Synthesis and post-polymerisation modification of an epoxy-functional polycarbonate

Paula K. Kuroishi, Michael J. Bennison, Andrew P. Dove*

Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK.

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

Table of Contents

Figure S1 SEC chromatograms (CHCl ₃ , RI) of PTMOC prepared from 4-methoxybenzyl alcohol catalysed by A) 5 mol% of DBU, B) 5 mol% of DBU and 5 mol% of TU, C) 5 mol% of TBD and D) 1	
mol% of TBD.	S2
Figure S2 ¹³ C NMR spectrum of PTMOC ₆₉ (CDCl ₃ , 125 MHz, 298 K).	S2
Figure S3 ¹ H NMR spectra of functionalisation of PTMOC with benzylamine with different catalysts (CDCl ₃ , 250 MHz, 298 K).	S3
Figure S4 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 12.5$ kg mol ⁻¹ ; $D_M = 1.15$) and	
after post-polymerisation functionalisation with benzylamine using different catalysts.	S3
Figure S5 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 9.7$ kg mol ⁻¹ ; $\mathcal{D}_M = 1.16$) and	
after post-polymerisation functionalisation with diisopropylamine ($M_n = 0.9$ kg mol ⁻¹ ; $D_M =$	
1.15).	S4
Figure S6 SEC chromatograms (CHCl ₃ , RI) of PTMOC before ($M_n = 7.5$ kg mol ⁻¹ ; $D_M = 1.23$) and	
after post-polymerisation functionalisation with 1-dodecanethiol catalysed by 12 mol% of LiOH	
$(M_n = 8.3 (0.5) \text{ kg mol}^{-1}; \mathcal{D}_M = 1.29 (1.04)).$	S4
Figure S7 SEC chromatograms (CHCl ₃ , RI) of PTMOC before ($M_n = 7.5$ kg mol ⁻¹ ; $\mathcal{D}_M = 1.23$) and	
after post-polymerisation functionalisation with 1.25 equivalents of benzylmercaptan catalysed	
by 2 mol% of LiOH (M_n = 9.6 kg mol ⁻¹ ; D_M = 1.17) and 5 mol% of LiOH (M_n = 9.6 (0.6) kg mol ⁻¹ ; D_M	
= 1.47 (1.09)).	S4
Figure S8 SEC chromatograms (CHCl ₃ , RI) of PTMOC before ($M_n = 12.1 \text{ kg mol}^{-1}$; $D_M = 1.28$) and	
after post-polymerisation functionalisation with 2.0 equivalents of benzylmercaptan catalysed	
by 2 mol% of LiOH (M_n = 13.9 kg mol ⁻¹ ; D_M = 1.26).	S5
Figure S9 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 14.2 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.21$) and	
after post-polymerisation functionalisation with 1.25 equivalents of thiophenol catalysed by 2	
mol% of LiOH (M_n = 18.8 kg mol ⁻¹ ; D_M = 1.19) and with 2.0 equivalents of thiophenol catalysed	
by 2 mol% of LiOH (M_n = 18.4 kg mol ⁻¹ ; D_M = 1.19).	S5
Figure S10 SEC chromatograms from the RI and UV detectors (DMF) of a post-polymerisation	
functionalisation of PTMOC with thiophenol catalysed by DBU.	S5
Figure S11. SEC chromatograms (DMR, RI) of PTMOC before ($M_n = 14.7 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.15$) and	
after post-polymerisation functionalisation with thiophenol catalysed by 2 mol% of DBU (M_n =	
19.0 kg mol ⁻¹ ; \mathcal{D}_{M} = 1.16), DMAP (M_{n} = 16.8 kg mol ⁻¹ ; \mathcal{D}_{M} = 1.10), TBD (M_{n} = 6.5 kg mol ⁻¹ ; \mathcal{D}_{M} =	
2.33) and without addition of any catalyst ($M_n = 16.4 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.10$).	S6
Figure S12 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 14.2 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.21$) and	
after post-polymerisation functionalisation with 4-methoxythiophenol ($M_n = 19.4 \text{ kg mol}^{-1}$; $\mathcal{D}_M =$	
1.19) and with 4-chlorothiophenol (M_n = 19.5 kg mol ⁻¹ ; D_M = 1.18).	S6



Figure S1 SEC chromatograms (CHCl₃, RI) of PTMOC prepared from 4-methoxybenzyl alcohol catalysed by A) 5 mol% of DBU, B) 5 mol% of DBU and 5 mol% of TU, C) 5 mol% of TBD and D) 1 mol% of TBD.



Figure S2 ¹³C NMR spectrum of PTMOC₆₉ (CDCl₃, 125 MHz, 298 K).



Figure S3 ¹H NMR spectra of functionalisation of PTMOC with benzylamine with different catalysts (CDCl₃, 250 MHz, 298 K).



Figure S4 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 12.5 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.15$) and after post-polymerisation functionalisation with benzylamine using different catalysts.



Figure S5 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 9.7$ kg mol⁻¹; $D_M = 1.16$) and after post-polymerisation functionalisation with diisopropylamine ($M_n = 0.9$ kg mol⁻¹; $D_M = 1.15$).



Figure S6 SEC chromatograms (CHCl₃, RI) of PTMOC before ($M_n = 7.5$ kg mol⁻¹; $\mathcal{D}_M = 1.23$) and after post-polymerisation functionalisation with 1-dodecanethiol catalysed by 12 mol% of LiOH ($M_n = 8.3$ (0.5) kg mol⁻¹; $\mathcal{D}_M = 1.29$ (1.04)).



Figure S7 SEC chromatograms (CHCl₃, RI) of PTMOC before ($M_n = 7.5 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.23$) and after post-polymerisation functionalisation with 1.25 equivalents of benzylmercaptan catalysed by 2 mol% of LiOH ($M_n = 9.6 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.17$) and 5 mol% of LiOH ($M_n = 9.6 \text{ (0.6) kg mol}^{-1}$; $\mathcal{D}_M = 1.47 (1.09)$).



Figure S8 SEC chromatograms (CHCl₃, RI) of PTMOC before ($M_n = 12.1 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.28$) and after post-polymerisation functionalisation with 2.0 equivalents of benzylmercaptan catalysed by 2 mol% of LiOH ($M_n = 13.9 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.26$).



Figure S9 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 14.2 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.21$) and after post-polymerisation functionalisation with 1.25 equivalents of thiophenol catalysed by 2 mol% of LiOH ($M_n = 18.8 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.19$) and with 2.0 equivalents of thiophenol catalysed by 2 mol% of LiOH ($M_n = 18.4 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.19$).



Figure S10 SEC chromatograms from the RI and UV detectors (DMF) of a post-polymerisation functionalisation of PTMOC with thiophenol catalysed by DBU.



Figure S11. SEC chromatograms (DMR, RI) of PTMOC before ($M_n = 14.7 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.15$) and after post-polymerisation functionalisation with thiophenol catalysed by 2 mol% of DBU ($M_n = 19.0 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.16$), DMAP ($M_n = 16.8 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.10$), TBD ($M_n = 6.5 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 2.33$) and without addition of any catalyst ($M_n = 16.4 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.10$).



Figure S12 SEC chromatograms (DMF, RI) of PTMOC before ($M_n = 14.2 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.21$) and after post-polymerisation functionalisation with 4-methoxythiophenol ($M_n = 19.4 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.19$) and with 4-chlorothiophenol ($M_n = 19.5 \text{ kg mol}^{-1}$; $\mathcal{D}_M = 1.18$).