Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to:

"Synthesis of degradable poly(ε-caprolactone)-based graft copolymers via a "grafting-from" approach"

Panagiotis Bexis[a], Anthony W. Thomas[a], Craig A. Bell[a,b,c], and Andrew P. Dove[a*]

[a] *Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, CV4 7AL, UK.*

[b] *Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, St Lucia, Queensland, 4072, Australia.*

[c] Centre for Advanced Imaging, The University of Queensland, St Lucia, Queensland, 4072, Australia.

Corresponding Authors

* a.p.dove@warwick.ac.uk

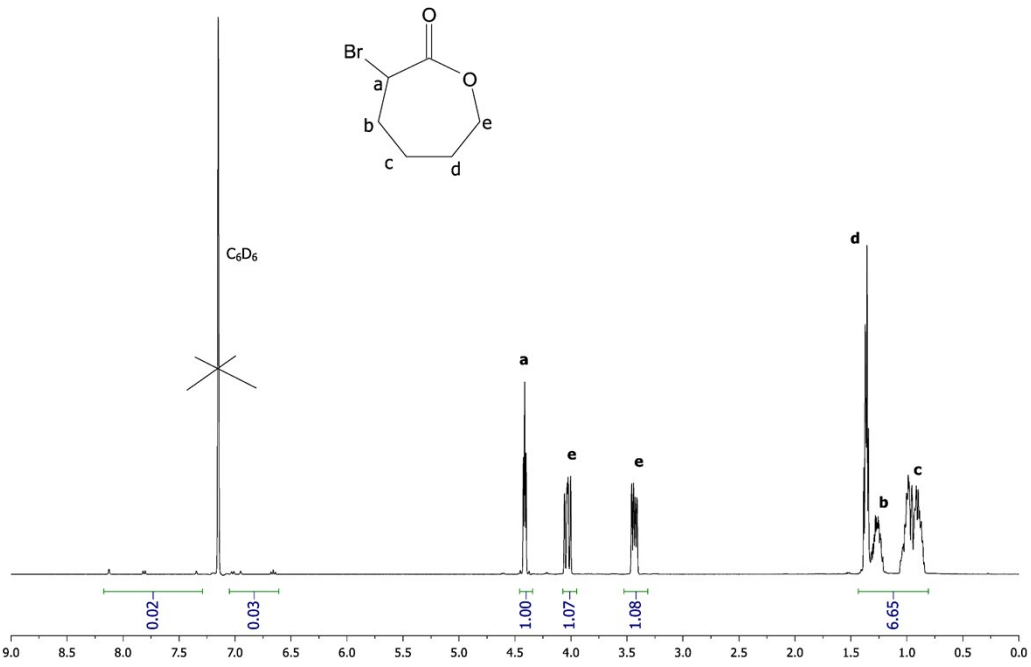

Figure S1. ^{1}H NMR (400 MHz, 298K, $CDCl_3$) spectrum of α-bromo-ε-caprolactone (αBrCL).

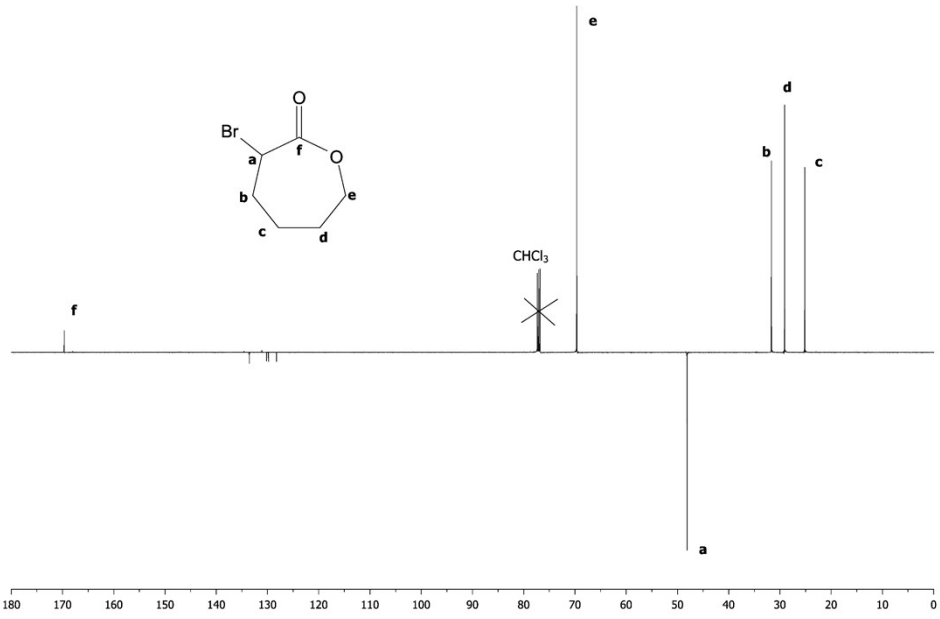

Figure S2. ^{13}C NMR (125 MHz, 298K, $CDCl_3$) spectrum of α-bromo-ε-caprolactone (αBrCL).

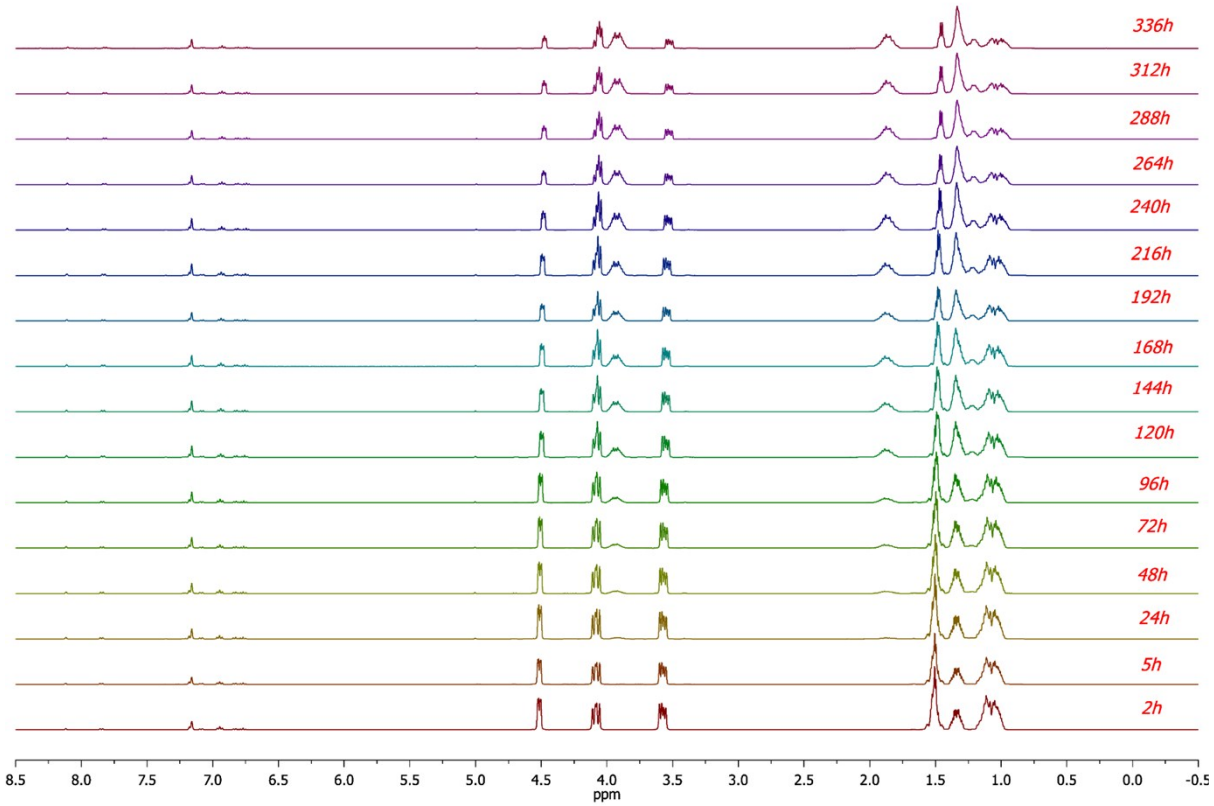

Figure S3. Stacked ^{1}H NMR spectra for the ROP of αBrCL against time (400 MHz, 298K, C_6D_6).

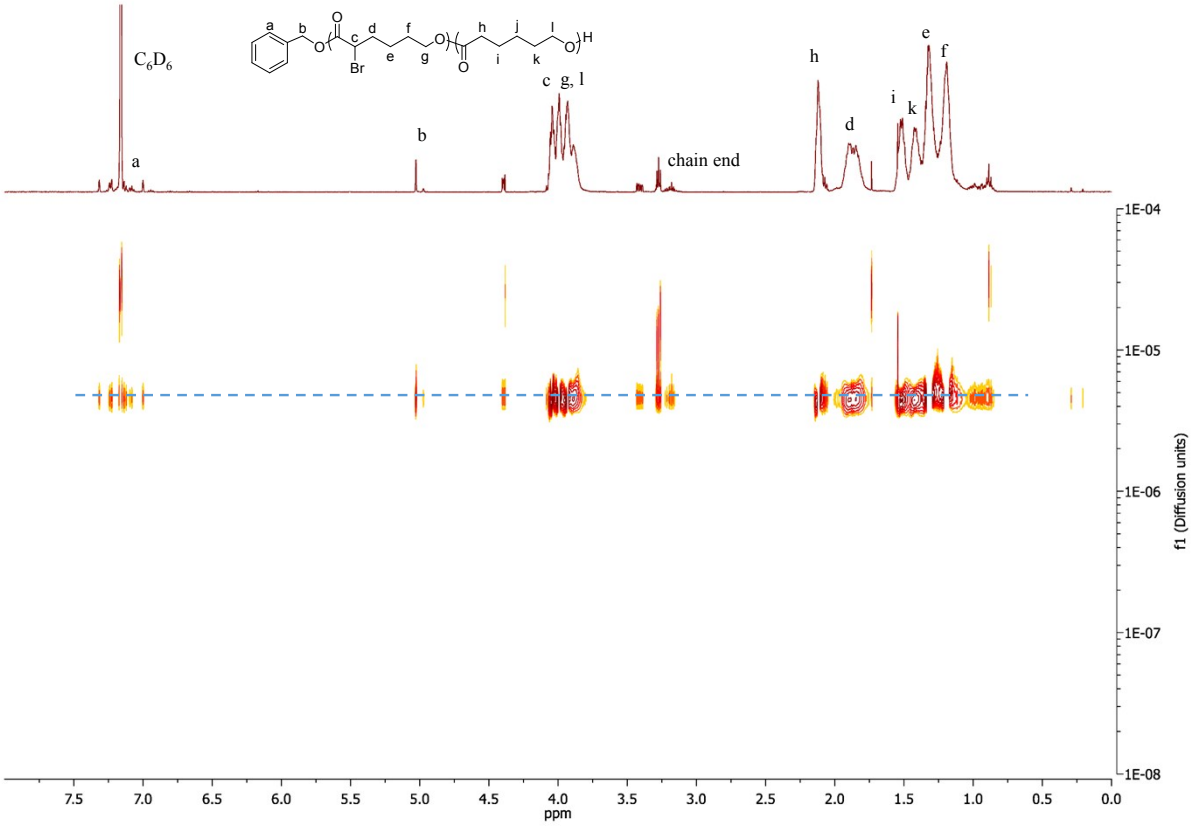

Figure S4. DOSY NMR spectrum of the P(αBrCL)-*co*-(CL) copolymer (400 MHz, 298K, C_6D_6).

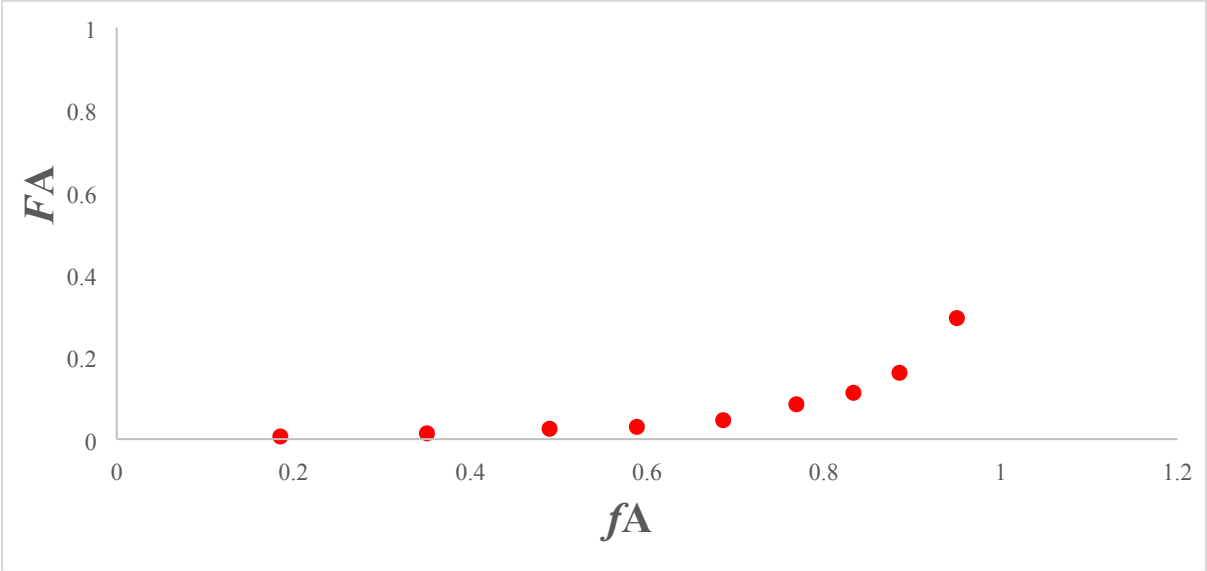

Figure S5. Plot of f_A vs F_A for the copolymerization of ε-CL [A] and αBrCL [B] catalysed by DPP in benzene leading to reactivity ratios results of $r_{\varepsilon\text{-CL}} = 39.25$ and $r_{\alpha\text{BrCL}} = 0.016$. (Nonlinear least squares (NLLS) method).

Table S1. Mole fraction of monomers in the initial feed and copolymers.

Target (αBrCL/CL)	CL feed[a]	BrCL feed[a]	CL conv. (%)[a]	αBrCL conv. (%)[a]	PCL ratio[a]	PBrCL ratio[a]
0/100	1	0	4		1	
10/90	0.9	0.1	4.74	4.6	0.51	0.49
20/80	0.8	0.2	5.3	0.85	0.86	0.14
30/70	0.72	0.28	5.4	1.3	0.8	0.2
40/60	0.62	0.38	5.9	0.7	0.89	0.11
50/50	0.52	0.48	4.9	3.6	0.57	0.43
60/40	0.42	0.58	4.7	0.2	0.96	0.04
70/30	0.33	0.67	5.6	0.15	0.97	0.03
80/20	0.21	0.79	5.3	0.16	0.97	0.03
90/10	0.1	0.9	5.6	1.23	0.82	0.18
100/0	0	1		6.4		1

[a]Determined by ^{1}H NMR spectroscopy.

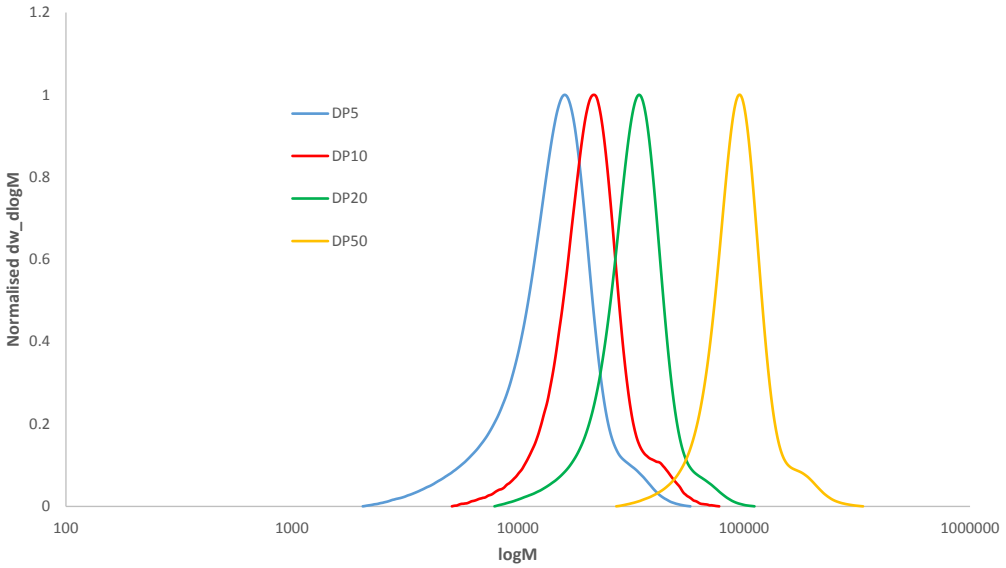

Figure S6. Size exclusion chromatograms of PMA polymers grafted-from the $PBrCL_{80}$ macroinitiator, in DMSO (SEC $CHCl_3$, Polystyrene used as standard).

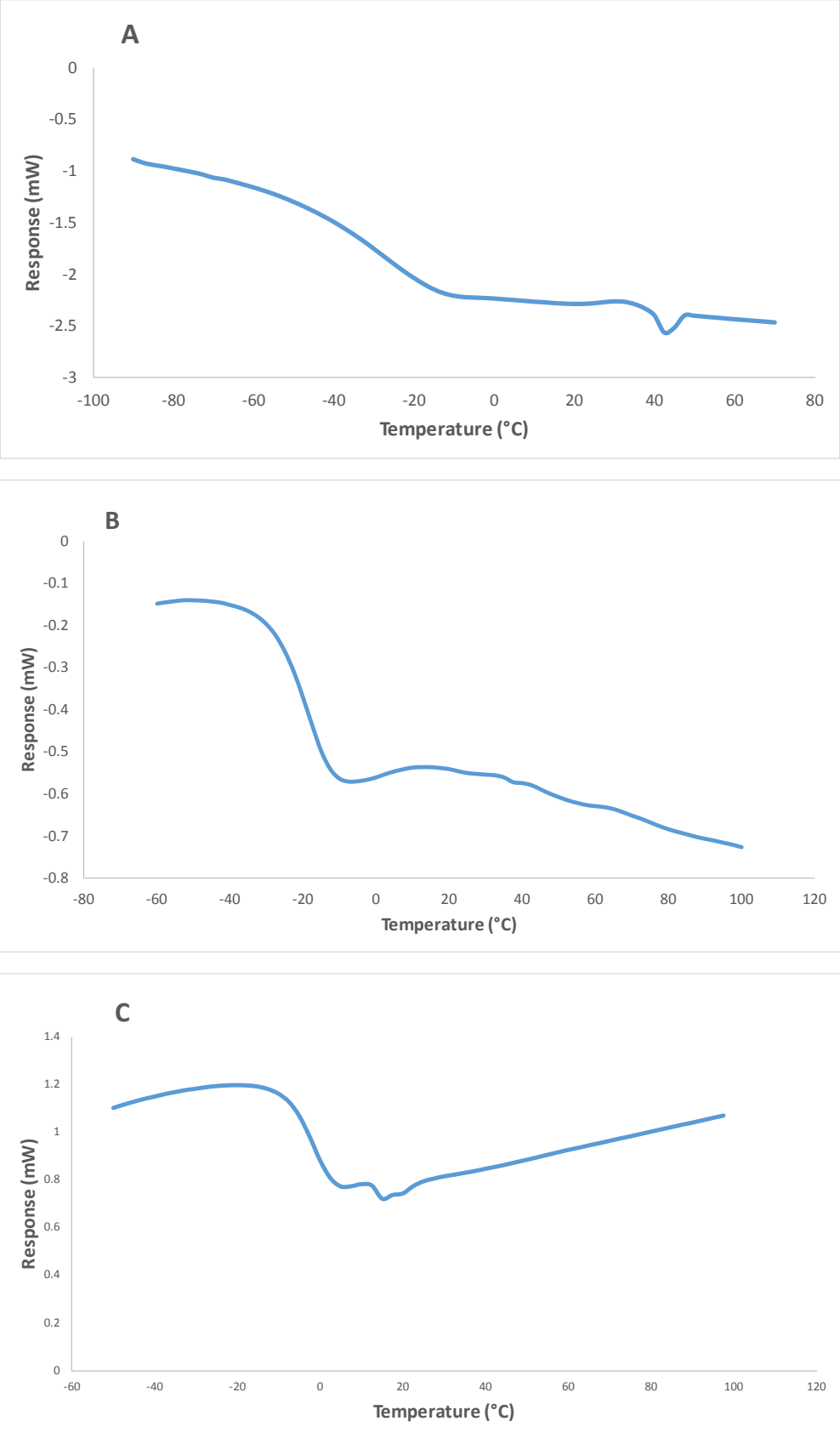

Figure S7. DSC thermograms of (PαBrCL-*co*-PCL)-*g*-PMA polymers (under N_2 atmosphere, second scan measurements, exo down); A) [PεCL$_{60}$-*co*-PαBrCL$_8$]-*g*-PMA$_{160}$, B) [PεCL$_{39}$-*co*-PαBrCL$_{18}$]-*g*-PMA$_{360}$, C) [PεCL$_{24}$-*co*-PαBrCL$_{30}$]-*g*-PMA$_{600}$.