

PROPERTY MODIFICATION VIA CROSSLINKING IN CBDO BASED
COPOLYTEREPHTHALATES

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ABSTRACT

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The work proposed here will focus on the effects of crosslinking CBDO containing copolymers. A series of CBDO containing copolymers with aromatic diols will be made. These will incorporate CBDO, bisphenol A, phloroglucinol and terephthaloyl chloride by solution polymerization. Phloroglucinol, a trifunctional aromatic alcohol, will serve as an aromatic crosslinking agent. A series of crosslinked homopolymers will be made with bisphenol A and CBDO. Both will be crosslinked with phloroglucinol by solution polymerization. Both homopolymers will be made via solution polymerization. Thermal and mechanical tests will be utilized to characterize the structure/property relationships of these crosslinked polymers.

This study revealed that bisphenol A is a detrimental factor in these series of polymers. With the crosslinked polymers, the T_g and T_d increase as the mol % of crosslinker increases. This is due to the fact that as the mol % crosslinker is increased, the overall % of bisphenol A decreases.

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1.0. INTRODUCTION

1.1 BACKGROUND

Thermoplastics with a glass transition temperature ≥ 100 °C and notched IZOD values < 100 J/m contain aromatic groups. As shown in Figure 1, polycarbonates, such as bisphenol A polycarbonate, contain aromatic diol units within the polymer chain¹.

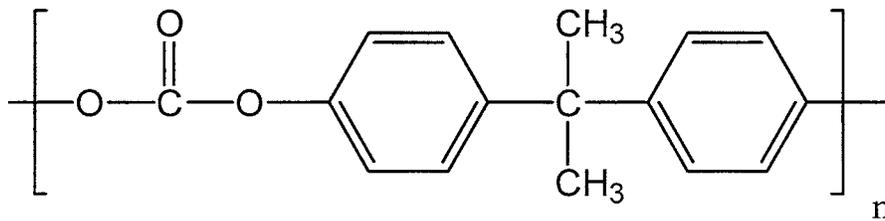


Figure 1 – Structure of Bisphenol A Polycarbonate²

Aromatic groups provide the rigidity necessary for a high T_g and notched IZOD values to exist. Bisphenol A polycarbonate is an amorphous thermoplastic that exhibits toughness, clarity and high heat-deflection temperatures. Polycarbonate was first discovered in 1898 by Einhorn². He noticed an insoluble, infusible solid while attempting to synthesize cyclic carbonates with hydroquinone and phosgene. In the late 1950's the General Electric Company in the United States and Bayer in Germany developed commercial versions of polycarbonate. Today more than one million tons are produced per year around the world².

The name polycarbonate is derived from the carbonate group (Figure 2) in the polymer repeat unit and bisphenol A (Figure 3) is the covalently bonded to the carbonate group. Bisphenol A polycarbonate is synthesized (scheme 1)

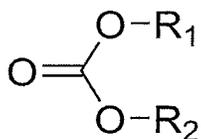


Figure 2 – Structure of Carbonate Functional Group⁴

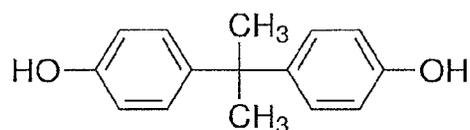
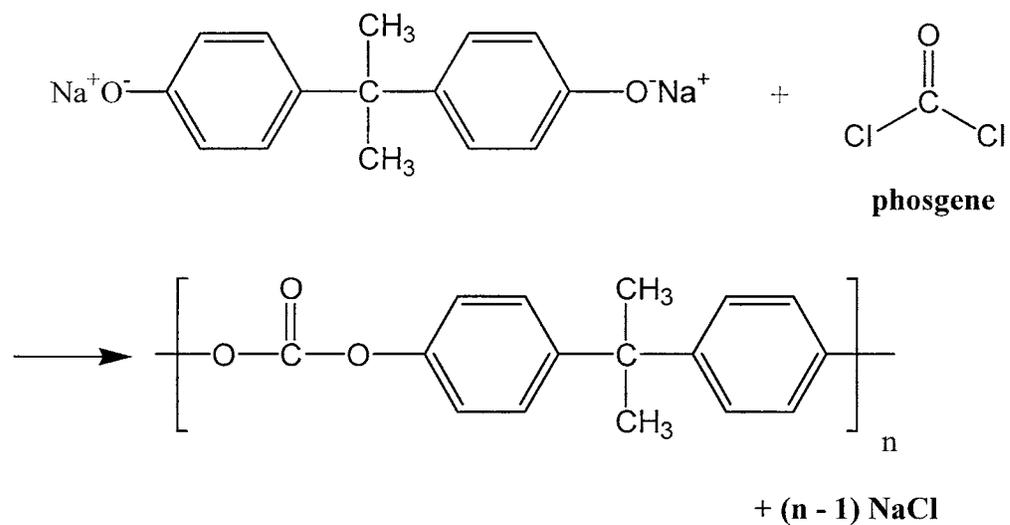


Figure 3 – Structure of Bisphenol A⁴

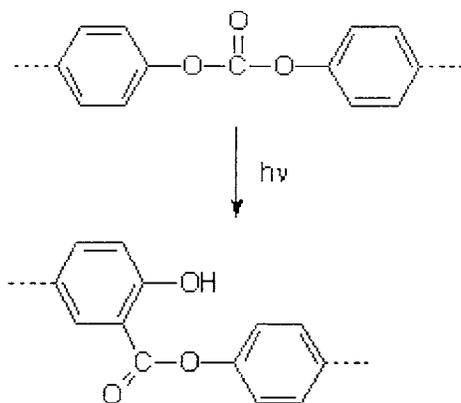


Scheme 1 – Synthesis of Bisphenol A Polycarbonate with Phosgene Gas

by reacting bisphenol A with sodium hydroxide to form a sodium salt of bisphenol A³. This is followed by a reaction with phosgene gas to produce the bisphenol A polycarbonate and HCl. This synthetic process allows for the production of bisphenol A polycarbonate with extremely high molecular weights. Because of the poisonous nature of phosgene gas, other methods for the synthesis of bisphenol A polycarbonate have been developed. These methods do not yield a product with the high molecular weights for the toughness associated with the former method⁴.

Modern thermoplastics commonly synthesized in industry, display glass transition temperatures, T_g 's $> 100^\circ\text{C}$ and notched IZOD values between 100 and 250 J/m. Polycarbonates exhibit a T_g of 100°C , and notched IZOD values of 650-850 J/m. These properties make them a desirable thermoplastic for a wide array of applications. These applications include battery boxes, household appliances, eyeglasses, mobile phones, automotive parts and even baby bottles⁴.

One problem associated with polycarbonates, is the of UV light stability (Scheme 3). UV light induces the photo-Fries rearrangement. A new repeat unit is introduced into the polymer. When this occurs, the polymer can absorb blue light and will give the



Scheme 2 – Photodegradation of Polycarbonates⁵

polymer a yellowish color. The polymer will become brittle⁵. This is undesirable for all applications, which require a colorless, tough polymer. For this reason, work has been done to produce a polyester or polycarbonate that will be resistant to degradation by UV light.⁵

1.2 ALIPHATIC-2,2,4,4-TETRAMETHYL-1,3-CYCLOBUTANEDIOL

Aliphatic monomers are easily incorporated into the polymer backbone. They traditionally do not provide the rigidity required for the development of useful thermoplastics. An exception is the 2,2,4,4-tetraalkyl-1,3-cyclobutane family. These monomers impart rigidity to the polymer. Of specific interest is 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) (Figure 4). A synthetic route for the production of CBDO was first proposed in 1906, by pyrolysis of either isobutyric acid or isobutyric anhydride to the ketene. The ketene forms the diketene by a 2 + 2 cycloaddition. Production of CBDO is realized by hydrogenation, using ruthenium, nickel or rhodium¹.

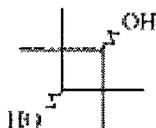


Figure 4 – 2,2,4,4-tetramethyl-1,3-cyclobutanediol⁷

CBDO is extremely rigid due to the lack of torsional mobility caused by the attachment of the four methyl groups and the four membered ring. The Rotational Isomeric State method and the Metropolis Monte-Carlo (RMMC) method have been used to investigate the effects of the methyl substituents on the four-membered ring. The RIS method studies the polymer conformation and predicts the materials stiffness. The Metropolis Monte Carlo method utilizes information gained from RIS to statistically provide a number for the chain lengths within the polymer⁶.

Poly(2,2,4,4-tetramethyl-1,3-cyclobutylene terephthalate) (CBDO), poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), poly(1,4-cyclohexylenedimethylene 2,5-dimethyl terephthalate) (DMPCT) and poly(1,4-cyclohexylenedimethylene 1,4-cyclohexylenedicarboxylate) (PCC) were studied via RMMC. The purpose of this study was to observe the effects of a four-membered ring in polyesters vs. six-membered rings, structures can be viewed in figure 5. As shown in Table 1, the rigidity of the CBDO monomer leads to extended chain morphology as compared to flexible six-membered ring monomers, such as cyclohexane diol. The length, l_6 , is a value that would be expected of a purely aromatic group. Also, due to the methyl substituents on the CBDO monomer, there is limited torsional mobility and therefore limited number of possible conformations⁶.

Table 1 - Geometrical Parameters of the Polyesters Studied via RMMC⁷

Bond Length (Å)	CBDO	PCT	DMPCT	PCC
l_1	1.36	1.36	1.36	1.36
l_2	2.90	2.90	2.90	1.52
l_3	2.90	2.90	2.90	3.00
l_4	1.36	1.36	1.36	1.52
l_5	1.42	1.42	1.42	1.36
l_6	2.17	1.54	1.54	1.42
l_7	1.42	3.00	3.00	1.54
l_8		1.54	1.54	3.00
l_9				1.54

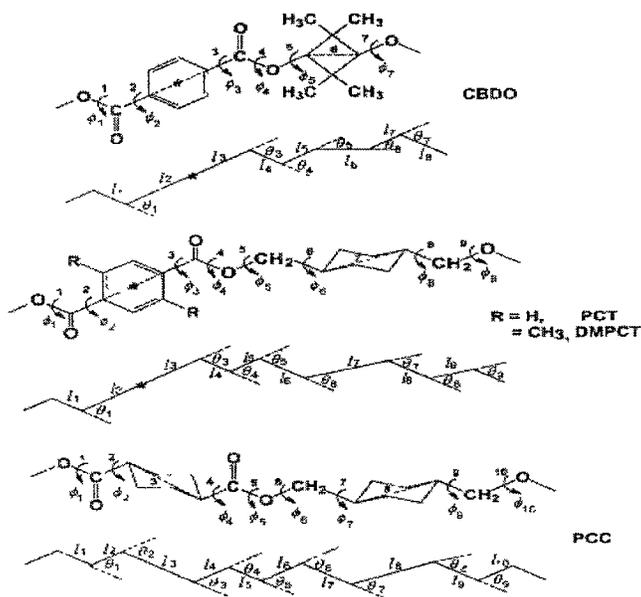


Figure 5 – Structure of the Repeat Units of the Polyesters Studied via RMMC⁷

1.3 ALIPHATIC-AROMATIC COPOLYCARBONATES

CBDO copolycarbonate (Figure 6) was the first academic study of CBDO within a polymer backbone. The R group in the polycarbonate, indicates which bisphenol (A, AP, TP, F, or HPF) was studied. One method of synthesis employed by the Macromolecular Studies Group at Louisiana State University was the direct transesterification of CBDO with the appropriate bisphenol and diphenyl carbonate⁷.

Another method for this synthesis is the reaction of liquid phosgene and CBDO at low temperatures to produce the bischloroformate. The bischloroformate was then reacted with the appropriate bisphenol to produce the CBDO polycarbonate. Figure 7 shows the repeat unit for the CBDO polycarbonate. All of the polycarbonates produced displayed T_g 's above 100°C and could be utilized within a large temperature range.

Molecular weights of these polymers ranged from 37,000 to 65,000 (Table 2). No mechanical properties were reported due to thermal decomposition of samples above T_g ⁷.

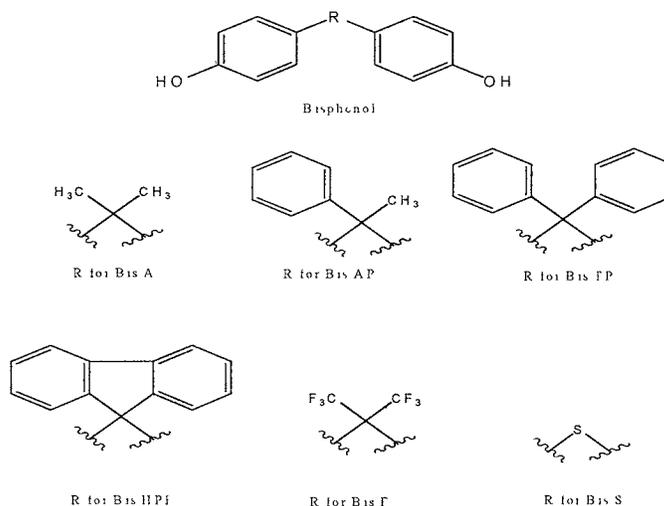


Figure 6 – Common Bisphenols Utilized in the Synthesis of CBDO Copolycarbonates⁷

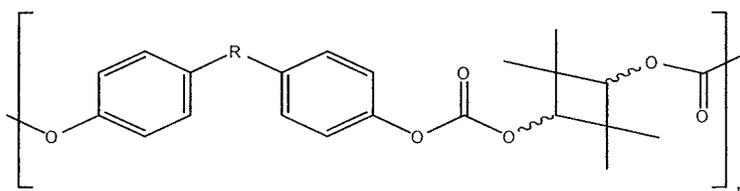


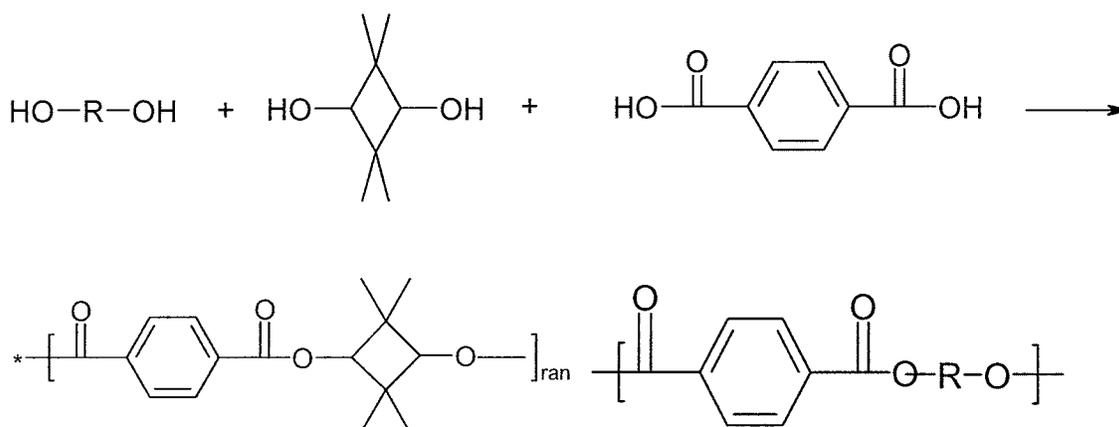
Figure 7 – Aliphatic Aromatic CBDO-Based Copolycarbonates⁷

Table 2 – CBDO Copolycarbonate Results⁷

Polymer	T_g (°C)	T_d (°C)	MW	Mol % cis-CBDO
Bis A/CBDO	130	352	42000	33
Bis AP/CBDO	149	357	38000	25
Bis HPF/CBDO	214	347	39000	36
Bis HF/CBDO	142	343	42000	34
Bis S/CBDO	107	341	65000	34

1.4 FLEXIBLE ALIPHATIC COPOLYESTER

The Shell Chemical Company reported the effects of flexible aliphatic diols incorporated into CBDO based copolyesters (Scheme 3). These aliphatic diols are used as spacers, which increases the thermal and UV stability and increase the T_g . The effects were studied with two, three and four carbon spacers. Propanediol, a three carbon spacer, was found to greatest positive affect on the polymer properties⁸.



Scheme 3 – Synthesis of CBDO Copolyesters with Aliphatic Diols⁸

Shell reported that as the % incorporation of CBDO is increased in the system, the thermal stability of the polymer increases and impact resistance decreases (Figure 8). They also found that unlike CBDO based polycarbonates, the CBDO polyesters with linear diols have high UV resistance. Molecular weights for these polymers ranged from 48,000-55,000, T_g 's were between 80-174 °C and notched IZOD values were between 140-1070 J/m. Although CBDO increases many of these properties, a balance can be found at CBDO concentrations of 40 mol %⁸. At 40 mol %, the T_g will be above 100 °C with a notched IZOD similar to that of polycarbonate.

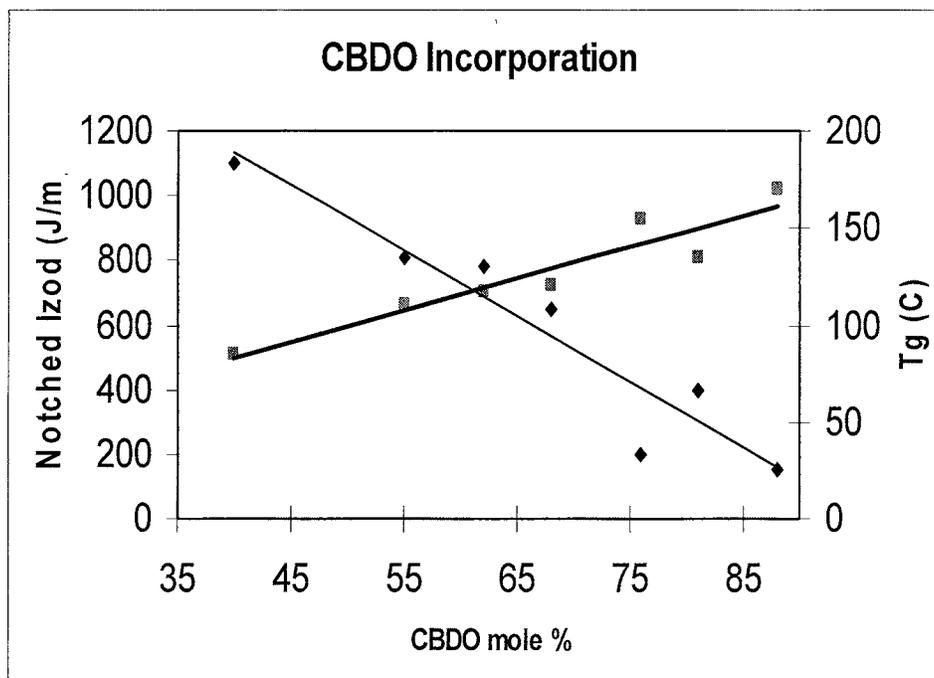


Figure 8 – Affects of the Incorporation of the CBDO Monomer⁸

1.5 PREVIOUS WORK AT TEXAS STATE UNIVERSITY-SAN MARCOS

The previous study Texas State University-San Marcos observed the affect of varying the molar feed ratio between various bisphenols (A, AF, HPF, and F) and CBDO. This study observed that as the CBDO mol % was increased the T_d decreased and the T_g increased. This trend was observed for all of the various bisphenols. The T_d and T_g can be tailored to suit the purposes of the experiment.

1.6 IMPACT AND BALISTIC REPORTS OF CBDO COPOLYTEREPHTHALATES

In 2006, Texas State University-San Marcos reported a CBDO polyester with an increase in impact and ballistic properties over polycarbonate. $^1\text{H-NMR}$ was used to determine the cis/trans ratio of CBDO. This study reported T_g 's around 98 °C and T_d 's around 355° C. Notched IZOD studies displays an average value of 912.2 J/m and an average Young's modulus of 8.87×10^8 Pa. Polycarbonate had an average Notched

IZOD value of 679.5 J/m and an average Young's modulus of 9.18×10^8 Pa. Ballistic tests, carried out independently, with plaques of areal density 111 g/cm^2 gave an FSP V50 rating of up to 355 m/s and similar sample of polycarbonate gave a rating of 241 m/s. A CBDO copolyterephthalate sample of areal density 167 g/cm^2 gave a maximum value of 464 m/s and a similar sized sample of polycarbonate gave a value of 341 m/s^9 . Areal density refers to the mass of a plaque at a given cross-sectional area.

2.0 PROSPECTUS OF RESEARCH

The work proposed here will focus on the effects of cross-linking on CBDO containing copolyesters. The mechanical properties are expected to change due to the fact that the material is now one complete molecule, instead of many chains interwoven. Typically accepted methods of cross-linking include: chemical, thermal and UV induced cross-linking. For the purposes of this research, chemical cross-linking will be the method utilized.

A linear CBDO copolyester will be made from bisphenol A, CBDO and terephthaloyl chloride. Along with the copolyester, a bisphenol A homopolymer, containing only bisphenol A and terephthaloyl chloride will be made and a CBDO homopolymer containing only CBDO and terephthaloyl will be made. Characterization will include: $^1\text{H-NMR}$, GPC, TGA, DSC and DMA.

A series of cross-linked CBDO copolyesters will be made from bisphenol A, CBDO, terephthaloyl chloride and a tri-functional crosslinker, phloroglucinol (Figure 9). A third series will be made from bisphenol A, terephthaloyl chloride and phloroglucinol. Finally, a series will be made from CBDO, terephthaloyl chloride and phloroglucinol. Characterization will include: TGA, DSC, DMA and a solvent swell study.

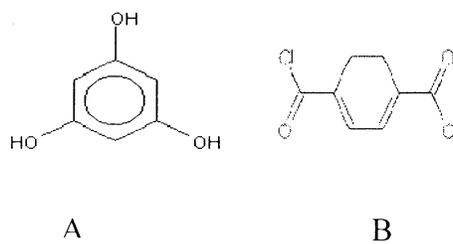


Figure 9 – Structures of Phlorglucinol (A) and Terephthaloyl Chloride (B)

3.0 EXPERIMENTAL

3.1 MATERIALS

CBDO (cis/trans ratio of 46/54 donated by Eastman Chemical) used for the following syntheses without further purification. In addition, polymer grade terephthaloyl chloride of 99+% (used as received), phloroglucinol (used as received) and ortho-dichlorobenzene (used as received) were purchased from Aldrich Chemical Company.

3.2 SYNTHETIC METHODS

3.2.1 SYNTHESIS OF LINEAR CBDO COPOLYESTERS

For this system, bisphenol A, CBDO and terephthaloyl chloride were used in the following molar ratio: 0.6:0.4:1.0. They were added to a flame-dried 250 ml 3-neck flask equipped with a magnetic stirrer. The flask was then be degassed with an argon purge using a Shlenk line and heated to reflux for 12 hours. The reaction flask was then cooled to room temperature and the polymers were dissolved in chloroform to remove from the flask.

3.2.2 PURIFICATION OF LINEAR CBDO COPOLYESTERS

After removal from the flask, the polymer was precipitated in methanol. The polymer was dissolved in chloroform and precipitated in methanol 3-4 times. The polymer was then dried in a vacuum oven for 48 hours prior to characterization.

3.2.3 SYNTHESIS OF CROSSLINKED COPOLYESTERS

For the CBDO copolyester system, a series of cross-linked polyesters have been made ranging from 8 mol % phloroglucinol to 20 mol %. For the polymer with 8 mol % phloroglucinol, three equivalents at 8 mol% of phloroglucinol were used. Two equivalents at 36.8 mol % of CBDO, two equivalents at 55.2 mol % bisphenol A and seven equivalents at 100 mol % of terephthaloyl chloride were used. Amounts in the rest of the series followed this pattern. They were added to a 250 ml 3-neck flask equipped with a magnetic stirrer. The flask was then degassed with an argon purge using a Schlenk line and heated to reflux until the contents of the flask become gelatinous. The cross-linked polymer was swollen with chloroform and removed from the flask.

For the system containing bisphenol A, terephthaloyl chloride and phloroglucinol, a series was synthesized with crosslink ranging from 9-15 mol %. For the polymer with 9 mol % phloroglucinol, three equivalents at 9 mol % phloroglucinol were used. Two equivalents at 91 mol % bisphenol A and five equivalents at 100 mol % terephthaloyl chloride were used. Amounts in the rest of the series followed this pattern. The syntheses were the same as the cross-linked polymer previously discussed.

For the system containing CBDO, terephthaloyl chloride and phloroglucinol, a series was synthesized with crosslink ranging from 8-15 mol %. For the polymer with 8 mol % phloroglucinol, three equivalents at 8 mol % phloroglucinol were used. Two equivalents at 92 mol % CBDO and five equivalents at 100 mol % terephthaloyl chloride were used. Amounts in the rest of the series followed this pattern. The syntheses were the same as the cross-linked polymer previously discussed.

3.2.4 PURIFICATION OF CROSSLINKED COPOLYESTERS

Once removed from the flask, the polymer was dried with methanol. The polymer was swollen in chloroform and dried with methanol 4-5 times. The polymer was then dried under vacuum for 48 hours prior to characterization.

3.3 FILM FORMATION

Prior to mechanical and crosslink characterizations, a polymeric film must be formed. This is done on a Carver Laboratory Press at 5000 psi with a temperature above the T_g of the polymer for 10 minutes.

3.4 CHARACTERIZATION METHODS

3.4.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

^1H -NMR spectra were performed on a 400 MHz Oxford NMR 400 spectrometer. To confirm the structure of the linear polymers, ^1H -NMR was run after synthesis. The polymers were dissolved in deuterated chloroform in 10 mm tubes. Samples were prepared by taking 1-2 mg of the monomer and dissolving it into approximately 0.75 ml of deuterated chloroform. ^1H -NMR was run in the range of 0-9 ppm, as all significant peaks were in this range and set to TMS standard. Peaks were integrated for further analysis.

3.4.2 THERMAL GRAVIMETRIC ANALYSIS (TGA)

TGA's were performed on TA Instrument Q50 Thermal Gravimetric Analyzer. TGA measures the heat capacity, weight loss and degradation temperatures of the polymer. It was run at ambient temperatures to 800° C at 10° C/min on 5-10 mg samples. The analysis was carried out in air.

3.4.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC's were performed on a TA Instrument Q200 Differential Scanning Calorimeter using heat/cool/heat cycle at 10 °C/min on 5-10 mg samples. Data taken from the DSC provided the T_g and any apparent crystal structure transition temperatures. Because amorphous polymers do not display a melting transition temperature, this transition was used to signify a semi-crystalline polymer. An argon environment must be maintained throughout the analysis.

3.4.4 DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA was performed on a TA Instrument Q800 Dynamic Mechanical Analysis. The DMA provides the materials storage and loss modulus and T_g .

3.4.5 GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC was performed on a Walters 600 Gel Permeation Chromatographer to determine the molecular weight of the linear, non-crosslinked polymers. Samples performed with a polystyrene standard and dissolved in chloroform.

3.4.6 SWELL STUDIES

Using the Flory-Huggins solvent interaction parameter and the following equation, the crosslink density and molecular weight between crosslink points was determined¹⁰.

$$M_c = \rho/v_e = V_0/v_e' = (v_2^{0.33} - v_2/2)/\{-[\ln(1-v_2) + v_2 + \chi v_2^2]/v_1\}$$

$$\chi = (V_m/RT)(\delta_s - \delta_p)^2$$

$$\delta = (\Delta H_{\text{vap}}/V_m)^{1/2}$$

δ = solubility parameters of solvent and polymer respectively.

V_m = molar volume of solvent

ΔH_{vap} = heat of vaporization of solvent/polymer

R = real gas constant

T = temperature at which the solute is dissolved by the solvent

M_c = molecular weight between crosslinks

ρ = polymer density

v_e = crosslink density in moles/ml

v_e' = moles of elastically effective network chains in volume V_0 of unswollen polymer

V_0 = volume of unswollen polymer

v_1 = molar volume of solvent

v_2 = geometric term related to swelling of polymer

$$v_2 = 1/(1+f)^3$$

$$f = (x_2 - x_1)/x_1$$

x_1 = original length of the sample

x_2 = length after swelling

Because this polymer/solvent system has never been studied before, some inference of the polymer and solvent solubility parameters must be done. Due to similarities between the CBDO polyester and poly(ethylene terephthalate) (PET), PET's solubility parameter in chloroform was used.

$$\delta_{(\text{PET})} = (21.9 \text{ MPa}^{1/2})^{11}$$

$$\delta_{(\text{chloroform})} = (17.92 \text{ MPa}^{1/2})^{12}$$

$$v_1 = 80.7 \text{ cm}^3/\text{mol}$$

$$\chi = 8.454 \text{ MPa}^{-1}$$

4.0 RESULTS AND DISCUSSION

4.1 $^1\text{H-NMR}$

$^1\text{H-NMR}$ confirmed the structure of the polymer. Figure 10 shows the $^1\text{H-NMR}$ for the linear copolyester. Signal A is for the protons on the ring of the terephthalate group. It is more deshielded due to the direct linkage to the electron withdrawing carbonyl group located directly next to the ring on either side. Signal B is due to the protons of the bisphenol unit. Signal C is due to solvent impurities left behind in the polymer.

Signal D of figure 10, is attributed to the protons on the ring of the trans-CBDO

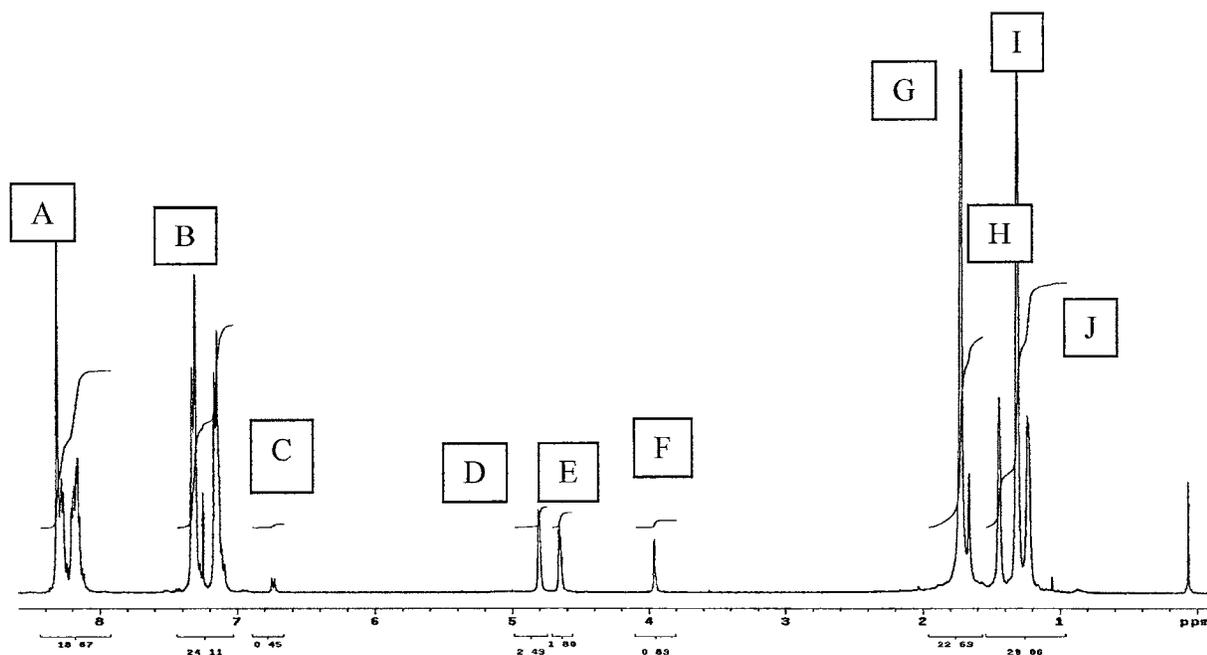


Figure 10 - Linear Copolyester NMR

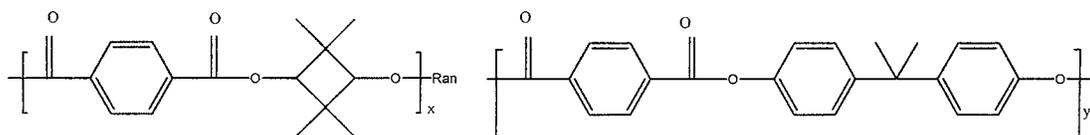


Figure 11 – Structure of Linear Copolyester Repeat Unit

unit. The trans-CBDO unit is more deshielded due to its closeness in proximity to the oxygens bonded to the ring. Signal E is attributed to the cis-CBDO unit. Signal F is attributed to an impurity due to the mass usage of NMR tubes.

Signal G is from the methyl groups located on the bisphenol unit. Signal H and J are from the methyl groups located on the cis-CBDO unit. Signal I is due to the trans-CBDO unit. The cis-CBDO unit shows two signal for the methyls because half of the methyls are non-equivalent. So each set of two methyls displays its own signal. For the trans-CBDO unit, all four methyl groups are chemically equivalent, therefore only one signal is observed.

Figure 12 displays the $^1\text{H-NMR}$ for the linear CBDO homopolymer. Signal A is due to the protons on the ring of the terephthalate unit. Signal B is attributed to residual chloroform within the polymer. Signal C is the protons located on the ring of the trans-CBDO unit. Signal D is due to the protons on the ring of the cis-CBDO unit. Signal E is due to an impurity. Signals F and H are attributed to the methyls of the cis-CBDO unit. Signal G is due to the methyls of the trans-CBDO unit. Proton NMR confirms the ratio of the cis/trans ratio. For the linear copolyester there was a 42.6/57.4 cis/trans ratio. Also,

the CBDO/Bis A ratio was 35.93/64.07. For the linear CBDO homopolymer there was a 44.6/55.4 cis/trans ratio.

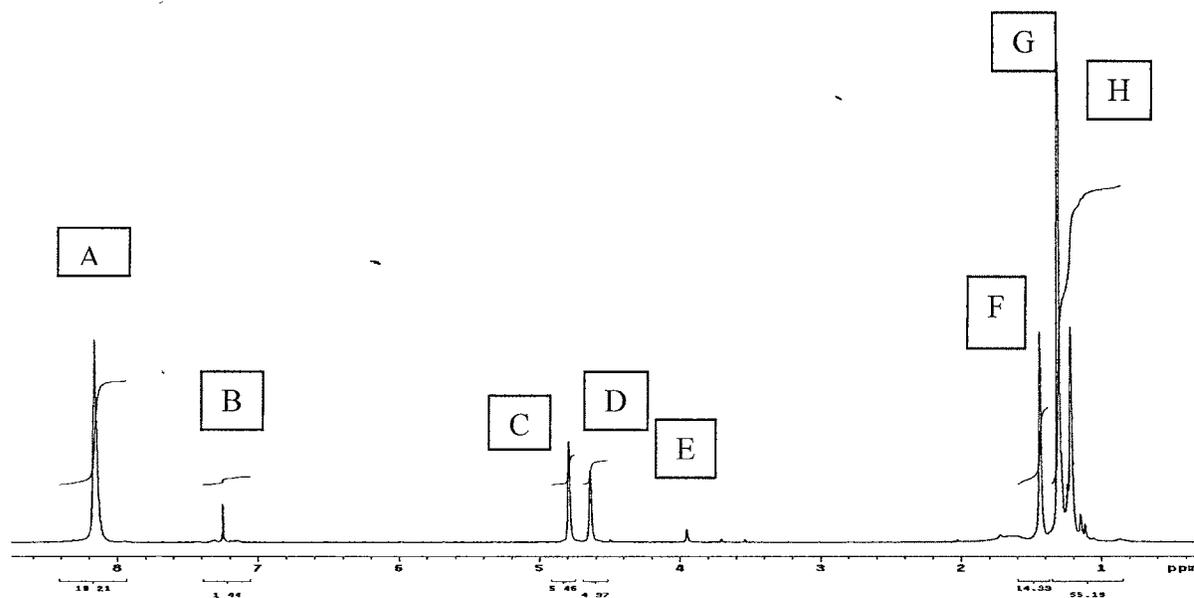


Figure 12 - Linear CBDO Homopolymer NMR

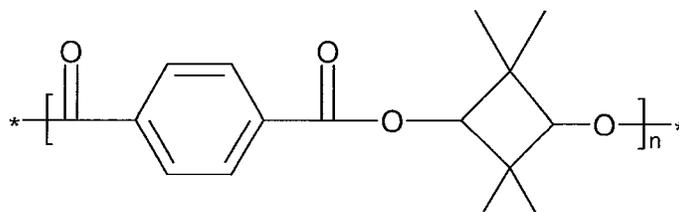


Figure 13 – Structure of Linear CBDO Homopolymer Repeat Unit

4.2 GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC was performed on the linear CBDO homopolymer and the linear copolyester. From this the Mn, Mw, MP, Mz, and PDI were obtained. GPC was not performed on Bisphenol A homopolymer due to the fact that it is only slightly soluble in chloroform at room temperature. Crosslinked samples were not performed on the GPC due to their inability to be dissolved.

Table 3 – Molecular Weight Determination Via GPC

	Linear Copolyester	Linear CBDO Homopolymer
Mn	8837	13506
Mw	15365	24487
PDI	1.74	1.81

Mn = number average molecular weight

Mw = weight average molecular weight

PDI = polydispersity index

4.3 THERMAL GRAVIMETRIC ANALYSIS (TGA)

TGA was performed in an air environment. This was used to determine the decomposition temperatures of the polymers. Decomposition temperature (T_d) is defined as the temperature in which the polymer has lost 10 percent of its initial mass. This temperature is important when attempting to process a polymer, to keep the polymer a

significant amount below this temperature. Decomposition temperatures, in air, for all of the polymers in this study appear in table 4, noting all alcohols and acids are kept in a 1:1 ratio.

Table 4 – Decomposition Temperatures of Polymers in Study

% Phloroglucinol	% CBDO	% Bisphenol	T _d (°C)
0	40	60	390
5	38	57	388
6	37.6	56.4	390
10	36	54	398
12	35.2	52.8	402
15	34	51	405
0	100	0	391
6	94	0	390
8	92	0	397
9	91	0	391
10	90	0	390
12	88	0	388
20	80	0	380
0	0	100	350

The linear copolyester has a T_d of 390° C which is not significantly lower than the crosslinked versions of this polymer. The crosslinked versions have a range of 388-405° C. The linear CBDO homopolymer has a T_d of 391 °C. All of the crosslinked versions

remain in the same range, from 380-397 °C. It is not believed that crosslinking of these specific polymers has much affect of the T_d . The linear bisphenol A homopolymer had a T_d of 350 °C. Thermal data on crosslinked versions could not be obtained as the synthesis did not work. Within 30 minutes of synthesis, the solution turned to wax. This wax would not dissolve in any solvent within the lab. The assumption is the polymer became insoluble in the solvent of choice once oligomers were formed.

4.4 DIFFERENTIAL SCANNING CALORIMITRY (DSC)

DSC was performed to determine the T_g of the sample as well as to determine the if the polymer displays any semi-crystallinity. Table 5 contains the T_g for every polymer as well as the crystallinity information. All polymers in this study had an alcohol:acid ratio of 1:1.

Table 5 – T_g/Crystallinity Data for Polymers in This Study

% Phloroglucinol	% CBDO	% Bisphenol A	T _g (°C)	Crystallinity
0	40	60	175	None
5	38	57	182	None
6	37.6	56.4	193	None
10	36	54	175	None
12	35.2	52.8	202	None
15	34	51	193	None
0	100	0	162	T _m =195° C
6	94	0	200	None
8	92	0	192	None
9	91	0	182	None
10	90	0	185	None
12	88	0	149	None
20	80	0	175	None
0	0	100	125	T _m =150° C

The linear copolyester had a T_g of 175 °C, which was not a significant amount lower than the crosslinked versions of this polymer, although crosslinking did seem to have more of an affect on the T_g than on the T_d. The T_g's of the crosslinked versions ranged from 175-202 °C. All copolyesters, linear or crosslinked, were purely amorphous.

The linear CBDO homopolymer had a T_g of 162 °C, which was not a significant amount higher than the crosslinked versions ranging from 149-200 °C. Unlike the

copolyesters, the linear CBDO did show a peak for crystallinity at 195 °C. After crosslinking was complete, the polymers were once again amorphous. The linear Bisphenol A homopolymer had a T_g of 125° C and had a crystallinity peak, T_c , of 150 °C. Once again, no thermal data will be reported for crosslinked versions of the bisphenol A polymers.

4.5 DYNAMIC MECHANICAL ANALYSIS (DMA)

DMA was performed to determine a multitude of thermal and physical properties, including: T_g , storage and loss modulus, Tan delta, Young's modulus, crosslink density and molecular weight between crosslink points (M_c). Table 6 contains all of the data obtained with the DMA.

Table 6 – Thermal and Physical Data Obtained Via DMA

% Phloroglucinol	% CBDO	T_g (°C)	Storage Modulus at 50 °C (MPa)	Loss Modulus at 50 °C (MPa)
6	94	219.5	1645.38	50
8	92	212.6	1583.34	45.83

The linear polymers, were not of sufficient molecular weight, therefore the films did not display the structural integrity needed to obtain films. During film formation of the crosslinked copolyesters, it was observed that the material was tough and took some force to break, but were too rigid to create a thin film for the DMA. The 6 and 8%,

showed significantly higher T_g 's from the DMA than from the DSC, 219.5 and 212.6 °C respectively. The DMA shows that the storage modulus decreases with increasing % crosslinker. This data confirms that the material stores less energy at fairly low temperature with increasing crosslinker percent. This means that the material will be more rigid. All crosslinked CBDO polymers above 8% were brittle and no films could be made of them. Due to the inability of film formation of the linear polymers, a comparison cannot be made between linear and crosslinked samples mechanical data.

4.6 SWELLING STUDIES

Table 7 – Crosslink Density and M_c Obtained Via Swelling Studies

% Phloroglucinol	% CBDO	Crosslink density (mol/cm ³)	M_c (g/mol)
6	94	1.2×10^{-3}	822.3
7	93	1.01×10^{-3}	970.73

5.0 CONCLUSIONS

Throughout this project some trends of the polymers have been noticed. During thermal characterization it has become evident that the absence of CBDO decreases the decomposition temperatures and the glass transition temperatures. With the presence of CBDO, the linear copolyester has a T_g of 175 °C and a T_d of 390 °C. The linear CBDO homopolymer has a T_g of 162 °C and a T_d of 391 °C. The linear bisphenol A homopolymer has a T_g of 125 °C and a T_d of 350 °C. The T_g for the linear bisphenol A homopolymer is at least 35 °C less than either the linear copolyester or the linear CBDO homopolymer. The T_d of the linear bisphenol A homopolymer is at least 40 °C less than either of the linear polymers.

This leads to the assumption that the CBDO unit has some affect on the polymers thermal properties. This is due to the fact that CBDO is extremely rigid. Despite the fact that it is an aliphatic unit, four methyl groups provide steric hindrance to provide the molecule with the same degree of rigidity that an aromatic monomer would possess. This rigid monomer incorporated into a polymer backbone will increase the T_g and the T_d of a polymer.

It can also be acknowledged that the full copolymer is amorphous, while the homopolymers of either the bisphenol A or the CBDO display semicrystallinity. The T_m for the linear CBDO homopolymer was 195 °C and the T_m for the bisphenol A homopolymer was 150 °C. The T_m indicates that the polymers possess some degree of

crystallinity. The reason the copolyester has no evidence of crystallinity is the fact that the polymer has two repeat units which are random. There is a very low possibility that a polymer consisting of 3 x units and 2 y units with the next chain consisting of 2 x units and 8 y units will be able to cohesively stack and form a semi-crystalline polymer. Once the polymers are crosslinked, the crystallinity has disappeared. This is due to the fact that the crosslinking monomer is not identical to the monomers themselves, therefore disrupting their ability to crystallize.

From all of these data, it can be assumed that Bisphenol A is the destructive factor for the polymers. In the fully crosslinked series of copolyesters, it can be affirmed that as the amount of crosslinker is increased the polymers T_g and T_d increase. This is attributed to the fact that with increasing mol % of phloroglucinol, the overall mol % of bisphenol A is decreasing. Thereby allowing the thermal properties of the polymer to increase.

APPENDIX

GPC DATA

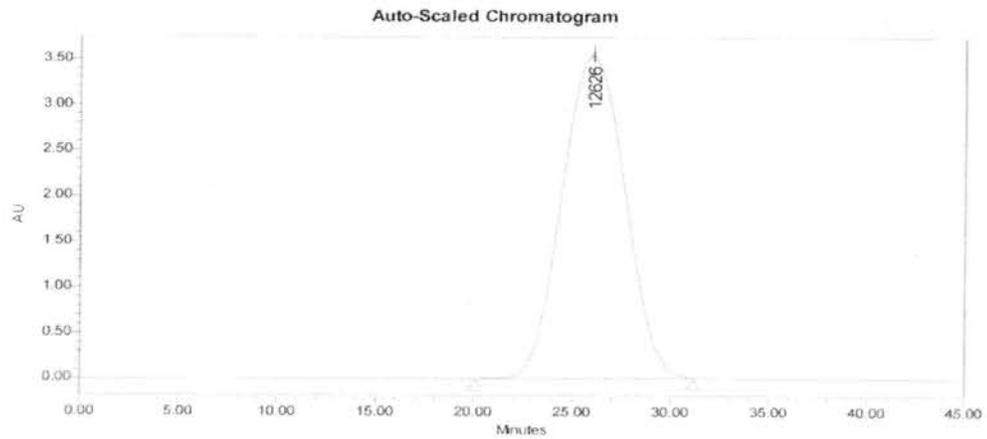


Figure 14 – Linear Copolyester GPC

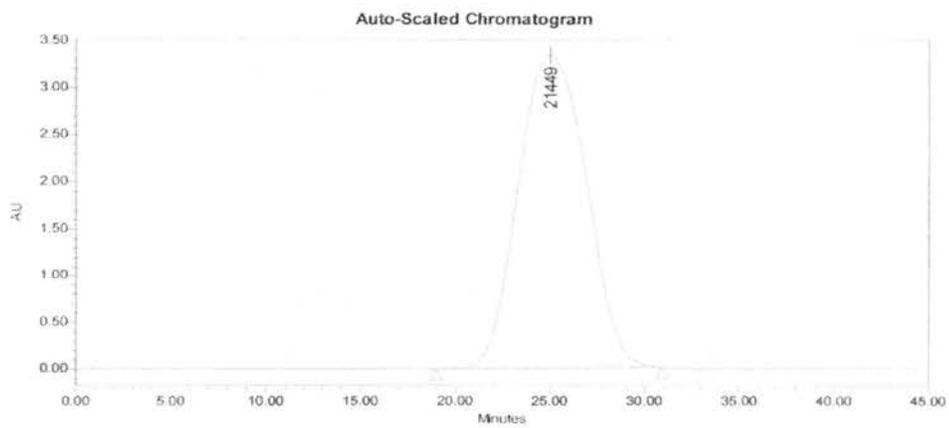


Figure 15 – CBDO Homopolymer GPC

TGA DATA

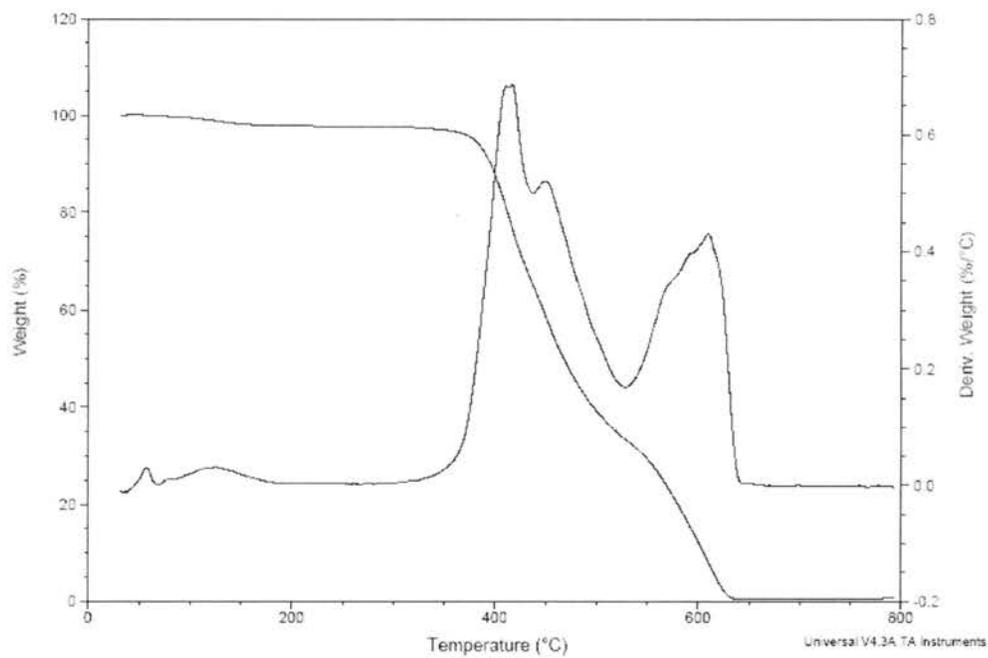


Figure 16 - Linear Copolyester TGA

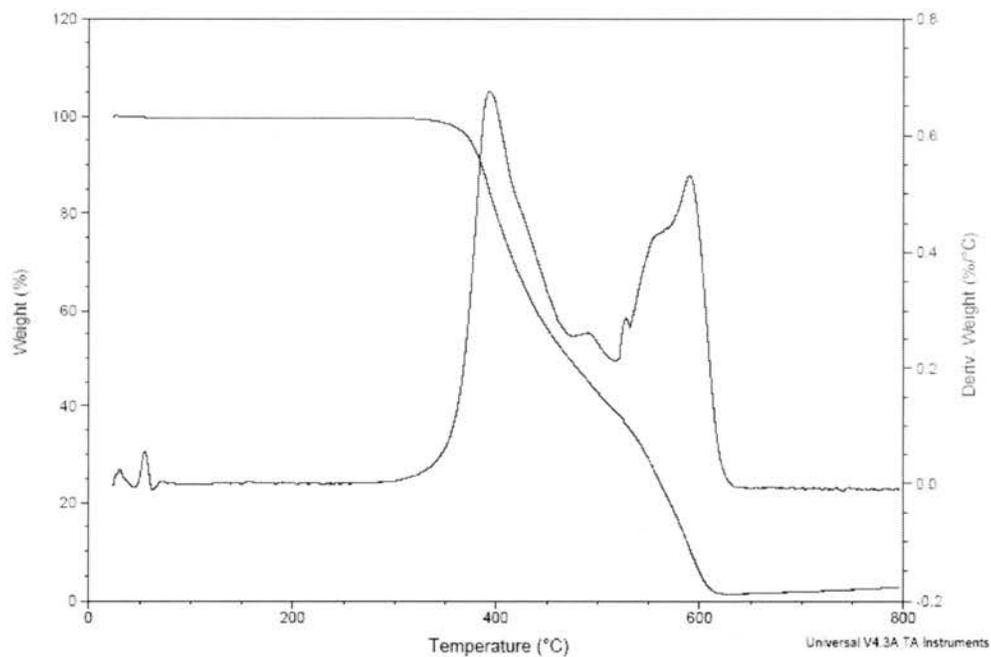


Figure 17 - 5% Crosslinked Copolyester TGA

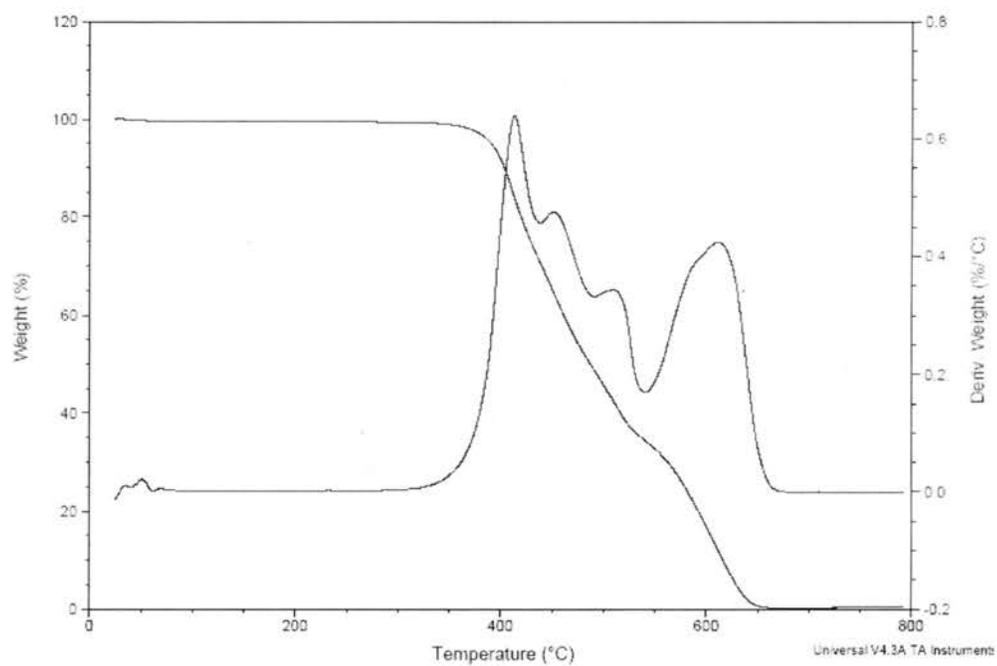


Figure 18 - 6% Crosslinked Copolyester TGA

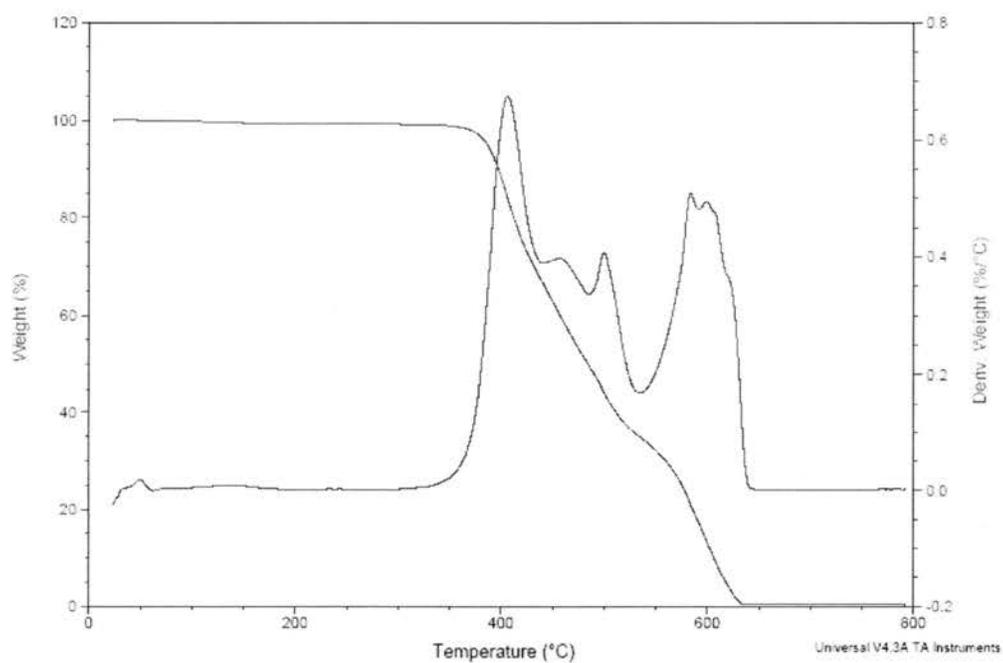


Figure 19 - 10% Crosslinked Copolyester TGA

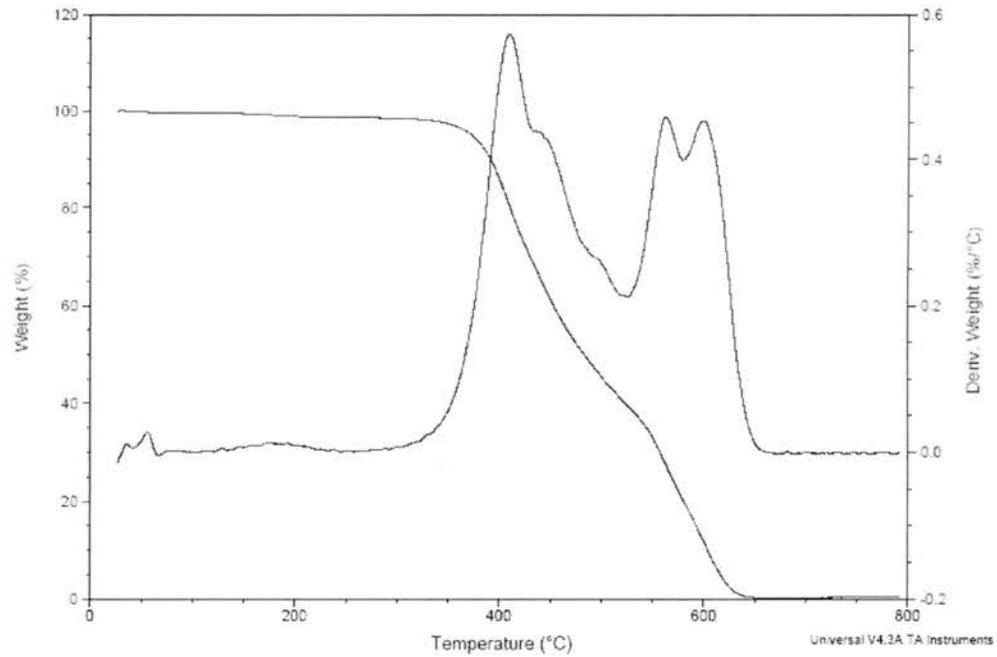


Figure 20 - 12% Crosslinked Copolyester TGA

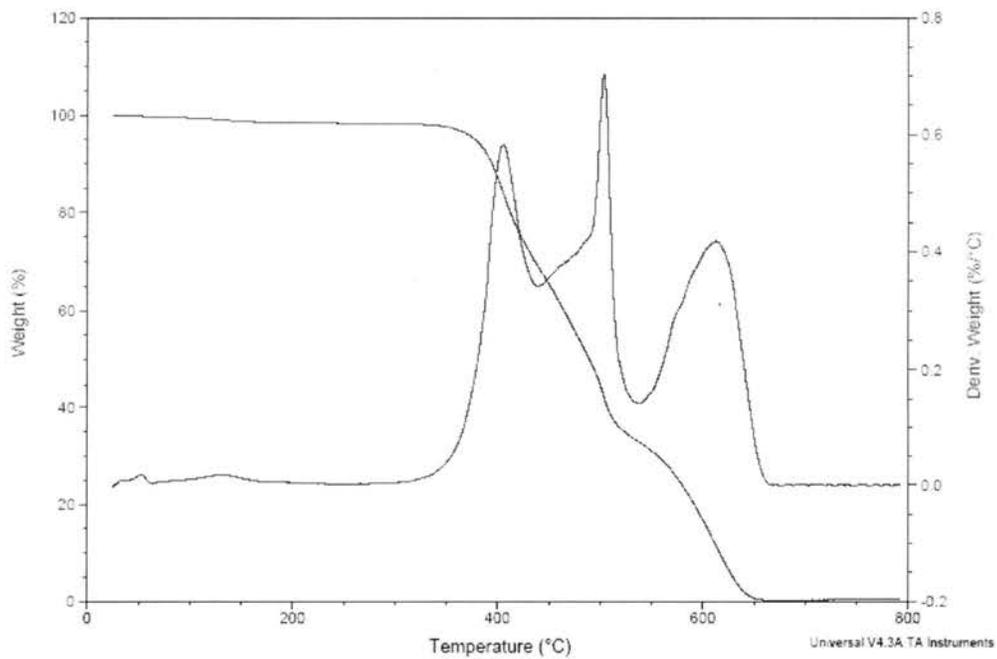


Figure 21 - 15% Crosslinked Copolyester TGA

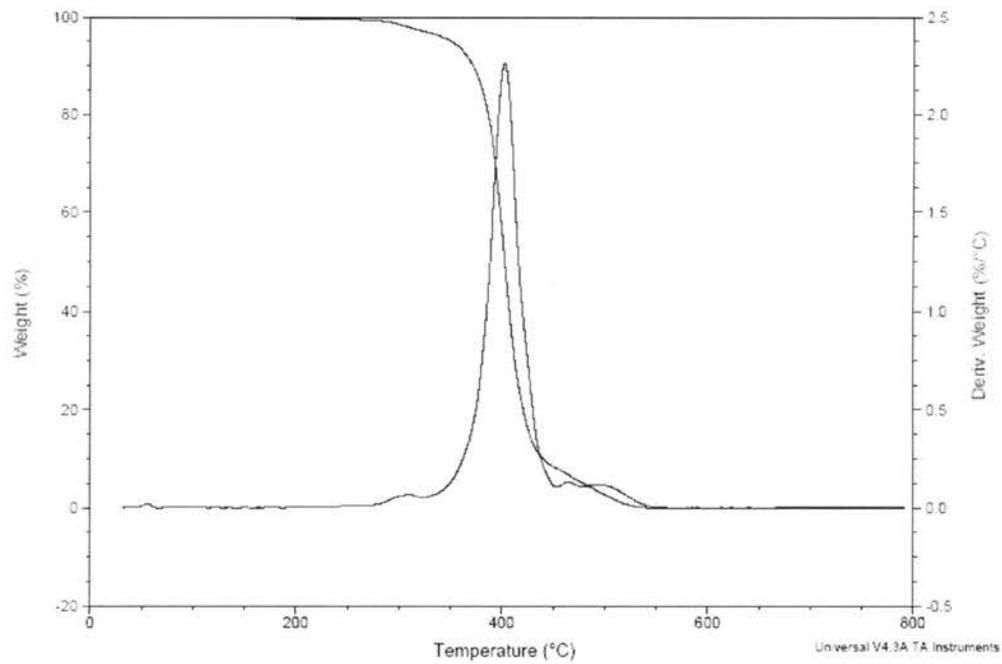


Figure 22 - Linear CBDO Homopolymer TGA

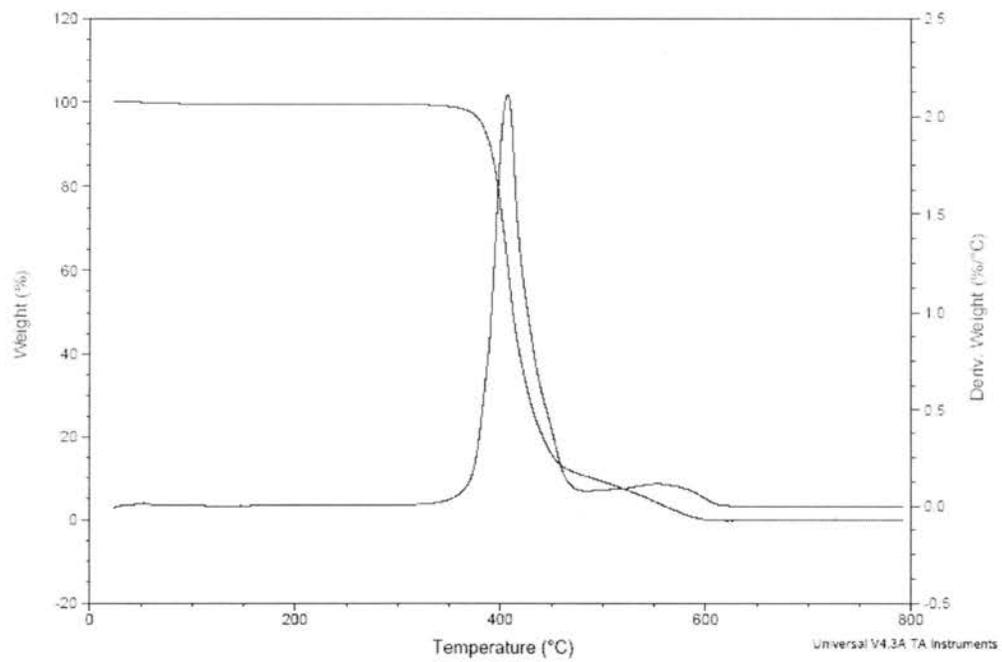


Figure 23 - 6% Crosslinked CBDO Copolyester TGA

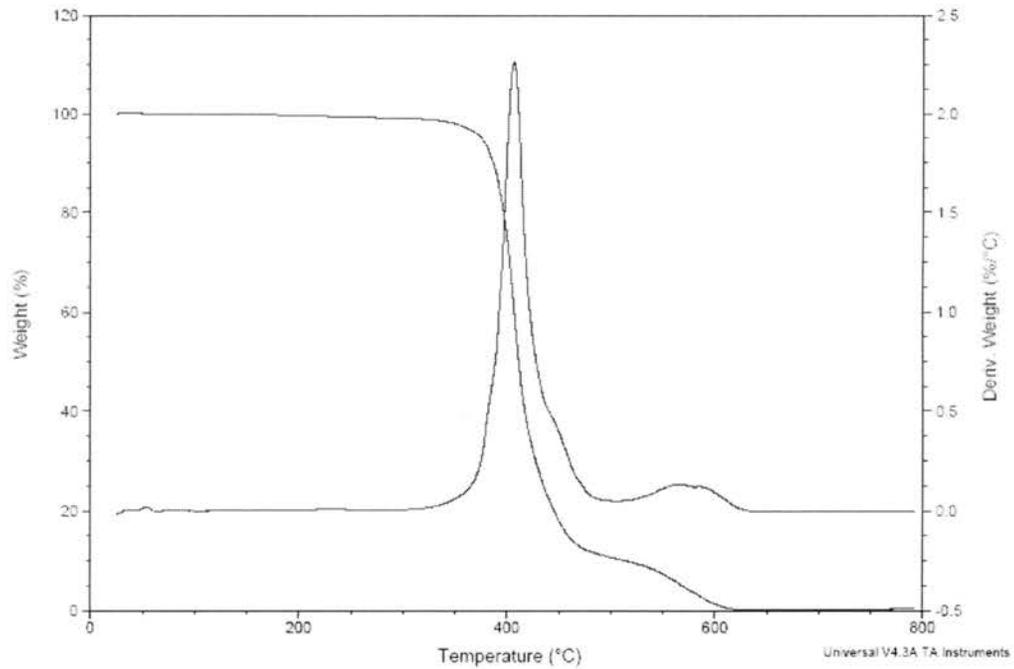


Figure 24 - 8% Crosslinked CBDO Copolyester TGA

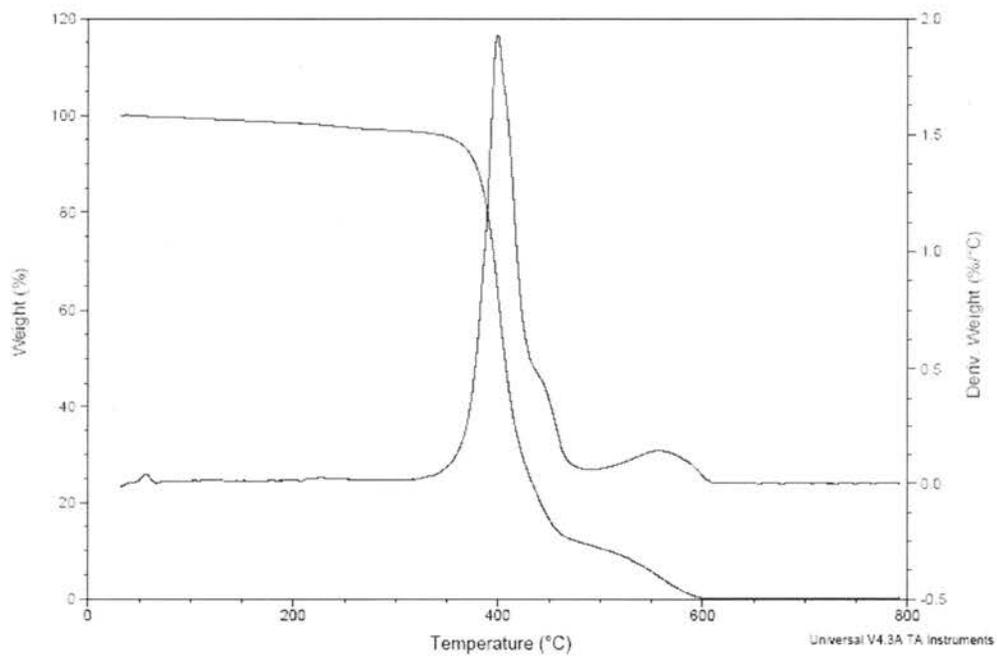


Figure 25 - 9% Crosslinked CBDO Copolyester TGA

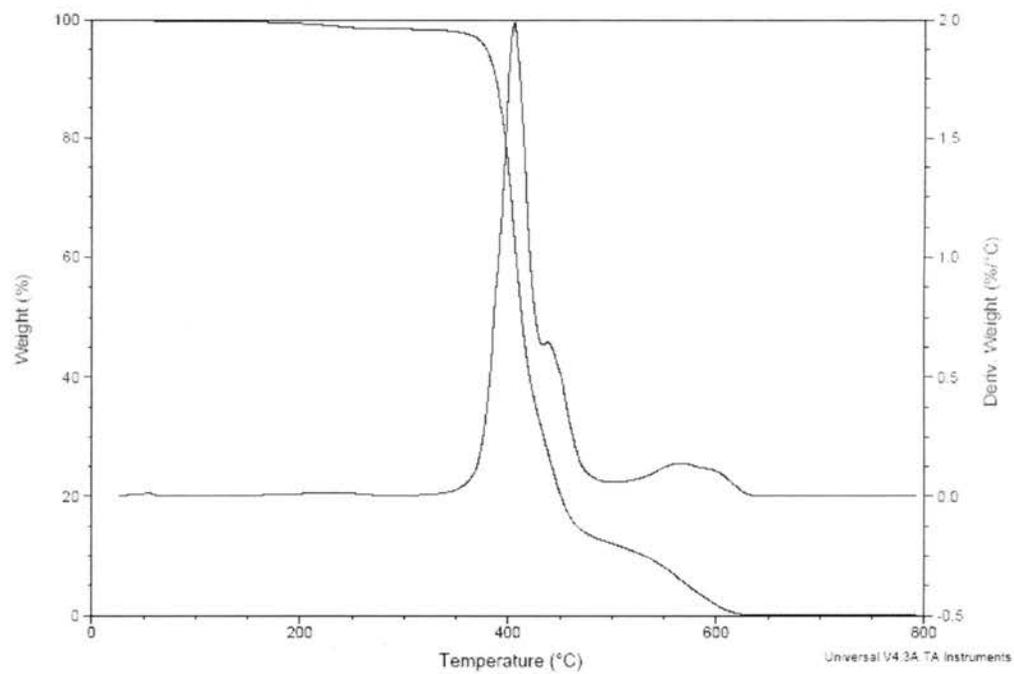


Figure 26 - 10% Crosslinked CBDO Copolyester TGA

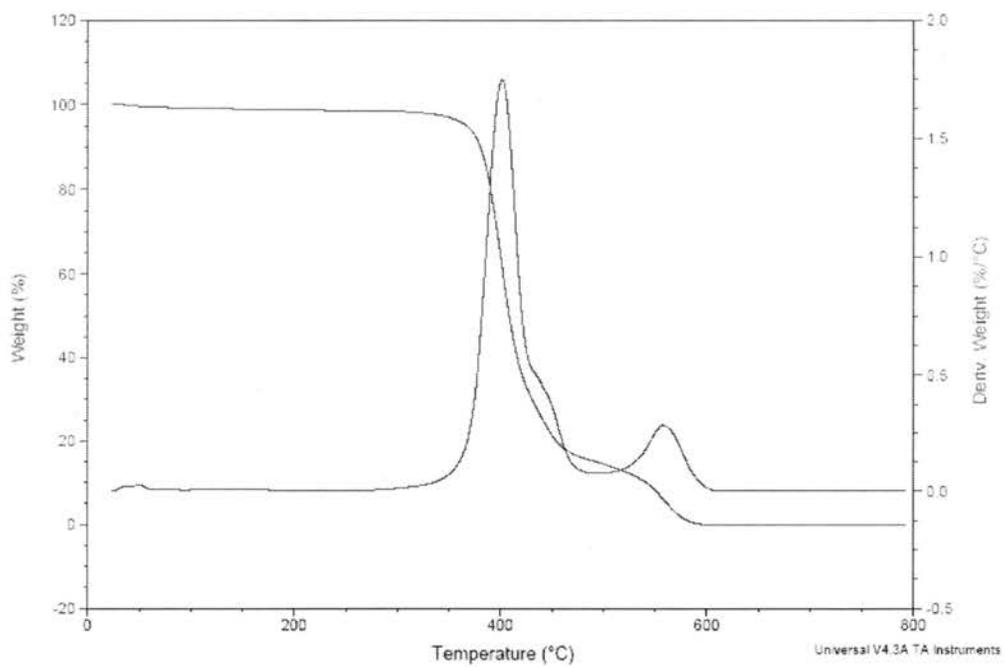


Figure 27 - 12% Crosslinked CBDO Copolyester TGA

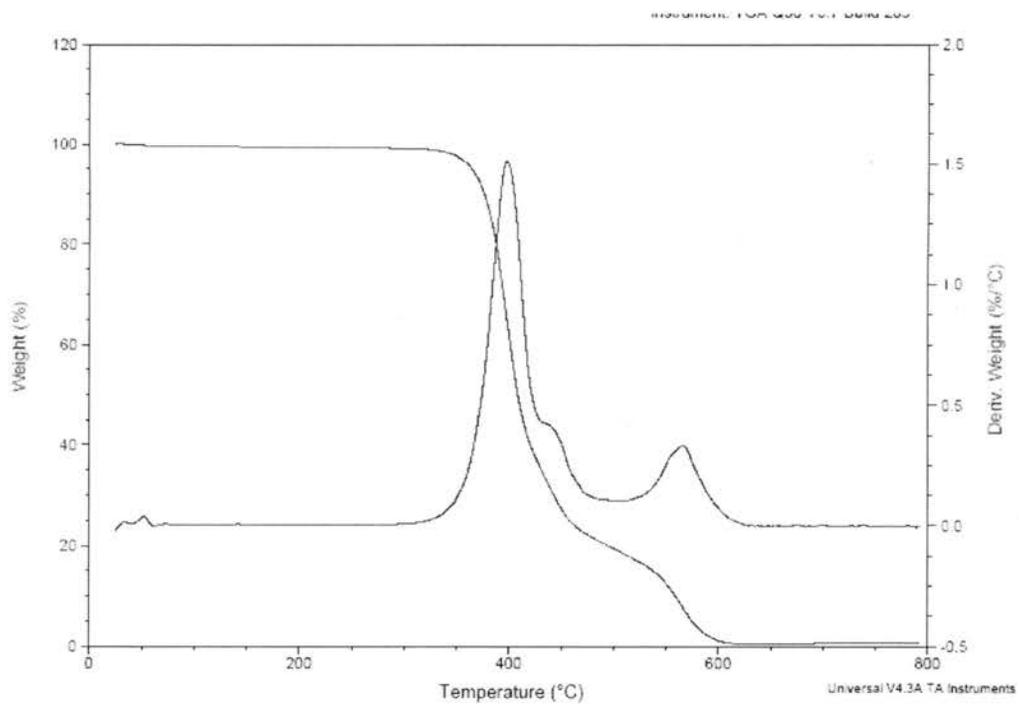


Figure 28 - 20% Crosslinked CBDO Copolyester TGA

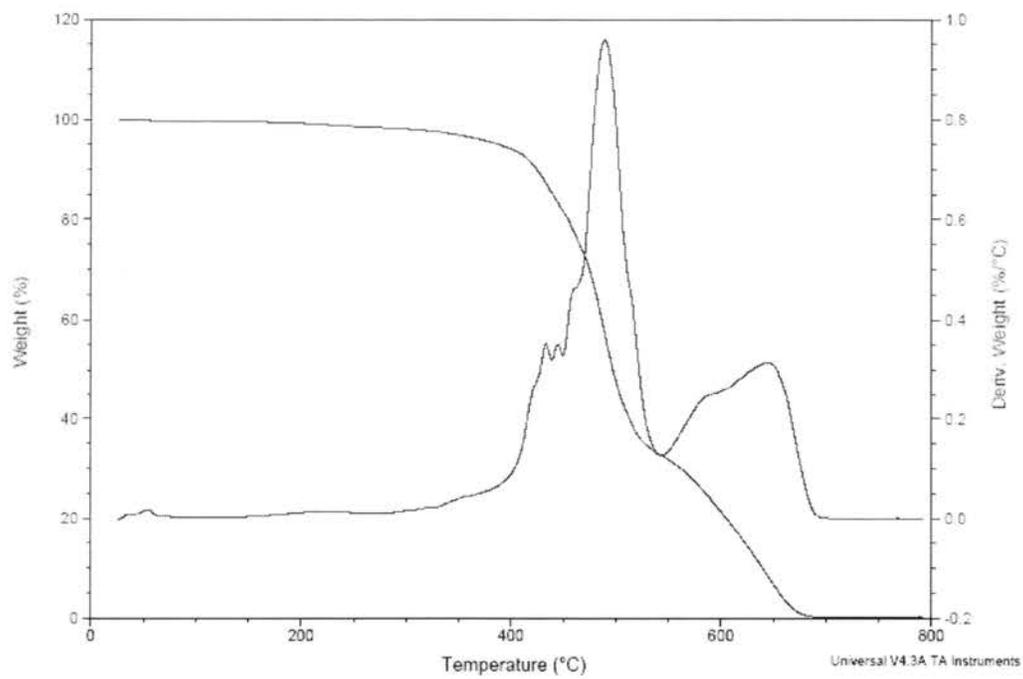


Figure 29 - Linear Bisphenol A Homopolymer TGA

DSC DATA

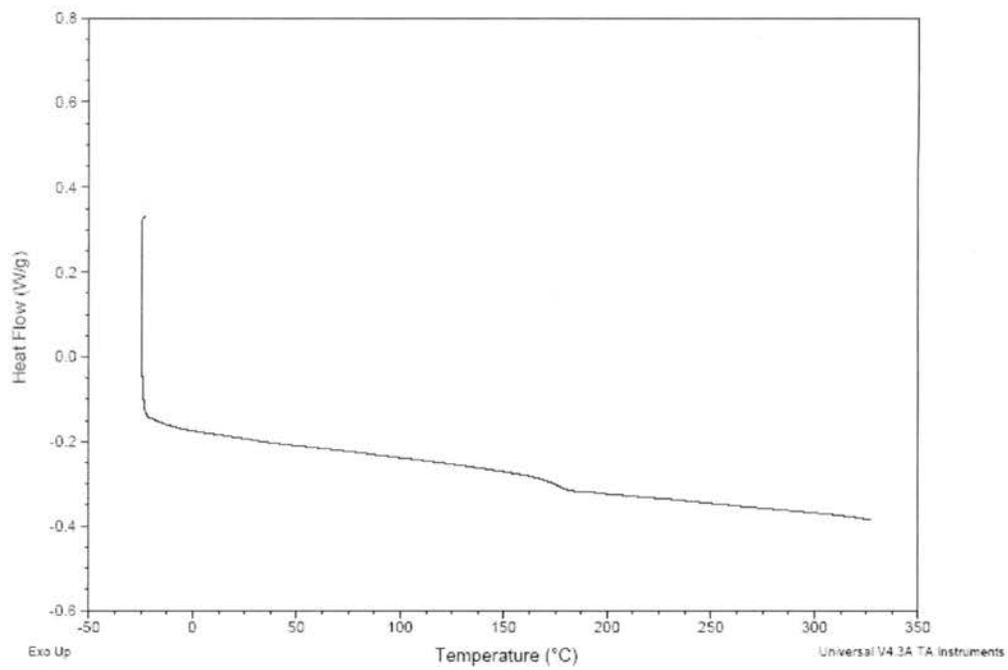


Figure 30 - Linear Polyester DSC

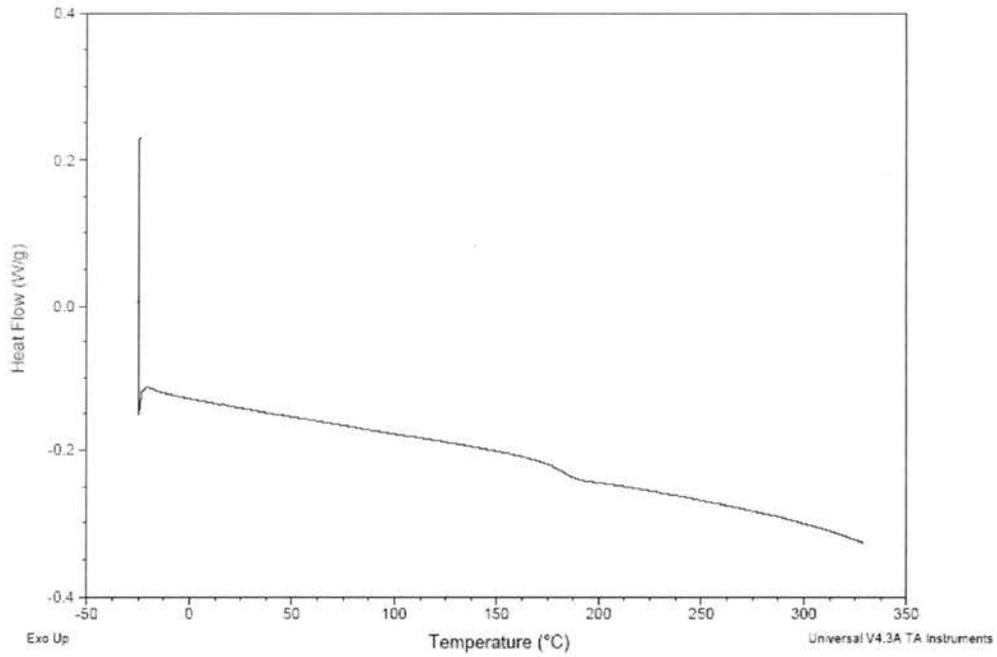


Figure 31 - 5% Crosslinked Copolyester DSC

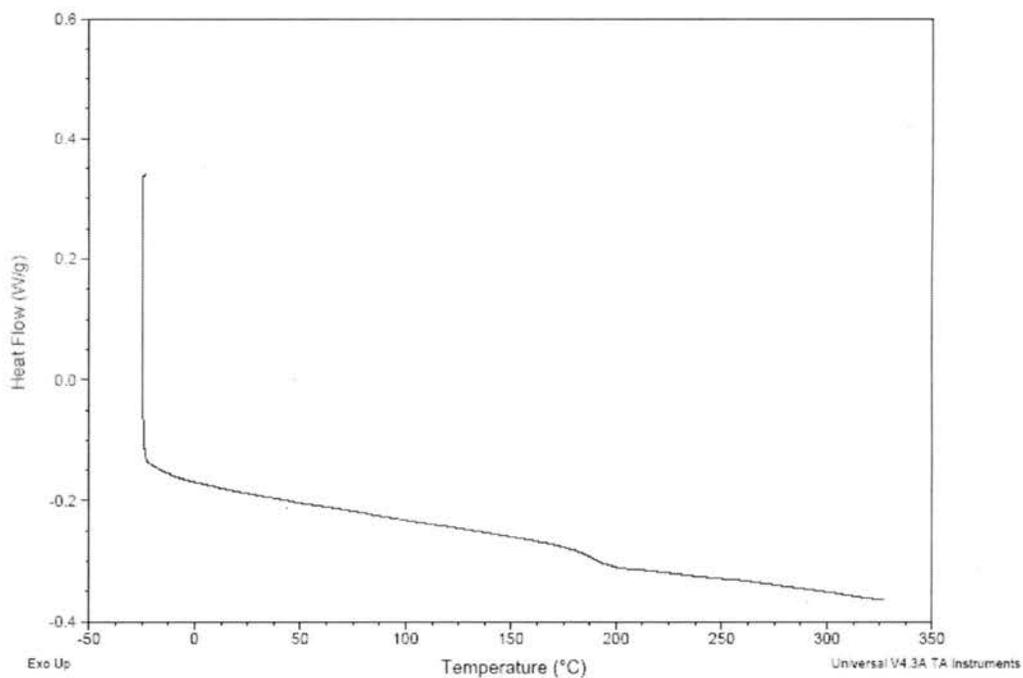


Figure 32 - 6% Crosslinked Copolyester DSC

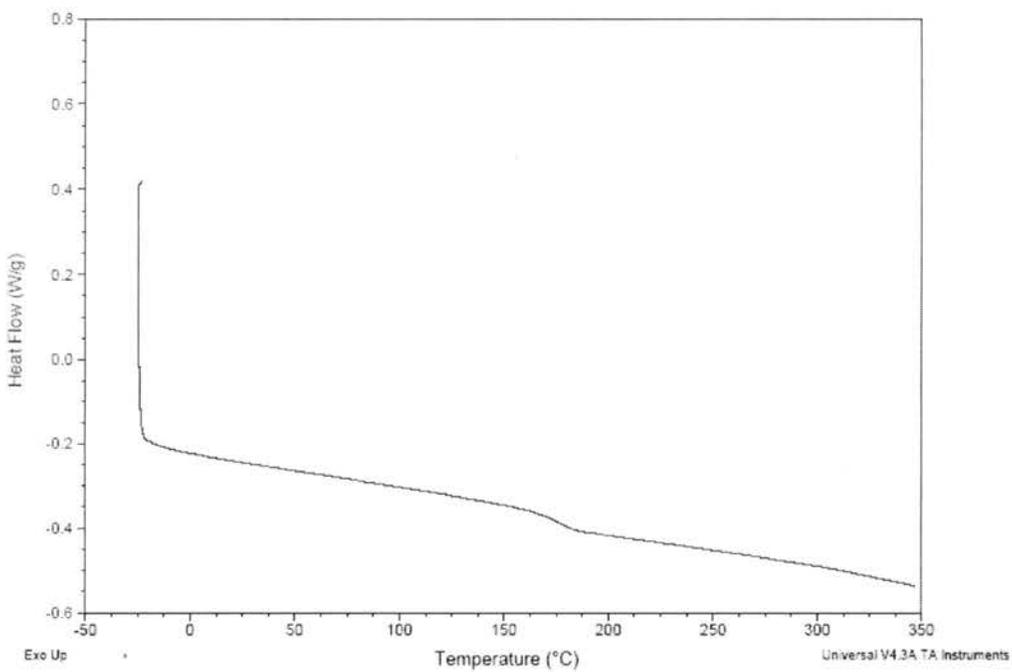


Figure 33 - 10% Crosslinked Copolyester DSC

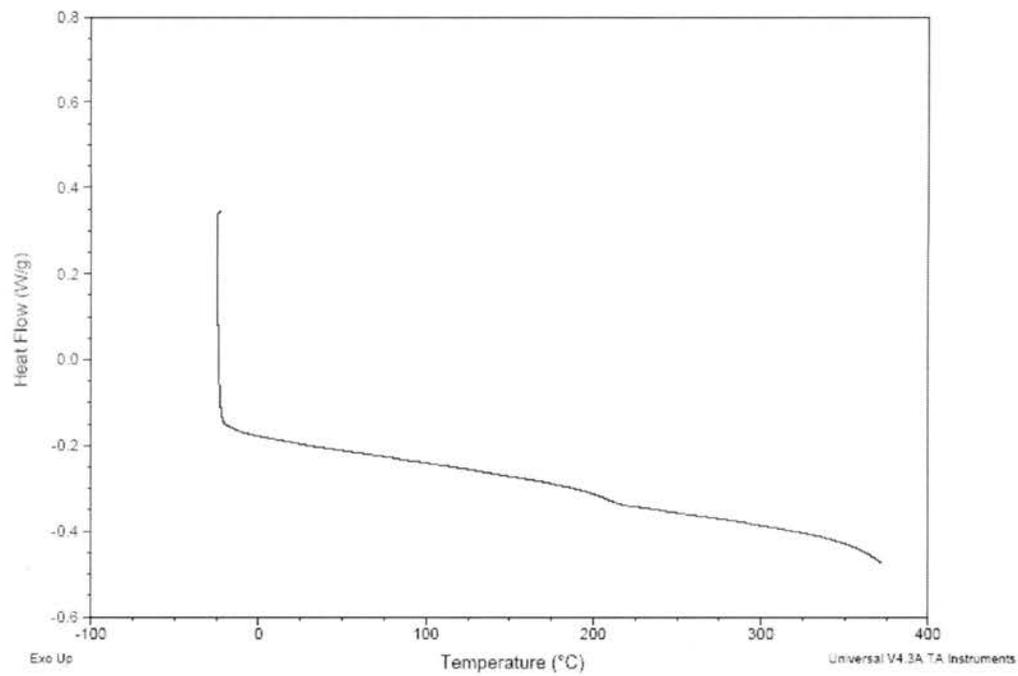


Figure 34 - 12% Crosslinked Copolyester DSC

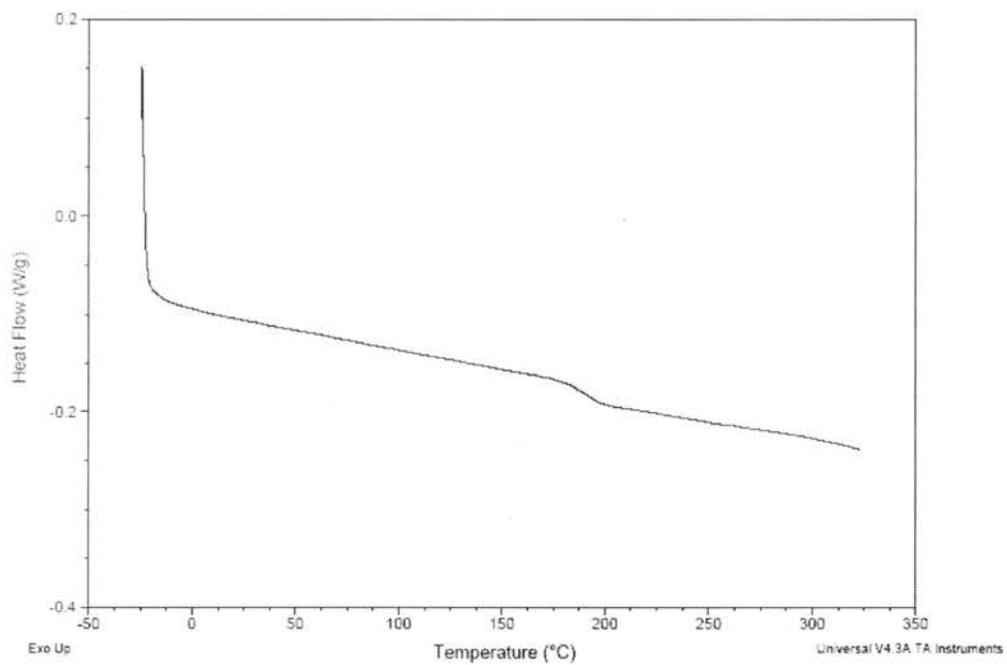


Figure 35 - 15% Crosslinked Copolyester DSC

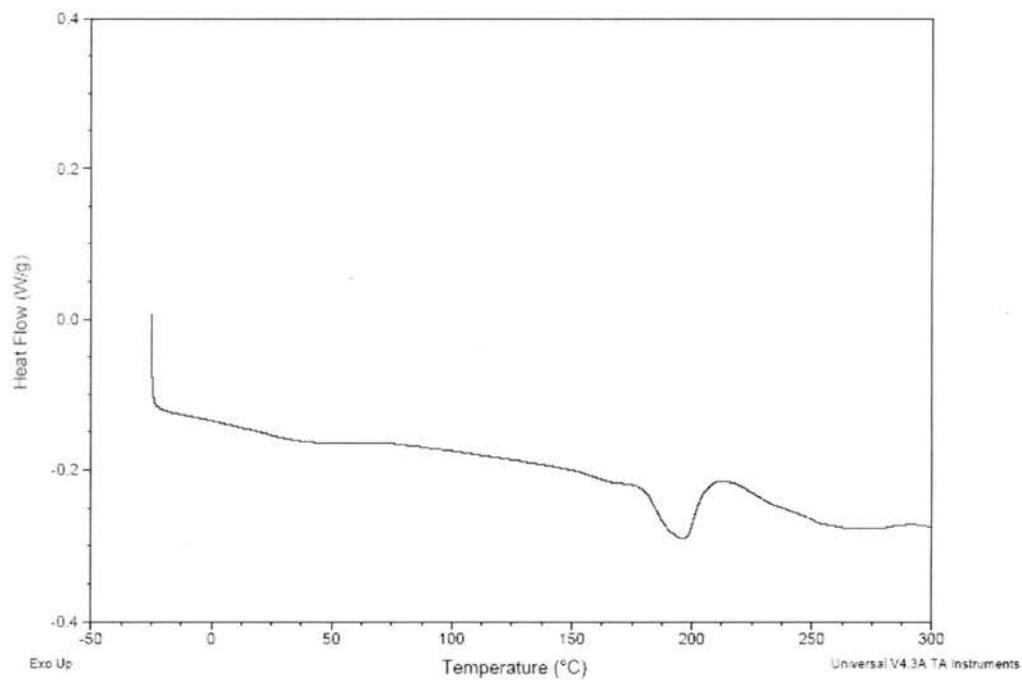


Figure 36 - Linear CBDO Homopolymer DSC

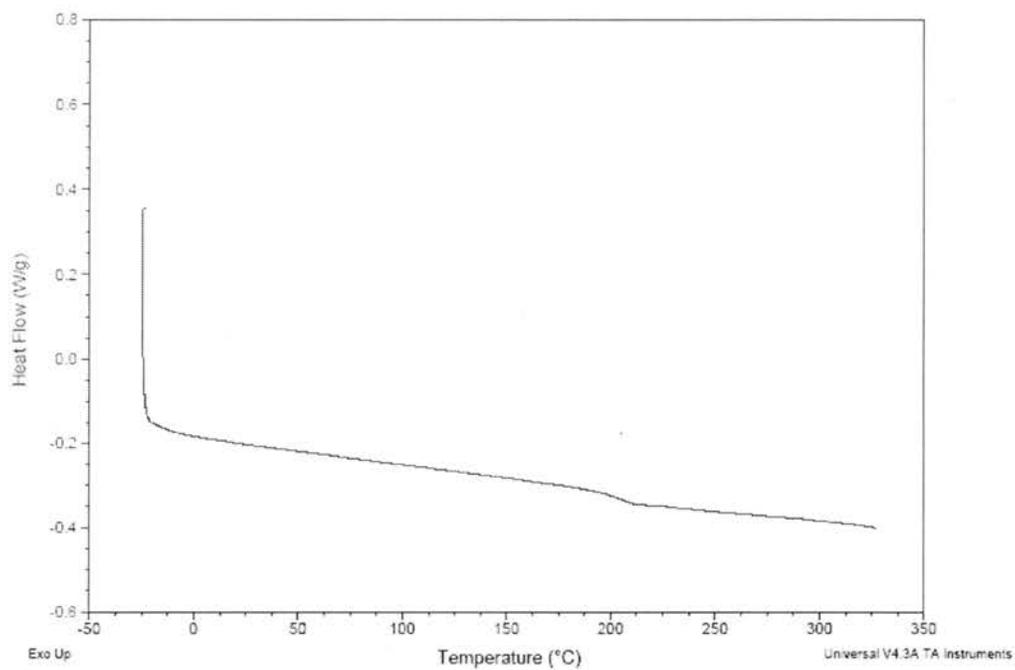


Figure 37 - 6% Crosslinked CBDO Copolyester DSC

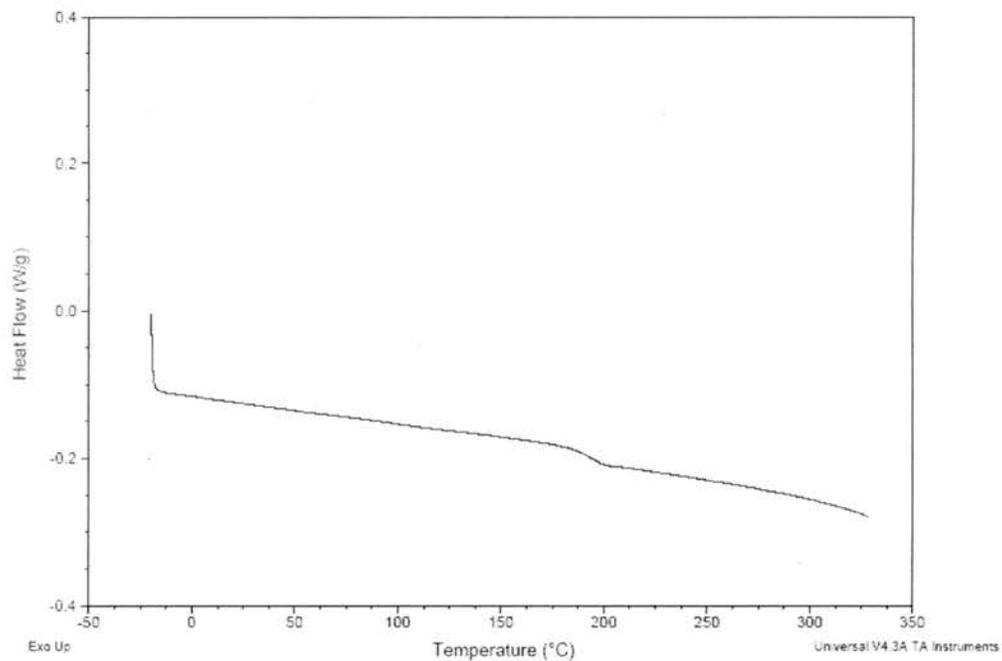


Figure 38 - 8% Crosslinked CBDO Copolyester DSC

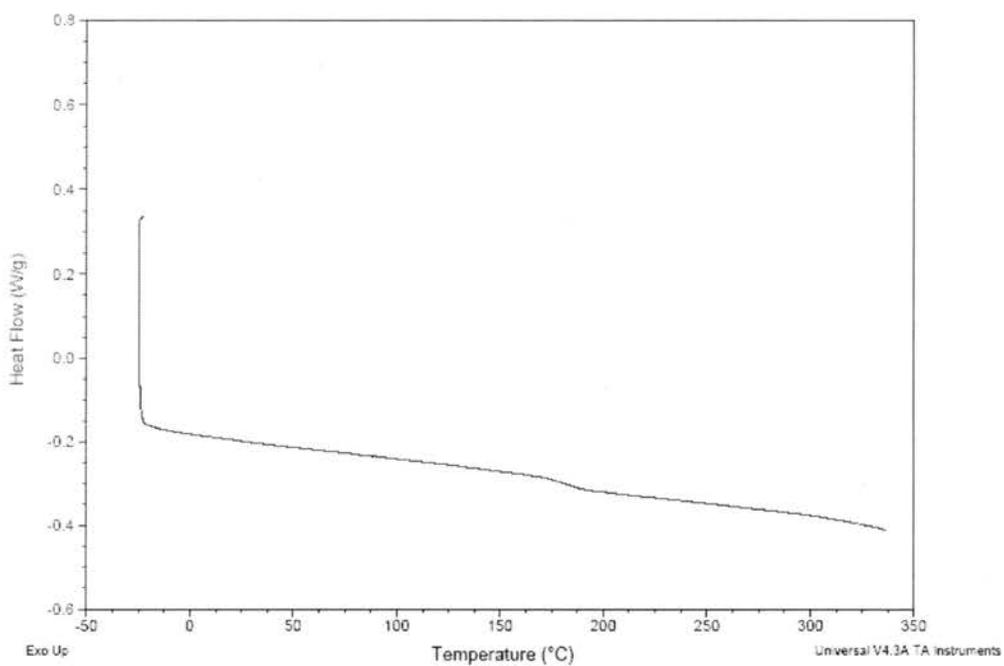


Figure 39 - 9% Crosslinked CBDO Copolyester DSC

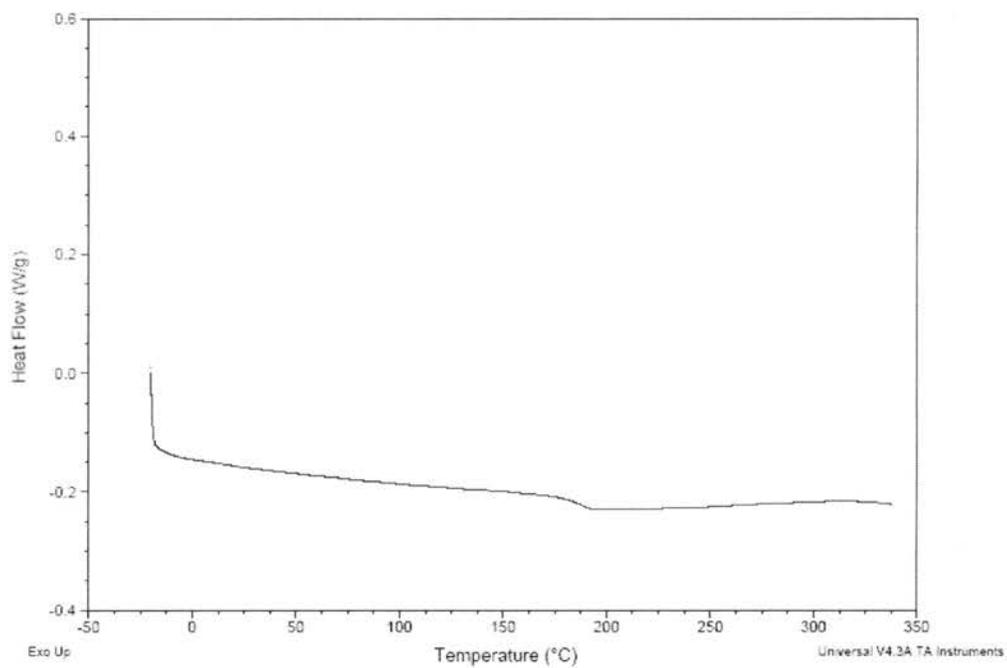


Figure 40 - 10% Crosslinked CBDO Copolyester DSC

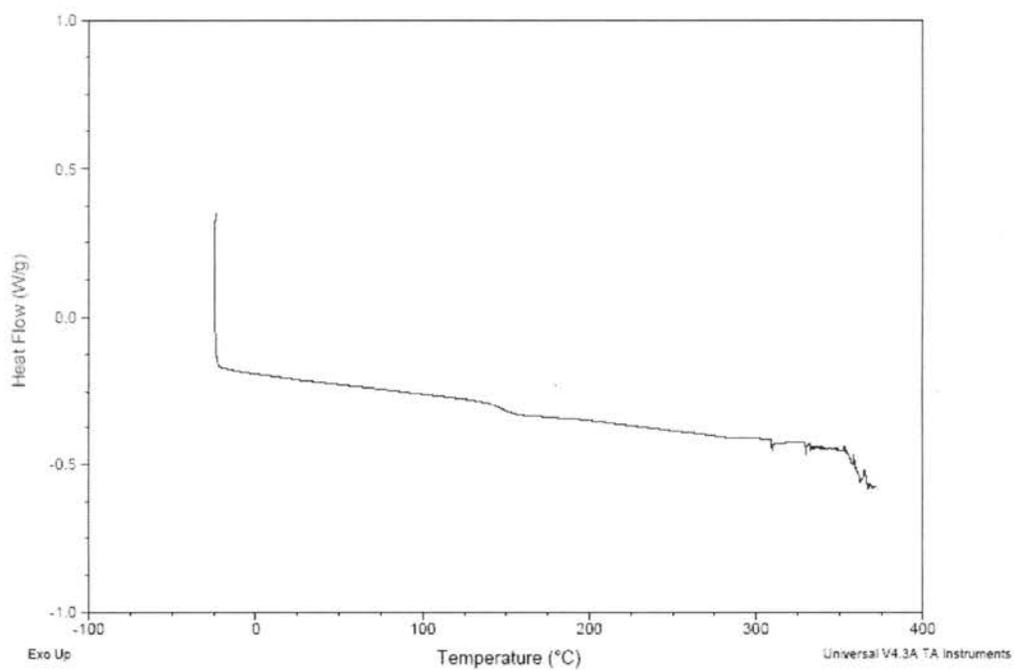


Figure 41 - 12% Crosslinked CBDO Copolyester DSC

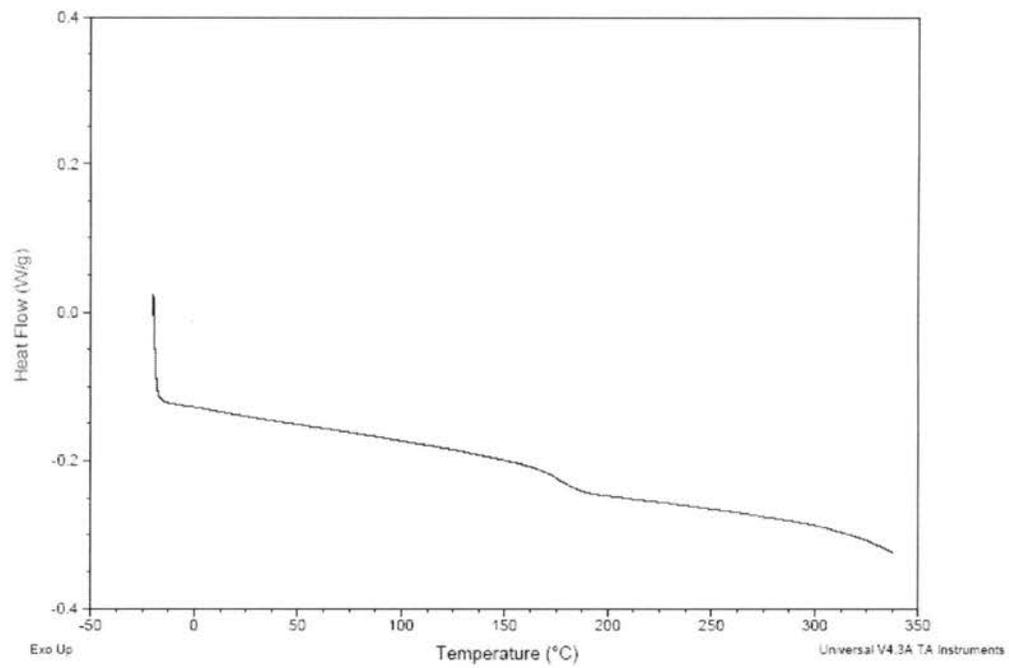


Figure 42 - 20% Crosslinked CBDO Copolyester DSC

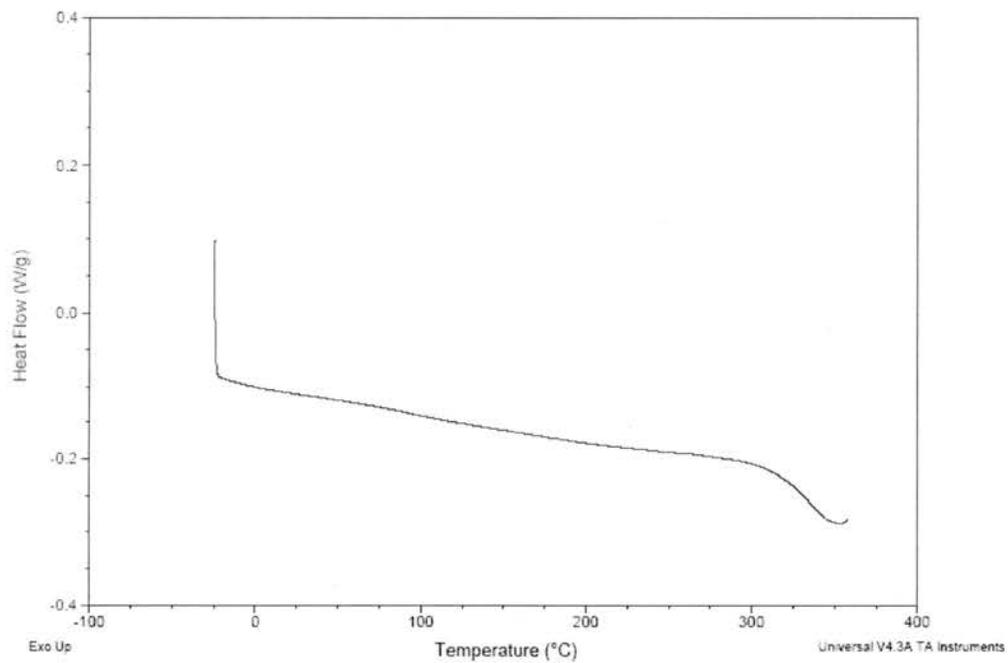


Figure 43 - Linear Bisphenol A Homopolymer DSC

DMA DATA

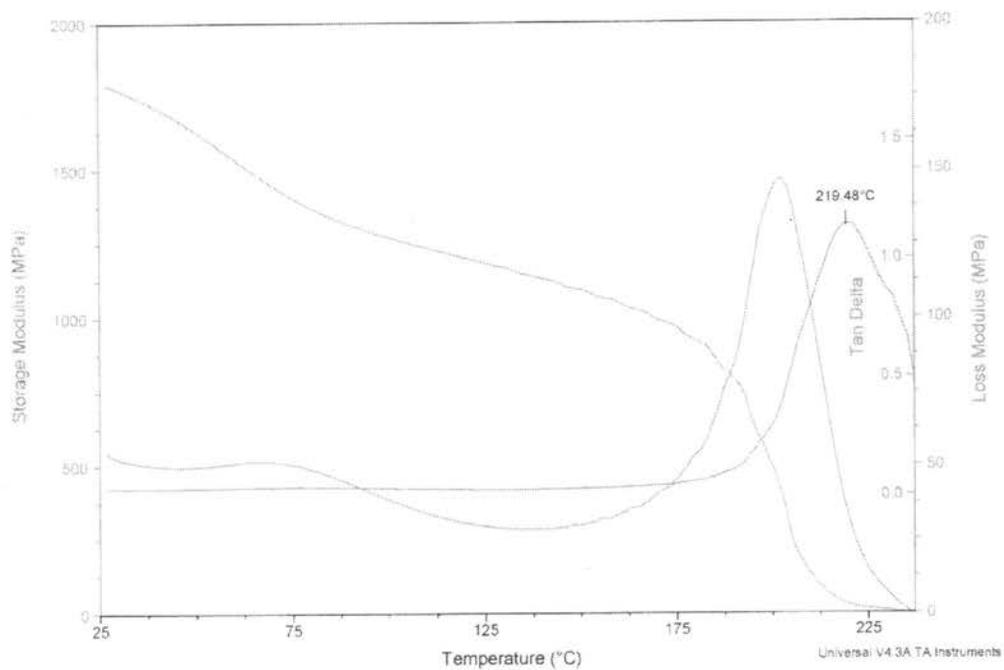


Figure 44 - 6% Crosslinked CBDO Copolyester DMA

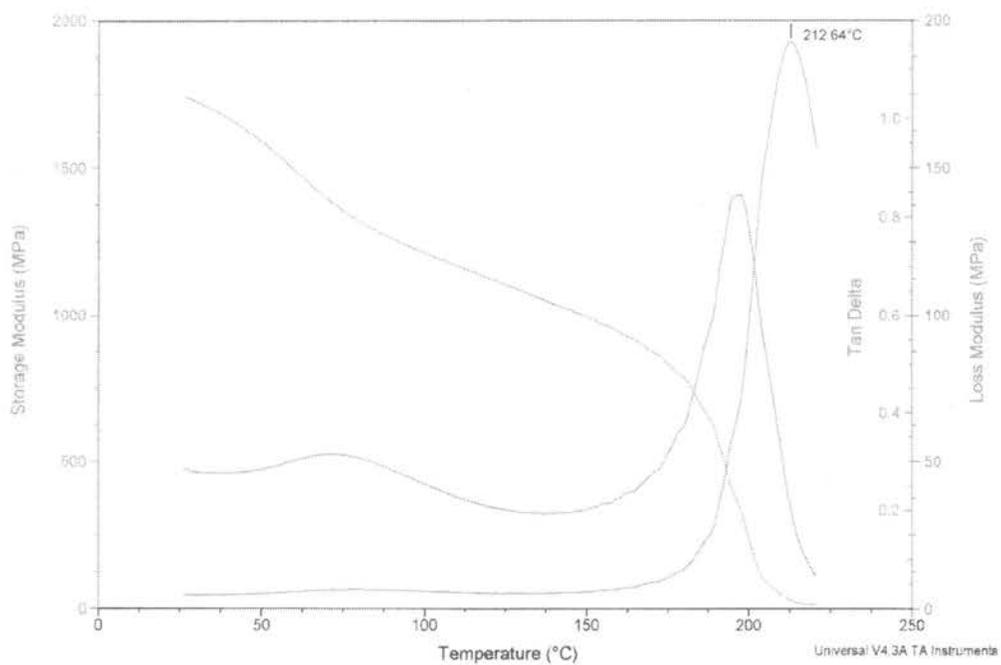


Figure 45 - 8% Crosslinked CBDO Copolyester DMA

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VITA

Amber Marie Douglas was born in Dallas, Texas, on October 3, 1980, the daughter of Sandra Lynn Gordon and Donald Eldon Gordon, Jr. After completing her work at Scarborough High School, Houston, Texas, in 1998, she entered Saint Edward's University, Austin, Texas. After receiving her Bachelor of Science from Saint Edward's University in May of 2003, she took two years off from school to care for her child. In August of 2005, she entered the Graduate College of Texas State University-San Marcos.

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