High Impact, Amorphous Terephthalate Copolyesters of Rigid 2,2,4,4-Tetramethyl-1,3-cyclobutanediol with Flexible Diols

Donald R. Kelsey,* Betty M. Scardino, Janusz S. Grebowicz, and Hoe H. Chuah

Shell Chemical Company, Westhollow Technology Center, PO Box 1380, Houston, Texas 77251

Received February 7, 2000; Revised Manuscript Received May 30, 2000

ABSTRACT: A new family of terephthalate-based copolyesters has been found to exhibit high impact resistance combined with good thermal properties, ultraviolet stability, optical clarity, and low color. These engineering thermoplastic compositions were prepared using conformationally rigid *cis*/*trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol [CBDO] and flexible C_2-C_4 aliphatic glycols. The copolymers were amorphous when the CBDO (~50/50 *cis*/*trans*) content was about 40 to 90 mol % of total diol. Glass transition temperatures were 80−168 °C, depending on the proportion of rigid CBDO units. Impact resistance was inversely proportional to CBDO content, and notched Izod values as high as 1000 J/m were obtained. Both high T_g (>100 °C) and high impact (250−750 J/m) can be realized simultaneously for compositions containing about 50−80 mol % CBDO. Accelerated weathering indicated good inherent resistance of 1,3-propanediol/CBDO copolyterephthalate to yellowing under ultraviolet radiation. Dibutyltin oxide was more effective for transesterification of CBDO with dimethyl terephthalate than other typical catalysts. Better color and higher molecular weights were obtained with this catalyst when the flexible diol was 1,3-propanediol or 1,4-butanediol rather than ethylene glycol.

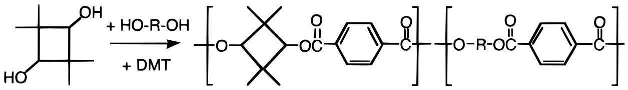
Introduction

Engineering thermoplastics[1] with useful properties at elevated temperatures (>100 °C) are usually composed of aromatic units, especially symmetrical aryl groups such as 1,4-phenylene, 4,4′-biphenylene, and 2,6-naphthalene. Aromatic groups impart molecular rigidity, which contributes to high glass transition temperatures and also, in the case of semicrystalline polymers, to high melting points. They also provide thermal stability, which is needed for processing these polymers.

Rigid, thermally stable, symmetrical *aliphatic* molecules suitable for polymers are rare. One class is the 2,2,4,4-tetraalkyl-1,3-cyclobutylenes. This molecular unit can be incorporated into polymers using, for example, *cis*/*trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediols [CBDO].[2−13] CBDO (**1**) is prepared in high yield by pyrolysis of isobutyric acid[2] or isobutyric anhydride[3] to form dimethylketene (**3**), which spontaneously dimerizes to cyclic diketone **2**, a molecule known since 1906[4] (Scheme 1). Hydrogenation of **2** using ruthenium,[5] nickel,[5,6] or rhodium[7] catalysts produces up to 98% yield of *cis*/*trans*-**1**. Isolation of the pure isomers is tedious and expensive,[8] so *cis*/*trans* mixtures of **1** have usually been used.

CBDO polycarbonate, the simplest polyester, is amorphous and exhibits a relatively high glass transition temperature (T_g = 105−120 °C) for an aliphatic structure and good weathering resistance.[9,10] Aromatic polyesters of CBDO reported to date have been primarily high melting, semicrystalline materials.[11] Melting points for the polyesters from dimethyl terephthalate and CBDO, i.e., the “homopolymers”, are 316−319 °C (38/62 *cis*/*trans*),[11a] 296−308 °C (*cis*),[11c] and >350 °C (*trans*).[11c] Many of the reported terephthalate copolyesters of CBDO with other diols also are semicrystalline. Examples include copolymers with 1,6-hexanediol (T_m = 180−190 °C[11a]) and 1,4-cyclohexanedimethanol (T_m = 192−204[11a] and 200−238 °C[11c]). A “segmented”, presumably semiblock, copolymer of about 15 mol % CBDO polyterephthalate with poly(ethylene terephthalate) also has been reported.[12]

The properties of random aromatic copolyesters of CBDO with small chain aliphatic diols over a range of compositions had not been reported when we undertook this study.[13] Because of the potential enhancement of the glass transition temperature by the rigid CBDO backbone unit, we prepared several terephthalate-based copolyesters (**4**) of CBDO combined with ethylene glycol, 1,3-propanediol [PDO], or 1,4-butanediol [BDO].[13a] Unlike aromatic diols such as bisphenol A and 4,4′-biphenol, which are difficult to copolymerize with aliphatic glycols, CBDO readily forms high molecular weight, random copolyterephthalates with PDO and BDO. This new family of *amorphous* CBDO copolyesters, especially compositions with PDO, has been found to exhibit attractive combinations of physical properties, including thermal stability, UV stability, clarity, low color, and glass transition temperatures (T_g) up to 168 °C. The rigid tetramethylcyclobutylene group not only enhanced the T_g but also resulted in compositions with unusually high impact resistance.



4a R = $(CH_2)_2$
4b R = $(CH_2)_3$
4c R = $(CH_2)_4$

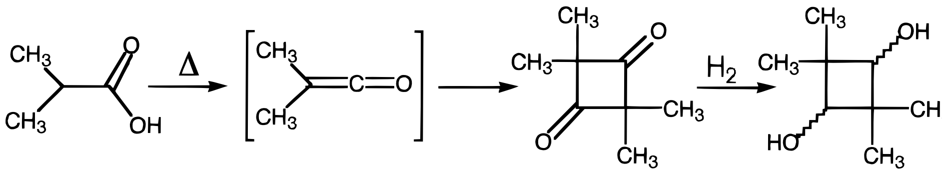
Results and Discussion

Synthesis. Because the CBDO hydroxyl groups are secondary and sterically hindered by adjacent methyl groups, we expected polymerizations using CBDO could be more difficult than for primary diols. Tin[11a] and lead[11b] catalysts have been used successfully with CBDO, although the latter tends to produce gray products. Some transesterification catalysts, such as titanium tetrabutoxide, showed surprisingly poor activity with CBDO in our tests.[12]

The reactivities of several typical polyester catalysts were estimated by measuring the rate of methanol

10.1021/ma000223+ CCC: $19.00

Scheme 1



3 **2** *cis/trans* **1**

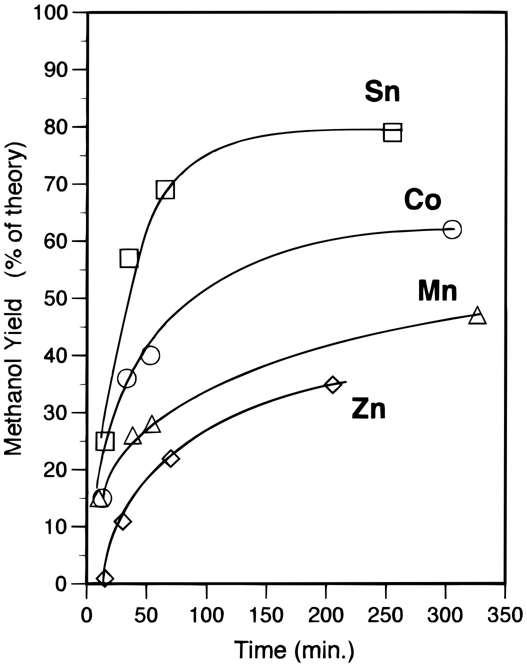


Figure 1. Methanol yields from transesterification of CBDO (**1**) with dimethyl terephthalate using various catalysts at 240 °C (lines show trends only).

produced from transesterification of CBDO with dimethyl terephthalate [DMT] at 240 °C. The relative rates were $SnOBu_2 > Co(OAc)_2 > Mn(OAc)_2 > Zn(OAc)_2$ (Figure 1). Similar experiments with $Ti(OBut)_4$ or NaOAc produced low methanol yields, and only trace amounts were observed using $Ge(OEt)_4$ or Sb_2O_3 catalysts.[13a]

Our results confirm that tin compounds[11a] are good catalysts for transesterification with CBDO. The reason why tin catalysts are so much better in this case than other typical polyester catalysts is not clear. Nor is it obvious why titanium butoxide was so sluggish. In model transesterification systems, titanium alkoxides have been reported to be more active catalysts than Co, Mn, and Zn compounds, which in turn were more active than antimony and germanium species.[14a] The reactivities of these catalysts for transesterification with CBDO might be affected, for example, by formation of stabilized cyclic complexes of *cis*-CBDO with some metal centers, such as Ti. Even though some catalysts, such as titanium butoxide, were not very reactive for CBDO transesterification, they could still be used in combination with the tin catalyst for preparing copolymers with linear diols (see Experimental Section).

Copolyesters **4** were prepared without solvent by bulk melt polymerization, a potentially inexpensive, scalable process. Transesterification of excess CBDO and linear diol with DMT using dibutyltin oxide, sometimes in combination with titanium butoxide, was conducted at 220−250 °C. The methanol byproduct was distilled, and excess diols were removed by heating at 250−260 °C under high vacuum to advance the molecular weight. In most cases, the "water white" transparent solid product was dissolved in methylene chloride, filtered, and coagulated into methanol. The polymerization also can be conducted in stages where only CBDO and DMT are reacted first with tin catalyst, and then the linear diol is added along with either tin or titanium catalyst (see Experimental Section). We anticipate that terephthalic acid, rather than its diester, also can be used to prepare these CBDO copolyesters.

The CBDO copolymers (**4**) of various compositions are summarized in Table 1. Incorporation of 1,3-propanediol [PDO] or 1,4-butanediol [BDO] produced copolymers (**4b** and **4c**) with intrinsic viscosities (IV) generally >0.6. On the basis of gel permeation chromatography using a laser light scattering detector, the typical IVs of 0.7−0.8 corresponded to 48 000−55 000 weight-average molecular weights. In the case of ethylene glycol [EG], the copolymer **4a** molecular weights achieved were borderline using the tin catalyst and even lower using other catalysts.[13a]

NMR analyses (Figure 2) showed that the CBDO/diol molar ratio in the final product was essentially the same as the CBDO/diol ratio used for the polymerization when PDO or BDO was the linear diol (Table 1). This may be due to fortuitously similar volatilities of CBDO, PDO, and BDO. With ethylene glycol, the CBDO/diol product ratio was enriched in CBDO because of the higher volatility of EG under vacuum. NMR of the copolymers also showed essentially the same *cis/trans* CBDO ratio as in the starting monomer. The NMR spectra showed no evidence of nonrandom sequence distributions, consistent with random copolymers.

The amorphous copolyesters made with 1,3-propanediol, including those with high CBDO levels, usually remained transparent and "water white" when cooled from the melt to room temperature. The 1,4-butanediol copolymers were very slightly discolored, but copolymers prepared using ethylene glycol were distinctly yellow. The yellowness index (YI) measured on compression molded samples increased in the order PDO < BDO ≪ EG (Table 1). In our experience, ethylene glycol can generate considerable color in the presence of "hot" transesterification catalysts, such as tin and titanium, especially titanium alkoxides. Fortunately, the longer chain diols, especially PDO, are less prone to color formation in the presence of the more reactive catalysts, which is an advantage.[14b] After our work was completed and disclosed, similar terephthalate-based copolyesters of CBDO with ethylene glycol (only) prepared using a combination of tin and zinc catalysts were reported. However, the color of these copolyesters was not mentioned.[13b]

Thermal Properties. a. Crystallinity. The crystalline behavior of the CBDO/diol terephthalate copolyesters is determined by the proportion of CBDO and also

Table 1. CBDO/Diol Terephthalate Copolyesters

			CBDO/diol						
DMT[i] (mol)	CBDO[a] (mol)	diol (mol)	charged	found[b]	exp method[c]	IV[d]	T_g[e] (°C)	T_m[e] (°C)	yellowness index
			Ethylene Glycol (**4a**)						
0.80	0.72	0.28	72/28	78/22	A2	0.52	155	A	83.6
0.20	0.15	0.10	60/40	69/31	B1	0.70	146	A	79.8
0.80	0.64	0.48	57/43	68/32	A1	0.52	142	A	86.9
			1,3-Propanediol (**4b**)						
0.80	1.04		100/0		A2	0.31	174	>310	
0.80	0.80	0.12	87/13	87/13	A2	0.57	168	A	
0.80	0.80	0.21	80/20	81/19	A1	0.67	154	A	
0.35	0.341	0.097[g]	78/22	82/18	B2	0.82[f]	150	A	
				81/19		0.70	139	A	
0.80	0.72	0.28	72/28	72/28	A2	0.65	136	A	
0.80	0.64	0.36	64/36	65/35	A1	0.83	122	A	15.7
0.80	0.64	0.36	64/36	64/36	A2	0.78	121	A	
0.35	0.284	0.153[g]	65/35	65/35	B2	0.84	119	A	
0.80	0.56	0.44	56/44	57/43	B1	0.73	112	A	15.9
0.03	0.0188	0.0188[h]	50/50	53/47	B2	0.86	101	A	
0.20	0.15	0.15	50/50		A2	0.53	98	A	
0.20	0.10	0.13	44/56		B2	0.52	80	A	
0.80	0.40	0.60	40/60	40/60	B1	0.72	87	A	
0.80	0.25	0.75	25/75		B1	0.92[f]	17	162	
0.80		1.04	0/100		A1	1.11[f]	59	235	
			1,4-Butanediol (**4c**)						
1.30	1.27	0.35	78/22	78/22	A2	0.73	145	A	
0.80	0.72	0.28	72/28	72/28	A2	0.61	129	A	18.9
0.80	0.64	0.36	64/36	64/36	A2	0.73	119	A	36.9

[a] *Cis/trans* = 48/52 unless otherwise noted. [b] NMR of final product. [c] See Experimental Section. [d] Intrinsic viscosity in hexafluoro-2-propanol at 35 °C. [e] By DSC on second heating; "A" indicates amorphous as molded and/or the second heating in the DSC showed no crystallization or melting transitions. [f] Polymer insoluble or partially soluble in methylene chloride. [g] CBDO *cis/trans* = 39/61. [h] CBDO *cis/trans* = 59/41. [i] DMT = dimethyl terephthalate.

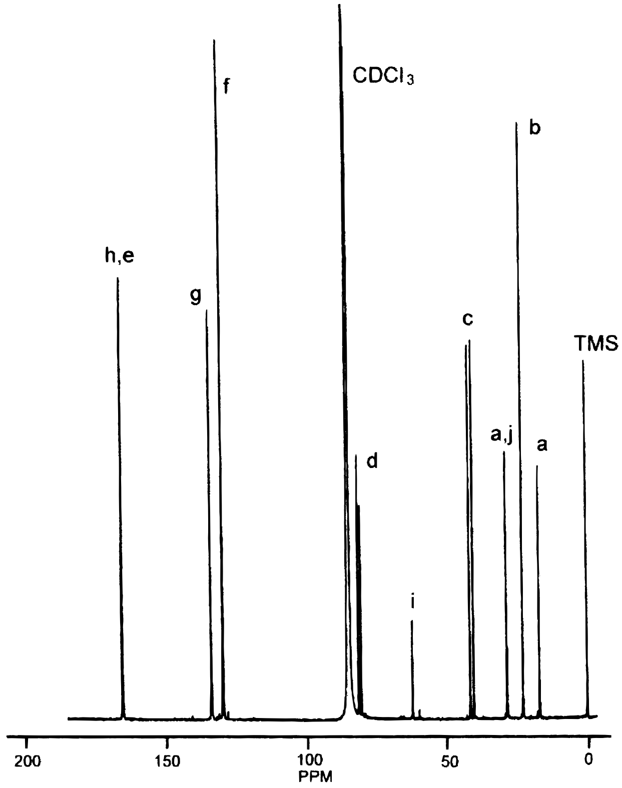


Figure 2. ^{13}C NMR spectrum of terephthalate copolyester **4b** with CBDO/PDO = 78/22 and *cis/trans* = 47/53; peak assignments are shown in the Experimental Section.

to some extent by the *cis/trans* isomer ratio, as summarized in Tables 1 and 2. The CBDO terephthalate "homopolymer" was semicrystalline, as expected, with a melting onset above 300 °C, similar to literature values.[11]

The copolyesters were amorphous, transparent materials and soluble in CH_2Cl_2 when the proportion of CBDO was about 40−90 mol % of total diol and the CBDO *cis/trans* ratio was near 50/50. Small transitions were observed occasionally during the first DSC heating, but these were absent on the second heating and in molded samples. The transient transitions were likely due to solvent-induced crystallization during work-up. X-ray analyses confirmed the amorphous nature of the as-made and molded copolymers. At 40% CBDO, crystallinity became borderline, as evidenced by two small melting transitions respectively in the first DSC scan, but the second heating gave no crystallization or melting transitions. X-ray analysis of the "as-made" sample showed some crystalline features, but a compression molded sample showed none. (See Supporting Information for examples of the X-ray spectra mentioned here.)

Below about 40 mol % CBDO, the CBDO/PDO copolyesters became semicrystalline. At 25% CBDO, the copolymer exhibited cold crystallization and a distinct melting transition. The X-ray spectrum showed peaks characteristic of a semicrystalline polymer (see Supporting Information).

Limited experiments suggest that higher *trans/cis* CBDO isomer ratios may promote crystallinity. With 61% *trans* isomer and 81% CBDO, the CBDO/PDO copolyester was opaque and only partially soluble in methylene chloride, unlike the similar composition made with 52% *trans* isomer. Both the insoluble and soluble fractions showed weak melting transitions on the first DSC heating (Table 2), but the second heating showed only a T_g.When the proportion of CBDO was decreased to 65 mol %, the as-made copolymer was slightly opaque but completely soluble in methylene chloride and amorphous by DSC.

b. Glass Transitions. The T_g for the homopolymer of CBDO (52% *trans*) and terephthalic acid was 174 °C,

Table 2. Crystallinity of CBDO/PDO Terephthalate Copolyester Compositions

cis/trans[a]	CBDO (mol %)	T_m[b] (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	DSC scan	
59/41	53	A				first	transparent; soluble[d]
48/52	100	317–325[c]				second	opaque; insoluble
	87–44	A				first	transparent; soluble
	40	127/157	10/4.3			first	transparent; soluble
		A				second	
	25	162	14	97	15	second	opaque; insoluble
39/61	81	227	5.7			first	opaque; insoluble fraction
		A				second	
		176/227	weak			first	soluble fraction
		A				second	
	65	A				first	slightly opaque; soluble

[a] Charged (see Experimental Section). [b] A = amorphous. [c] Onset. [d] In CH_2Cl_2.

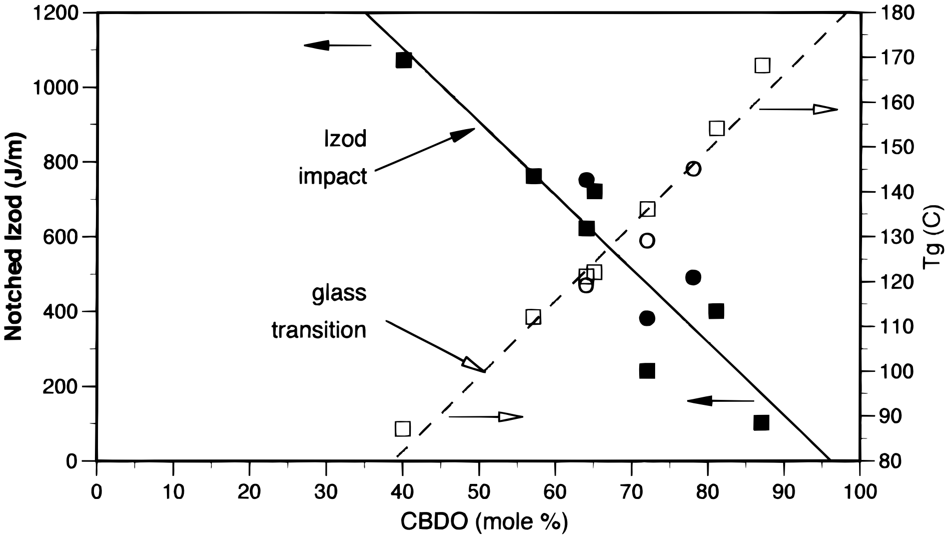


Figure 3. Effect of CBDO content on T_g (open symbols) and notched Izod impact (solid symbols) for terephthalate copolymers with 1,3-propanediol (squares) and 1,4-butanediol (circles); lines indicate trends.

which is close to the literature value (184 °C, 60% *trans*),[11d] and also may be slightly depressed due to the relatively lower molecular weight of this sample. Semicrystalline polyterephthalates such as PET, PTT, and PBT exhibit T_g's near 70 °C. But for quenched, amorphous samples, the T_g is lower, e.g., about 40 °C for amorphous poly(trimethylene terephthalate) [PTT]).[15] Therefore, the rigid CBDO unit boosts the glass transition by about 130–140 °C compared to the case of the corresponding polyterephthalate linear diol analogues.

The effect of the rigid CBDO unit on T_g is similar in magnitude to common rigid aromatic backbone groups. Using van Krevelen's group contribution method[16] and the T_g for CBDO terephthalate homopolymer (174–184 °C), we estimate that the group contribution (Y_g) for the ~50/50 *cis/trans*-2,2,4,4-tetramethyl-1,3-cyclobutylene [TMCB] residue is about 60–63. This compares favorably with Y_g's of common aromatic groups, such as 1,4-phenylene (29–41), terephthalate (62), 4,4′-biphenylene (70), and bisphenol A residue (87).[16]

To allow for the differences in molecular weight (because the van Krevelen correlations involve the group molecular weights[16]), we calculate a "molar group contribution" Y_g/M of ~0.56 for the TMCB unit. This value is higher than the Y_g/M, for example, of 1,4-phenylene (0.39–0.54), terephthalate (0.38), 4,4′-biphenylene (0.46), and bisphenol A residue (0.45). This suggests that the TMCB group is at least as effective for increasing T_g as some of the more common aromatic backbone units.

The effectiveness of the CBDO (or TMCB) group contribution to T_g also was borne out by the T_g's of the amorphous copolyesters containing 40–87 mol % CBDO, which ranged from 80 to 168 °C. Single T_g's were observed, consistent with random copolymer structures. The transition energies, ΔC_p, were generally 0.165–0.185 J/(g K). The expected general proportional trend of T_g with composition (Figure 3) is followed and indicates that a T_g above 100 °C requires >50 mol % CBDO. The calculated copolymer T_g's using the Fox equation[17] ($1/T = w_a/T_a + w_b/T_b$, where w's are the weight fractions and T's are the T_g's of the corresponding homopolymers *a* and *b*) generally agree with the experimental data to within <10 K, but only if the T_g for quenched, amorphous PTT homopolymer (~40 °C) is used rather than the T_g for semicrystalline PTT. The T_g's for the CBDO/EG copolymers were similar to the CBDO/PDO and CBDO/BDO copolymers, especially when the weight fraction of EG is taken into consideration. The T_g of 141° C recently reported for the 64/36 CBDO/EG copolyester[13b] is comparable to the T_g we observed for the 68/32 CBDO/EG composition (Table 1).

Interestingly, the T_g of the 25/75 CBDO/PDO semicrystalline copolymer was depressed compared to that of the PTT homopolymer. The T_g measured on the second DSC heating was 17 °C, and after this sample was annealed at 125 °C, the T_g was 10 °C ($\Delta C_p = 0.228$ J/(g K)). This transition temperature is significantly lower than the T_g of amorphous PTT homopolymer itself. The reason for this depressed T_g is not obvious to us and worth further study.

c. Thermal Stability. Thermogravimetric analyses confirmed that the copolyesters are thermally stable at temperatures needed for injection molding, at least with respect to degradation reactions which produce volatile byproducts. The 87/13 CBDO/PDO copolymer showed no weight loss up to onset at >380 °C under nitrogen and >360 °C in air; the 5% weight loss temperatures were about 417 and 392 °C, respectively. A 64/36 sample showed 5% weight loss temperatures of 393 and 382 °C in nitrogen and air, respectively.

Physical Properties. a. Impact Resistance. Polyterephthalates of C_2-C_4 linear diols (PET, PTT, and PBT) have poor impact resistance with typical notched Izod values <80 J/m.[1] Backbone groups that increase the rigidity of polymer chains by increasing steric interactions or by decreasing conformational flexibility often result in polymers with low impact resistance. Because the CBDO group effectively contributes to the glass transition temperature, as shown above, one might expect that the CBDO copolyesters would be brittle materials due to the incorporation of this rigid structure. However, the amorphous CBDO/diol terephthalate copolymers proved to be exceptionally tough materials with notched Izod impacts as high as 1070 J/m (~20 ft-lb/in.).

The Izod impact was inversely related to the CBDO content of the copolymers (**4b**, **4c**), as shown in Figure 3 for compositions made with 48/52 *cis/trans*-CBDO isomers. Because the glass transition temperatures are proportional to the CBDO content, there is a tradeoff between toughness and thermal resistance. Nevertheless, compositions in the range of about 50−80 mol % CBDO were found to have excellent toughness combined with T_g's >100 °C. The balance between T_g and toughness can be tailored to specific requirements by adjusting the proportion of CBDO in the composition.

The CBDO/EG terephthalate copolyesters disclosed recently[13b] after our study was completed showed similar impact behavior but reached a maximum of 660 J/m notched Izod impact at 64/36 CBDO/EG compared to maximum of 1070 J/m we found for 40/60 CBDO/PDO (Figure 3). The impact values for CBDO/EG compositions with less than about 50 mol % or more than 84% CBDO were <140 J/m.[13b]

Commercial engineering thermoplastics (unmodified with fillers, glass, or elastomers) with T_g's above 100 °C usually have Izod impacts <250 J/m (5 ft-lb/in.), often even below 100 J/m.[1] Poly(hexamethylene terephthalamide) and bisphenol A polycarbonate are two exceptions,[1] the latter exhibiting a notched Izod of 650−850 J/m (12−16 ft-lb/in.) and $T_g \sim 150$ °C.[1,18] The trends in Figure 3 show that the CBDO/diol terephthalate copolymers can match the Izod impact of polycarbonate when the proportion of CBDO is about 50−60 mol %, although the T_g's of these compositions are somewhat lower than that of polycarbonate. Conversely, the CBDO copolymer T_g can approach that of polycarbonate using about 70−80 mol % CBDO and still retain an Izod impact >250 J/m, which is adequate for many applications.

The high impact resistance of bisphenol A polycarbonate, which undergoes shear yielding under impact, has been attributed to cooperative chain motions that are related to sub-T_g (low energy) relaxations extending over several structural units.[19] Another example, albeit with T_g's below 100 °C, are the terephthalate copolyesters of ethylene glycol and 1,4-cyclohexanedimethanol (CHDM) which exhibit high Izod impact at room temperature (e.g., >1000 J/m), especially for compositions with high proportions of CHDM. The high impact of CHDM copolymers has been attributed to the conformational flexibility of the cyclohexylene rings and the influence of this flexibility on chain mobility.[20]

Table 3. Physical Properties of Molded Copolyesters

		CBDO/BDO	CBDO/PDO
CBDO/diol[a]	mol/mol	78/22	78/22
cis/trans[a]		49/51	49/51
IV (after molding)[b]		0.55	0.76
flexural modulus	GPa		1.81
tensile modulus	GPa	1.84	1.83
tensile strength	kPa	31.0	45.5
heat distortion at 264 psi	°C	105	114
T_g (DSC)	°C	145	150
Izod impact			
23 °C, $^1/_8$ in.	J/m	490 ± 50 CM	
23 °C, $^1/_8$ in.	J/m	280 ± 40 IM	390 ± 40 IM
23 °C, $^1/_4$ in.	J/m		210 ± 50 CM[c]
−30 °C, $^1/_8$ in.	J/m		130 ± 40 IM

[a] By NMR. [b] Intrinsic viscosity in hexafluoro-2-propanol at 35 °C. [c] IV = 0.81 after molding. CM = compression molded sample; IM = injection molded bars.

The CBDO terephthalate copolymers also appear to undergo shear yielding under impact (see fracture surface in Supporting Information). The very high impact resistance of these compositions seems remarkable because, unlike CHDM, the tetramethylcyclobutylene unit is conformationally rigid. The *inverse* relationship between impact and CBDO content, unlike the behavior of CHDM copolymers, is also intriguing. The molecular structure of CBDO is significantly different from the structures of either bisphenol A or CHDM, so the molecular basis for the high impact resistance of the CBDO/diol copolyterephthalates cannot be explained readily by our current understanding of how polymer structure affects impact behavior. Further study of these copolyesters and other polymers of CBDO should provide valuable insights into the molecular parameters that influence impact resistance.

b. Injection Molded Samples. Compositions with 78/22 CBDO/PDO (**4b**) and CBDO/BDO (**4c**) were chosen to obtain simultaneously a T_g ~140 °C and an impact resistance >250 J/m. The Izod impact values (Table 3) showed some variation depending on molding conditions[21] but were as high as 400−500 J/m, which confirmed the good impact behavior observed for the small batch experiments (see Figure 3).

Polycarbonate is notch sensitive, viz. the notched Izod impact decreases for thicker samples. For $^1/_4$ in. thickness, rather than the usual $^1/_8$ in. samples, the notched Izod value for the 78/22 CBDO/PDO copolyester was 210 J/m compared to 120 J/m reported for polycarbonate,[18] which indicates less notch sensitivity for the CBDO copolymer. The low-temperature impact (130 J/m at −30 °C) of the CBDO/PDO copolyester was also acceptable.

Flexural and tensile moduli (>1.8 GPa) and tensile strength (30−45 kPa) were very good, although these values are not necessarily optimum due to the disadvantages of working with laboratory samples and unoptimized molding conditions. Because of the relatively high moduli, the heat deflection temperatures for these copolymer compositions (105−114 °C at 264 psi) were reasonably comparable to the HDTs of polycarbonate (121−132 °C)[1,18]

c. Birefringence. The stress−optic coefficient of a molded copolyester sample containing 87 mol % CBDO was about 103−114 brewsters ($m^2/N \times 10^{-12}$), which is similar to that of polycarbonate (see Experimental Section).

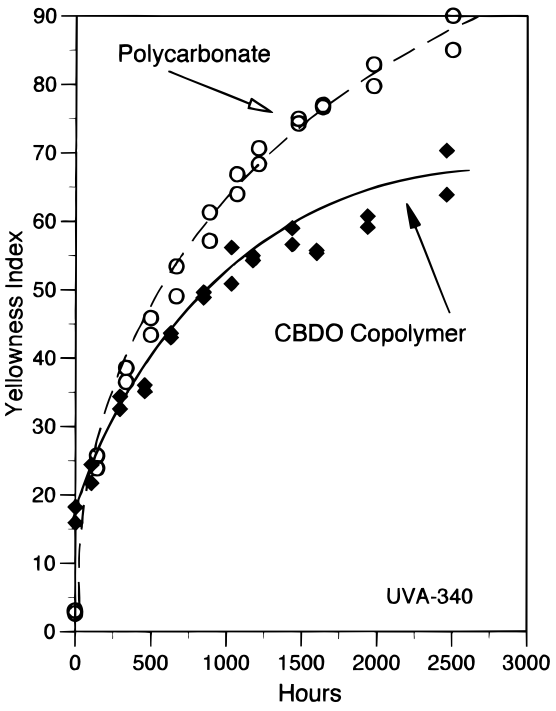


Figure 4. Yellowness (YI) during accelerated UV aging of CBDO/PDO copolyester and unstabilized polycarbonate.

Photooxidative Stability. Some aromatic polyesters, such as bisphenol A polycarbonate and polyarylate [poly(bisphenol A terephthalate)], undergo severe yellowing and chain degradation under ultraviolet exposure.[22] The chemistry involved has been attributed to photo-Fries rearrangements, which produce benzophenones and related species, and to photooxidative cleavage.[23]

The CBDO unit should be relatively stable under photooxidative conditions. Like the polyterephthalates of aliphatic diols, such as PET and PBT, CBDO polyesters should not be able to undergo photo-Fries rearrangements. The tetramethylcyclobutylene unit has two sterically hindered tertiary hydrogens, which could be susceptible to radical abstraction. But chain cleavage resulting from reactions at this site should be prevented by the cyclic structure, which can still maintain backbone connectivity even if one C−C bond is broken. To determine the relative UV stability, an accelerated UV weathering test was conducted on the CBDO/PDO terephthalate copolyester [**4b**; 78/22; 49/51 *cis*/*trans*] and on commercial polycarbonate not containing UV stabilizers.[24]

The CBDO/PDO copolyester samples showed less increase in yellowness index (YI) and lower absolute yellowness than the polycarbonate samples after 2500 h (Figure 4). The CBDO copolymer also retained somewhat higher Izod impact (90−150 vs 50−70 J/m), although both polymers showed substantial decreases from their initial values (Table 4). The changes in haze, gloss, and transmission were similar for the two polymers. These results confirm that the CBDO/diol terephthalate copolyesters have some inherent photooxidative stability, especially to yellowing.

Table 4. Accelerated (UV) Weathering of CBDO/PDO Copolyester and Bisphenol A Polycarbonate for 2500 h

	initial	final	change	
yellowness index[a]				
CBDO/PDO copolymer	17	67	+50	+294%
polycarbonate	3	87	+84	+2800%
haze[a] (%)				
CBDO/PDO copolymer	19	29	+10	+53%
polycarbonate	3	17	+14	+470%
transmission[a] (%)				
CBDO/PDO copolymer	70	63	−7	−10%
polycarbonate	87	72	−15	−17%
gloss[a] at 45°				
CBDOPDO copolymer	68	62	−6	−9%
polycarbonate	93	63	−30	−32%
gloss[a] at 60°				
CBDO/PDO copolymer	108	72	−36	−33%
polycarbonate	150	102	−48	−32%
notched Izod (J/m)				
CBDO/PDO copolymer	390	110	−280	−72%
polycarbonate	990	70	−920	−93%

[a] Optical values are averages of two samples.

Conclusions

The amorphous CBDO/diol terephthalate copolyester compositions we prepared with about 40−90 mol % CBDO exhibit unique combinations of useful properties not often realized in a single polymer family: high impact resistance, useful thermal behavior (high T_{g}), thermal stability, good photooxidative stability, transparency, and low color.

These random copolymers are easily prepared by bulk melt polymerization if a reactive catalyst, such as dibutyltin oxide, is used. 1,3-Propanediol is the preferred linear diol because it produces high molecular weight product with less color (yellow), particularly compared to ethylene glycol.

The rigid, aliphatic CBDO unit is responsible for the enhanced glass transition temperatures attained with these compositions. The CBDO group's influence on T_{g} is similar to the effect normally achieved using symmetrical, rigid aromatic backbone groups, such as 1,4-phenylene or 4,4′-biphenylene and the like.

Surprisingly, despite its rigid structure, the CBDO unit also enhances the impact resistance of these copolymers to a remarkable degree. The effect is inversely proportional to the CBDO content, reaching a maximum of $>$1000 J/m (notched Izod). The combination of impact resistance and T_{g} can be tailored by adjusting the relative proportions of CBDO and linear diol. These CBDO copolyester compositions may provide an opportunity to understand better the molecular mechanisms and structures required for designing high impact thermoplastics.

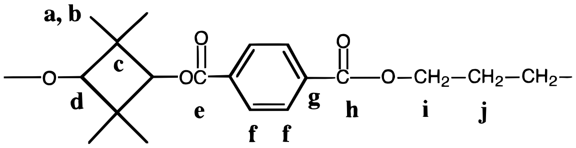
Experimental Section

General. CBDO (*cis*/*trans* = 48/52 by NMR and GC) from Eastern Chemical (Hauppauge, NY) was used for most syntheses. For batches prepared for injection molding, CBDO from several sources were blended to obtain an overall *cis*/*trans* = 47/53 before conversion into copolymer: Lark Enterprises (44/56 by GC after recrystallization from ethyl acetate), TCI (American Tokyo Kasei, Inc., 39/61), Pfaltz & Bauer (50/50), Eastern Chemical (59/41) and Fairfield Chemical (50/50 after recrystallization from ethyl acetate). Other reagents were DMT (Fluka, polymer grade, 99+%), 1,3-propanediol (Eastman Kodak, redistilled), 1,4-butanediol (Aldrich, 99+%), ethylene glycol (Union Carbide, polyester grade), dibutyltin oxide (Aldrich), titanium tetrabutoxide (Aldrich, 99%), Irganox 1098 (Ciba-Geigy), and hexafluoro-2-propanol [HFIPA] (duPont). **Caution***: HFIPA is very corrosive to skin and eyes and should be used with adequate safety precautions.*

Chromatography. Gas chromatography was conducted using an HP5880A with a 12 m × 0.2 mm × 0.33 μm crosslinked methylsilicone gum capillary column (HP-1) programmed from 60 to 220 °C; *cis*- and *trans*-CBDO isomers eluted at 22.7 and 22.9 min, respectively; 2,2,4,4-tetramethyl-3-hydroxycyclobutanone, an impurity in some samples removed by recrystallization, eluted at 21.4 min.

Gel permeation chromatography (GPC) was obtained on a Waters instrument with a refractive index detector (410) and a Wyatt Technology mini-DAWN laser light scattering detector (for M_w) with angles nominally at 45°, 90°, and 135°, a Schmadzu oven at 35 °C, and Phenomenex Phenogel 5 μm linear and Phenogel 5 μm 500A columns (7.8 × 300 mm) in series using HFIPA containing 0.01 M ammonium trifluoroacetate at 0.5 mL/min and sample concentration 0.005 g/dL. M_w/M_n was estimated by refractive index because light scattering tends to overestimate M_n. For 65/35 CBDO/PDO (0.83 IV): $M_w = 57\,000$, $M_w/M_n = 2.5$; for 87/13 CBDO/PDO (IV = 0.57): $M_w = 38\,500$, $M_w/M_n = 2.2$.

NMR. ^{13}C spectra were obtained on solutions in CD_3Cl containing 0.1 M TEMPO (relaxation agent for quantitative spectra) and TMS reference in 10 mm tubes using a Bruker AM-500 spectrometer programmed for 45° pulse-and-acquire sequence with composite pulse ^{1}H decoupling and 10 s recycle delay time for quantitative analysis. *J*-modulated spin-echo experiments (Attached Proton Test) were run to confirm the following peak assignments (ppm):



a = 17.0 and 28.6 (cis)
b = 23.0 (trans)
c = 40.3 and 41.7
d = 80.4 and 81.4
e = 165.1
f = 129.5
g = 133.7
h = 165.4
i = 62.3
j = 28.4

An example of an expanded spectrum is included in the Supporting Information. For BDO copolymers **4c**, the corresponding values for **i** and **j** were 65.0 and 25.6 ppm, respectively.

Thermal and Other Analyses. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer DSC7 using a heat/cool/heat cycle at 10 °C/min on 6−14 mg samples; T_g values were taken at the midpoint of the transitions. Thermal gravimetric analysis (TGA) was measured on a duPont 2100 from ambient to 500 °C at 20°/min on 5−7 mg samples. X-ray spectra were obtained using a wide-angle Philips APD3720 automated diffractometer at 40 kV and 35 mA by scanning the 2θ angle from 5° to 60°; spectra are shown in the Supporting Information. Color was measured on $^1/_8$ in. thick compression molded disks according to ASTM-1925 using a Gardner Colorgard System 05**.** A yellowness index (YI) of 15 corresponds to a value of about 6 on the *b** scale (Cielab 1976) and visually is almost “water white”. Intrinsic viscosity was measured on HFIPA solutions at ~0.15−0.5 g/dL at 35 °C.

Catalyst Reactivity. A 250 mL three-neck reaction flask fitted with a mechanical stirrer, graduated 10 mL Dean−Stark trap, and water-cooled condenser was charged with dimethyl terephthalate (0.10 mol, 19.4 g), 2,2,4,4-tetramethyl-1,3-cyclobutanediol (0.12 mol, 17.06 g), catalyst (0.06 mmol), and 0.035 g Irganox 1098 (free radical stabilizer). The mixture was degassed four times with argon using a Firestone valve and then heated in an oil bath to 240 °C (bath temperature) at atmospheric pressure. NaOAc, $Ti(OBut)_4$, $Ge(EtO)_4$, and Sb_2O_3 produced <0.5 mL methanol (theoretical 8.1 mL) in the trap after ~4 h or more. The results for But_2SnO, $Co(OAc)_2$, $Mn(OAc)_2$, and $Zn(OAc)_2$ are shown in Figure 1. Attempts to prepare terephthalate copolymers with CBDO and ethylene glycol using cobalt acetate, zinc acetate, and manganese acetate produced highly colored, low molecular weight products (IV < 0.23).[13]

Synthesis of CBDO Copolyester 4b (Example). A 1 L, three-neck reaction flask fitted with a mechanical stirrer and distillation head was charged with dimethyl terephthalate (155.36 g, 0.80 mol), 2,2,4,4-tetramethyl-1,3-cyclobutanediol (91.01 g, 0.64 mol), Irganox 1098 stabilizer (0.2555 g,), and dibutyltin oxide (0.1207 g, 0.485 mmol), degassed with argon using a Firestone valve, and heated in an oil bath at about 235−250 °C for about 5.5 h to distill out methanol (~35 g), and then the reaction was cooled to room temperature. 1,3-Propanediol (27.43 g, 0.36 mol, distilled) and titanium tetrabutoxide (0.535 g, 0.154 mmol) were added to the reaction mixture. The flask and contents were degassed with argon, heated at about 230−250 °C for about 6 h to distill out methanol (~13.9 g), and then cooled to room temperature. The distillation head was replaced by a short path vacuum distillation adapter with a collection flask cooled in dry ice. The reaction mixture was degassed and heated in the oil bath to about 260 °C. The pressure was gradually reduced to about less than ~2 mbar over about 15 min and then maintained under full vacuum for about 7 h to give a viscous, clear, transparent polymer melt (also obtained for compositions with 25−87 mol % CBDO). The cooled polymer was recovered by cutting it into pieces, dissolving in methylene chloride, filtering, coagulating into methanol (containing a small amount of 2,6-di-*tert*-butyl-4-methylphenol stabilizer) in a blender, washing the polymer twice with methanol, and drying in a vacuum oven with a N_2 bleed. Isolation by coagulation typically produced polymer fluff (powder) with low bulk density. The IV was 0.78. NMR analysis showed that the final polymer contained 64/36 molar ratio of CBDO/PDO units, which is the same ratio as the monomers charged to the reactor; the product CBDO *cis*/*trans* ratio was also the same as the monomer.

In the case of the copolymer prepared with 78/22 CBDO/PDO and 61% *trans*-CBDO, the white, opaque product was only partially soluble in methylene chloride Of the total 74 g polymer recovered, 48 g was insoluble (see Table 1). NMR analysis showed 34/66 and 38/62 *cis*/*trans* ratio for the insoluble and soluble polymer fractions, respectively.

Variations in the experimental procedure were as follows:

A1 = step 1: Dibutyltin oxide and titanium tetrabutoxide catalysts with all reagents charged initially to reactor and methanol distilled at atmospheric pressure; step 2: heated under vacuum.

A2 = step 1: Dibutyltin oxide catalyst with CBDO and DMT charged initially to reactor and methanol distilled at atmospheric pressure; step 2: linear diol and titanium tetrabutoxide catalyst added to reactor and methanol distillation resumed; step 3: heated under vacuum.

B1 = method A1 using only dibutyltin oxide catalyst.

B2 = method A2 using only dibutyltin oxide catalyst.

Injection Molding. Two batches of 78/22 CBDO/BDO copolymer were combined (370 g), and the dried polymer fluff was injection molded (25 ton Arburg Allrounder 221-55-250, 25 mm screw, barrel 250−272 °C, 50 °C mold, 1000 psi injection, 400 rpm) to provide transparent, slightly yellow test bars. Several laboratory batches of CBDO/PDO copolymer (1.4 kg total) were blended to make a composite feed with IV = 0.96. Attempts to mold the fluff led to unacceptable degradation in molecular weight apparently due to hydrolysis, even though the polymer was thoroughly dried and precautions were taken to minimize moisture takeup. Therefore, the dried fluff was compression molded into $^1/_8$ in. thick plaques, cut into $^1/_4$ in. square chips with a clean diamond band saw, redried, and molded successfully into test bars and disks in the clean Arburg injection molder (barrel 300−330 °C, mold 80 °C, injection 1500 psi, 110 rpm).

Heat deflection temperature was measured according to ASTM D-648−72; tensile modulus and strength (ASTM D-638) and flexural modulus (ASTM D-790) were measured using an Instron, series IX, at 0.2 in./min. Notched Izod was measured according to ASTM D-256A.

Accelerated Weathering. The copolymer (CBDO/PDO = 78/22) used for this test was prepared without hindered phenol stabilizer. Injection molded $^1/_8$ in. thick bars (11) were used for Izod tests; two compression molded disks were used to measure optical properties. Polycarbonate (GE Lexan 131 without UV stabilizers) was molded on the same machine using the recommended molding conditions (22 bars and 10 disks). Note that the CBDO copolymer samples were not as optically “clean” as the polycarbonate samples, which is not unusual for experimental polymer made in small laboratory runs. Consequently, the initial yellowness and haze of the CBDO copolymer samples were higher and initial transmission and gloss were lower compared to the commercial grade polycarbonate samples (Table 4).

The samples were placed in a Q-U-V accelerated weathering tester (Q-Panel Co.) and exposed continuously to UVA-340 lamps at ambient temperature (~50 °C) for a total of 2500 h. The panels were rotated twice weekly, and the lamp positions were changed every 400 h according to the accepted protocol. Yellowness index, gloss (ASTM D-523), and haze and transmission (ASTM D-1003) were measured about once per week on the same samples in duplicate. Samples were removed for notched Izod tests at intervals of 250−750 h; only one or two bars were tested each time because of the limited number of bars available.

Birefringence. Measurements were made by Strainoptic Technologies, Inc., North Wales, PA. Injection molded tensile bars about $^1/_2$ in. wide and $^1/_8$ in. thick of copolyester (87/13 CBDO/PDO) were tested at room temperature under tension using three increments of 5 lb stress. The stress−optic coefficient was 103−114 brewsters ($m^2/N \times 10^{-12}$) for the copolymer sample compared to 87 brewsters for a polycarbonate sample, the latter coefficient being in the range typically found for polycarbonate by this laboratory. The bars were then heated to about 165 °C (above T_g) in an oven for 1 h and then subjected to 30 psi tensile stress. The temperature was slowly decreased over 1.5 h to room temperature and the birefringence remeasured. The coefficients obtained on the “frozen” samples were about 11 000 brewsters for the copolyester compared to 6600 for polycarbonate. Because of the limited molding experience with the CBDO copolymers, these values should be regarded as preliminary.

Acknowledgment. We thank P. N. Tutunjian and S. C. Tang for providing NMR and X-ray analyses, respectively, and L. H. Oliveri, J. G. Bowers, M. S. Rodriguez, J. A. Kelley, and D. G. Waters for valuable technical assistance.

Supporting Information Available: Four figures showing X-ray spectra, one figure showing an expanded NMR spectrum (Figure 2), and one figure showing a scanning electron micrograph of the Izod fracture surface of CBDO/PDO (64/36) copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Deanin, R. D. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: New York, 1996; Vol. 3, p 2074. *Engineering Thermoplastics: Properties and Applications*; Margolis, J. M., Ed.; Marcel Dekker: New York, 1985. Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach: Basel, 1995.

(2) Mugno, M.; Bornengo, M. *Chim. Ind. (Milan)* **1963**, *45*, 1216.

(3) Hasek, R. H.; Elam, E. U. (Eastman Kodak) Brit. Patent 965,762, Aug 6, 1964. Mugno, M.; Bornengo, M. *Chim. Ind. (Milan)* **1964**, *46*, 5. Pregaglia, G. F.; Binaghi, M. *Macromol. Synth.* **1968**, *3*, 152. Sumner, C. E., Jr.; Gustafson, B. L.; Knight, J. R. (Eastman Kodak) U. S. Patent 5,169,994, Dec 8, 1992. Sumner, C. E., Jr.; Gustafson, B. L.; Knight, J. R. (Eastman Kodak) U.S. Patent 5,258,556, Nov 2, 1993. (b) Parker, L. M.; Bibby, D. M.; Miller, I. J. *J. Catal.* **1991**, *129*, 438.

(4) Diketone **2** can also be prepared from isobutyryl chloride: Miller, L. L.; Johnson, J. R. *J. Org. Chem.* **1936**, *1*, 135. Wedekind, E.; Weisswange, W. *Ber.* **1906**, *39*, 1631. Herzog, H. L.; Buchman, E. R. *J. Org. Chem.* **1951**, *16*, 99. Erickson, J. L. E.; Kitchens, G. C. *J. Am. Chem. Soc.* **1946**, *68*, 492. See also: Sauer, J. C. *J. Am. Chem. Soc.* **1947**, *69*, 2444. Williams, R. T., Jr.; Baber, S. C. *J. Chem. Educ.* **1964**, *41*, 563.

(5) Hasek, R. H.; Elam, E. U.; Martin, J. C.; Nations, R. G. *J. Org. Chem.* **1961**, *26*, 700. Hasek, R. H.; Elam, E. U. (Eastman Kodak) U.S. Patent 2,936,324, May 10, 1960.

(6) Elam, E. U.; Hasek, R. H. (Eastman Kodak) U.S. Patent 3,190,928, June 22, 1965; the type of catalyst and reaction temperature influence the *cis*/*trans* isomer ratio.

(7) Rylander, P. N. (Englhard Industries) U.S. Patent 3,329,722, July 4, 1967.

(8) Martin, J. C.; Elam, E. U. U.S. Patent 3,227,764, Jan 4, 1966.

(9) Matzner, M. (Union Carbide) Brit. Patent 1,156,222, June 25, 1969. Matzner, M. U.S. Patent 3,527,734, Sept 8, 1970. D'Onofrio, A. A. (Union Carbide) U.S. Patent 3,375,210, March 26, 1968. Daly, W. H. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1989**, *30*, 337.

(10) (a) Jackson, W. H., Jr.; Caldwell, J. R.; Perry, K. P. (Eastman Kodak) *J. Appl. Polym. Sci.* **1968**, *12*, 1713. Jackson, W. J., Jr.; Caldwell, J. R. *J. Appl. Polym. Sci.* **1967**, *11*, 227. Jackson, W. H., Jr.; Caldwell, J. R. U.S. Patent 3,386,935, June 4, 1968. Jackson, W. J., Jr.; Caldwell, J. R. *Am. Chem. Soc., Div. Org. Coat. Plast. Chem.*, Meeting **1966**, *26* (2), 170.

(11) (a) Caldwell, J. R.; Gilkey, R.; Kuhfuss, H. F. (Kodak) Brit. Patent 1,044,015, Sept 28, 1966, report a copolymer with 40% 1,6-hexanediol and a copolymer with 20% 1,4-cyclohexanedimethanol (70% *trans*-CHDM). (b) Caldwell, J. R.; Gilkey, R.; Kuhfuss, H. F. (Kodak) Fr. Patent 1,456,345, Oct 21, 1966, report a high melting homopolymer with 2,6-naphthalenedicarboxylate. (c) Elam, E. U.; Martin, J. C.; Gilkey, R. (Kodak) U.S. Patent 3,313,777, April 11, 1967, report a 50% copolymer (58% *trans*-CBDO) with CHDM (70% *trans*). (d) Jackson, W. J.; Gray, T. F.; Caldwell, J. R. *J. Appl. Polym. Sci.* **1970**, *14*, 685.

(12) Quesenberry, R. K. (duPont) U.S. Patent 3,249,652, May 3, 1966, report a relatively low molecular weight CBDO terephthalate homopolymer obtained after >19 h using NaHTi$(OBut)_6$ catalyst.

(13) (a) Kelsey, D. R. (Shell) U.S. Patent 5,705,575, Jan 6, 1998. European Patent Appl. 745628A2, published Dec 4, 1996; copolymers incorporating isophthalate and 2,6-naphthalate also were reported. (b) Morris, J. C.; Bradley, J. R. (Eastman Chemical) U.S. Patent 5,955,565, Sept 21, 1999 (provisional application filed Dec 28, 1996); only compositions with ethylene glycol were reported.

(14) (a) Otton, J.; Ratton, S.; Vasnev, V. A.; Markova, G. D.; Nametov, K. M.; Bakhmutov, V. I.; Lomarova, L. I.; Vinogradova, S. V.; Korshak, V. V. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2199. (b) Although catalyst and diol are two primary factors affecting polymer color, we also found after this study was completed that trace impurities in PDO can affect color. Therefore, CBDO/PDO copolyesters prepared using purer PDO than used in this study are expected to have even better color (lower yellowness index) than shown in Table 1. We do not expect further purification of EG will reduce the color of the CBDO/EG copolymers because very highly purified polyester grade EG was used in our experiments.

(15) Pyda, M.; Boller, A.; Grebowicz, J.; Chuah, H.; Lebedev, B. V.; Wunderlich, B. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 2499.

(16) van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990; pp 129−151.

(17) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(18) Modern Plastics Encyclopedia ‘92. *Mod. Plast.* **1991**, *68* (11), 378−428.

(19) Xiao, C.; Jho, J. Y.; Yee, A. F. *Macromolecules* **1994**, *27*, 2761. Plummer, C. J. G.; Soles, C. L.; Xiao, C.; Wu, J.; Kausch, H.-H.; Yee, A. F. *Macromolecules* **1995**, *28*, 7157.

(20) Chen, L. P.; Yee, A. F.; Goetz, J. M.; Schaefer, J. *Macromolecules* **1998**, *31*, 5371. Liu, J.; Yee, A. F. *Macromolecules* **1998**, *31*, 7865.

(21) The lower impact of injection molded CBDO/BDO compared to a compression molded sample (Table 3) is probably due to molecular weight degradation, e.g. hydrolysis, or defects caused by unoptimized molding conditions. In the case of the CBDO/PDO sample, the injection molded sample gave higher impact, due to better drying and additional molding experience.

(22) Pickett, J. E.; Barrenm, J. P.; Oliver, R. J. *Angew. Makromol. Chem.* **1997**, *247*, 1. Sherman, E. S.; Ram, A.; Kenig, S. *Polym. Eng. Sci.* **1982**, *22*, 457.

(23) See: Hoyle, C. E.; Shah, H.; Nelson, G. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1525. Shah, H.; Rufus, I. B.; Hoyle, C. E. *Macromolecules* **1994**, *27*, 553. Pankasem, S.; Kuczynski, J.; Thomas, J. K. *Macromolecules* **1994**, *27*, 3773 and references therein.

(24) Polymers made in laboratory quantities are at a disadvantage compared to commercially produced polymers in these tests, especially with regard to initial color and optical properties. However, the relative changes in properties still provide useful comparisons.

MA000223+