Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for:

Di-Magnesium and zinc catalysts for the copolymerization of phthalic anhydride and cyclohexene oxide

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Experimental Section

Materials and Methods

All experiments were carried out under N_2 using standard Sclenk techniques or in a Mbraun Unilab glovebox. The catalysts $[LMg_2(OAc)_2]$ (**1**) and $[LZn_2(OAc)_2]$ (**2**) were synthesized employing previously published methods.[1] All solvents and reagents were purchased from commercial sources (Aldrich and Merck) and used as received, unless stated otherwise. Toluene was distilled from sodium and stored under nitrogen. Cyclohexene oxide (CHO) was fractionally distilled, over magnesium sulfate, prior to use and stored under a nitrogen atmosphere. Research grade CO_2 (99.99995%), for use in copolymerization reactions, was purchased from BOC (Linde Gas). Phthalic Anhydride was purchased from Sigma Aldrich (98% purity) and purified by dissolving in benzene, filtering off impurities, recrystallizing from chloroform and then subliming.

^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker AV-400 spectrometer. *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 for *in situ* ATR-FTIR measurements. Certain frequencies are monitored and reported due to clarity and minimal signal overlap. Gel permeation chromatography (GPC) data were collected using a Polymer Laboratories PL GPC-50 instrument (Polymer Laboratories Mixed D columns) with THF as the eluent, at a flow rate of 1 mL min^{-1} at 40°C and narrow M_n polystyrene standards for calibration. MALDI-ToF spectrometry measurements were performed on Waters/Micromass MALDI micro MX spectrometer. The samples were dissolved in THF and mixed with the dithranol matrix and the cationizing additive: potassium trifluororacetate.

General copolymerization procedure (Table 1).

Reaction in toluene: Cyclohexene oxide (250 µL, 2.5 mmol, 100 eq.), phthalic anhydride (370 mg, 2.5 mmols, 100 eq.), **1** (17.9 mg, 25 µmols) and toluene (1 mL, 2.5 M concentration in CHO and PA) were added to Schlenck tube, in the glovebox. The vessel was heated with constant stirring, as described in Table **1**. The polymerization was stopped after a defined time period by exposure to air. The volatile components were removed, *in vacuo,* to yield the product as an off white powder. A sample of the crude product was analysed by ^{1}H NMR spectroscopy, to determine the conversion of the monomers.

Reactions in neat CHO: Cyclohexene oxide (2 mL, 19.8 mmol, 800 eq.), phthalic anhydride (366 mg, 2.47 mmol, 100 eq.), and **1** (17.9 mg, 25 μmol) were added to a Schlenk tube. The vessel was heated, at the appropriate temperature with constant stirring, for a defined time. The volatile components were removed, *in vacuo,* to yield the product as an off white powder. A sample of the crude product was analysed by ^{1}H NMR spectroscopy, to determine the conversion of the phthalic anhydride.

General terpolymerization procedure (Figure 4 & 6).

Cyclohexene oxide (2 mL, 19.8 mmol), phthalic anhydride (366 mg, 2.47 mmol, 100 eq.), and **1** (19.7 mg, 25 μmol) were added to a Schlenk tube. The vessel was degassed at 298 K, then CO_2 was added to 1 bar pressure. The vessel was left under a CO_2 atmosphere, at 298 K, for a few minutes and was then heated to 353 K, with continuous reaction stirring, for a defined time. A sample of the crude product was analysed by ^{1}H NMR spectroscopy to determine the conversion and selectivity. Any unreacted monomers were removed, *in vacuo,* to yield the product as an off white powder. The polymer was purified by precipitation from a THF solution using pentane.

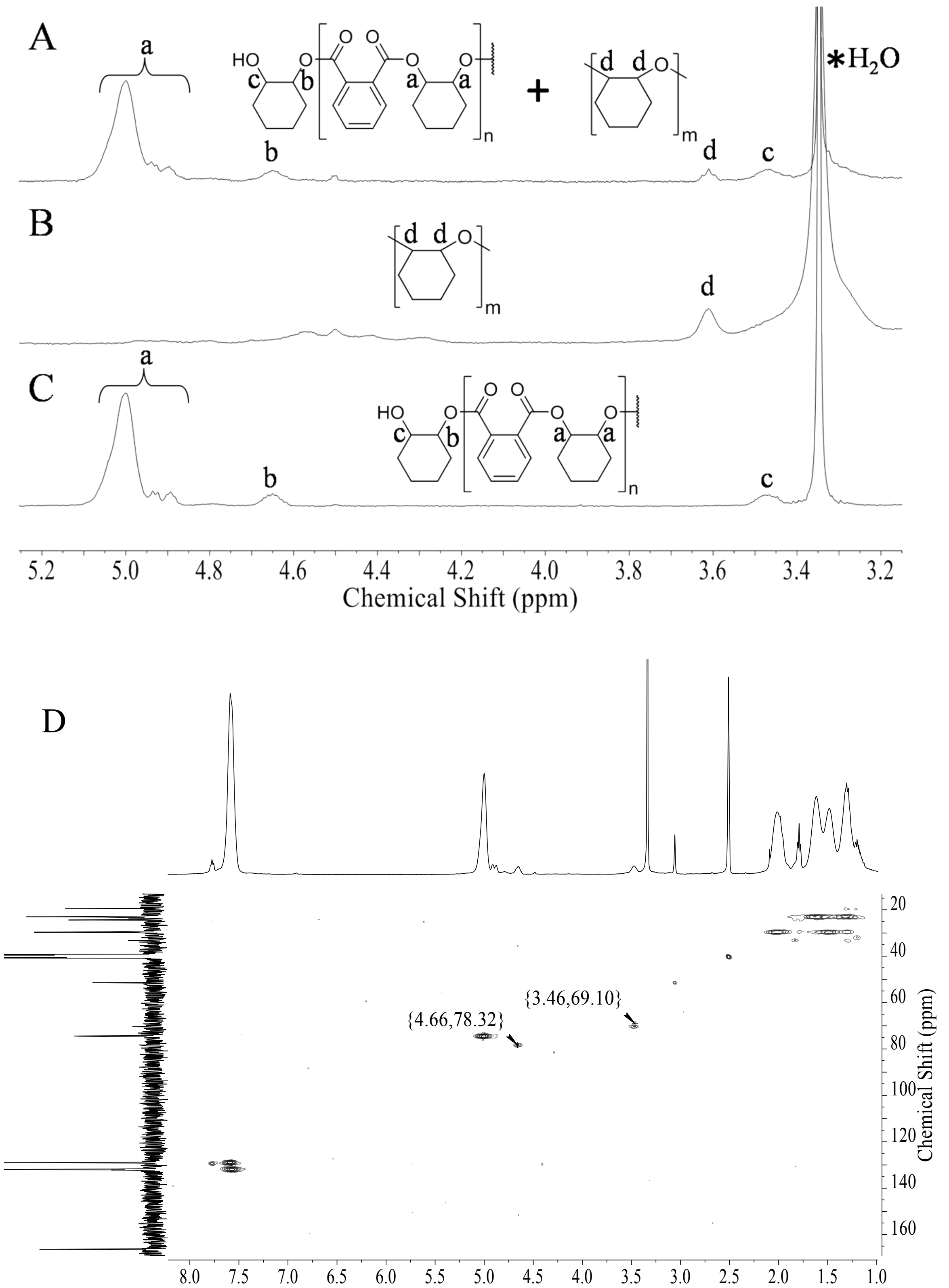
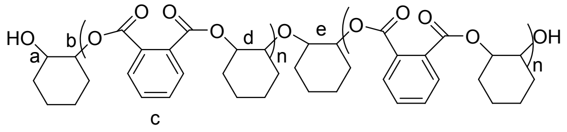


Fig. S1: (a) ^{1}H NMR spectrum of a mixture of polyester (PE) and polyether in DMSO-d_6; (b) ^{1}H NMR spectrum of polyether in DMSO-d_6 ; (c) ^{1}H NMR spectrum of polyester (PE) (without any ether linkages) in DMSO-d_6 (d) HSQC spectrum of a sample of polyester (PE) (without any ether linkages) showing that the signals at 3.46 and 4.66 ppm correspond to chain end groups. The ether linkage signal is absent (3.59 ppm).



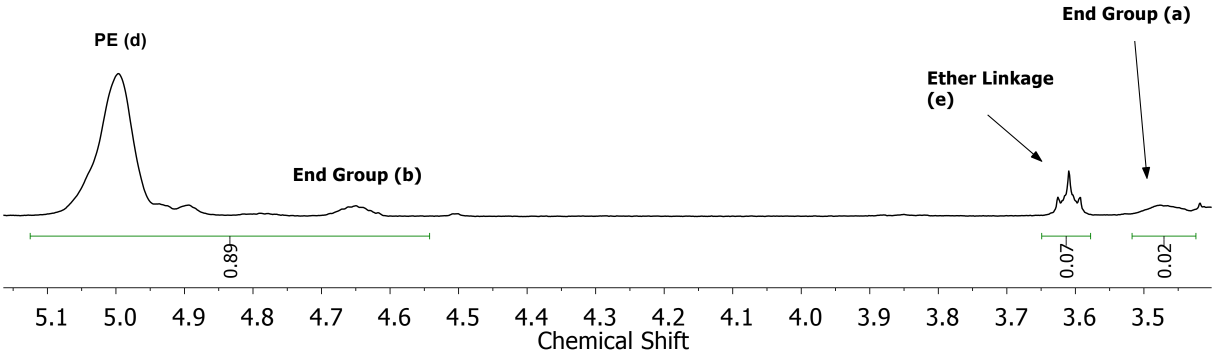


Fig. S2: ^{1}H NMR spectrum of polyester (PE) in DMSO-d_6 (Table 1 Run 3).

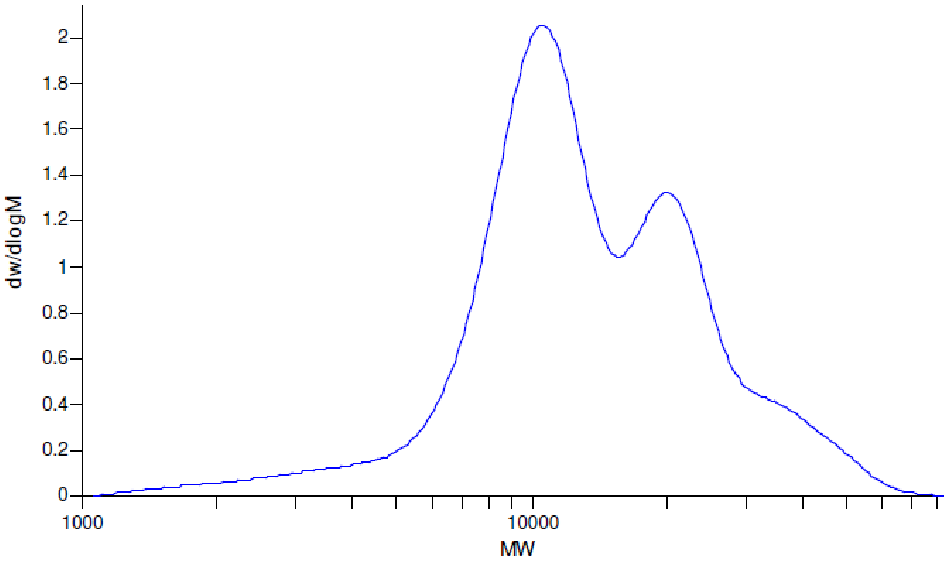


Fig. S3: Plot of M_w against dw/d(logM) for the polyester formed by catalyst **1** (Table 1 Run 1)

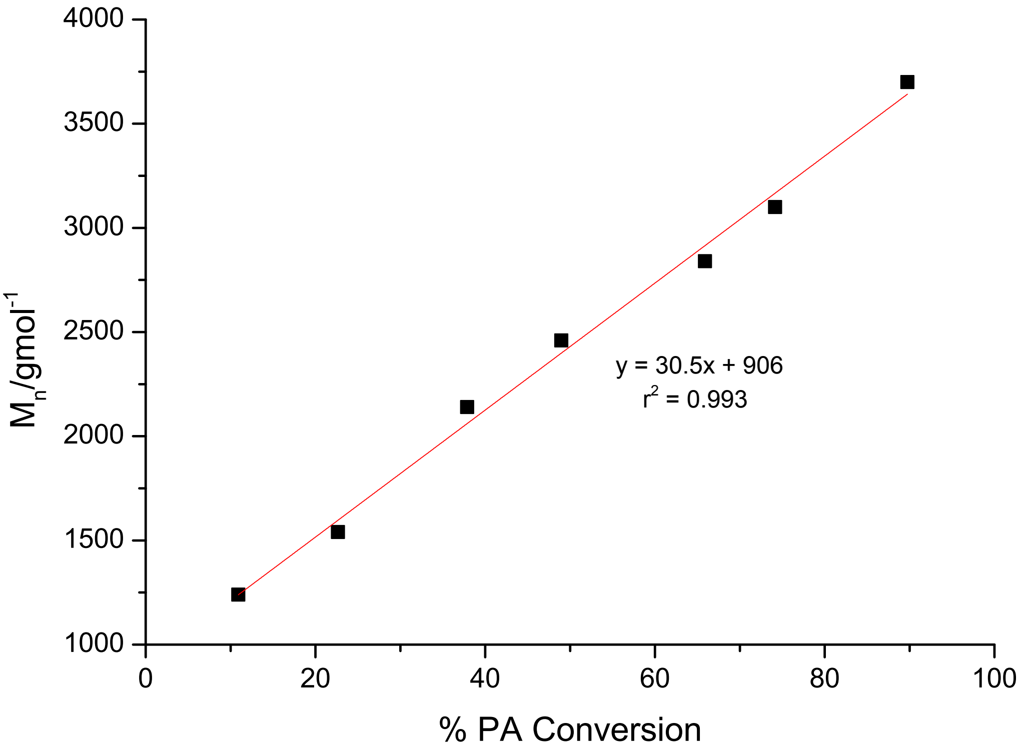


Fig. S4: Evolution of M_n against PA conversion for ROCOP initiated by **1**. Polymerization conditions: Cat.:PA:CHO = 1:100:800, 100 ° C. At higher PA conversions SEC data becomes bimodal and thus higher M_n of the two peaks taken.

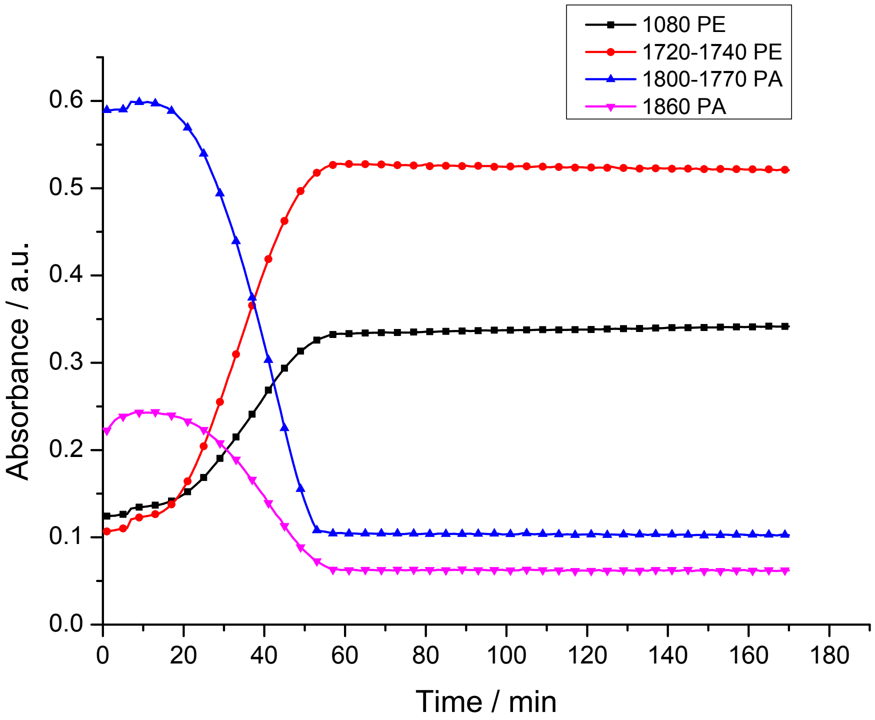


Fig. S5: Plot illustrating the absorption intensity vs. time for various signals in the IR spectra for PA/CHO copolymerization using **1**. This plot shows that rate of consumption of PA corresponds to zero reaction order. Reaction conditions: 1:100:800, cat:PA:CHO, 100 °C.

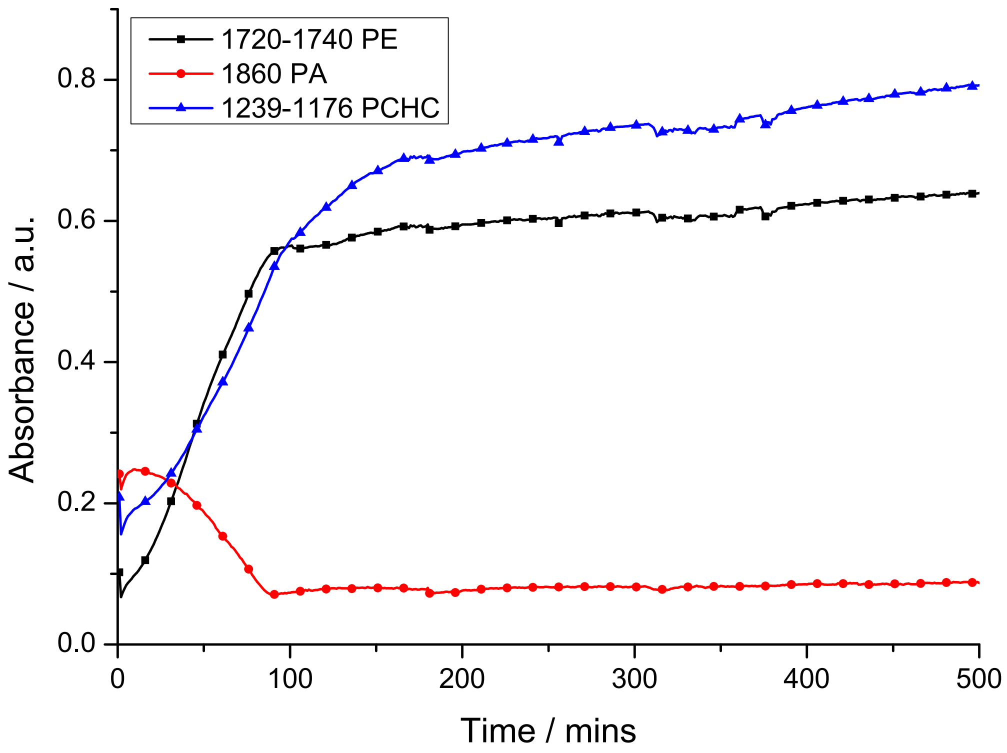


Fig. S6: Shows the changes in the intensity of the ATR-FTIR resonances observed during ROCOP of PA, CHO and CO_2 using complex **1**. Polymerization conditions: Cat.:PA:CHO = 1:100:800 under 1 bar CO_2.

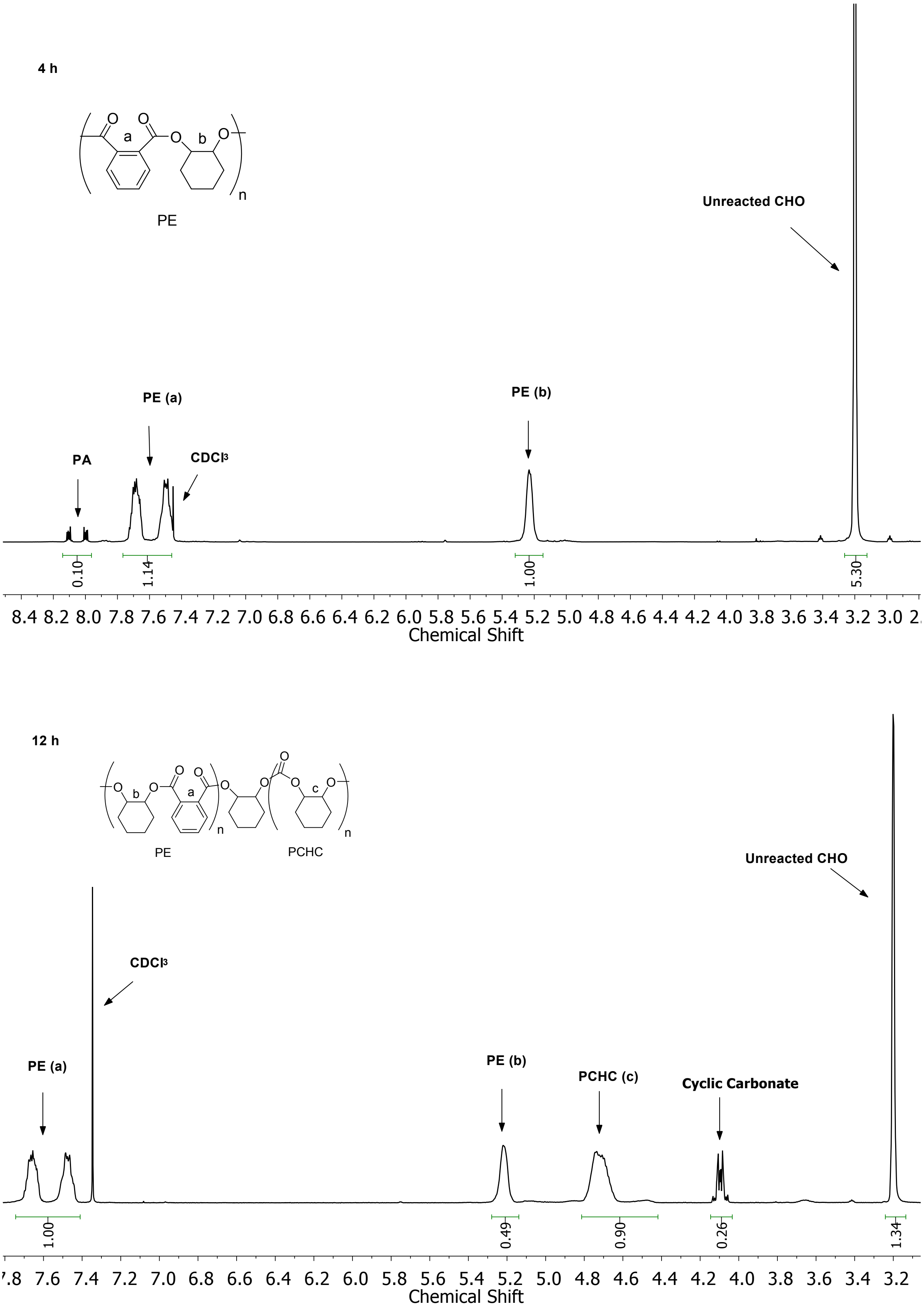


Fig. S7: ^{1}H NMR spectra for terpolymerization of CHO/PA/CO_2 using **2**. Reaction conditions: 1:100:800. Cat:PA:CHO, 100 °C, under 1 bar CO_2. Spectra show that PA is fully consumed before PCHC is formed.

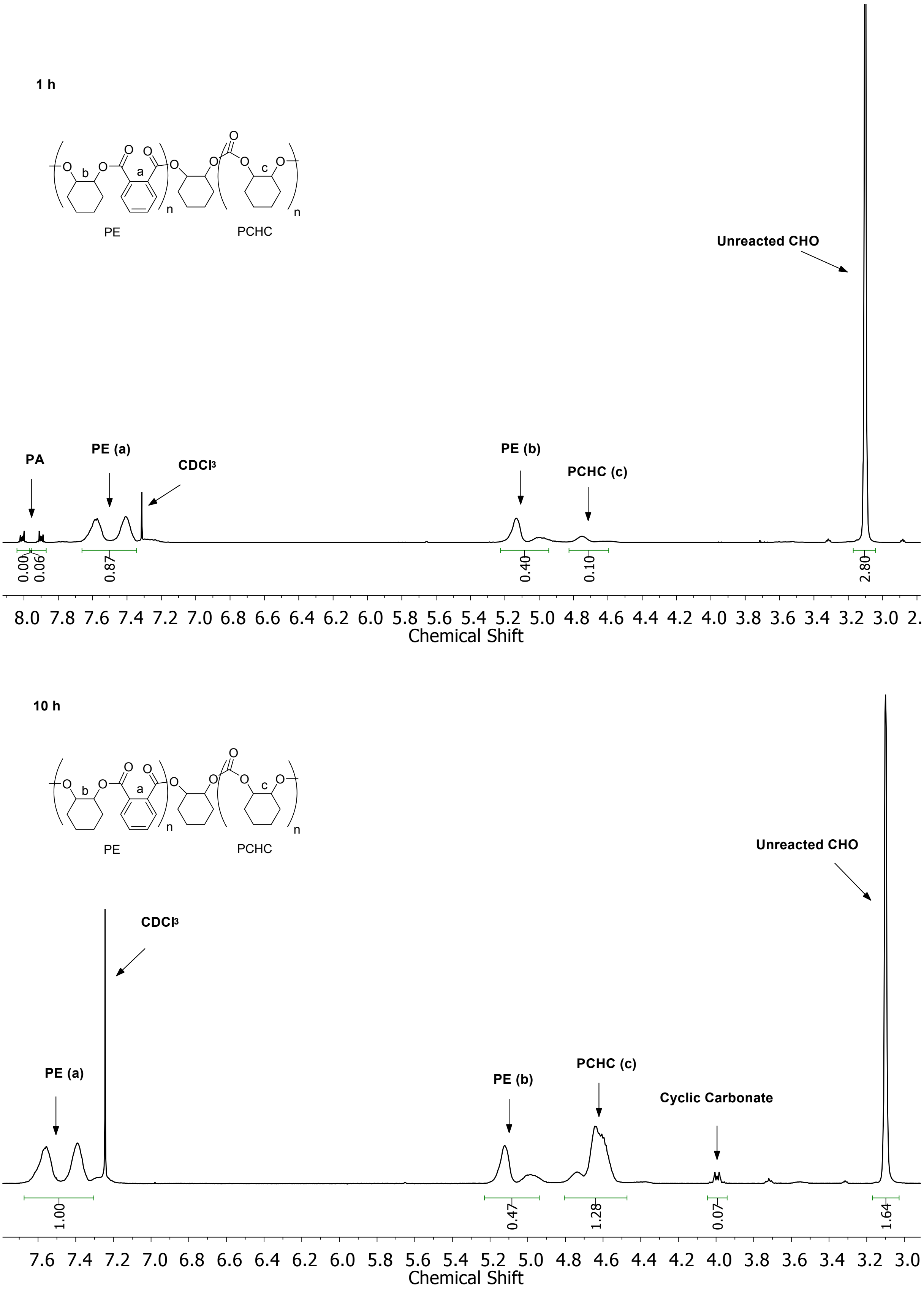


Fig. S8: ^{1}H NMR spectra for terpolymerization of CHO/PA/CO_2 using **1**. Reaction conditions: 1:100:800. Cat:PA:CHO, 100 °C under 1 bar CO_2. Spectra show that PCHC forms when PA is still present in a low concentration (95% PA conversion).

References

1. a) M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem. Int. Ed.,* 2009, 931-933; b) M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.,* 2012, ***134***, 15676-15679.