Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Guanidine as inexpensive dual function ligand and reducing agent for ATRP of methacrylates

Madson R.E. Santos[a‡] *Sílvia M. Ferreir*[b‡] *Patrícia V. Mendonça,*[*a] *Francesco De Bonb*[b] *Armenio C. Serra*[†] *and Jorge F. J. Coelho*[*†]

[a]CEMMPRE, Centre for Mechanical Engineering, Materials and Processes, Department of Chemical Engineering, University of Coimbra, Coimbra 3030-790, Portugal

[b]Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

[*]E-mail addresses: jcoelho@eq.uc.pt (Jorge F. J. Coelho) and patmend@eq.uc.pt (Patrícia V. Mendonça)

Table ST1. Results of the Cu^0-mediated ATRP of MMA using TMG as the ligand and freeze-thaw degassing procedure (replicate experiments). Conditions: $[MMA]_0/[EBPA]_0/[TMG]_0/[CuB_2]_{0;}$ 222/1/0.5/0.1, $[MMA]_0/[DMSO]$ = 1/0.5 (v/v); t = 6.5 h; T = 30 ºC; Cu^0_{wire}: l = 5 cm, d = 1 mm.

Entry	Conv. (%)	M_n^{th} x 10^{-3}	M_n^{SEC} x 10^{-3}	$Đ$	I_{eff} (%)
1	64	15.0	21.4	1.29	70
2	66	15.0	48.8	2.32	30
3	71	16.9	74.6	1.49	22

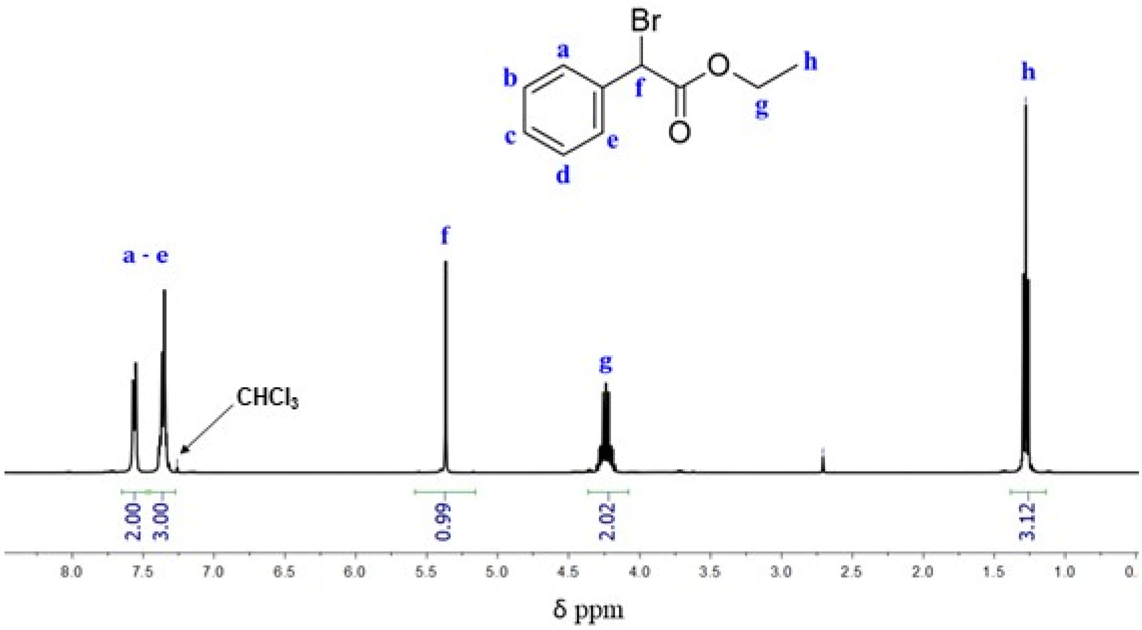

Figure SF1. 400 MHz [1]H NMR, in $CHCl_3$, of ethyl α-bromophenyl acetate (EBPA).

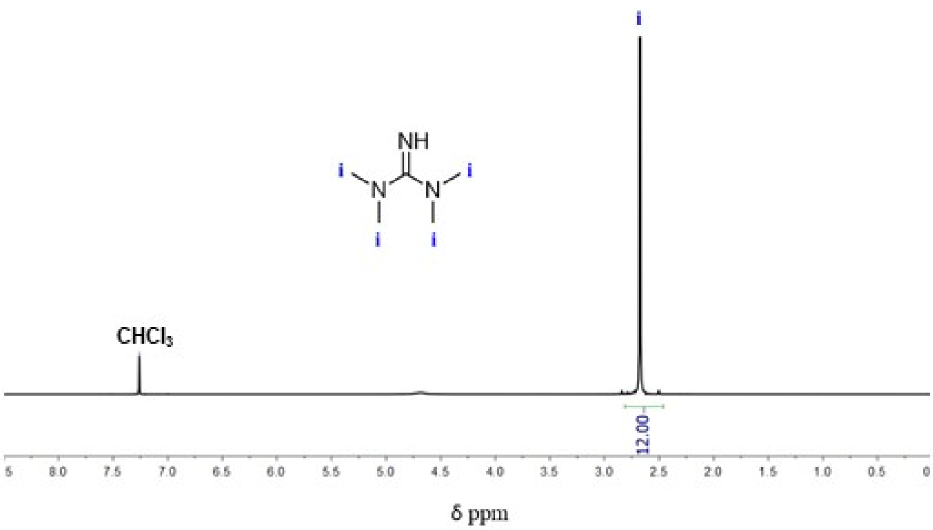

Figure SF2. 400 MHz [1]H NMR, in $CHCl_3$, of 1,1,3,3-tetramethylguanidine (TMG).

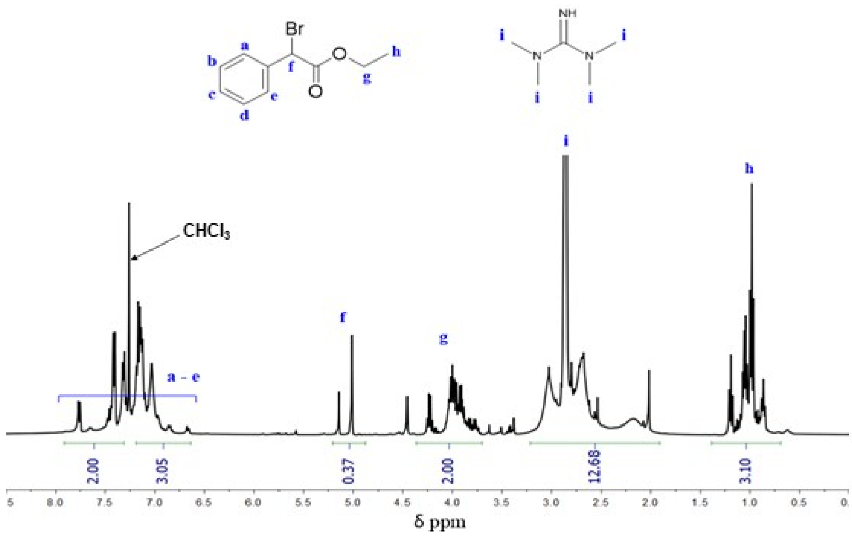

Figure SF3. 400 MHz ^{1}H NMR, in $CHCl_3$, of a $[EBPA]_0/[TMG]_0 = 1/1$ (molar)

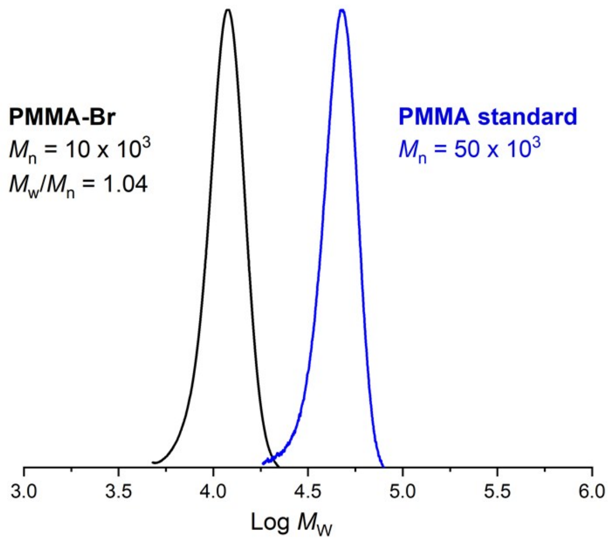

Figure SF 4. SEC traces of a PMMA-Br ($M_n^{SEC} = 10 \times 10^3$; $M_w/M_n = 1.12$) prepared by SARA ATRP using TMG as the ligand (black line) and a PMMA standard (blue line).

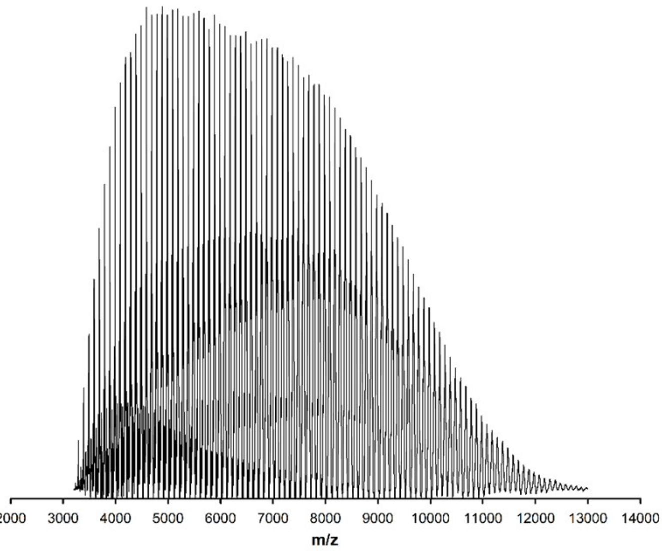

Figure SF5. MALDI-TOF MS spectrum of PMMA-Br (M_n^{SEC} = 7000, M_w/M_n = 1.14) from m/z 500 to 7500, using DCTB matrix.

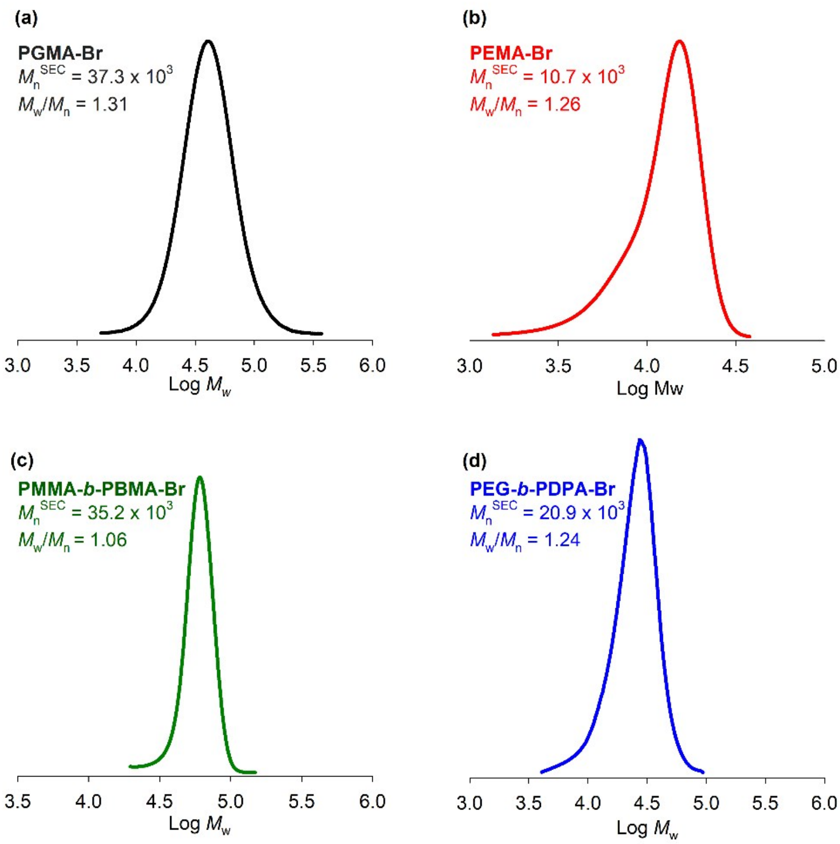

Figure SF6. SEC traces of the polymethacrylates obtained by SARA ATRP.

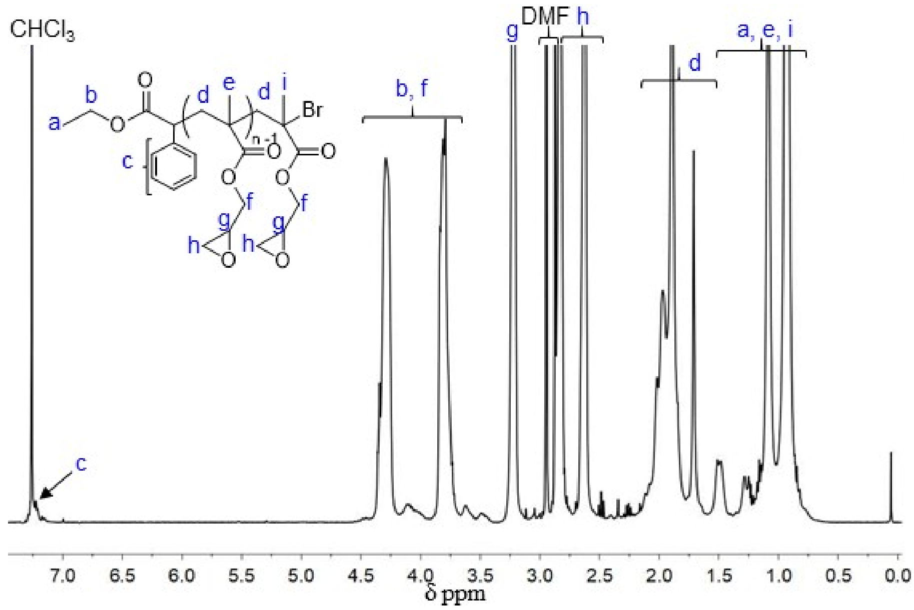

Figure SF7. 400 MHz [1]H NMR spectrum, in $CHCl_3$, of PGMA-Br homopolymer (M_n^{th} = 22600, M_n^{SEC} = 37300, M_w/M_n = 1.31).

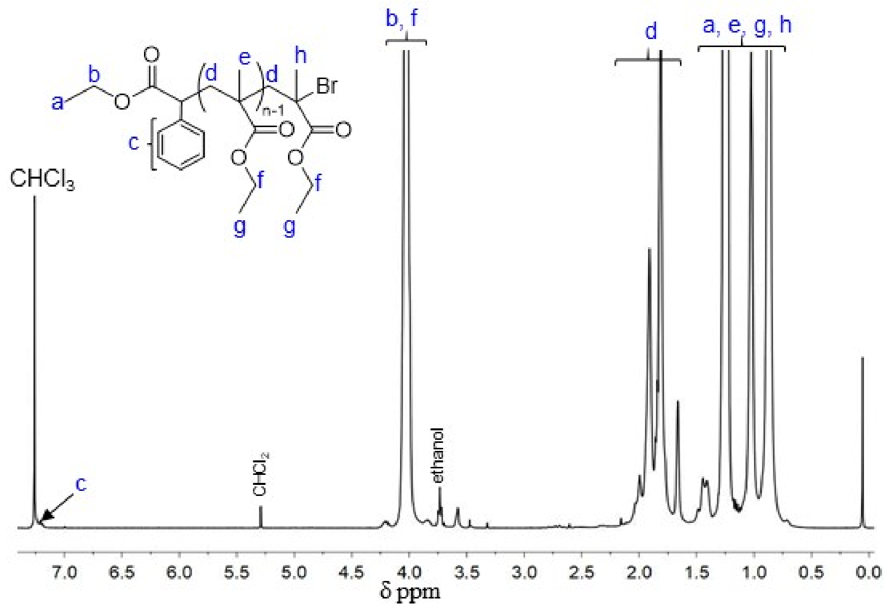

Figure SF8. 400 MHz [1]H NMR spectrum, in $CHCl_3$, of PEMA-Br homopolymer (M_n^{th} = 8340, M_n^{SEC} = 1070, M_w/M_n = 1.26).

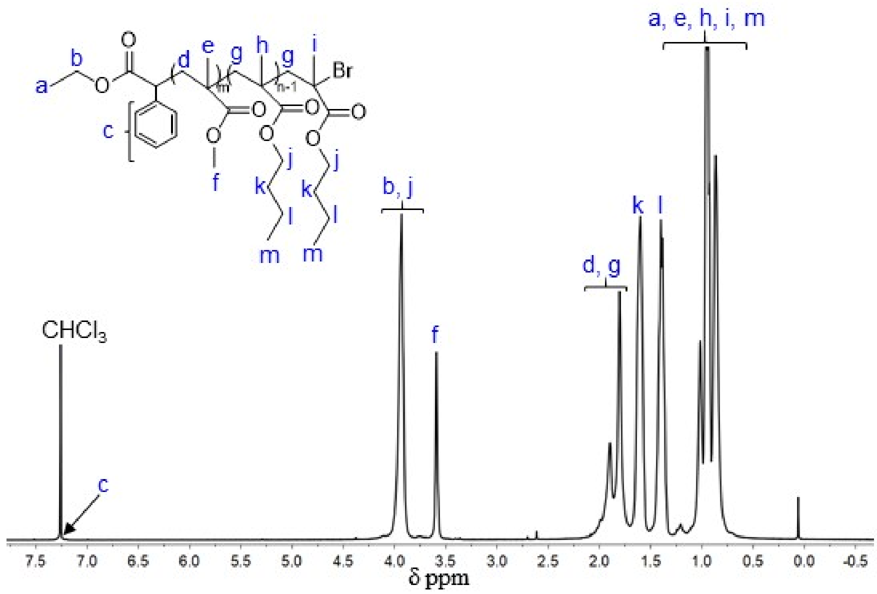

Figure SF9. 400 MHz ¹H NMR spectrum in $CHCl_3$ of PMMA-*b*-PBMA-Br copolymer (M_n^{th} = 27900, M_n^{SEC} = 35200, M_w/M_n = 1.06).

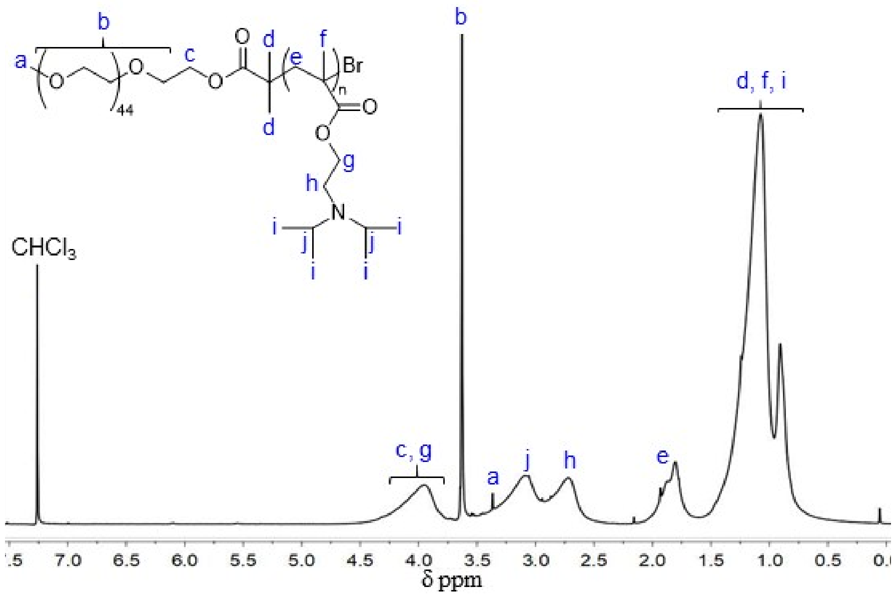

Figure SF10. 400 MHz ¹H NMR spectrum in $CHCl_3$ of PEG-*b*-PDPA-Br block copolymer (M_n^{th} = 20100, M_n^{SEC} = 20900, M_w/M_n = 1.24).

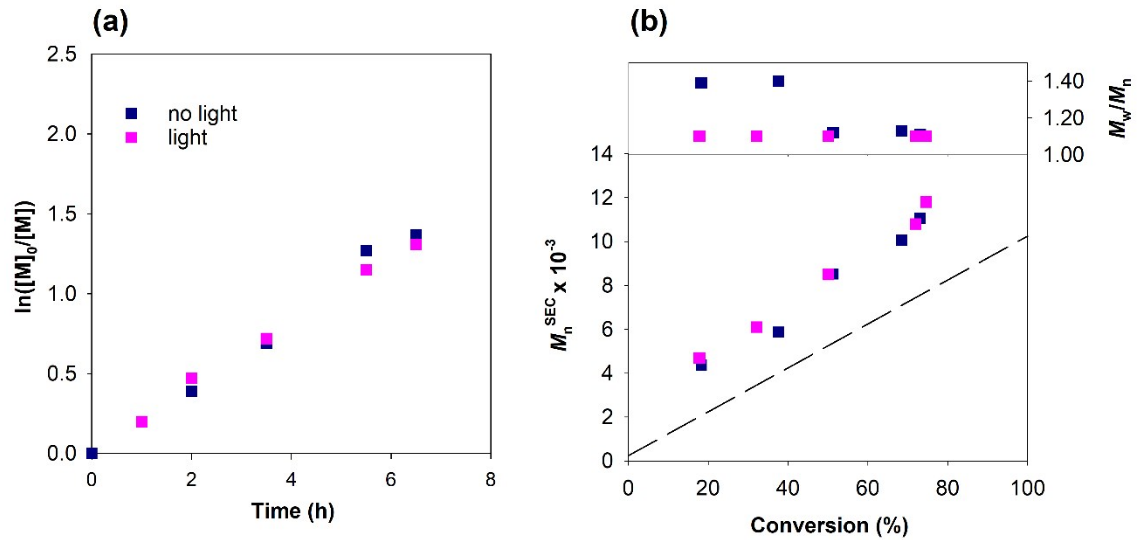

Figure SF11. Kinetic plots of (a) $\ln([M]_0/[M])$ *vs.* time and (b) M_n^{SEC} and M_w/M_n *vs.* monomer conversion for SARA ATRP of MMA at 30 °C in DMSO in the presence and absence of light. Conditions: $[MMA]_0/[DMSO] = 2/1$ (v/v); $[MMA]_0/[EBPA]_0/[CuBr_2]_0/[TMG]_0 = 100/1/0.1/2$; Cu^0 wire: $l = 5.0$ cm, $d = 1$ mm.