Supplementary information for

Ring-opening polymerisation of alkyl-substituted ε-caprolactones: Kinetic effects of substitution position

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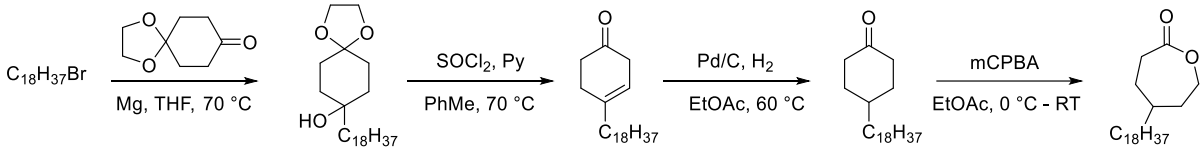
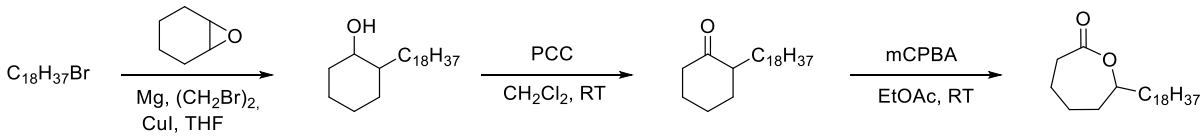
Experimental details

Synthesis of the alkyl substituted monomers: γC_{18}CL, εC_{18}CL and the mixture of the β- and δC_{18}CL isomers

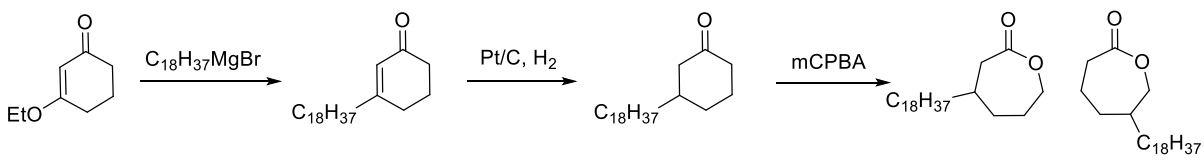
The alkyl substituted monomers were provided by Infineum UK Ltd. *via* a contract manufacturer. The synthesis was achieved as shown in Scheme S1-S3.



Scheme S1. Synthesis pathway of γC_{18}CL.



Scheme S2. Synthesis pathway of εC_{18}CL.



Scheme S3. Synthesis pathway of the mixture of the β and δC_{18}CL isomers.

γ(C_{18})(ε-caprolactone)

^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 4.38 – 4.07 (m, 2H), 2.76 – 2.49 (m, 2H), 1.94 (m, J = 14.0, 10.7, 7.0, 3.4, 1.7 Hz, 2H), 1.72 – 1.40 (m, 3H), 1.25 (s, 32H), 0.98 – 0.75 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 176.28 (*C*=O), 68.35 ((CO)O*C*H_2), 40.41 (*C*H_2(CO)OCH), 36.61, 35.55, 33.37, 32.08, 29.89, 29.85, 29.83, 29.81, 29.77, 29.73, 29.51, 29.08, 26.96, 22.84, 14.27.

β/δ(C_{18})(ε-caprolactone) isomers (1:1 mixture)

^{1}H NMR (300 MHz, C_6D_6, 299 K, ppm): δ = 3.73 – 3.57 (m, 1H), 5.54 – 3.36 (m, 1H), 2.44 – 2.21 (m, 1H), 2.15 – 1.96 (m, 1H), 1.48 – 0.99 (m, 38H), 0.97 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, C_6D_6, 299 K, ppm): δ = 173.80 (*C*=O), 173.03 (*C*=O), 71.51 ((CO)O*C*H_2), 67.88 ((CO)O*C*H_2), 39.69 (*C*H_2(CO)OCH), 38.53 (*C*H_2(CO)OCH), 34.51, 34.28, 34.01, 33.74, 31.99, 29.86, 29.83, 29.78, 29.76, 29.75, 29.71, 29.69, 29.65, 29.48, 26.83, 26.79, 22.76, 14.02.

ε(C_{18})(ε-caprolactone)

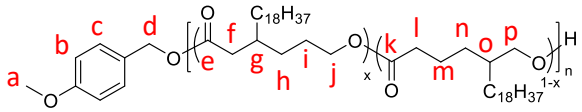
^{1}H NMR (300 MHz, C_6D_6, 299 K, ppm): δ = 3.63 (m, 1H), 2.48 – 2.33 (m, 1H), 2.07 – 1.90 (m, 1H), 1.58 – 1.09 (m, 40H), 0.97 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, C_6D_6, 299 K, ppm): δ = 176.01 (*C*=O), 80.76 ((CO)O*C*H), 36.59, 35.12, 34.72, 32.08, 29.85, 29.81, 29.79, 29.73, 29.67, 29.57, 29.51, 28.51, 25.58, 23.23, 22.84, 14.27 (*C*H_3).

General procedure for DPP catalysed polymerisations

Using standard glovebox techniques, a stock solution was prepared containing 4-methoxybenzyl alcohol initiator (55.0 mg, 0.40 mmol) and dry benzene-*d6* (500 μL). The stock solution (50 μL) was added to the appropriate monomer (2 mmol) and catalyst (50.0 mg, 0.20 mmol) in dry benzene-*d6* (1.95 mL) to form a 1 M solution. The solution was then transferred into a vial. Aliquots were taken at allotted time points and quenched by the addition of Amberlyst® A21 free base. After determining the polymer conversion by ^{1}H NMR spectroscopy, Amberlyst® was removed *via* filtration through a pipette plugged with cotton wool and the polymer was precipitated into cold MeOH, cooled using liquid nitrogen. Polymers were dried under vacuum.

β/δ(C_{18})poly(ε-caprolactone) isomers

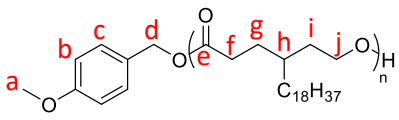


^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 6.88 (d, J = 8.7 Hz, 2H, H^b), 5.04 (s, 2H, H^d), 4.18–3.92 (m, 93H, H^j, H^p), 3.80 (s, 3H, H^a), 2.43–2.14 (m, 104H, H^f, H^l), 1.87 (s, 53H, CH_2, H^i), 1.76–1.51 (m, 135H, CH_2, H^h, H^m, H^n), 1.25 (s, 2035H, H^g, H^o, CH_2), 0.87 (d, J = 7.0 Hz, 177H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 173.6 (C^e, C^k), 66.9 (C^p, C^j), 36.9 (C^g, C^o), 34.5 (C^f, C^l), 32.0 (CH_2), 31.1 (CH_2), 30.9 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 26.6 (CH_2), 22.7 (CH_2), 22.2 (C^h, C^m), 14.2 (CH_3).

SEC ($CHCl_3$): M_n = 6350, M_w = 6900, $Đ_M$ = 1.09.

γ(C_{18})poly(ε-caprolactone)

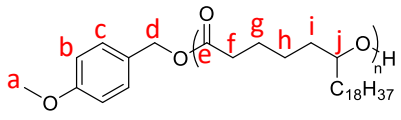


^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 6.96–6.77 (m, 2H, H^b), 5.04 (s, 2H, H^d), 4.08 (t, J = 7.1 Hz, 95H, H^j), 3.81 (s, 3H, H^a), 2.28 (t, J = 7.8 Hz, 103H, H^f), 1.86–1.35 (m, 208H, H^g, H^i, H^h), 1.37–1.14 (m, 1806H, CH_2), 0.99–0.63 (m, 155H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 173.9 (C^e), 62.8 (C^j), 61.0 (CH_2), 34.4 (C^h), 33.3 (CH_2), 32.3 (CH_2), 32.08 (C^g)f, 31.7 (C^f), 30.2 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 28.8 (C^i), 26.6 (CH_2), 22.8 (CH_2), 14.3 (CH_3).

SEC ($CHCl_3$): M_n = 11350, M_w = 12700, $Đ_M$ = 1.12.

ε(C_{18})poly(ε-caprolactone)



^{1}H NMR (400 MHz, $CDCl_3$, 299 K, ppm): δ = 6.81 (d, J = 8.7 Hz, 2H, H^b), 4.96 (s, 2H, H^d), 4.78 (t, J = 6.2 Hz, 48H, H^j), 3.73 (s, 3H, H^a), 2.19 (t, J = 7.6 Hz, 104H, H^f), 1.65–1.33 (m, 275H, H^g, H^i, H^h), 1.18 (d, J = 2.4 Hz, 1852H, CH_2), 0.81 (t, J = 6.7 Hz, 167H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 173.4 (C^e), 74.0 (C^j), 50.9 (CH_2), 34.5 (CH_2), 34.0 (CH_2), 33.9 (C^f), 32.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 25.4 (CH_2), 25.0 (CH_2), 25.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

SEC ($CHCl_3$): M_n = 10100, M_w = 12500, $Đ_M$ = 1.23.

Supplementary Figures

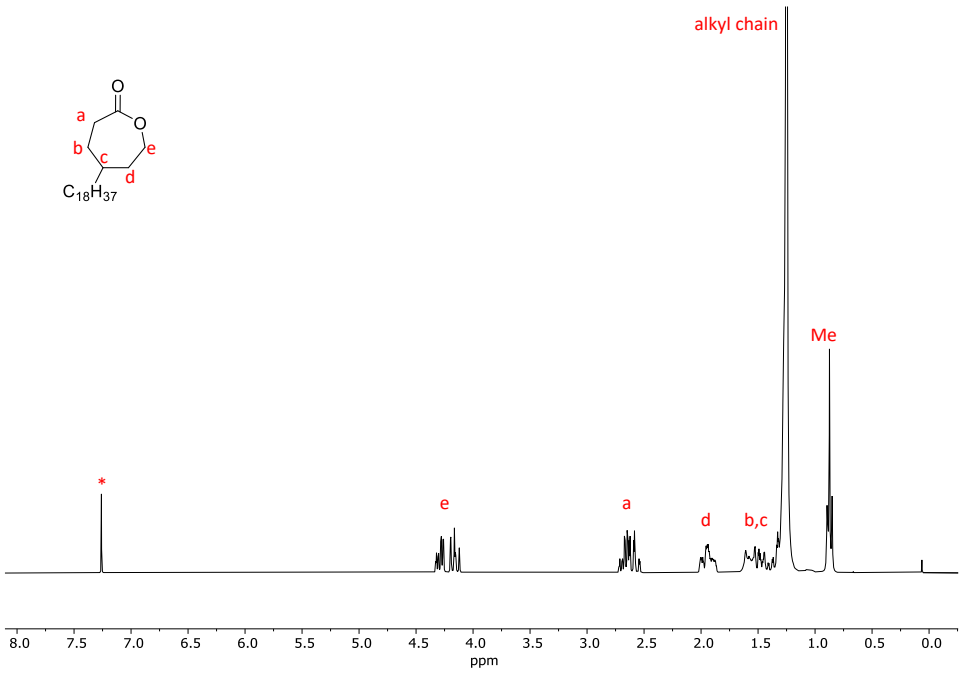


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of $\gamma C_{18}CL$. * = $CHCl_3$.

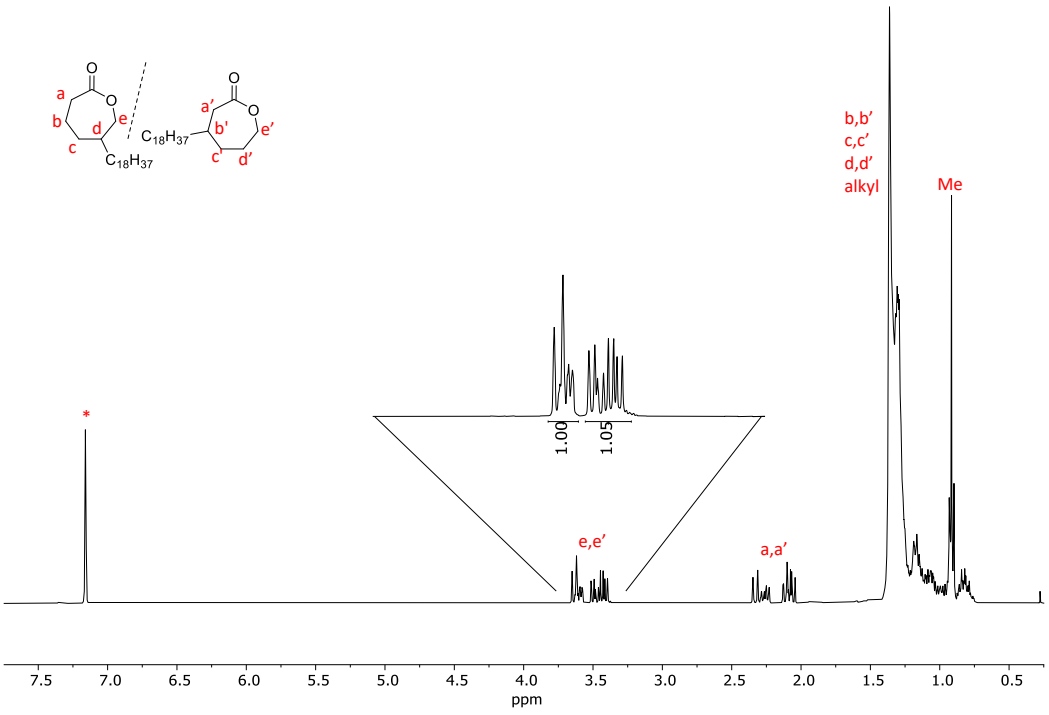


Figure S2. ^{1}H NMR spectrum (C_6D_6, 300 MHz) of $\beta/\delta C_{18}PCL$ isomers. * = C_6D_5H.

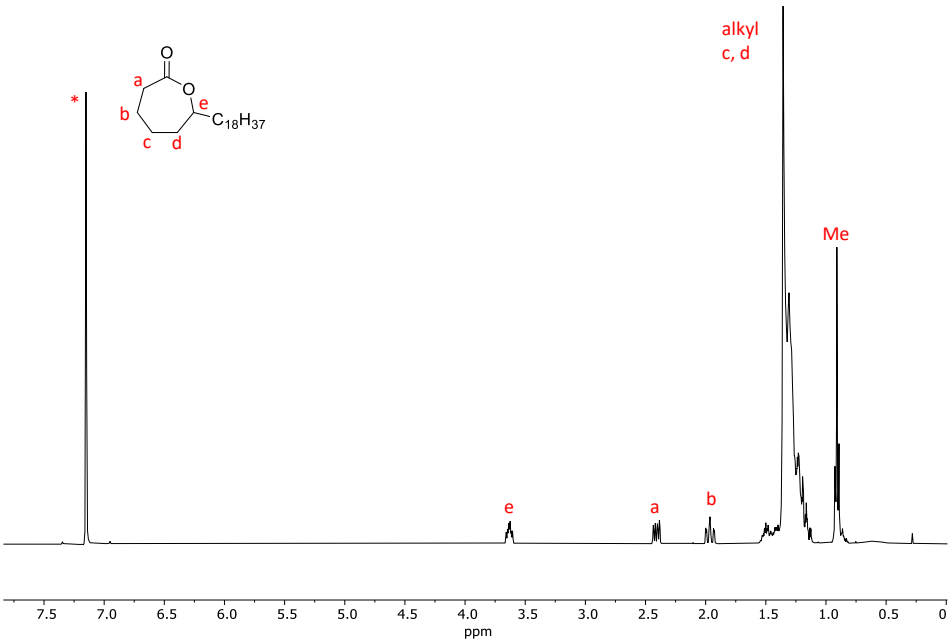


Figure S3. ^{1}H NMR spectrum (C_6D_6, 300 MHz) of $\varepsilon C_{18}CL$ isomers. * = C_6D_5H.

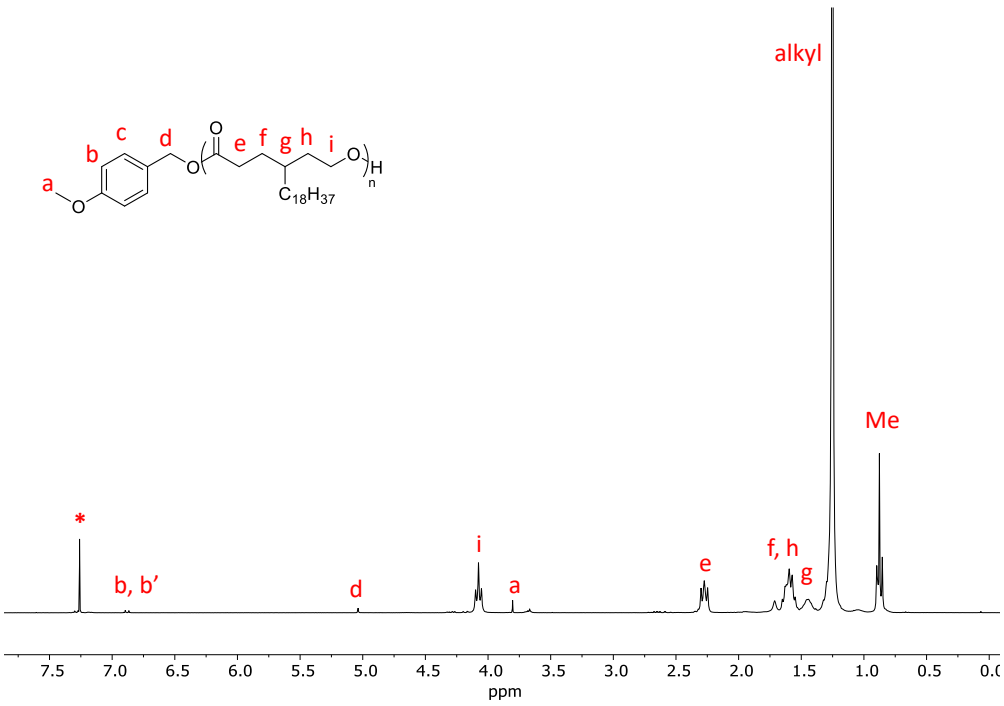


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of $\gamma C_{18}PCL$. * = $CHCl_3$.

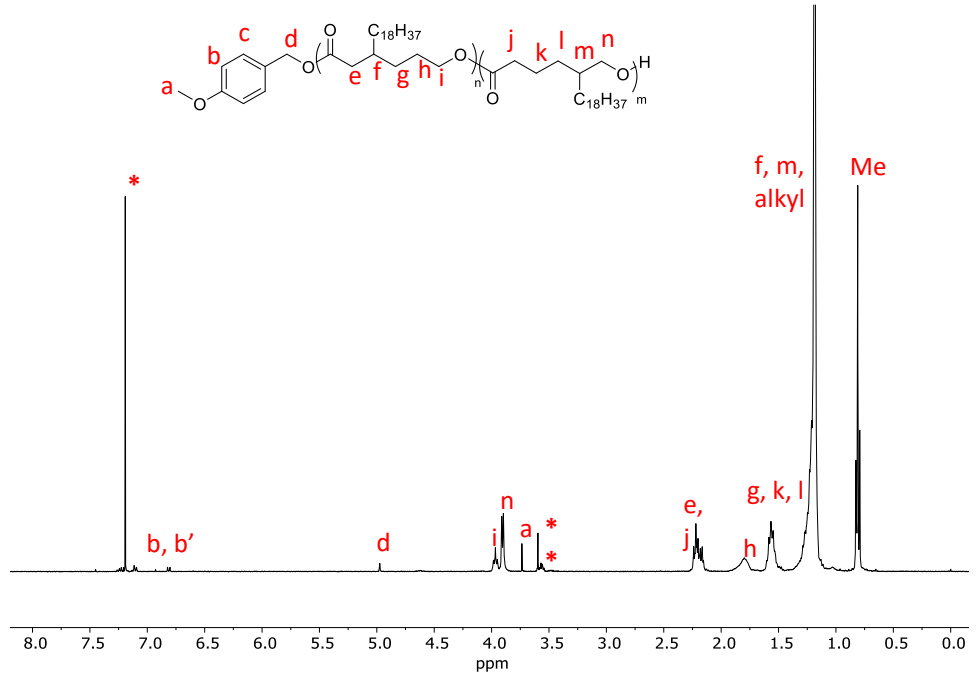


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of β/δC_{18}PCL isomers. * = $CHCl_3$. ** = MeOH.

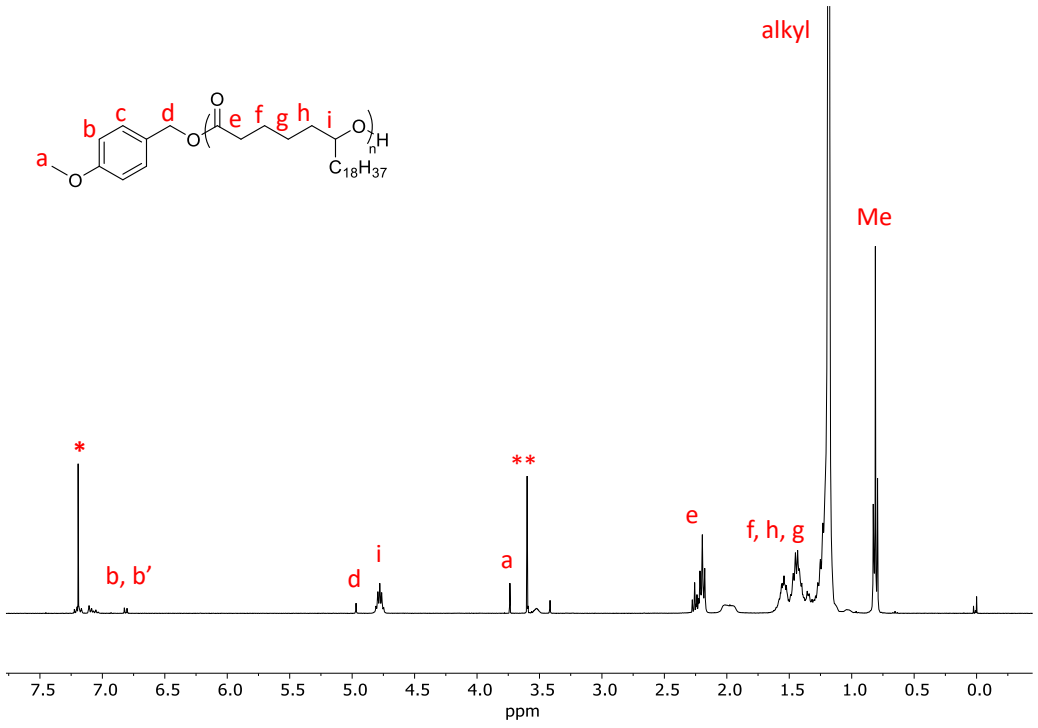


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of εC_{18}PCL. * = $CHCl_3$. ** = MeOH.

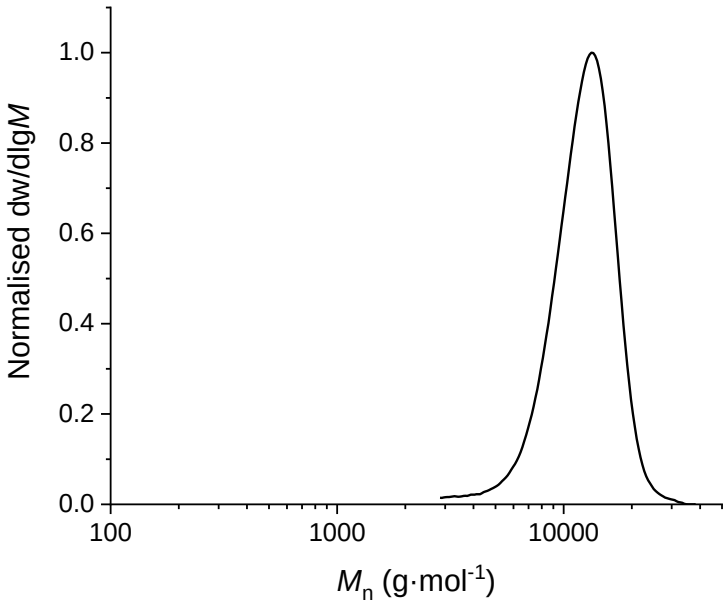


Figure S7. Size exclusion chromatogram of the molecular weight distribution of γC_{18}PCL using 4-methoxybenzyl alcohol as initiator ($[M]_0/[I]_0 = 50$). Molecular weight was determined against poly(styrene) standards using $CHCl_3$ (0.5% NEt_3) as eluent.

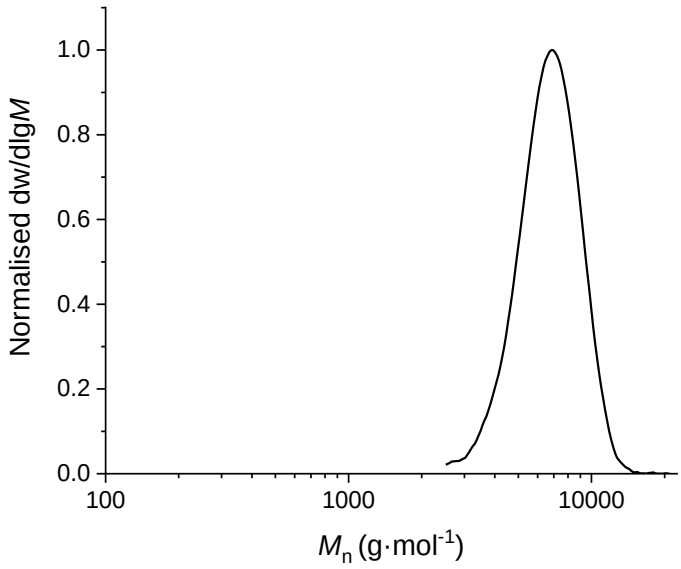


Figure S8. Size exclusion chromatogram of the molecular weight distribution of $\beta/\delta C_{18}$PCL using 4-methoxybenzyl alcohol as initiator ($[M]_0/[I]_0 = 50$). Molecular weight was determined against poly(styrene) standards using $CHCl_3$ (0.5% NEt_3) as eluent.

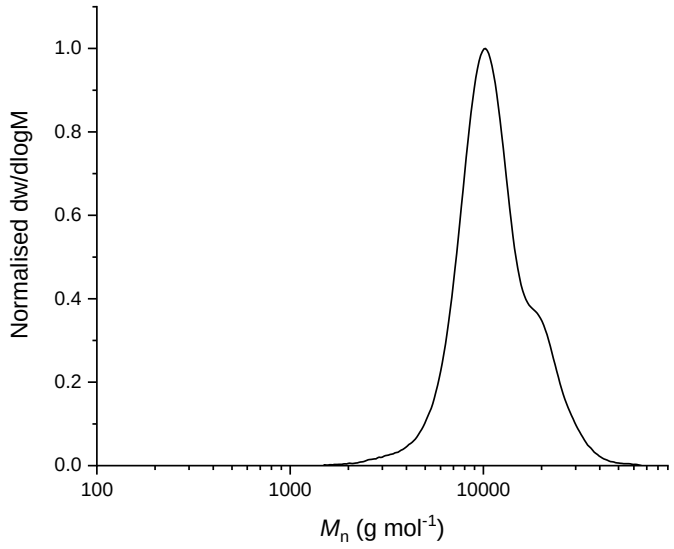


Figure S9. Size exclusion chromatogram of the molecular weight distribution of $\varepsilon C_{18}PCL$ using 4-methoxybenzyl alcohol as initiator ($[M]_0/[I]_0 = 50$) and DPP (10 mol%) as the catalyst at 25 °C. Molecular weight was determined against poly(styrene) standards using $CHCl_3$ (0.5% NEt_3) as eluent.

Table S1. Calculated monomer concentration over time for the kinetic resolution of the polymerisation of $\beta/\delta(C_{18})CL$ based on a 1:1 mixture of the isomers.

$\beta C_{18}CL$			**$\delta C_{18}CL$**		
Time (min)	Resolved conversion	Resolved $[M]_t$ [a]	Time (min)	Resolved conversion	Resolved $[M]_t$ [a]
0	0	0.5	0	0	0.5
15	12	0.44	15	18	0.41
30	14	0.43	30	40	0.3
60	14	0.43	60	64	0.18
90	28	0.36	90	76	0.12
120	30	0.35	120	88	0.06
240	52	0.24	240	-	-
360	68	0.16	360	-	-
420	72	0.14	420	-	-

[a] ROP of $\beta/\delta(C_{18})CL$ isomers using DPP and 4-methoxybenzyl alcohol as initiator ($[M]_0/[I]_0 = 50$). [M] = 1 M. Calculated from isomer ratios obtained by ^1H NMR spectroscopy based on a total monomer concentration of 1 M and a starting ratio of β isomer : δ isomer = 1:1.

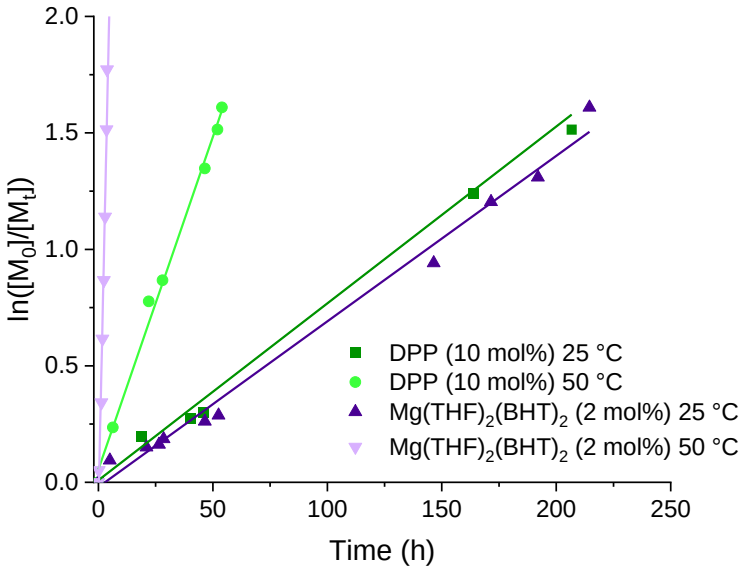


Figure S10. Kinetic plots of ln of initial monomer concentration by monomer concentration ($\ln([M]_0/[M]_t)$) against time for the ROP of $\varepsilon C_{18}CL$ using DPP (10 mol%) and $Mg(BHT)_2(THF)_2$ (2 mol%) at 25 °C and 50 °C, respectively.

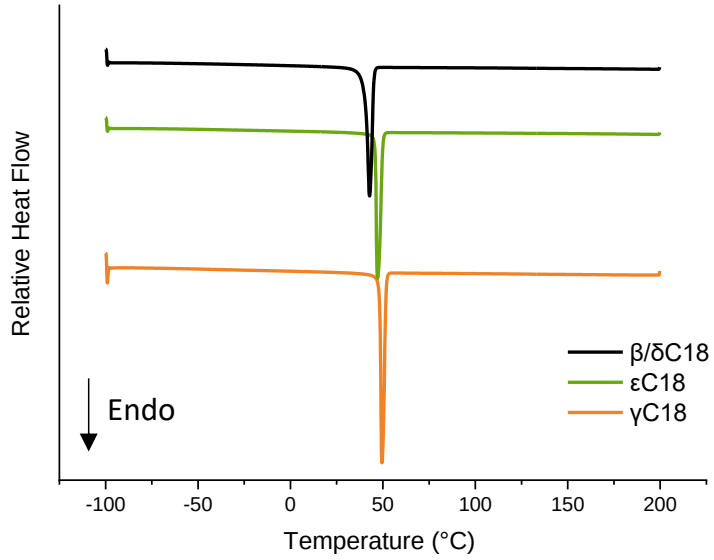


Figure S11. Differential scanning calorimetry (DSC) for 2nd heating cycle (200 to −100 °C, 10 °C min^{-1}) showing melting temperature of the polymers.