Supporting Information to Accompany

Uranium Mediated Ring Opening Polymerization of ε-Caprolactone: A Comparative Study

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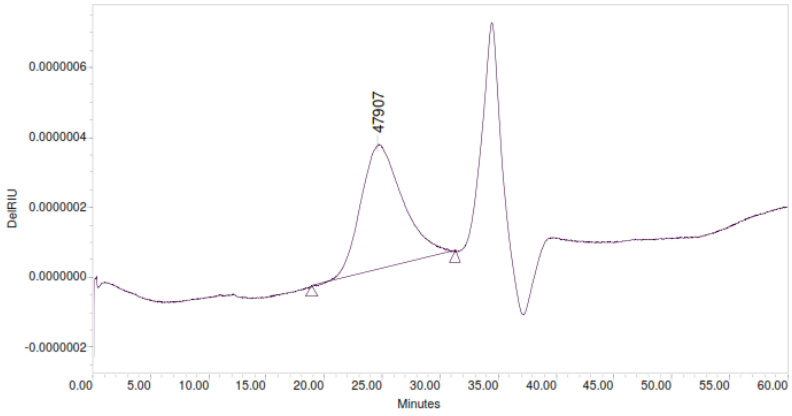
1. General Considerations

All manipulations of air sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a high vacuum line (10-5 torr), or in nitrogen filled Vacuum Atmospheres glovebox with a medium capacity recirculator (1-2 ppm oxygen). Argon and nitrogen were purified by passage through a MnO oxygen removal column and a Davison 4 Å molecular sieve column. Analytically pure solvents were dried and stored with Na/K alloy and degassed by three freeze-pump-thaw cycles prior to use (THF, hexane, toluene, benzene-d_6, toluene-d_8). ε-Caprolactone (Sigma Aldrich) was distilled under reduced pressure from CaH_2 and stored in the glovebox prior to use. NMR spectra were recorded on DPX 200, Avance 300 and Avance 500 Bruker spectrometers. Chemical shifts for ^{1}H NMR and ^{13}C NMR are reported in ppm and referenced using residual proton or carbon signals of the deuterated solvent relative to tetramethylsilane. GPC measurements were carried out on a Waters Breeze system with a styrogel RT column and with THF (HPLC grade, T.G. Baker) as mobile phase at 30 °C. Relative calibration was done with polystyrene standards (Aldrich, 2000 – 1800000 range). M_n values were multiplied by a factor of 0.56 and correlated to actual PCL values.[1]

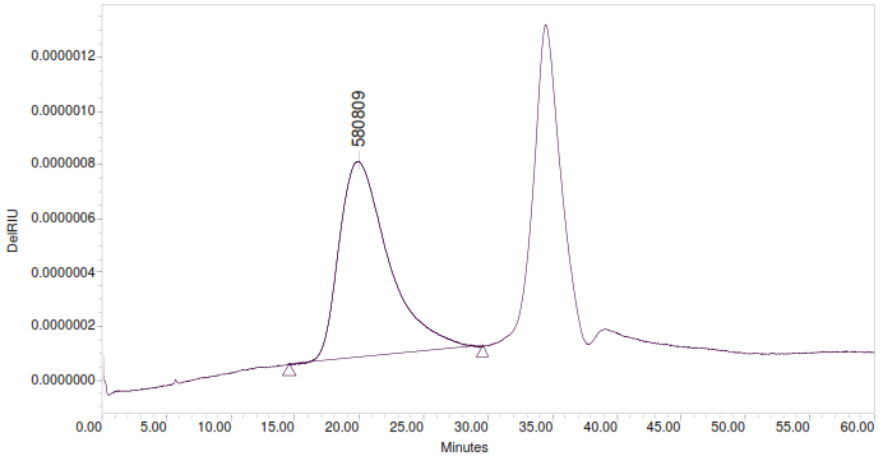
2. GPC results for PCL obtained with complex **3** as catalyst



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		21545	54752	47907	105647	175689	2.541299	1.929529	3.208790

This graph corresponds to the polymer obtained after a polymerization time of 60 minutes at room temperature using complex **3** as initiator and a catalyst to monomer ratio of 1 / 60 000 (entry 3 in Table 1).

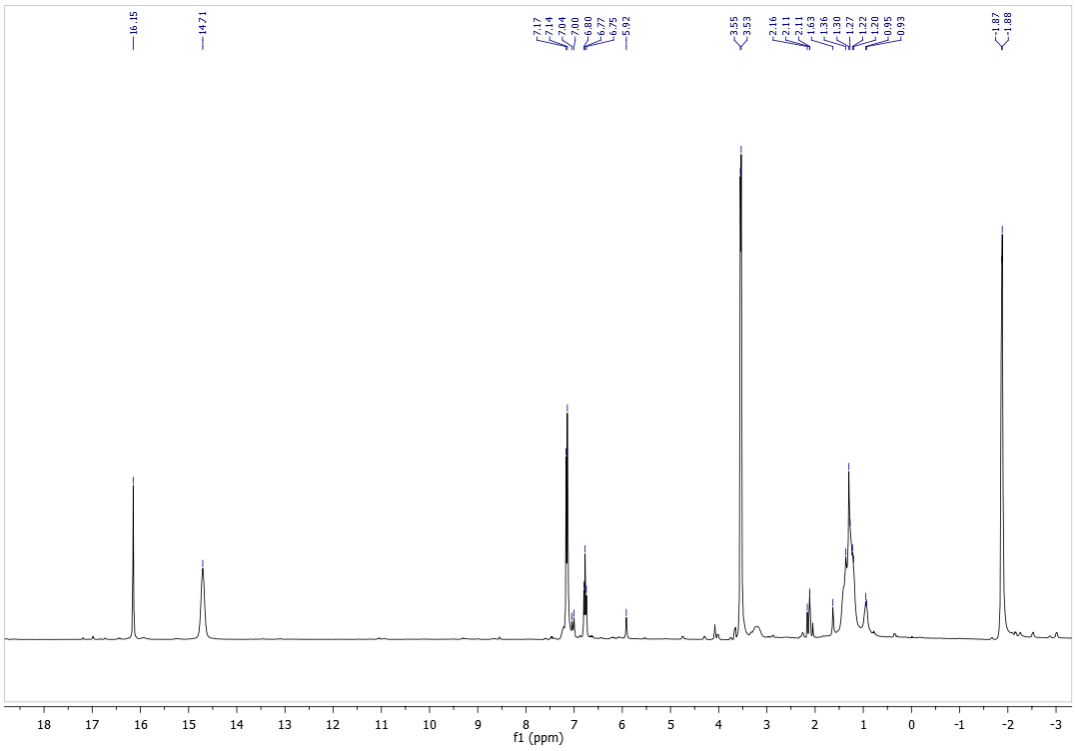


Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		162934	585469	580809	1044297	1482020	3.593284	1.783694	2.531338

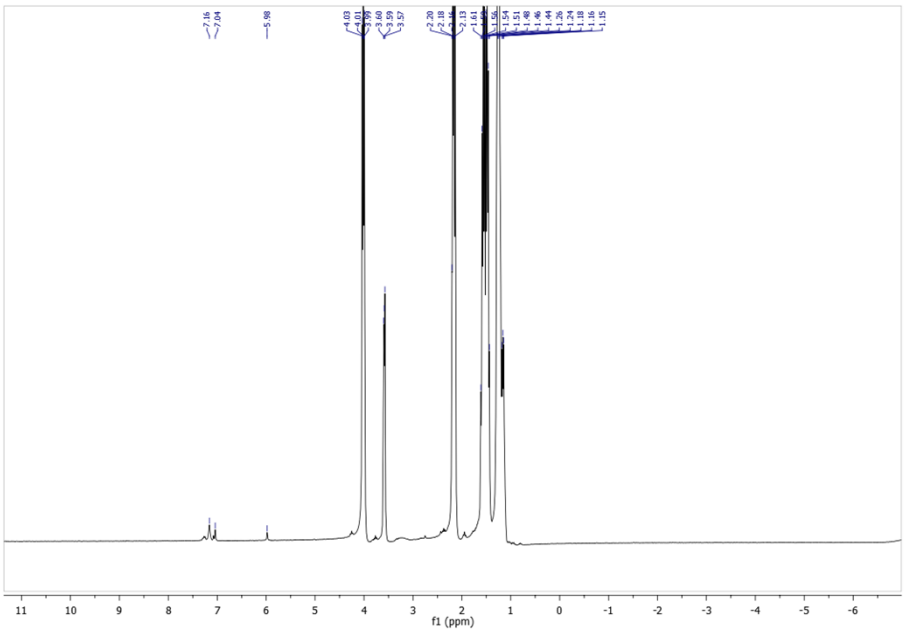
This graph corresponds to the polymer obtained after a polymerization time of 300 minutes at room temperature using complex **3** as initiator and a catalyst to monomer ratio of 1 / 60 000 (entry 5 in Table 1).

3. ^{1}H NMR spectrum for stoichiometric reaction of complex **3** and ε-caprolactone



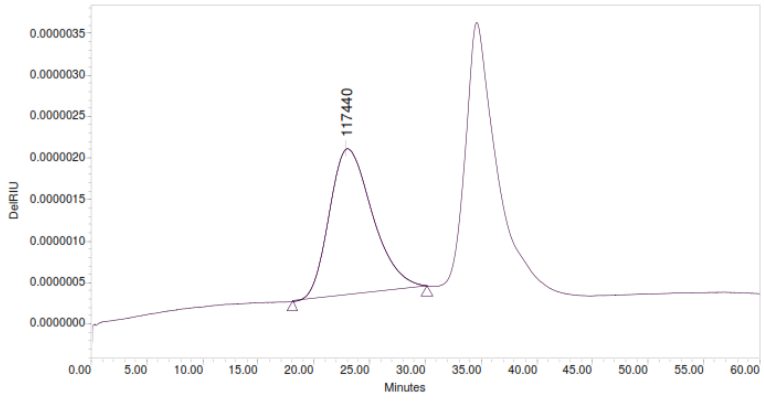
^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ (ppm) -1.88 (d, 24 H, ^{3}J = 5.25 Hz, N-C=C-CH(CH_3)$_2$) 0.93–0.95 (m, 6 H, HN(CH_2CH_3)(CH_3), 1.20-1.36 (m, 29 H, HN(CH_2CH_3)(CH_3) + CH_2 ε-CL + N-C=C-CH(CH_3)$_2$), 1.63 (m, 2 H, CH_2, ε-CL), 2.09-2.11 (m, 3 H, CH_2, ε-CL), 3.21 (brs, 2 H, HN(CH_2CH_3)(CH_3)), 3.53-3.55 (m, 28 H, -C=C-CH(CH_3)2 + CH_2, ε-CL), 5.92 (s, 2 H, CH, ε-CL), 6.75-6.80 (m, 2 H, H_{ar}), 7.14 – 7.17 (m, 6 H, H_{ar}), 14.71 (brs, 4 H, CH=CH), 16.15 (s, 4 H, H_{ar}).

4. In situ ^{1}H NMR spectrum of the polymerization of ε-caprolactone mediated by complex **3**.



^{1}H NMR (C_7D_8, 300 MHz, 25 °C) δ (ppm) 1.15 – 1.56 (m, CH_2, ε-CL), 1.59 – 1.61 (m, CH_2, PCL), 2.13 – 2.30 (m, CH_2, ε-CL and PCL), 3.57 -3.60 (m, CH_2, ε-CL), 3.99 -4.01 (m, CH_2, PCL), 5.98 (br, CH of caprolactonyl).

5. GPC results for PCL obtained with complex **4** as catalyst

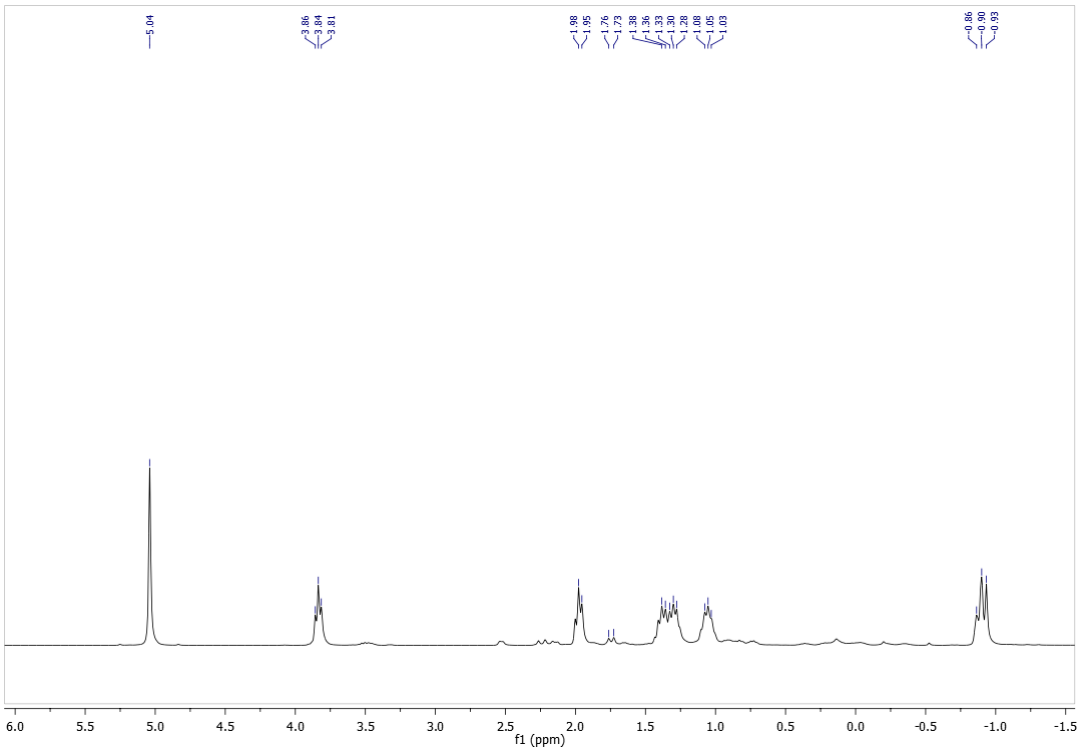


Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		50448	131284	117440	246967	379645	2.602362	1.881165	2.891785

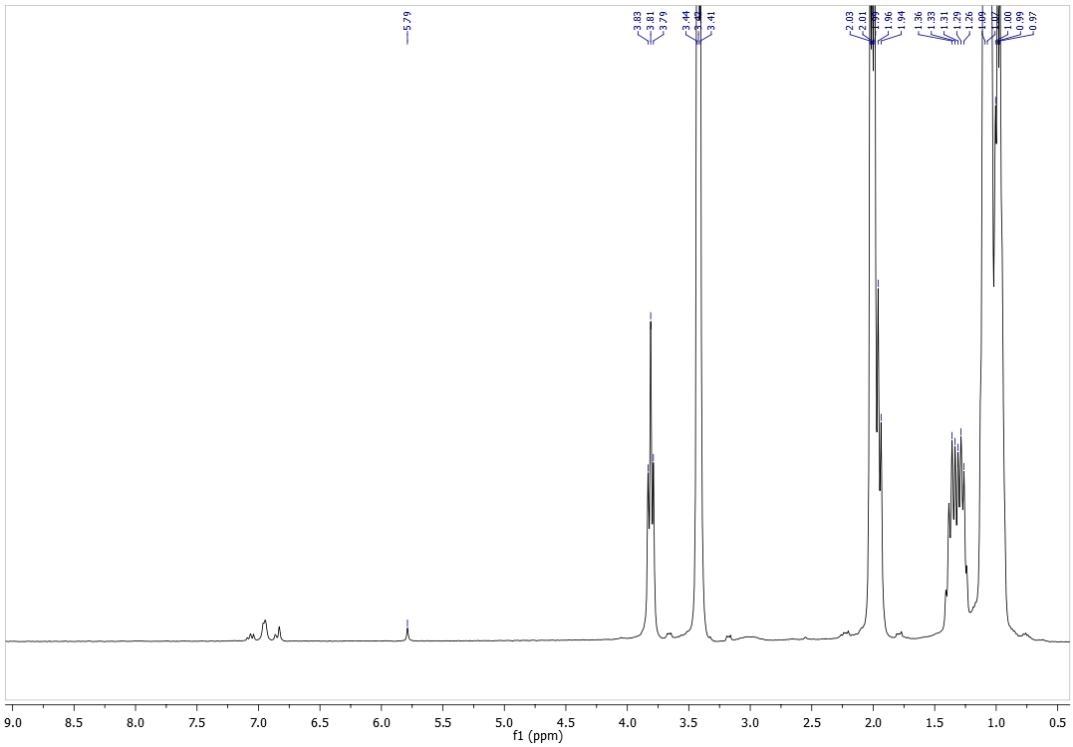
This graph corresponds to the polymer obtained after a polymerization time of 120 minutes at 90°C using complex **4** as initiator and a catalyst to monomer ratio of 1 / 1000 (entry 3 in Table 2).

6. ^{1}H NMR spectrum for the stoichiometric reaction of complex **4** and ε-caprolactone



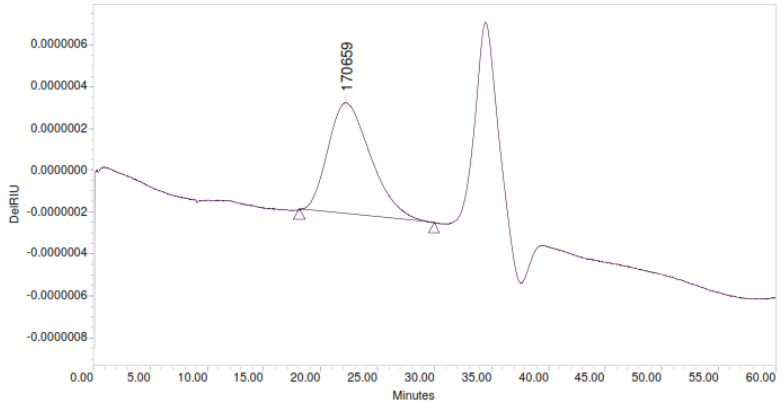
^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ (ppm) -0.93 - -0.86 (m, 36 H, CH_2, ε-CL), 1.01-1.08 (m, 30 H, CH_2, ε-CL), 1.28-1.38 (m, 44 H, CH_2, ε-CL), 1.73 (s, 3 H, N(CH_3)$_2$), 1.74 (s, 3 H, N(CH_3)$_2$), 1.95-1.98 (m, 21 H, CH_2, ε-CL), 5.04 (s, 30 H, C_5(CH_3)$_5$).

7. In situ ^{1}H NMR spectrum of the polymerization of ε-caprolactone mediated by complex **4**.



^{1}H NMR (C_7D_8, 300 MHz, 25 °C) δ (ppm) 0.97 – 1.09 (m, CH_2, ε-CL), 1.26 - 1.36(m, CH_2, PCL), 1.94 – 2.03 (m, CH_2, ε-CL and PCL), 3.41 – 3.44 (m, CH_2, ε-CL), 3.79 – 3.83 (m, CH_2, PCL), 5.79 (br, CH, caprolactonyl).

8. GPC results for PCL obtained with catalyst **5**

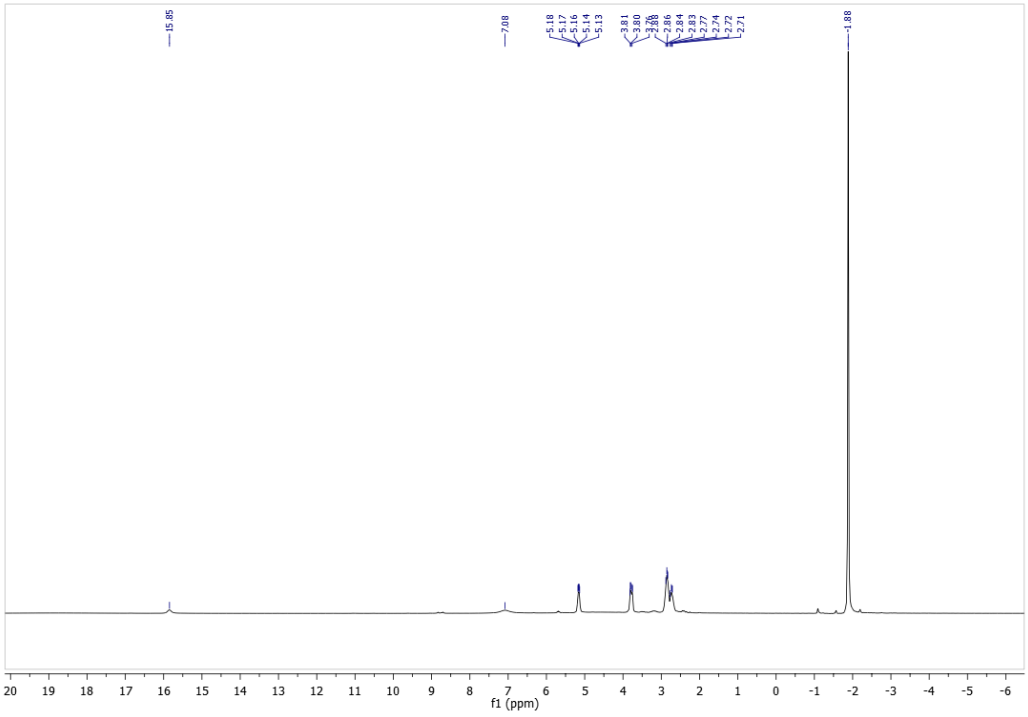


Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		76373	194117	170659	350698	516780	2.541711	1.806631	2.662208

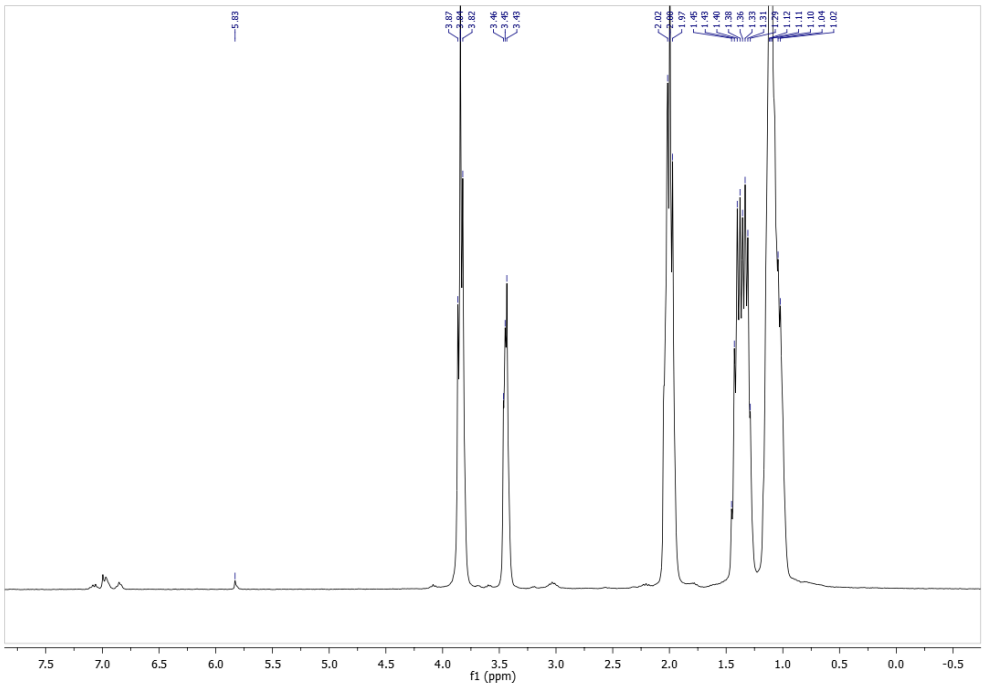
This graph corresponds to the polymer obtained after a polymerization time of 840 minutes at 90°C using complex **5** as initiator and a catalyst to monomer ratio of 1 / 1000 (entry 5 in Table 3).

9. ^{1}H NMR spectrum for the stoichiometric reaction of complex **5** and ε-caprolactone



^{1}H NMR (C_6D_6, 300 MHz, 25 °C) δ (ppm) -1.89 (s, 30 H, $C_5(CH_3)_5$), 2.71-2.88 (m, 33 H, CH_2, ε-CL), 3.76-3.81 (m, CH_2, ε-CL), 5.13-5.18 (m, CH_2, ε-CL), 7.08 (brs, 6 H, H_{ar}), 15.85 (brs, 3 H, CH_3).

10. In situ ^{1}H NMR spectrum of the ROP of ε-caprolactone mediated by complex **5**.



^{1}H NMR (C_7D_8, 300 MHz, 25 °C) δ (ppm) 1.02 – 1.29 (m, CH_2, ε-CL), 1.31 – 1.45 (m, CH_2, PCL), 1.97 – 2.02 (m, CH_2, ε-CL and PCL), 3.43 – 3.46 (m, CH_2, ε-CL), 3.82 – 3.87 (m, CH_2, PCL), 5.83 (br, CH caprolactonyl).

1. A. Duda, Z. Florjanczyk, A. Hofman, S. Slomkowski, S. Penczek, *Macromolecules*, 1990, **23**, 1640-1646.