

ARTICLE

Supporting information

Cu(0)-mediated living radical polymerisation in dimethyl lactamide (DML); An unusual green solvent with limited environmental impact

Olivier Bertrand,^a Paul Wilson^a, Gordon A. Bell,^b James A. Burns^b and David M. Haddleton^{*a}

Materials

Dimethyl lactamide (DML) was supplied by Syngenta.

Tris(2-(dimethylamino)ethyl)amine (Me₆TREN) was synthesized according to literature procedure and stored under a nitrogen atmosphere prior to use.^{1,2} The synthesis of pyrenyl-2-bromoisobutyrate (Py-BiB) was adapted from ref ³ Cholesteryl-2-bromoisobutyrate was synthesised as reported by ref ⁴. 3-dihydroxypropyl-2-bromoisobutyrate was synthesised according to literature procedure.⁵ N-succinimidyl 2-bromoisobutyrate was synthesised according to ref ⁶. 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (Mal-BiB) synthesised according to literature procedure.⁷. Adamantyl-2-bromoisobutyrate (Adam-BiB) was synthesised according to literature procedure.⁸

methyl acrylate (MA; Aldrich; 99%), n-butyl acrylate (nBA; Aldrich; 99%), lauryl acrylate (LauA; Aldrich; 90%), poly(ethylene glycole)methyl ether acrylate (PEGA; $M_n = 480$ g/mol; Aldrich) 2-hydroxyl acrylate (HEA; BASF) methyl methacrylate (MMA; Aldrich; 99%), n-butyl methacrylate (nBMA; Aldrich; 99%), lauryl methacrylate (LauMA; Aldrich; 96%), poly(ethylene glycole)methyl ether methacrylate (PEGMA; $M_n = 300$ g/mol; Aldrich) 2-hydroxyl methacrylate (HEMA; BASF) were filtered throw a basic aluminium oxide (Al₂O₃; Aldrich; Activated, basic, Brockmann I) prior to use. 2-(dimethylamino)ethyl acrylate (DMAEA; Aldrich; 98%), 2-(dimethylamino)ethyl methacrylate (DMAEMA; Aldrich; 98%) and N, N, N', N'', N'''-pentamethyldiethylenetriamine (PMDETA; Aldrich; 99%) were distilled prior to use.

Copper wire (diameter = 0.25 mm) was pre-treated by washing in hydrochloric acid for 15 min and rinsed thoroughly with MilliQ water, dried under nitrogen and used immediately. Copper(II) bromide (CuBr₂; Aldrich; 99%), ethyl-2-bromoisobutyrate (EBiB; Aldrich; 98%) and all other chemicals, unless otherwise stated, were used as received.

Instruments and analysis

¹H NMR spectra were recorded on Bruker DPX-250, DPX-300, DPX-400 and spectrometers using deuterated solvents obtained from Aldrich. SEC was conducted on Varian 390-LC system, equipped with refractive index, UV and viscometry detectors, 2 × PLgel 5 mm mixed- D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm) and autosampler. Narrow linear poly (methyl methacrylate) standards in range of 200 to 1.0×10^6 g·mol⁻¹ were used to calibrate the system. All samples were passed through 0.45 µm PTFE filter before analysis.

SEC was conducted on Varian 390-LC system in THF (Et₃N = 2 V%, BHT = 0.01 wt%, T = 30°C) or DMF (5 mM NHBf₄, T = 50°C), equipped with refractive index, UV and viscometry detectors, 2 × PLgel 5 mm mixed- D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm) and autosampler. Narrow linear poly (methyl methacrylate) standards in range of 200 to 1.0×10^6 g·mol⁻¹ were used to calibrate the system. All samples were passed through 0.45 µm PTFE filter before analysis.

UV/Vis spectra were recorded on Agilent Technologies Cary 60 UV-Vis in the range of 350-1100 nm using a cuvette with 10 mm optical length.

All reactions were carried out using standard Schlenk techniques under an inert atmosphere of oxygen-free nitrogen, unless otherwise stated.

Typical procedure for the disproportionation of CuBr in DML.

A Quartz cuvette was filled with CuBr (2.2 mg; 0.015 mmol; 1 eq.) and sealed with a rubber septum. A vial was filled with Me₆TREN (8.2 μ L, 0.03 mmol, 1 eq.) and DML (6ml). The solution was then degassed by nitrogen bubbling for 15 minutes. 3mL of the degassed solution were then introduced in the quartz cuvette with positive nitrogen flux. The solution absorbance was recorded after 0, 1, 10, 20, 30, 60 minutes.

Typical procedure for the polymerization by SET-LRP in DML.

A schlenk tube was filled with EBiB (75 μ L ; 0.29 mmol ; 1 eq.), DML (642 μ L), methyl acrylate (1.3 mL, 14.46 mmol, 50 eq.) and 161.5 μ L of a solution of CuBr₂/Me₆TREN in DML (C_{Cu} = 20 g/L; CuBr₂ : 3.2 mg ,0.014 mmol ,0.05 eq.; Me₆TREN : 9.3 μ L, 0.035 mmol, 0.12 eq.). This solution was degassed by nitrogen bubbling for 15 min. a magnetic barrel rubbed with 5cm of Cu wire was then introduced with positive nitrogen flux. The solution was immersed in an oil bath at 25°C ad stirred for 16h. The polymerization was quenched by quickly cooling the tube in a water–ice bath and exposing the reaction mixture to air. The reaction mixture was diluted with CH₂Cl₂ and washed with water. The organic phase was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The residue was precipitated in cold MeOH.

Typical procedure for the kinetic experiments.

A schlenk tube equipped with a rubber septum was filled with EBiB (100 μ L ; 0.38 mmol ; 1 eq.), DML (5.1 mL), n-butyl methacrylate (6.1 mL, 38.57 mmol, 100 eq.) and 215.4 μ L of a solution of CuBr₂/Me₆TREN in DML (C_{Cu} = 20 g/L; CuBr₂ : 4.3 mg ,0.019 mmol ,0.05 eq.; Me₆TREN : 12.4 μ L, 0.046 mmol, 0.12 eq.). This solution was degassed by nitrogen bubbling for 15 mins. A magnetic flea wrapped with 5cm of Cu wire was then introduced with positive nitrogen flux. The solution was immersed in an oil bath at 25°C ad stirred for 16h under positive nitrogen atmosphere. Sampling of the solution was realized with a cannula (t = 1, 2, 3, 4, 6, 8, 23 h). The samples were purified by the dilution of the polymerization mixture with CH₂Cl₂ and washed with water. The organic phase was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. The residue was precipitated in cold MeOH. The samples were then analysed by GPC.

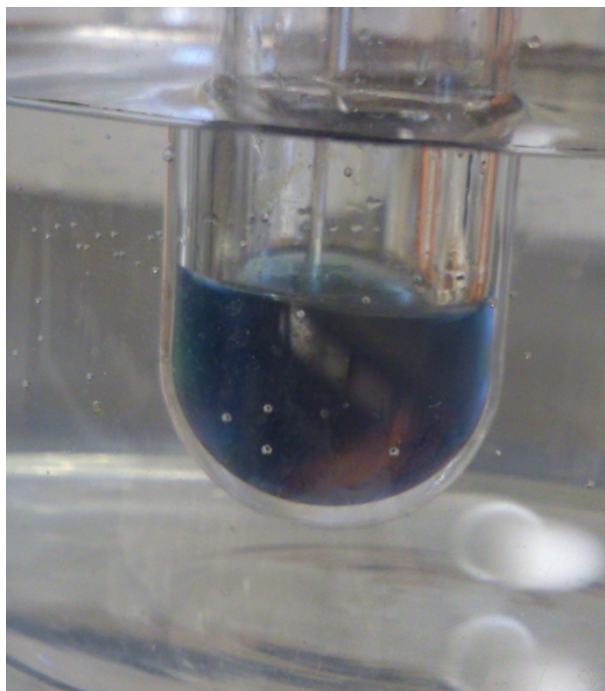


Figure S1: Electronic picture of a solution of CuBr/PMDETA in DML.

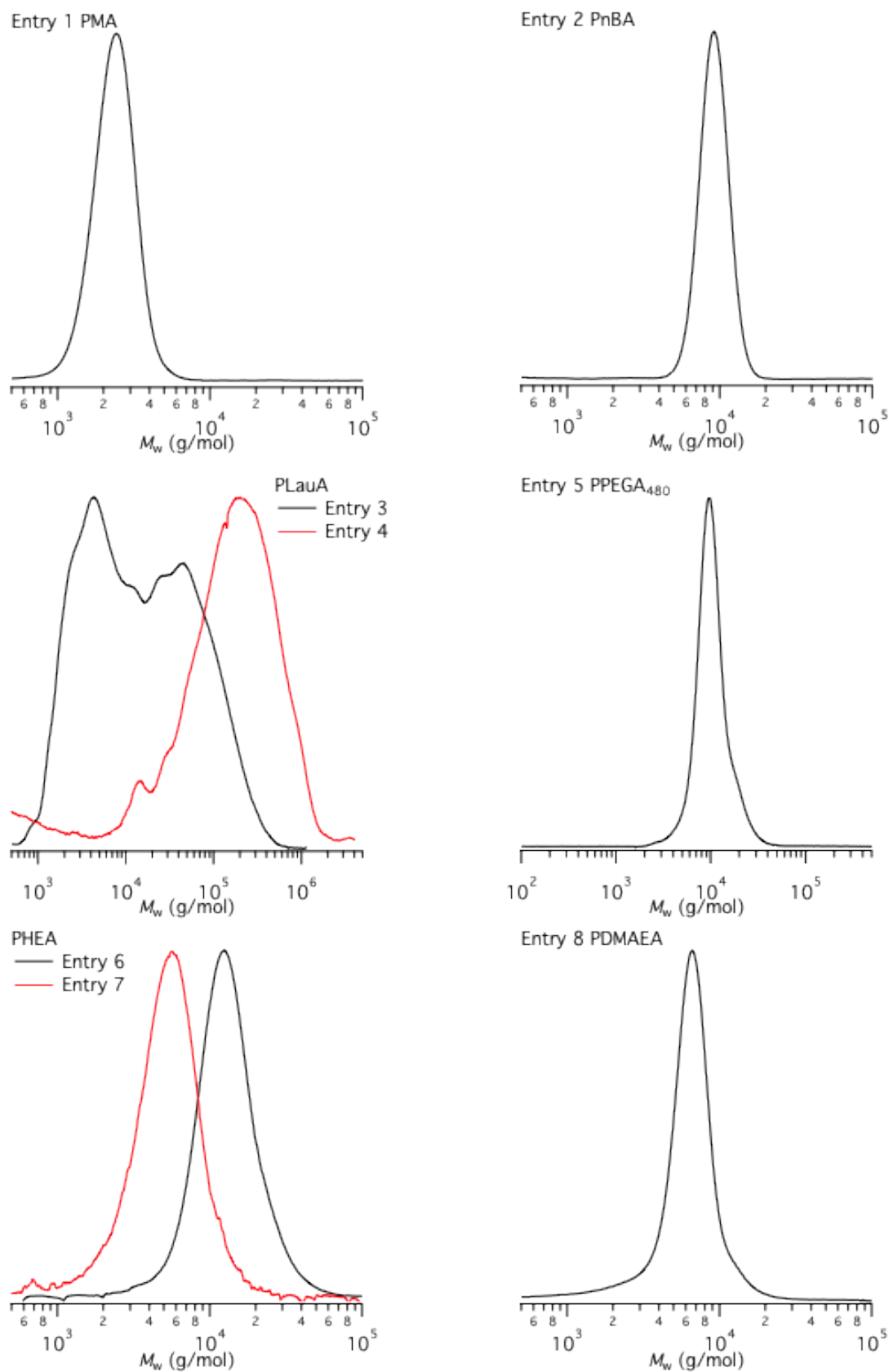


Figure S2: GPC chromatograms of poly(acrylate) synthesized by SET-LRP in DML from Table 1.

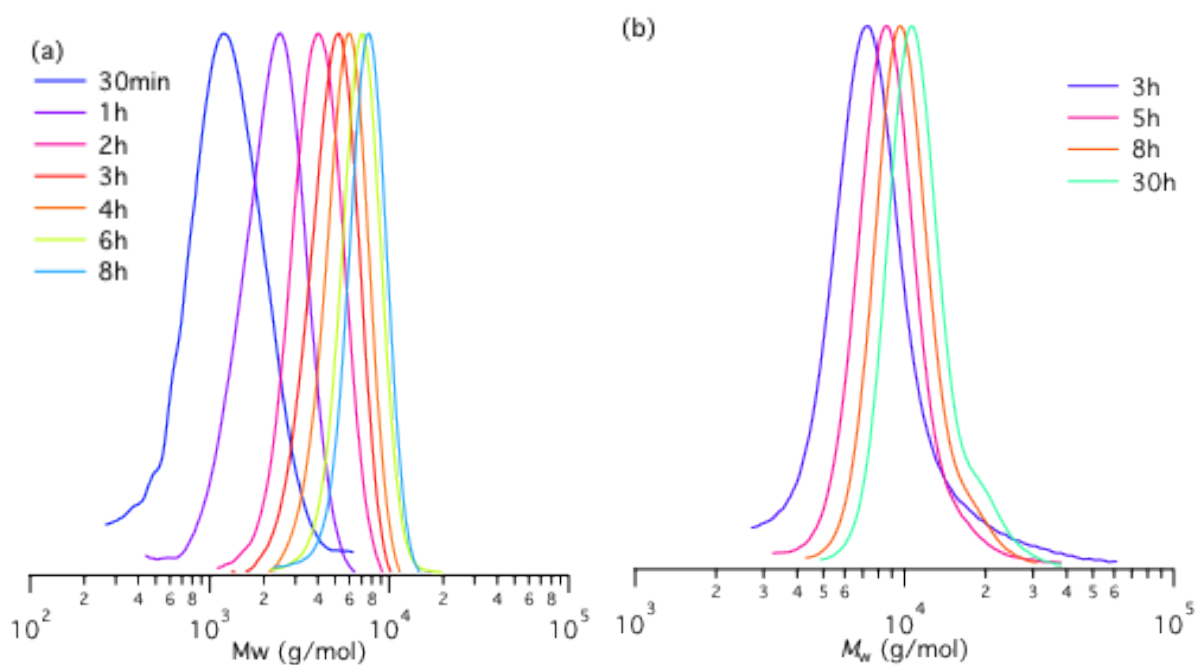


Figure S3: Evolution of the GPC chromatograms with time for the SET-LRP of (a) nBA and (b) PEGA in DML.

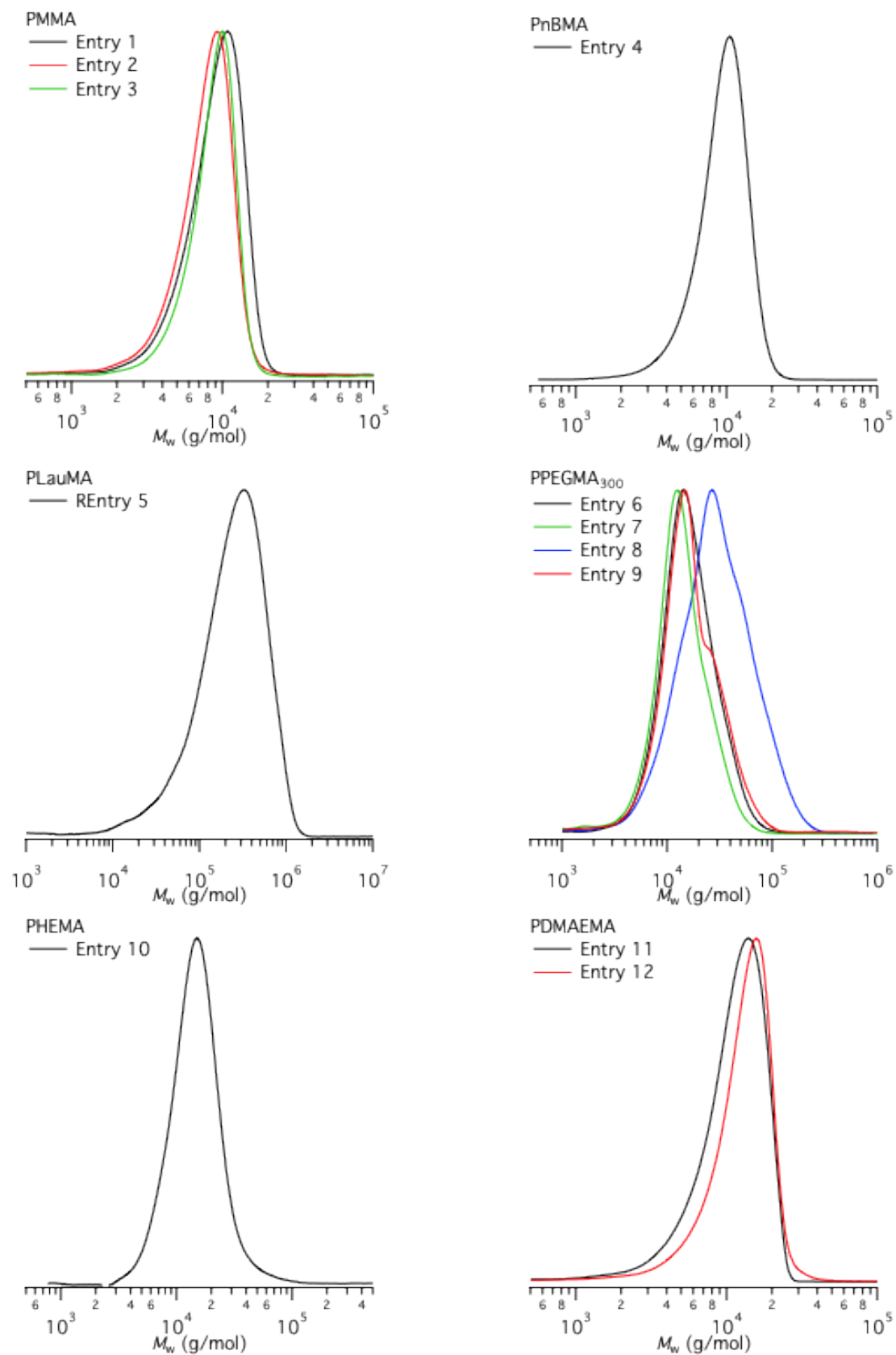


Figure S4: GPC chromatograms of poly(methacrylate) synthesized by SET-LRP in DML from Table 2.



Figure S5: Electronic picture of a solution of CuBr/PMDETA in DML with lauryl acrylate (right) and lauryl methacrylate (left).

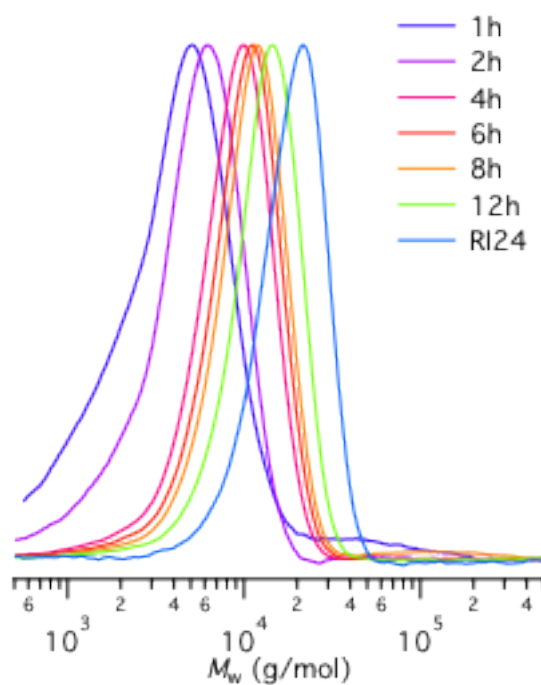


Figure S6: Evolution of the GPC chromatograms with time for the SET-LRP of nBMA in DML.

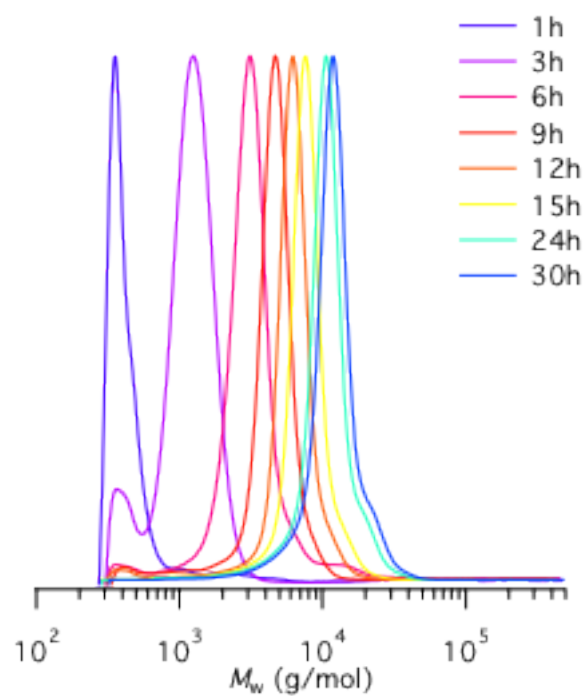
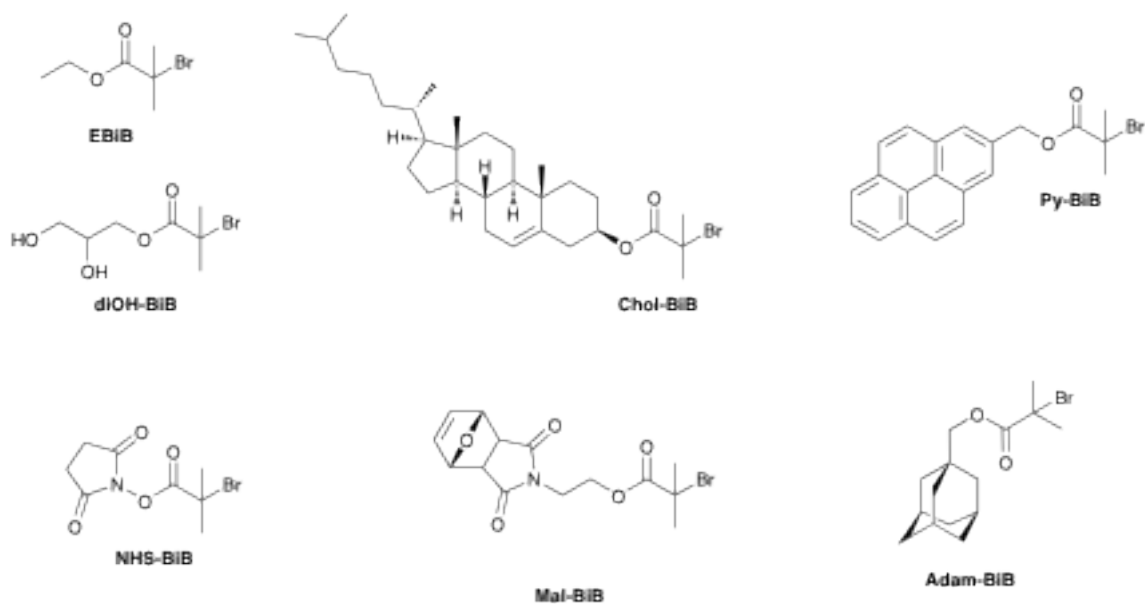


Figure S7: Evolution of the GPC chromatograms with time for the SET-LRP of styrene in DML.



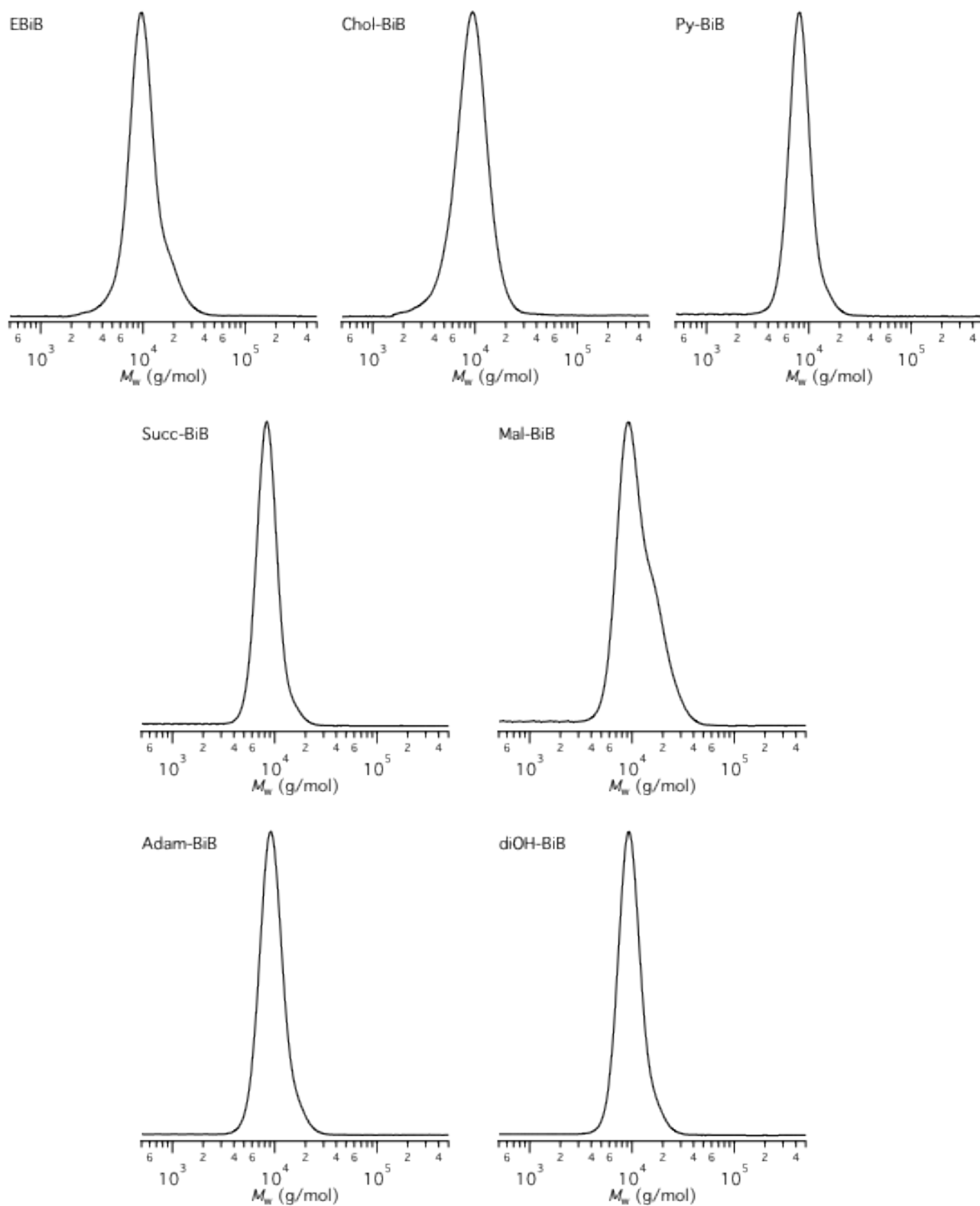


Figure S9: GPC chromatograms of the PPEGA synthesized with different initiator.

Polymerisation of PEGA with Chol-BiB

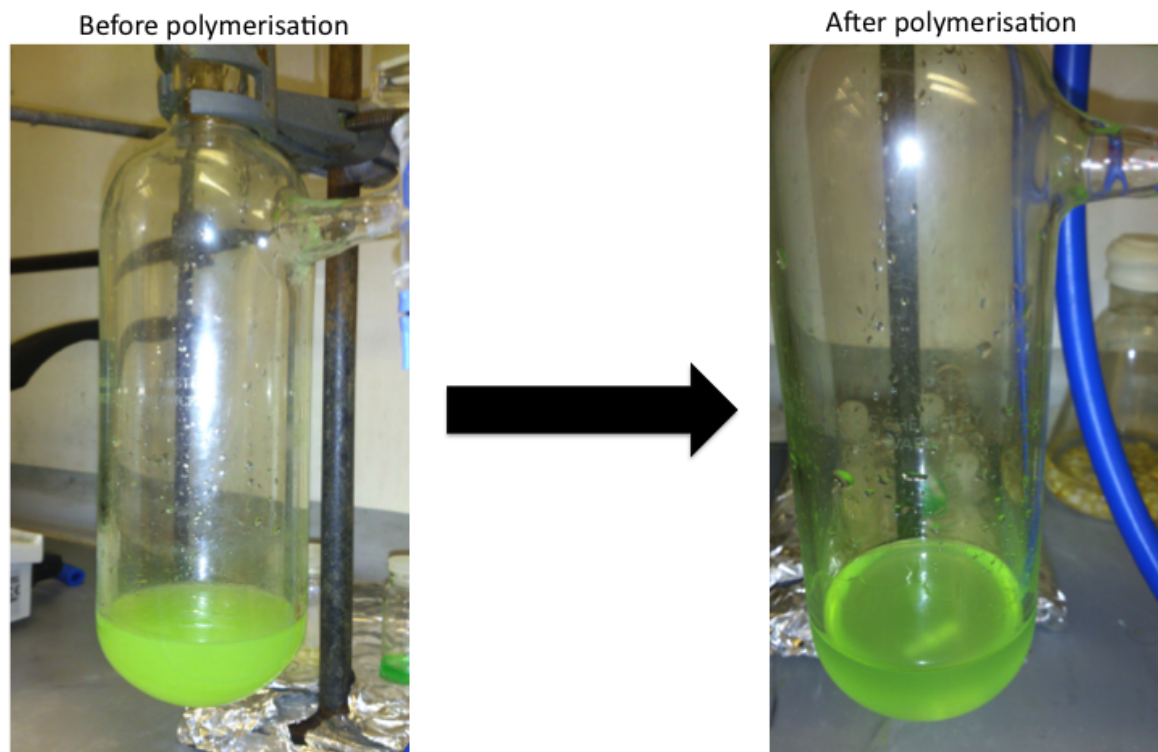


Figure S10: Electronic picture of the polymerization medium for the polymerization of PEGA with Cholesterol-2-bromoisobutyrate : before and after the polymerization.

Notes and references

^a Dept. of Chemistry, University of Warwick, Library Road, Coventry, UK, CV4 7AL. E-mail: D.M.Haddleton@warwick.ac.uk; Tel: +44 (0) 2476 523256

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41–44.
2. J. Queffelec, S. G. Gaynor, and K. Matyjaszewski, *Macromolecules*, 2000, **33**, 8629–8639.
3. J. Babin, M. Lepage, and Y. Zhao, *Macromolecules*, 2008, **41**, 1246–1253.
4. R. A. Cordeiro, N. Rocha, J. P. Mendes, K. Matyjaszewski, T. Gulashvili, A. C. Serra, and J. F. J. Coelho, *Polym. Chem.*, 2013, **4**, 3088.
5. S. Perrier, S. P. Armes, X. S. Wang, F. Malet, and D. M. Haddleton, *J. Polym. Sci. A Polym. Chem.*, 2001, **39**, 1696–1707.
6. F. Lecolley, L. Tao, G. Mantovani, I. Durkin, S. Lautru, and D. M. Haddleton, *Chem. Commun. (Camb.)*, 2004, 2026–2027.
7. G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. J. L. M. Cornelissen, and K. Velonia, *J. Am. Chem. Soc.*, 2005, **127**, 2966–2973.
8. A. Matsumoto and B. Giese, *Macromolecules*, 1996, **29**, 3758–3772.