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Electronic Supplementary Information for

Controlled Synthesis of Polycarbonate Diols and Their Polylactide Block Copolymers using Amino-bis(phenolate) Chromium Hydroxide Complexes

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Structure refinement details

Raw data images from the diffraction experiment were converted from Rigaku format to Bruker format via the program Eclipse (Parsons, Simon; 2010, ECLIPSE – Program for masking high pressure diffraction images and conversion between CCD image formats) for inspection, integration and scaling using APEX2 software (Bruker; 2007, Bruker AXS Inc., Madison, Wisconsin, USA). After integration, data were scaled and corrected for absorption using the program SADABS (Bruker; 2001, Bruker AXS Inc., Madison, Wisconsin, USA) to produce a merged, scaled HKLF file which was used for structure solution.

During refinement, badly disordered, partial occupancy toluene molecules were present, and were ultimately using the OLEX2 masking procedure. 593 electrons were recovered per unit cell in two voids (total volume 3075 $Å^3$). All hydrogen atoms were introduced in calculated positions and refined on a riding model, except H7 and H8. H7 and H8 were introduced from different map positions and were refined positionally with a distance restraint. Their isotropic displacements rode on the parent atoms (O7 and O8, respectively). All non-hydrogen atoms were refined anisotropically. Two disordered t-butyl groups are present. These were refined as PARTs, with distance and anisotropic restraints/constraints.

Bond valence sum calculations show the oxidation state of each Cr atom to be +3 and therefore the bridging oxygen atom is assigned as hydroxide, for charge balance purposes.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Table S1: Crystallographic and Structure Refinement Data

Compound	**4**
Chemical formula	$C_{66}H_{104}Cr_2N_2O_8$
Formula weight	1157.51
Temperature/K	153(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.509(5)
b/Å	17.346(5)
c/Å	29.415(8)
α/°	90
β/°	103.150(7)
γ/°	90
Volume/Å^3	8699(4)
Z	4
ρ_{calc}/g cm^{-3}	0.884
Radiation type	MoKα(λ = 0.71073)
μ(MoKα)/mm^{-1}	0.289
F(000)	2504.0
Crystal size/mm^3	0.16 × 0.14 × 0.08
Reflections collected	29311
Unique reflections	15222
R_{int}	0.0452
R_{sigma}	0.1009
R_1 (all)	0.1686
$wR(F_2)$ (all)	0.3753
R_1 (I > 2σ (I))[a]	0.1105
$wR(F_2)$ (I > 2σ (I))[b]	0.3459
Goodness of fit on F^2	1.160
CCDC Ref.	**2075754**

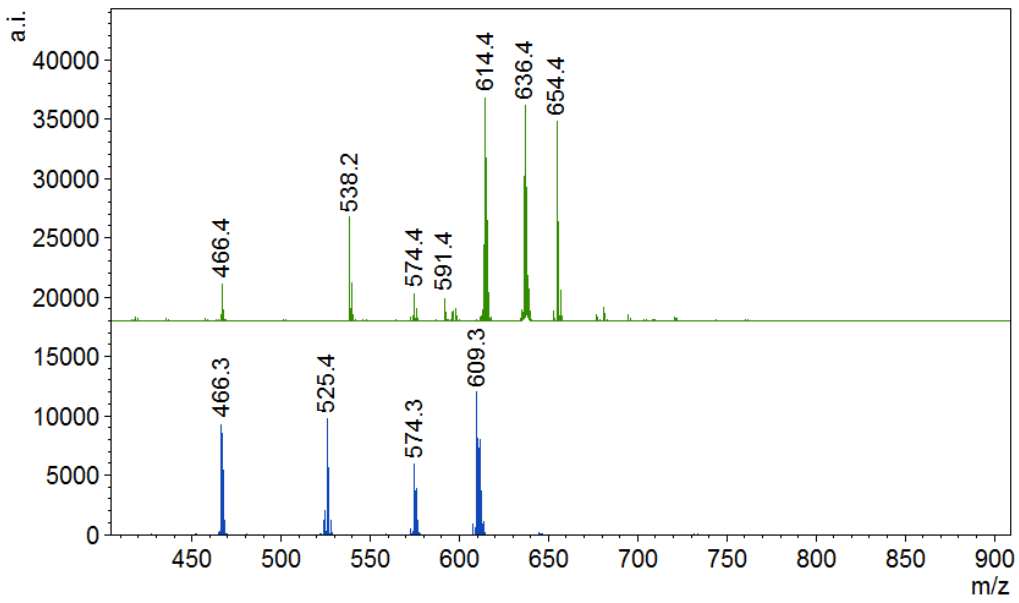

Figure S1. MALDI-TOF mass spectra of CrCl(THF)[**L**] (**1**) (blue, bottom) and CrOH[**L**] (**2**) (green, top).

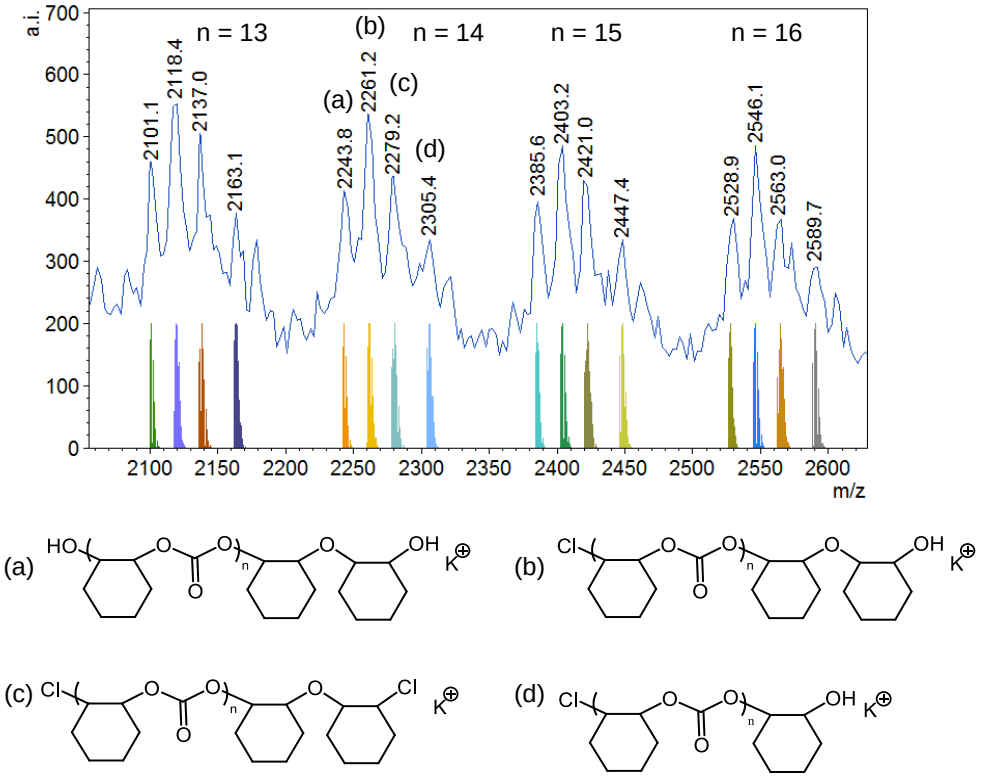

Figure S2. Magnified section of MALDI-TOF mass spectrum for PCHC (n = 13−16) obtained using **2** with PPNCl as cocatalyst (Table 1, entry 2). Modeled isotopic masses for polymers (a−d) containing different end groups are shown below the experimental spectrum.

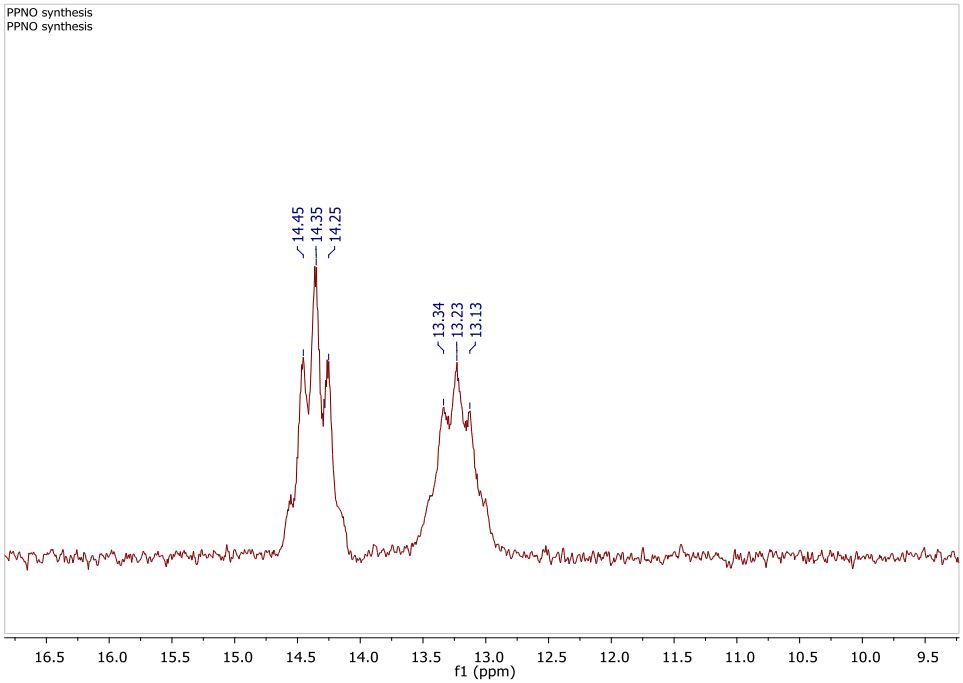

Figure S3. ^{31}P (^{1}H-coupled) NMR spectrum in $CDCl_3$ of $Ph_2P(O)NPPh_3$ obtained from PPNCl and NaOH.

(A)

(B)

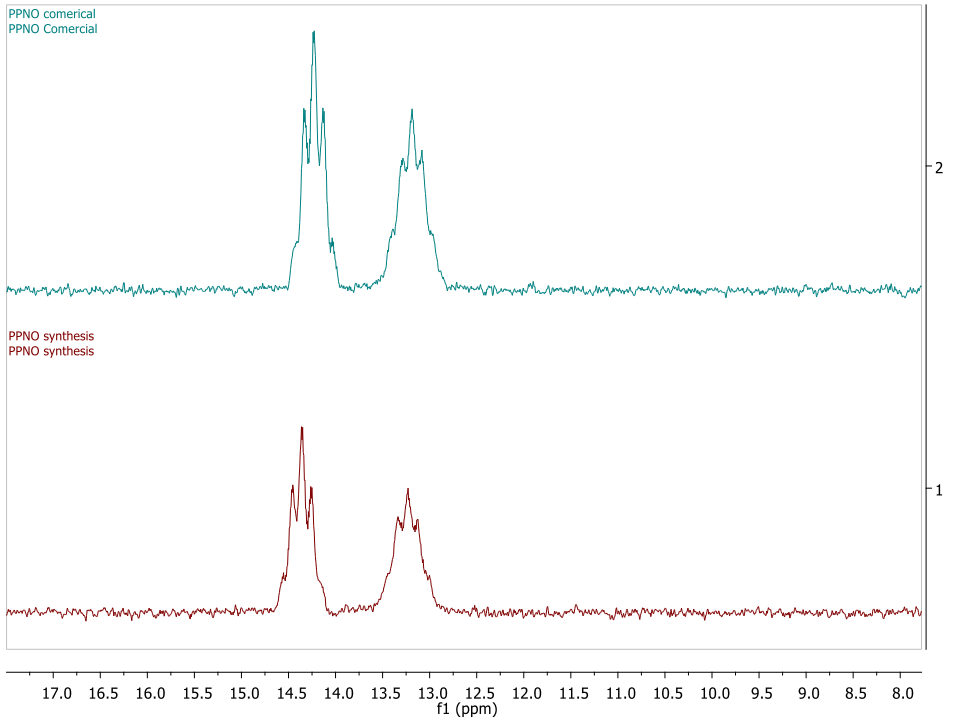

Figure S4. ^{31}P (^{1}H-coupled) NMR spectra in $CDCl_3$ of commercial $Ph_2P(O)NPPh_3$ (red, bottom) and $Ph_2P(O)NPPh_3$ obtained from PPNCl and NaOH (blue, top).

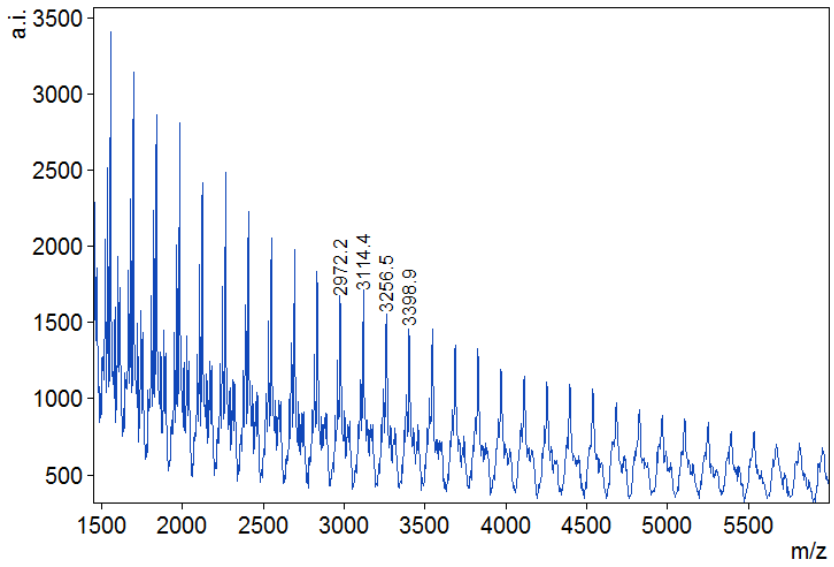

Figure S5. MALDI-TOF mass spectrum of PCHC using $Ph_2P(O)NPPh_3$ as cocatalyst (Table 1, entry 3).

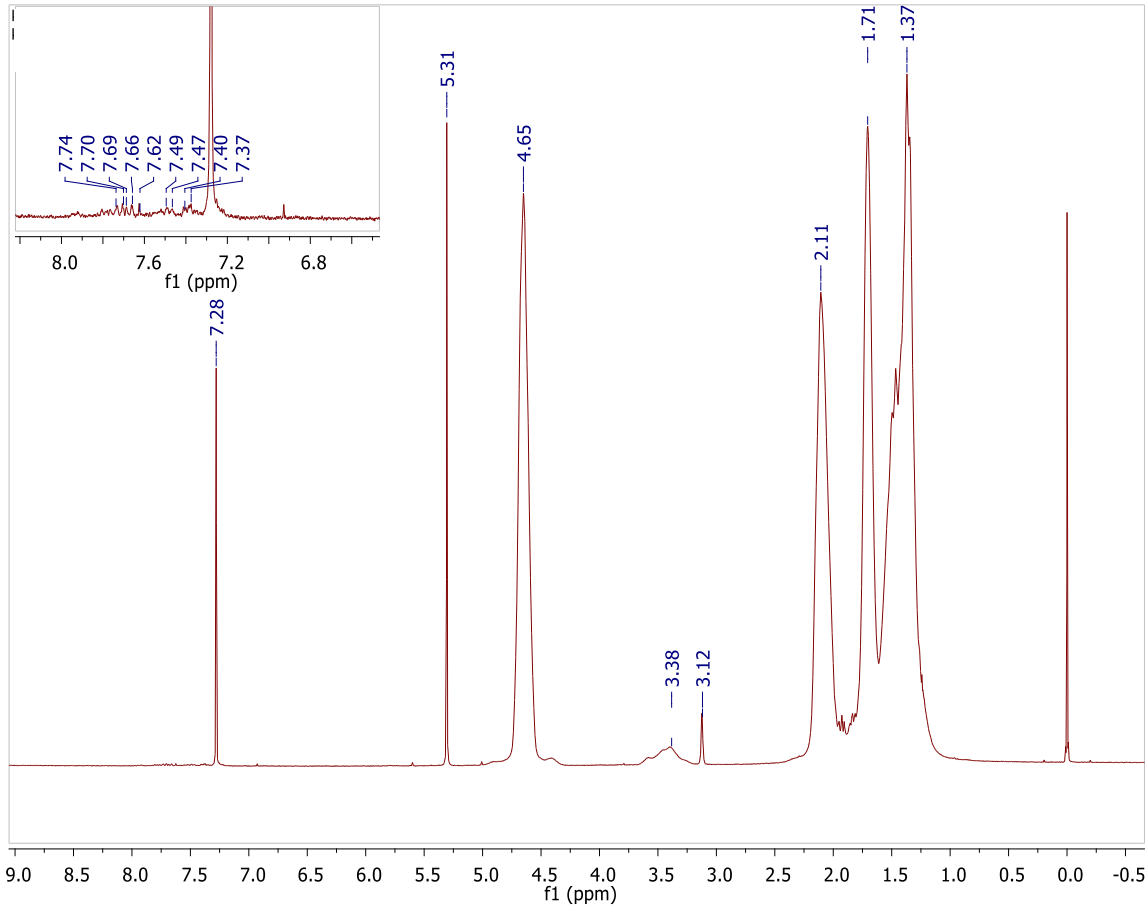

Figure S6. ^1H NMR spectrum in $CDCl_3$ of polycarbonate obtained from **2** and $Ph_2P(O)NPPh_3$ (Table 1, entry 3)

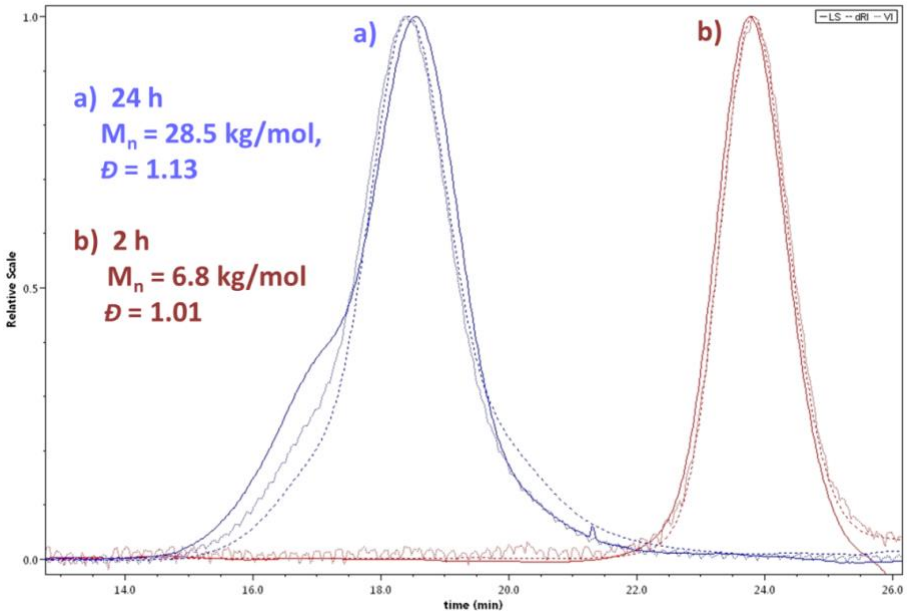

Figure S7. GPC traces determined by triple detection of the polymers obtained from CHO/CO_2 copolymerization by **2** and $Ph_2P(O)NPPh_3$ with different reaction times (a) 24 h (b) 2 h.

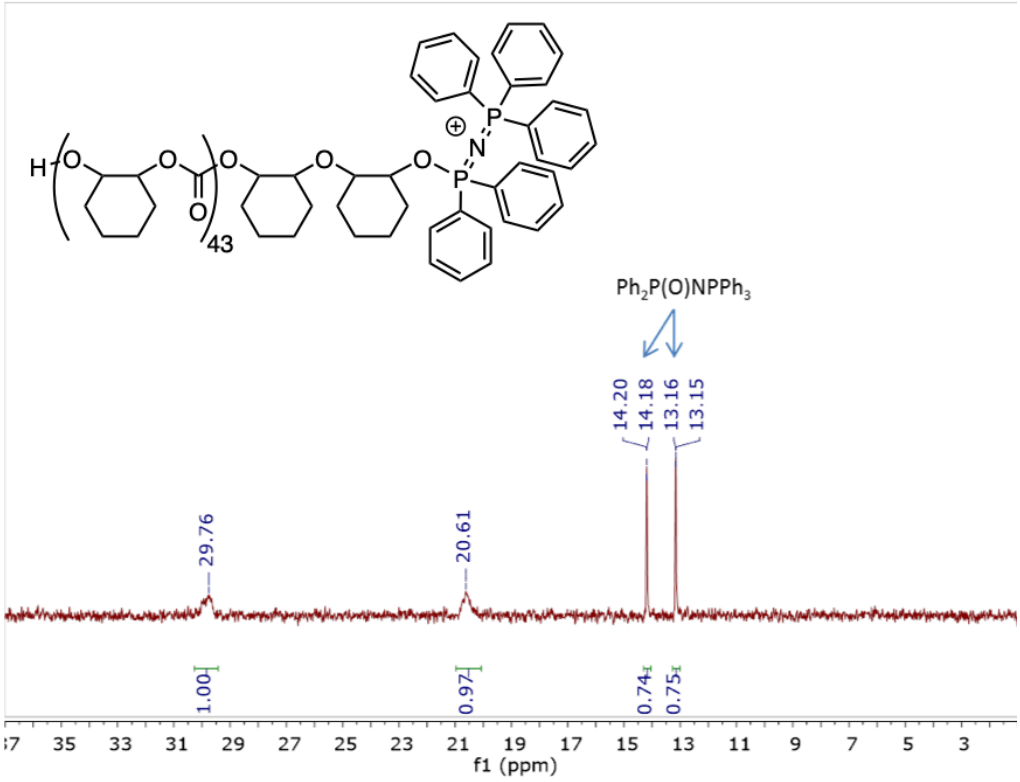

Figure S8. $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ of the polymer obtained from CHO/CO_2 copolymerization by **2** and $Ph_2P(O)NPPh_3$ for 2 h, with unreacted $Ph_2P(O)NPPh_3$ as shown.

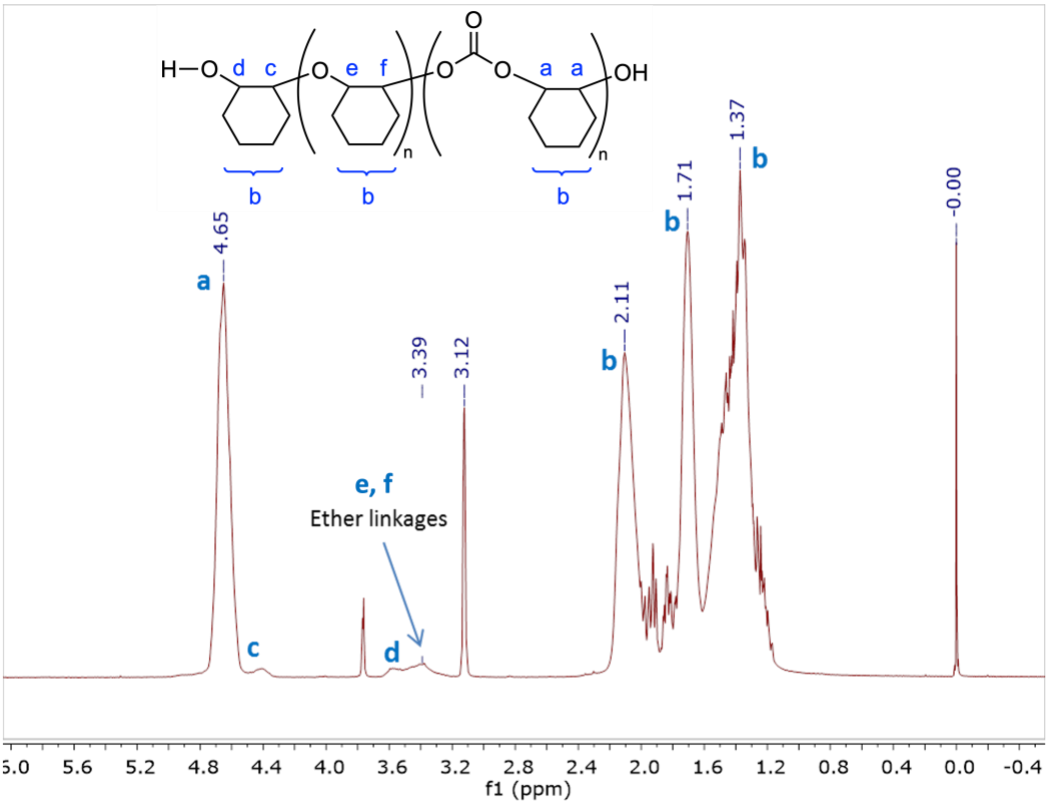

Figure S9. ^{1}H NMR spectrum in $CDCl_3$ of crude polycarbonate diol obtained from **2** and Bu_4NOH (Table 1, entry 4).

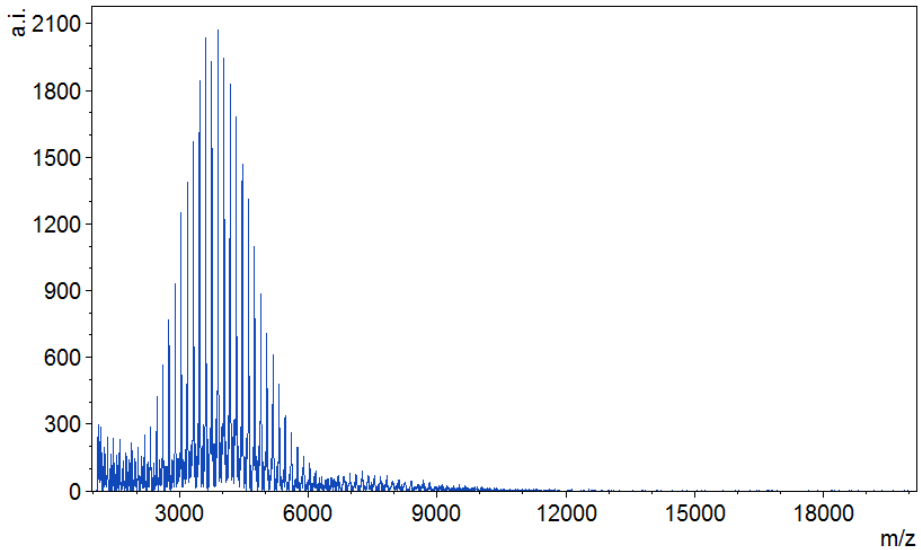

Figure S10. MALDI-TOF mass spectrum of PCHC using Bu_4NOH as cocatalyst (Table 1, entry 4).

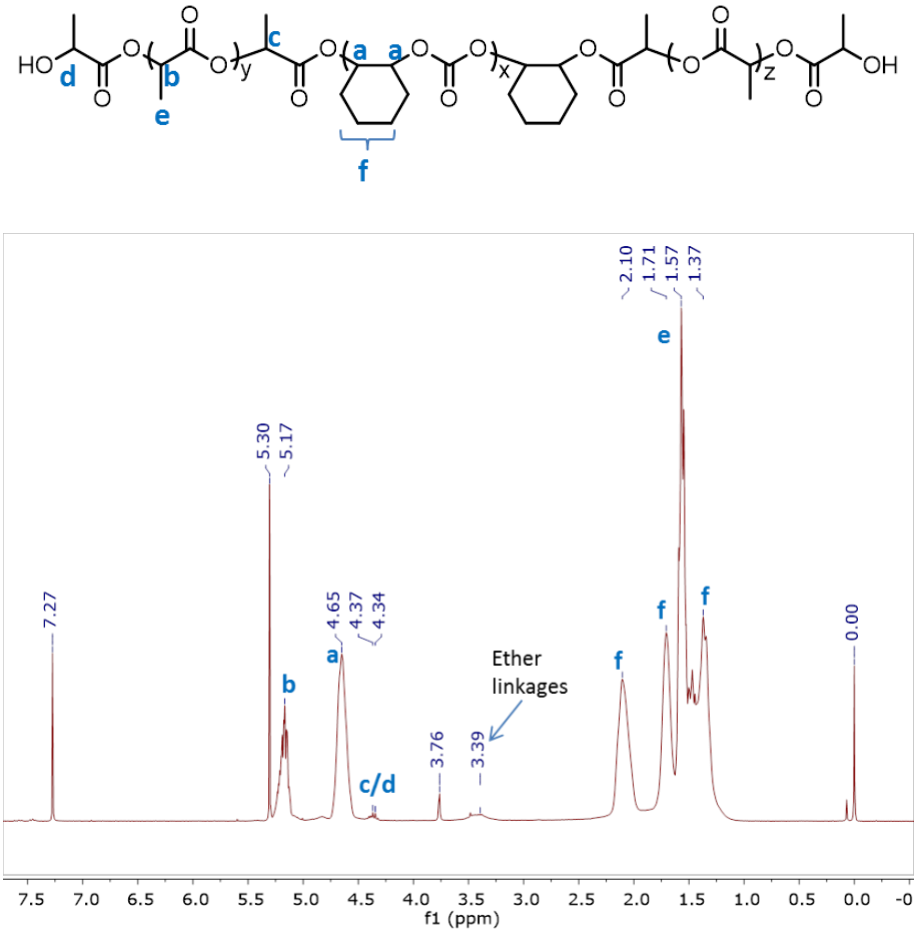

Figure S11. Representative ^{1}H NMR spectrum in $CDCl_3$ of triblock copolymer (Table 2, entry 2).

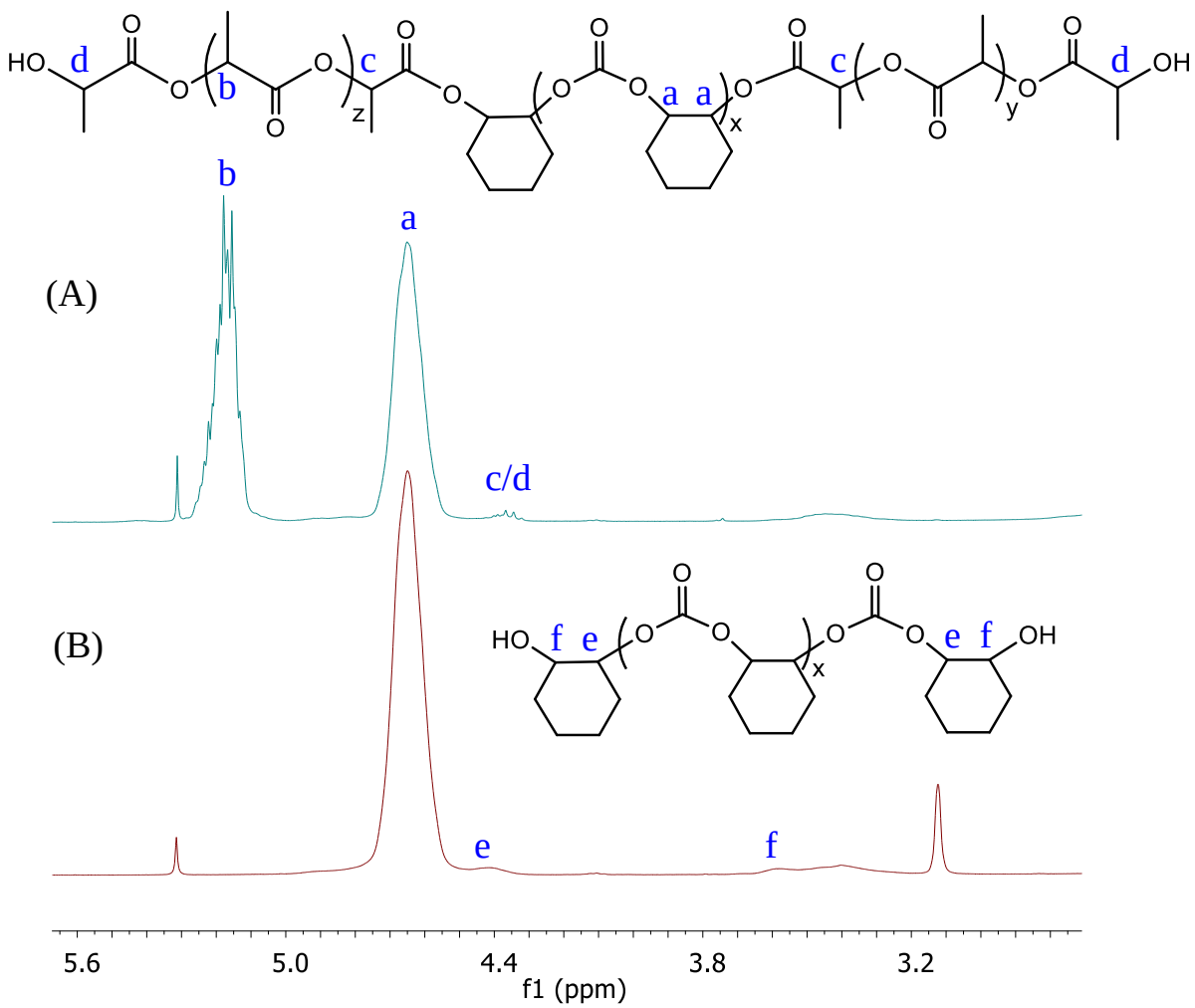

Figure S12. ^{1}H NMR spectra in $CDCl_3$ of (A) PLA-PCHC-PLA, (Table 2, entry 1), and (B) PCHC, (Table 1, entry 4). Resonances at 3.4 ppm and 5.3 ppm in spectra (A) and (B) correspond to ether linkages and CH_2Cl_2, respectively. The resonance at 3.1 ppm in (B) corresponds to unreacted cyclohexene oxide.

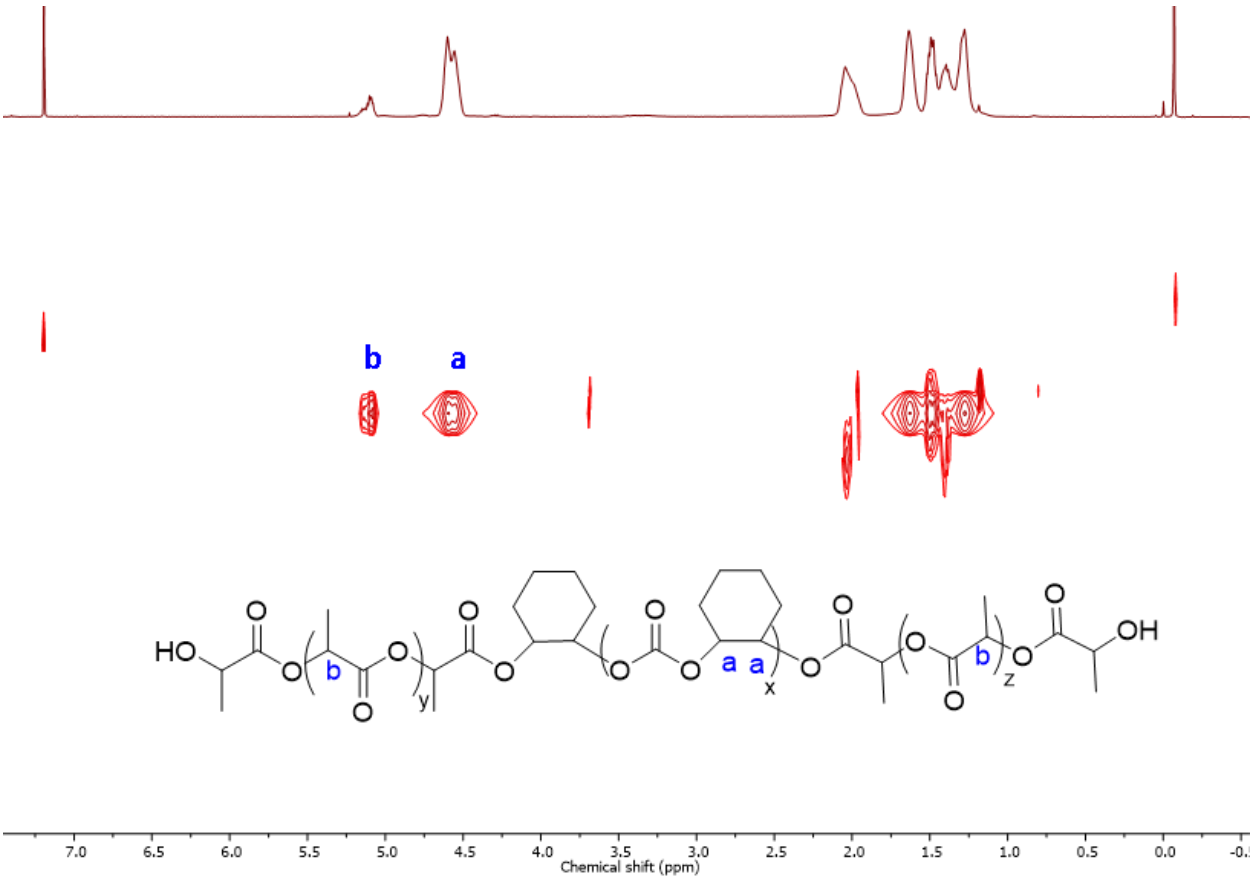

Figure S13. Representative ^{1}H DOSY NMR spectrum in $CDCl_3$ of triblock copolymer.

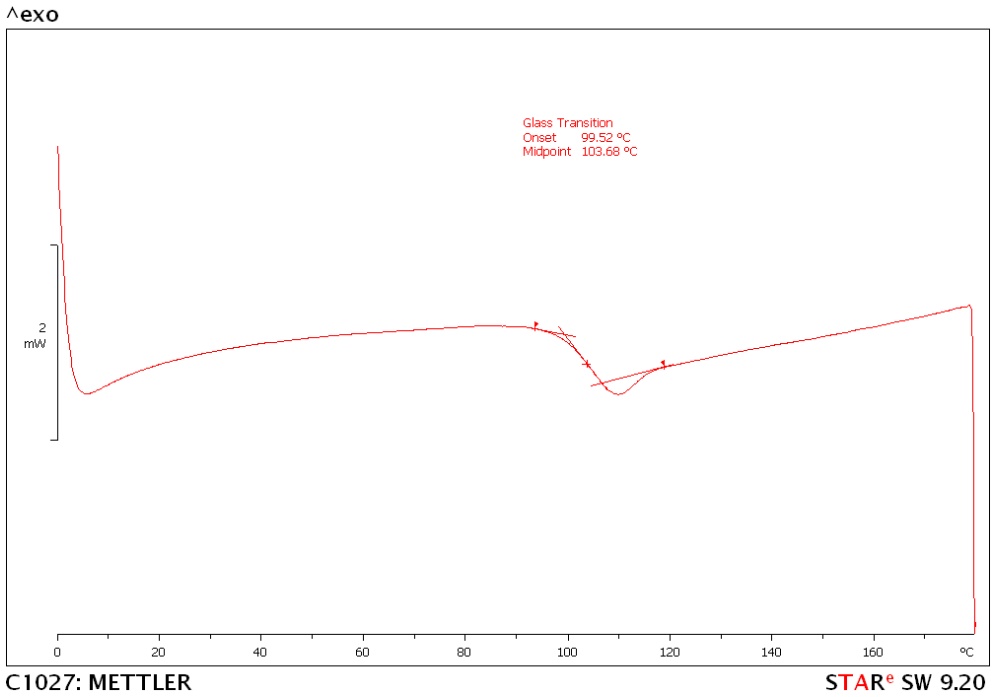

Figure S14. DSC second heating curves of polycarbonate obtained from **2** and PPNCl (Table 1, entry 2).

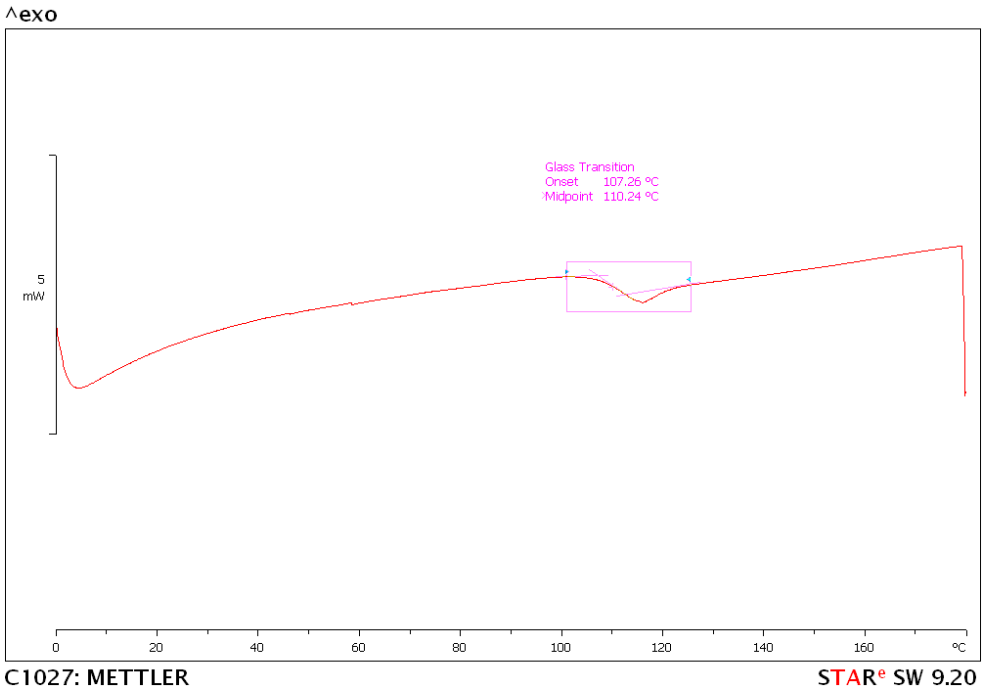

Figure S15. DSC second heating curves of polycarbonate obtained from **2** and $Ph_2P(O)NPPh_3$ (Table 1, entry 3).

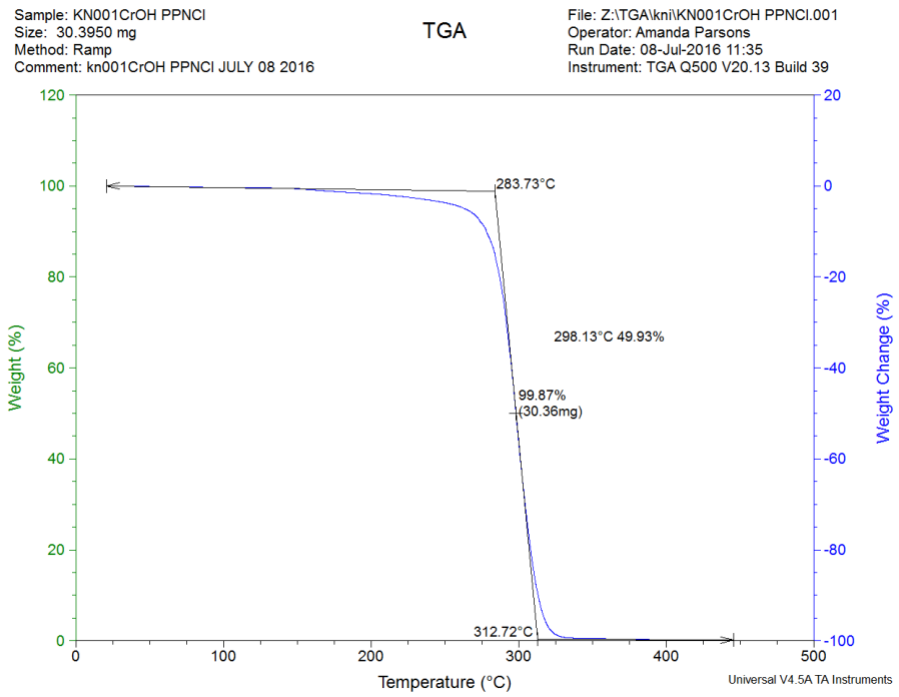

Figure S16. TGA curve of PCHC at a heating rate of 10 °C/min (Table 1, entry 2).

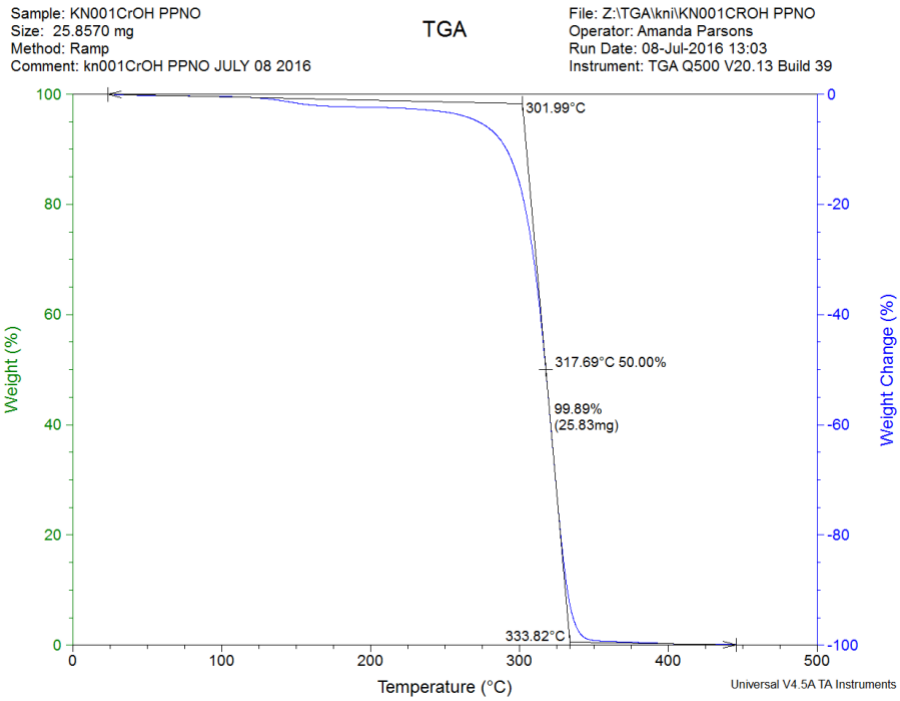

Figure S17. TGA curve of PCHC initiated by PPNO at a heating rate of 10 °C/min (Table 1, entry 3).

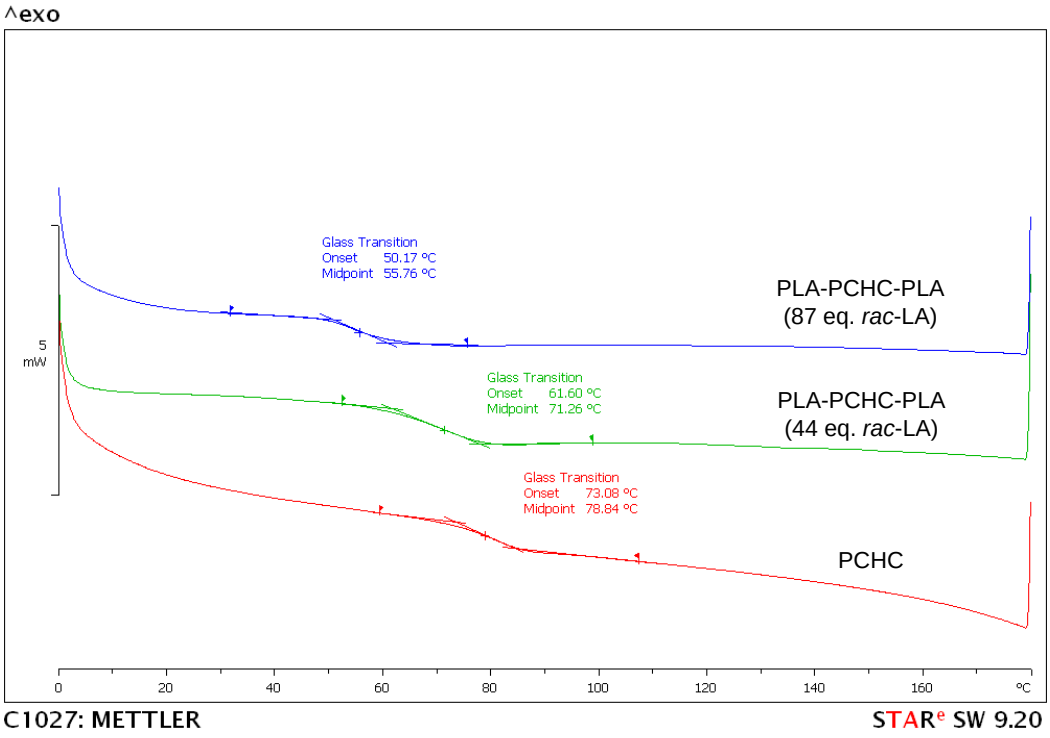

Figure S17. DSC second heating curves of PCHC (Table 1, entry 4) and PLA-PCHC-PLA (Table 2, entries 1 and 2).

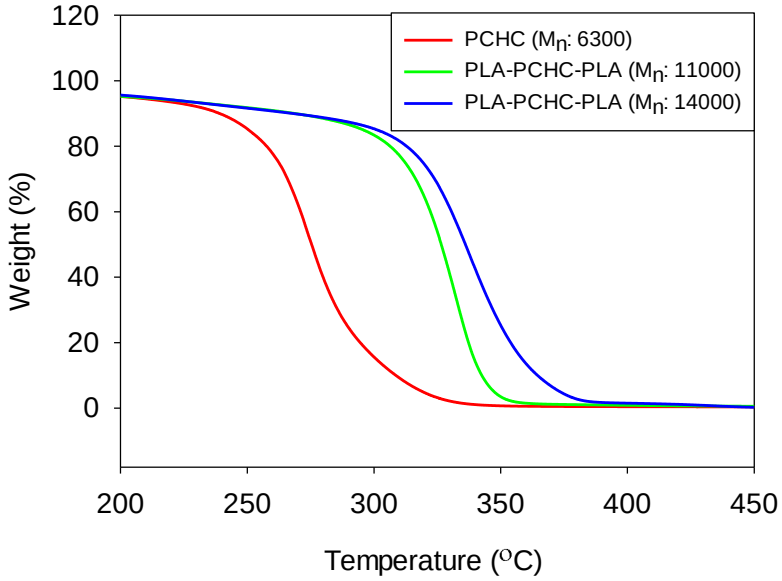

Figure S18. TGA curves of PCHC (Table 1, entry 4) and PLA-PCHC-PLA (Table 2, entries 1 and 2).