Supplemental information

Advancing the Development of Highly-Functionalizable Glucose-Based Polycarbonates by Tuning of the Glass Transition Temperature

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Materials and Methods.

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) and 2-ethylhexyl chloroformate were used as received from TCI America (Portland, OR). 4-Methylbenzyl alcohol was purified by recrystallization from petroleum ether and stored in a glovebox under Ar atmosphere. Amberlyst® 15 (H), ion exchange resin and *N,N,N′,N′*-tetramethylethylenediamine, 99% were purchased from Alfa Aesar, Thermo Fisher Scientific (Ward Hill, MA). Triphosgene was used as received from Oakwood Products, Inc. (Estill, SC). Dichloromethane (DCM) was purified by a solvent purification system (J. C. Meyer Solvent Systems, Inc., Laguna Beach, CA). Other reagents were used as received from Sigma-Aldrich, Co. (St. Louis, MO) unless otherwise noted.

Instrumentation.

^{1}H NMR and ^{13}C NMR spectra were acquired on a Varian Inova 500 spectrometer interfaced to a UNIX computer using VnmrJ software. Chemical shifts were referenced to the residual solvent resonance signals.

Fourier transform infrared (FT-IR) spectra were recorded on an IR Prestige 21 system (Shimadzu Corp., Japan), equipped with an attenuated total reflectance (ATR) accessory, and analyzed using IRsolution v. 1.40 software.

Size exclusion chromatography (SEC) eluting with THF was conducted on a Waters Chromatography, Inc. (Milford, MA) system equipped with an isocratic pump (model 1515), a differential refractometer (model 2414), and a four-column set, including a 5 μm Guard column (50 × 7.5 mm), a PLgel 5 μm Mixed C column (300 × 7.5 mm, Agilent Technologies) and two Styragel® columns (500 Å and 104 Å, 300 × 7.5 mm, Waters Chromatography, Inc.). The system was equilibrated at 40 °C in THF with the flow rate set to 1.0 mL/min. Data collection and analysis were performed with Waters Breeze™ software. Molar masses were determined relative to polystyrene standards (615-442800 Da) purchased from Polymer Laboratories, Inc. (Amherst, MA). Polymer solutions were prepared at a concentration of *ca.* 3 mg/mL with 0.05 vol% toluene added as a flow marker, and an injection volume of 200 μL was used.

Preparative size exclusion chromatography (prep SEC) eluting with chloroform was conducted on a JAI LC-9230II NEXT Chromatography, Inc. (Japan) system equipped with a reciprocating double plunger pump (model P-9104B), a UV-vis 4ch NEXT detector at four wavelengths (254 nm, 280 nm, 300 nm, 330 nm), and a two-column set, including a JAIGEL-H 40P Guard column and a JAIGEL-2H-40 HPLC column. The system was equilibrated at room temperature in chloroform with the flow rate set to 14.0 mL/min. Data collection and analysis were performed with JAI Scan™ software. Polymer solutions were prepared at a concentration of *ca*. 10 mg/mL in chloroform and an injection volume of 5 mL was used.

Thermogravimetric analysis (TGA) was performed under an Ar atmosphere using a Mettler-Toledo model TGA2/1100/464 with a heating rate of 10 °C/min. Data were analyzed using Mettler-Toledo STAR^e v. 15.00a software

Glass transitions (T_g) were measured by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC3/700/1190® (Mettler-Toledo, Inc., Columbus, OH) under $N_{2(g)}$. Measurements were performed with a heating rate of 10 °C/min and analyzed using Mettler-Toledo Star^e v. 15.00a software. The T_g was taken as the midpoint of the inflection tangent of the second heating scan.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using a Thermo Scientific Q Exactive Focus. The sample was directly infused at a flow rate of 10 μL/min. The Q-Exactive Focus HESI source was operated in full MS in positive mode. The mass resolution was tuned to 70000 FWHM at m/z 200. The spray voltage was set to 3.75 kV, and the sheath gas and auxiliary gas flow rates were set to 7 and 0 arbitrary units, respectively. The transfer capillary temperature was held at 320 °C. Exactive Series 2.8 SP1/Xcalibur 4.0 software was used for data acquisition and processing.

Matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) was performed on a microflex™ LRF mass spectrometer (Bruker Corporation, Billerica, MA) in positive linear mode. Ions were generated by a pulsed nitrogen laser (337 nm, 25 kV), and 200 laser pulses were used per spectrum. Trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) and potassium trifluoroacetate (KTFA) were used as a matrix and cationization reagent, respectively. The sample and matrix were prepared at 1 and 26 mg/mL, respectively, in chloroform, and KTFA was prepared at 1 mg/mL in acetone. The sample solution was mixed with the matrix and KTFA at a volumetric ratio of 2:2:1, and 1 μL of the mixture was deposited onto a stainless-steel sample holder and dried in air prior to the measurement.

Synthetic protocols.

Synthesis of the bicyclic glucose carbonate monomers were performed following previously reported procedures,[1] using the corresponding alkyl chloroformates as starting materials. For simplicity, these monomers (Scheme 1) are systematically named:

methyl-2,3-*O*-*n*-ethyloxycarbonyl-4,6-*O*-carbonyl-α-D-glucopyranoside GC(EEC) (**1**),

methyl-2,3-*O*-*n*-butyloxycarbonyl-4,6-*O*-carbonyl-α-D-glucopyranoside GC(BBC) (**2**),

methyl-2,3-*O*-*n*-hexyloxycarbonyl-4,6-*O*-carbonyl-α-D-glucopyranoside GC(HHC) (**3**),

methyl-2,3-*O*-isobutyloxycarbonyl-4,6-*O*-carbonyl-α-D-glucopyranoside GC(isoBBC) (**4**),

methyl-2,3-*O*-neopentyloxycarbonyl-4,6-*O*-carbonyl-α-D-glucopyranoside GC(neoPPC) (**5**), and methyl-2,3-*O*-2-ethylhexyloxycarbonyl-4,6-*O*-carbonyl-α-D-glucopyranoside GC(EHEHC) (**6**).

The monomers **1**–**5** were purified by column chromatography and recrystallization in ethyl acetate and hexanes, while monomer **6** was a liquid/wax like compound that was purified by column chromatography and extensive drying against phosphorous pentoxide under reduced pressure.

Monomer GC(BBC) (2): ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 5.40 (dd, *J* = 10, 10 Hz, 1H, 3-C*H*), 5.08 (d, *J* = 4 Hz, 1H, 1-C*H*), 4.71 (dd, *J* = 10, 4 Hz, 1H, 2-C*H*), 4.53 (m, 1H, 6-CH_2), 4.33 – 4.25 (m, 1H, 6-CH_2), 4.25 – 4.09 (m, 6H, 4-C*H*, 5-C*H*, 2,3-CHOCOC$H_2CH_2CH_2CH_3$), 3.47 (s, 3H, 1-CHOCH_3), 1.71 – 1.59 (m, 4H, 2,3-CHOCOCH_2C$H_2CH_2CH_3$), 1.40 (m, 4H, 2,3-CHOCOCH_2CH_2CH_2CH_3), 0.94 and 0.93 (t, *J* = 7 Hz, 6H, 2,3-CHOCO$CH_2CH_2CH_2$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.45, 154.04, 146.50, 97.97, 76.65, 73.63, 71.86, 69.43, 68.97, 68.94, 59.69, 56.37, 30.66, 30.62, 18.97, 18.93, 13.76, 13.73. FT-IR(ATR): 2950, 2870, 1782, 1749, 1460, 1394, 1361, 1268, 1244, 1193, 1151, 1109, 1050, 1025, 978, 931, 900, 848, 777, 656 cm^{-1}. HRMS (ESI^+) $C_{18}H_{28}O_{11}Na^+$ 443.1529, found ($M+Na^+$) 443.1515; $C_{18}H_{28}O_{11}H^+$ 421.1710, found 421.1698.

Monomer GC(HHC) (3): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.40 (m, *J* = 10, 10 Hz, 1H, 3-C*H*), 5.08 (d, *J* = 4 Hz, 1H, 1-C*H*), 4.70 (dd, *J* = 10, 4 Hz, 1H, 2-C*H*), 4.57 – 4.50 (m, 1H, 6-CH_2), 4.34 – 4.25 (m, 1H, 6-CH_2), 4.25 – 4.10 (m, 6H, 4-C*H*, 5-C*H*, 2,3-CHOCOC$H_2(CH_2)_4CH_3$), 3.46 (s, 3H, 1-CHOCH_3), 1.70 – 1.59 (m, 4H, 2,3-CHOCOCH_2C$H_2CH_2CH_2CH_2CH_3$), 1.41 – 1.22 (m, 12H, 2,3-CHOCOCH_2CH_2CH_2CH_2CH_2CH_3), 0.88 (t, *J* = 7 Hz, 6H, 2,3-CHOCO$(CH_2)_5$CH_3). ^{13}C

NMR (126 MHz, $CDCl_3$, ppm) δ 154.43, 154.02, 146.50, 97.95, 76.65, 73.62, 71.85, 69.42, 69.36, 69.26, 69.24, 59.67, 56.35, 31.49, 31.45, 28.59, 28.57, 25.39, 25.34, 22.60, 14.09, 14.08. FT-IR(ATR): 2927, 2857, 1782, 1736, 1460, 1390, 1329, 1263, 1240, 1193, 1146, 1114, 1058, 1025, 974, 908, 777, 670 cm^{-1}. HRMS (ESI^+) $C_{22}H_{36}O_{11}Na^+$ 499.2155, found ($M+Na^+$) 499.2145; $C_{22}H_{36}O_{11}H^+$ 477.2336, found 477.2327.

Monomer GC(isoBBC) (4): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.38 (dd, J = 10, 10 Hz, 1H, 3-CH), 5.08 (d, J = 4 Hz, 1H, 1-CH), 4.73 (dd, J = 10, 4 Hz, 1H, 2-CH), 4.54 (m, 1H, 6-CH_2), 4.34 – 4.16 (m, 3H, 6-CH_2, 4-CH, 5-CH), 4.04 – 3.88 (m, 4H, 2,3-CHOCOCH_2CH(CH_3)$_2$), 3.47 (s, 3H, 1-CHOCH_3), 1.98 (spt, J = 7 Hz, 2H, 2,3-CHOCOCH_2CH(CH_3)$_2$), 0.97 – 0.90 (m, 12H, 2,3-CHOCOCH_2CH(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.13, 153.84, 146.34, 97.51, 76.06, 74.50, 74.42, 73.32, 71.75, 69.06, 59.27, 55.80, 27.51, 27.46, 18.54, 18.51, 18.47, 18.46. FT-IR(ATR): 1962, 2880, 1777, 1749, 1459, 1375, 1268, 1240, 1193, 1146, 1104, 1053, 1030, 974, 894, 820, 777, 763, 670 cm^{-1}. HRMS (ESI^+) $C_{18}H_{28}O_{11}Na^+$ 443.1529, found ($M+Na^+$) 443.1514; $C_{18}H_{28}O_{11}H^+$ 421.1710, found 421.1698.

Monomer GC(neoPPC) (5): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.47 – 5.38 (m, 1H, 3-CH), 5.08 (d, J = 4 Hz, 1H, 1-CH), 4.74 (dd, J = 10, 4 Hz, 1H, 2-CH), 4.57 – 4.49 (m, 1H, 6-CH_2), 4.34 – 4.26 (m, 1H, 6-CH_2), 4.26 – 4.17 (m, 2H, 4-CH, 5-CH), 3.94 – 3.78 (m, 4H, 2,3-CHOCOCH_2C(CH_3)$_3$), 3.47 (s, 3H, 1-CHOCH_3), 0.94 and 0.93 (s, 18H, 2,3-CHOCOCH_2C(CH_3)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.74, 154.29, 146.52, 98.01, 78.26, 78.22, 76.65, 73.67, 71.82, 69.44, 59.73, 56.37, 31.75, 31.74, 26.34, 26.29, 26.27. FT-IR(ATR): 2963, 2880, 1782, 1750, 1469, 1400, 1371, 1268, 1240, 1198, 1156, 1110, 1057, 1029, 983, 950, 908, 773, 679 cm^{-1}. HRMS (ESI^+) $C_{20}H_{32}O_{11}Na^+$ 471.1842, found ($M+Na^+$) 471.1834; $C_{20}H_{32}O_{11}H^+$ 449.2023, found 449.2016.

Monomer GC(EHEHC) (6): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.40 (dd, J = 10 ,10 Hz, 1H, 3-CH), 5.08 (d, J = 4 Hz, 1H, 1-CH), 4.71 (dd, J = 10, 4 Hz, 1H, 2-CH), 4.57 – 4.49 (m, 1H, 6-CH_2), 4.32 – 4.15 (m, 3H, 6-CH_2, 4-CH, 5-CH), 4.15 – 3.99 (m, 4H, 2,3-CHOCOCH_2CH(CH_2CH_3)$CH_2CH_2CH_2CH_3$), 3.46 (s, 3H, 1-CHOCH_3), 1.66 – 1.55 (m, 2H, 2,3-CHOCOCH_2CH(CH_2CH_3)$CH_2CH_2CH_2CH_3$), 1.36 - 1.25 (m, 16 H, 2,3-CHOCOCH_2CH(C$H_2$$CH_3$)C$H_2CH_2CH_2$$CH_3$), 0.88 (m, 12H, 2,3-CHOCOCH_2CH(CH_2CH_3)$CH_2CH_2CH_2$CH_3). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.61, 154.18, 146.50, 97.95, 76.64, 73.63, 71.82, 71.59, 71.55, 71.52, 69.41, 59.67, 56.34, 38.93, 38.89, 38.87, 30.24, 30.15, 30.11, 30.07, 29.01, 28.98, 28.93, 28.89, 23.57, 23.50, 23.02, 14.13, 10.98, 10.96, 10.94. FT-IR(ATR): 2960, 2925, 2869, 1755, 1460, 1383, 1264, 1242, 1194, 1140, 1243, 1187, 1145, 1103, 1046, 980, 905, 785, 765, 670 cm^{-1}. HRMS (ESI^+) $C_{26}H_{44}O_{11}Na^+$ 555.2781, found ($M+Na^+$) 555.2777; $C_{26}H_{44}O_{11}H^+$ 533.2962, found 533.2956.

Synthesis of poly(α-D-glucose carbonate)s PGC(RRC) homopolymers: A solution of alkyloxycarbonyl protected glucose carbonate monomer GC(RRC) (200 mg, at predetermined equivalences) and 4-methylbenzyl alcohol (1 eq.) dissolved in *ca.* 1.0 mL of anhydrous DCM was transferred to a vial equipped with a stir bar and a rubber septum in a glovebox under Ar atmosphere, and the reaction was conducted in a -78 °C dry ice/acetone bath in a fume hood. A solution of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (*ca.* 0.5 eq.) in 0.1 mL of anhydrous DCM was injected quickly into the vial under -78 °C. The reaction mixture was allowed to stir at -78 °C for 5 min, then quenched by adding an excess amount of acetic acid. The product was purified by precipitation from DCM into methanol three times and dried under vacuum.

PGC(BBC): ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27 and 7.16 (AB_q, J = 8 Hz), 5.33 (dd, J = 10, 10 Hz), 5.00 (d, J = 4 Hz), 4.80 (t, J = 10 Hz), 4.70 (dd, J = 10, 4 Hz), 4.32 (d, J = 11 Hz), 4.23 – 4.06 (m), 4.06 – 4.01 (m), 3.40 (s), 2.34 (s), 1.66 – 1.60 (m), 1.36 – 1.22 (m), 0.93 and 0.92 (t, J = 7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.40, 154.34, 153.91, 96.46, 73.87, 73.60, 72.91, 68.67, 68.56, 66.89, 66.14, 55.76, 30.67, 30.65, 18.95, 18.92, 13.77, 13.75. FT-IR(ATR): 2959, 2868, 1752, 1456, 1394, 1232, 1163, 1110, 1032, 948, 846, 777 cm^{-1}. Yield: 91%. T_g = 68 °C. TGA in Ar: 270-393 °C, 87% mass loss. SEC (THF, PS standards): M_n = 15.5 kDa, $Đ$ = 1.06.

PGC(HHC): ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27 and 7.16 (AB_q, J = 8 Hz), 5.33 (dd, J = 10, 10 Hz), 5.00 (d, J = 4 Hz), 4.80 (t, J = 10 Hz), 4.71 (dd, J = 10, 4 Hz), 4.32 (d, J = 11 Hz), 4.24 – 4.03 (m), 3.41 (s), 2.35 (s), 1.71 – 1.57 (m), 1.55 (s), 1.44 – 1.31 (m), 0.92 (t, J = 7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.23, 154.15, 153.75, 129.19, 128.53, 96.30, 77.26, 77.00, 76.75, 73.74, 73.47, 72.77, 68.78, 68.70, 66.73, 65.96, 55.59, 31.37, 31.34, 31.19, 28.61, 28.46, 25.22, 25.20, 25.06, 22.46, 22.32, 13.95, 13.93. FT-IR(ATR): 2936, 2855, 1749, 1453, 1372, 1232, 1166, 1113, 1029, 977, 908, 778 cm^{-1}. Yield: 90%. T_g = 46 °C. TGA in Ar: 256-396 °C, 85% mass loss. SEC (THF, PS standards): M_n = 15.9 kDa, $Đ$ = 1.06.

PGC(isoBBC): ^1H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27 and 7.16 (AB_q, J = 8 Hz), 5.38 – 5.26 (m), 5.00 (t, J = 4 Hz), 4.86 – 4.76 (m), 4.76 – 4.67 (m), 4.32 (d, J = 11 Hz), 4.20 (dd, J = 12, 6

Hz), 4.09 – 4.01 (m), 4.00 – 3.83 (m), 3.41 (s), 2.34 (s), 1.95 (m), 0.92 and 0.91 (d, J = 7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.48, 154.40, 153.92, 129.36, 128.70, 96.47, 77.35, 74.76, 74.63, 73.88, 73.59, 72.94, 66.90, 66.18, 55.77, 27.89, 27.86, 18.94, 18.92, 18.90. FT-IR(ATR): 2959, 2876, 1751, 1459, 1378, 1231, 1169, 1110, 1035, 967, 777 cm^{-1}. Yield: 89%. T_g = 85 °C. TGA in Ar: 260-394 °C, 86% mass loss. SEC (THF, PS standards): M_n = 14.9 kDa, $Đ$ = 1.05.

PGC(neoPPC): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz), 5.36 (dd, J = 10, 10 Hz), 5.01 (d, J = 4 Hz), 4.80 (t, J = 10 Hz), 4.75 – 4.69 (m), 4.32 (d, J = 11 Hz), 4.19 (dd, J = 12, 6 Hz), 4.10 – 4.02 (m), 3.95 – 3.81 (m), 3.79 (dd, J = 10, 4 Hz), 3.41 (s), 3.44 – 3.33 (m), 2.35 (s), 0.93 and 0.92 (s). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.70, 154.57, 153.92, 128.71, 96.46, 77.98, 77.80, 77.35, 73.91, 73.55, 73.01, 66.90, 66.19, 55.78, 31.81, 31.72, 26.33, 26.32, 20.90. FT-IR(ATR): 2959, 2868, 1752, 1465, 1372, 1235, 1163, 1114, 1036, 958, 777 cm^{-1}. Yield: 91%. T_g = 125 °C. TGA in Ar: 266-398 °C, 89% mass loss. SEC (THF, PS standards): M_n = 15.7 kDa, $Đ$ = 1.06.

PGC(EHEHC): ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.27 and 7.16 (AB_q, J = 8 Hz), 5.33 (dd, J = 10, 10 Hz), 5.01 (d, J = 4 Hz), 4.79 (t, J = 10 Hz), 4.70 (dd, J = 10, 4 Hz), 4.32 (d, J = 11 Hz), 4.24 – 4.14 (m), 4.14 – 3.91 (m), 3.41 (s), 2.34 (s), 1.58 (br), 1.41 – 1.30 (m), 1.30 – 1.21 (br), 0.91 – 0.82 (m). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 154.58, 154.40, 153.93, 129.35, 128.69, 96.41, 77.14, 73.91, 73.62, 72.97, 71.30, 71.26, 71.17, 71.13, 66.85, 66.15, 55.75, 38.88, 30.18, 30.15, 30.11, 30.08, 29.00, 28.92, 23.54, 23.49, 23.06, 14.17, 14.16, 10.96, 10.93, 10.91. FT-IR(ATR): 2928, 2861, 1852, 1456, 1389, 1232, 1169, 1110, 1033, 967, 910, 777 cm^{-1}. Yield: 90%. T_g = 38 °C. TGA in Ar: 239-391 °C, 90% mass loss. SEC (THF, PS standards): M_n = 15.8 kDa, $Đ$ = 1.06.

Synthesis of oligomers and polymers with different molar mass of GC(neoPPC) and GC(EHEHC): Solutions of monomer and 4-methylbenzyl alcohol were dissolved in 0.5–1.0 mL of anhydrous DCM predetermined at different equivalence ratios. A solution of TBD (1% eq. of monomer) in 0.05 mL of anhydrous DCM was injected quickly into the reaction mixtures under -78 °C. After stirring for 5 min, the reaction was quenched by adding an excess amount of acetic acid. The products with DP_n > 6 were purified by precipitation from DCM into methanol three times; products with DP_n ≤ 5 were purified and separated using preparative SEC during up to 5 recycles, and dried under vacuum.

GC(neoPPC) unimer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.14 (s, 2H), 5.14 (dd, J = 10, 10 Hz, 1H), 4.97 (d, J = 4 Hz, 1H), 4.72 (dd, J = 10, 4 Hz, 1H), 4.49 (dd, J = 12, 4 Hz, 1H), 4.41 (dd, J = 12, 2 Hz, 1H), 3.86 – 3.78 (m, 5H), 3.68 (dd, J = 10, 9 Hz, 1H), 3.38 (s, 3H), 2.35 (s, 3H), 0.94 and 0.93 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 156.22, 155.58, 154.83, 138.68, 132.13, 129.40, 128.72, 128.51, 96.89, 78.13, 77.97, 76.69, 73.64, 70.13, 69.71, 69.37, 66.24, 55.57, 31.77, 31.73, 29.84, 26.33, 26.31, 26.27, 21.35. FT-IR(ATR): 3495, 2954, 2924, 2862, 1743, 1458, 1373, 1242, 1165, 1041, 980, 964, 918, 856, 787, 733 cm^{-1}. Yield: 10%. T_g = 13 °C. TGA in Ar: 164-373 °C, 81% mass loss.

GC(neoPPC) dimer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.33 (dd, J = 10, 10 Hz, 1H), 5.19 – 5.09 (m, 3H), 4.99 (dd, J = 12, 4 Hz, 2H), 4.91 (dd, J = 10, 9 Hz, 1H), 4.77 (dd, J = 10, 4 Hz, 1H), 4.71 (dd, J = 10, 4 Hz, 1H), 4.50 – 4.20 (m, 4H), 4.04 (3, 1H), 3.95 – 3.76 (m, 9H), 3.76 – 3.67 (m, 2H), 3.40 and 3.39 (s, 6H), 2.35 (s, 3H), 0.96 – 0.90 (m, 36H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 156.09, 155.03, 154.99, 154.84, 154.71, 154.25, 138.58, 132.17, 129.37, 128.67, 96.91, 78.04, 77.98, 77.99, 77.92, 76.63, 74.19, 73.79, 73.64, 72.99, 70.10, 69.42, 69.17, 66.97, 66.91, 65.56, 55.75, 55.61, 31.79, 31.76, 31.73, 26.35, 26.31, 26.29, 26.28, 26.25, 21.34. FT-IR(ATR): 3502, 2970, 1751, 1458, 1373, 1242, 1119, 1034, 964, 918, 864, 779, 756, 687 cm^{-1}. Yield: 19%. T_g = 50 °C. TGA in Ar: 205-369 °C, 79% mass loss.

GC(neoPPC) trimer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.37 and 5.33 (dd, J = 10, 10 Hz, 2H) 5.20 – 5.07 (m, 3H), 5.03 – 4.95 (m, 3H), 4.88 (m, 2H), 4.80 – 4.67 (m, 3H), 4.47 – 4.16 (m, 6H), 4.05 (m, 2H), 3.96 – 3.67 (m, 15H), 3.43 – 3.37 (m, 9H), 2.34 (s, 3H), 0.96 – 0.89 (m, 54H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 156.03, 155.00, 154.84, 154.71, 154.69, 154.65, 154.20, 153.96, 138.53, 132.25, 129.35, 128.68, 96.88, 96.64, 96.54, 78.01, 77.99, 77.93, 77.90, 77.84, 76.58, 74.21, 73.91, 73.83, 73.64, 73.51, 73.09, 72.97, 70.04, 69.44, 69.11, 67.07, 67.01, 66.89, 66.26, 65.62, 55.80, 55.71, 55.59, 31.80, 31.79, 31.76, 31.72, 31.70, 26.35, 26.31, 26.29, 21.34. FT-IR(ATR): 3502, 2963, 2878, 1751, 1558, 1466, 1373, 1242, 1119, 1034, 957, 756, 671 cm^{-1}. Yield: 28%. T_g = 65 °C. TGA in Ar: 211-377 °C, 83% mass loss.

GC(neoPPC) tetramer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.37 (dd, J = 10, 10 Hz, 2H), 5.32 (dd, J = 10, 10 Hz, 1H), 5.03 – 4.95 (m, 4H), 4.92 – 4.80 (m, 3H), 4.78 – 4.68 (m, 4H), 4.48 – 4.18 (m, 9H), 4.05 (m, 3H), 3.96 – 3.75 (m, 19H), 3.42 – 3.36 (m, 12H), 2.34 (s, 3H), 0.95 – 0.90 (m, 72H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 155.98, 155.00, 154.84, 154.72, 154.69, 154.69, 154.64, 154.19, 153.94, 153.92, 138.52, 132.25, 129.35, 128.68, 96.88, 96.63, 96.52, 96.51, 78.01, 78.00, 77.99, 77.89, 77.82, 76.54, 74.24, 73.94, 73.92, 73.86, 73.63, 73.49, 73.12, 73.02, 72.97, 70.04, 69.48, 69.05, 67.11, 67.04, 66.78, 66.37, 66.27, 65.61, 55.84, 55.75, 55.70, 55.58, 31.81, 31.80, 31.75, 31.72, 31.71, 26.35, 26.32, 26.30, 21.34. FT-IR(ATR): 3495, 2963, 2908, 1751, 1558, 1466, 1373, 1242, 1111, 1041, 964, 779, 664 cm^{-1}. Yield: 20%. T_g = 79 °C. TGA in Ar: 215-376 °C, 80% mass loss.

GC(EHEHC) unimer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.17 (AB_q, J = 8 Hz, 4H), 5.13 (s, 2H), 5.12 (dd, J = 10, 10 Hz, 1H), 4.97 (d, J = 4 Hz, 1H), 4.71 (dd, J = 10, 4 Hz, 1H), 4.49 (dd, J = 12, 4 Hz, 1H), 4.41 (dd, J = 12, 2 Hz, 1H), 4.13 – 3.99 (m, 5H), 3.84 (m, 1H), 3.68 (m, 1H), 3.37 (s, 3H), 2.35 (s, 3H), 1.40 – 1.22 (m, 16H), 0.93 – 0.83 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 156.18, 155.56, 154.70, 138.68, 132.12, 129.40, 128.72, 96.84, 76.71, 73.61, 71.50, 71.45, 71.30, 71.25, 70.12, 69.67, 69.41, 66.25, 55.56, 38.95, 38.91, 38.89, 30.21, 30.16, 30.15, 30.10, 29.01, 29.00, 28.94, 28.91, 23.58, 23.53, 23.06, 23.05, 21.35, 14.15, 10.99, 10.96. FT-IR(ATR): 3495, 2932, 2870, 1744, 1458, 1389, 1242, 1165, 1041, 972, 918, 787 cm^{-1}. Yield: 14%. T_g = -25 °C. TGA in Ar: 185-350 °C, 61% mass loss.

GC(EHEHC) dimer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.30 (dd, J = 10, 10 Hz, 1H), 5.17 – 5.08 (m, 3H), 4.99 (dd, J = 10, 4 Hz, 2H), 4.90 (dd, J = 10, 10 Hz, 1H), 4.74 (dd, J = 10, 4 Hz, 1H), 4.68 (dd, J = 10, 4 Hz, 1H), 4.39 (d, J = 4 Hz, 2H), 4.30 (d, J = 4 Hz, 2H), 4.14 – 3.94 (m, 10H), 3.39 and 3.38 (s, 6H), 2.34 (s, 3H), 1.41 – 1.20 (m, 32H), 0.88 (m, 24H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 1j56.00, 155.03, 154.92, 154.71, 154.59, 154.23, 138.57, 132.18, 129.37, 128.68, 96.87, 96.57, 76.62, 74.26, 73.78, 73.60, 72.99, 71.38, 71.33, 71.32, 71.31, 71.25, 71.20, 70.09, 69.42, 69.18, 66.91, 65.56, 55.74, 55.60, 38.95, 38.91, 38.89, 38.85, 30.21, 30.17, 30.15, 30.13, 30.10, 30.09, 29.01, 28.99, 28.96, 28.94, 28.92, 23.58, 23.52, 23.48, 23.05, 21.34, 14.15, 10.97, 10.96, 10.93. FT-IR(ATR): 3503, 2931, 2870, 1751, 1458, 1389, 1242, 1165, 1111, 1034, 972, 786 cm^{-1}. Yield: 23%. T_g = -8 °C. TGA in Ar: 190-364 °C, 82% mass loss.

GC(EHEHC) trimer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.35 (dd, J = 10, 10 Hz, 1H), 5.31 (s, 2H), 5.30 (dd, J = 10, 10 Hz, 1H), 5.17 – 5.08 (m, 3H), 5.00 (dd, J = 10, 4 Hz, 2H), 4.97 (d, J = 4 Hz, 1H), 4.87 (m, 2H), 4.74 (td, J = 10, 4 Hz, 2H), 4.38 (m, 3H), 4.29 (m, 2H), 4.19 (m, 1H), 4.14 – 3.93 (m, 15H), 3.82 (m, 1H), 3.71 (m, 1H), 3.40, 3.39, and 3.37 (s, 9H), 2.34 (s, 3H), 1.43 – 1.19 (m, 48H), 0.91 – 0.82 (m, 36H). ^{13}C NMR (126

MHz, $CDCl_3$, ppm) δ 155.96, 155.00, 154.96, 154.71, 154.60, 154.58, 154.52, 154.20, 153.96, 138.53, 132.26, 129.35, 128.69, 96.86, 96.85, 96.60, 96.46, 76.55, 73.89, 73.83, 73.59, 73.54, 73.05, 73.00, 71.37, 71.31, 71.27, 71.24, 71.21, 71.19, 70.05, 69.44, 69.07, 69.06, 69.05, 67.03, 67.00, 66.84, 66.27, 65.61, 55.79, 55.70, 55.59, 38.94, 38.88, 30.16, 30.14, 30.09, 29.00, 28.95, 28.92, 23.57, 23.51, 23.06, 21.34, 14.16, 10.96, 10.92. FT-IR(ATR): 3502, 2932, 2870, 2168, 1752, 1458, 1389, 1242, 1173, 1034, 972, 779 cm^{-1}. Yield: 30%. T_g = 4 °C. TGA in Ar: 197-365 °C, 81% mass loss.

GC(EHEHC) tetramer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.35 (dd, J = 10, 10 Hz, 2H), 5.30 (s, 2H), 5.29 (dd, J = 10, 10 Hz, 1H), 5.18 – 5.08 (m, 3H), 5.04 – 4.96 (m, 4H), 4.93 – 4.79 (m, 3H), 4.78 – 4.65 (m, 4H), 4.49 – 4.19 (m, 8H), 4.15 – 3.93 (m, 21H), 3.84 (s, 1H), 3.72 (s, 1H), 3.42, 3.40 and 3.37 (s, 12H), 2.35 (s, 3H), 1.43 – 1.21 (m, 64H), 0.92 – 0.84 (m, 48H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 155.90, 155.00, 154.96, 154.72, 154.61, 154.60, 154.58, 154.57, 154.49, 154.19, 153.95, 153.93, 138.51, 132.27, 129.35, 128.69, 96.86, 96.60, 96.46, 76.53, 74.39, 73.94, 73.90, 73.87, 73.62, 73.59, 73.57, 73.51, 73.11, 73.01, 71.36, 71.34, 71.31, 71.28, 71.27, 71.23, 71.21, 71.18, 70.03, 69.47, 69.01, 67.07, 67.03, 66.71, 66.43, 66.35, 66.27, 65.62, 65.51, 55.82, 55.74, 55.68, 55.57, 38.94, 38.88, 30.16, 30.12, 30.09, 29.00, 28.96, 28.95, 28.92, 23.57, 23.52, 23.50, 23.06, 21.33, 14.17, 14.15, 10.96, 10.94, 10.91. FT-IR(ATR): 3502, 2932, 2870, 1751, 1458, 1389, 1234, 1173, 1034, 964, 779 cm^{-1}. Yield: 17%. T_g = 8 °C. TGA in Ar: 187-363 °C, 80% mass loss.

GC(EHEHC) pentamer: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.28 and 7.16 (AB_q, J = 8 Hz, 4H), 5.39 – 5.31 (m, 4H), 5.18 – 5.06 (m, 3H), 5.05 – 4.95 (m, 5H), 4.92 – 4.76 (m, 4H), 4.76 – 4.58 (m, 5H), 4.49 – 4.15 (m, 10H), 4.15 – 3.89 (m, 26H), 3.41, 3.40, 3.39 and 3.36 (s, 15H), 2.34 (s, 3H), 1.44 – 1.18 (m, 80H), 0.88 (m, 60H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ 155.88, 154.97, 154.71, 154.59, 154.56, 154.48, 154.45, 154.18, 153.95, 153.91, 138.52, 132.27, 129.35, 128.69, 96.83, 96.59, 96.44, 74.43, 74.41, 73.94, 73.88, 73.62, 73.58, 73.54, 73.50, 73.04, 73.01, 72.99, 71.31, 71.20, 71.16, 70.03, 69.48, 69.00, 67.07, 66.87, 66.67, 66.40, 66.23, 65.62, 55.79, 55.77, 55.71, 55.67, 55.56, 38.93, 38.88, 30.21, 30.15, 30.11, 30.08, 29.84, 29.00, 28.93, 28.91, 23.56, 23.50, 23.06, 21.33, 14.17, 14.15, 10.96, 10.94, 10.91. FT-IT(ATR): 2932, 2870, 1751, 1458, 1389, 1234, 1172, 1110, 1034, 964, 779, 678 cm^{-1}. Yield: 6%. T_g = 11 °C. TGA in Ar: 190-362 °C, 77% mass loss.

Supplemental Table:

Table S1. Data for PGC(RRC) with Different Alkyloxycarbonyl Side Chains

Entry	Polymer[a]	$M_{n,\,SEC}$[b] (kDa)	$Đ$[b]	T_g[c] (°C)	T_d[d] (°C)
1	$PGC(EEC)_{51}$	16.0	1.04	120	332
2	$PGC(BBC)_{40}$	15.5	1.06	68	330
3	$PGC(HHC)_{36}$	15.9	1.06	46	335
4	$PGC(isoBBC)_{42}$	14.9	1.05	85	341
5	$PGC(neoPPC)_{40}$	15.7	1.06	125	342
6	$PGC(EHEHC)_{30}$	15.8	1.06	38	345

[a]Repeating units were calculated based on [1]H NMR spectroscopic analysis. [b]$M_{n,\,SEC}$ and $Đ$ were measured by SEC [c]T_g was measured by DSC, performed with a heating rate of 10 °C/min. [d]T_d was measured from the onset of TGA analysis, heating from 25 to 500 °C.

Table S2. Data for Oligo/PolyGC(neoPPC) (Entries 7-12) and Oligo/PolyGC(EHEHC) (Entries 13-19)

Entry	Oligo/Polymer[a]	M_n[b] (Da)	$Đ$	T_g (°C)	T_d (°C)
7	$OGC(neoPPC)_1$	571	1.00	13	266
8	$OGC(neoPPC)_2$	1019	1.00	50	266
9	$OGC(neoPPC)_3$	1468	1.00	65	284
10	$OGC(neoPPC)_4$	1916	1.00	79	295
11	$PGC(neoPPC)_7$	3020	1.07	85	328
12	$PGC(neoPPC)_{20}$	8800	1.06	118	331
13	$OGC(EHEHC)_1$	655	1.00	-25	254
14	$OGC(EHEHC)_2$	1187	1.00	-8	268
15	$OGC(EHEHC)_3$	1720	1.00	4	270
16	$OGC(EHEHC)_4$	2252	1.00	8	273
17	$OGC(EHEHC)_5$	2785	1.00	11	271
18	$PGC(EHEHC)_{10}$	5360	1.06	26	304
19	$PGC(EHEHC)_{17}$	9080	1.06	32	322

[a]DP_n values for polymers were determined by SEC results. [b]M_n for discrete oligomers were calculated from DP_n.

Supplementary Figures:

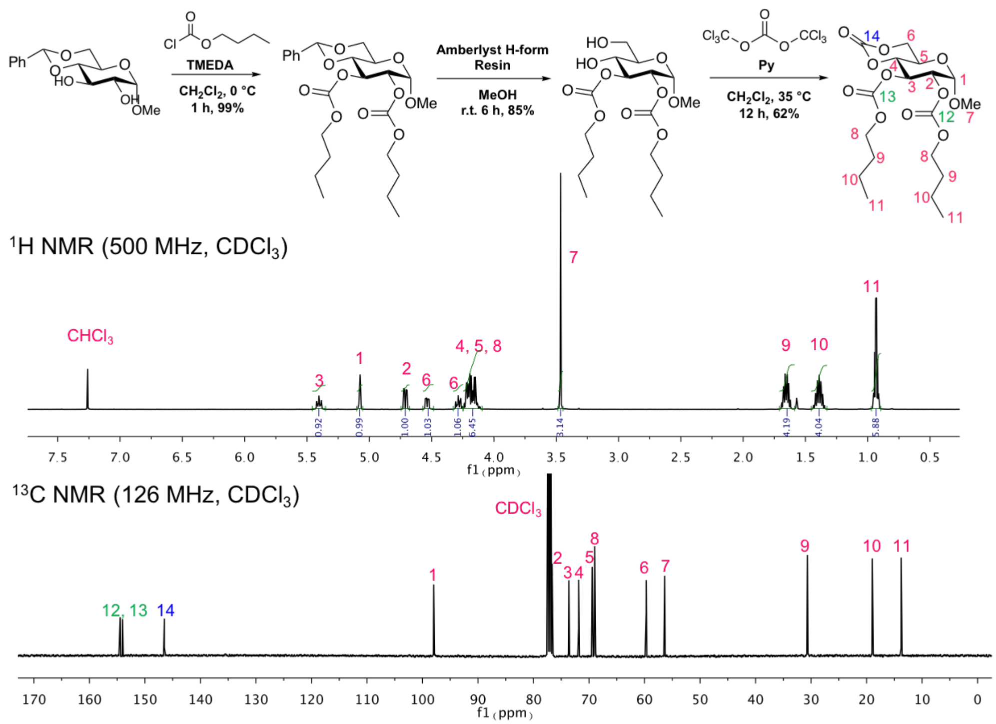

Figure S1. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of GC(BBC) (**2**) in $CDCl_3$.

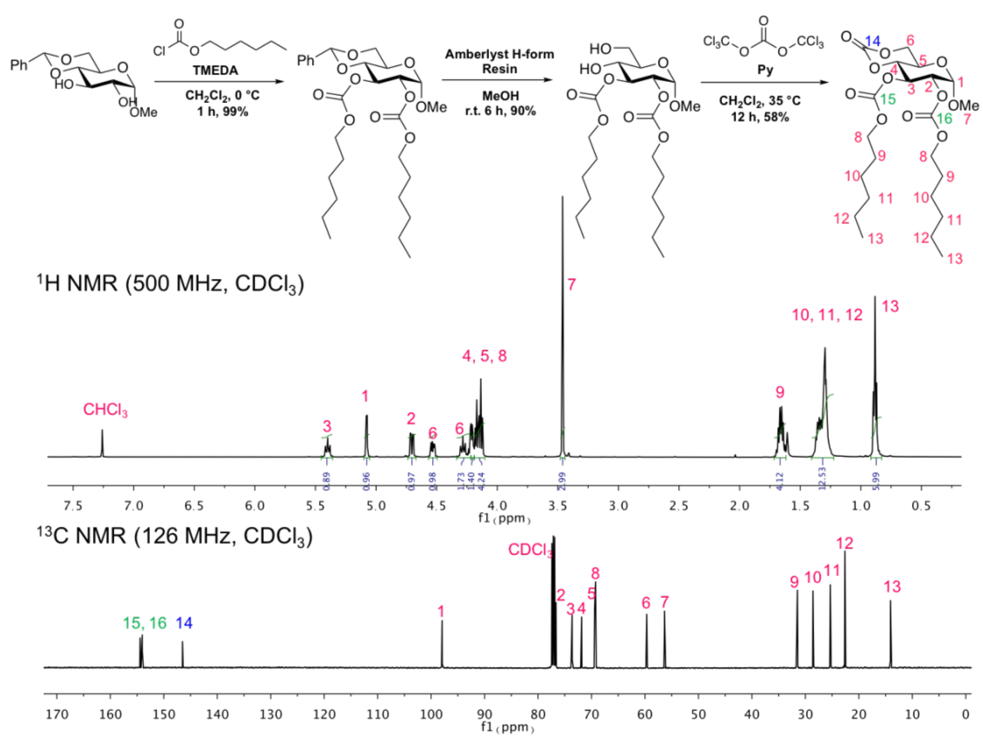

Figure S2. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of GC(HHC) (**3**) in $CDCl_3$.

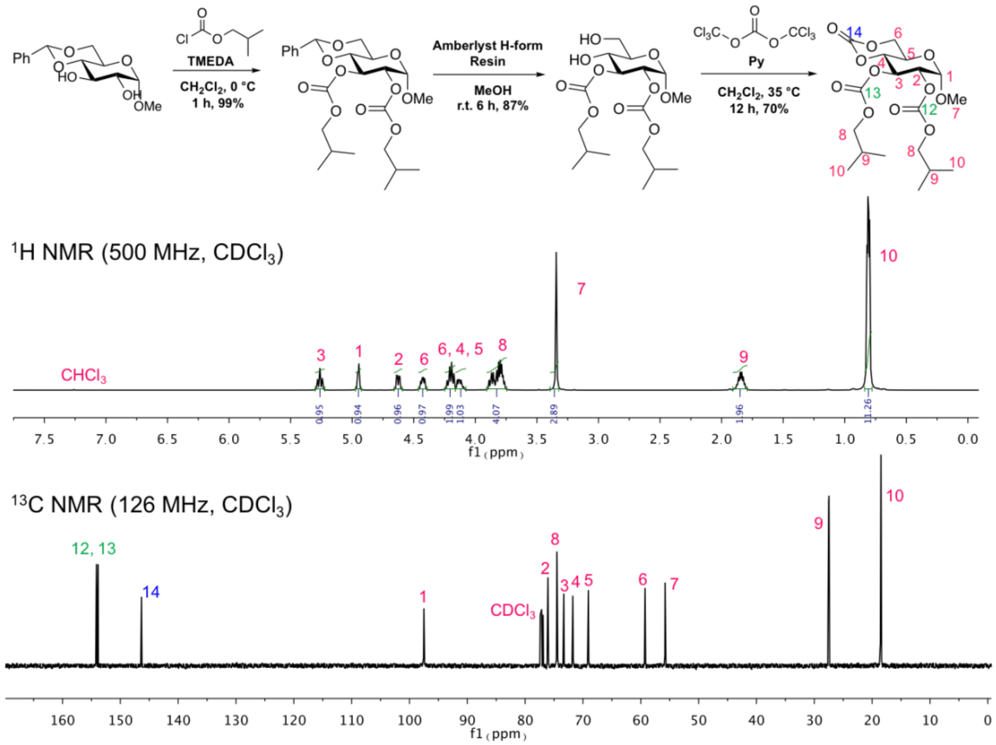

Figure S3. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of GC(isoBBC) (**4**) in $CDCl_3$.

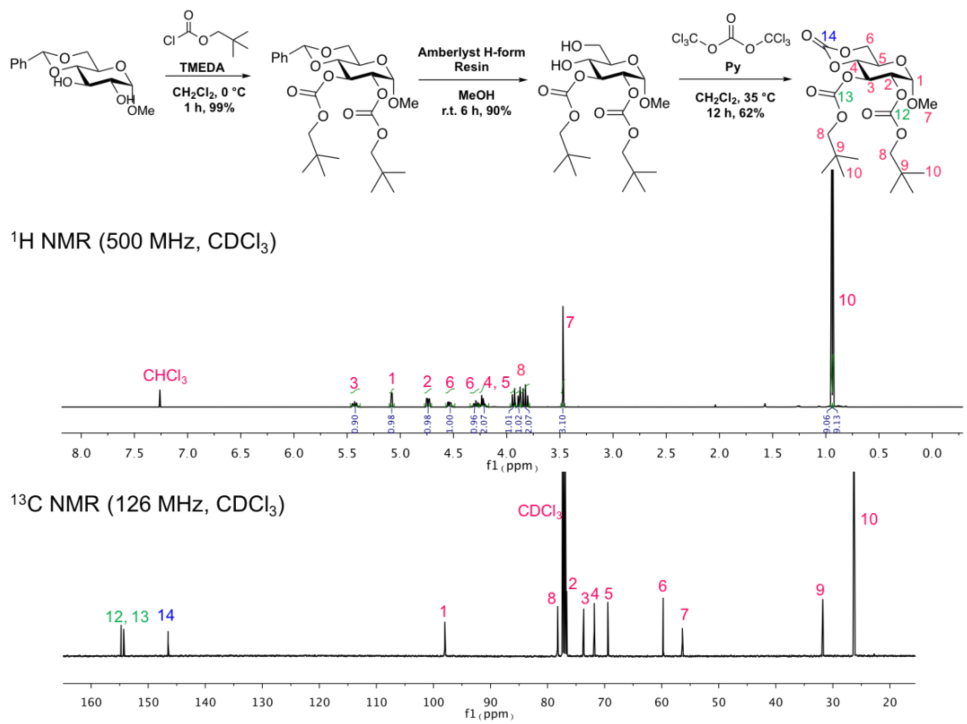

Figure S4. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of GC(neoPPC) (**5**) in $CDCl_3$.

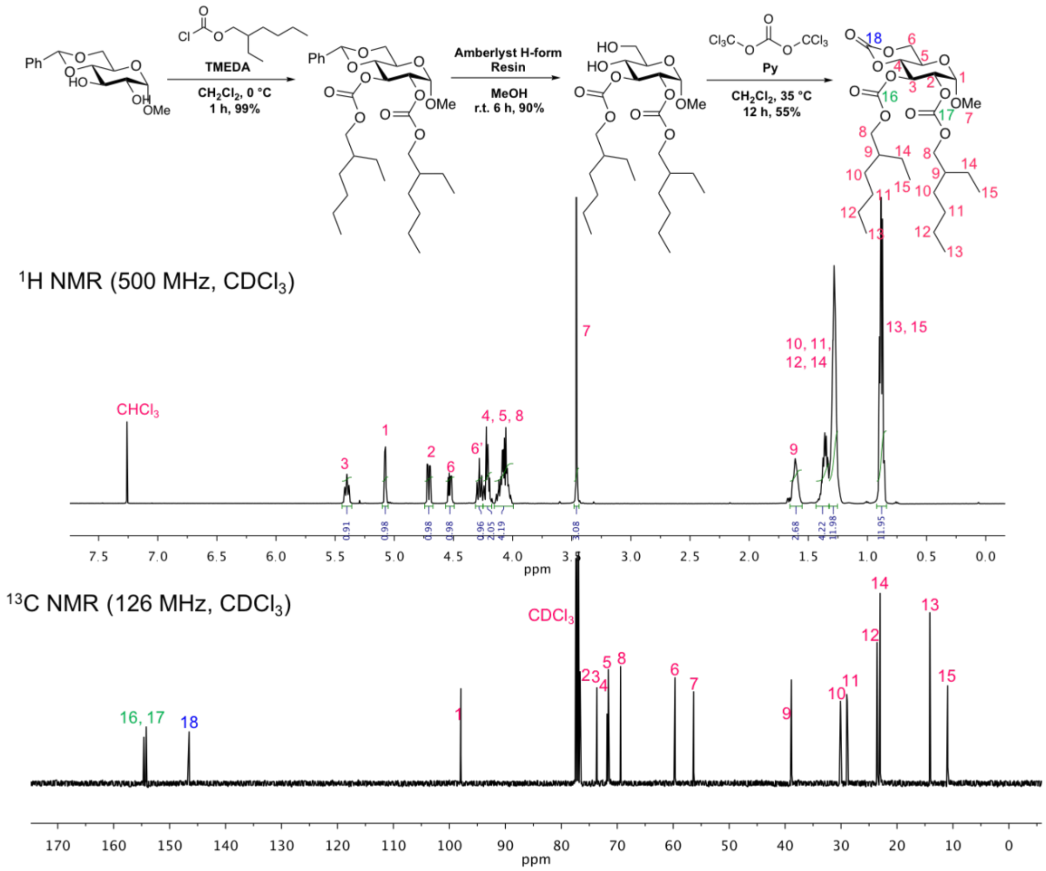

Figure S5. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of GC(EHEHC) (**6**) in $CDCl_3$.

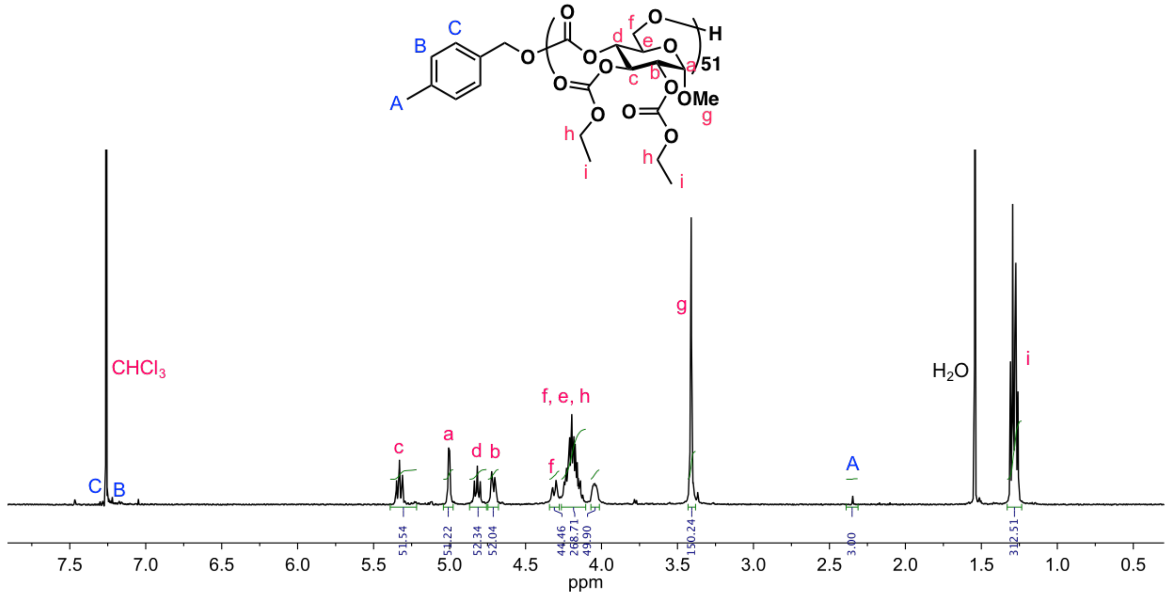

Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PGC(EEC)$_{51}$.

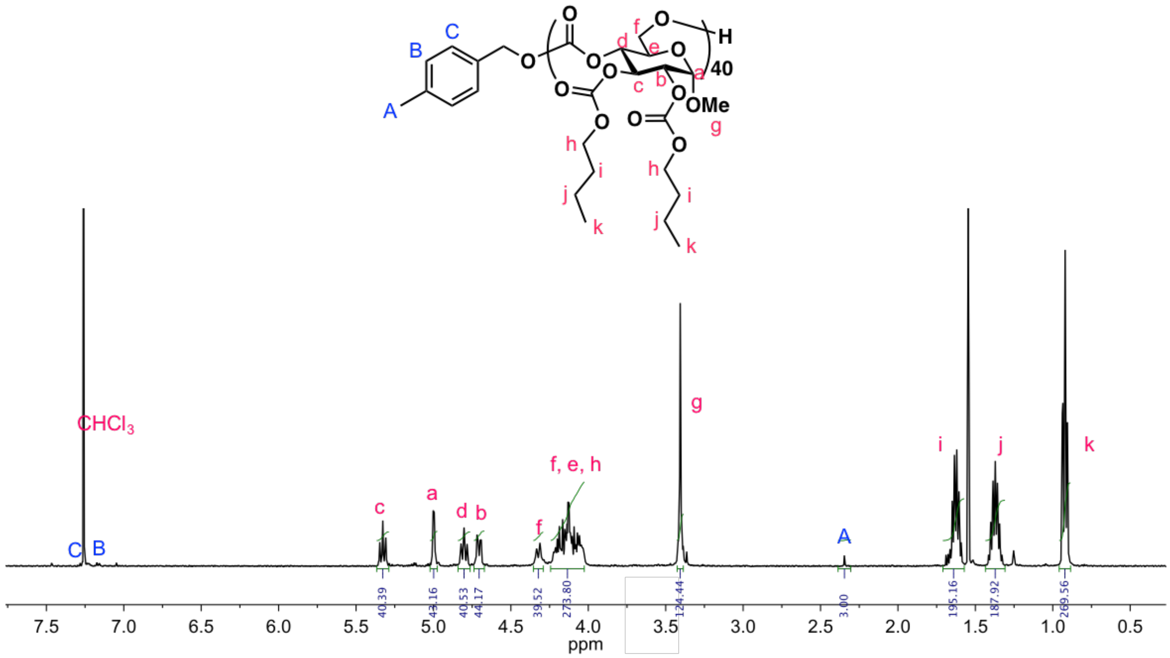

Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PGC(BBC)$_{40}$.

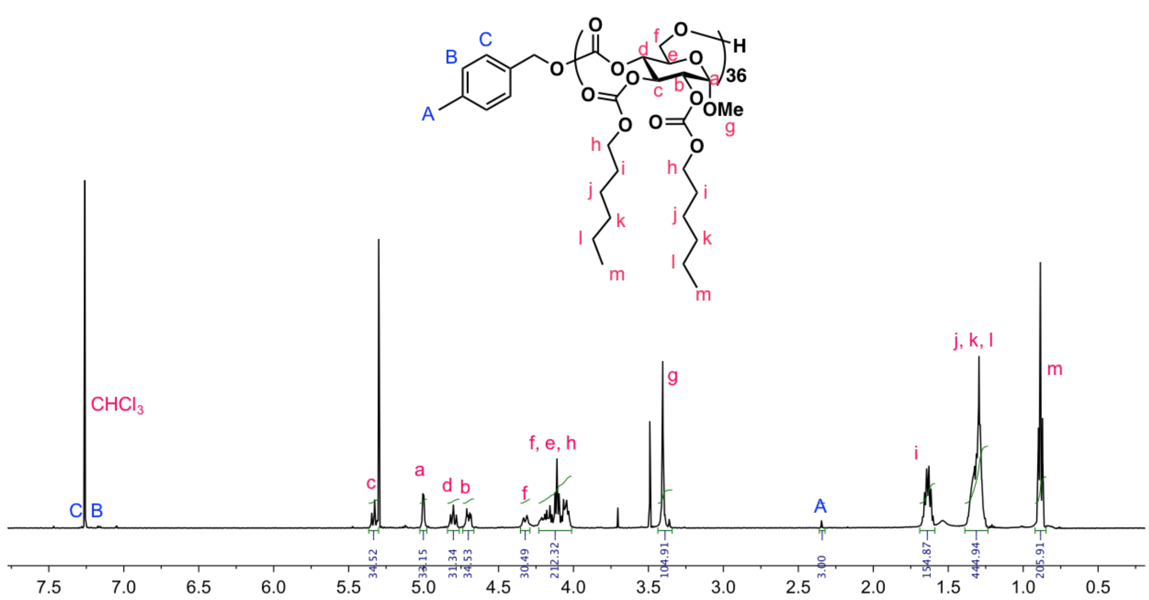

Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PGC(HHC)$_{36}$.

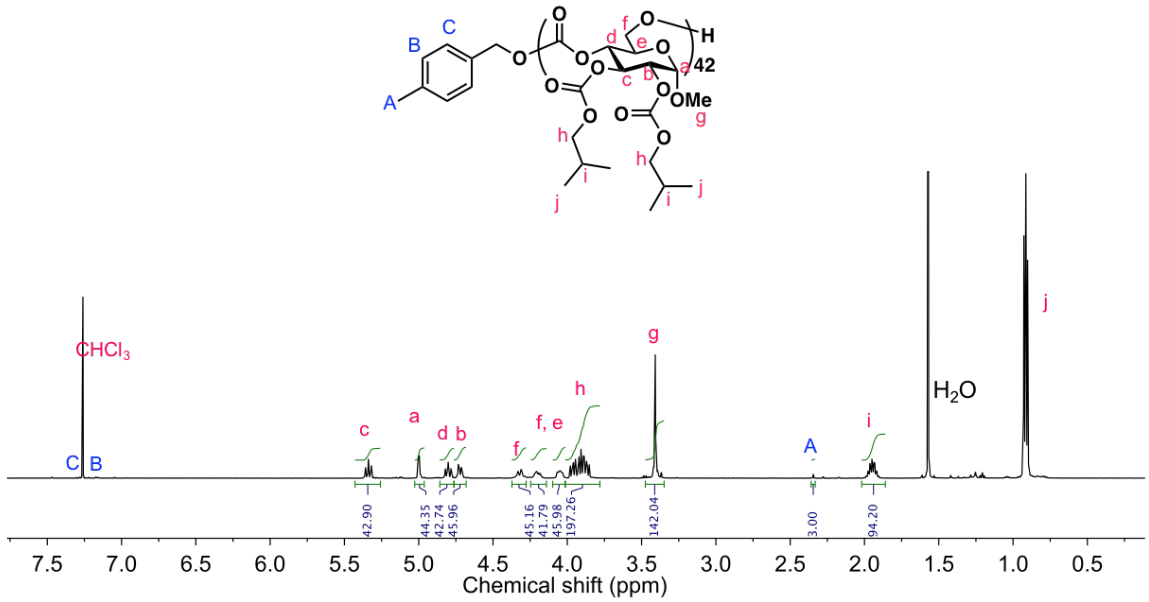

Figure S9. [1]H NMR (500 MHz, $CDCl_3$) spectrum of PGC(isoBBC)$_{42}$.

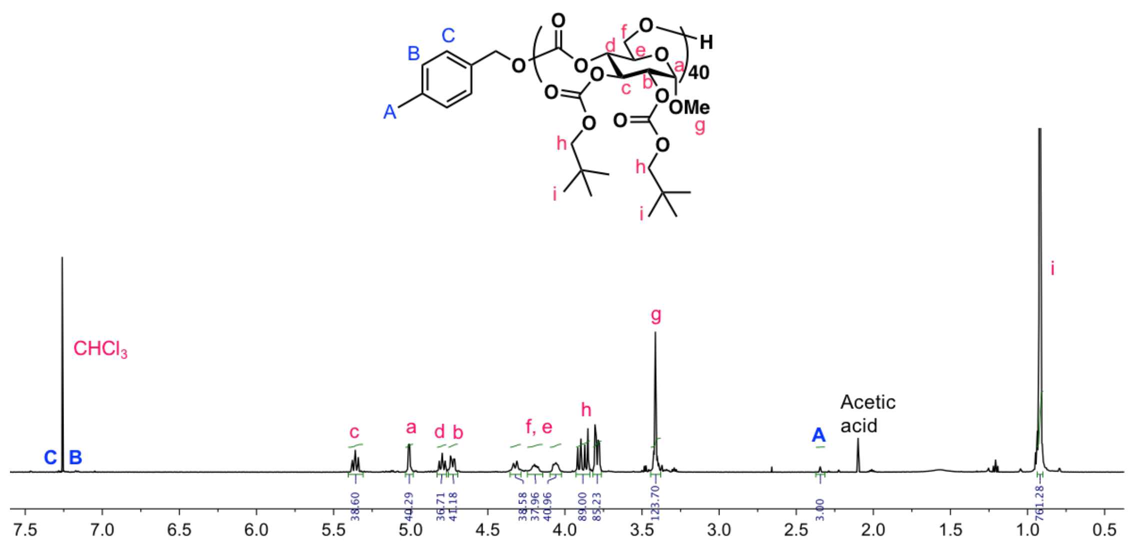

Figure S10. [1]H NMR (500 MHz, $CDCl_3$) spectrum of PGC(neoPPC)$_{40}$.

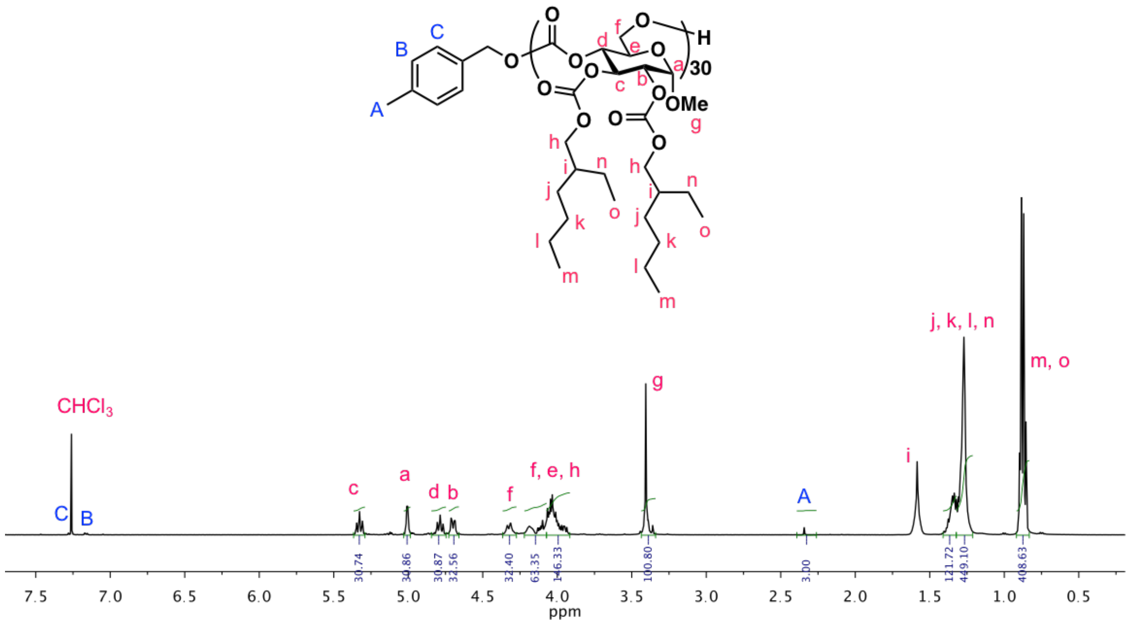

Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of PGC(EHEHC)$_{30}$.

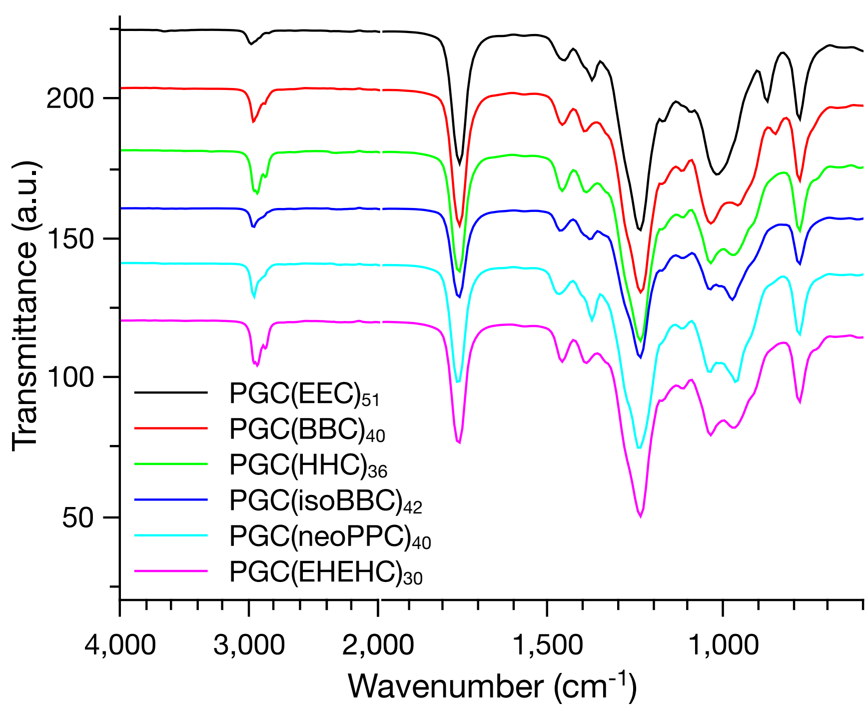

Figure S12. FT-IR(ATR) spectra of PGC(RRC).

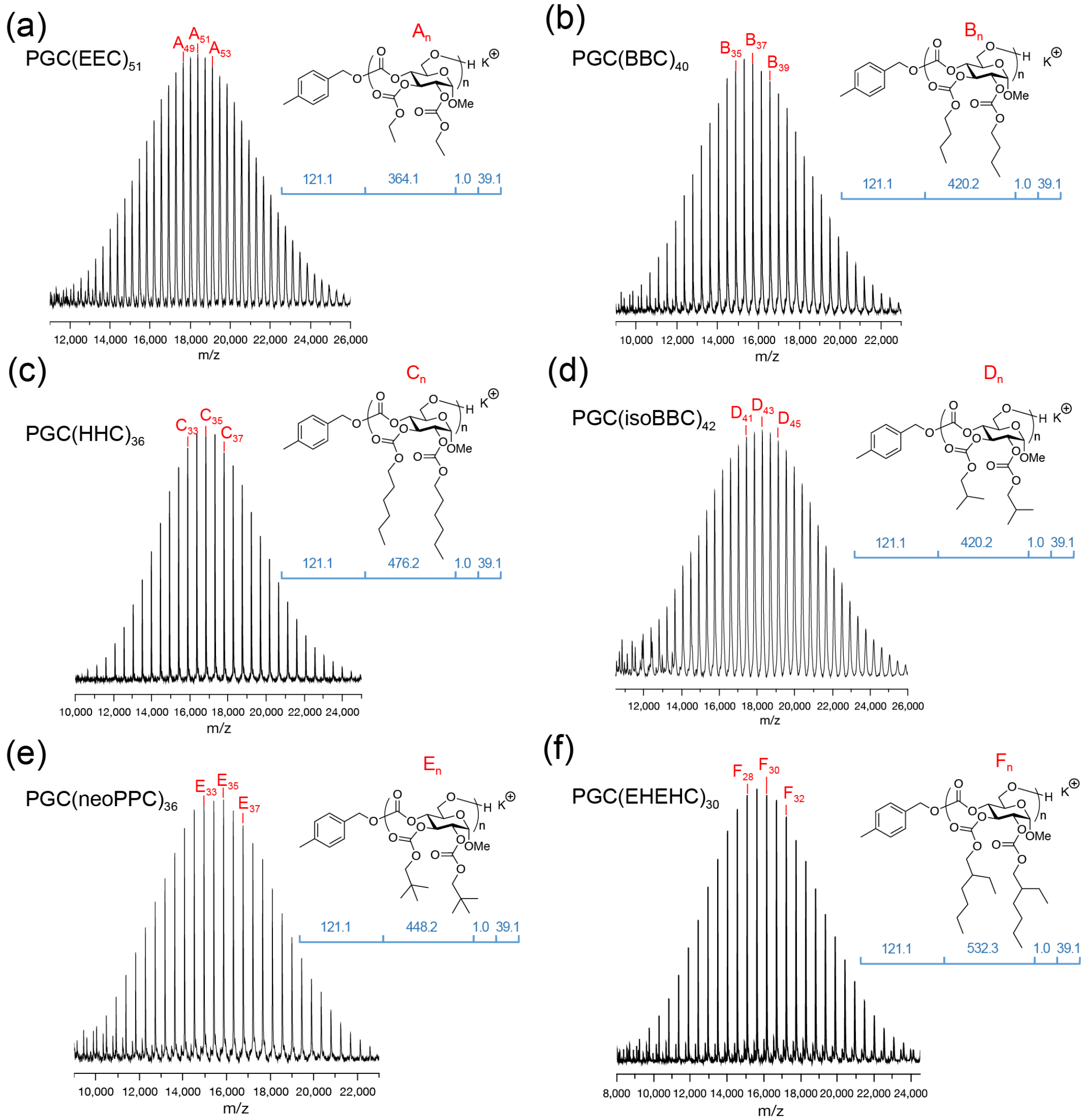

Figure S13. MALDI-TOF MS spectra of PGC(RRC): (a) PGC(EEC)$_{51}$, (b) PGC(BBC)$_{40}$, (c) PGC(HHC)$_{36}$, (d) PGC(isoBBC)$_{42}$, (e) PGC(neoPPC)$_{40}$, and (f) PGC(EHEHC)$_{30}$. *DP*$_n$ values were calculated from ^{1}H NMR spectroscopy.

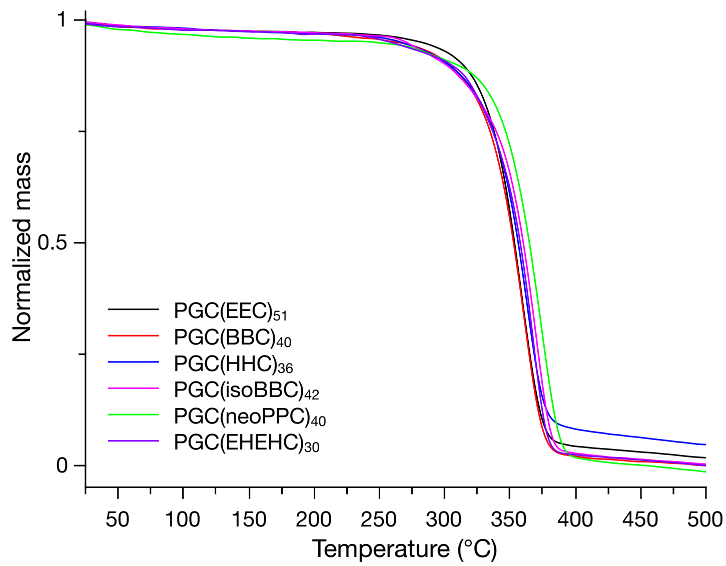

Figure S14. TGA traces (25 – 500 °C, 10 °C/min) of PGC(RRC).

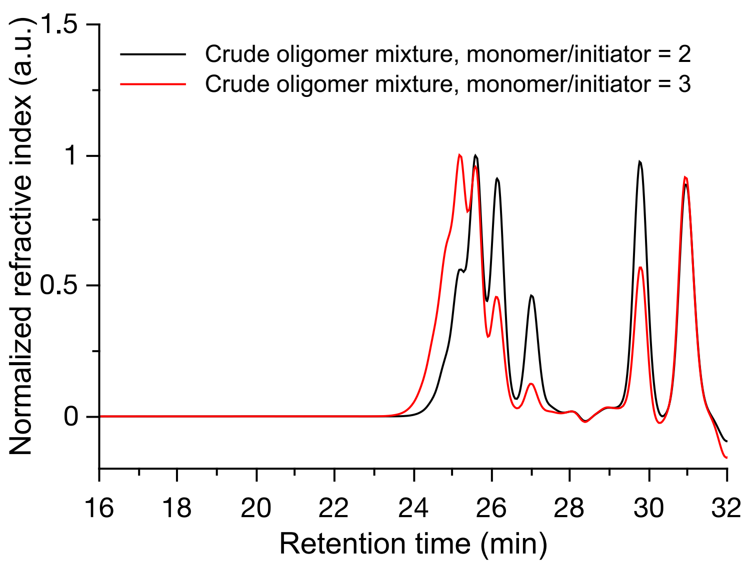

Figure S15. SEC chromatograms (THF as eluent, 1.0 mL/min) of the crude mixtures of oligomers prepared by ROP of GC(neoPPC).

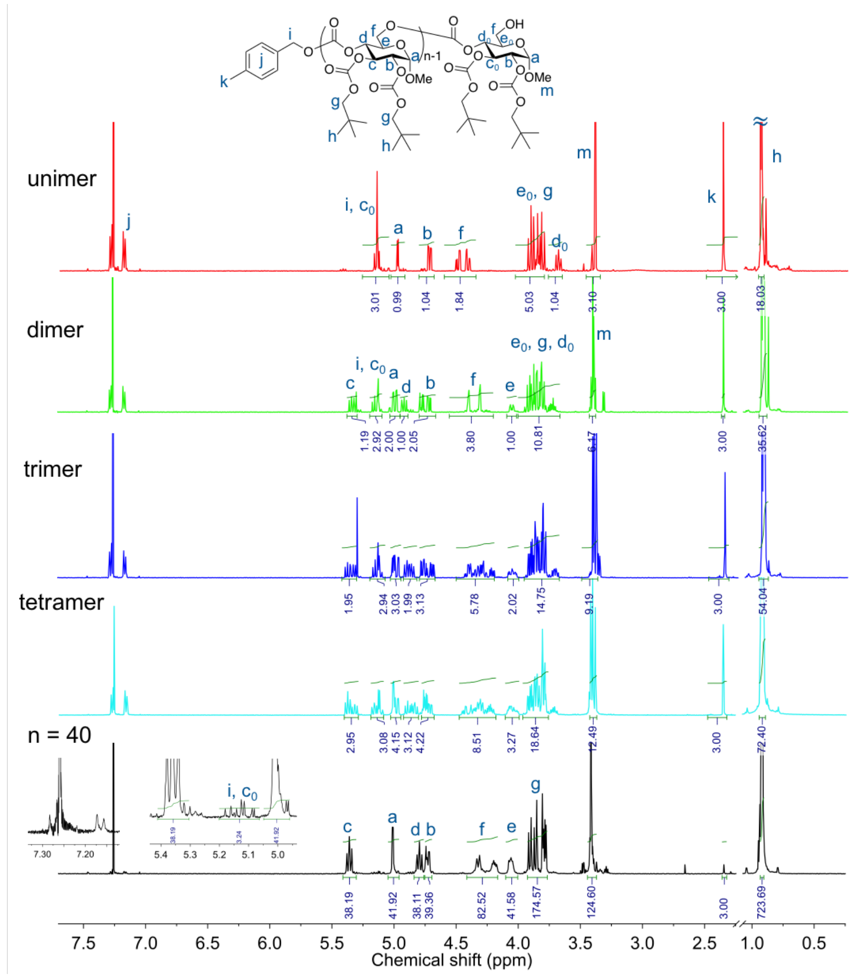

Figure S16. [1]H NMR (500 MHz, $CDCl_3$) spectra of oligo/polyGC(neoPPC).

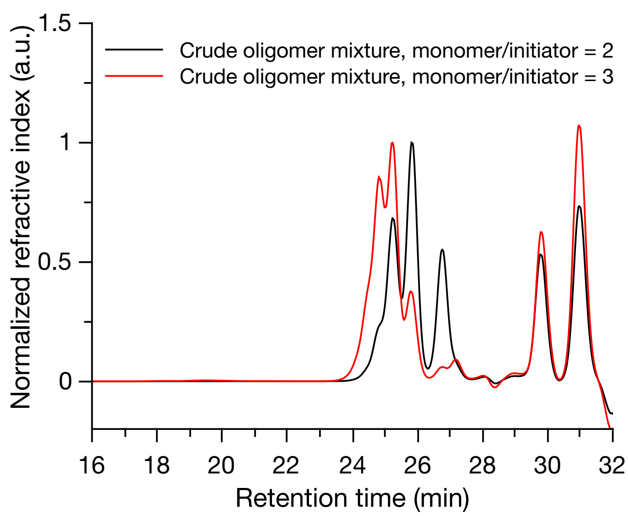

Figure S17. SEC chromatograms (THF as eluent, 1.0 mL/min) of the crude mixtures of oligomers prepared by ROP of GC(EHEHC).

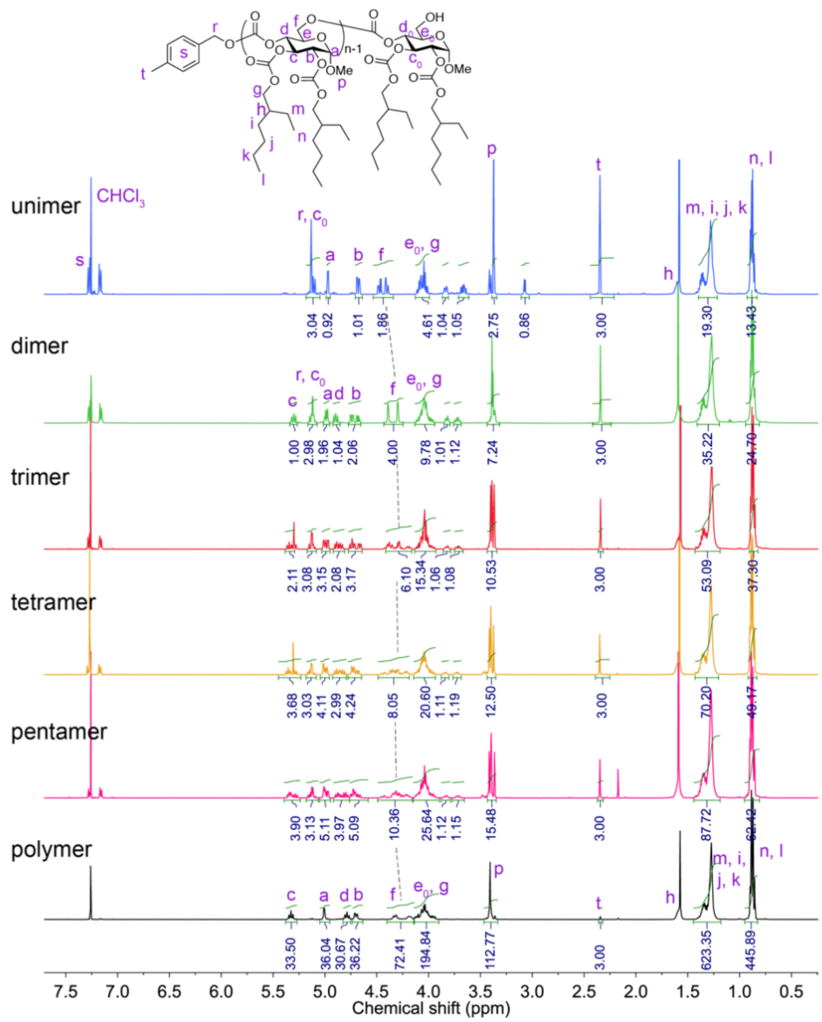

Figure S18. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of oligo/polyGC(EHEHC).

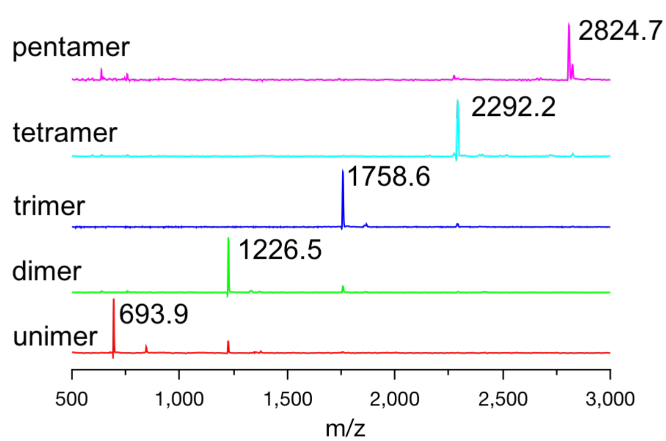

Figure S19. MALDI-TOF MS spectra (with K^+ as the adduct ion) of the discrete oligomers of GC(EHEHC).

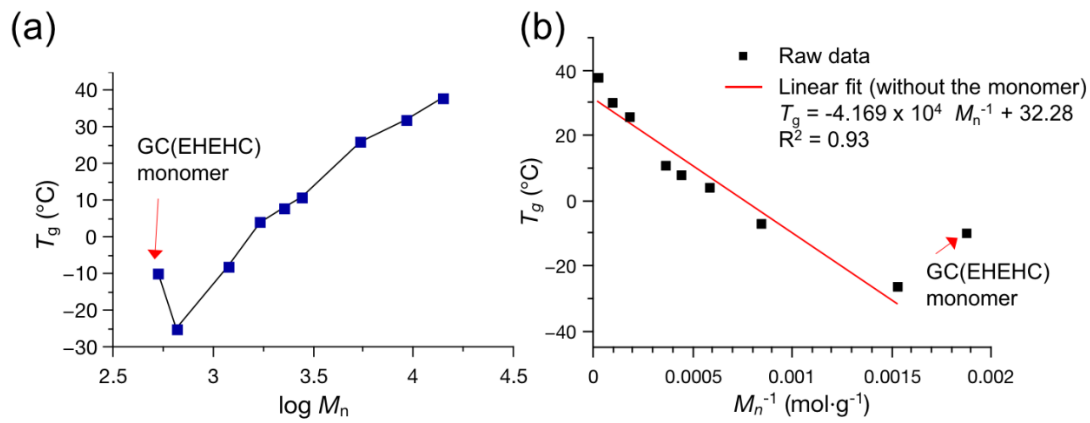

Figure S20. Plots of (a) T_g *vs*. log M_n and (b) M_n^{-1} of oligo/polyGC(EHEHC).

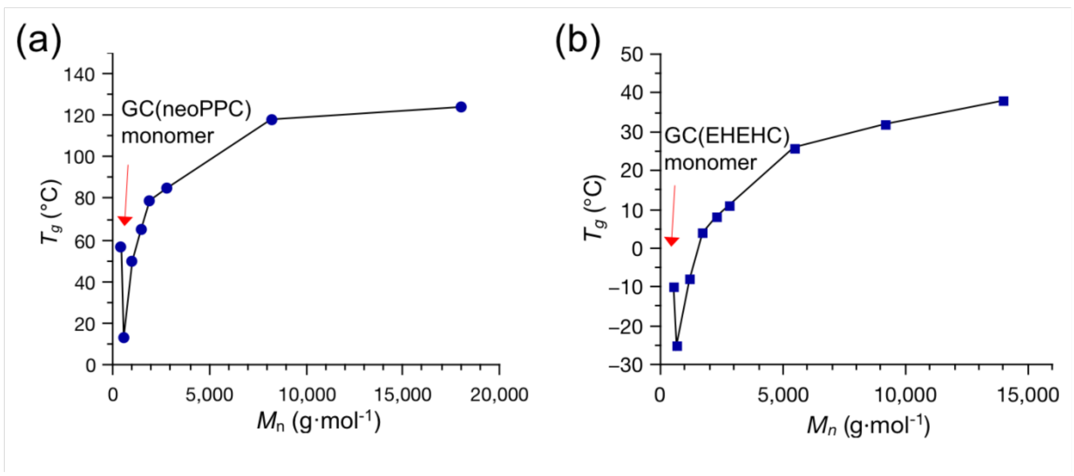

Figure S21. Plots of (a) T_g *vs*. M_n for oligo/polyGC(neoPPC) and (b) oligo/polyGC(EHEHC).

Reference:

(1) Su, L.; Khan, S.; Fan, J. W.; Lin, Y. N.; Wang, H.; Gustafson, T. P.; Zhang, F. W.; Wooley, K. L., Functional sugar-based polymers and nanostructures comprised of degradable poly(D-glucose carbonate)s. *Polym. Chem.* **2017,** *8* (10), 1699-1707.