Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

for

Polymerization of long chain [meth]acrylates by Cu(0)-mediated and catalytic chain transfer polymerisation (CCTP): High fidelity end group incorporation and modification

Athina Anastasaki,[a] *Christopher Waldron,*[a] *Vasiliki Nikolaou,*[a] *Paul Wilson,*[a] *Ronan McHale,*[a] *Tim Smith*[b] *and David M. Haddleton*[a]*

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

Email : D.M.Haddleton@warwick.ac.uk

Supplementary Figures

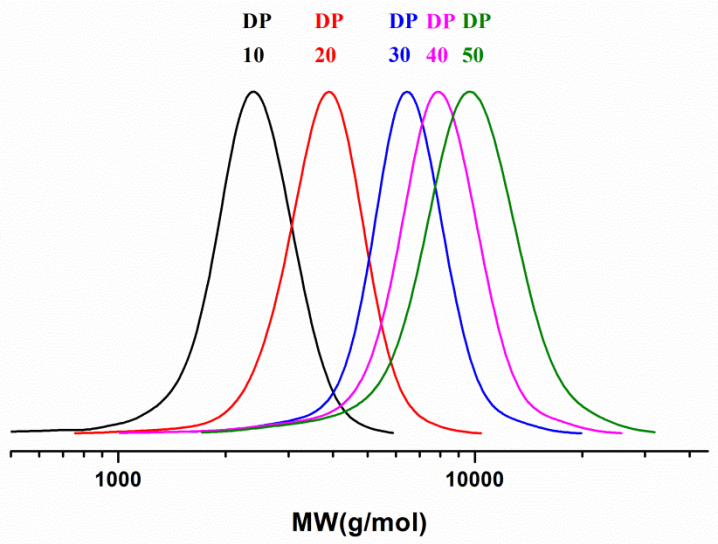


Fig S1. GPC analysis of poly(LA) with DP = 10-50 in IPA (cf table 1 in the manuscript).

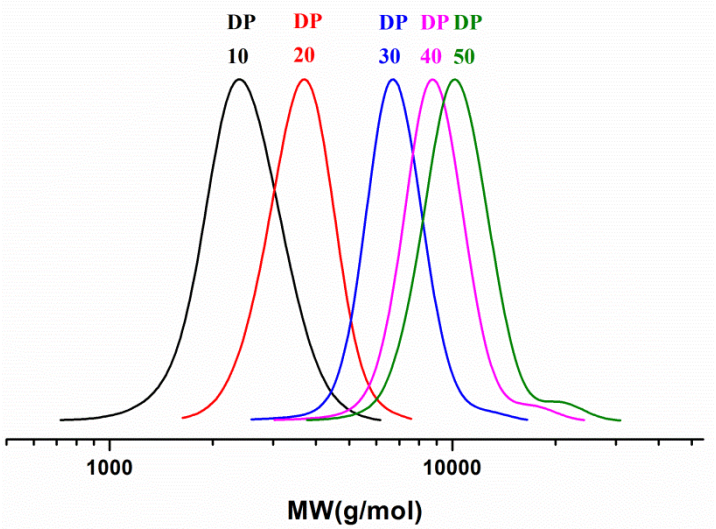


Fig S2. GPC analysis of poly(LA) with DP = 10-50 in toluene/methanol (80/20 v/v) (cf table 1 in the manuscript).

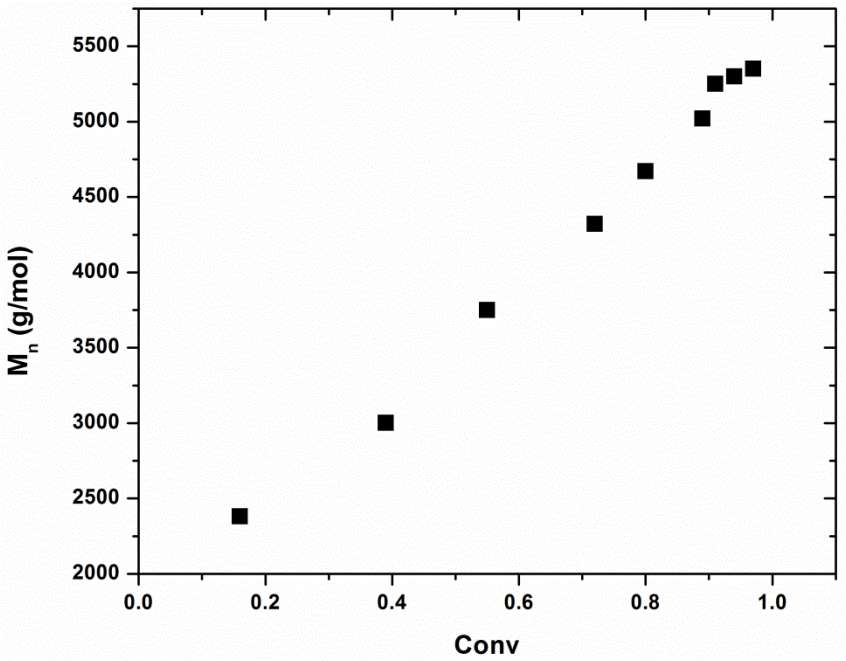


Fig S3. Linear evolution of molecular weight with conversion during the polymerization of LA in toluene/methanol (80/20 v/v) solvent system.

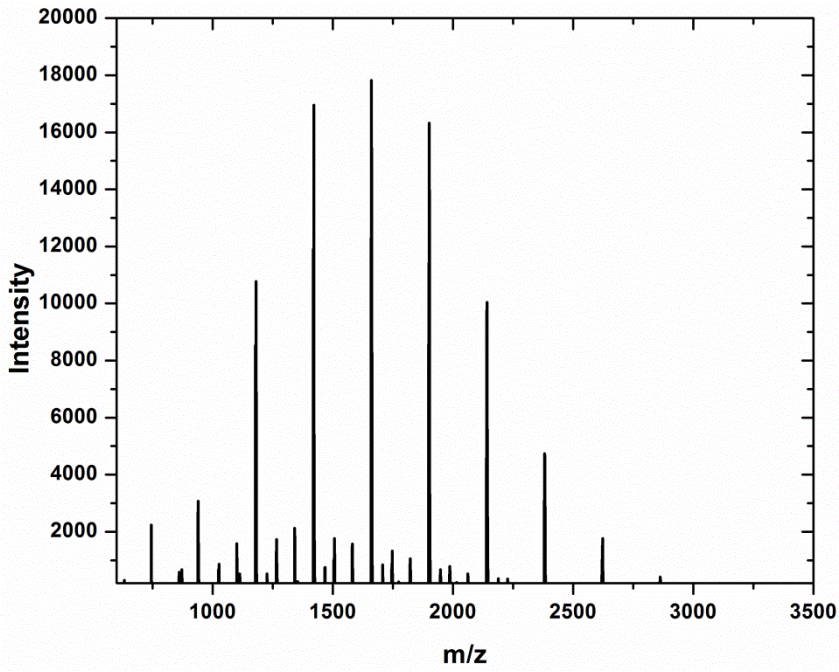


Fig S4a. MALDI-TOF-MS of poly(LA) synthesised in the toluene/methanol (80/20 v/v) solvent system.

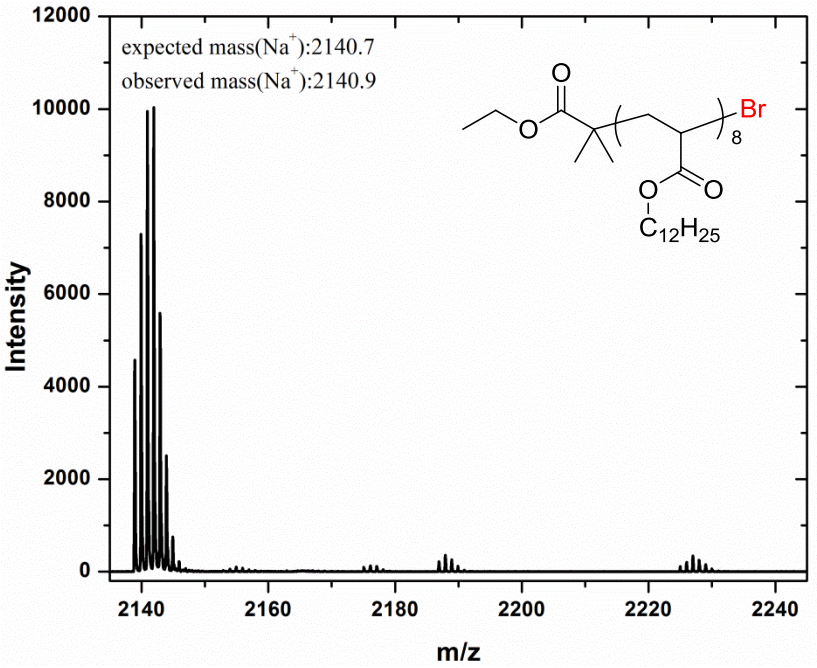
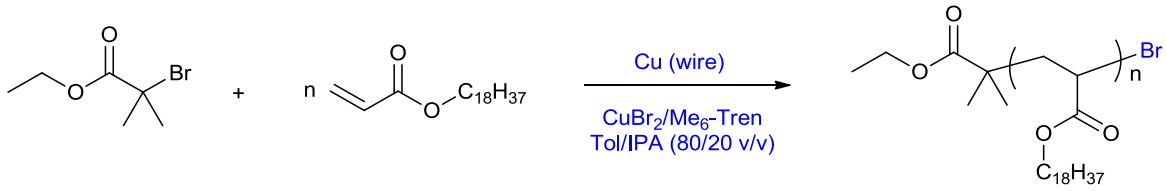


Fig S4b. Zoomed MALDI-TOF-MS of poly(LA) synthesised in the toluene/methanol (80/20 v/v) solvent system displaying near perfect *ω*-bromo end group fidelity.



Scheme S1: Cu(0)-mediated polymerization of stearyl acrylate (SA).

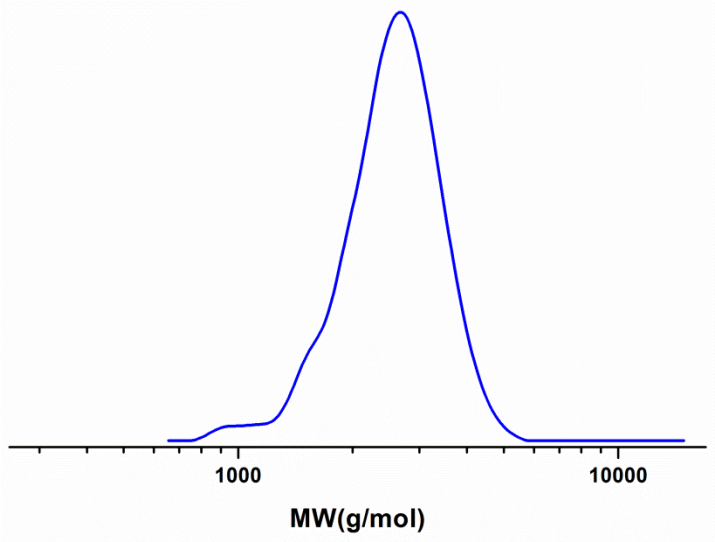


Fig S5. GPC trace of poly(stearyl acrylate) in $CHCl_3$. M_n = ~~???~~ 2500 PDi = 1.09

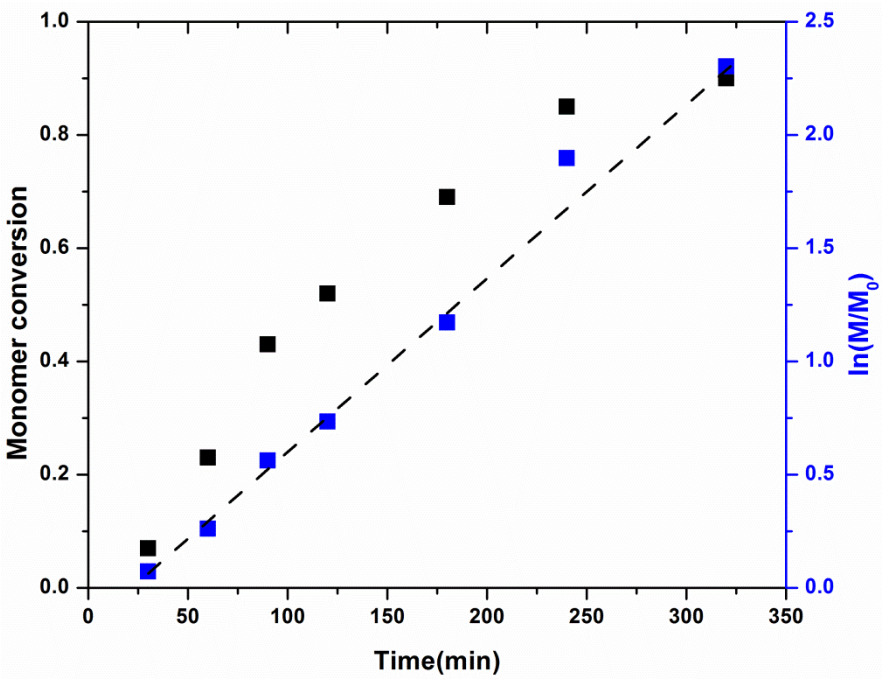


Fig S6a. First order kinetics obtained for the Cu(0)-mediated polymerization of stearyl acrylate.

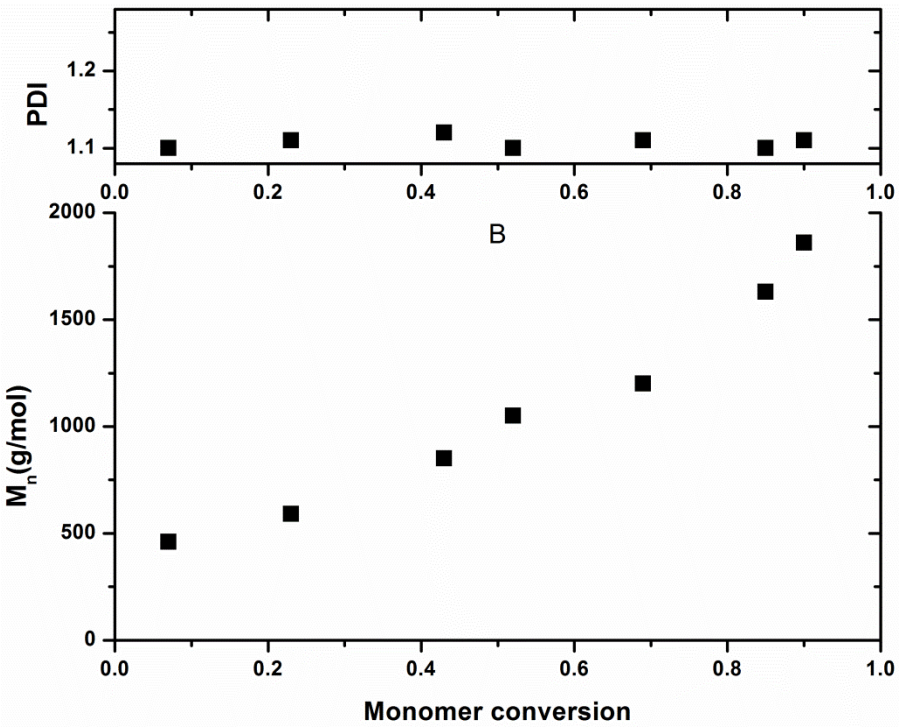


Fig S6b. Molecular weight and PDi evolution during the Cu(0)-mediated polymerization of stearyl acrylate.

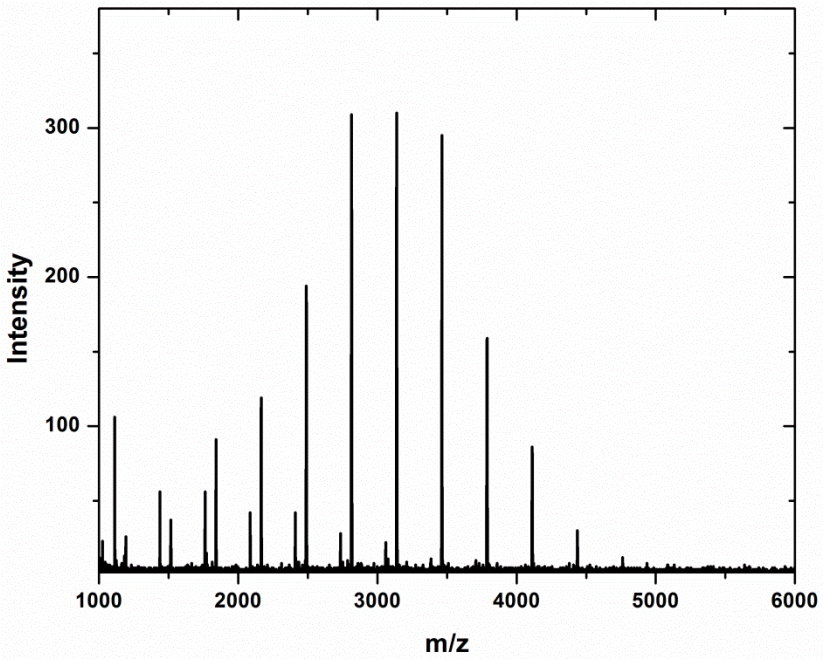


Fig S7a. MALDI-TOF-MS of poly(SA) synthesised in the toluene/IPA (80/20 v/v) solvent system.

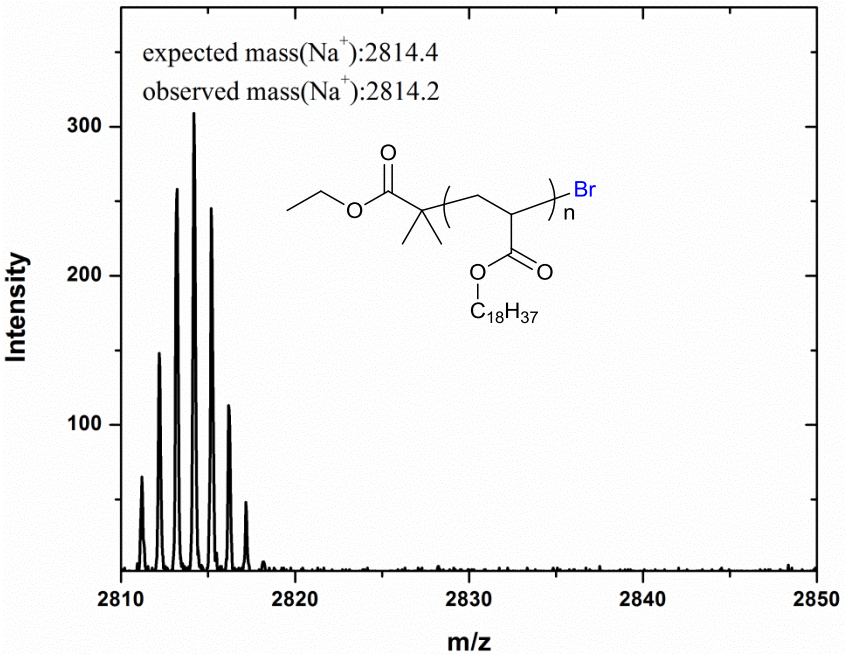
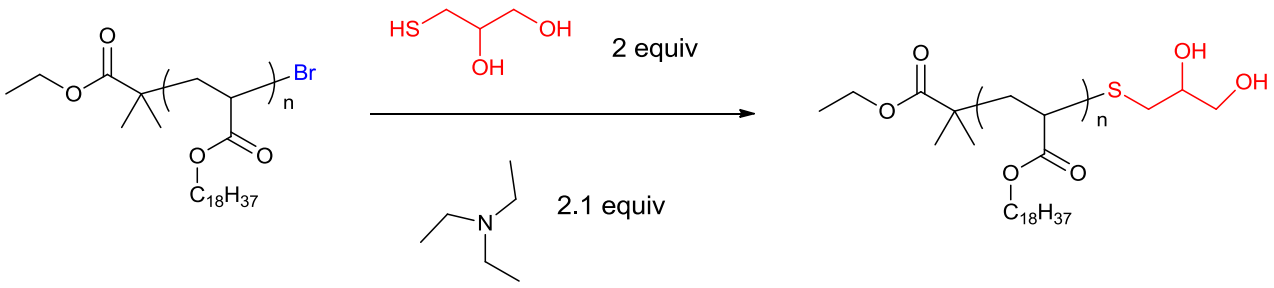


Fig S7b. Zoomed MALDI-TOF-MS of poly(SA) synthesised in the toluene/IPA (80/20 v/v) solvent system displaying near perfect *ω*-bromo end group fidelity.



Scheme S2: Nucleophilic thio-bromo substitution of poly(SA).

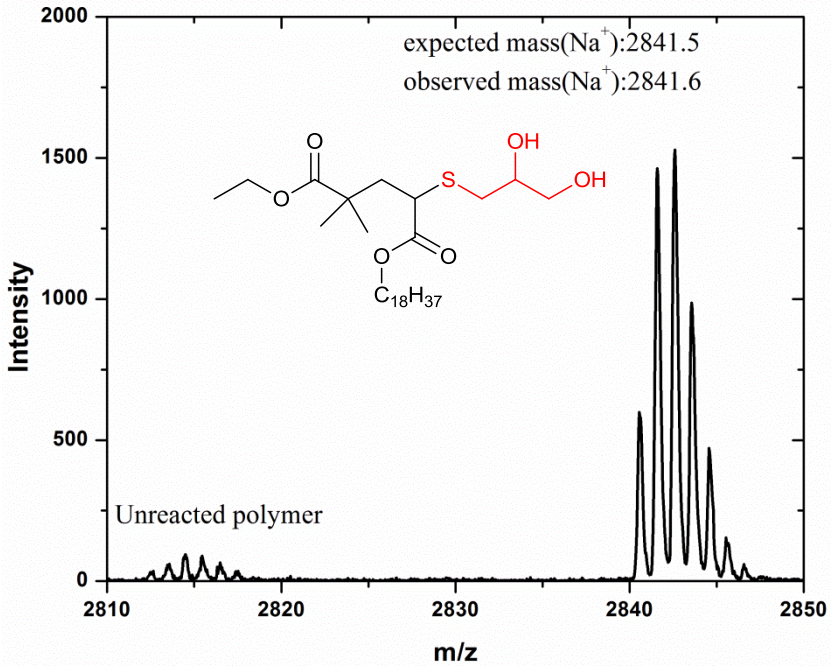


Fig S8. Zoomed MALDI-TOF-MS of thioglycerol functionalised poly(SA) .