

SYNTHESIS AND THERMAL CHARACTERIZATION OF A SERIES OF
COPOLYESTERS SYNTHESIZED FROM TEREPHTHALOYL CHLORIDE,
2,2,4,4-TETRAMETHYL-1,3-CYCLOBUTANEDIOL,
AND BISPHENOL A, AF, F, AND HPF

THESIS

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ABSTRACT

**SYNTHESIS AND THERMAL CHARACTERIZATION OF A SERIES OF
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AND BISPHENOL A, AF, F, and HPF**

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The synthesis of copolyesters which contain both aromatic as well as aliphatic diol monomer units has been conducted. The rigidity of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) makes it a viable candidate to replace or use along with rigid aromatic diols. Bisphenols A, AF, F, and HPF have also been used as the aforementioned aromatic diols due to their common industrial use. Copolymers of CBDO, terephthaloyl chloride, and the various bisphenols were synthesized and characterized for structure and thermal properties. The percent incorporation of the CBDO and bisphenol were varied in order to examine the effect on thermal properties. The structure of these various copolymers was verified by fourier-transform infrared spectroscopy (FTIR), as well as gel-permeation chromatography (GPC), and nuclear magnetic resonance spectroscopy (NMR). The latter yielding information not only about the structure, but also about the percent cis and trans CBDO, as well as the percent

CBDO in the copolyester. The cis to trans ratio did not fluctuate from the original CBDO monomer, while the percent CBDO in the copolyesters remained within 5% of the feed ratio initially used for the reaction. GPC was used to determine the weight average molecular weight of the copolymers, these ranged from 6,415 to 28,826. The decomposition temperatures of these copolymers, determined by thermal gravimetric analysis (TGA), ranged from 359 °C for the Bisphenol-F copolymer to 472 °C for the Bisphenol-HPF copolymer. The glass transition temperatures, determined by differential scanning calorimetry (DSC), ranged from 163 °C for the Bisphenol-HPF copolymer to 215 °C for the Bisphenol-AF copolymer. Although the molecular weights were low compared to commercial polymers, glass transitions higher than 100 °C and decomposition temperatures higher than 350 °C were obtained and make for very useful optical plastic materials.

1.0 INTRODUCTION

1.1 Background

Bisphenol-A polycarbonate (figure 1) is an amorphous engineering thermoplastic with excellent balance of toughness, clarity, and high-heat deflection temperatures. It also exhibits good dimensional stability, excellent electrical properties, and inherent ignition-resistant characteristics. Polycarbonate was first developed in Germany in 1958 and today more than one million tons are produced per year around the world ¹⁰

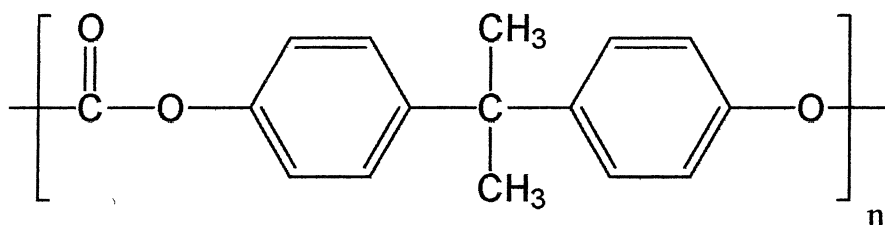


Figure 1 – Structure of bisphenol-A polycarbonate.

Polycarbonate gets its name from the carbonate group found in its backbone. It is made by reacting bisphenol-A with sodium hydroxide to get the sodium salt of bisphenol-A (Figure 2).

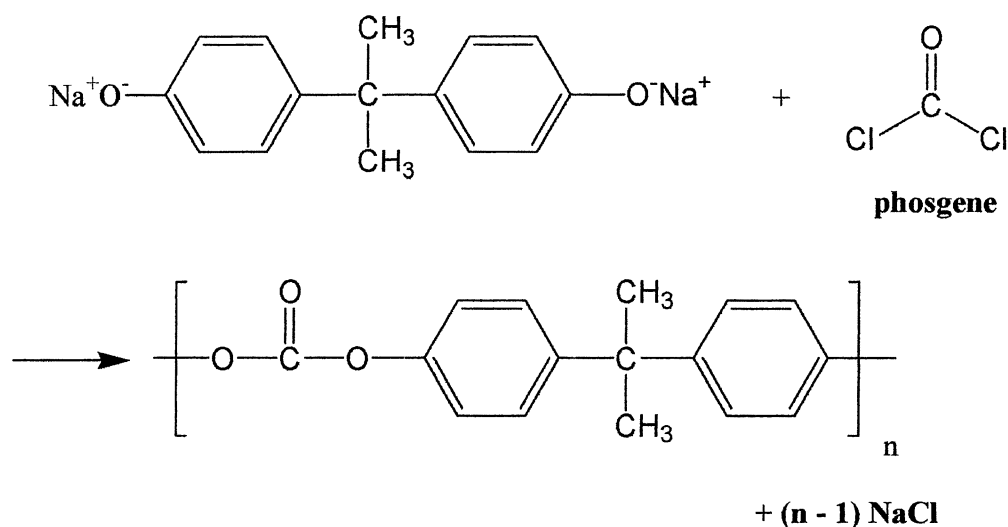


Figure 2 – Reaction of a bisphenol-A salt with phosgene gas.

This salt is then reacted with phosgene gas to produce the Bisphenol-A polycarbonate. Molecular weights for typical polycarbonates vary from 22,000 to 35,000.

Most engineering thermoplastics with glass transition temperatures above 100 °C usually have Izod impacts less than 250 J/m and quite often they are lower than 100 J/m.¹⁰ Bisphenol-A polycarbonate is one example of a thermoplastic that goes against this trend, giving a notched Izod of 650-850 J/m and glass transition of 150 °C.^{10,12} This high impact resistance and glass transition temperature allows Bisphenol-A polycarbonate to be used as an optically clear safety device (i.e. safety goggles, riot shields, etc.).

Polycarbonate is easy to work with, as it can be easily machined with standard metal working tools. No special tools are needed, and finished parts can be polished to a high gloss. With the benefits, there are a few drawbacks to the use of polycarbonate. Due to the aromatic nature of polycarbonate, exposure to ultraviolet (UV) radiation causes yellowing and chain degradation. This is attributed to the production of benzophenones via photooxidative cleavage.¹³ Prolonged exposure to UV radiation causes polycarbonate

to turn yellow, become hazy, and reduces the amount of light transmitted.⁷ Additionally, polycarbonate suffers from poor long-term hydrolytic stability at elevated temperatures.¹⁰

Polycarbonate can be melt-processed using all the traditional methods such as injection molding, extrusion and blow molding. To prevent decomposition during the molding process, polycarbonate must be dried to remove all water immediately prior to the molding process. Because of the versatility of polycarbonate, it can be used in a variety of applications. Everything from headlamps to instrument and as alloy body panels for the automotive industry are made from polycarbonate. Other applications include, but are not restricted to electronics, lighting, appliances, bottles, and even compact discs.

The ring structure of aromatic compounds imparts a degree of rigidity upon the backbones of many polymers. It is this rigidity that contributes to enhanced physical properties in these compounds. Such enhancements include higher glass transition temperatures and increased structural integrity.¹ One of the drawbacks to synthesizing polymers using all aromatic monomers is that as one increases the structural rigidity, the brittleness tends to increase as well.

Incorporation of a rigid aliphatic monomer instead of an aromatic monomer has been shown to decrease this brittleness, thereby allowing an increase in the physical properties without increasing flexibility in the polymeric molecule. One such example of these rigid aliphatic monomers is 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO). Due to a large amount of bond angle strain in this molecule, its structural rigidity closely resembles that of an aromatic ring. This is important in forming aromatic-like polymers with increased physical properties.

The advantage of incorporating a four-membered ring such as CBDO rather than a six membered aliphatic ring such as cyclohexane diol has been examined using the RIS Metropolis Monte-Carlo (RMMC) method.¹¹ In this study, it was shown that the rather rigid backbone in the CBDO chain leads to more extended chain lengths than the more flexible cyclohexane chains. This is closer to what would be expected for a fully aromatic polycarbonate chain. Figure 3 illustrates that the trans-trans conformation of the polycarbonate showed an increase in chain extension along with polydispersity as compared to similar polyesters using cyclohexane derivatives such as poly(1,4-cyclohexylenedimethylene terephthalate) [PCT], poly(1,4-cyclohexylenedimethylene cyclohexylenedicarboxylate) [PCC], and poly(1,4-cyclohexylenedimethylene 2,5-dimethylterephthalate) [DMPCT] which are shown below in figure 4.¹¹

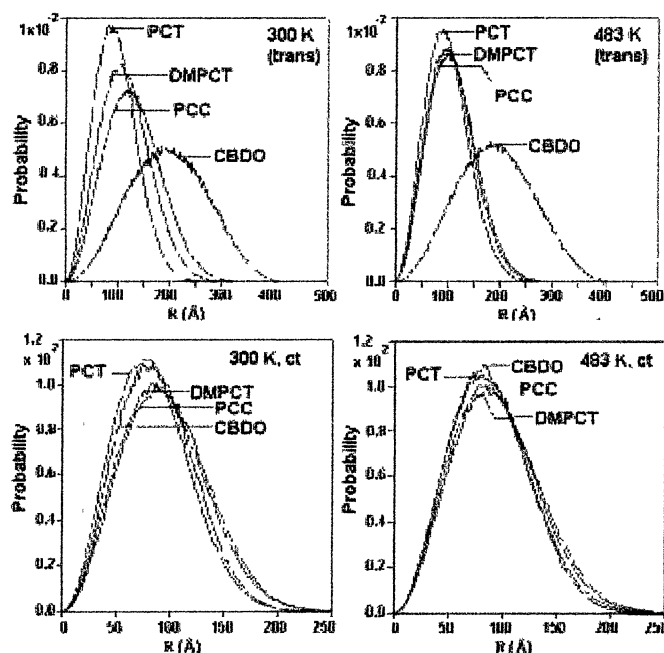


Figure 3 – End-to-end distributions for the cis-trans and trans-trans conformations of the polyesters in Figure 4. (taken from reference 11)

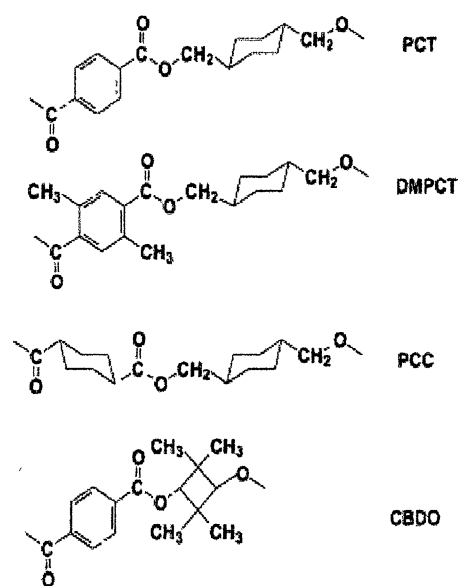


Figure 4 - Geometry of the repeat units of polyesters in the trans conformation. (taken from reference 11)

In the trans-trans case of the CBDO polyester, this finding is exaggerated due to the limited torsional flexibility of the bonds in the repeat unit. This limits the number of preferable conformations possible. This exhibition of high chain dimensions in CBDO polyesters compared to other polyesters gives support to the theory that a rather rigid backbone exists.

1.2 Aliphatic-Aromatic Copolycarbonates

Recent interest has been given to copolycarbonates synthesized using CBDO as an aliphatic diol monomer. One reason is that polycarbonates of CBDO have been shown to exhibit improved physical properties when compared to commercial grade polycarbonate. These properties include higher glass transition temperatures, increased structural integrity, as well as a greater toughness.¹ These properties lend themselves to excellent optical plastics that can be used for safety glass for many different applications.

The discovery of a simple method for production of CBDO² was not formulated until 1961. This new process opened the door to the formation of polycarbonates using CBDO, which is a field that has been extensively studied.³ This research has been conducted not using polycarbonates which contain CBDO, as well as copolycarbonates which contain CBDO. One study that exhibits the effects of different monomeric precursors mixed with the CBDO and their properties is that conducted by Daly et.al. His group synthesized a large number of CBDO based copolycarbonates and studied the co-monomer effects. They used a series of aromatic bisphenols,³ including BisA, BisAP, BisTP, BisHPF, BisF, and BisS (Figure 5).

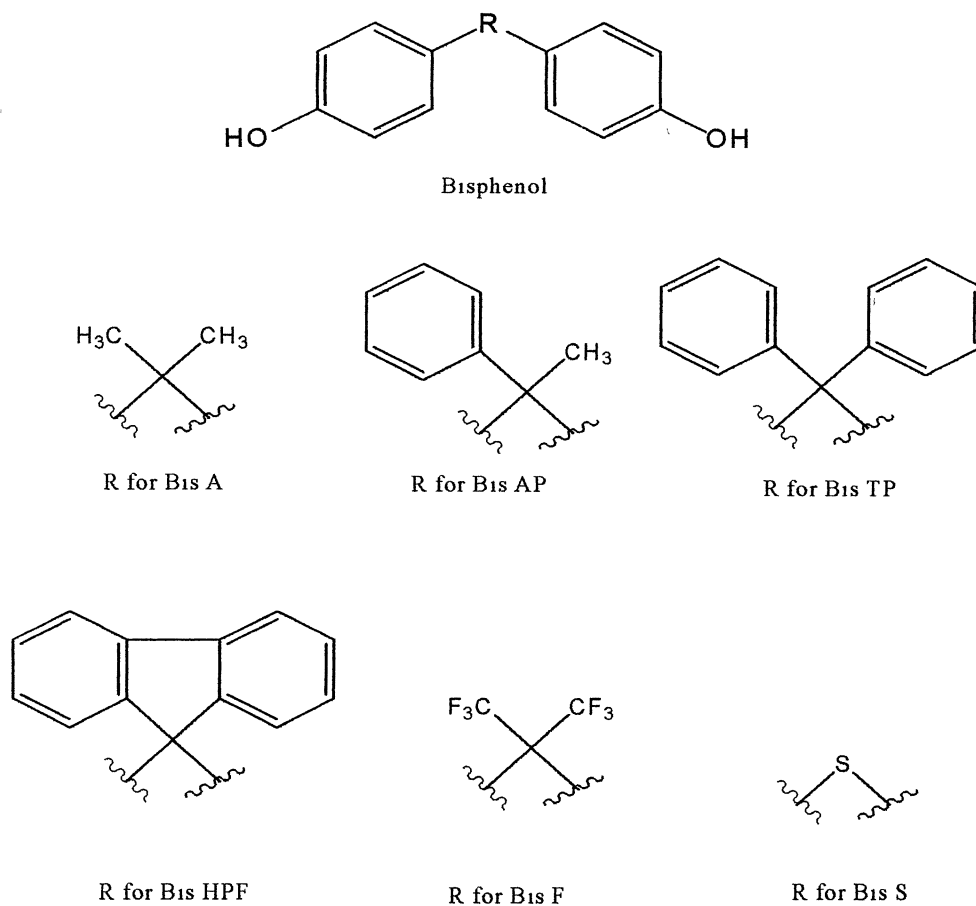


Figure 5 - Typical bisphenols used in the synthesis of CBDO copolyesters.

The aliphatic-aromatic copolycarbonates (Figure 6) were prepared using both melt polymerizations⁴ and solution polymerizations.⁵ One of the drawbacks found to using the

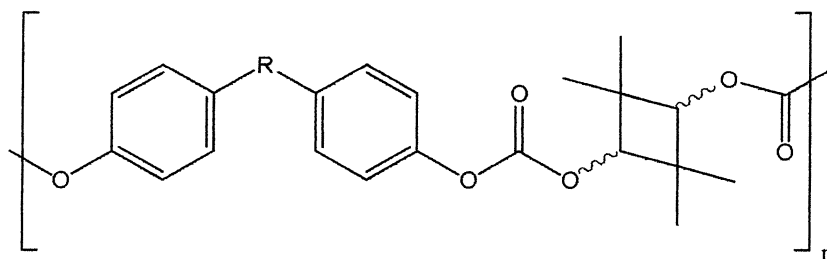


Figure 6 – Generic representation of a CBDO/Bisphenol copolycarbonate.

melt polymerization technique was that thermal degradation of the CBDO monomer occurred due to the high temperatures needed to melt the starting compounds. This degradation led to decreased yields and changes in cis/trans ratio with the CBDO, when

compared to the starting CBDO monomer.⁴ The Daly group reported this degradation, and therefore used solution polymerization to synthesize their series of polymers. This alleviated the thermal degradation of the CBDO and produced alternating copolymers.³

Incorporation of the various bisphenol monomer units into the CBDO copolycarbonate, as shown in Figure 6, resulted in a rather wide range of thermal data.

Polymer	T _g (°C)	T _d (°C)	MW	Mol % cis-CBDO
BisA/CBDO	130	352	42000	33
BisAP/CBDO	149	357	38000	25
BisHPF/CBDO	214	347	39000	36
BisF/CBDO	142	343	42000	34
BisS/CBDO	107	341	65000	34

Table 1 – CBDO copolycarbonate results from reference 3.

Changes in the bisphenol monomer showed a glass transition range greater than 100°C, shown in table 1. Incorporation of bisphenol-S into the copolymer displayed the lowest T_g, 107° C, while incorporation of bisphenol-HPF showed the highest T_g, 214° C. This range of glass transition temperatures can be explained by examining the degree of flexibility of the bisphenol unit incorporated. As the flexibility increases, the glass transition temperature decreases. Data for bisphenol-A copolycarbonate was also measured and gave a glass transition of 130° C.³ The decomposition range for the various bisphenols was less dependent on the bisphenol used. An average value of 350° C was reported. Bisphenol-A was reported to have a decomposition temperature of 352° C.³

The findings of the Daly group showed that copolycarbonates with the incorporation of CBDO and various bisphenol monomers could be synthesized via solution polymerization with high yield and molecular weight. These copolycarbonates exhibited

glass transition temperatures above 100° C and have large temperature ranges in which they could be used as structural plastics.³

1.3 Flexible Aliphatic Copolyesters

The formation of polyesters using dimethyl terephthalate and CBDO has been studied in detail by a number of groups (Figure 7).^{6,9} It has been shown that these CBDO based polyesters are amorphous and exhibit relatively high glass transition temperatures that range between 105-120°C.⁶

Many diols can be used to form copolyesters by substituting themselves into the polyester chain in place of the CBDO. Of the CBDO based copolyesters that can be formed, perhaps the most interesting are those that use flexible diols as diol co-monomers. The Shell Chemical Co. studied the effects of diols with two, three, and four carbon spacers on the physical properties of such copolyesters (Figure 8). Shell found that using such a flexible spacer unit increased thermal stability, increased UV stability, increased clarity, decreased color, and increased glass transition temperatures. Shell also found that the rigidity of the CBDO group imparted an unusually high impact resistance.⁷

Unlike the copolycarbonates formed by the Daly group, the copolyesters were synthesized using a melt polymerization technique. This was possible since the flexible diols used in their research acted as a solvent for the DMT and CBDO. The process was driven by removing the excess diol and the methanol byproduct under high vacuum. Doing such allowed molecular weights of 48000-55000 to be attained.

CBDO/1,3-Propanediol	T_g (°C)	T_m (°C)
100/0	174	>310
78/22	150	A
50/50	101	A
25/75	17	162
0/100	59	235

Table 2 – CBDO/PDO copolyester results.

The homopolymer (Figure 7a) made using CBDO and DMT was shown to have a glass transition temperature of 174 °C (Table 2) ⁷ This value approximates the previously

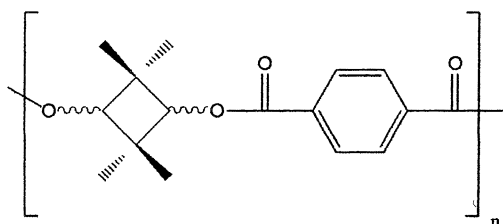


Figure 7a – Homopolymer made with CBDO and DMT.

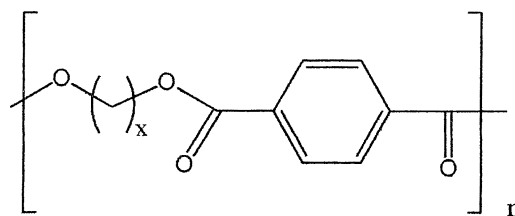


Figure 7b – Homopolymer made with CBDO and flexible diol (x=2, 3, or 4)

reported literature value of 184 °C, ⁸ and was theorized to be slightly low due to lower molecular weight. Glass transition temperatures for flexible diol polyesters (figure 7b) of dimethyl terephthalate such as amorphous poly(trimethylene terephthalate) [PTT] are around 40 °C ⁹ This shows that addition of CBDO to the polyester chain increases the glass transition temperature by 130-140 °C. This also shows that the aliphatic CBDO acts in a very similar way to an aromatic bisphenol giving comparable increases in glass transition temperature ⁷ Kelsey's group also was able to assign a trend in glass transition temperature corresponding to the amount of CBDO incorporated into the polymer. They found that in order to obtain a glass transition of 100 °C, the mole percent of CBDO must be at least 50%. Anything lower would be insufficient to increase the glass transition temperature to 100 °C.

The polyesters made using flexible diols, such as PTT, exhibit poor impact resistance giving typical notched Izod values of less than 80 J/m.¹⁰ Incorporation of CBDO into these same polymer systems by creating CBDO copolymers (figure 8) increases the

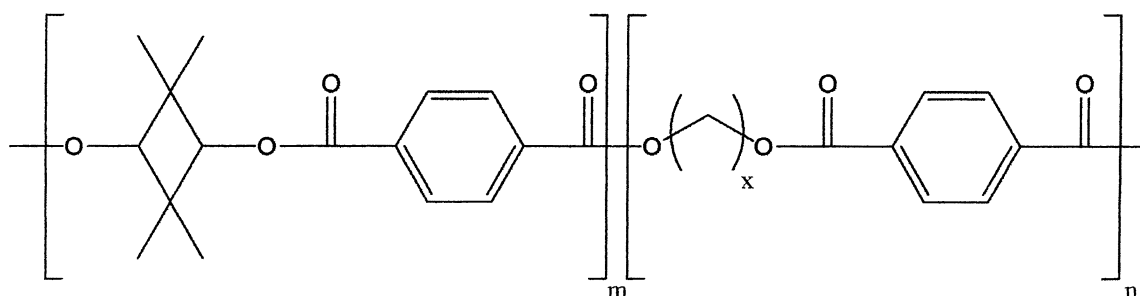


Figure 8 – Copolymer consisting of CBDO, DMT, and flexible diol

toughness of the polymer, and improves the notched Izod impact resistance to as much as 1070 J/m⁷ This increase of almost 1000 J/m is attributed to the extremely rigid CBDO structure. The Kelsey group found that impact resistance was inversely related to the percent incorporation of the CBDO content in the copolyester. This trend is reversed from the glass transition data seen earlier, and therefore a tradeoff must be made between strength and thermal stability when using CBDO and flexible diols in copolyesters⁷

Through studying the effects of percent incorporation of CBDO and flexible diol used in a series of copolyterephthalates, many interesting discoveries have been made about the nature of CBDO. One such observation is that as CBDO is added to the system, thermal resistance increases. Another of these observations is that as CBDO content increases, impact resistance decreases, however the impact properties even at high concentrations of CBDO are still better than copolyterephthalates containing no CBDO. The study has also shown that, when compared to CBDO containing polycarbonates, the optical properties as well as UV resistance of the CBDO polyterephthalate are improved.⁷

2.0 PROSPECTUS OF RESEARCH

Polycarbonates are amorphous engineering thermal plastics with surprisingly useful properties. Relatively high glass transition temperatures, degradation temperatures, and excellent toughness make polycarbonate a preferred commercial polymer for optical safety devices.³ The most significant drawback to the production of mass quantities of polycarbonate is the use of deadly phosgene gas in its production

As seen in Figure 2, the sodium salt of bisphenol-A is used along with phosgene gas to make bisphenol-A polycarbonate. According to the Agency for Toxic Substances and Disease Registry, phosgene is a colorless, fuming liquid below 8 °C and a colorless, nonflammable gas above this temperature. Phosgene is slightly soluble in water and is hydrolyzed slowly by moisture to form hydrochloric acid. Because the odor threshold, or concentration needed to smell the gas, is five times greater than the concentration deemed hazardous by OSHA, odor provides insufficient warning of hazardous concentrations. Phosgene's irritating quality can be mild and delayed, which may result in a lack of avoidance leading to exposure for prolonged periods. Phosgene is heavier than air and may cause asphyxiation in poorly ventilated, low-lying, or enclosed spaces. Exposure to small amounts usually causes eye, nose, and throat irritation. However, the irritating effects can be so mild at first that the person does not leave the area of exposure. Generally, the higher the exposure, the more severe the symptoms. Extended exposure

can cause severe breathing difficulty, which may lead to chemical pneumonia and death. Severe breathing problems may not develop for as long as 48 hours after exposure.

Due to the high risk associated with polymerizations using phosgene gas, new methods of producing polycarbonate have been developed. The drawback is that these methods don't produce polycarbonate as cheap or with the same impact properties. Scientists, therefore, have been looking into other polymer systems that have high glass transition temperatures, as well as mechanical and thermal stability.

Two of the polymeric systems that fit the criterion to replace bisphenol-A polycarbonate were introduced earlier. Using CBDO as a structurally rigid aliphatic diol, polycarbonates and polyesters were formed in order to increase mechanical stability without decreasing the glass transition of the polymer. By forming a copolyterephthalate of CBDO and various bisphenols, it is thought that these numbers can be increased in such a way as to optimize the mechanical stability as well as keeping a relatively high glass transition.

This thesis reports the synthesis and thermal characterization of copolyterephthalates comprised of CBDO, dimethyl terephthalate, and a series of bisphenols. These bisphenols include Bisphenol-A, AF, F, and HPF. These systems will be an improvement upon the properties of Bisphenol-A polycarbonate. The synthesis of these copolyterephthalates involves a solution polymerization using o-dichlorobenzene with the acid chloride of terephthalic acid.

Shell reported an inverse relationship between the glass transition temperature and the impact resistance as percent incorporation of CBDO was varied. It is thought that this trend should also hold true if bisphenol is substituted for the flexible diols. Bisphenol-A

is the main component in Bisphenol-A polycarbonate; therefore it is believed that the structural integrity of a polymer with a large percent of bisphenol-A will have structural properties similar to those of polycarbonate.

This study reports the synthesis of a series of copolyesters which incorporate CBDO, terephthaloyl chloride, and bisphenol-A, bisphenol-AF, bisphenol-HPF, and bisphenol-F. These bisphenols will be incorporated into a copolyterephthalate with appropriate molar ratios of CBDO and terephthaloyl chloride in order to produce copolyterephthalates of CBDO and various bisphenols. The four bisphenols studied were picked on the basis of availability and structural integrity.

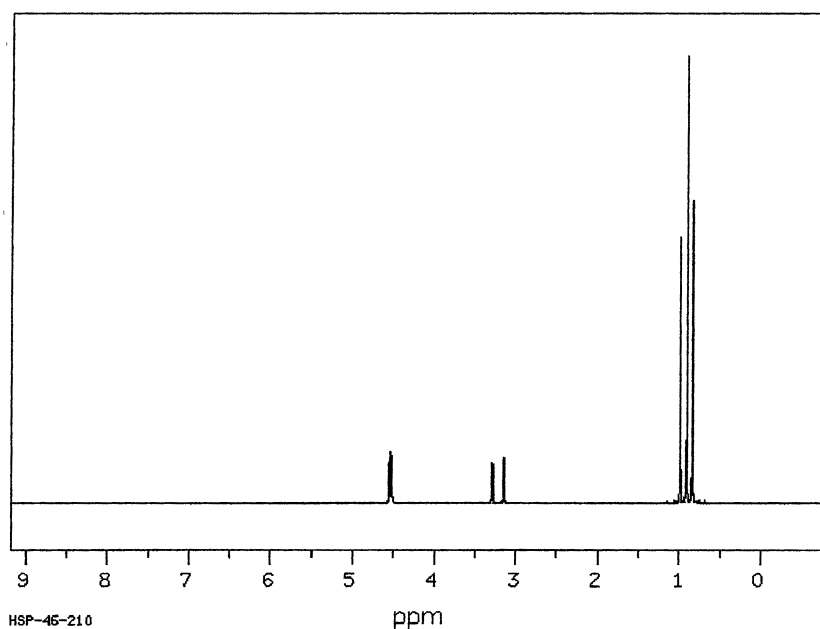


Figure 9 – NMR spectrum of CBDO monomer

After synthesis of the copolyterephthalates, a series of tests have been run to determine product identity and thermal properties. CBDO content of the copolyterephthalate has been determined using nuclear magnetic resonance spectroscopy (NMR). This technique can also determine the amount of cis/trans character of the

CBDO incorporated into the copolyterephthalate by looking at the two peaks at 3.2 and 3.4 ppm (figure 9). NMR also allows for determination of the structure of the copolymer synthesized, and comparison to the structures of the monomer units. Weight average molecular weight as well as polydispersity of the copolymers has been determined using gel-permeation chromatography (GPC). Thermal degradation temperature has been determined using thermal gravimetric analysis (TGA). Differential scanning calorimetry (DSC) has been used to determine both the glass transition temperature as well as the percent crystallinity of the copolymers.

3.0 EXPERIMENTAL

3.1 Materials

CBDO in a cis/trans ratio of 37/63 (by NMR) was purchased from TCI America, Tokyo Kasei, Inc. and was used for all syntheses. Polymer grade terephthaloyl chloride of 99+% purity was purchased from Aldrich Chemical Company and will be used without further purification. Bisphenol-A of 99% purity was purchased from Aldrich Chemical Company and then purified further via sublimation at 145 °C under vacuum. Central Glass Co. LTD in Japan donated bisphenol-AF of 99% purity. It was purified via sublimation at 160 °C under vacuum. Bisphenol-F was purchased from Isonova and purified by recrystallization from anisole. Bisphenol-HPF of 99.8% purity was purchased from Isonova and purified by washing in dichloromethane. Solvation in ethyl acetate and precipitation in petroleum ether further purified the bisphenol-HPF.

3.2 Synthetic Methods

3.2.1 Synthesis of Copolyterephthalates

A flame dried 500 mL three-neck reaction flask fitted with a magnetic stirrer and distillation head was filled with terephthaloyl chloride (2.00 g, 0.010 mol), CBDO (0.71 g, 0.005 mol), bisphenol-A (1.12 g, 0.005 mol), o-dichlorobenzene (16 mL), and 5 drops of pyridine. The flask was then degassed with an argon purge using a Schlenk line, and heated in an oil bath to 176 °C for 24 hours. After this time, the reaction flask was cooled

to room temperature. The cooled polymer gel was dissolved in chloroform to effectively remove it from the flask, and then precipitated into acidic methanol.

3.2.2 Purification

Purification methods for all the copolymers were carried out in the same manner. First, the copolymer/chloroform solution was precipitated into acidic methanol. After filtering the polymer, it was dried overnight in a vacuum oven. The process of dissolving in chloroform and then precipitating into methanol was repeated three times. The copolymer was then placed into a Soxhlet extractor and washed with methanol for two days. The resulting copolyester was then dried in the vacuum oven at 80 °C for two days to ensure dryness.

3.3 Characterization Methods

3.3.1 Nuclear Magnetic Resonance Spectroscopy

¹H-NMR spectra were obtained in solutions of deuterated chloroform in 10 mm tubes using a 400-MHz Oxford NMR 400 spectrometer. Samples were prepared by taking 1-2 mg of copolyester and dissolving it into approximately 0.75 ml of deuterated chloroform. NMR spectra were then run in the range of 0-9ppm as all significant peaks were in this range. Peaks were integrated for further analysis.

3.3.2 Fourier-Transform Infrared Spectroscopy

FTIR spectrometry was carried out using a Perkin-Elmer Spectrum One FTIR spectrometer at ambient temperature and humidity. Each spectrum was obtained using an average of five scans with a wavenumber range of 400-4000 cm⁻¹ and a resolution of 2.00 cm⁻¹. Samples were prepared by mixing 2.5 mg of copolymer sample with 15 mg of KBr with a WIG-L-BUGTM grinding mill to achieve homogeneity. Pressing the KBr mixture

using a hand press produced transparent IR pellets. Peaks were then labeled as appropriate using the software for the Perkin-Elmer Spectrum One FTIR.

3.3.3 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was obtained on a Waters model 600 GPC in conjunction with a Waters 2410 refractive index detector (410). Calibration was carried out using a series of ten polystyrene standards of varying molecular weights from 1.32×10^3 – 3.15×10^6 . Samples were prepared by mixing 6.6 mg of copolymer with a milliliter of chloroform. The samples were filtered using a 0.45 micron Teflon Cameo 30F syringe filter. Samples were injected at a volume of 50 μ L.

3.3.4 Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was measured on a TA Instruments Q50 thermal gravimetric analyzer from ambient to 800 °C at 20 °C/min on 5-10 mg samples. This analysis was carried out in both air and argon and was analyzed for 10% weight loss of the copolymer sample as well as char yield.

3.3.5 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was measured on a TA Instruments DSC 2920 Modulated DSC using a heat/cool/heat cycle at 10 °C/min on 5 mg samples. Data was taken on the first cool and second heat cycles of the run. An argon environment was maintained throughout the analysis. Data was analyzed to determine glass transition as well as percent crystallinity. Glass transition peak values were taken at the midpoint of the transitions.

4.0 RESULTS AND DISCUSSION

4.1 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to confirm the presence of both saturated and unsaturated carbon hydrogen stretches in the copolymer compounds. These stretching frequencies generally occurred at 3050 cm^{-1} for the unsaturated stretches and had multiple peaks centered around 2930 cm^{-1} for the saturated stretches. The presence of the carbon-oxygen double bond of the carbonyl moiety in the ester portion of the copolyterephthalates was generally seen at 1740 cm^{-1} for all permutations of the copolymer studied. Other rocking and bending modes were seen in the fingerprint region of the spectra, but were not used for confirmation of the presence of copolymers made with CBDO, bisphenol-A and terephthalate monomers.

Due to the solution polymerization method used to synthesize each of the copolymers, the possibility for solvent to be trapped in the chain entanglements was high. FTIR was used to insure the polymers were dry before further testing. Representative spectra for the copolymer synthesized with bisphenol-A and terephthaloyl chloride can be seen in figure 10.

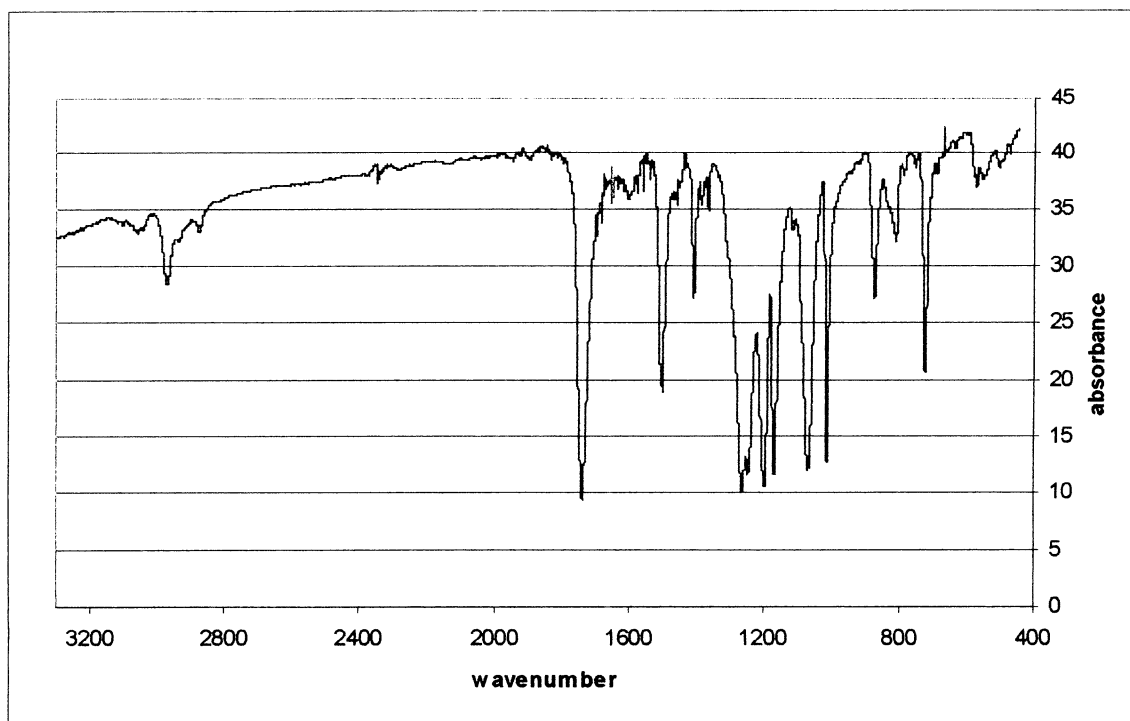


Figure 10 – IR spectrum for poly(bisphenol-A)terephthalate homopolymer

4.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy was used in conjunction with FTIR in order to determine purity, structure, percent CBDO in the cis and trans conformation, and percent CBDO in the copolymer. All ^1H NMR spectra were compared to those of the homopolymers in order to determine the percent incorporation of the individual monomers in the copolymer system. These values were then compared to the monomer feed ratio used in the synthesis to determine the exact percent compositions. The differing environments of the aromatic protons on the terephthalate monomer facilitated determination of this calculation. The aromatic protons of the terephthalate monomer nearest the CBDO monomer showed a resonance of 8.153 ppm (Figure 11), while those

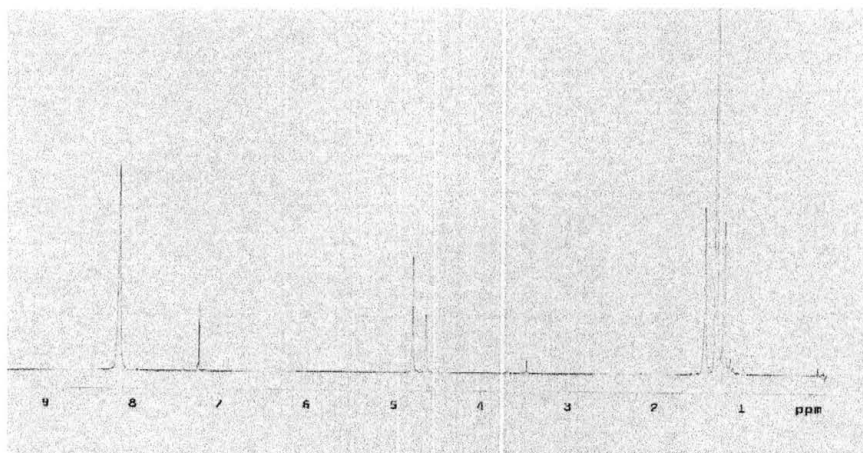


Figure 11 – NMR spectrum of CBDO Homopolymer

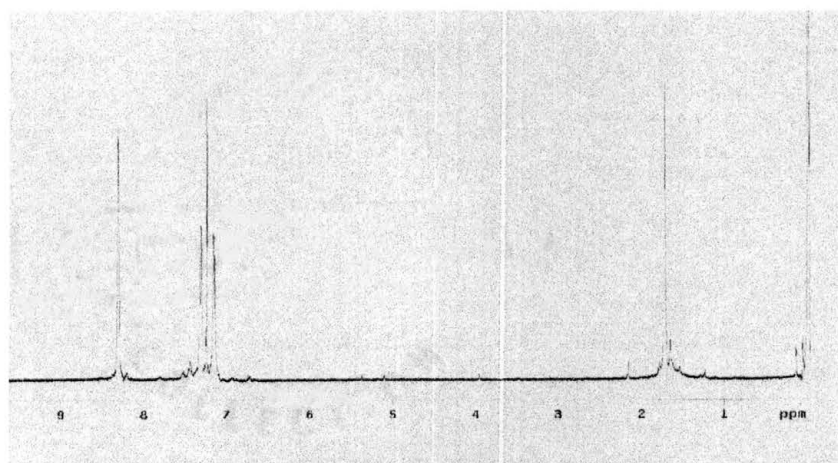


Figure 12 – NMR spectrum of Bisphenol-A Homopolymer

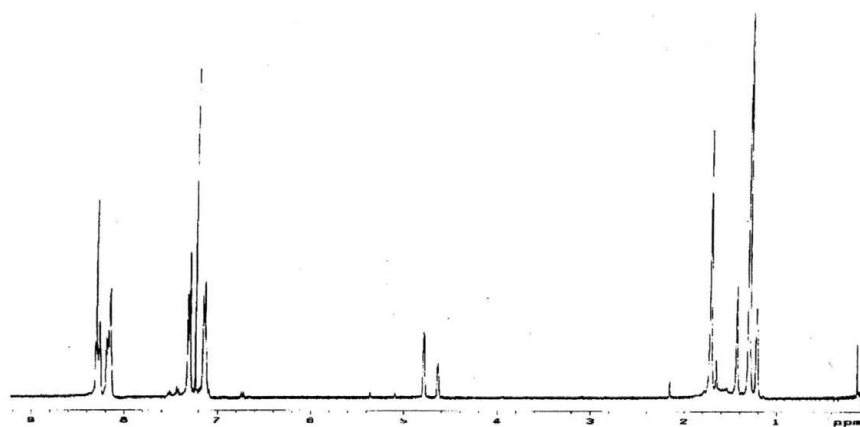


Figure 13 – NMR spectrum of 50/50 CBDO/Bisphenol-A copolymer

protons nearest the bisphenol monomer showed a resonance of 8.308 ppm (Figure 12).

Both of these peaks are seen in the copolymer as shown in Figure 13. This difference in proton environments allowed calculation of percent CBDO by simple integration of these two signals. Table 3 gives the exact percent CBDO in each copolymer.

Data obtained from the NMR include the percent CBDO that exist in the cis and trans conformers. The protons on the cyclobutane ring of the CBDO structure exhibit different resonances depending on whether they are in the cis or the trans conformation. The trans

Initial % CBDO	Initial % Bisphenol	Actual % CBDO	Actual % Bisphenol
	Bisphenol-A		
25%	75%	29%	71%
50%	50%	51%	49%
75%	25%	76%	24%
	Bisphenol-AF		
25%	75%	29%	71%
50%	50%	47%	53%
75%	25%	79%	21%
	Bisphenol-HPF		
25%	75%	66%	34%
50%	50%	49%	51%
75%	25%	73%	27%

Table 3 – Exact CBDO incorporation into copolymers from NMR data

protons give a resonance peak around 4.8 ppm, while the cis protons have a peak just above 4.6 ppm (Figure 11). Using integration values from these two peaks, it is possible to determine the percent cis to trans of the CBDO in the copolymer synthesized. Since all the CBDO was purchased from the same manufacturer, the cis to trans ratio was approximately 35% cis and 65% trans. All NMR spectra showed that this relationship was maintained in the polymer.

More peaks of importance include the aromatic proton peaks on the various bisphenols. These two peaks resulting from the two rings fell around 7.15 and 7.25 ppm

The methyl protons from the CBDO were also seen to reside as three singlets around 1.3 ppm. The methyl protons in bisphenol-A generally coincided with a resonance of 1.75 ppm.

4.2.1 Bisphenol-A Copolymer Series

NMR peak assignments are as follows for the following protons. δ 1.22 (s, 3H, CH_3 -CBDO), 1.31 (s, 3H, CH_3 -CBDO), 1.44 (s, 3H, CH_3 -CBDO), 1.72 (s, 6H, CH_3 -Bisphenol-A), 4.65 (s, 1H, cis-CBDO ring proton), 4.80 (s, 1H, trans-CBDO ring proton), 7.14 (d, 4H, inner aromatic Bisphenol-A protons), 7.32 (d, 4H, outer aromatic Bisphenol-A protons), 8.15 (d, 4H, aromatic terephthalate protons nearest CBDO monomer), 8.31 (d, 4H, aromatic terephthalate protons nearest Bisphenol-A monomer). In the case of bisphenol-A, the percent incorporated approaches the percent initially used as the initial percentage approaches 100%. For the copolymer that had 75% CBDO, the copolymer had 75.97% CBDO.

4.2.2 Bisphenol-AF Copolymer Series

NMR peak assignments are as follows for the following protons. δ 1.22 (s, 3H, CH_3 -CBDO), 1.31 (s, 3H, CH_3 -CBDO), 1.44 (s, 3H, CH_3 -CBDO), 4.65 (s, 1H, cis-CBDO ring proton), 4.80 (s, 1H, trans-CBDO ring proton), 7.14 (d, 4H, inner aromatic Bisphenol-AF protons), 7.33 (d, 4H, outer aromatic Bisphenol-AF protons), 8.16 (d, 4H, aromatic terephthalate protons nearest CBDO monomer), 8.31 (d, 4H, aromatic terephthalate protons nearest Bisphenol-AF monomer). NMR results for the Bisphenol-AF copolymer series showed that the correlation between initial molar percentage of CBDO and the actual percentage in the final copolymer was not as predictable as for the Bisphenol-A copolymer series. Again, peaks indicating the protons on the aromatic ring

of terephthalate were used to determine amounts of the CBDO monomer and Bisphenol-AF monomer. This was again facilitated by the differing environments of these protons' proximity to either CBDO or Bisphenol-AF.

4.2.3 Bisphenol-HPF Copolymer Series

NMR peak assignments are as follows for the following protons: δ 1.22 (s, 3H, CH_3 -CBDO), 1.11 (s, 3H, CH_3 -CBDO), 1.44 (s, 3H, CH_3 -CBDO), 4.64 (s, 1H, cis-CBDO ring proton), 4.80 (s, 1H, trans-CBDO ring proton), 7.14 (d, 4H, inner aromatic Bisphenol-HPF protons), 7.32 (d, 4H, outer aromatic Bisphenol-HPF protons), 8.15 (d, 4H, aromatic terephthalate protons nearest CBDO monomer), 8.30 (d, 4H, aromatic terephthalate protons nearest Bisphenol-AF monomer). The copolymer with 25% molar feed ratio of CBDO was shown to have 66% CBDO. The reason for this is unknown, but may have stemmed from poor control of initial feed ratio. Overall for the remaining two copolymers the actual percentage of CBDO was lower than the initial mole percent added to the reaction vessel.

4.3 Gel-Permeation Chromatography Data

Gel-permeation chromatography (GPC) was conducted for all copolymer sets except the Bisphenol-F copolymer which was insoluble in chloroform. Elution times were compared for all samples against a polystyrene standard. These peaks were then analyzed based on the weight average molecular weight and the polydispersity of the copolymers synthesized. This data is shown in table 4.

4.3.1 GPC Analysis of Bisphenol-A Copolymer Series

Weight average molecular weight from GPC for the series of Bisphenol-A copolymers varied from approximately 6,000 to 19,000. A general trend for this data is

that as percent CBDO increases, the molecular weight also increases. This trend did not hold up for the copolymer with approximately 30% CBDO as it had the highest molecular weight. It is possible that this trend is nothing more than a coincidence based on slight variance in the way these polymers were synthesized. Slight differences in reaction time and temperature could account for this variance in the molecular weight.

Actual % CBDO	Actual % Bisphenol	M _w	Polydispersity
	Bisphenol-A		
0%	100%	6,415	4.2
29.49%	70.51%	19,916	2.0
51.46%	48.54%	13,904	1.9
75.97%	24.03%	14,045	8.0
100%	0%	17,475	9.5
	Bisphenol-AF		
0%	100%	6,592	3.8
29.38%	70.62%	25,374	4.3
46.55%	53.45%	22,500	21.4
78.95%	21.05%	11,545	78.7
	Bisphenol-HPF		
0%	100%	28,826	2.7
49.34%	50.66%	15,277	5.1
66.28%	33.72%	1,788	1.6
72.98%	27.02%	13,826	4.8

Table 4 – Weight average molecular weight and polydispersity of copolymers by GPC data

4.3.2 GPC Analysis of Bisphenol-AF Copolymer Series

The Bisphenol-AF copolymer series showed weight average molecular weights ranging from approximately 6,000 to 25,000. This was very similar to what was seen previously for the Bisphenol-A copolymer series, however the Bisphenol-AF copolymer was able to reach a higher molecular weight than its counterpart. Both copolymer series showed approximately 6,000 for the homopolymer made up of only the bisphenol-And terephthaloyl chloride. Copolymers with approximately 30% CBDO showed the highest

molecular weights. In the case of the Bisphenol-AF copolymer series this molecular weight was 25,374. Polydispersities for this series of copolymers were extremely high with the highest peaking at almost 80. This high polydispersity makes for a poor determination of molecular weight as chain lengths are a vast number of different sizes.

4.3.3 GPC Analysis of Bisphenol-HPF Copolymer Series

GPC data for the Bisphenol-HPF copolymer series showed the broadest weight average molecular weight distribution of all the bisphenol copolymers. This range was from approximately 2,000 to 29,000. This molecular weight range was offset by a small variance in polydispersity ranging from 1.6-5.1. Due to such a narrow distribution of polydispersities, the molecular weights are more accurate than for any other system. There is not as large a difference in chain length for these polymers. The highest molecular weight recorded for these copolymers was near 30,000 for the Bisphenol-HPF homopolymer. This is counterintuitive when compared to the other series, as the lowest molecular weights were observed for the homopolymers of these series. As would be expected the polydispersity for the 66% CBDO copolymer with molecular weight around 2,000 was the lowest seen by far at 1.612. This stems from the fact that such small chains will tend to be the same length due to such a small number of monomers needed to create these chains. It is possible that this copolymer did not have sufficient time to react in order to increase its molecular weight.

4.4 Thermal Gravimetric Analysis Data

Thermal Gravimetric Analysis (TGA) was obtained in both air and argon. Decomposition temperatures are defined as the temperature at which the polymer has lost ten percent of initial mass. Knowing this temperature allows for future studies to be

made which utilize the decomposition temperature as a guide for processing the polymer.

Decomposition data for all the copolymers in this study appear in table 5.

Actual % CBDO	Actual % Bisphenol	T_d (°C)	T_d (°C)
	Bisphenol-A	Air	Argon
0%	100%	444	481
29.49%	70.51%	410	421
51.46%	48.54%	390	398
75.97%	24.03%	386	392
100%	0%	377	386
	Bisphenol-AF		
0%	100%	468	496
29.38%	70.62%	399	414
46.55%	53.45%	388	390
78.95%	21.05%	384	380
	Bisphenol-HPF		
0%	100%	472	493
49.34%	50.66%	366	367
66.28%	33.72%	362	367
72.98%	27.02%	373	380
	Bisphenol-F		
0%	100%	390	466
25%	75%	374	394
50%	50%	359	389
75%	25%	375	380

Table 5 – Degradation temperatures of copolymers by TGA data

Further comparison of this data with that of the copolycarbonates in table 3 shows that the T_d for CBDO-bisphenol copolyterephthalates is approximately 80°C higher than that for the respective CBDO-bisphenol copolycarbonates. This suggests that the thermal stability of the copolymer systems is further enhanced by using the terephthalate monomer as a linker rather than relying on the carbonate linkage unit.

4.4.1 TGA Analysis of Bisphenol-A Copolymer Series

Degradation temperatures under both atmospheric and argon conditions yielded good results for the Bisphenol-A copolymers. According to the data collected, as percent CBDO was increased, degradation temperature decreased. This shows that incorporation of CBDO hindered the thermal stability of the copolymers studied. The difference under atmospheric conditions showed that in argon the T_d was approximately ten degrees higher than in open-air conditions. For the Bisphenol-A homopolymer this difference was even more pronounced giving a difference of almost forty degrees.

4.4.2 TGA Analysis of Bisphenol-AF Copolymer Series

TGA results for the Bisphenol-AF copolymer series followed the same trend as those for the Bisphenol-A copolymer series. The highest degradation temperature was seen for the Bisphenol-AF homopolymer, while the lowest degradation temperature was exhibited by the 79% CBDO copolymer. The thermal degradation temperature of 380°C for this copolymer in argon is even lower than that of the CBDO homopolymer which has 100% CBDO. This information does not follow the trend, but a difference of six degrees can be attributed to human error in the measurement of this data. The 79% CBDO sample may have been slightly wet during the testing which would lead to a lower degradation temperature based on a 10% weight loss. Although the samples were normalized to remove this error due to trapped solvent, the method for normalization may have provided skewed results for this sample. These skewed results would explain why the trend of CBDO incorporation decreasing thermal degradation temperature does not carry through this one piece of data while holding true for all others.

4.4.3 TGA Analysis of Bisphenol-HPF Copolymer Series

TGA results for the Bisphenol-HPF copolymer series were similar to those of the Bisphenol-A and the Bisphenol-AF series. Using this data a trend is beginning to form in which the bisphenol homopolymer shows the highest degradation temperature while that for the CBDO homopolymer shows the lowest. Differing percent compositions between these extremes show degradation temperatures between those of the two. This case also shows that in an argon environment the T_d is higher than for the same in an atmospheric environment. Again, the T_D for the 73% CBDO case is lower than that for the CBDO homopolymer. This leads to the idea that perhaps the data for the copolymer series are not skewed, and that of the CBDO homopolymer may be exhibiting an abnormally high T_d . This would lead to the results shown with the ~75% CBDO copolymers having lower T_d 's than the homopolymer. Once again a reason for this skewing of data could come from the normalization of all the data.

4.4.4 TGA Analysis of Bisphenol-F Copolymer Series

The TGA results for the Bisphenol-F copolymer series were almost identical to those of the prior series. The main difference was that in air, the 50% CBDO copolymer had a lower T_d than the 75% CBDO copolymer. This abnormality can not be accounted for in the argon samples and can be seen as a difference in analysis techniques as the normalization used for the other samples was not used in this one. The reason for not running the normalization on this sample is that another technician who was uninformed analyzed it. The rest of the data conforms to the trend and therefore validate it.

4.5 Differential Scanning Calorimetry Data

Differential Scanning Calorimetry (DSC) was carried out on all polymers in order to analyze for glass transition temperatures as well as percent crystallinity. The copolymers studied were semi-crystalline due to the purification procedures used, in which the polymer was dissolved in a solvent and then precipitated from acidic methanol. This procedure imparted a certain degree of crystallinity to the polymer. Annealing the polymer at temperatures above the glass transition temperature allowed for crystalline polymer chains to flow, causing the polymer to become amorphous in an irreversible way. Therefore on the first cool and the second heat only, the glass transition was observed showing a lower temperature on the cool than the heat. All data for glass transition temperatures is tabulated in table 6.

4.5.1 DSC Analysis of Bisphenol-A Copolymer Series

Glass transition temperatures for the Bisphenol-A copolymer were between 170 and 185°C. The glass transition temperatures were randomly scattered throughout this range, following no discernible trend. Although no clear-cut trend could be seen, it can be noticed that as the percent CBDO increases, the T_g also increases slightly with variations due to human error in analyzing the glass transition temperature from the DSC plot. These variations may have stemmed from imprecise determination of a T_g temperature.

Actual % CBDO	Actual % Bisphenol	T _g (°C)
	Bisphenol-A	
0%	100%	171.62
29.49%	70.51%	170.11
51.46%	48.54%	181.67
75.97%	24.03%	180.20
100%	0%	185.22
	Bisphenol-AF	
0%	100%	163.55
29.38%	70.62%	214.77
46.55%	53.45%	203.45
78.95%	21.05%	189.59
	Bisphenol-HPF	
0%	100%	169.41
49.34%	50.66%	163.18
66.28%	33.72%	147.34
72.98%	27.02%	162.56
	Bisphenol-F	
0%	100%	199.67
25%	75%	171.49
50%	50%	182.24
75%	25%	195.06

Table 6 – Glass transition temperatures of copolymers by DSC data

4.5.2 DSC Analysis of Bisphenol-AF Copolymer Series

The DSC data for the Bisphenol-AF copolymer series seems to show no direct correlation between CBDO content and glass transition temperature. If the Bisphenol-AF homopolymer data is thrown out, however, a direct correlation can be determined in which T_g decreases with increasing CBDO content. This is the direct opposite of the trend seen in the Bisphenol-A copolymer series previously. This could be simple coincidence based on imprecision in determining the glass transition temperature from the DSC data provided.

4.5.3 DSC Analysis of Bisphenol-HPF Copolymer Series

With the exception of the suspect 66% CBDO copolymer in this series, the glass transition temperature decreases with increasing CBDO content. This trend also goes against that of the Bisphenol-A copolymer series, but matches that of the Bisphenol-AF series. After these analyses it would appear that glass transition is more dependent on the bisphenol used than the amount of CBDO incorporated into the copolymer system. Predictions for other copolymer systems using CBDO as a monomer cannot be made using this data, as each series of bisphenol copolymers seems to have its own tendency.

4.5.4 DSC Analysis of Bisphenol-F Copolymer Series

Once again with the exception of the Bisphenol-F homopolymer the Bisphenol-F copolymer series matches the trend of the Bisphenol-A series in which increase of CBDO content increases glass transition temperature. The presence of this trend leads to two pair of tendencies: one for Bisphenol-A and Bisphenol-F copolymer series which is a direct relationship between the CBDO content and the T_g , and another for Bisphenol-AF and Bisphenol-HPF copolymer series in which an indirect correlation can be drawn.

5.0 CONCLUSIONS

Four different series of poly(bisphenol – CBDO)terephthalate copolymers were synthesized via solution polymerization techniques. The identity of these compounds was then verified using both FTIR and NMR analyses. Degree of polymerization as well as polydispersity was obtained by GPC methods. Thermal properties were then determined using both TGA and DSC.

Thermal analysis provided the first true result of the addition of CBDO into a poly(Bisphenol-A)terephthalate system. By comparing degradation temperatures in argon it has been shown that the addition of CBDO into the system lowers the decomposition temperature. This detrimental trend is countered by an opposite trend for glass transition temperatures for the same systems. Given this fact, it is imperative to note that in order to raise the glass transition temperature; one must forfeit some thermal stability in the form of degradation temperature.

In order to determine the usefulness of these copoly(bisphenol-CBDO)terephthalates, it is imperative that mechanical analysis is run in addition to thermal analysis. This data was beyond the scope of the research conducted, but will help gain a better understanding of the relationship between these copolymers and Bisphenol-A polycarbonate. As seen before, Bisphenol-A polycarbonates exhibit higher glass transition temperatures, increased structural integrity, as well as a greater toughness. These new copolyterephthalates have been shown to exhibit this same higher glass transition

temperature and structural integrity, however the toughness of these polymers is unknown at the present time.

Additional research is required in order to completely determine the extent to which this new copolymer can be used industrially. One such obstacle is the improvement of the molecular weight, as these, made by solution polymerizations, were low compared to industrially useful polymers. One way to overcome this would be to thermally drive the polymerization to high molecular weight after solution polymerization had taken place. Since degradation temperatures are high for all the copolymers, a rise in temperature to 200°C may be enough to dramatically increase the molecular weights of these polymers. Once the molecular weight has been raised to an acceptable level, it should be possible to process these polymers using melt injection in order to make Izod bars for structural stability testing, such as impact resistance and even glass transition verification using a dynamic mechanical thermal analyzer.

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