

Structural and Kinetic Studies of the Polymerization Reactions of ϵ -Caprolactone Mediated by (Pyrazol-1-ylmethyl)pyridine Cu(II) and Zn(II) Complexes

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Supplementary Information

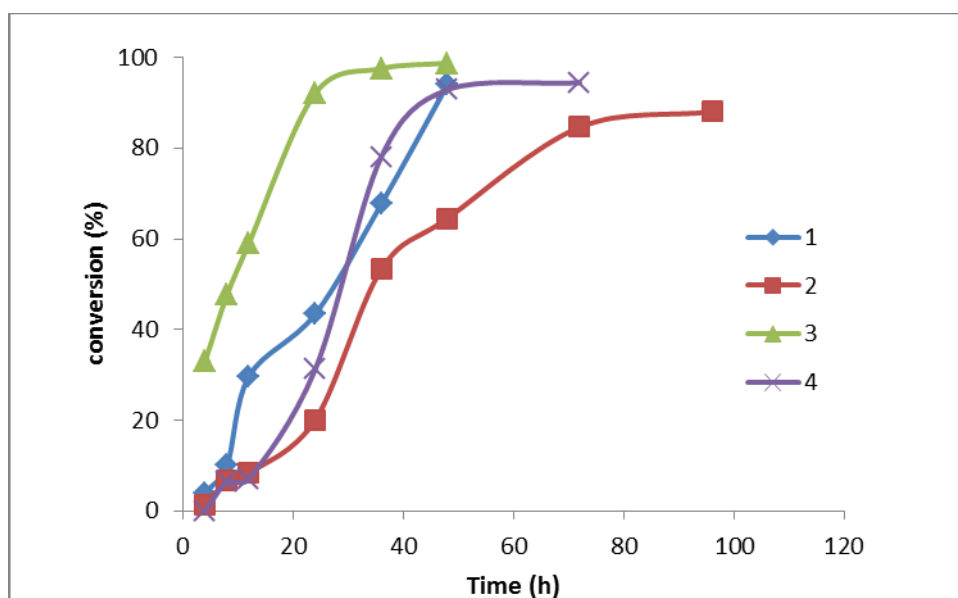


Figure S1: Bulk polymerization of ϵ -CL to PCL with time for catalyst initiators **1-4** at $[\text{CL}]_0/[\text{I}] = 100$, $[\text{CL}] = 0.01$ mol, $[\text{cat}] = 0.0001$ mol.

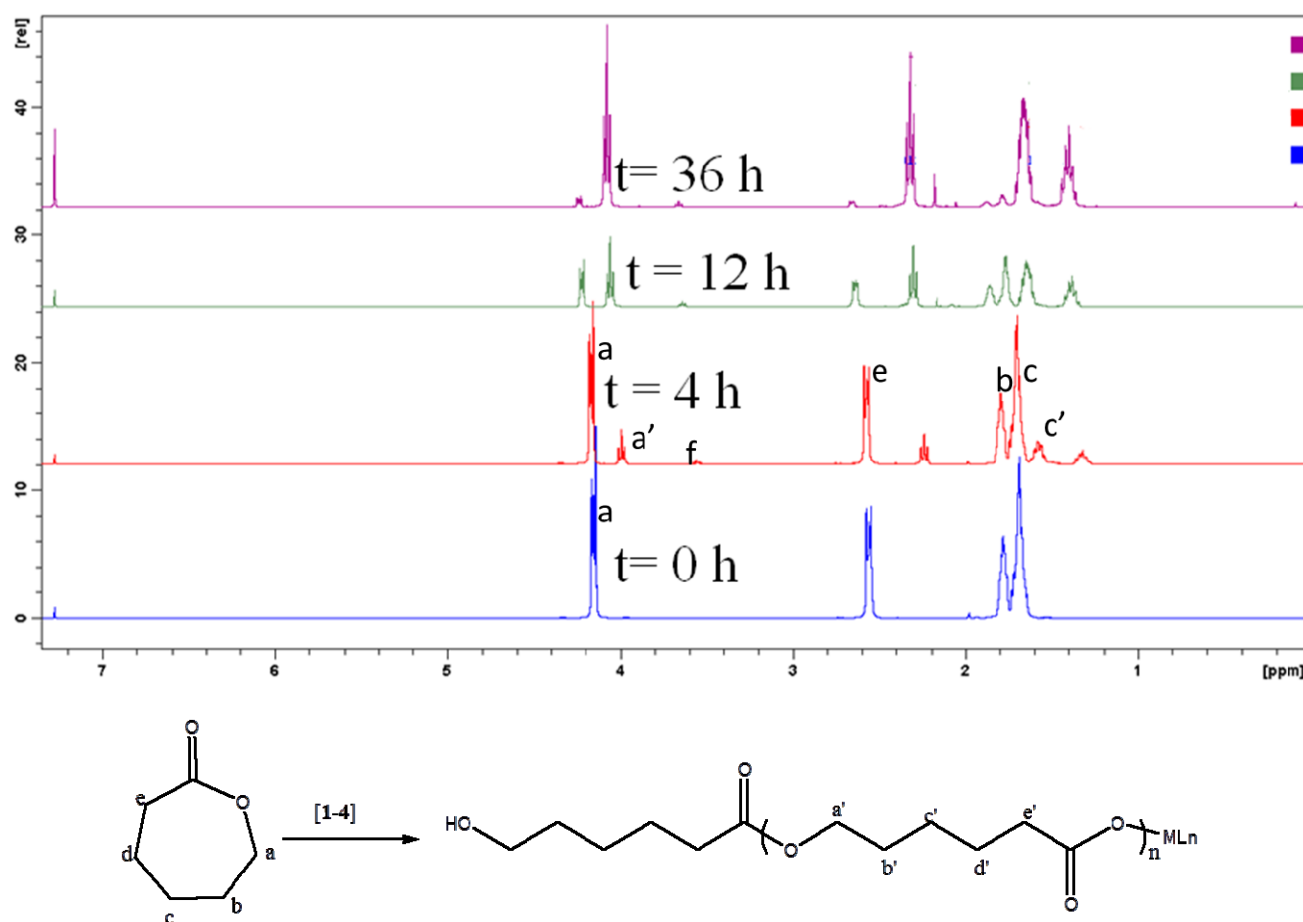


Figure S2: ^1H NMR spectra of PCL showing the rates of conversion of ϵ -CL to PCL with time using catalyst **1**, $M/I = 100$, $[\text{CL}]_0 = 0.01$ mol, $[1] = 0.0001$ mol. The intensities of the O-CH₂ signals at 4.2 ppm for CL and 4.0 ppm for PCL were used to determine the percentage conversion of ϵ -CL to PCL with time.

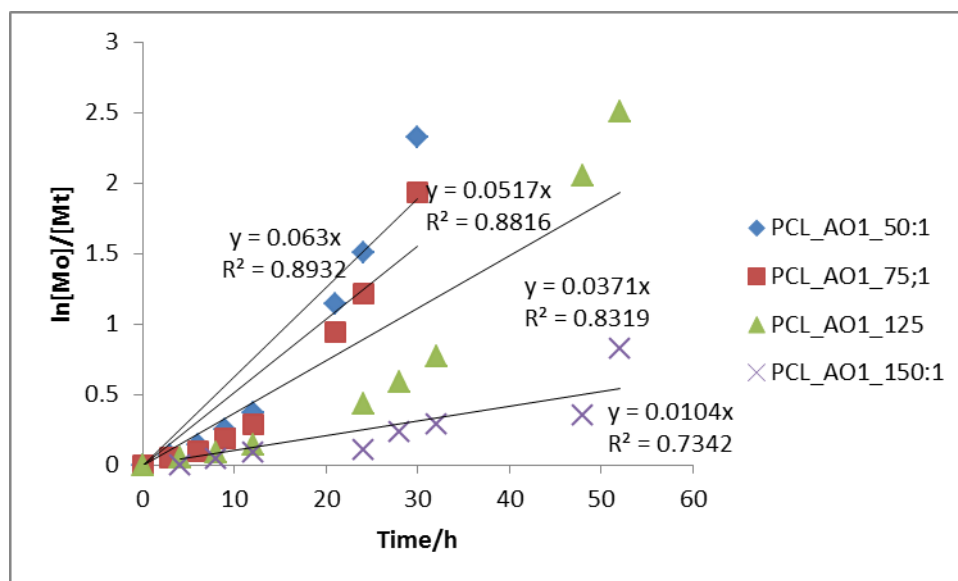


Figure S3: Plot $\ln[M]_0/[M]_t$ vs time for catalyst **1** at different M/I ratios for the determination of order of reaction with respect to initiator **1**. $[M]_0 = 0.01$ mol, temperature 110 °C.

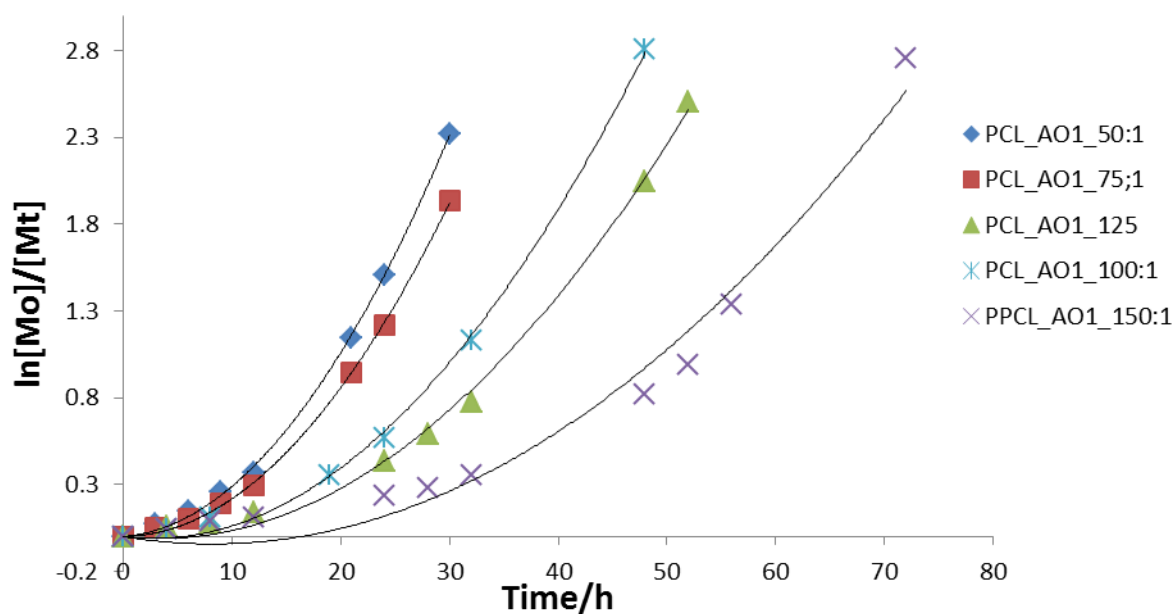


Figure S4: Polymerization kinetics of ϵ -CL at different catalyst/initiator concentrations copper catalyst **2** showing longer induction periods at low catalyst concentrations. The plot was non-linear hence the order of reaction with respect to **2** could not be determined. $[M]_0 = 0.01$ mol, temperature, 110 °C.

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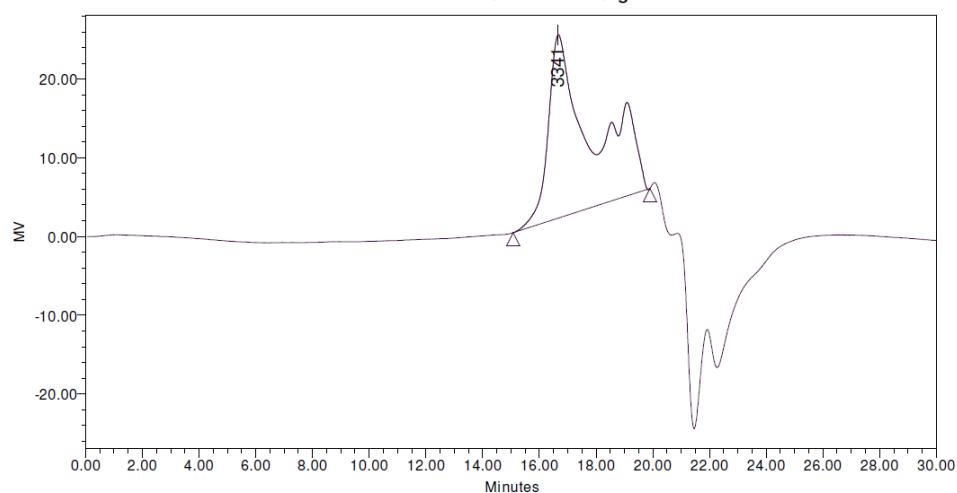
Reported by User: System



SAMPLE INFORMATION

Sample Name:	W3-4	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	2012/10/17 04:19:34 PM
Vial:	11	Acq. Method:	GPC_im_UV254_320
Injection #:	1	Date Processed:	2012/10/18 06:55:08 AM
Injection Volume:	100.00 ul	Channel Name:	410
Run Time:	30.00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name	Sample Set GPC20121017 UKZN

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	677	2121	3341	3781	5174	3.131904	1.782599	2.439615

Broad Unknown by Relative Calibration

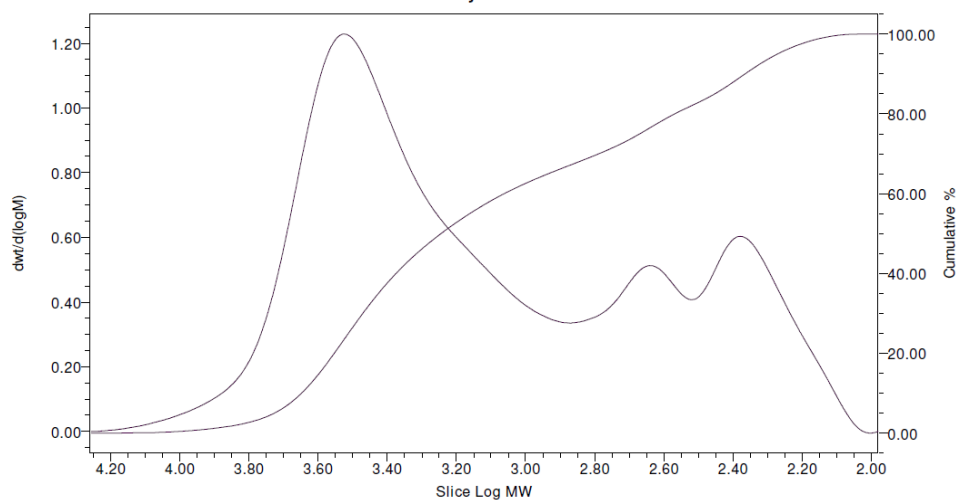


Figure S5: GPC traces of PCL obtained from catalyst **1**, M/I = 100, time, 4 h, temperature, 110 °C showing the broad molecular weight distribution of the polymer obtained.

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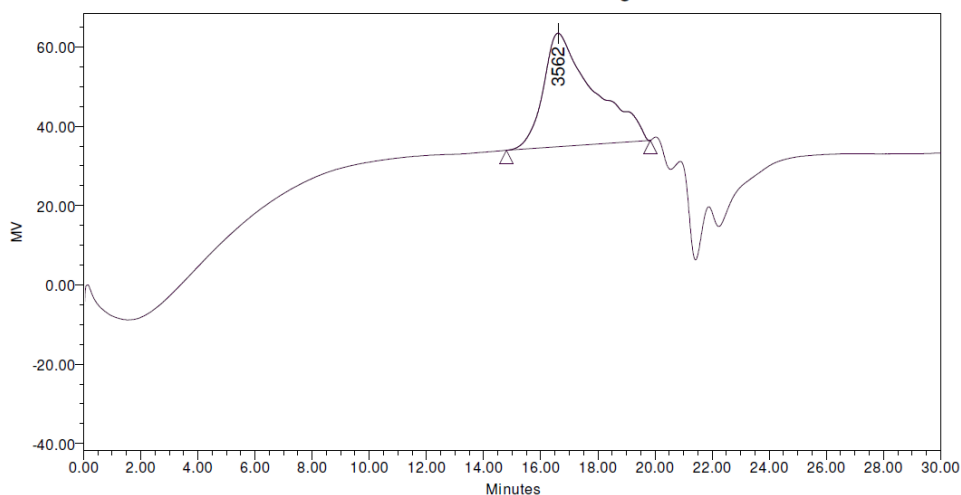
Project Name: GPC2006
Reported by User: System



SAMPLE INFORMATION

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Sample Type:	Broad Unknown	Date Acquired:	2012/10/17 07:31:47 PM
Vial:	17	Acq. Method:	GPC_im_UV254_320
Injection #:	1	Date Processed:	2012/10/18 06:55:08 AM
Injection Volume:	100.00 ul	Channel Name:	410
Run Time:	30.00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name	Sample Set GPC20121017 UKZN

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	969	2749	3562	4911	7018	2.836583	1.786602	2.553387

Broad Unknown by Relative Calibration

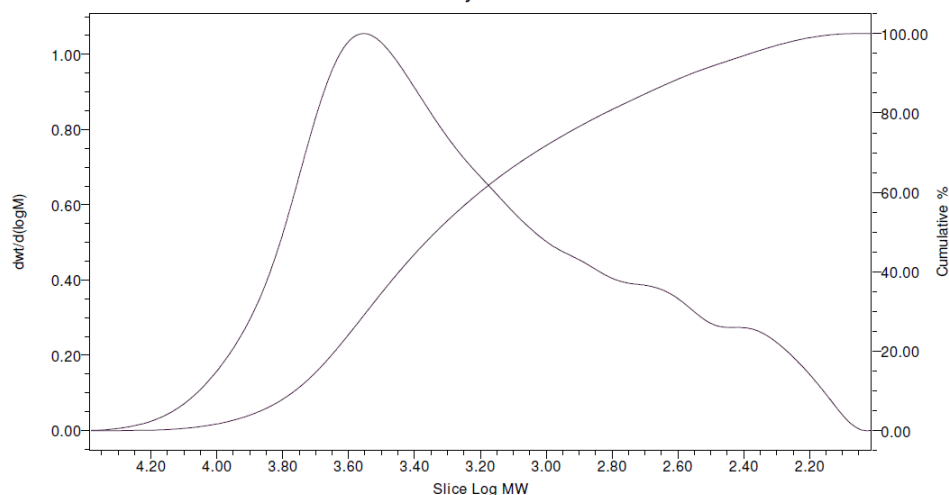


Figure S6: GPC traces of PCL obtained from catalyst **1**, M/I = 100, time, 48 h, temperature, 110 °C showing a broad molecular weight distribution of the polymer obtained.

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Project Name: GPC2006

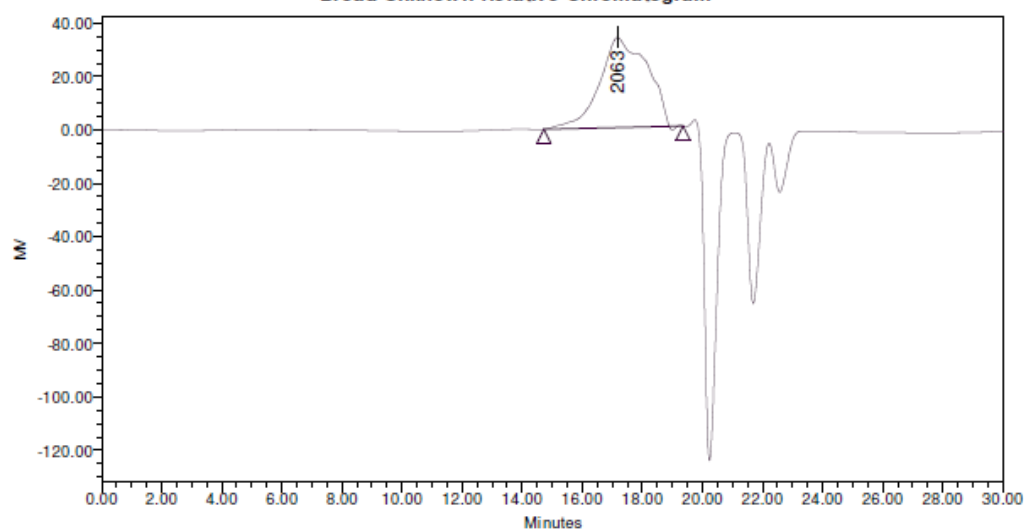
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	PCLT_005	Acquired By:	System
Sample Type:	Broad Unknown	Date Acquired:	2013/03/12 05:35:12 AM
Vial:	23	Acq. Method:	GPC_im_UV254_320
Injection #:	1	Date Processed:	2013/03/12 08:03:00 AM
Injection Volume:	100.00 ul	Channel Name:	410
Run Time:	30.00 Minutes	Channel Desc.:	RI Detector
Column Type:		Sample Set Name	20130312

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		1202	2407	2063	5703	11799	2.002711	2.369697	4.902691

Broad Unknown by Relative Calibration

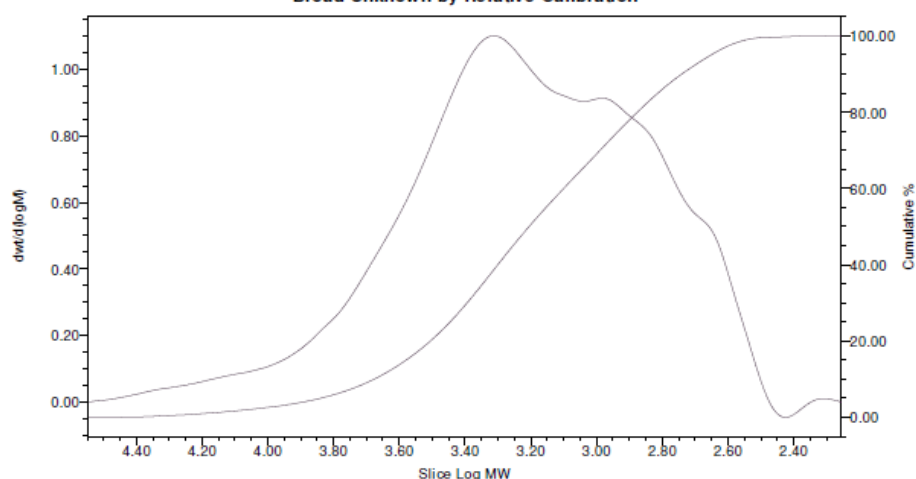


Figure S7: GPC traces of PCL obtained from catalyst **1**, $[CL]_0/[1] = 50$, time, 32 h (99%), solvent, methanol temperature, 110 °C showing a relatively narrow molecular weight distribution of the polymer obtained.