Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Polyglycocarbonates Through Polycondensation of Glucopyranosides with CO_2

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Experimental Section:

Synthesis of α-methyl 4,6-O-benzylidene D-glucopyranoside;

α-methyl-4,6-*O*-benzylidene D-glucopyranoside was synthesized from α-methyl D-glucopyranoside (MDG) following previously reported literature.[1] In a 250 mL of round bottom flask, α-methyl D-glucopyranoside (10 g, 51.5 mmol), benzaldehyde dimethyl acetal (8.62 g, 56.65 mmol), *para*-toluene sulphonic acid (44 mg, 257.49 μmol) and 40 mL anhydrous DMF were added. The mixture was heated at 60^{o}C for 1 h under reduced pressure. Then DMF was distilled out from the reaction mixture and colorless residue was obtained. 50 mL water containing sodium hydrogen carbonate (1 g) was added to the round bottom flask and heated to 100^{o}C under stirring conditions. The insoluble precipitation was filtered, the filtrate was dried and recrystallized in 1-propanol to obtain a colorless white powder (10.0 g, 69 % Yield).

^{1}H NMR (400MHz, $CDCl_3$): δ 2.36 (d, J = 9.4 Hz, 1H), 2.85 (d, J = 2.1 Hz, 1H), 3.45 (s, 3H), 3.49 (t, J = 9.3 Hz, 1H), 3.62 (td, J = 9.3, 3.9 Hz, 1H), 3.86 – 3.69 (m, 2H), 3.92 (td, J = 9.2, 2.0 Hz, 1H), 4.29 (dd, J = 9.6, 4.2 Hz, 1H), 4.79 (d, J = 3.9 Hz, 1H), 5.53 (s, 1H), 7.37 (dd, J = 5.1, 1.9 Hz, 3H), 7.49 (dd, J = 6.6, 3.0 Hz, 2H).

^{13}C NMR (100MHz, $CDCl_3$): δ 55.56 (1C), 62.34 (1C), 68.91 (1C), 71.75 (1C), 72.85 (1C), 80.89 (1C), 99.73 (1C), 101.92 (1C), 126.28 (1C), 128.31 (1C), 128.31 (2C), 129.24 (2C), 137.00 (1C).

Synthesis of α*-methyl-2,3-di-O-methyl-4,6-O-benzylidene D-glucopyranoside (**MDG-Ket**);*

In a 100 mL of round bottom flask, α-methyl-4,6-*O*-benzylidene D-glucopyranoside (2 g, 7.08 mmol) was added and dissolved with 20 mL anhydrous DMF. Sodium hydride (60%, 0.85 g, 21.25 mmol) was added to the solution under inert conditions at 0^{o}C and kept for stirring for 30

mins. After completion of hydrogen evolving, methyl iodide (2.51 g, 17.71 mmol) in 10 mL of DMF was further added to the reaction mixture. The reaction mixture was kept stirring for 12 h at room temperature. Then the reaction mixture was diluted with dichloromethane and washed with 1 (N) HCl to remove the undesired salts. The organic layer was dried over anhydrous sodium sulphate and concentrated under vacuum (Scheme 1). The compound was characterized by ^{1}H and ^{13}C NMR (2.0 g, 90% Yield).

^{1}H NMR (400MHz, $CDCl_3$): δ 2.3 (dd, J=9.3 and 3.6 Hz, 1H), 3.44 (s, 3H), 3.55 (s, 3H), 3.63 (s, 3H), 3.67-3.85 (m, 3H), 4.28 (dd, J=9.3 and 3.6 Hz, 1H), 4.86 (d, J=3.6 Hz, 1H), 5.54 (s, 1H), 7.34-7.40 (m, 3H), 7.48-7.51 (m, 2H).

^{13}C NMR (100MHz, $CDCl_3$): δ 55.26 (1C), 61.01 (1C), 62.21 (1C), 69.04 (1C), 79.82 (1C), 81.38 (1C), 82.11 (1C), 98.35 (1C), 101.34 (1C), 126.05 (2C), 128.18 (2C), 128.92 (1C), 137.31 (1C).

*Synthesis of α-methyl-2,3-di-O-methyl D-glucopyranoside (**MDMG**);*

α-Methyl-2,3-di-*O*-methyl D-glucopyranoside (**MDMG**) was synthesized from α-methyl-2,3-di-*O*-methyl-4,6-*O*-benzylidene D-glucopyranoside (**MDG-Ket**) following the published literature.[2] **MDG-Ket** (3.0 g, 9.67 mmol) was dissolved in 10 mL of dioxane and 10% Pd-C (1 g) was added into a 100 mL high pressure reactor. Followed by addition of a few drops of concentrated hydrochloric acid, hydrogen gas was charged into the reactor to 30 bar and kept stirring for 16 h at room temperature. The completion of the reaction was confirmed by TLC and α-methyl-2,3-di-*O*-methyl D-glucopyranoside was isolated and characterized by ^{1}H and ^{13}C NMR (1.75 g, 81% Yield).

^{1}H NMR (400MHz, $CDCl_3$): δ 2.3 (bs, 1H), 2.98 (bs, 1H), 3.21 (dd, J=9.3 and 3.6 Hz, 1H), 3.42-3.53 (m, 8H), 3.60-3.66 (m, 4H), 3.77-3.86 (m, 2H), 4.84 (d, J=3.6 Hz, 1H).

^{13}C NMR (100MHz, $CDCl_3$): δ 55.23 (1C), 58.50 (1C), 61.23 (1C), 62.27 (1C), 70.21 (1C), 70.73 (1C), 81.87 (1C), 82.77 (1C), 97.5 (1C).

IR Data

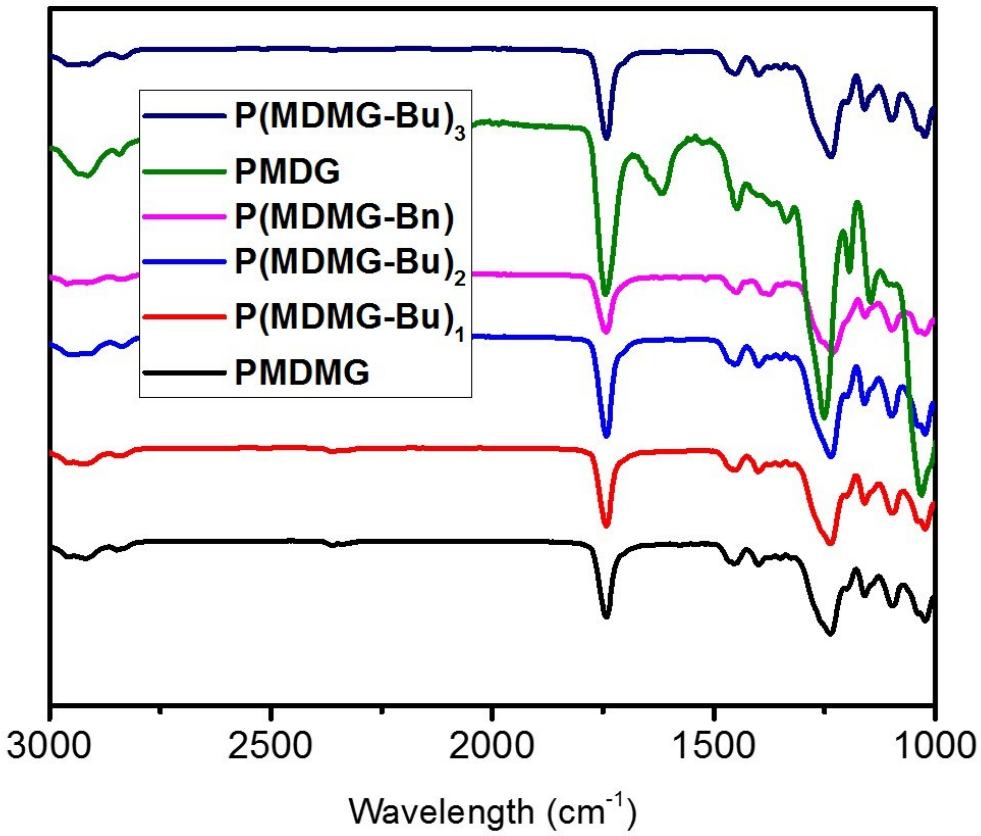

Figure S1: The infrared spectra of the synthesized Linear polyglycocarbonates (ῡ-1750 cm^{-1}).

HRMS Data

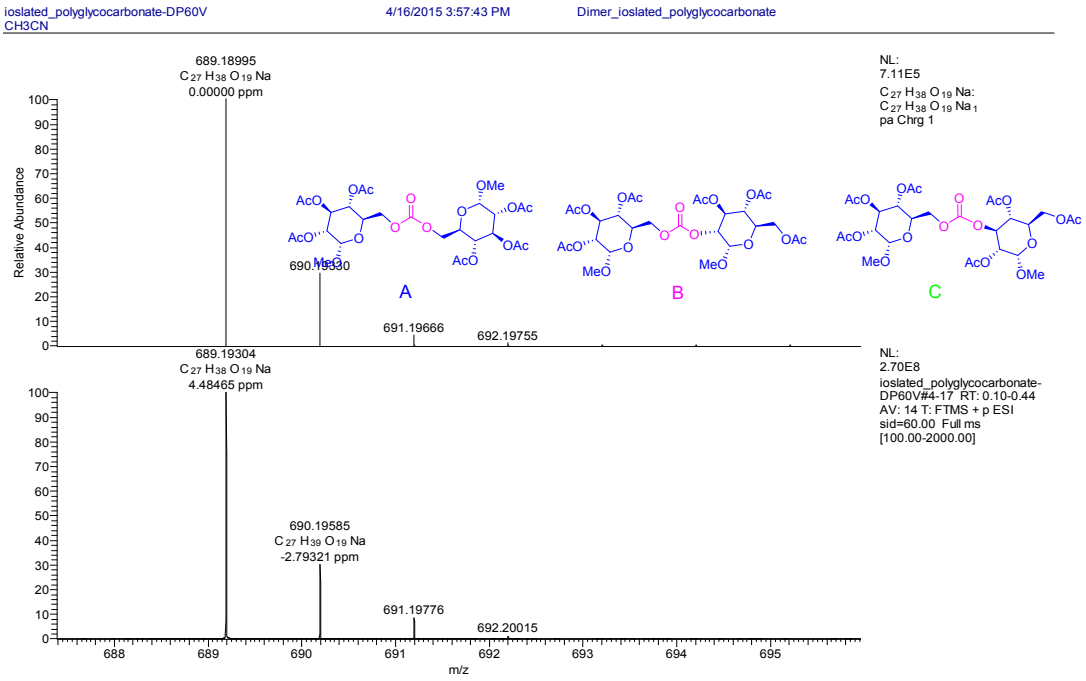

Figure S2: The HRMS spectrum of the isolated dimer linear glycocarbonates acetate. The calculated mass $[M+Na]^+$ is 689.1899 and peaks appeared at 689.1930.

NMR Data

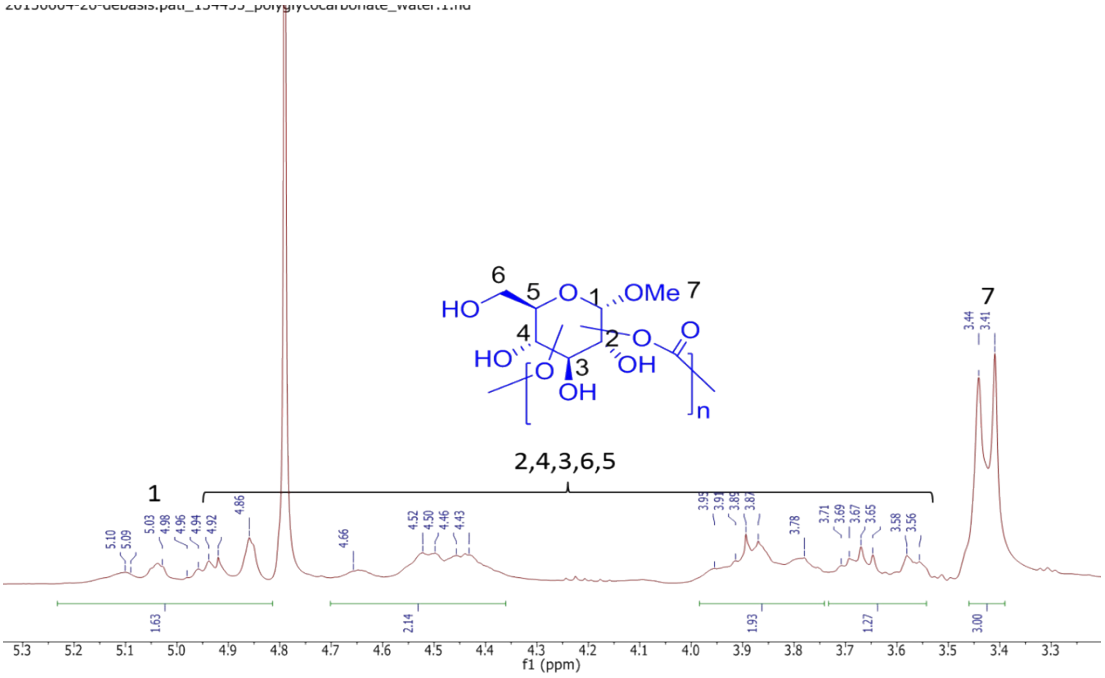

Figure S3: ^{1}H spectrum of the linear polyglycocarbonates (**PMDG**).

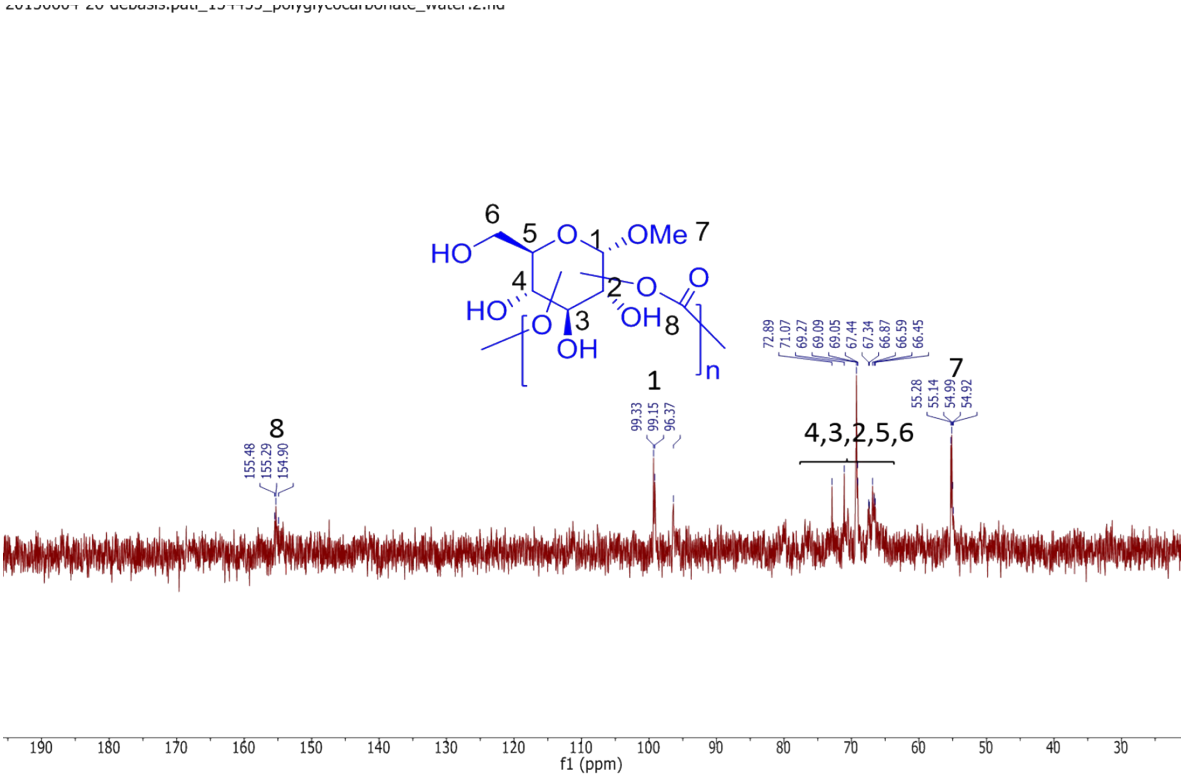

Figure S4: ^{13}C spectrum of the linear polyglycocarbonates (**PMDG**).

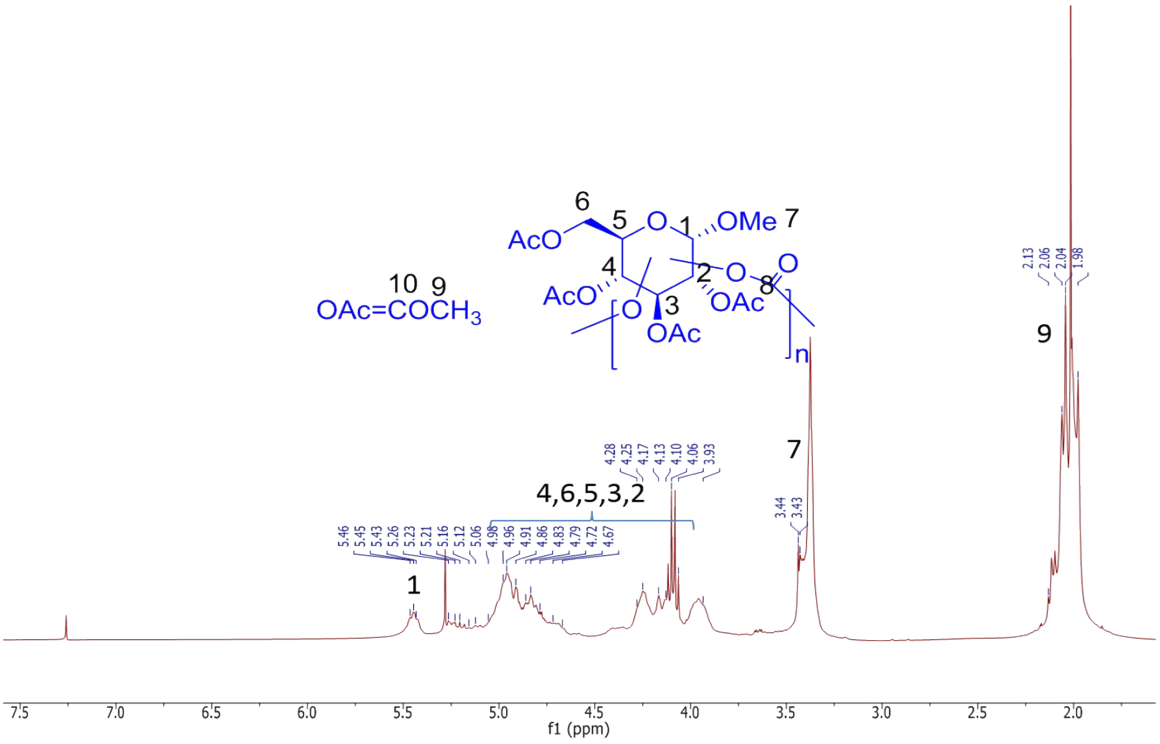

Figure S5: ^{1}H spectrum of the linear polyglycocarbonates acetate (**PMDG-Ac**).

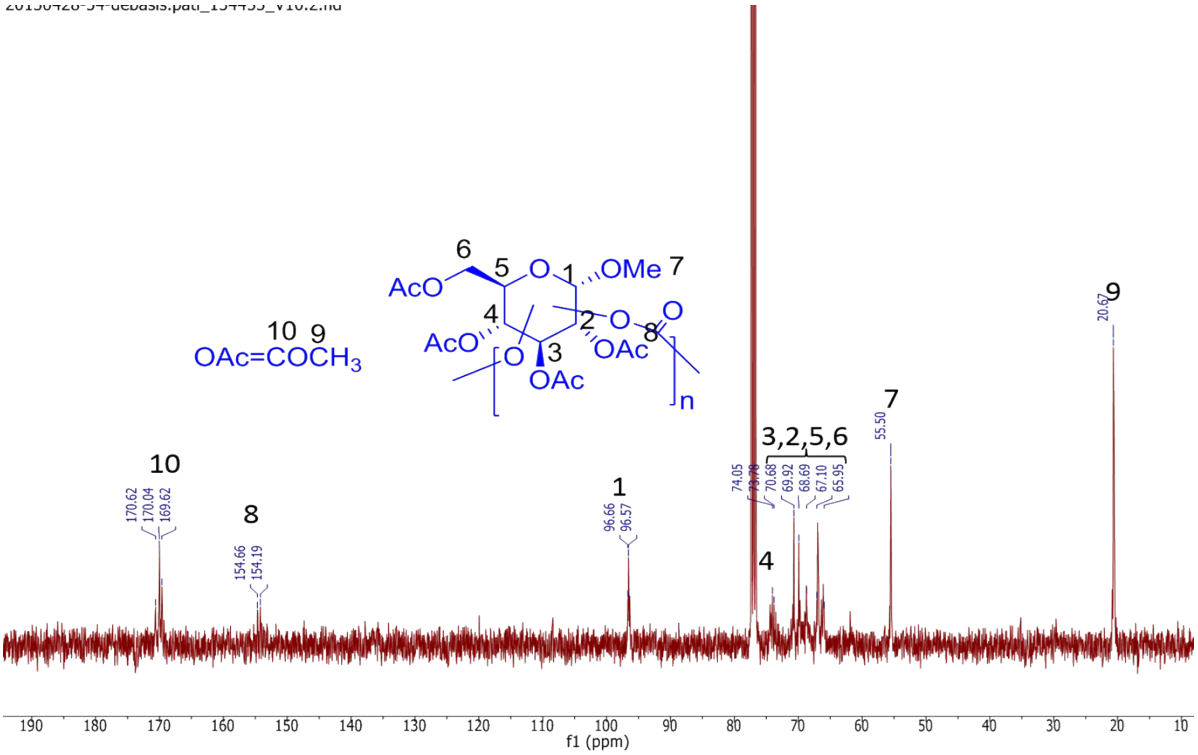

Figure S6: ^{13}C spectrum of the linear polyglycocarbonates acetate (**PMDG-Ac**).

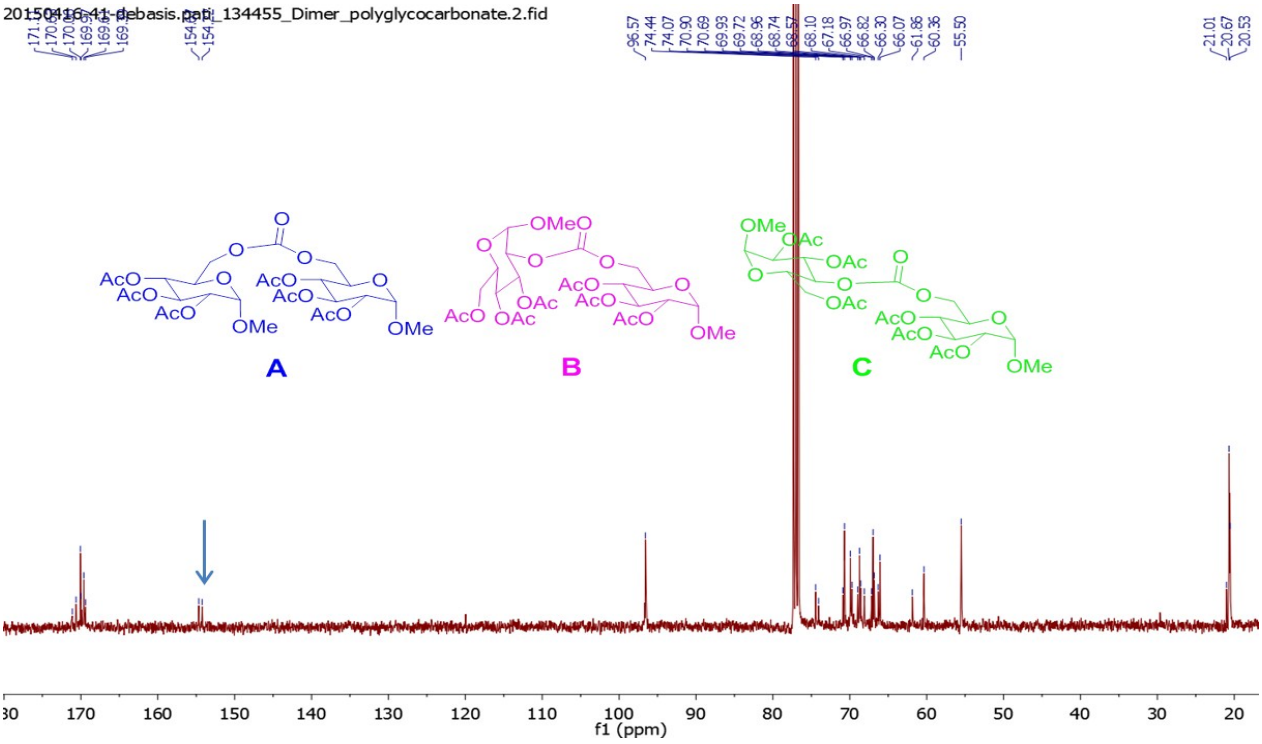

Figure S7: ^{13}C spectrum of the isolated linear dimer glycocarbonates acetate.

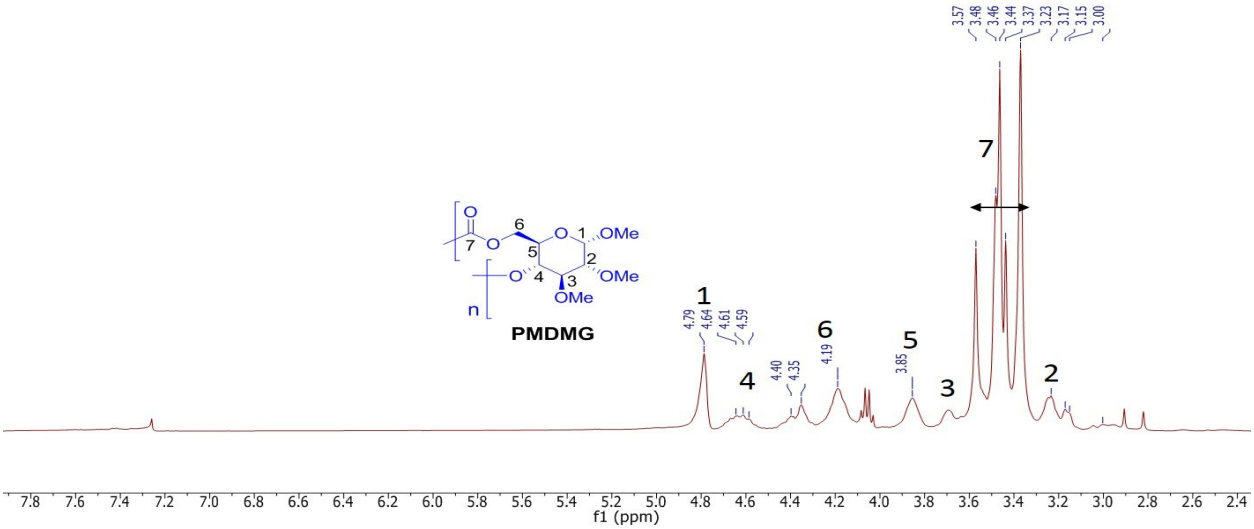

Figure S8: ^{1}H spectrum of the linear polyglycocarbonates (**PMDMG**).

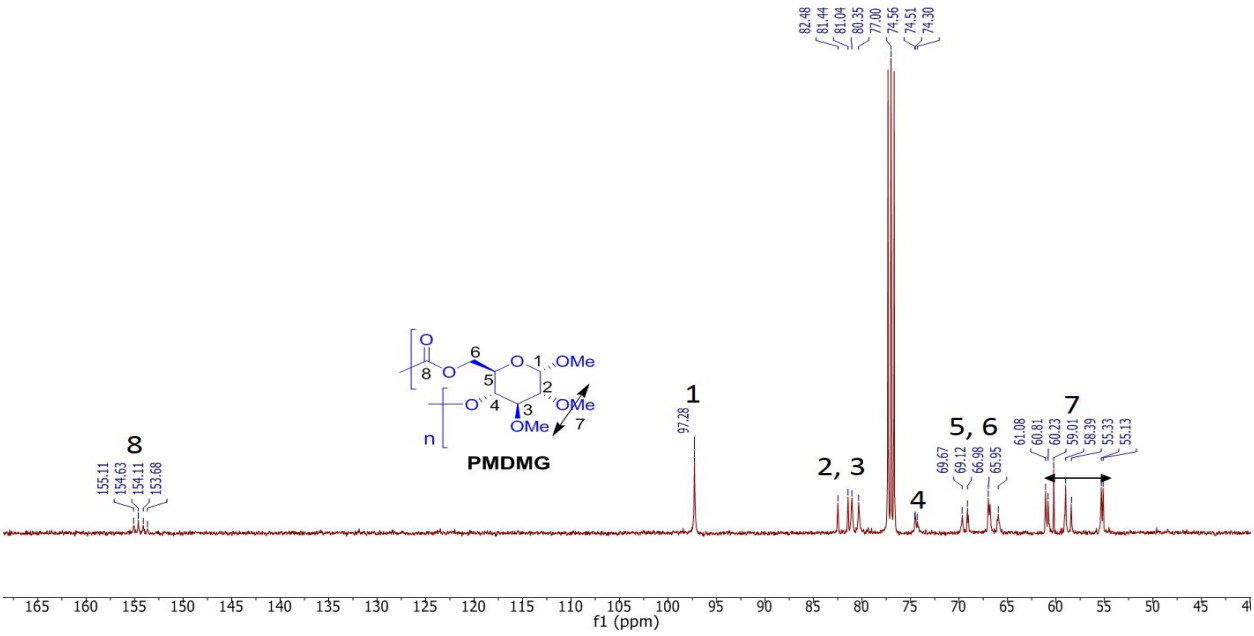

Figure S9: ^{13}C spectrum of the linear polyglycocarbonates (**PMDMG**).

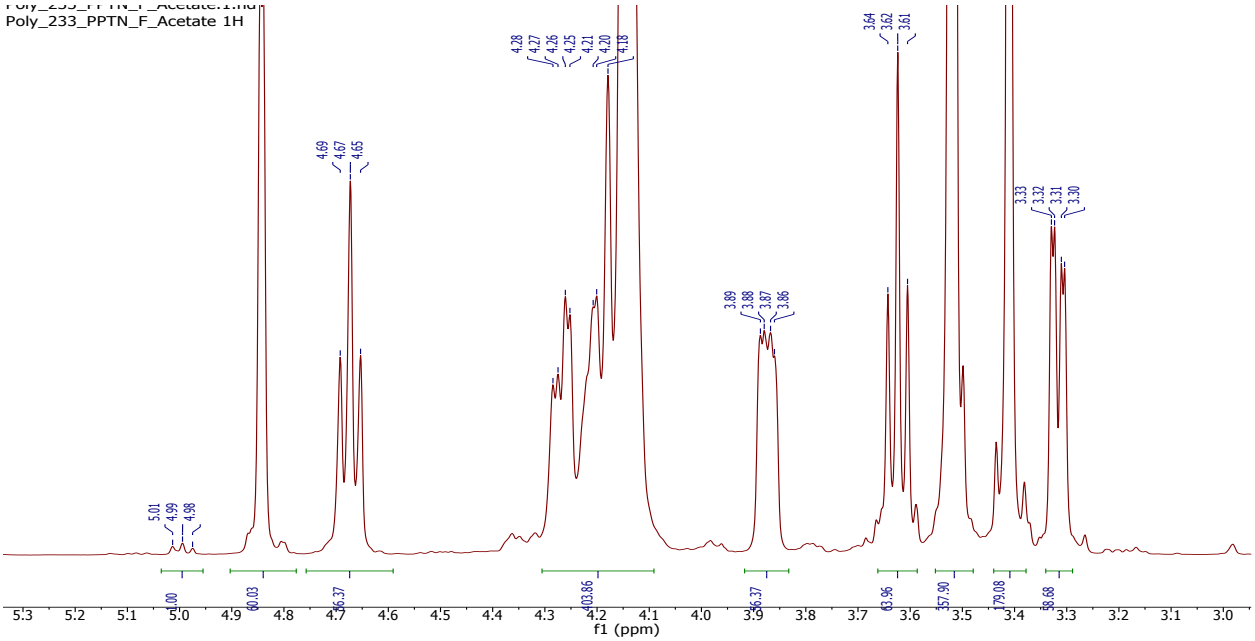

Figure S10: ^{1}H NMR spectrum of the polyglycocarbonates **P(MDMG-Bu)$_1$** after derivatization of the remaining end hydroxyls of the polymer into their corresponding esters by trifluoroacetic anhydride.

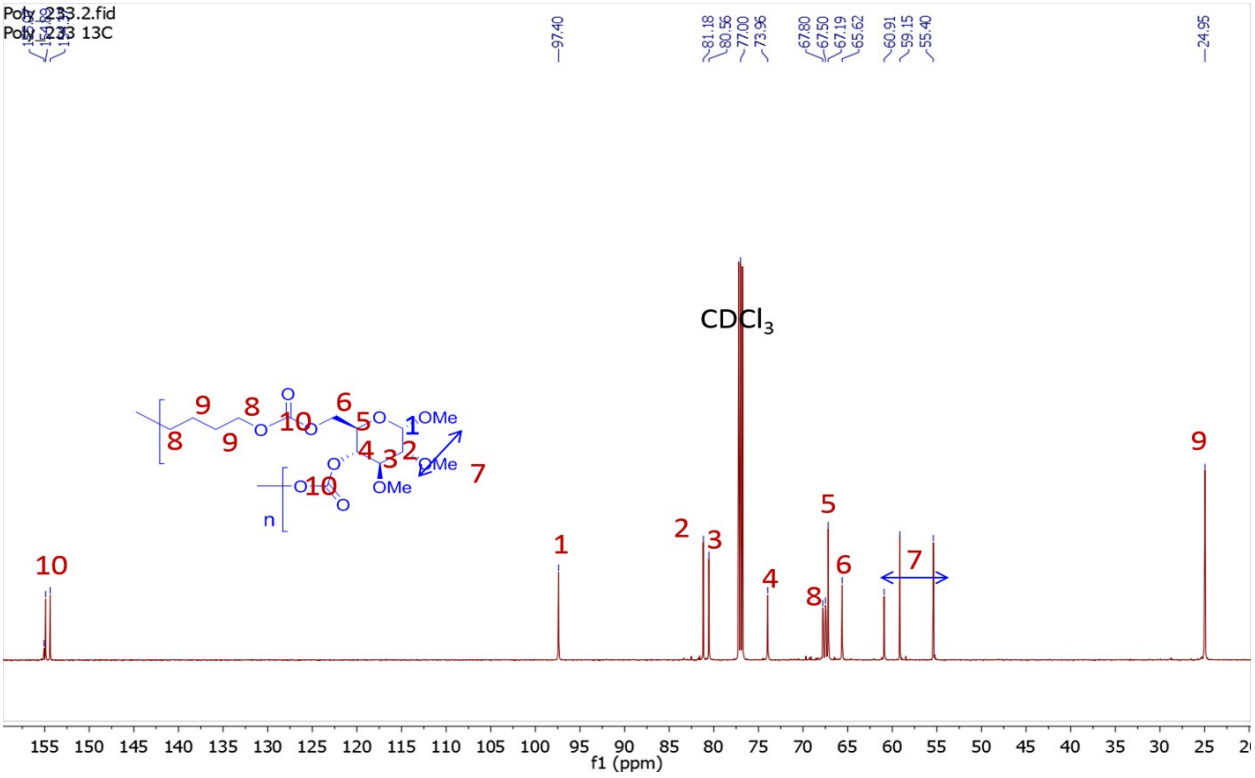

Figure S11: ^{13}C spectrum of the linear polyglycocarbonates **P(MDMG-Bu)$_1$.**

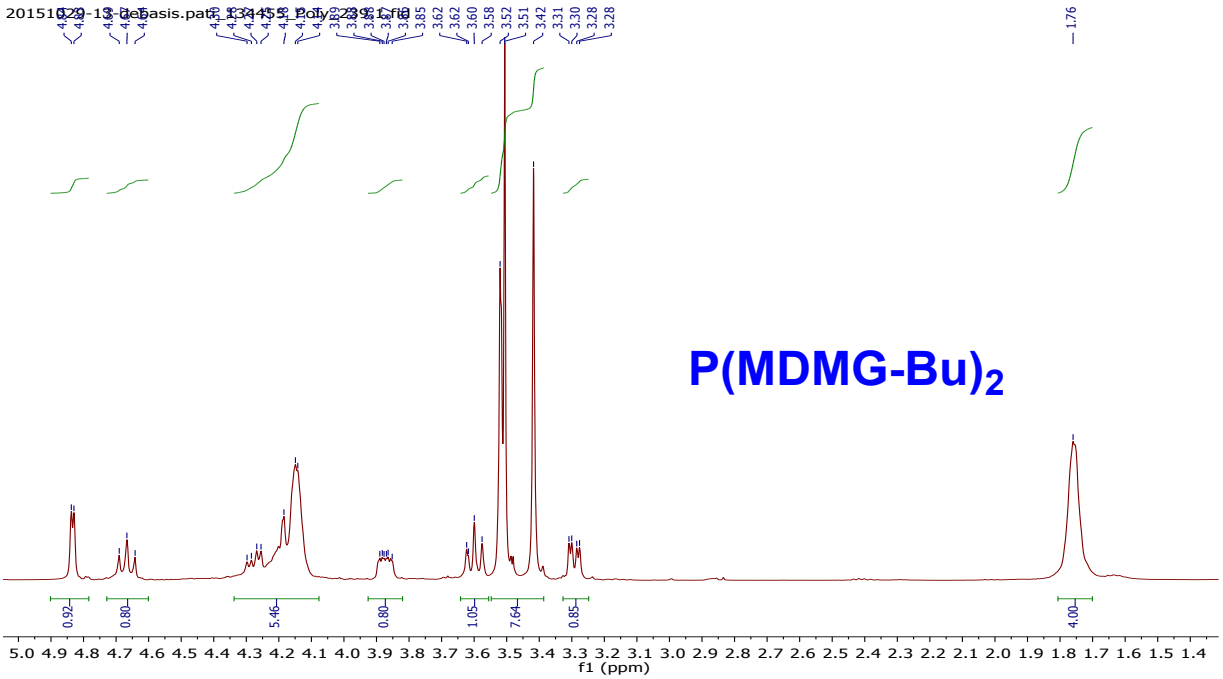

Figure S12: ^{1}H spectrum of the linear polyglycocarbonates **P(MDMG-Bu)$_2$.**

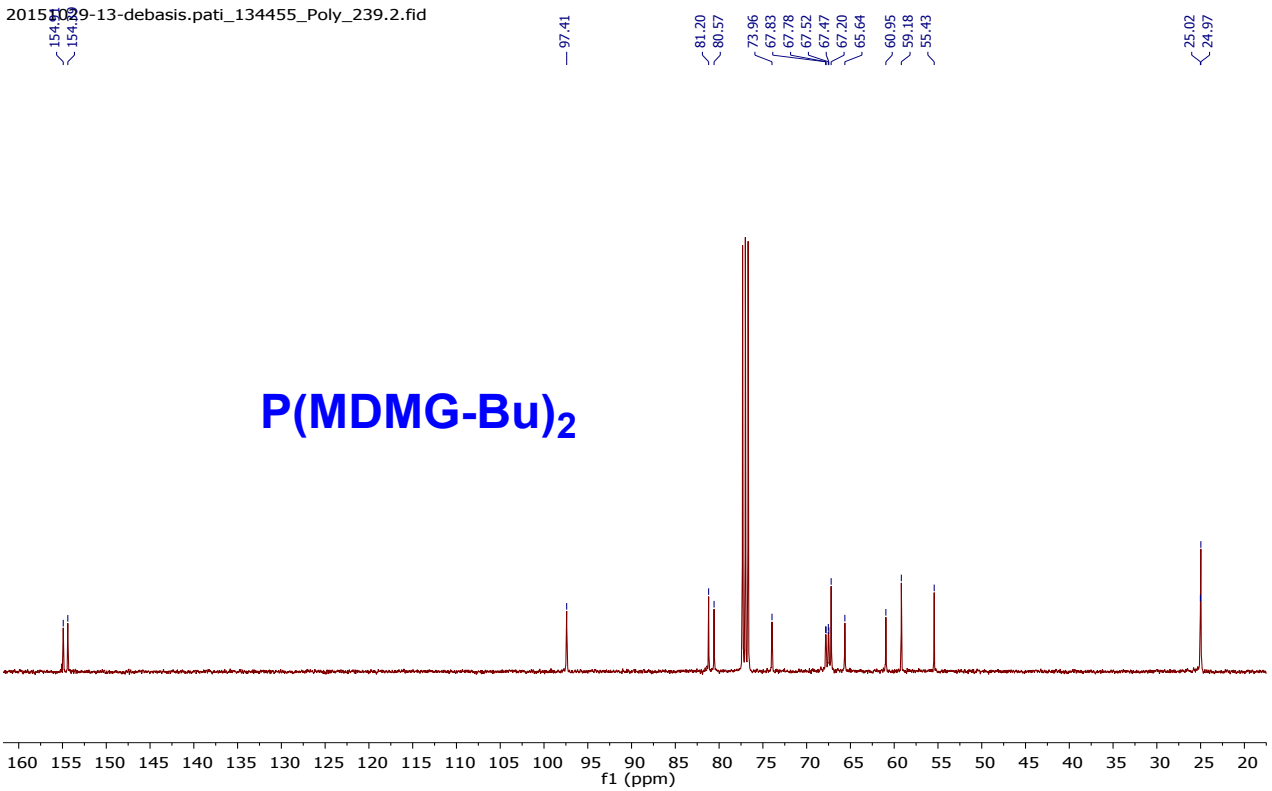

Figure S13: ^{13}C spectrum of the linear polyglycocarbonates **P(MDMG-Bu)$_2$.**

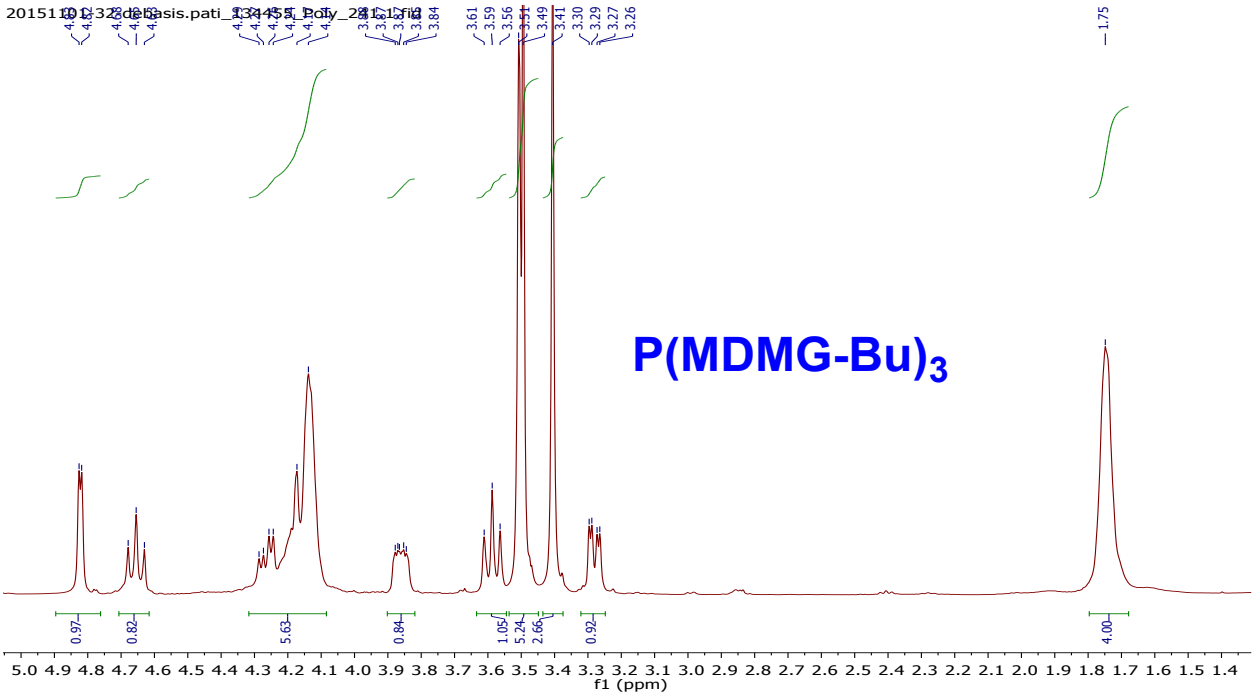

Figure S14: ^{1}H spectrum of the linear polyglycocarbonates **P(MDMG-Bu)$_3$.**

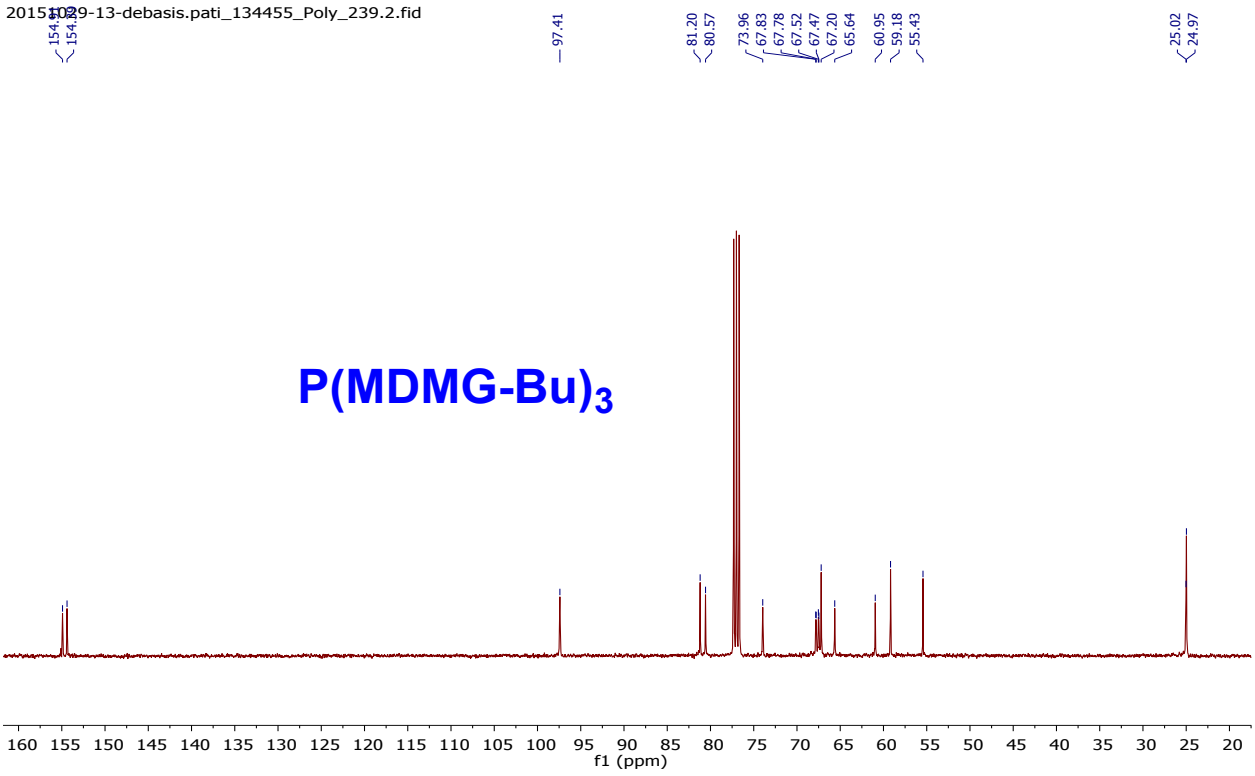

Figure S15: ^{13}C spectrum of the linear polyglycocarbonates **P(MDMG-Bu)$_3$.**

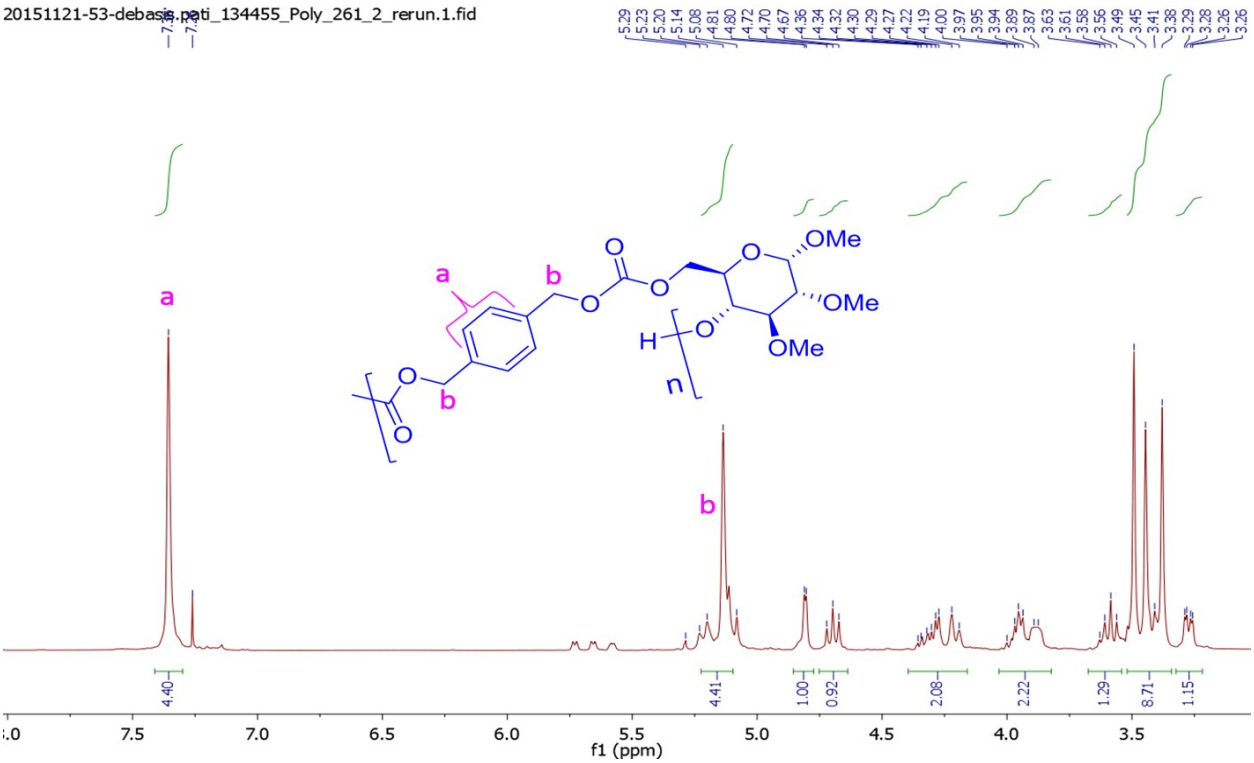

Figure S16: ^{1}H spectrum of the linear polyglycocarbonates **P(MDMG-Bn)**.

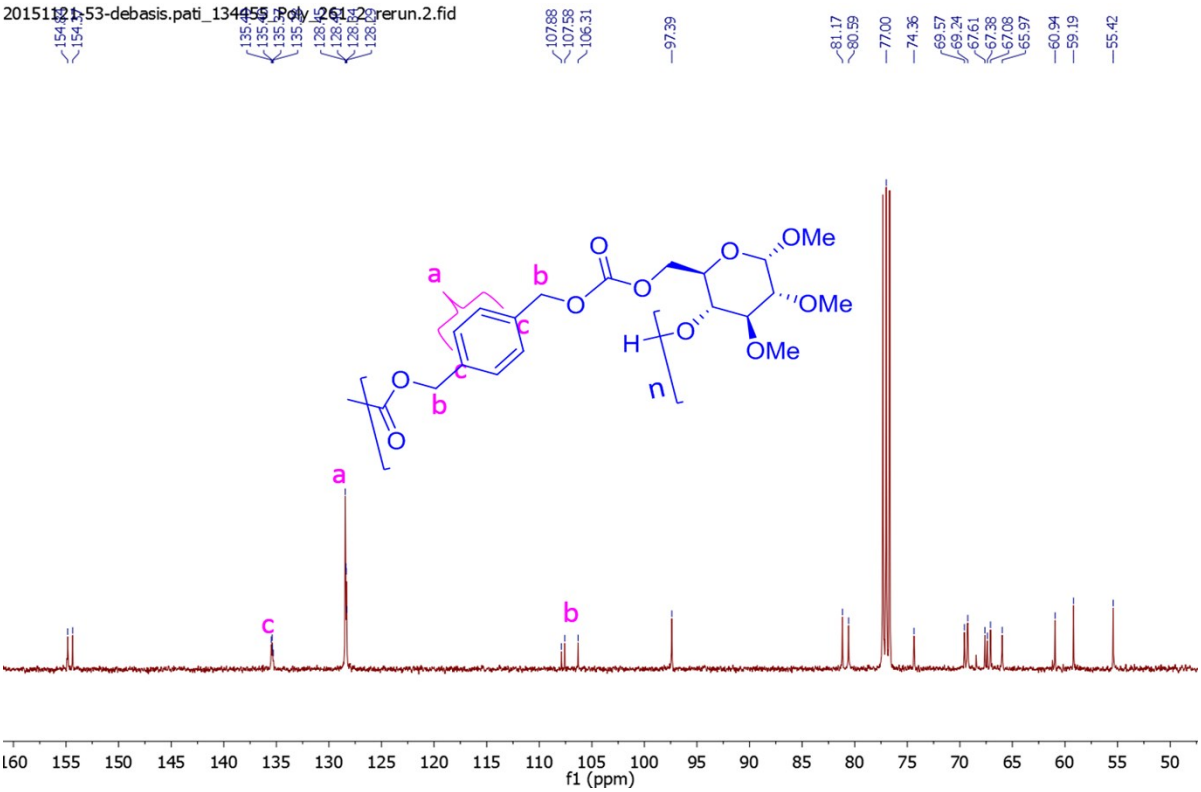

Figure S17: ^{13}C spectrum of the linear polyglycocarbonates **P(MDMG-Bn)**.

MALDI-TOF

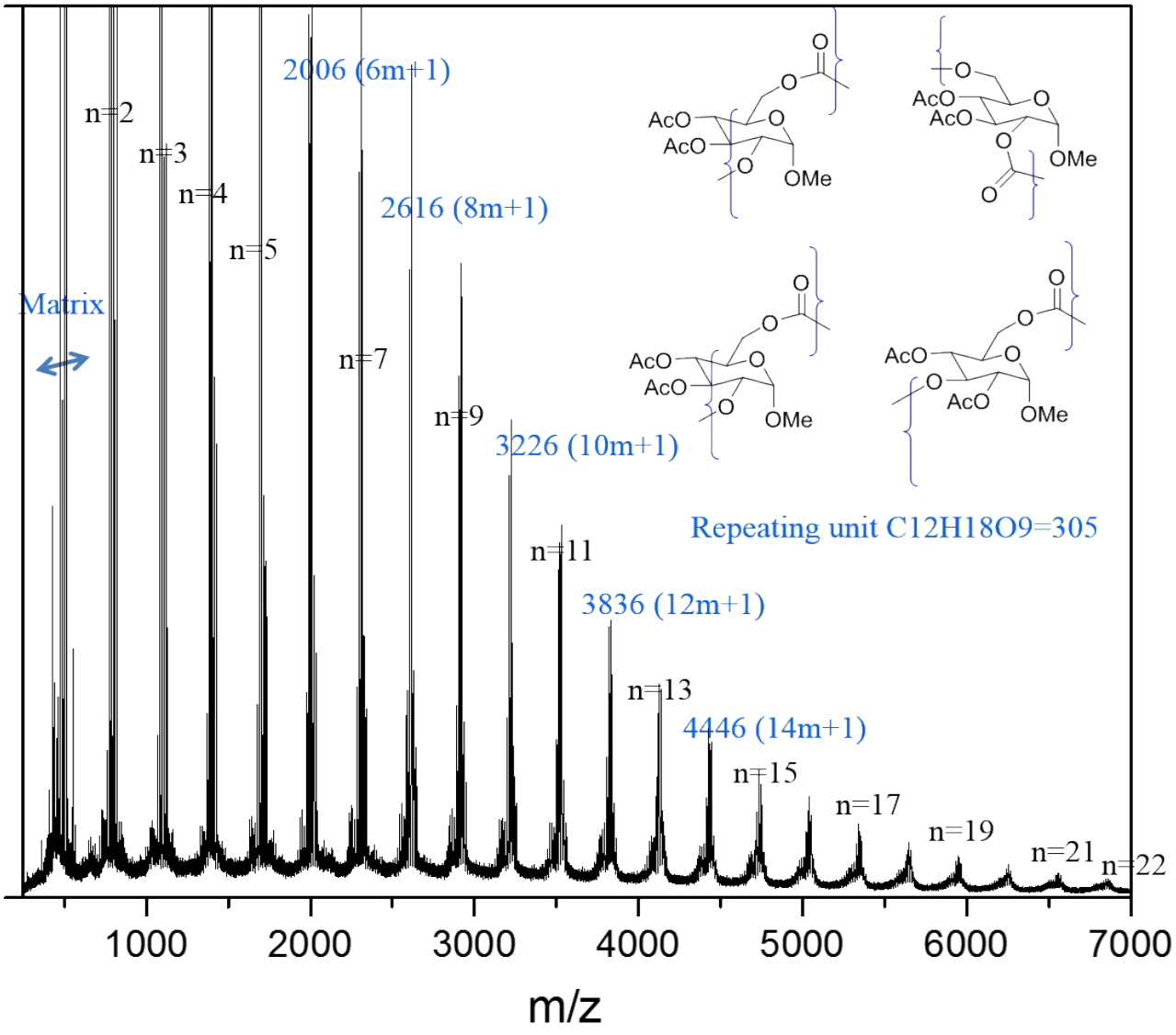

Figure S18: MALDI-TOF of the Linear polyglycocarbonates acetate (**PMDG-Ac**).

P-XRD Data:

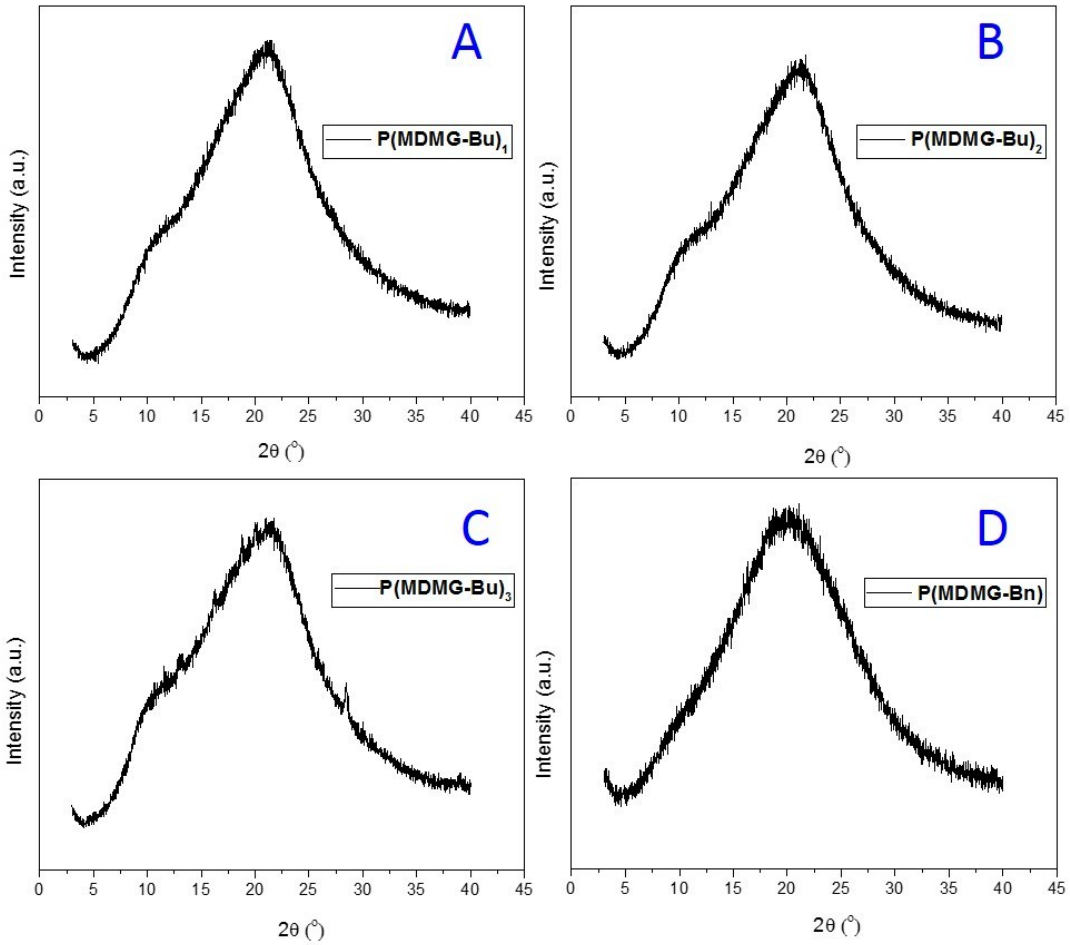

Figure S19: P-XRD of polyglycocarbonates; A) **P(MDMG-Bu)$_1$**, B) **P(MDMG-Bu)$_2$**, C) **P(MDMG-Bu)$_3$** and D) **P(MDMG-Bn)**.

References:

[1] K. Hashimoto, K. Yaginuma, S.-i. Nara, H. Okawa, *Polym J* **2005**, *37*, 384-390.
[2] Mikami, K.; Lonnecker, A. T.; Gustafson, T. P.; Zinnel, N. F.; Pai, P. J.; Russell, D. H.; Wooley, K. L., *J. Am. Chem. Soc.* **2013,** *135* (18), 6826-9.