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Synthesis and Characterization of BPA-free Polyesters by Incorporating a Semi-rigid Cyclobutanediol Monomer

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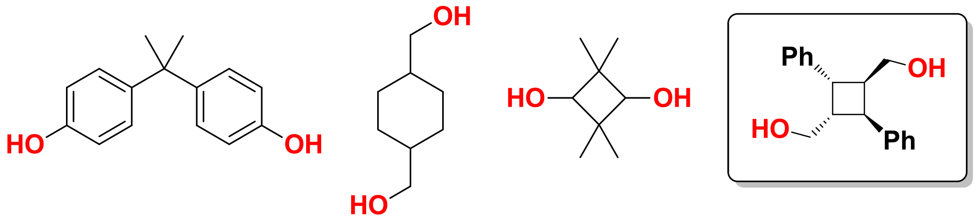
Abstract

The ability of diol monomers, such as 1,4-cyclohexanedimethanol (CHDM) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD), to replace the potentially hazardous BPA in the production of polyesters and polycarbonates with excellent thermal, optical, and mechanical properties, has not only gained considerable academic interest but has also garnered significant commercial success. Herein, we report a novel strategy to synthesize a semi-rigid diol, *trans*-1,3-cyclobutane dimethanol (CBDO-1), a versatile building block which may also serve as a phenol-free BPA replacement. It was synthesized using a facile photoreaction and subsequent reduction. Specifically, an initial photodimerization of *trans*-cinnamic acid using 365 nm blacklight was carried out to form a *trans*-1,3-cyclobutane diacid, CBDA-1, which was then reduced with either $NaBH_4$ in the presence of I_2, or by catalytic hydrogenation using CuO-CrO_3, to give the desired CBDO-1 in excellent yield. To highlight the potential application of this useful primary diol, CBDO-1 and various diacids were used to synthesize novel polyesters via conventional melt polymerization. The thermal properties of this new series of polyesters were studied, including the glass transition temperature, which ranged from 33 to 114 °C, and the decomposition temperature, which ranged from 381 to 424 °C. The ease of synthesis of this cyclobutane-containing CBDO-1 monomer, coupled with its desirable properties, will not only help in the development of alternatives for the widely used BPA, but will also lead to novel and useful materials that are not accessible employing thermal reactions alone.

Introduction

Synthetic polymers[1] have become a prime material of choice around the globe because of their diverse applications, ranging from commodity to high tech, such as food and beverage packaging, electronics, as well as the automotive and architectural industries. Among these, bisphenol A (BPA) based polymers have proven to be essential thermoplastics. For example, BPA-based polycarbonates[2] and epoxy resins[3] exhibit exceptional thermal, mechanical, and optical properties, making them perfect for durable goods and engineering applications. Their success can be attested by their considerable market consumption of 2.7 billion pounds worldwide annually. Some of this use includes reusable water bottles; food can linings, spectacle lenses, and construction. The use of BPA-based polymers, however, has recently come under scrutiny due to the potential carcinogenic and disruptive endocrine effects of BPA.[4] This has boosted widespread research and development of health- and environment-friendly polyesters with similar thermal and mechanical properties.[5,6,7]

One strategy to achieve excellent thermal and mechanical properties similar to those of BPA-derived polymers is to incorporate semi-rigid cyclic monomers, such as octahydro-2,5-pentalenediol and isohexides, into the polymer structure.[5] These cyclic monomers bridge the gap in rigidity between their flexible aliphatic-chain and rigid aromatic counterparts, and some of them have been proven to be useful in synthesizing polyesters with the desired properties. Introduction of the semi-rigid aliphatic units can be used to tune the glass transition temperature, to improve optical clarity of the polymeric materials by reducing their crystallinity, and to make them more UV-stable due to the absence of phenol groups. Among these cyclic aliphatic diol monomers, 1,4-cyclohexane dimethanol (CHDM)[6,8] and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD or CBDO)[7,8] have achieved significant commercial success (Figure 1). They have been used in a variety of polyester and co-polyester products, including BPA-free water and baby bottles, which are now hugely popular.[8,9] However, the ability to introduce functional groups onto the cyclobutane ring of TMCD to tune the properties of the corresponding polymers (e.g., Tritan copolyester) is inherently limited because TMCD is mainly produced through flash vacuum pyrolysis (FVP).[10] Moreover, it is challenging to achieve polymers with high molecular weight using TMCD due to the low reactivity of the secondary diol (a mixture of trans and cis isomers) and its relatively high melting point (126 to 134 °C). Because of these limitations, copolymers are usually synthesized using a mixture of TMCD and another diol (e.g., CHDM).[8,11]



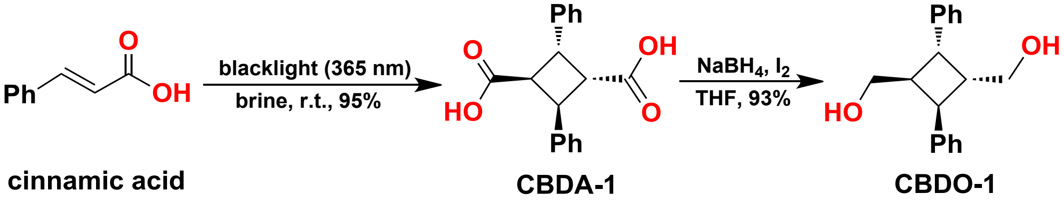
BPA CHDM TMCD CBDO-1

Fig 1. Comparison of different diols with BPA: CBDO-1 shares structural similarities with BPA, CHDM, and TMCD

Trans-1,3-cyclobutane dimethanol (CBDO-1) on the other hand has not gained much attention from researchers, although it was discovered contemporaneously with TMCD. Characterization of the diol was limited to melting point determination and elemental analysis at that time.[12] To the best of our knowledge, no detailed investigation of CBDO-1's physical properties and its application in synthesizing polymers can be found in the literature up to now. In this study, we report the synthesis and application of CBDO-1 monomer as part of our systematic efforts in designing and constructing useful cyclobutane-containing building blocks (CBs) using photoreaction.[13] The performance of CBDO-1 in synthesizing a series of cyclobutane-containing polyesters, as well as their thermal properties, molecular weight distribution, and structural details were investigated. On the one hand, CBDO-1 does not contain a phenol group, which enables BPA to trigger estrogenic pathways in the body.[4] On the other hand, this novel primary diol building block has two rigid phenyl rings like BPA and shares structural similarities with both CHDM and TMCD. Thus it may also serve as a novel BPA replacement like these monomers (Figure 1). Besides CBDO-1, other CBDOs with different substituents can also be readily prepared via similar reduction from the cyclobutane diacids (CBDAs) reported by our group and others,[13] which allow the properties of the corresponding polymers to be tuned by changing the structure of the CBDOs according to specific needs. In addition, since CBDO-1 is a primary diol, CBDO-1 can be easily used in polymer synthesis without the need of adding another diol, due to its higher reactivity and lower melting point compared to those of TMCD.

Results and discussion

Solvent-free dimerization of *trans*-cinnamic acid under residential blacklight (365 nm) resulted in *rctt*-2,4-diphenylcyclobutane-1,3-dicarboxylic acid (CBDA-1), in nearly quantitative yield. The photoreaction can also be carried out in slurry conditions, using brine as a medium in which the commercially available crystalline powder of cinnamic acid is stirred under blacklight. Compared to reported procedures,[13a,14] this innovative slurry photoreaction using brine and blacklight has merits of simplicity and easy scalability (see Figure S2 in the ESI). CBDO-1 (*rctt*-2,4-diphenyl-1,3-cyclobutanedimethanol) was then synthesized in 93% isolated yield by the reduction of CBDA-1 using sodium borohydride ($NaBH_4$) in the presence of iodine (I_2) as an electrophile, and tetrahydrofuran (THF) as the solvent (Scheme 1).



Scheme 1. Synthesis of CBDO-1 from *trans*-cinnamic acid.

Although $LiAlH_4$ is known to be able to reduce carboxylic acids to alcohols, its high reactivity makes it difficult to handle, and extra precautions are required.[15] The milder reagent $NaBH_4$ is not reactive enough to reduce carboxylic acids to alcohols by itself, however, the combination of $NaBH_4$ and I_2 was successfully able to reduce CBDA-1 to CBDO-1.[16] The role of I_2 is unique because of its ability to work either as an electrophile or nucleophile. The mechanism of the reduction of acids to alcohols by metal hydrides shows that the rate-determining step is the hydride transfer from the metal hydride to the carbonyl carbon. Unfortunately, the carbonyl carbon on the acid is not susceptible to a hydride attack in the case of $NaBH_4$. However, the presence of I_2 can facilitate the hydride transfer in this reaction.[17] CBDA-1 has good solubility in THF, so using this solvent gave a better yield (93%) of CBDO-1 when compared to the yield with diethyl ether (74%). As a side note, the solvent does not need to be dried before use in this reaction, unlike when using $LiAiH_4$. In terms of reaction stoichiometry, for every mole of the diacid, a significant excess of the hydride regent (7 moles, 3.5 equivalents for each acid functional group) was required to assure the completion of the reduction. CBDO-1 was obtained as a white solid, which was further purified by recrystallization from ethyl acetate and hexane. The chemical structure was fully characterized by HRMS, FT-IR, and ^{1}H and ^{13}C NMR spectroscopy (see ESI).

Besides having optimized reaction conditions to synthesize CBDO-1 from CBDA-1 in the lab using $NaBH_4/I_2$, we have also successfully applied a model protocol used in industry to this reduction. Specifically, the transformation was accomplished by an efficient and cost-effective heterogeneous catalytic hydrogenation method using an inexpensive and commercially available catalyst, $CuO\text{-}CrO_3$, at elevated pressure and temperature in a stainless steel reactor.

To further characterize this promising diol, rhombic crystals of CBDO-1 were obtained from an ethyl acetate and hexane (3:1) solution by slow evaporation at room temperature. Single crystal X-ray diffraction was used to elucidate the structure of CBDO-1. The crystal structure revealed that the two methanol groups are on the 1 and 3 positions of the cyclobutane ring and are trans to each other, which is the same configuration as their parent carboxylic acid groups in the starting material, CBDA-1 (Fig 2a). The space group is $Pna2_{1,}$ and there are two molecules in each asymmetric unit cell. The two cyclobutane rings in each asymmetric unit adopt about 18.61 and 22.02° puckered conformations (Fig 2b and ESI), respectively, indicating a certain degree of flexibility of the four-membered ring structure.[18] The angles in the cyclobutane ring are 89.00, 88.55, 90.06, and 88.13° (Fig 2a & b). Each hydroxyl group forms two hydrogen bonds with the two hydroxyl groups of the two neighboring molecules (Fig 2c) to form a supramolecular helix, which plays an important role in determining the melting point of CBDO-1 (m.p. 106.4 – 107.0 °C). For comparison, the melting point of its diacid parent molecule, CBDA-1, is about 175 ^{o}C higher. The distance between oxygen atoms in the four hydrogen bonds is 2.734, 2.758, 2.764, and 2.769 Å, respectively. Although the hydrogen-bonded helix is chiral, each crystal is racemic. CBDO-1 is soluble in many common organic solvents, such as acetone, ethyl acetate, diethyl ether, and chloroform. Its relatively low melting point and high solubility demonstrate its potential processability in polymer synthesis.

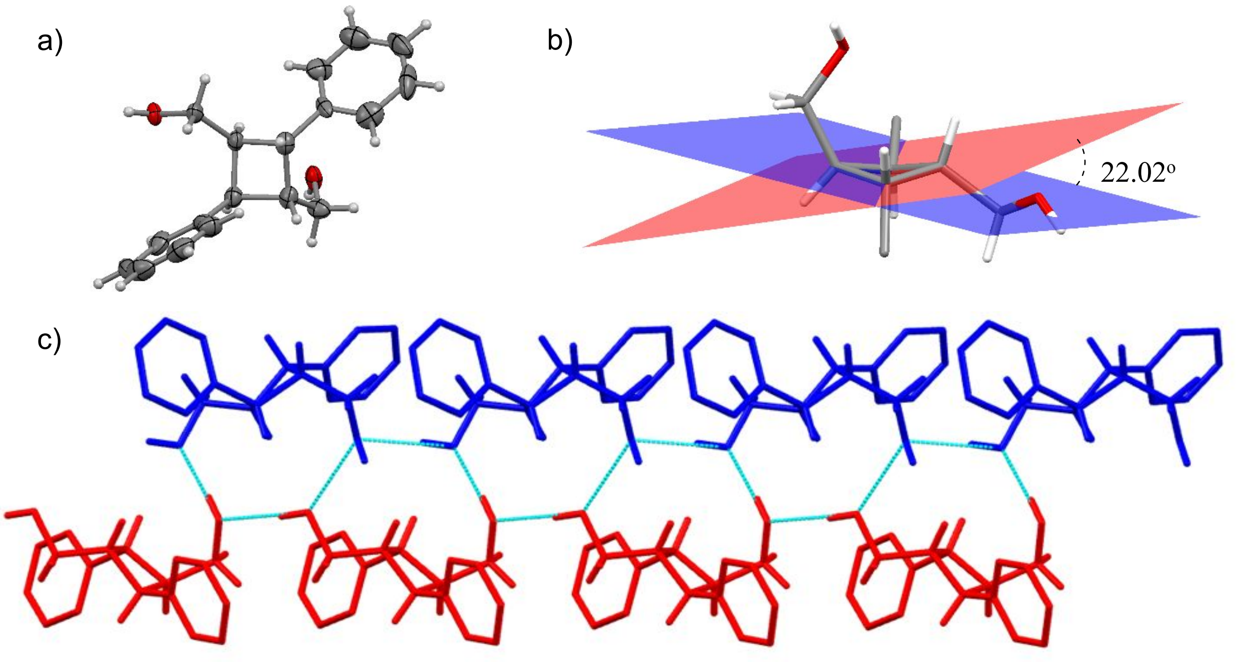
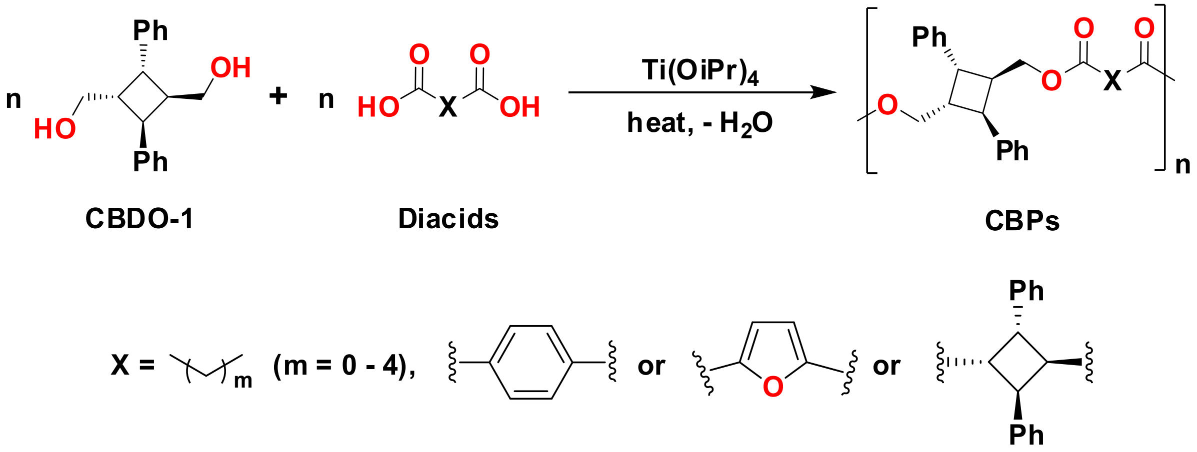


Fig 2. X-ray single-crystal structure of **CBDO-1**: (a) One molecule shown as Oak Ridge Thermal Ellipsoid Plot (ORTEP) representing 50% electron density; (b) The puckered conformation adopted by cyclobutane rings (the phenyl groups are replaced with carbon atoms for clarity); (c) Side view of supramolecular helix formed via hydrogen bonding (the molecules with the same symmetry equivalence are shown in the same color).

Synthesis of polymers

To demonstrate the potential application of CBDO-1 in materials, a series of polyesters were synthesized using a conventional polycondensation procedure.[19] The two-step polycondensation was performed using titanium (IV) isopropoxide as a catalyst (1.25 mol %). The pre-polymerization was first carried out at 160 °C for 12 h, followed by further polycondensation at 210 - 215 °C for 2h under reduced pressure in the second step (Scheme 2). This melt polycondensation involved the reaction of CBDO-1 with one equivalent of an aromatic or aliphatic diacid. Specifically, these diacids were oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, terephthalic acid, 2,5-furandicarboxylic acid, and CBDA-1, which yielded eight corresponding cyclobutane-containing polymers (CBPs):[20] polycyclobutane oxalate (PCBO), polycyclobutane malonate (PCBM), polycyclobutane succinate (PCBS), polycyclobutane glutarate (PCBG), polycyclobutane adipate (PCBA), polycyclobutane terephthalate (PCBT), polycyclobutane furandicarboxylate (PCBF), and polycyclobutane-1,3-cyclobutane-dicarboxylate (PCBC). Out of the eight polyesters synthesized, PCBS, PCBT, and PCBC appeared as white amorphous solids, PCBO had an earth color, and PCBM had a very distinct bright orange color. PCBF, PCBG, and PCBA were found to have a light yellow, tan, and brown color, respectively. The color observed in the polymers prompted us to replace magnetic stirring with external mechanical stirring in the polycondensation, which resulted in polyesters with negligible color (See Figure S3 in the ESI and TOC). The success of this subtle change in the process supported our hypothesis that ineffective magnetic stirring to the melted reaction mixture with high viscosity might result in localized overheating and degradation of some polymer at high temperature. The tiny amount of the degraded products might be responsible for the color in the final polymers, although they were undetectable using NMR and FT-IR. Furthermore, a white translucent film (2 cm X 1 cm) of PCBS, as shown in Fig 3, was obtained by solution casting using dichloromethane (DCM) as the solvent, showing the processability of these polyesters.



Scheme 2. Synthesis of **CBDO-1** based polyesters.

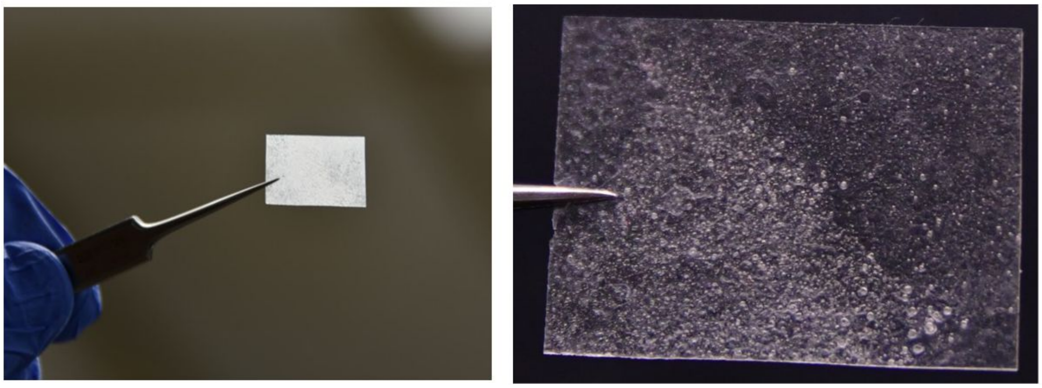


Fig 3. Images of the synthesized polycyclobutane succinate (PCBS).

It is worth noting that many of the diacids used in the polyester syntheses, such as succinic acid[21] and 2,5-furandicarboxylic acid,[22] can be produced from various biomass-derived precursors. The starting material for making both CBDA-1 and CBDO-1, *trans*-cinnamic acid, can also be obtained from glucose or Dried Distillers Grains with Solubles (DDGS), which is generated as a side product of dry mill ethanol production on a large scale and used as livestock feed.[23] Due to the possible environmentally-friendly origin of the starting materials, the CBPs are even greener compared to BPA-based polymers.

The polymers synthesized by the polycondensation were subjected to further purification by first dissolving them in a solution of chloroform and trifluoroacetic acid (TFA) in a 6:1 ratio, and then precipitating them by adding methanol. All the polyesters precipitated as amorphous powders with excellent isolated yields of 72 – 87%. NMR and FT-IR spectroscopy confirmed the structures of all the polyesters (see ESI). The molecular weight and molecular weight distribution of the CBPs were measured by Gel Permeation Chromatography (GPC) and compared with the weight average molecular weight (M_w) data obtained from Diffusion Ordered NMR Spectroscopy (DOSY).[24] DOSY linearly relates the chemical shifts of ^{1}H NMR resonances to the translational diffusion coefficient of a particular molecular species, which can be applied to determine M_w of polymers in dilute solutions. In diluted conditions, viscosity and density remain consistent throughout the solution, hence the linear relation between Log D_a and Log M_w using the Stokes-Einstein equation.[25] Commercial polystyrene (PS) standards were selected to obtain the D – M_w calibration curve due to its widespread use in GPC standards. Chloroform-d was used as a solvent due to its ability to dissolve most of the polyesters. Table S3 and Figure S38 in the ESI show the PS calibration curve in chloroform-d, with good linearity of Log D_a – Log M_w demonstrated by a high value of r^2 value of 0.9969. Furthermore, by extrapolating the calibration curve to the low molecular range, the M_w of chloroform-d was estimated as 122.97 g/mol with only 2.1% deviation from its calculated value, 120.38 g/mol. After the establishment of a calibration curve, diffusion coefficients of the CBP samples were fitted to the PS calibration curve to calculate the M_w. As shown in Table 1 and Fig 4, the M_w of CBPs obtained from DOSY ranged between 7,200 and

35,600 g/mol, which were consistent with the results from GPC (6,900 - 34,900 g/mol). The polydispersity indice (PDI) of the CBPs ranged from 1.55 – 2.91.

Table 1. Molecular weight distribution from GPC and externally referenced DOSY

Sample	**Molecular weight distribution GPC**			**Molecular weight data DOSY[a]**	
	M_n g/mol	**M_w g/mol**	**PDI**	**D_a m^2/s (10^{-10})**	**M_w g/mol**
PCBA	8,800	25,600	2.91	1.38	25,700
PCBG	5,300	8,900	1.66	2.33	9,500
PCBM	4,400	6,900	1.55	2.71	7,200
PCBO	6,300	14,900	2.28	1.79	15,700
PCBS	12,100	26,800	2.21	1.33	27,100
PCBT	11,000	23,100	2.11	1.48	22,300
PCBF	3,600	6,900	1.89	2.66	7,500
PCBC	23,400	34,900	1.49	1.15	35,600

[a] M_w (DOSY) were calculated using the PS calibration curve incorporating the experimental D values of the CBP samples

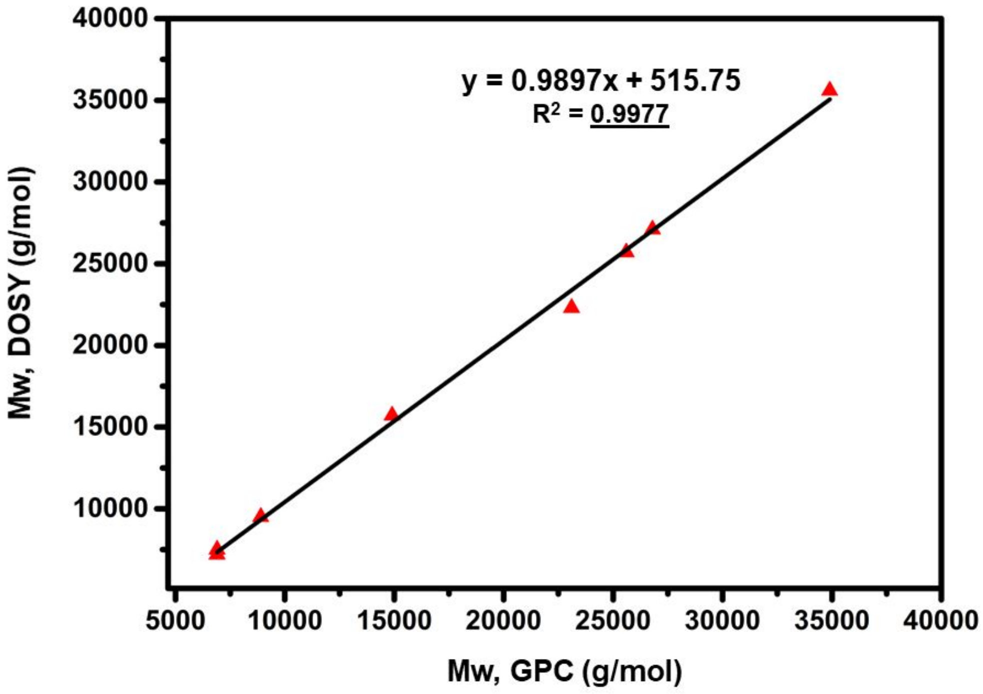


Fig 4. Comparison of M_w analysis of CBP samples by DOSY and GPC

To obtain more detailed structural information, MALDI-TOF mass spectrometry was performed on the CBPs. Fragments and oligomers with low mass (< 5000 Da), which had the same repeat units and possible end groups as high mass components, were studied to get structural information. Positive ion MALDI-TOF spectra were obtained for PCBS, PCBT, PCBF, and PCBC, and their results are summarized in Figures S34 – S37 (see ESI for the spectra and proposed structures). In general, the spectra of the CBPs were highly asymmetric and had dispersed fragment and oligomer distributions, which is expected for polycondensates. The individual repeated units are well displayed: 350 Da for PCBS, 398 Da for PCBT, 388 Da for PCBF, and 528 Da for PCBC, respectively.

In PCBS and PCBF, four main series of repeated units and oligomers are marked in Figures S34 and S36 and shown in different colors: cyclic (blue), linear with two acid end groups (yellow), linear with one acid and one alcohol end group (red), and linear with two alcohol end groups (purple). In contrast, peaks corresponding to the cyclic oligomers were not found in PCBT and PCBC, as shown Figures S35 and S37, due to the linear orientation and rigidity of the diacid moieties (i.e., terephthalic acid and CBDA-1). PCBT showed a series of high-intensity peaks from linear fragments with two alcohol end groups and a series of low-intensity peaks from linear fragments with both acid and alcohol end groups. In the case of PCBC, a series of peaks from linear fragments with two acid end groups were prominent, and two series of medium-intensity peaks were also observed, corresponding to the other two possible linear fragments. Interestingly, one additional series of strong peaks with a mass 148 Da less than the high-intensity peak at 2962 Da were observed. These peaks were presumably due to cleavage of the cyclobutane ring of the CBDA-1 moieties present in the polymer chains during the process of the MALDI experiment, which led to the formation of fragments with one end group as cinnamate (coded with black in Figure S37 of the ESI).

The thermal properties of the polyesters were analyzed using differential scanning calorimetry (DSC) under N_2 atmosphere. The samples were heated from 0 to 200 °C at a rate of 20 °C/min. After this step, they were isothermally held at 200 °C for 5 min, then cooled to 0 °C at a rate of 20 °C / min. DSC did not show a melting transition in any of the polymer samples, suggesting that all the materials are amorphous thermoplastics. As anticipated, the semi-rigid structure of the CBDO-1 monomer unit has a profound effect on thermal properties such as the glass transition temperatures (T_gs) of the final polyesters (Fig 5a). For instance, the substitution of the ethylene glycol unit with the cyclobutane unit increased the T_gs of the polymers substantially. The T_gs of the polyesters derived from CBDO-1 and aliphatic diacids such as succinic acid (PCBS) and adipic acid (PCBA) were approximately 50 °C and 80 °C higher than their ethylene glycol analogs, polyethylene succinate and polyethylene adipate, respectively (see Table S1 in the ESI). The effect of carbon chain length of the homologous diacids on the T_g of the polyesters is graphically represented in Fig 5b. This representation shows a considerable decrease in T_g with an increasing length of the carbon chain of the diacid; PCBG was found to have the lowest T_g amongst all the aliphatic polyesters, 33 °C, while PCBO had the highest T_g at 62 °C. This decrease was anticipated and can be attributed to the increase of chain mobility with higher flexible aliphatic content from 2-carbon oxalic acid to 6-carbon adipic acid. Interestingly, the polyesters with an even-numbered carbon chain (PCBO, PCBS, and PCBA) showed a higher T_g than the polyesters with odd-numbered carbon chains (PCBM, PCBG). This odd-even difference in T_gs shows that the packing and stereochemical properties of the even-numbered carbon chains form a better-organized structure in the solid phase, which requires more energy to move apart.[26]

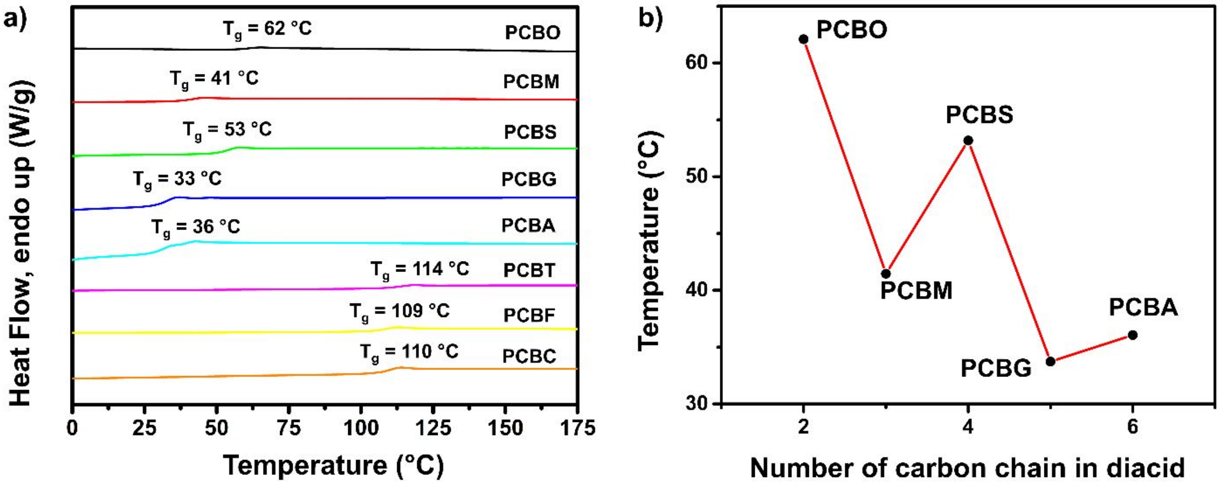


Fig 5. The DSC analyses of CBDO-1 polymers: a) second heating DSC curves of polymers derived form CBDO-1 at a heating rate of 20 °C/min under N_2. b) The plot of T_gs of polymers against carbon chain length of aliphatic diacids showing the odd-even difference.

Similarly, the introduction of CBDO-1 in conjunction with the rigid aromatic diacids also showed a clear impact on the T_g of the polyesters. It was observed that the T_gs of polyesters synthesized from CBDO-1 with terephthalic acid (PCBT), and 2,5-furan dicarboxylic acid (PCBF), were higher than those of the polyesters derived from aliphatic diacids, with PCBT and PCBF having T_gs of 114 and 109 °C, respectively. It should be noted that PET (polyethylene terephthalate) and PEF (polyethylene 2,5-furandicarboxylate) synthesized under similar conditions were shown to have T_gs of 80 °C and 87 °C, correspondingly, meaning that the replacement of flexible ethylene glycol with the semi-rigid CBDO-1 with its two phenyl substituents in the above two polymers significantly improved their T_gs. Furthermore, a sample of the popular Tritan copolyester, which is produced from polycondensation between DMT (dimethyl terephthalate) with both CHDM and TMCD (Fig 1), was shown to have a T_g of 109 °C.[10a] When CBDO-1 was used to replace CHDM and TMCD in this Tritan polyester, it was also not a surprise that a higher T_g was observed (PCBT: 114 ^oC), even at relatively low M_w, under the current experimental conditions (see Table 1). The obvious improvement in T_g can be attributed to the unique structure of the CBDO-1 monomer, which contains a semi-rigid cyclobutane backbone as well as two rigid and bulky phenyl substituents roughly perpendicular to the backbone. The phenyl groups stick out from the polymer backbone and restrict the movement of the polyester chains, resulting in a high T_g. For the same reason, the T_g of PCBC (the polyester synthesized from CBDO-1 and CBDA-1) was as high as 110 °C, which is comparable to those of the corresponding polyesters made from CBDO-1 and a rigid diacid such as terephthalic acid (PCBT with T_g of 114 °C) or 2,5-furan dicarboxylic acid (PCBF with T_g of 109 °C). Compared to the polyesters derived from CBDO-1 and the other aliphatic diacids, incorporating CBDA-1 in the polymer chain boosts the T_g of the polyesters by approximately 50 °C or more (Fig 5a).

The thermal stabilities of the CBPs were examined by comparing the temperatures at which the onset of decomposition, $T_{5\%}$ (5% weight loss), and maximum rate of decomposition (T_d) occur. Thermogravimetric analysis (TGA) was employed to measure these characteristics under a N_2 atmosphere, as shown in Figs 6a and 6b. As expected, the morphology of CBDO-1 does affect the decomposition temperatures of the synthesized polyesters. Fig 6 reveals that most of the CBPs showed high thermal stability without any significant weight loss below at 300 °C. PCBM exhibited a decomposition onset temperature ($T_{5\%}$) of 266 °C, while PCBA exhibited the highest $T_{5\%}$ of the CBPs using aliphatic diacids, at 350 °C. The thermal stability of CBPs increases slightly with increasing length of the linear diacids used in synthesizing the polyesters.[27] In the case of the aromatic diacids, PCBT and PCBF showed similar $T_{5\%}$ values, 363 °C and 341 °C, respectively. When CBDA-1 was used as the diacid, PCBC was obtained, which showed a $T_{5\%}$ of 383 °C, among the highest of all CBPs synthesized in this study. Notably, the maximum decomposition temperatures (T_d) of the CBPs were in the range of 380 to 424 °C, with less significant differences compared to those of the $T_{5\%}$, suggesting the decomposition of these polyesters might be governed by cleavage of cyclobutane moieties.

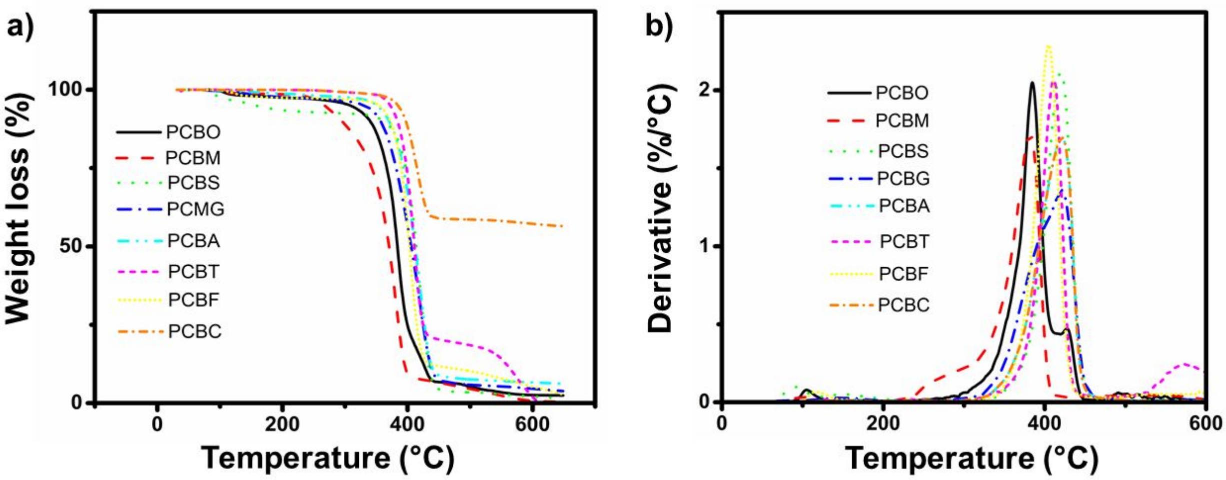


Fig 6. The TGA analyses of CBDO-1 polymers: a) TGA traces of CBDO-1 based polymers recorded from 30 to 600 °C at 20 °C/min under N_2. b) The plot of the first derivative of TGA traces (%/°C) against temperature.

It is important to point out that, besides polyesters, CBDOs can also be used to produce other industrially relevant polymers such as polyurethanes, polycarbonates, and polysilylethers, which are challenging to obtain from the previously reported CBDAs.

Thus, exemplified by CBDO-1 in this work, the use of CBDOs will largely extend the scope of novel polymers with desirable properties that utilize CBs.

Conclusion

A *trans*-1,3-cyclobutane-containing diol (CBDO-1) has been synthesized and introduced to materials science as a versatile monomer. In the first stage of the CBDO-1 synthesis, a diacid was yielded by dimerizing *trans*-cinnamic acid using 365 nm residential blacklight. The diacid was then reduced using a reliable and operator-friendly $NaBH_4/I_2$ system or by catalytic hydrogenation with an inexpensive catalyst, $CuO\text{-}CrO_3$, used in industry. This whole synthetic route is safe, efficient, and scalable. CBDO-1 was fully characterized, and its single crystal structure confirmed that the two methanol arms attached to the cyclobutane ring are trans to each other, showing this molecule's potential to serve as a monomer. As a phenol-free monomer, CBDO-1 shares structural similarities to BPA, as well as its replacements CHDM and TMCD, which have been used in producing the popular Tritan copolyester. The unique semi-rigid nature and thermal stability of the primary diol were then translated into a series of novel polyesters via a two-step melt polycondensation using titanium isopropoxide as a catalyst. The thermal properties, molecular weight distribution, and structural details of the CBDO-1 polyesters were investigated and discussed to evaluate the potential utilizations of these polymers as BPA-free polyesters. Compared to polyesters with established industrial importance such as PET, PEF, and Tritan copolyester, the amorphous cyclobutane-containing polyesters derived from CBDO-1 showed excellent thermal properties (e.g., high T_g, $\mathrm{T}_{d5\%}$, and T_d) due to the unique structure of CBDO-1. However, under the current polymerization conditions, the M_w of these polyesters was still inferior to their commercially available Tritan-based counterparts, suggesting efforts are still needed to further improve the molecular weight of the CBPs. Nevertheless, the successful synthesis of Tritan-like polymers, possessing desirable thermal properties, and not relying on the required petroleum feedstock of TMCD monomer, support CBDO-1 as a promising building block in the area of BPA-free thermoplastics.

Experimental

Materials and method

All chemicals were purchased from Alfa Aesar, Sigma-Aldrich, or Acros and used without further purification. Blacklight used in the photoreaction was produced by E27 40-watts HD 159 compact fluorescent bulbs or 15W Eiko EK15526 F15T8/BLs. The solution phase nuclear magnetic resonance spectra (NMR) were recorded with a Bruker AVANCE (1H: 500 MHz, 13C: 125 MHz). Proton and carbon chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) or using the resonance of corresponding deuterated solvent as an internal standard. ^{1}H NMR data were reported as follows: chemical shift (ppm), s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, and integration. Single crystal X-ray data were collected on a Bruker Kappa Apex II Duo X-Ray Diffractometer with Cu $K\alpha$ (λ = 1.54178 Å). Infrared spectroscopy (IR) was recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer. The mass spectrometric analyses were performed using a high-resolution time of flight G1969A with electrospray (atmospheric pressure chemical) ionization (Agilent, Santa Clara, CA, USA) and reported as m/z (relative intensity). Differential scanning calorimetry

(DSC) was recorded with a Perkin Elmer Jade DSC with a ramping rate of 20 ^{o}C/min under nitrogen protection. Heat flow was recorded from both the first heating and cooling curves. Thermogravimetric analysis (TGA) was carried out with a Hi-Res TGA Q500 from TA Instruments using alumina pans at a heating rate of 20 °C/min under nitrogen with a sample weight of about 10 mg. The molecular weight and distribution were measured using a 1220 Infinity II HPLC (Agilent, Santa Clara, CA), with Agilent OpenLab CDS software/GPC module, VWD detector, and Agilent Plgel Minimix-D reversed-phase column (5 mm pore size, 250 mm length, 4.6 mm ID) with molecular weight lower and upper limits of 200 and 400,000 Da respectively. All sample and calibration injection volumes were 30 uL, and the flow rate was 0.3 mL/min. Tetrahydrofuran (THF) was used as the solvent to dissolve the samples, and the mobile phase solvent was also THF. The concentration of CBPs in the solution was about 1 mg/mL, and the eluent flow rate was 0.35 mL/min. The PS standards were available in the range of 580 to 271,800 Mp, while PMMA standards were available from 550 to 56,600 Mp. The PS standards that covered this range well, without overlap, were 580, 1480, 5030, 8450, 38100, 70950, and 271800 Mp. PMMA standards that covered the PMMA range as well were 550, 960, 2880, 4640, 10280, 17810, and 56600 M_p. The PS and PMMA values above are presented with their peak molecular weights and general retention times in Table S2 (see ESI). Retention times are routinely measured in thousandths of a minute but vary somewhat with individual sequences; thus, the retention times listed in Table S2 are only listed to tenths of a minute.

Diffusion ordered spectroscopy (DOSY) experiments

NMR tubes were flame-dried in advance, and experiments were performed at 25 ± 1 °C. The data collection was done after stabilizing the NMR sample at RT for 30 min. For polystyrene standard samples, each NMR tube contained 0.5 mg of polystyrene and 1 mL of deuterated chloroform ($CDCl_3$). For CBP samples, each NMR tube contained 0.5 mg of polyester and 1 mL of chloroform-$CDCl_3$. DOSY experiments were performed on a Bruker AVANCE 500 spectrometer equipped with a z-axis gradient coil. All experiments were run without spinning to avoid convection. The maximum gradient strength was 0.214 T/m. The standard Bruker pulse program, stebpgp1s, employing a stimulated echo sequence and 1 spoil gradient, was utilized. Bipolar rectangular gradients were used with a total duration of 0.5−10 ms. Gradient recovery delays were 0.5−1 μs. Diffusion times were between 100 and 2000 ms. The number of gradient steps was set to be 16. Individual rows of the quasi-2-D diffusion databases were phased, and baseline corrected. DOSY spectra were processed by Topspin 1.3 software. The diffusion dimension was generated using inverse Laplace transform driven by the maximum entropy method. Diffusion coefficients of a chosen narrow chemical shift range were extracted from the T1/T2 analysis module of Topspin 1.3.

Synthesis of CBDA-1:

Method 1: Solid State Approach

The method used here was modified from the previously reported procedure by our group. It involves the use of operator-friendly household black lights as a source of irradiation. The photosynthesis was carried out on an 8 x 4-inch glass plate. 2.00 g of powdered *trans*-cinnamic acid was dispersed uniformly over the glass plate. This plate was irradiated with six 15W Eiko EK15526 F15T8/BL bulbs, three on top, and the other three on the bottom. The distance between the light source and glass plate was about 1.0 cm, as shown in Figure S1 (see ESI). The progress of the reaction was monitored by ^{1}H NMR spectroscopy. The powder was periodically re-blended uniformly to ensure even irradiation. After a total of about 60 h, the powder was collected and washed with 3 mL ethanol to obtain the product as a white solid (1.94 g, 97% yield). The product was determined as the titled compound, consistent with the previous reports.

Method 2: Brine Slurry Approach

This method is suitable for larger-scale reactions and is more operator friendly. Specifically, 5.00 g *trans*-cinnamic acid powder was suspended in 2 L of brine solution in a crystallizing dish or beaker with magnetic stirring. Three E27 40W HD 159 black lights were immersed in the crystallizing dish, as shown in Figure S2 (see ESI). The slurry was continuously stirred under the black lights for 72 h. To ensure that the brine was as transparent as possible, 25 mL water was added into the brine before the reaction and each day during the slurry photoreaction. The slurry was then filtered, and the solid was washed with 10 mL ice-cold water. After air-drying, the desired product was obtained as a white solid (4.75 g, 95% yield). The same slurry photoreaction that was done by suspending cinnamic acid powder in water only gave a yield of 78% (3.9 g) mainly due to the solubility of cinnamic acid and CBDA-1 in water. Additionally, it’s much easier to disperse cinnamic acid powder in brine than in water because cinnamic acid can easily accumulate on the surface of the glassware in the latter case, which slows down the reaction and makes it difficult to collect the product.

Synthesis of CBDO-1

Method 1: Reduction with $NaBH_4/I_2$

In a 100 mL round bottom flask fitted with a Claisen head adaptor, a magnetic stir bar and finely powered $NaBH_4$ (0.89 g, 23.59 mmol – 7 molar equivalent) was added to 25 mL of THF. This suspension was stirred for 10 min, and then CBDA-1 (1.00 g, 3.37 mmol) was added to the suspension. The addition resulted in bubbling (CAUTION: hydrogen gas is flammable). When the reaction mixture stopped bubbling, a solution of I_2 (1.71 g, 6.74 mmol) in THF (15 mL) was added dropwise, using a dropping funnel attached to the Claisen head, over a period of 45 - 60 min. The addition of I_2 is an exothermic reaction and resulted in significant evolution of H_2 gas. During this addition, the color of the mixture changed from red to yellow to colorless, indicating the disappearance of I_2. After the disappearance of all I_2, a water condenser was attached to the Claisen head, and the solution was heated to reflux. After 16 h of refluxing, the reaction mixture was analyzed using TLC (10 % Methanol in Dichloromethane as solvent) to verify the absence of the starting material. Approximately 40 mL of THF was removed using a rotary evaporator, and a white solid was collected from the flask. To this white solid, 20 mL of cyclohexane and 30 mL of 10% NaOH solution were added and stirred until bubbling from the mixture ceased (approximately 30 min). After 1 hour, a white solid precipitated, which was filtered using a Buchner funnel, and subseuently washed with 3 X 10 mL of 3M NH_4OH, then with 10 mL of 12 % $NaHSO_3$ to remove leftover I_2. The white solid obtained after filtration was dissolved in chloroform, and this organic layer was washed three times with a saturated brine solution. The removal of chloroform yielded the desired product CBDO-

1 (0.84 g; 93% yield) as a white solid, which was confirmed by NMR using $CDCl_3$ as the solvent. Melting point: 106.4 – 107.0 °C (Three concordant melting point readings were taken: (i). 106.5-106.9 °C; (ii). 106.4- 107.0 °C; (iii). 106.4-107.0 °C). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.07 (s, 2H), 3.12-3.18 (m, 2H), 3.40-3.47 (m, 4H) 3.49-3.52 (m, 2H), 7.13-7.27 (m, 12H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 36.37, 37.64. 58.45, 121.80, 122.90, 123.87, 134.92 ppm. FT-IR (solid): v = 3307.12, 2931.36, 1448.66, 1496.15, 1014.64, 1600.72, 743.33, 696.68 cm^{-1}. HRMS (ESI/TOF): Calculated for $[M +Na]^+$, $C_{18}H_{20}O_2Na^+$: 291.1361 g/mol ; Found: 291.1370 g/mol.

Method 2: Catalytic hydrogenation

CBDA-1 (1.69 mmol) and CuO-CrO_3 (100 mg) were added to 20 ml of water/ dioxane mixture (1:1) in a stainless steel reactor equipped with a magnetic stirrer and pressure regulator. The reactor was then sealed and purged with argon, then with hydrogen, and this process was repeated three times. Hydrogen gas was introduced at a pressure of 15 MPa, and the temperature was raised to 180 °C. The reaction mixture was allowed to stir for 12 h. Next, the reaction mixture was filtered through celite, and the filtrate was extracted with EtOAc (3 X 5 mL). The extract was dried with $MgSO_4$, and subsequent evaporation of the solvent afforded the product, CBDO-1, as a white solid, which was confirmed by NMR.

General method of polycondensation

Polycondensation was conducted in a 15 mL round bottom flask containing a magnetic stir bar equipped with a Claisen head, one neck being attached to an Argon gas inlet and the other neck connected to a water condenser. The reaction flask was charged with a finely ground mixture of CBDO-1 (1.06 mmol) and a dicarboxylic acid (1.28 mmol). The setup was placed under a vacuum and purged with argon gas - this process was repeated three times. The polycondensation was then performed in two steps. In the first step, the reaction was carried out under argon gas to promote the formation of oligomers. The reaction mixture was heated in a sand bath at 130 °C for 15 min with constant stirring. When complete melting of the mixture was observed, the catalyst titanium isopropoxide $Ti(OiPr)_4$ (1.25 mol%), in 1 mL of toluene, was then added to the reaction flask under a continuous flow of argon gas. Afterward, the temperature was increased to 170 °C and allowed to stir for 12 h, and finally to 200-215 °C for 1.5 h to complete the first step. In the second step of polycondensation, to connect the oligomers to form a long chain, a vacuum was gradually applied to the flask at 210-215 °C for 2 h (Scheme S1 in ESI). After reaction completion, the reaction mixture was cooled to room temperature under the flow of argon gas. The polymer was further purified by dissolving it in 5 mL of chloroform-TFA mixture (6:1). It was then precipitated by adding 50 mL of methanol, filtered, and dried under vacuum at 40 °C for 12 h to yield the desired powder. When using an external mechanical stirrer, a 3-neck 100 mL round bottom flask was used, one neck being attached to the argon inlet and the other two for the mechanical stirrer and water condenser, respectively.

PCBO: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.29-3.72 (m, 2H), 4.05 (s, 2H), 7.30 (s, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.10, 41.86, 63.44, 67.07, 127.41, 128.09, 128.33, 129.04, 129.21 ppm; FT-IR (solid): v =3026.52, 2938.94, 1740.28, 1234.35, 1080.48 cm^{-1}.

PCBM : ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.91 (s, 2H), 3.34 (s, 2H), 3.58 (s, 2H), 3.90 (s, 2H), 7.23-7.31 (m, 10H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.14, 41.31, 42.03, 66.01, 127.18, 128.08, 128.92, 138.93, 166.37 ppm; FT-IR (solid): *v* = 2944.19, 1728.12, 1143.08, 1004.63 cm^{-1}.

PCBS : ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.20 (s, 2H), 3.37 (s, 1H), 3.63 (s, 1H), 3.93 (m, 2H) 7.23-7.32 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.05, 39.38, 42.09, 65.25, 127.08, 128.13, 128.87, 139.20, 172.30 ppm; FT-IR (solid): *v* = 2924.51, 1728, 1150.50 cm^{-1}.

PCBG : ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.57 (s, 1H), 1.98 (s, 2H), 3.39 (s, 1H), 3.64 (s, 1H), 3.94 (s, 2H), 7.22-7.32 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.10, 33.31, 39.57, 42.21, 65.01, 127.09, 128.24, 128.87, 139.27, 173.03 ppm; FT-IR (solid): *v* = 2942.10, 1727.41, 1147.00 cm^{-1}.

PCBA: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 2H), 2.02 (s, 2H), 3.43 (t, 1H), 3.67 (t, 1H), 3.94 (m, 2H), 7.23-7.32 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.44, 33.94, 39.52, 42.19, 64.98, 127.07, 128.86, 139.31, 173.46 ppm. FT-IR (solid): *v* = 2942.45, 1727.52, 1139.05 cm^{-1}.

PCBT: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.16 (m, 1H), 3.35 (s, 1H), 3.80 (m, 2H), 6.76-6.93 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.59, 37.04, 60.55, 121.96, 122.94, 123.76, 124.38, 128.74, 133.85, 160.56 ppm. FT-IR (solid): *v* = 2941.32, 1708.74, 1264.18, 1100.43 cm^{-1}.

PCBF: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.53 - 3.60 (m, 1H), 3.76 (t, 1H), 4.16 - 4.24 (m, 2H), 6.83 (s, 1H), 7.18 (t, 1H), 7.29 (t, 2H), 7.24 (d, 2H), ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.20, 41.75, 65.45, 118.11, 126.81, 127.62, 127.79, 128.54, 138.43, 146.47, 157.53 ppm. FT-IR (solid): *v* = 2942.85, 1716.13, 12.67.72, 1220.04, 1129.77 cm^{-1}.

PCBC: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.70 – 4.17 (m, 6H), 7.04 – 7.08 (d, 2H), 7.17 – 7.23 (m, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): 39.27, 41.37, 41.97, 47.10, 64.74, 127.05, 127.41, 127.63, 127.92, 128.22, 128.81, 139.16, 139.24, 172.00 ppm. FT-IR (solid; *v* = 3027.52, 1723.96, 1167.70, 695.43 cm^{-1}.

Conflicts of interest

There are no conflicts to declare

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A *trans*-1,3-cyclobutane-containing diol (CBDO-1) has been synthesized and introduced to materials science as a versatile monomer and a possible phenol-free BPA replacement.