

Supplementary Information

Improved Reactivity in the Ring-Opening Polymerization of ϵ -Caprolactone with a Trinuclear Titanium(IV) Oxochloroneopentoxide as Initiator

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Table S1. Crystal and structure refinement data for $[\text{Ti}_3(\mu_3\text{-O})(\mu_3\text{-Cl})(\mu\text{-ONep})_3(\text{ONep})_6]\cdot\text{C}_7\text{H}_8$ (complex **B**)

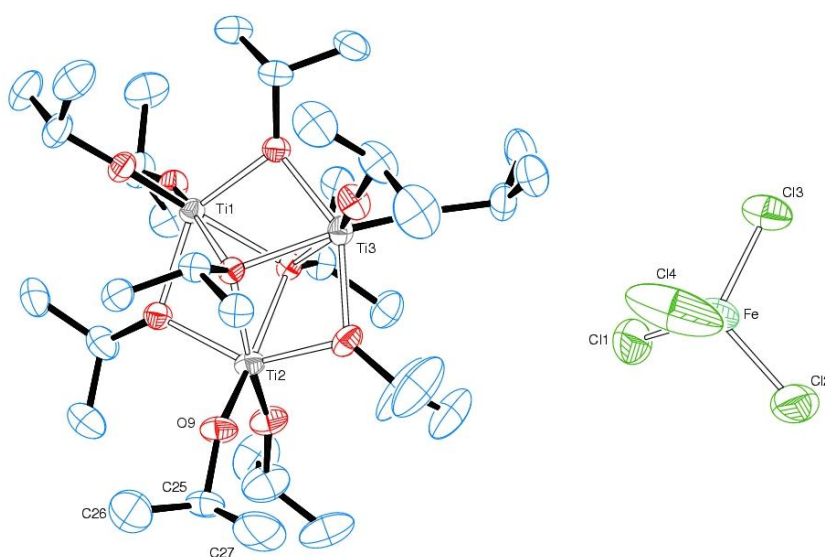
	B
Empirical formula	$\text{C}_{45}\text{H}_{99}\text{ClO}_{10}\text{Ti}_3\cdot\text{C}_7\text{H}_8$
Formula weight / (g mol^{-1})	1071.52
Temperature / K	100(2)
Crystal system	monoclinic
Space group	Pn (No.7)
a / Å	15.2819(9)
b / Å	13.4787(8)
c / Å	15.4311(10)
β / degree	97.214(2)
V / Å ³	3153.3(3)
Z	2
μ / mm^{-1}	0.460
θ_{max}	25.5
Reflections collected	113847
Independent reflections	11747
R_{int}	0.082
Reflections with $I > 2\sigma_1$	11571
R_1 ($I > 2\sigma_1$) ^a	0.038
w R_2 ($I > 2\sigma_1$) ^a	0.099
R_1 all data ^a	0.039
w R_2 all data ^a	0.100
Goodness-of-fit on F^2	1.049
Largest diff. peak and hole / $\text{e}\text{Å}^{-3}$	0.64, -0.31

^aAs defined by the SHELXL program.¹

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Table S2. Selected bond (Å) and angles (°) for $[\text{Ti}_3(\mu_3\text{-O})(\mu_3\text{-Cl})(\mu\text{-ONep})_3(\text{ONep})_6]$ in **B**

Ti(1)···Ti(3)	3.0375(8)	Ti(1)-Ti(3)-Ti(2)	60.10(2)
Ti(1)···Ti(2)	3.0487(9)	O(5)-Ti(1)-O(99)	160.89(11)
Ti(2)···Ti(3)	3.0504(9)	O(8)-Ti(1)-O(4)	142.01(10)
Ti(1)-O(4)	2.040(3)	O(7)-Ti(1)-Cl(4)	175.04(10)
Ti(1)-O(5)	1.794(3)	O(99)-Ti(1)-Cl(4)	76.74(7)
Ti(1)-O(7)	1.774(3)	O(3)-Ti(2)-O(99)	157.59(12)
Ti(1)-O(8)	2.033(3)	O(4)-Ti(2)-O(9)	141.54(10)
Ti(1)-O(99)	1.943(2)	O(2)-Ti(2)-Cl(4)	176.94(10)
Ti(1)-Cl(4)	2.7540(10)	O(99)-Ti(2)-Cl(4)	75.01(7)
Ti(2)-O(2)	1.788(3)	O(1)-Ti(3)-O(99)	159.46(12)
Ti(2)-O(3)	1.794(3)	O(8)-Ti(3)-O(9)	142.09(10)
Ti(2)-O(4)	2.027(2)	O(6)-Ti(3)-Cl(4)	176.38(10)
Ti(2)-O(9)	2.038(3)	O(99)-Ti(3)-Cl(4)	75.89(8)
Ti(2)-O(99)	1.936(3)	Ti(2)-O(4)-Ti(1)	97.11(10)
Ti(2)-Cl(4)	2.8264(10)	Ti(1)-O(8)-Ti(3)	96.67(10)
Ti(3)-O(1)	1.792(3)	Ti(2)-O(9)-Ti(3)	96.90(11)
Ti(3)-O(6)	1.779(3)	Ti(2)-O(99)-Ti(3)	103.87(12)
Ti(3)-O(8)	2.033(2)	Ti(2)-O(99)-Ti(1)	103.61(11)
Ti(3)-O(9)	2.038(3)	Ti(3)-O(99)-Ti(1)	103.01(11)
Ti(3)-O(99)	1.938(2)	Ti(1)-Cl(4)-Ti(3)	66.43(3)
Ti(3)-Cl(4)	2.7906(10)	Ti(1)-Cl(4)-Ti(2)	66.21(3)
Ti(3)-Ti(1)-Ti(2)	60.16(2)	Ti(3)-Cl(4)-Ti(2)	65.78(3)
Ti(1)-Ti(2)-Ti(3)	59.74(2)		

**Figure S1.** ORTEP representation of $[\text{Ti}_3(\mu_3\text{-OPr})_2(\mu\text{-OPr})_3(\text{OPr})_6][\text{FeCl}_4]$ (**A**).²

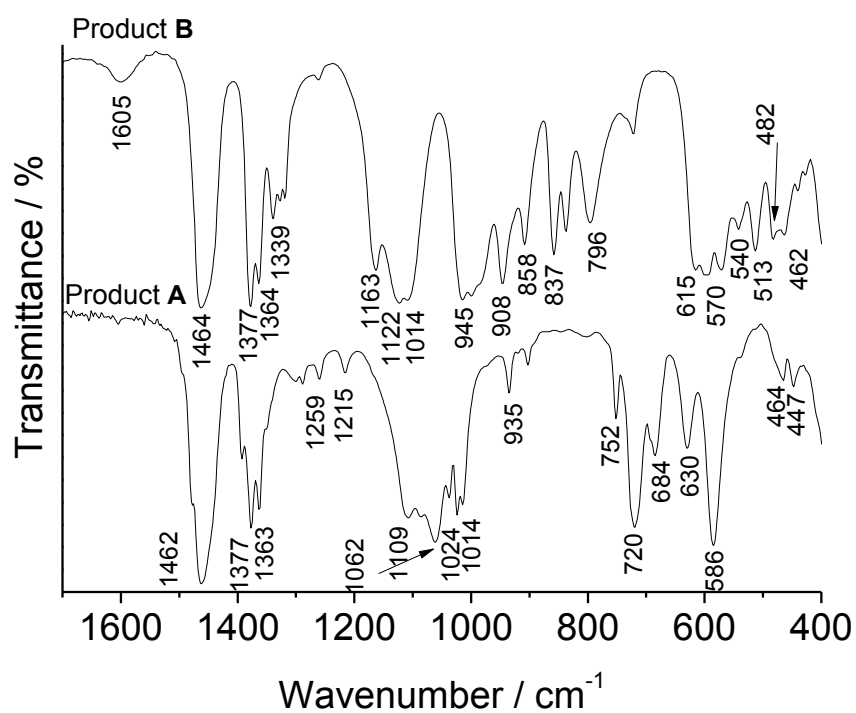
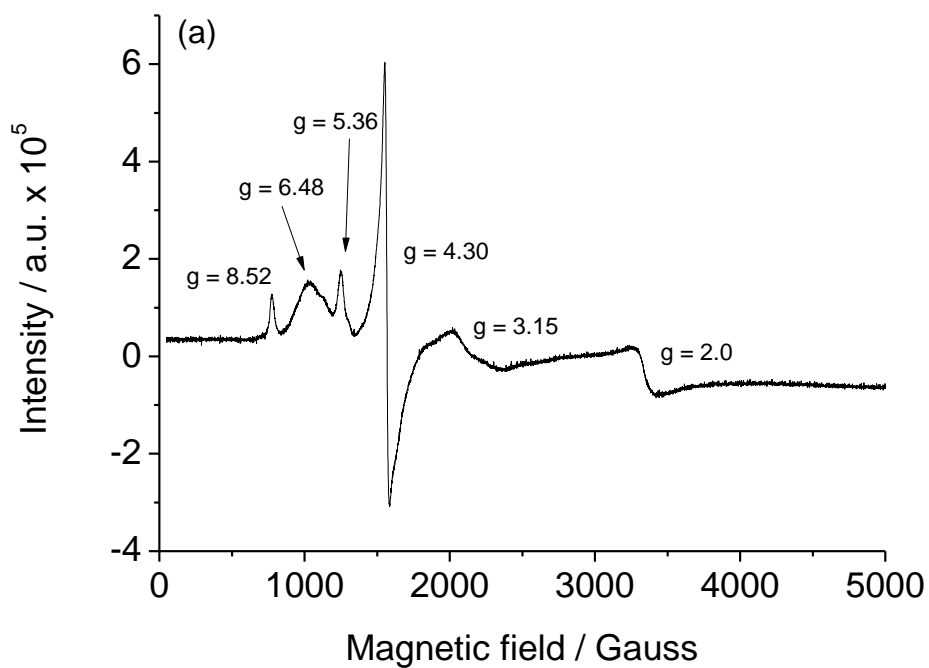


Figure S2. FTIR spectra registered in Nujol mulls for $[\text{Ti}_3(\text{O}^i\text{Pr})_{11}][\text{FeCl}_4]$ (A) and $[\text{Ti}_3\text{OCl}(\text{ONep})_9]$ (B).



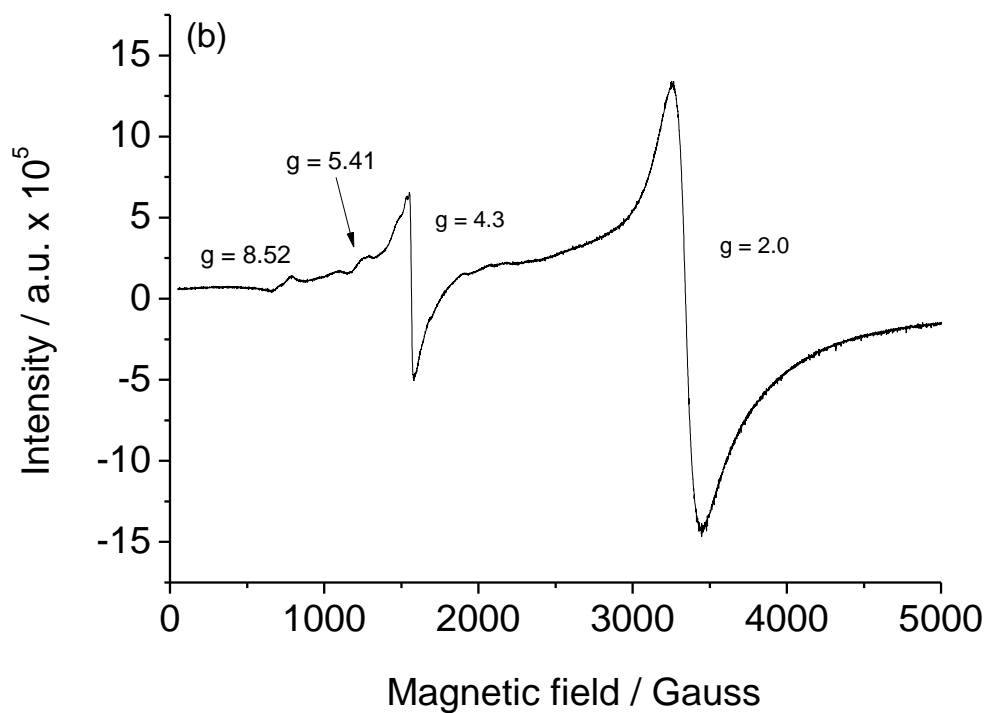


Figure S3. (a) EPR spectrum of the viscous yellow oil in toluene solution (77 K); (b) EPR spectrum of the mixture of C and D in THF solution (77 K).

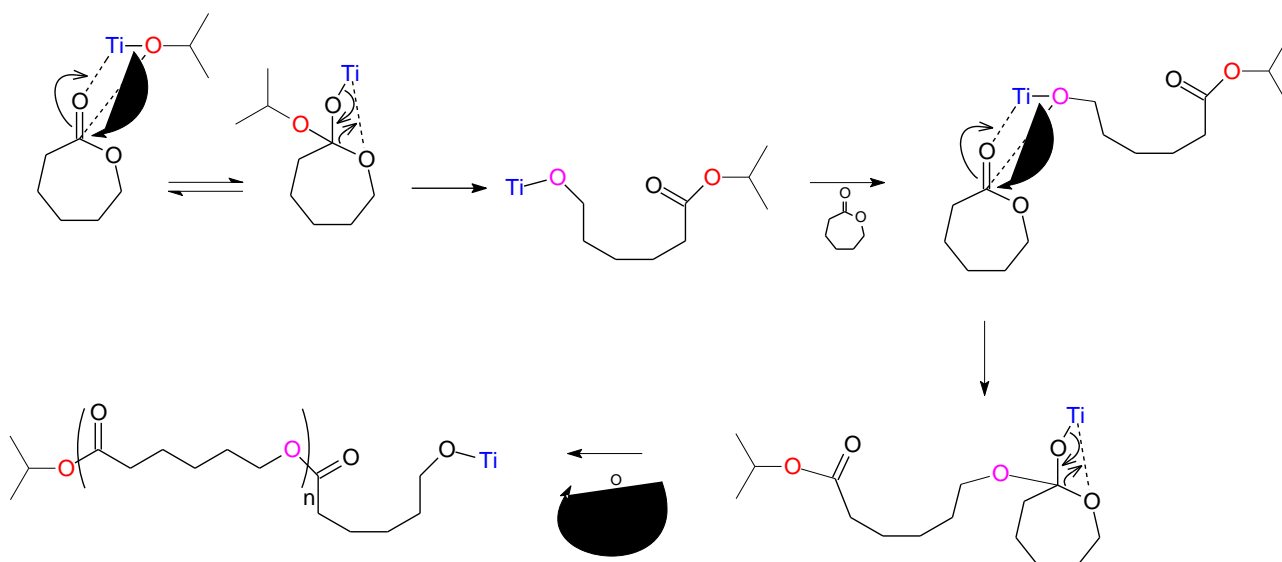


Figure S4. Representation of the coordination-insertion mechanism of the ROP reaction initiated by alkoxides (adapted).³

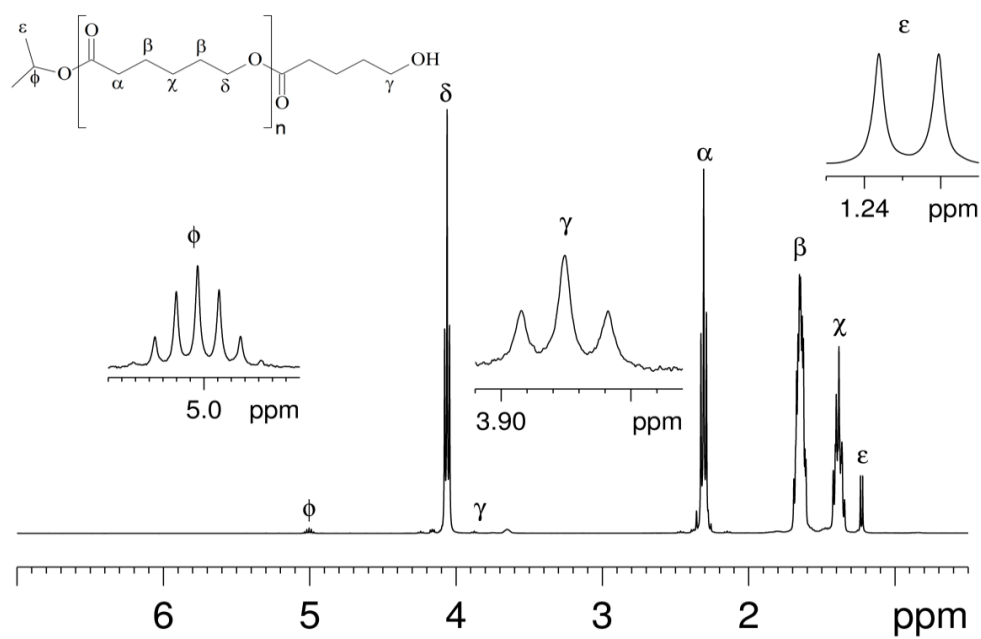
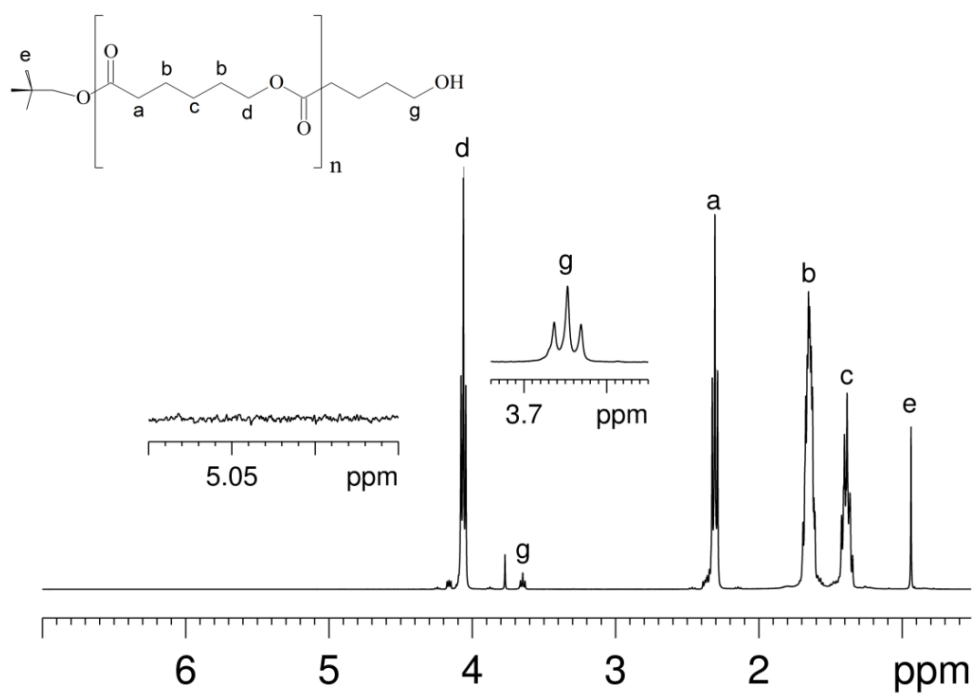


Figure S5. ¹H NMR (440 MHz, CDCl₃) spectra of representative PCL samples obtained with **B** (top) and **A** (bottom) as initiators.

The calculation of molecular weights (M_n) for the PCL samples by ^1H NMR spectroscopy employs the intensity ratio between the signals given by the repetitive CH_2 groups in the polymer chain and the terminal end group. In the case of the PCL obtained from **A**, this ratio involves the terminal isopropyl group at 5.0 ppm, $(\text{CH}_3)_2\text{CH}$, and the methylene signals at 2.34 ppm multiplied by the monomer mass, giving the $M_{n(\text{H NMR})}$ values.⁴ The PCL samples produced from $[\text{Ti}_3(\mu_3\text{-O})(\mu_3\text{-Cl})(\mu\text{-ONep})_3(\text{ONep})_6]$ (**B**), in turn, show a different terminal end group (neopentyl), according to the coordination-insertion mechanism. Thus, the methodology to calculate $M_{n(\text{H NMR})}$ for samples produced with **B** was adapted from that already described in the literature.⁴ In this case, we employed the ratio between the signal intensities at 0.94 ppm, $(\text{CH}_3)_3\text{CCH}_2$ - (terminal neopentyl group), and the methylene groups at 4.09 ppm, multiplied by 114.14 (monomer molar mass, equation S1).

$$M_n = \frac{I_{(4.09 \text{ ppm})}}{I_{(0.94 \text{ ppm})}} \times 114.14 \quad (\text{S1})$$

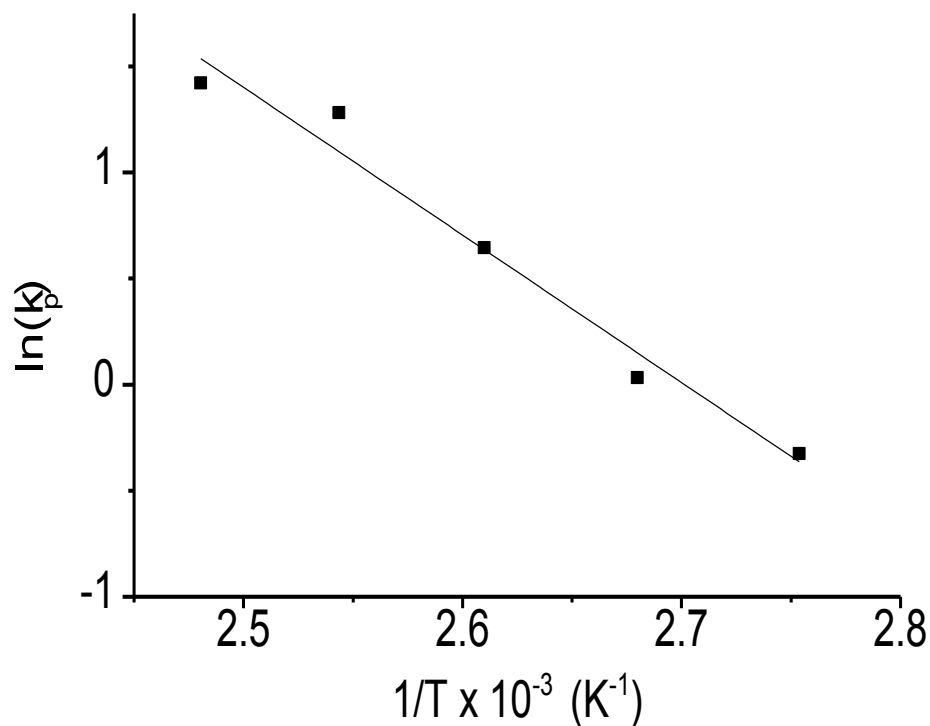


Figure S6. Plot of $\ln(k_p)$ vs. $1/T$ obtained from the kinetic data gathered for **B**.

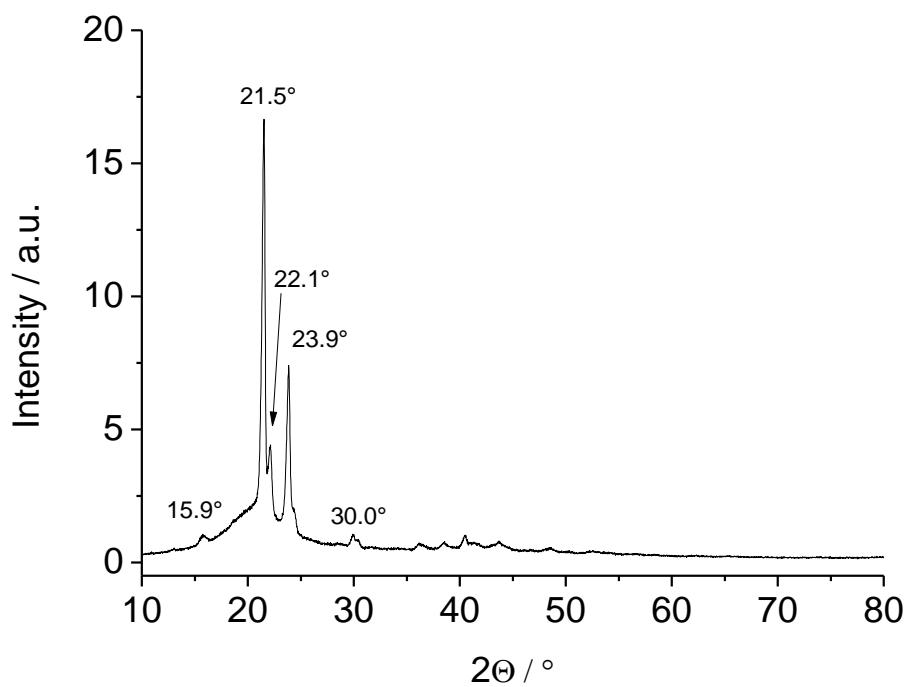


Figure S7. Powder X-ray diffraction pattern of a representative poly(ϵ -caprolactone) sample obtained with **B** as initiator.

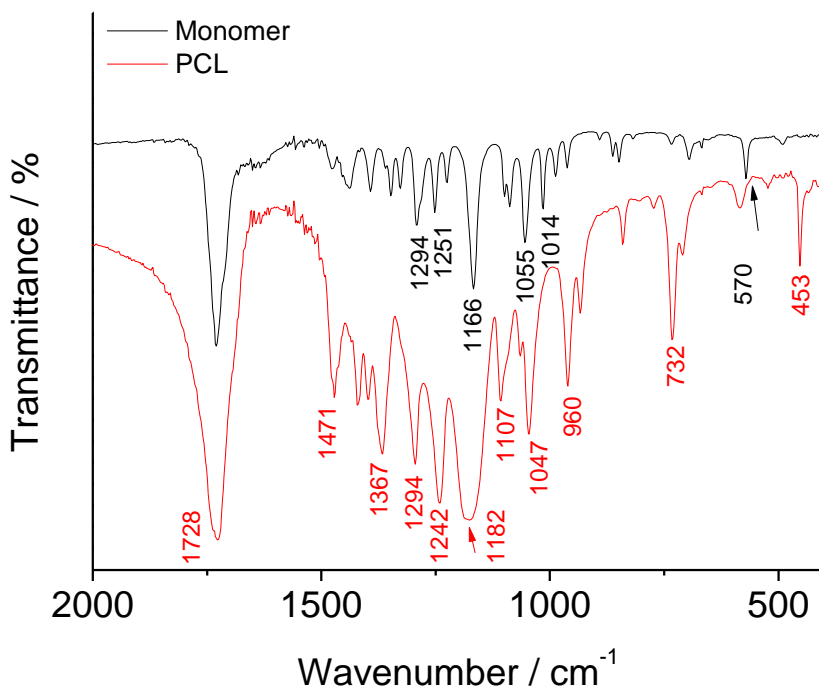


Figure S8. FTIR spectra (KBr pellets) of ϵ -caprolactone and of a representative poly(ϵ -caprolactone) sample produced with initiator **B**.

Table S3. Tentative assignments of the mid-infrared absorptions registered for ϵ -caprolactone (ϵ -CL) and poly(ϵ -caprolactone) (PCL)⁵

ϵ -CL	PCL	Tentative assigns
2937	2947	$\nu_{as}(\text{CH}_2)$
2862	2868	$\nu_s(\text{CH}_2)$
1728	1728	$\nu(\text{C}=\text{O})$
1294	1294	$\nu(\text{C}-\text{C}) + \nu_{as}(\text{COC})$
1251	1242	$\nu_{as}(\text{COC})$
1166	1182	$\nu(\text{OCO})$

References

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