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Complete List of Authors:	Lillie, Leon; University of Minnesota, Chemistry; University of Minnesota Tolman, William; Washington University in Saint Louis College of Arts and Sciences, Chemistry Reineke, Theresa; University of Minnesota, Chemistry

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Degradable and Renewably-sourced Poly(ester-thioethers) by Photo-initiated Thiol-ene Polymerization

Leon M. Lillie,[a] William B. Tolman,*[b] and Theresa M. Reineke*[a]

With the aim of preparing sustainable and degradable polymers from sugar-derived precursors, a family of five poly(ester-thioethers) were synthesized by photoinitiated thiol-ene polymerization of monomers incorporating D-glucaro-1,4:6,3-dilactone (GDL). Various dithiols were used to produce linear poly(ester-thioethers) of glucarodilactone 10-undecenoate (GDLU) to probe the effect of the dithiols on the observed mechanical performance and degradability. The samples exhibited glass transition (Tg) values from -8.7 to 19 °C. The polymers with the simplest dithiols, 1,2-ethanedithiol (EtDT) and 3,6-dioxa-1,8-octane-dithiol (DODT), were found to exhibit crystallinity, while the more structurally complex and rigid dithiol structures were found to produce amorphous materials. Due to the GDL units in the polymers, rapid degradation under basic aqueous conditions and stability in acidic and neutral conditions were observed. Tensile testing of these materials showed robust mechanical properties, including tunable moduli (0.011 to 0.29 GPa), strength (21 to 42 MPa), and ductility (410 to 590 %).

Introduction

The preparation of sustainable materials with exceptional performance and competitive cost are key research goals for many applications and industries;[1,2] the use of bio-sourced and degradable building blocks is important in efforts to meet these goals.[3,4,5,6] Carbohydrates and their derivatives have been widely explored as feedstocks for the next generation of high performance and degradable materials.[2,7,8,9] Isosorbide (Scheme 1) is a commercially available, rigid bicyclic diol derived from glucose, and has been extensively studied for its potential as a drop-in replacement for a wide array of polymeric applications.[9-13] The commercial relevance of these materials has been realized through the release of DURABIO™, an isosorbide-based polycarbonate resin.[14] Building on the successful use of isosorbide to produce high performance and, in some cases, degradable materials, we postulated that both rapid triggered degradability and commercially relevant mechanical performance may be imparted with the incorporation of D-glucaro-1,4:6,3-dilactone (glucarodilactone, GDL, Scheme 1), a lesser studied chemical analog of isosorbide, into polyester materials.

[a.] Department of Chemistry and Center for Sustainable Polymers, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431. Email: treineke@umn.edu
[b.] Department of Chemistry, One Brookings Drive, Campus Box 1134, Washington University in St. Louis, St. Louis, MO 63130-4899. Email: wbtolman@wustl.edu

In previous work, we found that polyesters with GDL as a component of the backbone possessed excellent hydrolytic degradability and tunable and commercially relevant mechanical properties.[15,16] In that work, GDL was pre-functionalized with 10-undecenoic acid (Scheme 1), a castor oil derivative, to form the α,ω-diene glucarodilactone 10-undecenoate (GDLU, Scheme 2).[15,16] This diene was found to be suitable for use as a substrate in acyclic diene metathesis (ADMET) polymerization. Using this route, moderate molecular weight polyesters (30-60 kDa) were obtained through homopolymerization and copolymerization with the congener, isosorbide 10-undecenoate (IU, Scheme S2).[15,16] Direct comparisons of the homopolymer of isosorbide 10-undecenoate, P(IU), with GDL-containing materials showed the latter to be more susceptible to degradation under basic conditions and to exhibit industrially relevant and tunable
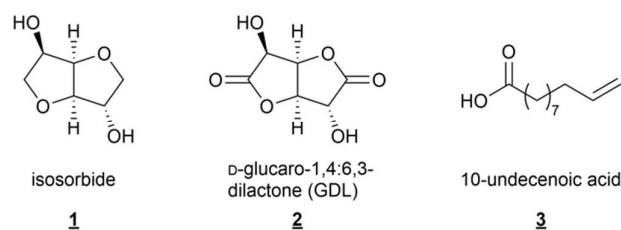
Scheme 1. Molecular structures of isosorbide **1**, D-glucaro-1,4:6,3-dilactone (glucarodilactone, GDL) **2**, and 10-undecenoic acid **3**.

mechanical properties that were dependent on GDL content.[16] Yet, while high performance and degradable materials were produced via ADMET polymerization, the method had several disadvantages, including the need for high temperatures, the
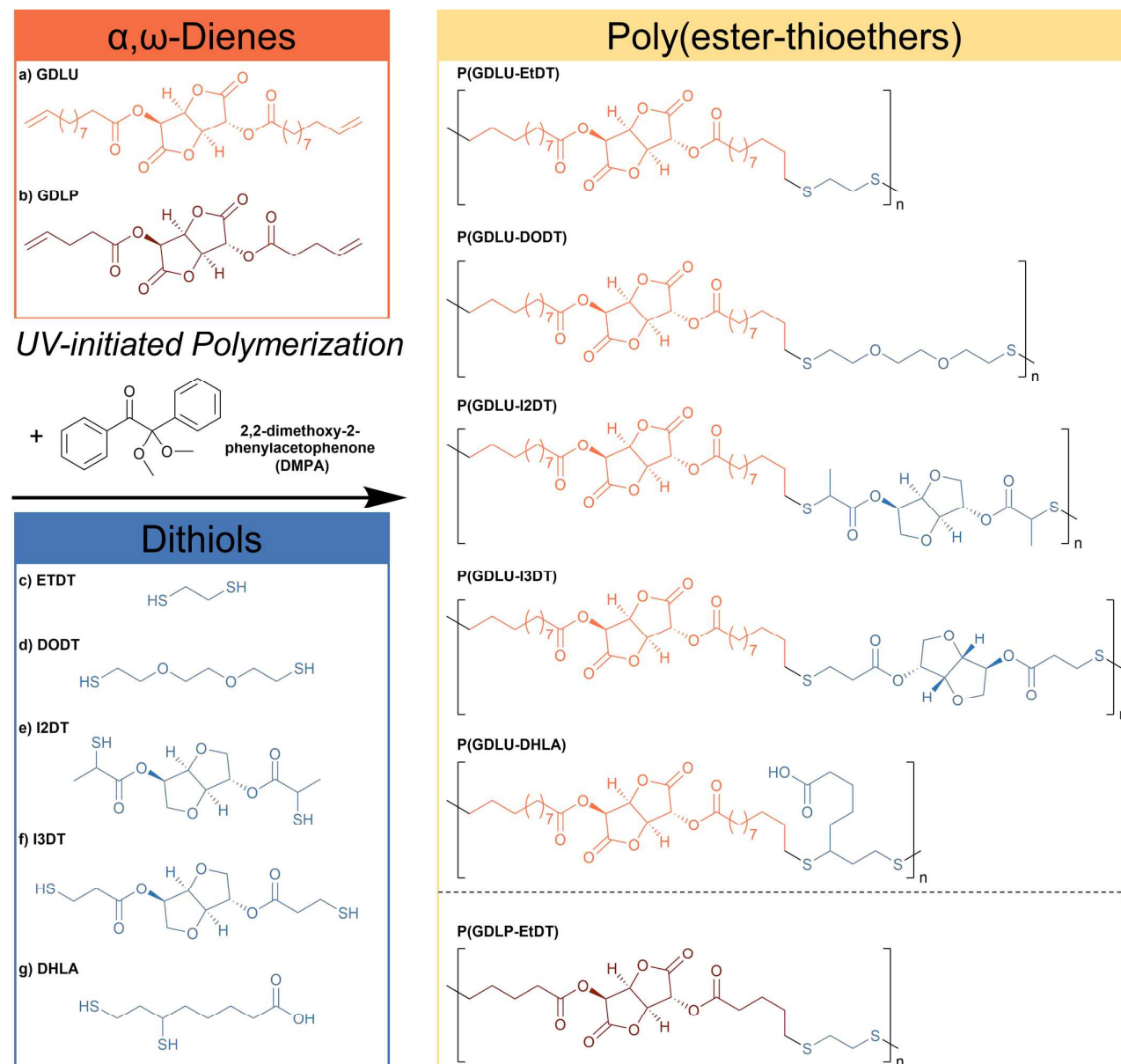
Scheme 2. Schematic representation of the alkenes and dithiols used to prepare the indicated poly(ester-thioethers) through photopolymerization. A) glucarodilactone 10-undecenoate (GDLU), b) glucarodilactone 4-pentenoate (GDLP), c) 1,2-ethanedithiol (EtDT), d) 3,6-dioxa-1,8-octane-dithiol (DODT), e) isosorbide 2-mercaptopropionate (I2DT), f) isosorbide 3-mercaptopropionate (I3DT), g) dihydrolipoic acid (DHLA).

requirement for expensive ruthenium-based catalysts, and difficulties with removal of ruthenium impurities that left the materials deeply colored.[15,16]

With the aim of circumventing these issues and developing a more cost-effective route for incorporating the degradable sugar derivative, GDL, into polymeric materials, we looked towards an alternative synthetic route. One such route involves thiol-ene "click" photopolymerization to couple GDLU with various dithiol molecules. This "click" reaction is a 100% atom-efficient process with well-defined reactivity patterns, which often reaches quantitative or near-quantitative conversions and exceptional control over polymer structure.[17] While the bulk of the reports of thiol-ene click chemistry in material applications are focused on the formation of crosslinked materials or post-functionalization of polymers, there is precedence for using this chemistry for linear polymer formation, notwithstanding difficulties in accessing high molecular weights due the step-growth process.[18,19]

Herein, we demonstrate the use of thiol-ene photopolymerization for the synthesis of GDLU-containing poly(ester-thioethers) (Scheme 2). The structure/property relationships of the distance between rigid components and flexibility of the backbone on physical properties such as glass transition temperature (T_g) and crystallinity were explored. We also discovered that the nature of the dithiols (primary vs. secondary) does not seem to play a role in the ability to produce moderately high molecular weight materials. Finally, we show that through the choice of linker we were able to match or supersede the mechanical performance of the GDLU-containing polyesters obtained with ADMET polymerization, while maintaining degradability of this system.

Experimental

Materials

Isosorbide was obtained as a gift from Archer Daniels Midland Company (Chicago, Illinois, USA). D-glucaro-1,4:6,3-dilactone was synthesized using previously reported procedures from calcium D-saccharate tetrahydrate, which was obtained from Carbosynth Limited (Compton, Berkshire, UK).[20] Rac-α-lipoic acid was also obtained from Carbosynth Limited. Deuterated chloroform (CDCl$_3$) was obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA). 4-Pentenoic acid, N,N'-diisopropylcarbodiimide (DIC), and 4-dimethylaminopyridine were obtained from Oakwood Products, Inc. (Estill, South Carolina, USA.). All other reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA). Purchased compounds were used directly without further purification. Glucarodilactone 10-undecenoate (GDLU) was synthesized as described previously.[16] All glassware was oven-dried prior to use.

Characterization Methods

^{1}H NMR and ^{13}C NMR spectra were obtained in deuterated chloroform on a Bruker Avance HD-500. ^{1}H NMR spectra of polymeric samples were obtained with at least 64 scans with a 5 second acquisition time and 10 second delay time. All spectra were referenced to tetramethylsilane (TMS). Polymer molecular weights (M_w, M_n) and dispersities (Đ) were calculated after performing size exclusion chromatography (SEC) using an Agilent 1260 Infinity instrument with a Wyatt DAWN Heleos II 10-angle light scattering detector at 662.6 nm and a Wyatt Optilab EX RI detector. The instrument was setup using Waters Styragel HR6, HR4, HR1 columns with a tetrahydrofuran mobile phase at 25 °C with a 1.0 mL/min flow rate. High-resolution mass spectrometry (HRMS) of novel diene and dithiols was performed using a Bruker Bio-TOF II in positive mode.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 under a nitrogen atmosphere with a heating rate of 10 °C/min using samples of 8-15 mg. Samples were heated from room temperature (RT) to 550 °C. Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Q-1000. Samples were tested in hermetically sealed aluminum pans. Each sample was equilibrated to -50 °C and then heated to 125 °C at a rate of 10 °C/min. The samples were then cooled to -50 °C at a rate of -10 °C/min. Lastly, the samples were heated to 150 °C at 10 °C/min. Glass transition temperatures and melting temperatures were measured during the second heating ramp.

Mechanical testing was performed on polymer samples that were melt processed in a Carver Lab Press. Polymer samples were placed between two Teflon sheets and melt processed at 100 °C under 10,000 lbs. of force for 10 minutes. The samples were then removed from the hot press and allowed to cool to RT. If bubbles or other defects were present in the samples after pressing, samples were cut into smaller pieces and reprocessed using the same conditions described above until uniform samples were obtained. Tensile testing was performed on a Shimadzu AFS-X tensile tester at room temperature with tensile bars possessing approximate gauge dimensions of 6 mm x 1 mm x 0.3 mm. Samples were each extended at 50 mm/min and at least six replicate runs were performed for each polymer sample.

Synthesis of Glucarodilactone 4-Pentenoate (GDLP)

GDL (5.2 g, 0.03 mol, 1 equiv.) was added to an oven dried 500 mL round bottom flask (RBF) along with 4-pentenoic acid (8.7 mL, d=0.981g/mL, 0.063 mol, 2.1 equiv.) and catalytic amounts of 4-dimethylaminopyridine (DMAP, 0.26 g, 0.015 mol, 0.05 equiv.). Dichloromethane (CH$_2$Cl$_2$, 100 mL) and tetrahydrofuran (THF, 15mL) were added to the RBF, dissolving GDL and 4-pentenoic acid. The flask was sealed with a rubber septum, placed under nitrogen, and submerged into an ice water bath prior to N,N'-diisopropylcarbodiimide (DIC) addition. DIC (19.1 mL, d=0.806 g/mL, 0.089 mol, 3 equiv.) was added directly to the chilled reaction flask in a dropwise manner via syringe. The reaction was allowed to heat to room temperature as the ice melted (30 min) and was allowed to react for 3 h, with progress monitored via TLC (silica gel, CH$_2$Cl$_2$ eluent). During the reaction, N,N'-diisopropylurea precipitates from solution. After the reaction is complete, N,N'-

diisopropylurea was filtered from the reaction mixture and the solvent was removed *in vacuo* to obtain a dark green solid. This crude mixture was subjected to purification via column chromatography (silica gel, Hexanes: CH_2Cl_2 = 1:1) and pure glucarodilactone 4-pentenoate (GDLP) was obtained as a white solid (4.2 g, 42% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.82 (ttd, *J* = 16.9, 6.6, 3.3 Hz, 2H), 5.55 – 5.44 (m, 1H), 5.37 (d, *J* = 6.7 Hz, 1H), 5.14 – 5.00 (m, 5H), 4.98 (s, 1H), 2.68 – 2.51 (m, 4H), 2.44 (dp, *J* = 14.2, 7.1 Hz, 5H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 172.64, 172.14, 169.08, 168.87, 135.80, 135.63, 116.57, 116.36, 78.90, 74.64, 73.05, 67.35, 32.74, 32.52, 28.56. **HRMS (ESI-TOF, *m/z*)** calculated for $C_{16}H_{18}O_8Na^+$: 361.0894; found: 361.0894.

Synthesis of Isosorbide 2-Mercaptopropionate (I2DT) and Isosorbide 3-Mercaptopropionate (I3DT)

The synthesis of isosorbide 2-mercaptopropionate (I2DT) and isosorbide 3-mercaptopropionate (I3DT) was previously reported in a patent.[21] Since these dithiols are simple structural isomers of each other, one synthetic method can be used to produce both I2DT and I3DT. Thus, for simplicity, the synthesis of I2DT is described herein. Isosorbide (11.3 g, 0.078 mol, 1 equiv.) and 2-mercaptopropionic acid (14.5 mL, d=1.196 g/mL, 0.16 mol, 2.1 equiv.) were added to an oven dried 500 mL round bottom flask (RBF). Toluene (100 mL) followed by p-toluenesulfonic acid (0.74 g, 0.004 mol, 0.05 equiv.) were then added to the flask. The flask was equipped with a heating mantle and Dean-Stark apparatus. The reaction was heated to reflux under magnetic stirring and the reaction was monitored via the volume of water collected in the Dean-Stark apparatus. After completion of the reaction (approximately 3 h), the flask was then removed from heat and allowed to cool to room temperature. The remaining 2-mercaptopropionic acid was removed via an extraction from the toluene solution with saturated sodium bicarbonate (3 x 100 mL) and brine (1x 150 mL), the resulting toluene layer was dried with magnesium sulfate and the solvent removed *in vacuo*, yielding 22.4 g (90% yield) of isosorbide 2-mercaptopropionate (I2DT) as a viscous colorless oil.

I2DT – ^{1}H NMR (I2DT, 500 MHz, Chloroform-*d*) δ 5.24 (d, *J* = 3.1 Hz, 1H), 5.18 (p, *J* = 5.5 Hz, 1H), 4.90 (td, *J* = 6.8, 3.1 Hz, 1H), 4.51 (t, *J* = 5.7 Hz, 1H), 4.08 – 3.97 (m, 2H), 3.95 (dq, *J* = 8.4, 2.6 Hz, 1H), 3.88 (ddt, *J* = 10.2, 4.9, 3.0 Hz, 1H), 3.62 – 3.53 (m, 1H), 3.47 (dddd, *J* = 16.8, 9.0, 7.0, 2.0 Hz, 1H), 2.26 – 2.11 (m, 2H), 1.59 – 1.49 (m, 6H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 173.11, 172.91, 85.95, 80.90, 78.65, 74.73, 74.70, 73.25, 35.52, 35.48, 20.79. **HRMS (ESI-TOF, *m/z*)** calculated for $C_{12}H_{18}O_2S_2Na^+$: 345.0437; found: 345.0445.

I3DT – ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.25 (t, *J* = 2.2 Hz, 1H), 5.19 (q, *J* = 5.5 Hz, 1H), 4.86 (t, *J* = 5.2 Hz, 1H), 4.50 (d, *J* = 4.7 Hz, 1H), 4.03 – 3.90 (m, 3H), 3.84 (dd, *J* = 10.0, 5.1 Hz, 1H), 2.85 – 2.70 (m, 6H), 1.72 (t, *J* = 8.2 Hz, 1H), 1.64 (dd, *J* = 16.2, 7.9 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 170.99, 170.72, 85.96, 80.79, 78.26, 74.23, 73.39, 70.51, 38.34, 38.27, 19.71. **HRMS (ESI-TOF, *m/z*)** calculated for $C_{12}H_{18}O_2S_2Na^+$: 345.0437; found: 345.0431.

Reduction of Lipoic Acid and Purification of rac-Dihydrolipoic Acid

The procedure used for the synthesis of rac-dihydrolipoic acid was modified from a previous report.[22] The reaction was performed using the same scale, stoichiometry, and temperatures. Dichloromethane was used as an extraction solvent rather than toluene, and evaporation of the solvent yielded 11.9 g (97% theoretical yield) of rac-dihydrolipoic acid as a slightly yellow oil. The ^{1}H NMR data matched previously reported chemical shifts for rac-dihydrolipoic acid.[22]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.98 – 2.87 (m, 1H), 2.80 – 2.62 (m, 2H), 2.38 (t, *J* = 7.3 Hz, 2H), 1.91 (dtd, *J* = 14.3, 7.8, 4.4 Hz, 1H), 1.81 – 1.40 (m, 7H), 1.36 (t, *J* = 8.0 Hz, 1H), 1.31 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (126 MHz, Chloroform-*d*)** δ 180.03, 42.87, 39.40, 38.81, 34.00, 26.57, 24.39, 22.41.

Representative Thiol-ene Photopolymerization Procedure

The representative procedure for P(GDLU-EtDT) is described herein: the other thiol-ene polymers were synthesized similarly on a similar scale. GDLU (3.0 g, 0.006 mol, 1 equiv.) and 1,2-ethanedithiol (0.50 mL, d=1.123 g/mL, 0.006 mol, 1 equiv.) were loaded into a 25mL glass scintillation vial. This mixture was dissolved in enough THF (anhydrous, 18 mL) to make a 0.33M solution in ene-monomer, with 2 mL spared for the dissolution of the photo initiator. GDLU typically was slow to dissolve in THF, so the mixture was initially allowed to stir for 5 min protected from light. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 0.031 g, 0.0001 mol, 0.01 equiv.) was measured into a separate scintillation vial, then dissolved in the remaining 2 mL THF and quickly added to the polymerization vial. The reaction vial was allowed to mix for 1 minute before UV exposure. A MelodySusie® 36W UV Nail Dryer was used as the UV cure chamber and was placed on top of a magnetic stir plate to allow for mixing during polymerization. Samples were exposed to UV light for 30 min, then removed from the cure chamber. Slight warming was observed, so samples were allowed to cool to room temperature (RT) prior to precipitation into methanol (MeOH). Polymer samples were then dried at 50 °C overnight in a vacuum oven before further characterization.

Solvent was used to form a homogenous mixture of the crystalline GDLU, dithiol, and crystalline DMPA. Tetrahydrofuran was found to ensure solubility of the polymer during polymerization. Toluene was found to form homogenous solutions of monomers and photoinitiator but was unable to solubilize all polymers during photopolymerization, likely limiting achievable molecular weight.

Hydrolytic Stability Testing

Solvent cast polymer films were characterized in aqueous solutions (0.25 M NaOH, neutral, and 0.25 M HCl) following our previously reported hydrolytic stability testing method.[15,16]

Results and Discussion

Monomer Selection and Synthesis

Three types of dithiol molecules were selected for copolymerization with GDLU (Scheme 2): (a) commercially available simple dithiols (EtDT and DODT), (b) rigid isosorbide-based dithiols (I2DT and I3DT), and (c) a 100% bio-sourced dithiol (DHLA). The type (a) dithiols were selected for their chemical simplicity, allowing the low-cost production of polymers with the highest similarity to previously reported materials prepared by ADMET polymerization.[15,16] The isosorbide-based dithiols were employed to reduce the distance between rigid components in the backbone, elucidating the structure/property relationship between the rigid and flexible components of our backbone, and to access higher T_g materials. Finally, with the aim of obtaining essentially entirely bio-based materials, we targeted DHLA, dihydrolipoic acid, which is available from the reduction of lipoic acid, a naturally occurring organosulfur compound.[22,23]

As an alternative route to increase the rigid component and accessible T_g's, we replaced 10-undecenoic acid with 4-pentenoic acid. Glucarodilactone 4-pentenoate (GDLP) was synthesized though the Steglich esterification of GDL with 4-pentenoic acid using N,N'-diisopropylcarbodiimide and catalytic amounts of 4-dimethylaminopyridine (DMAP).[24] The previously used route involving scandium triflate-catalyzed esterification of 10-undecenoic anhydride with GDL was not used because of the strong, persistent odor of 4-pentenoic anhydride prepared via the published method.[16,25]

Synthesis and Characterization of GDLU-containing Polymers

Photoinitiated thiol-ene polymerization was employed to produce a family of polymers of GDLU and the various dithiols depicted in Scheme 2. Polymerizations were conducted in tetrahydrofuran (THF) without inhibitor initiated with 2,2-dimethoxy-2-phenylacetophenone (DMPA, 1 mol%) in air at room temperature using UV exposure. The polymers were obtained as colorless solids or amorphous melts by precipitation in methanol, which significantly reduced the odor arising from the presence of low-valent organosulfur impurities. After drying in a vacuum oven at 50 °C, the polymers were characterized by ^{1}H NMR spectroscopy, thermogravimetric analysis, differential scanning calorimetry, MALLS-SEC, uniaxial tensile testing, and degradation analysis.

In general, polymers of moderate molecular weight (16-49 kg/mol) and expected step-growth dispersities (1.1-2.0) were obtained (Table 1). Thermogravimetric analysis indicated decomposition temperatures at 5% mass loss ranging from 200 °C to 246 °C, a level of stability similar to GDL-containing polyesters reported previously.[15,16] The introduction of the thioether linkage between GDLU units led to an overall reduction in observed T_g when comparing to P(GDLU) (T_g = 32 °C) obtained by ADMET polymerization.[15,16] Introduction of EtDT led to a 16 °C reduction in T_g. DODT further increased the distance and chain-flexibility between rigid backbone components leading to the lowest observed T_g of the dithiol linkers at -8.7 °C. These poly(ester-thioethers) were found to

be semi-crystalline by differential scanning calorimetry (Table 1, Figure S19). The asymmetric backbone of the DHLA dithiol and pendant carboxylic acid group were found to lower the T_g (3.8 °C) and eliminated crystallinity in these materials (Table 1, Figure S19). To access higher T_gs, we reduced the distance between rigid units using the isosorbide-derived I2DT and I3DT. While I2DT did lead to a slight increase in T_g (19 °C) over EtDT, its constitutional isomer I3DT significantly reduced the observed T_g (-1.3 °C). I2DT and I3DT were also observed to be amorphous (Table 1, Figure S19); indicative of the importance of maintaining a long, uninterrupted flexible unit between rigid sugar-derivatives for crystallization. These findings merit a more detailed exploration, which will be a focus of future studies.

Table 1. Data summary for the GDLU-containing thiol-ene polymer system.

P(GDLU-x) Where x =	M_n[a] (kg/mol)	Đ[a]	T_g[b] (°C)	T_m[b] (°C)	$T_{d,5\%}$[c] (°C)
EtDT	29	1.6	16	49 & 64	200
DODT	24	1.9	-8.7	44	208
I2DT	49	1.6	19	Am.	246
I3DT	17	2.0	-1.3	Am.	216
DHLA	16	1.4	3.8	Am.	234

[a]Number average molecular weight and dispersity determined via SEC-MALLS in THF at 25 °C. [b]Glass transition temperature and melting temperature were determined by differential scanning calorimetry (DSC). [c]Decomposition temperatures were determined at the 5% weight loss level by thermal gravimetric analysis (TGA). "Am." indicates amorphous sample with no observable melting feature (T_m) in DSC.

The effect of the dithiol linkers on mechanical performance at room temperature was characterized via tensile analysis (Fig. 1, Table 2). P(GDLU-EtDT) was found to be a high performance ductile plastic (with a modulus of 0.29 GPa) with high stress at break (σ_x, 32 MPa) and large strain at break (ε_x, 410%). These room temperature properties are akin to that of polypropylene.[26] The use of DODT as the dithiol linker maintained the ductile behavior, albeit with a lower modulus (0.065 GPa) and strength (11 MPa) and slightly increased deformability (480 %). The room temperature tensile characterization of the amorphous P(GDLU-I2DT) and P(GDLU-I3DT) was performed above their respective T_gs, and showed these materials to possess low moduli (11 and 16 MPa) and strength (26 and 42 MPa) comparable to or exceeding those of commercial elastomers.[27] P(GDLU-DHLA) was molten at room temperature and thus we were unable to obtain viable tensile specimen for tensile characterization.
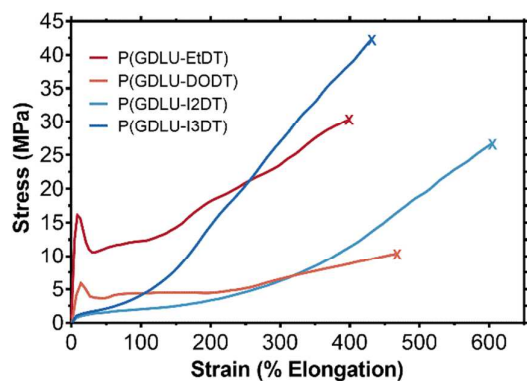
Fig. 1 Uniaxial extensional tensile testing of the GDLU-containing thiol-ene polymer family. Samples were deformed at a uniform rate of 50 mm/min until break (denoted with X). Representative data from at least 5 replicates are shown for each composition.

Table 2. Tensile properties of the GDLU-containing thiol-ene polymer system.

P(GDLU-x) Where x =	Young's Modulus[a] (GPa)	σ_x[b] (MPa)	ε_x[c] (%)
EtDT	0.29 ± 0.02	32 ± 3	410 ± 13
DODT	0.065 ± 0.005	11 ± 0.3	480 ± 16
I2DT	0.011 ± 0.003	26 ± 5	590 ± 20
I3DT	0.016 ± 0.001	42 ± 2	440 ± 16

[a]Young's modulus was calculated from the first 5% elongation during uniaxial tensile testing. [b]Average stress (σ_x, MPa) and [c]Average maximum elongation at break (ε_x, %) from at least 5 measurements.

Hydrolytic Stability Testing

The hydrolytic stability of the GDL-containing poly(ester-thioethers) was explored under neutral, acidic (0.25 M HCl), and basic (0.25 M NaOH) aqueous conditions (Figure 2). Under basic hydrolytic conditions, we observed complete degradation (0 % insoluble mass) in 1-3 days. The materials were found to be relatively stable under the neutral and acidic conditions, with minimal mass loss observed during the testing period (Figure S24). These results mirror those for the previously reported GDL-containing polymers, further showcasing the potency of GDL in imparting rapid hydrolytic degradation characteristics to polymeric materials.[15,16]
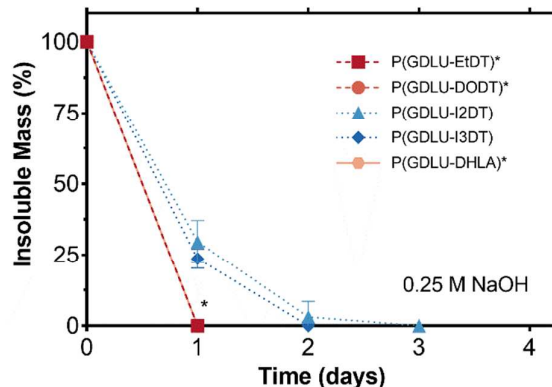
Fig. 2 Hydrolytic stability testing of the thiol-ene polymer system in basic (0.25 M NaOH) aqueous conditions. Samples in triplicate were exposed to 0.25 M NaOH for 24-hour periods, dried and insoluble mass was measured. Then samples were exposed to new aqueous insult for the next 24-hour period. This process was repeated over the course of six 24-hour periods. *P(GDLU-EtDT), P(GDLU-DODT), and P(GDLU-DHLA) were found to degrade completely during the first day of testing.

4-Pentenoate-based Polymer Synthesis and Characterization

Thiol-ene photopolymerization of glucarodilactone 4-pentenoate (GDLP) and 1,2-ethanedithol (EtDT) produced a poly(ester-thiolether) of similar molecular weight (14 kg/mol versus 29 kg/mol) and slightly lower dispersity (1.1 versus 1.6) as P(GDLU-EtDT) (Table 3). Reducing the distance between the rigid GDL units of the backbone increased the observed T_g of this sample from 16 °C observed in P(GDLU-EtDT) to 28 °C for P(GDLP-EtDT). Also, no melting features were observed in further thermal characterization of this GDLP-containing poly(ester-thiother). Both routes we used for reducing the distance between the GDL units of the backbone, shorter diene and use of isosorbide-derived dithiols, led to the loss of crystallinity in these materials. Parallel structure/property relationships were previously observed in analogous isosorbide-based polyesters, where reducing the number of methylene units between isosorbide units of the backbone yielded similar increases in T_g and loss of crystallinity.[28,29] The high T_g and amorphous nature of P(GDLP-EtDT) resulted a material that was found to be too brittle to produce viable samples for tensile testing.

Table 3. Characterization summary between the 10-undecenoic acid- and 4-pentenoic acid-containing polymers.

Sample	M_n[a] (kg/mol)	Đ[a]	T_g[b] (°C)	T_m[b] (°C)	$T_{d,5\%}$[c] (°C)
P(GDLU-EtDT)	29	1.6	16	49, 64	200
P(GDLP-EtDT)	14	1.1	28	*Am.*	202

[a]Number average molecular weight and dispersity determined via SEC-MALLS in THF at 25 °C. [b]Glass transition temperature and melting temperature were determined by differential scanning calorimetry (DSC). [c]Decompositon temperatures were determined at the 5% weight loss level by thermal gravimetric analysis (TGA). "Am" indicates amorphous sample with no observable T_m feature.

Conclusions

We have shown the feasibility of the use of thiol-ene photopolymerization as a rapid, metal-free, and low-cost way to incorporate GDL into colorless linear polymers. The thermal and mechanical characteristics of the polymers were found to be tunable based on the identity of the dithiol coupling agent. The use of the chemically simple dithiols, DODT and EtDT, yielded ductile materials with industrially relevant mechanical characteristics (σ_x from 11-32 MPa, ε_x from 410-480 %). Where Isosorbide-based dithiols were used, the resulting amorphous materials were found to be exceptionally strong (σ_x from 26-42 MPa) and no longer exhibited plastic deformation during tensile testing. We also discovered the importance of a long flexible aliphatic unit in imparting crystallinity in these materials, as well as the performance implications of the loss of crystallinity. The naturally-derived dithiol dihydrolipoic acid was used to produce degradable polymers with 100 percent renewable content. This work also further confirms the potential of GDL to enhance the degradability of polymeric materials when added, intact, to their backbone.

Conflicts of interest

Authors declare no conflicts of interest.

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References

1 D. K. Schneiderman and M. A. Hillmyer, *Macromolecules*, 2017, **50**, 3733-3749.

2 Y. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, **540**, 354-362.

3 J. J. Kolstad, E. T. H. Vink, B. De Wilde and L. Debeer, *Poly. Degrad. and Stab.*, 2012, **97**, 1131-1141.

4 M. J. Krause and T. G. Townsend, *Environ. Sci. Tech. Lett.*, 2016, **3**, 166-169.

5 J. Ren, *Biodegradable Poly(Lactic Acid) : Synthesis, Modification, Processing and Applications*, Beijing: Tsinghua University Press; Heidelberg; New York: Springer, Beijing: Heidelberg; New York, 2011.

6 S. Lambert and M. Wagner, *Chem. Soc. Rev.*, 2017, **46**, 6855-6871.

7 J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, **12**, 539-554.

8 R. De Clercq, M. Dusselier and B. F. Sels, *Green Chem.*, 2017, **19**, 5012-5040.

9 J. A. Galbis and M. G. García-Martín, in *Carbohydrates in Sustainable Development II*, eds. A. P. Rauter, P. Vogel and Y. Queneau, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, DOI: 10.1007/128_2010_57, pp. 147-176.

10 M. Rose and R. Palkovits, *ChemSusChem*, 2012, **5**, 167-176

11 F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup and J. P. Pascault, *Prog. Polym. Sci.*, 2010, **35**, 578-622.

12 J. J. Gallagher, M. A. Hillmyer and T. M. Reineke, *ACS Sustainable Chem. Eng.*, 2015, **3**, 662-667.

13 J. J. Gallagher, M. A. Hillmyer and T. M. Reineke, *ACS Sustainable Chem. Eng.*, 2016, **4**, 3379-3387.

14 Mitsubishi Chemical Develops New Grade of Bio-based Engineering Plastic DURABIO(TM) for Automotive Touch Panels. https://www.m-chemical.co.jp/en/news/kagaku/00004.html (accessed 02/22/2018).

15 W. C. Shearouse, L. M. Lillie, T. M. Reineke and W. B. Tolman, *ACS Macro Lett.*, 2015, **4**, 284-288.

16 L. M. Lillie, W. B. Tolman and T. M. Reineke, *Polym. Chem.*, 2017, **8**, 3746-3754.

17 N. B. Cramer, T. Davies, A. K. O'Brien and C. N. Bowman, *Macromolecules*, 2003, **36**, 4631-4636.

18 J. M. Sarapas and G. N. Tew, *Macromolecules*, 2016, **49**, 1154-1162.

19 K. L. Poetz, O. Z. Durham and D. A. Shipp, *Poly. Chem.*, 2015, **6**, 5464-5469.

20 T. C. Gehret, A. S. Frobese, J. S. Zerbe and H. K. Chenault, *J. Org. Chem.*, 2009, **74**, 8373-8376.

21 Owusu-Adom, K.; Lewandowski, K. M.; Janoski, J. E. US Pat., WO2013090138 A1, 2013.

22 H. T. Uyeda, I. L. Medintz, J. K. Jaiswal, S. M. Simon and H. Mattoussi, *J. Am. Chem. Soc.*, 2005, **127**, 3870-3878.

23 K. P. Shay, R. F. Moreau, E. J. Smith, A. R. Smith and T. M. Hagen, *Biochim. et Biophys. Acta, Gen. Subj.*, 2009, **1790**, 1149-1160.

24 B. Neises and W. Steglich, *Angew. Chem. Int. Ed. Engl.*, 1978, **17**, 522-524.

25 H. L. Wehrmeister and D. E. Robertson, *J. Org. Chem.*, 1968, **33**, 4173-4176.

26 D. W. A. Rees, in *Mechanics of Optimal Structural Design*, John Wiley & Sons, Ltd, 2009, DOI: 10.1002/9780470749784.app1, pp. 521-524.

27 G. Holden, H.R. Kricheldorf, R. P. Quirk, in *Thermoplastic Elastomers*, Hanser Gardner Publications, Inc., Cincinnati, Ohio, 3rd ed., 2004, ch. 3, pp. 51-56.

28 D. Braun and M. Bergmann, *J. Prakt. Chem.*, 1992, **334**, 298-310.

29 M. Okada, Y. Okada, A. Tao and K. Aoi, *J. of Appl. Polym. Sci.*, 1996, **62**, 2257-2265.