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

Nino Malic\textsuperscript{A} and Richard A. Evans\textsuperscript{A,B,C}

\textsuperscript{A} CSIRO Molecular & Health Technologies, Bag 10, Clayton VIC 3169 Australia and The Cooperative Research Centre for Polymers, 8 Redwood Drive, Notting Hill, VIC 3168, Australia.

\textsuperscript{B} Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW, 2052, Australia.

\textsuperscript{C} Corresponding author. Email: richard.evans@csiro.au

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 ($M_n = 1,555$ g mol$^{-1}$)

Figure 2. GPC trace of compound 5b ($M_n = 2,597$ 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 ($M_n = 7,136$ g mol$^{-1}$)

Figure 6. GPC trace of compound 5f ($M_n = 8,293$ g mol$^{-1}$)
Figure 7. GPC trace of compound 6a ($M_n = 1,290$ g mol$^{-1}$).

Figure 8. GPC trace of compound 6b ($M_n = 3,261$ g mol$^{-1}$).
Figure 9. GPC trace of compound 6c ($M_n = 6,541$ g mol$^{-1}$).

Figure 10. GPC trace of compound 6d ($M_n = 8,161$ g mol$^{-1}$).
Figure 11. GPC trace of compound 6e ($M_n = 10,037$ g mol$^{-1}$).

Figure 12. GPC trace of compound 6f ($M_n = 11,572$ g mol$^{-1}$).
Figure 13. First-order kinetic plot and polydispersity vs. time for the RAFT mediated polymerisations of styrene, (\(\ln [M]_0/[M] \square\), PD ■), giving polystyrene products 5a-5f.

Figure 14. First-order kinetic plot and polydispersity vs. time for the RAFT mediated polymerisations of \(n\)-butyl acrylate, (\(\ln [M]_0/[M] \square\), PD ■), 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, ($\ln [M]_0/[M] \square$, PD ■), giving products 9a-9f.