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: γC₁₈CL, εC₁₈CL** and the mixture of the β- and δC₁₈CL 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 γC₁₈CL.

**Scheme S2.** Synthesis pathway of εC₁₈CL.

**Scheme S3.** Synthesis pathway of the mixture of the β and δC₁₈CL isomers.
γ(C18)(ε-caprolactone)

$^1$H NMR (300 MHz, CDCl$_3$, 299 K, ppm): $\delta = 4.38 – 4.07$ (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): $\delta = 176.28$ (C=O), 68.35 ((CO)OCH$_2$), 40.41 (CH$_2$(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(C18)(ε-caprolactone) isomers (1:1 mixture)

$^1$H NMR (300 MHz, C$_6$D$_6$, 299 K, ppm): $\delta = 3.73 – 3.57$ (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$_6$D$_6$, 299 K, ppm): $\delta = 173.80$ (C=O), 173.03 (C=O), 71.51 ((CO)OCH$_2$), 67.88 ((CO)OCH$_2$), 39.69 (CH$_2$(CO)OCH), 38.53 (CH$_2$(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(C18)(ε-caprolactone)

$^1$H NMR (300 MHz, C$_6$D$_6$, 299 K, ppm): $\delta = 3.63$ (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$_6$D$_6$, 299 K, ppm): $\delta = 176.01$ (C=O), 80.76 ((CO)OCH), 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 (CH$_3$).
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 1H 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(C18) poly(ε-caprolactone) isomers

\[ \text{1H NMR (300 MHz, CDCl}_3, 299 \text{ K, ppm): } \delta = 6.88 (d, J = 8.7 \text{ Hz, H}^b), 5.04 (s, 2H, H^d), 4.18–3.92 (m, 93H, H^f, H^g), 3.80 (s, 3H, H^o), 2.43–2.14 (m, 104H, H^i, H^j), 1.87 (s, 53H, CH2, H^k), 1.76–1.51 (m, 135H, CH2, H^l, H^m, H^p), 1.25 (s, 2035H, H^o, CH2), 0.87 (d, J = 7.0 Hz, 177H, CH3). \]

\[ \text{13C NMR (101 MHz, CDCl}_3, 299 \text{ K, ppm): } \delta = 173.6 (C^e, C^b), 66.9 (C^o, C^i), 36.9 (C^g, C^n), 34.5 (C^f, C^i), 32.0 (CH2), 31.1 (CH2), 30.9 (CH2), 30.0 (CH2), 29.8 (CH2), 29.7 (CH2), 29.7 (CH2), 29.4 (CH2), 26.7 (CH2), 26.6 (CH2), 22.7 (CH2), 22.2 (CH^h, CH^m), 14.2 (CH3). \]

SEC (CHCl3): \( M_n = 6350, M_w = 6900, D_M = 1.09. \)

γ(C18) poly(ε-caprolactone)

\[ \text{1H NMR (300 MHz, CDCl}_3, 299 \text{ K, ppm): } \delta = 6.96–6.77 (m, 2H, H^b), 5.04 (s, 2H, H^d), 4.08 (t, J = 7.1 \text{ Hz, 95H, H}^f), 3.81 (s, 3H, H^o), 2.28 (t, J = 7.8 \text{ Hz, 103H, H}^i), 1.86–1.35 (m, 208H, H^o, H^i, H^p), 1.37–1.14 (m, 1806H, CH2), 0.99–0.63 (m, 155H, CH3). \]

\[ \text{13C NMR (101 MHz, CDCl}_3, 299 \text{ K, ppm): } \delta = 173.9 (C^e), 62.8 (C^i), 61.0 (CH2), 34.4 (CH^b), 33.3 (CH2), 32.3 (CH2), 32.08 (CH^f), 31.7 (C^i), 30.2 (CH2), 29.9 (CH2), 29.9 (CH2), 29.8 (CH2), 29.5 (CH2), 28.8 (C^o), 26.6 (CH2), 22.8 (CH2), 14.3 (CH3). \]

SEC (CHCl3): \( M_n = 11350, M_w = 12700, D_M = 1.12. \)
ε(C\textsubscript{18})poly(ε-caprolactone)

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

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}, 299 K, ppm): \( \delta = 173.4 \) (C\textsuperscript{e}), 74.0 (C\textsuperscript{i}), 50.9 (CH\textsubscript{2}), 34.5 (CH\textsubscript{2}), 34.0 (CH\textsubscript{2}), 33.9 (C\textsuperscript{i}), 32.0 (CH\textsubscript{2}), 29.8 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 29.7 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 29.4 (CH\textsubscript{2}), 25.4 (CH\textsubscript{2}), 25.0 (CH\textsubscript{2}), 25.0 (CH\textsubscript{2}), 22.7 (CH\textsubscript{2}), 14.1 (CH\textsubscript{3}).

SEC (CHCl\textsubscript{3}): \( M_n = 10100, M_w = 12500, D_M = 1.23 \).
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$_6$D$_6$, 300 MHz) of $\beta/\delta$C$_{18}$PCL isomers. * = C$_6$D$_3$H.
Figure S3. $^1$H NMR spectrum (C$_6$D$_6$, 300 MHz) of $\varepsilon$C$_{18}$CL isomers. * = C$_6$D$_5$H.

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 $\beta/\delta$C$_{18}$PCL isomers. * = CHCl$_3$. ** = MeOH.

Figure S6. $^1$H NMR spectrum (CDCl$_3$, 400 MHz) of $\varepsilon$C$_{18}$PCL. * = CHCl$_3$. ** = MeOH.
**Figure S7.** Size exclusion chromatogram of the molecular weight distribution of $\gamma\text{C}_{18}\text{PCL}$ 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 $\beta/\delta\text{C}_{18}\text{PCL}$ 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 εC_{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 CHCl₃ (0.5% NEt₃) as eluent.

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

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*ROP of β/δ(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 \( \text{Mg(BHT)}_2(\text{THF})_2 \) (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.