

Electronic Supplementary Information for:
Carbon Dioxide Capture and Utilization: Using Dinuclear Catalysts to Prepare Polycarbonates

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1. Results

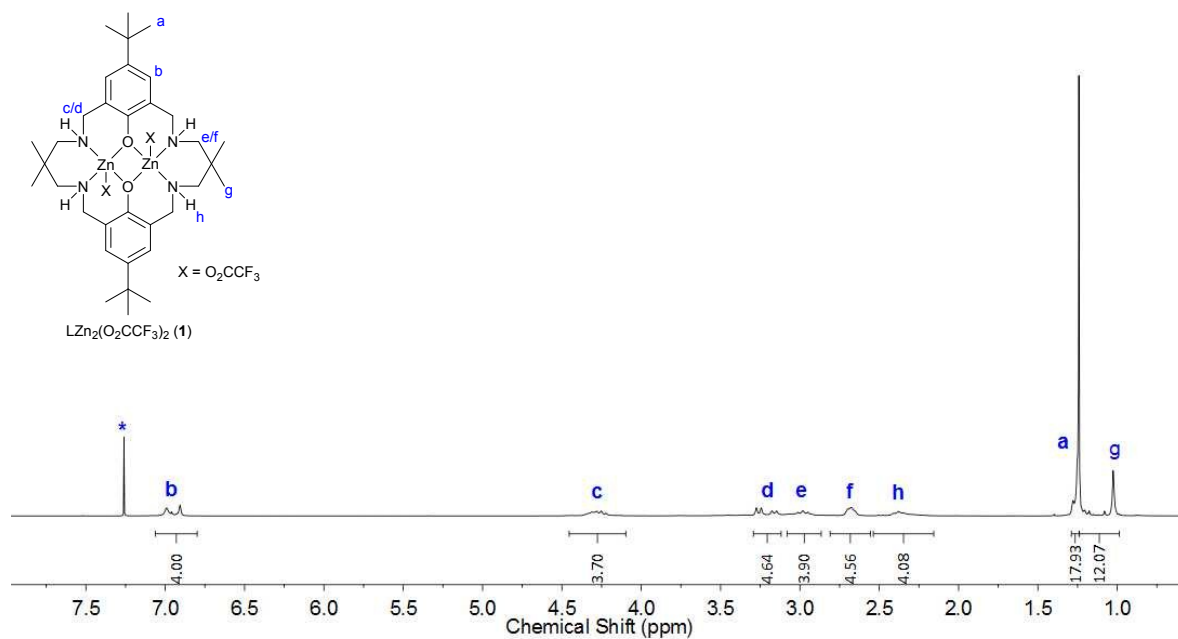


Figure S1. ¹H NMR (400.0 MHz, CDCl₃-d₁, 298 K) spectrum of LZn₂(O₂CCF₃)₂ (1). The asterisk denotes the residual protio-solvent.

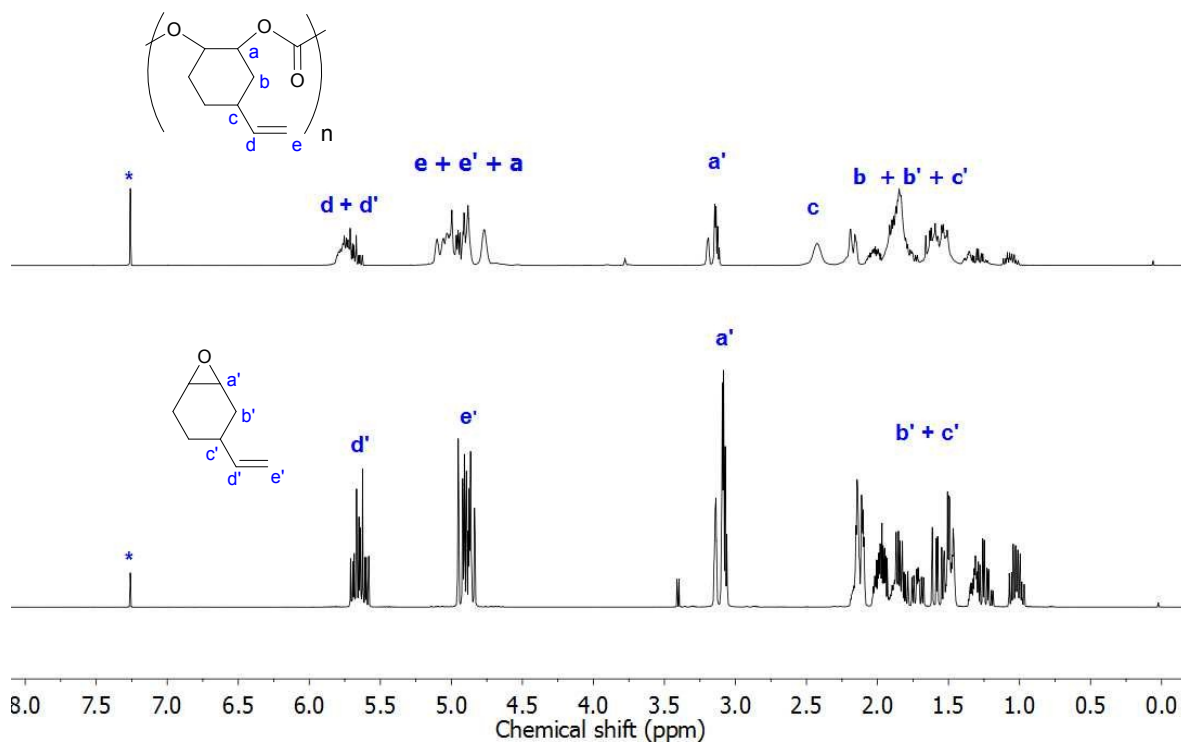


Figure S2. Top: ^1H NMR (400.0 MHz, CDCl_3-d_1 , 298 K) spectrum of crude poly(vinyl-cyclohexene oxide) reaction mixture. Bottom: ^1H NMR (400.0 MHz, CDCl_3-d_1 , 298 K) spectrum of vinyl cyclohexene oxide monomer. The conversion of V-CHO to PVCHC was calculated by the ratio of integration of c to the integration of $d+d'$. The asterisk denotes the residual protio-solvent.

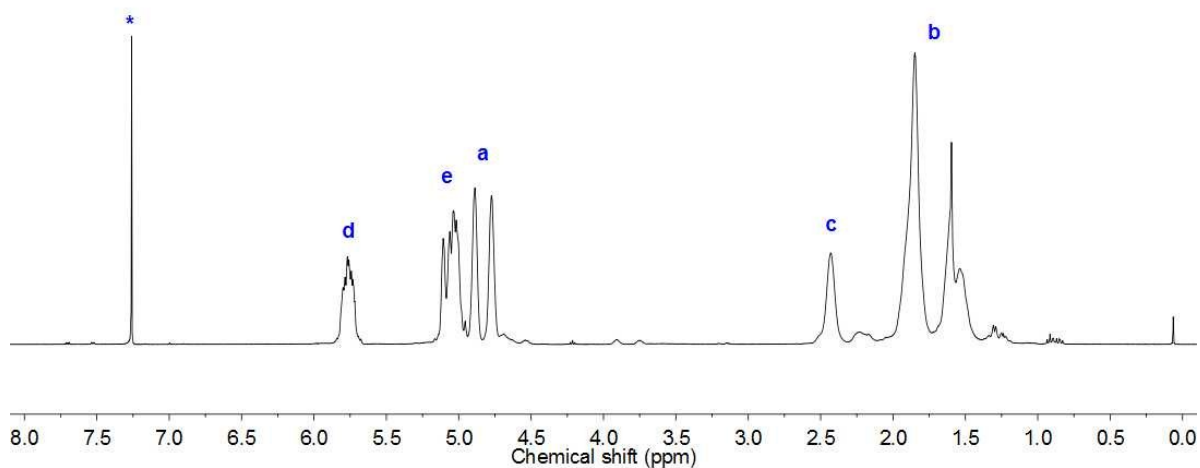


Figure S3. ^1H NMR (400.0 MHz, CDCl_3-d_1 , 298 K) spectrum of isolated poly(vinyl-cyclohexene oxide) (PvCHC, $M_n = 6,700 \text{ g mol}^{-1}$). The asterisk denotes the residual protio-solvent.

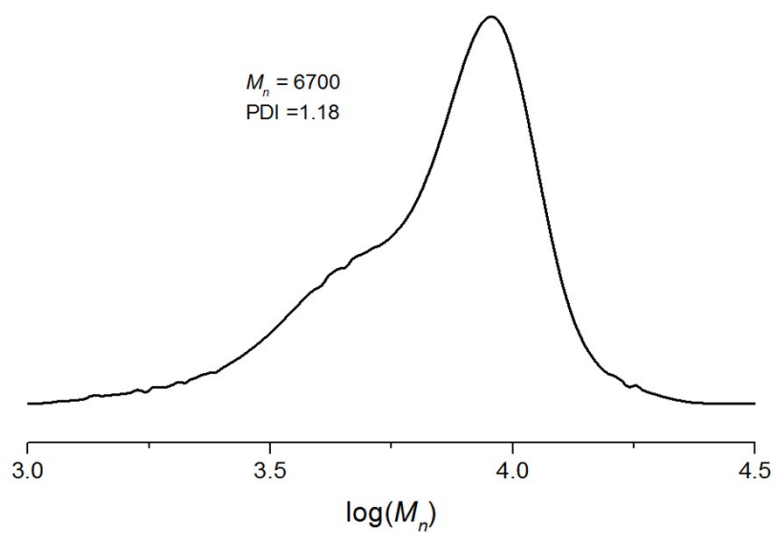


Figure S4. Bimodal molecular weight distribution of the isolated PvCHC polymer (Table 1 Entry 4), obtained by SEC using narrow M_w polystyrene calibration.

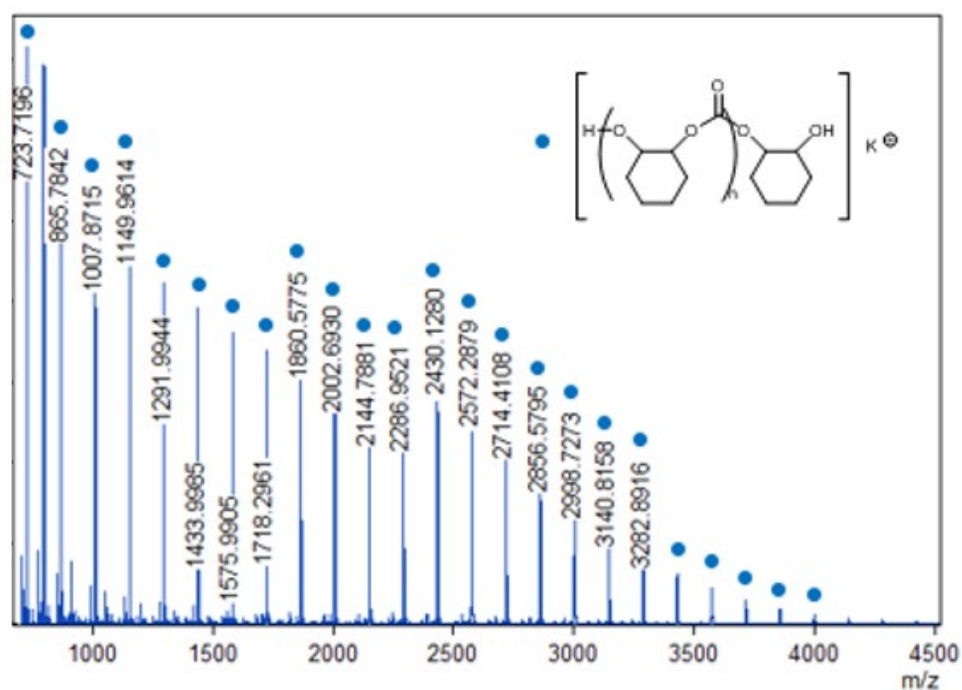
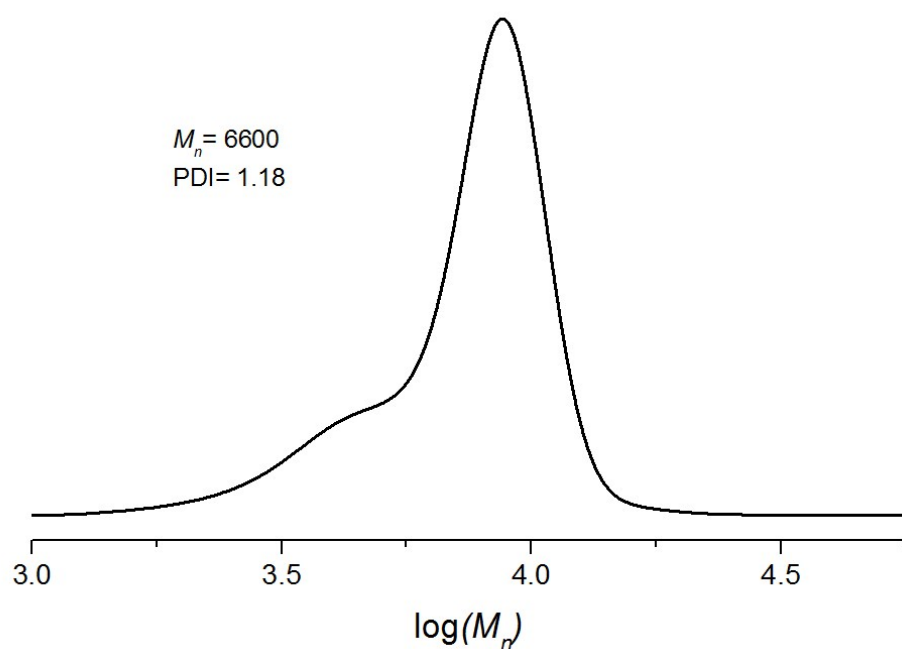


Figure S5. Top: bimodal molecular weight distribution of the isolated PCHC polymer (Table 1 Entry 2), obtained by SEC using narrow M_w polystyrene calibration. Bottom: MALDI-ToF spectrum of the PCHC produced in Table 1 Entry 2, showing the polyol series $[\text{HO}(\text{C}_7\text{H}_{10}\text{O}_3)_n\text{C}_6\text{H}_{11}\text{O}_2]^+\text{K}^\ominus = [(142.15)_n+116.16+39.1]$

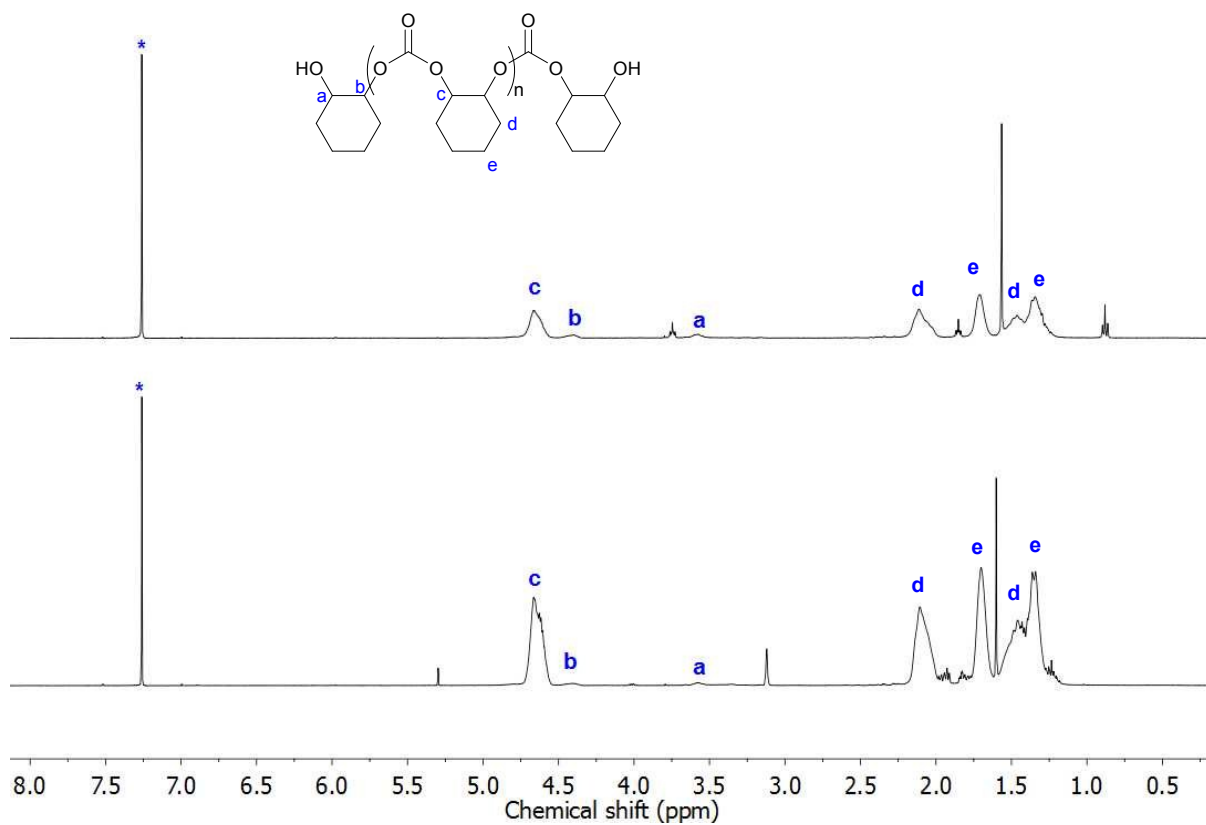


Figure S6. ¹H NMR (400.0 MHz, CDCl₃-d₁, 298 K) spectra of separated fractions (Top: low M_n fraction, Bottom: high M_n fraction) of PCHC produced in Table 1 Entry 2. The asterisks denote the residual solvent.

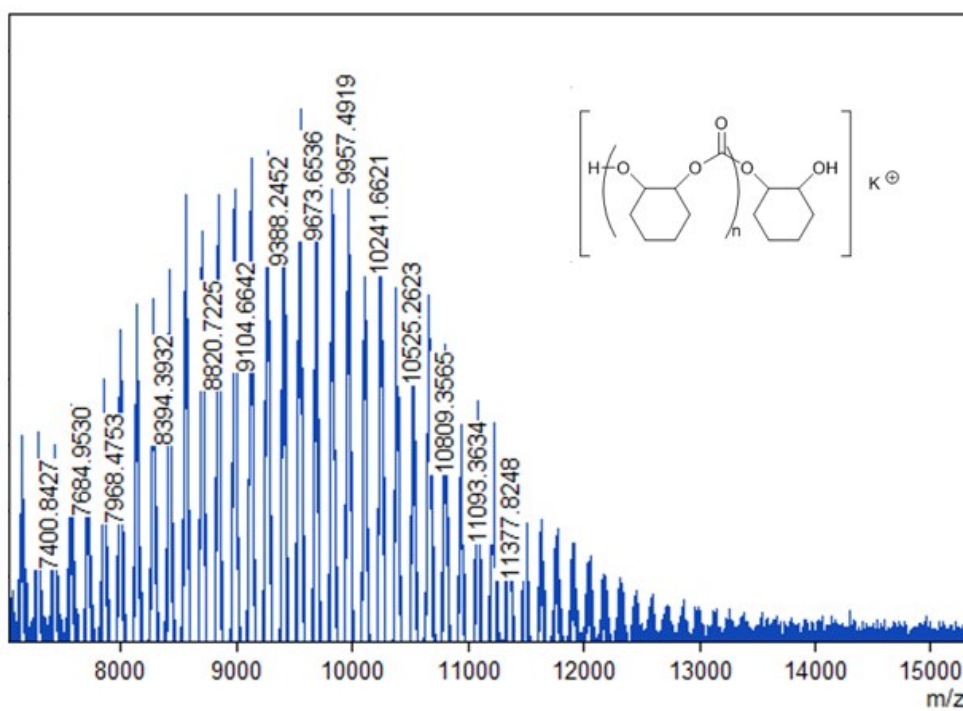
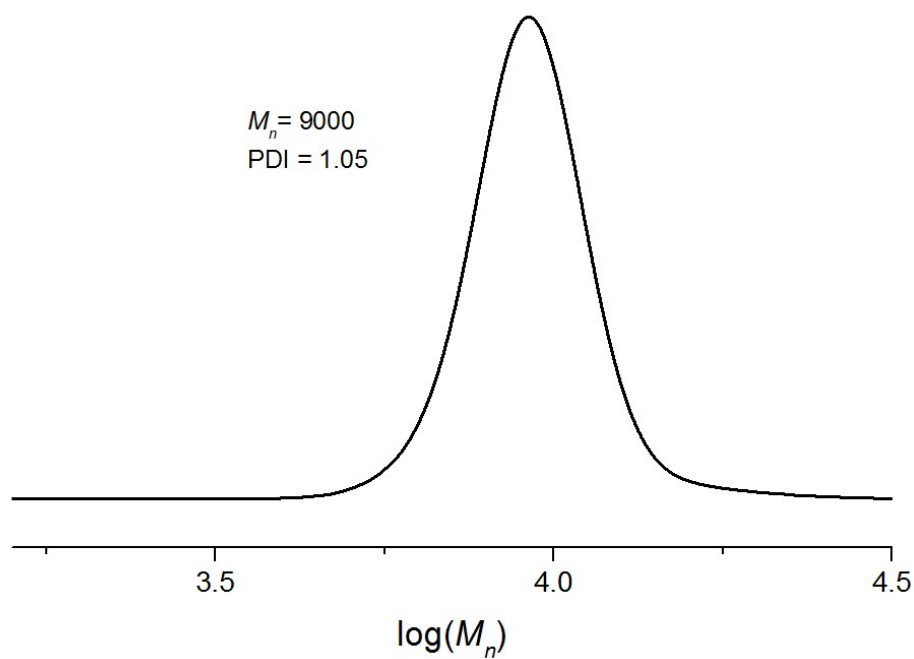


Figure S7. Top: molecular weight distribution of the isolated high M_n fraction of PCHC polymer (Table 1 Entry 2), obtained by SEC using narrow M_w polystyrene calibration. Bottom: MALDI-ToF spectrum of the high M_n fraction of the PCHC produced in Table 1 Entry 2, showing the polyol series $[\text{HO}(\text{C}_7\text{H}_{10}\text{O}_3)_n\text{C}_6\text{H}_{11}\text{O}_2]\text{K}^+ = [(142.15)_n + 116.16 + 39.1]$

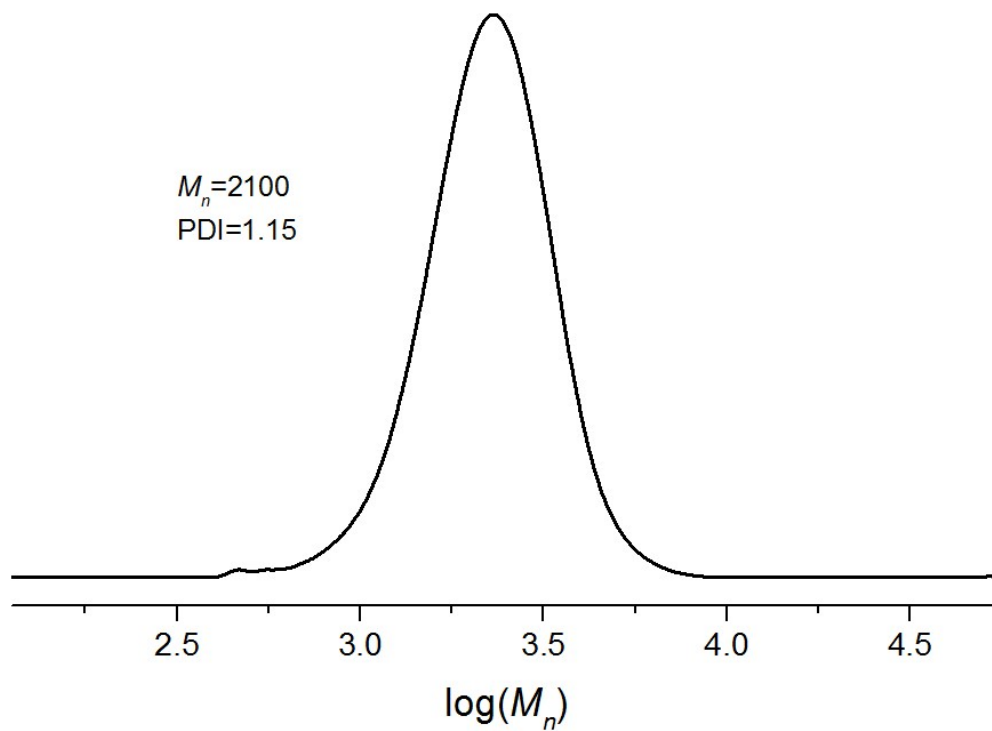


Figure S8. Monomodal molecular weight distribution of the PCHC polymer using 10 equiv. CHD in the polymerization (Table 3 Entry 2), obtained by SEC using narrow M_w polystyrene calibration.

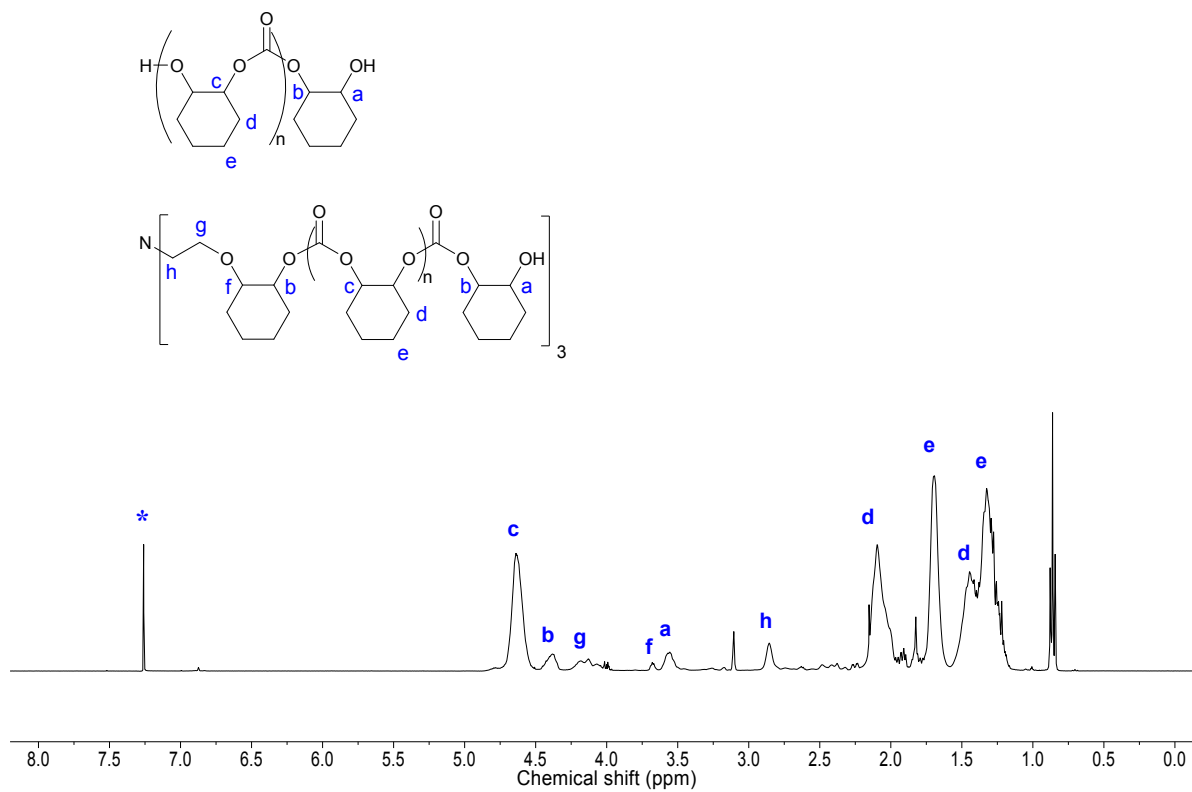


Figure S9. ¹H NMR (400.0 MHz, CDCl₃-d₁, 298 K) spectrum of isolated poly(cyclohexene oxide) produced in the polymerization with TEA additive ($M_n = 1,500 \text{ gmol}^{-1}$, Table 3, Entry 5). The asterisk denotes the residual protio-solvent.

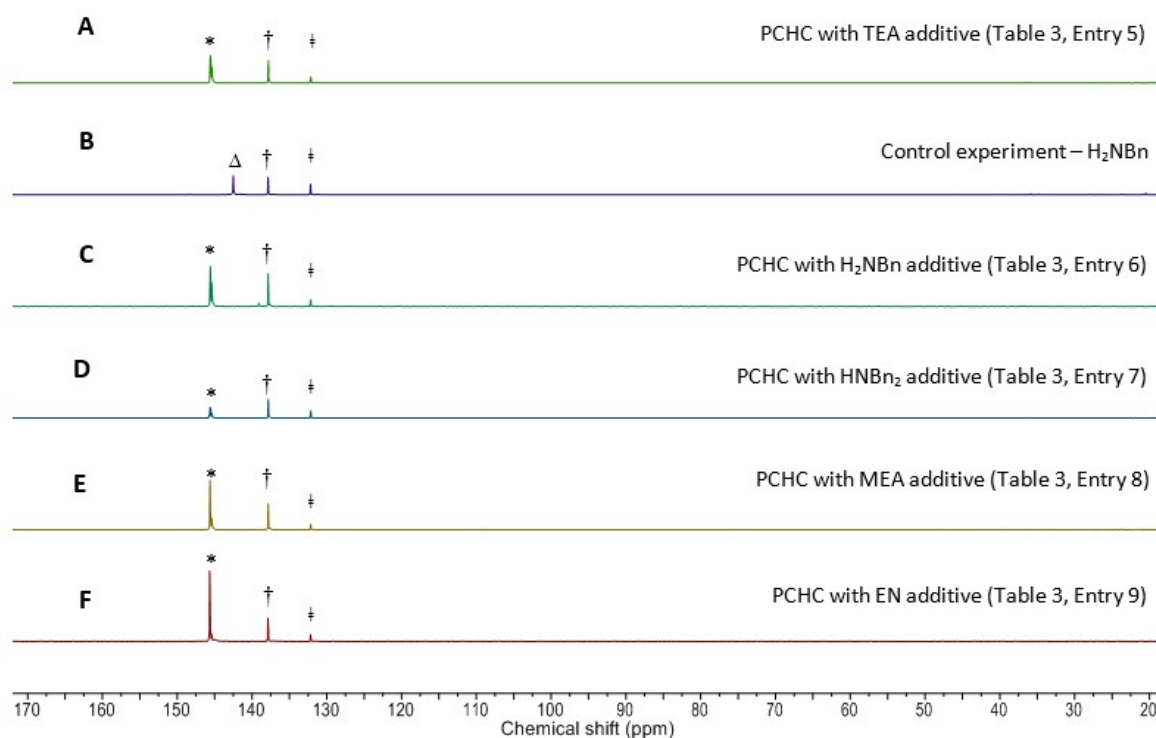
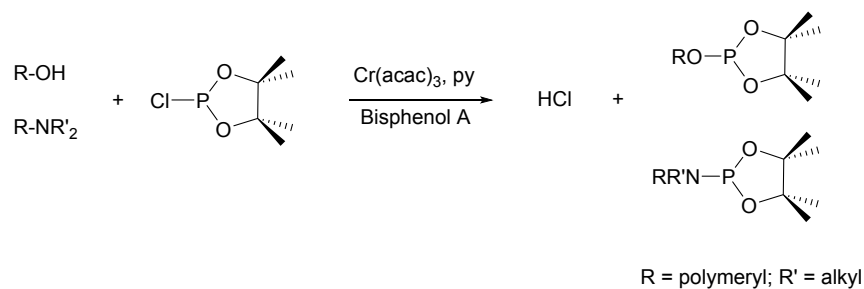


Figure S10. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162.1 MHz, CDCl_3-d_1 , 298 K) of the products of the reactions between the amine reagent (H_2NBn , **B**) or polymer end groups (**A and B-F**) and 2-chloro-4,4,5,5-tetramethyl dioxaphospholane. The asterisks, triangle, daggers and double daggers denote resonances corresponding to the product of the dioxaphospholane with secondary alcohol ($\delta = 145.5$ ppm), primary amine ($\delta = 142.5$ ppm), Bisphenol A ($\delta = 138.0$ ppm) and water ($\delta = 132.0$ ppm), respectively.

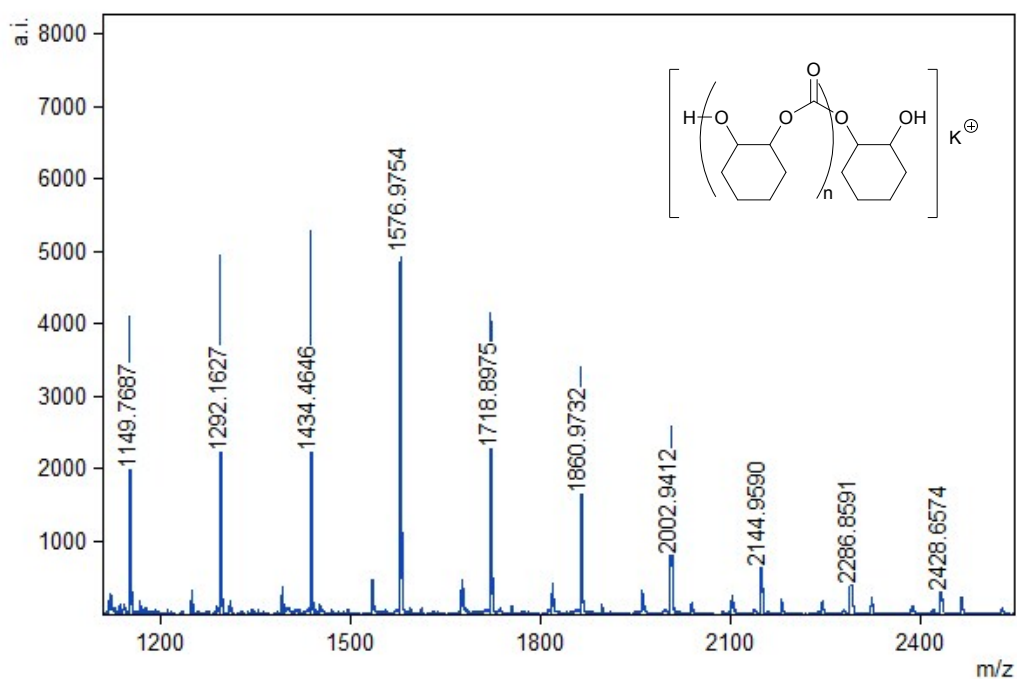


Figure S11. MALDI-ToF spectrum of the isolated PCHC ($M_n = 1,500 \text{ g mol}^{-1}$, PDI = 1.23) produced in the polymerization with TEA additive (Table 3, Entry 5), showing the polyol series $[\text{HO}(\text{C}_7\text{H}_{10}\text{O}_3)_n\text{C}_6\text{H}_{11}\text{O}_2]\text{K}^+ = [(142.15)_n + 116.16 + 39.1]$.

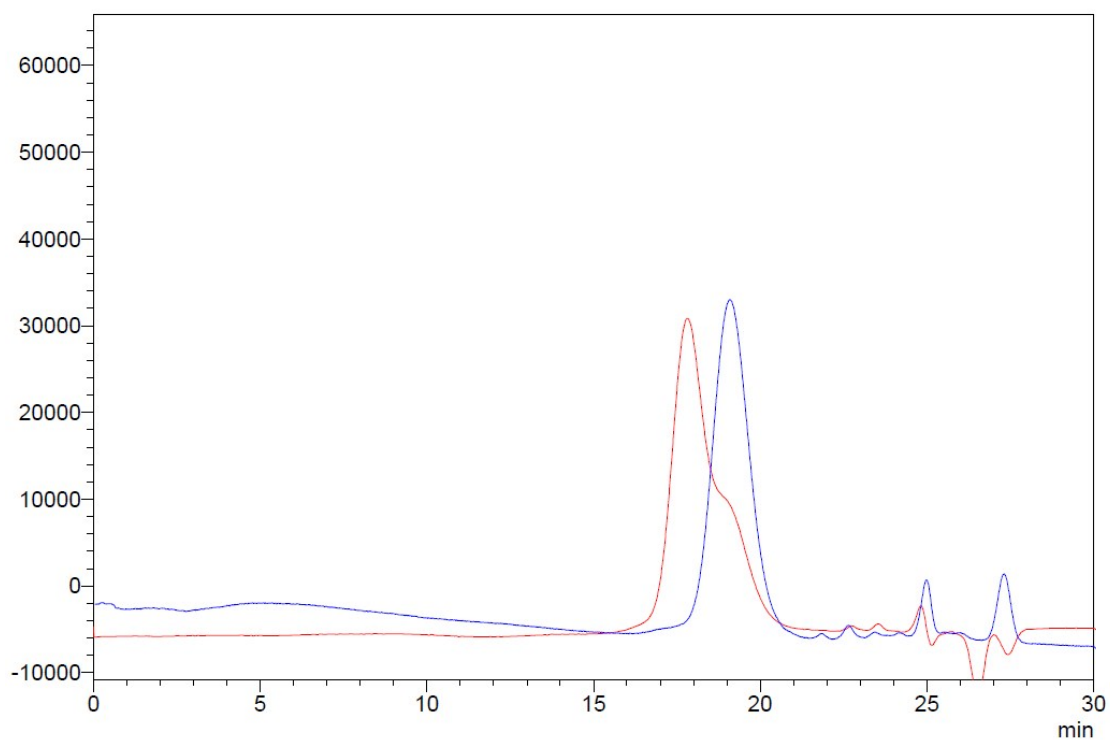


Figure S12. Combined SEC traces of PCHC produced using 20 equiv. HNBn_2 in Table 3 Entry 5, with RI detection (red) and UV detection (blue), using THF as the eluent.

2. References

1. M. R. Kember, J. Copley, A. Buchard and C. K. Williams, *Polym. Chem.*, 2012, **3**, 1196-1201.