

Synthesis and modification of thermoresponsive poly(oligoethylene glycol) methacrylate *via* catalytic chain transfer polymerization and thiol-ene Michael addition

5 Alexander H. Soeriyadi,^a Guang-Zhao Li,^{b,c} Stacy Slavin,^b Mathew W. Jones,^b Catherine M. Amos,^b C.
Remzi Becer,^b Michael R. Whittaker,^a David M. Haddleton,^b Cyrille Boyer,^a Thomas P. Davis^{a*}

^a*Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom.*

^b*Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering,*

The University of New South Wales, Sydney, NSW 2052, Australia.

Table S1. Series of polymerization that was done for the kinetic study (C_s calculation) of catalytic chain transfer polymerization of oligo ethylene glycol methacrylate. All reaction was done in acetonitrile at 70 °C.

| | CoBF (moles) | CoBF/DEGMEMA | M_n (NMR) | $1/DP_n$ |
|----------|---------------------|------------------------------------|-------------------------------|----------------------------|
| 1 | 1.96E-08 | 3.44E-06 | 6566 | 0.0286 |
| 2 | 3.92E-08 | 7.38E-06 | 3794 | 0.0496 |
| 3 | 5.23E-08 | 9.52E-06 | 2200 | 0.0855 |
| 4 | 7.85E-08 | 1.45E-05 | 1765 | 0.1065 |
| 5 | 1.05E-07 | 1.96E-05 | 1236 | 0.1521 |
| | CoBF (moles) | CoBF/PEGMEMA₄₇₅ | M_n | $1/DP_n$ |
| 5 | 2.73E-08 | 1.29E-05 | 15223 | 0.0312 |
| 1 | 3.92E-08 | 1.83E-05 | 15426 | 0.0308 |
| 3 | 5.47E-08 | 2.58E-05 | 9178 | 0.0518 |
| 2 | 7.85E-08 | 3.74E-05 | 6220 | 0.0764 |
| 4 | 1.64E-07 | 7.59E-05 | 3355 | 0.1416 |
| | CoBF (moles) | CoBF/PEGMEMA₁₁₀₀ | M_n | $1/DP_n$ |
| 4 | 2.95E-08 | 6.26E-05 | 63621 | 0.0173 |
| 3 | 5.23E-08 | 1.17E-04 | 41316 | 0.0266 |
| 2 | 1.05E-07 | 2.31E-04 | 21505 | 0.0512 |
| 1 | 1.57E-07 | 2.86E-04 | 16697 | 0.0659 |
| 6 | 1.91E-07 | 4.32E-04 | 12837 | 0.0857 |
| 5 | 2.19E-07 | 4.84E-04 | 12200 | 0.0902 |

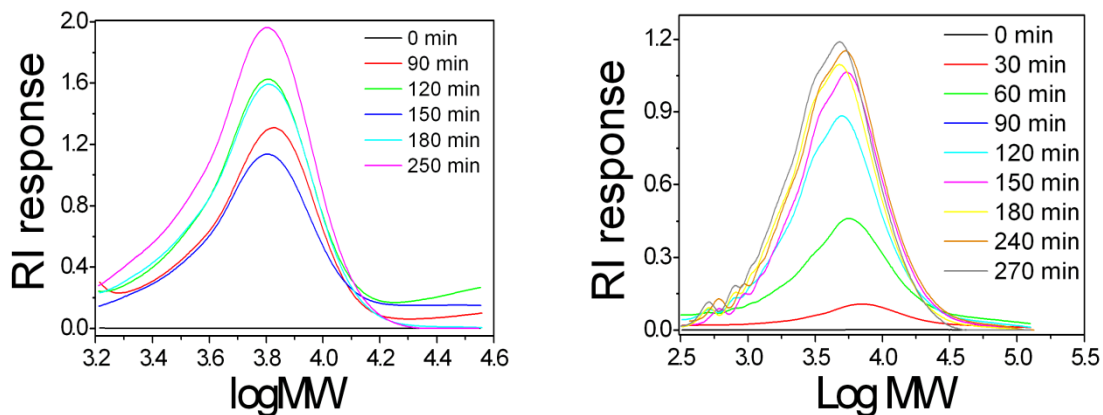


Figure S1. Comparison of GPC traces for one pot (left – P3) and feed mechanisms (right – P2) and the corresponding conversions showing steadier conversion for system employing starve feed process.

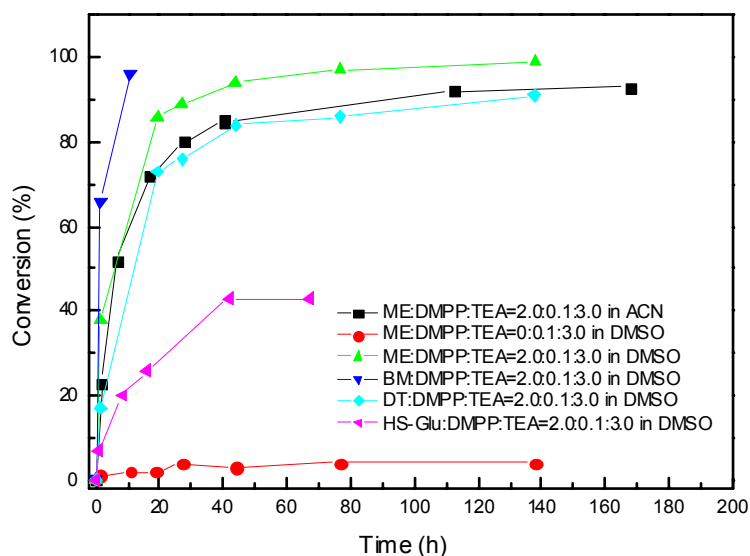


Figure S2. Conversion versus time plot for the DMPP catalyzed thiol-Michael addition of different thiols.

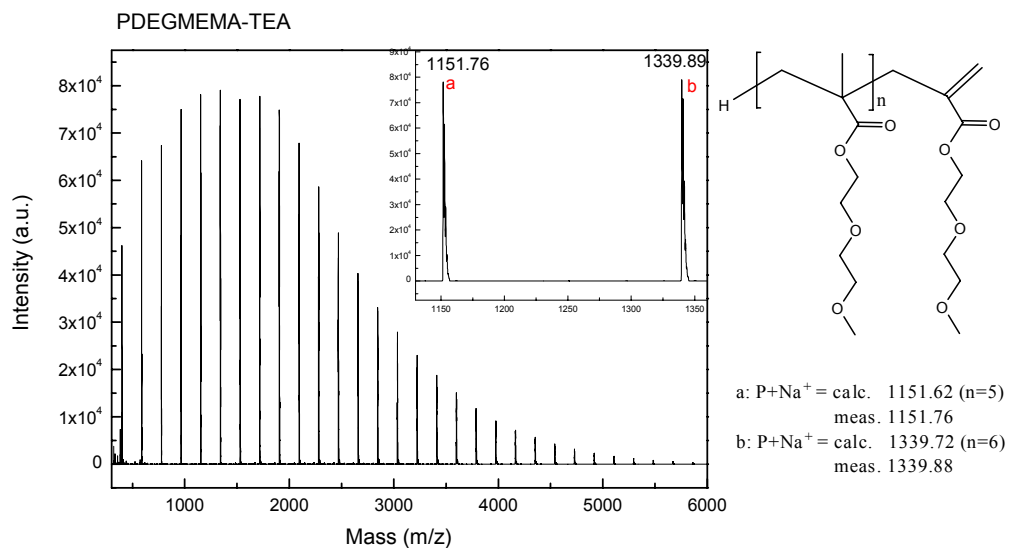


Figure S3. MALDI-ToF MS of poly(DEGMEMA) in the presence of TEA. There is no TEA adduct detected in the MALDI-ToF MS.

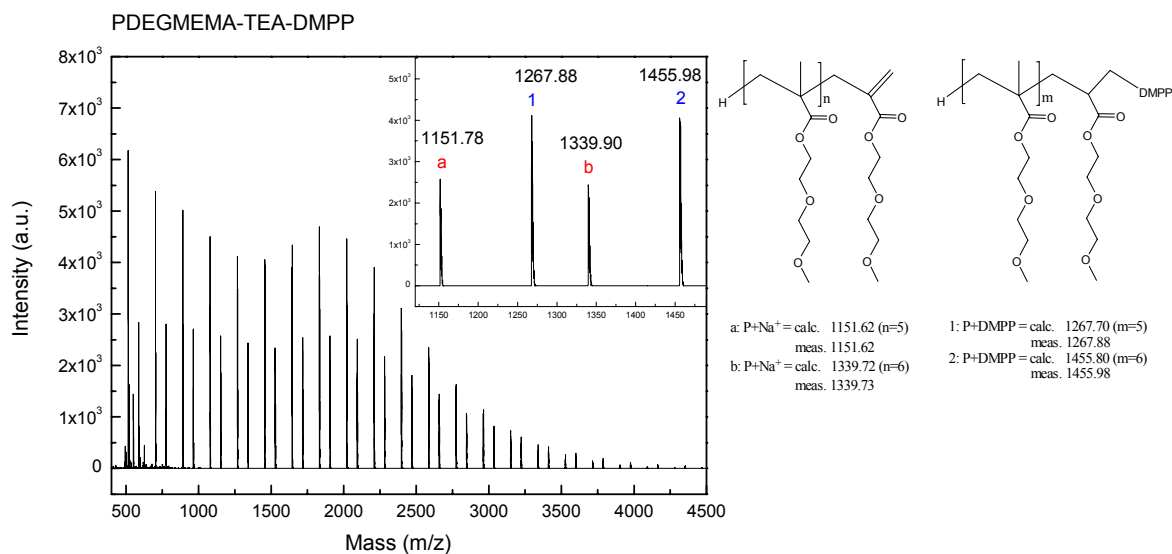


Figure S4. MALDI-ToF MS of poly(DEGMEMA) in the presence of TEA and DMPP. There is no TEA adduct detected in the MALDI-ToF MS whereas the DMPP adducts are clearly visible.

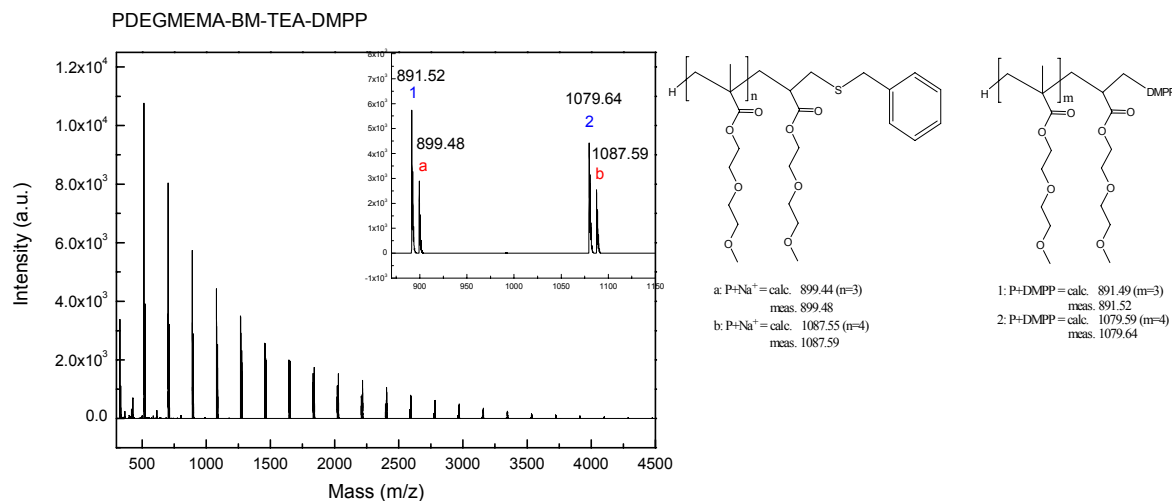


Figure S5. MALDI-ToF MS of poly(DEGMEMA) reacted with benzyl mercaptan in the presence of TEA and DMPP. The large peak corresponds to the DMPP adduct although it does not give a quantitative comparison with the product.

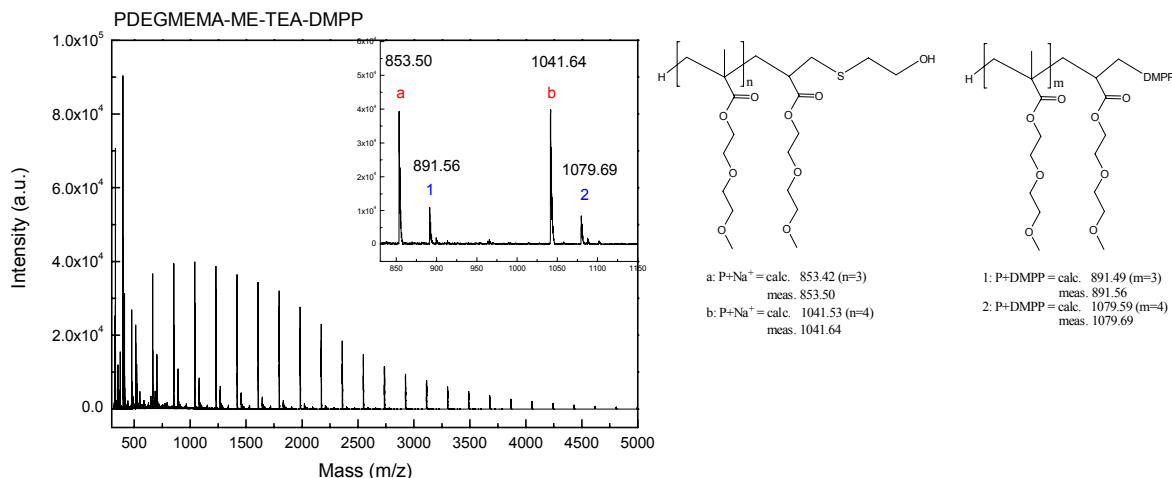


Figure S6. MALDI-ToF MS of poly(DEGMEMA) reacted with 2-mercaptoethanol in the presence of TEA and DMPP. The small peak corresponds to the DMPP adduct although it does not give a quantitative comparison with the product.

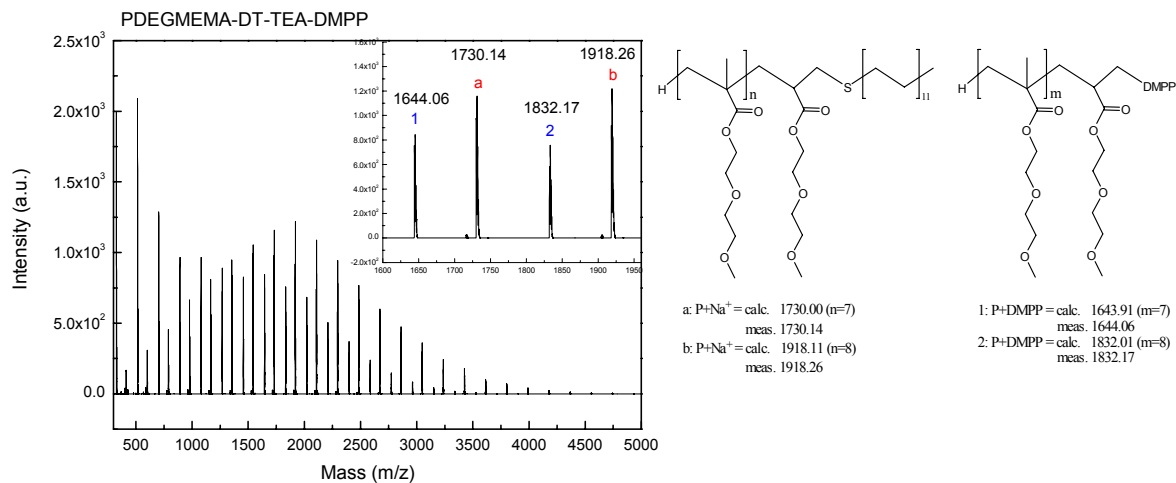


Figure S7. MALDI-ToF MS of poly(DEGMEMA) reacted with 1-dodecanthiol in the presence of TEA and DMPP. The small peak corresponds to the DMPP adduct although it does not give a quantitative comparison.

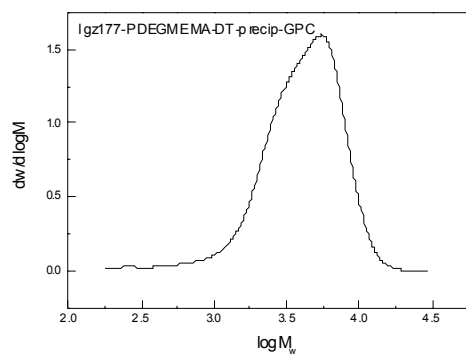


Figure S8. Size exclusion chromatography of 2-dodecanethiol conjugated poly(diethylene glycol) methacrylate catalyzed with hexylamine.

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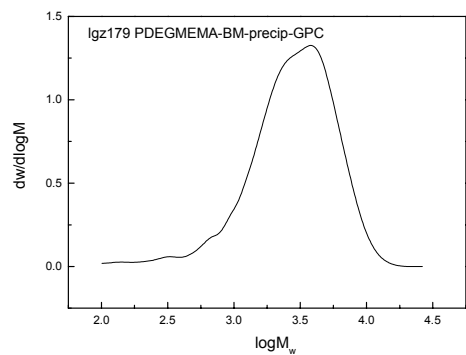


Figure S9. Size exclusion chromatography of benzene mercaptan conjugated poly(diethylene glycol) methacrylate catalyzed with hexylamine.

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