

New Reactivity of the Uranyl Ion: Ring Opening Polymerization of Epoxides

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References

Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. Toluene and THF were distilled over potassium, whilst diethyl ether was distilled over Na/K. ^1H and ^{13}C NMR spectra were recorded on either a Bruker AV400 spectrometer operating at 400.13 (^1H) or 100.65 (^{13}C) or a Bruker Avance II 600 NMR with a TCI cryoprobe operating at 150.92 MHz (^{13}C), and were referenced to the residual ^1H or ^{13}C resonances of the solvent used. EXSY spectra were recorded using Bruker's NOESY pulse sequence; a number of mixing times were examined and 1 second was deemed optimal for all experiments. Kinetic data were extracted using the methodology described in reference 1. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 with ATR. DSC spectra were recorded on a Perkin Elmer Diamond DSC. Mass spectra were measured on a MALDI QTOF Premier MS system. GPC data was recorded on a Varian ProStar with a 350 RI detector using a PLgel 5 μm MIXED-D column and calibrated with EasiCal polystyrene standards. Optical rotation measurements were made on a Rudolph Research Analytical Autopol IV instrument. The complexes $[\text{UO}_2\text{Cl}_2(\text{THF})_2]_2$ ² and $[\text{UO}_2(\text{OAr})_2(\text{THF})_2]$ ³ were prepared by the literature procedure and all other reagents were obtained from commercial sources, dried over CaH_2 and distilled under Ar before use.

Polymerisation Experiments. In a typical reaction, **1** was dissolved in PhMe or THF (10 cm³) and placed in an oil bath set to the required temperature. After equilibrating for 15 minutes propylene oxide (1 cm³, 14.3 mmol) was added via syringe and the reaction vigorously stirred. After completion, MeOH/HCl (90:10) was added to quench the reaction and the polymer obtained as a solid or oil. This was washed with MeOH and dried under vacuum.

Determination of % conversion. During the course of the reaction, aliquots (ca. 1 cm³) of the reaction mixture were removed, treated with one drop of MeOH and the ^1H NMR spectra were recorded. % conversion calculated from the relative integrals of the monomer (PO: 1.29 ppm; CHO 2.91 ppm) and polymer (PO: 1.10-1.26 ppm; CHO 3.55 ppm).

Figure S1. EXSY spectrum of **1** and >2 equivalents of 2,3-dimethyl-2,3-epoxybutane ($C_6D_5CD_3$, $T = 298\text{ K}$, $t_m = 1\text{ s}$)

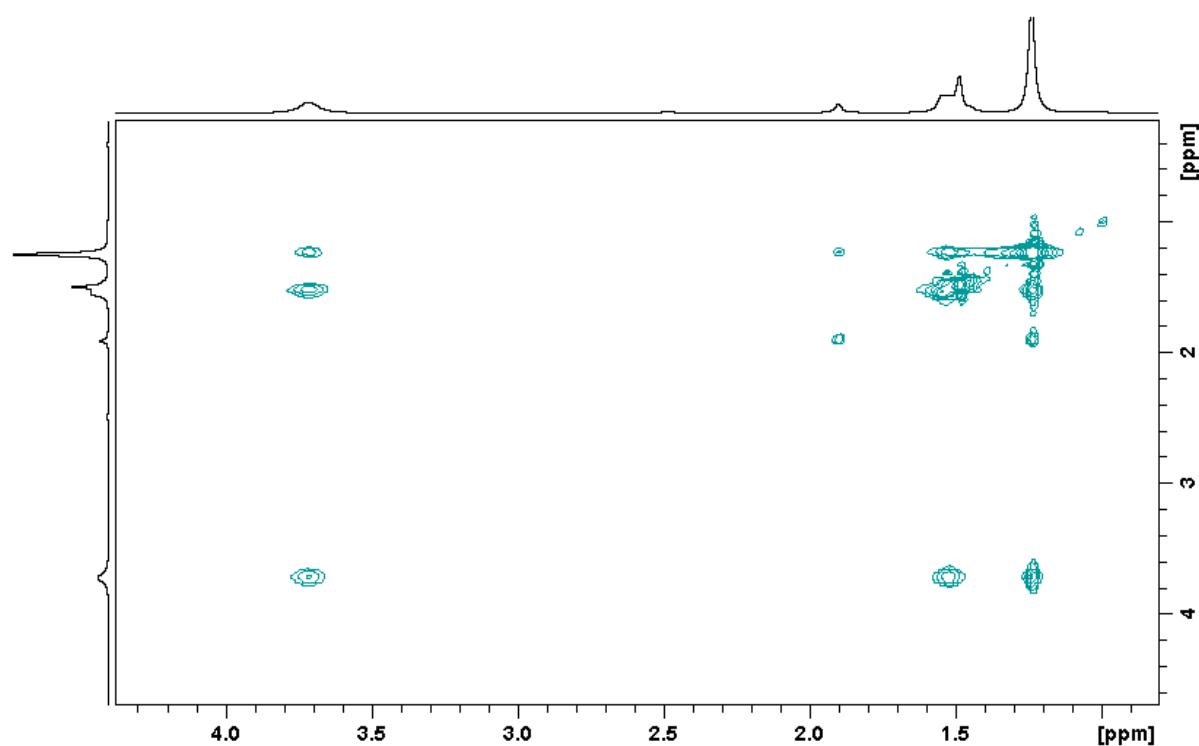


Figure S2. Arrhenius and Eyring plots for exchange of PO with THF in **1**.

T (°C)	k	st dev	lnk	st dev	1/T	ln(k/T)	st dev
22	0.02760876	0.00156636	-3.5896221	0.05627628	0.04545455	-6.681726	0.05627628
30	0.01944362	0.00146285	-3.9402363	0.07589514	0.03333333	-7.3433426	0.07589514
40	0.05602309	0.02535099	-2.8819914	0.54753929	0.025	-6.6969248	0.54753929
50	0.10454478	0.02346813	-2.2581398	0.23234602	0.02	-6.1912869	0.23234602

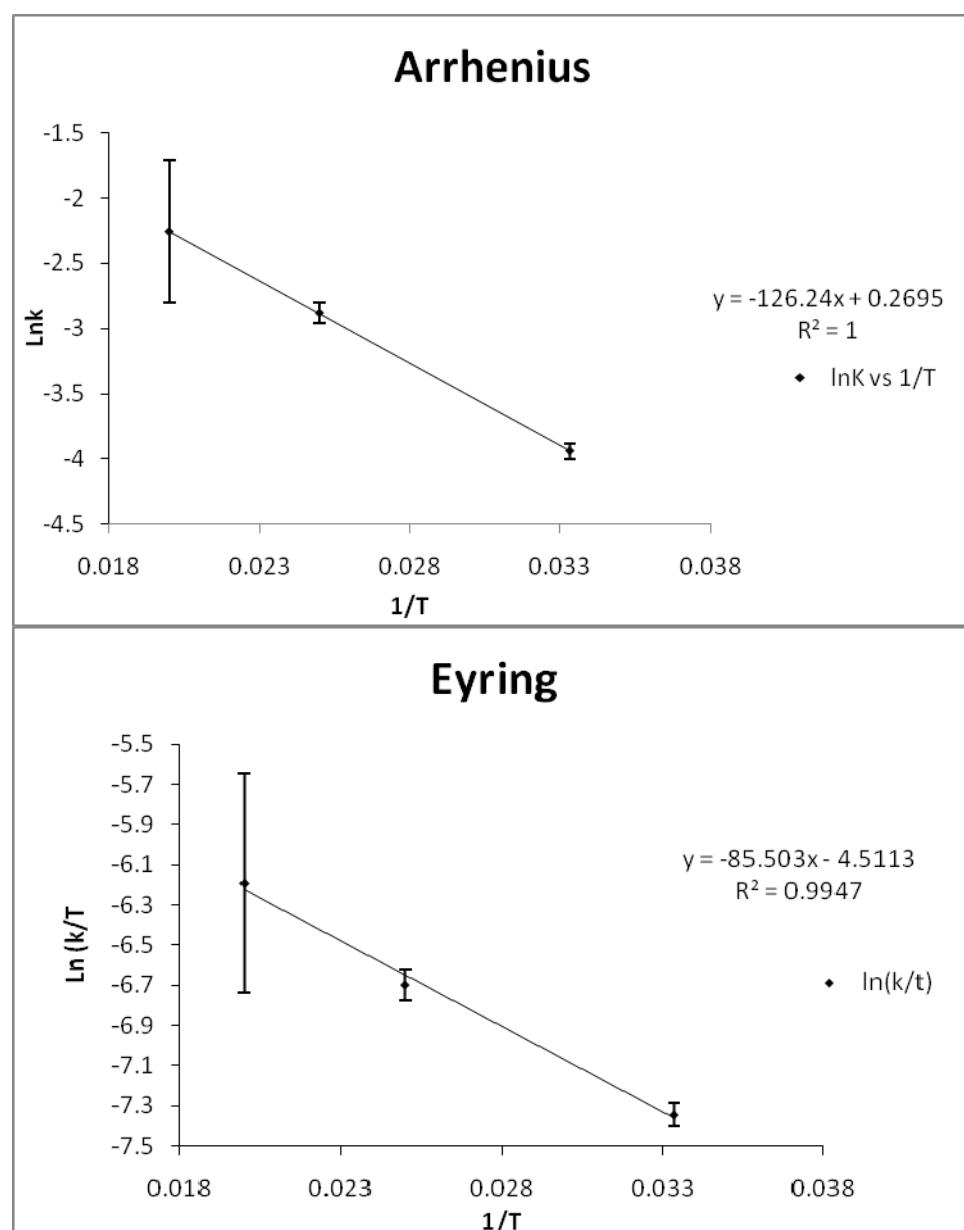


Figure S3. 400 MHz ^1H NMR spectrum of **1** and >2 equivalents of CHO ($\text{C}_6\text{D}_5\text{CD}_3$, T = 298 K)

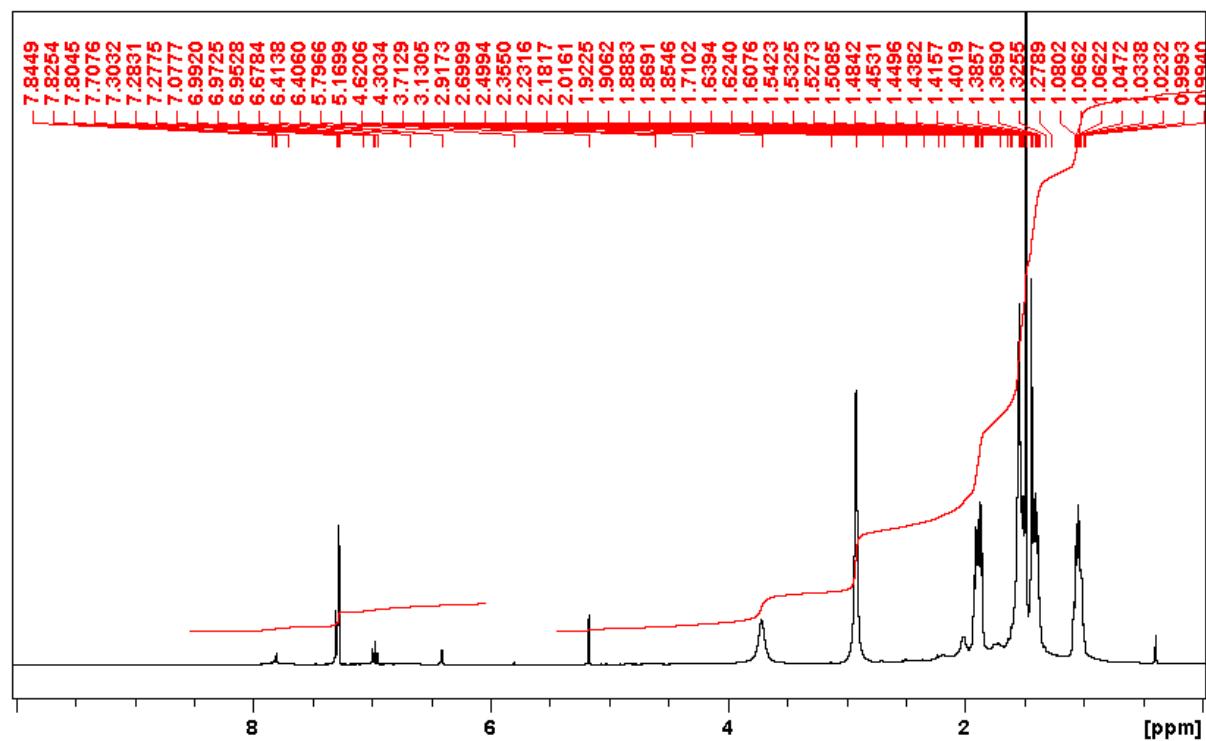


Figure S4. H-H COSY of poly(PO) catalysed by **1** in THF showing connectivity between aryl and polymer moieties.

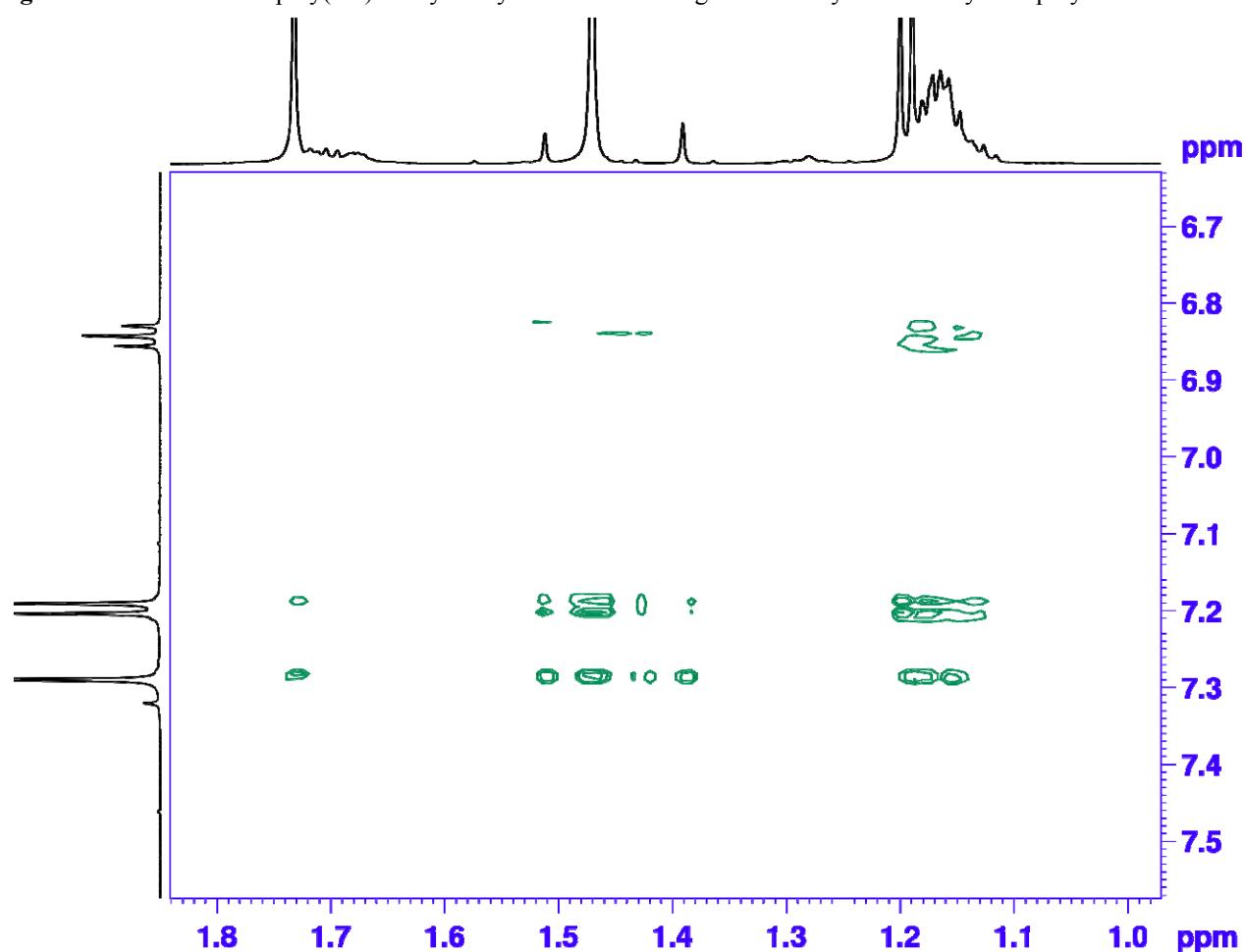


Figure S5. Selective TOCSY of polymer obtained from **3** and cyclohexene oxide. Top: irradiation at $\delta_H = 3.735$ ppm shows protons attached to cyclohexane ring with Cl end-group; Middle: irradiation at $\delta_H = 2.955$ ppm shows protons attached to cyclohexane ring with OMe end-group; Bottom: full spectrum.

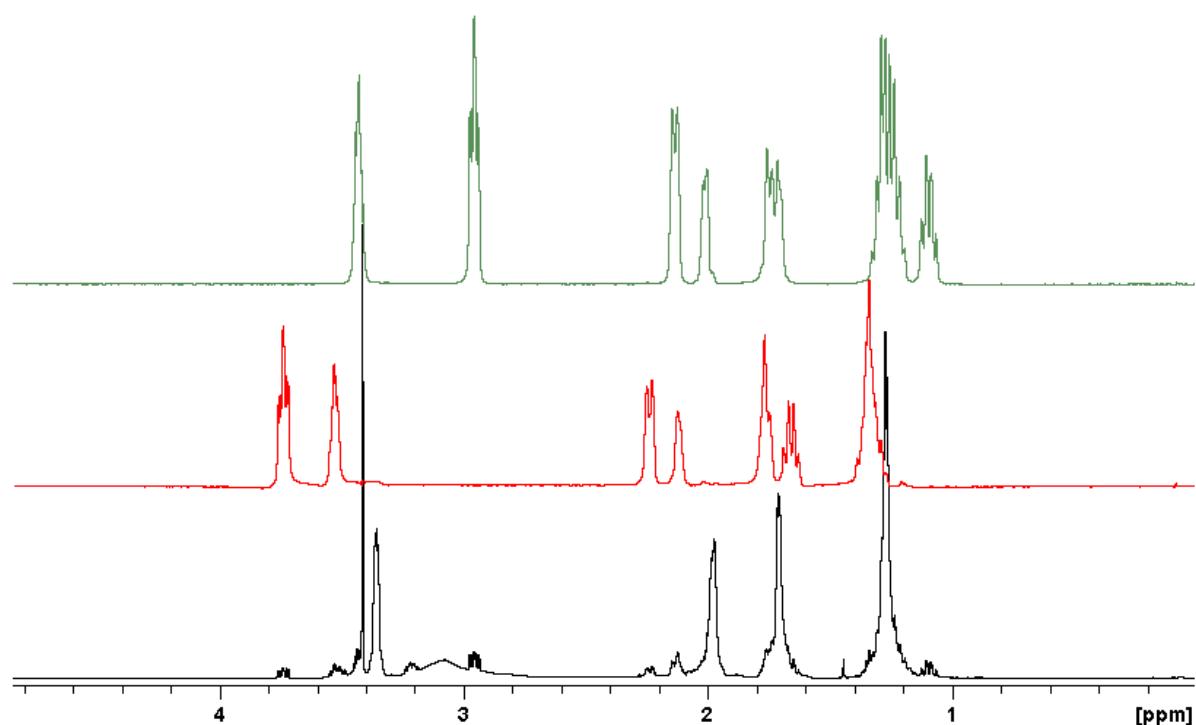


Figure S6. DSC spectra of poly(propyleneoxide) (top) and poly(cyclohexene oxide) (bottom) obtained from catalyst **1**.

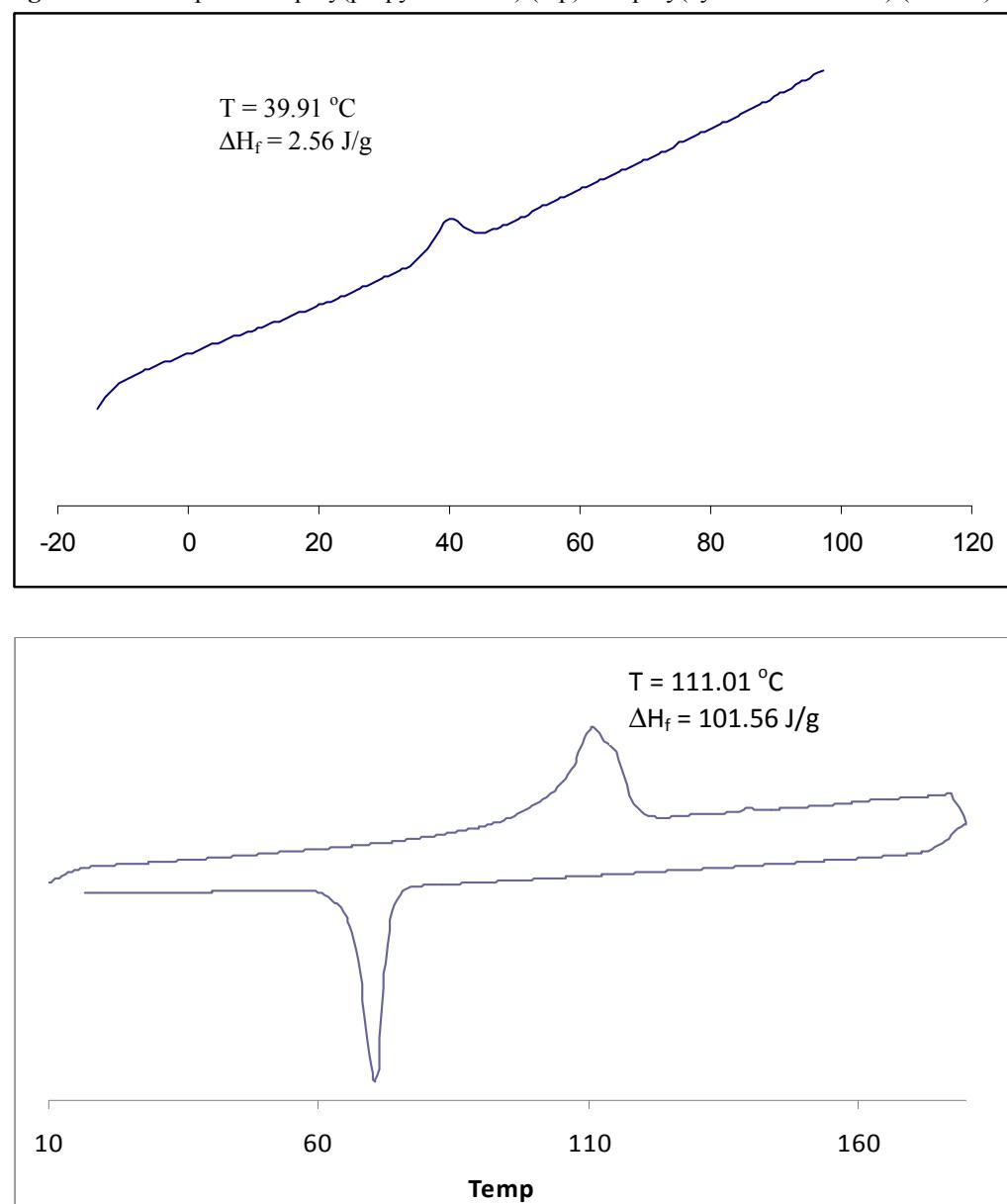
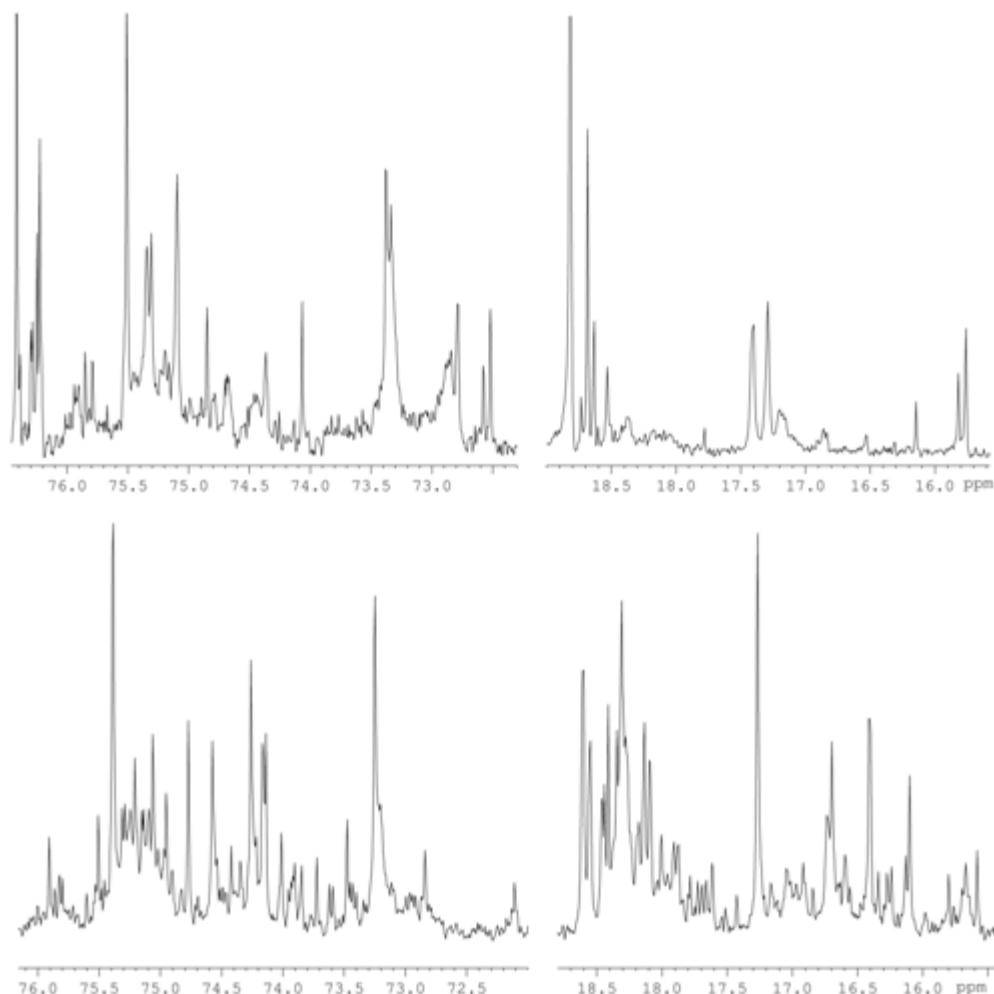


Figure S7. $^{13}\text{C}\{\text{H}\}$ NMR of poly(PO) obtained from **1** and *rac*-PO in THF (top) and poly(PO) obtained from **1** and *s*-PO in THF (bottom).



References

- [1] H. Günther, *NMR spectroscopy: basic principles, concepts, and applications in chemistry*, 2nd edn, Wiley, Chichester, 1995.
- [2] M. P. Wilkerson, C. J. Burns, R. T. Paine and Brian L. Scott, *Inorg. Chem.* **1999**, *38*, 4156-4158.
- [3] M. P. Wilkerson, C. J. Burns, D. E. Morris, R. T. Paine and B. L. Scott, *Inorg. Chem.* **2002**, *41*, 3110-3120.