Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary information for

Controlling the crystallinity and solubility of functional PCL with efficient post-polymerisation modification

Cinzia Clamor[1], Beatrice N. Cattoz[2], Peter M. Wright[2], Rachel K. O'Reilly[1*], Andrew P. Dove[1*]

[1] School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

[2] Infineum UK Ltd, Milton Hill, Abingdon OX13 6BB, United Kingdom

Experimental details

Synthesis of $Mg(BHT)_2(THF)_2$

Using standard glovebox techniques, to a solution of the dimer $(Mg(BHT)_2)_2$ (5.00 g, 5.40 mmol) in dry pentane (27 mL) was added dropwise THF (4.67 g, 64.8 mmol) and the solution was stirred overnight. The solvent was removed under vacuum and the solid was recrystallised from pentane in the glovebox to obtain $Mg(BHT)_2(THF)_2$ as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$, 299 K, ppm): δ = 7.29 (d, J = 0.8 Hz, 4H, C$H_{aromatic}$), 3.62 (ddt, J = 5.8, 4.1, 1.4 Hz, 8H, OCH_2), 2.43 (s, 6H, CH_3), 1.63 (s, 37H, *t*-Bu), 1.24-1.13 (m, 8H, OCH_2CH_2). ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 160.9 (aromatic *C*), 137.0 (aromatic *C*), 126.1 (aromatic *C*H), 121.2 (aromatic *C*), 70.7 (O*C*H_2), 35.5 (*C*CH_3), 32.0 (*t*-Bu), 24.8 (OCH_2CH_2), 21.7 (*C*H_3).

Poly(ε-allyl-ε-caprolactone) functionalised with 2-ethylhexanethiol

^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 6.90–6.84 (m, 2H, -C$H_{aromatic}$), 5.02 (s, 2H, -$CH_{aromatic}$-CH_2), 4.85 (p, J = 6.0 Hz, 60H, -COOC*H*), 3.79 (s, 3H, -OCH_3), 2.46 (dd, J = 7.7, 6.2 Hz, 263H, -CH_2SCH_2), 2.25 (t, J = 7.6 Hz, 133H, -COOCH_2), 1.88–1.15 (m, 1596H, -CH_2), 0.87 (dt, J = 9.8, 6.7 Hz, 497H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 172,1 (O(*C*O)),137.9 (*C*H=CH_2), 122.0 (CH=*C*H_2), 77.2 (O*C*HCH_2), 42.9 (*C*H_2CH=CH_2), 38.7 (O(CO)*C*H_2), 37.5 (OCH*C*H_2), 29.2 (O(CO)CH_2*C*H_2, O(CO)CH_2CH_2*C*H_2); SEC ($CHCl_3$): M_n = 16400, M_w = 21300, $Đ_M$ = 1.30.

Poly(ε-allyl-ε-caprolactone) functionalised with 1-hexanethiol

δ = 6.82 (d, J = 8.7 Hz, 2H, C$H_{aromatic}$), 4.97 (s, 2H, $CH_{aromatic}$CH_2), 4.87–4.70 (m, 55H, (CO)OC*H*), 3.74 (s, 3H, OCH_3), 2.42 (td, J = 7.3, 4.9 Hz, 242H, CH_2SCH_2), 2.21 (t, J = 7.6 Hz, 125H, COOCH_2), 1.67 – 1.37 (m, 550H, CH_2), 1.40 – 1.11 (m, 361H, CH_2), 0.88 – 0.72 (m, 144H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 173.3 (O(*C*O)), 73.5 (*C*HO), 34.6 (CH_2SCH_2), 34.0 (CH_2S*C*H_2), 33.3 (*C*H_2), 32.3 (*C*H_2), 32.1 (*C*H_2), 31.6 (*C*H_2), 29.8 (*C*H_2), 28.8 (*C*H_2), 25.51 (*C*H_2), 25.1 (*C*H_2), 25.1 (*C*H_2), 22.7 (*C*H_2), 14.2 (*C*H_3); SEC ($CHCl_3$): M_n = 14700, M_w = 19500 $Đ_M$ = 1.33.

Poly(ε-allyl-ε-caprolactone) functionalised with 1-octanethiol

^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 6.88 (d, J = 8.7 Hz, 2H, -C$H_{aromatic}$), 5.03 (s, 2H, -$CH_{aromatic}$-CH_2), 4.87 (p, J = 6.7 Hz, 57H, -COOCH), 3.80 (s, 3H, -OCH_3), 2.57-2.42 (m, 244H, -CH_2SCH_2), 2.27 (t, J = 7.6 Hz, 132H, -COOCH_2), 1.77–1.45 (m, 638H, -CH_2), 1.44-1.16 (m, 795H, -CH_2), 0.94–0.80 (m, 200H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ= 173.6 (O(*C*O)), 73.8 (*C*HO), 34.8 (CH_2SCH_2), 34.3 (CH_2S*C*H$_2$), 33.6 (*C*H$_2$), 32.6 (*C*H$_2$), 32.3 (*C*H$_2$), 32.2 (*C*H$_2$), 30.1 (*C*H$_2$), 29.6 (*C*H$_2$), 29.6 (*C*H$_2$), 29.4 (*C*H$_2$), 25.8 (*C*H$_2$), 25.3 (*C*H$_2$), 23.1 (*C*H$_2$), 14.7 (*C*H$_3$); SEC ($CHCl_3$): M_n = 13800, M_w = 18500, $Đ_M$ = 1.34.

Poly(ε-allyl-ε-caprolactone) functionalised with 1-decanethiol

^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 4.87 (p, J = 6.1 Hz, 59H), 3.81 (s, 3H), 2.49 (td, J = 7.2, 5.2 Hz, 253H), 2.27 (t, J = 7.6 Hz, 131H), 1.74–1.45 (m, 718H), 1.27 (d, J = 4.9 Hz, 1207H), 0.96–0.78 (m, 210H); ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ= 173.6 (O(*C*O)), 73.9 (*C*HO), 34.5 (CH_2SCH_2), 34.0 (CH_2S*C*H$_2$), 32.3 (*C*H$_2$), 32.1 (*C*H$_2$), 29.9 (*C*H$_2$), 29.7 (*C*H$_2$), 29.5 (*C*H$_2$), 29.1 (*C*H$_2$), 25.5 (*C*H$_2$), 25.1 (*C*H$_2$), 22.8 (*C*H$_3$); SEC ($CHCl_3$): M_n = 13400, M_w = 17700, $Đ_M$ = 1.31.

Poly(ε-allyl-ε-caprolactone) functionalised with 1-dodecanethiol

^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 5.03 (s, 2H, -$CH_{aromatic}$-CH_2), 4.86 (p, J = 6.1 Hz, 53H, -COOCH), 3.80 (s, 3H, -OCH_3), 2.59–2.38 (m, 234H, -CH_2SCH_2), 2.27 (t, J = 7.6 Hz, 125H, -COOCH_2), 1.84–1.11 (m, 1970H, -CH_2), 1.00–0.76 (m, 266H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ= 173.6 (O(*C*O)), 73.71 (*C*HO), 34.8 (CH_2SCH_2), 34.3 (CH_2S*C*H$_2$), 33.6 (*C*H$_2$), 32.6 (*C*H$_2$), 32.3 (*C*H$_2$), 30.1 (*C*H$_2$), 30.0 (*C*H$_2$), 29.8 (*C*H$_2$), 29.7 (*C*H$_2$), 29.6 (*C*H$_2$), 29.4 (*C*H$_2$), 28.9 (*C*H$_2$), 25.7 (*C*H$_2$), 25.3 (*C*H$_2$), 25.2 (*C*H$_2$), 23.1 (*C*H$_2$), 14.3 (*C*H$_3$); SEC ($CHCl_3$): M_n = 1930, M_w = 24800, $Đ_M$ = 1.29.

Poly(ε-allyl-ε-caprolactone) functionalised with 1-hexadecanethiol

^{1}H NMR (300 MHz, $CDCl_3$, 299 K, ppm): δ = 6.88 (d, J = 8.6 Hz, 2H, -C$H_{aromatic}$), 5.04 (s, 2H, -$CH_{aromatic}$-CH_2), 4.88 (m, 58H, -COOCH), 3.81 (s, 3H, -OCH_3), 2.58–2.41 (m, 229H, -CH_2SCH_2), 2.27 (t, J = 7.6 Hz, 143H, -COOCH_2), 1.25 (s, 2900H, -CH_2), 0.98–0.75 (m, 205H,

-CH_3); ^{13}C NMR (101 MHz, $CDCl_3$, 299 K, ppm): δ = 173.2 (O(*C*O)), 73.4 (*C*HO), 34.5 (CH_2SCH_2), 34.0 (CH_2SCH_2), 33.3 (*C*H_2), 32.3 (*C*H_2), 32.0 (*C*H_2), 29.8 (*C*H_2), 29.7 (*C*H_2), 29.5 (*C*H_2), 29.4 (*C*H_2), 29.3 (*C*H_2), 29.1 (*C*H_2), 28.6 (*C*H_2), 25.5 (*C*H_2), 25.1 (*C*H_2), 24.9 (*C*H_2), 22.8 (*C*H_2), 14.2 (*C*H_3), M_w = 30150, $Đ_M$ = 1.34.

Supplementary Figures

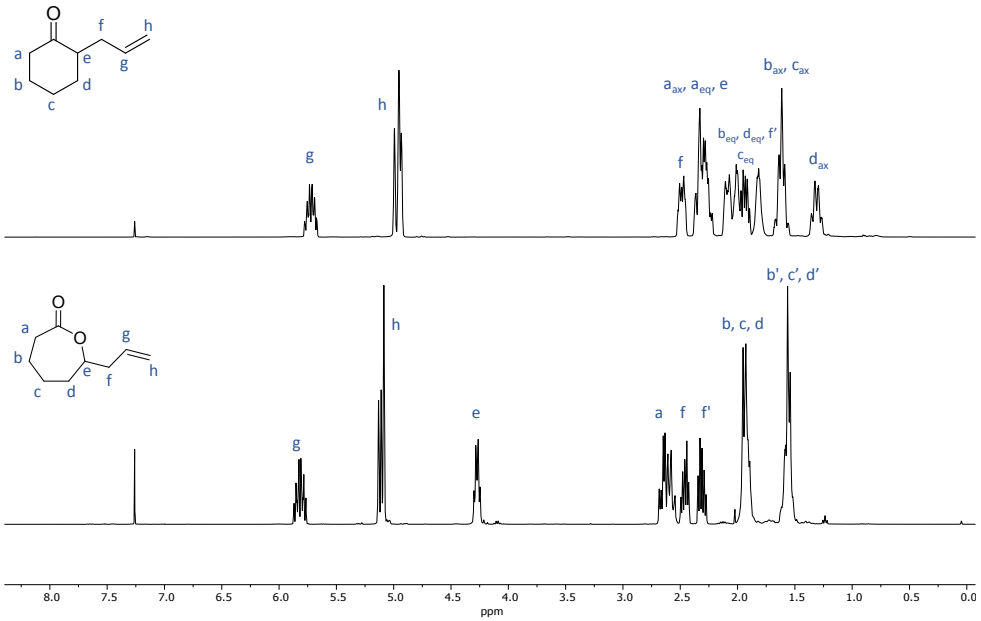

Figure S1 Stacked ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of 2-allylcyclohexanone (top) and ε-allyl-ε-caprolactone (bottom).

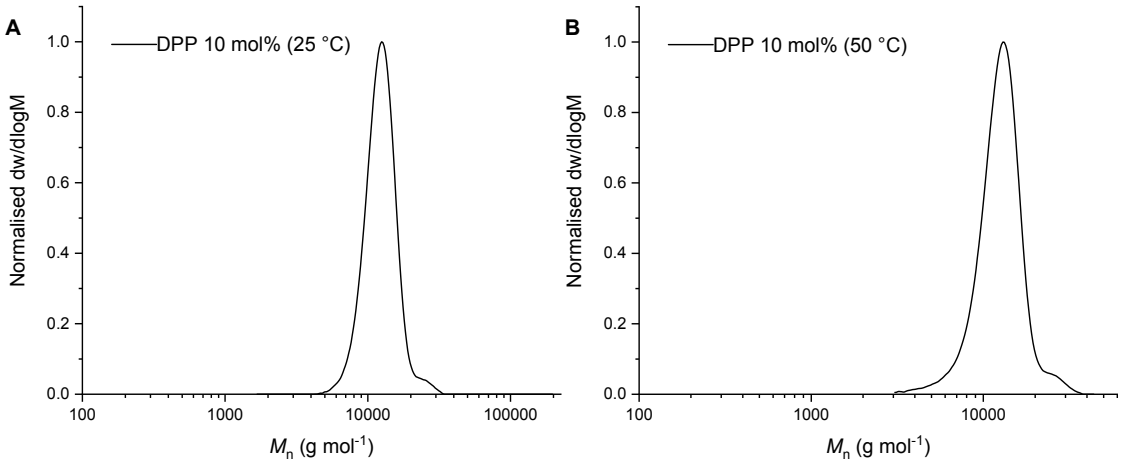

Figure S2 Size exclusion chromatogram of the molecular weight distribution of poly(ε-allyl-ε-caprolactone) catalysed by DPP (10 mol%) at (a) 25 °C and (b) 50 °C. Molecular weight was determined against poly(styrene) standards using $CHCl_3$ (0.5% NEt_3) as eluent.

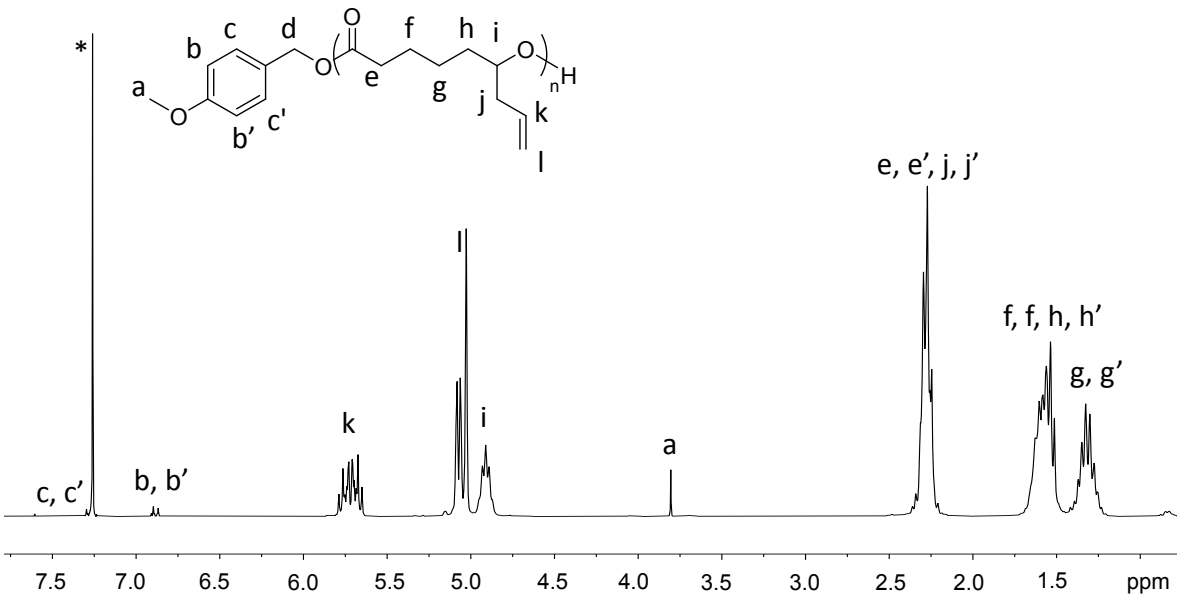

Figure S3 ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of AεPCL.

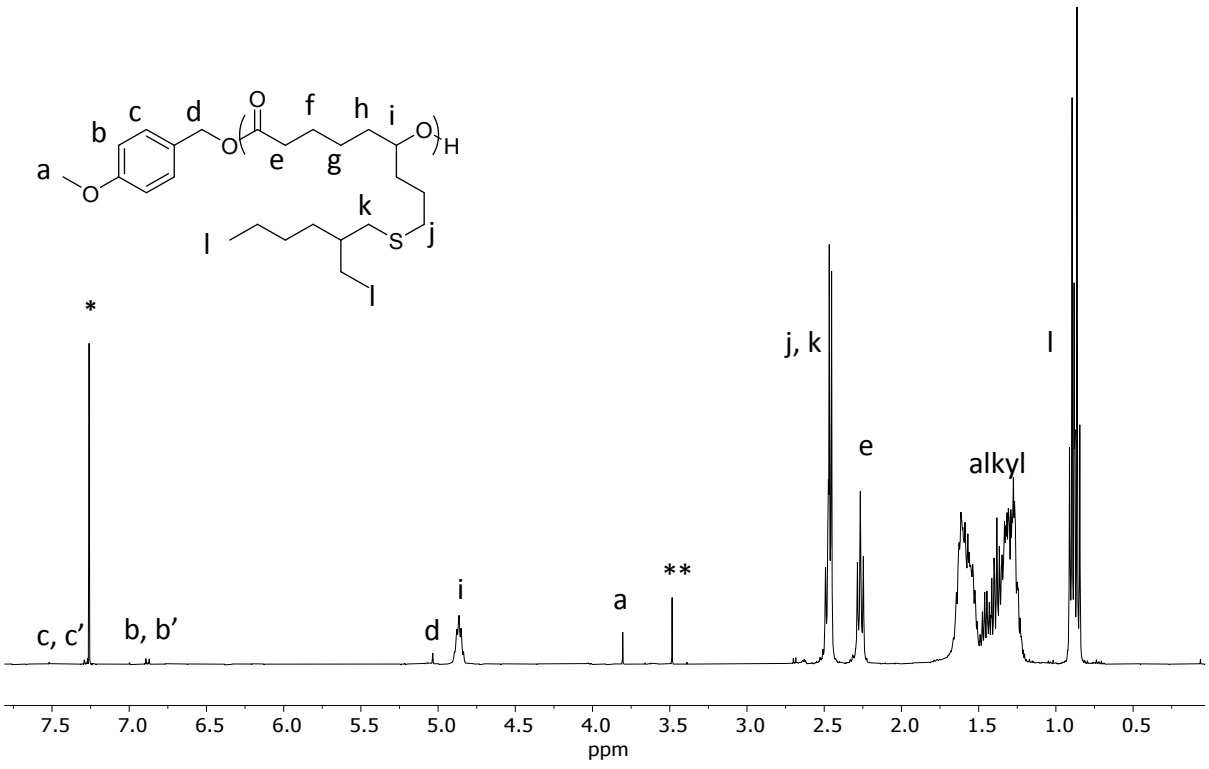

Figure S4 ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of poly(ε-allyl-ε-caprolactone) functionalised with (a) 2-ethyl hexanethiol. * = $CHCl_3$. ** = MeOH.

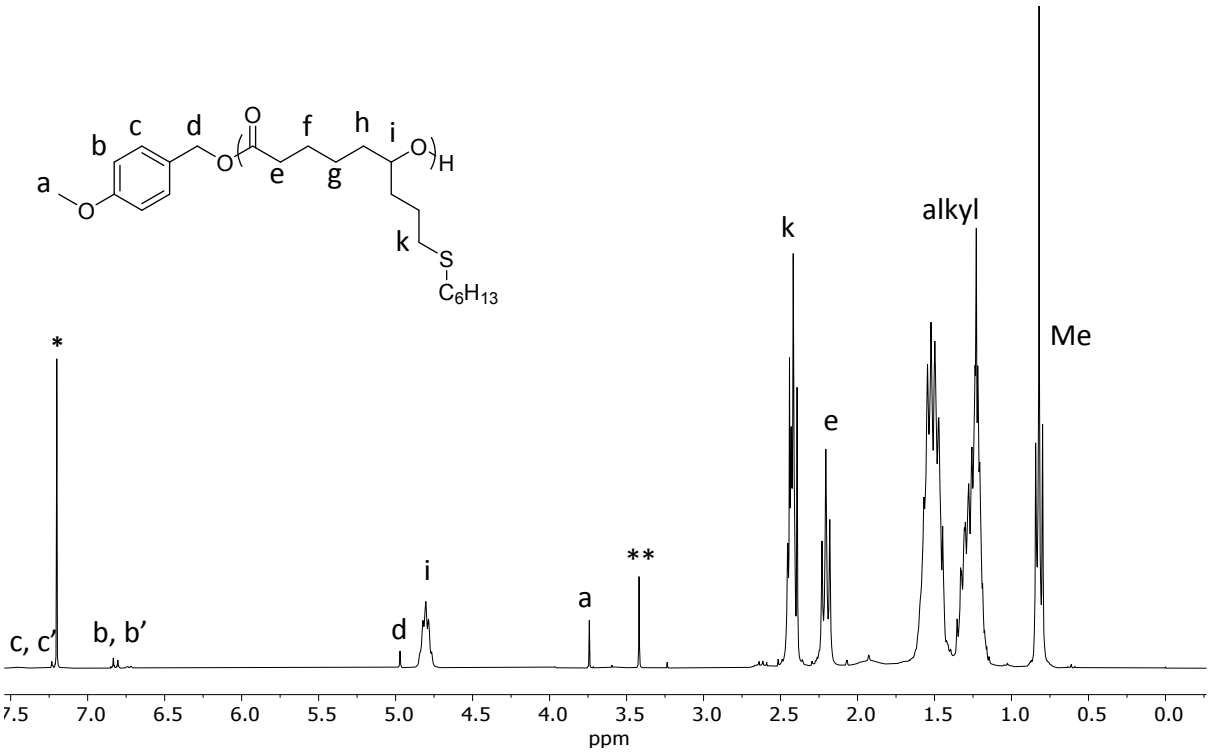

Figure S5 ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of poly(ε-allyl-ε-caprolactone) functionalised with 1-hexanethiol. * = $CHCl_3$. ** = MeOH.

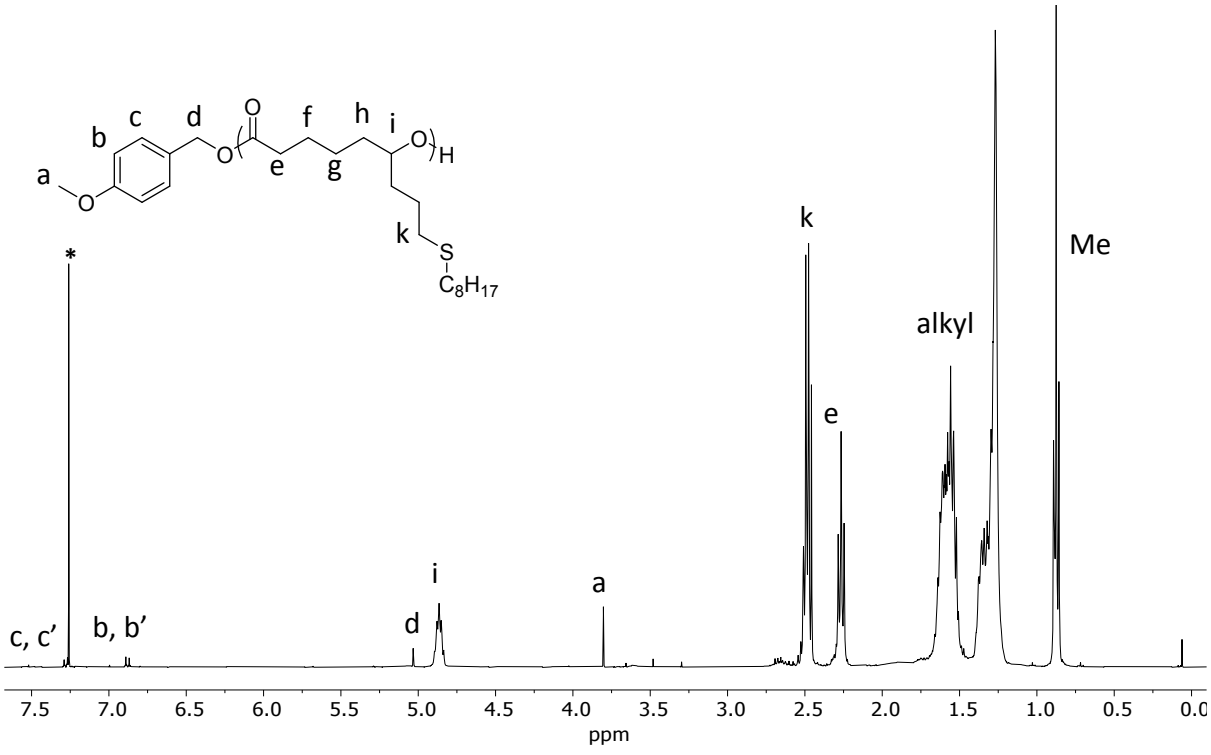

Figure S6 ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of poly(ε-allyl-ε-caprolactone) functionalised with 1-octanethiol. * = $CHCl_3$. ** = MeOH.

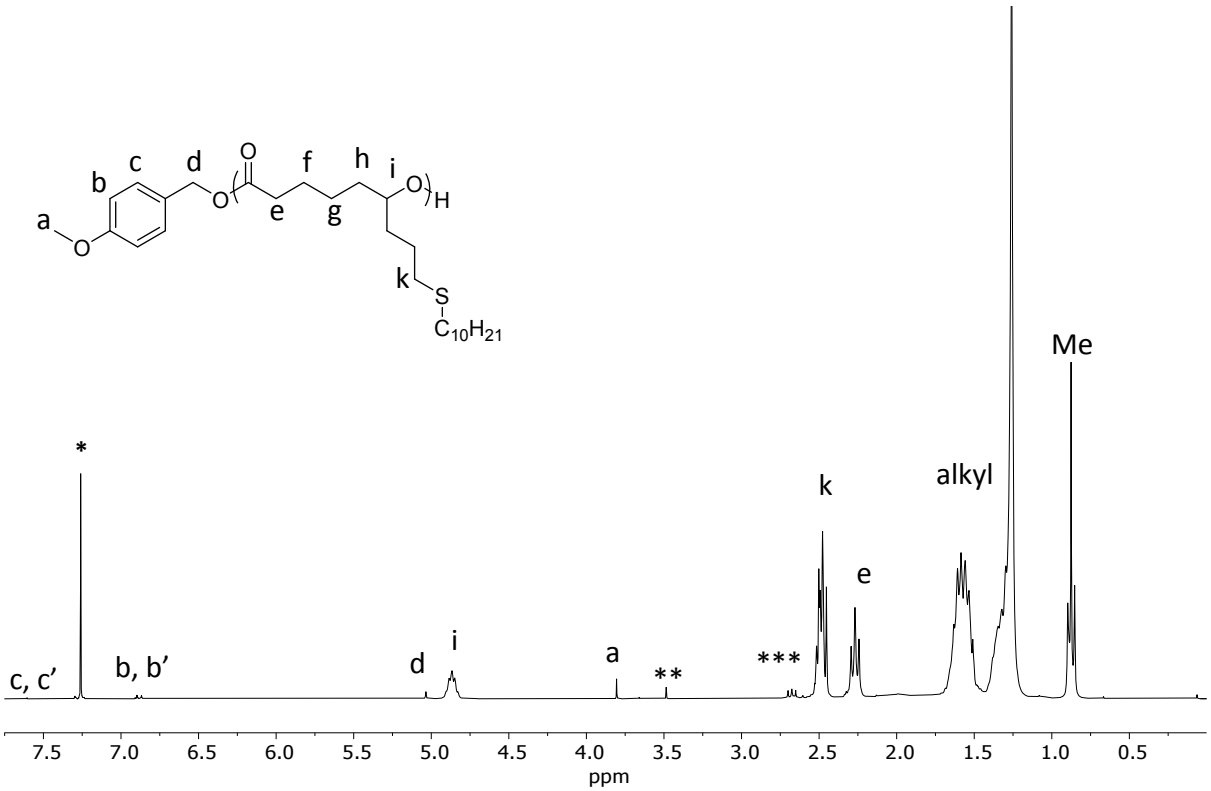

Figure S7 ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of poly(ε-allyl-ε-caprolactone) functionalised with 1-decanethiol. * = $CHCl_3$. ** = MeOH. *** = unknown impurity.

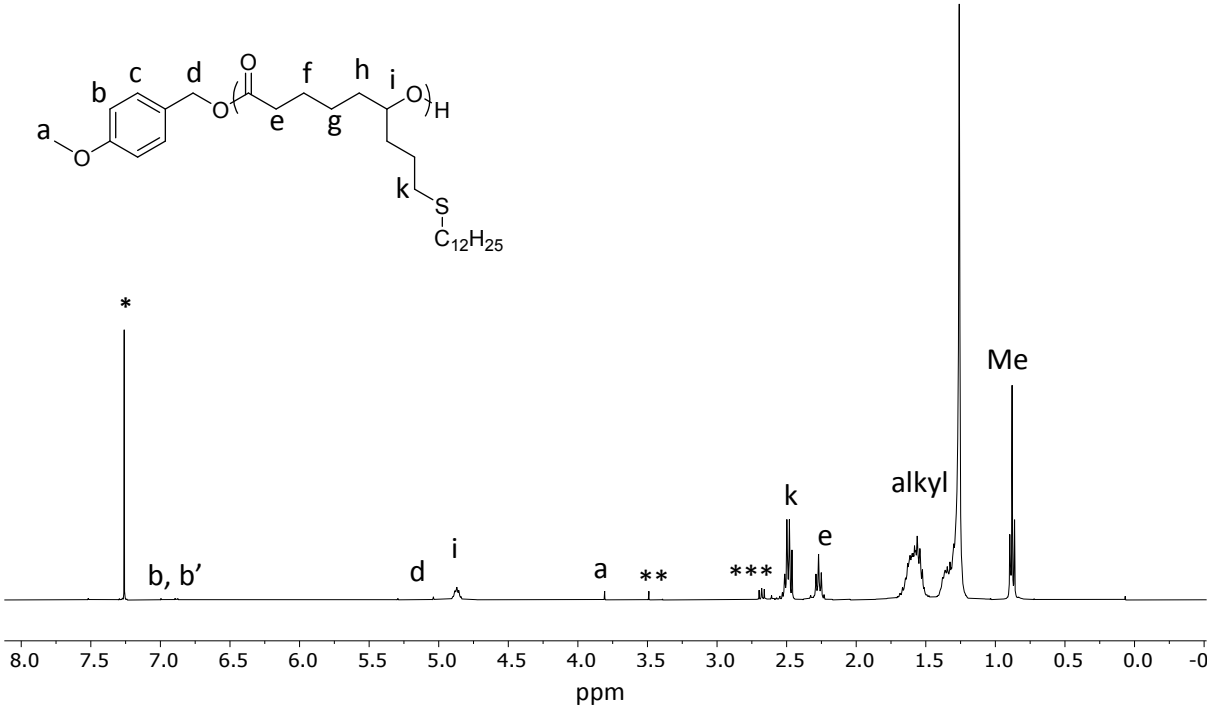

Figure S8 ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of poly(ε-allyl-ε-caprolactone) functionalised with 1-dodecanethiol. * = $CHCl_3$. ** = MeOH. *** = unknown impurity.

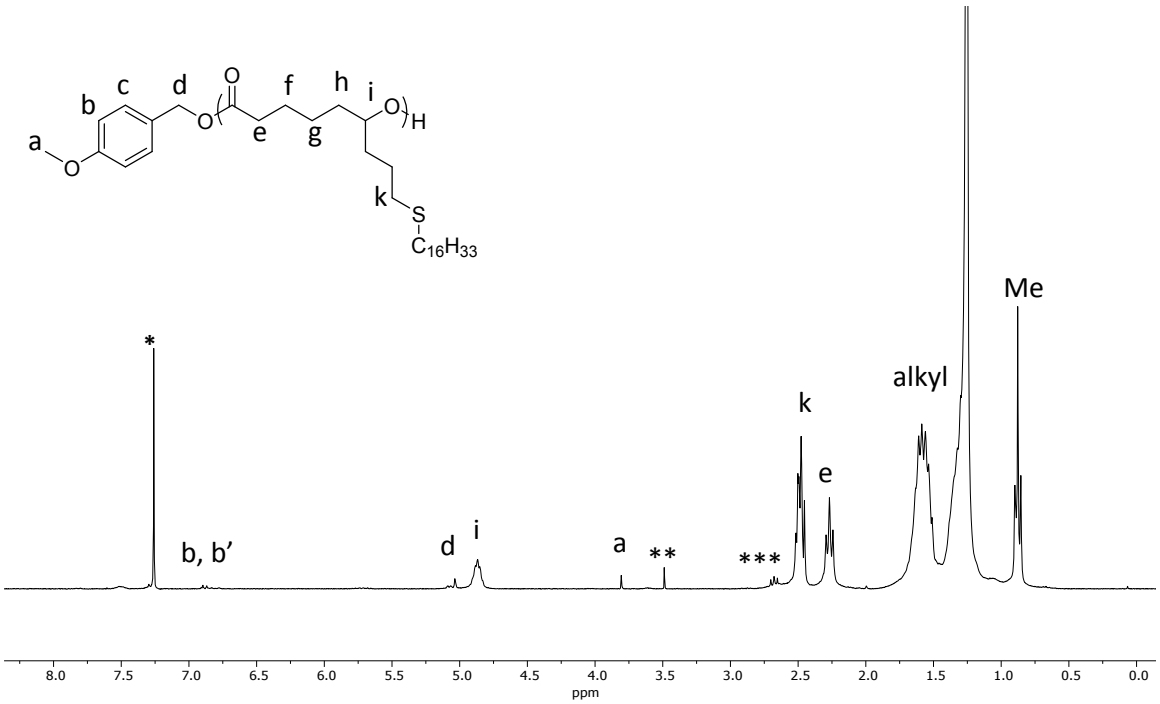

Figure S9 ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of poly(ε-allyl-ε-caprolactone) functionalised with 1-hexadecanethiol. * = $CHCl_3$. ** = MeOH. *** = unknown impurity.

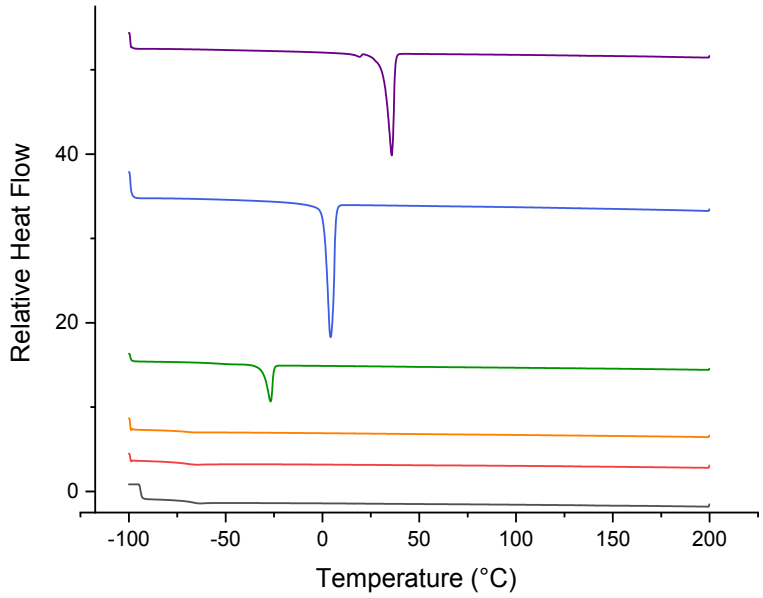

Figure S10 Differential scanning calorimetry thermograms of poly(ε-allyl-ε-caprolactone) functionalised with 2-ethyl hexanethiol, 1-hexanethiol 1-octanetiol, 1-decanethiol, 1-dodecanethiol and 1-hexadecanethiol for 2nd heating cycle (10 °C min^{-1}).

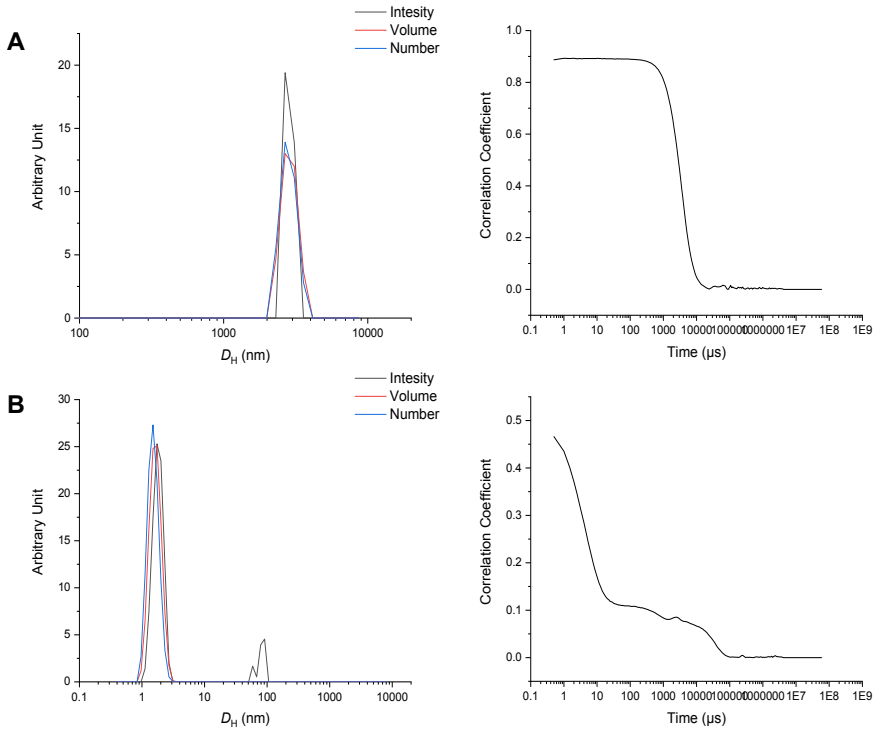

Figure S11 Dynamic light scattering (DLS) particle size distributions and correlograms from poly(ε-allyl-ε-caprolactone) functionalised with 1-octanethiol at 40 mg mL^{-1} concentration in *n*-dodecane measured at a) 20 °C and b) 90 °C.

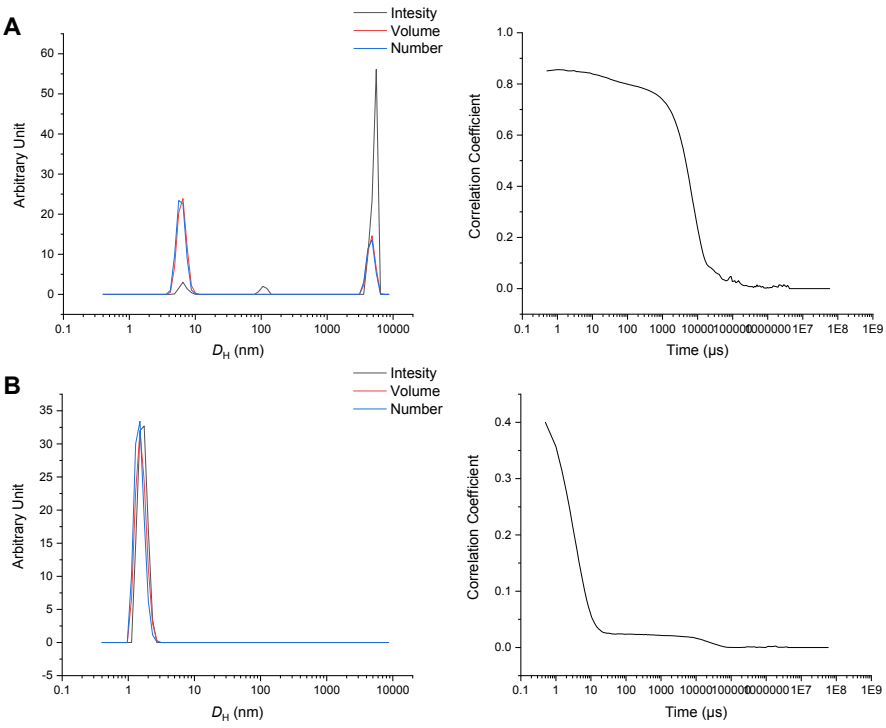

Figure S12 Dynamic light scattering (DLS) particle size distributions and correlograms from poly(ε-allyl-ε-caprolactone) functionalised with 2-ethyl hexanethiol at 40 mg mL^{-1} concentration in *n*-dodecane measured at a) 20 °C and b) 90 °C.

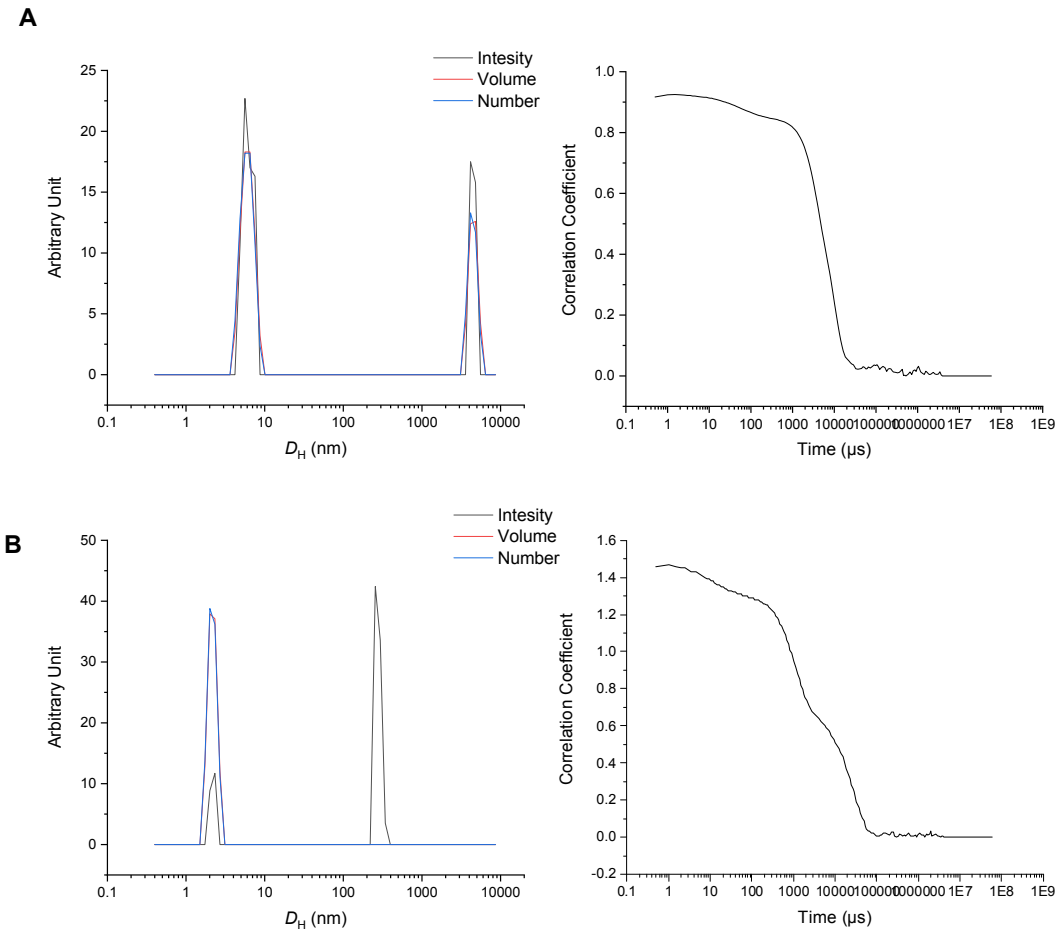

Figure S13 Dynamic light scattering (DLS) particle size distributions and correlograms from poly(ε-allyl-ε-caprolactone) functionalised with 1-decanethiol at 40 mg mL^{-1} concentration in *n*-dodecane measured at a) 20 °C and b) 90 °C.

Figure S14 40 mg mL^{-1} solution of poly(ε-allyl-ε-caprolactone) functionalised with 1-decanethiol in *n*-dodecane. A laser pen was used to monitor Tyndall effect.

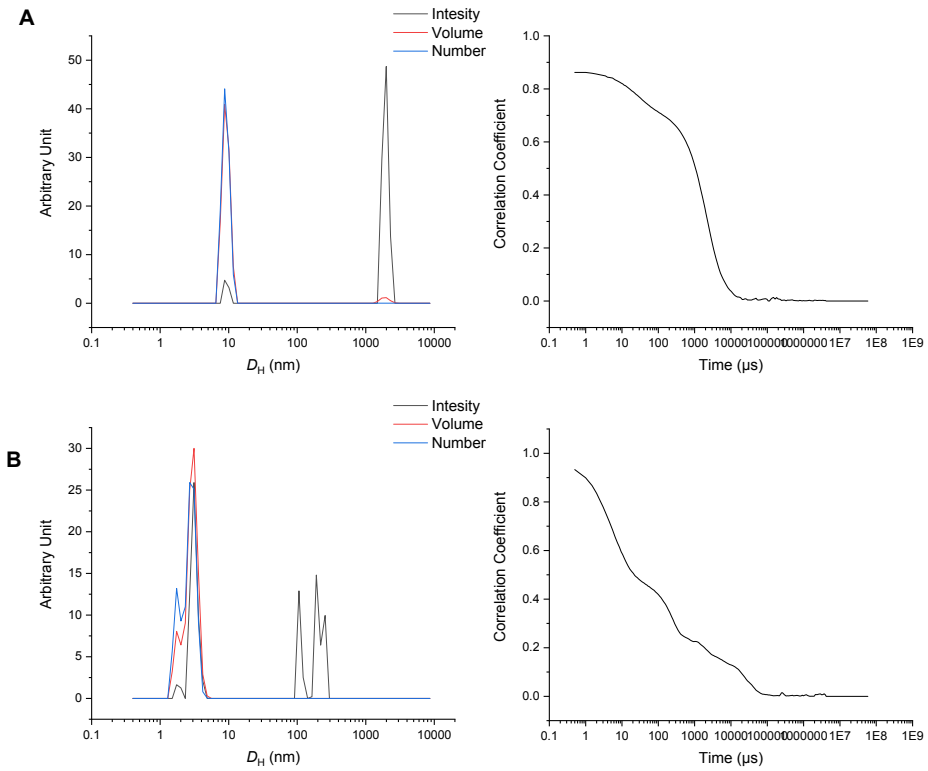

Figure S15 Dynamic light scattering (DLS) particle size distributions and correlograms from poly(ε-allyl-ε-caprolactone) functionalised with 1-decanethiol at 40 mg mL^{-1} concentration in *n*-decane measured at a) 20 °C and b) 90 °C.

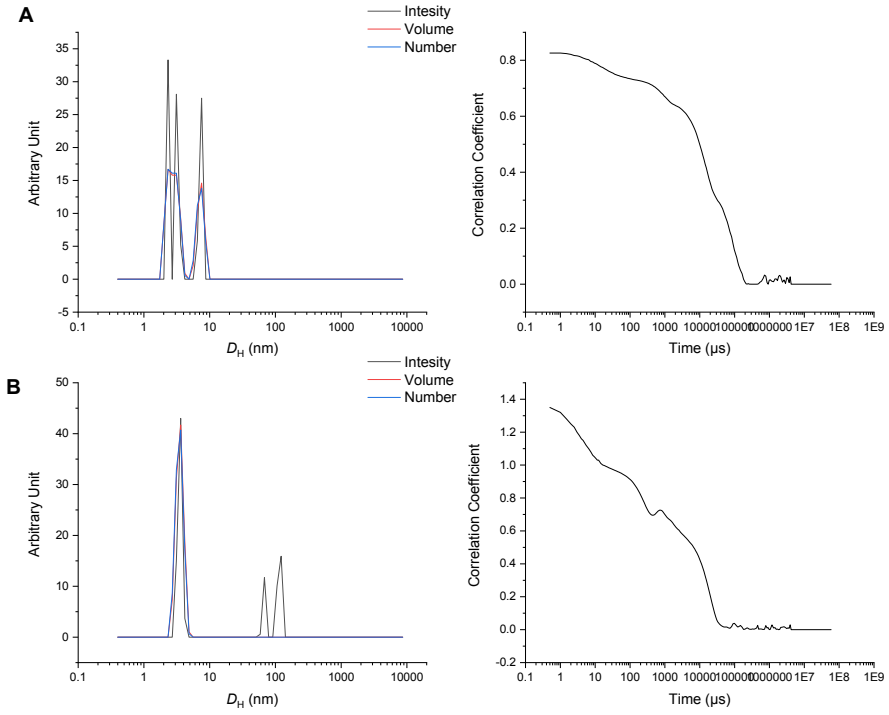

Figure S16 Dynamic light scattering (DLS) particle size distributions and correlograms from poly(ε-allyl-ε-caprolactone) functionalised with 1-decanethiol at 40 mg mL^{-1} concentration in *n*-octane measured at a) 20 °C and b) 90 °C.