

**Mono-, di- and tetra-zinc complexes derived from an amino-
benzotriazole phenolate ligand containing a bulkier *N*-alkyl pendant
arm: synthesis, structure and catalysis for ring-opening
polymerization of cyclic esters**

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Fig. S1 ORTEP drawing of **1** with probability ellipsoids drawn at the 40% level. All hydrogen atoms except H1 are omitted for clarity.

Fig. S2 Polymerization of ϵ -CL catalysed by **2** in the presence of 9-AnOH. The relationship between Mn(■)/(PDI(□)) of polymer and the initial mole ratio $[\epsilon\text{-CL}]_0/[\text{Zn}]_0$ is shown.

Fig. S3 ¹H NMR spectrum of PCL-25 (Table 1, entry 5) initiated by **3**.

Fig. S4 Polymerization of β -BL catalysed by **2** in presence of 9-AnOH. The relationship between Mn(■)/(PDI(□)) of polymer and the initial mole ratio $[\beta\text{-BL}]_0/[\text{Zn}]_0$ is shown.

Fig. S5 Polymerization of β -BL catalysed by **3**. The relationship between Mn(■)/(PDI(□)) of polymer and the initial mole ratio $[\beta\text{-BL}]_0/[\text{Zn}]_0$ is shown.

Fig. S6 ¹H NMR spectrum of PHB-25 (Table 2, entry 1) initiated by **2** in the presence of 9-AnOH.

Fig. S7 ¹H NMR spectrum of PHB-25 (Table 2, entry 5) initiated by **3**.

Table S1 Crystallographic data of complexes **1-5**

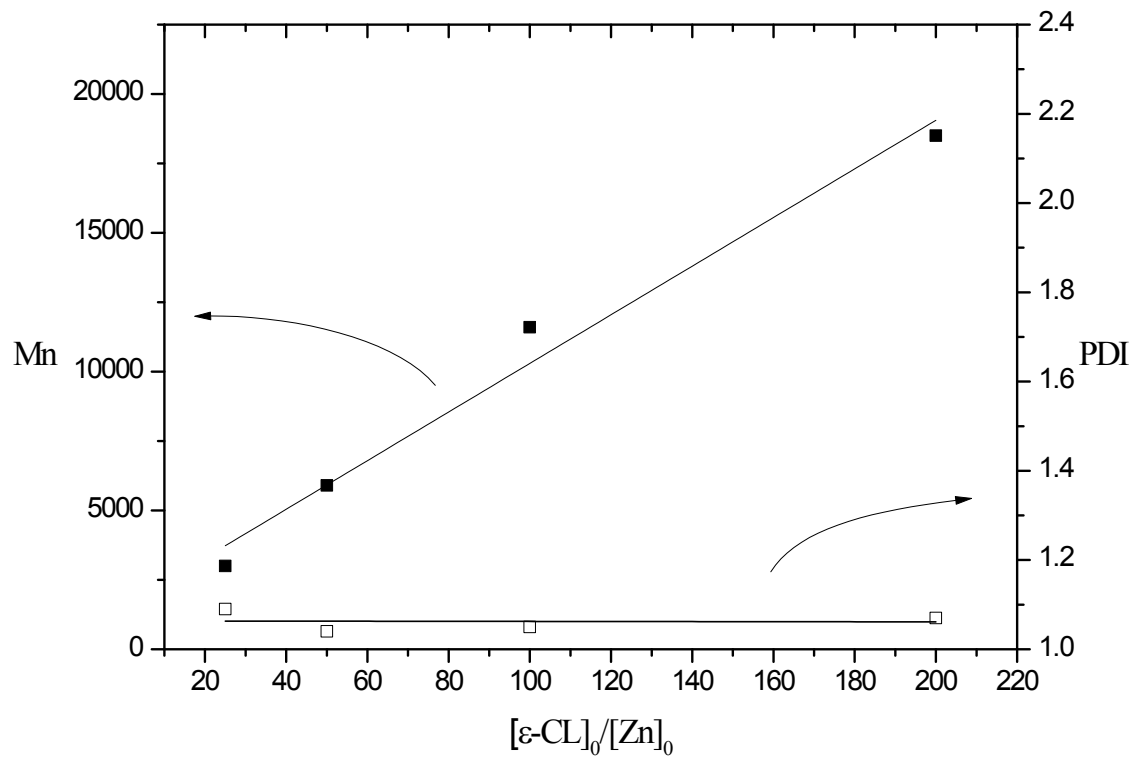


Fig. S2 Polymerization of ϵ -CL catalysed by **2** in the presence of 9-AnOH. The relationship between Mn(■)/(PDI(□)) of polymer and the initial mole ratio $[\epsilon\text{-CL}]_0/[\text{Zn}]_0$ is shown.

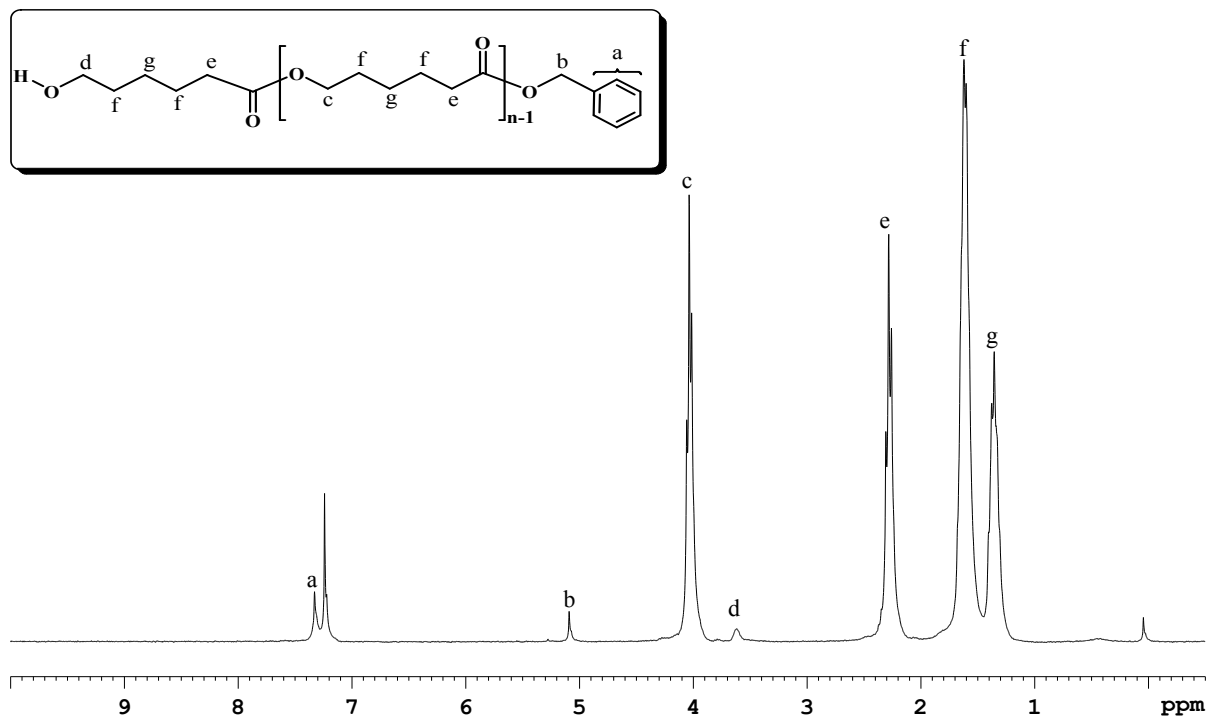


Fig. S3 ^1H NMR spectrum of PCL-25 (Table 1, entry 5) initiated by **3**.

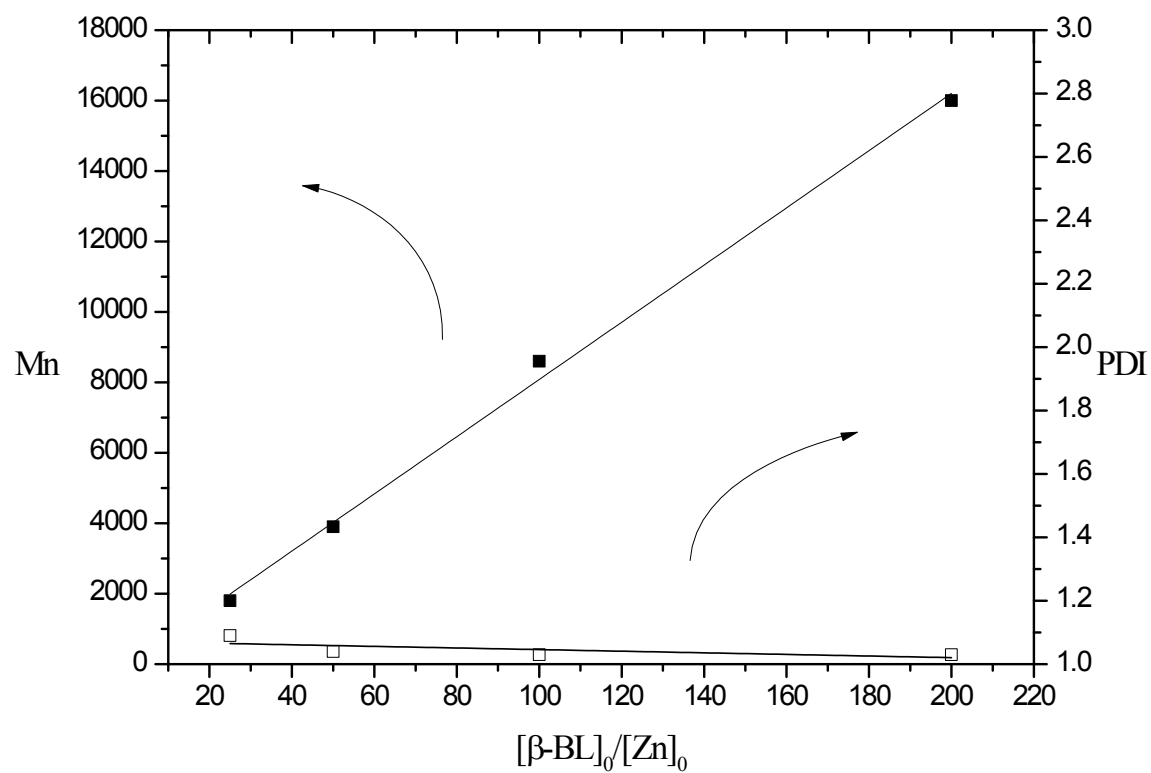


Fig. S4 Polymerization of β -BL catalysed by **2** in presence of 9-AnOH. The relationship between Mn(■)/(PDI(□)) of polymer and the initial mole ratio $[\beta\text{-BL}]_0/[\text{Zn}]_0$ is shown.

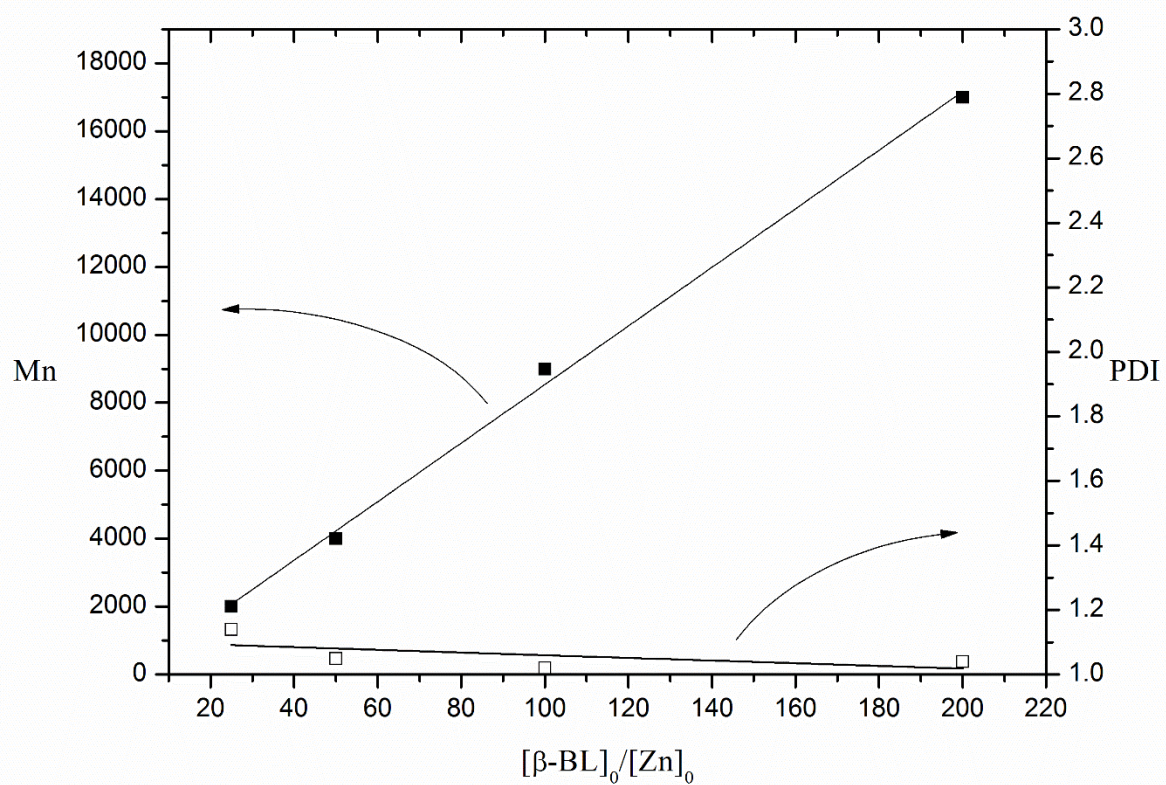


Fig. S5 Polymerization of β -BL catalysed by **3**. The relationship between Mn(■)/(PDI(□)) of polymer and the initial mole ratio $[\beta\text{-BL}]_0/[\text{Zn}]_0$ is shown.

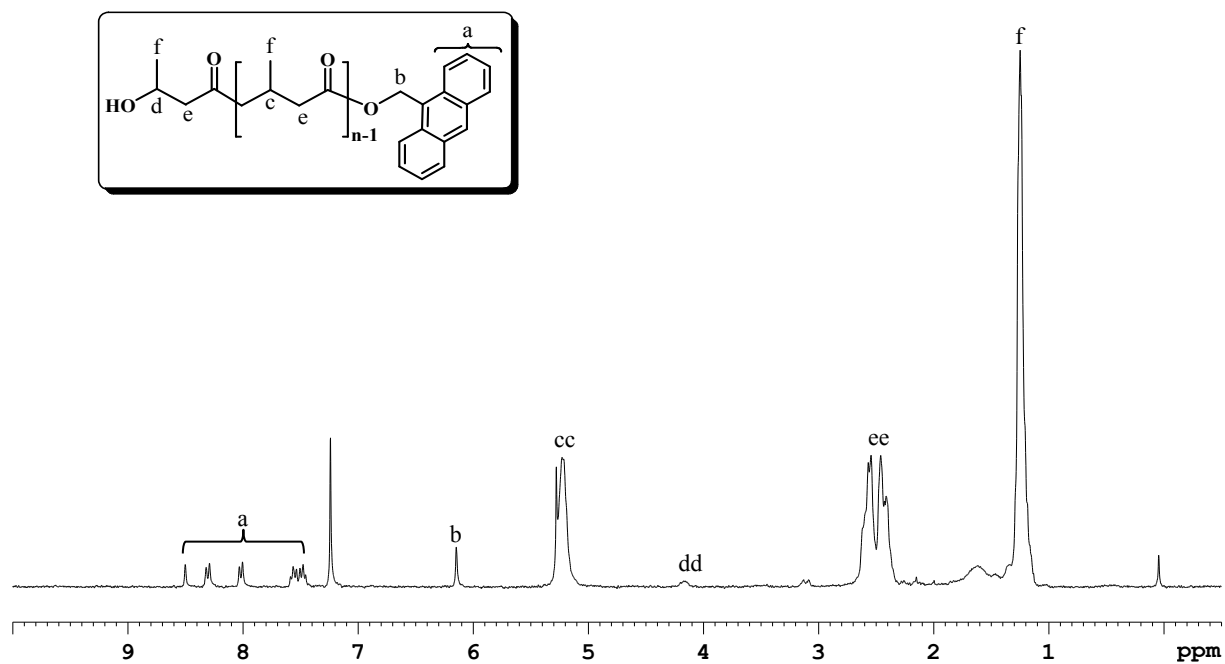


Fig. S6 ¹H NMR spectrum of PHB-25 (Table 2, entry 1) initiated by **2** in the presence of 9-AnOH.

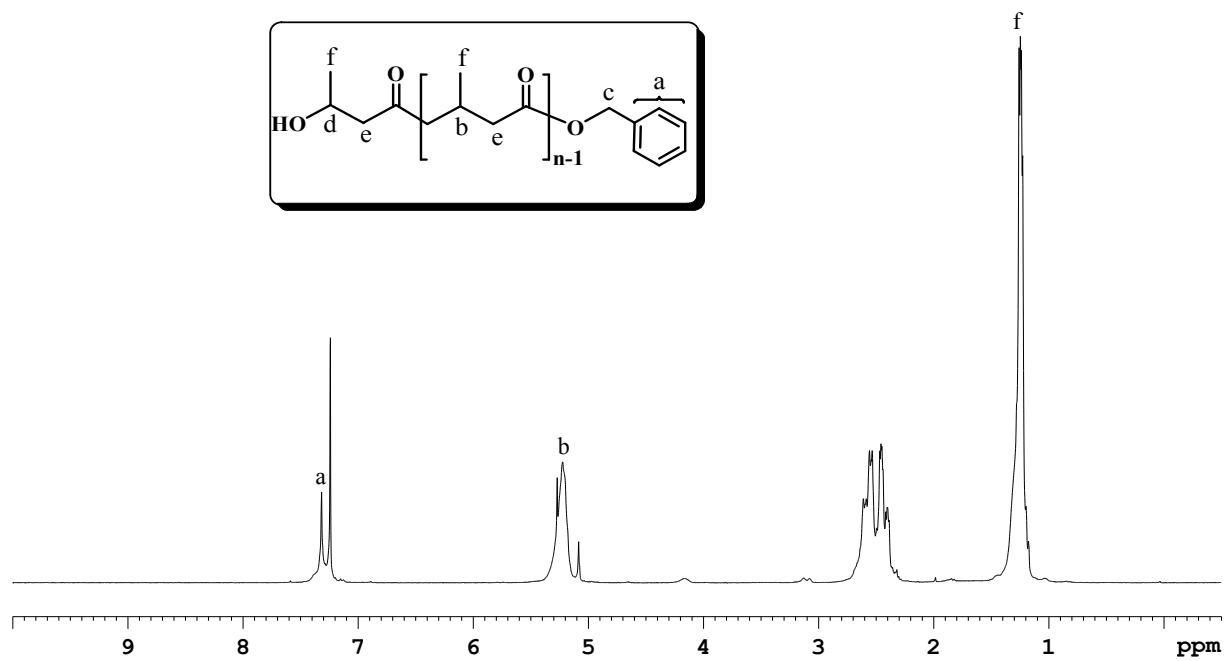


Fig. S7 ¹H NMR spectrum of PHB-25 (Table 2, entry 5) initiated by **3**.

Table S1 Crystallographic data of complexes **1-5**

	1	2	3	4	5
Formula	C ₂₇ H ₄₀ N ₄ O	C ₅₈ H ₈₈ N ₈ O ₂ Zn ₂	C ₁₃₆ H ₁₇₆ N ₁₆ O ₈ Zn ₄	C ₈₂ H ₁₀₂ N ₁₂ O ₄ Zn ₂	C ₆₄ H ₈₈ N ₁₀ O ₂ Zn
Formula weight	436.63	1060.10	2424.49	1450.50	1094.81
Temp (K)	173(2)	100(2)	100(2)	150(2)	100(2)
Crystal system	Monoclinic	Triclinic	Tetragonal	Monoclinic	Triclinic
Space group	<i>C 2/c</i>	<i>P -1</i>	<i>I -4 2 d</i>	<i>C 2/c</i>	<i>P -1</i>
a (Å)	12.1385(2)	10.8086(3)	29.5765 (4)	18.5857(7)	12.4319(2)
b (Å)	10.0974(2)	16.7967(4)	29.5765 (4)	15.3783(6)	15.4687(2)
c (Å)	41.5355(7)	18.1461(5)	16.4015 (2)	29.9998(10)	17.8328(3)
α (deg)	90	66.4510(10)	90	90	68.3750(10)
β (deg)	92.4890(10)	74.5920(10)	90	98.205(3)	88.3680(10)
γ (deg)	90	76.1620(10)	90	90	76.6330(10)
$V(\text{Å}^3)$	5086.09(16)	2878.33(13)	14347.5 (3)	8486.7(5)	3095.50(8)
Z	8	2	4	4	2
$D_{\text{calc}}(\text{Mg/m}^3)$	1.140	1.223	1.122	1.135	1.175
μ (Mo K α)(mm ⁻¹)	0.070	0.880	0.716	0.617	0.447
$F(000)$	1904	1136	5152	3080	1176
Reflections collected	23327	51272	68891	34040	56113
No. of parameters	299	651	403	459	745
Indep. reflns (R_{int})	6327(0.0227)	14206(0.0249)	8967 (0.0701)	9185(0.0287)	15357(0.0886)
$R1[I > 2\sigma(I)]$	0.0457	0.0307	0.0444	0.0456	0.0469
$wR2 [I > 2\sigma(I)]$	0.1151	0.0775	0.0995	0.1617	0.1292
Goodness-of-fit on F^2	1.054	1.022	1.007	1.038	1.027