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Ketene-Based Route to rigid Cyclobutanediol Monomers for the Replacement of BPA in High Performance Polyesters

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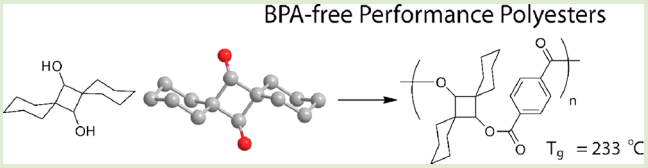
Supporting Information

ABSTRACT: Recently, polyesters based on the diol monomer 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBDO) have been shown to exhibit excellent thermal stability, mechanical properties, and optical clarity. In particular, the ability of TMCBDO to replace bisphenol A as a diol monomer in polycarbonates and polyesters has resulted in significant commercial and academic interest in these types of monomers. Herein, we report a versatile synthetic strategy based on the dimerization of ketenes derived from the thermal treatment of Meldrum's acid for the synthesis of structurally diverse cyclobutanediol (CBDO) monomers. This strategy allows a library of CBDO monomers amenable to standard polyester polymerization procedures to be prepared and the structural diversity of these CBDO monomers provides polymers with tunable physical properties, such as glass transition temperature ranging from 120 to 230 °C. The versatility and modularity of this Meldrum's acid-based approach to substituted cyclobutanediols, combined with the ease of synthesis, will be important for the further development of high-performance polyester materials that are not based on bisphenol A.



Thermoplastics have demonstrated their importance as commodity materials in a variety of applications ranging from digital media storage, to bullet-resistant glass and beverage containers.[1−3] In this field, the most widely used amorphous thermoplastic is polycarbonate (PC), a polymer synthesized via a condensation polymerization of bisphenol A (BPA) with either phosgene or diphenylcarbonate.[4] The success of PC is a result of its processability combined with beneficial properties such as high glass transition temperature (T_g), optical clarity, and high impact resistance.[3,5] PC, however, has recently come under significant scrutiny because of major issues with UV-instability, residual stress in molded objects, and most importantly, the leaching of potentially hazardous BPA monomer into food storage containers.[1,5−11] The fact that BPA is a known carcinogenic compound and endocrine disruptor has sparked significant interest in the development of replacement materials that are not based on BPA.[12−15]

The search for thermoplastics to replace PC is complicated by the fact that conventional, aliphatic polycarbonates and polyesters do not meet the necessary thermal and mechanical requirements when compared to BPA-containing materials.[1] Recently, the design and synthesis of cyclic, rigid aliphatic diols to replace BPA has emerged as a viable solution, especially with the commercial success of Tritan, Eastman Chemical Company's high performance copolyester. The key technological breakthrough for Tritan is the use of *cis*/*trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBDO) as a rigid, aliphatic diol in condensation-type polyester polymerizations.[16−21] This polymer has gained significant attention due to its exceptional physical and mechanical properties, as compared to PC, while completely eliminating the use of BPA as a monomer.[16−21]

Synthetically, the rigid cyclobutane ring is accessed through the [2 + 2] dimerization of a ketene functional group.[22] The commercial synthesis of TMCBDO involves flash vacuum pyrolysis (FVP) of isobutyric anhydride to produce dimethylketene, ketene dimerization to provide tetramethyl cyclobutanedione, and subsequent hydrogenation (Scheme 1A).[20,22] This synthetic procedure, however, inherently limits access to diverse cyclobutanediols due to the limited availability of substituted anhydrides and the necessity of obtaining a low molecular weight, volatile ketene for purification purposes. Due to these synthetic challenges, the study of substituted derivatives of these commercially valuable cyclobutanediols in commodity polymer production has been underdeveloped.

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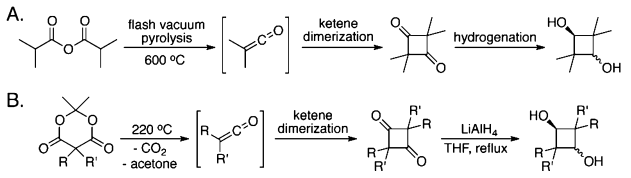
Scheme 1. (A) Synthetic Procedure Used Commercially for the Preparation of 2,2,4,4-Tetramethyl-1,3-cyclobutanediol (TMCBDO); (B) General Route to Make Cyclobutanediols from Meldrum's Acid Derivatives

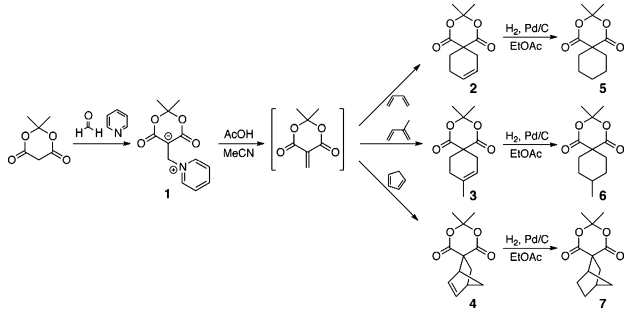


Herein, the synthesis of a variety of substituted cyclobutanediols and the evaluation of their potential as replacement diols for high performance polyesters is reported. The key synthetic step involves the quantitative generation of substituted ketenes by thermal treatment of 5,5′-dialkyl Meldrum's acid derivatives (Scheme 1B).[23] The advantages of ketene generation from Meldrum's acid include significantly lower temperature demands as compared to FVP, the simple removal of the volatile reaction byproducts of acetone and carbon dioxide, and the rich array of possible substitutions for the generated ketenes.[24] Our group has exploited these benefits in the application of a ketene based strategy to cross-link and functionalize polymer films,[24] enhance the processing and synthesis of polyolefins/polyesters,[25] and stabilize nanostructured materials.[26] In this study, the versatile chemistry of Meldrum's acid is exploited to prepare a variety of ketenes, providing a structural array of cyclobutanediol monomers. The performance of these cyclobutanediols in polyester materials is demonstrated.

The general strategy for the preparation of cyclobutanediol monomers from Meldrum's acid derivatives is shown in Scheme 1B and demonstrates the importance, as well as the opportunities, afforded by the substituents R and R′ present in the original Meldrum's acid skeleton. Key to this synthetic strategy is the rich chemistry associated with the acidic methylene group of Meldrum's acid, which can act as a nucleophile in alkylation reactions, or can alternatively be used to synthesize a highly reactive dieneophile for Diels–Alder chemistry, to produce a range of structurally diverse CBDO monomers. The quantitative formation of substituted ketenes from Meldrum's acid derivatives upon thermolysis (ca. 220 °C) is well documented,[23−27] with the facile nature of this reaction being evidenced in our hands by the short reaction time of 10 min and the high yields of cyclobutanedione derivatives.

To introduce dense, rigid functionality, and in some cases asymmetry, into the cyclobutanediol building block, spirocyclic Meldrum's acid derivatives were prepared by Diels–Alder cycloaddition chemistry with the zwitterion **1** employed as a stable precursor to the methylene Meldrum's acid.[28a] Multigram synthesis of **1** was achieved by condensation of Meldrum's acid with formaldehyde and pyridine, which on treatment with acid generates a dienophile in situ that is reactive with a wide variety of Diels–Alder dienes (Scheme 2).[28] Initially, simple dienes were selected to demonstrate the versatility of this approach as well as the structural diversity inherent in the corresponding Meldrum's acid and cyclobutanediol derivatives. Reaction with butadiene, isoprene and cyclopentadiene all proceeded with high yields to afford the desired Diels–Alder adducts **2**–**4**. These spirocyclic MA derivatives were hydrogenated to produce **5**–**7**, which removed the remaining alkenes to prevent retro-Diels–Alder reactions

Scheme 2. Synthesis of Spirocyclic Meldrum's Acid Derivatives Employing Diels-Alder Cycloadditions from the Common Starting Material 1



during ketene formation. Heating of the fully saturated cyclic derivatives to 220 °C resulted in rapid (10 min) formation of the ketene and in situ [2 + 2] cycloaddition to give the 2,2,4,4-cyclobutanediones. After filtration over a small plug of silica, the cyclobutanediones were obtained in yields typically exceeding 90%. Subsequent reduction with lithium aluminum hydride gave the desired mixture of *syn* and *anti* cyclobutanediols, **8**–**10**, in quantitative yields (Figure 1).

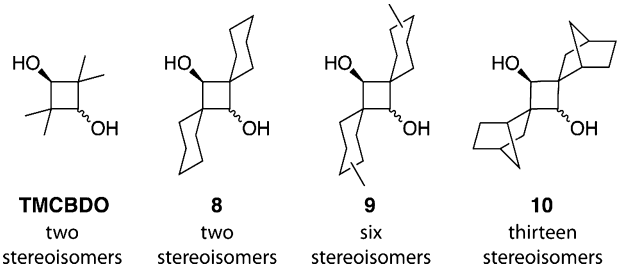


Figure 1. Diol monomers, **8**–**10**, prepared from spriocyclic Meldrum's acid derivatives.

For all of these monomers, stereochemistry of the cyclobutanediol impacts the final material properties.[20] Generally, mixtures of isomers in the polymer are thought to be advantageous by inhibiting crystallinity and thus improving clarity. For TMCBDO and the cyclohexyl-substituted monomer **8**, only *syn*- and *anti*-alcohol isomers are possible. With the reported methodology, the number of stereoisomers can be significantly increased by employing complex dienes that react under the regiorandom nature of the Diels–Alder conditions. In this case, we hope to employ structurally similar isomers that can provide enhanced disorder to inhibit crystallinity while still maintaining beneficial thermal properties. During the course of the synthesis of monomer **9**, for example, reaction with isoprene can occur in two possible ways, placing the methyl group on either the 3 or 4 position of the cyclohexyl ring. As a result, the number of isomers is increased to 3 upon ketene dimerization, and then doubled to 6 upon reduction to the diol. Characterization of this stereochemical complexity was possible through ^{1}H NMR analysis of Meldrum's acid derivative, **3**, with the major product being the 4-methylcyclohexene derivative (93%) and the minor product being the 3-isomer (7%), with excellent batch-to-batch consistency. The complexity of the monomer set increases further for the norbornene derivative, **10**, with as many as 13 different isomers being possible in the final diol. While these complex monomer mixtures are advantageous for a number of polymer properties, for example

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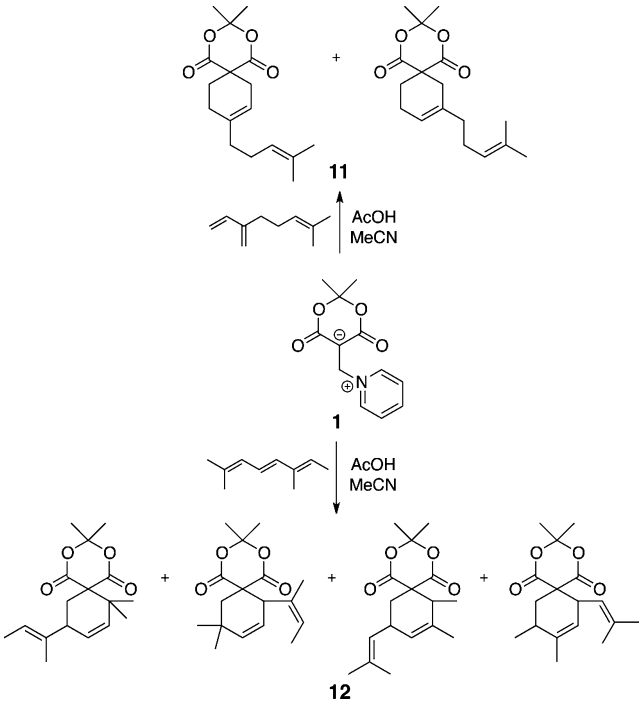
clarity, they do pose challenges in determining monomer purity. To address this issue, extensive GC-MS and HPLC-MS analysis was performed on the monomer mixtures. Significantly, chromatographs with multiple peaks were observed with each peak corresponding to the expected mass for the respective monomer units, demonstrating the high purity of the desired cyclobutanediol monomer units despite the complex mixture of isomers.

Our success synthesizing and characterizing complex cyclobutanediol products led us to consider more readily available and structurally diverse dienes. Specifically, employing renewable, nonpetroleum based dienes would make these cyclobutanediol monomers attractive as bioplastics.[29] Terpene derivatives provide a number of inexpensive, commercially available dienes that are isolated from plant species. Myrcene, for example, contains a reactive diene and can be used to introduce a prenyl group, while alloocimene, having two reactive diene sites, provides a number of interesting regioisomeric cycloaddition products (Scheme 3). As expected,

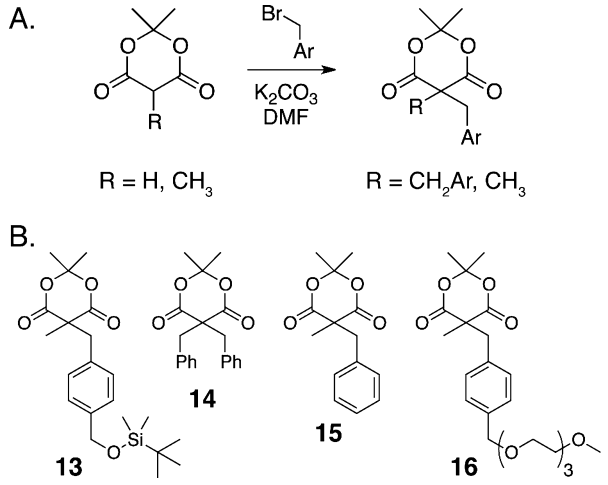
Scheme 3. Simple Terpenes Provide a Range of Densely Functionalized, Rigid Spirocyclic Meldrum's Acid Derivatives: the Mix of Isomers is Carried Through Monomer Synthesis



one major isomer was observed for compound **11**, whereas a complex mixture of products was isolated in the case of **12** due to the mixture of regioisomers as well as the lack of stereospecificity. However, the successfully synthesized Diels–Alder adducts for both of these products were carried on through synthesis as mixtures of isomers.

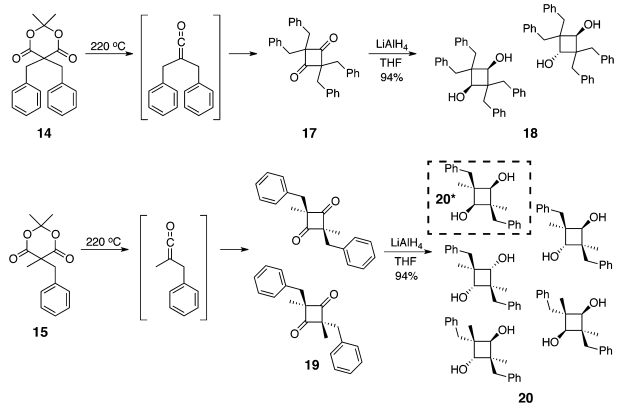
Along with the spirocyclic CBDO structures accessible through Diels–Alder reactions, the rich chemistry of Meldrum's acid also allows the acidic methylene group to participate in nucleophilic substitution. When K_2CO_3 is used as a base in DMF, a series of derivatives were prepared from both Meldrum's Acid and commercially available 5-methyl-Meldrum's acid, as shown in Scheme 4. This synthetic route

Scheme 4. Meldrum's Acid Derivatives Prepared by Alkylation Chemistry



allowed access to an array of functional Meldrum's acid derivatives, including the hydrophilic, ethylene glycol-based monomer **16** and the protected alcohol-functional Meldrum's acid **13**. For these derivatives, however, it is instructive to compare monomers **14** and **15**. Both compound **14** and its resulting cyclobutanedione, **17**, are highly symmetric, crystalline materials. The resulting monomer, like both TMCBDO and **8**, is simple to analyze as it contains only two isomers arising from the relative positions of the alcohols. In contrast, thermolysis and dimerization of **15** provides cyclobutanedione **19** as a mixture of two isomers. Reduction with lithium aluminum hydride results in the dibenzyldimethyl monomer **20** as a complex mixture of five stereoisomers (Scheme 5). Interest-

Scheme 5. Symmetric Meldrum's Acid 14 Provides only Two Stereoisomers of 18, while Asymmetric 15 Provides a Mixture of Five Distinct Stereoisomers



ingly, this mixture was enriched with isomer **20***, which contains both alcohols and both benzyl groups on the same face of the cyclobutane ring. The enrichment of the cyclobutanedione with both benzyl groups on the same side is expected from the antarafacial nature of the ketene cycloaddition, which favors placing the largest substituents on the same face of the crowded ring-system.[30] This stereochemistry then allows the hydride to attack more readily from the less hindered, methyl-group functional face. This stereodefined isomer could be simply isolated by recrystallization from the

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mixture of isomers, with single crystal X-ray diffraction providing confirmation of the stereochemistry (Supporting Information).

Having successfully prepared a library of high purity cyclobutanediol monomers, the procedure of Hoppens et al. was followed for polymer synthesis.[21] This procedure involved reaction of the diol monomer with 1 equiv of terephthaloyl chloride in the presence of catalytic pyridine in *o*-dichlorobenzene under a flow of argon. Moderate molecular weights, based on polystyrene standards, were obtained in all cases with the deviation in molecular weight between polymers being due to a combination of inherent variations in the condensation polymerization conditions (e.g., stoichiometry, scale) and likely the steric hindrance in the different monomers. Further, thermal characterization data has been obtained on each polymer through the use of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA; Table 1). It should be noted that a commercial sample of Tritan was shown to have a T_g of 109 °C and is known to be a copolymer containing TMCBDO and other diol monomers.

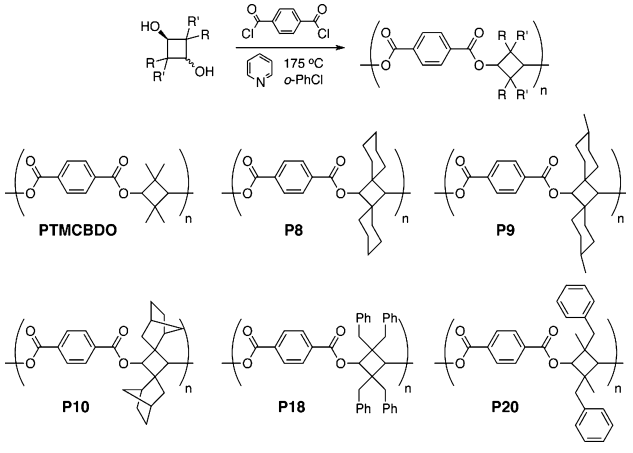
Table 1. Physical and Thermal Characterization of Polyesters

	M_n[a] (kg/mol)	M_w (kg/mol)	PDI	T_d[b] (°C)	T_g (°C)
tritan	26.5	53.1	2.0	365	109
PTMCBDO	13.5	29.5	2.2	350	200
P8	11.4	23.0	2.7	368	233
P9	3.6	11.8	3.3	364	211
P10	4.5	10.3	2.3	331	205
P20	3.2	6.7	2.1	290	122
P20*	4.2	8.0	1.9	298	137

[a]Molecular weights are relative to polystyrene standards. [b]T_d was determined as the temperature for 5 wt % mass loss.

To better compare these novel cyclobutanediol monomers, we synthesized a homopolymer of the commercially available TMCBDO with terephthaloyl chloride using Hoppens procedure (Scheme 6). The polymer containing only TMCBDO displayed a T_g of 200 °C, which is in accordance with previous literature.[20g] No melting transition was observed by DSC in any of the polymer samples, indicating that all materials are amorphous thermoplastics.

Scheme 6. Polyester Synthesis Is Carried out with Terephthaloyl Chloride and Structurally Diverse Cyclobutanediols to Provide a Library of Polymeric Materials



As expected, the structure of the cyclobutanediol monomer unit has a profound effect on the thermal properties of the final polymer. For example, subtle synthetic variations in molecular structure led to an ability to tune the T_gs of the polyesters from 120 to 230 °C. Significantly, the methodology presented here allows for the discovery of alternative CBDO-based monomers. Spirocyclic derivatives **8**−**10** produce polymers (**P8**−**P10**) with higher T_gs and decomposition temperatures than that of PTMCBDO, even at lower molecular weights (Table 1).

Moving to CBDOs with more flexible side chains, such as the benzyl groups on **P20**, drastically decreases the T_g of the material to 122 °C. With the ability to purify a single stereoisomer from the mixture of diols of **20**, however, a polymer could be made of the isomer **20***. Interestingly, the polymer made from **20*** showed similar molecular weight to **P20** while displaying a T_g of 137 °C and no melting point, which is expected for a polymer made of exclusively *syn*-diols.[31] This difference in T_g for a stereodefined polymer shows that stereochemistry of the CBDO does affect the final thermal properties of the polymer, and this phenomenon can be employed as a synthetic handle to further tune the structure/property relationships in these polymer systems.

In addition, the steric bulk of the substituents on the CBDO was shown to impact the polymerization of these monomers. In the spirocyclic family of monomers, it was observed that the polymers of the norbornyl substituted monomer **10** were typically lower molecular weight when compared to those derived from monomers **8** and **9**, although comparably sized polymers could be isolated by fractional precipitation or preparative SEC. Similarly, polymers were not accessible from the highly crowded tetrabenzyl CBDO **18** under our conditions, with only methanol-soluble oligomers being observed. These results point to the delicate balance between the need for rigid and compact CBDO substituents, such as the methyl, cyclohexyl, and methylcyclohexyl derivatives that show improved properties, with the restriction of limiting steric bulk around the secondary alcohol.

In conclusion, a versatile and modular strategy for the synthesis of 2,2,4,4-tetrasubstituted-1,3-cyclobutanediol monomers and their corresponding high performance polyesters has been developed. The use of Meldrum's acid as a thermolytic ketene precursor allows for the study of the structure/property relationships for different substitution patterns on these cyclobutanediol monomers. The potential to increase the thermal properties of the polymers while maintaining or decreasing the required feed of cyclobutanediol monomers in the production of Tritan-like polymers makes these monomers promising building blocks for the production of BPA-free amorphous thermoplastics. Further work is required to study the polymerizability of these substituted cyclobutanediols which will allow high molecular weight polymers to be obtained and the mechanical properties to be evaluated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Methods, synthetic procedures, and complete characterization of materials. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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