Electronic Supplementary Material (ESI) for Green Chemistry.

Renewable Polycarbonates and Polyesters from 1,4-Cyclohexadiene

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1. Materials

1,4-Cyclohexadiene (97 %,Sigma Aldrich), *meta*-chloroperoxybenzoic acid (≤77 %,Sigma Aldrich), oxone® (potassium peroxymonosulfate, Sigma Aldrich) were used as received. Cyclohexene oxide (98 %, Sigma Aldrich) (CHO) was dried over $MgSO_4$ and fractionally distilled under nitrogen. Phthalic anhydride (≥99 %, Sigma-Aldrich) was washed with benzene, re-crystallized from chloroform and sublimated at 100°C and reduced pressure (approx. 10^{-2} mbar). *Bis*(triphenylphosphoranylidene)ammonium chloride (PPN-Cl, 97 %, Sigma Aldrich) was re-crystallized from dry chloroform. Research grade CO_2 for polymerization reactions was purchased from BOC (Linde Gas). (*R*,*R*)-(-)-*N*,*N*'-*Bis*(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt(II) ([(*R*,*R*)SalcyCo(II)], (Strem chemicals), (1*R*,2*R*)-(-)-*N*,*N*'-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride (**C4**). Catalyst **C1** - **C3** were synthesized according to literature procedures.[1,2] Pd(en)/C was synthesized according to a known literature procedure.[3] Epoxide **1**, **3a** and **3b** were prepared by standard oxidation using *m*CPBA as already described in literature.[4,5]

2. Characterization

In situ ATR-FTIR measurements were performed on a Mettler-Toledo ReactIR 4000 spectrometer equipped with a MCT detector and a silver halide DiComp probe. Molecular weights of the polymers were determined by size exclusion chromatography (SEC) using a Polymer Laboratories PL GPC 50 instrument (Polymer Laboratories Mixed D columns) operating with THF as the eluent, at a flow rate of 1 mL min^{-1} at 40°C. The SEC instrument was calibrated with polystyrene standards.^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker AV 400. All samples were dissolved in $CDCl_3$ and the chemical shifts δ are reported in ppm relative to TMS. Mass spectrometry measurements were performed using a MALDI micro MX micromass instrument. The matrix used was dithranol with KTFA as the ionising agent and THF as the solvent. Differential scanning calorimetry (DSC) experiments were carried out on a DSC4000 (Perkin Elmer) calorimeter under nitrogen atmosphere at a heating rate of 10 °C per min^{-1} up to a temperature of 130 °C / 200°C, using a sample mass of approximately 5 mg. Data from second heating scans are reported. TGA measurements were performed on a TGA4000 (Perkin Elmer) instrument. A heating rate of 1°C / min was used.

3. Experimental procedure

General procedure for the epoxidation of 1,4-Cyclohexadiene using oxone® adapted from the literature[6]

To 1 g of 1,4 cylohexadiene (12.5 mmol) in 50 mL dichloromethane, 5 mL acetone and 100 mL of a saturated solution of $NaHCO_3$, a solution of 3.84 g oxone® (12.5 mmol) in 60 mL water was added drop-wise to the ice cooled solution. The reaction mixture was vigorously stirred at 0°C for 30 min and at room temperature for 6 h. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried over $NaSO_4$ and CH_2Cl_2 was carefully removed under reduced pressure (40°C, >80 - 100 mbar). Fractionated distillation under reduced pressure afforded epoxide **1** (0.73 g, yield 65 %).

^1H-NMR ($CDCl_3$, 400 MHz) δ / ppm: 5.43 (s, 2H, -C*H*=C*H*-), 3.24 (s, 2H, -C*H*-O-C*H*-) 2.64 – 2.36 (m, 4H, $-CH_2-$)

^{13}C-NMR ($CDCl_3$, 100 MHz) δ / ppm: 121.5, 49.8, 24.8.

General procedure for the one-pot epoxidation of 1,4-Cyclohexadiene using oxone®

To 1 g of 1,4 cylohexadiene (12.5 mmol) in 50 mL dichloromethane, 5 mL acetone and 100 mL of a saturated solution of $NaHCO_3$, a solution of oxone® (1, 2 or 4 equivalents) in 60 mL water was added drop wise to the ice cooled solution. The reaction mixture was vigorously stirred at 0°C for 30 min and at room temperature for 6 h. After TLC and ^1H-NMR analysis of the crude reaction mixture showed full conversion of the 1,4-cyclohexadiene, the organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried over $NaSO_4$ and CH_2Cl_2 was carefully removed under reduced pressure (40°C, >80 - 100 mbar). The content of the respective epoxide was estimated by ^1H-NMR spectroscopy.

Table S 1: Results of the one-pot epoxidation using varying amounts of oxone®.

Entry	***Oxone® [equivalents]***[a]	***1 [%]***[b]	***3a + 3b [%]***[b]
1	1	79.5	20.5
2	2	67.0	33.0
3	4	49.5	50.5

[a] equivalents respective to 1,4-cyclohexadiene, [b] determined by ^{1}H-NMR

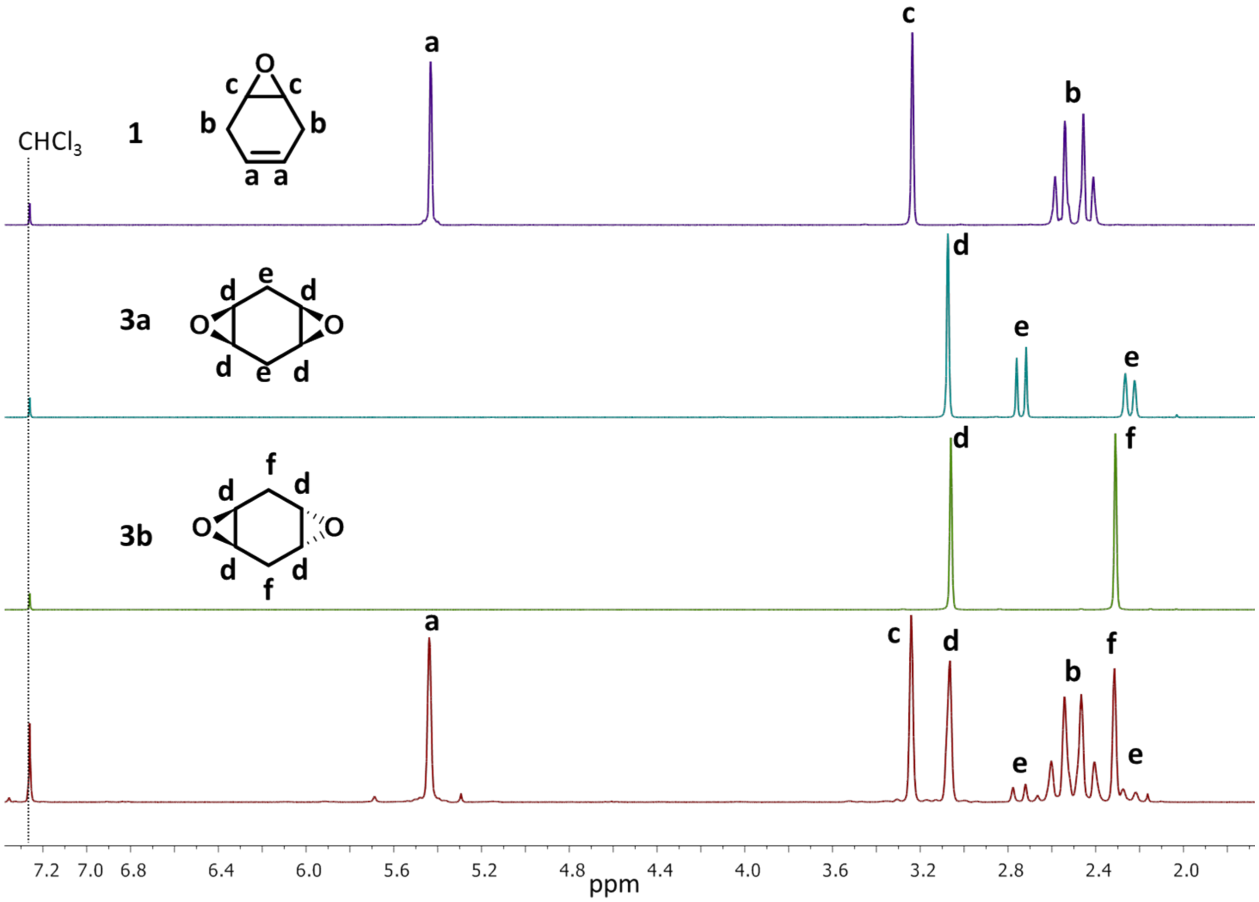

Figure S1: Overlay of the ^{1}H-NMR (400 MHz, CDCl$_3$) of the crude reaction mixture (bottom), epoxide **1**, **3a** and **3b**.

General procedure for the reduction of CHDO 1 by Pd/C or Pd(en)/C

To 1 g of 1,4-cyclohexadiene oxide (10.4 mmol) in 10 mL ethyl acetate or THF, 0.1 g of the palladium catalyst (Pd/C or Pd(en)/C[3,7], 10 wt%) was added. The reaction mixture was stirred for 24 h under a hydrogen atmosphere (balloon). The crude reaction mixture was then filtered through a pore filter to remove the palladium catalyst. After evaporation of the solvent the crude product mixture was analysed by 1H NMR spectroscopy and GC analysis showing presence of CHO.

CO_2 co-polymerization of monomer 1

Monomer **1** and the catalyst (and co-catalyst) were weighted in a Schlenk flask. For reactions at atmospheric pressure of CO_2, the Schlenk flask was shortly evacuated and back-filled with CO_2 two times to generate a carbon dioxide atmosphere. Then, the reaction mixture was heated to the desired temperature and stirred for the given time. The polymer was precipitated in cold methanol from THF. For the analysis of the polymer by GPC and NMR, a sample was taken of the crude reaction mixture.

Reactions under CO_2 pressure were performed in a Parr 5513 100 mL bench reactor. Therefore, the pre-dried reactor was set under a CO_2 atmosphere and the reaction mixture was injected. Then, the reaction mixture was stirred at an evaluated pressure and temperature for the given time.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ / ppm: 5.57 (s, 2H, -C*H*=C*H*-), 4.96 (s, 2H, -C*H*-O-), 2.77 – 2.15 (m, 4H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ / ppm: 154.0, 123.4, 73.7, 29.9.

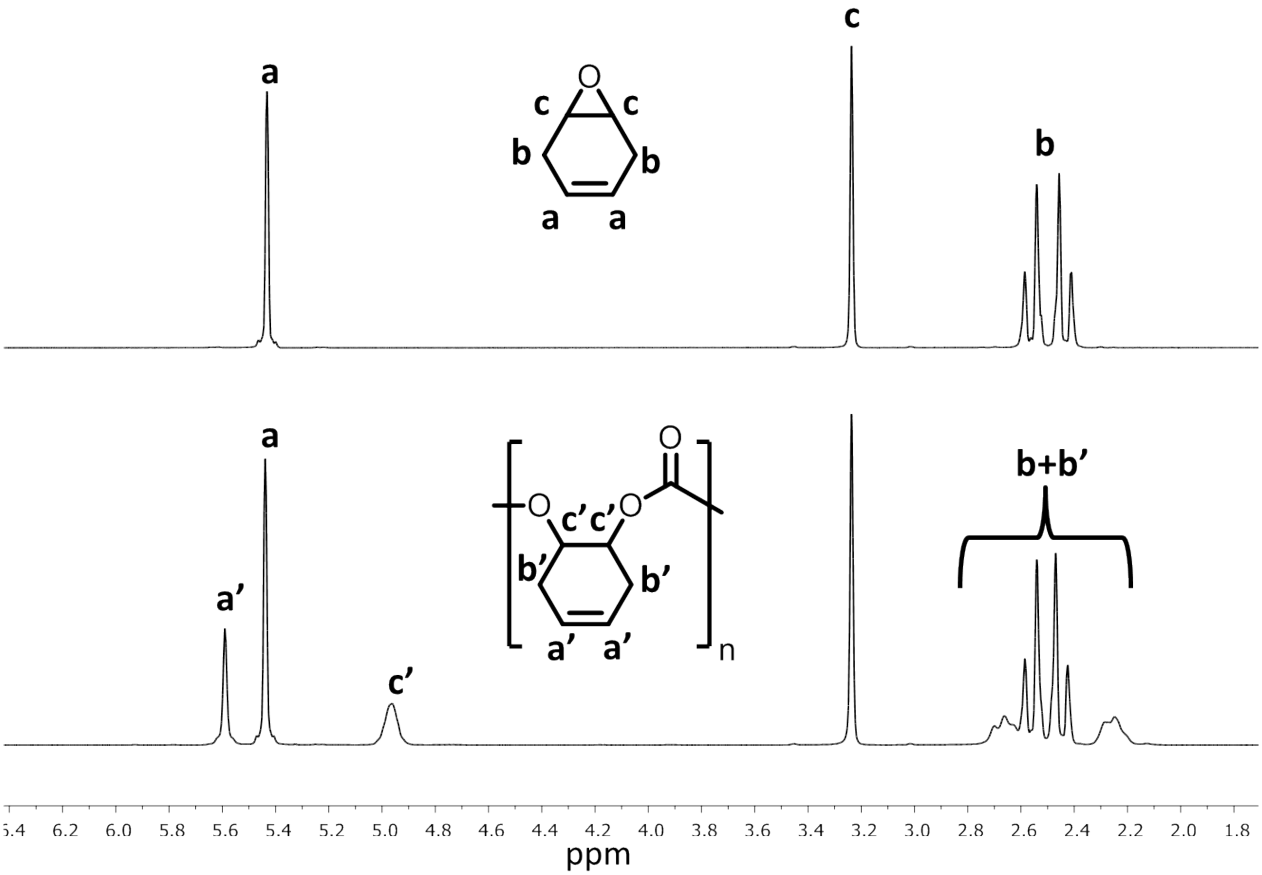

Figure S2: ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of the crude reaction mixture (bottom) and monomer **1** (top) between 2 - 6 ppm.

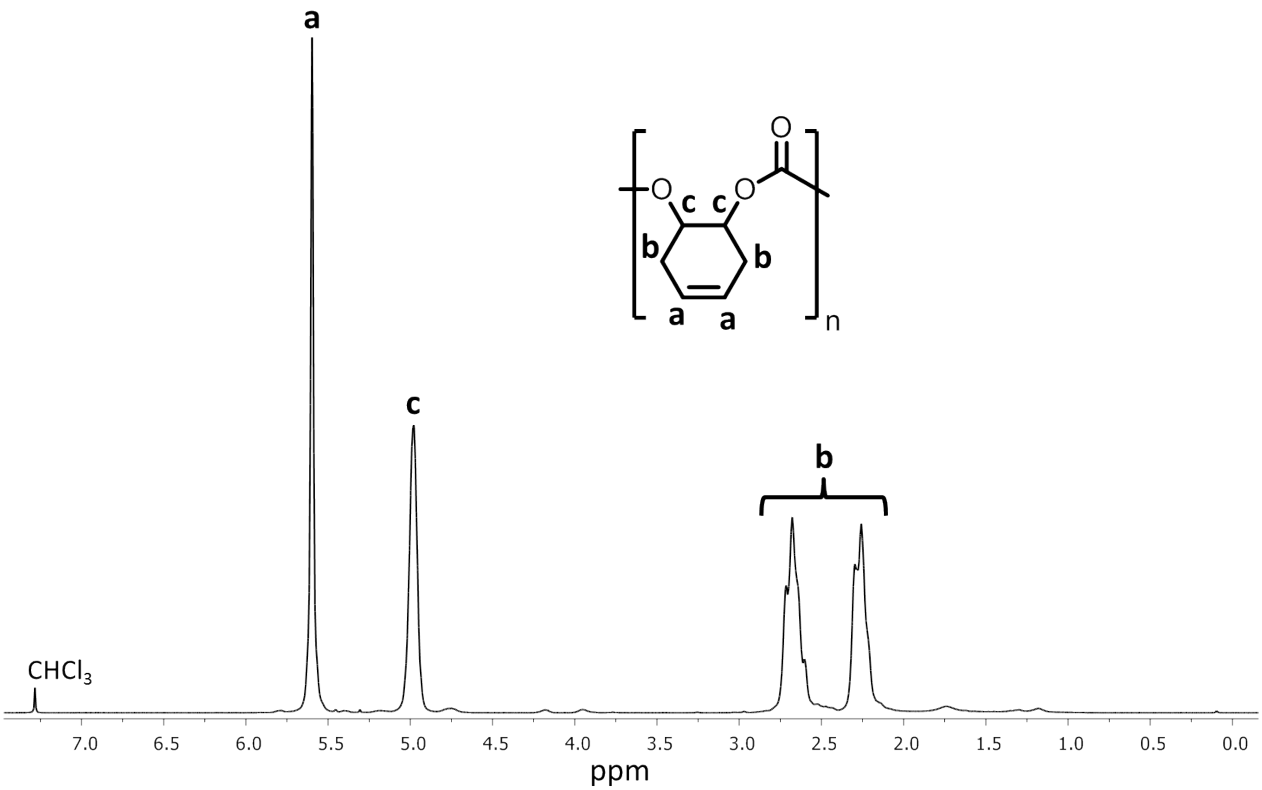

Figure S3: ^{1}H-NMR (400 MHz, $CDCl_3$) of polymer P3 (conditions as described in Table 1).

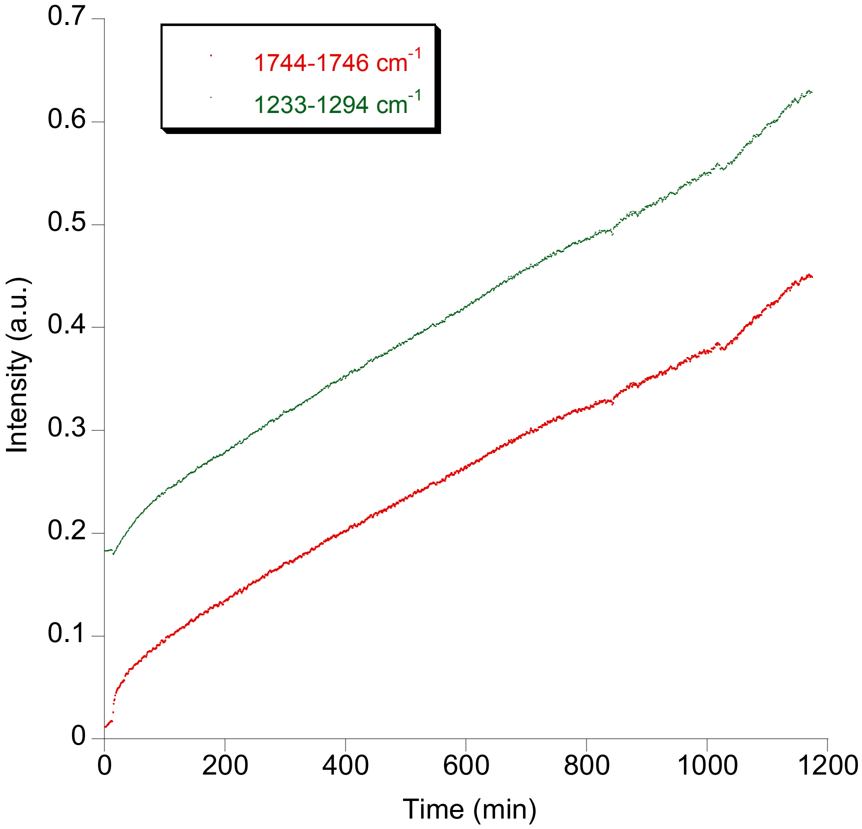

Figure S4: Changes in intensity of IR resonances for **1**/CO_2 copolymerization in the presence of **C1**.

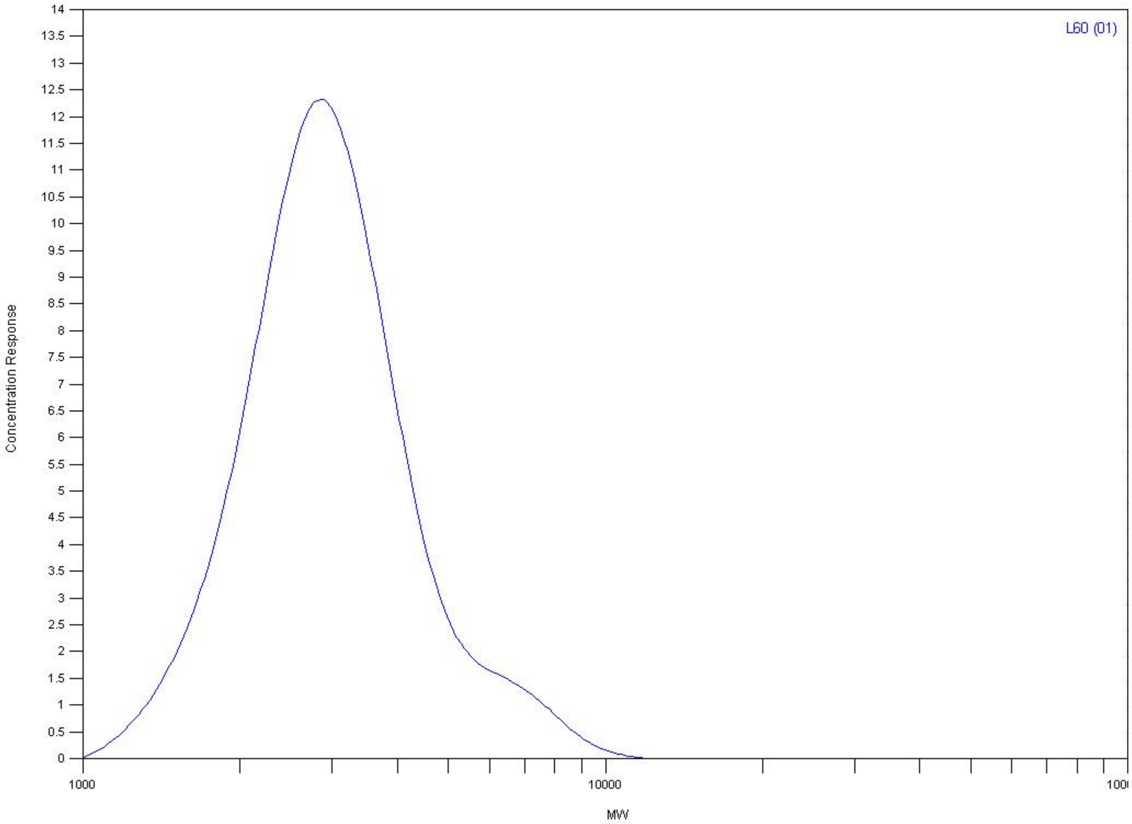

Figure S5: Molecular weight distribution of **P5** (M_n = 2800 g/mol, PDI = 1.15), (conditions as described in Table 1).

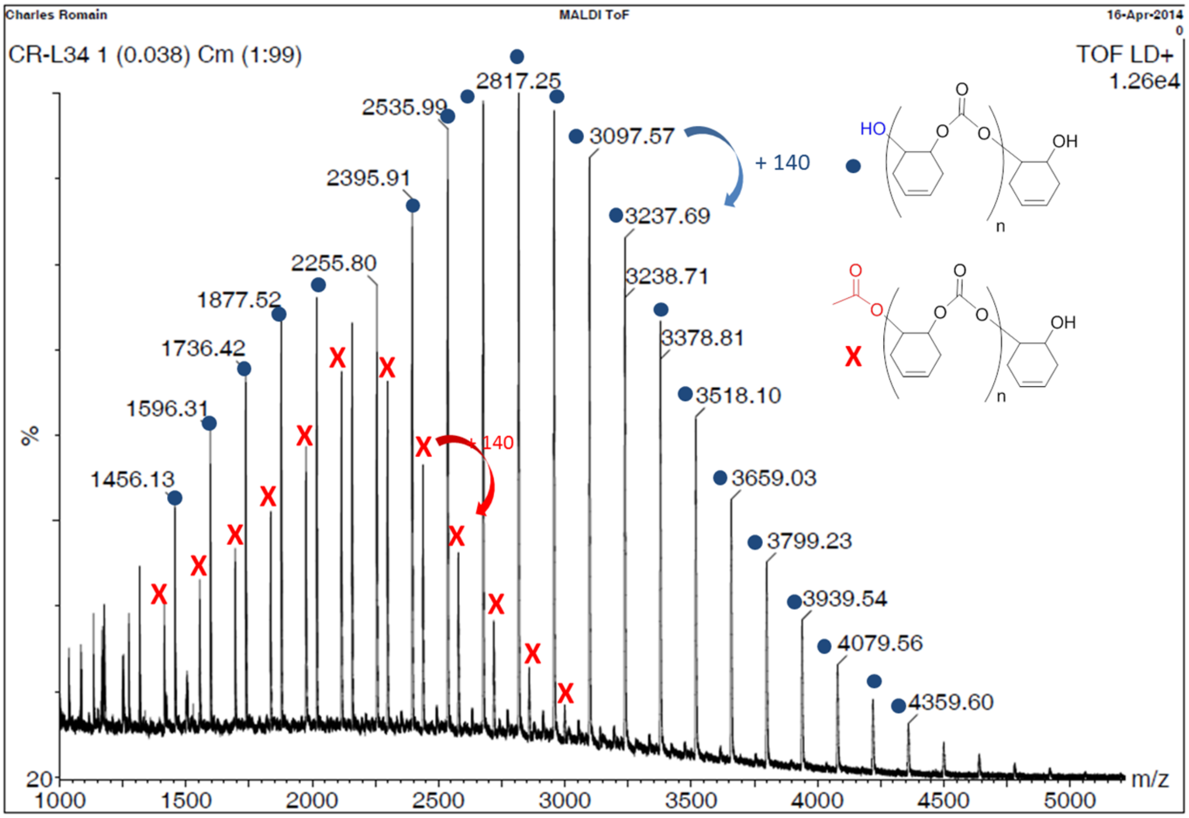

Figure S6: MALDI_ToF-MS of polymer **P3** prepared by co-polymerisation of CO_2 and monomer **1** (conditions as described in Table 1).

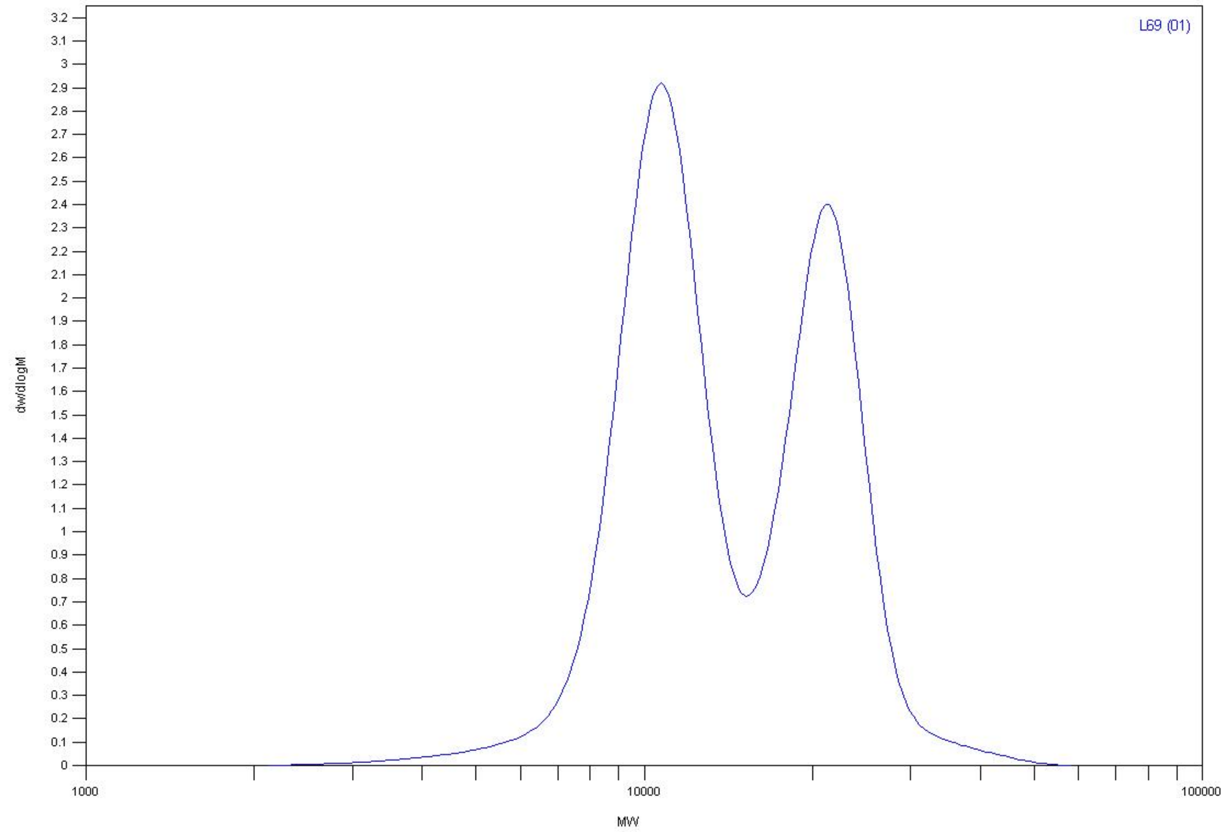

Figure S7: Molecular weight distribution of **P7**, M_n = 12.9 kg/mol and PDI = 1.19 (conditions as described in Table **1**).

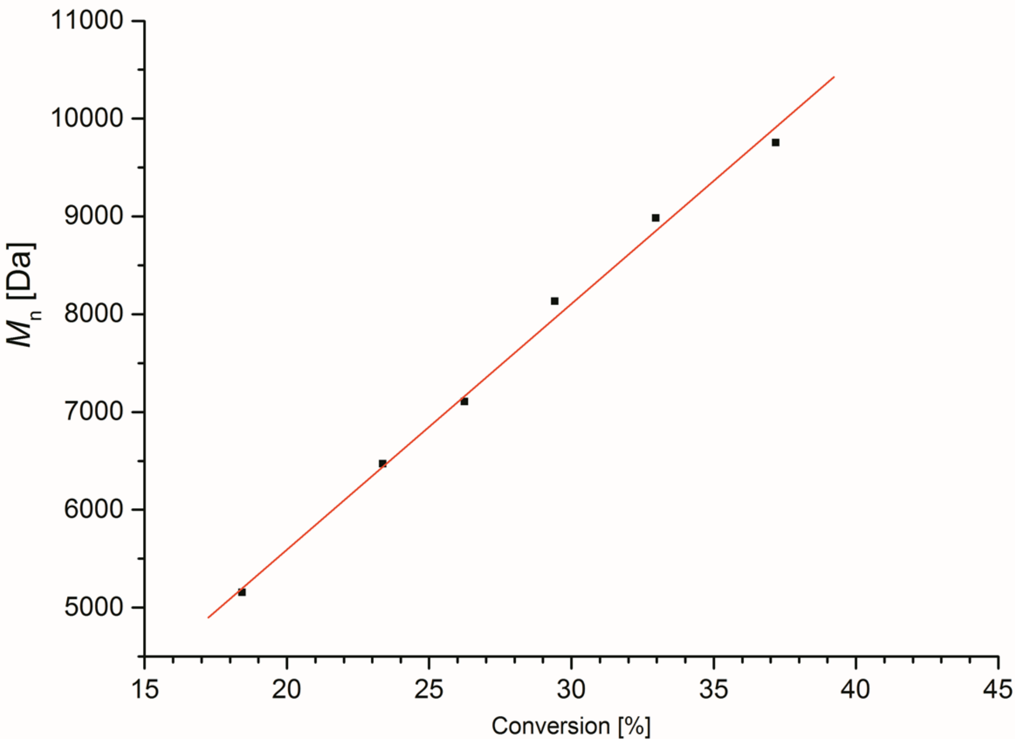

Figure S8: Plot showing the molecular weight of the polycarbonate against epoxide conversion for the co-polymerisation of monomer **1** and CO_2 performed at 28°C, under a CO_2 pressure of 20 bar.

Terpolymerization of CO_2, monomer 1 and cyclohexene oxide 2

CO_2 –mediated terpolymerizations of monomer **1** and cyclohexene oxide **2** were performed according to the procedure given for the CO_2 copolymerization of monomer **1**.

^{1}H-NMR ($CDCl_3$, 400 MHz) δ / ppm: 5.57 (s, 2H, -C*H*=C*H*-), 4.96 (s, 2H, -C*H*-O-C*H*-), 4.66 (s, 2H, -C*H*-O-C*H*-), 2.85 – 2.17 (m, 4H, -CH_2-), 2.16 – 1.62 (m, 4H, -CH_2-), 1.61 – 1.18 (m, 4H, -CH_2-).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ / ppm: 154.00, 153.62, 123.42, 123.33, 73.70, 29.88, 29.56.

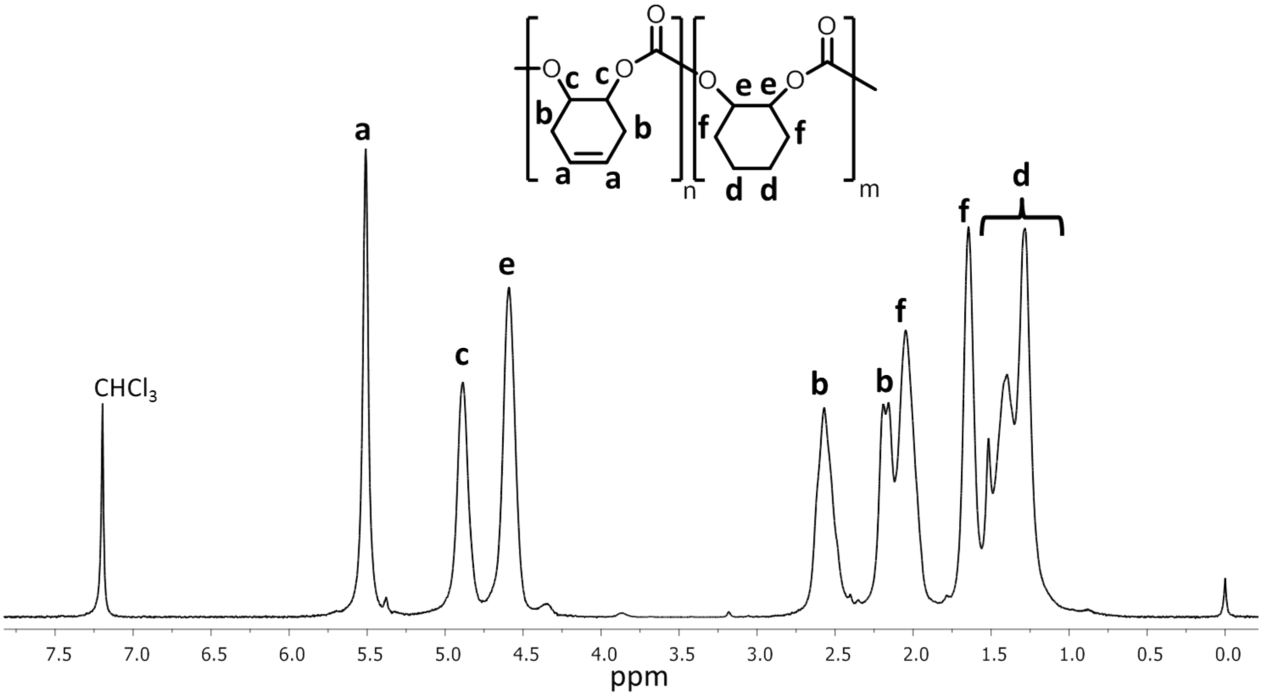

Figure S9: ^{1}H-NMR (400 MHz, CDCl$_3$) of polymer **P8** (conditions as described in Table 1).

Co-polymerisation of epoxide 1 and phthalic anhydride

Under nitrogen atmosohere, phthalic anhydride, monomer **1**, and the catalyst (and co-catalyst) were weighed into a 2 mL vial. Dry toluene was added if reactions were performed in a 2.5M solution. The reaction mixture was heated to 110°C and stirred for the given time. The polymer was precipitated in methanol from THF. For the analysis of the polymer by GPC and NMR, a sample was taken of the crude reaction mixture.

^{1}H-NMR (CDCl$_3$, 300 MHz) δ / ppm: 7.66 – 7.36 (m, 4H, -C*H$_{arom}$*-), 5.62 (s, 2H, -C*H*=C*H*), 5.42 (s, 2H, -C*H*-O-), 2.87 – 2.22 (m, 4H, -C*H*$_2$-).

^{13}C-NMR (CDCl$_3$, 100 MHz) δ / ppm: 166.7, 132.1, 132.0, 131.3, 129.1-128.8, 123.9- 123.6, 71.2-70.8, 29.8, 29.7.

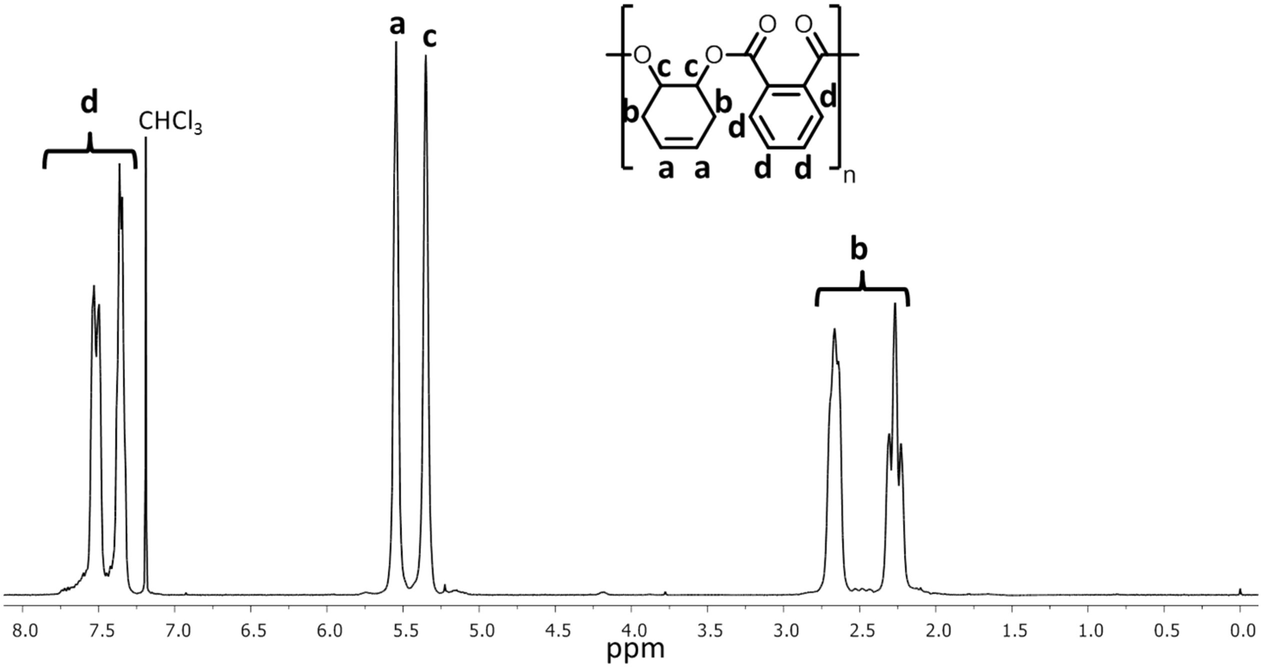

Figure S10: ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of polymer **P13**.

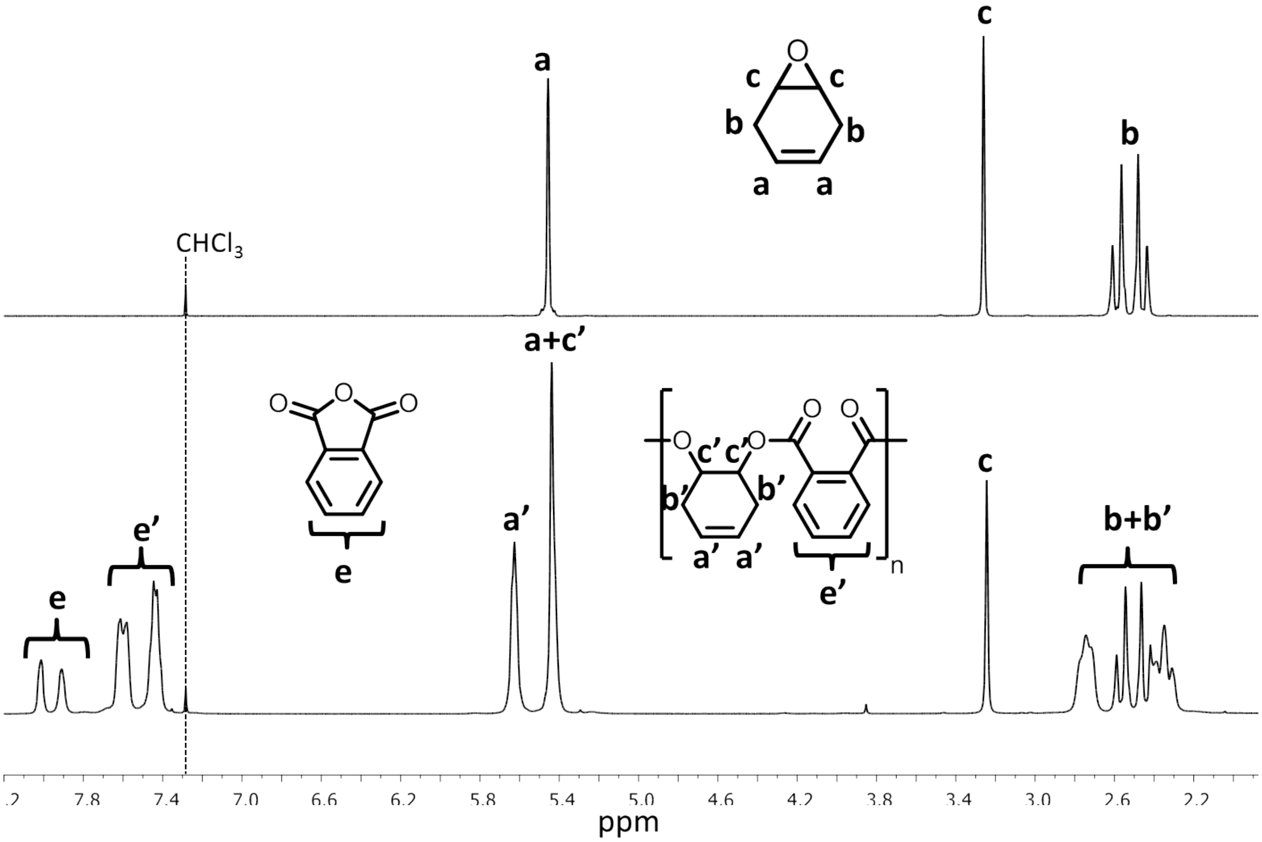

Figure S 11: ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of monomer **1** (top) and the crude reaction mixture (bottom).

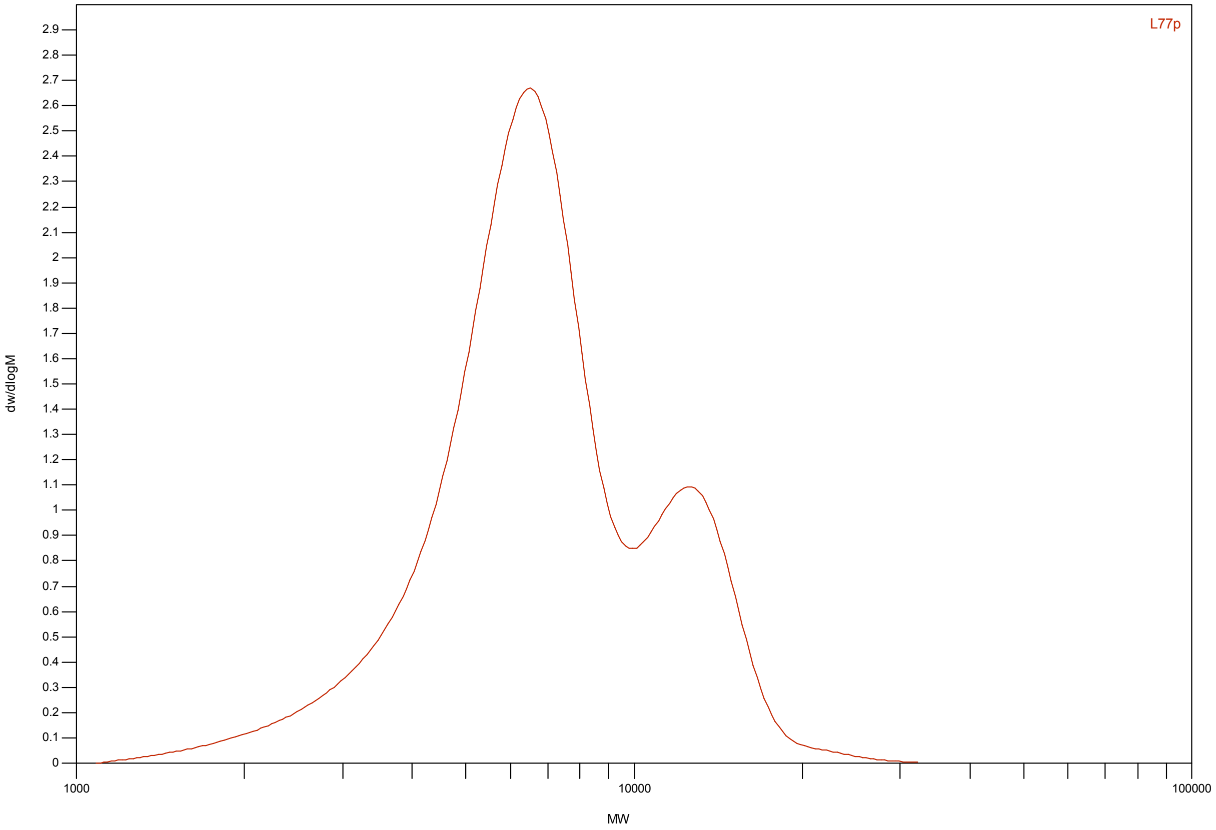

Figure S12: Molecular weight distribution of polyester obtained by **1**/PA copolymerization, M_n = 6,050 g/mol aand PDI = 1.25 (conditions as described in table **1** for **P13** but at stopped at 65 % conversion).

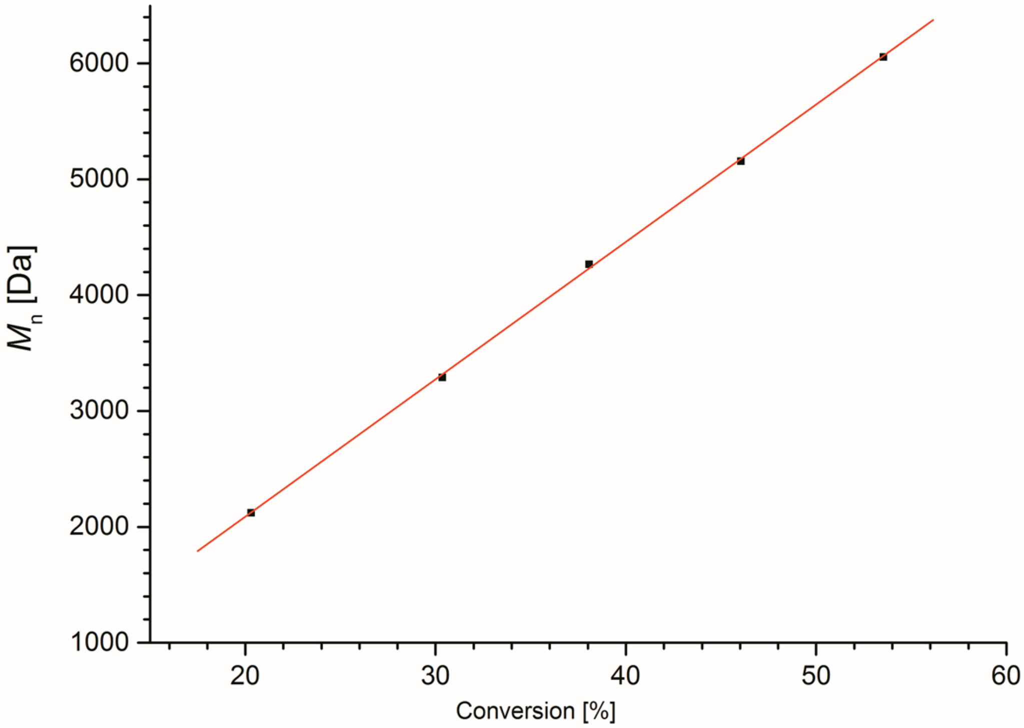

Figure S13: Plot of M_n vs. conversion for the co-polymerization of monomer **1** and PA performed at 110°C.

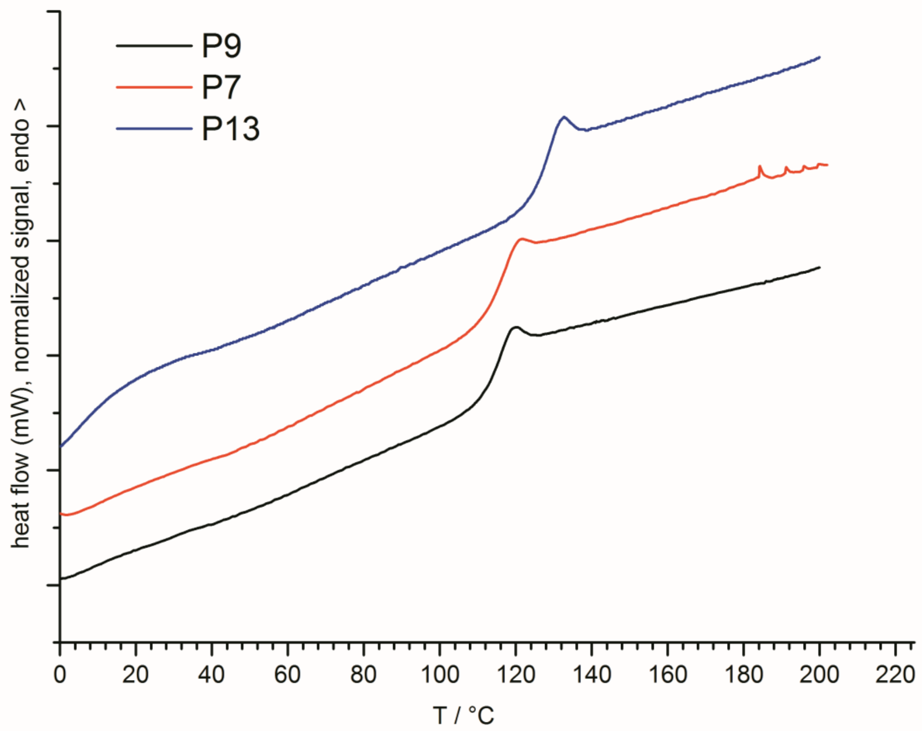

Figure S14: DSC traces of **P9**, **P7** and **P13**. Thermal data are reported from the second heating scan (heating rate 10 K/min).

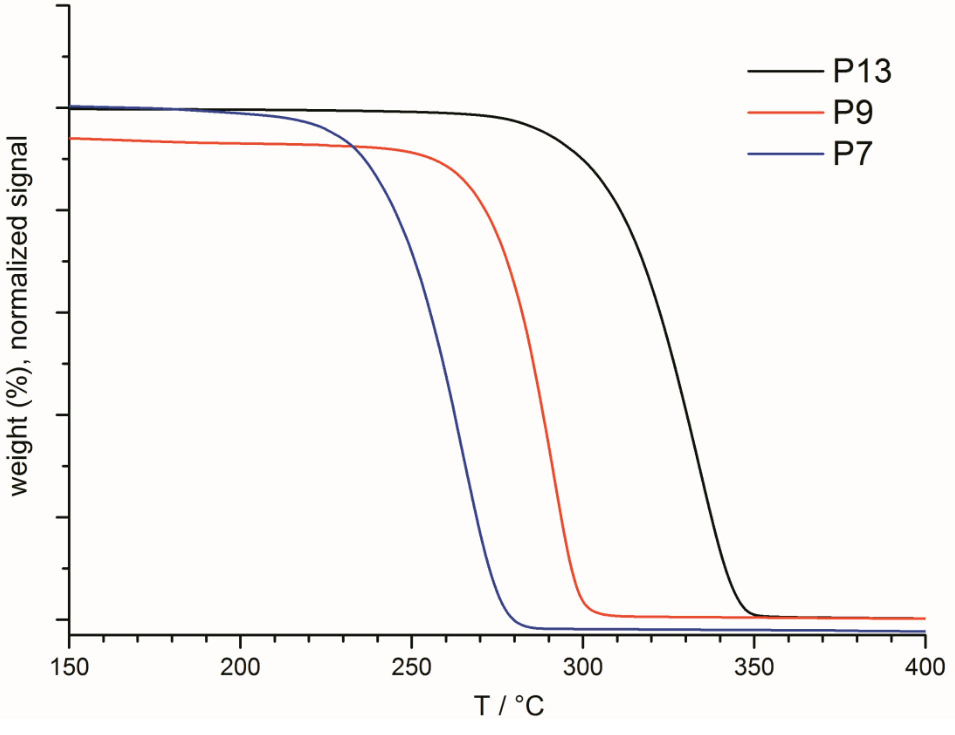

Figure S15: TGA traces of **P13**, **P9** and **P7**.

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