

THERMAL AND MECHANICAL ANALYSIS OF A NOVEL CBDO-BASED
COPOLYESTER

by

Marcus B. Newsome, B. A.

A thesis submitted to the Graduate Council of
Texas State University in partial fulfillment
of the requirements for the degree of
Master of Science
with a Major in Chemistry
August 2015

Committee Members:

Gary Beall, Chair

Jennifer Irvin

William Brittain

COPYRIGHT

by

Marcus B. Newsome

2015

FAIR USE AND AUTHOR'S PERMISSION STATEMENT

Fair Use

This work is protected by the Copyright Laws of the United States (Public Law 94-553, section 107). Consistent with fair use as defined in the Copyright Laws, brief quotations from this material are allowed with proper acknowledgement. Use of this material for financial gain without the author's express written permission is not allowed.

Duplication Permission

As the copyright holder of this work I, Marcus B. Newsome, refuse permission to copy in excess of the "Fair Use" exemption without my written permission.

ACKNOWLEDGEMENTS

I would like to thank my chair, Dr. Gary Beall, for introducing me to this line of research and for encouraging me to develop my skills as an independent worker, scientist and thinker. I couldn't have started or ended this project without the disciplined help of Dr. Yelena Nash, who showed me all there was to know about CBDO. Leah Cromwell was also invaluable for the recrystallization process. Thanks to Dr. Powell, as well, for having extended conversations about anything related to polymers with me. I'm indebted to my committee members, Dr. Jennifer Irvin and Dr. William Brittain, for their extremely valuable feedback. I would also like to thank the Beall Research Group, especially: Amber Douglas, for her insight on the work; Brandon Henderson, for his help with the processing and analysis help; and to Haoran Chen, for willing to have extended conversations about everything and anything related to this topic. I'd like to thank the department for helping us to develop skills in a small and nurturing academic environment. Finally, I would like to thank my family, especially my mom, for encouraging me to reach my goals, no matter what the circumstance.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS.....	iv
LIST OF TABLES.....	vi
LIST OF FIGURES	vii
CHAPTER	
I. INTRODUCTION	1
II. MATERIALS AND METHODS.....	14
III. RESULTS AND DISCUSSION	24
REFERENCES	37

LIST OF TABLES

Table	Page
1. Thermal and Mechanical Properties of CBDO Copolyesters	5
2. Notched Izod Data for CBDO Copolyester and Polycarbonate.....	7
3. Ballistic Data for CBDO Copolyester and Polycarbonate	8
4. <i>cis</i> -CBDO ¹ H NMR Peak Shifts and Relative Intensities.....	25
5. <i>trans</i> -CBDO ¹ H NMR Peak Shifts and Relative Intensities	26
6. <i>cis</i> -CBDO/NPG and DMT Copolyester ¹ H NMR Peak Shifts and Relative Intensities	26
7. GPC Data of <i>cis</i> -CBDO/NPG and DMT Copolyester	29
8. TGA Data of <i>cis</i> -CBDO/NPG and DMT Copolyester	30
9. DSC Data of <i>cis</i> -CBDO/NPG and DMT Copolyester	31
10. DMA Data of <i>cis</i> -CBDO/NPG and DMT Copolyester	33

LIST OF FIGURES

Figure	Page
1. <i>cis</i> and <i>trans</i> CBDO isomer structures.....	2
2. Typical <i>cis</i> -CBDO and <i>trans</i> -CBDO isomers.....	2
3. Reaction of CBDO with 1,3-propanediol and dimethyl terephthalate to produce a CBDO copolyester	3
4. Effect of CBDO content on T_g and notched Izod impact for terephthalate copolymers with PDO and BDO	6
5. Dent in <i>cis</i> copolyester and full shape recovery using a heat gun	9
6. DSC and TGA data of the <i>trans</i> -rich, 43C:57T and <i>cis</i> -rich polymers	9
7. DMA data of the <i>trans</i> -rich, 43C:57T and <i>cis</i> -rich polymers.....	10
8. Molecular model of a CBDO-based copolyester utilizing the <i>cis</i> isomer	11
9. Molecular model of a CBDO-based copolyester utilizing the <i>trans</i> isomer.....	11
10. Structural comparison of 1,3-propanediol and neopentyl glycol.....	12
11. Synthesis of the <i>cis</i> -CBDO/NPG and DMT copolyester.....	17
12. Proposed mechanism of acid-catalyzed transesterification (using dibutyltin oxide) of DMT with <i>cis</i> -CBDO and NPG	18
13. ^1H NMR of <i>cis</i> -CBDO in DMSO-d_6	24
14. ^1H NMR of <i>trans</i> -CBDO in DMSO-d_6	25
15. ^1H NMR of <i>cis</i> -CBDO/NPG and DMT copolyester in CDCl_3	27
16. <i>cis</i> -CBDO/NPG and DMT copolyester with labeled NMR protons.....	28

17. Sample 2 TGA of the <i>cis</i> -CBDO/NPG and DMT copolyester, with a ramp of 10 °C/min.....	31
18. Sample 3 DSC of the <i>cis</i> -CBDO/NPG and DMT copolyester, with a 2 nd ramp of 5 °C/min.....	32
19. Sample 2 DMA of the <i>cis</i> -CBDO/NPG and DMT copolyester, using a single cantilever at 1 Hz and a ramp of 3 °C/min	33

CHAPTER I

INTRODUCTION

The polymer industry has been evolving at an exponential rate by discovering, modifying and commercializing everyday products. These apply to thermoplastics, resins and thermosets that exhibit a wide range of properties. While some exhibit better thermal stability at the cost of lowered strength, some may exhibit superior strength while lacking resistance to UV degradation, causing constant refinement of a polymer at every level of development. In the military realm, there is a high level of interest in transparent, high impact materials for soldier protection. The applications can include windows in vehicles, protective goggles, face shields and riot shields.

As it stands, the polyamide Kevlar[®] is the standard for body armor and impact-related protection due to its high impact resistant properties (1). The molecular reason for this lies behind the hydrogen bonding between the carbonyl and amine groups, as well as the pi-bond stacking interactions between the aromatic groups (2). Given the crystalline nature of this polyamide (3), though, its opaqueness is not suitable in applications requiring transparency, such as bullet-proof windows. In these types of applications, polycarbonate would be a more appropriate choice due to its unusually high impact strength and transparency (4). This is why it is used in laboratory safety shields, bullet-proof windows, safety helmets and other similar products.

High impact polymers are typically composed of aromatic units so that molecular rigidity is enforced, which contributes to high glass transition temperatures and, in the case of semi-crystalline polymers, higher melting points (5). Since aromaticity is almost necessary for rigid and thermally stable polymers, aliphatic molecules (non-aromatic

compounds) are not commonly used. The exception to this rule is the class of 2,2,4,4-tetraalkyl-1,3-cyclobutylenes. For instance, this molecular template can be incorporated into polymers in the form of *cis/trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), as seen in Figures 1 and 2 (6).

The polyesters of *cis/trans*-CBDO and dimethyl terephthalate (DMT) exhibit relatively high melting points and good weathering resistance (7,8). Their subsequent polycondensation with linear, aliphatic diols (40-90 mol % CBDO) produce amorphous, random copolyesters with high impact resistance, high glass transition temperature (T_g), thermal stability, transparency, and low color.

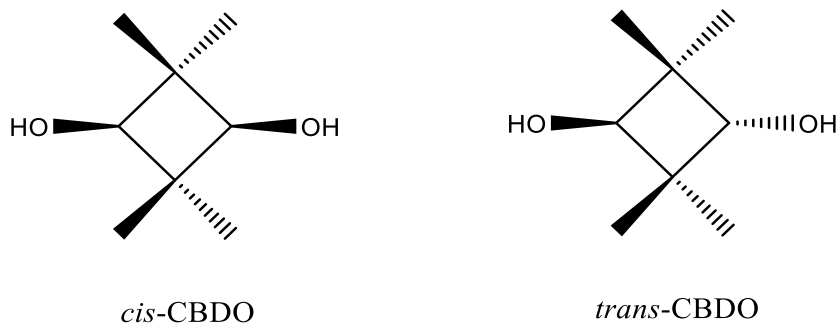


Figure 1. *cis* and *trans* CBDO isomer structures.

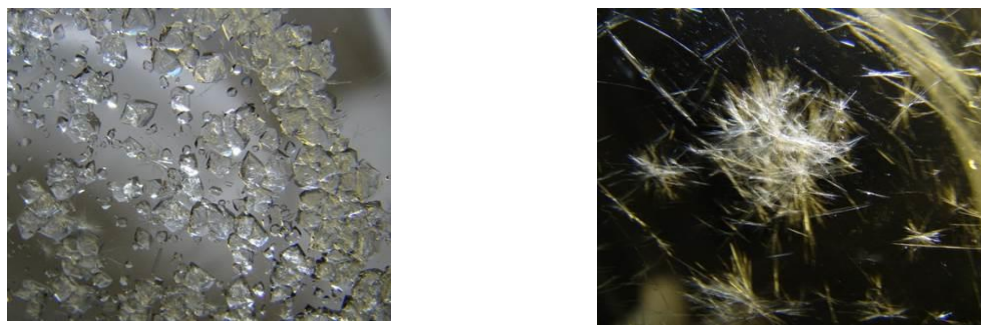


Figure 2. Typical *cis*-CBDO (left) and *trans*-CBDO (right) isomers (Photo Credit: Dr. Yelena Nash).

In particular, 1,3-propanediol (PDO) is the linear, aliphatic diol of choice since it yielded a high molecular weight product with less yellow color (9). Most importantly, the aforementioned qualities of this polymer (copolyester) can be attributed to the rigid, aliphatic CBDO unit (especially for the enhanced T_g and the enhanced impact resistance) (5). Figure 3 shows a typical synthesis of CBDO with PDO and DMT.

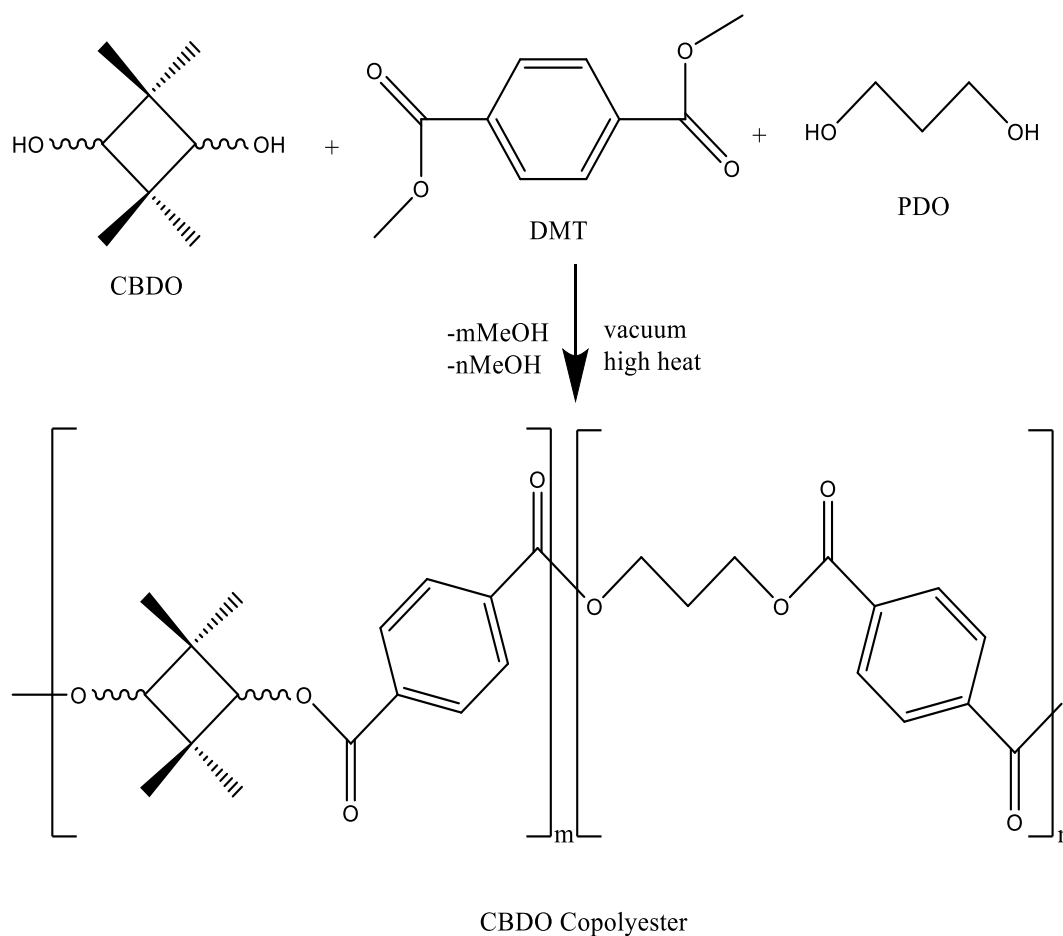


Figure 3. Reaction of CBDO with 1,3-propanediol and dimethyl terephthalate to produce a CBDO copolyester (9).

The polycondensation of CBDO copolyesters are typically carried out by melt polymerization since it is a potentially inexpensive, scalable process (9). The products

obtained by this process are also generally pure and no additional product purification steps are needed. Although not a technique used in recent literature to produce CBDO copolyesters, solution polymerization is a potential polymerization technique that can be utilized since it is already used in industry to produce certain types of polyesters. It is most frequently used when melt polymerization is impossible or too difficult because of the high melting point of the resulting polymer (10).

In solution polymerization, the formed polymer may be readily soluble in the solvent being used or the solution may contain only the monomer in which the polymer is only slightly soluble or not at all. This polymerization technique takes place at lower temperatures than melt polymerizations and enables an efficient heat transfer to be maintained. However, it requires polymer separation from the solution, repurification of the solvent and polymer washing and drying (10). Additionally, a solvent that can withstand high temperatures without evaporating and being distilled over is necessary for the technique to be successful. Since CBDO copolyesters have relatively low melting points (220-250 °C for 40 mol % CBDO), though, melt polymerization is a more feasible technique. On top of that, all known solvents that will dissolve the polymer have low boiling points, meaning that they would distill out before they could be of any use.

Data from Table 1 show early results of the mixed isomer CBDO with 1,4-butanediol (BDO) and PDO displaying impressive properties in their polymeric forms. It can be seen that a relatively high T_g (as high as 150°C) is still achieved with the 78 mol % incorporation of the aliphatic CBDO. Additionally, mechanical integrity is still kept intact, with an observed 1.81 GPa flexural modulus observed for the PDO-based polymer.

Table 1. Thermal and Mechanical Properties of CBDO Copolyesters (9).

		CBDO/BDO	CBDO/PDO
CBDO/diol ^a	mol/mol	78/22	78/22
<i>cis/trans</i> ^a		49/51	49/51
IV (after molding) ^b		0.55	0.76
flexural modulus	GPa		1.81
tensile modulus	GPa	1.84	1.83
tensile strength	kPa	31.0	45.5
heat distortion at 264 psi	°C	105	114
T_g (DSC)	°C	145	150
Izod impact			
23 °C, 1/8 in.	J/m	490 ± 50 CM	
23 °C, 1/8 in.	J/m	280 ± 40 IM	390 ± 40 IM
23 °C, 1/4 in.	J/m		210 ± 50 CM ^c
-30 °C, 1/8 in.	J/m		130 ± 40 IM

Additionally, varying the CBDO:diol ratio (C3-C4 diol) changed the properties of the polymer, with a higher CBDO mol % (and conversely, a lower C3-C4 diol mol %) increasing the T_g while a lower CBDO mol % (and conversely, a higher C3-C4 diol mol %) increased the Notched Izod impact strength. This pattern explains the lowered Notched Izod strength for both polymers in Table 1 while still maintaining a high T_g .

Figure 4 maps out the patterns and, as it can be seen, a 40 CBDO mol % is ideal for producing polymers with a higher impact resistance. This would be ideal for potential military applications.

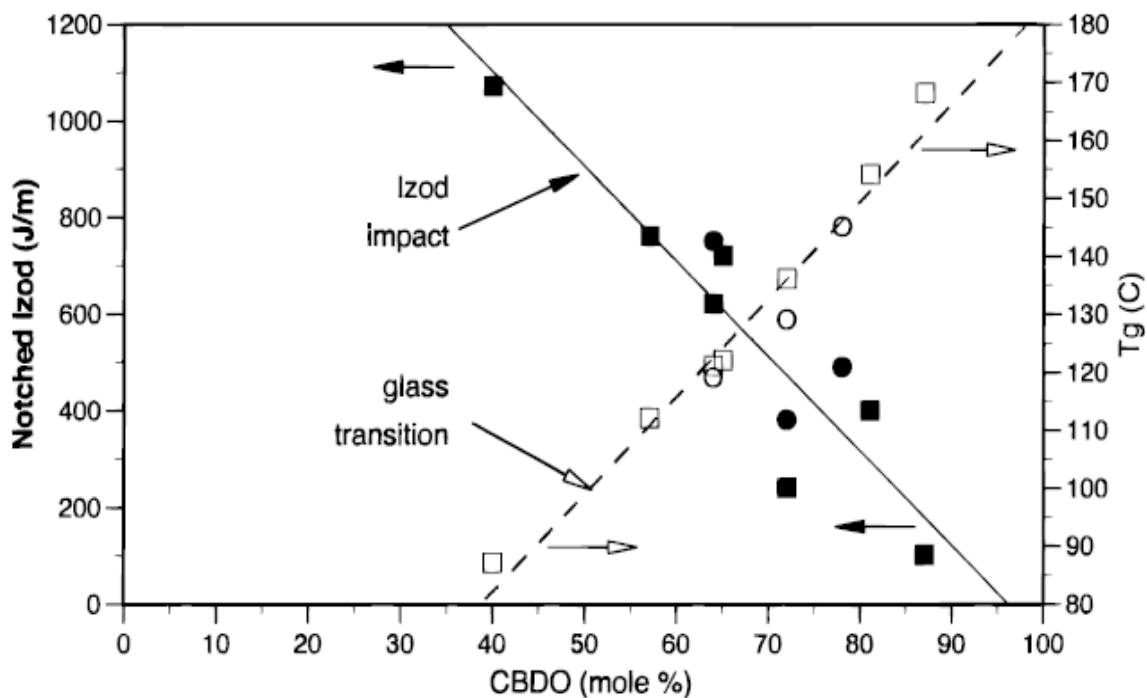


Figure 4. Effect of CBDO content on T_g (open symbols) and notched Izod impact (solid symbols) for terephthalate copolymers with PDO (squares) and BDO (circles). Dashed line shows T_g trend and solid line shows notched Izod impact trend (9).

Typically, copolyterephthalates containing greater than ~45 CBDO mol % are semi-crystalline when polymerized with C2-C4 diols (9). Additionally, CBDO-based copolyesters incorporating a higher percentage of the *trans* isomer showed evidence of higher degrees of crystallinity (9), which would most likely have an unfavorable effect on the polymer's impact and ballistic resistance (11).

However, this tradeoff may be desirable for developing products where long-term thermal stability is the main concern, such as protective materials for certain electronic products. A *cis*-rich copolymer, though, may affect the properties such that a similar toughness and T_g is observed over a wider range of CBDO mol %. This could, for example, cut down on production costs since half the amount of *cis*-CBDO could be used

to produce a copolymer with similar properties to its *cis/trans*-CBDO-based copolymer counterpart.

Table 2 shows that further investigation of a (46:54 *cis/trans*) CBDO, PDO, and DMT copolyester (Eastman material, 0.4:0.6 CBDO:PDO) displayed higher impact resistance and fewer breaks than bisphenol A polycarbonate, the industry standard (11).

Table 2. Notched Izod Data for CBDO Copolyester and Polycarbonate (11).

Material	Run	Impact value (J/m)	Comment
Polycarbonate	1	685.7	Partial break
	2	667.7	Partial break
	3	680.5	Partial break
	4	684.0	Partial break
	Average	679.5	
Eastman material	1	878.3	No break
	2	901.6	Partial break
	3	956.6	No break
	Average	912.2	

This same study also showed the CBDO copolyester exhibiting enhanced ballistics properties in relation to polycarbonate. The ballistic testing used (FSP V50 tests) is considered to be the standard “first test” for all ballistic materials and a standard ballistic test for military qualification (11). Table 3 shows that compression molded plaques of 0.64 cm thickness (areal density of up to 113 g/cm²) gave an FSP V50 rating of up to 355 m/s, while a similar sample of polycarbonate had a rating of only 241 m/s. This means that the steel pellets fired at each of these plaques (50% of the pellets had to penetrate a plaque before velocities were recorded) required a higher velocity to penetrate the CBDO plaque. Additionally, the 0.95 cm thick plaques (areal density of up to 172

g/cm²) gave a high value of 464 m/s, while a polycarbonate sample of the same thickness was only 341 m/s.

Table 3. Ballistic Data for CBDO Copolyester and Polycarbonate (11).

Areal density (g/cm ²)	% <i>cis/trans</i> for CBDO monomer	CBDO copolyterephthalate (m/s)	Polycarbonate (m/s)
107	35/65	198	N/A
109	35/65	215	241
111	46/54	355	N/A
111	46/54	321	N/A
113	46/54	247	N/A
162	N/A	N/A	341
165	46/54	457	N/A
167	46/54	464	N/A
172	35/65	323	N/A

A positive correlation between impact testing and ballistics testing was noticed from this research. Furthermore, the CBDO copolyesters with a higher *cis* ratio also had higher ratings, meaning that plaques with a higher *cis* content could withstand higher pellet velocities under ballistics testing.

The desirable properties of shape memory and self-healing were also observed in Figure 5, which was tested by hammering a dent into a plaque and then heating with a heat gun for over a minute above its T_g (11). This phenomenon was attributed to the *cis* monomer, which tends to promote kinks and coils within the polymer, but when stressed, becomes somewhat straightened out. However, when the polymer was heated at or above its T_g , it spontaneously returned to a coiled state (11). This gave rise to the possibility that increasing the *cis*-CBDO ratios could further enhance mechanical properties.

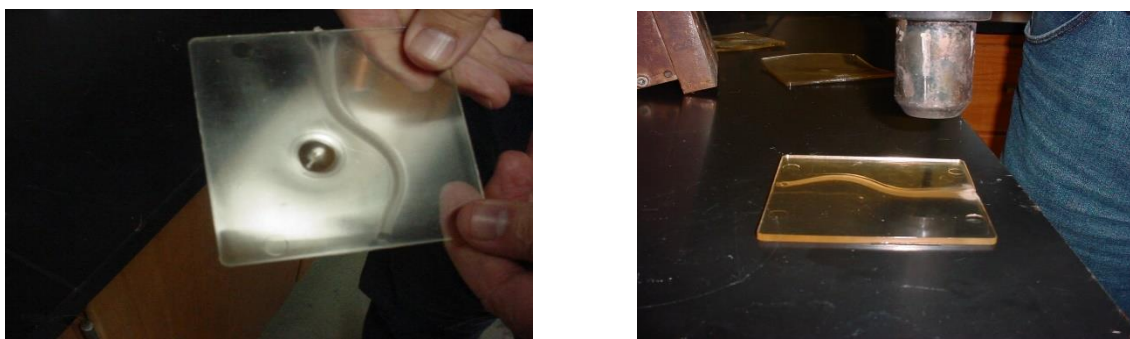


Figure 5. Dent in *cis* copolyester (left) and full shape recovery using a heat gun (right) (11).

Further research was then carried out to exploit the properties of isomer-specific copolyesters. The *cis*-copolyester demonstrated higher Izod impact strength test results (1,095 J/m) in relation to the 43:57 *cis:trans* (944 J/m) or *trans*-copolyesters (841 J/m) (12).

Other thermal and mechanical data also followed suit, with the *cis*-based polymer exhibiting a higher T_d and T_g (Figure 6), along with a higher storage modulus (Figure 7) than the mixed or *trans*-based polymers (12).

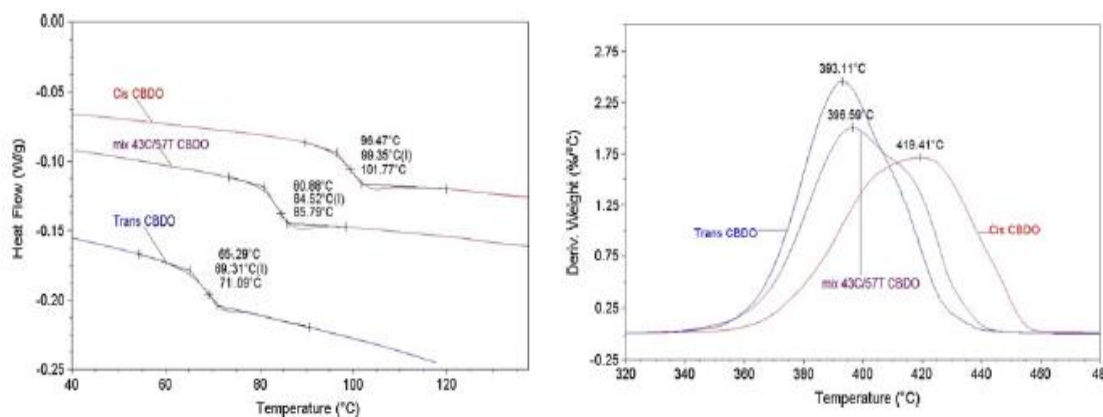


Figure 6. DSC (left) and TGA (right) data of the *trans*-rich, 43C:57T and *cis*-rich polymers (12).

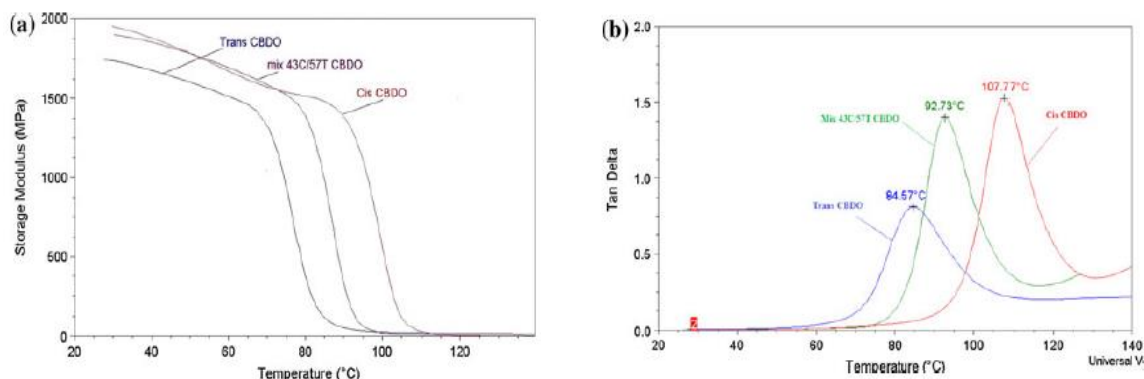


Figure 7. DMA data of the *trans*-rich, 43C:57T and *cis*-rich polymers, with storage modulus on the left and T_g on the right (12).

However, sufficient material was not produced to conduct ballistics testing. Additionally, it proved to have shape memory and self-healing properties after it completely recovered its original shape, which is consistent with previous studies (11,12). This last property would be of great use on the battlefield, since it would allow relatively quick repair of damage from surface scratches and minor impact events.

Molecular modeling was used to understand the interactions between the polymers for each type of isomer. As can be seen in Figure 8, the two polymer chains simulated for the polymer containing the *cis* isomer show no order and appear to be heavily coiled. This is in contrast to the polymer containing the *trans* isomer in Figure 9, which displays a more linear shape. With the polymer chains appearing more regular and orderly, this could explain the crystalline nature of the *trans* polymer. This also makes it more likely for stronger intermolecular interactions (dipole-dipole) to develop between polymer chains. X-ray diffraction analysis confirms the crystalline nature of the *trans* copolyester (12).

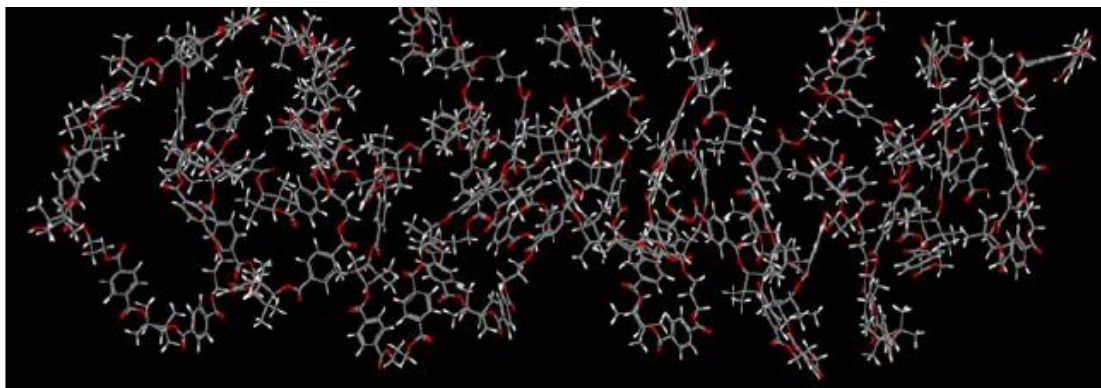


Figure 8. Molecular model of a CBDO-based copolyester utilizing the *cis* isomer (12).

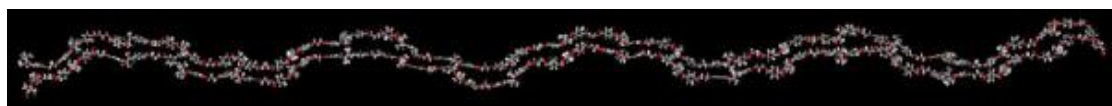


Figure 9. Molecular model of a CBDO-based copolyester utilizing the *trans* isomer (12).

Because of these results, the Army Natick Soldier Systems Group has a great interest in further understanding this class of polymers. Specifically, they want to further investigate the improved ballistics performance and shape memory properties of the *cis*-based copolyester (11,12). However, they also want to explore the *trans*-based copolyester for potentially high strength fiber applications.

The first part of this project was to separate *cis*- and *trans*-CBDO via several recrystallizations using excess ethyl acetate. 2.5 kg of copolyesters utilizing *cis*-CBDO (40%), PDO (60%) and DMT (100%) were then produced, along with another 2.5 kg of copolyesters utilizing *trans*-CBDO (40%), PDO (60%) and DMT (100%). Each of the 2.5 kg of product required 10-12 polymerizations. These polymers were then sent to the Army Natick Group for processing and analysis.

Due to the impressive mechanical and thermal properties exhibited by the *cis*-CBDO polymer, it was hypothesized that the diol component could be manipulated to improve the polymer's properties. PDO only has secondary carbons, but using a diol with a tertiary carbon or even a quaternary carbon could increase the glass transition temperature, decomposition temperature and storage modulus. Typically, the diol neopentyl glycol (2,2-dimethyl-1,3-propanediol, NPG) can enhance the product's stability towards heat, light and water when incorporated into a polyester (13). When it's transesterified with a carboxylic acid, a synthetic lubricating ester can be produced with reduced potential towards oxidation or hydrolysis (14).

NPG has the same structure as PDO, but with a central, quaternary carbon, in contrast to the central, secondary carbon in PDO (Figure 10). It was believed that this would fortify the polymer and lead to improvements in its thermal and mechanical properties. Improvements to T_g have been demonstrated in representative polycarbonates when methyl groups were substituted for their hydrogens symmetrically (11).



Figure 10. Structural comparison of 1,3-propanediol (left) and neopentyl glycol (right).

Additionally, a recent patent utilized NPG as the diol component and showed that, using a 4:1 NPG:CBDO ratio (67:33 *cis:trans*), a glass transition temperature of 156 °C was achieved (15).

The second part of this project involved polymerizing the *cis*-CBDO isomer (40%), the NPG monomer (60%), and the DMT monomer (100%), which then gave rise to an amorphous polymer. The properties of this novel polymer were then characterized (¹H NMR, GPC). Thermal tests (TGA, DSC) and a mechanical test (DMA) were also run. These data were then compared to those of the PDO-based polymer.

CHAPTER II

MATERIALS AND METHODS

I. Materials

General Reagents

Ethyl acetate was purchased from BDH Solvents (Radnor, PA) while chloroform (biotechnology grade) was purchased from Amresco (Solong, Ohio). Dimethyl terephthalate (99%) was purchased from Acros Organics (New Jersey) while 1,3-propanediol was acquired from Shell Chemicals (polymer grade, marked for CBDO synthesis only). Both neopentyl glycol and dibutyltin oxide were purchased from Sigma Aldrich (St. Louis, MO). CBDO was donated by Eastman Chemicals (Houston, TX). All monomers were used as received. The NMR reagents, deuterated chloroform (CDCl_3) and dimethyl sulfoxide (DMSO-d_6) were also purchased from Sigma Aldrich (St. Louis, MO).

II. Methods

Recrystallization

A step-wise recrystallization technique was used to separate the *cis* isomers from the *trans* isomers. This was the most time-consuming part of the whole project. A 1:4 CBDO:ethyl acetate ratio was used (50 g: 200 mL), with the monomer completely dissolved into the solvent and left to recrystallize overnight (using a 1 L beaker). The following day, both isomers had fallen out of solution as slightly bigger crystals (for

more visual distinction), and then were loosened so that the crystals were floating freely in solution. The solution was then carefully heated at medium power while being stirred so that nearly all the *trans* isomers would dissolve back into solution. This was visually confirmed by taking the beaker off of the hot plate and stirring the solution around under sufficient lighting to see if enough *trans* needles (dependent upon the skill of the researcher) had fallen back into solution. It was better to still have a few *trans* isomers that hadn't dissolved than to start having *cis* isomers dissolving into solution. Generally (up to a certain size of the crystals involved), the *trans* isomers fall into solution before the *cis* isomers due to their weaker molecular interactions. This correlates with their melting points: 162.5-163 °C for the *cis* isomer and 147-148 °C for the *trans* isomer (16).

Once this time-sensitive step occurred, the solution (~80% *trans*-rich) was immediately decanted into a beaker, leaving behind the ~80% *cis*-rich crystals. The same step would be performed one to two more times, with the goal being to get as close to >99% *cis* or >99% *trans* crystals.

If a *cis*-rich beaker was believed to still contain a few *trans* crystals upon visual inspection, then excess ethyl acetate would be added to obtain a dilute solution and all the crystals would be heated and dissolved back into solution. Afterward, bigger *cis* crystals would fall out over a longer period of time, but this dilution helped ensure almost no *trans* crystals would fall out. The same case would hold for a *trans*-rich beaker, even though the *cis* isomer recrystallizes sooner than the *trans* isomer because of its higher melting point. The shape of the *cis* crystals ranged from small, hexagonal-like to flat, elongated cylinders. The shape of the *trans* crystals was almost always fiber-like, although in more dilute solution, they appeared more needle-like.

With enough training and skill, about 15-20 g of each isomer could be collected on a daily basis when starting out with 50 g total. However, dilution parameters (consolidating beakers with few monomers or using a rotary evaporator to reset a recrystallization) and the timing of the decantation were critical to ensuring enough of each isomer was collected.

Polycondensation/Transesterification

The *cis*-CBDO/PDO and DMT copolyester production alternated every week with the *trans* copolyester (depending on the availability of the isomer). The synthesis can be seen in Figure 3. A 0.4 mol: 0.8 mol CBDO:PDO ratio was used, with approximately 57.70 g and 60.87 g of each monomer used, respectively. PDO was added in excess (0.2 mol) to prevent undesired future reactions (17). DMT (1.0 mol, 194.20 g) and a catalyst, dibutyltin oxide (0.003 mol, 0.65 g), were also added into the 500 mL 3-neck round bottom flask. Future polymerizations for this particular copolyester required doubling each monomer amount and using a 1 L flask instead, along with a larger PTFE stirring blade (reinforced with a smaller steel template).

Catalyst is used in these polymerizations because the CBDO (in addition to being a secondary alcohol) has secondary hydroxyl groups that are sterically hindered by adjacent methyl groups (9). Furthermore, dibutyltin oxide was found to be the better catalyst based on its 80% methanol yield from a transesterification of CBDO and DMT at 240 °C for 250 hours (9).

The *cis*-CBDO/NPG and DMT copolyester, however (Figure 11), used a 0.20 mol:0.32 mol *cis*-CBDO:NPG ratio, with approximately 28.84 g and 33.33 g of each

monomer added, respectively. DMT (0.50 mol, 97.10 g) and dibutyltin oxide (0.001 mol, 0.33 g) were added as well. A possible mechanism for this reaction can be seen in Figure 12 (18).

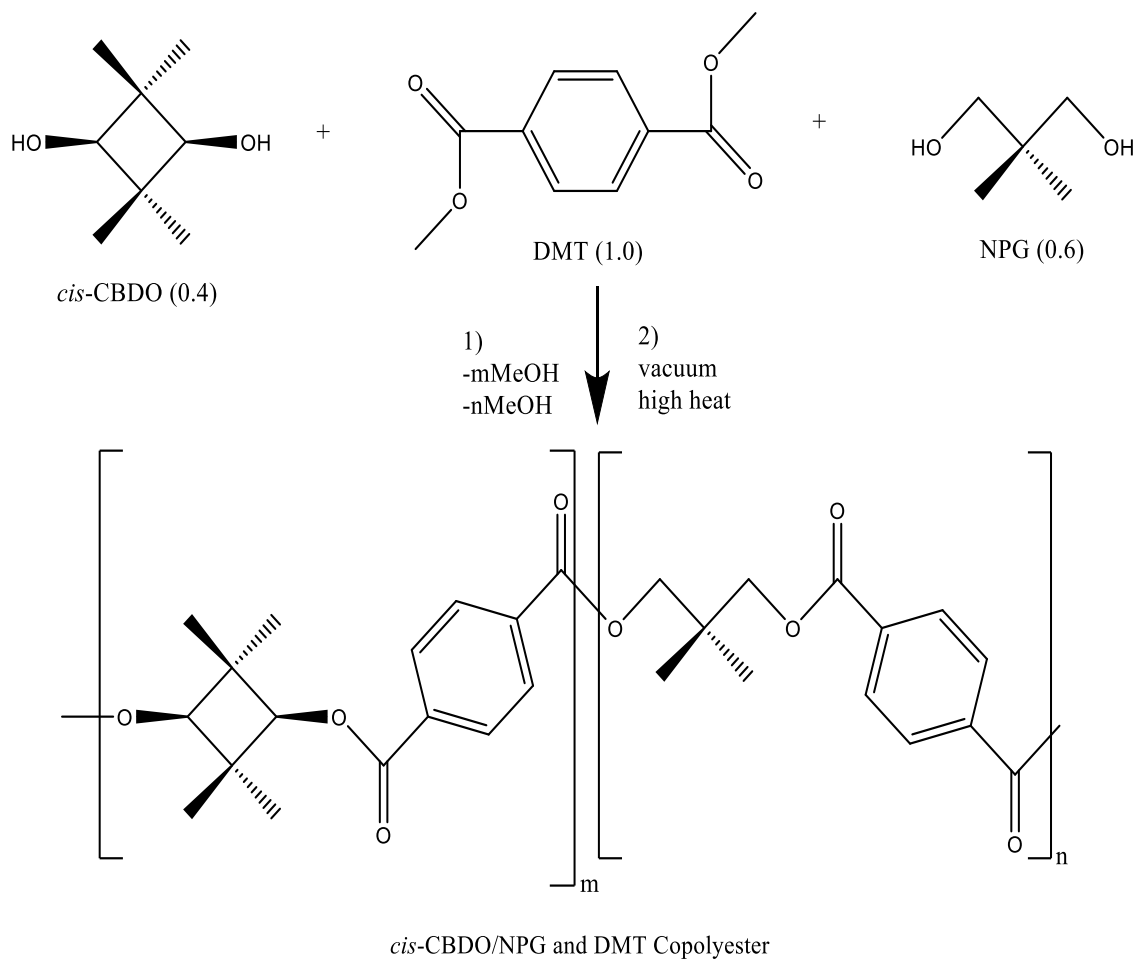


Figure 11. Synthesis of the *cis*-CBDO/NPG and DMT copolyester.

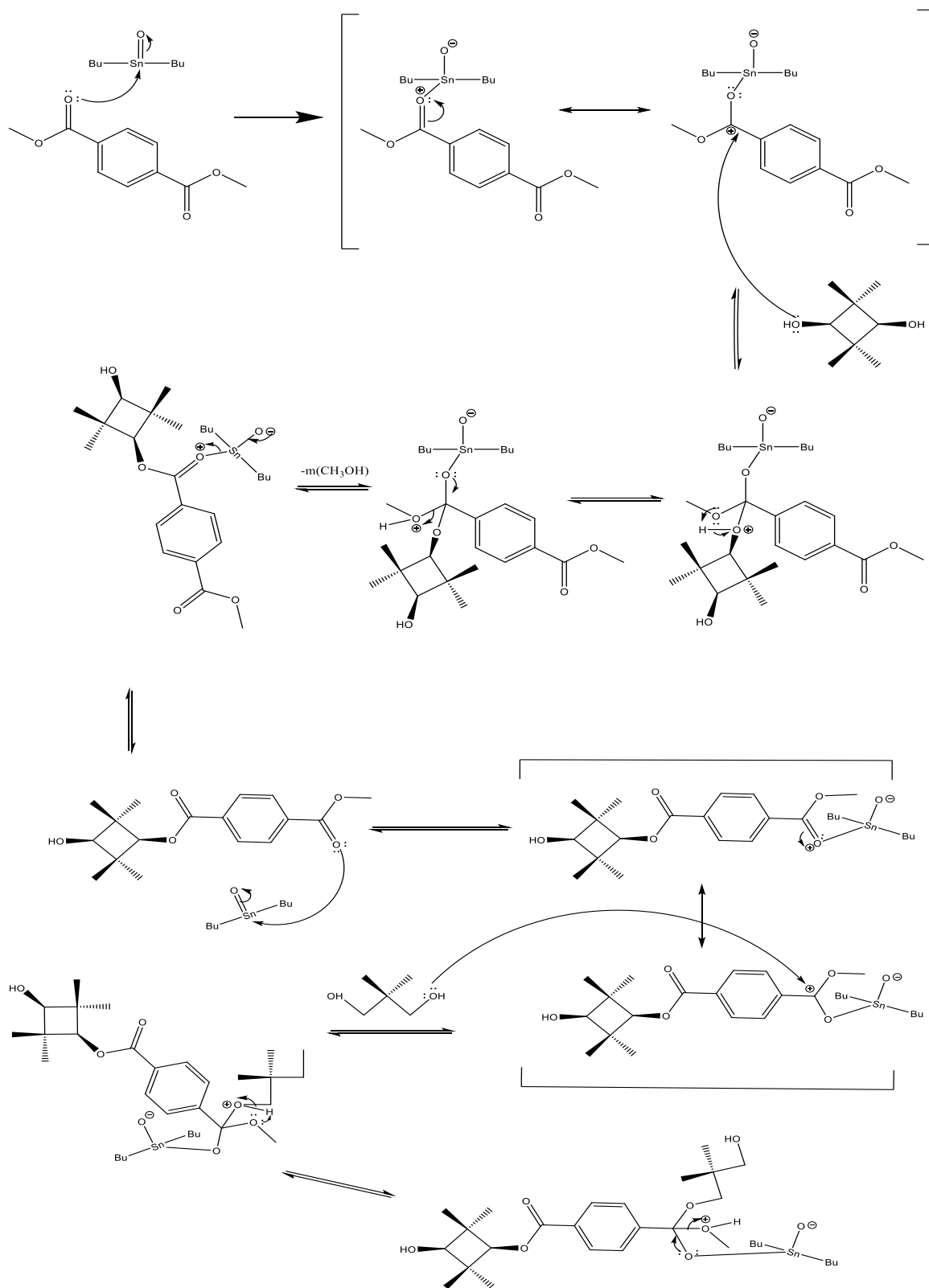


Figure 12. Proposed mechanism of acid-catalyzed transesterification (using dibutyltin oxide) of DMT with *cis*-CBDO and NPG (18).

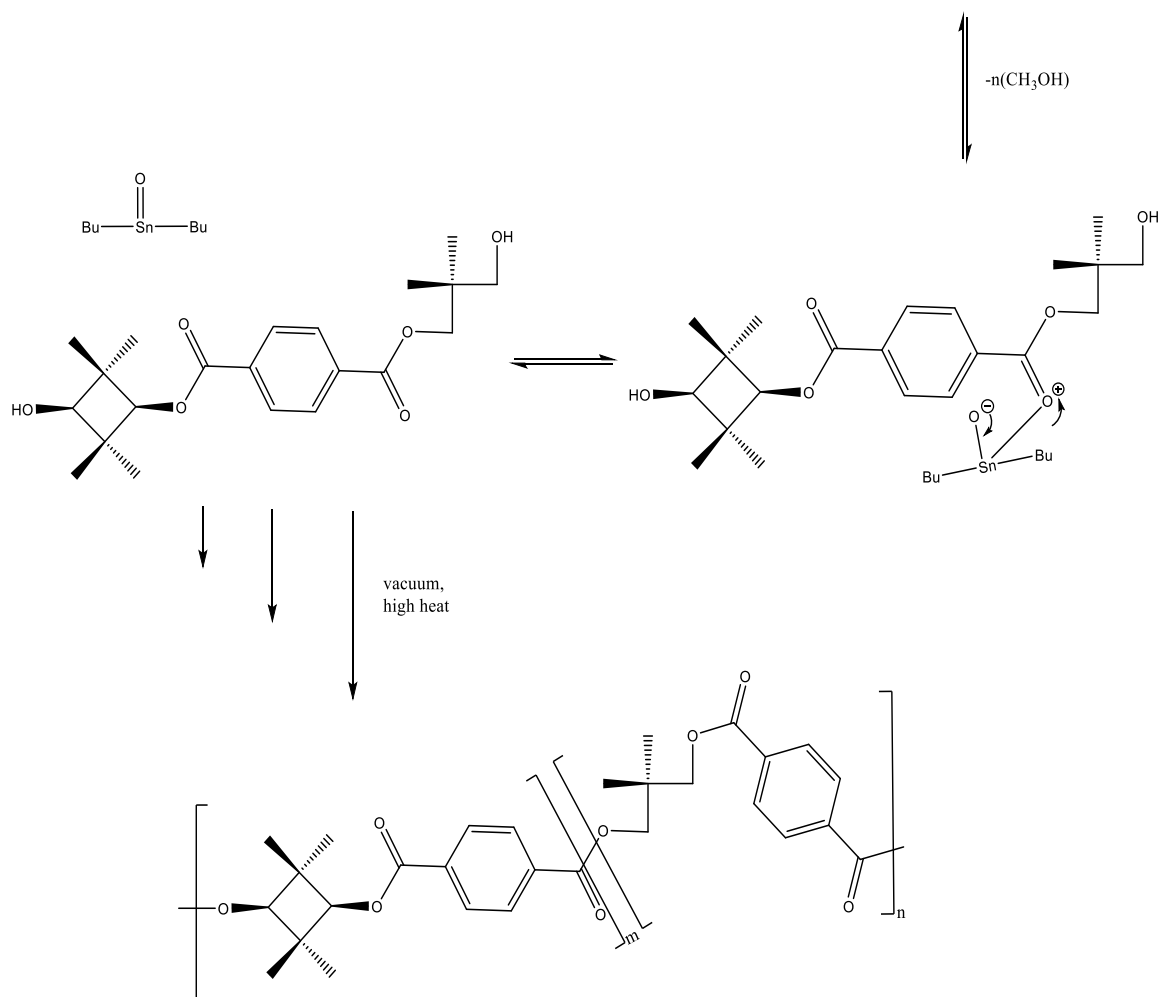


Figure 12 Continued.

For step 1 (under argon) utilizing the PDO monomer, either CBDO isomer, and a 500 mL flask, the initial temperature was set to 150 °C on the controller and ramped by 10°C about every 45 min, depending on if the rate of distillation had slowed down enough to justify increasing the temperature. Stirring (using a PTFE stir blade) began once a system melt had been achieved, and an end temperature of approximately 235 °C was held to ensure no more methanol or excess diol needed to be distilled out. For step 1 using a 1 L flask, an initial temperature of 135 °C was used for the *cis* isomer and 120 °C

for the *trans* isomer (to prevent premature sublimation and subsequent condensation from occurring in the distillation adapter). Step 1 for the PDO-based copolyester (for both the 500 mL and 1 L flasks) took approximately 6 hours and ~80% methanol yield was usually collected each time.

For step 1 (under argon) utilizing the NPG monomer, the initial temperature was set to 135 °C on the controller and ramped by 5 °C about every 30 min, depending on if the rate of distillation had slowed down enough to justify increasing the temperature. A mechanical stirrer was set at 50 rpm to stir the reaction mixture using a PTFE stir blade. This occurred once the monomers had sufficiently reached a mass melt at 163 °C. Slight recondensation of the *cis*-CBDO monomer occurred at around 210 °C (after it had sublimed) at the flask/distillation adapter interface. This signaled prolonging the current temperature in an attempt to make sure the crystals fell back into the melt. If it looked as if the crystals would not melt at the current temperature, only a 5 °C ramp was carried out so that further recrystallization would not occur. An end temperature of 238 °C was reached and held for an hour. This end temperature ensured that excess NPG monomer could be boiled off since this was above its boiling point (15). Methanol (ca. 32 mL) was collected (80% methanol recovery in theory (9)), and *cis*-CBDO crystals (ca. 0.25 g, 0.002 mol) were collected out of the adapter. Step 1 lasted about 6 hours.

The purpose of step 2 (the following day) was to remove excess PDO or NPG, to distill out residual methanol and to also increase the molecular weight of the polymer. The initial temperature was set to 120 °C on the controller and held for approximately 40 minutes. Stirring was then turned on to 50 rpm since mass melting had been achieved and a temperature ramp of 10 °C/~30 min was carried out. This rate was varied,

depending on how much condensation had built up in the adapter. A torque rate of 25 J was initially observed for the 500 mL flask (33 J for the 1 L flask) and once the system had reached 200 °C, it was held at this temperature (~3 hours) until a torque rate of about 31 J (46 J for the 1 L flask) was reached. The temperature controller setting was then ramped from 190 °C to 225 °C (245 °C in the system). Initially, the torque dropped to about 29J (42 J for the 1 L flask), but then reached 37 J (55 J for the 1 L flask) after about 3.5 hours. The *trans* copolyesters didn't display nearly as high a torque as their *cis* copolyester counterparts, which could be explained by their semi-crystalline state (12), and therefore, would reach their endpoint quicker (which is consistent with previous studies (12)).

The end of step 2 was marked by a sharp drop in torque due to nearly the entire polymer remaining on top of the stir blade. For the *cis* copolyester in the 1 L flask, the end of step 2 was also marked by a disjoint between the stir shaft and the female coupling that rotated it. Step 2 lasted about 10 hours and approximately 110 g of the NPG copolyester was produced. For the PDO copolyesters, approximately 250 g of polymer from the 1 L flask was collected (~115 g from the 500 mL flask). The scale-up to the 1 L flasks took place after a couple of runs using the 500 mL flask for each isomer. Regardless of the flask size, step 2 for these copolyesters also took about 8-10 hours, and ultimately, 2.5 kg of copolyester for each isomer (5 kg in total) were produced.

¹H NMR

¹H NMR was carried out on a Bruker/Spectrospin Cryomagnet (400 MHz, NMR Spectroscopy) to confirm the isomer identities and to map out the polymer itself.

Approximately 7 mg of the polymer was dissolved in 1 mL of CDCl_3 (19), and about 7 mg of each CBDO isomer was dissolved in 1 mL of DMSO-d_6 (20).

Gel Permeation Chromatography (GPC)

GPC was run using a Viscotek 270 Dual Detector (for RALS and LALS) and a VE 3580 RI Detector. A Viskotek VE 1122 Solvent Delivery System was used along with a VE 7510 GPC Degasser System. The column used was a Viscotek T600M General Mixed column (Org. 300 x 7.8 mm, crosslinked-PS and styrene-DVB).

Approximately 2 mg of sample was dissolved in 1 mL of HPLC chloroform (Fisher Scientific) for about 5 minutes, and 0.1 μL of sample (filtered through a 0.2 μm PTFE filter beforehand) was then injected at a flow rate of 1 mL/min (1.4 MPa). A PolyCAL Polystyrene Standard—PS99K was used, with the following information: weight average molecular weight (M_w) = 98,251; number average molecular weight (M_n) = 96,722; intrinsic viscosity (IV) = 0.477 (30 $^\circ\text{C}$, tetrahydrofuran); weight= 10.51 mg.

Thermogravimetric Analysis (TGA)

A Q50 Series TGA instrument was used first to determine the decomposition temperature. This data also aided in selecting appropriate thermal and process parameters for future analyses. Approximately 6-10 mg of sample was used in each run, with the temperature ramped up to 600 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$ in air.

Differential Scanning Calorimetry (DSC)

A Q200 Series DSC instrument was used to determine the glass transition temperature. Approximately 4-8 mg of sample was used in each run, and the temperature

was ramped up to 150 °C at 10 °C/min for the first part so that the sample could be “homogenized”. It was then cooled back down to 30 °C, and then ramped back up at a slower rate of 5 °C/min for the actual T_g recording.

Injection Molding

Dog bones (17.5 mm x 5 mm x 1.5 mm.) were produced for future DMA testing utilizing a Haake MiniJet injection molder. Approximately 2 g of sample was used to produce each dog bone, with the sample being chipped into small pieces such that pelletizing was not necessary. Samples were placed under vacuum overnight. The cylinder temperature was set to 230 °C and the mold temperature was set to 120 °C. The inject and post pressures were each at 4,500 psi held for 5 sec.

Dynamic Mechanical Analysis (DMA)

A Q800 Series DMA instrument was used to determine the storage and loss moduli. The glass transition temperature determined using DSC was also confirmed by using the tan delta (loss modulus:storage modulus). A single cantilever clamp under a multi-frequency strain mode was used, with an amplitude of 15 μm at a frequency of 1 Hz, with the frequency of 1 Hz being held constant and a temperature ramp of 3 °C/min to a max temperature of 130 °C.

CHAPTER III

RESULTS AND DISCUSSION

I. Results

Structural Elucidation Using NMR Spectroscopy

^1H NMR spectra were used to verify the identities of the *cis* isomer (Figure 13) and the *trans* isomer (Figure 14). The 2.50 ppm peaks correspond to DMSO and the 3.37 ppm peaks most likely correspond to residual diethyl ether (21). Actual shifts matched those found on the SDBS database (20). Chemical shifts and relative intensities are tabulated in Tables 4 (*cis*-CBDO) and 5 (*trans*-CBDO).

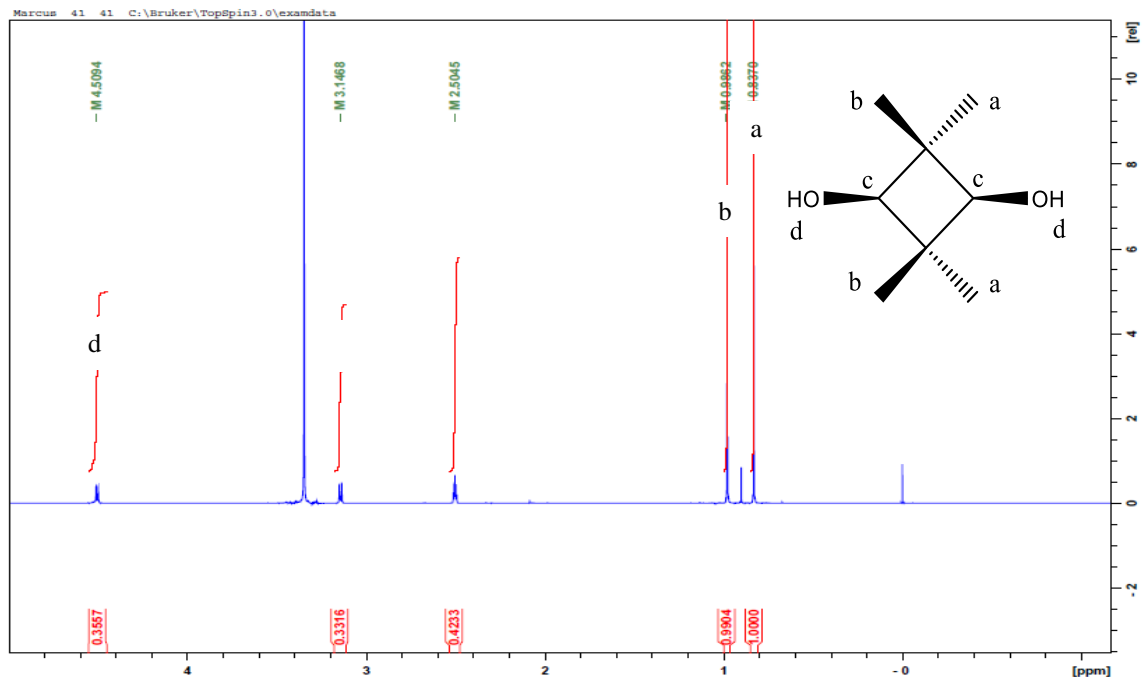


Figure 13. ^1H NMR of *cis*-CBDO in DMSO-d_6 .

Table 4. *cis*-CBDO ^1H NMR Peak Shifts and Relative Intensities.

Peak	Shift (ppm)	Relative Intensity
a	0.84	1.00
b	0.99	0.99
c	3.15	0.33
d	4.51	0.36

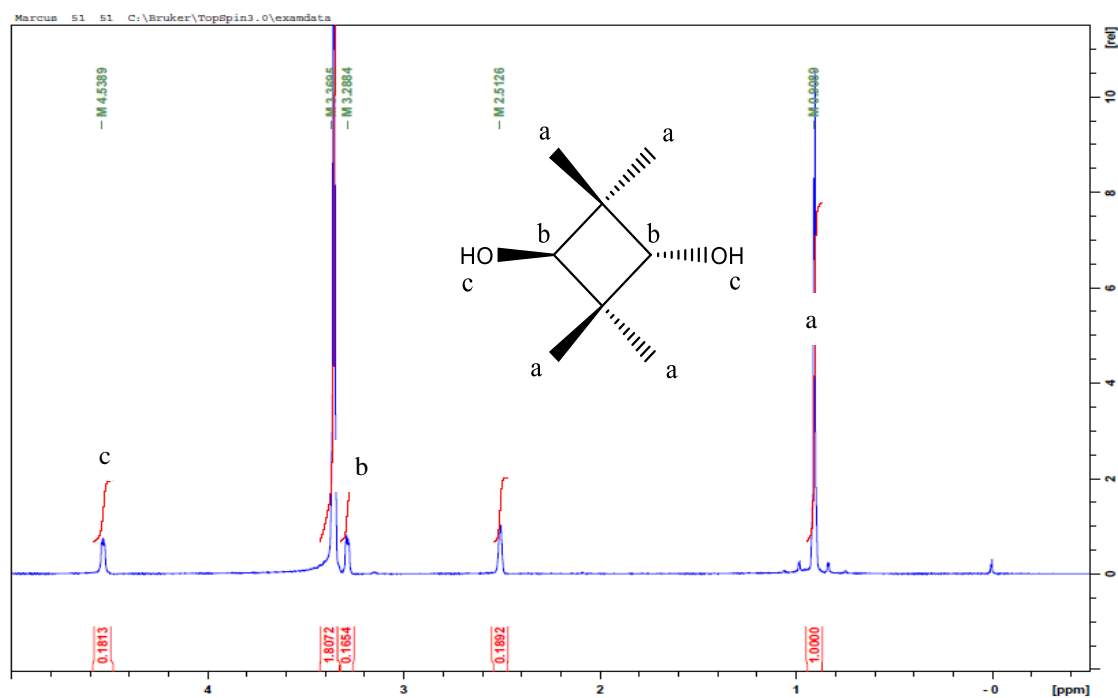


Figure 14. ^1H NMR of *trans*-CBDO in DMSO-d_6 .

Table 5. *trans*-CBDO ¹H NMR Peak Shifts and Relative Intensities.

Peak	Shift (ppm)	Relative Intensity
a	0.91	1.00
b	3.29	0.17
c	4.54	0.18

As can be seen, the relative intensities match the number of protons for each isomer. Chemical shifts are consistent with those reported in the literature (20, 22); methyl groups are seen upfield due to shielding effects and protons near or on the hydroxyl groups are seen downfield due to the deshielding effects of the oxygen. The hydrogens on the hydroxyl carbons and the hydroxyls themselves are deshielded more on the *cis* isomer due to their proximity to the opposite oxygen.

Table 6. *cis*-CBDO/NPG and DMT Copolyester ¹H NMR Peak Shifts and Relative Intensities.

Peak	Shift (ppm)	Relative Intensity
a	0.91	1.00
b	1.45	0.71
c	1.61	0.74
(d)	(4.23)	(0.23)
e	4.30	0.70
f	4.66	0.21
g	8.14	1.19

The ^1H NMR spectrum of the *cis*-CBDO/NPG and DMT copolyester can be seen in Figure 15. Relative intensities for the polymer in Table 6 coincided with the amount of protons expected on the polymer chain in Figure 16. It can be seen that besides the aromatic protons, every other peak was shifted downfield significantly, in relation to their respective monomer shift values. This can be attributed to the aromatic rings and carbonyl groups pulling away electron density. It should be noted that (d) represents the hydrogen on that particular carbon (on CBDO) that is connected to an unreacted hydroxyl group. This is also verified with the doublet multiplicity.

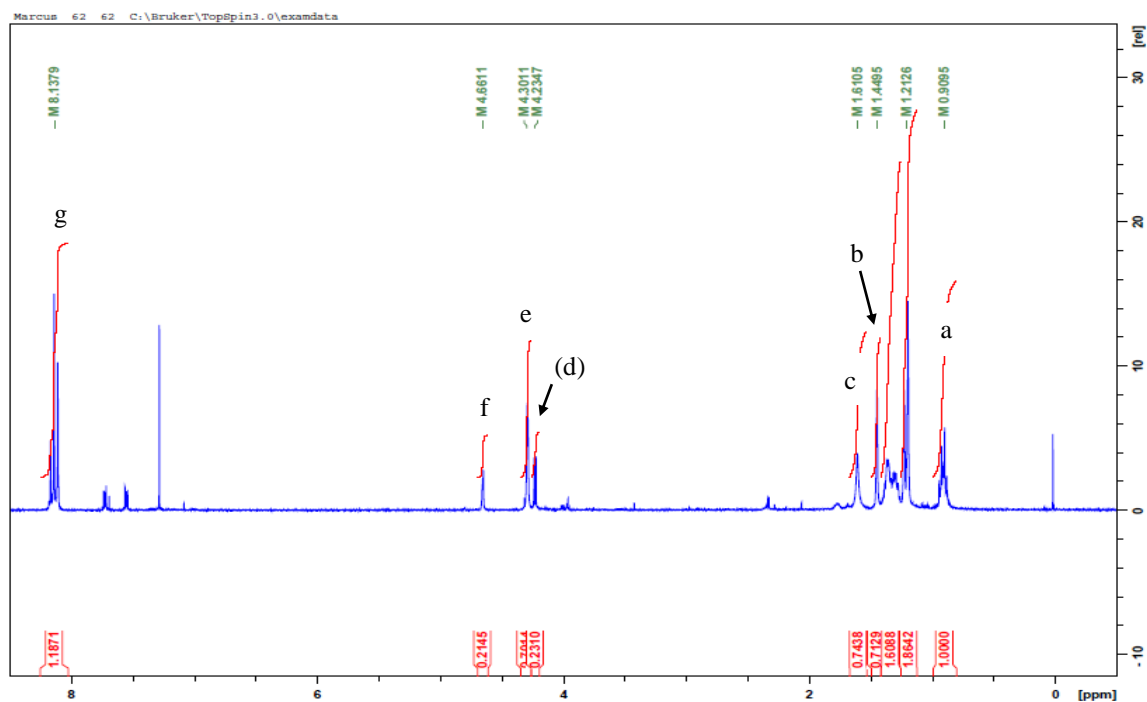


Figure 15. ^1H NMR of *cis*-CBDO/NPG and DMT copolyester in CDCl_3 .

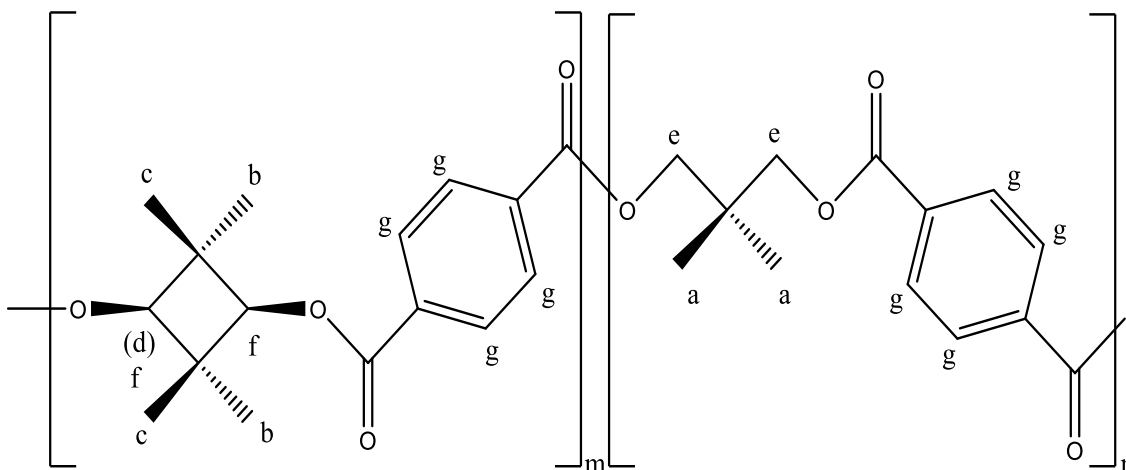


Figure 16. *cis*-CBDO/NPG and DMT copolyester with labeled NMR protons.

Long-range coupling, which tends to occur in rigid structures like aromatics (22), is observed with peaks at around 7.6 and 7.8 ppm. The peak at 7.26 ppm corresponds to residual CDCl_3 solvent (22). Other unreacted end groups (such as methyl groups on DMT) do not appear on the spectrum, but if there were unreacted end groups on NPG, it would have the same shift as those of its methylene protons at 4.30 ppm. End groups being present on NPG are possible since it was added in slight excess. However, this doesn't seem as probable due to NPG being a primary alcohol, meaning that it will react faster with DMT than the secondary alcohol CBDO would. Slight DMT was also pulled out during step 2 due to vacuum, so it's valid to see unreacted CBDO end groups present due to the nonstoichiometry introduced. Finally, the multiple peaks in the 1.2-1.4 ppm range consistently showed up on every spectrum, and they could be attributed to dibutyltin oxide.

Molecular Weight Determination Using GPC

Molecular weights of the polymers were determined using gel permeation chromatography (GPC, Table 7). The weight average molecular weight (M_w) was found to range from 10 kDa to 11 kDa and the number average molecular weight (M_n) was found to range from 6 kDa to 7 kDa. The PDI therefore ranged from 1.58 to 1.95.

Table 7. GPC Data of *cis*-CBDO/NPG and DMT Copolyester

	M_w (kDa)	M_n (kDa)	PDI
Sample 1	11	7	1.6
Sample 2	11	6	1.8
Sample 3	11	6	1.8

These lower than usual molecular weights might be attributed to nonstoichiometry, mainly caused by 1) loss of monomer(s) during the vacuum phase, 2) the excess diol (either *cis*-CBDO or NPG) not distilling out and 3) impurities inherent to using the as-received PDO and NPG. If the nonstoichiometry is too large, the polymer molecular weight will be too low (17). Higher conversions and the appropriate stoichiometric ratio are required to obtain higher degrees of polymerization, which lead to higher molecular weights. Previous studies utilizing PDO obtained molecular weights of 72-74 kDa (12).

Another likely cause for low molecular weight is the polymer building up viscosity too quickly, rising up the shaft and staying on top of the stir blade, effectively halting the reaction and limiting the molecular weight. Even with the polymer being

continuously stirred, though, the low surface area within the 500 mL flask doesn't allow excess diol to distill out due to the long path it would have to take.

Thermal and Mechanical Analysis

Polymer decomposition temperatures (T_d) were determined using thermogravimetric analysis (TGA). The T_d temperatures in Table 8 ranged from approximately 423 °C to 450 °C, with one example being shown in Figure 17. These values are higher than the PDO-based copolyester, and could be attributed to the increase in methyl substitution along the polymer backbone.

Table 8. TGA Data of *cis*-CBDO/NPG and DMT Copolyester.

	Amount (mg)	Decomposition Temperature, T_d (°C)
Sample 1	7.7	439
Sample 2	8.1	450
Sample 3	6.8	423
	Average	437
PDO-based Copolyester (12)		419

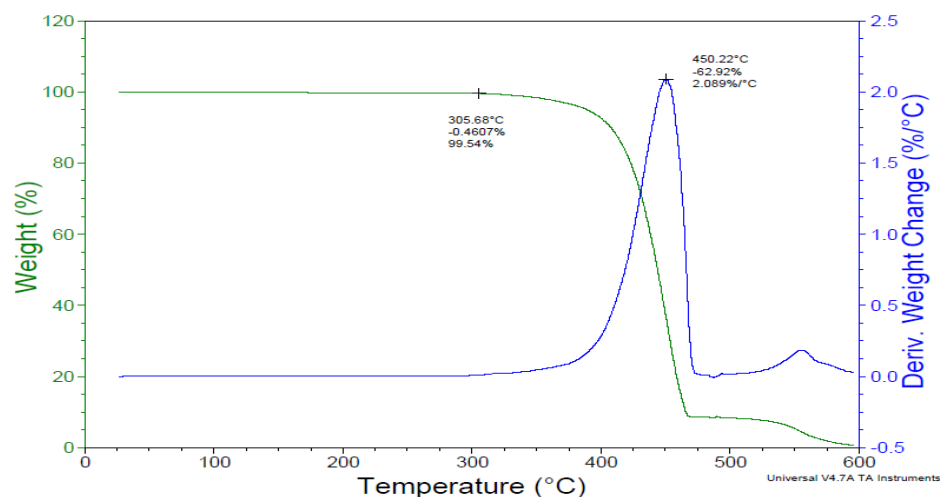


Figure 17. Sample 2 TGA of the *cis*-CBDO/NPG and DMT copolyester, with a ramp of 10 °C/min.

Polymer glass transition temperatures (T_g) were determined using differential scanning calorimetry (DSC). In addition to a higher T_d , DSC testing showed that a higher T_g was achieved relative to the PDO-based copolyester, with values staying around 109 °C (Table 9). A representative sample is shown in Figure 18.

Table 9. DSC Data of *cis*-CBDO/NPG and DMT Copolyester.

	Amount (mg)	Glass Transition Temperature, T_g (°C)
Sample 1	4.7	107
Sample 2	8.1	109
Sample 3	6.2	110
Average		109
PDO-based Copolyester (12)		99

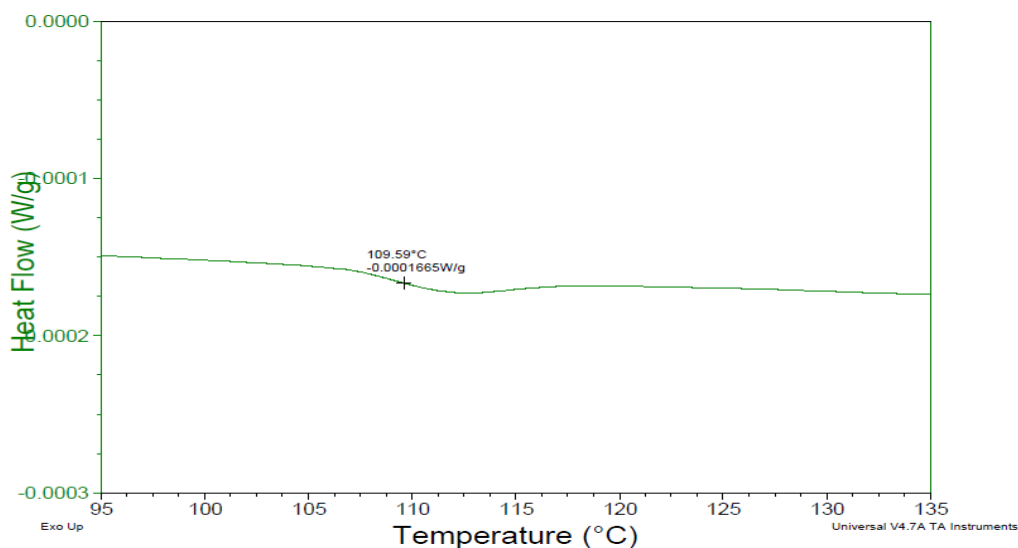


Figure 18. Sample 3 DSC of the *cis*-CBDO/NPG and DMT copolyester, with a 2nd ramp of 5 °C/min.

Since the T_g can depend on the free volume between atoms, the methyl groups on NPG will cause this value to decrease (10). Additionally, only one transition was observed, confirming that the copolyester is random.

Dynamic mechanical analysis (DMA) was used to further evaluate the thermal and mechanical properties of the polymer. A representative DMA analysis is shown in Figure 19 for sample 2. Storage moduli ranged from 1,530 MPa to 2,120 MPa at 40 °C (Table 10), with approximately 125 °C being the endpoint for the samples (although Sample 3 failed at 103 °C). The tan delta gave an average T_g of 113 °C, which is higher than the tan delta value of previous studies.

Table 10. DMA Data of *cis*-CBDO/NPG and DMT Copolyester.

	Storage Modulus at	Tan Delta
	40 °C (MPa)	(°C)
Sample 1	1,530	113
Sample 2	2,120	112
Sample 3	1,920	N/A
Average	1,860	113
PDO-based Copolyester (12)	1,820	108

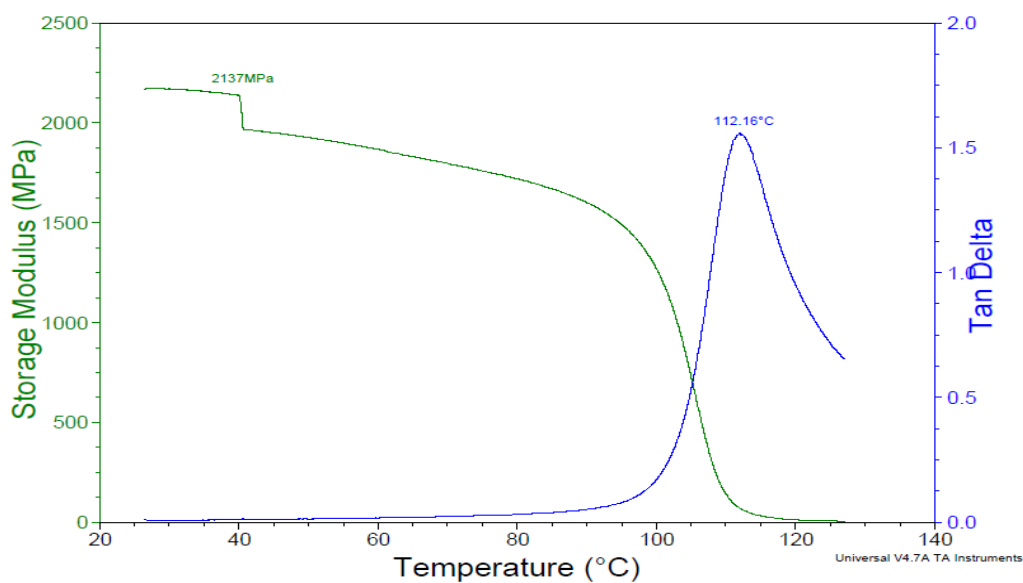


Figure 19. Sample 2 DMA of the *cis*-CBDO/NPG and DMT copolyester, using a single cantilever at 1 Hz and a ramp of 3 °C/min.

Compared to the storage modulus of the polymer utilizing PDO (ca. 1,820 MPa, 12), NPG seems to strengthen the polymer a bit more. Mechanical properties can strongly depend on molecular weight, so ensuring optimal stoichiometry during the polycondensation stage could produce polymers with increased storage moduli.

II. Discussion

Summary and Conclusions

The goals of this project were to improve the separation technique of the *cis* and *trans* CBDO isomers and to polymerize a novel CBDO-based copolyester by using NPG in place of the previously studied PDO diol. We also wanted to characterize it by using ^1H NMR and GPC, and to also put it through basic thermal and mechanical tests.

A more efficient separation technique was established during this project. Seeing as previous research utilized more reagents and purifying steps (16), simply modifying the concentration of the CBDO isomers in only one reagent (ethyl acetate) offers a more streamlined method for isomer separation.

Unlike the copolyesters utilizing PDO, where the polymer tended to climb the shaft to signal the end of the process, all the NPG-based polymers marked the end of the process by staying above the stir blade.

Low molecular weight polymers may not exhibit the same properties as high molecular weight polymers because increasing the degree of polymerization correlate with higher melting temperature and higher mechanical strength (23). Additionally, most

mechanical properties depend on and vary considerably with molecular weight (17). However, polymer chains with stronger intermolecular forces (such as polyesters) develop sufficient strength to be useful at lower molecular weights than polymers having weaker intermolecular forces (such as polyethylene) (24). This may have been the reason as to why an impressive storage modulus was still observed.

Overall, improved thermal properties were confirmed from TGA and DSC analyses by observing a higher T_g and a higher T_d . DMA confirmed this higher T_g and also showed a higher storage modulus, meaning that the polymer has one improved mechanical property. This could correlate to better results in future ballistics testing than previous CBDO-based polymers. The thermal stability over an even wider range of temperatures is also very encouraging since it has a wider margin for processing.

Future Studies

The Army Natick Soldier Systems Group is in the process of producing test plaques for ballistics testing of the *cis* copolyester and producing spun fiber with the *trans* copolyester to test for use in Kevlar-type applications. Unfortunately, the polymers have not been processed in time to be included in this thesis, but when the data becomes available, it will be included in open literature publications.

Priority will be given to improving the polycondensation method (as described in the aforementioned set-up) so that 1) excess diol can be distilled out more easily, and 2) the polymer melt can continue to build up molecular weight. Care will also be taken to improve the stoichiometric balance. Solution polymerization might also be a potential technique to use in future runs.

Additional funding was provided to continue research on the *cis*-CBDO/NPG and DMT class of copolyesters. The goal will be to map out impact strength and T_g (among other properties) of varied *cis*-CBDO mol % polymers (similar to Figure 4) and to see what optimal ratio of *cis*-CBDO to NPG produces polymers with high impact strength for potential future use in military applications.

From a qualitative standpoint, the polymer was difficult to break with considerable force using a hammer. Notched Izod would be valuable to run and to see how these results compare to previous impact values that utilize the mixed isomer CBDO with PDO. Those results were already higher than traditional polycarbonate (11). Tensile testing can also be carried out to collect a wider variety of mechanical data.

Looking into the weathering and degradation resistance of this novel polymer would be critical if it is to be commercialized. In general, aromatic-based polymers tend to undergo UV degradation more readily than their aliphatic counterparts (25), but a recent patent has shown that a CBDO-based poly(ether ketone) exhibited good thermal properties without suffering from the UV and photo-oxidative limitations of polymers only containing aromatic groups (26).

REFERENCES

1. Cheng, M.; Chen, W. *J. Engn. Mater. Tech.* **2005**, 127, 197-203.
2. Petty, M.C. *Molecular Electronics: From Principles to Practice*; John Wiley & Sons Ltd: Chicester, U.K., 2007.
3. Chatzi, E. G. and Koenig, J. L. *Polym.-Plast. Technol. Eng.* **1987**, 26(3 & 4), 229-270.
4. Agranoff, J. (Ed.). *Modern Plastics Encyclopedia*, Vol. 61; McGraw-Hill: New York, 1984-1985; pp 449-704.
5. Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach: Basel, 1995.
6. Mugno, M.; Bornengo, M. *Chim. Ind. (Milan)* **1963**, 45, 1216-1221.
7. Jackson, W. J.; Gray, T. F.; Caldwell, J. R. *J. Appl. Polym. Sci.* **1970**, 14, 685-698.
8. Jackson, W. H., Jr.; Caldwell, J. R.; Perry, K. P. (Eastman Kodak). *J. Appl. Polym. Sci.* **1968**, 12, 1713-1733.
9. Kelsey, D. R.; Scardino, B. M.; Grebowicz, J. S.; Chuah, H. H. *Macromolecules* **2000**, 33, 5810-5818.
10. Cheremisinoff, N. P. *Handbook of Polymer Science and Technology*, Vol. 1; Marcel Dekker Inc.: New York, 1989.
11. Booth, C. J.; Kindinger, M.; McKenzie, H. R.; Hancock, J.; Bray, A.V.; Beall, G. W. *Polymer* **2006**, 47, 6398-6405.
12. Nash, Y.; Nash, T. L.; Henderson, B.; Duraia, E. M.; Powell, C. E.; Sanderson, B.; Beall, G. W. *J. Mater. Sci.* **2013**, 48, 8588-8595.
13. Lide, D. R. *Handbook of Chemistry and Physics*, 87th ed.; CRC Press: Boca Raton, FL, 1998.

14. Weissermel, K.; Arpe, H.-J.; Lindley, C. R. *Industrial Organic Chemistry*, 4th ed.; Wiley-VCH: Germany, 2003.
15. US 8623483, Percy et al., "Copolyesters containing neopentyl glycol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol", issued 7 January 2014.
16. US 3227764, James C. Martin and Edward U. Elam, "Separation of cis and trans isomers of tetraalkyl-1,3-cyclobutanediols and novel compound obtained thereby", issued 4 January 1966.
17. Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons: New Jersey, 2004.
18. Denmark, S. E.; Jones, T. K. *J. Org. Chem.* **1982**, 47, 4595-4597.
19. Douglas, A. M. and Booth, C. J. *Int. J. Polym. Mater.* **2008**, 57, 806-814.
20. *Spectral Database for Organic Compounds (SDBS)*; ¹H NMR; SDBS No.: 3493; HSP-46-210; http://sdb.db.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi (accessed July 5, 2015).
21. *Common ¹H NMR Impurities*; http://www.chem.sc.edu/faculty/shimizu/site/Group_Stuff_files/HNMR%20Solvents%20List.pdf (accessed July 5, 2015).
22. Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds*, 7th ed.; John Wiley & Sons: New Jersey, 2005.
23. Stevens, M. P. *Polymer Chemistry—An Introduction*, 3rd ed.; Oxford University Press: New York, 1999.
24. Flory, P.J. and Vrij, A. *J. Am. Chem. Soc.* **1963**, 85(22), 3548-3553.
25. Strong, A. B. *Fundamentals of Composites Manufacturing: Materials, Methods, and Applications*, 2nd ed.; Society of Manufacturing Engineers: U.S.A., 2008.

26. WO 2014/096269, Taylor et al., "Poly(ether ketone) polymers containing cycloaliphatic units", issued 26 June 2014.