STRONGER PLASTICS AND BETTER ANTI-GLARE COATINGS:

EXPLORING THE PROPERTIES OF A FLUORINATED CBDO STRUCTURE

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EXPLORING THE PROPERTIES OF A FLUORINATED CBDO STRUCTURE

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ABSTRACT

STRONGER PLASTICS AND BETTER ANTI-GLARE COATINGS:
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by

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Exciting advances have been made in recent years regarding both polymers that incorporate fluorine atoms or groups and polymers that incorporate 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) based monomers into their backbone. A wide range of polymers have incorporated fluorine into their systems, usually in the form of trifluoromethyl ($-CF_3$) groups. These groups increase the thermal and thermooxidative stability, flame resistance, mechanical stability, and optical transparency. The latter, especially, makes these systems optimal for anti-glare coatings for eyeglasses, military and commercial aircraft windows, and spacecraft windows. Incorporating trifluoromethyl groups into a polymer system via a cyclic structure opens the door to the potential for some particularly exciting properties, especially those of mechanical and

thermal stability. A process for the preparation of the novel compound 2,2,4,4-tetrakis(trifluoromethyl)cyclobutane-1,3-diol (F_{12}-CBDO) is described. Polymers incorporating this new monomer were expected to show superior mechanical and thermal stability, flame resistance, optical transparency, and other properties compared to their non-fluorinated counterparts. They were also expected to show superior properties compared to systems that did not incorporate a CBDO monomer at all. While successful synthesis of the F_{12}-CBDO monomer was not achieved in the time constraints of this experiment, several considerations for future research concerning this monomer are discussed.

I.   DEFINITIONS OF TERMS

Organic. In Chemistry, the term *organic* refers to any molecule with a
hydrocarbon backbone. That is, if the main section of the molecule consists of carbon
atoms with attached hydrogen atoms, the molecule is considered organic. Because
carbon shows a high affinity for having four bonds at any given moment, hydrogen tends
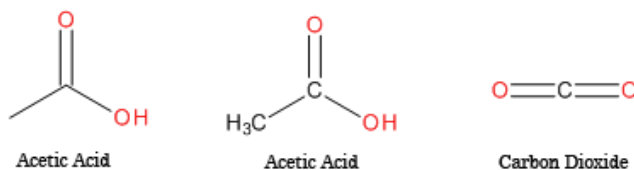to fill any gap where carbon is unbonded to any other molecule.

| Acetic Acid | Acetic Acid | Carbon Dioxide |

Figure 1. Examples of organic versus inorganic molecules.
Shown are the skeletal structure of acetic acid, the explicit
structure of acetic acid, and carbon dioxide.

Figure 1 depicts the difference between organic and inorganic molecules. Here is
shown the structures of acetic acid (CH_3COOH), which is organic, and carbon dioxide
(CO_2), which is inorganic. Though both contain carbon and oxygen, acetic acid also
contains hydrogen, fulfilling the requirements for an organic molecule. Also shown in
Figure 1 is a common method for drawing organic molecules, the skeletal formula. On
the left is shown the skeletal formula of acetic acid, in which carbons are shown as
vertices (bends) and termini (ends) in the line, hydrogens are understood to fill any gaps
where any carbon would otherwise have less than four bonds, and all other atoms are
expressly drawn (such as the oxygen, as well as the hydrogen bonded to the oxygen in the

–OH group); in the middle is shown the structural formula, in which each atom is shown explicitly. Skeletal formulae will be used for drawing the molecules contained in this text.

Functional Groups. Figure 2 depicts some organic functional groups that are important for understanding the structures shown in this text. A R-OH group is called an alcohol, where the R depicts any hydrocarbon—in the case of ethyl alcohol, the R group is CH_2CH_3. Alcohols are often shortened to the suffix "-ol" when naming compounds; for instance, ethyl alcohol can also be named ethanol. A R-COOH group, such as that seen in acetic acid, is a carboxylic acid. The -OH group in acetic acid is not considered an alcohol because of its affiliation with the carbonyl group. A R-(C=O)-R' group is called a ketone, abbreviated to the suffix "-one" when naming compounds; R and R' can be different hydrocarbon groups, though both are CH_3 groups in the case of propanone. A R-COO-R' group is called an ester; like a ketone, R and R' can be different, but are both CH_3 in the case of methyl acetate.

Ethyl Alcohol   Acetic Acid   Propanone   Methyl Acetate
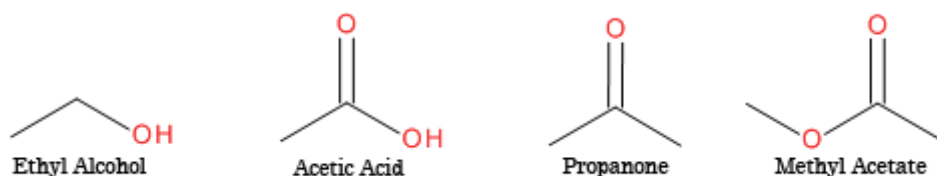
Figure 2. Relevant functional groups demonstrated. Structures for ethyl alcohol, acetic acid, propanone, and methyl acetate are shown. These structures demostrate the alcohol, carboxylic acid, ketone, and ester functional groups, respectively.

Synthesis. Synthesis is the formation of a target molecule through a chemical reaction or series of reactions. Synthesis can utilize organic compounds, inorganic compounds, or a combination of both. It can also apply techniques ranging from the very simple, such as merely heating to overcome a reaction's transition energy threshold and

allow the reaction to proceed, to highly complex. Organic synthesis often requires multiple steps, collectively called the synthesis scheme, to obtain a target molecule.

Aliphatic and aromatic compounds. An aromatic compound is a compound which contains a cyclic delocalized π-electron system. As it pertains to this text, the definition can be simplified to a compound which contains a benzene ring consisting of six carbons.[1] An aliphatic compound is simply a compound that is not aromatic; that is, aliphatic compounds are those that do not contain a benzene ring.[1]

Monomers and polymers. A monomer is a single unit that can be repeated as part of a longer chain.[1] A polymer is defined as a macromolecule comprising repeating monomers, though there are many ways in which these monomers can link together.[1] The easiest way to understand polymers is to think of something like paperclips, with each monomer represented as a single paperclip. A single monomer type (red paperclips) can be linked together to form a long chain of red paperclips, or different monomers can be linked together in various configurations, such as A-B (red-blue). Additionally, an amorphous polymer is one in which monomers are oriented randomly in the polymer and may intertwine (like cooked spaghetti) rather than being oriented in an ordered or predictable manner; semicrystalline polymers, often formed from linear polymers (shaped like uncooked spaghetti), are examples of ordered systems. Amorphous polymers tend to have a transparent appearance and are preferable for optical applications.

Optical properties. Optical properties refer to the amount of light that is transmitted through, absorbed by, or reflected off of a material. Good optical properties as discussed here relate to high transmittance. This means that less glare (reflection) will

be present and higher clarity will be seen through the material. These materials are excellent for uses such as windshields and eyeglass lenses, or for coatings on such.

Dielectric constant. The dielectric constant of a material refers to the ratio of the electric displacement in a medium to the electric field strength.[1] Therefore, a low dielectric constant grants a material some resistance to breakdown when subjected to applied electric fields and allows them to act as insulators. However, materials with high dielectric constants are generally preferred when making capacitors (for storing charge). For the polymers for which the synthesis is discussed in this text, low dielectric constants are preferable.

Glass transition temperature (T_g). T_g is "the temperature at which an amorphous polymer is transformed, in a reversible way, from a viscous or rubbery condition to a hard and relatively brittle one."[1] At temperatures lower than the T_g, the material is hard, whereas above the T_g, the material is rubbery. An example of this phenomenon can be seen by dipping a rubber band in liquid nitrogen. At very cold temperatures, the rubber band becomes hard and brittle and can be broken, but, at room temperature, the material is soft and rubbery and can be folded or stretched to an extent without breaking.[2]

Nuclear magnetic resonance (NMR). NMR is a spectroscopic technique that employs magnets to separate energy levels in nuclei and radio waves to analyze the nuclei. Due to the methods employed by NMR spectroscopy, only certain isotopes (those with quantum spin states equal to $\pm 1/2$) can be easily analyzed this way—namely ^1H, ^{13}C, ^{19}F, and a few others. Experiments involving these three atoms in particular analyze for the specific isotope named in the experiment title, though ^{13}C is sometimes analyzed by a

QDEPT experiment, which is a faster version of a true ^{13}C NMR. Various information

can be determined by NMR experiments, including the number of nuclei of the target

isotope in the sample species, the environment surrounding each nucleus, and sometimes

nearby atoms and overall molecular structure. NMR samples are often dissolved in

deuterated solvents such as chloroform-d ($CDCl_3$) because the deuterium—^2H—isotope

is invisible to NMR experiments, though the small proportion of non-deuterated solvent,

such as chloroform ($CHCl_3$), included in the mixture as an impurity still shows up as a

peak.

Melting point. Melting point analysis entails measuring the melting point range

of a sample using a special apparatus. Melting points are generally not a single

temperature, but comprise a range—usually narrow in the case of pure samples—of

temperatures. Because melting point is an intrinsic property, it is the same no matter how

much material is present; as such, it can be used as a confirmation of a species' identity,

though it is generally accompanied by other tests.

II.   INTRODUCTION

Exciting advances have been made in recent years regarding two sets of materials. One of these sets is polymers containing fluorinated organic monomers, especially those containing trifluoromethyl (CF_3) groups. The other set is polymers or copolymers containing cyclobutanediol derivatives. In this text, a combination of the two—a cyclobutanediol derivative containing trifluoromethyl groups—was studied. The specific materials being studied were 2,2,4,4-tetrakis(trifluoromethyl)-1,3-cyclobutanediol (F_{12}-CBDO) and polymers containing F_{12}-CBDO monomers. The synthesis of these materials was explored with the goal of comparing their properties to those of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO), the non-fluorinated analog of F_{12}-CBDO, and the same polymers containing CBDO monomers to allow for analysis of the effect of adding trifluoromethyl groups to these materials. Figure 3 shows the structures of F_{12}-CBDO and CBDO. Note that the only difference is that the four methyl (CH_3) groups have been replaced with trifluoromethyl groups.
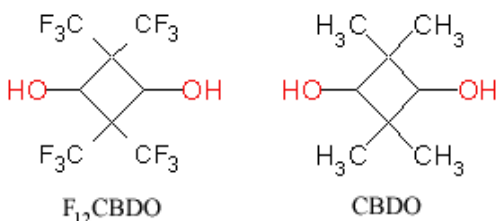

Figure 3. Structures of F_{12}-CBDO and CBDO. The analogous structures of these two compounds can be easily discerned by visual inspection.

Fluorinated polymers have received significant attention as advanced materials for use in films, coatings, and gas separation membranes.[3] Additionally, adding fluorine atoms into polymer chains showed advantages over non-fluorinated polymers with regards to their solubility, flame resistance, thermal stability, glass transition temperature, decreased color, crystallinity, dielectric constant, and moisture absorption.[3] These advantages extended specifically to systems incorporating trifluoromethyl groups, with additional uses as seals, soluble polymers, and additional high-temperature applications, and added benefits of oxidation resistance and environmental stability.[4] These benefits make these materials ideal for aerospace and electronic applications.[3] Some of the benefits listed here are exemplarized in Teflon® AF, which contains fluorine atoms attached directly to the polymer chain as well as in the form of attached trifluoromethyl groups. The dielectric constant of Teflon® AF is the lowest of any known solid polymer, and its refractive index is the lowest of any polymer family—especially as trifluoromethyl-group concentration is increased in the polymer system.[5] Optical transmission in Teflon® AF is particularly impressive, with greater than 90% transmission through most of the UV, visible, and near-IR ranges with no absorbance peaks appearing in this range.[5]

CBDO has the unique properties of being an aliphatic diol with high rigidity, thermal stability, and symmetricality, as well as reactivity similar to aromatic monomers.[6] Booth et al. showed the incorporation of the CBDO monomers into copolyesters to increase thermal properties, impact properties, ballistic properties, and that the materials displayed shape memory.[7] The latter was particularly impressive, as dents were shown to heal completely with mere heating, while cracks from ballistics resistance testing were

shown to heal almost completely.[7] CBDO exists in both a *cis* and *trans* configuration. The *cis* configuration was suspected of being responsible for the shape memory, as it caused coiling or kinking in the copolyester that stretched under strain but returned to its original configuration upon heating.[7]

Based on these prior studies, systems containing the F_{12}-CBDO monomer were expected to display improved thermal stability, glass transition temperature, flame resistance, optical properties, rigidity, impact properties, ballistic properties, shape memory, color, crystallinity, dielectric constant, moisture absorption, oxidation resistance, solubility, and environmental stability over analogous copolymers that contain neither fluorine nor CBDO monomers. Additionally, copolymers containing F_{12}-CBDO monomers, because they contain both trifluoromethyl groups and CBDO monomers, are expected to exhibit some improved properties over copolymers that contain either trifluoromethyl groups or CBDO monomers, but not both.

III.   EXPERIMENTAL

All solvents used were dried on an Innovative Technology PureSolv PS-MD-7 solvent system filled by Airgas nitrogen (compressed) and evacuated by an integrated vacuum pump. Argon was obtained from Airgas. Melting points were measured with a Laboratory Devices, Inc. Mel-Temp II melting point apparatus. Cyclohexanecarboxylic acid (98%) was purchased from Alfa Aesar and used as received. The 2,2-bis(trifluoromethyl)acetic acid (purity not listed) was purchased from VWR and used as received. Thionyl chloride (99+%) was purchased from Sigma-Aldrich and used as received. Toluene (anhydrous) was used fresh from the solvent-drying system. Triethylamine (99%) was purchased from Alfa Aesar and used as received; it was stored under argon. Tetrahydrofuran (anhydrous) for dry uses was used fresh from the solvent-drying system; tetrahydrofuran (99+%) for other uses was purchased from Fischer Scientific. Diethyl ether (99.9%) was purchased from J. T. Baker. Filter agent (standard supercell, acid washed) was purchased from Sigma-Aldrich. Sodium borohydride (98%) was purchased from Sigma-Aldrich. Ethanol (100%) was purchased from Sigma-Aldrich. Dichloromethane (DCM) (99.5%) was purchased from EMD Chemicals. Sodium hydroxide pellets (97+%, ACS Reagent grade) was purchased from Sigma-Aldrich. Aqueous hydrochloric acid (Certified ACS Plus) was purchased from Fischer Scientific. Methanol (99.8%) was purchased from EMD Chemicals. CBDO monomer (98.0%) was purchased from TCI America. Terephthaloyl chloride (99%) was purchased

from TCI America. Benzyltriethylammonium chloride (99%) was purchased from Alfa

Aesar. Deuterated chloroform (99.8%, +0.05% V/V TMS) was purchased from

Cambridge Isotope Laboratories, Inc. All structures shown in this text were drawn using

Symyx Accelrys Draw 4.0.[8] All NMR spectra were obtained from a 400 MHz Bruker in
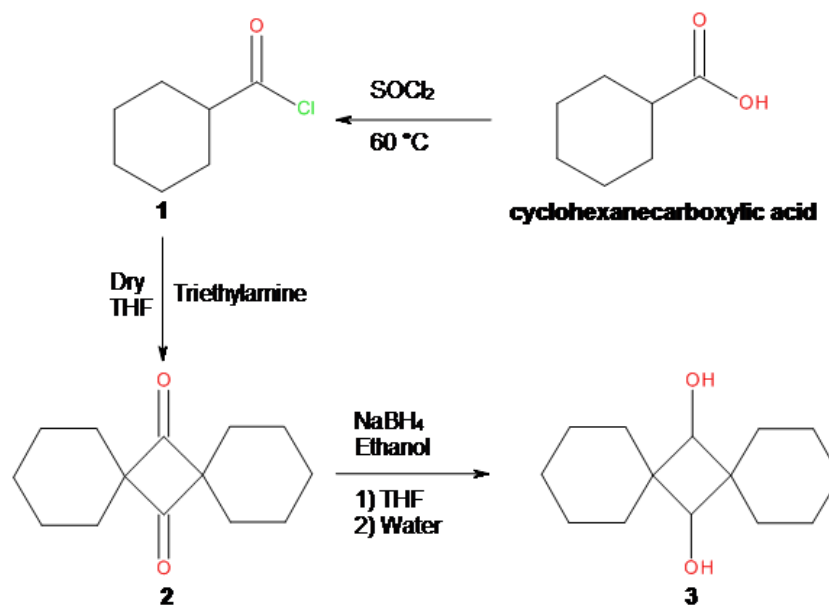
CDCl$_3$.

Figure 4. The overall synthesis scheme for the preparation of
dispiro[5.1.5.1]tetradecane-7,14-diol.

F$_{12}$-CBDO was obtained from 2,2-bis(trifluoromethyl)acetic acid via a three-step

synthesis. This synthesis scheme was based on an analogous scheme for the synthesis of

dispiro[5.1.5.1]tetradecane-7,14-diol (**3**) performed previously, described below.[9] The

overall synthesis of **3**, adapted for use in the synthesis of F$_{12}$-CBDO, is depicted in Figure

4.

Cyclohexanecarbonyl chloride (1). Cyclohexanecarboxylic acid (1 mmol) was

reacted with thionyl chloride (1.5 mmol). The bottle of cyclohexanecarboxylic acid

(melting point 35 ^{o}C) was placed in a water bath at 45 ^{o}C for 30 minutes prior to use, and

the acid was used as a liquid. The mixture was allowed to stir under a static argon atmosphere at 60 $^{\circ}$C for 4 hours while connected to a condenser to prevent evaporation of the reactants, solvent, or product. After 4 hours, the $SOCl_2$ was removed by vacuum distillation at 60 $^{\circ}$C. Liquid **1** was stored in a sealed flask under static argon in the freezer for no longer than 48 hours until it could be used in further reactions.

Dispiro[5.1.5.1]tetradecane-7,14-dione (2). Two units of compound **1** were "clicked" together. This reaction proceeded by adding **1** (1 mmol) to dry THF solvent (10 mmol) and reducing the solution to 0 $^{\circ}$C under an argon stream. Triethylamine (1.7 mmol) was added dropwise to the mixture with stirring over 10 minutes. The mixture was allowed to return to room temperature before being heated to reflux in THF under static argon for at least 8 hours. A large amount of off-white precipitate was observed. The mixture was separated by extraction in ether and water (precipitate dissolved readily in water). **2** was insoluble in both ether and water and was extracted by filtration. The solid was then recrystallized from boiling hexane and hot-filtered. The product (31.2% yield) was recovered as white crystals: ^{1}H NMR (CDCl$_3$): δ 1.44 (multiplet, 4H), 1.64 (multiplet, 8H), 1.73 (multiplet, 8H); melting point: 164-165 $^{\circ}$C.

Dispiro[5.1.5.1]tetradecane-7,14-diol (3). Compound **2** was reduced to its diol form by dissolving it (1 mmol) in THF (10 mmol), to which was added ethanol (4 mmol). Sodium borohydride (1 mmol) was added with stirring to the mixture slowly over 5 minutes and allowed to dissolve. The solution was allowed to stir at room temperature for 15 minutes before being quenched with water (10 mmol). The solution was then refluxed for 30 minutes. **3** was separated by extraction with DCM and water. The DCM layer was filtered, and the filtrate was distilled. The residue was recrystallized in hexane.

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3 (13.3% yield) was recovered as a white powder: [^1]H NMR (CDCl_3): δ 1.53 (multiplet, 20H, cyclohexane rings), 3.32 (d, 2H, OH), 3.55 (d, 2H, cyclobutane ring *cis*), 3.91 (d, 2H, cyclobutane ring *trans*).

2,2-bis(trifluoromethyl)acetyl chloride (4). 2,2-bis(trifluoromethyl)acetic acid (1 mmol) was reacted with thionyl chloride (3 mmol). The mixture was allowed to stir under a static argon atmosphere at 50 ^{o}C for 4 hours while connected to a condenser to prevent evaporation of the reactants, solvent, or product. After 4 hours, the mixture was cooled and placed in a freezer at -4 ^{o}C for at least 1 hour to allow **4** to precipitate as white crystals. The crystals were separated by vacuum filtration under a constant argon stream and rinsed with cold (0 ^{o}C) hexane. Purification by sublimation was attempted but found to be ineffective, as the starting acid was also found to readily sublime. The crystals were stored in a sealed flask under static argon in the freezer for no longer than 48 hours until they were used in further reactions. **4** (22.6% yield) was recovered as needle-like white crystals: [^1]H NMR (CDCl_3): δ 4.03 (septuplet, 1H, acetyl), 7.69 (s, 1H, acid). 2,2-bis(trifluoromethyl)acetic acid was received as white crystals: [^1]H NMR (CDCl_3): δ 4.04 (septuplet, 1H, acetyl), 11.19 (s, 1H, acid).

2,2,4,4-tetrakis(trifluoromethyl)-1,3-cyclobutanedione (5). Two units of compound **4** were clicked together. This reaction proceeded by adding **4** (1 mmol) to dry THF solvent (10 mmol) and reducing the solution to 0 ^{o}C under an argon stream. Triethylamine (1.7 mmol) was added dropwise to the mixture with stirring over 10 minutes. The mixture was allowed to return to room temperature before being heated to reflux in THF under static argon for at least 8 hours. The THF was distilled off and the

solid residue was separated by extraction with diethyl ether. Yield was too low to allow

for proper characterization.

IV.   RESULTS AND DISCUSSION

Dispiro[5.1.5.1]tetradecane-7,14-dione (**2**) was successfully synthesized, as confirmed by melting point and NMR.[10] Dispiro[5.1.5.1]tetradecane-7,14-diol (**3**) was successfully synthesized from cyclohexanecarboxylic acid, as confirmed using ^{1}H NMR. A slightly modified version of this synthesis scheme was successfully applied in literature to synthesize 2,2,4,4-tetrakis(trifluoromethyl)-1,3-cyclobutanediol (F_{12}-CBDO) with a yield of 35%.[9] However, reproduction of the synthesis of F_{12}-CBDO using this synthesis scheme was unsuccessful up to this point.

The synthesis of 2,2-bis(trifluoromethyl)acetyl chloride (**4**) proved to be far more problematic than anticipated. Though the same procedure used to synthesize cyclohexanecarbonyl chloride (**1**) reproduceably was applied to produce **4**, the results differed significantly. **4** was seen to hydrolize far more readily in atmosphere than **1**, so much stricter conditions to keep conditions as dry as possible were necessary. When a product was produced that was expected to be pure **4**, NMR analysis showed a broad peak upfield from the normal acid peak that integrated with the expected peak in a 1:1 ratio. This was thought to be a peak from the hydrolized acid, shifted upfield due to the different chemical environment caused by interaction with the solvent during hydrolysis in the $CDCl_3$ solution. However, if this was the case, then some amount of **4** was thought to have been necessary in solution in order for it to hydrolize.

Because of this reasoning, the synthesis of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-cyclobutanedione (**5**) was attempted as described above. However, the synthesis was unsuccessful, as the yield of product recovered was too low even to test in order to confirm the production of any amount of **5**. This may have been due to too high a volume of THF used during the synthesis, or it could have been caused by inappropriately-dried glassware used during reflux. This step was not given a great deal of attention, though; most of the efforts of synthesis in this experiment were focused on attempting to successfully produce and characterize pure **4**. Unfortunately, because **5** could not be successfully synthesized, the final synthesis of F_{12}-CBDO was not attempted.

One attempted batch of **4** was lost to a vacuum system when it was discovered to sublime readily. This factor was attempted to be utilized as a method of purification, but the product showed to be purely the starting acid. Upon further analysis, the starting acid, though it had a much higher boiling point, was also discovered to readily sublime, so that avenue was abandoned.

One piece of empirical evidence was observed, however, that **4** was successfully synthesized. During the reaction to synthesize **4**, condensation was seen on the inside of the reaction flask. Because the boiling point of the other possible compounds in solution (thionyl chloride and 2,2-bis(trifluoromethyl)acetic acid at 76 $^{\circ}$C and 126-128 $^{\circ}$C, respectively) were far higher than the reaction temperature (about 50 $^{\circ}$C), this condensation was thought to be indicative of the existence of **4** (boiling point of 54 $^{\circ}$C) in the reaction solution.[11-13]

V. CONCLUSIONS

Dispiro[5.1.5.1]tetradecane-7,14-diol (**3**) was confirmed to be synthesized successfully with 13.3% yield. The same synthesis scheme was attempted for the analogous novel compound 2,2,4,4-tetrakis(trifluoromethyl)-1,3-cyclobutanediol (F_{12}-CBDO), but this synthesis was unable to be synthesized successfully in the time constraints of this experiment. The precursor compound, 2,2-bis(trifluoromethyl)acetyl chloride (**4**), was attempted to be synthesized and purified in various ways and was thought to have been synthesized, but this was unable to be confirmed. The synthesis of the intermediate compound, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-cyclobutanedione (**5**), was attempted from unconfirmed **4** but was also unsuccessful.

The lack of successful synthesis in the course of this experiment was probably caused by inadequate drying of materials and equipment used prior to exposure to moisture-sensitive compounds. This was unexpected, as the techniques utilized in this experiment were adequate for use with the analogous compound cyclohexanecarbonyl chloride (**1**). Several other problems arose in the course of this experiment, such as unexpected sublimation of materials and loss of product during extractions. Future trials under this design should be carried out with the utmost care to avoid any exposure to moisture. Furthermore, solvent levels should be carefully minimized to avoid loss during filtration, recrystallization, and extraction.

Future considerations with these materials include finishing the work proposed in this text, including characterization of F_{12}-CBDO, which was expected to show heightened properties over compounds that incorporate trifluoromethyl (CF_3) groups or CBDO groups but not both. Additionally, upon successful synthesis of F_{12}-CBDO, this compound should be incorporated into polymer systems and tested. Polymer systems incorporating F_{12}-CBDO monomers are expected to exhibit many improved properties over both systems that contain neither CF_3 nor CBDO groups and systems that contain one or the other of these groups. These polymers should have applications in commercial, military, aerospace, and electrical markets as plastics and coatings.

F_{12}-CBDO is believed to be possible to synthesize based on the findings of this experiment. However, the conditions for synthesis must be much more strictly established than expected at the outset of this experiment, particularly where the lack of moisture in the reactions and on equipment is concerned. Due to the novel nature of this synthesis, some delays were expected, but the rewards for successful synthesis of these materials warrant continued efforts to that end.

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