Synthesis of Carboxylic Acid and Ester Mid-Functionalised Polymers *via* RAFT Polymerisation and ATRP

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Supplementary Material

Below are the actual GPC traces (Figures 1-12) of the carboxylic acid mid-functionalised polystyrene polymers 5a - 5f and poly(butyl acrylate) polymers 6a - 6f. They show the development of a shoulder on the right hand side of the major elution peak as molecular weight (M_n) increases.



Figure 1. GPC trace of compound **5a** ($M_n = 1,555 \text{ g mol}^{-1}$)



Figure 2. GPC trace of compound **5b** ($M_n = 2,597 \text{ g mol}^{-1}$)



Figure 3. GPC trace of compound **5c** ($M_n = 3,735 \text{ g mol}^{-1}$)



Figure 4. GPC trace of compound **5d** ($M_n = 4,682 \text{ g mol}^{-1}$)



Figure 5. GPC trace of compound **5e** ($M_n = 7,136 \text{ g mol}^{-1}$)



Figure 6. GPC trace of compound **5f** ($M_n = 8,293 \text{ g mol}^{-1}$)



Figure 7. GPC trace of compound **6a** ($M_n = 1,290 \text{ g mol}^{-1}$).



Figure 8. GPC trace of compound **6b** ($M_n = 3,261 \text{ g mol}^{-1}$).



Figure 9. GPC trace of compound **6c** $(M_n = 6,541 \text{ g mol}^{-1})$.



Figure 10. GPC trace of compound **6d** $(M_n = 8,161 \text{ g mol}^{-1})$.



Figure 11. GPC trace of compound **6e** ($M_n = 10,037 \text{ g mol}^{-1}$).



Figure 12. GPC trace of compound **6f** ($M_n = 11,572 \text{ g mol}^{-1}$).



Figure 13. First-order kinetic plot and polydispersity *vs*. time for the RAFT mediated polymerisations of styrene, $(\ln [M]_0/[M] \Box, PD \bullet)$, giving polystyrene products **5a-5f**.



Figure 14. First-order kinetic plot and polydispersity *vs.* time for the RAFT mediated polymerisations of *n*-butyl acrylate, $(\ln [M]_0/[M] \Box, PD \blacksquare)$, giving poly(*n*-butyl acrylate) products **6a-6f**.



Figure 15. First-order kinetic plot and polydispersity *vs.* time for the ATRP of *n*-butyl acrylate using 9-fluorenylmethyl functionalised ATRP macroinitiator **8**, $(\ln [M]_0/[M] \Box$, PD **•**), giving products **9a-9f**.