Supporting Information for

Efficient Magnesium Catalysts for the Copolymerization of Epoxides and CO_2; Using Water to Synthesize Polycarbonate Polyols

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Experimental

General procedures

The synthesis of H_2L^1 and **1** have previously been reported.[1] Anhydrous complexation reactions were conducted, under an atmosphere of nitrogen, using either standard anaerobic techniques or in a nitrogen-filled glovebox. All solvents and reagents were obtained from commercial sources (Aldrich and Strem) and used as received, unless stated otherwise. THF and toluene were distilled from sodium and stored under nitrogen. Cyclohexene oxide and methylene chloride were distilled, from CaH_2, and stored under nitrogen.

^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker AV-400 instrument, unless otherwise stated. All mass spectrometry measurements were performed using a Fisons Analytical (VG) Autospec spectrometer. Elemental analyses were determined by Mr Stephen Boyer at LondonMetropolitanUniversity, North Campus, Holloway Road, London, N7. SEC data were collected using an Agilent PL GPC-50 instrument, with THF as the eluent, at a flow rate of $1 mLmin^{-1}$. Two Polymer labs Mixed D columns were used in series. Narrow M_w polystyrene standards were used to calibrate the instrument. MALDI-ToF MS experiments carried out on using a dithranol matrix in THF at a loading of 1:5 with KOAc as the cationizing agent.

Synthesis of catalysts **2a** and **2b**

H_2L^1 (0.37 g, 0.67 mmol) was dissolved in dry THF (10 mL) in a Schlenk tube; the solution was transferred into another Schlenk tube containing KH (0.081 g, 2.0 mmol) and stirred at -78 °C. The solution was allowed to warm to room temperature, after which it was stirred for a further hour, before being filtered and transferred into another Schlenk tube containing MgX_2 (1.34 mmol) and left to stir overnight. The solvent was removed *in vacuo*, and the product taken up in toluene and filtered. The solvent was then removed *in vacuo* and the product dried overnight under vacuum.

2a (0.41 g, 0.57 mmol, 86 %)^1H NMR (d_2-TCE, 400 MHz, 373K): δ 6.95 (s, 4H, Ar-*H*), 4.23 (br s, 4H), 3.06 (br s, 4H), 2.97 (t, J = 12.3 Hz, 4H), 2.55 (d, *J* = 11.2 Hz, 4H), 1.97 (t, *J* = 13.7 Hz, 4H), 1.84 (br s, 6H, Ac-CH_3), 1.32 (s, 18H), 1.24 (s, 6H), 1.03 (s, 6H). $^{13}C\{1H\}$ NMR (d_2-TCE, 100 MHz, 373 K): δ 176.9, 160.0, 137.9, 127.8, 124.8, 62.0, 55.0, 34.0, 33.3, 31.5, 28.3, 22.0, 21.0. *m/z* (LSIMS): 657 ([M – OAc]$^+$, 100 %). Anal. Calc. for $C_{38}H_{60}Mg_2N_4O_6$: C, 63.61; H, 8.43; N, 7.81. Found: C, 63.75; H, 8.57; N, 7.81.

2b (0.35 g, 0.46 mmol, 69 %). ^{1}H NMR (d_2-TCE, 400 MHz, 373K): δ6.95 (s, 4H, Ar-*H*), 4.62 (t, *J* = 12.3 Hz, 4H), 3.10 (d, *J* = 12.4 Hz, 4H), 2.97 (t, *J*= 12.7 Hz, 1H), 2.65 (d, *J* = 12.2 Hz, 4H), 2.13 (t,*J* = 12.5 Hz, 4H), 1.34 (s, 18H), 1.23 (s, 6H), 1.01 (s, 6H). ^{13}C{^{1}H} NMR (d_2-TCE, 100 MHz, 373 K): δ 158.2, 139.1, 128.1, 125.3, 62.7, 55.6, 34.2, 33.6, 31.7, 28.1, 21.9. *m/z* (LSIMS): 679 ([M –Br]$^+$, 100 %). Anal. Calc. for $C_{34}H_{54}Br_2Mg_2N_4O_2$: C, 53.79; H, 7.17; N, 7.38. Found: C, 53.68; H, 7.24; N, 7.36.

Synthesis of **2c**

2b (0.25g, 0.33 mmol) and potassium trifluoroacetate (0.10 g, 0.66 mmol) were dissolved in THF (5 mL) in a centrifuge tube and the solution stirred at 298 K, for 20 h, in a glovebox. The solution was filtered by centrifugation, the solvent removed under vacuum and the crude product taken up in toluene. The solution was filtered, by centrifugation, and the solvent removed under vacuum, giving a white powder (0.24 g, 0.29 mmol, 88 %).

^{1}H NMR (d_2-TCE, 400 MHz, 373K): δ 6.96 (s, 4H), 4.11 (t, *J* = 12.2 Hz, 4H), 3.16 (d, *J* = 11.8 Hz, 4H), 2.87 (t, *J* = 12.6 Hz, 4H), 2.64 (d, *J* = 11.6 Hz, 4H), 1.96 (t,*J* = 12.0 Hz, 4H), 1.31 (s, 18H), 1.27 (s, 6H), 1.06 (s, 6H). ^{13}C{^{1}H}NMR (d_2-TCE, 100 MHz, 373 K): δ161.1 (q, *J* = 35 Hz), 160.9, 135.9, 127.8, 123.3, 116.2 (q, *J* = 100 Hz), 62.3, 55.1, 34.0. 33.2, 31.4, 28.3, 20.6. ^{19}F{^{1}H} NMR: (d_2-TCE, 400 MHz, 373K) δ -75.3 (s, 3F), - 77.2 (s, 3F). *m/z* (LSIMS): 712 ([M – O_2CCF_3]$^+$, 100 %). Anal. Calc. for $C_{38}H_{54}F_6Mg_2N_4O_6$: C, 55.29; H, 6.59; N, 6.79. Found: C, 55.15; H, 6.54; N, 6.66.

Low pressure copolymerisation procedure

Cyclohexene oxide (2.5 mL, 25 mmol) and the catalyst (0.025 mmol) were added to a Schlenk tube. The cyclohexene oxide was de-gassed, before being left stirring under 1 atm CO_2, at temperature for a certain number of hours. The crude reaction mixture was then taken up in CH_2Cl_2 and HCl/MeOH (0.2 mL of a 5%solution)was added.The solution was evaporated in air, after which the product was dried, *in vacuo,* for 24 h. No further purification of the polymer was undertaken as the vacuum was sufficient to remove unreacted cyclohexene oxide.

Low pressure copolymerisation for polyol formation

This procedure follows that described above, except a known quantity of water was added prior to the degassing of CHO.

High pressure copolymerisation procedure

The 100 mL Parr reaction vessel was dried in an oven at 140 ˚C for 20 h, prior to use, after which the reactor was assembled and placed under vacuum for 2-3 hours. Separately, the catalyst (0.0148 mmol) was dissolved in cyclohexene oxide (15 mL, 148.3 mmol) in a Schlenk tube. This was transferred into the Parr reaction vessel, under a nitrogen atmosphere. The vessel was evacuated, then charged with 12 bar CO_2 pressure and sealed whilst stirring. The vessel was recharged with CO_2 3 times following a dip in pressure due to dissolution of CO_2 in epoxide, before being sealed and heated to 100 °C and left for the chosen reaction time. Work-up was carried out in the same manner as above.

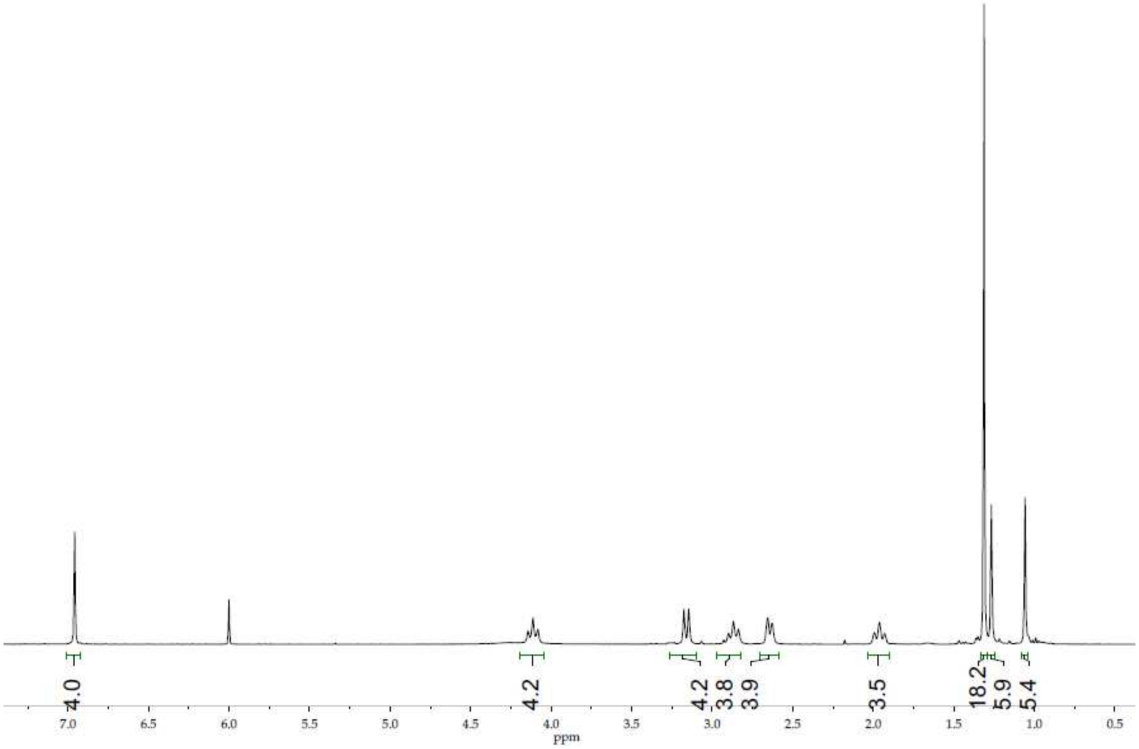


Figure S1. ^{1}H NMR spectrum of **2c** in d_2-TCE at 100 °C. NMR solvent peak at 6.0 ppm.

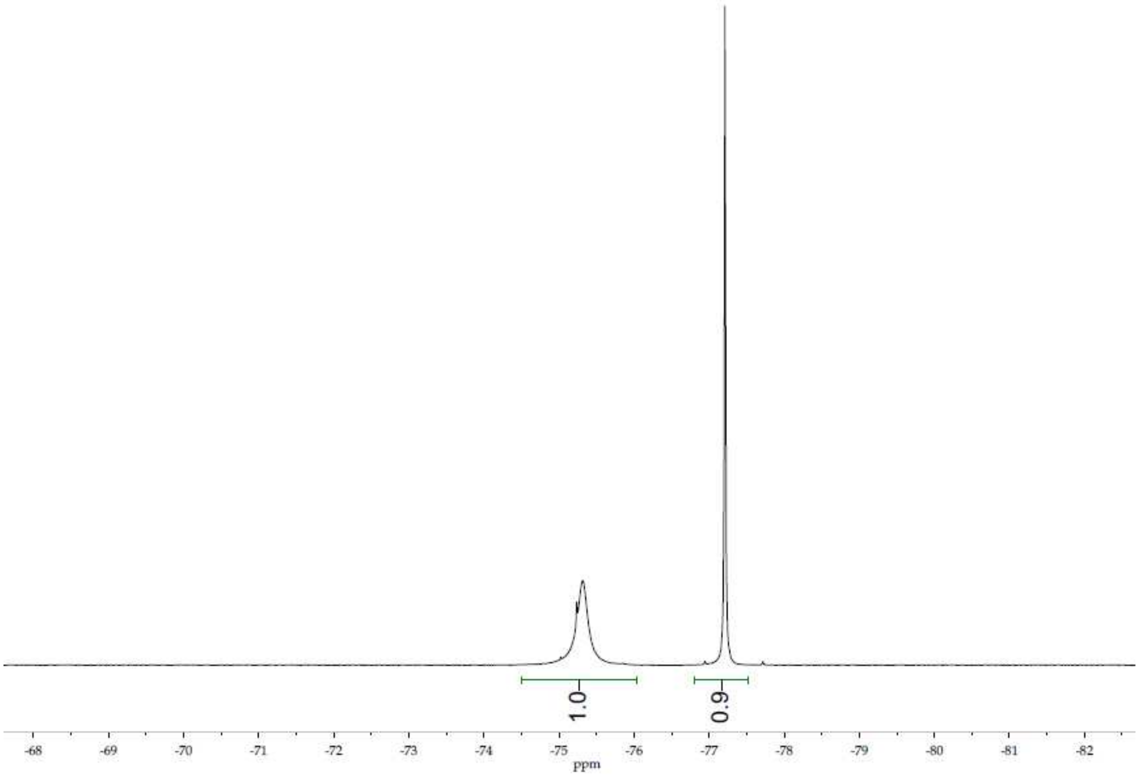
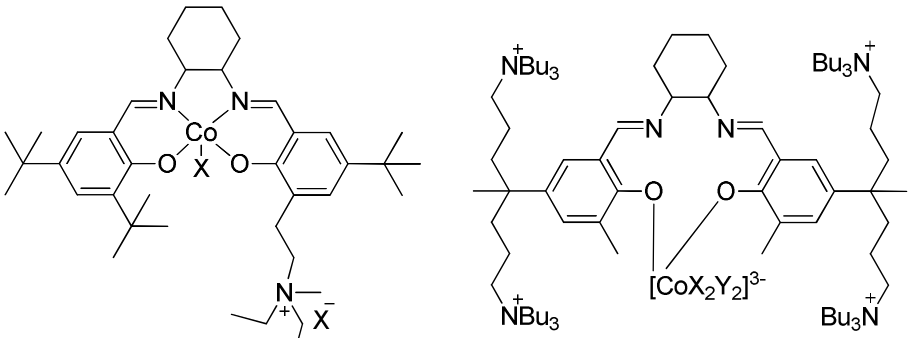


Figure S2. ^{19}F NMR spectrum of **2c** in d_2-TCE at 100 °C.



3 X = 2,4-dinitrophenolate

4 X = dinitrophenolate
Y = [X...H...X]

Figure S3. Structures of **3**[2] and **4**.[3]

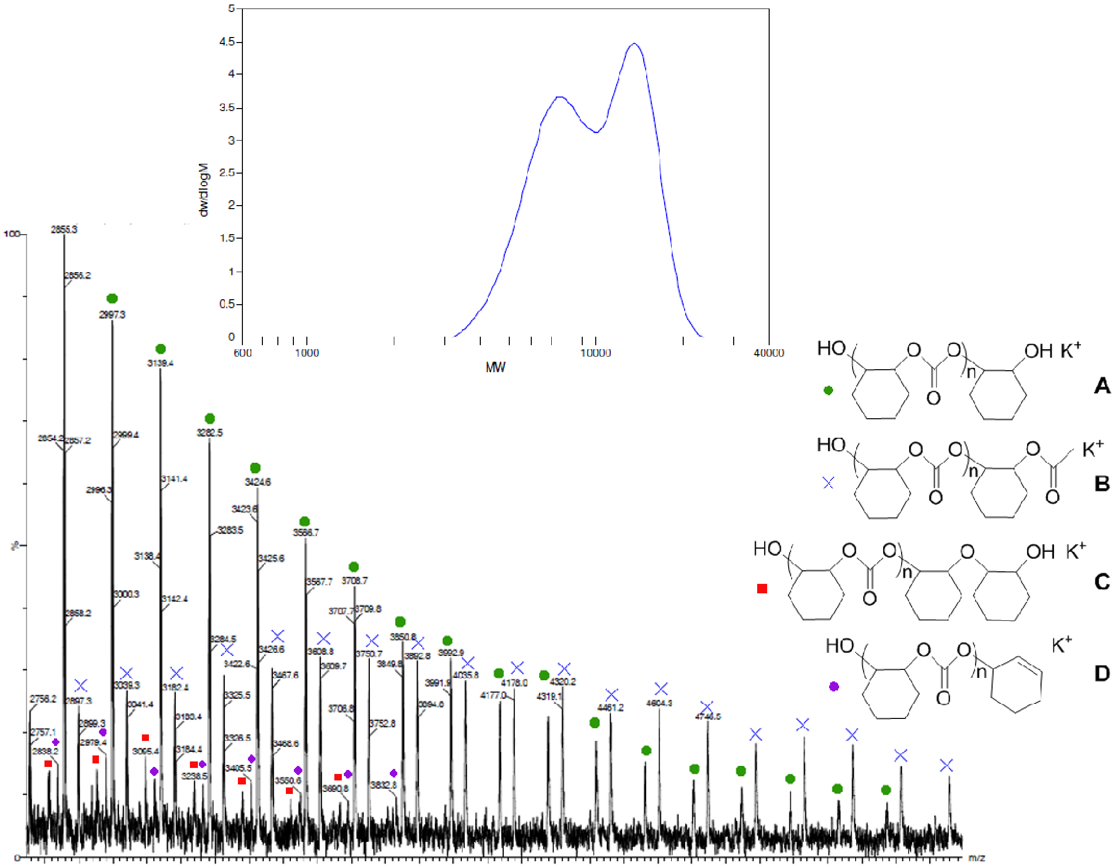


Figure S4. MALDI-ToF spectrum of (lower weight fraction of) copolymer produced by **2a** at 100 °C, 12 atm CO_2 pressure and 1:10000 loading with corresponding GPC trace inset. Expected high M_n polyol (A) series above detection limit. Polyol series (**A**, green dots) calculated for $[(C_6H_{10}O_3)_n + C_6H_{12}O_2 + K]^+ = [(142.15)n + 116.16 + 39.1]^+$. Mono-ol series **B** (blue crosses) calculated for $[(C_6H_{10}O_3)_n + C_8H_{14}O_3 + K]^+ = [(142.15)n + 158.19 + 39.1]^+$. A small polyol series (**C**, red squares) was detected at lower weight due to the presence of one ether linkage $[(C_6H_{10}O_3)_n + C_{12}H_{22}O_3 + K]^+ = [(142.15)n + 214.30 + 39.1]^+$. A small amount of series **D** (purple dots) observed due to change transfer with trace amounts of cyclohexanol/cyclohexenol, either present as a trace impurity in CHO or from MPVO side reactions with catalyst[4]: $[(C_6H_{10}O_3)_n + C_6H_{10}O + K]^+ = [(142.15)n + 98.14 + 39.1]^+$.

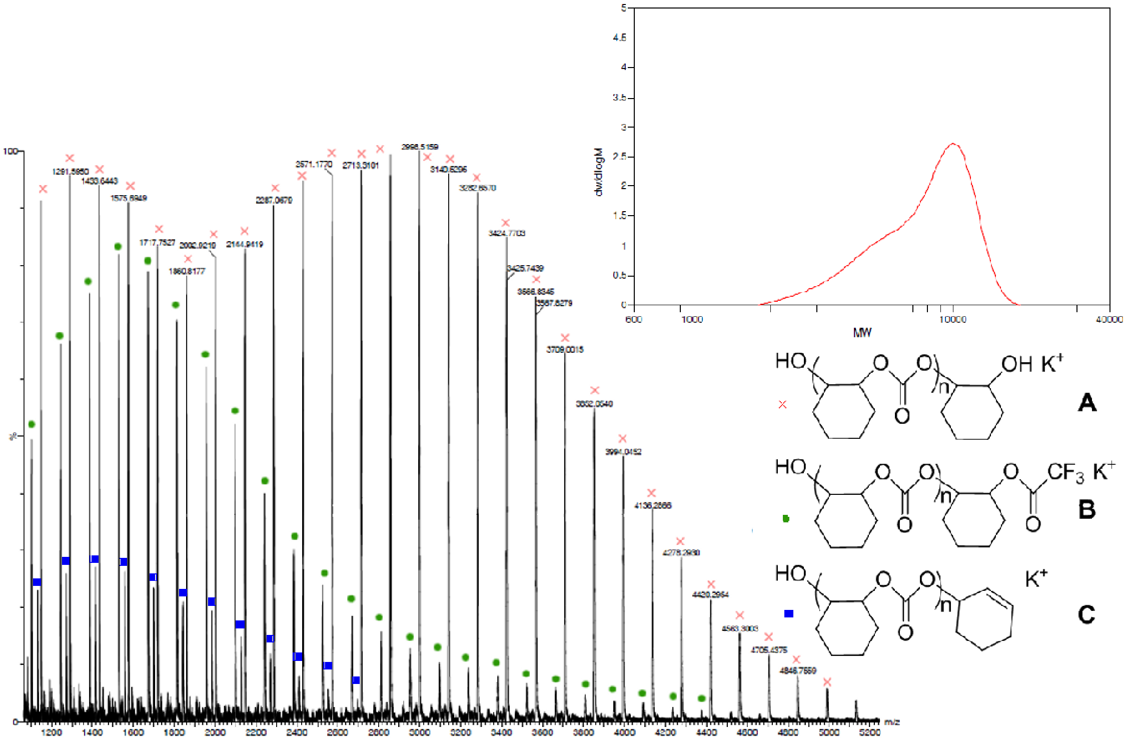


Figure S5: MALDI-ToF mass spectrum of PCHC sample produced by **2c** at 100 °C and 1 atm CO_2 with corresponding GPC trace inset. Polyol series **A** (pink crosses) calculated for $[(C_6H_{10}O_3)_n + C_6H_{12}O_2 + K]^+ = [(142.15)n + 116.16 + 39.1]^+$. Mono-ol series **B** (green dots) calculated for $[(C_6H_{10}O_3)_n + C_8H_{11}F_3O_3 + K]^+ = [(142.15)n + 212.17 + 39.1]^+$. Mono-ol series **C** (blue squares) $[(C_6H_{10}O_3)_n + C_6H_{10}O + K]^+ = [(142.15)n + 98.14 + 39.1$.

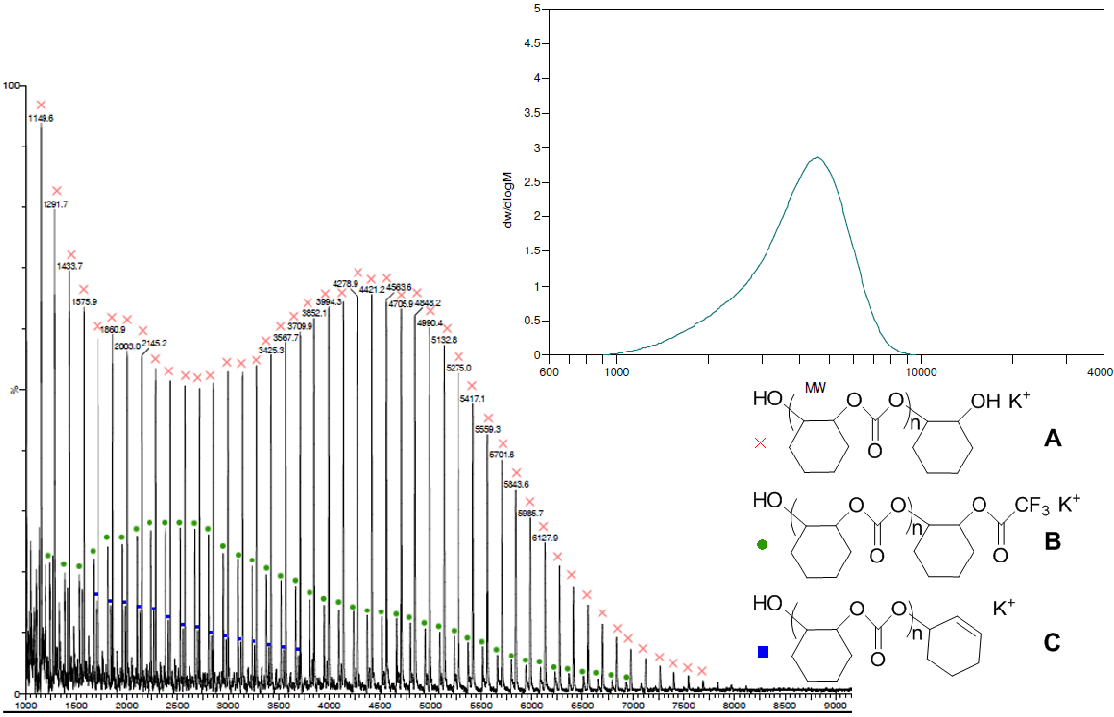


Figure S6. MALDI-ToF mass spectrum of PCHC sample from **2c** at 100 °C and 1 atm CO_2 with 10 equivalents of water and corresponding GPC trace (inset).

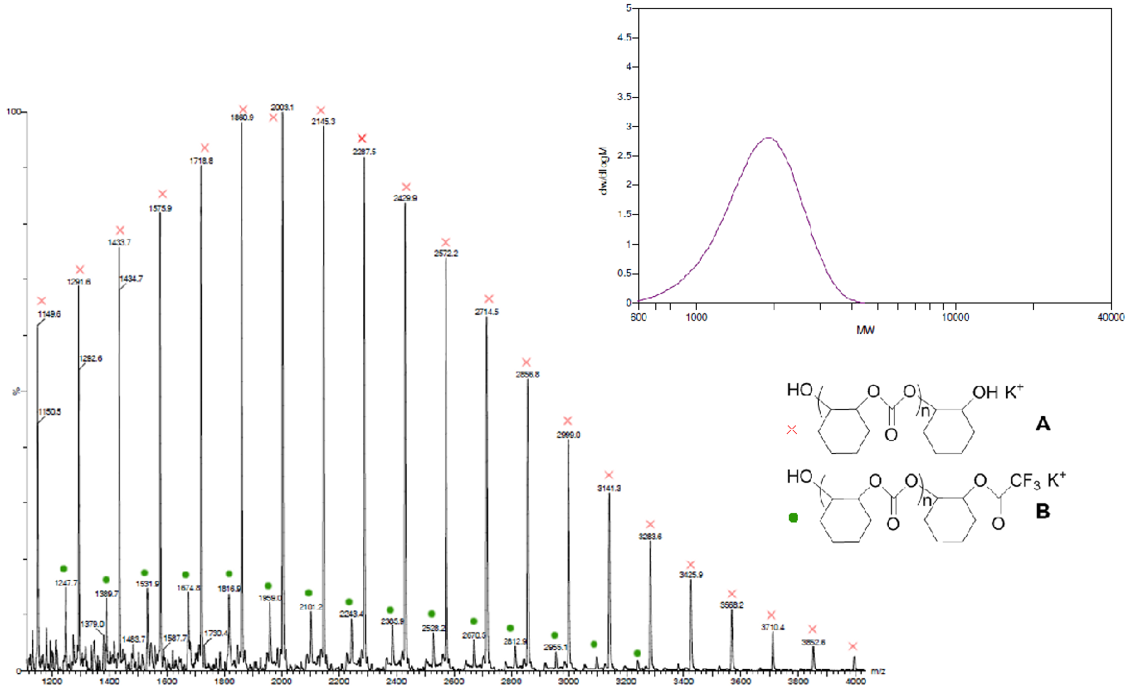


Figure S7. MALDI-ToF mass spectrum of PCHC sample from **2c** at 100 °C and 1 atm CO_2 with 30 equivalents of water with corresponding GPC trace inset.

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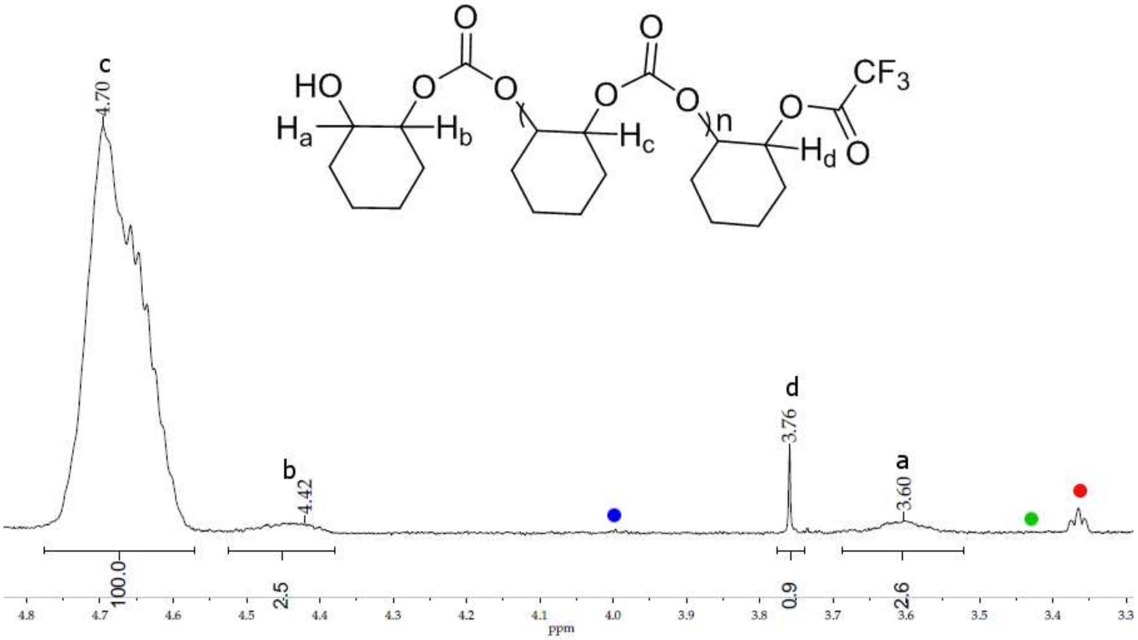

Figure S8. ^{1}H NMR of crude PCHC reaction mixture produced by **2c** at 80 °C, 1 atm CO_2 and 1:1000 loading in $CDCl_3$.

i) Assignments: Peak denoted by red circle is satellite peak of unreacted CHO from crude reaction mixture. Peak at 4.6-4.8 ppm corresponds to the methyne protons (H_c) in carbonate linkages. Peaks at 4.4 and 3.6 ppm correspond to the methyne protons on the OH end group, $OC\mathit{H}C_4H_8CHOH$ (H_b) and $OCHC_4H_8C\mathit{H}OH$ (H_a) respectively.[5] Absence of ether linkages confirmed by lack of resonance at 3.45 ppm (green circle), and >99 selectivity for polycarbonate confirmed by absence of significant resonance at 4.00 ppm corresponding to cyclohexene carbonate (blue circle).

ii) Assessment of selectivity: Resonance at 3.76 ppm assigned to H_d on basis of its absence from copolymers synthesized with different initiating groups, on the observation of similar peaks at different shifts due to OAc (4.1 ppm)[1] and Cl (3.7 ppm) end groups in copolymers formed with other initiating groups, on its decrease with increasing concentrations of water relative to catalyst and on the chemical shift of model compound methyl trifluoroacetate (3.98 ppm).[6] Peak at 3.6 ppm a composite of two $OCHC_4H_8C\mathit{H}OH$ (H_a) end groups from the diol, and one at the other end of the trifluoroacetate terminated mono-ol. For comparison of integrals of OH and O_2CCF_3 end groups, OH end group resulting from mono-ol subtracted from integral of H_a resonance at 3.6 ppm (i.e. 2.6 – 0.9 = 1.7). This value divided by 2 as polyol contains two OH end groups c.f. one O_2CCF_3 end group in mono-ol (1.7/2 = 0.85). 0.9:0.85 ~ 50 % mono-ol:polyol.

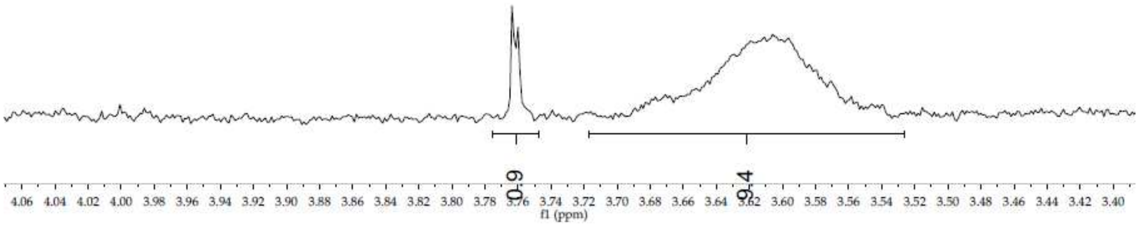

Figure S9. ^{1}H NMR of crude PCHC produced by **2c** and 30 equivalents of water. Absence of ether linkages confirmed by lack of resonance at 3.45 ppm, and >99 selectivity for polycarbonate confirmed by absence of significant resonance at 4.00 ppm corresponding to cyclohexene carbonate. Relative proportion of polyol calculated as (9.4-0.9)/2 = 4.25. Mono-ol:polyol = 0.9:4.25, ~83 % polyol.

(1) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 931-933.

(2) Ren, W.-M.; Zhang, X.; Liu, Y.; Li, J.-F.; Wang, H.; Lu, X.-B. *Macromolecules* **2010**, *43*, 1396-1402.

(3) Seong, J. E.; Na, S. J.; Cyriac, A.; Kim, B.-W.; Lee, B. Y. *Macromolecules* **2010**, *43*, 903-908.

(4) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2005**, *38*, 7306-7313.

(5) Xiao, Y.; Wang, Z.; Ding, K. *Macromolecules* **2005**, *39*, 128-137.

(6) See Spectral Database for Organic Compounds SDBS: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi