Copolyterephthalates containing tetramethylcyclobutane with impact and ballistic properties greater than bisphenol A polycarbonate

Chad J. Booth [a],*, Megan Kindinger [a], Heather R. McKenzie [a], Jesse Handcock [a,b], Alan V. Bray [b], Gary W. Beall [a]

[a] Polymer Research Group, Department of Chemistry and Biochemistry, Texas State University, 601 University Drive, San Marcos, TX 78666, United States
[b] Systems and Materials Research Corporation, 19300 Crosswind Circle, Spicewood, TX 78669, United States

Abstract

For the past 40 years bisphenol A polycarbonate has been the industry standard for lightweight transparent armor protection. More recently, researchers at the Shell Chemical Company developed a co-polyester derived from 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), 1,3-propanediol (PDO), and dimethyl terephthalate (DMT). By varying the percent incorporation of the monomers, the thermal/mechanical properties of this copolyterephthalate are tunable. Shell found that interesting impact properties arose from the material when 40 mol% CBDO was incorporated into the polymer. This material displayed a notched Izod value of 1070 J/m while maintaining T_g near 100 °C. The work discussed here focuses on the mechanical, impact, and ballistic characterizations of this material. Tensile, notched Izod, and .22 FSP V50 data are reported. This new material shows improvement over bisphenol A polycarbonate in both notched Izod as well as ballistic impact values.
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1. Introduction

In today's ever changing world the need for higher impact transparent materials is of utmost importance. For the past 40 years the material of choice for both military and civilian security and protection applications has been bisphenol A polycarbonate. Bisphenol A polycarbonate has a notched Izod impact value of around 850 J/m [1]. Since 1960s there have been reports, mostly in the patent literature [2–6], about a co-polyester [7] which incorporates an unique aliphatic diol monomer, 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), shown in Fig. 1. The polyester (shown in Fig. 2) synthesis utilizes dimethyl terephthalate (DMT) as the diacid component with 1,3-propanediol (PDO) and CBDO as the diol components. In 2000, Kelsey et al. reported that this material displays a notched Izod impact strength of up to 1070 J/m, depending on exact copolymer composition. In addition, Kelsey also reported that the material displays better UV [7] stability than does bisphenol A polycarbonate, presumably because of its lack of aromatic character. With this said, the CBDO based material will still require a UV protective coating if designed to be used in outdoor applications.

The material is synthesized via a process very similar to that used in industry to synthesize poly(ethylene terephthalate) (PET) and as such will be easy to scale-up. The most interesting finding from the work done by Kelsey et al. [7] was that the thermal/mechanical properties of the copolyterephthalate were adjustable. They found an inverse relationship between T_g and notched Izod impact strength with increasing mole percent incorporation of the CBDO monomer. Simply stated, the CBDO increased the impact resistance over the material without CBDO but reached a maximum value around 40 mol%. Above 40% the impact value decreased but remained higher than the material without CBDO incorporated.

* Corresponding author. Tel.: +1 512 245 8789; fax: +1 512 245 2374.
E-mail address: chadbooth@txstate.edu (C.J. Booth).
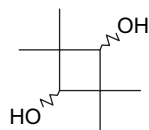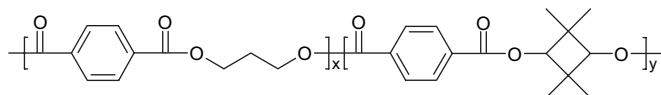
Fig. 1. Structure of CBDO.

Fig. 2. CBDO based co-polyester.

Typically, materials with large amounts of aromatic character display relatively high glass transition and melt temperatures but suffer in that the aromatic units lower the UV and solvent resistance (to date chloroform is the only solvent that has been shown to dissolve this material) [8]. While the CBDO is aliphatic, it has also been shown to display a high degree of rigidity [9,10] and therefore contributes to the material's mechanical properties, specifically to the impact and ballistic resistance, without the detrimental effects to the UV and solvent resistance. The presence of the four methyl groups on the cyclobutane ring forces it into a planar configuration due to steric crowding contributing to the stiffness of the monomer. Shell found that varying the ratio of diol monomers (PDO/CBDO) had a direct impact on the mechanical and thermal properties. Highest impact values, 1070 J/m, were obtained with CBDO concentrations of 40 mol%. This value did, however, provide a glass transition temperature of around 90 °C. At percent incorporations of CBDO greater than 40 mol%, the T_g does increase but the notched Izod value is lowered. This allows for a material with tunable properties which is capable of impact values 30% higher than those displayed by bisphenol A polycarbonate.

Work reported by Geiger and Daly [10,11] utilized a copolycarbonate of CBDO and a series of bisphenols, shown in generic form in Fig. 3. The materials reported by Geiger and Daly [10,11] suffered in that they displayed a thermal degradation slightly above the T_g and as such, no mechanical properties were reported. In addition, the homopolycarbonate of CBDO has also been reported [12,13]. This material was synthesized using an ester interchange and was originally reported by Gawlak et al. While little work has been done with respect to the mechanical properties of these materials, Aguilar-Vega and Paul [14] extensively studied the gas transport properties of this material. They found that the material displayed permeability coefficients which were larger than the corresponding aromatic bisphenol A polycarbonates. Additionally, Acar and Brunelle [15] reported a CBDO homopolycarbonate which differed from those discussed above, referenced as [12,13], in that these materials were synthesized utilizing more industrially
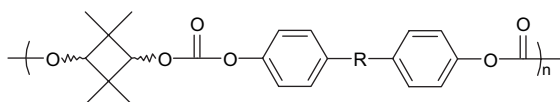

Fig. 3. Copolycarbonate reported by Daly et al.

useful transesterification techniques. This polymer displays poor impact resistance but scratch resistance higher than that of bisphenol A polycarbonate.

2. Experimental

2.1. Characterization

Infrared spectra were obtained using a Perkin–Elmer Spectrum One FTIR spectrometer at ambient temperature. Each spectrum consisted of five scans with wavenumbers in the range of 4000–400 cm^{-1} and a resolution of 2.00 cm^{-1}. Scans were run by dissolving the polymer in CHCl$_3$ and placing 1 ml of the solution onto a polyethylene substrate card. The CHCl$_3$ was then allowed to evaporate, leaving a thin film of the polymer.

Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were obtained using a 400-MHz Oxford NMR 400 spectrometer. Solution spectra were measured at ambient temperature with deuterated chloroform being the preferred solvent.

Gel permeation chromatography (GPC) was performed on a 6.6 mg/ml copolymer solution in chloroform at 25 °C with a Waters model 600 GPC using a Waters 2410 refractive index detector. Molecular weights and dispersions were based upon calibration with polystyrene standards.

Differential scanning calorimetry (DSC) was performed using 5 mg copolymer samples with a TA Instruments differential scanning calorimeter in an argon environment at a heating rate of 10 °C/min. Data were collected on the first cooling and second heating runs.

Thermal gravimetric analysis (TGA) was performed on 5–10 mg copolymer samples with a TA Instruments thermal gravimetric analyzer in both argon and air environments at a heating rate of 20 °C/min from ambient to 800 °C. All reported decomposition temperatures were taken from the temperature value at which 10% weight loss had occurred.

Dynamic mechanical analysis (DMA) was performed on TA Instruments Q800. All samples were run at a frequency of 1 Hz with a temperature range of 25–130 °C at 10 °C/min in air.

All modulus data were determined using a MTS/Sintech Model 1D Tensile Tester equipped with a Pentium data station. Samples were standardized and tested according to ASTM D628.

Impact resistance data were obtained using a Notched Izod Impact tester equipped with a 2 pound hammer under conditions specified in ASTM D256.

Ballistic data were determined by .22 FSP V50 tests conducted by Simula, a division of Armor Holdings Aerospace & Defense Group in Phoenix, Arizona. This type of testing is considered to be the standard "first test" for all ballistic materials and a standard ballistic test for military qualification. This test utilizes a measure of the velocity required to create a 50% failure in a material of a given areal density. It utilizes 0.22 cal steel pellets fired at controlled velocities. The velocity data are recorded at the point during which 50% of the pellets

penetrate the plaque. Areal density is the weight of a plaque divided by the plaque's area at a given thickness. Plaques of two different thicknesses were utilized in this study, one being 0.64 cm and the other being 0.95 cm. It is not atypical for areal density values to vary slightly due to small variations in the actual dimensions of the plaque. It should be noted that "standard" V50 tests are run on monolithic plaques that have been sheet extruded with minimum dimensions of 30 cm × 30 cm. The samples reported here are reported for compression molded samples of monolithic plaques of dimensions 15 cm × 15 cm. There are several potential issues with this size of plaque and compression molding. The first of which is that compression molded targets or plaques give inherently lower test results than do sheet extruded targets. Secondly, the smaller targets also give inherently lower test results than do larger ones, in most cases due to edge effects. While complete "misses" are not typically a problem, "hits" which occur near the edges are a problem. These typically give lower values and negate data collection from secondary shots.

Wide angle X-ray diffraction was performed on a Bruker D8 powder diffractometer equipped with a Cu X-ray tube and an energy dispersive Sol-X detector.

2.2. Chemicals

CBDO monomer was obtained from two sources. CBDO monomer with *cis/trans* ratio of 35/65 was purchased from TCI America. CBDO monomer with a *cis/trans* ratio of 46/54 was donated by the Eastman Chemical Company (Kingsport, TN). DMT and PDO were purchased from Aldrich Chemical Company and used as supplied. In addition a 100 pound batch of the co-polyester described here was provided by the Eastman Chemical Company. This material was synthesized using a chemical formulation identical to that carried out at Texas State, discussed below. The only difference is that Eastman synthesized a large batch utilizing their available batch reactors, while the group at Texas State utilized standard glassware. Data are provided for both the materials provided by Eastman as well as that synthesized at Texas State. The exception being that all ballistic and impact data are from the material provided by Eastman Chemical, due simply to material quantity. All polycarbonate samples, which are included as a reference, were obtained from GE – Plastics (Pittsfield, MA) in pelletized form and used as supplied. The polycarbonate was processed using the procedures as described in Section 2.4.

2.3. Synthetic procedure

All polymers were synthesized using techniques similar to those reported by Kelsey et al. [7]. To a 500 ml three-neck flask, equipped with digital mechanical overhead stirrer, were added CBDO (57.7 g, 0.40 mol), PDO (60.9 g, 0.80 mol), DMT (194 g, 1.00 mol), and dibutyl tin oxide (0.65 g). The system was purged with dry argon for a period of 15 min followed by evacuation under vacuum. The vacuum was maintained for 15 min and this purge procedure was repeated a total of three times. The system was then heated, under static argon,

to 180 °C at which time the generation of methanol was noted. Methanol was removed using simple distillation and the temperature was increased in 10 °C increments, up to 220 °C, to maintain constant production of methanol. The system was then cooled to room temperature at which time another 0.65 g of dibutyl tin oxide was added. The system was then again purged using the procedure described above. Under vacuum, the system was then heated to 250 °C to remove excess PDO and to drive the polymer to high molecular weight. The viscosity increased over a 4 h period of time. The reaction was considered complete when the polymeric material "climbed" the stainless steel stir shaft and was no longer being stirred. The system was cooled to 150 °C and argon was introduced before cooling to room temperature. The polymer was removed from the flask by breaking the flask and grinding away any residual glass stuck on the polymer surface. The polymer was then broken into smaller pieces and, without further purification, characterized and/or processed into plaques (described in Section 2.4).

All polymer structure was determined using IR and ^{1}H NMR techniques. The materials were determined to contain a percent incorporation of CBDO of 38% which matches, within 3%, the monomer feed ratio of the CBDO. In addition, it was determined via ^{1}H NMR utilizing techniques previously reported [2] that the *cis/trans* ratio of the CBDO units in the final polymer materials did not differ from that of the monomer. In both cases the *cis/trans* ratio was found to be 35% *cis* and 65% *trans* and 46% *cis* and 54% *trans*. These data were in agreement with the material purchased from TCI America and provided by Eastman Chemical Company.

2.4. Processing parameters

Compression molding was used to generate plaques of sizes 5 cm × 5 cm, 10 cm × 10 cm, or 15 cm × 15 cm. Plaques were made by placing the bulk polymer into 5 cm × 5 cm, 10 cm × 10 cm, or 15 cm × 15 cm aluminum frame molds at a temperature of 120 °C without pressure. The polymer was then allowed to sit until completely softened, approximately 90 min. The top mold plate was then attached and the material was pressed into its final shape with an applied load of 103 MPa for a period of 8 h, with the mold being rotated 90° each hour. The mold was then removed and allowed to cool.

Notched Izod bars were made by compression molding. The bars were made by placing the bulk polymer into an ASTM standard Izod cavity mold at a temperature of 120 °C for the CBDO based material and 150 °C for the polycarbonate. The polymer was then allowed to set until complete softening occurred. The top mold plate was then set in place and minimal pressure applied until mold closed, approximately 2 min. The mold was then removed and allowed to cool.

All injection molded samples were prepared at Southern Clay Products (Gonzales, TX). Samples were molded using a Demag Ergotech 35 injection molder. Injection molding of plaques of sizes 9 cm × 9 cm was carried out at Southern Clay Products (Gonzales, TX). The screw and die temperatures

were set to 150 °C, while an injection pressure of 69 MPa was used.

2.5. Molecular modeling

Molecular modeling was carried out utilizing the commercially available Cerius 2 software package. All calculations were atomistic forcefield based and were conducted using the COMPASS forcefield reported by Sun et al. [16] and Sun [17]. The monomers for all the polymers were produced using the 3D sketcher. The monomers were then assigned charges in the Open Forcefield Setup module and minimized using the Open Forcefield Methods module. The COMPASS forcefield was utilized in all calculations. The copolymers were generated using Polymer Builder. In order to generate the polymers, the monomers were constructed to be a unit of CBDO bonded to a terephthalate and a unit of 1,3-propanediol bonded to a terephthalate. This allowed the mole ratio of CBDO to be easily controlled. The polymers generated were 20 units in length. The partial charges on the polymers were recalculated and were iterated through several cycles of minimization and molecular dynamics.

3. Results and discussion

3.1. Thermal properties

Glass transitions of the polymers were determined using DMA tan δ values. The data correlated to that previously reported by Shell, around 98 °C for the material described here. All the materials discussed in this manuscript were found to be amorphous, as confirmed by the lack of corresponding peaks in the DSC scans and no crystalline peaks in the X-ray diffraction patterns. The decomposition temperatures were determined using TGA. The materials synthesized at Texas State gave a T_d on the order of 355 °C in both air as well as argon. The material provided by Eastman gave T_d values on the order of 360 °C in both air and argon. The thermal stability of the polymer is very encouraging since processing can be carried out at below 150 °C which gives a very wide margin for processing.

3.2. Physical properties

3.2.1. Impact properties

Impact data were obtained via notched Izod testing [18] with a 908 g hammer. The data are shown in Table 1 and include polycarbonate (for reference) and the material provided by Eastman. Shell originally reported that the highest impact properties are obtained by incorporating 40% CBDO with 60% PDO along with the appropriate amount of DMT. As such, the material used for this work contained 40 mol% CBDO and displays an average notched Izod impact resistance (see Table 1) of 912 J/m, when compression molded, compared to polycarbonates value of 680 J/m, also when compression molded. Shell reported that injection molded samples of this material display notched Izod impact values up to 1070 J/m. The data not only show that this material gives a 34% higher

Table 1
Notched Izod data

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	

notched Izod value than does the polycarbonate, with several of the samples displaying "no breaks", but also that it does such with non-optimized samples (i.e. compression molding versus sheet extrusion).

3.2.2. Modulus

The tensile modulus of the polymer samples was determined using data collected according to specifications contained in ASTM D638 [19]. The values for polycarbonate (processed using the same conditions as the CBDO copolyterephthalate), the material provided by Eastman, and the material synthesized at Texas State are shown in Table 2. Data were collected via a MTS/Sintech Tensile Tester. These data include peak stress, stress at break, elongation at break, percent strain at break, and tensile modulus. As with the impact and ballistic data (reported below), ballistic grade polycarbonate, processed using the same procedure, was run for comparison purposes. The CBDO copolyterephthalate gives properties very similar to those shown for polycarbonate, the exception being lower stress at break and slightly lower peak stress. The material does, however, give higher percent strain at break, which is typical of materials which display higher impact properties since they typically show larger degrees of plastic behavior. This is a very rough correlation since the strain rate in a tensile test is orders of magnitude lower than that of ballistic test.

3.3. Ballistic data

The ballistic data, shown in Table 3, were obtained using both material synthesized at Texas State as well as material provided by Eastman. The data show that plaques with thicknesses around 0.64 cm (areal density of around 73–76 depending on actual weight of plaque) give an FSP V50 rating of up to 355 m/s. A similar sample of polycarbonate gave a rating of 241 m/s albeit with at slightly lower areal density. Likewise, 0.95 cm thick plaques (areal density of around 110–117 depending on actual weight of plaque) gave a maximum value of 464 m/s as compared to 341 m/s for polycarbonate. In addition, samples synthesized more recently which contain CBDO monomer with a 46/54 *cis/trans* ratio, rather than the previously used 35/65 *cis/trans* ratio, displayed significantly higher ballistic data, the sample with areal density of 74.2 Pa for example. This material displays a V50 rating which is 26 m/s below that of polycarbonate. The samples synthesized with

Table 2
Modulus data

Material	Sample	Peak stress ($\times 10^8$ Pa)	Stress at break ($\times 10^7$ Pa)	Elongation at break (mm)	% Strain at break	Modulus ($\times 10^8$ Pa)
Polycarbonate	1	1.22	9.45	17.8	69.9	8.66
	2	1.24	9.22	12.7	54.2	9.69
	Average	1.23	9.34	15.3	62.1	9.18
Eastman material	1	1.03	6.25	17.8	73.5	8.66
	2	1.00	6.68	20.3	81.6	8.42
	3	0.97	6.22	12.7	50.0	8.91
	Average	1.00	6.38	16.9	68.4	8.66
Texas State material	1	1.01	6.26	10.2	43.3	9.38
	2	1.05	6.35	22.9	88.4	8.52
	3	1.03	6.07	17.8	69.5	8.71
	Average	1.03	6.23	17.0	67.0	8.87

Table 3
Ballistic data

Areal density (g/cm^2)	% *cis/trans* 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

the higher *cis* containing monomer out performed the lower *cis* containing polymer by over 40%. While it has not yet been confirmed, this enhanced ballistic resistance is potentially due to the higher degree of kinking and coiling displayed by materials with higher percent incorporation of the *cis* CBDO monomer. This theory of kinking is discussed in Section 3.5. The kinks in the backbone of the polymer may potentially act like springs which absorb and dissipate the energy of the ballistic impact. Additionally, the kinking caused by increased percentages of the *cis* isomer may lead to larger interchain distances, due to the inability of the chains to pack effectively, and thereby lowers the overall density of the material. An opposite argument can also be made, in that an increase in the percentage of *trans* isomer will increase the material's ability to pack and therefore increase the crystallinity. Kelsey et al. [7] reported that CBDO based copolyterephthalates with higher percentages of the *trans* isomer showed evidence of higher degrees of crystallinity. An increase in the material's crystallinity would certainly have a detrimental effect on the materials' impact and ballistic resistance.

3.4. Molecular weight data

Molecular weights were determined for the CBDO copolymer synthesized at Texas State and the material provided by Eastman Chemical as well as the polycarbonate utilized for comparison. Each sample was run twice and the data are summarized in Table 4.

3.5. Shape memory

In addition to the enhancement of mechanical behavior, this material exhibits some very unique properties of shape memory and self-healing, which have not been shown in bisphenol A polycarbonate. The shape memory effect can be seen in Fig. 4, where an injection molded plaque of the material is shown after an impact from a 4 pound weight at a distance of 4 ft (Fig. 4a). The impact left a dent of approximately 1 cm in diameter and 0.5 cm deep. The middle photograph (Fig. 4b) shows the plaque being heated by a heat gun for a period of 1 min. In the last photo (Fig. 4c) it is interesting to note that the dent has completely disappeared. It is believed that this phenomenon is a product of the *cis* CBDO monomer that promotes kinks and coiling in the polymer that when stressed is straightened out somewhat and then when heated near or above the T_g spontaneously returns to a coiled or kinked state. In other samples that have been tested for ballistics resistance where actual cracks formed by the heat gun treatment healed most of the cracks to the point that the cracks could only be discerned as small raised features on the plaque surface.

This shape memory effect is not new to polyesters. Choi et al. [20] reported a polycaprolactone (PCL) − poly(butylene terephthalate) (PBT) co-polyester, in which the PBT segment served as a physical crosslinking agent and that as the degree of dispersion of the PBT segment increased, the shape memory effect decreased. They furthermore attributed this effect

Table 4
Molecular weight data

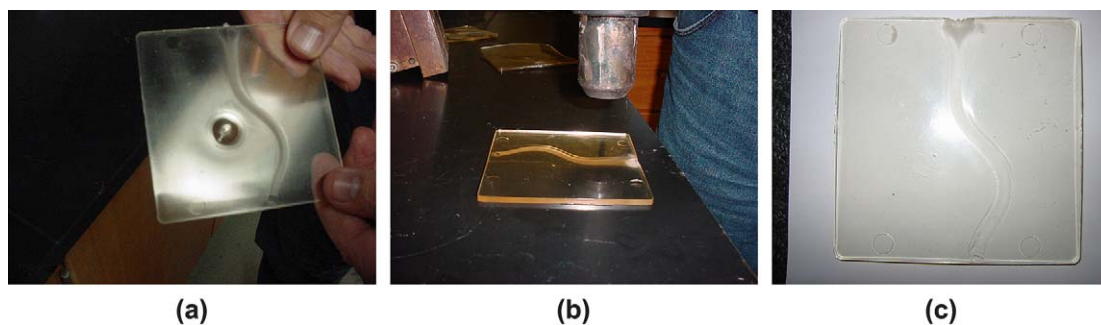| Material	M_n (g/mol)	M_w (g/mol)	PDI
Eastman	16,766	48,821	2.91
	19,140	48,382	2.53
Texas State	17,286	38,547	2.23
	13,900	33,638	2.42
Polycarbonate	26,070	69,340	2.66
	24,182	70,997	2.94

Fig. 4. Injection molded plaque showing (a) impact dent, (b) heat being applied, and (c) result of heat application (loss of impact dent).

to the enhanced dispersion of the PBT segment as the degree of transesterification increased. In addition, several studies have reported [21,22] crosslinked poly(ethylene terephthalate) (PET) and poly(ethylene glycol) (PEG) copolymers. Results show that with both glycol and sulfoisophthalate crosslinkers [21], as well as, maleic anhydride crosslinker [22] the materials display the highest levels of shape memory when the PET segment was incorporated in large molar percents. With this said, it is important to point out that the materials discussed here are not crosslinked and therefore the phenomenon of shape memory reported here cannot be attributed to crosslinking.

Molecular modeling has been conducted on two end members of the copolyterephthalate family of polymers discussed here. The two polymers were modeled with the molar ratios of CBDO/PDO, the same as those utilized in this paper. The two polymer systems differed in that either pure *cis* or *trans* isomers were utilized. Fig. 5 is a comparison of the overall structural architecture of the two polymers. It is obvious that the two isomers produce very different secondary structures. The *trans* version tends to be rather linear and in fact if one examines closely the geometry around the *trans* CBDO, it causes the polymer to retain this fairly linear shape.

Fig. 6 is a zoomed in model of the geometry around the *trans* form of the CBDO; clearly showing the tendency toward linearity. The perspective in Fig. 6 is parallel to the plane of cyclobutane ring with the methyl groups superimposed to illustrate the planar character of the butane ring.

Fig. 7 illustrates the same region of the polymer backbone as in Fig. 5 with the *cis* CBDO monomer. The angle imposed on the backbone by the *cis* form is striking; imparting very
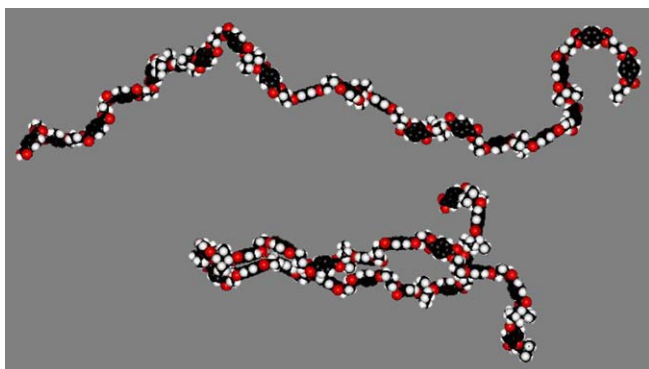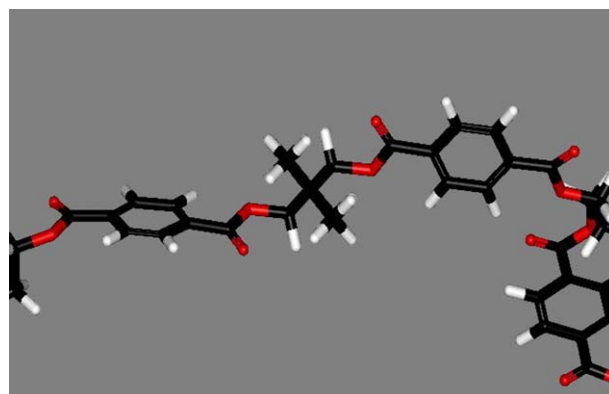

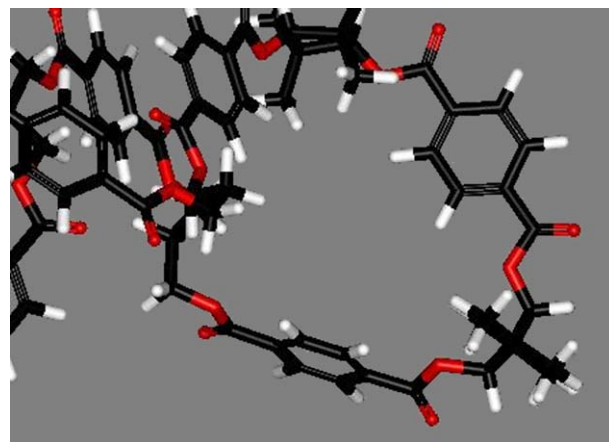Fig. 6. Expanded view of the geometry around the *trans* CBDO monomer.

Fig. 7. Expanded view of the geometry around the *cis* CBDO monomer.

substantial kinks in the overall secondary structure of the polymer. As can be seen in Fig. 7 this result in loops that allow the polymer to come back on itself. The asymmetry in electron density with the attached terephthalate groups causes a slight distortion of the cyclobutane ring. As in Fig. 6, the perspective is parallel to the plane of butane ring with the methyl groups superimposed.

In Fig. 8 it appears that the aromatic rings of two terephthalates are forming π−π interactions. The distance between the planes of the two rings is approximately 3.3 Å which is in agreement with distances observed for this type of interaction.
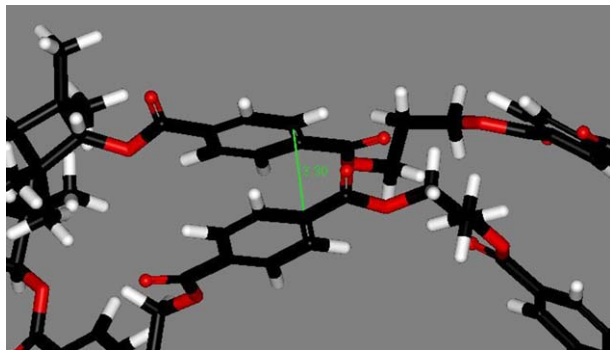

Fig. 5. Overall structure of both the *cis* and *trans* polymers.

Fig. 8. π−π stacking interactions between aromatic rings.

4. Conclusions

The amorphous polymer discussed herein displays higher impact resistance than bisphenol A polycarbonate, without the addition of additives. This copolymer is a mixture of (46:54 *cis/trans*) CBDO, PDO, and DMT. A typical structure for the copolymer is shown in Fig. 2. The data discussed above shows that the CBDO based copolyterephthalates have enhanced ballistic and impact resistance over modern bisphenol A polycarbonate. While it is not completely understood why this material displays enhanced ballistic and impact resistance, it is apparent that the introduction of the CBDO monomer contributes to this phenomenon since polymers such as PET or PPT do not display this unusually high impact behavior [23]. The situation then becomes further complicated when one considers that the impact resistance is related to the percent incorporation of the CBDO monomer into the polymer backbone in a complex way [7]. In simple terms, the CBDO must be present to enhance the impact properties, but there is an upper level limit to the CBDO monomers influence. One must recall that the *cis/trans* ratio of the CBDO monomer utilized herein is approximately 46:54. Several preliminary studies done using a CBDO monomer with a *cis/trans* ratio of 35:65 gave much lower impact values. It is therefore believed that the copolyterephthalate described here, if synthesized with a CBDO monomer of higher *cis* percentage, would display higher impact properties. One argument for this behavior is that the *cis* conformation contributes to higher degrees of kinking and potential coiling. The separation of the *cis/trans* isomers are currently being investigated and should shed light on this theory. If this theory is true, then it would conceivably be possible to increase the percent incorporation of the CBDO monomer while maintaining or even increasing the impact properties. It is believed that while the CBDO contributes to the impact resistance of the polymeric material, the upper level limit arises from the *trans* isomer's detrimental effects to the materials kinking and coiling behavior. Gawlak and Rose reported the use of pure isomeric forms of the CBDO [12] in the synthesis of polycarbonates of CBDO and bis(ethyl carbonate) esters. While no thorough thermal/mechanical evaluation was performed, they did report that the polymers containing between 61 and 100% *trans* CBDO were not soluble and displayed decomposition before melting and therefore

could not be molded. The polymers containing larger amounts of the *cis* CBDO (>50%) could be molded at temperatures near 265 °C and could be solvent cast into sustainable films.

Studies have shown that the four membered ring of the CBDO is planar and not puckered as would be expected for an unsubstituted four membered ring [9,10]. The introduction of CBDO into the polymer backbone would therefore be expected to increase the rigidity of the material, and as such increase the brittleness of the material. But, as stated above, the presence of the *cis* isomer creates a ''kink'' in the polymer chains. This not only contributes to the material's amorphous behavior but also to the ability to absorb impact via chain uncoiling. It is believed that the polymer chains in these copolyterephthalates are coiled. Upon impact, these coils have the ability to absorb the force of impact via partial/temporary chain uncoiling.

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