Supplementary information for

## Synthesis of aliphatic polycarbonates with a tuneable thermal response

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## SUPPLEMENTARY EXPERIMENTAL DETAILS

**Synthesis of poly**(*L*-lactide)-*b*-poly(AOMEC)-*b*-poly(*L*-lactide) (PLLA-b-PAOMEC-b-PLLA). PAOMEC (50 mg, 3.2 μmol,  $M_n = 15,800$  g mol<sup>-1</sup>) and *L*-lactide (42 mg, 300 μmol) were dissolved in CDCl<sub>3</sub> (500 μL). DBU (1 mol% to lactide) was then added to catalyse the polymerisation of lactide. The polymerisation was monitored by <sup>1</sup>H NMR spectroscopy. At completion, the polymerisation was quenched by addition of acidic Amberlyst A15 ion exchange resin. The resulting copolymer was then purified by repeated precipitations into cold *n*-hexane to yield pure PLLA-*b*-PAOMEC-*b*-PLLA. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): *δ* 5.91-5.77 (m, 1H, CH<sub>2</sub>-CH=CH<sub>2</sub>), 5.28-5.08 (m, 2H, + 1H, CH<sub>2</sub>-CH=CH<sub>2</sub>, C(O)-C(CH<sub>3</sub>)*H*-O, 4.13-4.05 (m, 4H, O-CH<sub>2</sub>-C-CH<sub>2</sub>-O), 3.91 (dd, <sup>3</sup>*J*<sub>H-H</sub> = 5.4 Hz, <sup>2</sup>*J*<sub>H-H</sub> = 1.7 Hz, 2H, O-CH<sub>2</sub>-CH), 3.31 (s, 2H, C-CH<sub>2</sub>-O), 1.65 (d, <sup>3</sup>*J*<sub>H-H</sub> = 1.6 Hz 2H, C(O)-CH-CH<sub>3</sub>), 1.47 (q, <sup>3</sup>*J*<sub>H-H</sub> = 7.5 Hz, 2H, C-CH<sub>2</sub>-CH<sub>3</sub>), 0.86 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.6 Hz, 3H, CH<sub>2</sub>-CH<sub>3</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): *δ* 169.6 (CH-*C*(O)-CO), 155.0 (O-*C*(O)-O), 134.6 (CH<sub>2</sub>-CH=CH<sub>2</sub>), 116.6 (C-CH=CH<sub>2</sub>), 72.1 (O-CH<sub>2</sub>-CH), 69.3 (C(O)-O-CH<sub>2</sub>), 67.7 (C-CH<sub>2</sub>-O), 41.8 (*C*(CH<sub>2</sub>)<sub>4</sub>), 22.5 (CH<sub>3</sub>-CH<sub>2</sub>-C), 16.7 (CH<sub>3</sub>-CH-C(O), 7.3 (CH<sub>3</sub>-CH<sub>2</sub>-C). *M*<sub>n</sub> = 29,400 g mol<sup>-1</sup> (determined by <sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>). *M*<sub>n</sub> = 30,100 g mol<sup>-1</sup>, *D*<sub>M</sub> = 1.12 (determined by SEC using RI detection and CHCl<sub>3</sub> as eluent).

Synthesis of PAOMEC-*b*-PEG-*b*-PAOMEC. PEG (40 mg, 2 × 10<sup>-5</sup> mol,  $M_n$  = 2,000 g mol<sup>-1</sup>,  $D_M$  = 1.04) and AOMEC (200 mg, 1 mmol) were dissolved in CDCl<sub>3</sub> (250 µL). DBU (5 mol% to monomer) and thiourea (5 mol% to monomer) catalysts were dissolved in the same solvent (250 µL) in a separate vessel and added to the initiator/monomer solution. The conversion of AOMEC to PAOMEC was monitored by <sup>1</sup>H NMR spectroscopy. At 80% monomer conversion, the polymerisation was quenched by addition of acidic Amberlyst A15 ion exchange resin. The resulting copolymer was then purified by repeated precipitation into cold *n*-hexane to yield pure PAOMEC-*b*-PEG-*b*-PAOMEC. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  5.92-5.78 (m, 1H, CH<sub>2</sub>-CH=CH<sub>2</sub>), 5.28-5.08 (m, 2H, CH=CH<sub>2</sub>), 4.13-4.05 (m, 4H, O-CH<sub>2</sub>-C-CH<sub>2</sub>-O), 3.91 (dd, <sup>3</sup>J<sub>H-H</sub> = 5.4 Hz, <sup>2</sup>J<sub>H-H</sub> = 1.7 Hz, 2H, O-CH<sub>2</sub>-CH=CH<sub>2</sub>), 3.66-3.64 (m, <sup>3</sup>J<sub>H-H</sub> = 1.7 Hz, 2H, PAOMEC-O-CH<sub>2</sub>(PEG)), 3.64 (s, 4H, O-CH<sub>2</sub>-CH<sub>2</sub>-O(PEG)), 3.31 (s, 2H, C-CH<sub>2</sub>-O), 1.47 (q, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 2H, C-CH<sub>2</sub>-CH<sub>3</sub>), 0.86 (t,  ${}^{3}J_{H-H}$  = 7.6 Hz, 3H, CH<sub>2</sub>-CH<sub>3</sub>).  $M_{n}$  = 9,200 g mol<sup>-1</sup> (determined by <sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>),  $M_{n}$  = 13,300 g mol<sup>-1</sup>,  $D_{M}$  = 1.07 (determined by SEC using RI detection and CHCl<sub>3</sub> as eluent).

Post-polymerisation functionalisation of PAOMEC with 1-dodecanethiol (DDT). PAOMEC (20 mg, DP 20, 5 µmol) and 1-dodecanethiol (2 equivalents to polymer alkene groups, 202 mg, 1 mmol) were dissolved in 1,4-dioxane (0.4 mL). The radical photoinitiator, 2-benzyl-2-(dimethylamino)-4'morpholinobutyrophenone (0.37 mg, 1 µmol) was dissolved separately in the same solvent (0.1 ml) and added to the polymer/thiol solution. The solution was then transferred to an NMR tube, sealed, placed in a UV light box and irradiated with light ( $\lambda$  = 365 nm) for 30 minutes. The functionalised polymer was purified by repeated precipitations into cold methanol to yield the purified product. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.02 (m, 4H, O-CH<sub>2</sub>-C-CH<sub>2</sub>-O), 3.40 (t, <sup>3</sup>J<sub>H-H</sub> = 5.4 Hz, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), 3.25 (s, 2H, C-CH<sub>2</sub>-O), 2.48 (t, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S), 2.42 (t, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.74 (dt, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S), 1.58-1.45 (m, 2H, S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>), 1.40 (q, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 2H, C-CH<sub>2</sub>-CH<sub>3</sub>), 1.34-1.19 (m, 20H, S- $CH_2-CH_2-(CH_2)_{10}-CH_3)$ , 0.81 (t,  ${}^{3}J_{H-H} = 7.6$  Hz, 6H,  $CH_3-CH_2$ ).  ${}^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  155.3 (O-C(O)-O), 70.3-70.0 (C-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>), 68.0 (O-CH<sub>2</sub>-C-CH<sub>2</sub>-O), 42.0 (O-CH<sub>2</sub>-C-CH<sub>2</sub>-O), 32.3 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>), 32.1 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-CH<sub>2</sub>), 29.8-28.9 (O-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 22.8 (CH<sub>3</sub>-CH<sub>2</sub>-C, S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 14.3 (S-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>10</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 7.7 (CH<sub>3</sub>-CH<sub>2</sub>-C). For DP 24 polymer,  $M_{\rm n}$  = 9,000 g mol<sup>-1</sup> (determined by <sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>),  $M_{\rm n}$  = 10,600 g mol<sup>-1</sup>,  $D_{\rm M}$  = 1.13 (determined by SEC using RI detection and CHCl<sub>3</sub> as eluent).

Post-polymerisation functionalisation of PAOMEC with 3-mercaptopropionic acid (3-MPA). Functionalisation of PAOMEC with 3-mercaptopropionic acid (3-MPA) was carried out using the method described for the functionalisation of PAOMEC with DDT, with the exceptions of the use of ten equivalents of thiol to alkene groups, and purification which was carried out by repeated precipitations into cold *n*-hexane. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  4.14 (m, 4H, O-CH<sub>2</sub>-C-CH<sub>2</sub>-O), 3.53 (t, <sup>3</sup>J<sub>H-H</sub> = 5.4 Hz, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>), 3.38 (s, 2H, C-CH<sub>2</sub>-O), 2.77 (dt, <sup>4</sup>J<sub>H-H</sub> = 12.7, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz, 2H, CH<sub>2</sub>-C(O)OH), 2.66 – 2.59 (m, 4H, CH<sub>2</sub>-S-CH<sub>2</sub>), 1.84 (dt, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>-S), 1.48 (q, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz, 2H, C-  $CH_2$ -CH<sub>3</sub>), 0.87 (t,  ${}^{3}J_{H-H}$  = 7.6 Hz, 6H,  $CH_3$ -CH<sub>2</sub>). For DP 79 polymer,  $M_n$  = 24,800 g mol<sup>-1</sup> (determined by  ${}^{1}$ H NMR, 400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO),  $M_n$  = 19,800 g mol<sup>-1</sup>,  $\mathcal{D}_M$  = 1.10 (determined by SEC using RI detection and DMF as eluent).

Post-polymerisation functionalisation of PAOMEC with benzyl mercaptan (BnSH). Functionalisation of PAOMEC with benzyl mercaptan was carried out using the method described for functionalisations using 3-MPA. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  7.42-7.18 (m, 5H, Ar*H*), 4.20-4.07 (m, 4H, O-C*H*<sub>2</sub>-C-C*H*<sub>2</sub>-O), 3.75 (s, 2H, S-C*H*<sub>2</sub>-Ar), 3.58-3.40 (t, <sup>3</sup>*J*<sub>H-H</sub> = 5.4 Hz, 2H, O-C*H*<sub>2</sub>-CH<sub>2</sub>), 3.34 (s, 2H, C-C*H*<sub>2</sub>-O), 2.51 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.2 Hz, 2H, CH<sub>2</sub>-C*H*<sub>2</sub>-S), 1.87-1.71 (dt, 2H, O-CH<sub>2</sub>-CH<sub>2</sub>-C), 1.46 (q, <sup>3</sup>*J*<sub>H-H</sub> = 7.5 Hz, 2H, C-C*H*<sub>2</sub>-CH<sub>3</sub>), 0.88 (t, <sup>3</sup>*J*<sub>H-H</sub> = 7.6 Hz, 6H, C*H*<sub>3</sub>-CH<sub>2</sub>). For DP 79 polymer, *M*<sub>n</sub> = 25,600 g mol<sup>-1</sup> (determined by <sup>1</sup>H NMR, 400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO), *M*<sub>n</sub> = 16,800 g mol<sup>-1</sup>, *D*<sub>M</sub> = 1.16 (determined by SEC using RI detection and DMF as eluent).

## SUPPLEMENTARY FIGURES



**Figure S1**. <sup>1</sup>H NMR spectrum of 2-allyloxymethyl-2-ethyltrimethylene carbonate (AOMEC) post-distillation (400 MHz, 293 K, CDCl<sub>3</sub>).



**Figure S2**. <sup>1</sup>H NMR spectrum of AOMEC polymerisation taken at 62% monomer conversion.  $[M]_0:[I]_0 = 30$ , initiated from benzyl alcohol, using a catalyst system of 1 mol% DBU and 5 mol% TU (400 MHz, 293 K, CDCl<sub>3</sub>; \* = CHCl<sub>3</sub>).



**Figure S3**. Plot of number-average molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}_M$ ) against % monomer conversion for the homopolymerisation of AOMEC. Conditions: [AOMEC] = 2.0 M in CDCl<sub>3</sub>, [M]<sub>0</sub>:[I]<sub>0</sub> = 50 using 1,4-butanediol as initiator, 5 mol% DBU and 5 mol% TU as catalysts.



**Figure S4**. Plot of number-average molecular weight ( $M_n$ ) and dispersity ( $\mathcal{D}_M$ ) against initial monomer-to-initiator concentration ratio, [M]<sub>0</sub>:[I]<sub>0</sub> for the homopolymerisation of AOMEC. Conditions: [AOMEC] = 2.0 M in CDCl<sub>3</sub>, 1,4-butanediol used as initiator, 5 mol% DBU and 5 mol% TU used as catalysts.



**Figure S5**. <sup>1</sup>H NMR spectrum of PAOMEC<sub>13</sub>-*b*-PEG<sub>62</sub>-*b*-PAOMEC<sub>13</sub> triblock copolymer synthesised using a catalyst system of 5 mol% DBU and 5 mol% TU (400 MHz, 293 K, CDCl<sub>3</sub>;  $* = CHCl_3$ ).



**Figure S6**. Size exclusion chromatograms of PEG prior to chain growth ( $M_n = 2,000 \text{ g mol}^{-1}$ ,  $\mathcal{D}_M = 1.04$ ) and PAOMEC-*b*-PEG-*b*-PAOMEC triblock ( $M_n = 13,300 \text{ g mol}^{-1}$ ,  $\mathcal{D}_M = 1.07$ ). Samples measured against polystyrene standards using CHCl<sub>3</sub> as eluent.



**Figure S7**. <sup>1</sup>H NMR spectrum of  $PLA_{93}$ -*b*-PAOMEC<sub>80</sub>-*b*-PLA<sub>93</sub> triblock copolymer synthesised using a catalyst system of 1 mol% DBU (400 MHz, 293 K, CDCl<sub>3</sub>; \* = CHCl<sub>3</sub>; \*\* = residual hexane from precipitation).



**Figure S8**. Size exclusion chromatograms of PAOMEC prior to chain extension ( $M_n = 15,800 \text{ g mol}^{-1}$ ,  $D_M = 1.13$ ) and PLLA-*b*-PAOMEC-*b*-PLLA triblock copolymer ( $M_n = 30,100 \text{ g mol}^{-1}$ ,  $D_M = 1.12$ ). Samples measured against polystyrene standards using CHCl<sub>3</sub> as eluent.



**Figure S9**. <sup>1</sup>H NMR spectrum of DP 24 PAOMEC functionalised with 1-dodecanethiol. Note the absence of alkene resonances at *ca*.  $\delta$  = 5.8 and 5.15 ppm, which indicates that complete functionalisation has taken place. (400 MHz, 293 K, CDCl<sub>3</sub>; \* = CHCl<sub>3</sub>).



**Figure S10**. Size exclusion chromatograms of DP 24 PAOMEC initiated from pentaerythritol dibenzyl ether ( $M_n = 5,200 \text{ g} \text{ mol}^{-1}$ ,  $\mathcal{D}_M = 1.11$ ) and DP 24 PAOMEC following post-polymerisation functionalisation with 1-dodecanethiol ( $M_n = 10,600 \text{ g} \text{ mol}^{-1}$ ,  $\mathcal{D}_M = 1.13$ ). Samples measured against polystyrene standards using CHCl<sub>3</sub> as eluent.



**Figure S11**. Size exclusion chromatograms showing effect on dispersity of varying exposure time to UV light during functionalisation of PAOMEC with 2 eq. of 3-mercaptopropionic acid per alkene group. No clear effect on dispersity can be observed, with  $D_{\rm M} = ca$ . 1.20 for all samples. Samples measured against poly(methyl methacrylate) standards using DMF as eluent.



**Figure S12**. Size exclusion chromatograms showing effect on dispersity of varying thiol equivalents for functionalisation of PAOMEC with 3-mercaptopropionic acid. Samples measured against poly(methyl methacrylate) standards using DMF as eluent.



**Figure S13**. Graphical representation of dispersity ( $\mathcal{D}_{M}$ ) from SEC to show effect of varying thiol equivalents for functionalisation of PAOMEC with 3-mercaptopropionic acid.



**Figure S14**. <sup>1</sup>H NMR spectrum of PAOMEC<sub>19</sub> grafted with 3-MPA (400 MHz, 293 K,  $(CD_3)_2CO$ ; \* =  $(CH_3)_2CO$ , \*\* = residual 1,4-dioxane).



**Figure S15**. <sup>1</sup>H NMR spectrum of PAOMEC<sub>19</sub> grafted with benzyl mercaptan (400 MHz, 293 K,  $(CD_3)_2CO$ ; \* =  $(CD_3)_2CO$ , \*\* = PDE initiator, \*\*\* = H<sub>2</sub>O).



**Figure S16.** Size exclusion chromatograms of PAOMEC<sub>79</sub> functionalised with 3-MPA and BnSH. Samples measured against poly(methyl methacrylate) standards using DMF as eluent.



**Figure S17**. <sup>1</sup>H NMR spectrum of MeO-PEG<sub>550</sub>-SH (400 MHz, 293 K,  $CDCl_3$ ; \* =  $CHCl_3$ ; \*\* = residual  $CH_2Cl_2$  from washing).



**Figure S18**. Size exclusion chromatogram of MeO-PEG<sub>550</sub>-SH. ( $M_n = 1,150 \text{ g mol}^{-1}, D_M = 1.08$ ). Sample measured against polystyrene standards using CHCl<sub>3</sub> as eluent.



**Figure S19**. <sup>1</sup>H NMR spectrum of PAOMEC-*g*-PEG<sub>550</sub>-OMe (400 MHz, 293 K, CDCl<sub>3</sub>; \* = H<sub>2</sub>O, \*\* = CDCl<sub>3</sub>).



**Figure S20**. Plots of normalised transmittance as a function of temperature for PAOMEC-*g*-PEG<sub>550</sub>-OMe over heating and cooling cycles, indicating low polymer hysteresis.



**Figure S21**. <sup>1</sup>H NMR spectrum of PAOMEC-*g*-PEG<sub>210/550</sub>-SH showing relative integrals for AOMEC region and PEG repeat units, highlighted in orange and blue respectively. (400 MHz, 293 K, CDCl<sub>3</sub>).



**Figure S22**. Plots of normalised transmittance as a function of temperature for PAOMEC-*g*-PEG-OMe with varying average PEG molecular weights prepared by simultaneous grafting of two separate PEG-thiol precursors to PAOMEC.