Degradable High $T_g$ Sugar Derived Polycarbonates from Isosorbide and Dihydroxyacetone

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Materials and methods

1,1’-Carbonyldiimidazole (CDI), isosorbide (Iso) and dihydroxyacetone (DHA) were purchased from Carbosynth (Berkshire, UK). Isosorbide (98%) was purified by re-crystallization from acetone prior to use in polymerizations. All other chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. HPLC grade solvents were used for all synthetic procedures, and dried over vacuum/heat-activated molecular sieves (3Å) prior to use. DBU was dried and stored over 3Å molecular sieves. All glassware and magnets were flame dried under vacuum and filled with argon prior to use.

NMR ($^1$H and $^{13}$C) experiments were performed on a Bruker Avance 400 (100) MHz NMR instrument. $^1$H NMR were referenced to the residual solvent peak of DMSO-$d_6$ δ 2.50, CDCl$_3$ δ 7.26 and D$_2$O δ 4.79, and $^{13}$C NMR to DMSO-$d_6$ δ 39.52 and CDCl$_3$ δ 77.16. Quantitative $^{13}$C-NMR was carried out with 200 mg sample in 0.8 mL DMSO-$d_6$ with 20 mM Chromium (III) acetylacetonate and a relaxation time of 10 s. 2D NMR techniques; COSY, HSQC, HMBC, DEPT and NOESY, were used to assign $^1$H and $^{13}$C shifts.

Size Exclusion Chromatography (SEC) was carried out on a TOSOH EcoSEC-HLC-8320GPC system equipped with an EcoSES RI detector and three columns from PSS GmbH were used (PSS PFG 5 μm; Microguard, 100 Å and 300 Å). A mobile phase of DMF with 0.01M LiBr (0.2 mL min$^{-1}$) at 50 °C was used together with a linear polymethylmethacrylate (PMMA) calibration method.

Differential Scanning Calorimetry (DSC) was performed on a Mettler Toledo DSC820, at a heating/cooling rate of 10°C min$^{-1}$ under nitrogen flow (50 mL min$^{-1}$). Glass transition temperature ($T_g$) was taken as the midpoint of transition on the second heating scan (20°C to 200°C).

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC1, using the STARre software to process the data. A sample of 5 mg was placed in a 70 µL ceramic crucible and heated from 40°C to 450°C at a rate of 10°C min$^{-1}$ under nitrogen flow (50 mL min$^{-1}$).

Melt-processing by compression molding of polymer films was performed using a TPB400 laboratory press (Fontijne Grotnes BV, Vlaardingen, The Netherlands) with a pressure of 20 kN for 10 min followed by 100 kN for 10 min, at 110 °C. Sample powders were pressed between two PET-films into a stainless steel mold, geometry 250 μm thickness by 3.4 cm in diameter.

Dynamic mechanical analysis (DMA) characterization was performed on a TA Instruments (New Castle, DE, USA) DMA Q800 in three-point bending mode, with the geometry of (20 × 6.5 × 2.5 mm). Temperature ramp was performed going from 25°C with a heating rate of 5°C min$^{-1}$ up to 100°C, with a frequency of 1 Hz and a strain-amplitude of 20 μm.
Experimental procedures

Synthesis of dihydroxyacetone dimethylacetal ((MeO)$_2$DHA)
Dihydroxyacetone (DHA) (100 g, 1.11 mol), trimethylorthoformate (118.4 g, 1.11 mol), and $p$-toluenesulfonic acid (422 mg, 2.22 mmol), were combined with 1.1 L of methanol and stirred for 19 h. After which 1.17 g (10.0 mmol) of Na$_2$CO$_3$ was added and stirred for another 12 h. The reaction was then filtered and concentrated in vacuo, followed by recrystallization of the resulting solid in diethyl ether, affording 70.2 g (47%) of white crystals. $^1$H NMR (D$_2$O): $\delta$ 3.63 (s, 4H, CH$_2$ 1 and 3), 3.29 (s, 6H, COCH$_3$ 4' and 4'').

Synthesis of isosorbide-biscarbonylimidazolide(Iso-bis-Im)
Isosorbide (40 g, 0.274 mol) was dissolved in 800 mL of acetone. 1,1'-carbonyldiimidazole (CDI) (111 g, 0.684 mol) was slowly added under argon flow and stirred for 4h. Product precipitated out of solution and was collected in a glass filter and washed with diethyl ether to afford a white powder, yield 83.0 g (89%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.15 (s, 1H), 8.10 (s, 1H), 7.44 (s, 1H), 7.38 (s, 1H), 7.09 (s, 1H), 7.07 (s, 1H), 5.47 (d, 1H, $J$ = 3.1 Hz, H2), 5.42 (td, 1H, $J$ = 3.8 and 5.6 Hz, H5), 5.08 (t, 1H, $J$ = 5.3 Hz, H4), 4.69 (d, 1H, $J$ = 4.8 Hz, H3), 4.18 (m, 1H, H1'), 4.12 (m, 1H, H6'), 4.05-4.01 (m, 2H, H1'' and H6''). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 148.1 (C8), 147.8 (C7), 137.22, 137.19, 131.19, 131.15, 117.24, 117.16, 85.9 (C3), 81.2 (C4), 81.0 (C2), 77.1 (C5), 73.0 (C1), 71.0 (C6). Peaks between $\delta_C$ 137.22 to 117.16 ppm and $\delta_H$ 8.15 to 7.07 ppm correspond to carbonylimidazoles.

Synthesis of (MeO)$_2$DHA-biscarbonylimidazolide ((MeO)$_2$DHA-bis-Im)
CDI (14.9 g, 91.8 mmol) was suspended in ethyl acetate (35 mL). (MeO)$_2$DHA (5 g, 36.7 mmol) was added portion wise to avoid cyclization of the 1,3-diol. After addition of (MeO)$_2$DHA, suspension turns into a yellow solution, followed by product precipitation. Solids were collected in a glass filter and washed with diethyl ether to afford pure product as a white powder, 4.0 g (34%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.16 (s, 2H, H5), 7.43 (s, 2H, H7), 7.10 (s, 2H, H6), 4.51 (s, 4H, CH$_2$ 1 and 3), 3.37 (s, 6H, COCH$_3$ 4' and 4''). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 148.1 (C8), 137.3 (C5), 131.2 (C6), 117.2 (C7), 98.4 (C2), 62.9 (C1 and C3), 49.0 (C4' and C4'').
Synthesis of ethyl 1-imidazolecarboxylate
To a mixture of ethanol 3.6 mL (61.7 mmol) and ethyl acetate 60 mL, CDI (10 g, 61.7 mmol) was added and allowed to stir for 1 hour. The resulting solution was filtered through a silica plug and eluted with excess ethyl acetate. The filtrate was concentrated in vacuo to afford the pure product as a transparent oil, 5.15 g, 60%. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.13 (s, 1H, H3), 7.42 (s, 1H, H5), 7.06 (s, 1H, H4), 4.47 (q, 2H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\)), 1.43 (t, 3H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\)).

Synthesis of (MeO)\(_2\)DHA-diethyl carbonate ((MeO)\(_2\)DHA-DEC)
(MeO)\(_2\)DHA (2 g, 14.7 mmol), Cesium Fluoride (112 mg, 0.734 mmol) and ethyl 1-imidazolecarboxylate (5.15 g, 36.7 mmol) were mixed under neat conditions and allowed to stir over night. After which precipitated imidazole was filtered off and product was purified by column chromatography (Ethyl acetate/heptane), using an ethyl acetate gradient from 0% to 30%. Product was isolated as a transparent oil 3.49 g, 85%. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 4.21 (s, 4H, CCH\(_2\)O 1 and 3), 4.20 (q, 4H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\) 5' and H5'), 3.28 (s, 6H, OCH\(_3\) 4' and 4''), 1.31 (t, 6H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\) 6' and 6''). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 154.7 (O(CO)O 7' and 7''), 98.6 (C2), 64.4 (C5' and C5''), 63.0 (C1 and C3), 48.6 (C4' and C4''), 14.3 (C6' and 6'').

Synthesis of DHA-diethyl carbonate (DHA-DEC)
(MeO)\(_2\)DHA-DEC (3.0 g, 10.7 mmol) and triphenylcarbonium tetrafluoroborate (Ph\(_3\)CBF\(_4\)) (3.53 g, 10.7 mmol) were added to 200 mL of dichloromethane and allowed to stir for 1h. To the stirring reaction aqueous NaHCO\(_3\) (10%) was added and later washed with distilled water. The organic phase was dried over Na\(_2\)SO\(_4\) and purified by column chromatography (Ethyl acetate/heptane), using an ethyl acetate gradient from 0% to 35%. Product was isolated as a white powder 2.36 g, 94%. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 4.81 (s, 4H, CH\(_2\)(CO)CH\(_2\) 1 and 3), 4.25 (q, 4H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\) 4' and 4''), 1.34 (t, 6H, \(J = 7.1\) Hz, OCH\(_2\)CH\(_3\) 5' and 5''). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 197.9 (CH\(_2\)(CO)CH\(_2\)), 154.6 (O(CO)O 6' and 6''), 69.2 (C1 and C3), 65.2 (C4' and 4''), 14.3 (C5' and C5'').
Representative procedure for polymerization of poly(isosorbide-co-(MeO)$_2$DHA)

All polymerizations were performed in 50-100 mL round-bottom flasks, fitted with magnetic stir bars, flame dried under vacuum. Varying feed ratios of (MeO)$_2$DHA (1), bis-carbonylimidazolide (2 or 4) and isosorbide (3) were added in powder form (1:1 eq. diol to bis-carbonylimidazolide), sealed and cycled with vacuum/Argon three times. Stock solutions of DBU and solvent (CHCl$_3$ or MeCN), were dried overnight on vacuum/heat activated 3Å molecular sieves, and added to reaction vessel using a syringe. Final catalytic loading was 1 mol-% DBU with regard to bis-carbonylimidazolide. Solvent reactions were either carried out at room temperature or at 50°C under magnetic stirring for 5h to 16h. Neat reactions were carried out at 100 °C to 120 °C, adding catalyst directly to reaction vessel and reacting for 3h to 4h. After which the DBU was quenched with 5 eq. acetic acid and precipitated in methanol, forming a white powder precipitate, in scales of 2 to 10 g and yields of 87-97%. $^1$H NMR (CDCl$_3$, 400 MHz): δ 5.05-5.11 (2H, br m, H$_7$ and H$_{10}$), 4.89 (1H, br t, H$_9$), 4.53 (1H, br d, H$_8$), 4.29-4.17 (4H, br m, CH$_2$1 and 3), 4.10-3.97 (2H, br m, CH$_2$6), 3.96-3.85 (2H, br m, CH$_2$11), 3.27 (6H, br s, CH$_3$ 4). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 154.1-153.2 (m, O(CO)O), 98.3 (C2), 85.8 (C8), 81.6 (C7), 81.1 (C9), 77.3 (C10), 73.2 (C6), 70.6 (C11), 63.3 (CH$_2$(CO) CH$_2$1 and 3), 48.6 (CH$_3$ 4).

Representative procedure for deprotection of poly(isosorbide-co-(MeO)$_2$DHA)

Deprotection of the dimethyl ketal was performed using trityl tetrafluoroborate Ph$_3$CBF$_4$ (1 eq.) in DCM.$^4$ To a round-bottom flask fitted with a magnetic stir bar, 300 mL of CH$_2$Cl$_2$, poly(Iso$_x$-co-(MeO)$_2$DHA$_y$) (3.00 g, 8.98 mmol), Ph$_3$CBF$_4$ (2.96 g, 8.98 mmol, 1 eq. per (MeO)$_2$DHA repeating unit) and H$_2$O (180 µL, 8.98 mmol). Reaction was allowed to stir at room temperature for 1h. After which solvent was removed in vacuo and purified by precipitation into methanol, affording 2 to 10 g (87-97 %) of polymer as white powder. $^1$H NMR ((CD$_3$)$_2$SO, 400 MHz): δ 5.07 (1H, br m, H6), 5.01 (1H, br m, H9), 4.97 (4H, br m, CH$_2$ 1 and 3), 4.85 (1H, br m, H7), 4.78 (1H, br m, H8), 3.99 (1H, br m, H10). 3.85 (3H, br m, H5, H5’ and H10’). $^{13}$C NMR ((CD$_3$)$_2$SO, 100 MHz): δ 197.6 (C2), 153.5-153.2 (C4, C4’), 85.2 (C8), 81.2 (C9), 80.6 (C7), 77.3 (C6), 72.3 (C10), 70.3 (C5), 68.8 (C1 and C3).
Kinetics of DBU polymerization

Diazabicycloundecene (DBU) is a highly potent organocatalyst for ring-opening polymerization (ROP). To evaluate the catalytic potential of DBU for step-growth polymerization of biscarbonylimidazolides (bis-Im) and diols, a model substrate (1,6-hexane diol) was chosen. This gave better baseline resolution for $^1$H NMR to follow the reaction kinetics. Polymerizations were performed in CDCl$_3$ using an initial bis-Im concentration of 1.88 M and a DBU loading of 0.0188 M and 0.094 M respectively. Aliquots were taken at specific time points and diluted in CDCl$_3$ and acetic acid (5 eq. per DBU) to quench the DBU. Data in Figure 1 suggest second-order kinetics with respect to hydroxyl-concentration, consistent with traditional step-growth polymerizations. The sharp rate increase going from 1% to 5% DBU indicated a satisfactory catalytic effect for polymerization reactions.

Figure S1. Second-order kinetics plot for 1% and 5% DBU catalyzed polymerizations
Cyclization during polymerization

Figure S2. Crude $^1$H-NMR spectra for step-growth polymerization of diol monomer (1), indicating cyclization into six-membered carbonate analogue (5) with singlet peaks at $\delta$ 4.28 and 3.31 ppm, corresponding to CH$_2$ and CH$_3$ respectively.
Scrambling of 1,3-diol for statistically random co-polymers

Integration of $^{13}$C-NMR carbonyl peaks for co-polymer V and VI, using inverse-gated decoupling $^{13}$C-NMR with 20 mM Chromium (III) acetylacetonate and a relaxation time of 10 s in (CD$_3$)$_2$SO. Dyad content $N_{A/A}$, $N_{B/A}$ and $N_{B/B}$ refers to integrals of carbonyl shifts of corresponding AA, AB/BA and BB dyads.$^5$

Table S1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>DHA/iso</th>
<th>$N_{A/A}$</th>
<th>$N_{A/B}$</th>
<th>$N_{B/B}$</th>
<th>$L_{nA}$</th>
<th>$L_{nB}$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>50/50</td>
<td>22.7</td>
<td>53.4</td>
<td>23.9</td>
<td>1.85</td>
<td>1.90</td>
<td>1.07</td>
</tr>
<tr>
<td>VI</td>
<td>25/75</td>
<td>2.7</td>
<td>24.7</td>
<td>72.6</td>
<td>1.22</td>
<td>6.87</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Number average sequence length ($L_{nA}$) of dyad A:

$$L_{nA} = \frac{N_{A\beta} + 2N_{A/A}}{N_{A\beta}}$$

Number average sequence length ($L_{nB}$) of dyad B:

$$L_{nB} = \frac{N_{A\beta} + 2N_{B\beta}}{N_{A\beta}}$$

Degree of randomness $R$:

$$R = \frac{1}{L_{nA}} + \frac{1}{L_{nB}}$$
Model compound degradation study

Kinetic study

Degradation reaction:

\[
\begin{align*}
[A] & \xrightleftharpoons[k_{-1}]{k_1} [B] \xrightarrow{k_2} [C] \xrightleftharpoons[k_{-3}]{k_3} [D] \xrightarrow{k_4} [E] \xrightleftharpoons[k_{-5}]{k_5} [F] \\
\end{align*}
\]

Equilibrium approximation:

\[
k_1, k_{-1}, k_3, k_{-3}, k_5 \text{ and } k_{-5} \gg k_2 \text{ and } k_4
\]

Simplified consecutive degradation reaction:

\[
[A+B] \xrightarrow{k'} [C+D] \xrightarrow{k''} [E+F]
\]

Integrated rate expressions:

\[
[A + B] = [A + B]_0 e^{-k't}
\]

\[
[C + D] = \frac{k[A + B]_0}{k'' - k'} (e^{-k't} - e^{-k''t})
\]

\[
[E + F] = [A + B]_0 \left[ 1 + \frac{1}{k'' - k'} (k'' e^{-k't} - k' e^{-k''t}) \right]
\]

Figure S3. Observed rate constants \((k_{obs})\) for the hydrolysis of A and B, over a pH* range of 5 to 9.6.
Table S2. Kinetic data for degradation of DHA-(EC)...

<table>
<thead>
<tr>
<th>pH* (D₂O)</th>
<th>pH* (D₂O/CD₃CN)</th>
<th>$K_{obs, EtOH}$ (h⁻¹)</th>
<th>$K_{obs,B}$ (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>9.6</td>
<td>3.7 × 10⁻¹</td>
<td>4.5 × 10⁻¹</td>
</tr>
<tr>
<td>8.1</td>
<td>8.8</td>
<td>2.4 × 10⁻¹</td>
<td>3.5 × 10⁻¹</td>
</tr>
<tr>
<td>7.6</td>
<td>8.3</td>
<td>1.3 × 10⁻¹</td>
<td>2.2 × 10⁻¹</td>
</tr>
<tr>
<td>7.4</td>
<td>8.0</td>
<td>8.8 × 10⁻²</td>
<td>1.4 × 10⁻¹</td>
</tr>
<tr>
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<td>5.9 × 10⁻²</td>
<td>9.1 × 10⁻²</td>
</tr>
<tr>
<td>7.0</td>
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<td>5.2 × 10⁻²</td>
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</tr>
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<td>7.3</td>
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<td>2.1 × 10⁻²</td>
</tr>
<tr>
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<td>6.7</td>
<td>2.8 × 10⁻³</td>
<td>3.7 × 10⁻³</td>
</tr>
<tr>
<td>4.9</td>
<td>5.8</td>
<td>6.0 × 10⁻⁴</td>
<td>9.0 × 10⁻⁴</td>
</tr>
<tr>
<td>4.1</td>
<td>5.0</td>
<td>1.0 × 10⁻⁴</td>
<td>3.0 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Figure S4. Hydrolysis over time at different pH* in D₂O/MeCN (60/40 v/v), buffered using 50 mM acetate or phosphate; (a) 7.3, (b) 7.5, (c) 7.9, and (d) 8.0. Lines represent a best fit to the integrated rate law of a two-step consecutive reaction.
NMR assignment of model compound and intermediate hydrolysis products

NMR assignments of unique CH$_2$ groups of each compound were carried out using $^1$H-NMR, $^{13}$C-NMR, HMBC and HSQC, supported by dilution studies of A and E in D$_2$O/CD$_3$CN using $^1$H-NMR. All shifts were referenced to the solvent residual of CD$_3$CN at $\delta$ 1.94 ppm.

Figure S5. $^1$H-NMR (400 MHz) assignment of model compound and hydrolysis products (D$_2$O and CD$_3$CN (60/40 v/v)

(A) $\delta$ 4.82 (s, 4H, CH$_2$(CO)CH$_2$ C1 and C3)

(B) $\delta$ 4.04 (s, 4H, CH$_2$(C(OH)$_2$)CH$_2$ C1 and C3)

(C) $\delta$ 4.83 (s, 2H, CH$_2$(CO)CH$_2$ C1), 4.26 (s, 2H, CH$_2$(CO)CH$_2$OH C3)

(D) $\delta$ 4.04 (s, 2H, CH$_2$(C(OH)$_2$)CH$_2$ C1), 3.42 (s, 2H, CH$_2$(C(OH)$_2$)CH$_2$OH C3)

(E) $\delta$ 4.26 (s, 4H, CH$_2$(CO)CH$_2$ C1 and C3)

(F) $\delta$ 3.42 (s, 4H, CH$_2$(C(OH)$_2$)CH$_2$ C1 and C3)

Solving for each component:

[A] and [C] are solved by integration

[E] is given by integral at 4.26 ppm subtracting C1

[F] is achieved from the equilibrium constant $K_{EF} = [F]/[E] = 0.11$

[D] is achieved by subtraction F1,3 to get D3

[B] is given by the integral at 4.04 ppm subtracting D1

$[A]_0 = [A] + [B] + [C] + [D] + [E] + [F] = 17.31$ mM
Figure S6. $^1$H-$^{13}$C HMBC NMR spectrum (A) and zoomed in spectrum (B) (D$_2$O) for the degradation of DHA-(EC)$_2$ at 298K in D$_2$O/MeCN-d$_3$ (60/40 v/v) and 50 mM phosphate buffer at pH* = 8.0. Spectrum was recorded on a Bruker Avance 400 (100) MHz NMR instrument, with 115 scans using the HMBCGPNQDF pulse sequence.
Figure S7. $^1$H-$^{13}$C HSQC-edited NMR spectrum (D$_2$O) for the degradation of DHA-(EC)$_2$ at 298K in D$_2$O/MeCN-$d_3$ (60/40 v/v) and 50 mM phosphate buffer at pH* = 8.0. Spectrum was recorded on a Bruker Avance 400 (100) MHz NMR instrument, with 4 scans using the phase sensitive HSQCEDETGP pulse sequence.
Polymer degradation study

Figure S8. Polymer pellet

Structural characterization

Figure S9. $^1$H NMR spectrum of dihydroxyacetone dimethylacetal ([(MeO)$_2$DHA] (1) (400 MHz, CDCl$_3$).
Figure S10. $^1$H NMR spectrum of isosorbide-biscarbonylimidazolide (2) (400 MHz, CDCl$_3$).

Figure S11. $^{13}$C NMR spectrum of isosorbide-biscarbonylimidazolide (2) (100 MHz, CDCl$_3$).
Figure S12. HSQC-edited NMR spectrum of isosorbide-biscarbonylimidazolide (2) (400 (100) MHz, CDCl$_3$).

Figure S13. HMBC NMR spectrum of isosorbide-biscarbonylimidazolide (2) (400 (100) MHz, CDCl$_3$).
Figure S14. COSY NMR spectrum of isosorbide-biscarbonylimidazolide (2) (400 MHz, CDCl₃).
Figure S15. NOESY 1D NMR (SELNO1H) spectrum of isosorbide-biscarbonylimidazolide (2) (400 MHz, CDCl₃).
Figure S16. $^1$H NMR spectrum of (MeO)$_2$DHA-biscarbonylimidazolide (4) (400 MHz, CDCl$_3$).

Figure S17. $^{13}$C NMR spectrum of (MeO)$_2$DHA-biscarbonylimidazolide (4) (100 MHz, CDCl$_3$).
Figure S18. $^1$H NMR spectrum of ethyl 1-imidazolecarboxylate (400 MHz, CDCl$_3$).
Figure S19. $^1$H NMR spectrum of (MeO)$_2$DHA-diethyl carbonate (400 MHz, CDCl$_3$).

Figure S20. $^{13}$C NMR spectrum of (MeO)$_2$DHA-diethylcarbonate (100 MHz, CDCl$_3$).
Figure S21. $^1$H NMR spectrum of dihydroxyacetone-diethyl carbonate (DHA-(EC)$_2$) (400 MHz, CDCl$_3$).

Figure S22. $^{13}$C NMR spectrum of dihydroxyacetone-diethyl carbonate (DHA-(EC)$_2$) (100 MHz, CDCl$_3$).
Figure S23. $^1$H NMR spectrum of poly(Iso-alt-(MeO)$_2$DHA) (400 MHz, CDCl$_3$).

Figure S24. $^{13}$C NMR spectrum of poly(Iso-alt-(MeO)$_2$DHA) (100 MHz, CDCl$_3$).
Figure S25. $^{13}$C DEPT (135, 90) NMR spectrum of poly(Iso-alt-(MeO)$_2$DHA) (100 MHz, CDCl$_3$).

Figure S26. HSQC-edited NMR spectrum of poly(Iso-alt-(MeO)$_2$DHA) (100 MHz, CDCl$_3$).
Figure S27. $^1$H NMR spectrum of poly(isosorbide-alt-DHA) (400 MHz, CDCl$_3$).

Figure S28. $^{13}$C NMR spectrum of poly(isosorbide-alt-DHA) (100 MHz, CDCl$_3$). *Trityl functional end-groups
Figure S29. HSQC-edited NMR spectrum of poly(isosorbide-alt-DHA) (100 MHz, (CD$_3$)$_2$SO).

References