Property Modification via Crosslinking in CBDO-Based Copolyterephthalates

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The work discussed herein focuses on the examination of the effects of crosslinking CBDO containing copolyterephthalates. A series of copolyterephthalates containing the aliphatic CBDO monomer along with aromatic diols was examined. These materials incorporate CBDO, bisphenol A, phloroglucinol, and terephthaloyl chloride and were made using standard solution polymerization techniques. The phloroglucinol, a trifunctional aromatic alcohol, was used as the crosslinking agent. The series of materials examined included both linear and crosslinked systems. The percent incorporations of the selected monomers, CBDO, bisphenol A, phloroglucinol, and terephthaloyl chloride, was varied to create a homologous series of polymers. Each polymer material was characterized for both thermal and mechanical performance.

INTRODUCTION

Typically, thermoplastics which display a glass transition temperature $\geq 100^{\circ}$C and notched Izod values >100 J/m contain aromatic groups within the polymer backbone. Aromatic groups provide the rigidity necessary for these properties to exist [1]. Bisphenol A polycarbonate is an amorphous thermoplastic that exhibits toughness, clarity and high heat-deflection temperatures. The aromatic monomers do, however, suffer with respect to their poor UV stability [2]. Polymer materials with higher percentage incorporation of aliphatic monomers are therefore desirable.
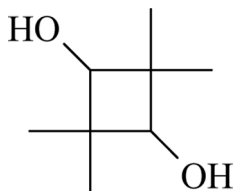
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FIGURE 1 2,2,4,4-tetramethyl 1,3-cyclobutanediol (CBDO).

While aliphatic monomers are easily incorporated into the polymer backbone, they traditionally do not provide the rigidity required for the development of useful thermoplastics. An exception to this is the 2,2,4,4-tetraalkyl-1, 3-cyclobutene family. These monomers have been shown to impart rigidity to the polymer. Of specific interest is 2,2,4,4-tetramethyl-1, 3-cyclobutanediol (CBDO) (Figure 1). A synthetic route for the production of CBDO was first proposed in 1906 [3], by pyrolysis of either isobutyric acid or isobutyric anhydride, followed by hydrogenation, using ruthenium, nickel or rhodium.

Rotational Isomeric State and similar methods have been employed to examine the CBDO monomer. The findings indicate that the lack of torsional mobility caused by the attachment of the four methyl groups creates an extremely rigid CBDO monomer [4]. This knowledge has recently led to an explosion of research with CBDO-containing polycarbonates [5] and copolyesters [6–9]. The work discussed in this article will focus on the examination of the effects of crosslinking CBDO containing copolyterephthalates.

EXPERIMENTAL

Materials

CBDO monomer was donated by Eastman Chemical and used without further purification. Polymerization grade terephthaloyl chloride, phloroglucinol (shown in Figure 2), and *o*-dichlorobenzene were purchased from Aldrich Chemical Company. Unless otherwise noted, all chemicals were used as received.

Synthetic Methods

Linear polymers were synthesized using the procedure outlined below. Molar ratios were modified according to the individual systems being synthesized. For the system of bisphenol A, CBDO, and terephthaloyl chloride (given as an example), molar ratios of 0.6:0.4:1.0 were used.
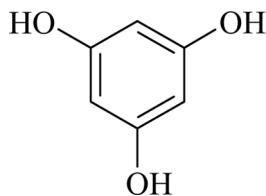
FIGURE 2 Phloroglucinol.

The monomers were added to a flame-dried 250 ml 3-neck flask equipped with a magnetic stirrer. The flask was then degassed with an argon purge using a Shlenk line and heated to reflux temperature for 12 h. The reaction flask was then cooled to room temperature and the linear polymer was diluted with chloroform and removed from the flask.

After removal from the flask, the polymer was precipitated in methanol. This process was repeated 3–4 times and the resulting white solid was thoroughly dried prior to characterization.

All crosslinked polymers were synthesized using the procedure outlined below. As with the linear systems, the molar ratios were varied according to the specific system being synthesized. Two series of crosslinked polymers were synthesized; one series containing CBDO, terephthaloyl chloride, and phloroglucinol; and a second containing bisphenol A, terephthaloyl chloride, and phloroglucinol. For the first system, the CBDO-based materials, the mole percent phloroglucinol added ranged from 8 mol% to 20 mol%. For the second system, the bisphenol A-based materials, the mole percent phloroglucinol ranged from 9 to 15 mol%. The monomers were added to a 250 ml 3-neck flask equipped with a magnetic stirrer. The flask was then degassed with an argon purge using a Schlenk line and heated to reflux until the contents of the flask became gelatinous. The crosslinked polymer was further swollen with chloroform and removed from the flask in pieces.

Once removed from the flask, the crosslinked polymers were dried with methanol. The process of swelling and drying (de-swelling) was performed 4–5 times. The polymer was then dried under vacuum for 48 h prior to characterization.

Characterization Methods

^{1}H-NMR spectra were performed using a Varian 400 MHz Oxford NMR 400 spectrometer. To confirm the structure of the linear polymers, ^{1}H-NMR was run after synthesis. The polymers were dissolved in deuterated chloroform in 10 mm tubes. Samples were prepared by

taking 1–2 mg of the polymer and dissolving it into approximately 0.75 ml of deuterated chloroform. ^{1}H-NMR was run in the range of 0–9 ppm, as all significant peaks were in this range. Peaks were integrated for further analysis. All spectra were consistent with the proposed structures.

Thermal gravimetric analysis (TGA) was performed using TA Instruments Q50 Thermal Gravimetric Analyzer. Scans were run from ambient temperature to 800°C at 10°C/min on 5–10 mg samples. All analyses was carried out in air.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q200 Differential Scanning Calorimeter using a heat/cool/heat cycle at 10°C/min on 5–10 mg samples. An argon environment was maintained throughout all analyses.

Dynamic mechanical analysis (DMA) was performed using a TA Instruments Q800 Dynamic Mechanical Analysis.

Gel permeation chromatography (GPC) was performed on a Walters 600 Gel Permeation Chromatographer to determine the molecular weight of the linear, non-crosslinked polymers.

Crosslink densities were calculated for crosslinked polymer samples. Using Flory-Huggins solvent interaction parameters and Eq. 1, the crosslink density and molecular weight between crosslink points were determined [10].

$$\mathrm{M_c} = \rho/\nu_e = \mathrm{V_o}/\nu_{e'} = (\nu_2^{0.33} - \nu_2/2)/\{-[\ln(1 - \nu_2) + \nu_2 + \chi\nu_2^2]/\nu_1\} \quad (1)$$

Because this polymer/solvent system has never been studied before, some inference of the polymer and solvent solubility parameters must be done. Due to similarities between the CBDO-based copolyterephthalate and poly(ethylene terephthalate) (PET), solubility parameters for PET in chloroform were used. These values [11] are: $\delta_{(PET)} = (21.9\,\mathrm{Mpa}^{\frac{1}{2}}), \delta_{(chloroform)} = (17.92\,\mathrm{Mpa}^{1/2}), \upsilon_1 = 80.7\,\mathrm{cm}^3/\mathrm{mol}$, and $\chi = 8.454\,\mathrm{MPa}^{-1}$.

RESULTS

GPC was performed on the linear CBDO homopolymer (shown in Figure 3) as well as the linear CBDO/bisphenol A polymer (shown in Figure 4) and the results are shown in Table 1. GPC was not performed on the bisphenol A homopolymer (shown in Figure 5) because the material is only slightly soluble in chloroform at room temperature. Crosslinked samples were not tried in the GPC due to their insolubility. Decomposition temperatures, in air, for all of the polymers in this study appear in Table 2.
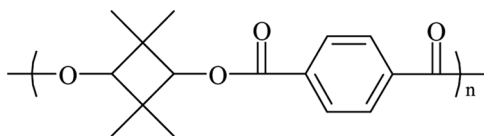
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FIGURE 3 CBDO homopolymer.

It is interesting to note that the decomposition temperature of the linear CBDO-based copolyester is not significantly different than that of the crosslinked analogues of this polymer. The crosslinked materials display decomposition temperatures in the range of 388–405°C, while the linear CBDO homopolymer has a T_d of 391°C. In contrast, the linear bisphenol A homopolymer displayed a decomposition temperature of T_d of 350°C, compared to its crosslinked analogues which display decomposition temperature 380 and 397°C.

DSC was performed to determine the T_g of the samples as well as to determine the amount of crystallinity, if any. Table 3 contains the T_g for the polymers examined as well as the amount of crystallinity, if present.

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

The linear CBDO homopolymer had a T_g of 162°C, which was not significantly higher than the crosslinked versions ranging from 149–200°C. Unlike the copolyesters, the linear CBDO did show a peak for crystallinity at 195°C. After crosslinking was complete, the polymers were once again amorphous. The linear bisphenol A homopolymer had a T_g of 125°C and had a crystallinity peak, T_c, of 150°C. Once again, no thermal data will be reported for crosslinked versions of the bisphenol A polymers.

DMA was performed to determine a multitude of thermal and physical properties, including: T_g, storage and loss modulus, Tangent delta, Young's modulus, crosslink density and molecular weight
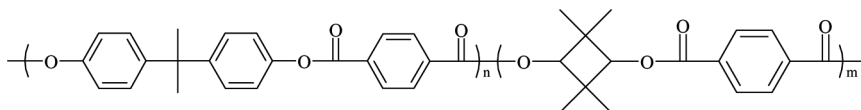

FIGURE 4 Linear CBDO/bisphenol A polymer.

TABLE 1 Molecular Weight for Linear Polymers

Polymer Sample	Mn (g/mol)	Mw (g/mol)	PDI
Linear Copolyester	8837	15365	1.74
Linear CBDO Homopolymer	13506	24487	1.81

between crosslink points (M_c). Table 4 contains data obtained from DMA analysis of the materials.

The linear polymers were not of sufficient molecular weight, therefore the films did not display the structural integrity needed to obtain mechanical data. During film formation of the crosslinked copolyesters, it was observed that the material was tough and took some force to break, but was too rigid to create a thin film for the DMA. The 6 and 8% showed significantly higher T_g's (based on DMA) than those observed in the DSC, 219.5 and 212.6°C, respectively. The DMA shows that the storage modulus decreases with increasing % crosslinker. These data confirm that the material stores less energy at fairly low temperature with increasing crosslinker percent, indicating a more rigid material. All crosslinked CBDO polymers above 8% were brittle and no films could be made. Due to the inability of film formation of the linear polymers, a comparison cannot be made between linear and crosslinked samples' mechanical data.

Swelling studies were carried out in order to determine the molecular weight between netpoints. The data (shown in Table 5) show that the crosslinked systems examined via swelling correlate with the percent phloroglucinol used to synthesize the material. That is to say that the higher percentage of crosslinker displays a lower molecular weight between netpoints and a higher crosslink density. The opposite is true for the system examined which had a lower percent of phloroglucinol.

CONCLUSIONS

The work discussed in this article focuses on CBDO-based copolyterephthalates and the effect of crosslinking on the thermal/mechanical properties. The most interesting observations are those related to the
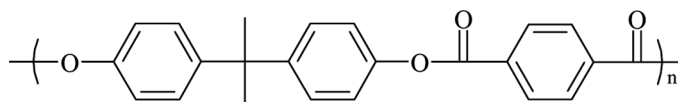

FIGURE 5 Bisphenol A homopolymer.

TABLE 2 Decomposition Temperatures

% Phloroglucinol	% CBDO	% Bisphenol A	T_d (°C)
0	40	60	390
5	38	57	388
6	38	56	390
10	36	54	398
12	35	53	402
15	34	51	405
0	100	0	391
6	94	0	390
8	92	0	397
9	91	0	391
10	90	0	390
12	88	0	388
20	80	0	380
0	0	100	350

decomposition temperatures and percent crystallinity. Upon examination of the decomposition temperature data, it becomes apparent that for the crosslinked systems which maintain a relatively constant percent incorporation of the CBDO monomer ($34-40\%$), the decomposition temperature also remains fairly constant: $T_d = 390-405$°C. In contrast, the crosslinked polymer systems which contain varying amounts of the CBDO monomer (80–100%) display decomposition temperatures which slightly decrease with decreasing percent incorporation of the CBDO

TABLE 3 T_g/Crystallinity Data for Polymers in This Study

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

TABLE 4 Thermal and Physical Data Obtained Via DMA

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

TABLE 5 Crosslink Density and M_c Obtained Via Swelling Studies

% Phloroglucinol	% CBDO	Crosslink density (mol/cm^3)	M_c (g/mol)
6	94	1.01×10^{-3}	970.7
7	93	1.2×10^{-3}	822.3

monomer. This is an indication that the CBDO monomer is a source of thermal decomposition and that its incorporation can be related to the decomposition temperature.

The second noticeable effect of crosslinking these polymeric systems is that it leads to a complete loss of crystallinity. This is most apparent in the systems which contain a percentage of the CBDO monomer greater than 45%. Previous work [6] has shown that copolyterephthalates containing greater than ≈45% of CBDO are semi-crystalline in nature. While the data show that the polymer system containing 100% CBDO (non-crosslinked) is semi-crystalline, all of the crosslinked polymer systems containing >45% CBDO are completely amorphous. This confirms the disruption of polymer chain packing via crosslinking.

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