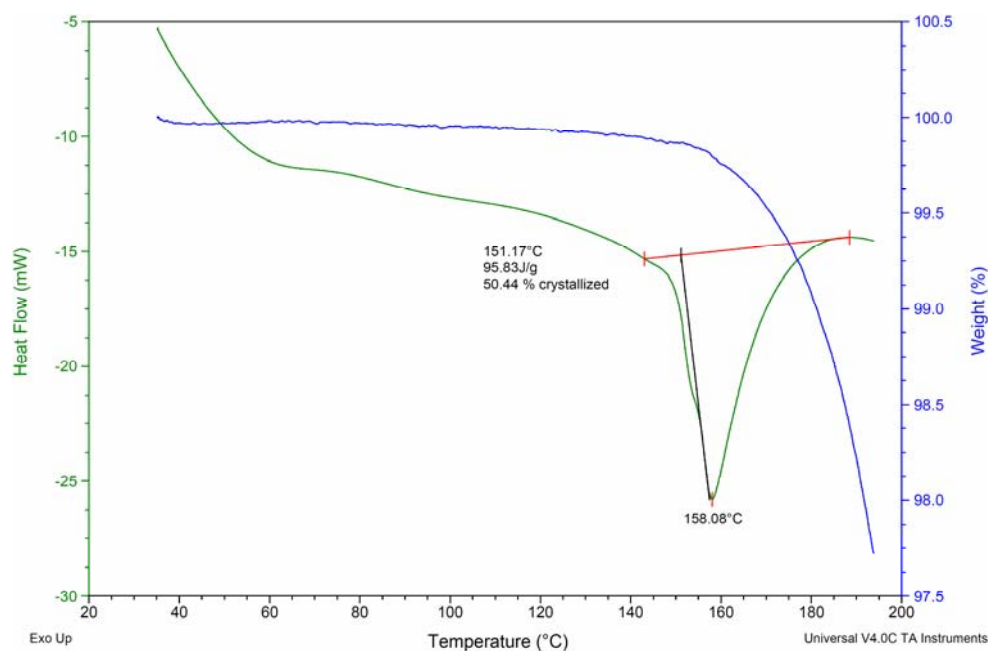


Figure 3.1. Melting endotherm for 12.25 mol% incorporation 4-ethyl-1,3-dioxolane/trioxane copolymer from differential scanning calorimetry.

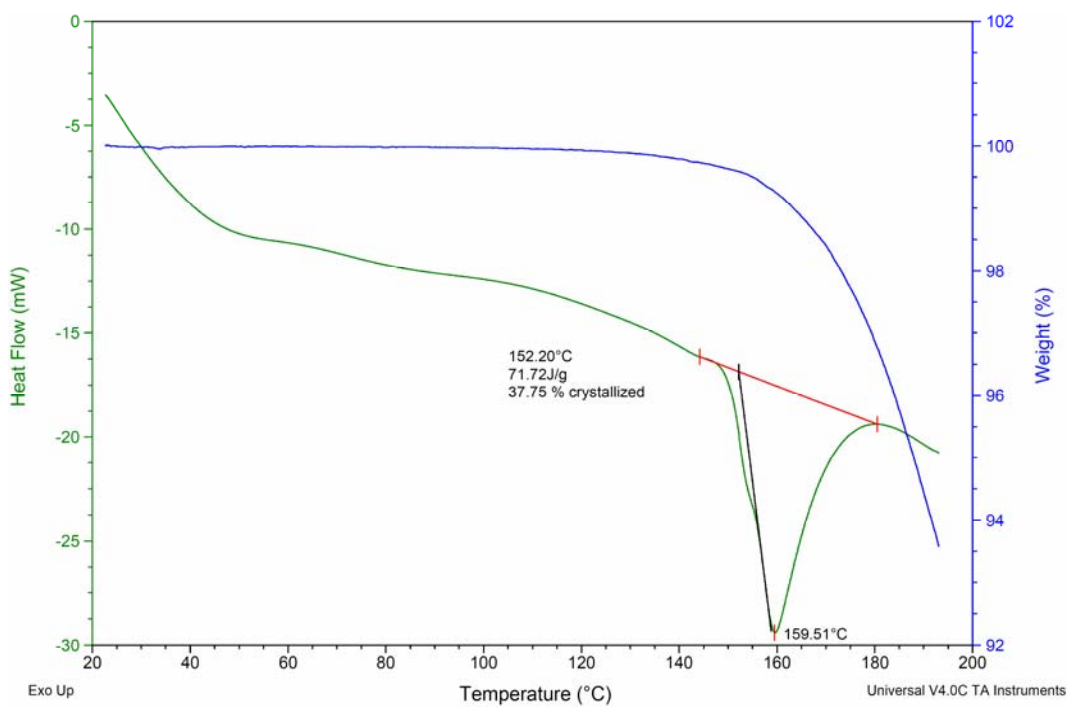


Figure 3.2. Melting endotherm for 11.51 mol% incorporation 4-butyl-1,3-dioxolane/trioxane copolymer from differential scanning calorimetry.

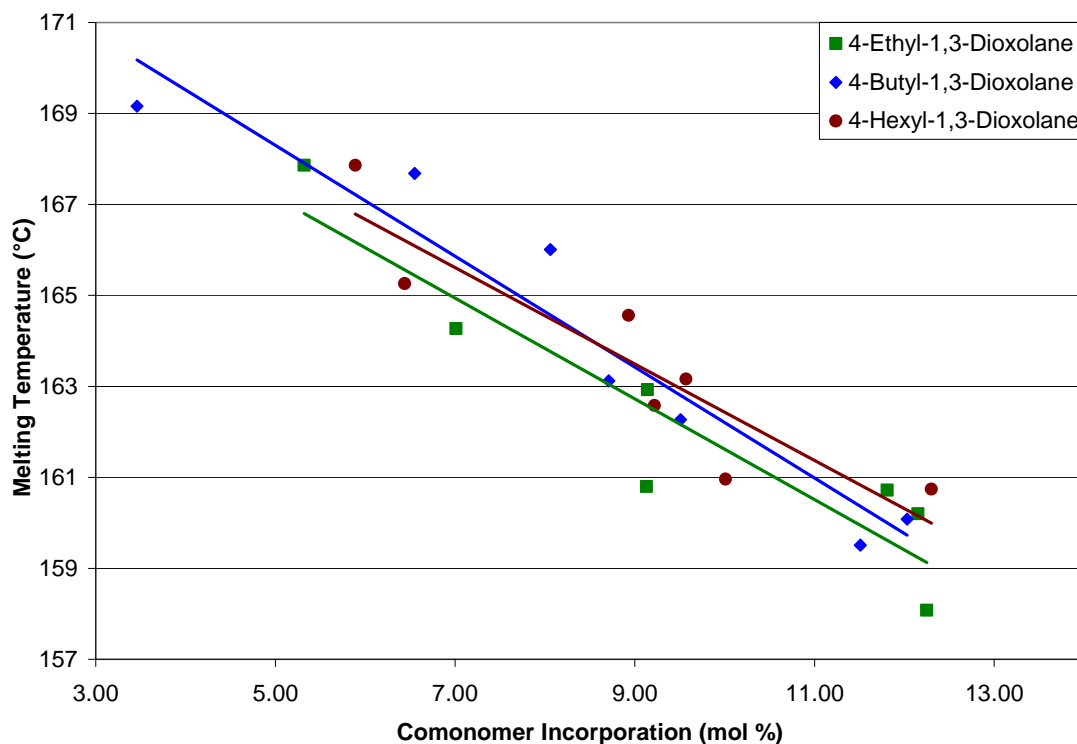


Figure 3.3. Copolymer melting temperatures versus mol% comonomer incorporation for various alkyldioxolane/trioxane copolymers.

The length of the branching in the alkyldioxolane/trioxane copolymers has a similar effect as with the epoxyalkane/trioxane copolymers except these copolymers follow a better linear trendline. The short-, medium-, and long-branched alkyldioxolanes have the same trend (slope) for the depression of melting temperature in relation to mol% incorporation (Figure 3.3). The alkyldioxolane/trioxane copolymers follow the projected outcome made with the comparison of ethylene being copolymerized with an α -olefin and was also seen with the epoxyalkane/trioxane copolymers. That is, the melting point depression is only affected by the amount of comonomer incorporation and not the length of the alkyl

branch. A comparison was made between alkyldioxolane/trioxane copolymers and α -olefin/ethylene copolymers by looking at the degree of branching versus melting temperature and can be seen in Figure 3.4. Both types of copolymers follow a linear

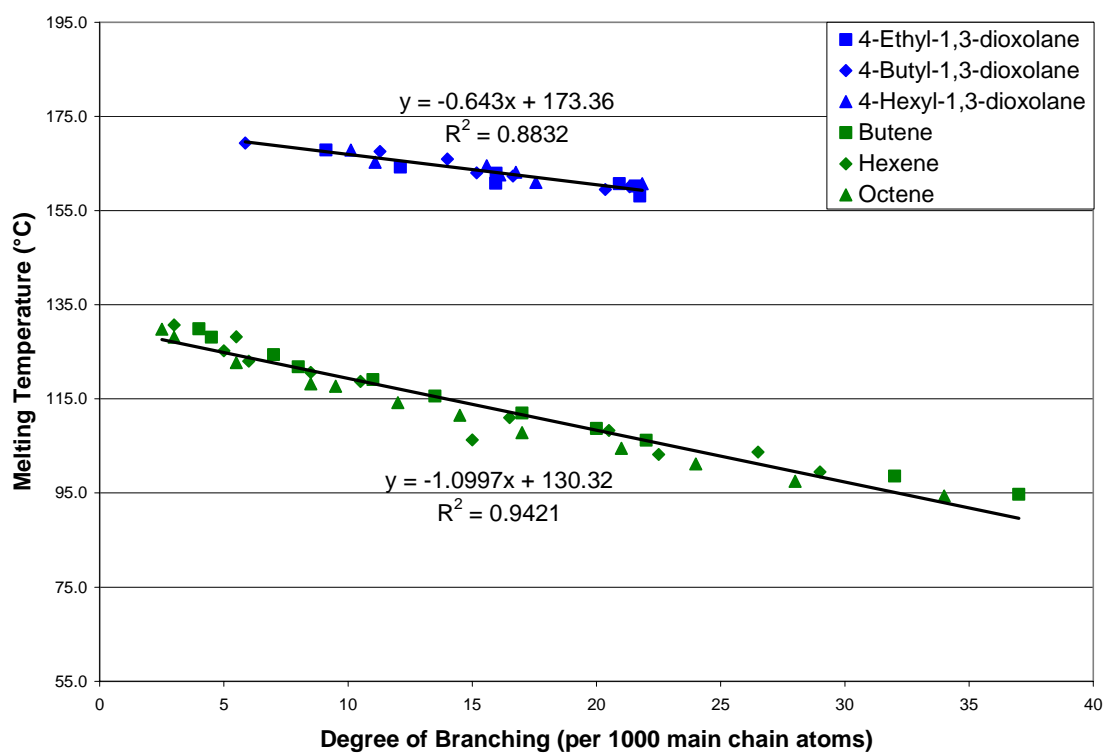


Figure 3.4. Comparison of degree of branching versus melting temperature for α -olefin/ethylene copolymers (green)³⁴ and alkyldioxolane/trioxane copolymers (blue).

trend regardless of the type of branch; however, the slopes differ greatly due to the main chain backbones. The alkyldioxolane/trioxane copolymers have a carbon-oxygen main chain backbone, while α -olefin/ethylene copolymers have a carbon-carbon main chain backbone. The oxygen from polyoxymethylene gives the

copolymer a lower crystallinity and a significantly larger dipole moment compared to polyethylene. Polyethylene is able to form a lamellar crystallite by chain folding that allows the long chains to form strong bond connections, whereas polyoxymethylene has stronger dipole-dipole interactions. By introducing branches into polyethylene there is a greater disturbance between chains, and this results in the melting temperature being depressed more with a minimal amount of branch, as compared to polyoxymethylene.

A comparison was made between the 4-ethyl-1,3-dioxolane, 4-butyl-1,3-dioxolane, and 4-hexyl-1,3-dioxolane with trioxane copolymers and the 1,2-epoxybutane, 1,2-epoxyhexane, and 1,2-epoxyoctane with trioxane copolymers by comparing the degree of branching per 1000 main chain atoms for each type of copolymer. Figure 3.5 shows a fairly linear trend regardless of whether the comonomer is an epoxyalkane or an alkyldioxolane. The melting points were not as depressed for the alkyldioxolane/trioxane copolymers as compared to the epoxyalkane/trioxane copolymers. However, this is likely due to an increased amount of epoxyalkane comonomer incorporated and the same effect should be seen if the amount of feed was increased for the alkyldioxolane/trioxane copolymers. This also suggests that the amount of feed can be increased for the alkyldioxolane/trioxane copolymers to obtain observations similar to the higher incorporated epoxyalkane/trioxane copolymers. There is an outlier being 20 mol% feed of epoxyoctane that will need to be further investigated in order to determine if it is a result of experimental error or if something else is occurring.

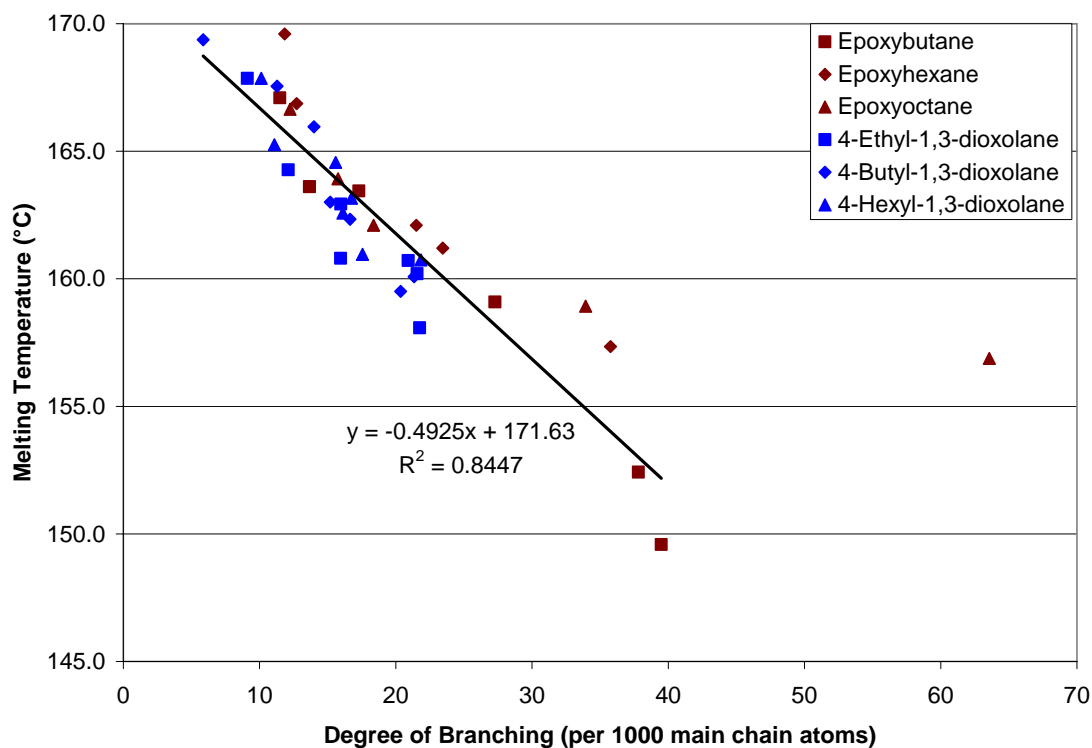


Figure 3.5. Copolymer melting temperatures versus degree of branching (per 1000 main chain atoms) comparing the alkyldioxolane/trioxane copolymers and epoxyalkane/trioxane copolymers.

The crystallinity of the alkyldioxolane/trioxane copolymers (Figure 3.6) shows that there is no linear trendline as there was for the epoxyalkane/trioxane copolymers. There is a similarity in the loss of crystallinity between the 1,2-epoxypropane/trioxane copolymers and 4-hexyl-1,3-dioxolane/trioxane copolymers, where there are two different linear trendlines. Regardless of the type of branch from the alkyldioxolane/trioxane copolymer, there is a large decrease in crystallinity when the alkyldioxolane comonomer feed was 3 mol%. Each alkyldioxolane/trioxane copolymer has a lower % crystallinity for the first polymerization and then there is

somewhat of a linear trend from 10-30 mol%. This could be a result of the polymerization occurring very rapidly for the 3 mol% while the larger feed amounts take a longer amount of time to polymerize, but more studies will be needed to confirm this result.

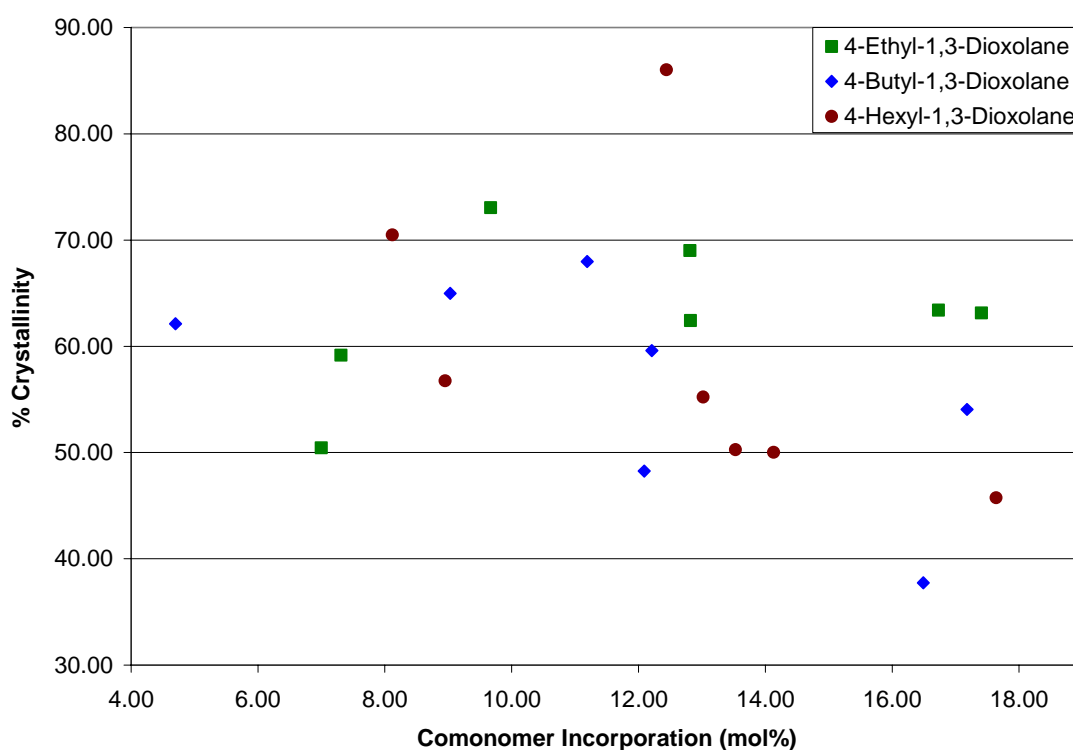


Figure 3.6. Copolymer % crystallinity versus mol% comonomer incorporation for various alkyldioxolane/trioxane copolymers.

The 4-ethyl-1,3-dioxolane/trioxane copolymers give the best results of all the alkyldioxolane comonomers investigated, as quantified by the most linear depression in melting temperature from POM (180 °C – 181 °C) and the greatest depression in

crystallinity. The 4-ethyl-1,3-dioxolane comonomer is a good choice as the starting materials (1,2-butane diol and paraformaldehyde) can be made from biorenewable resources.

Experimental

Materials. All polymerizations were carried out using standard glove box and Schlenk line techniques under a dry nitrogen atmosphere. 1,2-Dichloroethane, cyclohexane, and all dioxolanes (4-ethyl-1,3-dioxolane, 4-butyl-1,3-dioxolane, 4-hexyl-1,3-dioxolane) were distilled from calcium hydride before use. 1,3,5-Trioxane and boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{OEt}_2$) were used as received. Dowex 50 was prepared by washing with a 5% HCl solution followed by continuous washings with water until effluent was neutral.

4-Ethyl-1,3-Dioxolane Synthesis. In a 200 mL round bottom flask, 30.0 g of 1,2-butane diol (0.33 mol), 9.31 g of paraformaldehyde (0.31 mol), and 5.00 g Dowex 50 was added and attached to a short path condenser and heated to 110°C. The reaction was stopped once there was no more liquid distilled off (about 6 mL of water). The top layer dioxolane was separated and distilled from calcium hydride. ^1H NMR (CDCl_3 , 300 MHz) δ 0.59 (t, $^3J_{\text{HH}} = 2.99$ Hz, 3H, CH_3), 1.09-1.31 (m, 2H, CH_2CH_3), 2.98-3.06 (m, 1H, $\text{CH}_2\text{CH}(\text{O})\text{CH}_2\text{CH}_3$), 3.47-3.57 (m, 2H, $\text{OCH}_2\text{CH}(\text{O})\text{CH}_2\text{CH}_3$), 4.43 (s, 1H, OCH_2O), 4.58 (s, 1H, OCH_2O).

4-Butyl-1,3-Dioxolane Synthesis. In a 200 mL round bottom flask, 50.0 g of 1,2-hexane diol (0.42 mol), 9.61 g of paraformaldehyde (0.32 mol), and 5.00 g Dowex 50 was added and attached to a short path condenser and heated to 120 °C. Once all the water was distilled off, the top layer of dioxolane from the original round bottom flask was separated and distilled from calcium hydride. ¹H NMR (CDCl₃, 300 MHz) δ 0.69 (t, ³J_{HH} = 3.03 Hz, 3H, CH₃), 1.10-1.42 (m, 6H, CH(CH₂)₃CH₃), 3.13-3.20 (m, 1H, CH₂CH(O)(CH₂)₃CH₃), 3.69-3.72 (m, 2H, OCH₂CH(O)(CH₂)₃CH₃), 4.60 (s, 1H, OCH₂O), 4.76 (s, 1H, OCH₂O).

4-Hexyl-1,3-Dioxolane Synthesis. In a 200 mL round bottom flask, 50.0 g of 1,2-octane diol (0.34 mol), 9.61 g of paraformaldehyde (0.32 mol), and 5.00 g Dowex 50 was added and attached to a short path condenser and heated to 120 °C. Once all the water was distilled off, the top layer of dioxolane from the original round bottom flask was separated and distilled from calcium hydride. ¹H NMR (CDCl₃, 300 MHz) δ 0.62 (t, ³J_{HH} = 3.04 Hz, 3H, CH₃), 0.98-1.36 (m, 10H, CH(CH₂)₅CH₃), 3.03-3.10 (m, 1H, CH₂CH(O)(CH₂)₅CH₃), 3.58-3.65 (m, 2H, OCH₂CH(O)(CH₂)₅CH₃), 4.49 (s, 1H, OCH₂O), 4.65 (s, 1H, OCH₂O).

General Polymerization Procedure. The various feed fractions of alkyl dioxolane were syringed into a solution of trioxane (5.00 g, 56.0 mmol) and 1,2-dichloroethane (5.00 mL) at 42 °C under a dry-nitrogen atmosphere, followed by the addition of 0.074 g boron trifluoride diethyl etherate initiator (0.514 mmol) in 2.50 mL cyclohexane. The polymerization times for 3, 7.4, 10, 15, 20 mol% of alkyl dioxolane were 30 minutes; 25 mol% was one hour; and 30 mol% was 1.5

hours. The polymerizations were quenched with 5% aqueous Na_2CO_3 , washed with copious amounts of water and acetone, and air dried via vacuum filtration.

Instrumentation. Approximately 80.0 mg of polymer was dissolved in ~1.00 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and the ^1H NMR spectra of polymer samples were recorded on a Mercury 300 spectrometer at room temperature after obtaining a lock on deuterated chloroform. The thermal behavior of the copolymers was analyzed using a TA Instruments Q600 SDT differential scanning calorimeter under an argon atmosphere. The reported melting temperatures were for the cured copolymers and were obtained during the second heating cycle. Using the software program with the instrument, the melting enthalpy and crystallinity were calculated by integrating the area under the melting endotherm of the DSC trace. The theoretical value for the melting enthalpy of 100% crystalline polyoxymethylene used was 190 J/g.³⁹

CHAPTER IV

SUMMARY AND CONCLUSIONS

The synthesis of several 1,2-epoxyalkane/trioxane copolymers and 4-alkyl-1,3-dioxolane/trioxane copolymers were successful via cationic initiators. The most suitable cationic initiator is boron trifluoride diethyl etherate instead of trifluoromethanesulfonic acid due to the ability to successfully incorporate the comonomer (epoxyalkane or alkyldioxolane) in high amounts into the copolymer. The polymerization conditions were optimized in order to obtain copolymers with good yields and comonomer incorporations.

Even though the polymers are similar in structure (Figure 1.5), there are marked differences between these two copolymer families. The epoxyalkane/trioxane copolymers melting point depression was notably greater than the alkyldioxolane/trioxane copolymers for a given mol% of comonomer incorporation. However, when looking at the degree of branching (per 1000 main chain atoms) the alkyldioxolane/trioxane copolymers need to be performed with greater comonomer feeds in order to get a similar melting point depression. Regardless of whether the comonomer is an epoxyalkane or alkyldioxolane, the comonomers with the short alkyl branches give the greatest depressed melting point with the lowest amount of feed introduced, which suggests they may be better suited

for future applications. The 1,2-epoxybutane and 4-ethyl-1,3-dioxolane comonomers are of greater interest compared to the other comonomers, at least when considering that they can be synthesized from biorenewable resources. These results indicate that epoxyalkane comonomers (especially epoxybutane) may be superior to alkyldioxolane comonomers for disrupting crystallinity because of the steeper dependence of the copolymer melting temperature on mol% comonomer incorporation. The differences in crystallinity between the two comonomers may be due to the ability of the comonomer to be incorporated. Each of the comonomers has different pK_b 's with epoxyalkane being the lower value of alkyldioxolane and trioxane.

The mechanical properties (impact strength, tensile strength, and tensile modulus) will be explored in the future and will help to reveal the differences between the epoxyalkane/trioxane copolymers and the alkyldioxolane/trioxane copolymers and the effects of each type of individual branch on the copolymers. Longer reaction times for higher feed percentages are currently underway in an attempt to obtain a copolymer with higher amounts of comonomer incorporation. Although longer reaction times are not feasible for industrial production, it will help to further explain the effects of the branch if lower melting temperatures can be obtained for the longer branched epoxyalkanes and alkyldioxolanes.

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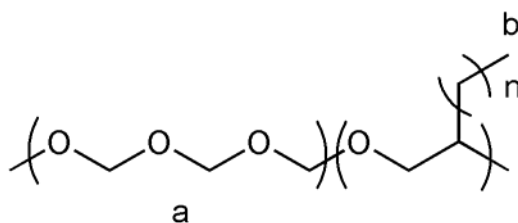
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APPENDIX A

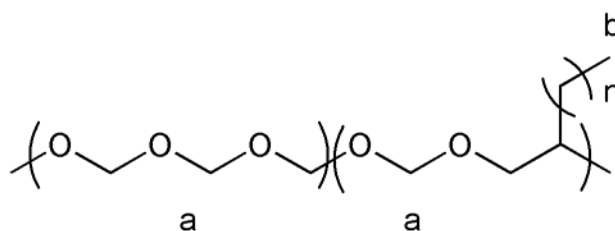
NMR SPECTRA

Epoxyalkane mol% Incorporation NMR Calculation



$$\text{mol\%} = \frac{J_{CH_3}(b)/3}{(J_{CH_2}(a)/6) + (J_{CH_3}(b)/3)}$$

Alkyldioxolane mol% Incorporation NMR Calculation



$$\text{mol\%} = \frac{J_{CH_3}(b)/3}{\frac{J_{CH_2}(a) - \frac{2}{3}J_{CH_3}(b)}{6} + J_{CH_3}(b)/3}$$

Epoxyalkane/Trioxane Copolymer Degree of Branching Calculation

$x = \text{mole fraction (mol\% incorporation/100)}$

$\# \text{ atoms} = 3x \text{ atoms} + 6(1-x) \text{ atoms}$

$\text{DB} = (x/\# \text{ atoms}) * 1000$

Alkyldioxolane/Trioxane Copolymer Degree of Branching Calculation

$x = \text{mole fraction (mol\% incorporation/100)}$

$\# \text{ atoms} = 5x \text{ atoms} + 6(1-x) \text{ atoms}$

$\text{DB} = (x/\# \text{ atoms}) * 1000$

Chapter II: Trioxane and 1,2-Epoxyalkanes Copolymers from Table 2.1

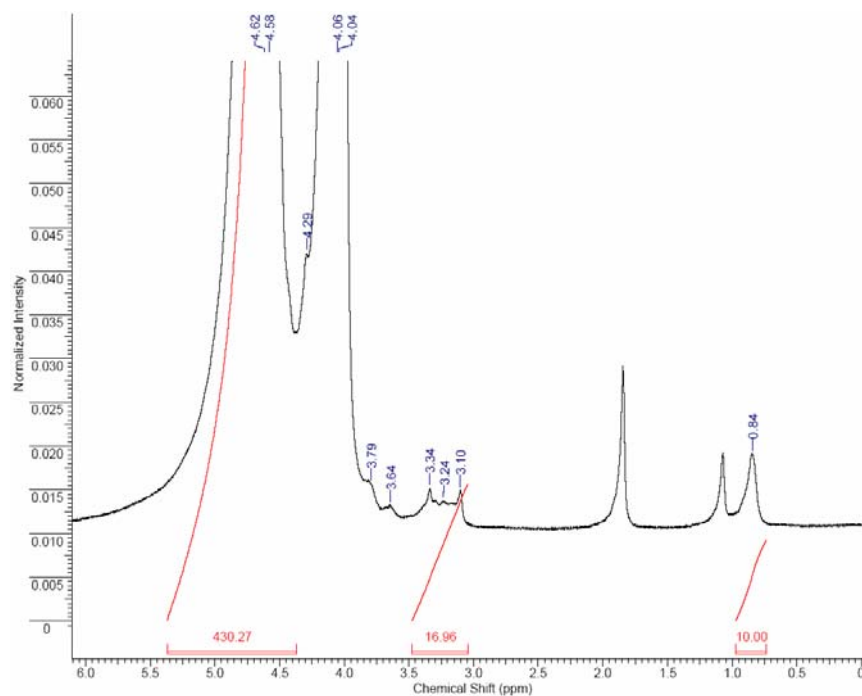


Figure A.1. 3 mol% feed 1,2-Epoxypropane 5.49 mol% incorporation

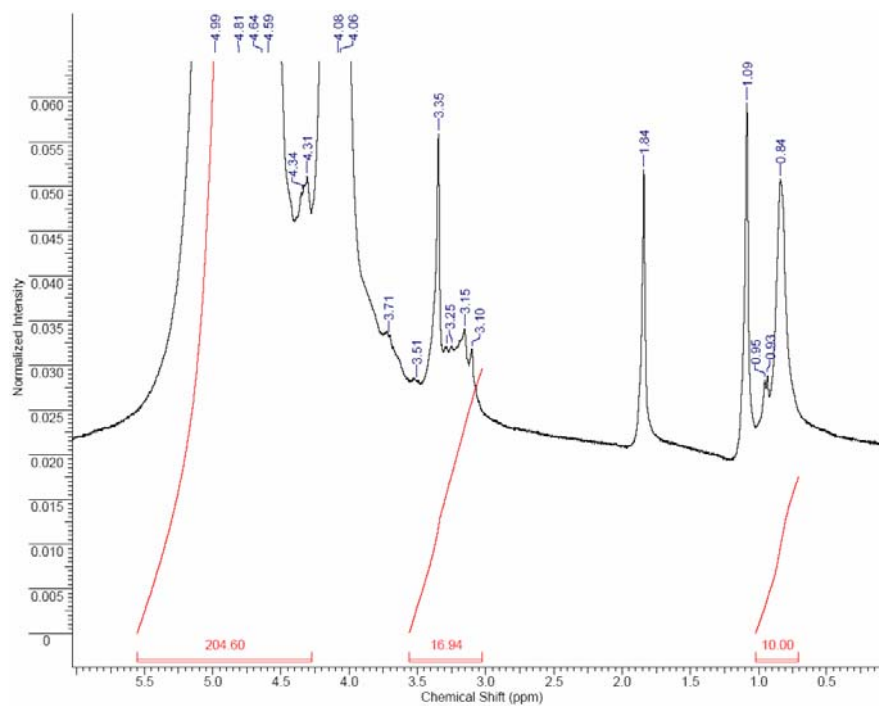


Figure A.2. 7.4 mol% feed 1,2-Epoxypropane 11.26 mol% incorporation

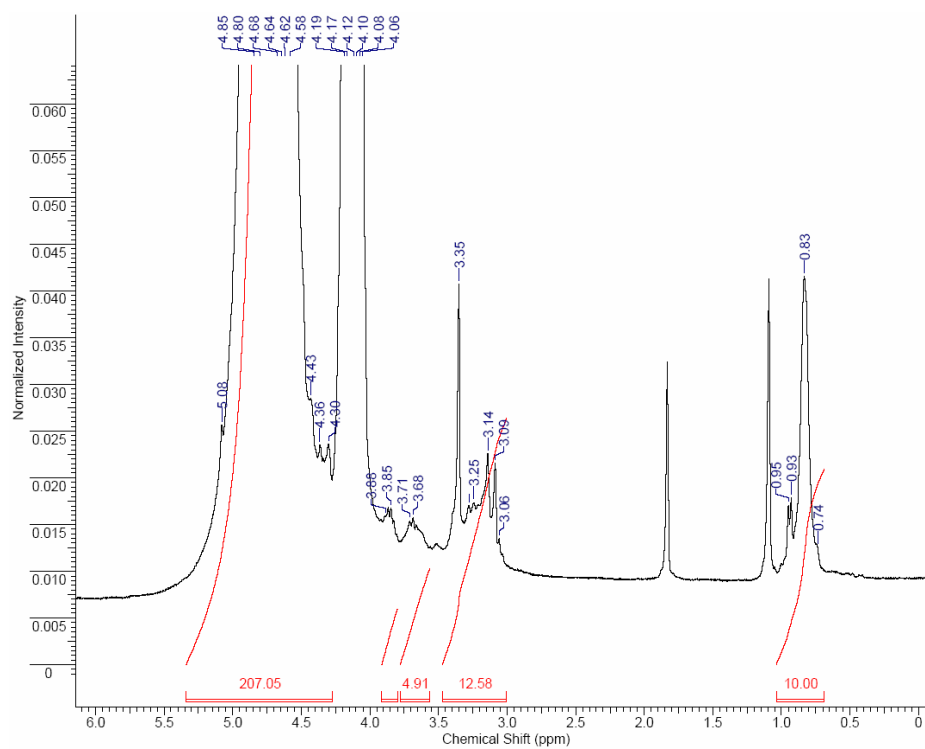


Figure A.3. 10 mol% feed 1,2-Epoxypropane 12.34 mol% incorporation

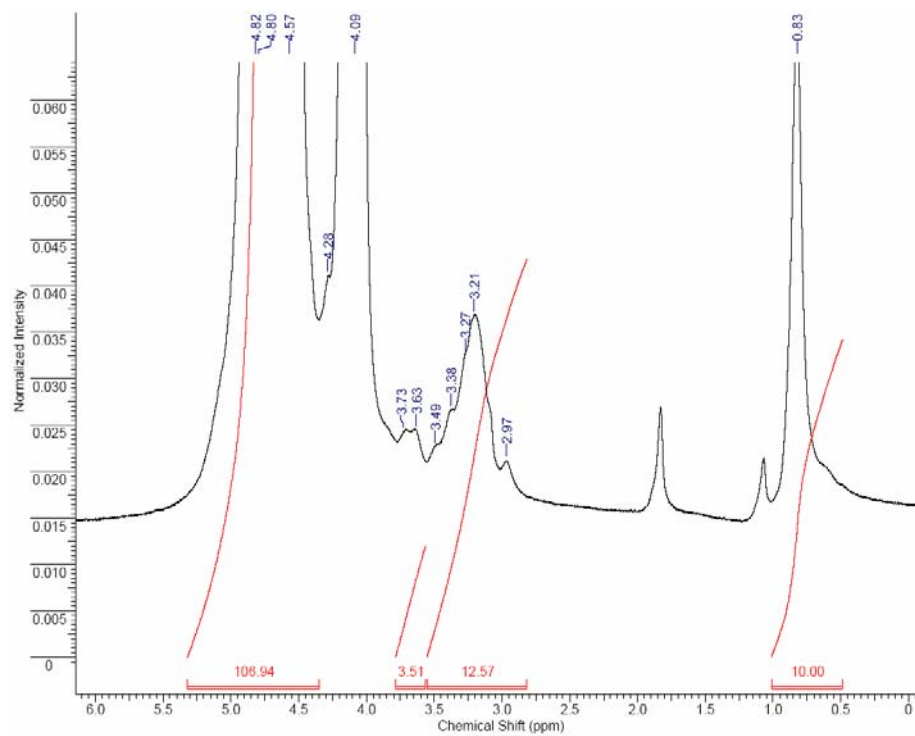


Figure A.4. 15 mol% feed 1,2-Epoxypropane 16.85 mol% incorporation

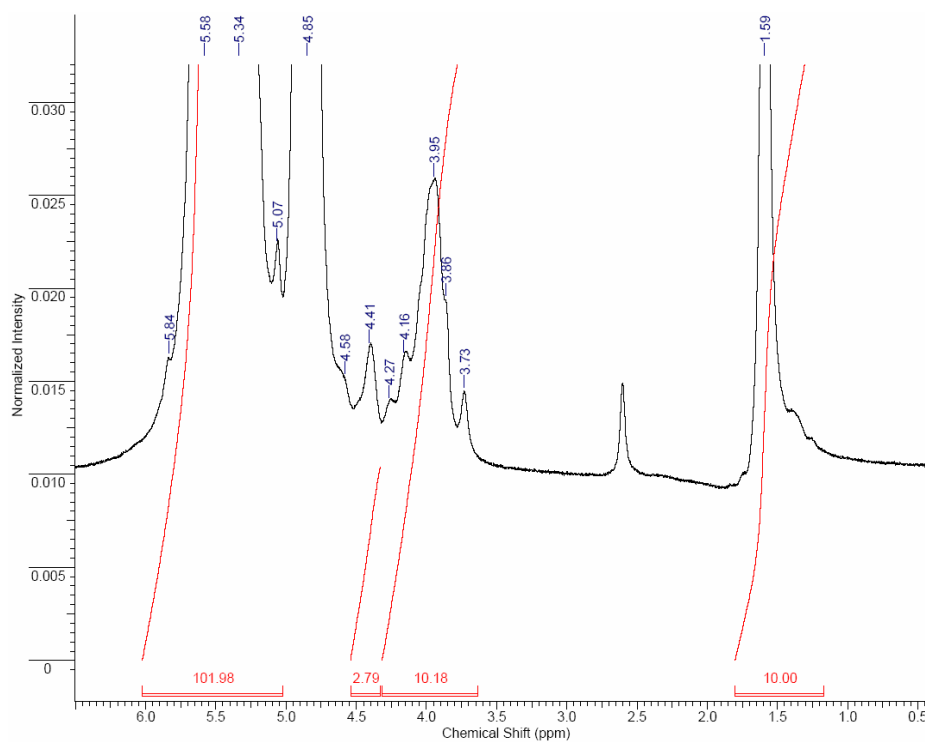


Figure A.5. 20 mol% feed 1,2-Epoxypropane 17.98 mol% incorporation

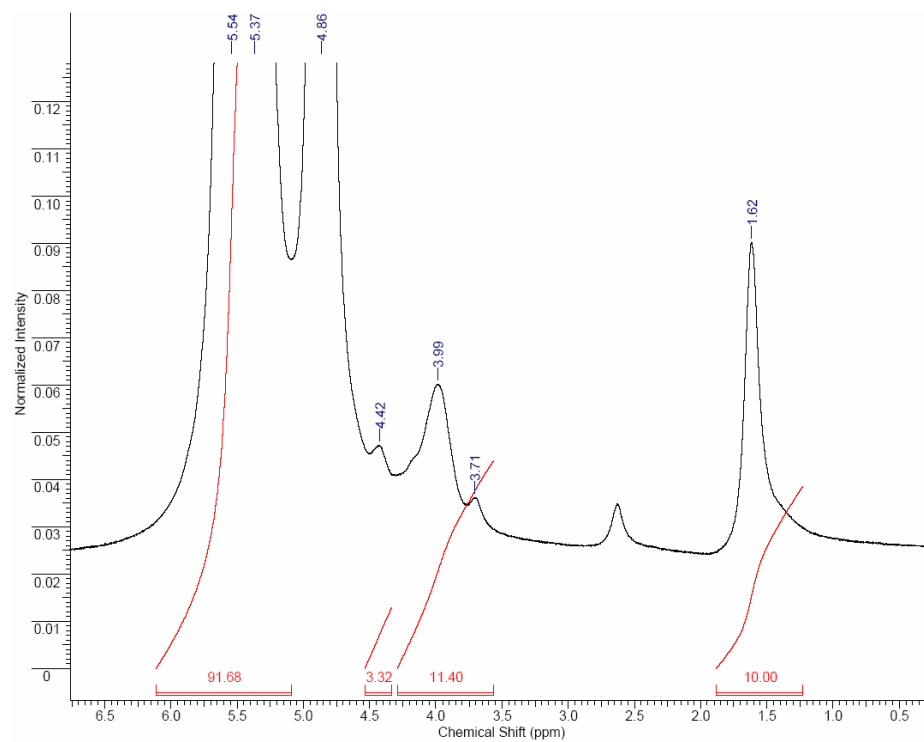


Figure A.6. 25 mol% feed 1,2-Epoxypropane 21.07 mol% incorporation

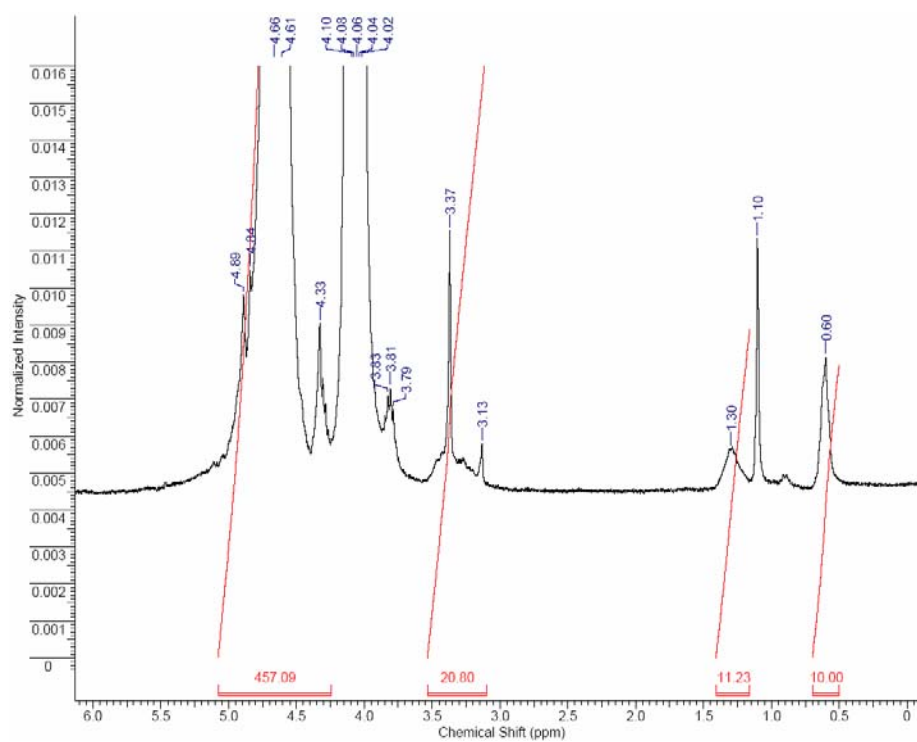


Figure A.7. 3 mol% feed 1,2-Epoxybutane 6.66 mol% incorporation

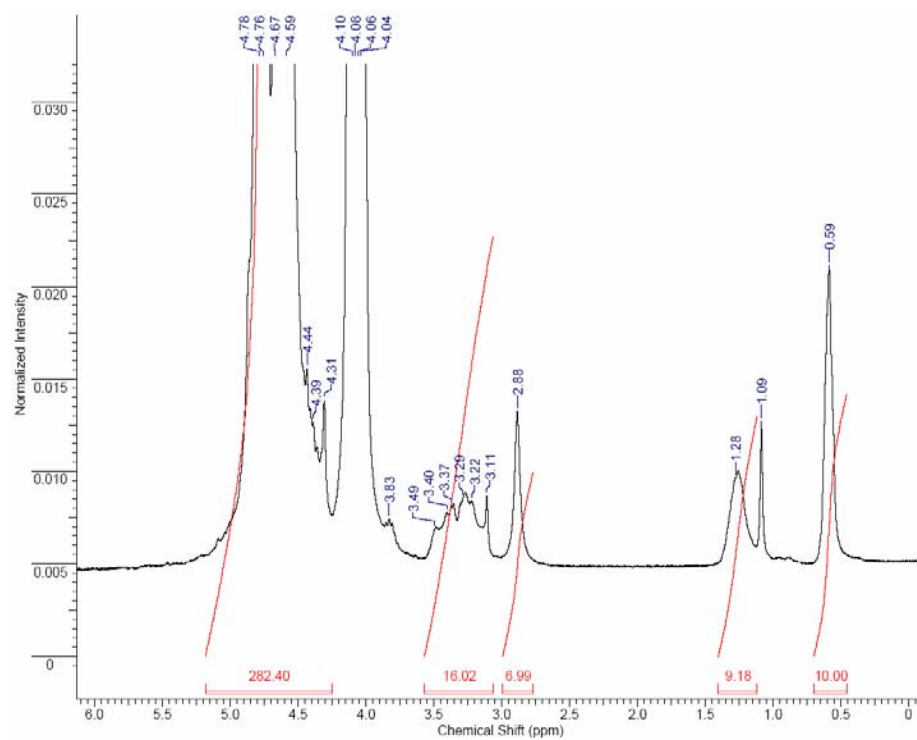


Figure A.8. 7.4 mol% feed 1,2-Epoxybutane 7.88 mol% incorporation

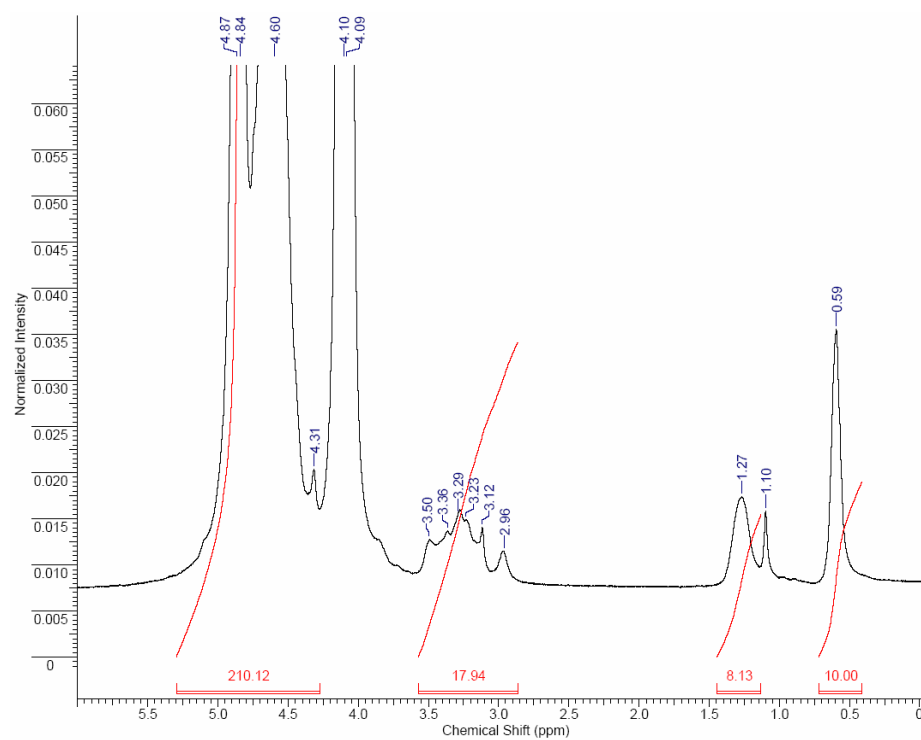


Figure A.9. 10 mol% feed 1,2-Epoxybutane 9.86 mol% incorporation

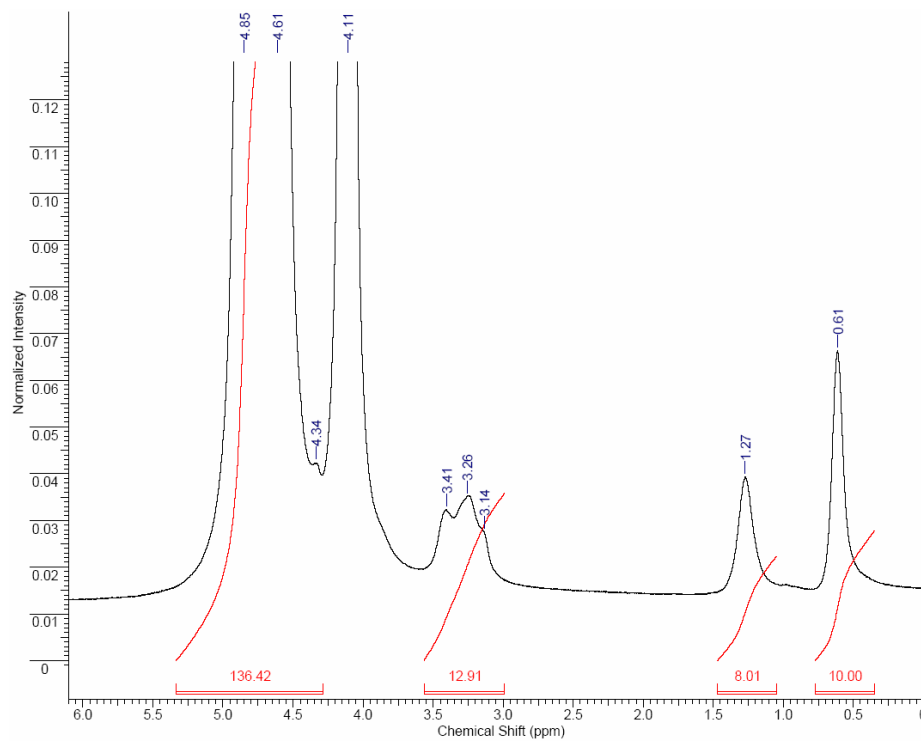


Figure A.10. 15 mol% feed 1,2-Epoxybutane 15.13 mol% incorporation

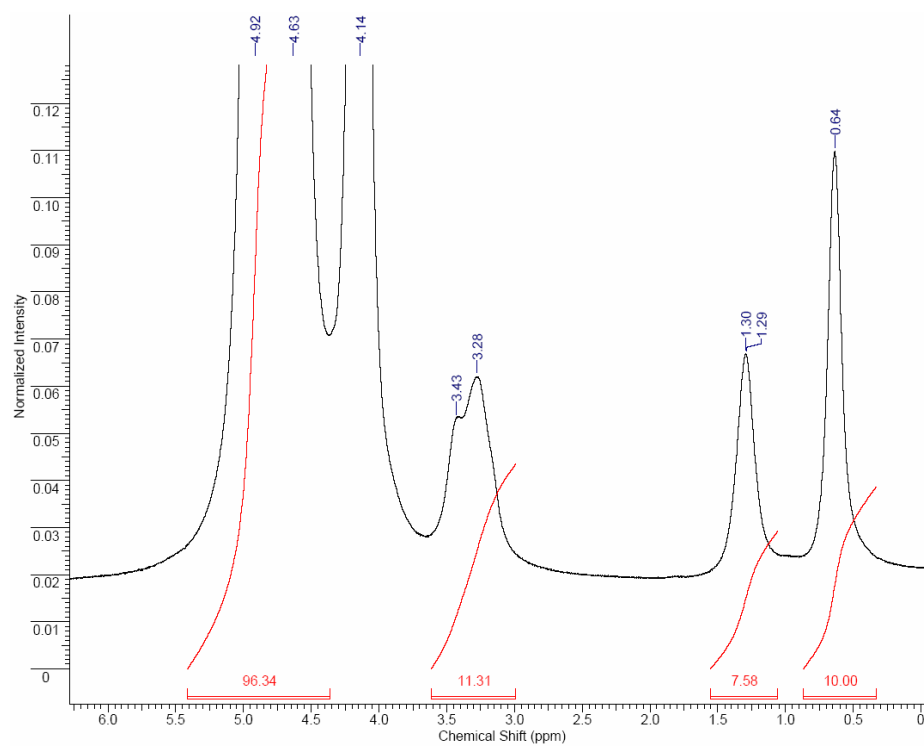


Figure A.11. 20 mol% feed 1,2-Epoxybutane 20.37 mol% incorporation

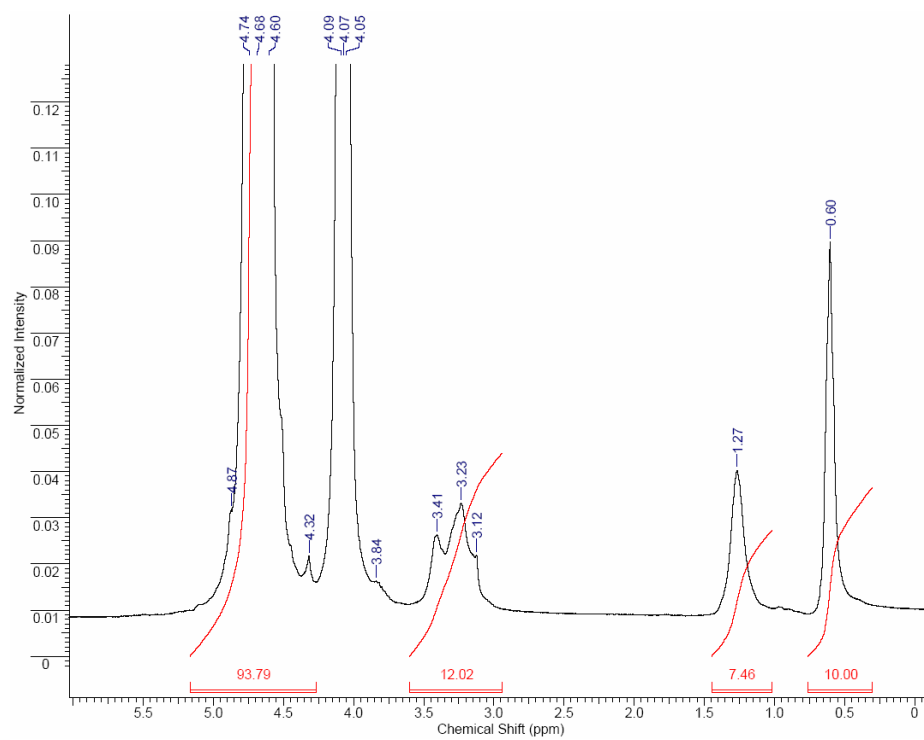


Figure A.12. 25 mol% feed 1,2-Epoxybutane 21.18 mol% incorporation

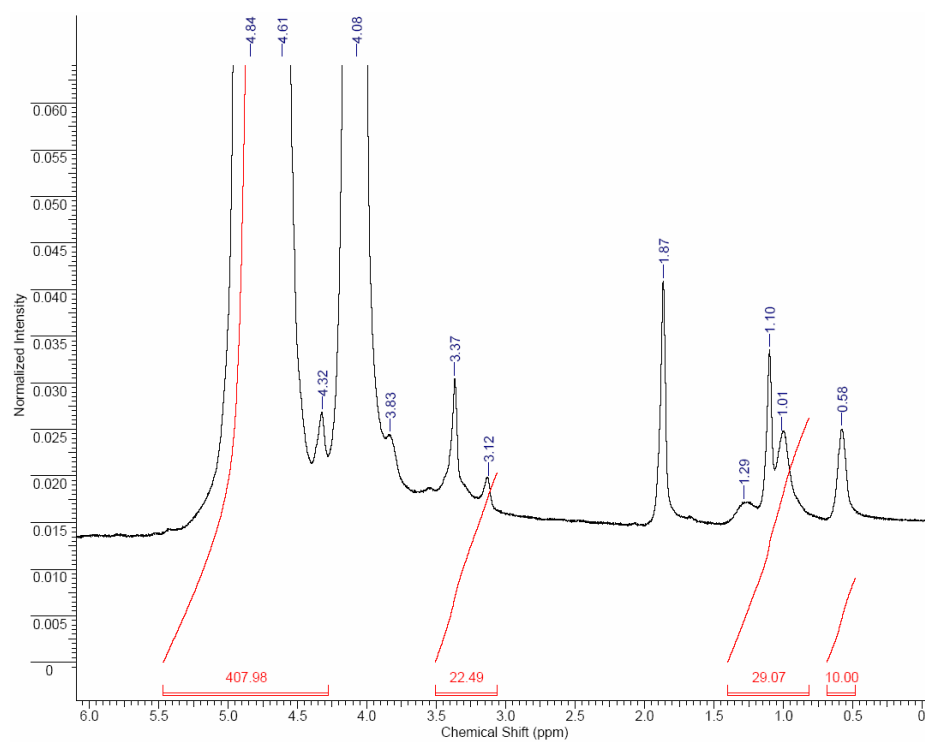


Figure A.13. 3 mol% feed 1,2-Epoxyhexane 6.86 mol% incorporation

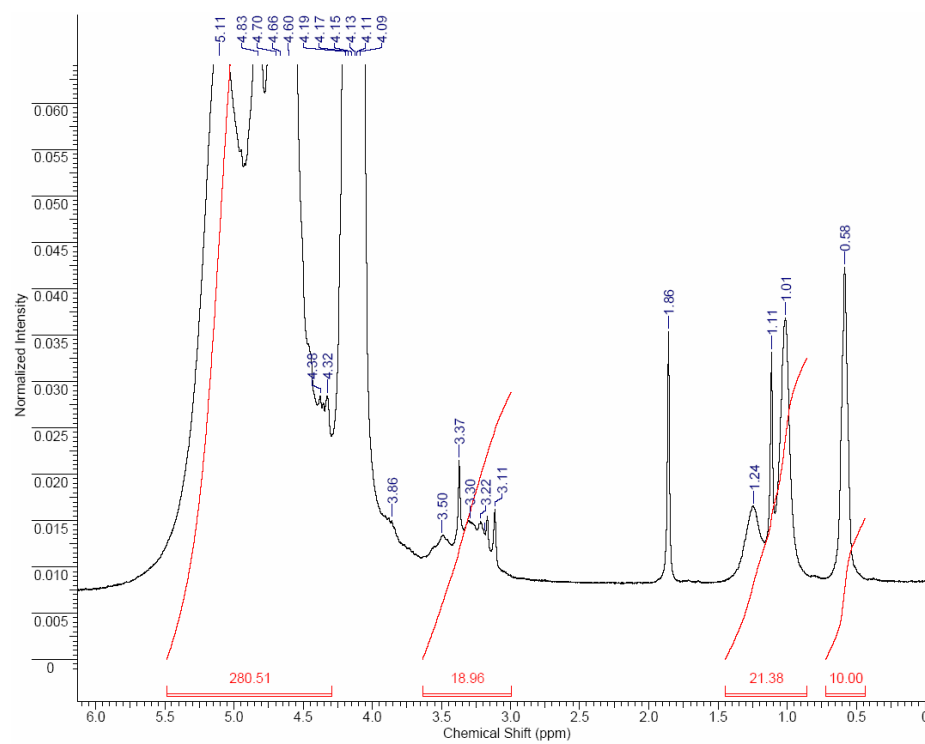


Figure A.14. 7.4 mol% feed 1,2-Epoxyhexane 7.35 mol% incorporation

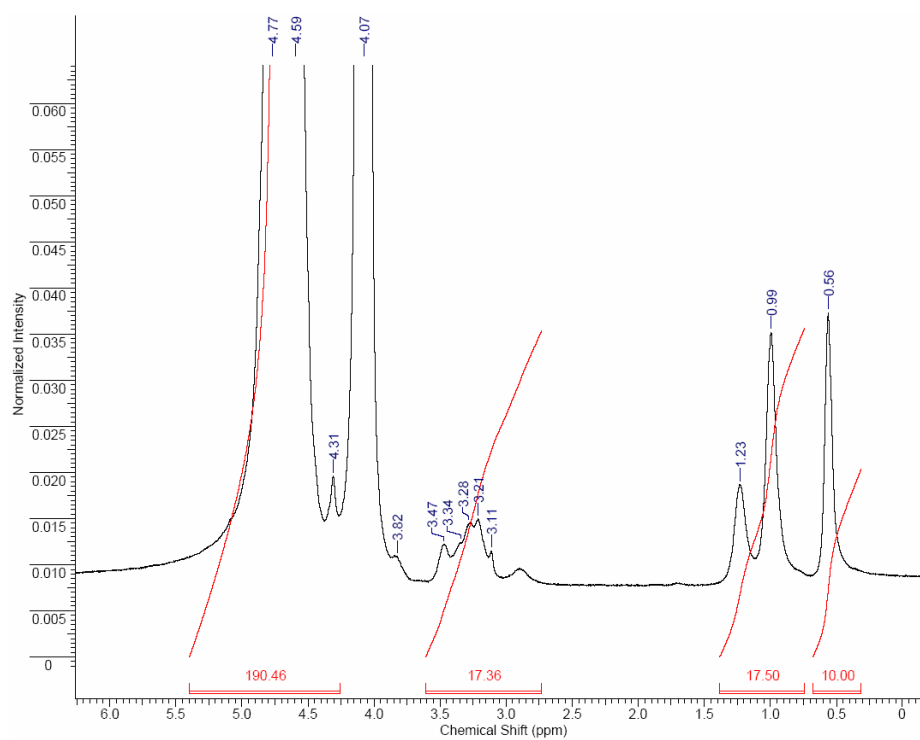


Figure A.15. 10 mol% feed 1,2-Epoxyhexane 12.12 mol% incorporation

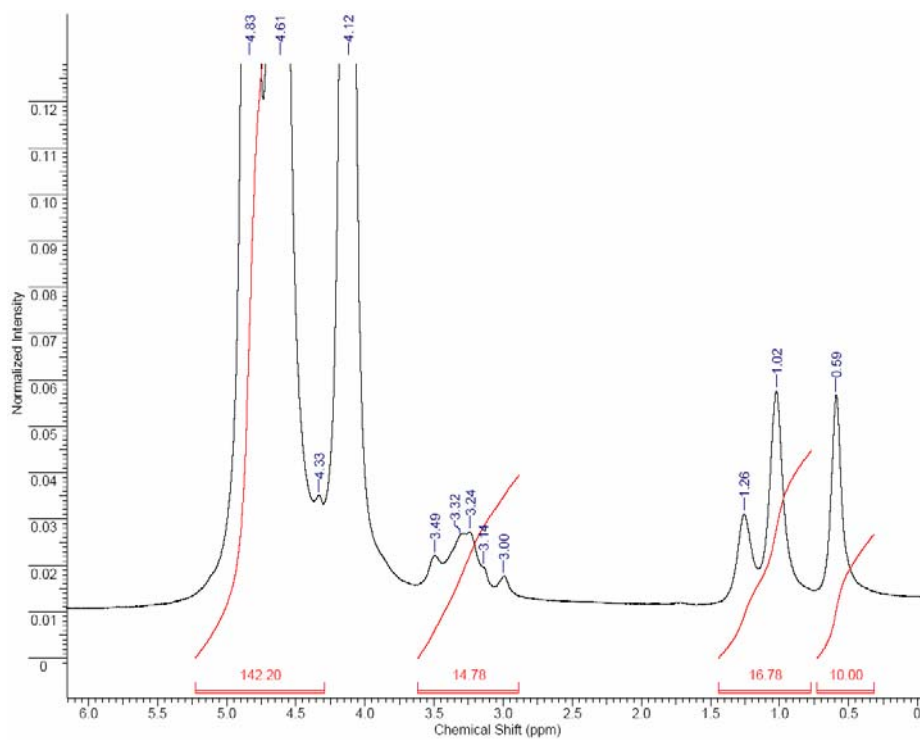


Figure A.16. 15 mol% feed 1,2-Epoxyhexane 13.14 mol% incorporation

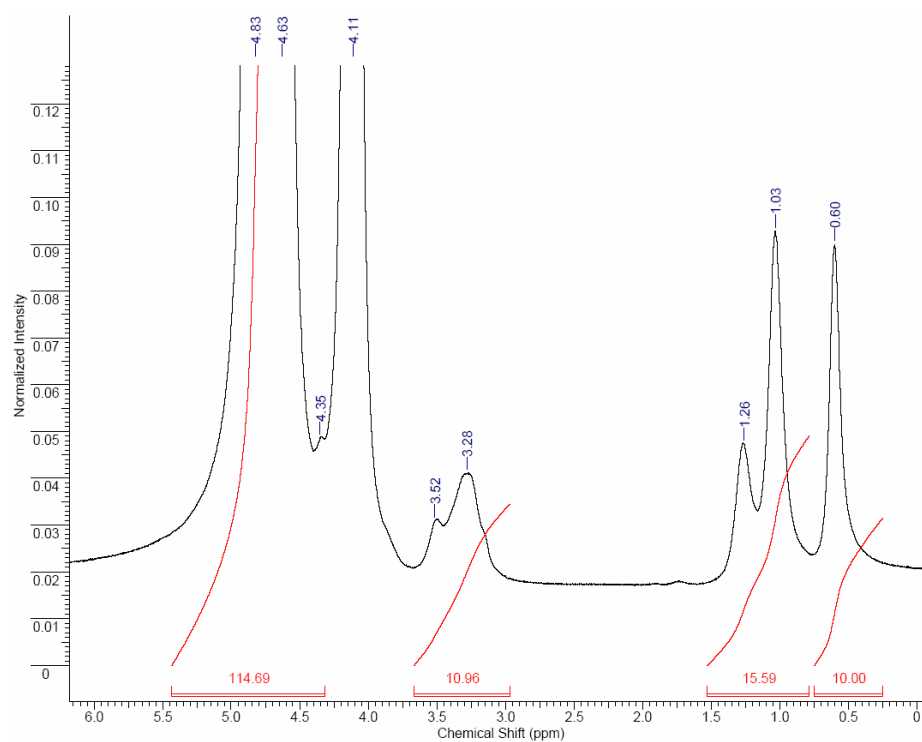


Figure A.17. 20 mol% feed 1,2-Epoxyhexane 19.38 mol% incorporation

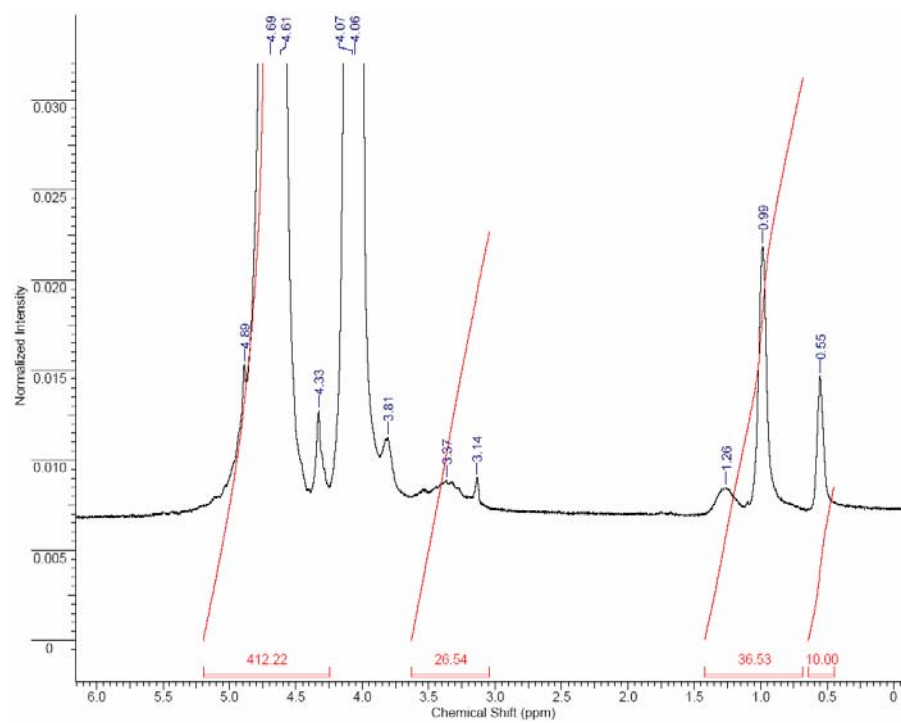


Figure A.18. 3 mol% feed 1,2-Epoxyoctane 7.08 mol% incorporation

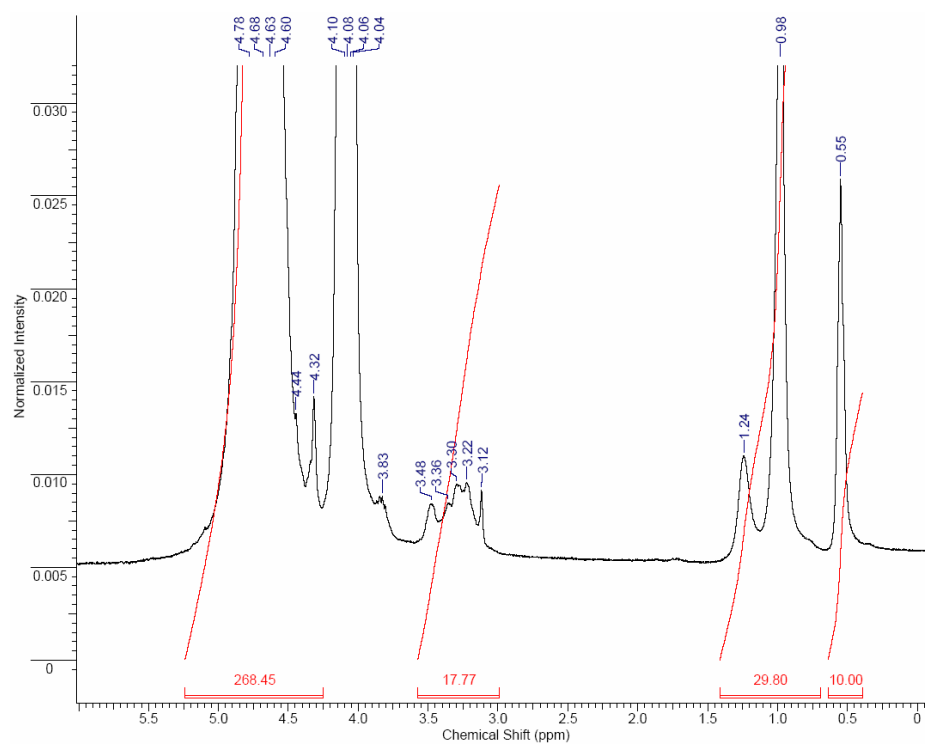


Figure A.19. 7.4 mol% feed 1,2-Epoxyoctane 9.03 mol% incorporation

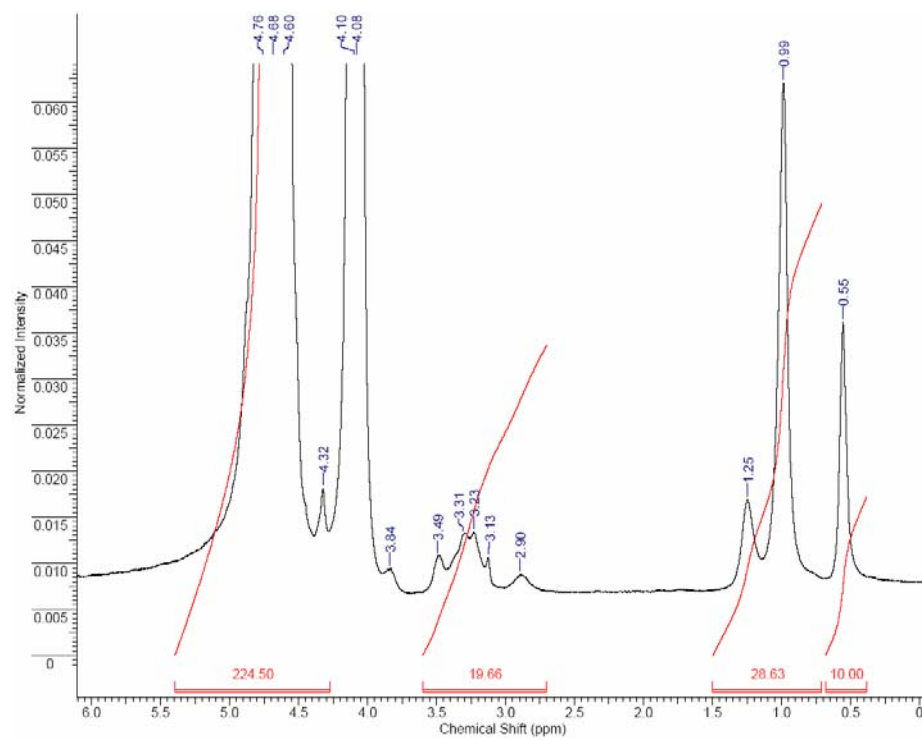


Figure A.20. 10 mol% feed 1,2-Epoxyoctane 10.44 mol% incorporation

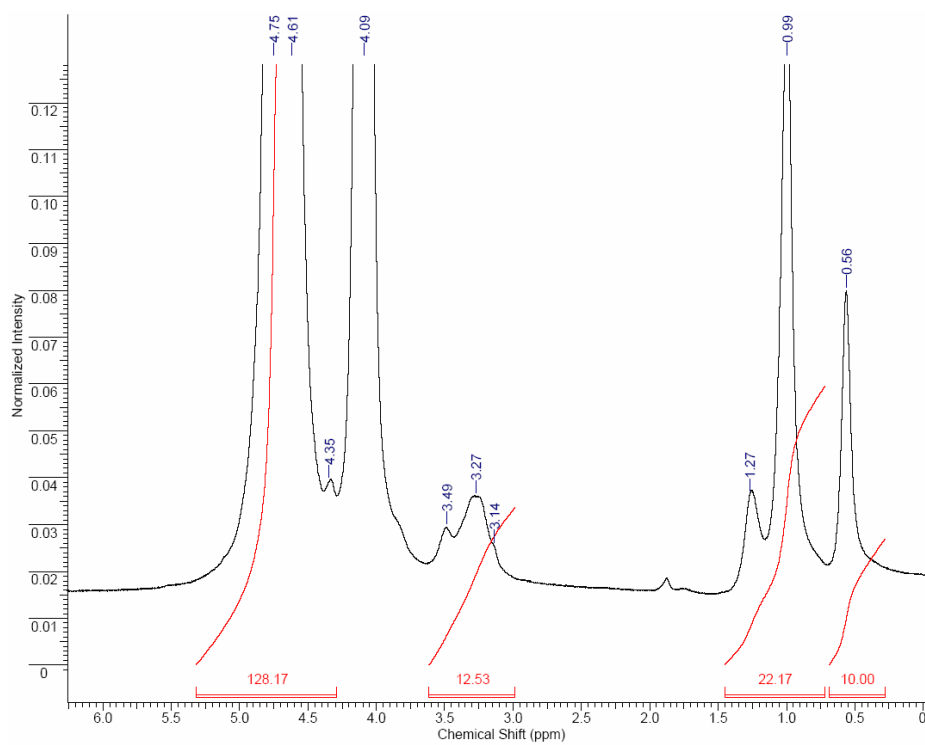


Figure A.21. 15 mol% feed 1,2-Epoxyoctane 18.48 mol% incorporation

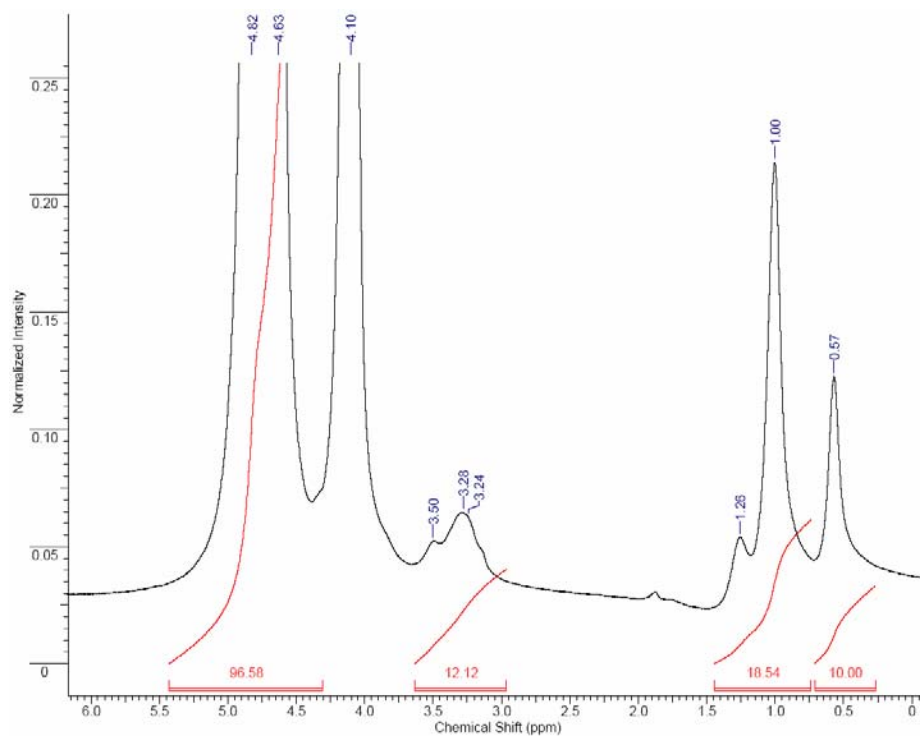


Figure A.22. 20 mol% feed 1,2-Epoxyoctane 32.03 mol% incorporation

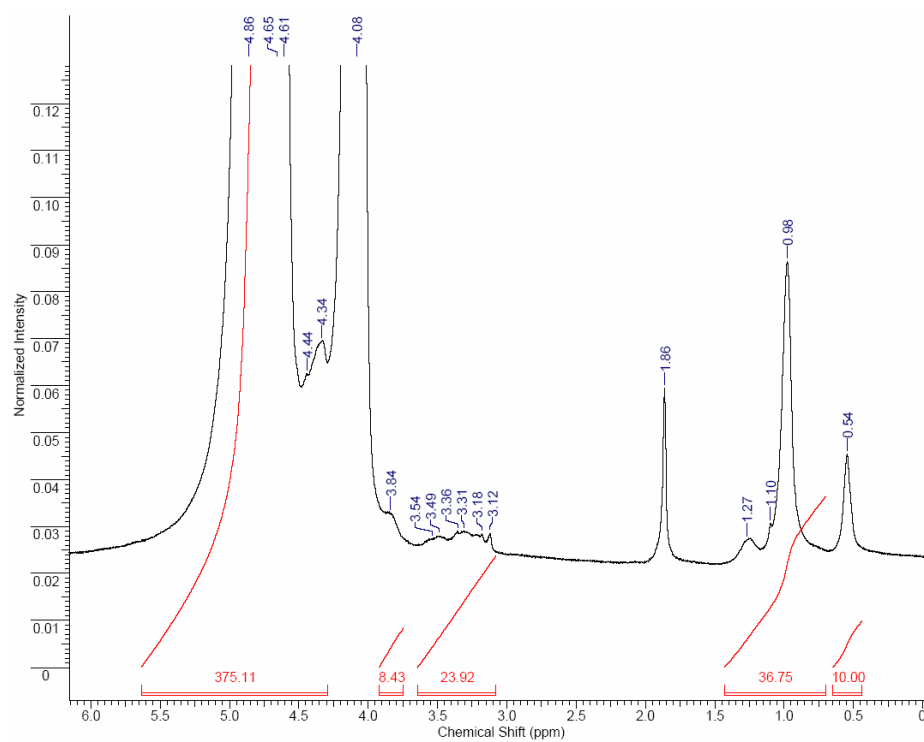


Figure A.23. 3 mol% feed 1,2-Epoxydecane 5.96 mol% incorporation

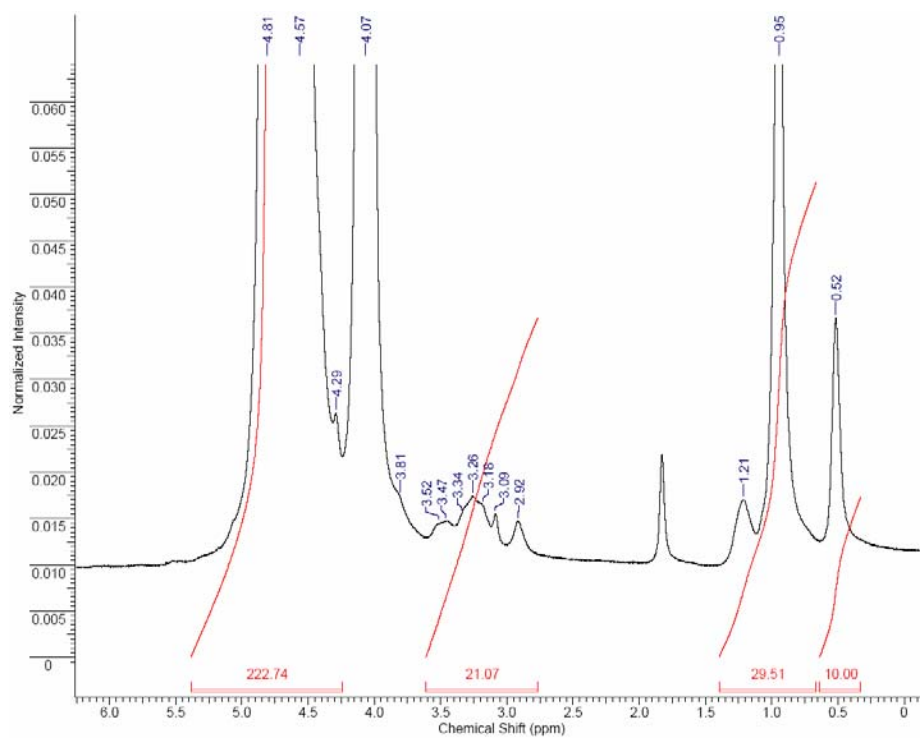


Figure A.24. 7.4 mol% feed 1,2-Epoxydecane 10.48 mol% incorporation

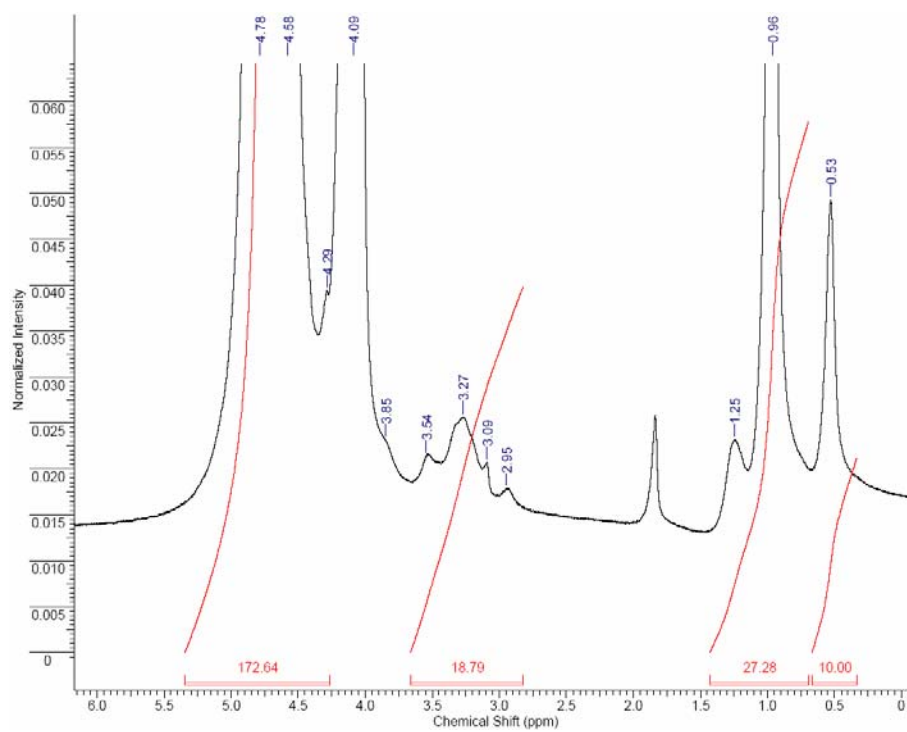


Figure A.25. 10 mol% feed 1,2-Epoxydecane 11.99 mol% incorporation

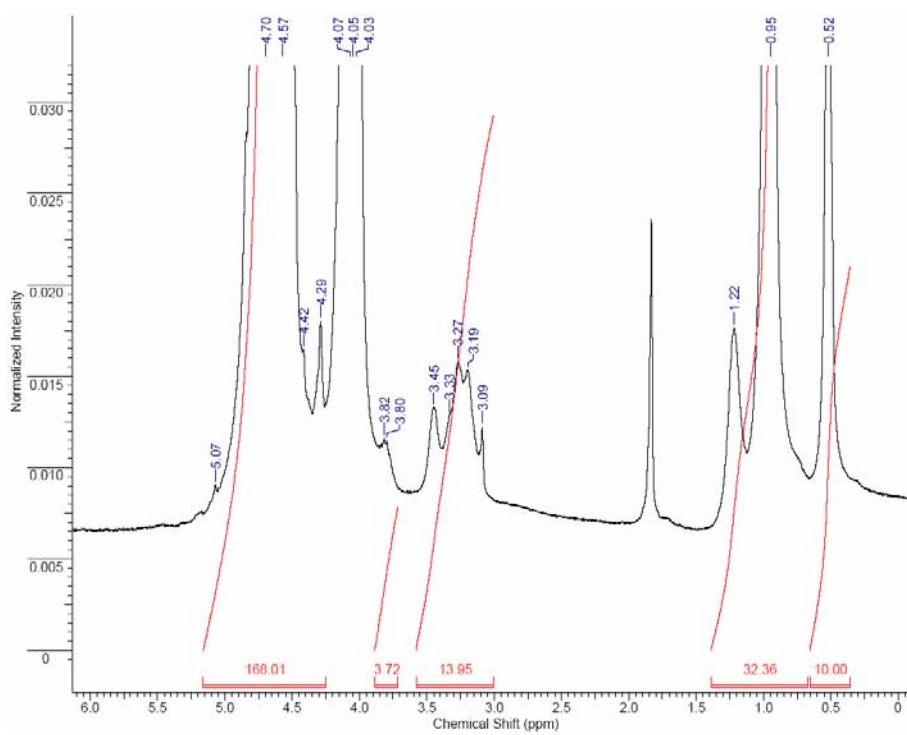


Figure A.26. 15 mol% feed 1,2-Epoxydecane 14.33 mol% incorporation

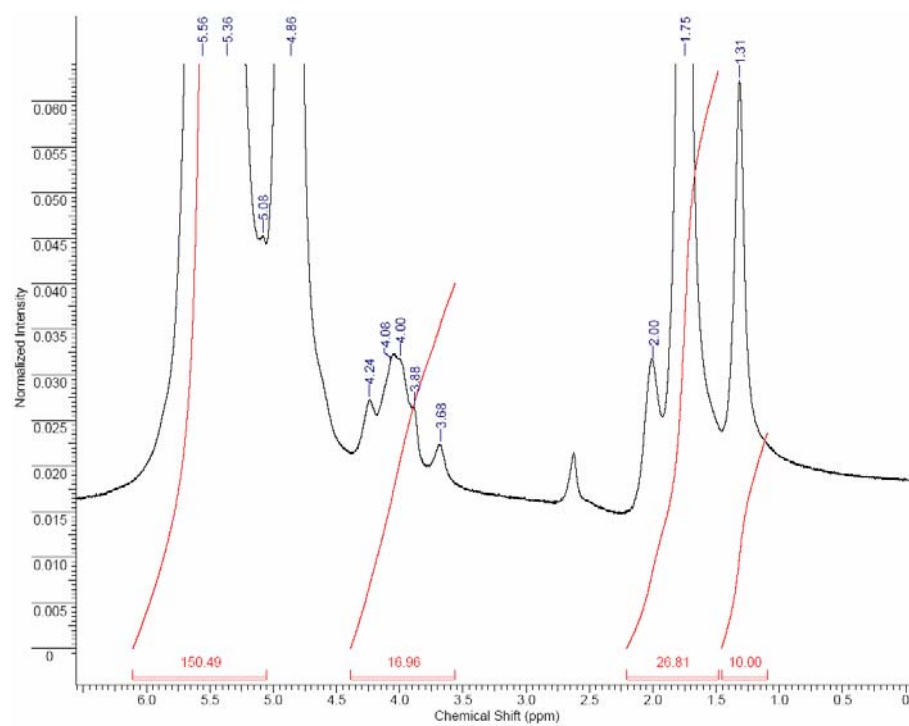


Figure A.27. 20 mol% feed 1,2-Epoxydecane 15.14 mol% incorporation

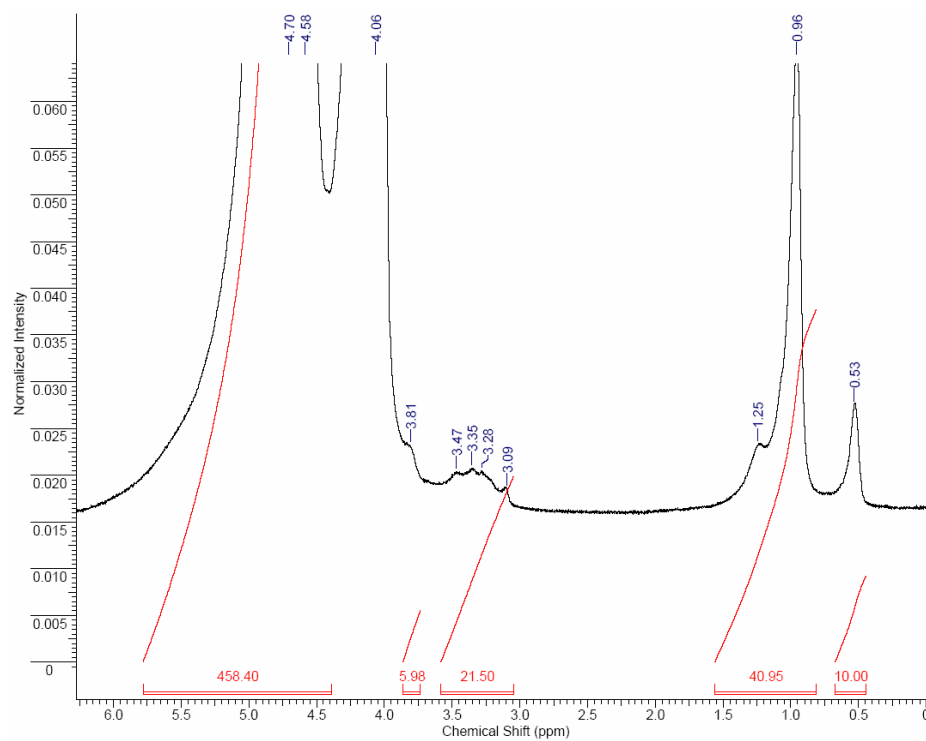


Figure A.28. 3 mol% feed 1,2-Epoxydodecane 5.93 mol% incorporation

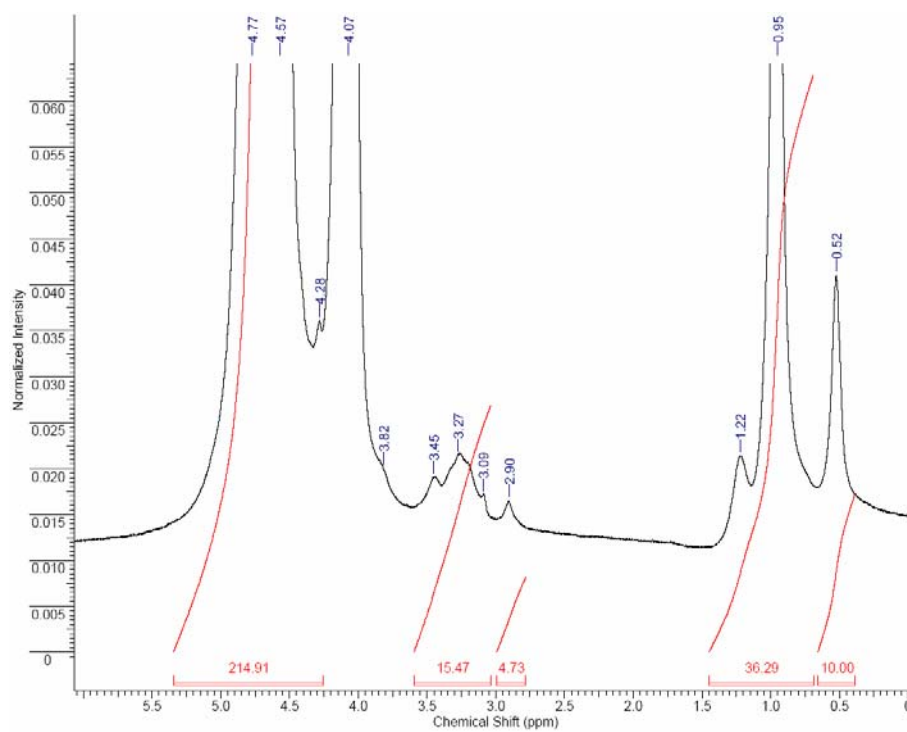


Figure A.29. 7.4 mol% feed 1,2-Epoxydodecane 9.93 mol% incorporation

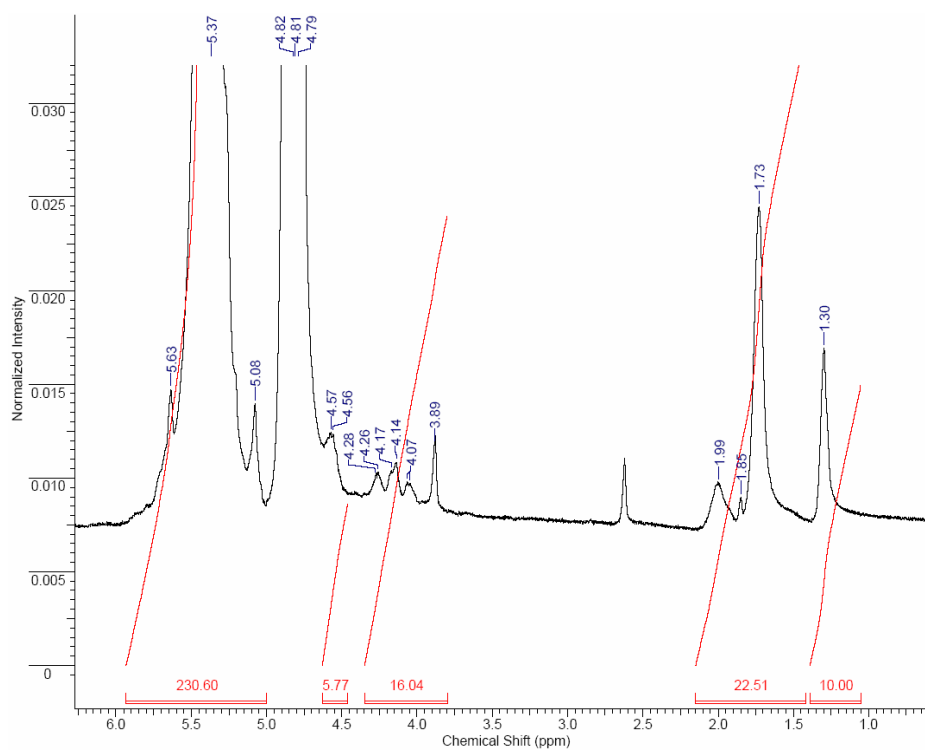


Figure A.30. 10 mol% feed 1,2-Epoxydodecane 11.47 mol% incorporation

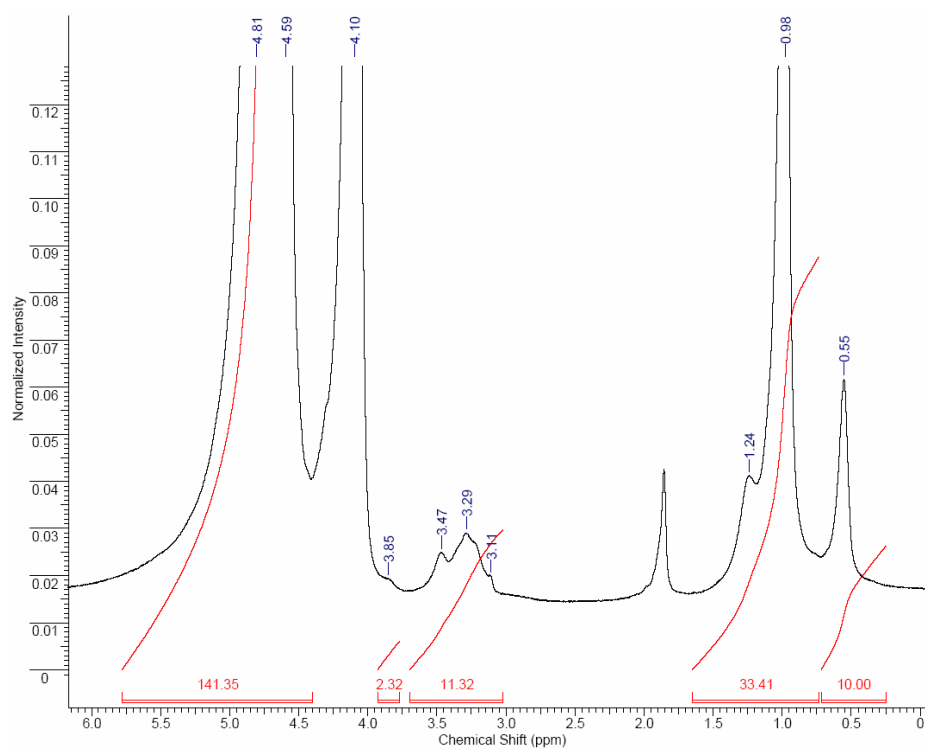


Figure A.31. 15 mol% feed 1,2-Epoxydodecane 16.41 mol% incorporation

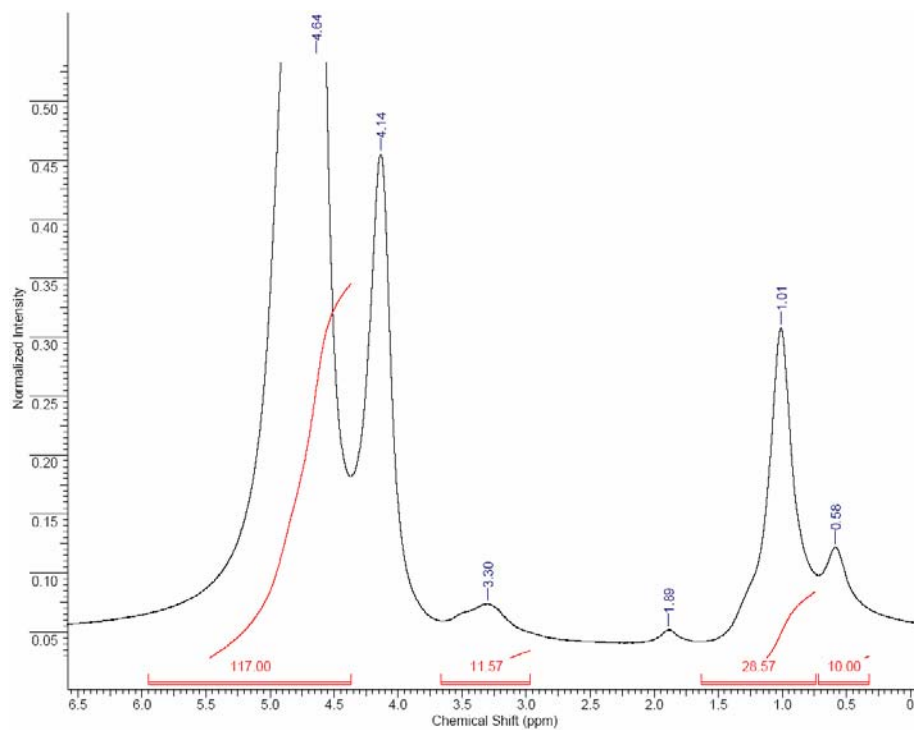
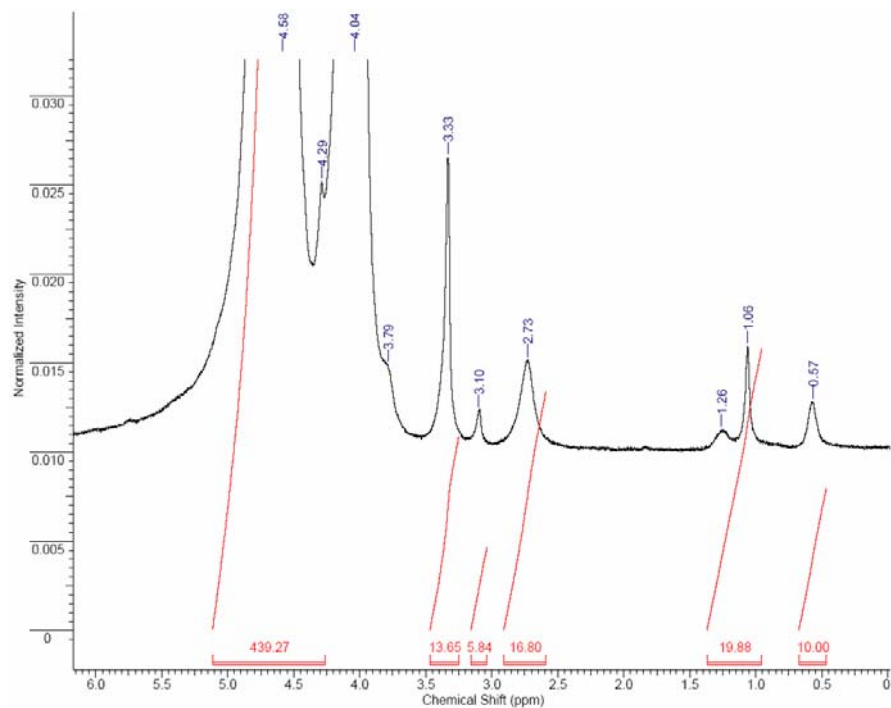
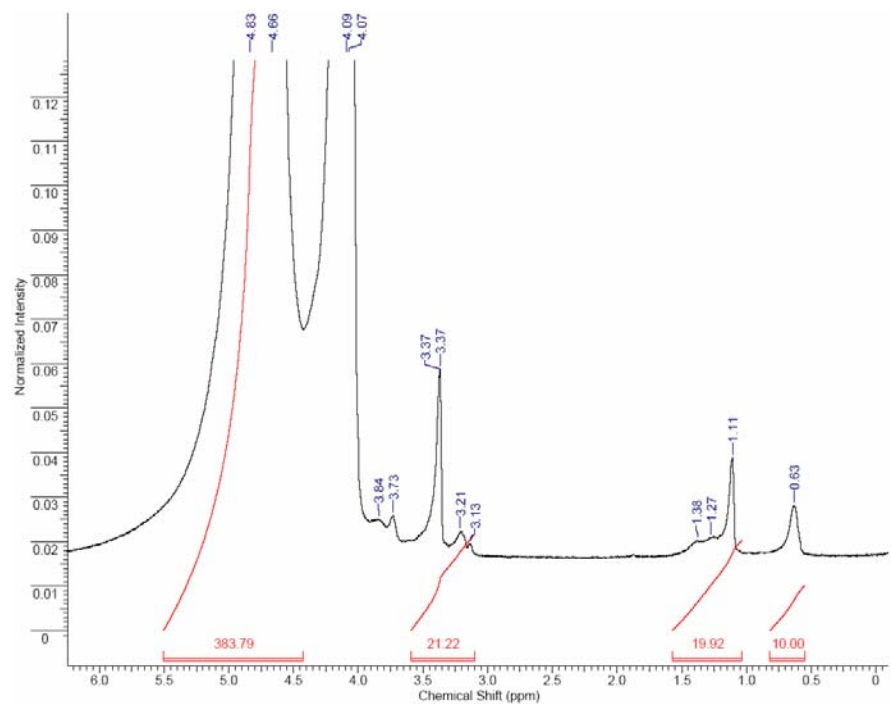


Figure A.32. 20 mol% feed 1,2-Epoxydodecane 22.29 mol% incorporation

Chapter III: Trioxane and 4-Alkyl-1,3-Dioxolanes Copolymers from Table 3.1**Figure A.33.** 3 mol% feed 4-Ethyl-1,3-Dioxolane 5.32 mol% incorporation**Figure A.34.** 7.4 mol% feed 4-Ethyl-1,3-Dioxolane 7.01 mol% incorporation

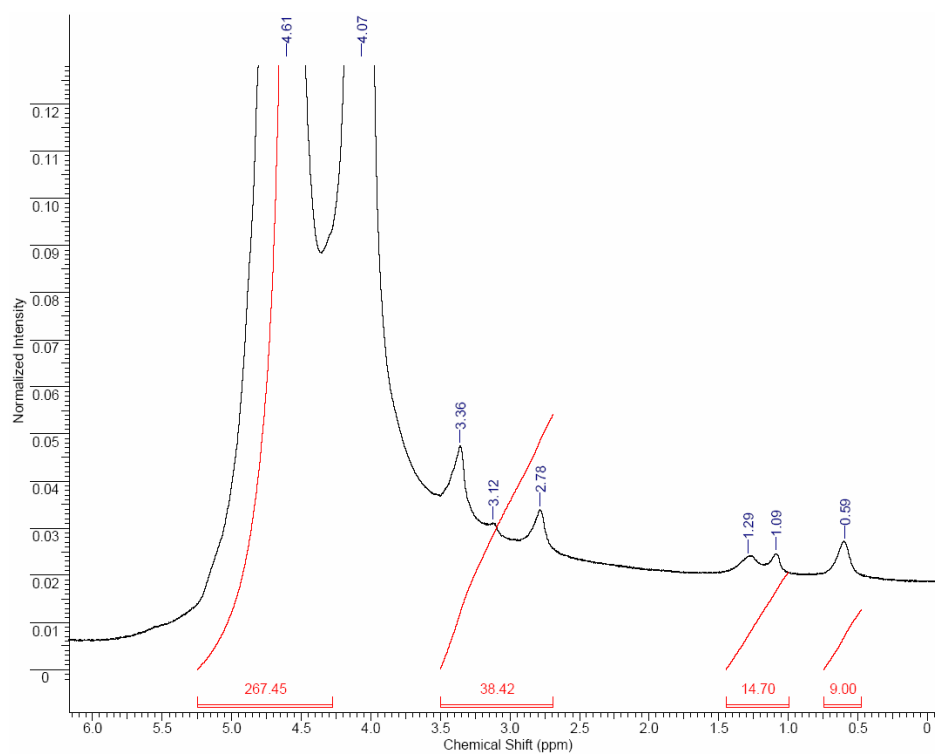


Figure A.35. 10 mol% feed 4-Ethyl-1,3-Dioxolane 9.14 mol% incorporation

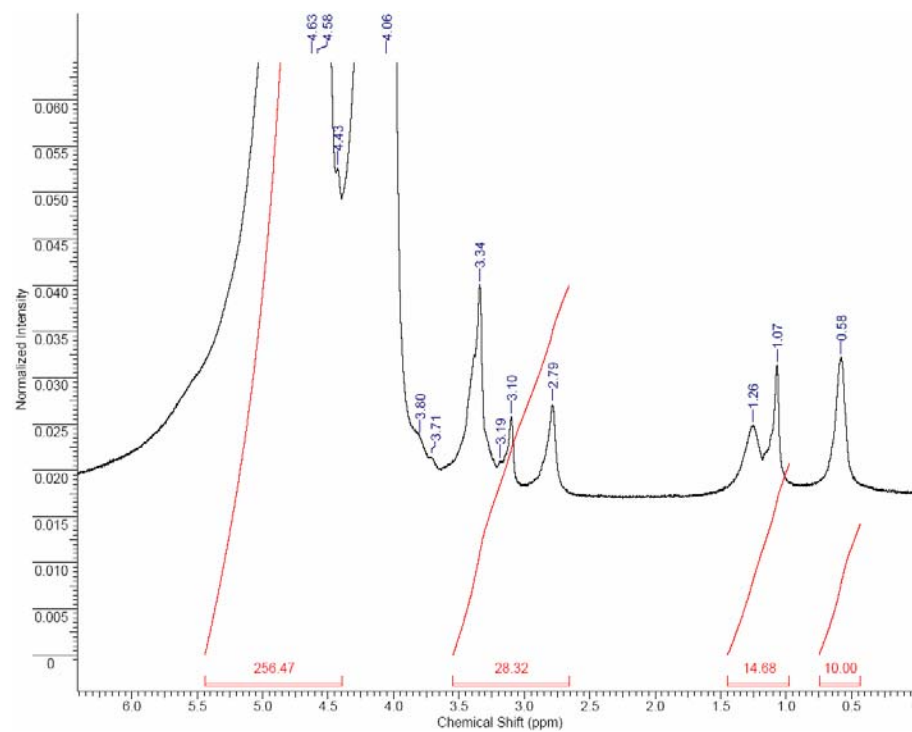


Figure A.36. 15 mol% feed 4-Ethyl-1,3-Dioxolane 9.13 mol% incorporation

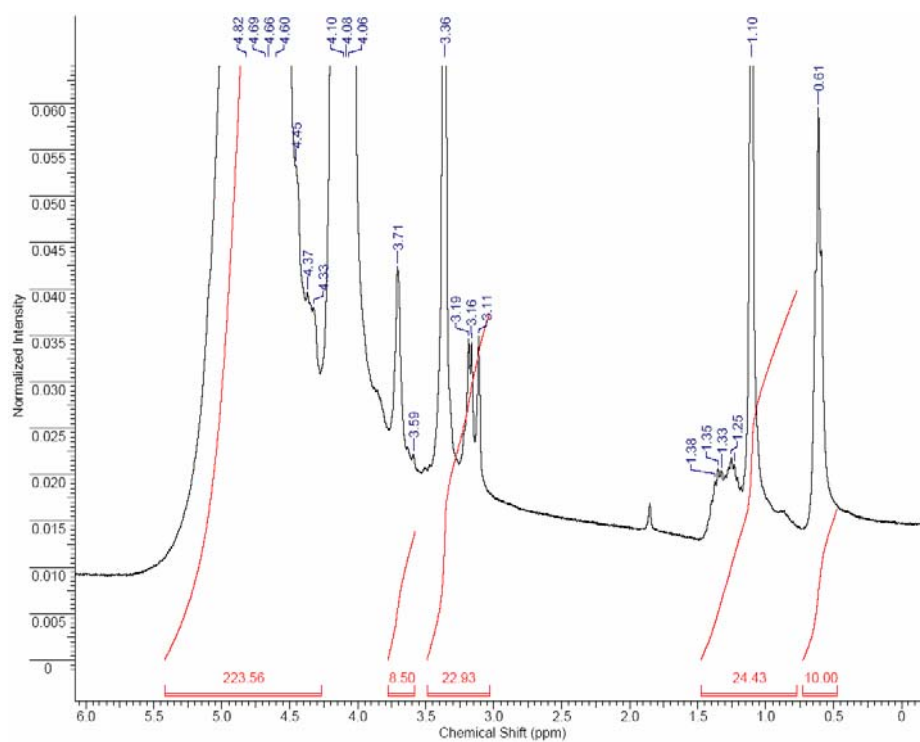


Figure A.37. 20 mol% feed 4-Ethyl-1,3-Dioxolane 11.81 mol% incorporation

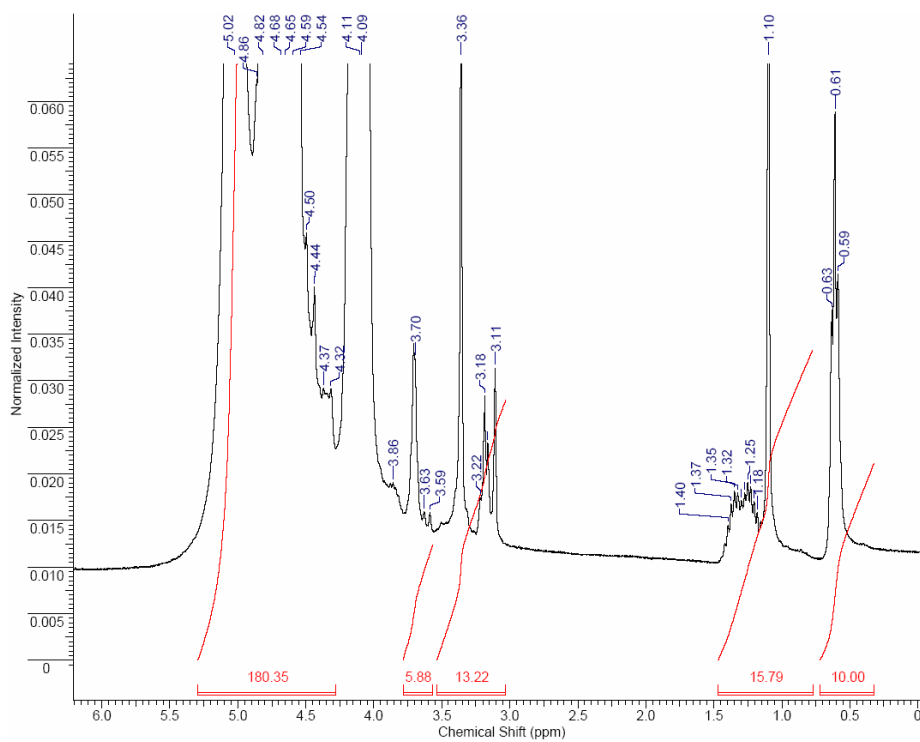


Figure A.38. 25 mol% feed 4-Ethyl-1,3-Dioxolane 12.15 mol% incorporation

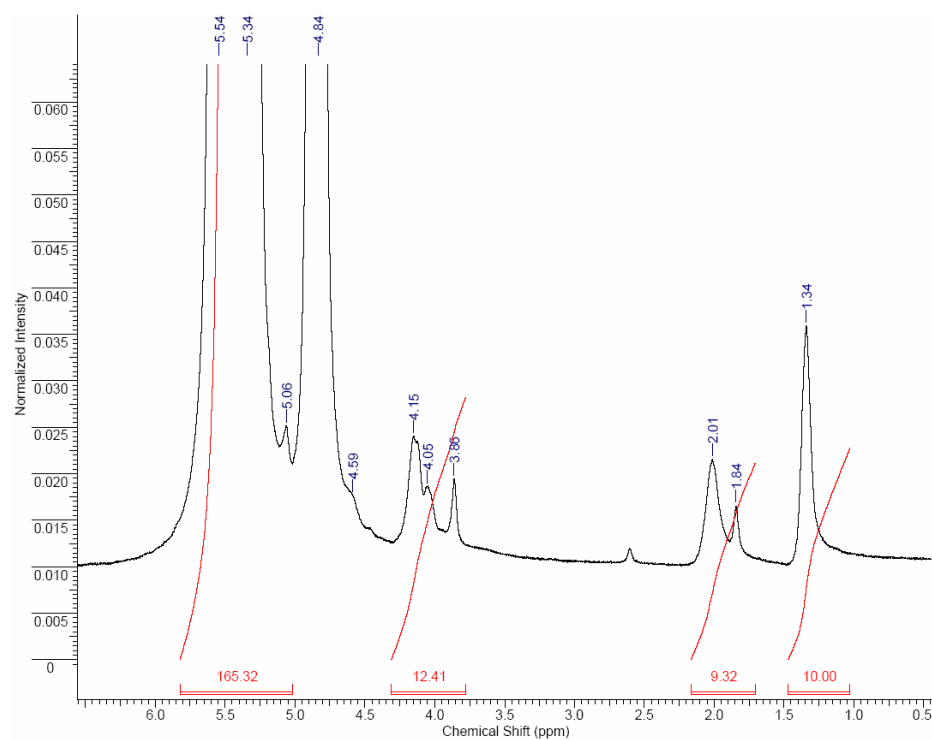


Figure A.39. 30 mol% feed 4-Ethyl-1,3-Dioxolane 12.25 mol% incorporation

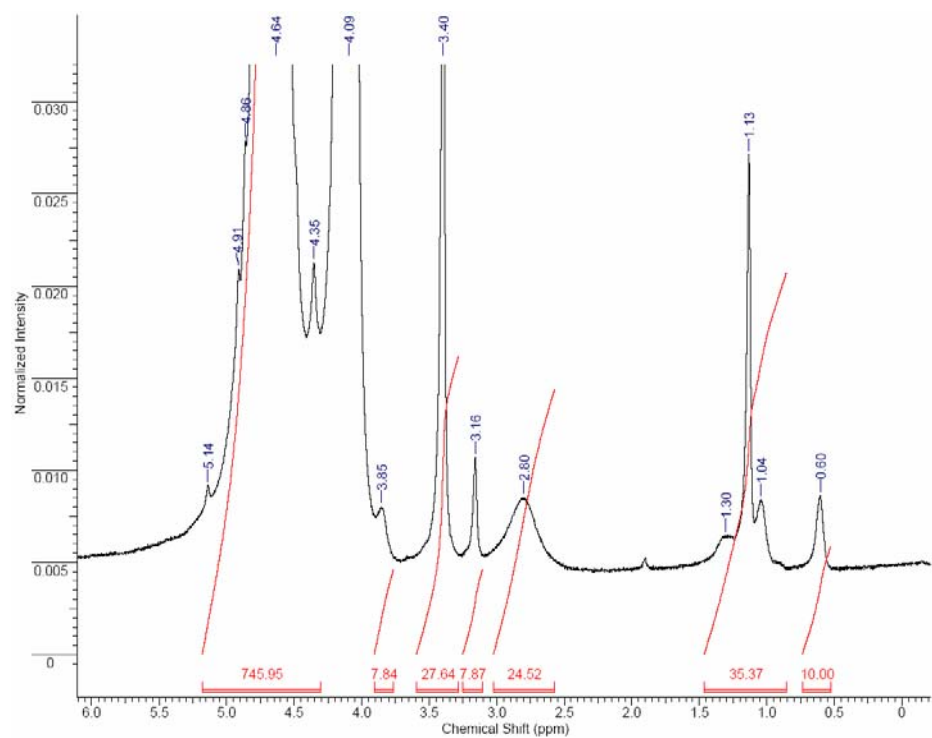


Figure A.40. 3 mol% feed 4-Butyl-1,3-Dioxolane 3.46 mol% incorporation

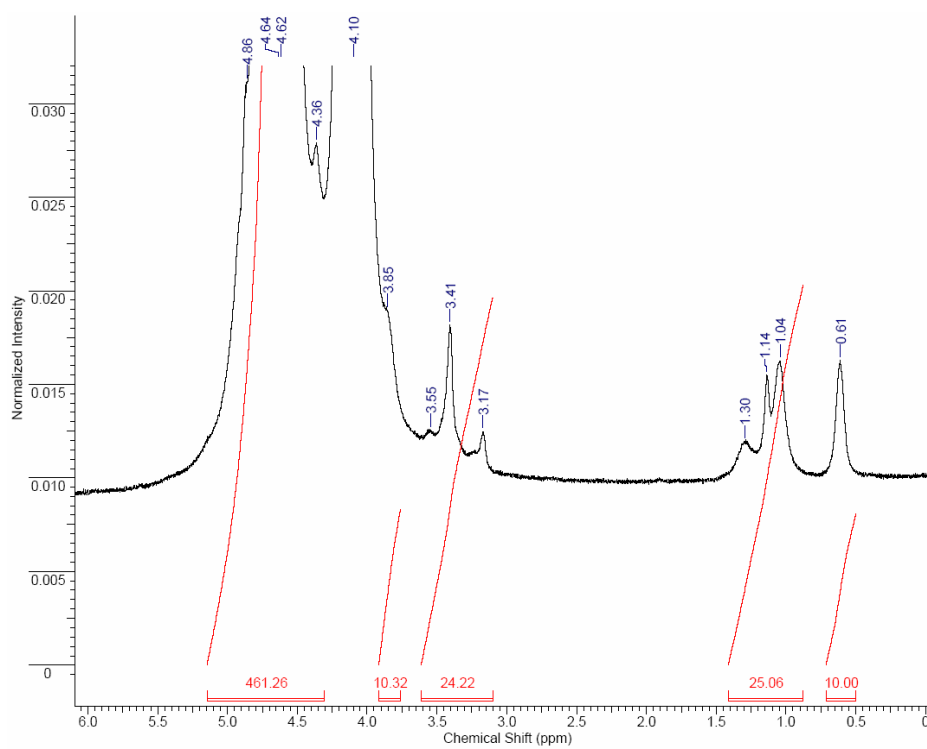


Figure A.41. 7.4 mol% feed 4-Butyl-1,3-Dioxolane 6.55 mol% incorporation

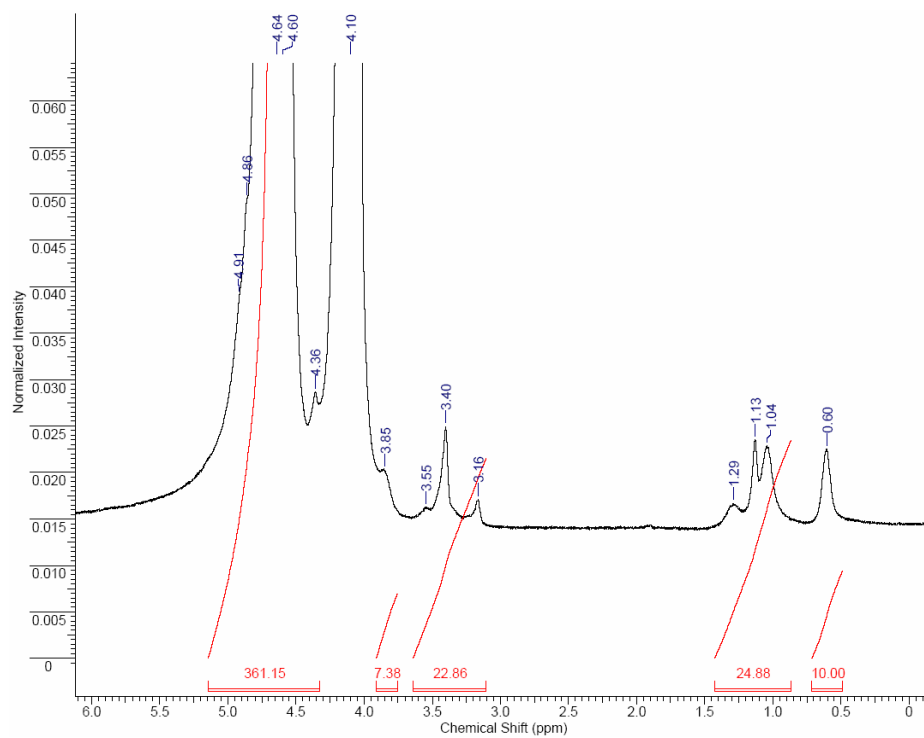


Figure A.42. 10 mol% feed 4-Butyl-1,3-Dioxolane 8.06 mol% incorporation

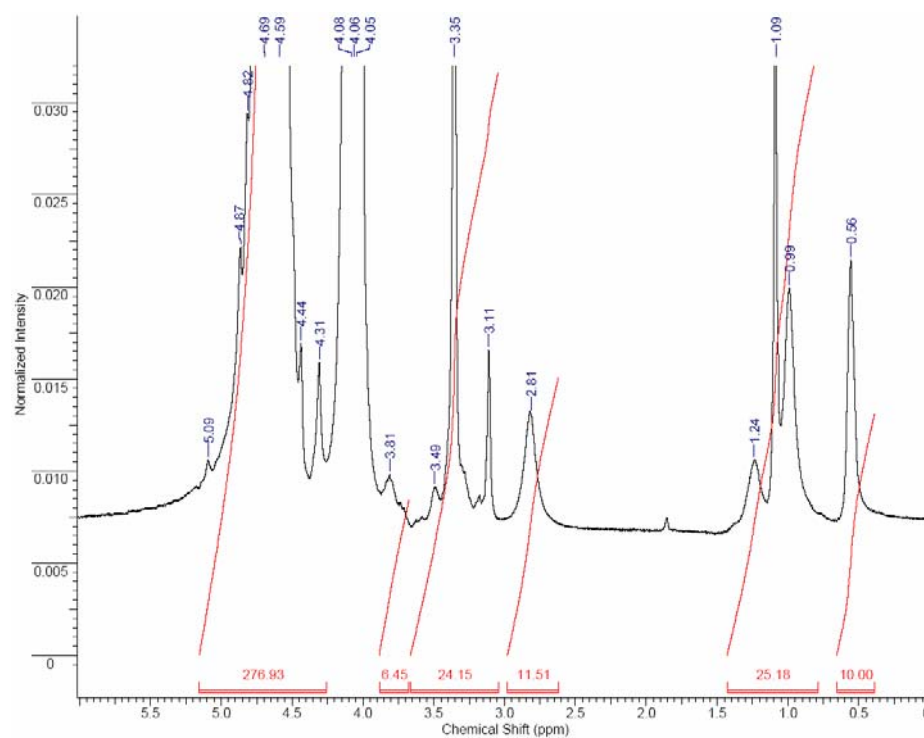


Figure A.43. 15 mol% feed 4-Butyl-1,3-Dioxolane 8.71 mol% incorporation

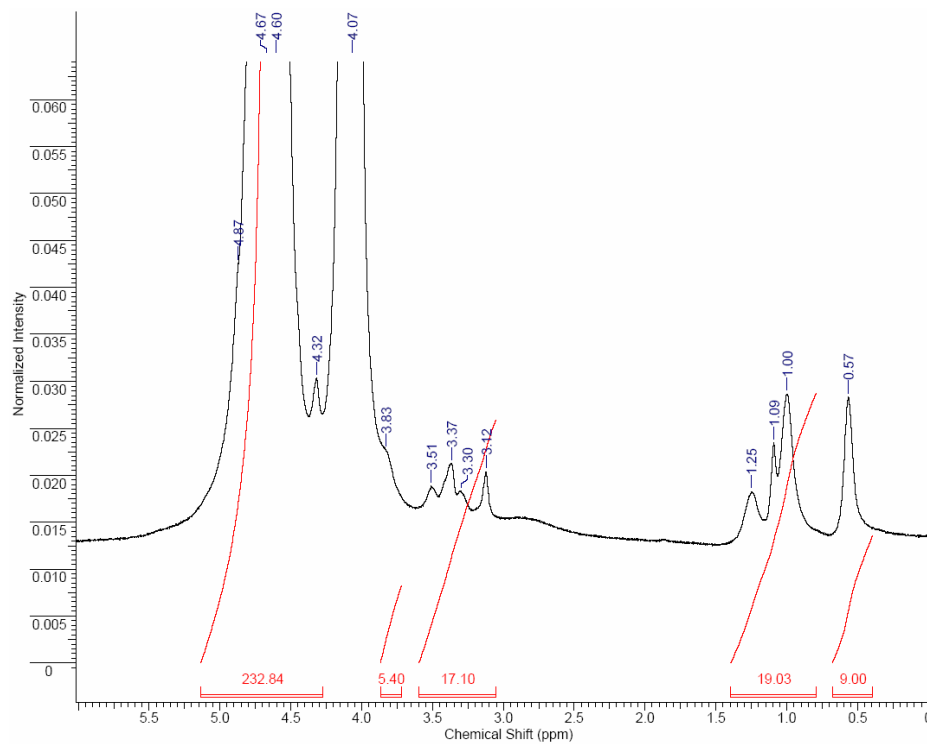


Figure A.44. 20 mol% feed 4-Butyl-1,3-Dioxolane 9.51 mol% incorporation

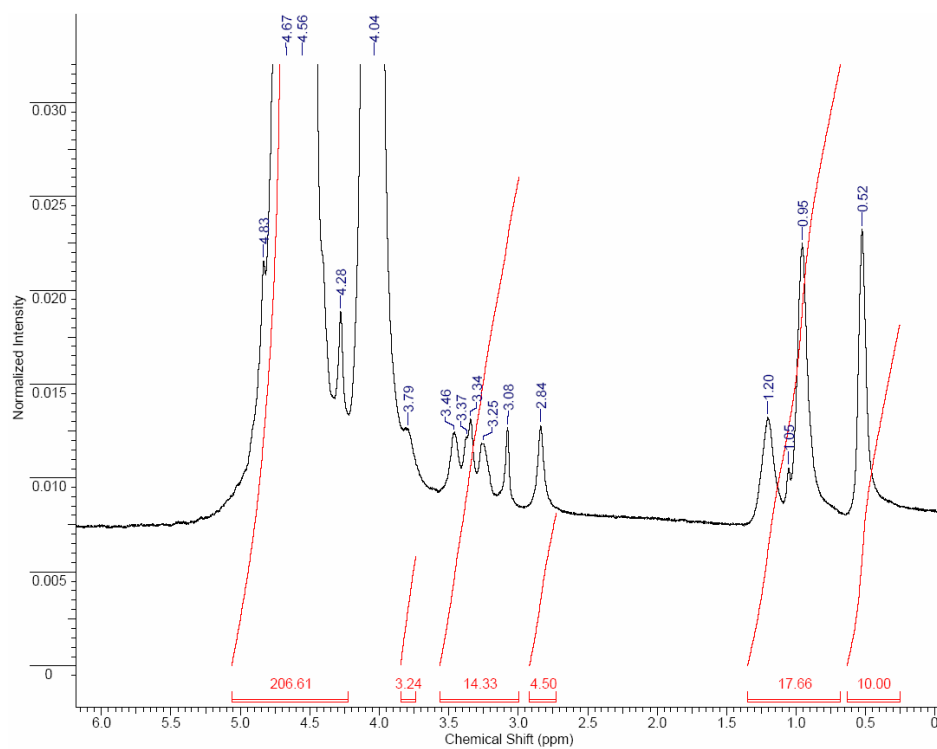


Figure A.45. 25 mol% feed 4-Butyl-1,3-Dioxolane 12.03 mol% incorporation

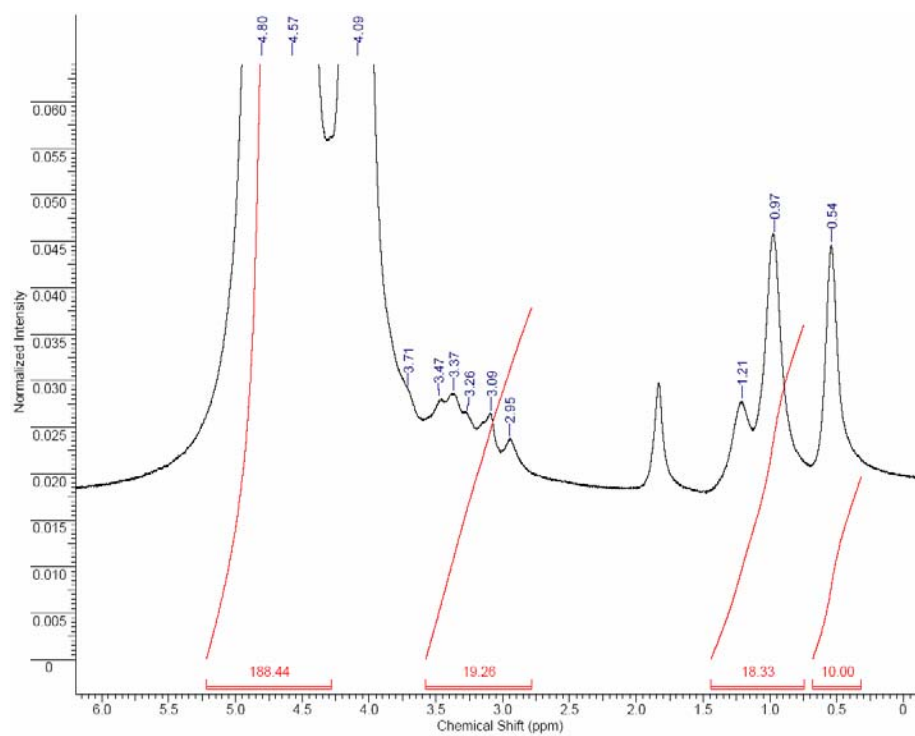


Figure A.46. 30 mol% feed 4-Butyl-1,3-Dioxolane 11.51 mol% incorporation

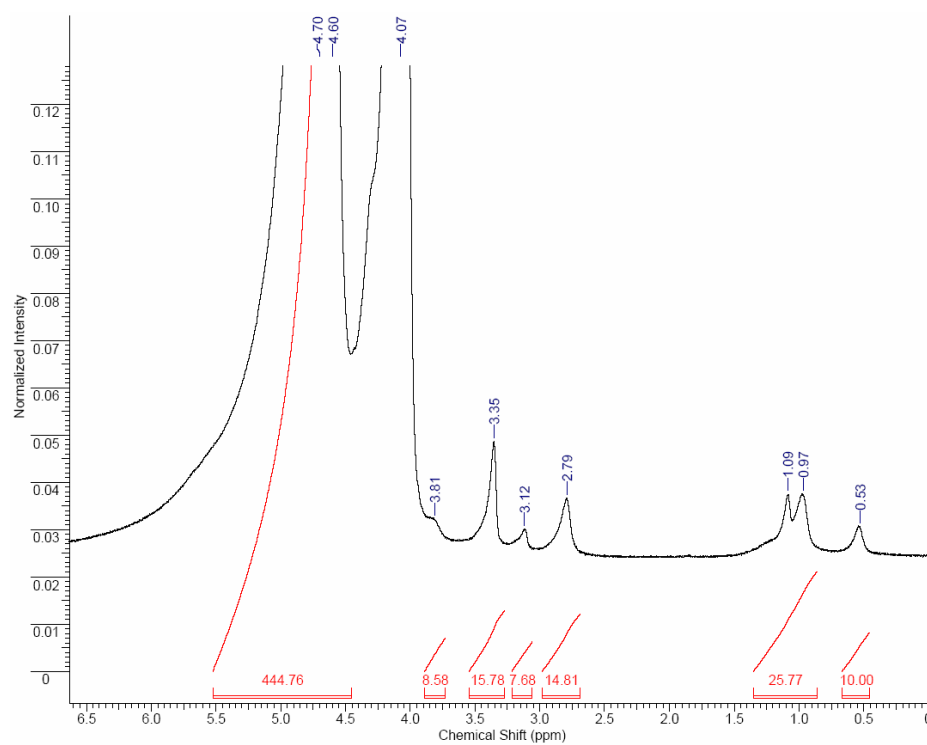


Figure A.47. 3 mol% feed 4-Hexyl-1,3-Dioxolane 5.89 mol% incorporation

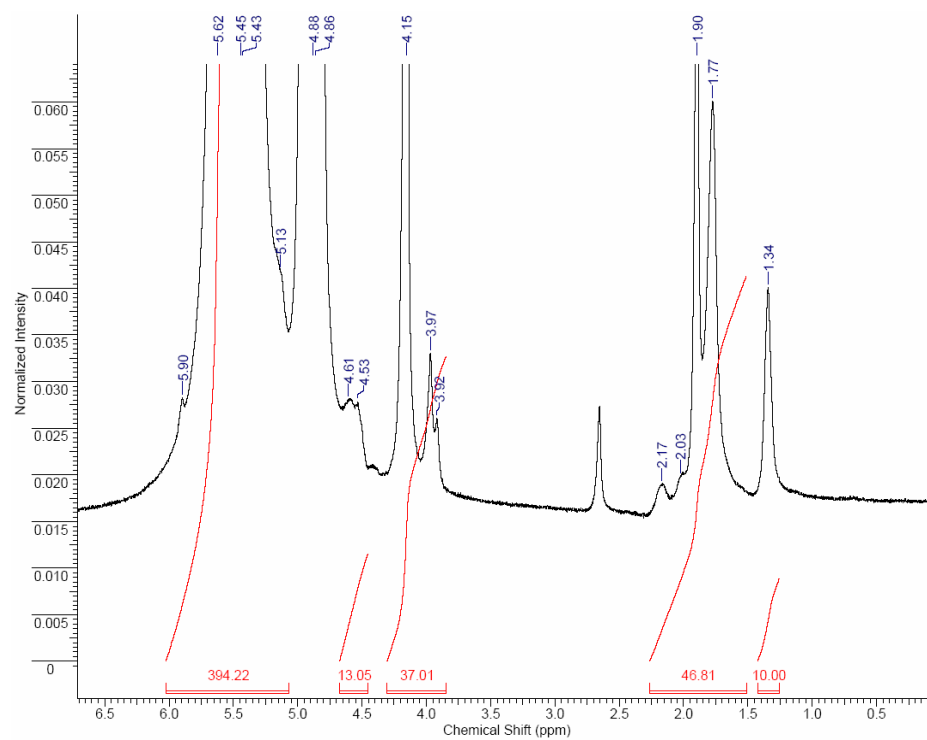


Figure A.48. 7.4 mol% feed 4-Hexyl-1,3-Dioxolane 8.93 mol% incorporation

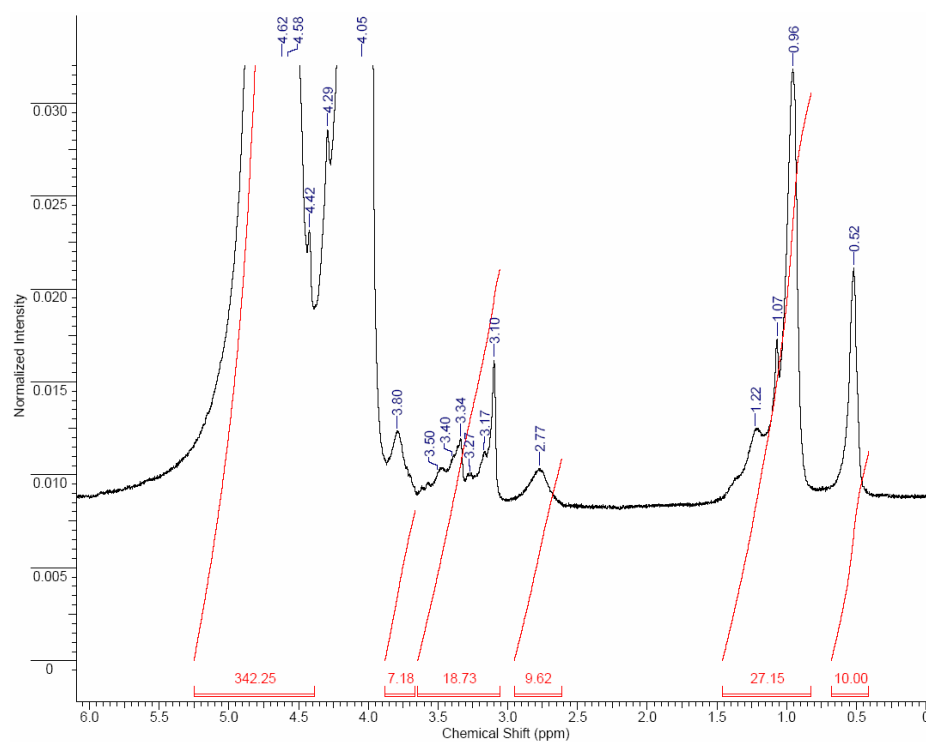


Figure A.49. 10 mol% feed 4-Hexyl-1,3-Dioxolane 6.44 mol% incorporation

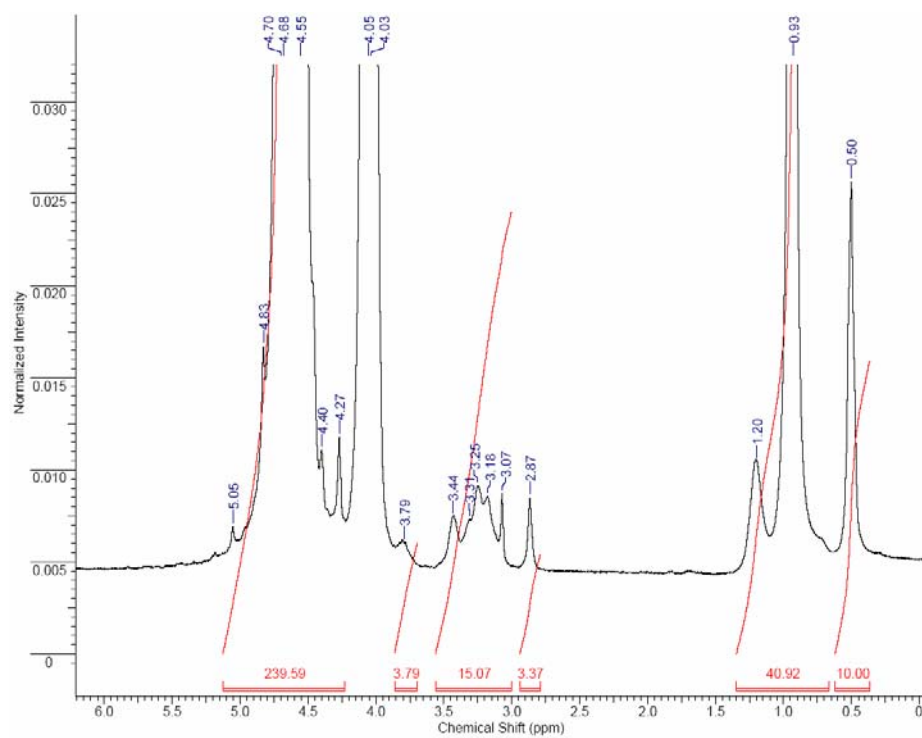


Figure A.50. 15 mol% feed 4-Hexyl-1,3-Dioxolane 9.57 mol% incorporation

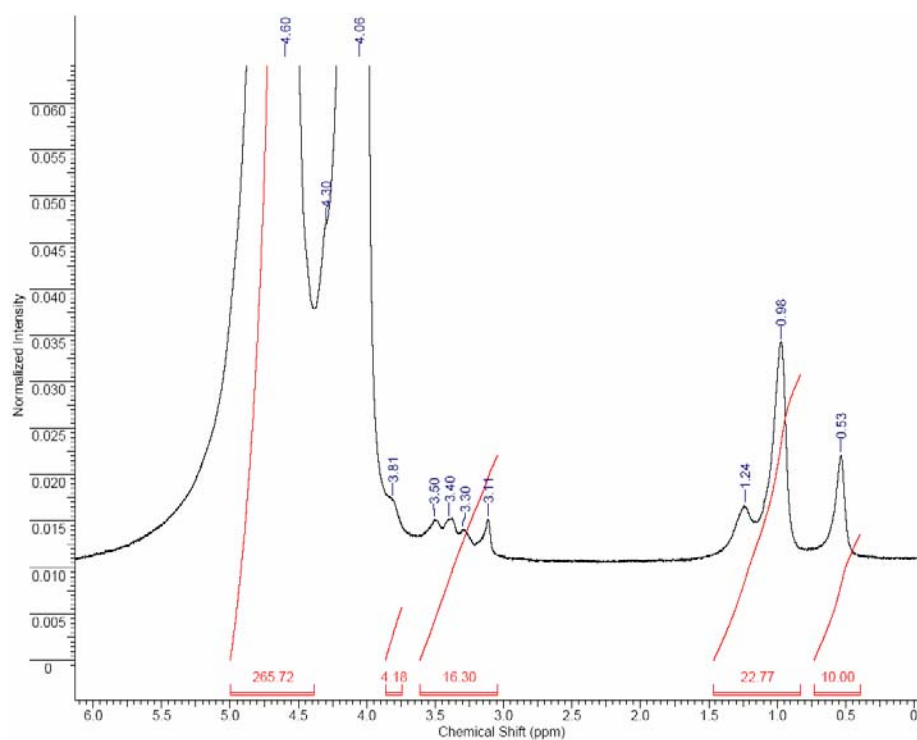


Figure A.51. 20 mol% feed 4-Hexyl-1,3-Dioxolane 10.01 mol% incorporation

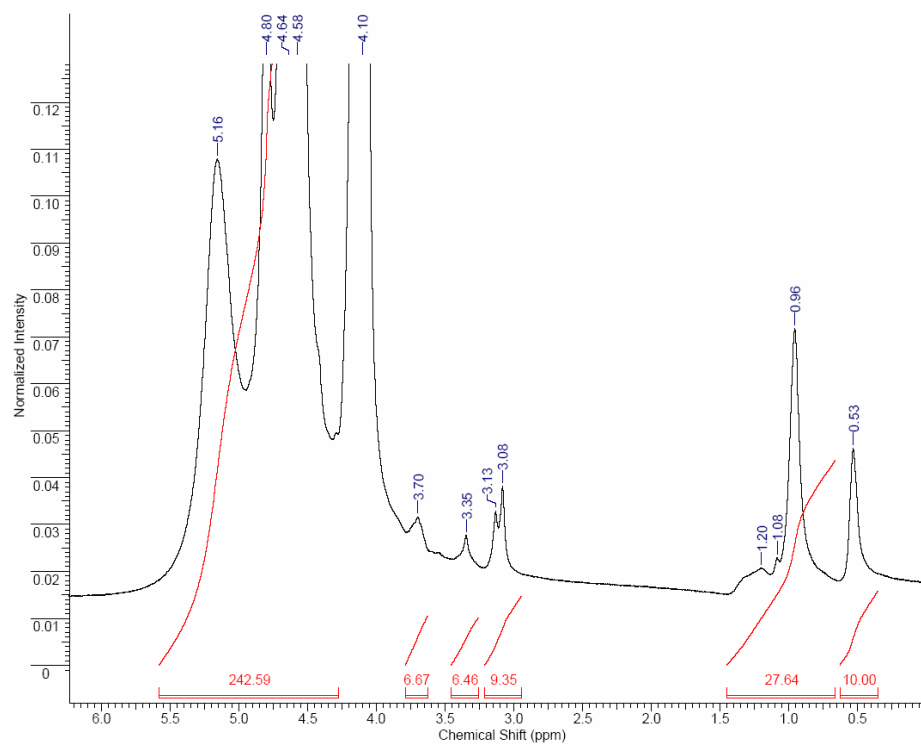


Figure A.52. 25 mol% feed 4-Hexyl-1,3-Dioxolane 9.22 mol% incorporation

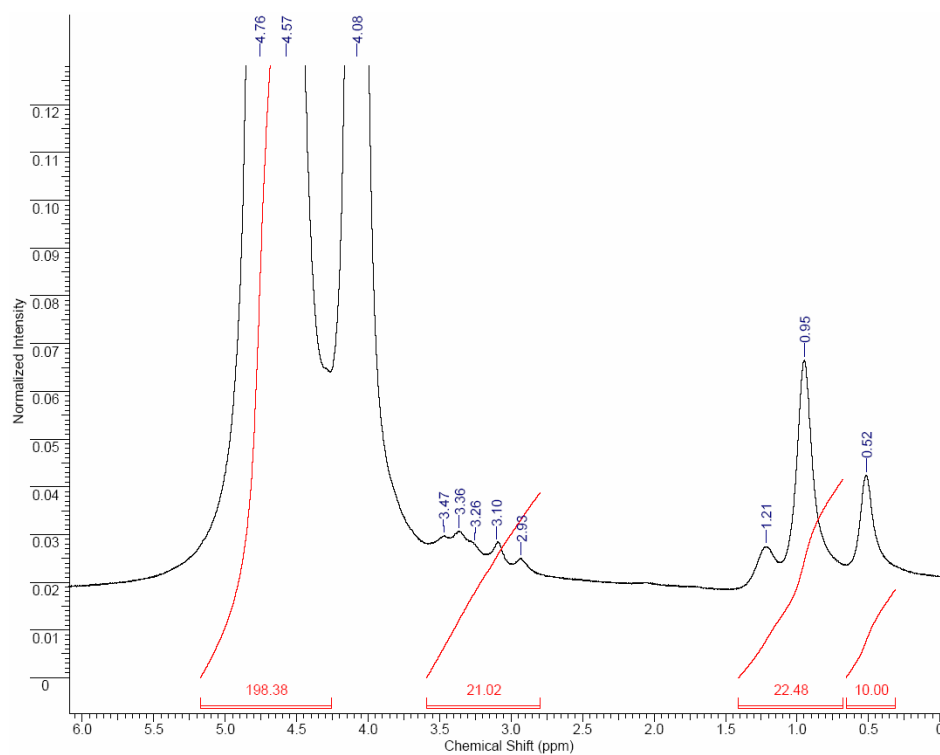


Figure A.53. 30 mol% feed 4-Hexyl-1,3-Dioxolane 12.30 mol% incorporation

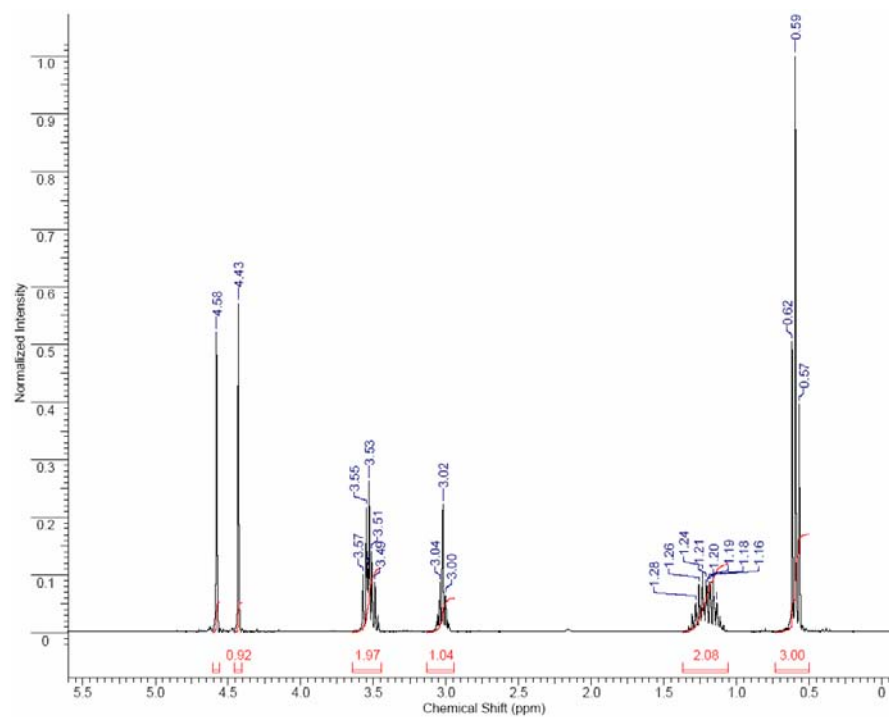


Figure A.54. 4-Ethyl-1,3-Dioxolane

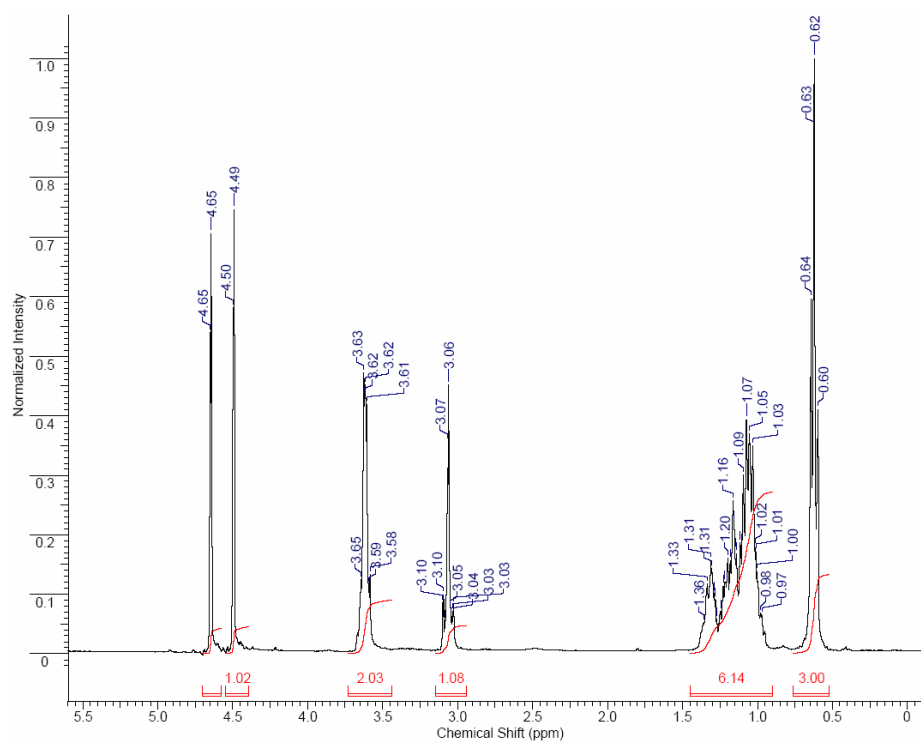


Figure A.54. 4-Butyl-1,3-Dioxolane

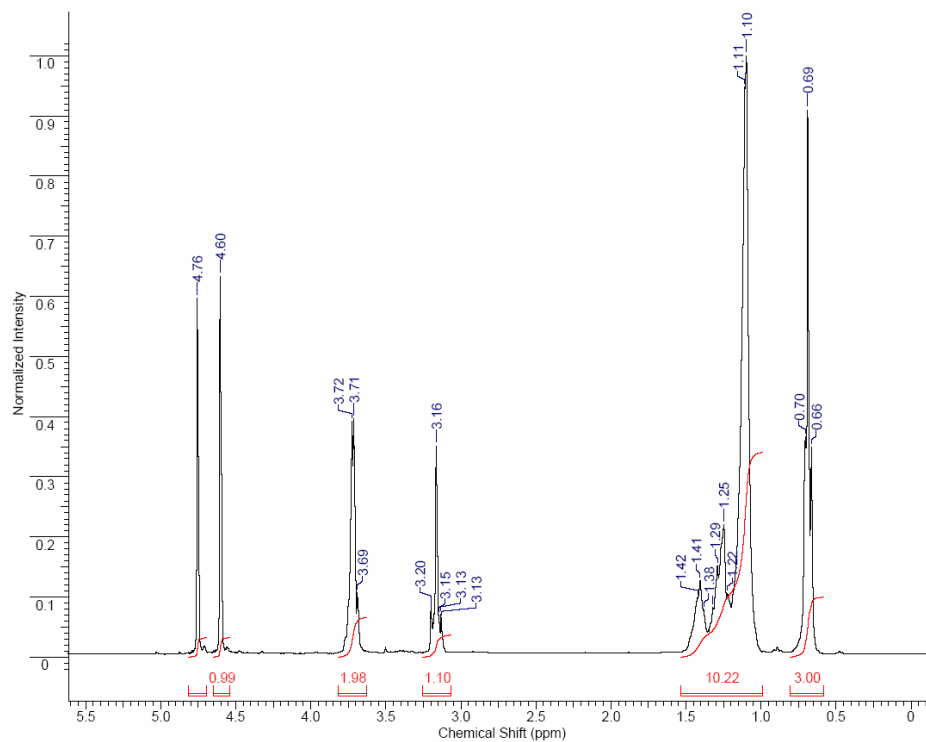


Figure A.54. 4-Hexyl-1,3-Dioxolane

APPENDIX B

DSC DATA

Mol% Incorporation Calculation after Cure

1 = before cure

2 = after cure

$$wt\%1 = \frac{(mol\%_{NMR} / 100) * MW_{comonomer}}{(mol\%_{NMR} / 100) * MW_{comonomer} + ((1 - mol\%_{NMR}) / 100) * MW_{TOX}} * 100$$

$$wt_{comonomer} 1 = (wt\%1 / 100) * sampleweight(DSC)$$

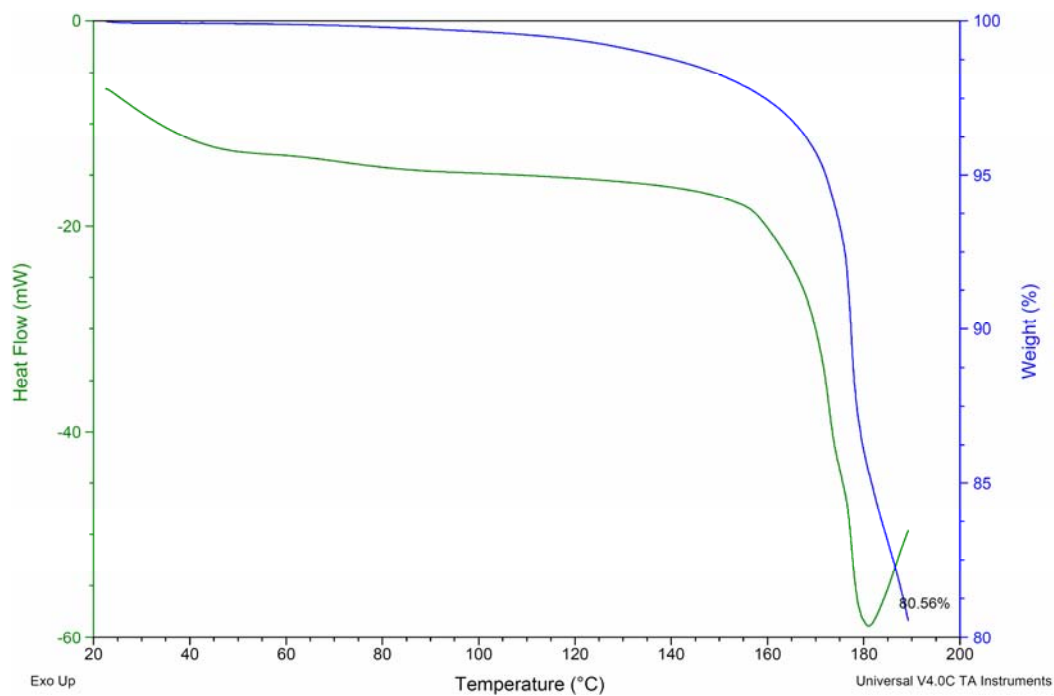
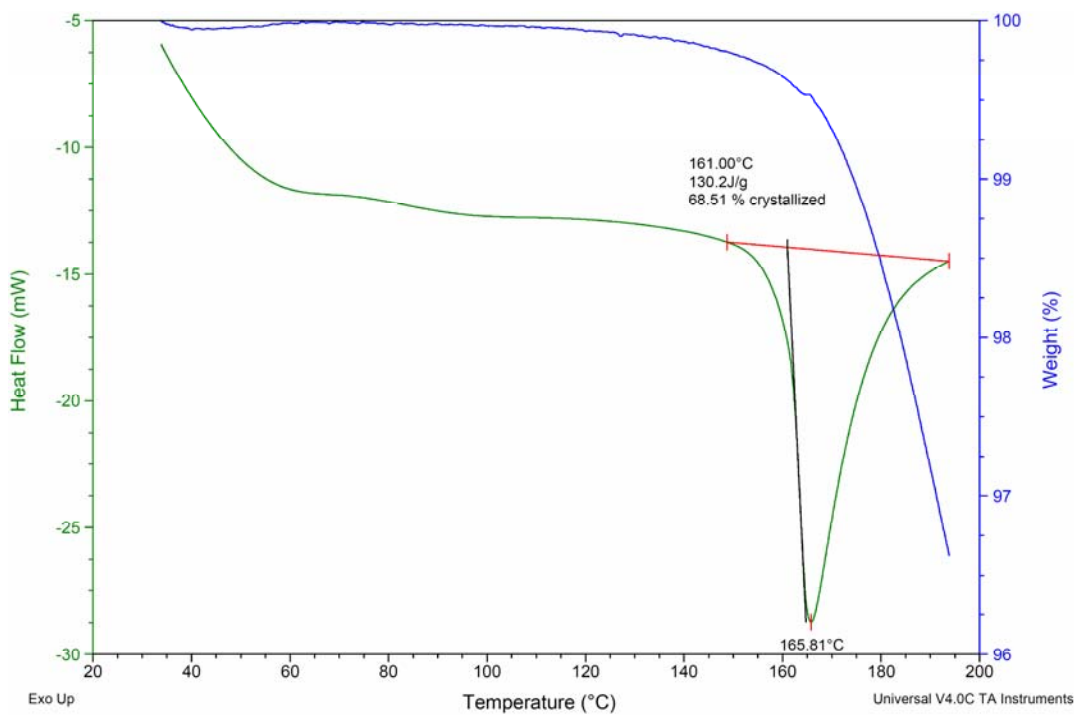
$$wt_{TOX} 1 = (1 - wt\%1 / 100) * sampleweight(DSC)$$

$$wt_{TOX} 2 = wt_{TOX} 1 - (\%wtloss * sampleweight(DSC) / 100)$$

$$wt_{comonomer} 2 = wt_{comonomer} 1$$

$$wt\%2 = \frac{wt_{comonomer} 2}{wt_{TOX} 2 + wt_{comonomer} 2} * 100$$

$$mol\%2 = \frac{(wt\%2 / 100) / MW_{comonomer}}{(wt\%2 / 100) / MW_{comonomer} + ((1 - wt\%2) / 100) / MW_{TOX}} * 100$$

Chapter II: Trioxane and 1,2-Epoxyalkanes Copolymers from Table 2.1**Figure B.1.** 3 mol% feed 1,2-Epoxypropane 1st Scan 5.49 mol% incorporation**Figure B.2.** 3 mol% feed 1,2-Epoxypropane 2nd Scan 5.49 mol% incorporation

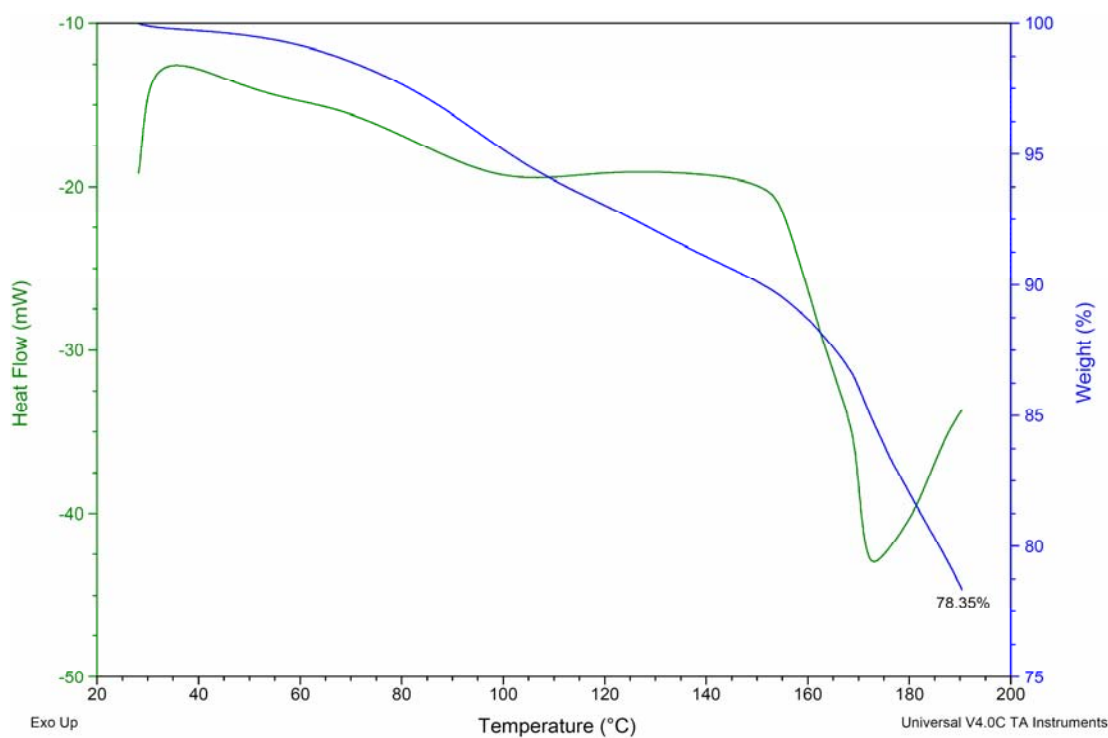


Figure B.3. 7.4 mol% feed 1,2-Epoxypropane 1st Scan 11.26 mol% incorporation

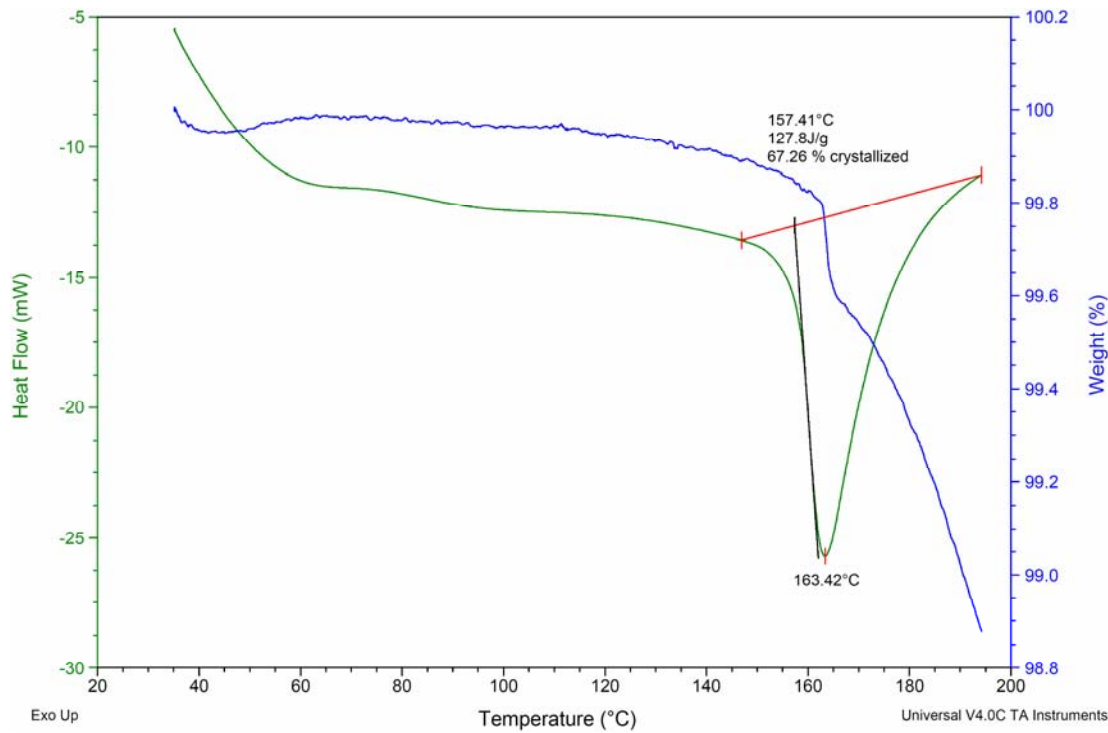


Figure B.4. 7.4 mol% feed 1,2-Epoxypropane 2nd Scan 11.26 mol% incorporation

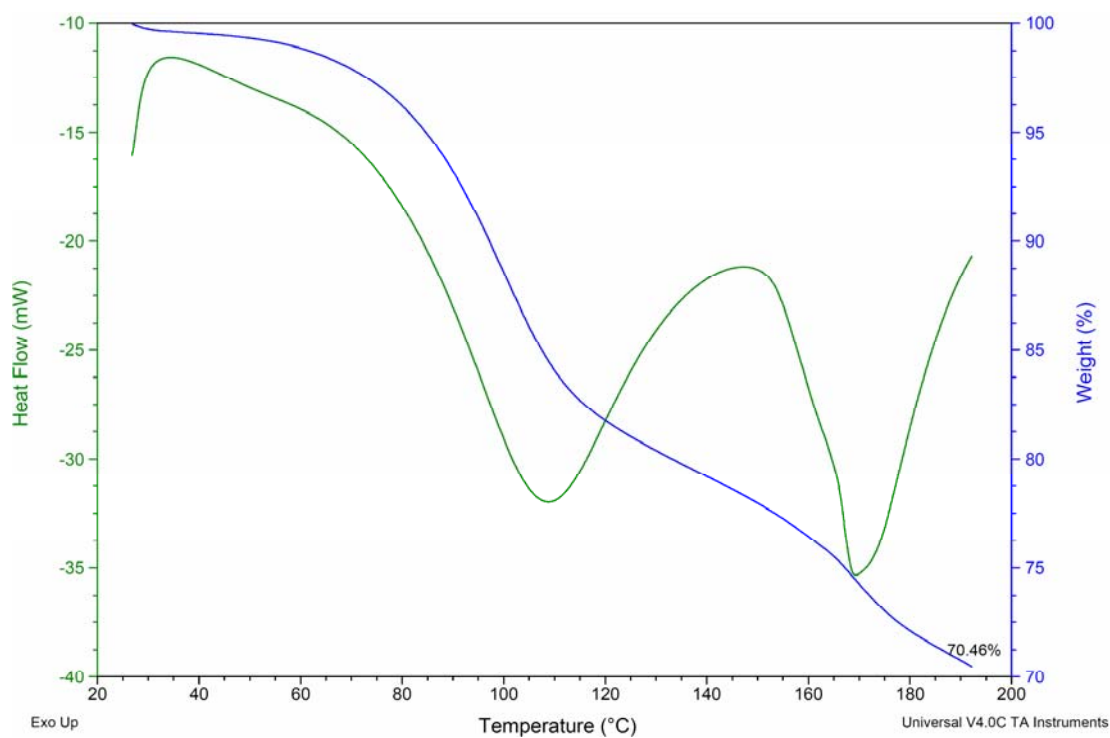


Figure B.5. 10 mol% feed 1,2-Epoxypropane 1st Scan 12.34 mol% incorporation

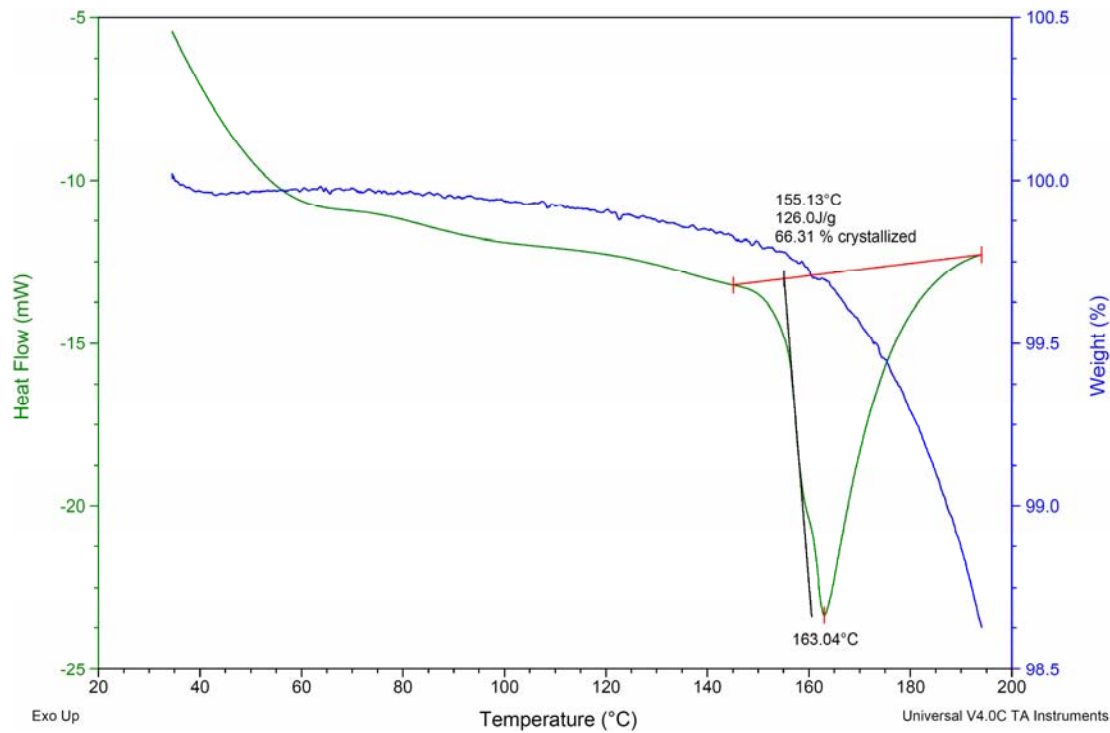


Figure B.6. 10 mol% feed 1,2-Epoxypropane 2nd Scan 12.34 mol% incorporation

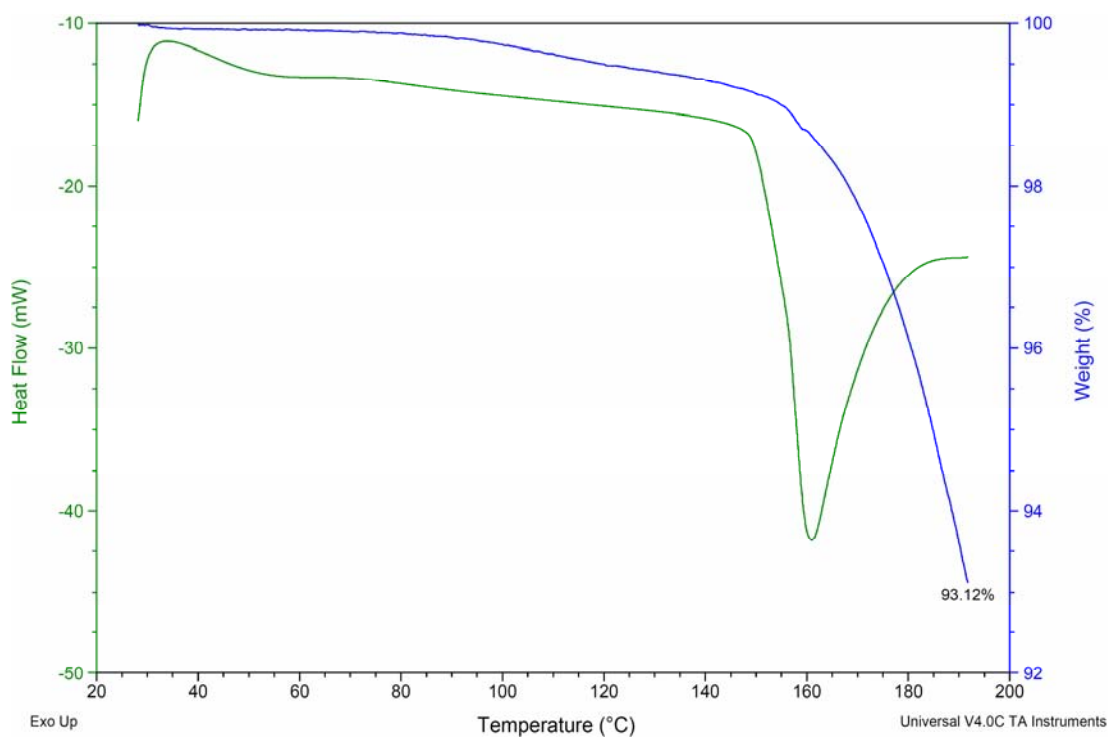


Figure B.7. 15 mol% feed 1,2-Epoxypropane 1st Scan 16.85 mol% incorporation

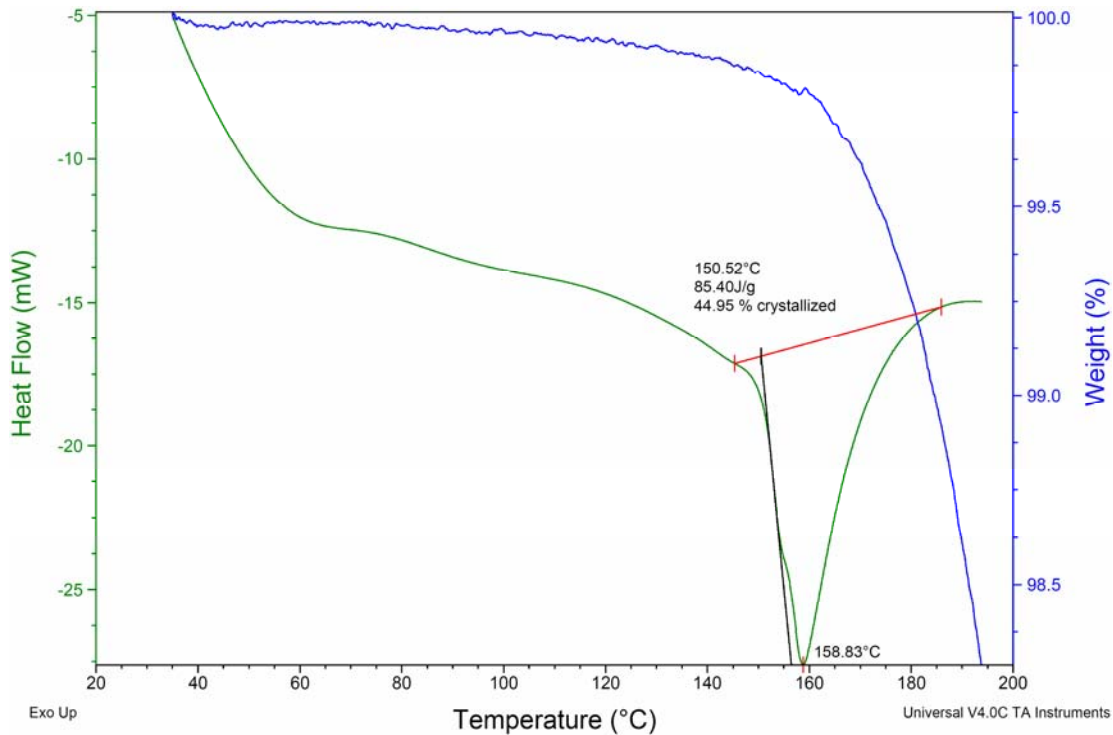


Figure B.8. 15 mol% feed 1,2-Epoxypropane 2nd Scan 16.85 mol% incorporation

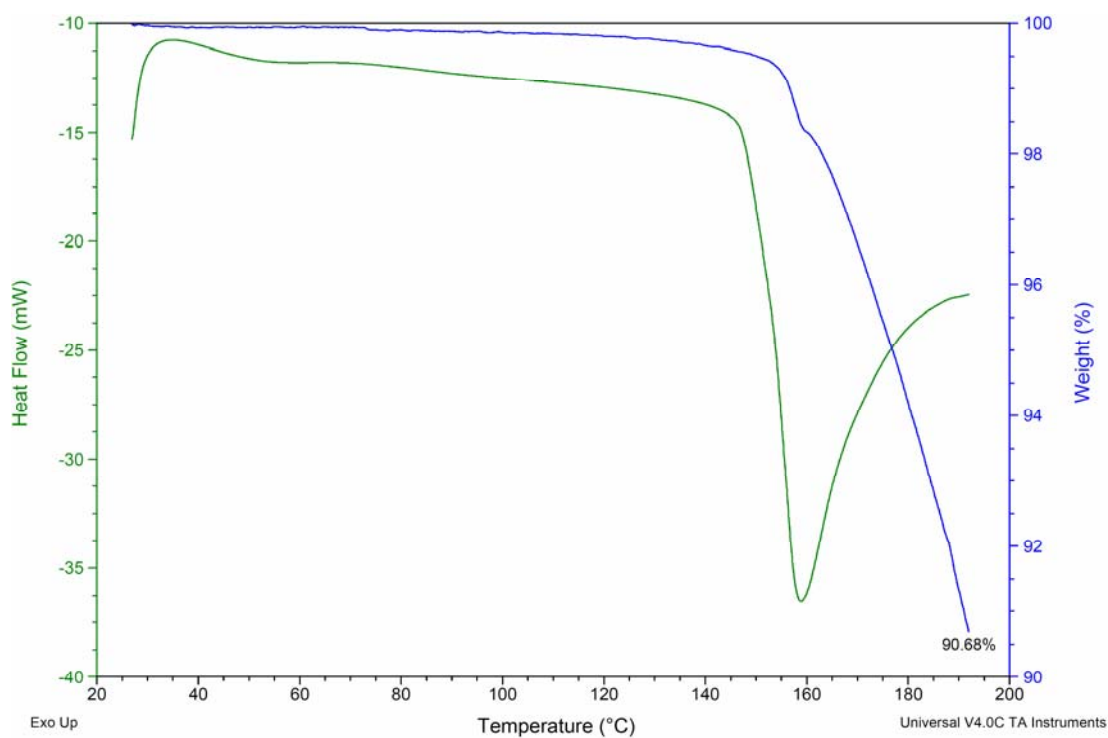


Figure B.9. 20 mol% feed 1,2-Epoxypropane 1st Scan 17.98 mol% incorporation

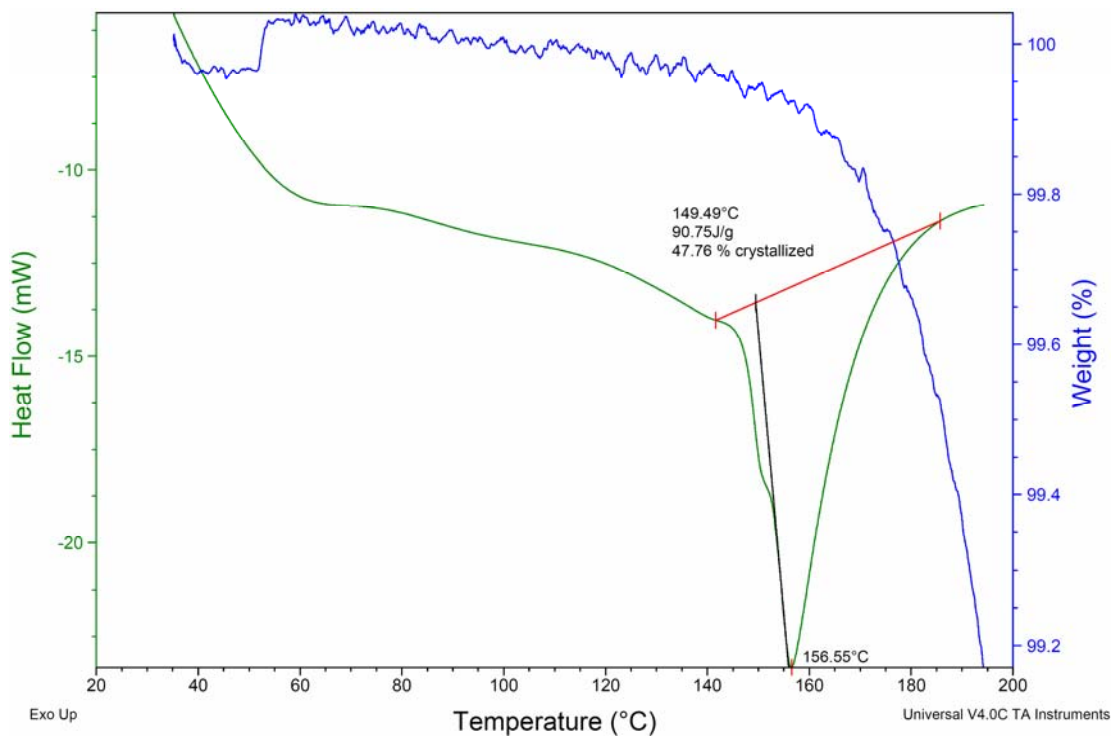


Figure B.10. 20 mol% feed 1,2-Epoxypropane 2nd Scan 17.98 mol% incorporation

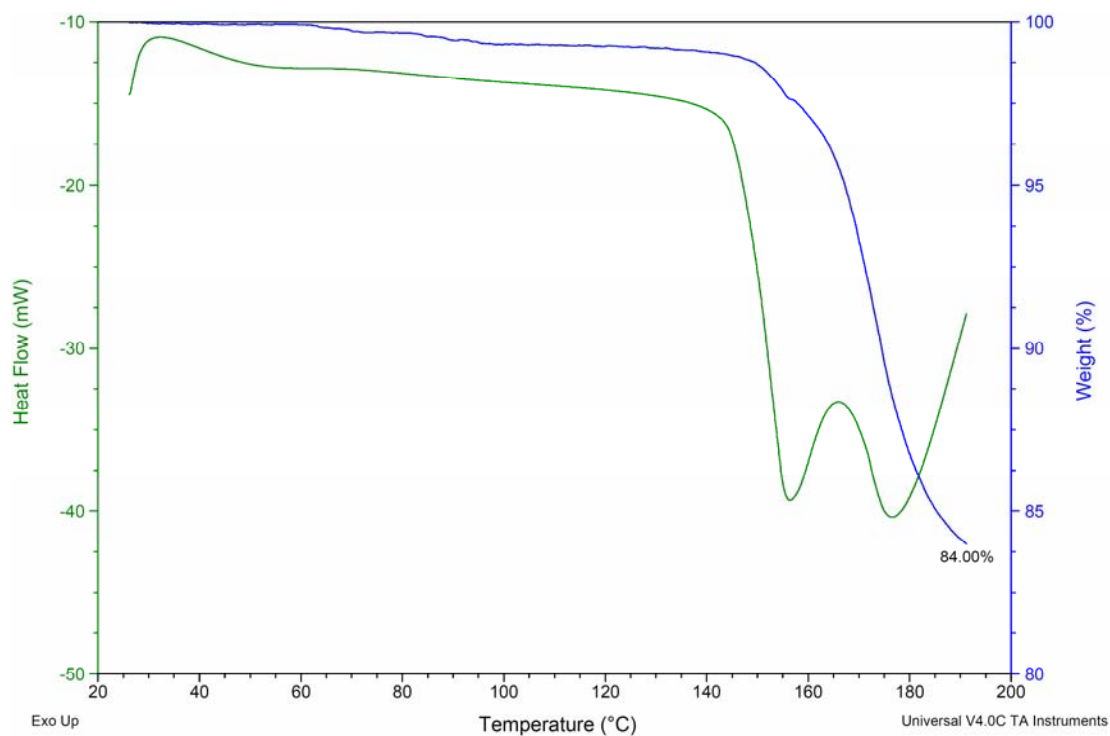


Figure B.11. 25 mol% feed 1,2-Epoxypropane 1st Scan 21.07 mol% incorporation

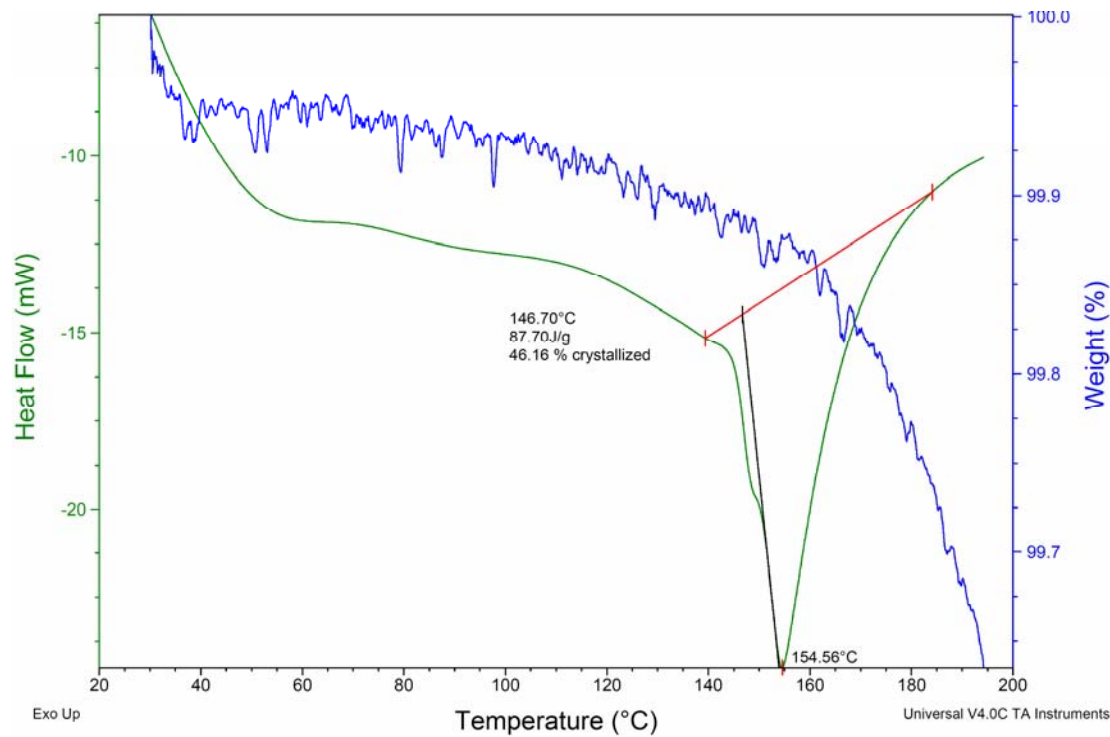


Figure B.12. 25 mol% feed 1,2-Epoxypropane 2nd Scan 21.07 mol% incorporation

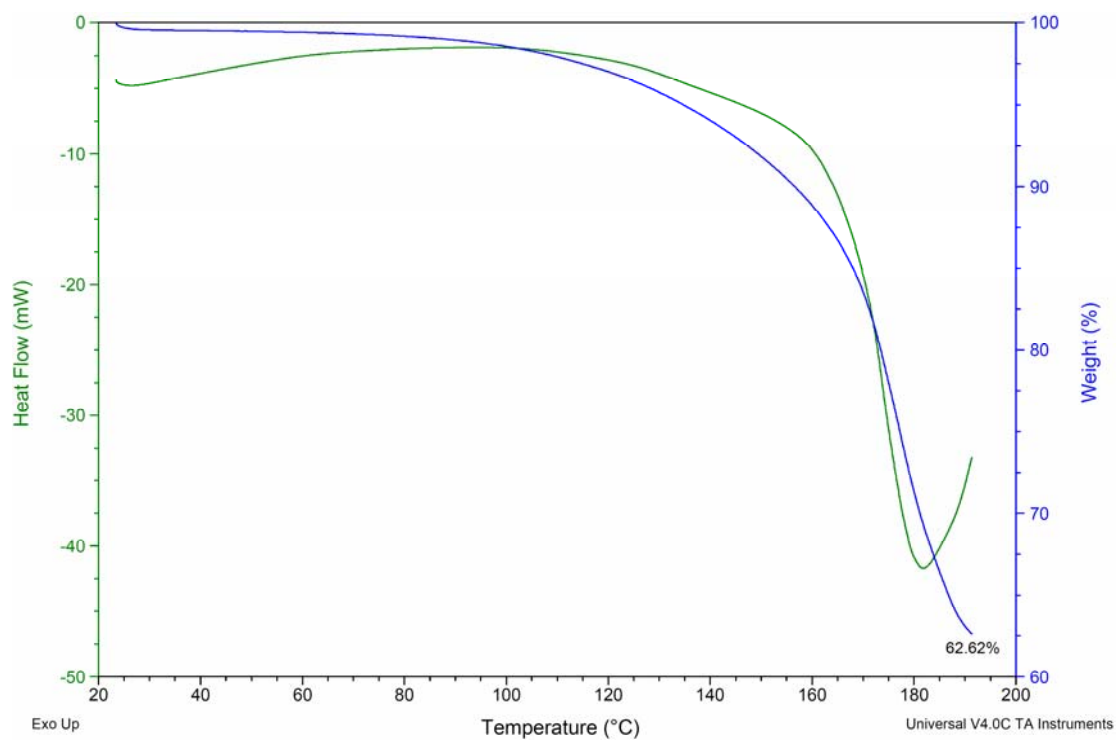


Figure B.13. 3 mol% feed 1,2-Epoxybutane 1st Scan 6.66 mol% incorporation

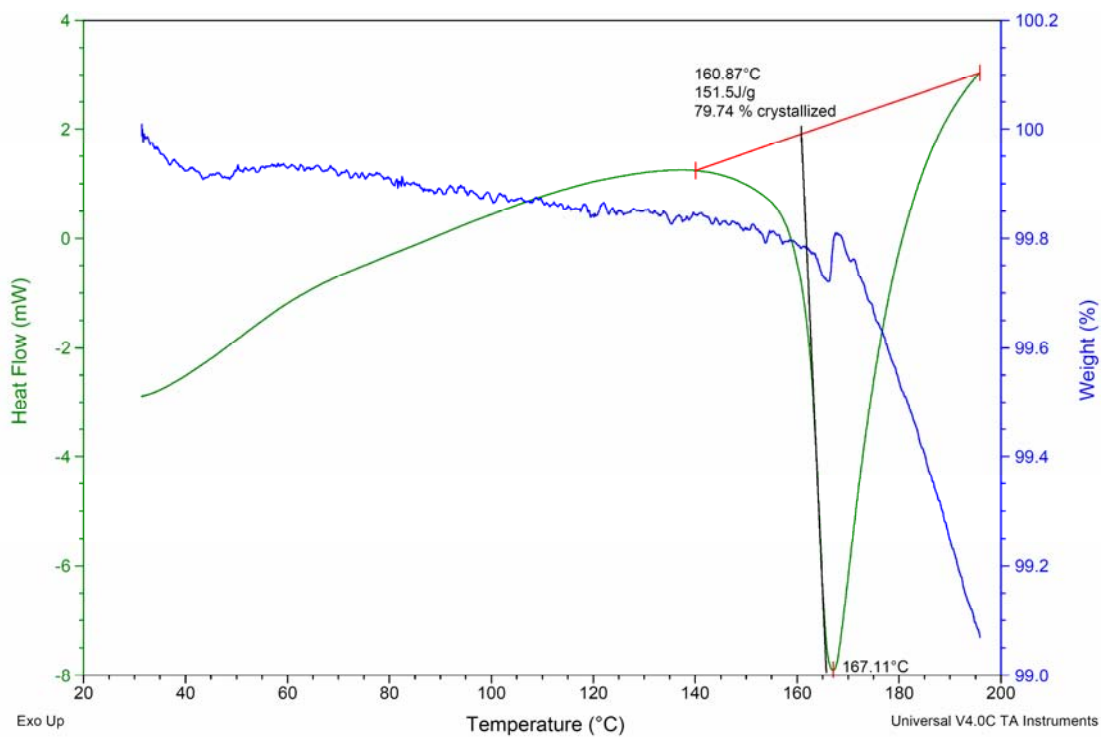


Figure B.14. 3 mol% feed 1,2-Epoxybutane 2nd Scan 6.66 mol% incorporation

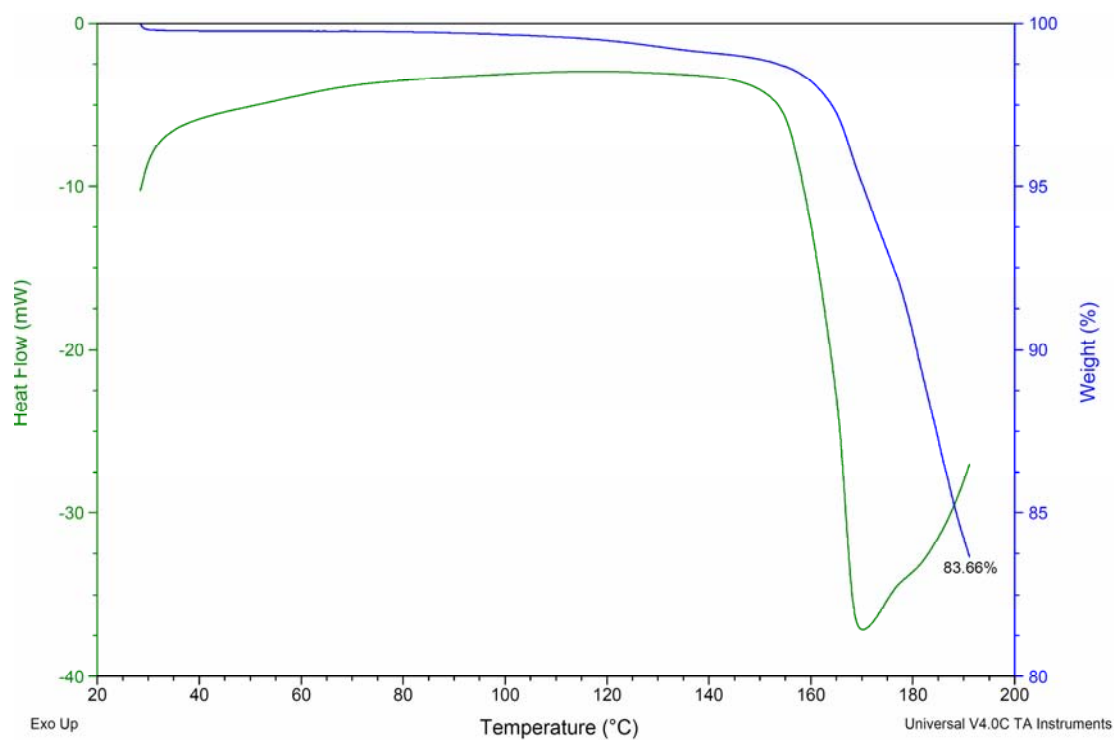


Figure B.15. 7.4 mol% feed 1,2-Epoxybutane 1st Scan 7.88 mol% incorporation

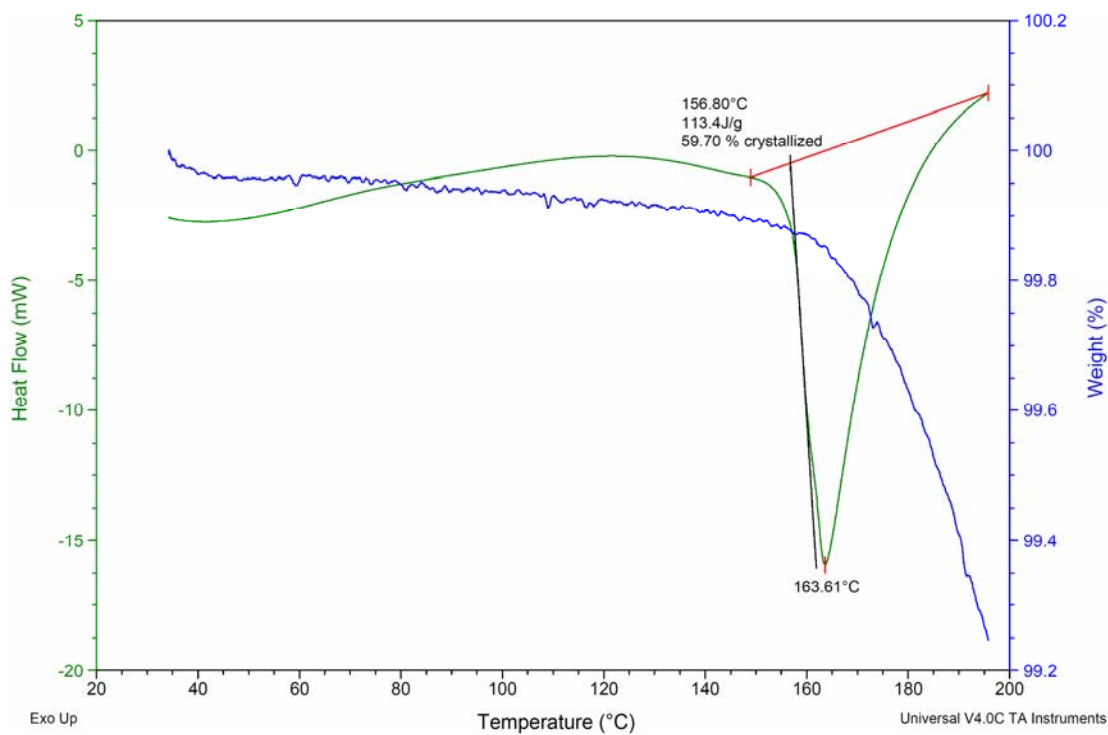


Figure B.16. 7.4 mol% feed 1,2-Epoxybutane 2nd Scan 7.88 mol% incorporation

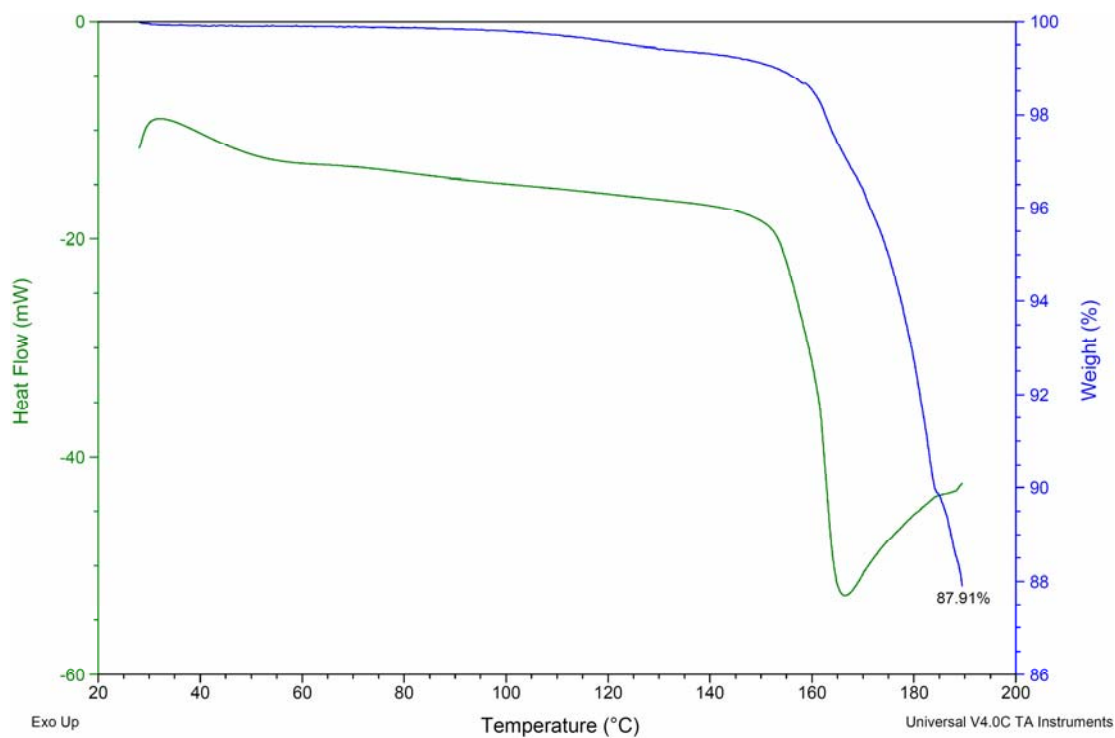


Figure B.17. 10 mol% feed 1,2-Epoxybutane 1st Scan 9.86 mol% incorporation

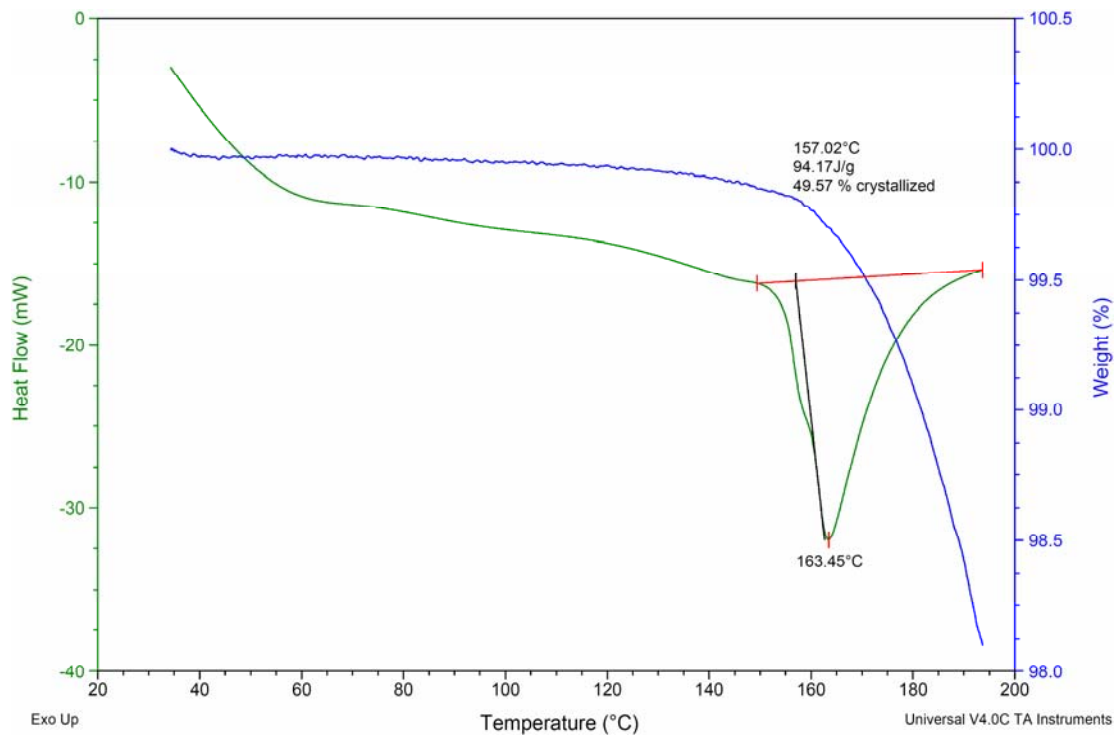


Figure B.18. 10 mol% feed 1,2-Epoxybutane 2nd Scan 9.86 mol% incorporation

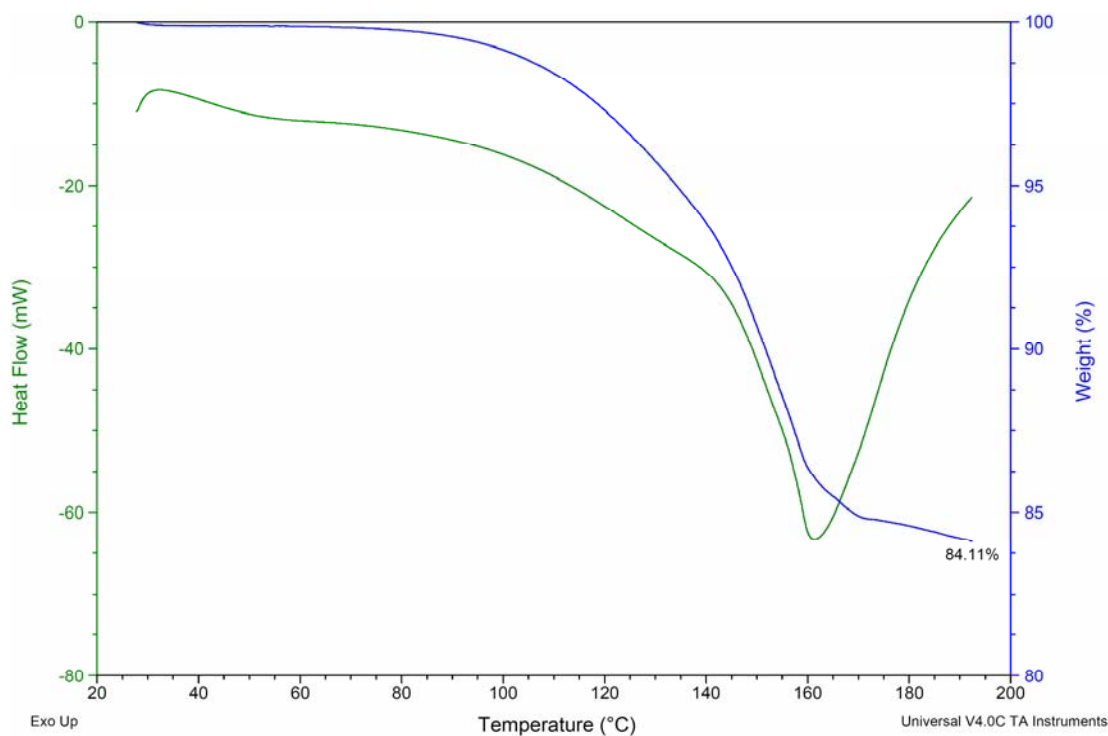


Figure B.19. 15 mol% feed 1,2-Epoxybutane 1st Scan 15.13 mol% incorporation

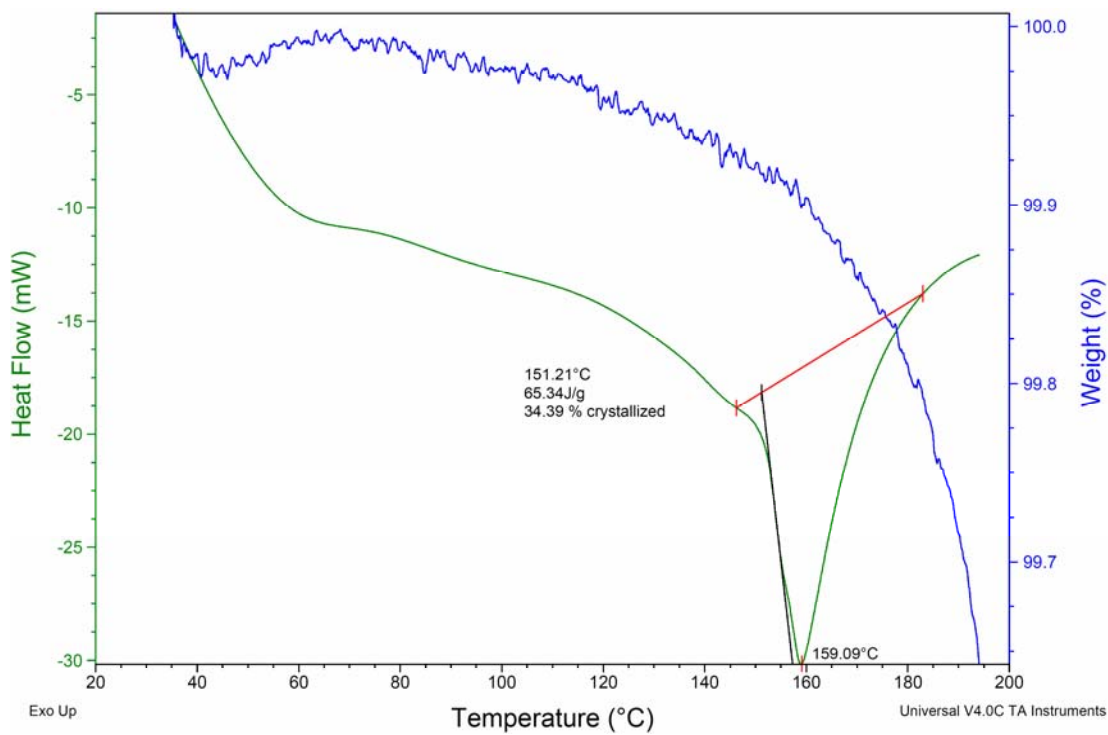


Figure B.20. 15 mol% feed 1,2-Epoxybutane 2nd Scan 15.13 mol% incorporation

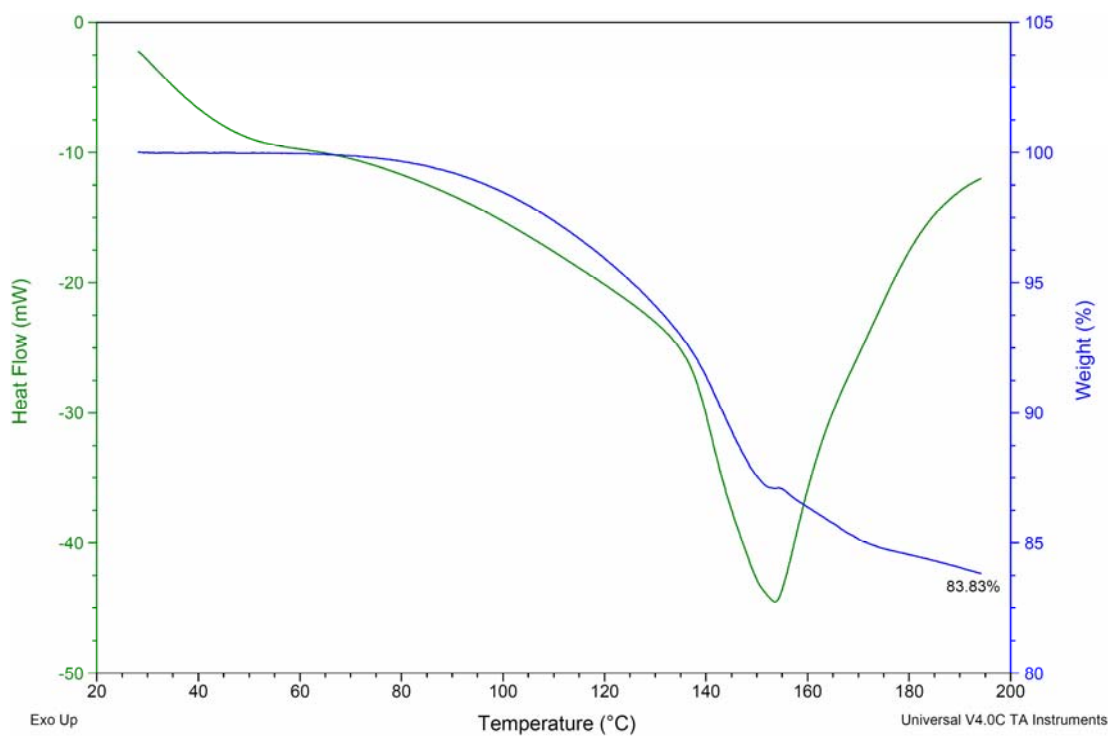


Figure B.21. 20 mol% feed 1,2-Epoxybutane 1st Scan 20.37 mol% incorporation

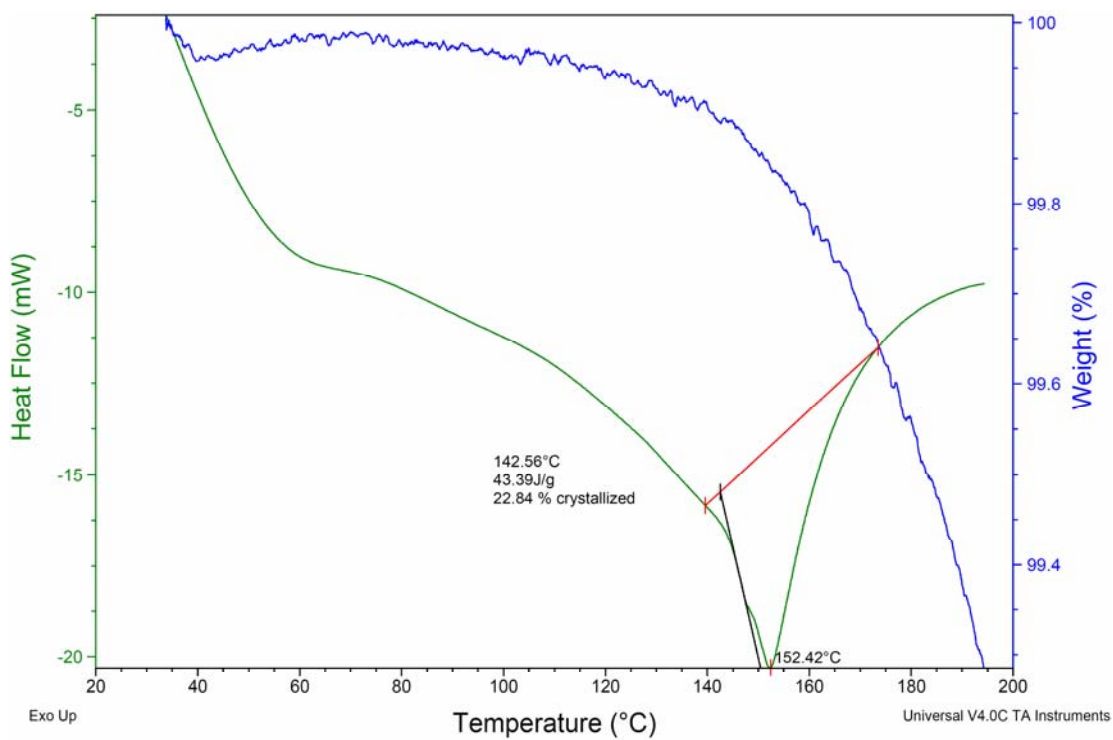


Figure B.22. 20 mol% feed 1,2-Epoxybutane 2nd Scan 20.37 mol% incorporation

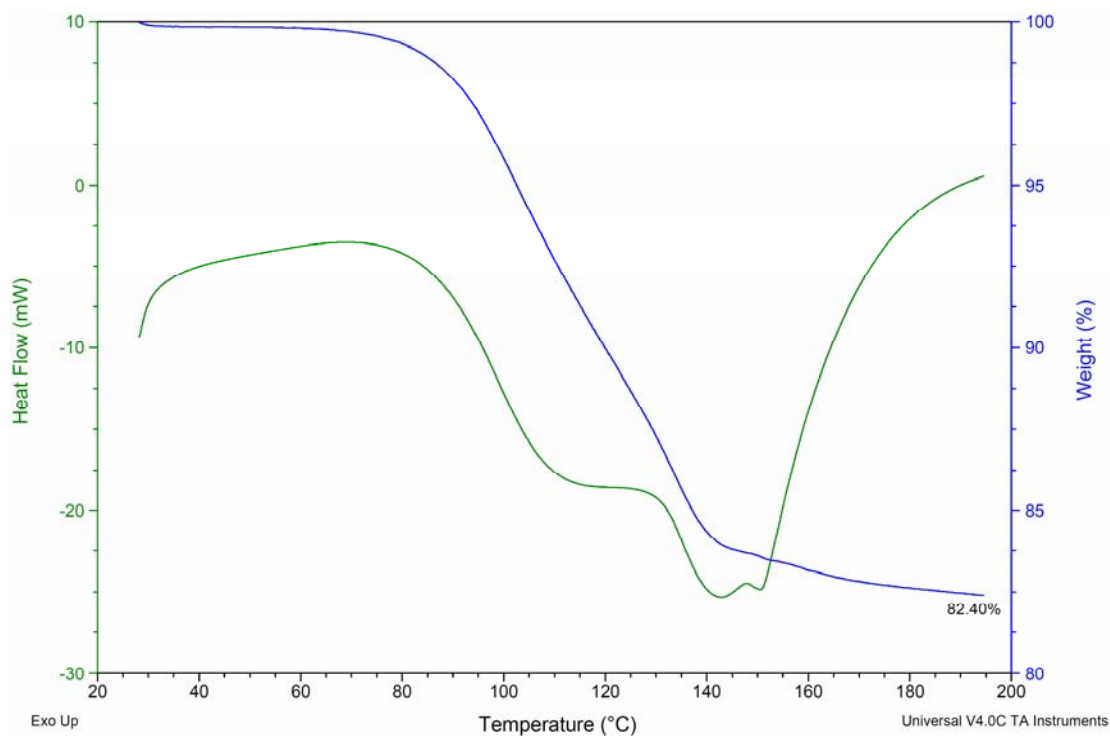


Figure B.23. 25 mol% feed 1,2-Epoxybutane 1st Scan 21.18 mol% incorporation

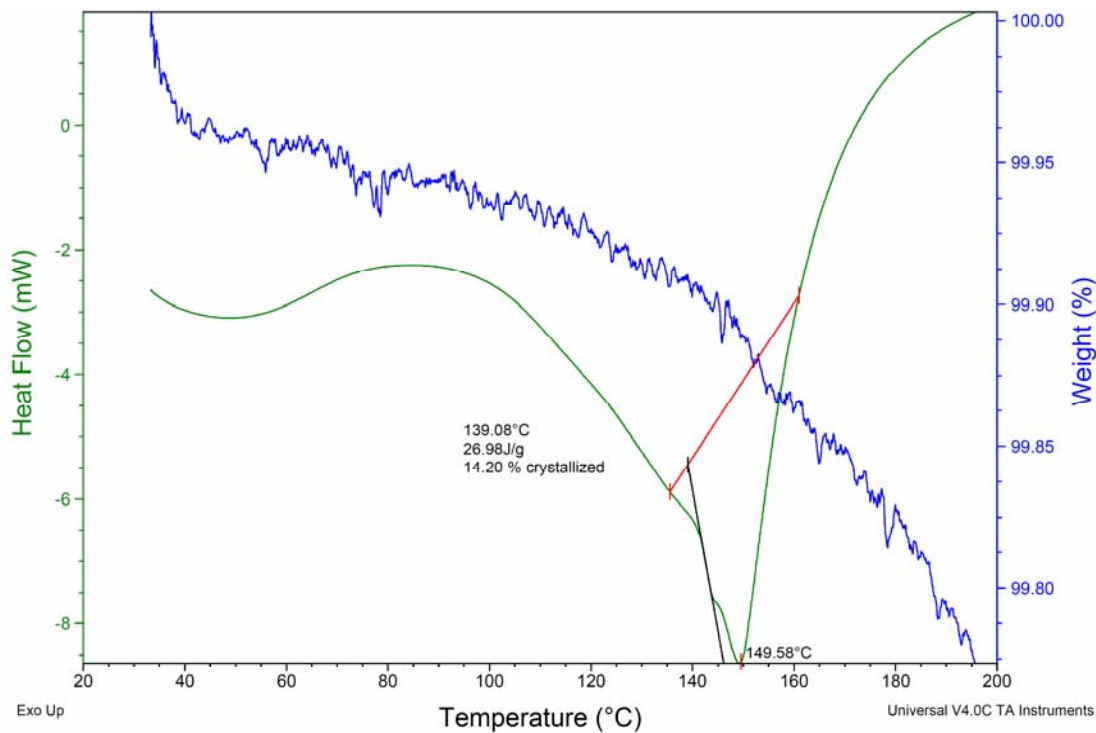


Figure B.24. 25 mol% feed 1,2-Epoxybutane 2nd Scan 21.18 mol% incorporation

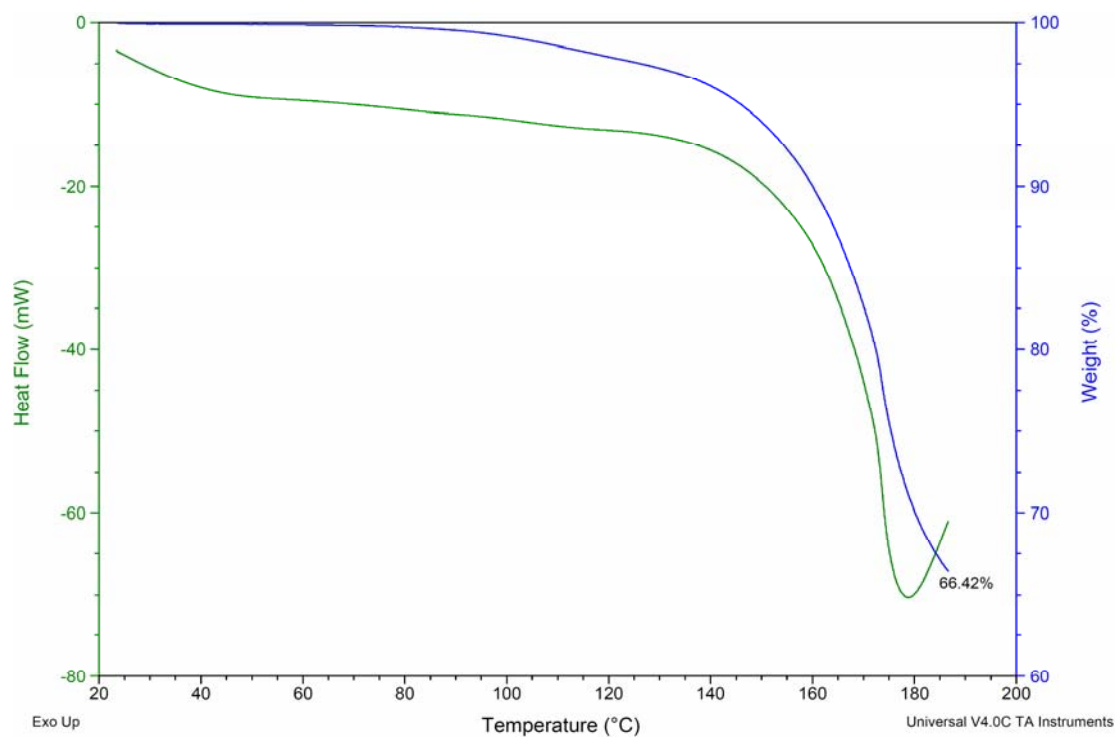


Figure B.25. 3 mol% feed 1,2-Epoxyhexane 1st Scan 6.86 mol% incorporation

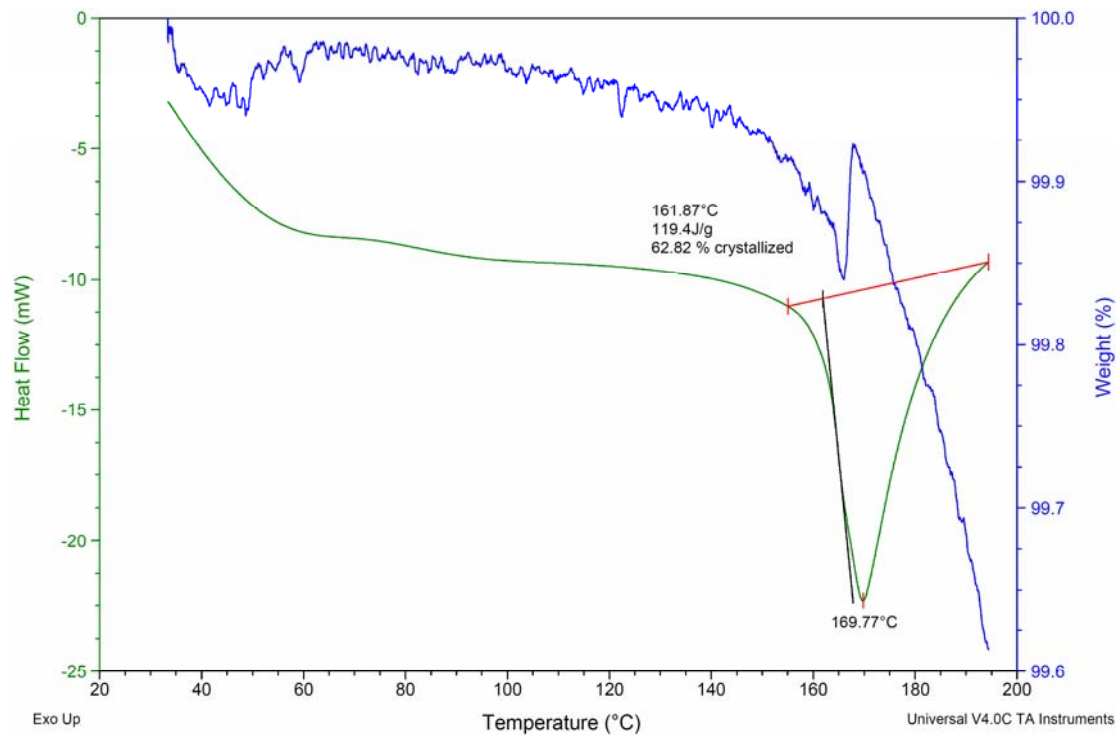


Figure B.26. 3 mol% feed 1,2-Epoxyhexane 2nd Scan 6.86 mol% incorporation

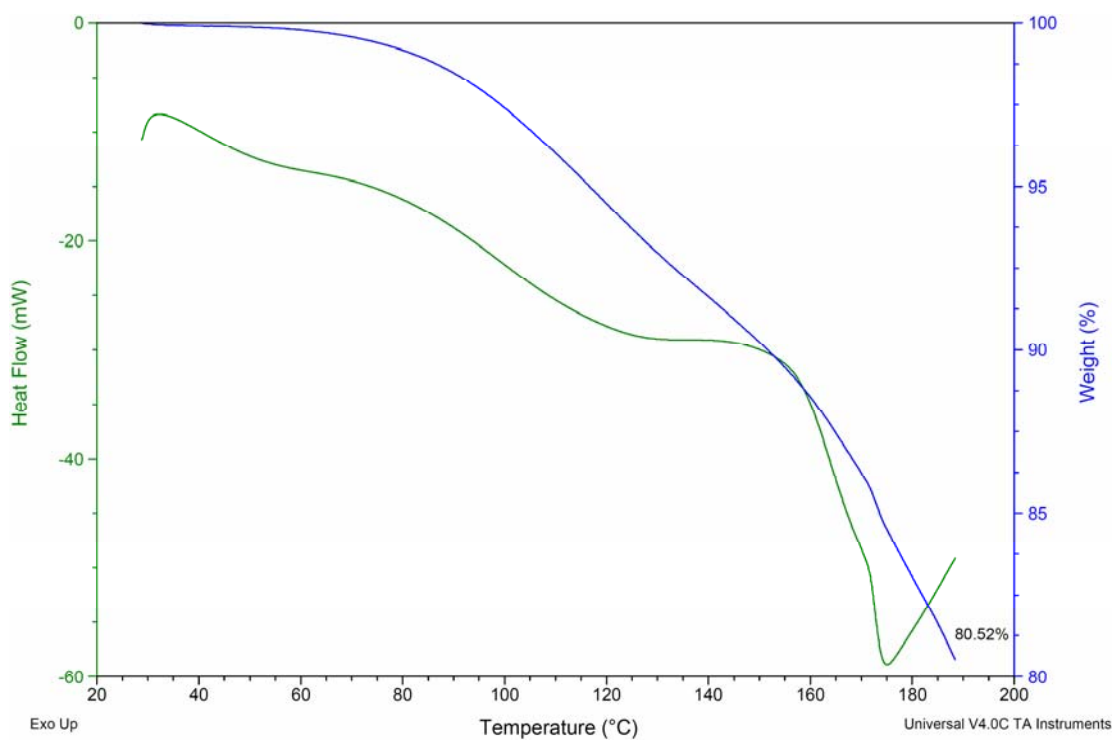


Figure B.27. 7.4 mol% feed 1,2-Epoxyhexane 1st Scan 7.35 mol% incorporation

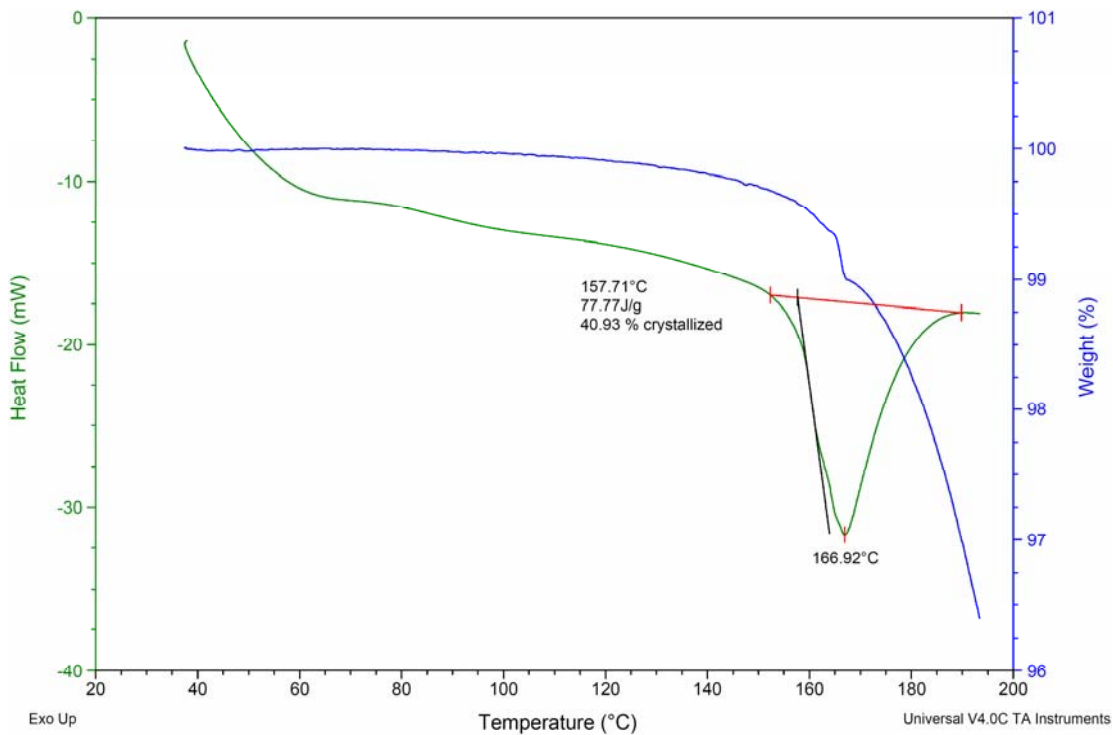


Figure B.28. 7.4 mol% feed 1,2-Epoxyhexane 2nd Scan 7.35 mol% incorporation

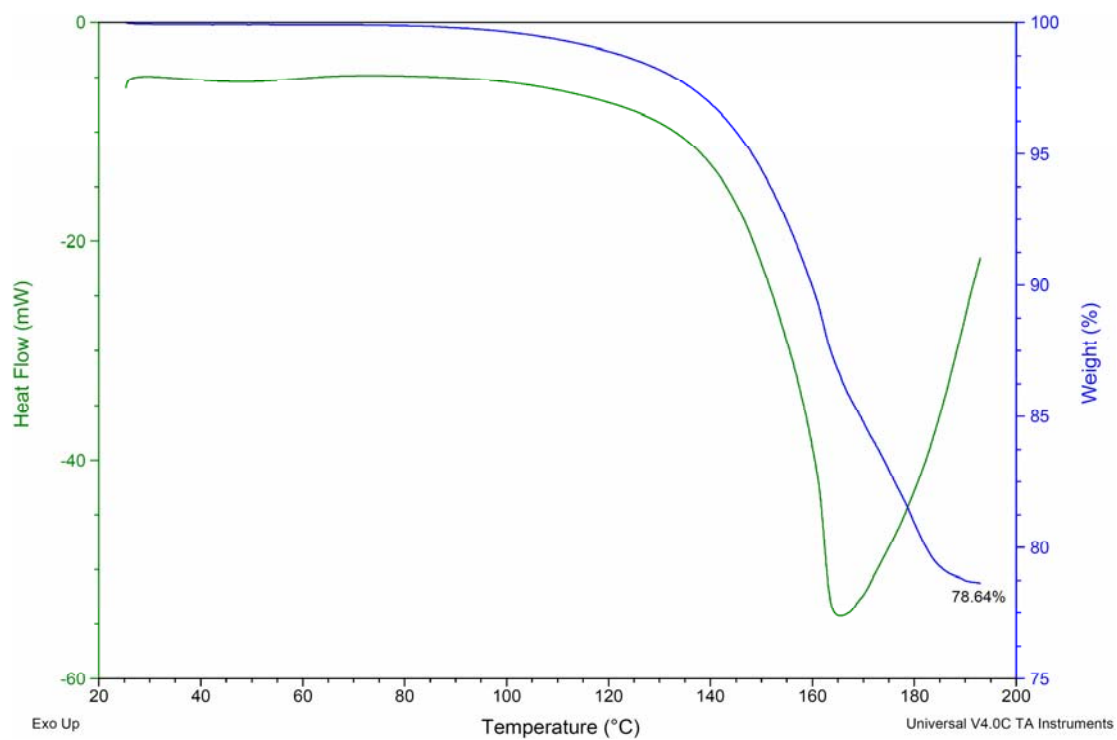


Figure B.29. 10 mol% feed 1,2-Epoxyhexane 1st Scan 12.12 mol% incorporation

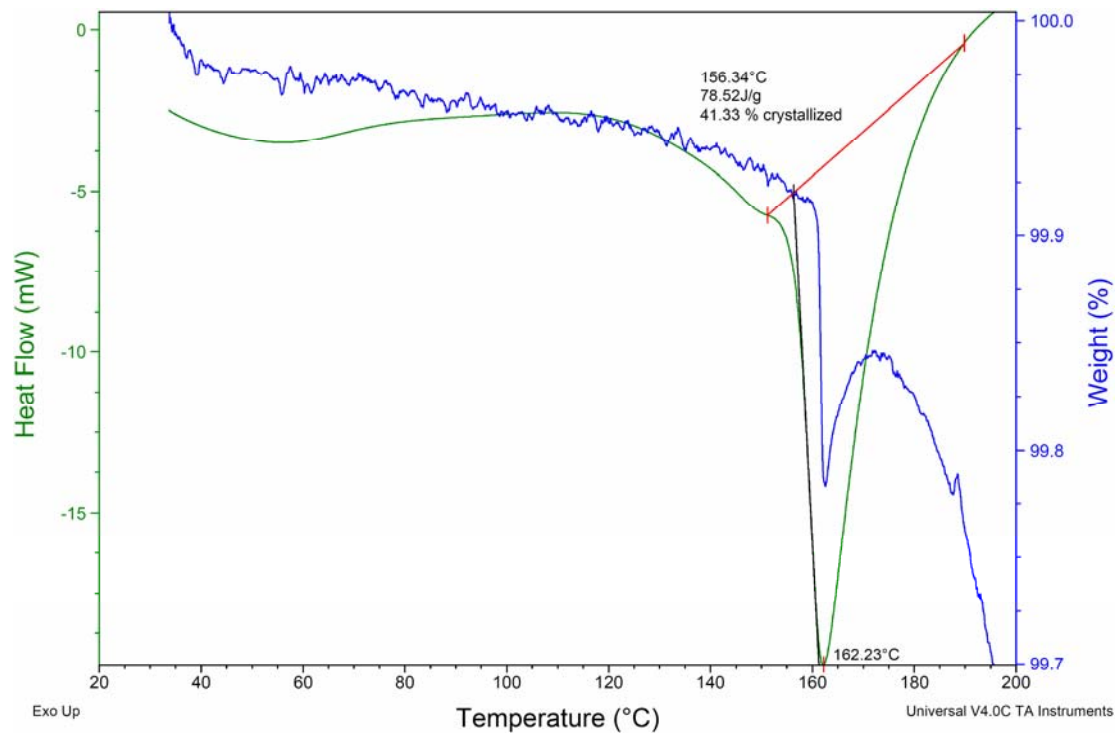


Figure B.30. 10 mol% feed 1,2-Epoxyhexane 2nd Scan 12.12 mol% incorporation

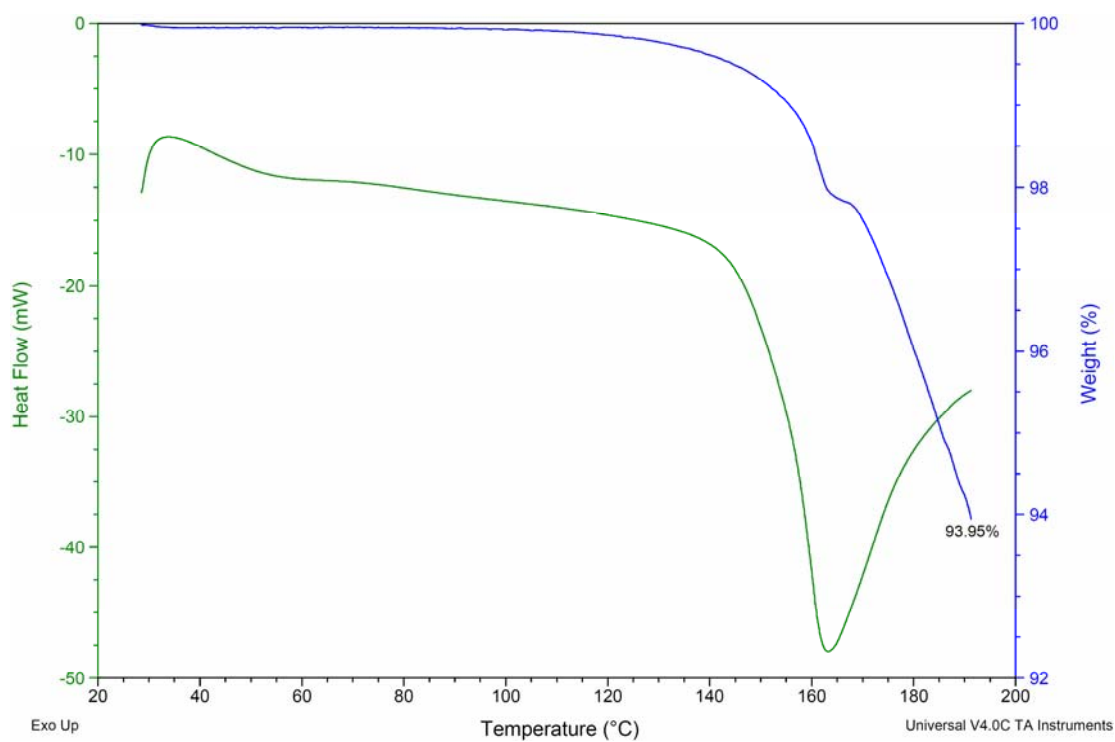


Figure B.31. 15 mol% feed 1,2-Epoxyhexane 1st Scan 13.14 mol% incorporation

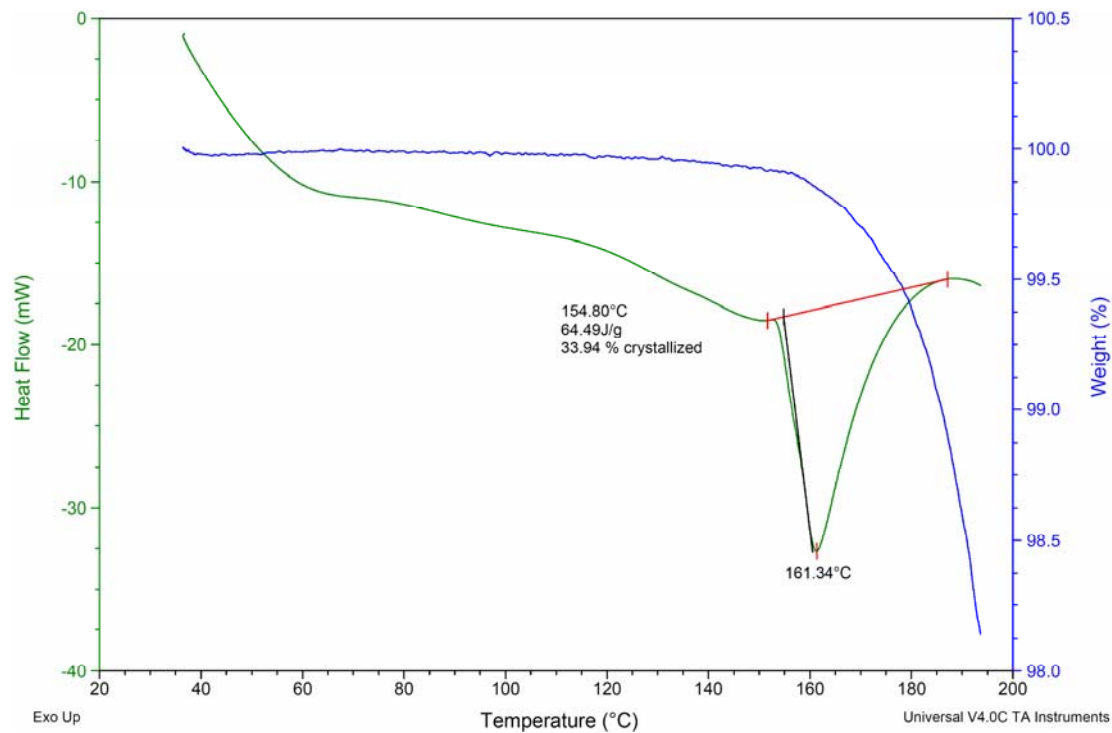


Figure B.32. 15 mol% feed 1,2-Epoxyhexane 2nd Scan 13.14 mol% incorporation

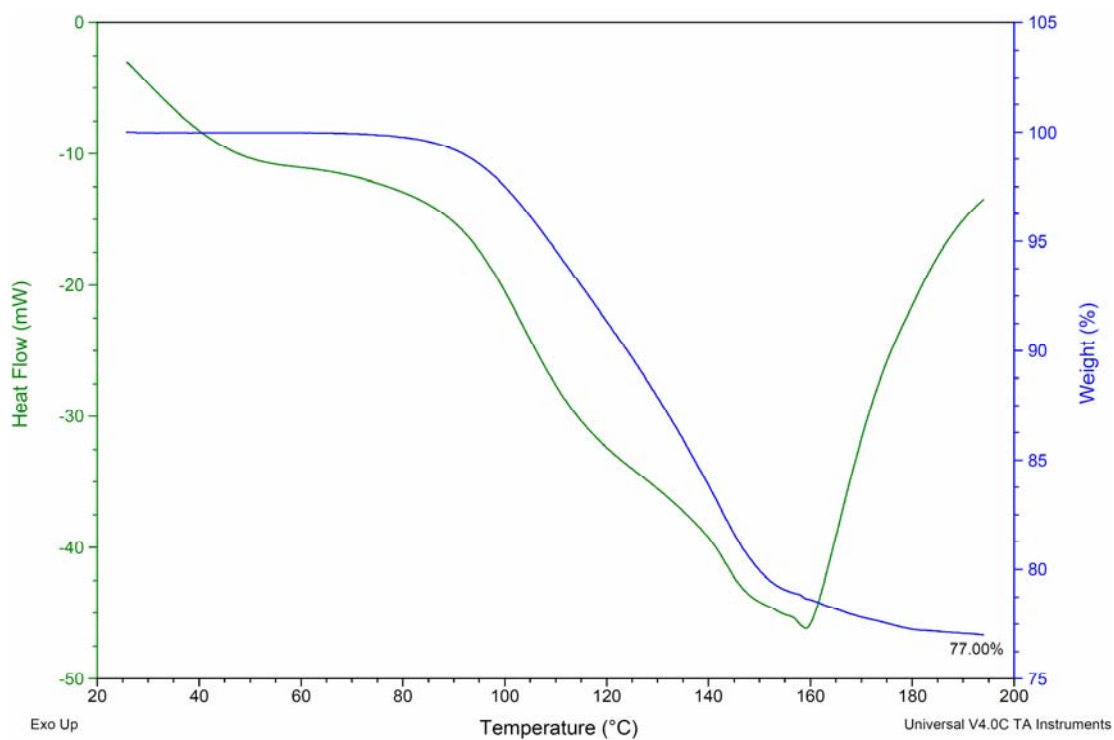


Figure B.33. 20 mol% feed 1,2-Epoxyhexane 1st Scan 19.38 mol% incorporation

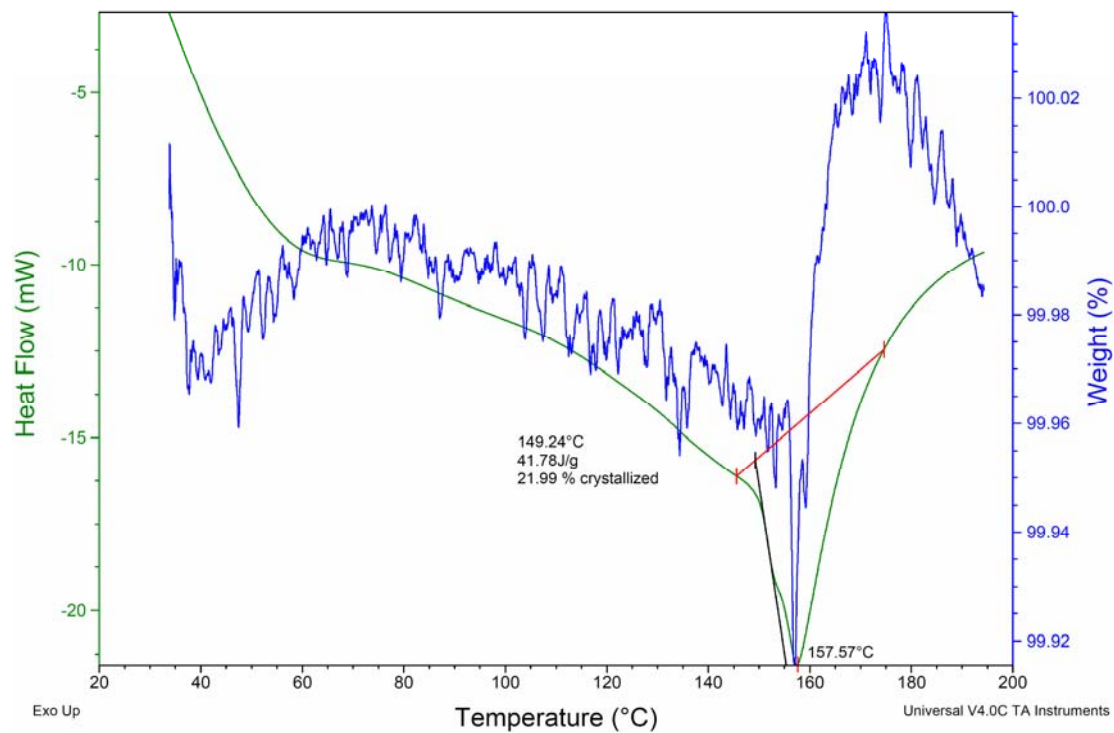


Figure B.34. 20 mol% feed 1,2-Epoxyhexane 2nd Scan 19.38 mol% incorporation

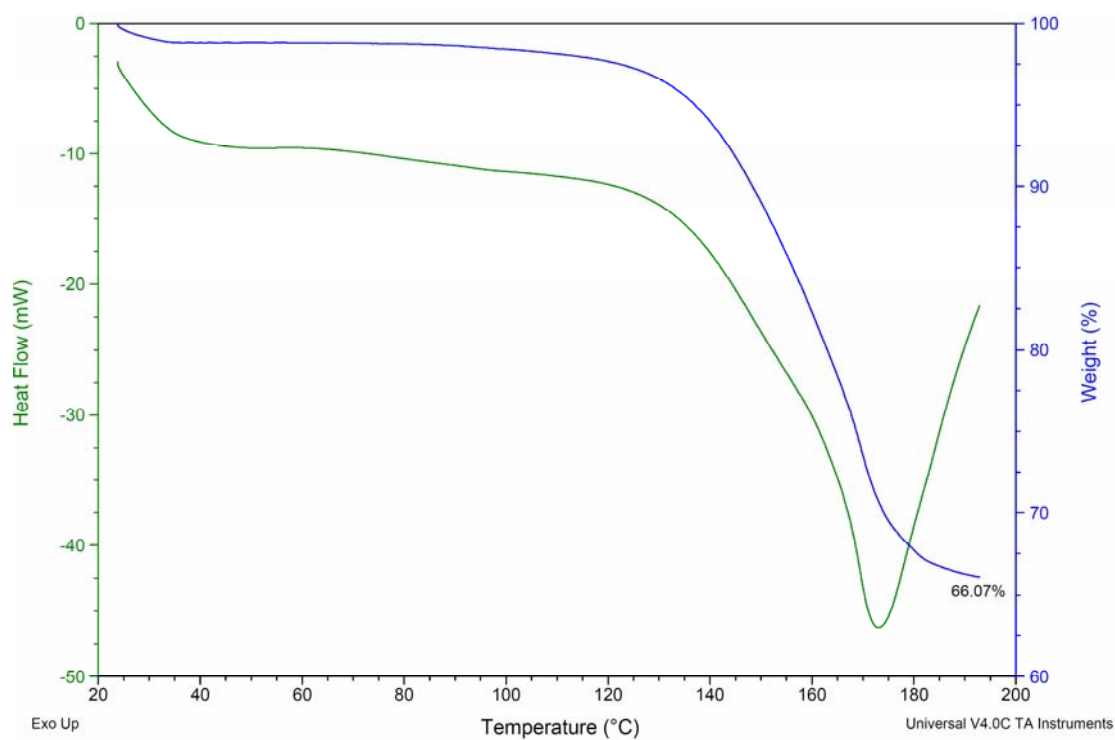


Figure B.35. 3 mol% feed 1,2-Epoxyoctane 1st Scan 7.08 mol% incorporation

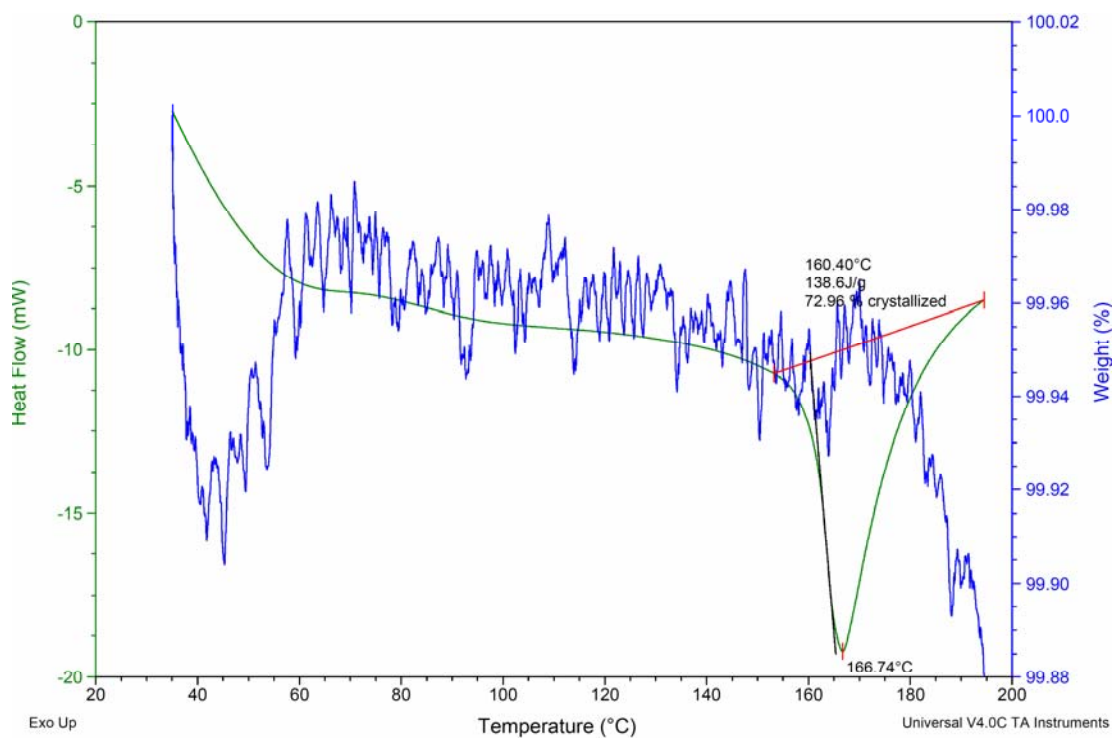


Figure B.36. 3 mol% feed 1,2-Epoxyoctane 2nd Scan 7.08 mol% incorporation

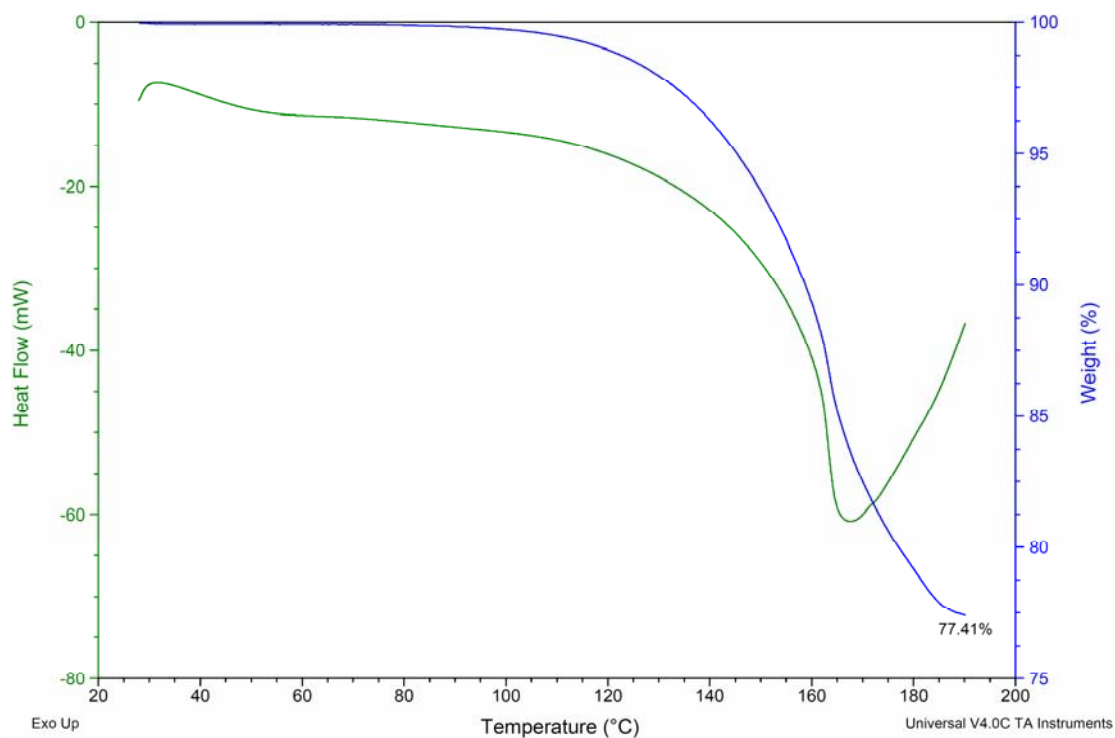


Figure B.37. 7.4 mol% feed 1,2-Epoxyoctane 1st Scan 9.03 mol% incorporation

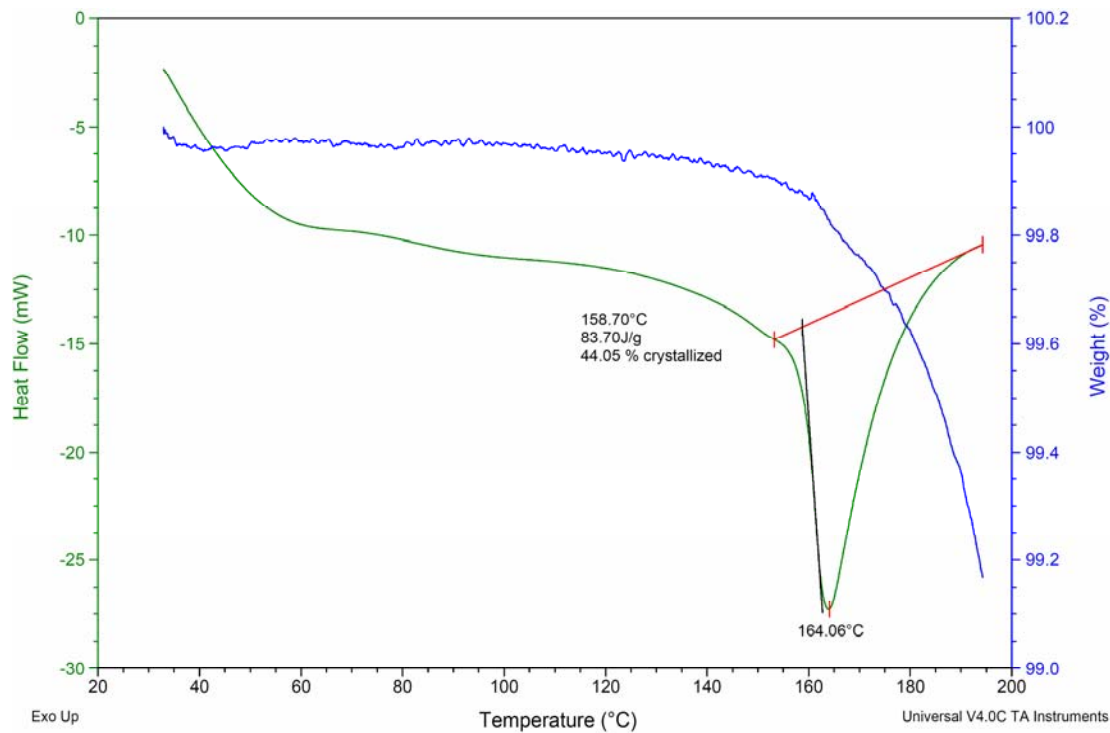


Figure B.38. 7.4 mol% feed 1,2-Epoxyoctane 2nd Scan 9.03 mol% incorporation

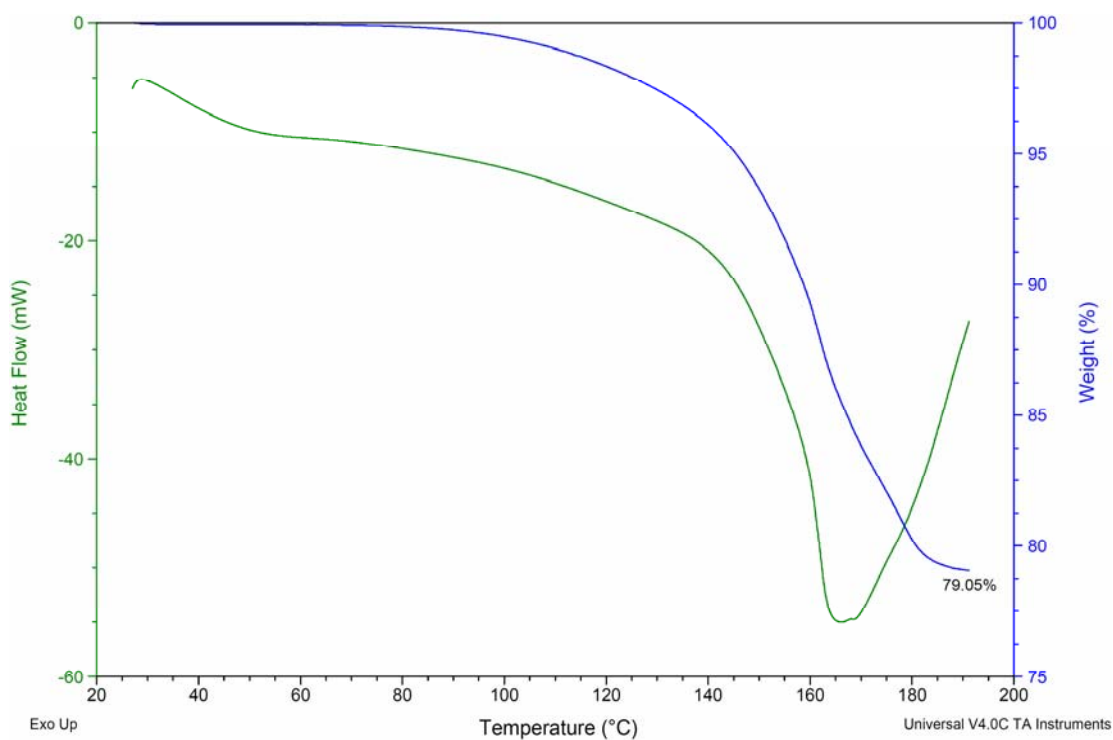


Figure B.39. 10 mol% feed 1,2-Epoxyoctane 1st Scan 10.44 mol% incorporation

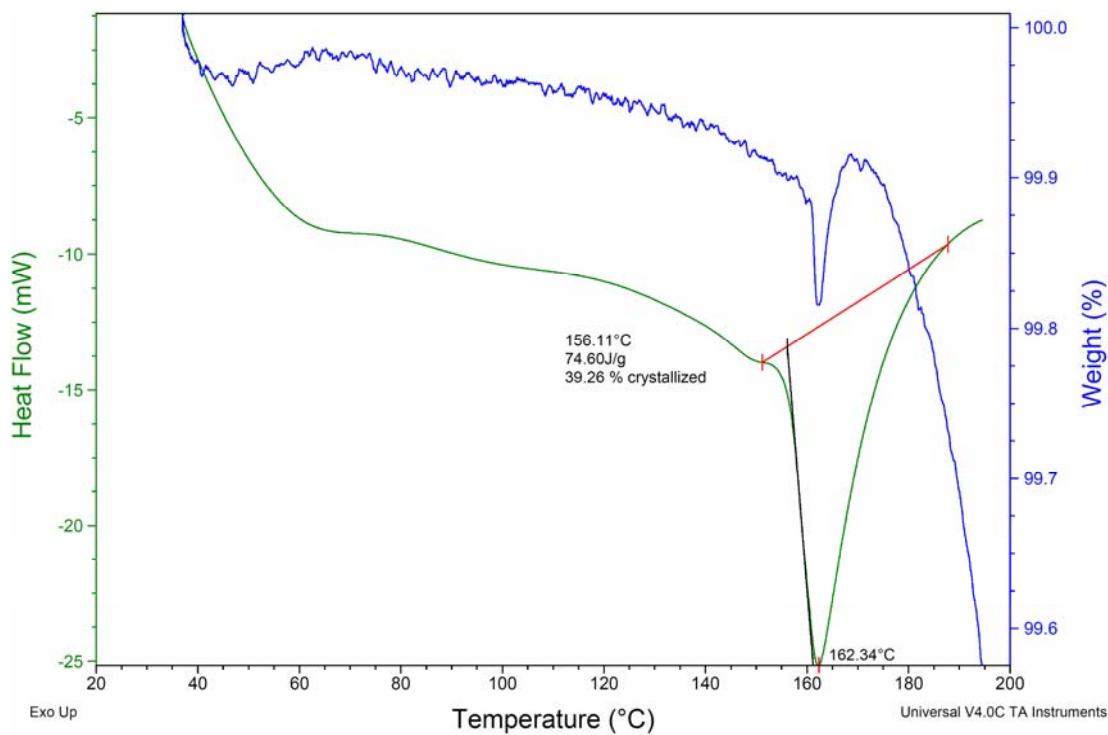


Figure B.40. 10 mol% feed 1,2-Epoxyoctane 2nd Scan 10.44 mol% incorporation

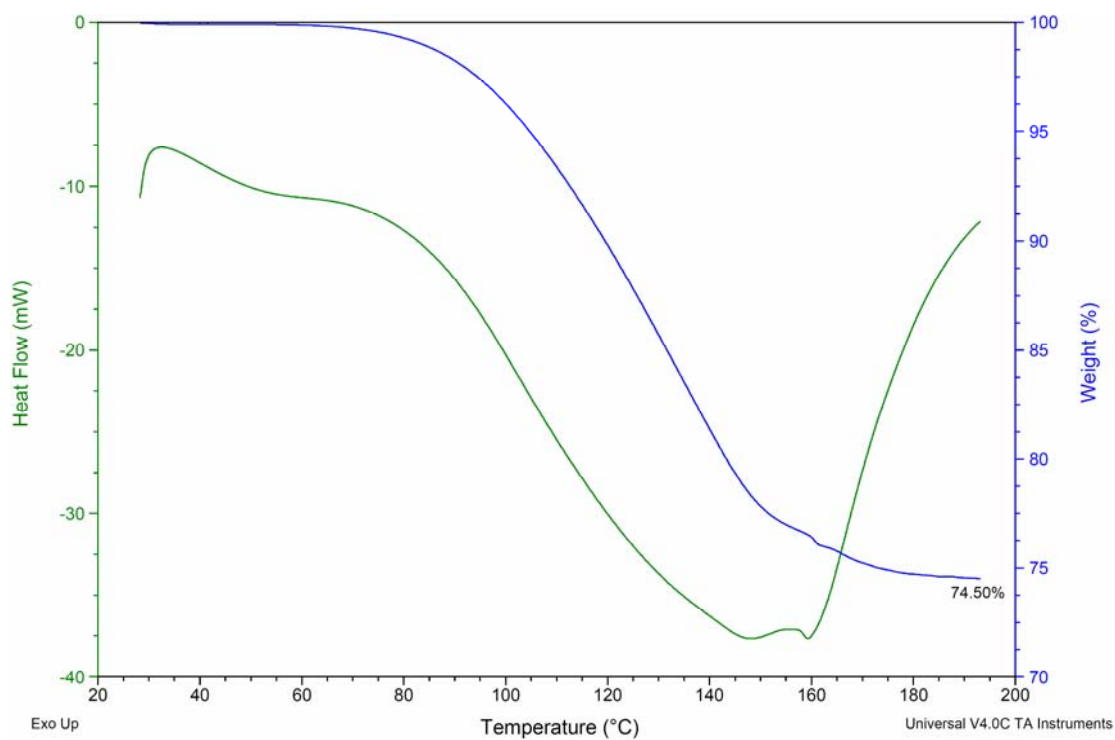


Figure B.41. 15 mol% feed 1,2-Epoxyoctane 1st Scan 18.48 mol% incorporation

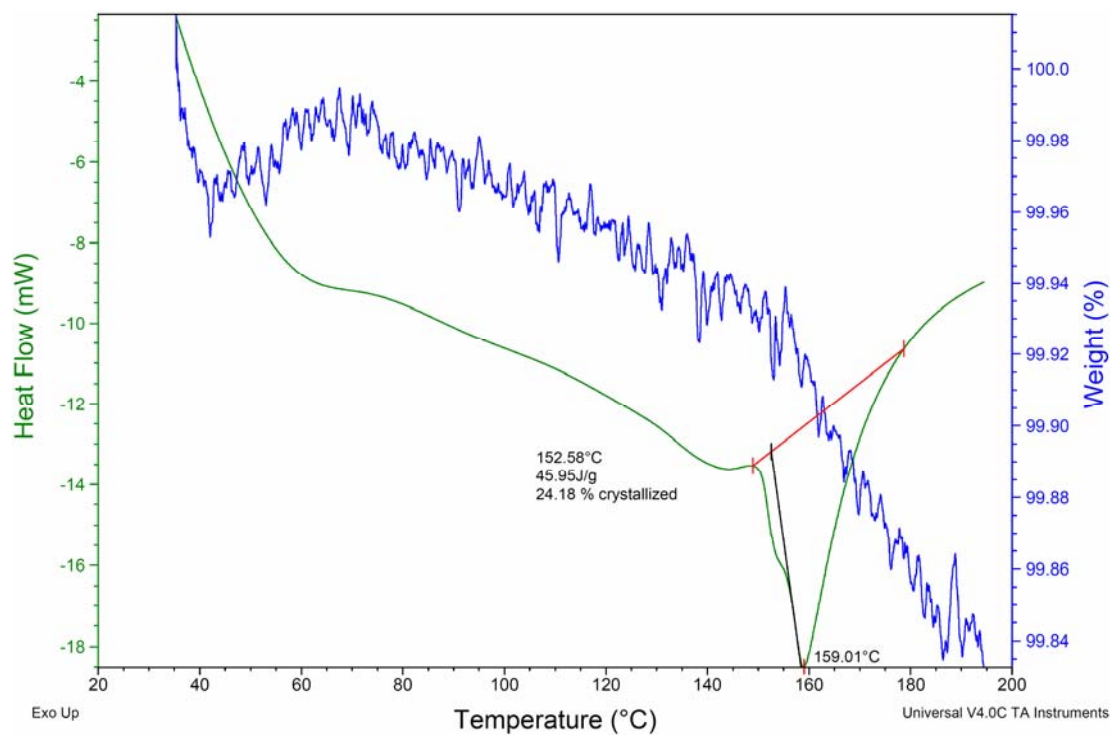


Figure B.42. 15 mol% feed 1,2-Epoxyoctane 2nd Scan 18.48 mol% incorporation

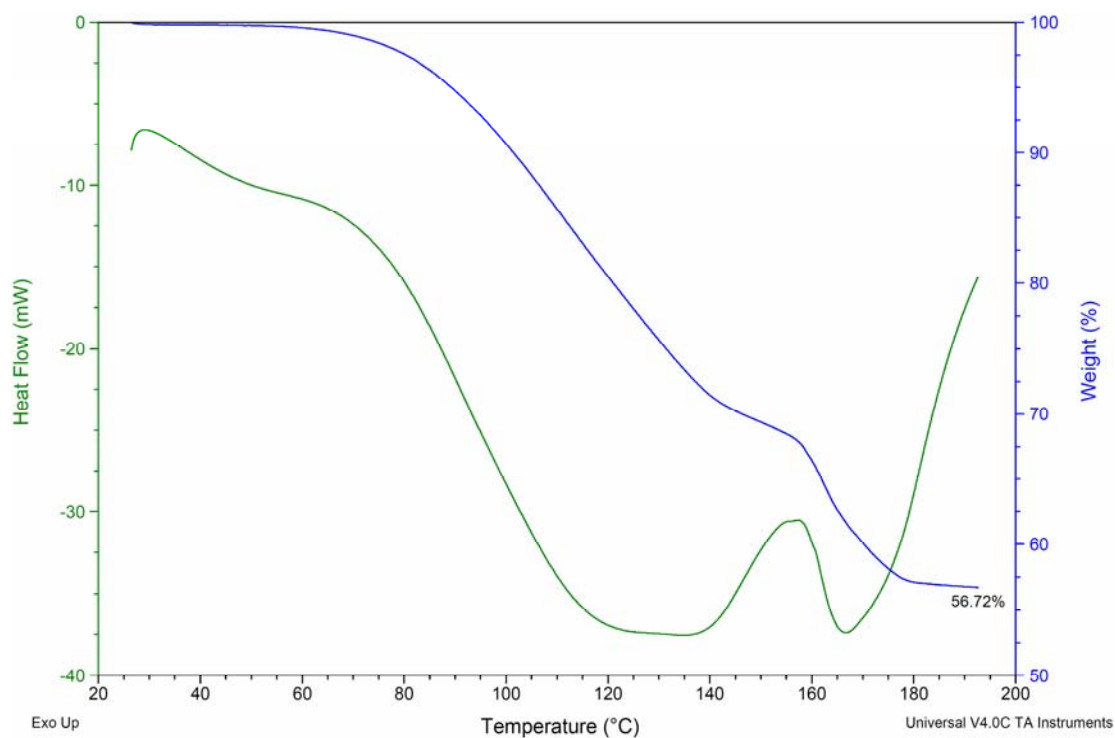


Figure B.43. 20 mol% feed 1,2-Epoxyoctane 1st Scan 32.03 mol% incorporation

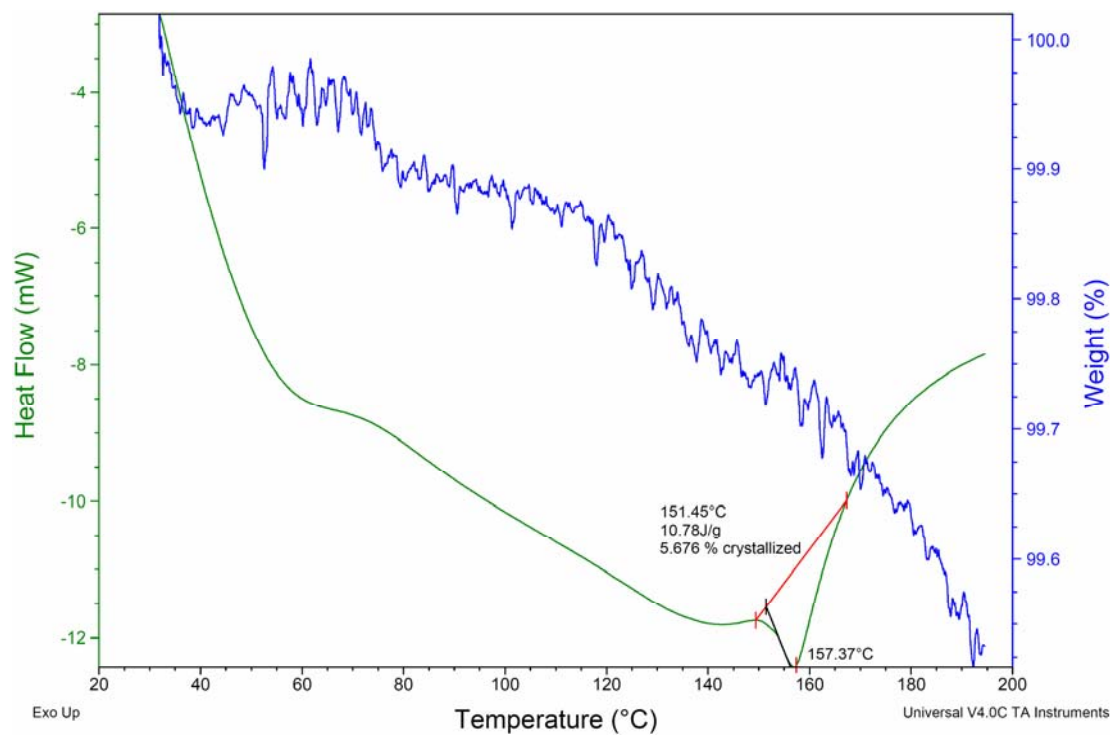


Figure B.44. 20 mol% feed 1,2-Epoxyoctane 2nd Scan 32.03 mol% incorporation

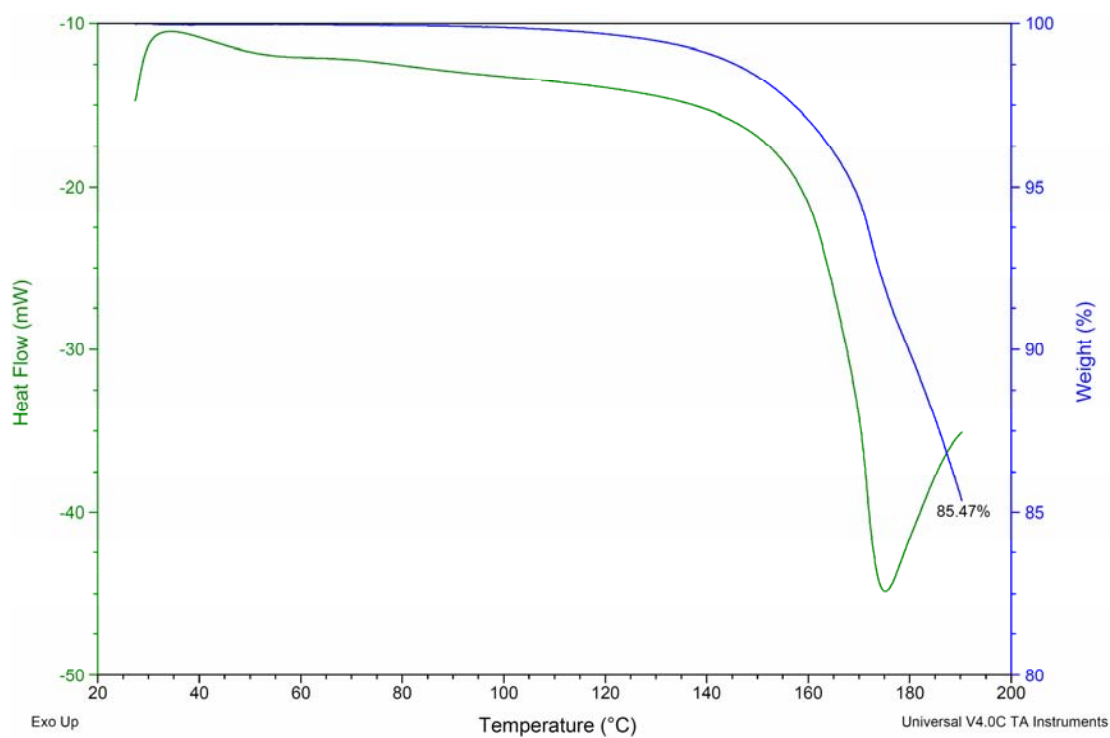


Figure B.45. 3 mol% feed 1,2-Epoxydecane 1st Scan 5.96 mol% incorporation

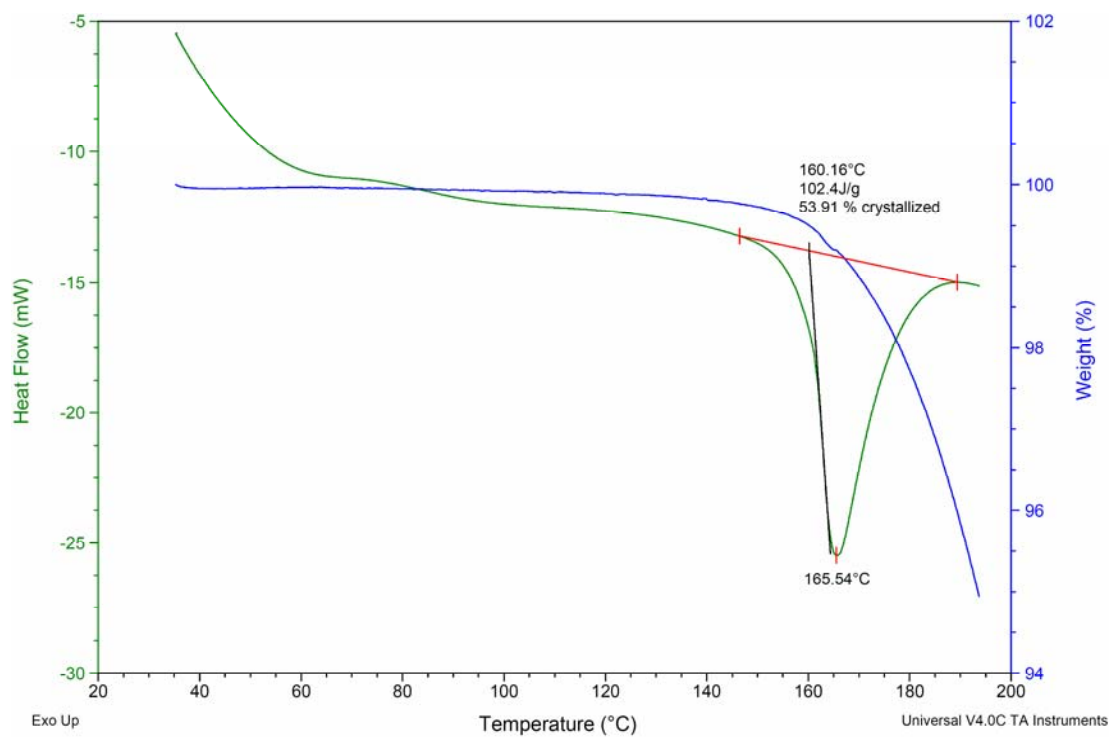


Figure B.46. 3 mol% feed 1,2-Epoxydecane 2nd Scan 5.96 mol% incorporation

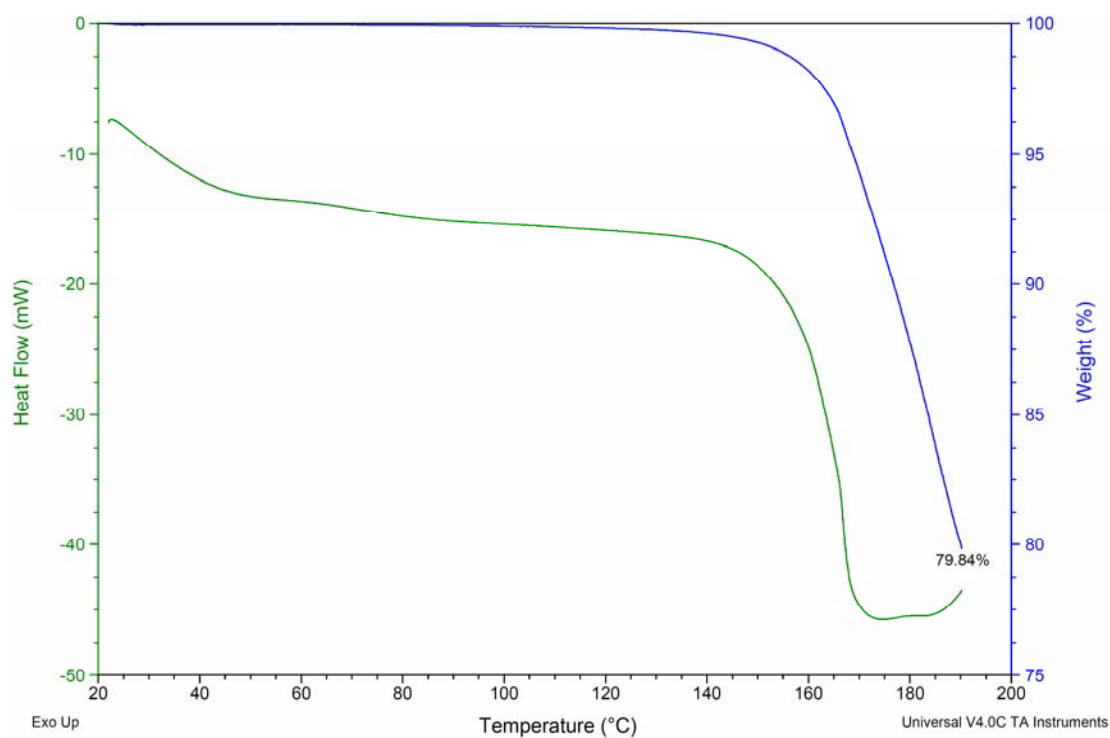


Figure B.47. 7.4 mol% feed 1,2-Epoxydecane 1st Scan 10.48 mol% incorporation

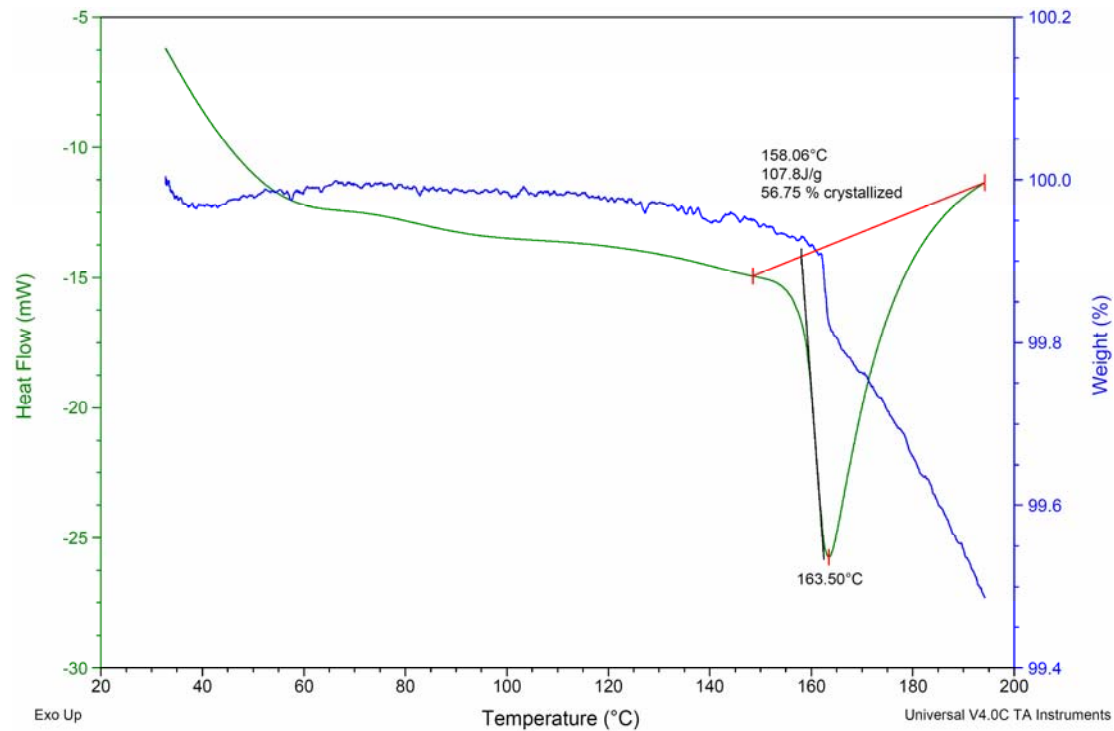


Figure B.48. 7.4 mol% feed 1,2-Epoxydecane 2nd Scan 10.48 mol% incorporation

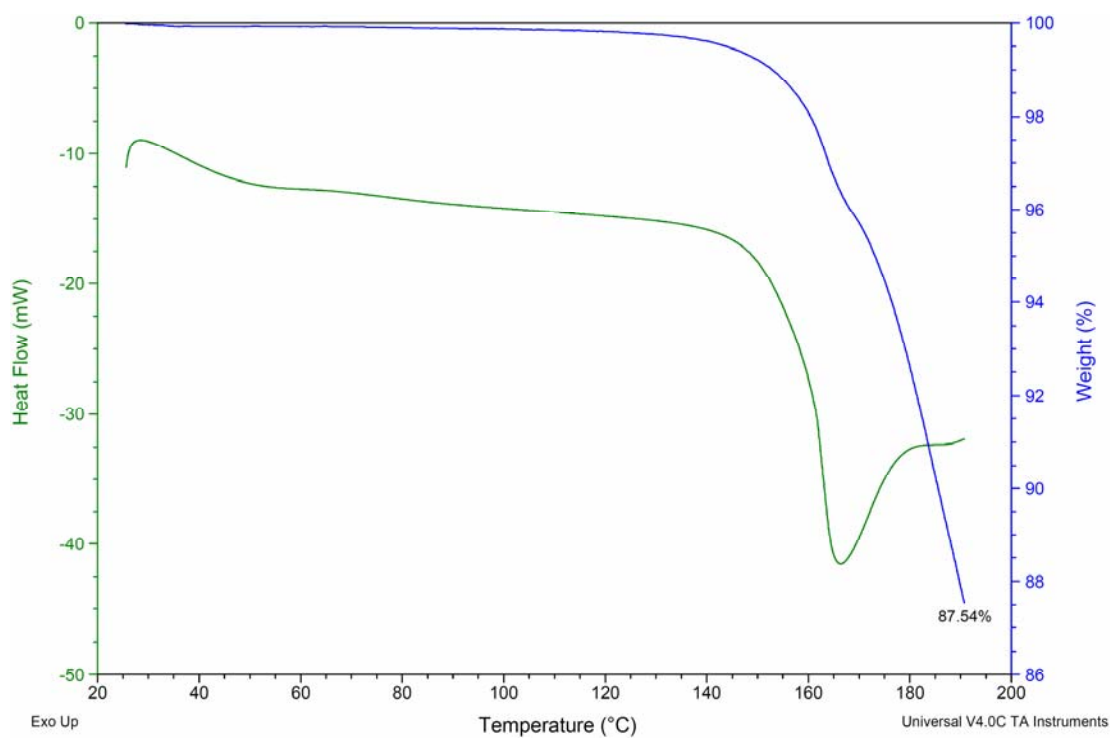


Figure B.49. 10 mol% feed 1,2-Epoxydecane 1st Scan 11.99 mol% incorporation

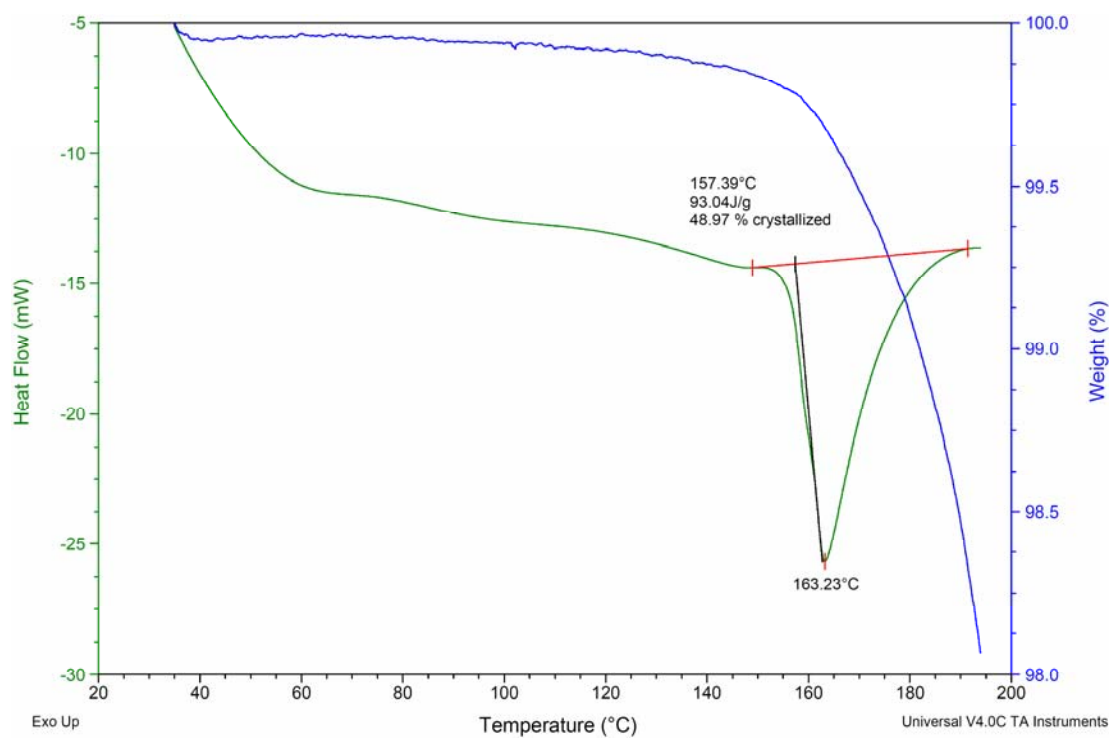


Figure B.50. 10 mol% feed 1,2-Epoxydecane 2nd Scan 11.99 mol% incorporation

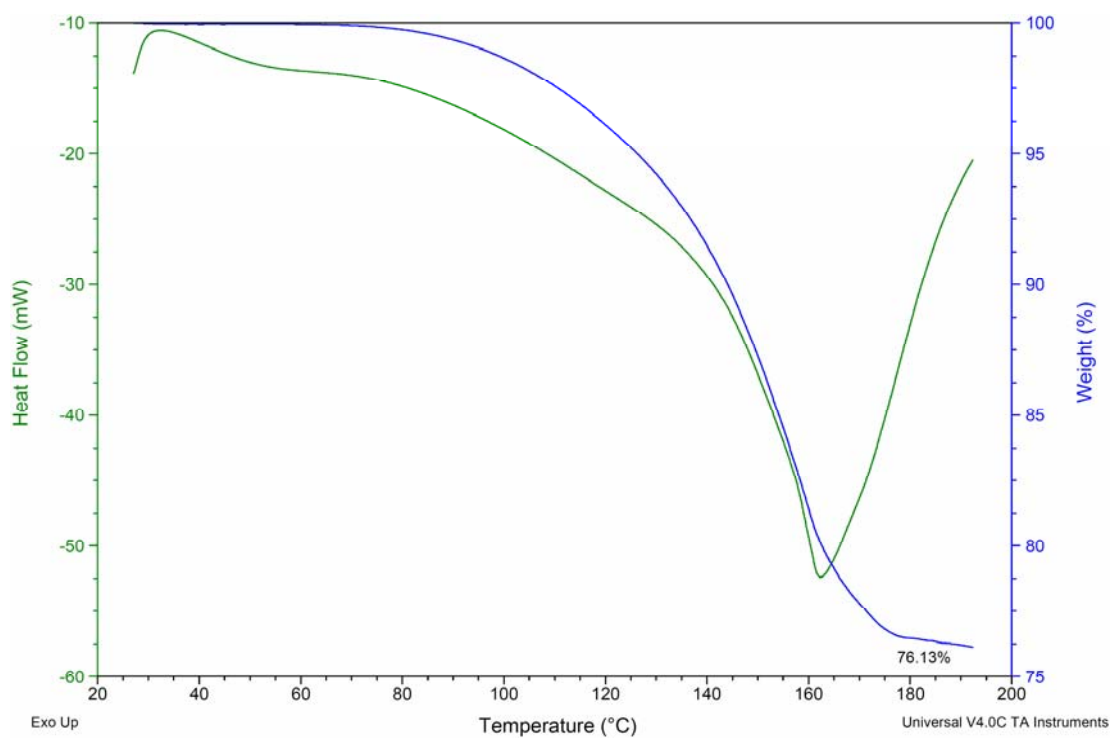


Figure B.51. 15 mol% feed 1,2-Epoxydecane 1st Scan 14.33 mol% incorporation

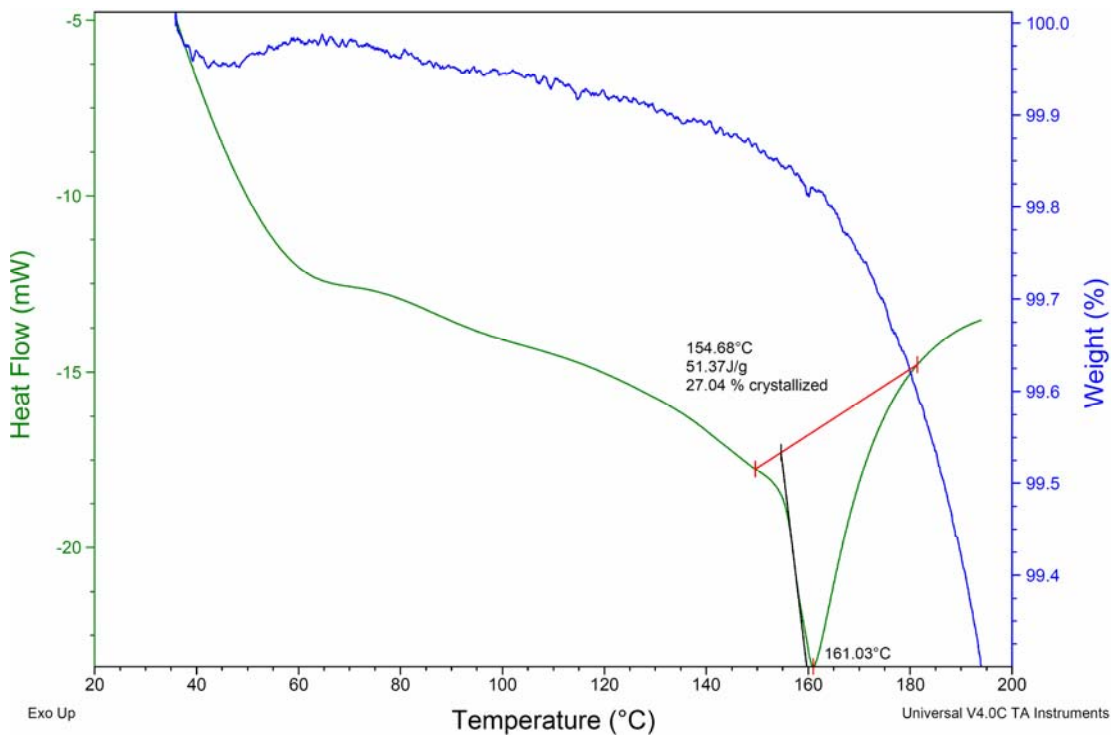


Figure B.52. 15 mol% feed 1,2-Epoxydecane 2nd Scan 14.33 mol% incorporation

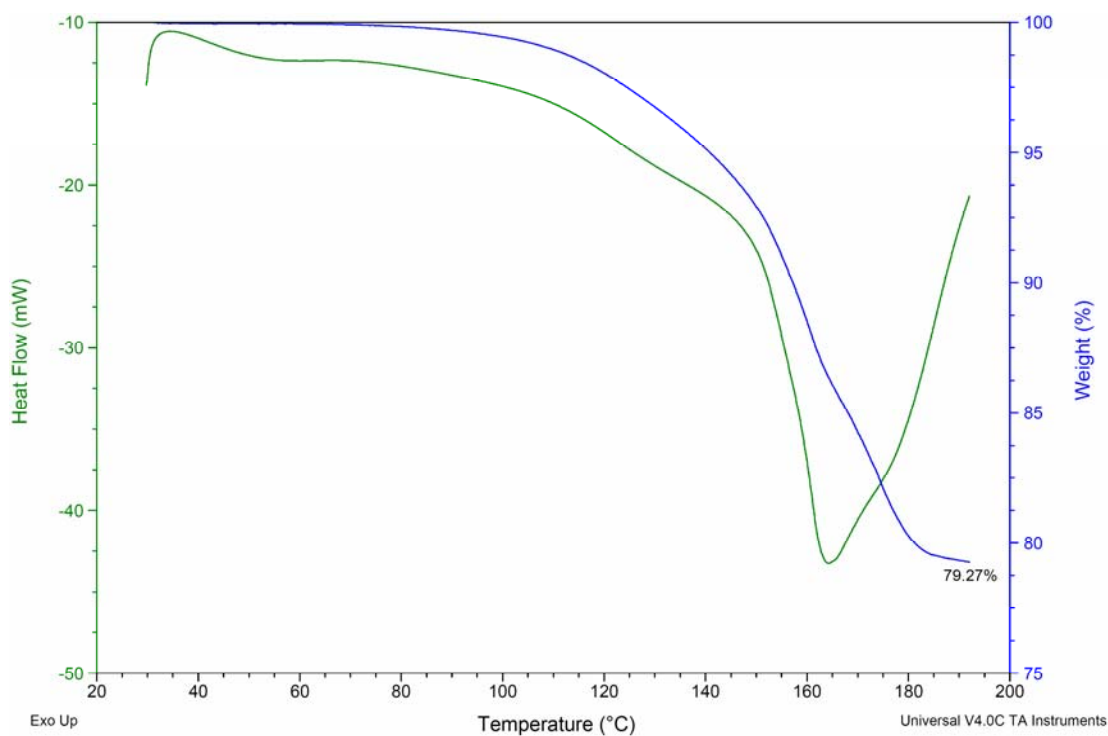


Figure B.53. 20 mol% feed 1,2-Epoxydecane 1st Scan 15.14 mol% incorporation

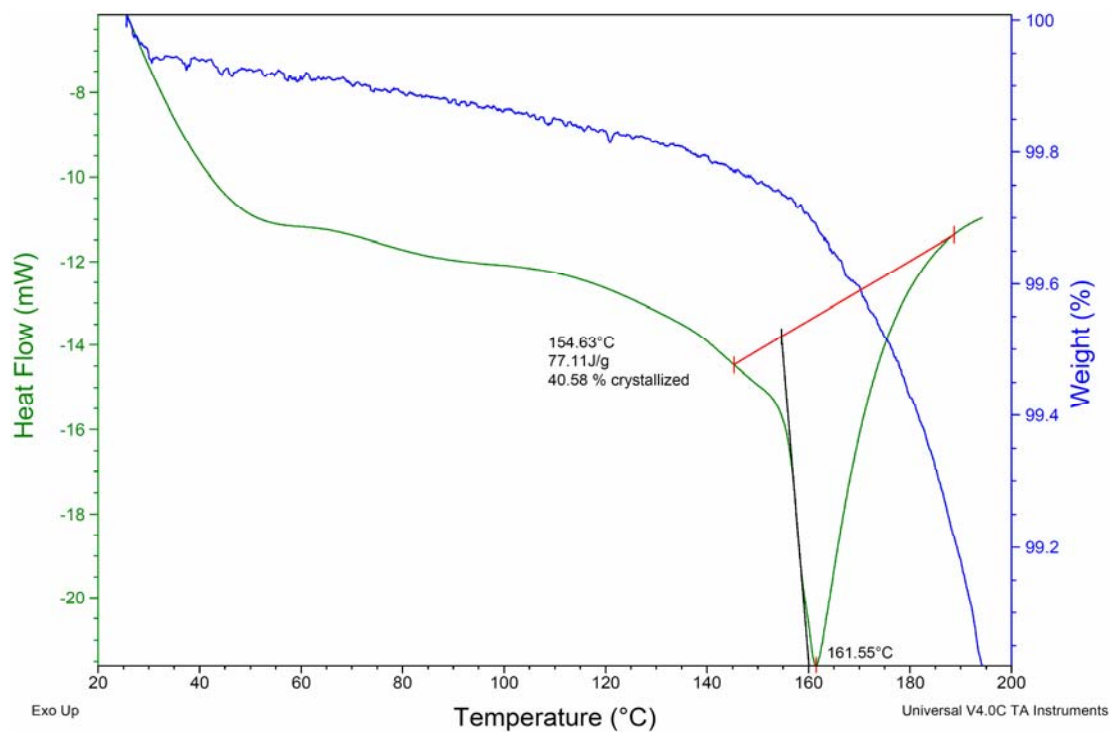


Figure B.54. 20 mol% feed 1,2-Epoxydecane 2nd Scan 15.14 mol% incorporation

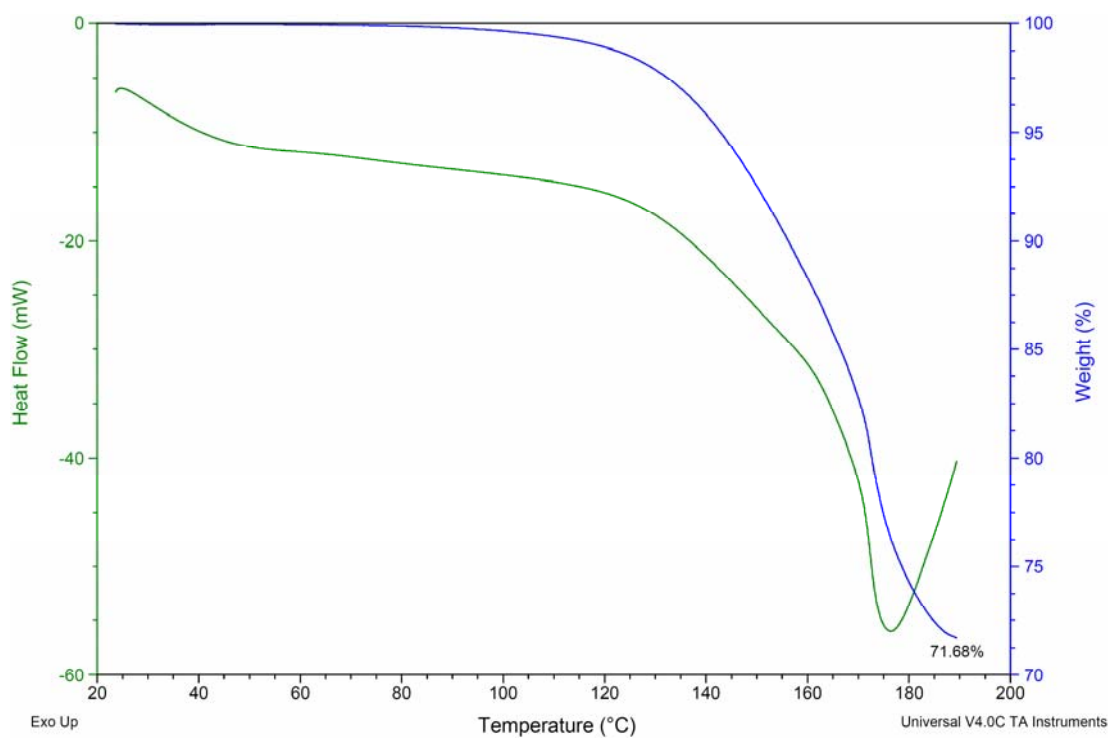


Figure B.55. 3 mol% feed 1,2-Epoxydodecane 1st Scan 5.93 mol% incorporation

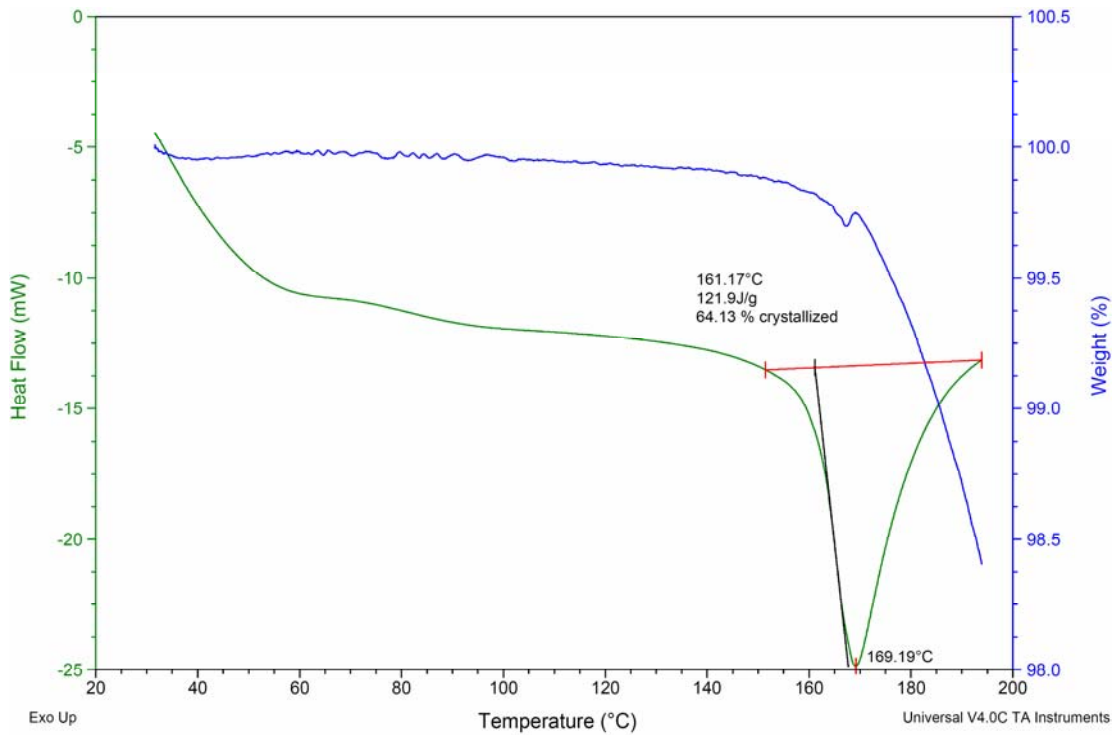


Figure B.56. 3 mol% feed 1,2-Epoxydodecane 2nd Scan 5.93 mol% incorporation

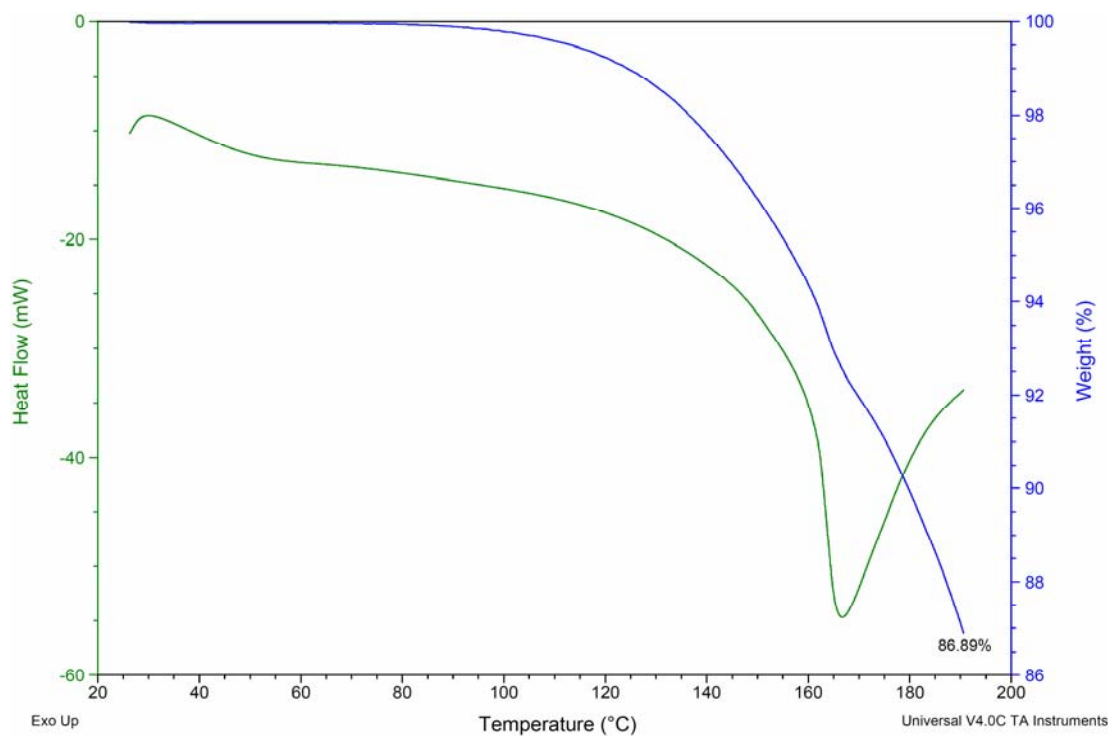


Figure B.57. 7.4 mol% feed 1,2-Epoxydodecane 1st Scan 9.93 mol% incorporation

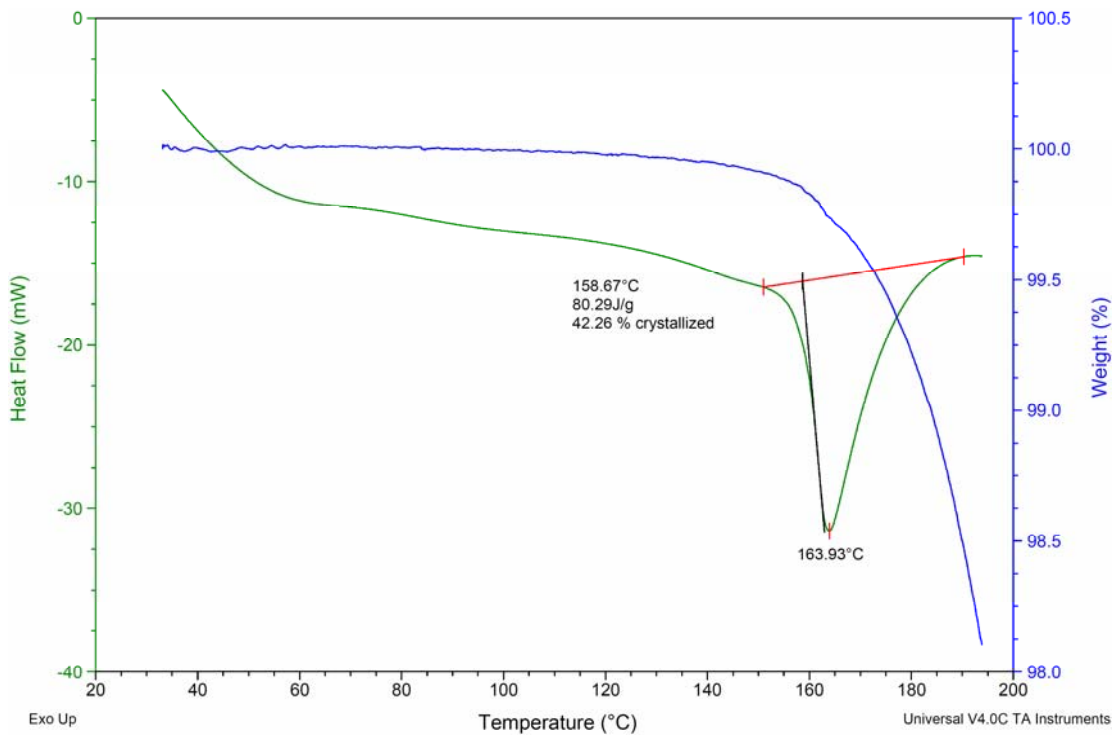


Figure B.58. 7.4 mol% feed 1,2-Epoxydodecane 2nd Scan 9.93 mol% incorporation

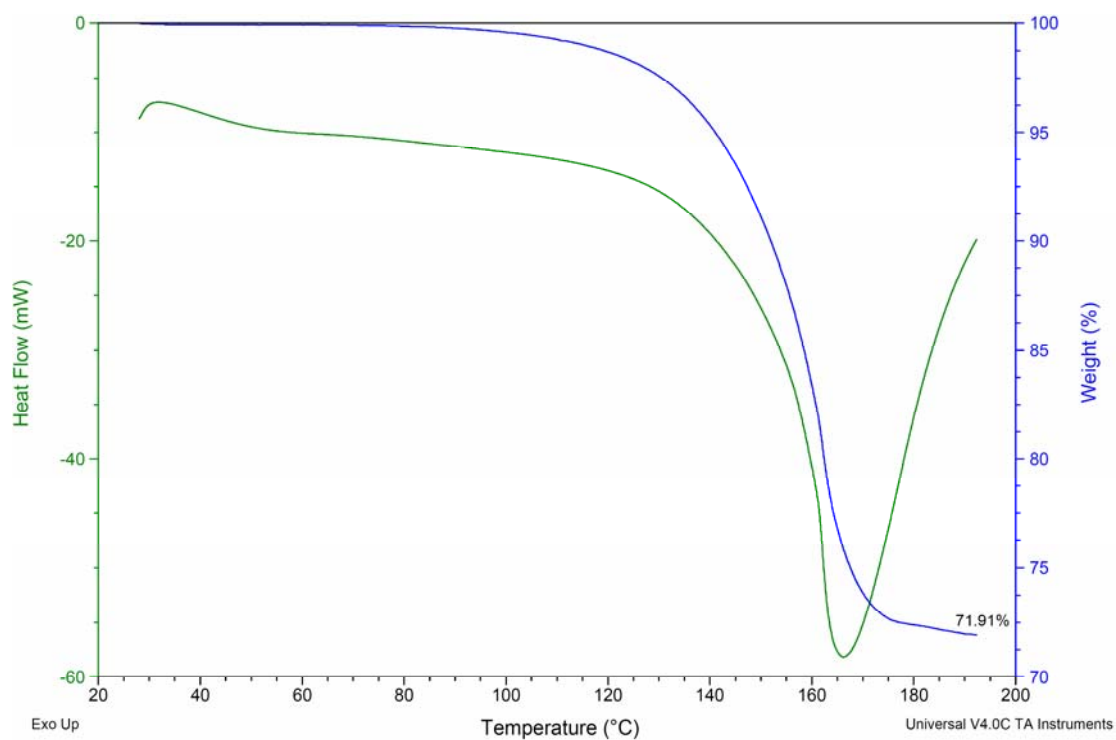


Figure B.59. 10 mol% feed 1,2-Epoxydodecane 1st Scan 11.47 mol% incorporation

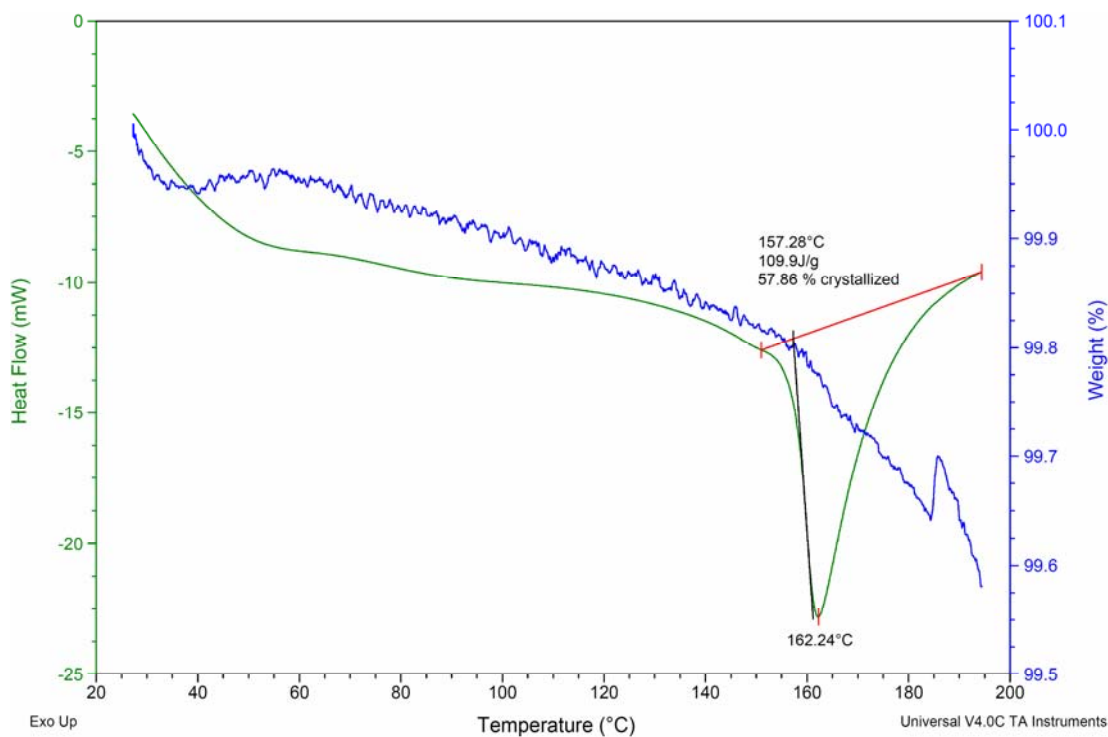


Figure B.60. 10 mol% feed 1,2-Epoxydodecane 2nd Scan 11.47 mol% incorporation

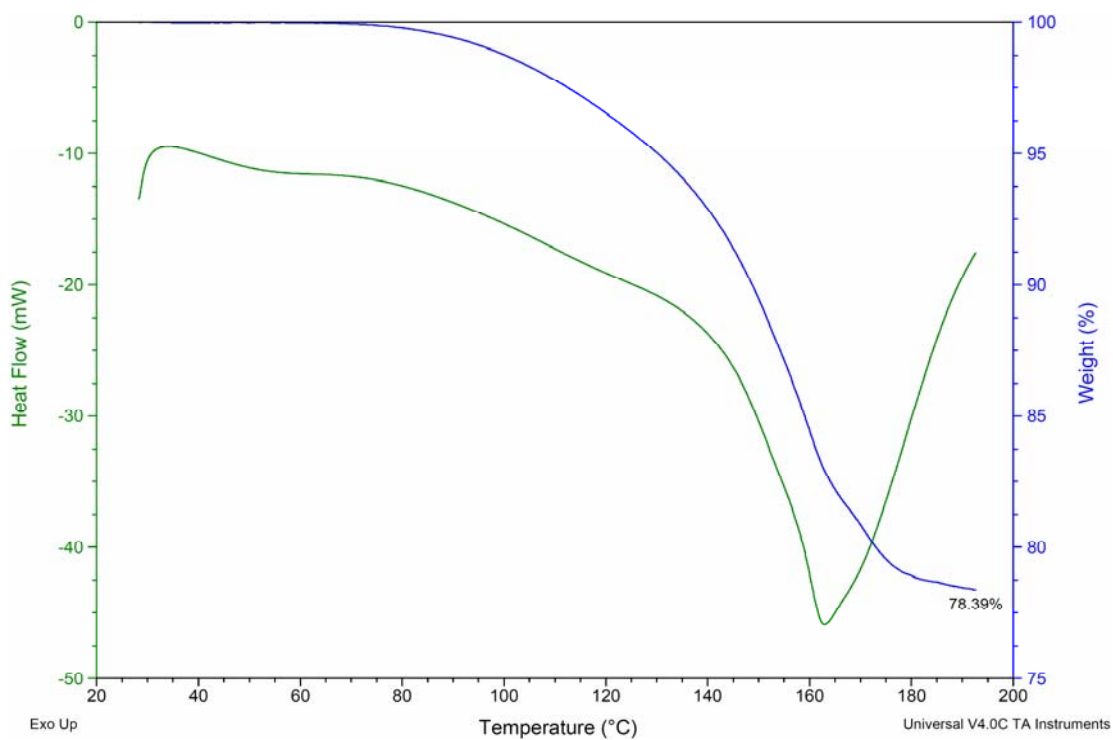


Figure B.61. 15 mol% feed 1,2-Epoxydodecane 1st Scan 16.41 mol% incorporation

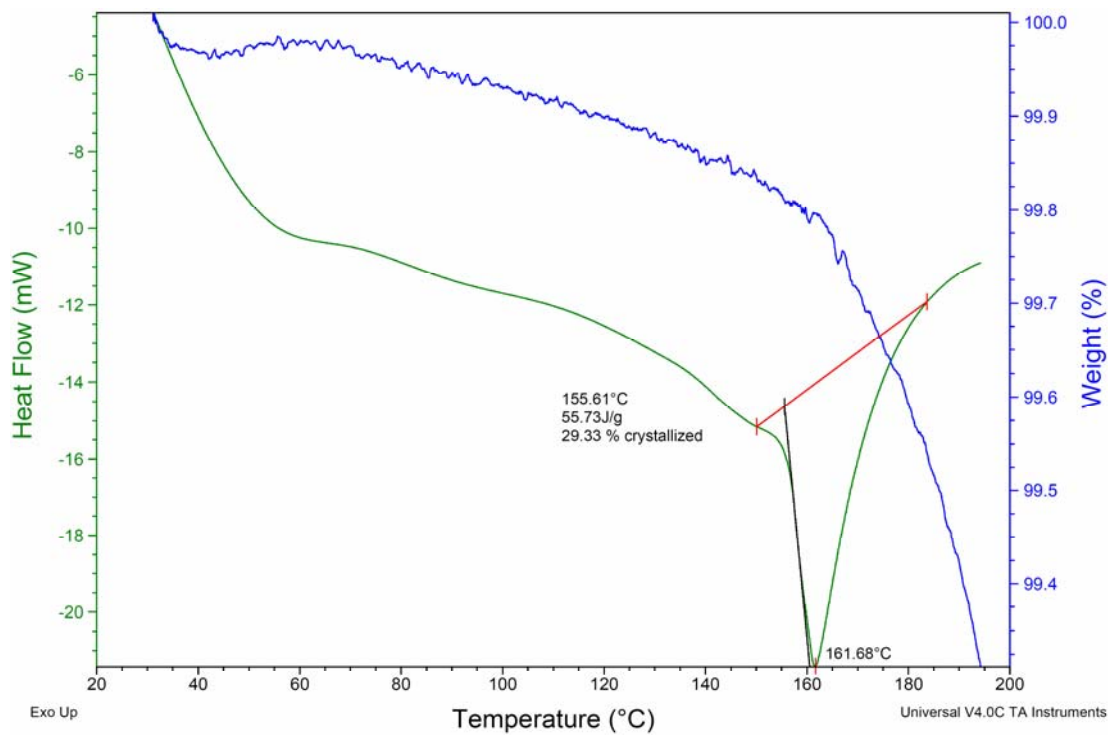


Figure B.62. 15 mol% feed 1,2-Epoxydodecane 2nd Scan 16.41 mol% incorporation

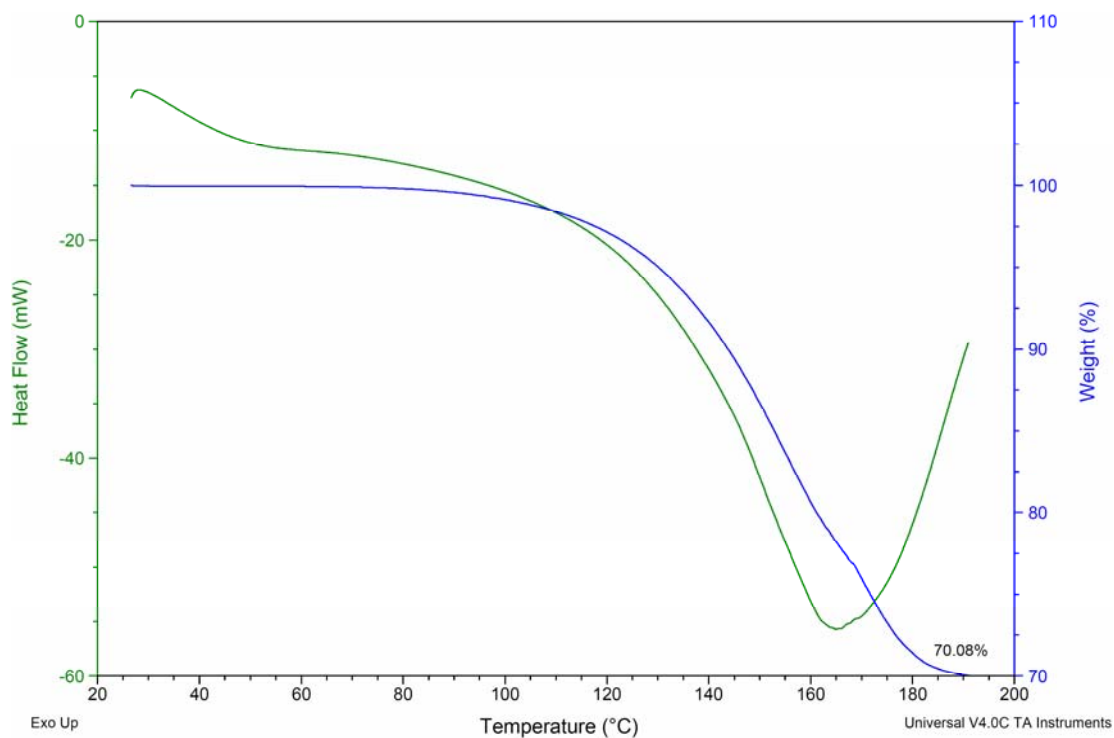


Figure B.63. 20 mol% feed 1,2-Epoxydodecane 1st Scan 22.29 mol% incorporation

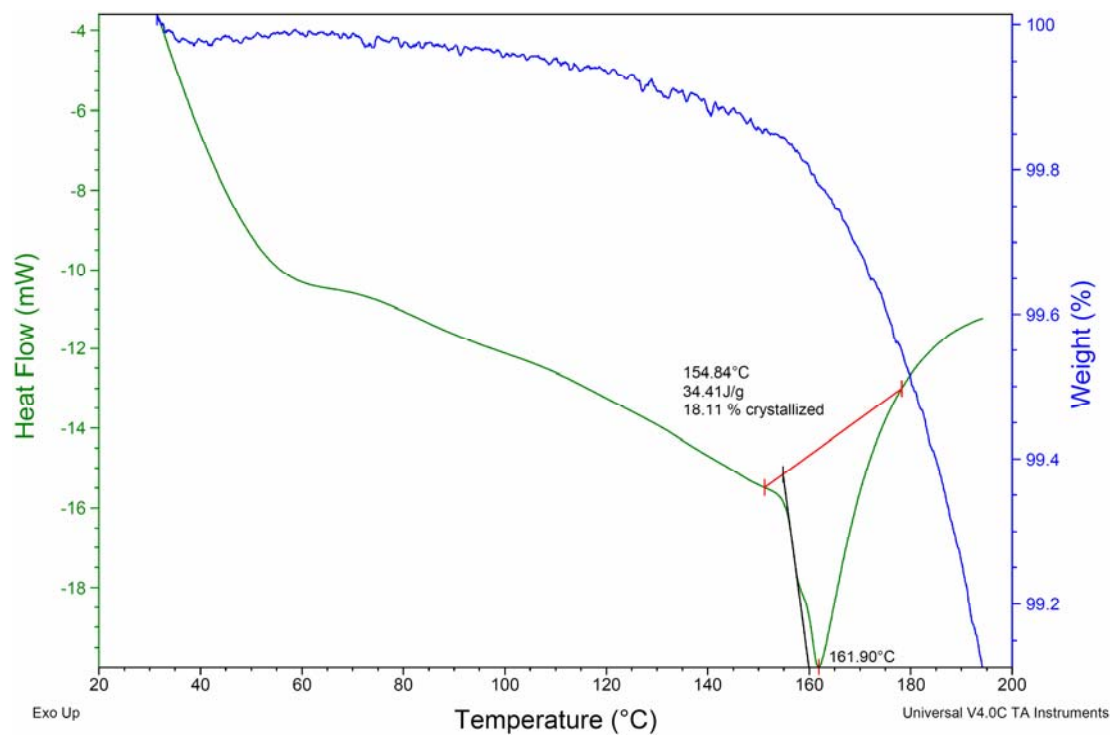
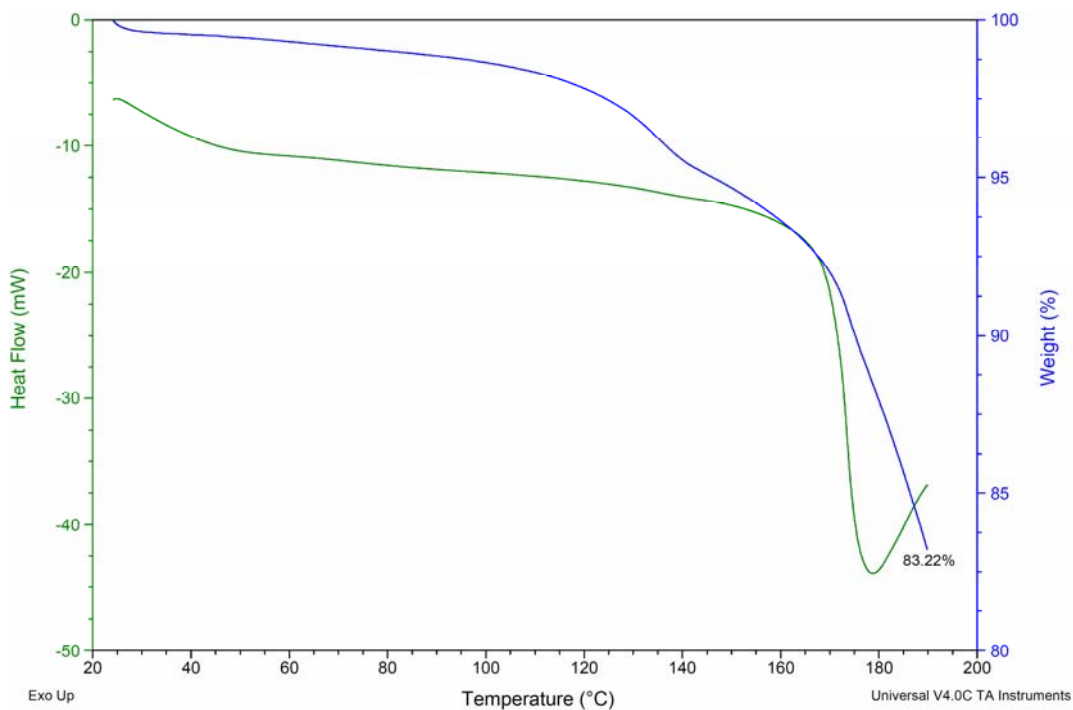
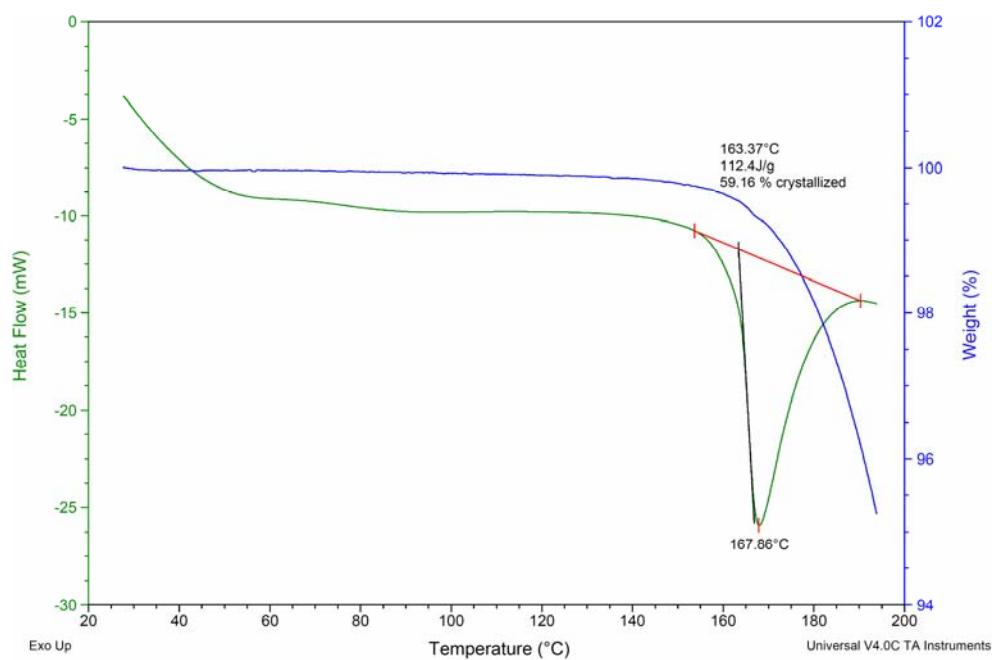


Figure B.64. 20 mol% feed 1,2-Epoxydodecane 2nd Scan 22.29 mol% incorporation

Chapter III: Trioxane and 4-Alkyl-1,3-Dioxolanes Copolymers from Table 3.1**Figure B.65.** 3 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 5.32 mol% incorporation**Figure B.66.** 3 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 5.32 mol% incorporation

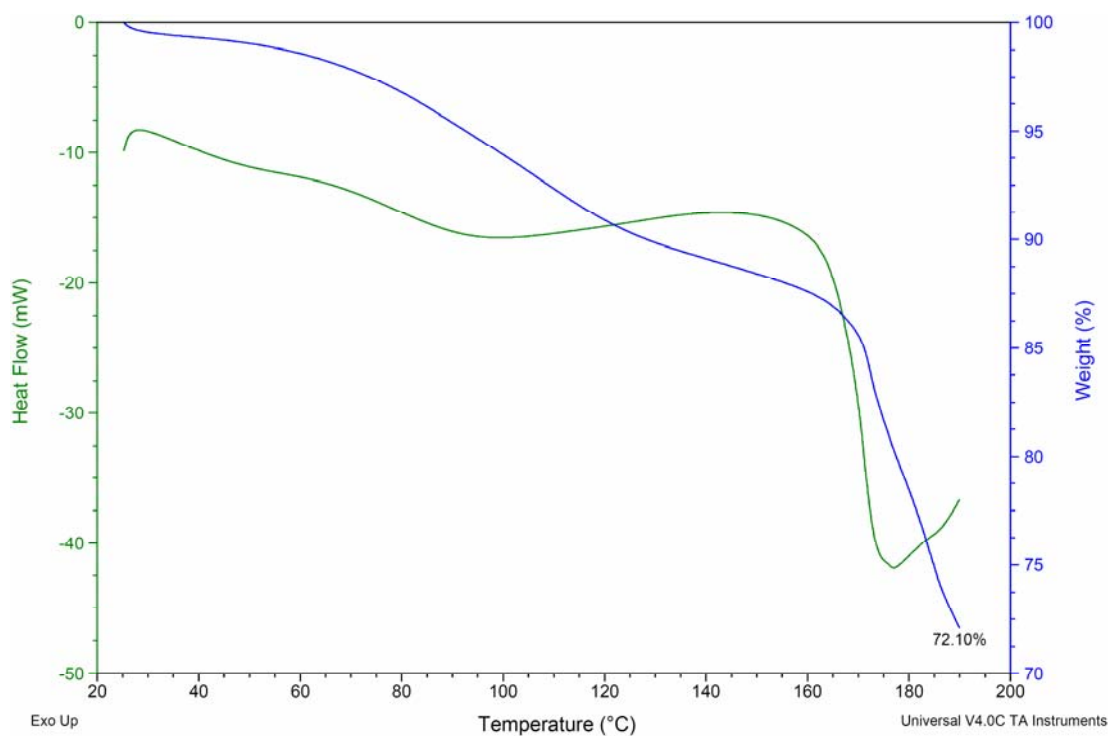


Figure B.67. 7.4 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 7.01 mol% incorporation

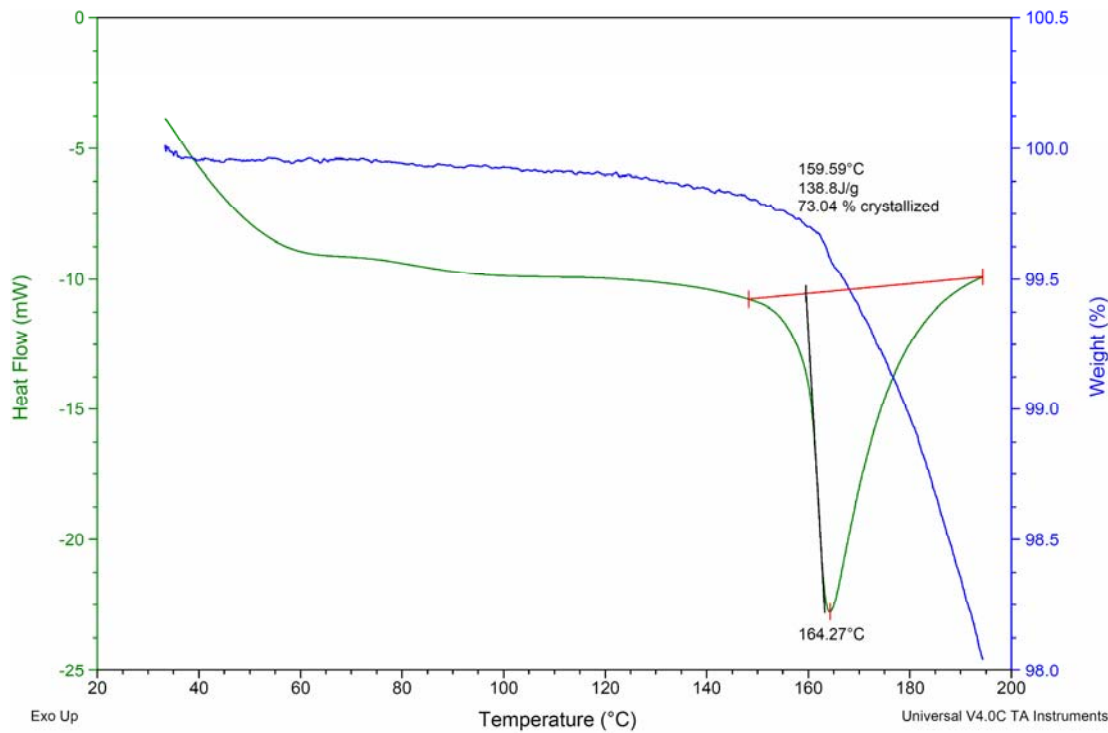


Figure B.68. 7.4 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 7.01 mol% incorporation

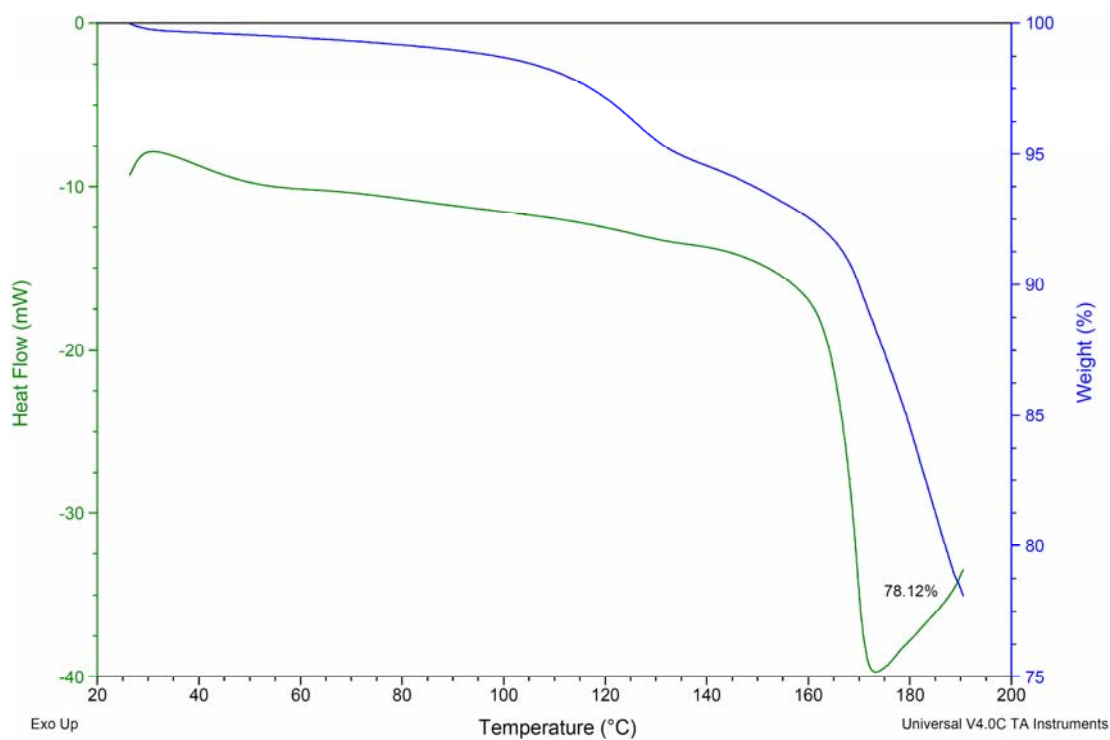


Figure B.69. 10 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 9.14 mol% incorporation

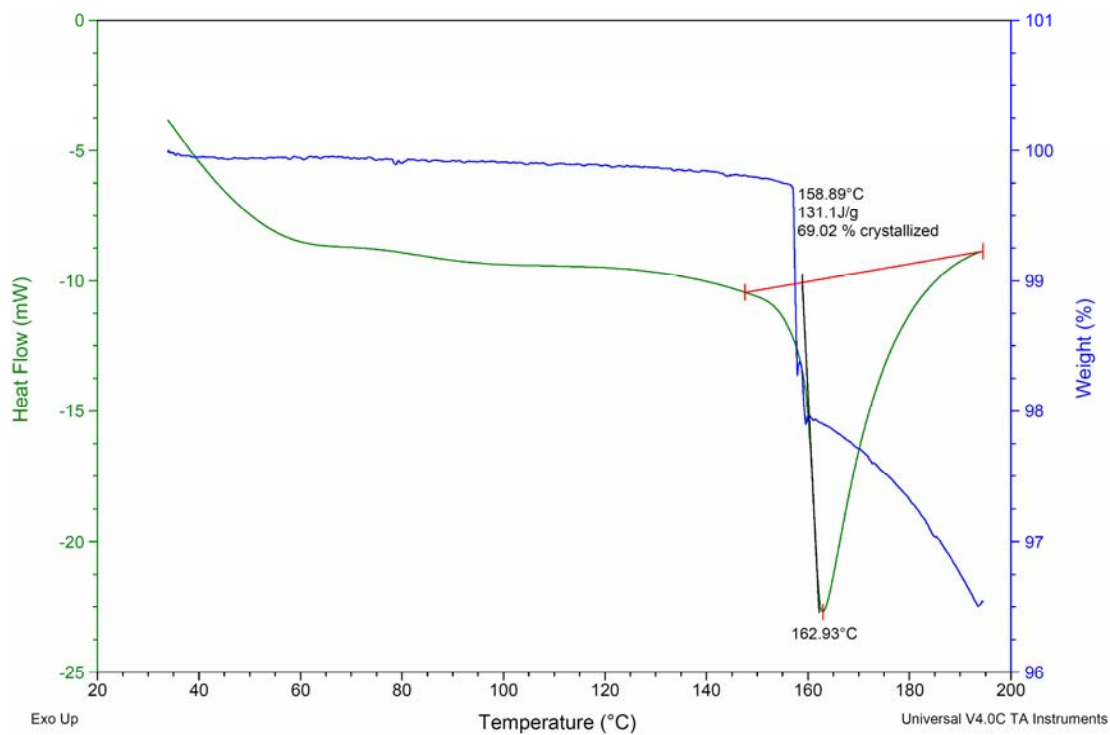


Figure B.70. 10 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 9.14 mol% incorporation

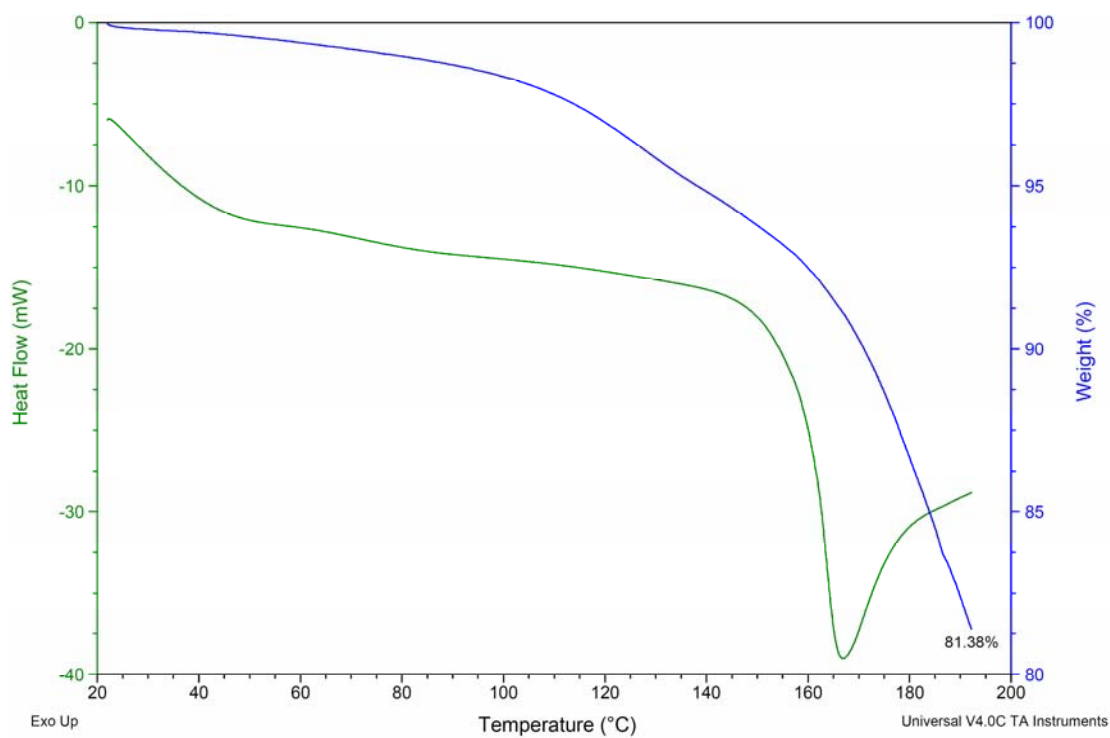


Figure B.71. 15 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 9.13 mol% incorporation

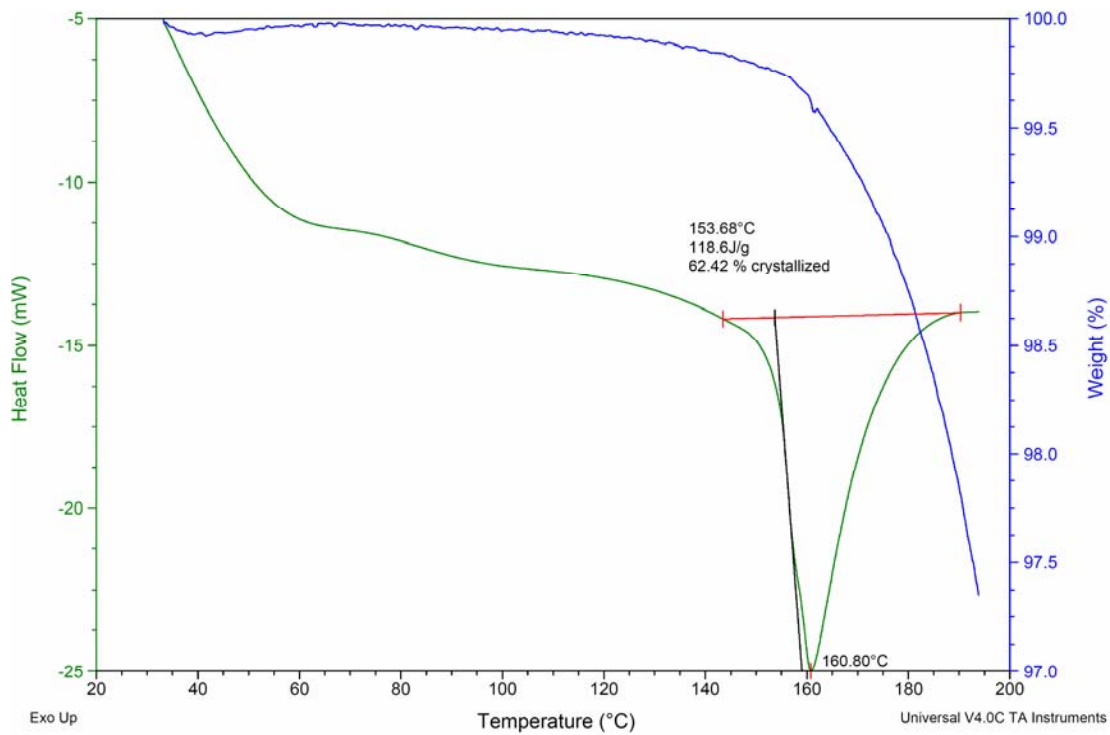


Figure B.72. 15 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 9.13 mol% incorporation

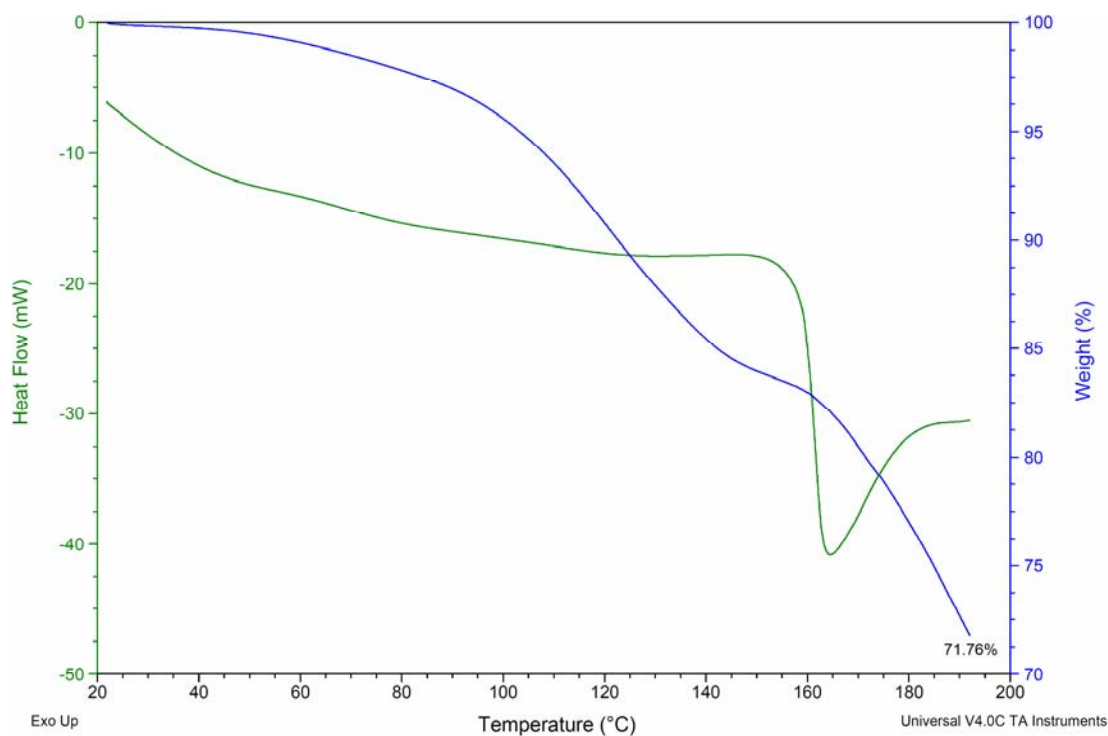


Figure B.73. 20 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 11.81 mol% incorporation

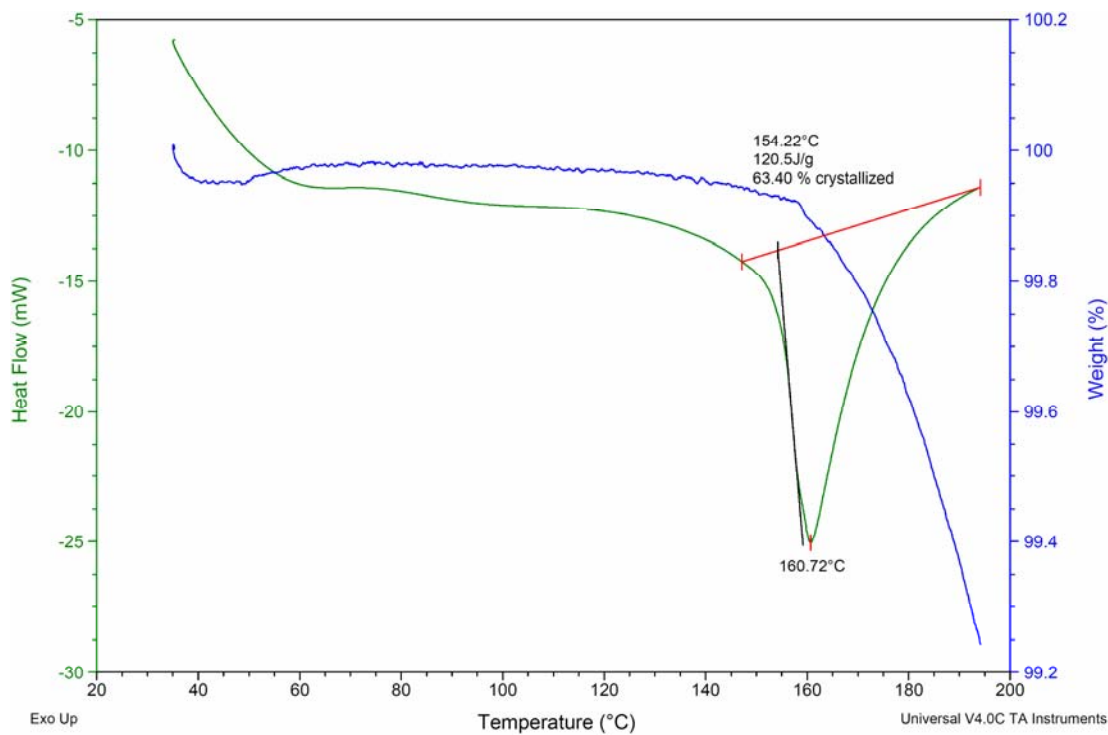


Figure B.74. 20 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 11.81 mol% incorporation

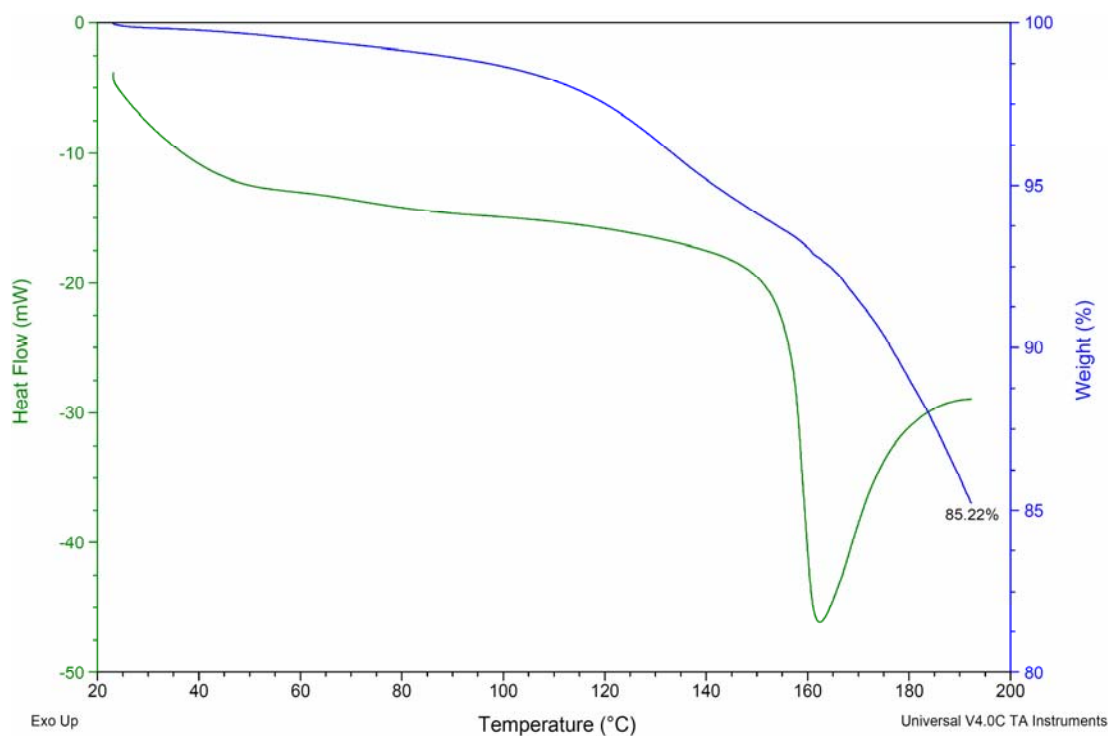


Figure B.75. 25 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 12.15 mol% incorporation

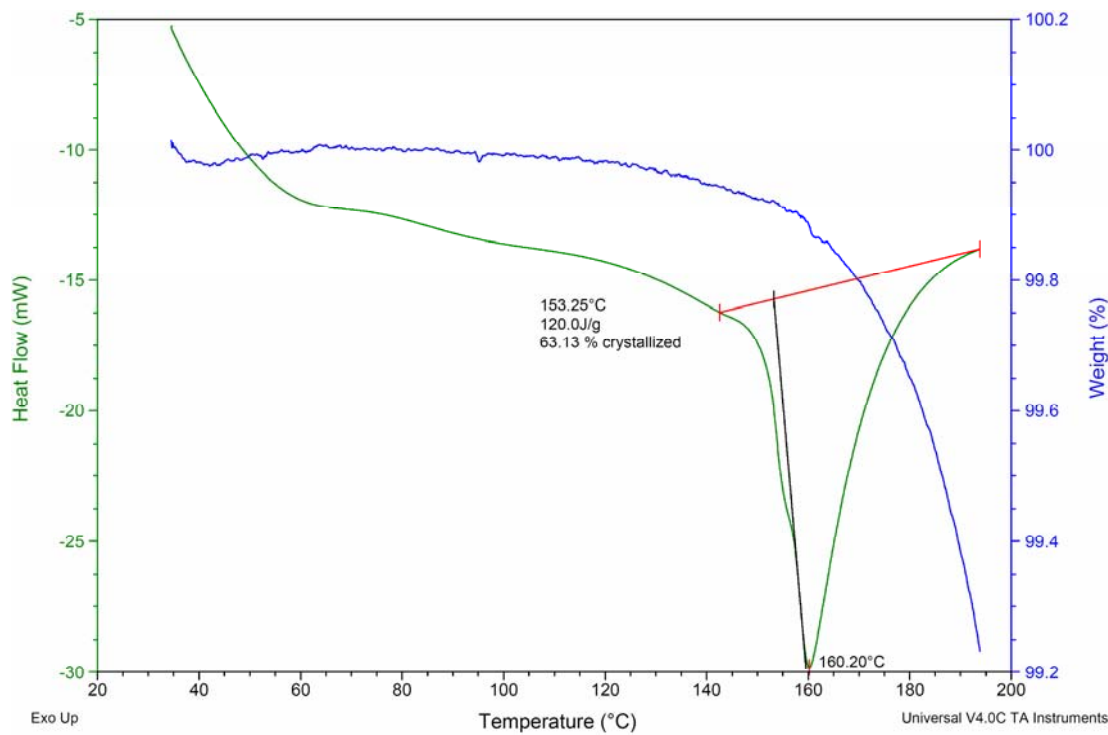


Figure B.76. 25 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 12.15 mol% incorporation

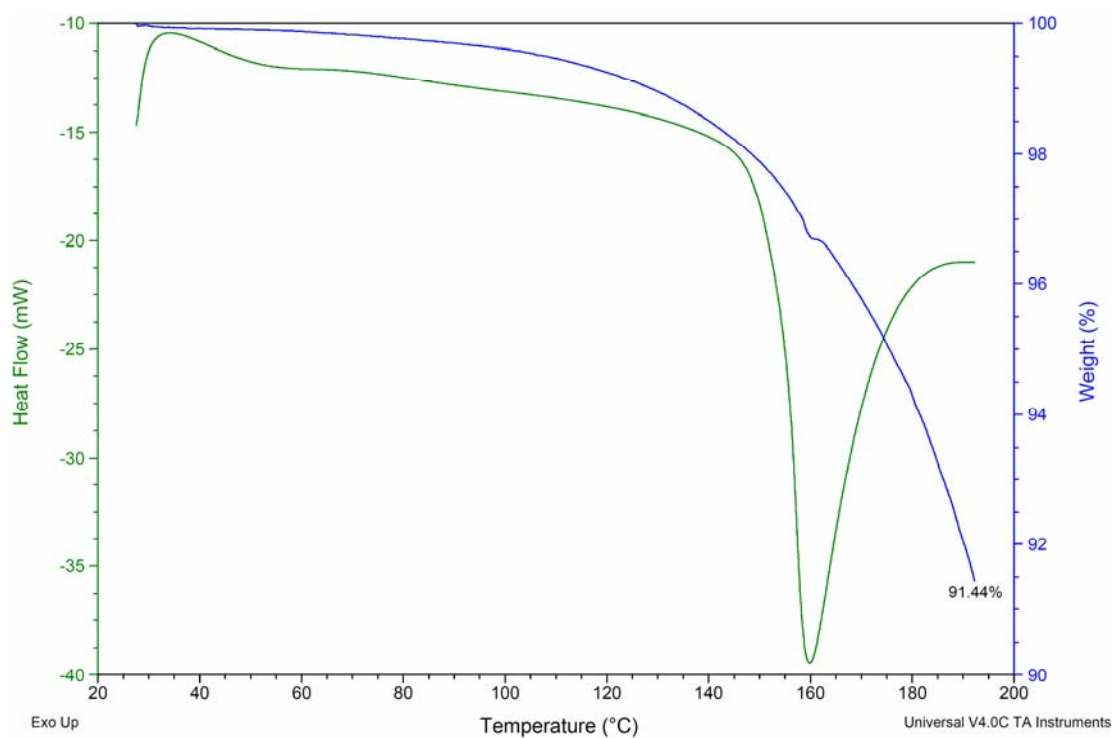


Figure B.77. 30 mol% feed 4-Ethyl-1,3-Dioxolane 1st Scan 12.25 mol% incorporation

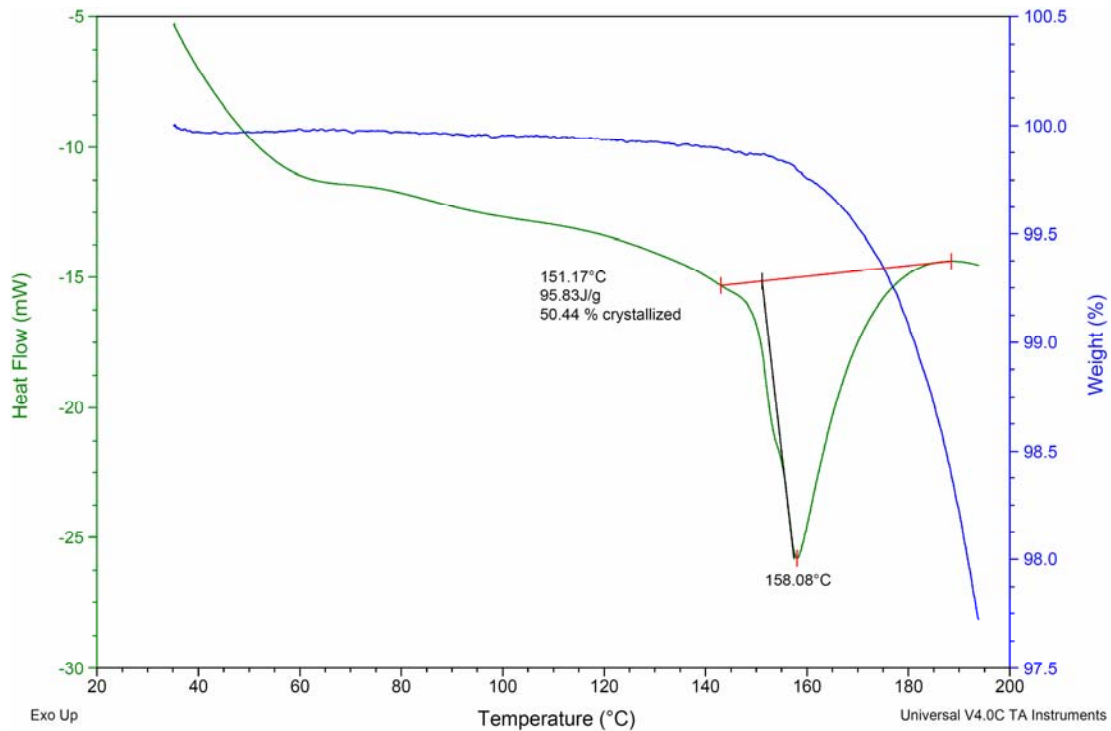


Figure B.78. 30 mol% feed 4-Ethyl-1,3-Dioxolane 2nd Scan 12.25 mol% incorporation

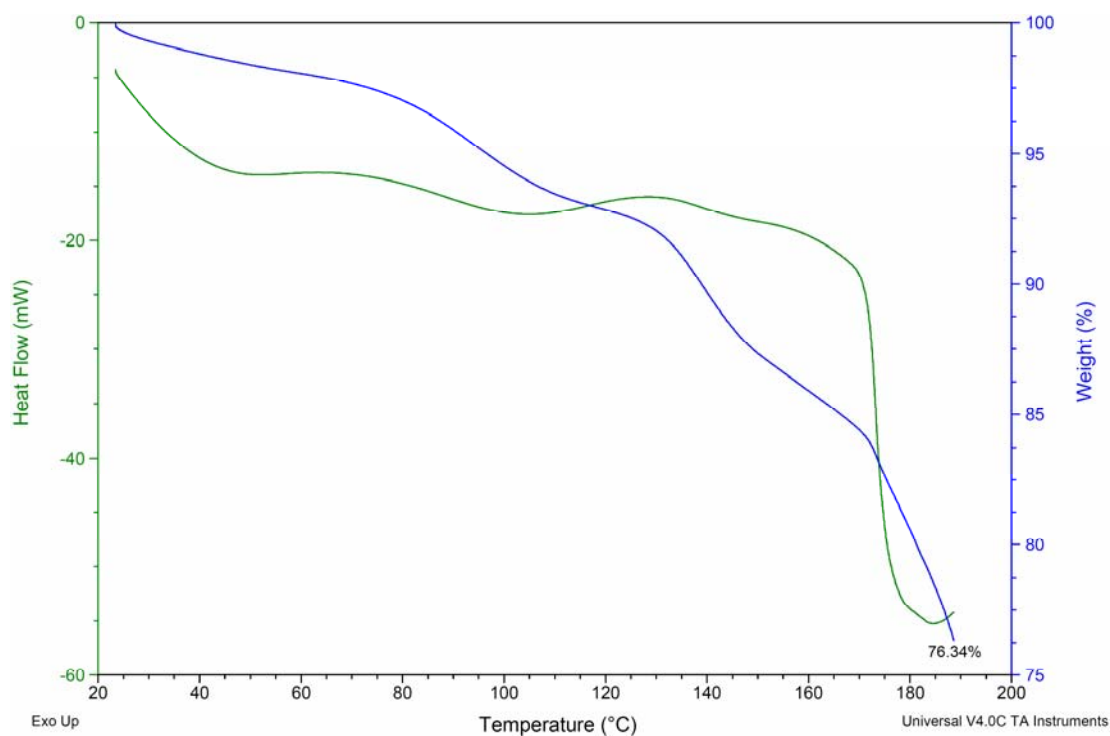


Figure B.79. 3 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 3.46 mol% incorporation

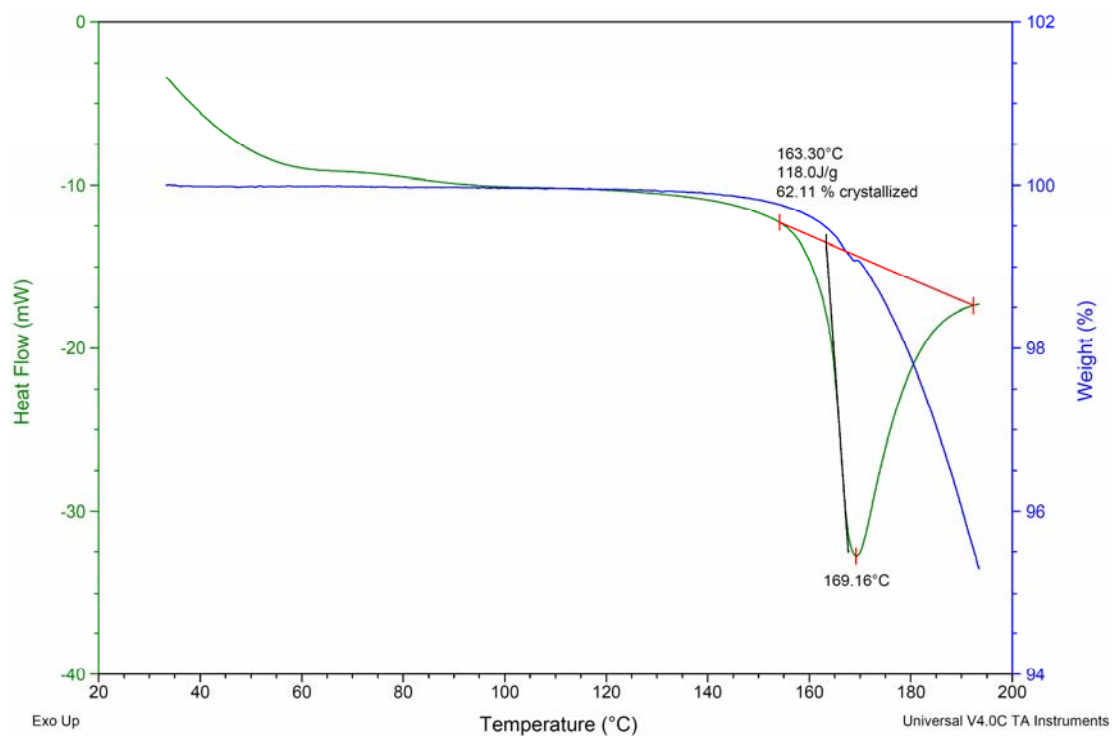


Figure B.80. 3 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 3.46 mol% incorporation

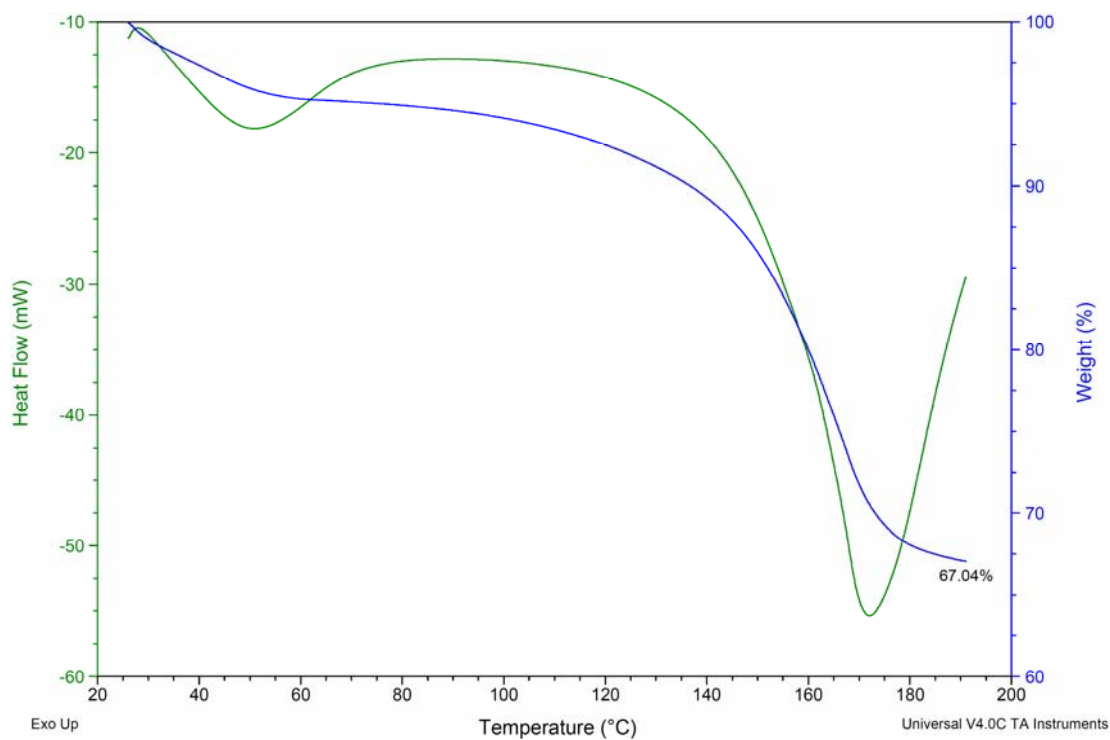


Figure B.81. 7.4 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 6.55 mol% incorporation

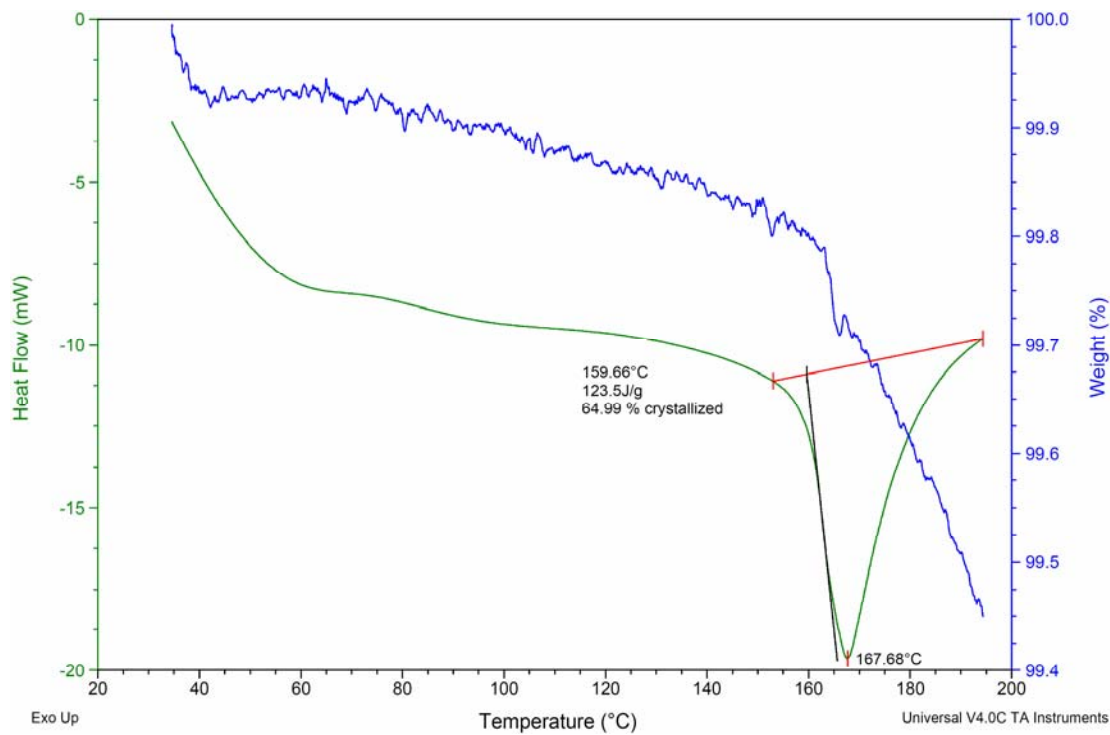


Figure B.82. 7.4 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 6.55 mol% incorporation

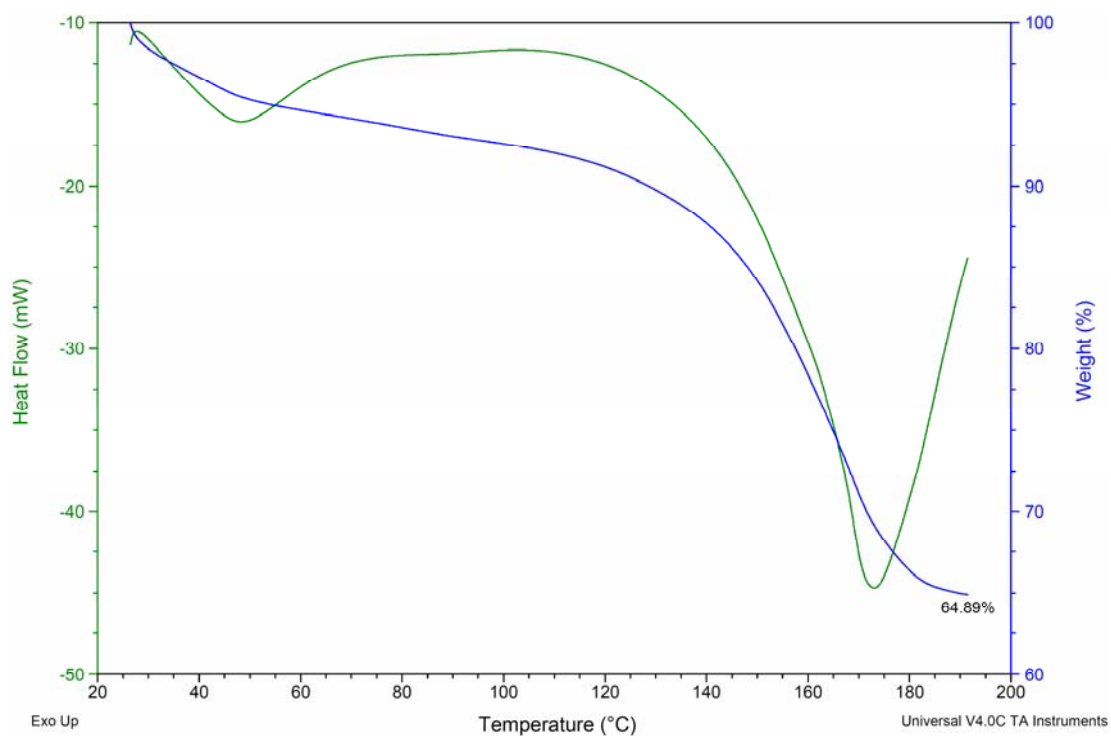


Figure B.83. 10 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 8.06 mol% incorporation

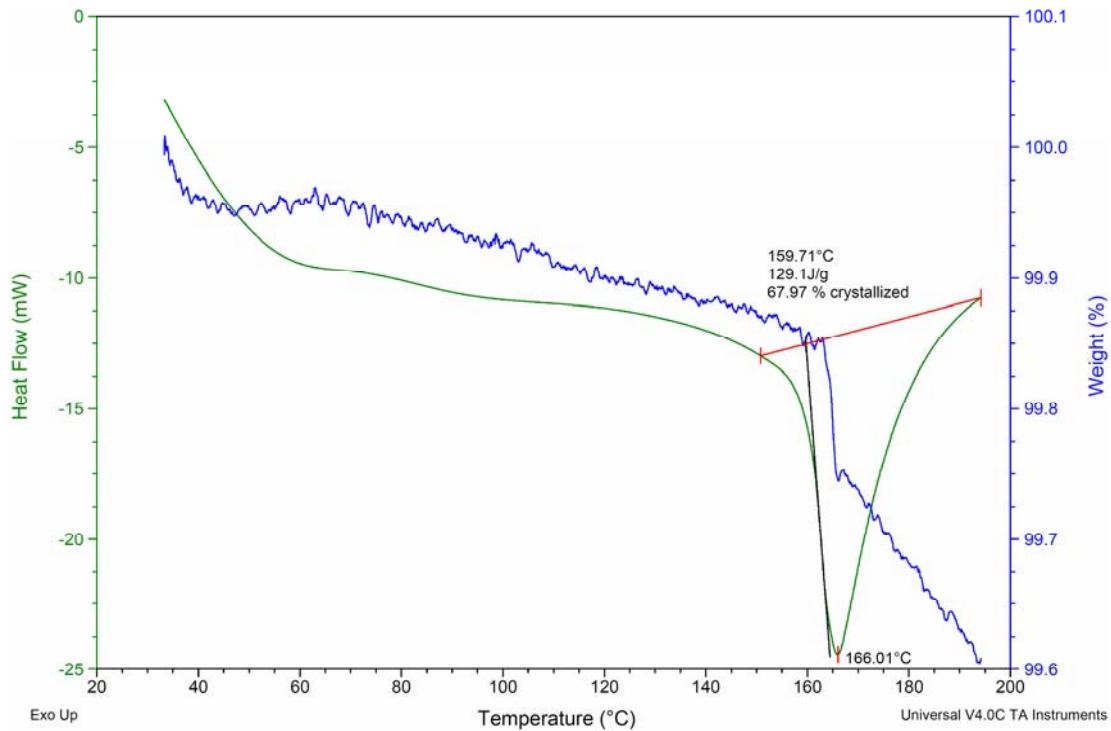


Figure B.84. 10 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 8.06 mol% incorporation

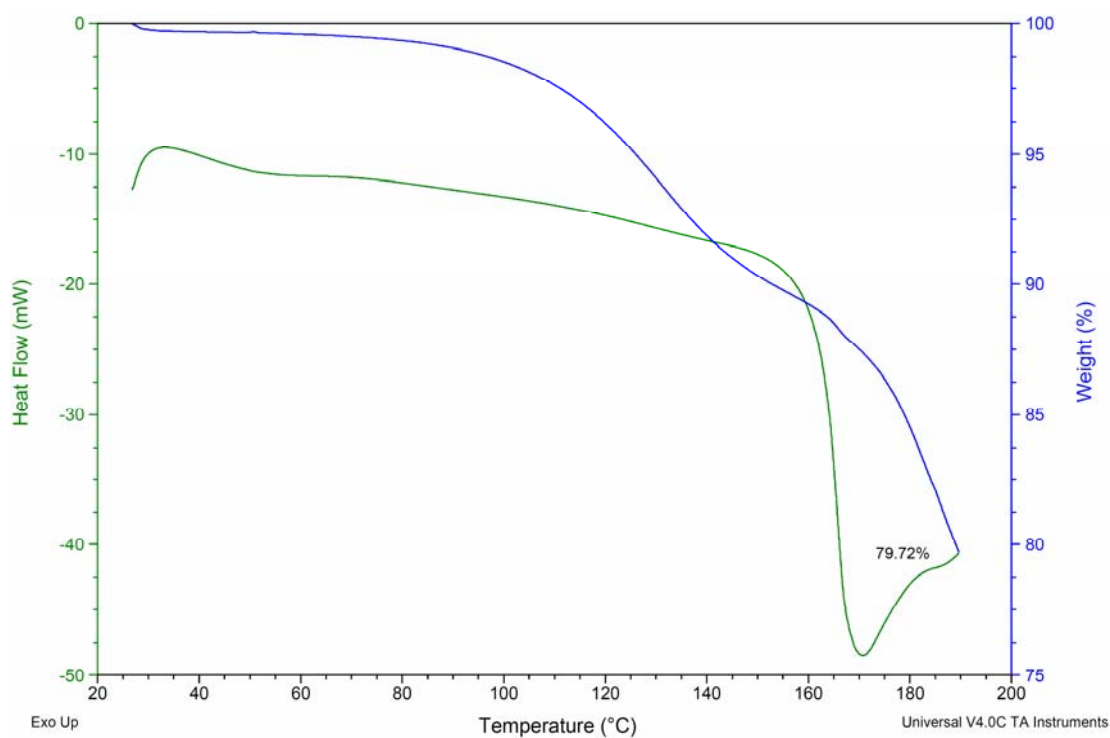


Figure B.85. 15 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 8.71 mol% incorporation

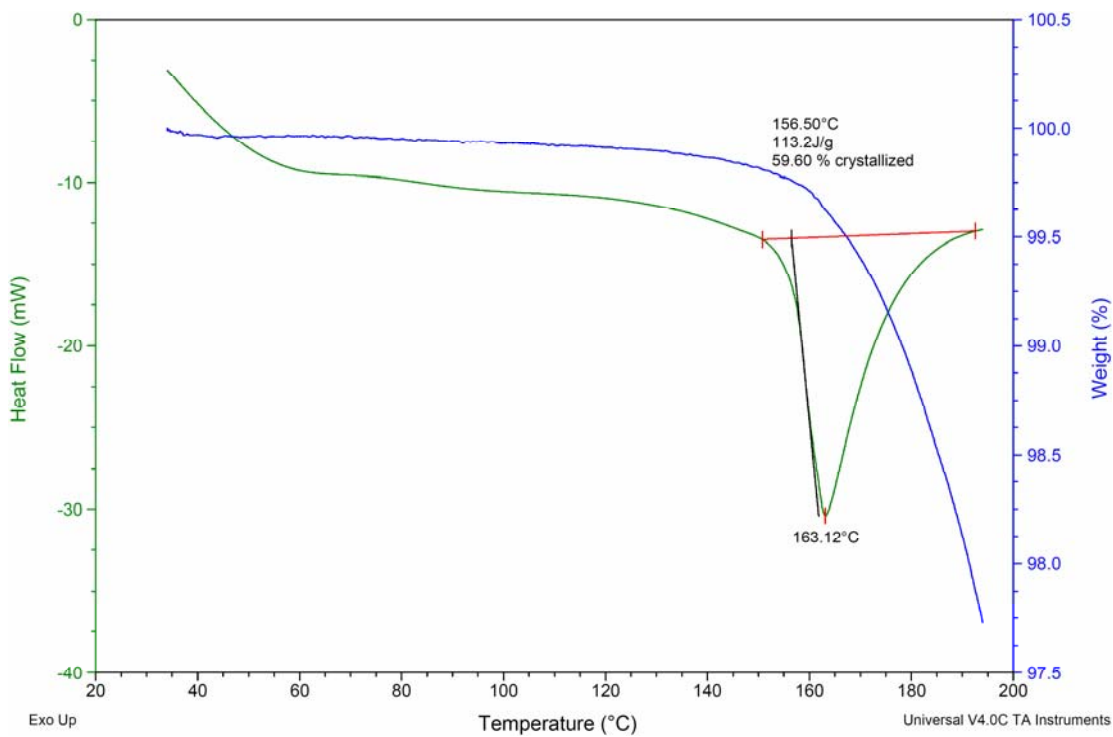


Figure B.86. 15 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 8.71 mol% incorporation

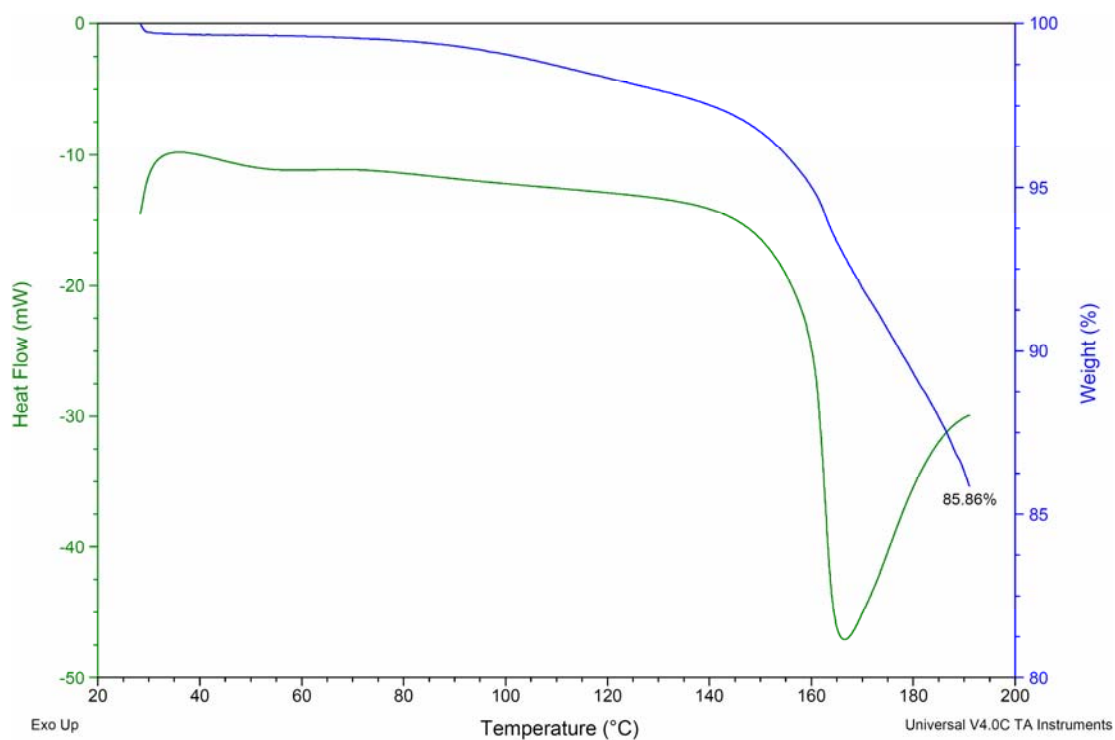


Figure B.87. 20 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 9.51 mol% incorporation

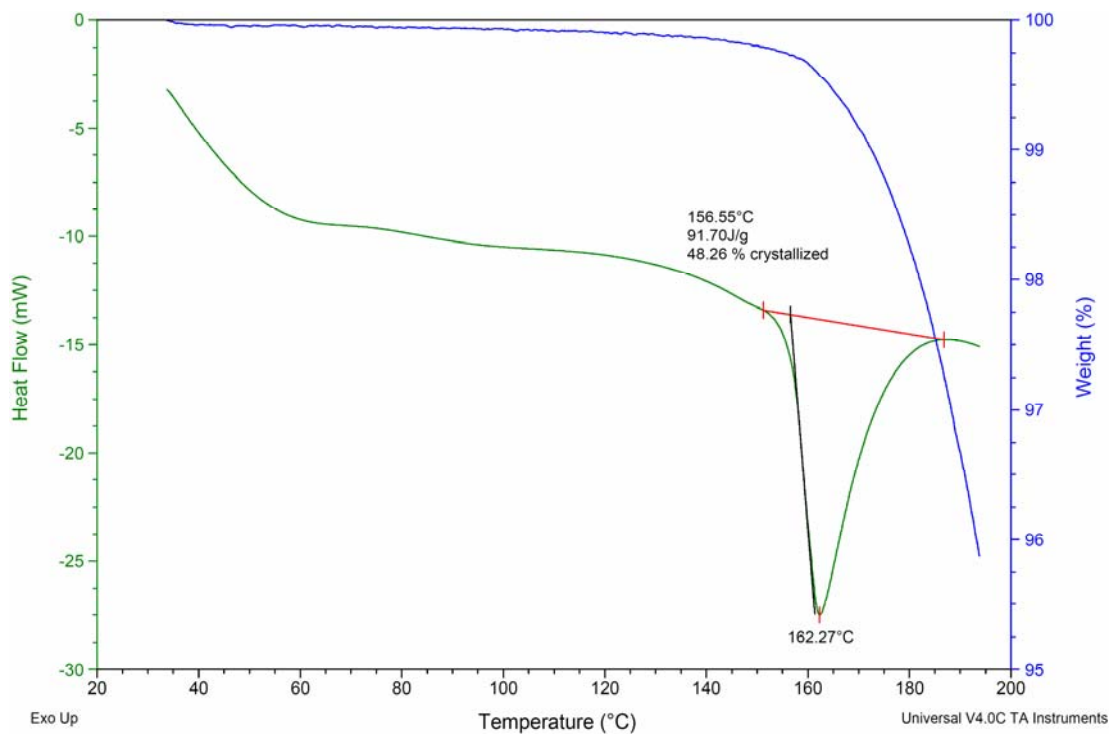


Figure B.88. 20 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 9.51 mol% incorporation

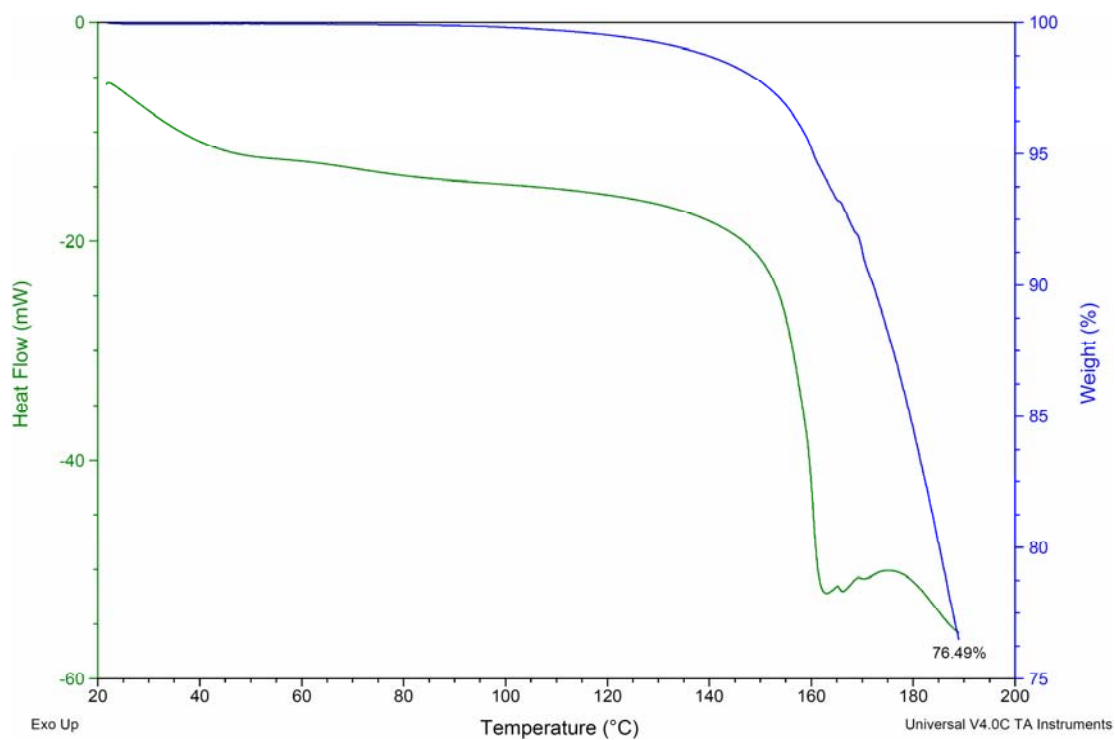


Figure B.89. 25 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 12.03 mol% incorporation

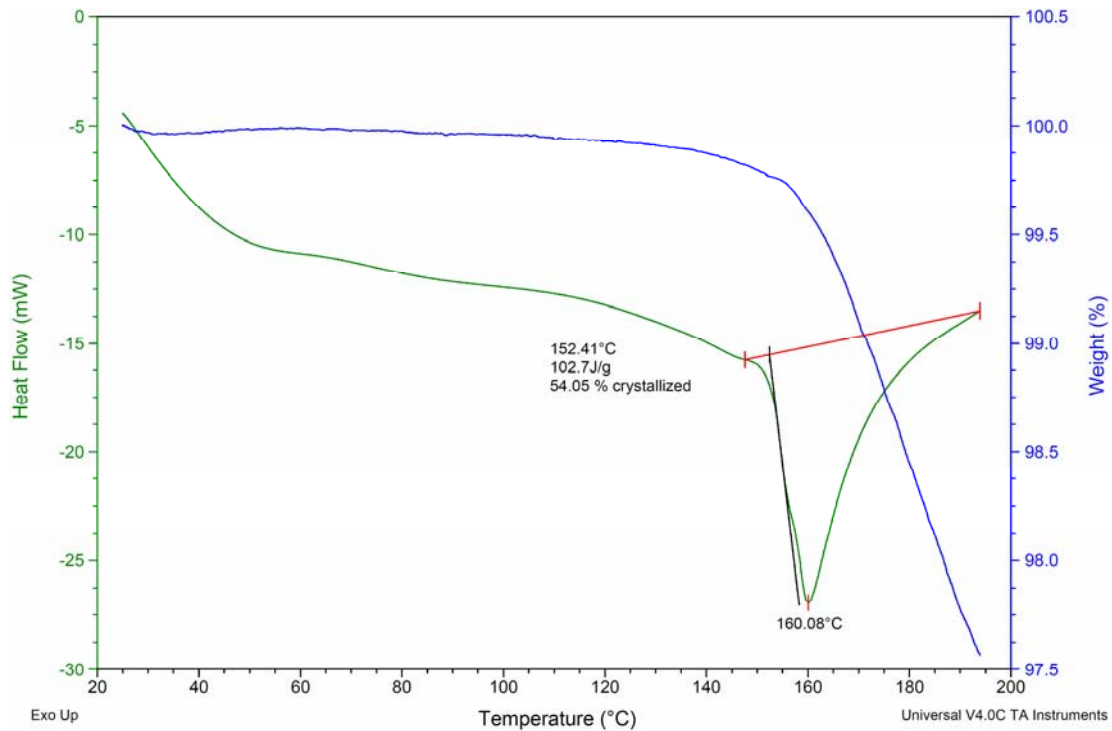


Figure B.90. 25 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 12.03 mol% incorporation

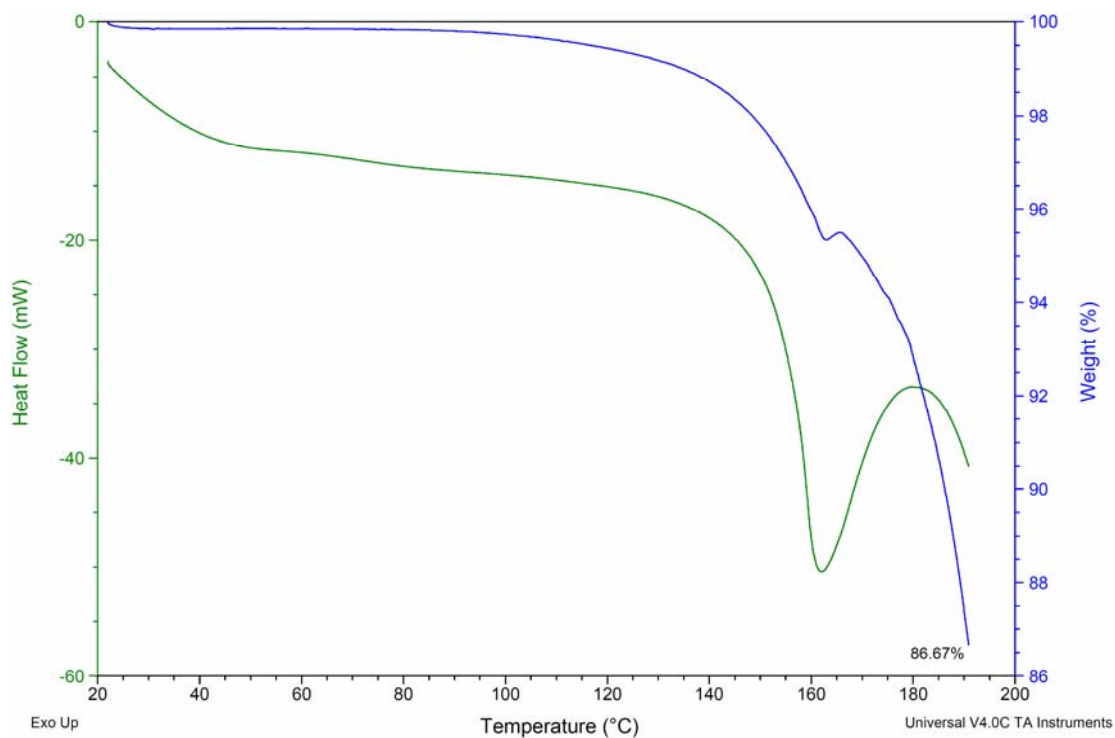


Figure B.91. 30 mol% feed 4-Butyl-1,3-Dioxolane 1st Scan 11.51 mol% incorporation

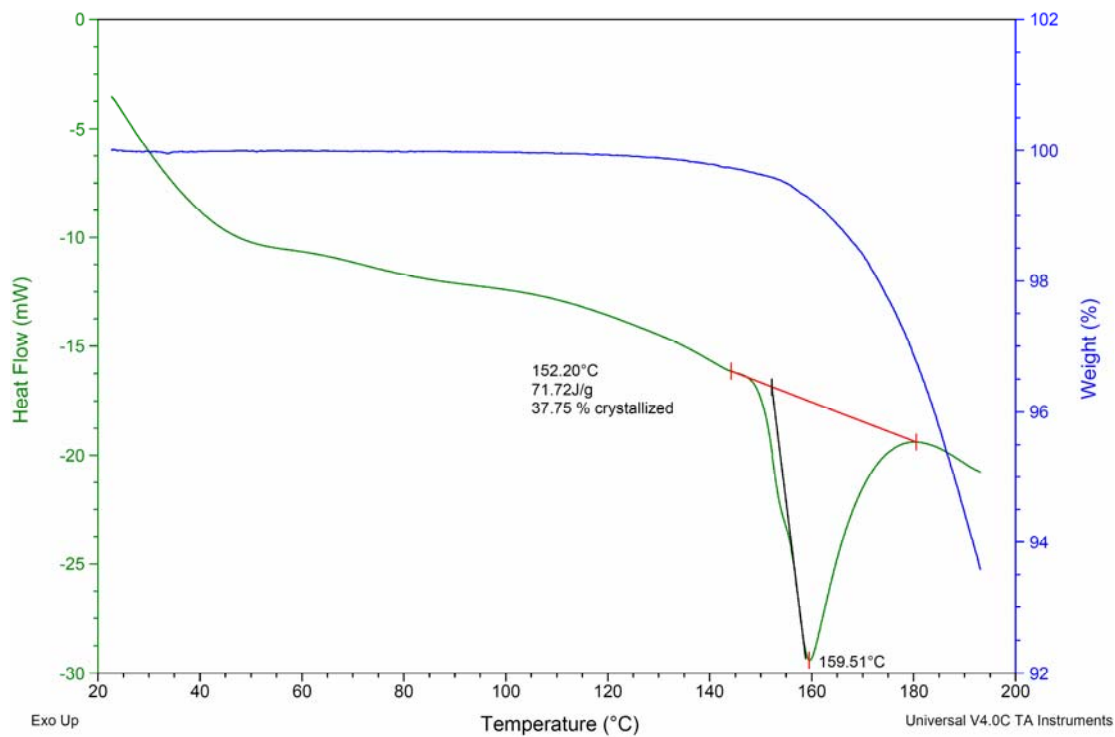


Figure B.92. 30 mol% feed 4-Butyl-1,3-Dioxolane 2nd Scan 11.51 mol% incorporation

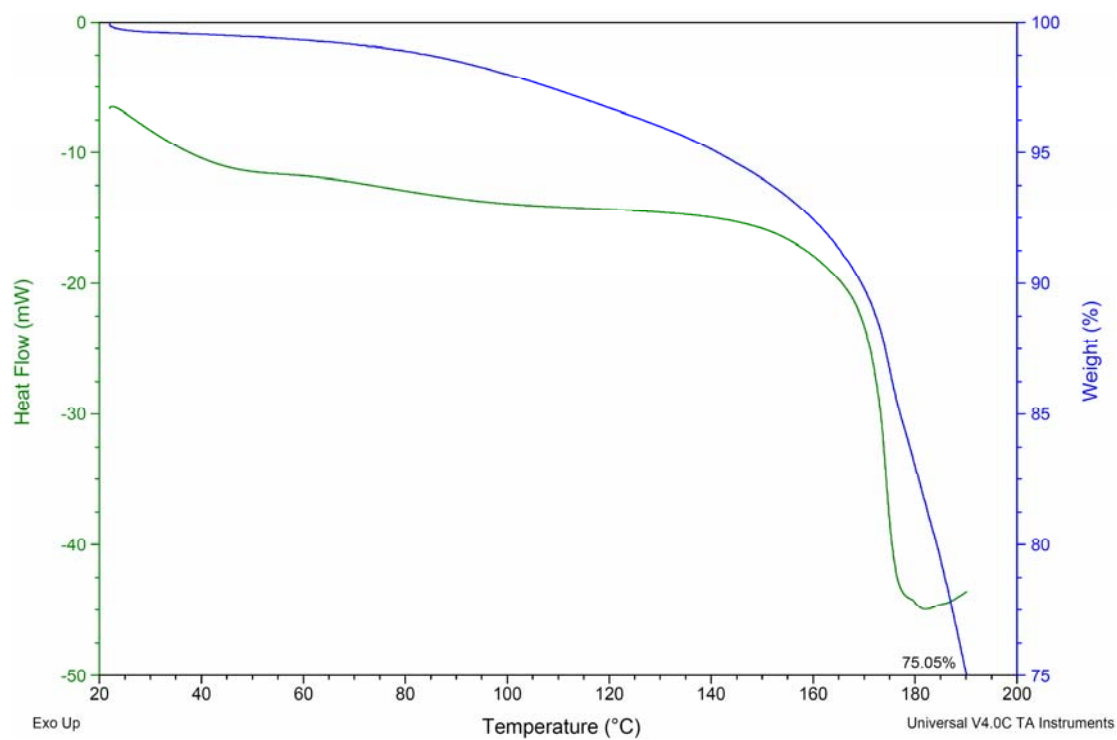


Figure B.93. 3 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 5.89 mol% incorporation

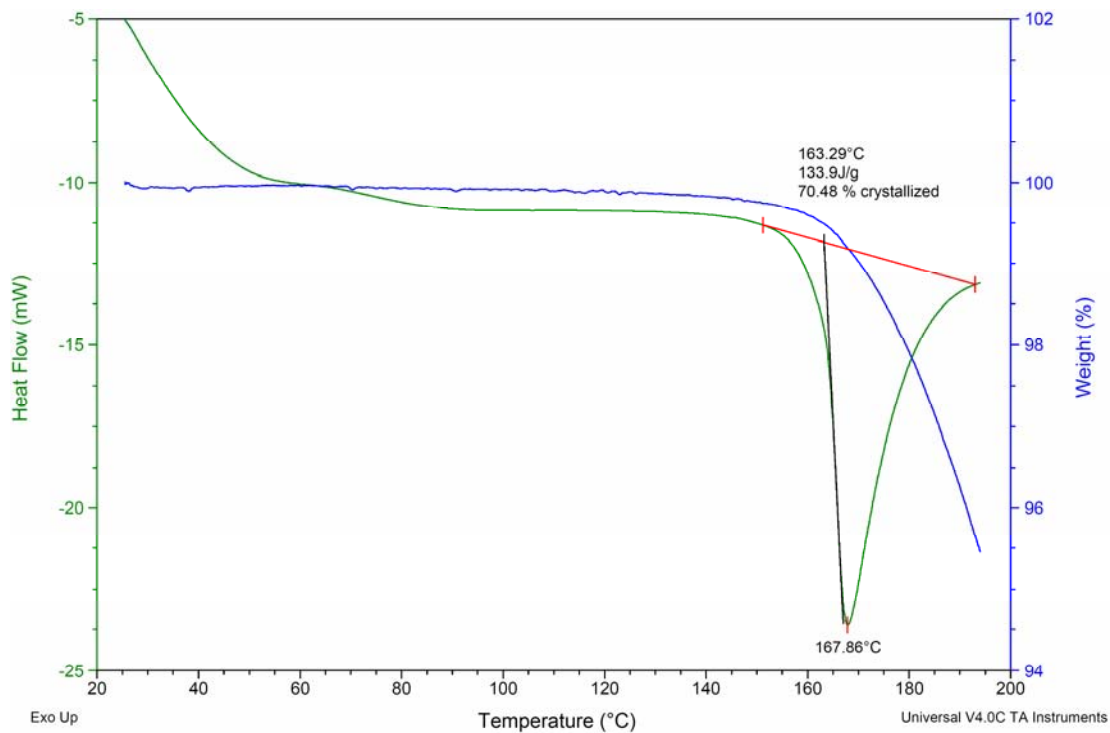


Figure B.94. 3 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 5.89 mol% incorporation

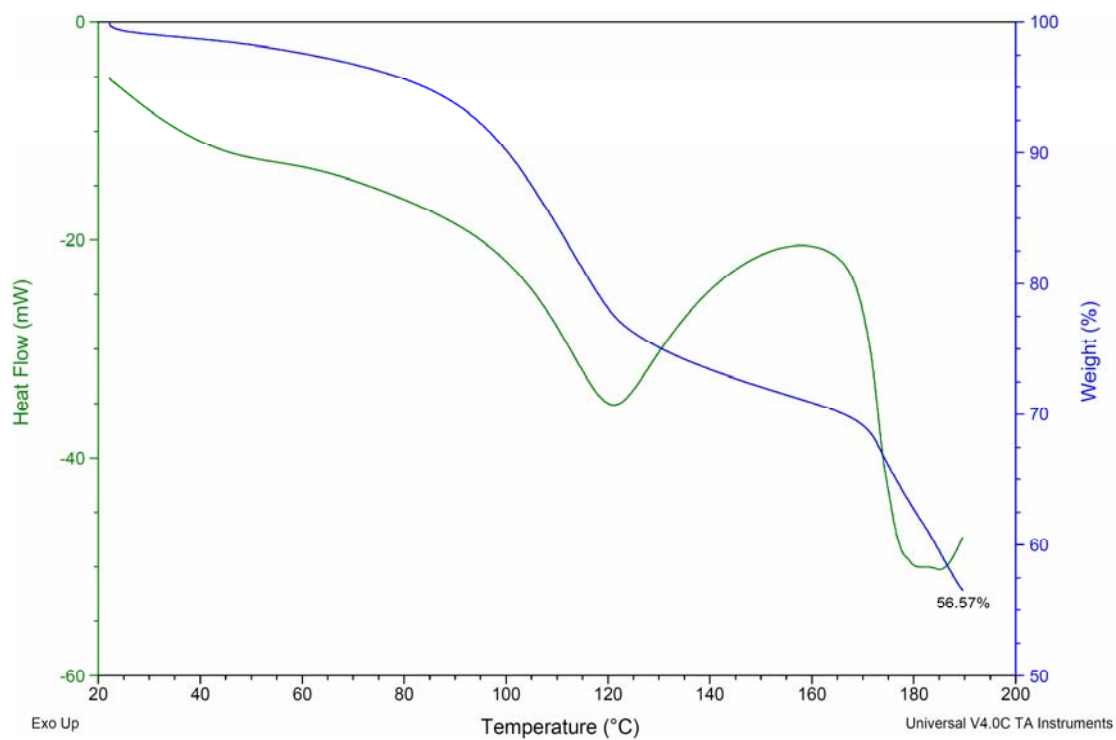


Figure B.95. 7.4 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 8.93 mol% incorporation

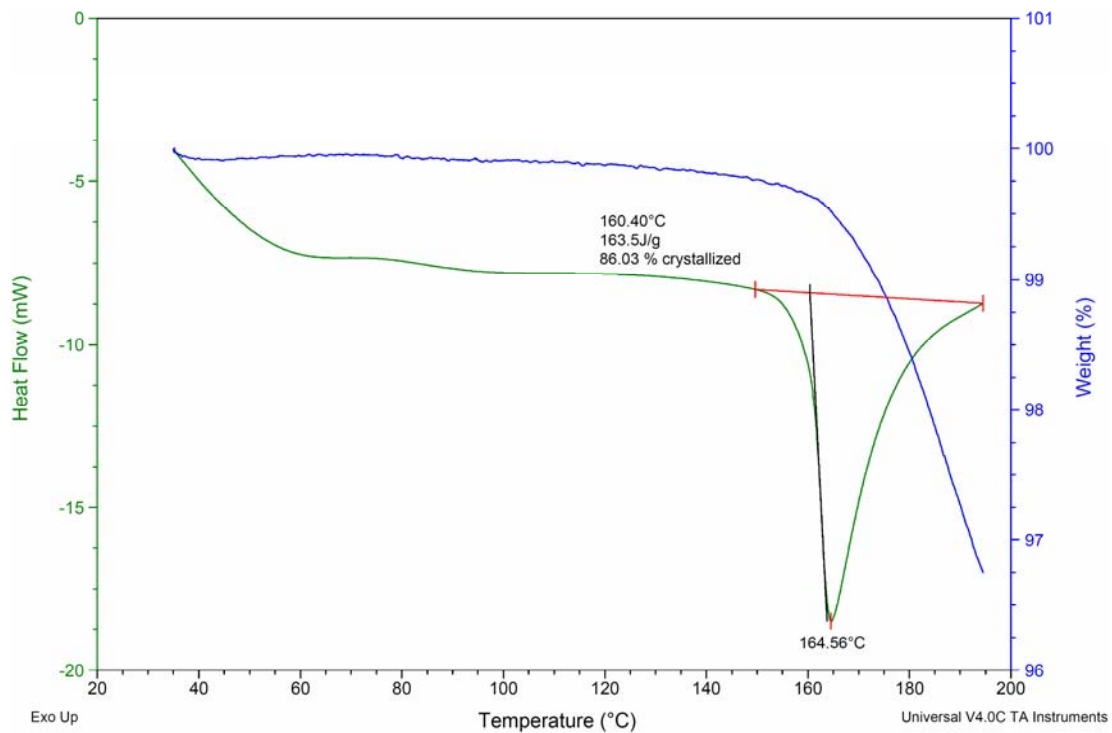


Figure B.96. 7.4 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 8.93 mol% incorporation

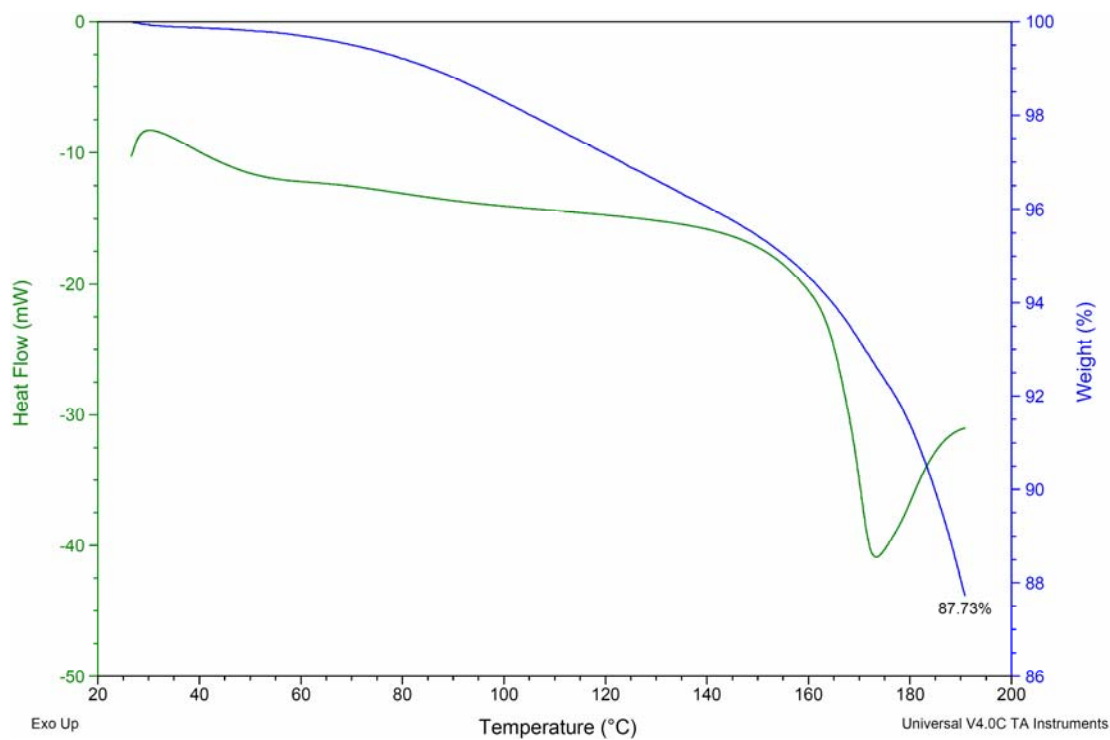


Figure B.97. 10 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 6.44 mol% incorporation

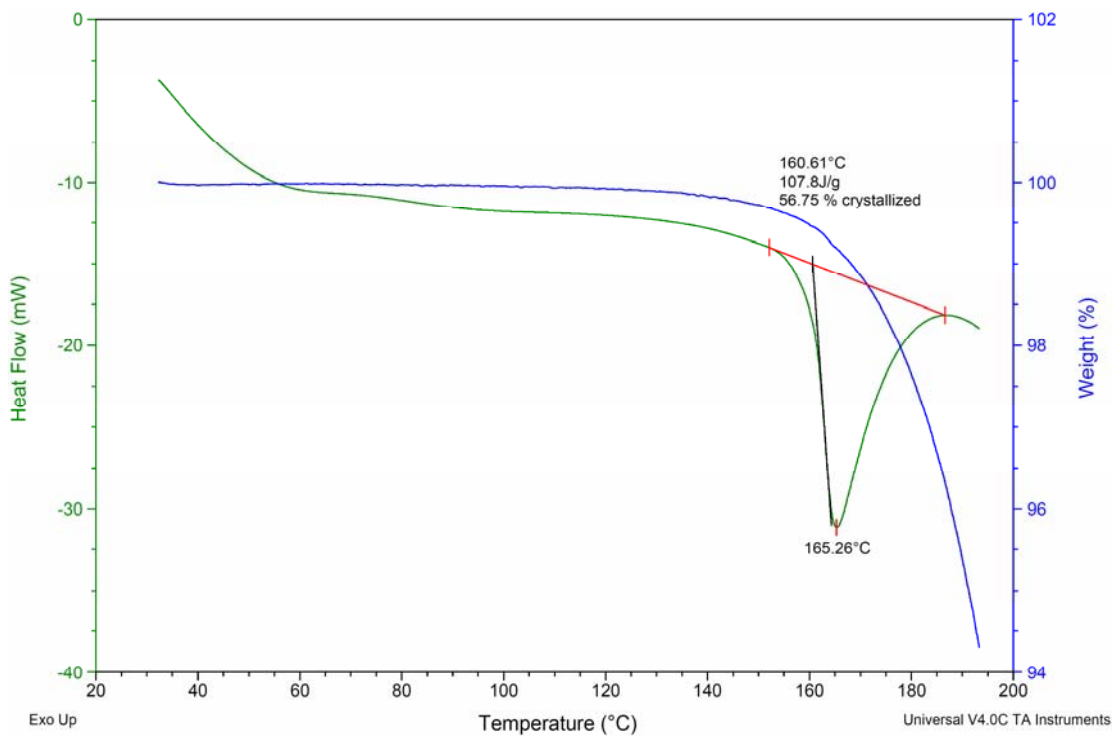


Figure B.98. 10 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 6.44 mol% incorporation

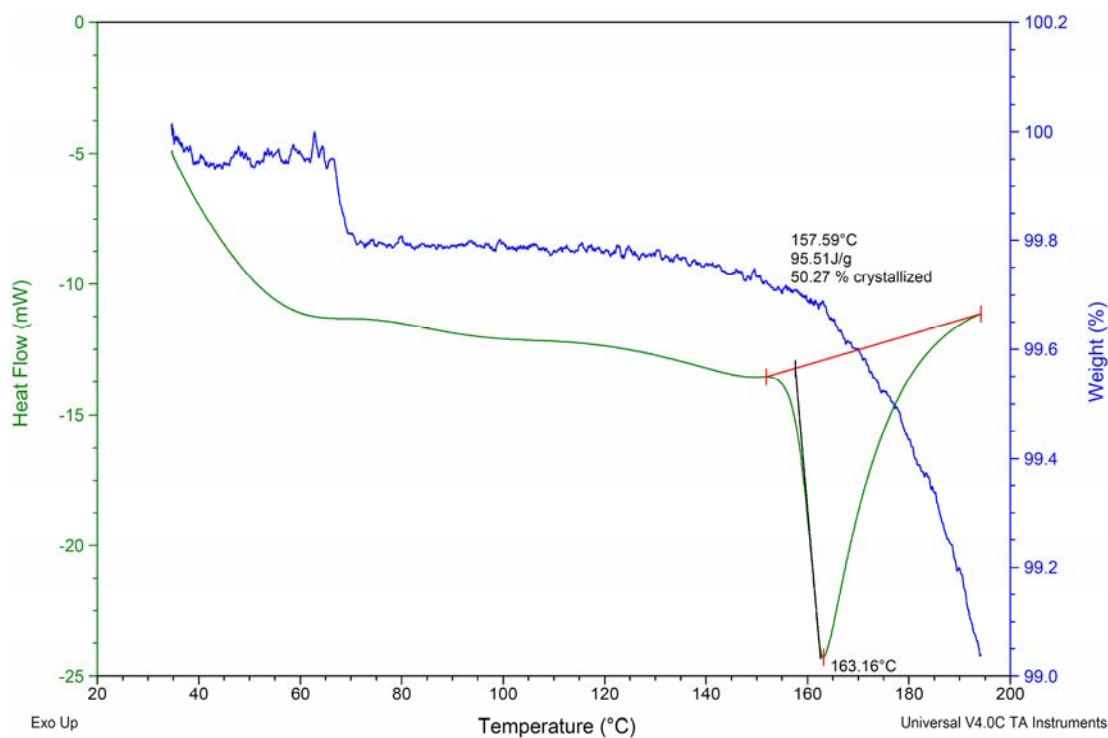


Figure B.99. 15 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 9.57 mol% incorporation

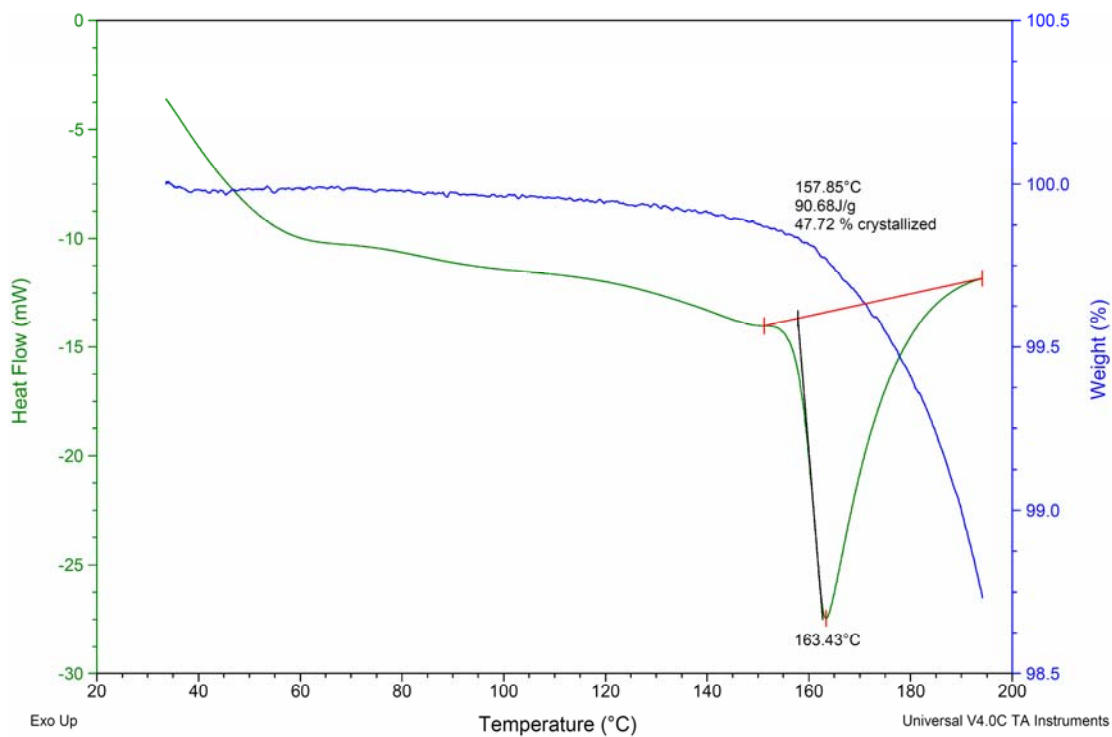


Figure B.100. 15 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 9.57 mol% incorporation

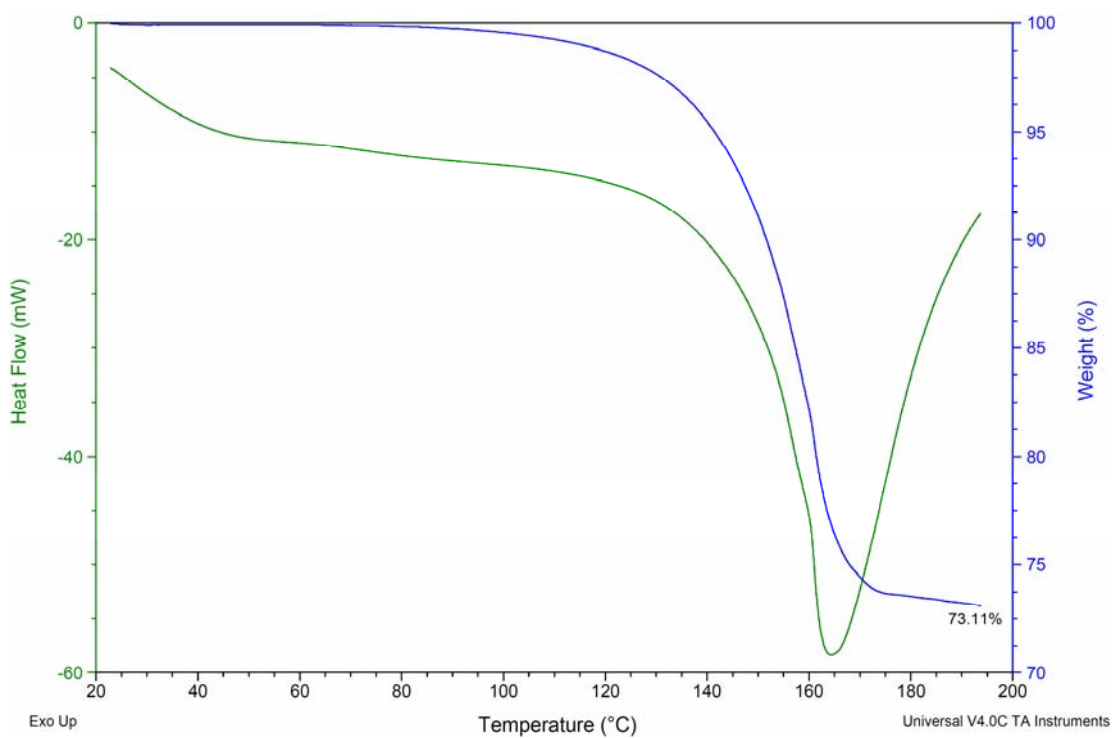


Figure B.101. 20 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 10.01 mol% incorporation

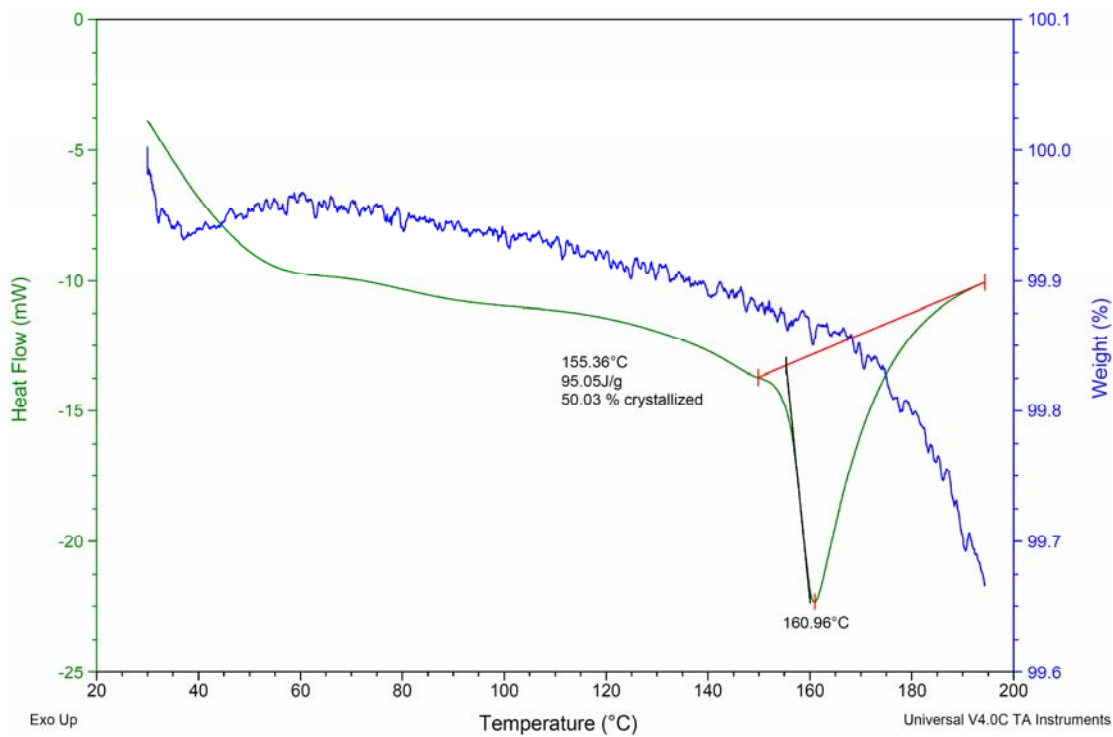


Figure B.102. 20 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 10.01 mol% incorporation

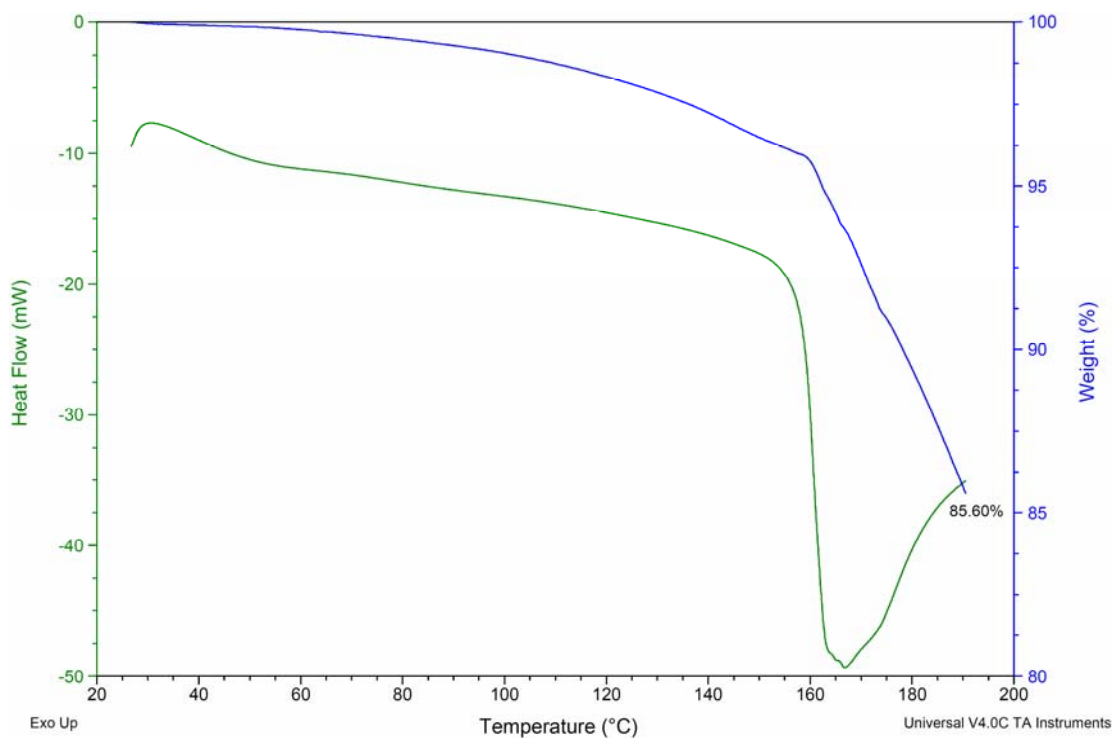


Figure B.103. 25 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 9.22 mol% incorporation

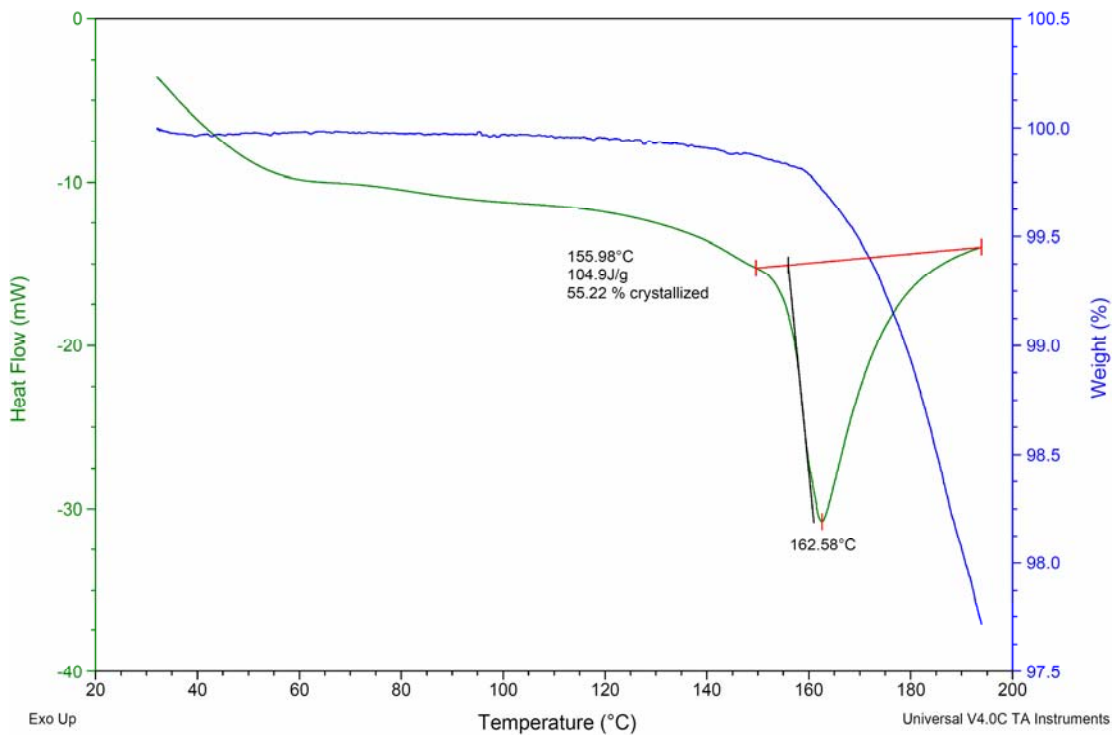


Figure B.104. 25 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 9.22 mol% incorporation

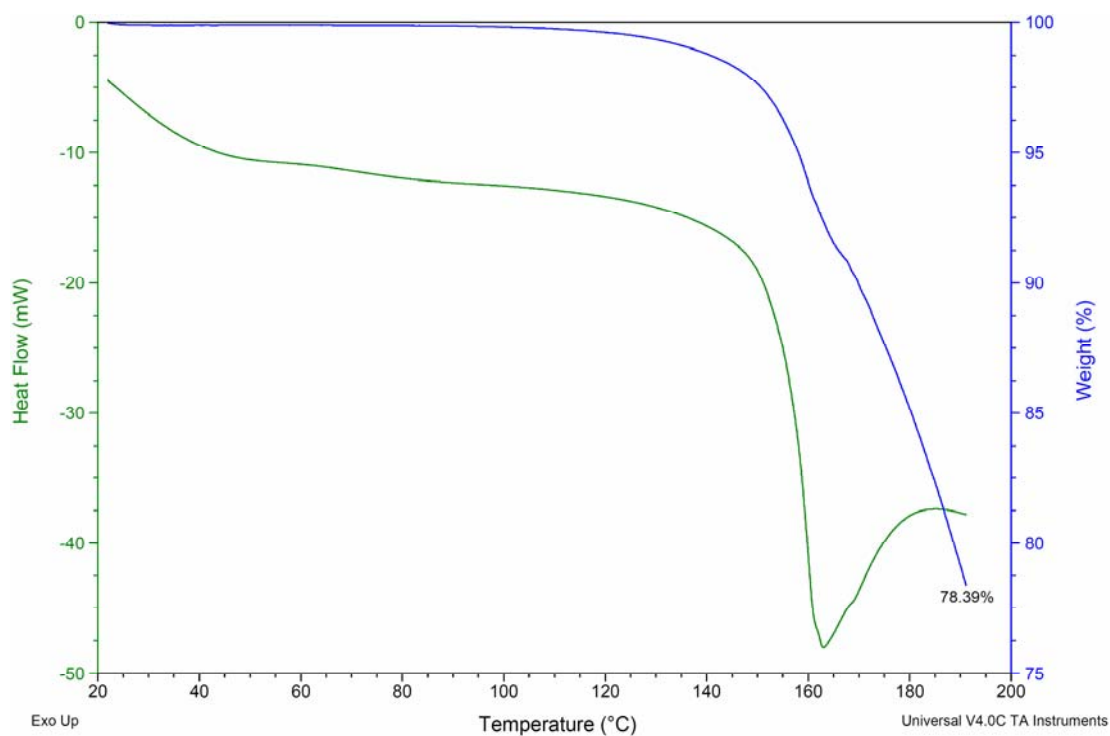


Figure B.105. 30 mol% feed 4-Hexyl-1,3-Dioxolane 1st Scan 12.30 mol% incorporation

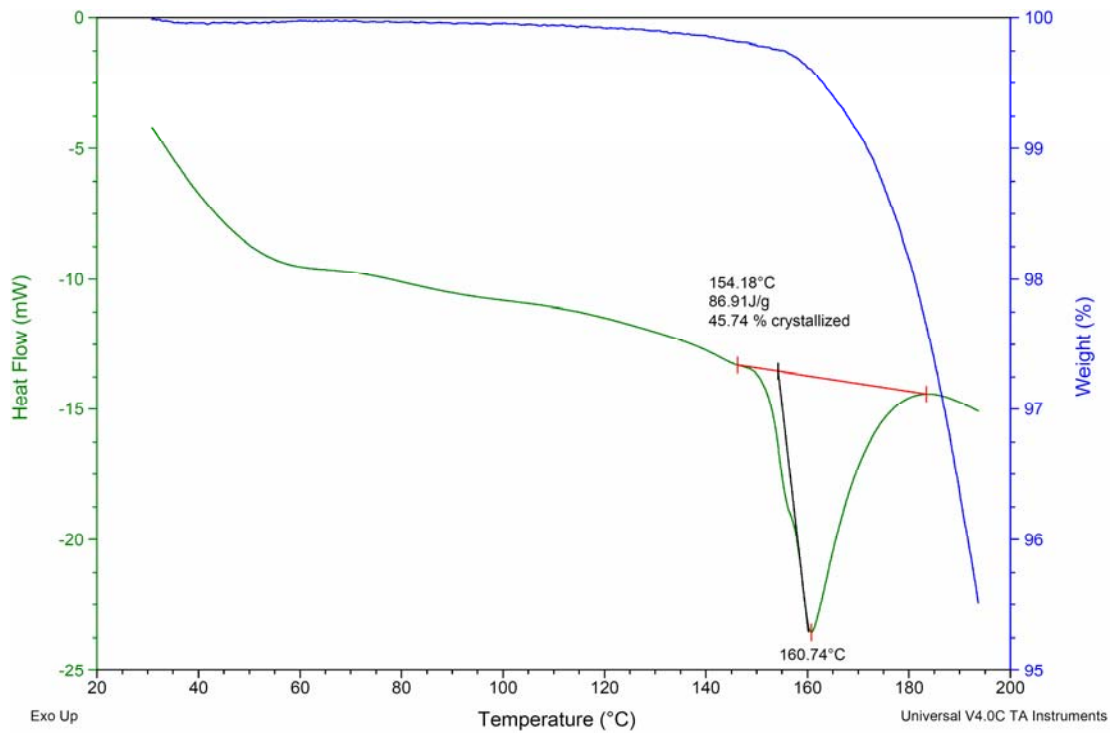


Figure B.106. 30 mol% feed 4-Hexyl-1,3-Dioxolane 2nd Scan 12.30 mol% incorporation

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2006 – 62nd Southwest Regional ACS Symposium, Houston, TX “The Effect of Branch Density on Polyoxymethylene Copolymers” Poster Presentation.

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