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 [CL]₀/I] = 100, [CL] = 0.01 mol, [cat] = 0.0001 mol.
Figure S2: $^1$H NMR spectra of PCL showing the rates of conversion of ε-CL to PCL with time using catalyst 1, M/I = 100, [CL]$_0$ = 0.01 mol, [1] = 0.0001 mol. The intensities of the O-CH$_2$ 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 $\varepsilon$-CL at different catalysts 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.
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.
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.
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.