Supporting Information for:

Ring-opening polymerization of cyclohexene oxide using aluminum amine-phenolate complexes

Hart Plommer,[a] Immanuel Reim,[a] and Francesca M. Kerton*[a]

a) Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, A1B 3X7, Canada

* Corresponding author, e-mail: fkerton@mun.ca

Experimental

General

All experiments involving metal complexes were carried out under nitrogen atmosphere in an inert atmosphere workstation under nitrogen. Ligands were prepared according to literature procedures.[1-3] Cyclohexene oxide (CHO) and other epoxides were dried over CaH_2, distilled, and stored under nitrogen. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance 300 or 500 MHz spectrometer at 25 °C and are referenced internally to residual signals of the solvent. Kinetic studies were performed on a Bruker Avance 500 Mz spectrometer using a co-axial NMR tube and $CDCl_3$ as the lock solvent. Polymer GPC data was collected from a setup consisting of a miniDawn TREOS light scattering detector, a Viscostar-II viscometer, and an Optilab T-rEX differential refractive index detector (Wyatt Technology) connected to an Agilent Infinity 1260 HPLC system equipped with a ResiPore 250×4.6 mm column. Samples were prepared in chloroform at a typical concentration of 2 mg/mL, filtered, and analyzed at a flow rate of 0.3 mL/min and 25 °C. Molecular weights were calculated using a *d*n/*d*c value of 0.0795 mL/g (obtained from standard calibration analyses by injecting known concentrations of PCHO in chloroform directly into the refractive index detector). DSC data were collected on a Mettler Toledo DSC1 Star^e System with a scanning rate of 10 °C/min and nitrogen gas flow of 50 mL/min. Samples were heated from 25 to 100 °C three times in order to eliminate the difference in sample history and all glass transition temperatures were taken from the third heating cycle. Polymer samples were analyzed by MALDI-TOF MS using an Applied Biosystems 4800 TOF-

TOF mass spectrometer, with spectra recorded in reflectron mode. The matrix was 2,5-dihydroxybenzoic acid, with tetrahydrofuran as the solvent. Spectra were modelled using mMass software (www.mmass.org). Microwave reactions were carried out using a Biotage Initiator microwave reactor with sealed 2 mL vials.

Synthetic procedures

Synthesis of **1** and **2** has been reported previously.[4]

[$O_2NO^{tBu,tBu}$]AlCl (**3**). In a glovebox at room temperature, 2.10 g (4.10 mmol) of **L3**H was added to an Erlenmeyer flask and dissolved in a sufficient amount of dry toluene. To this a solution of Et_2AlCl (25% w/w in toluene; 0.495 g, 4.10 mmol) was added dropwise while rapidly stirring. The reaction was allowed to stir for two hours, after which the toluene was removed *in vacuo*. The resulting fluffy solid was washed with 5 mL pentane and dried under vacuum, yielding a white powdery solid. Compound **3** was obtained as a white powdery solid. Yield (2.34 g, 100%). Anal. Calcd for $C_{33}H_{51}AlClNO_3$: C, 69.27; H, 8.98; N, 2.45. Found: C, 69.28; H, 8.99; N, 2.40. ^{1}H NMR (C_7D_8, 300 MHz, 298 K) δ 7.53 (2H, d, Ar*H*), 6.73 (2H, d, Ar*H*), 3.45 (3H, s, OC*H*$_3$), 3.26 (2H, d, $^2J_{HH}$=13 Hz, Ar-C*H*$_2$-N-C*H*$_2$-Ar), 3.10 (2H, d, $^2J_{HH}$=13 Hz, Ar-C*H*$_2$-N-C*H*$_2$-Ar), 2.60 (2H, t, N-C*H*$_2$-CH$_2$), 1.96 (2H, t, CH$_2$-C*H*$_2$-O), 1.73 (s, 18H, Ar-C{C*H*$_3$}$_3$), 1.39 (s, 18H, Ar-C{C*H*$_3$}$_3$); ^{13}C{^{1}H} NMR (C_7D_8, 125 MHz, 298 K) δ 155.6, 140.1, 139.9, 124.9, 123.7, 120.6 (Ar*C*), 68.6 (N-*C*H$_2$-CH$_2$), 64.0 (O*C*H$_3$), 58.4 (Ar-*C*H$_2$-N), 48.5 (CH$_2$-*C*H$_2$-O), 35.5 (Ar-*C*{CH$_3$}$_3$), 34.4 (Ar-*C*{CH$_3$}$_3$), 32.0 (Ar-C{*C*H$_3$}$_3$), 29.9 (Ar-C{*C*H$_3$}$_3$).

Typical ROP procedure

A desired amount of catalyst was weighed into a vial and epoxide (cyclohexene oxide, propylene oxide, styrene oxide, limonene oxide, or epichlorohydrin) was added with stirring. For lower catalyst loadings, the use of a standardized solution of the catalyst in toluene was necessary to accurately measure out known amounts of catalyst, followed by removal of the toluene via vacuum prior to epoxide addition. Reactions were typically terminated once they were unable to be stirred further, by removing the vial from the glovebox and opening it to air. A small amount was taken for ^{1}H NMR analysis to determine conversion of epoxide monomer to polymer. The crude polymer was dissolved in chloroform (or methylene chloride), precipitated from cold methanol acidified with a small amount of 1 M HCl, and isolated by suction filtration or

centrifugation. Finally, the polymer was dried in a vacuum oven to yield the PCHO that was analyzed by GPC and DSC.

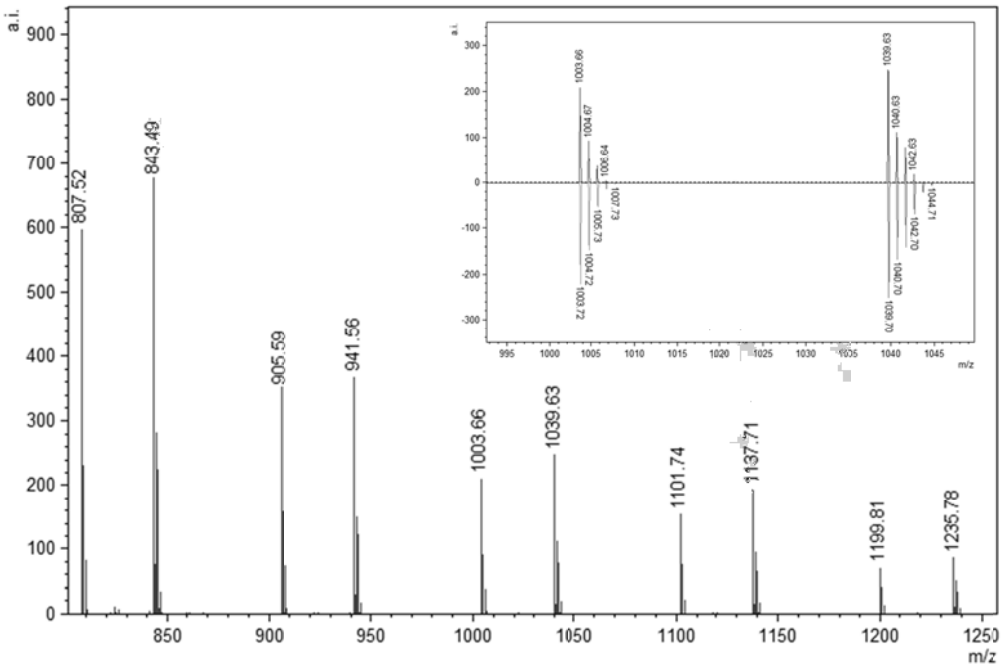

Figure S1: MALDI-TOF mass spectrum of PCHO (Table 1, entry 9), inset showing isotopic match for ($\{CHO\}_{10}\cdot Na^+$) and ($Cl\{CHO\}_{10}H\cdot Na^+$)

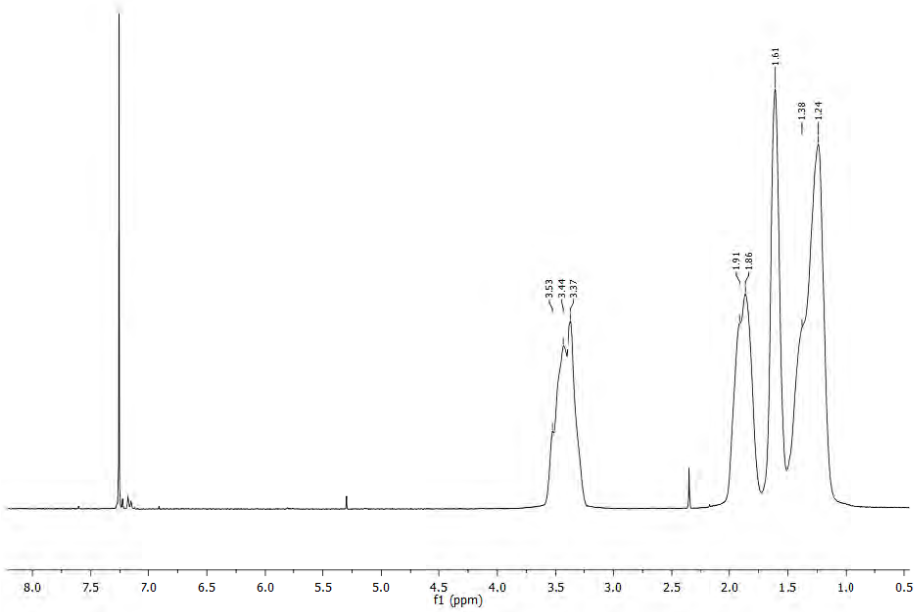

Figure S2: Typical ^1H NMR spectrum of PCHO

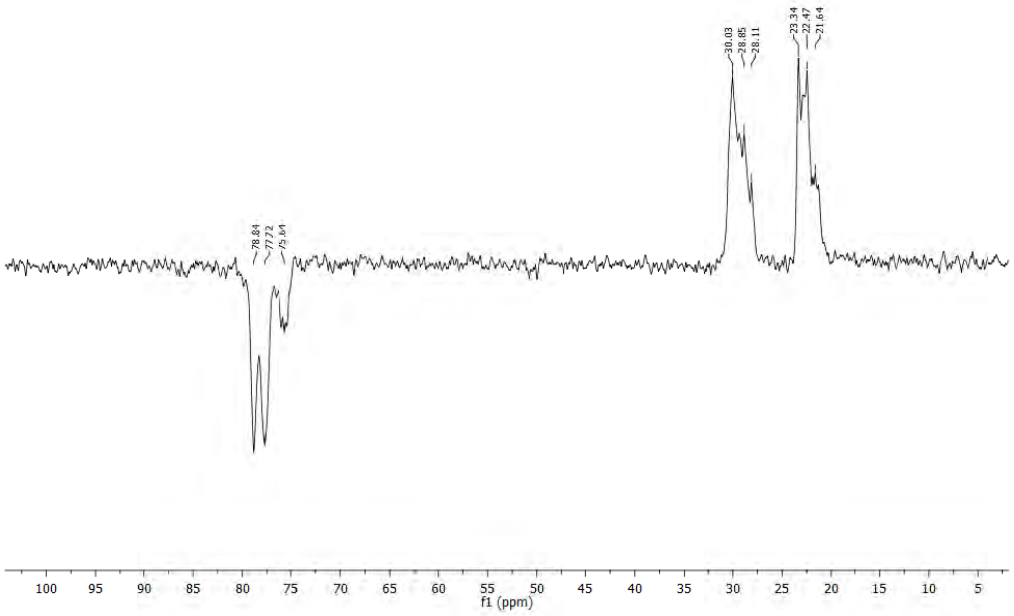

Figure S3: Typical ^{13}C DEPT-135 NMR spectrum of PCHO

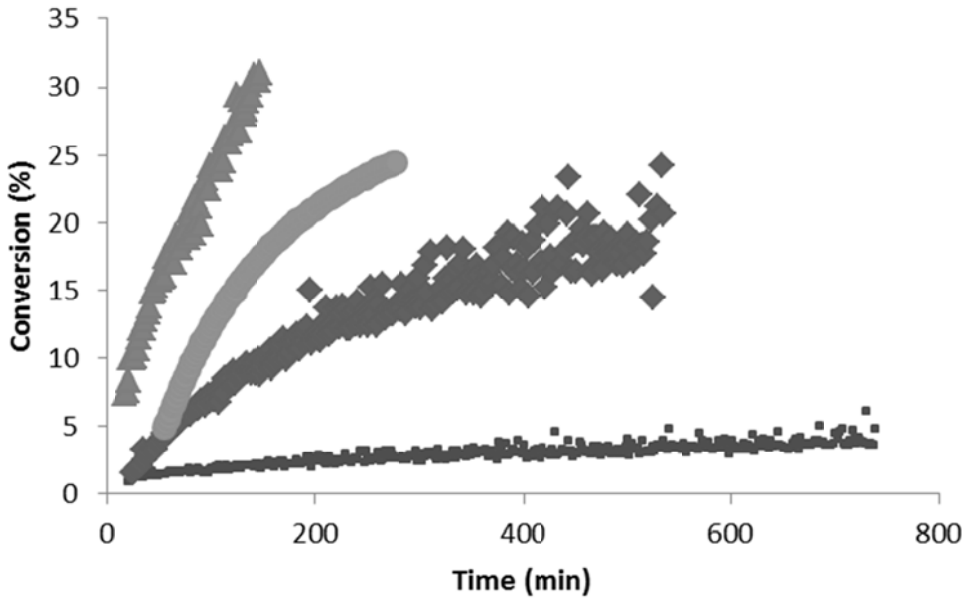

Figure S4: Plot of CHO conversion versus time for the polymerization of CHO using **2** at various concentrations (0.4 mol%, 0.2 mol%, 0.1 mol%, 0.01 mol%). Data collected via ^{1}H NMR spectroscopy using a co-axial NMR tube containing $CDCl_3$ for lock.

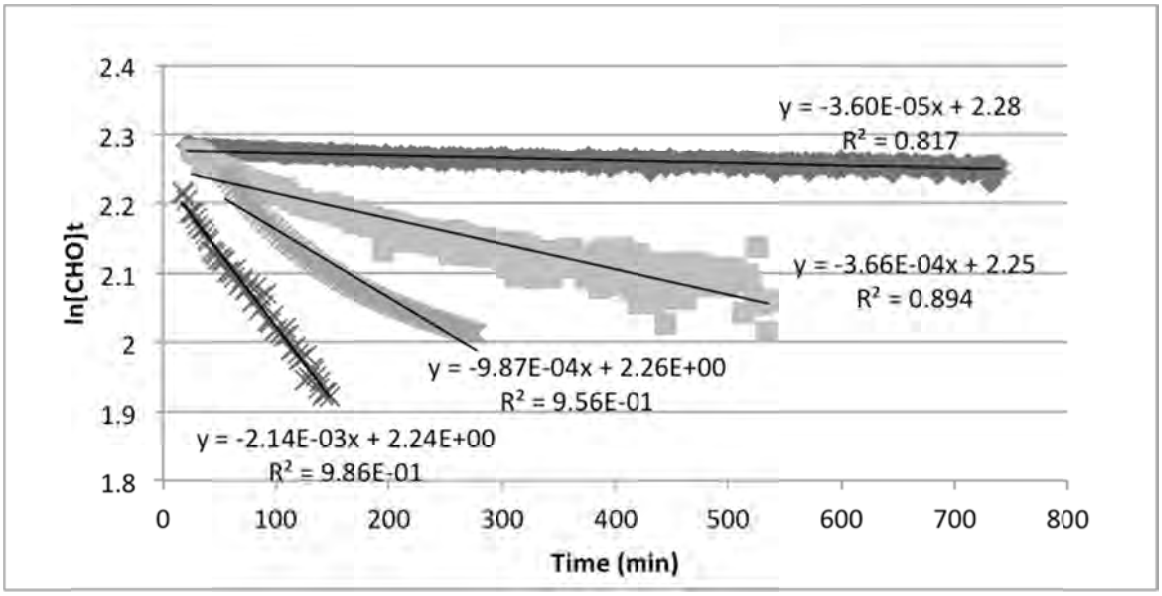

Figure S5: Detailed plot (with equations for fit of data to straight lines) of ln[CHO] against time at catalyst loadings 0.01, 0.1, 0.2, and 0.4 mol% using **2**.

Table S1: Attempted ROP of other epoxides using **1**, **2**, and **3** (PO = propylene oxide; SO = styrene oxide; LO = (-)-limonene oxide; ECH = epichlorohydrin)[a]

Entry	Epoxide	Complex	t/h
1	PO	**1**	24
2	PO	**2**	24
3	SO	**1**	24
4	SO	**2**	24
5	LO	**1**	24
6	ECH	**1**	24
7[b]	PO	**1**	0.33
8[c]	LO	**1**	1.67
9[d]	PO	**3**	4
10[d]	SO	**3**	4

[a] Reactions were performed neat at room temperature for the time indicated with 0.5 mol% complex (unless otherwise indicated). All samples showed 0% conversion according to ^{1}H NMR spectroscopy. [b] Performed in a microwave reactor at 60 °C with 2.7 mol% **1**. [c] Performed in a microwave reactor at 130 °C with 2.7 mol% **1**. [d] 0.2 mol% **3**

References

1. E. Y. Tshuva, S. Groysman, I. Goldberg, M. Kol and Z. Goldschmidt, *Organometallics*, 2002, **21**, 662-670.
2. N. Ikpo, L. N. Saunders, J. L. Walsh, J. M. B. Smith, L. N. Dawe and F. M. Kerton, *European Journal of Inorganic Chemistry*, 2011, **2011**, 5347-5359.
3. F. M. Kerton, S. Holloway, A. Power, R. G. Soper, K. Sheridan, J. M. Lynam, A. C. Whitwood and C. E. Willans, *Canadian Journal of Chemistry*, 2008, **86**, 435-443.
4. N. Ikpo, S. M. Barbon, M. W. Drover, L. N. Dawe and F. M. Kerton, *Organometallics*, 2012, **31**, 8145-8158.