

Supporting Information

Ambient temperature rapid SARA ATRP of acrylates and methacrylates in alcohol/water solutions mediated by mixed sulfites/Cu(II)Br₂ catalytic system

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Results

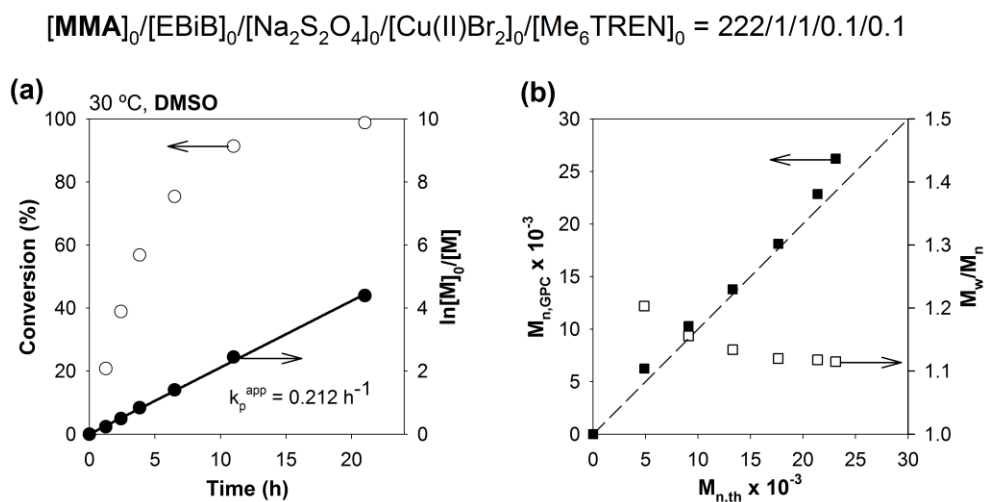


Fig. S1 Kinetic plot of conversion and $\ln[M]_0/[M]$ vs. time (a) and plot of number average molecular weights ($M_{n, GPC}$) and dispersity (M_w/M_n) vs. theoretical number-average molecular weights ($M_{n, th}$) (b) for ATRP of MMA catalyzed with $Na_2S_2O_4$ in the presence of $Cu(II)Br_2/Me_6TREN$ at 30 °C in DMSO. Conditions: $[MMA]_0/[DMSO] = 2/1$ (v/v); $[MMA]_0/[EBiB]_0/[Na_2S_2O_4]_0/[Cu(II)Br_2]_0/[Me_6TREN]_0 = 222/1/1/0.1/0.1$.

1H NMR and MALDI-TOF-MS analyses

The structure of PMA-Br obtained ($M_{n, GPC} = 4400$, $M_w/M_n = 1.04$) using the catalytic system $[Na_2S_2O_4]/[Cu(II)Br_2]/[Me_6TREN]$ in $EtOH/H_2O$ [90/10 (v/v)] was studied by 1H -NMR (Fig. S2) and MALDI-TOF-MS (Fig. S3).

The assignment of proton resonances have been done according to references: (e, g, f, f'),¹⁻³ (a, b, c),^{1,4} (dr, dm).^{1,5-8} The signal of protons **dr** is partially overlapped with the signal of water trace in $CDCl_3$ at 1.6 ppm.^{1,9} The fractions of syndiotactic and isotactic diads (**dr** and **dm** respectively) were obtained by measuring the integrals of signals **dm** and **dr**.⁵⁻⁸ The percentage of the chain-end functionality was calculated as follows: % functionality = $[I(g)/(I(c)/6)] \times 100\%$; where $I(g)$ is the integral of the PMA terminal bromo chain-end $-CH_2-CH_gBr(CO_2Me)$ at 4.24 ppm and $I(c)$ is the

integral of the initiator fragment $-\text{CH}(\text{CH}_3)_2\text{CO}_2\text{Et}$ at 1.10 and 1.15 ppm.¹ The PMA NMR molar mass was calculated using the equation $M_{n,\text{NMR}} = \{[\text{I}(\mathbf{e})]/(\text{I}(\mathbf{g})) + 1\} \times \text{MW}_{\text{MA}} + \text{MW}_{\text{EBiB}}$, where $\text{I}(\mathbf{e})$ is the integral of the PMA main chain C-H proton $-\text{CH}_2-\text{CH}_e(\text{CO}_2\text{Me})-$ at 2.3 ppm and $\text{I}(\mathbf{g})$ is the integral of the active chain end $---\text{CH}_g\text{Br}$ at 4.24 ppm).

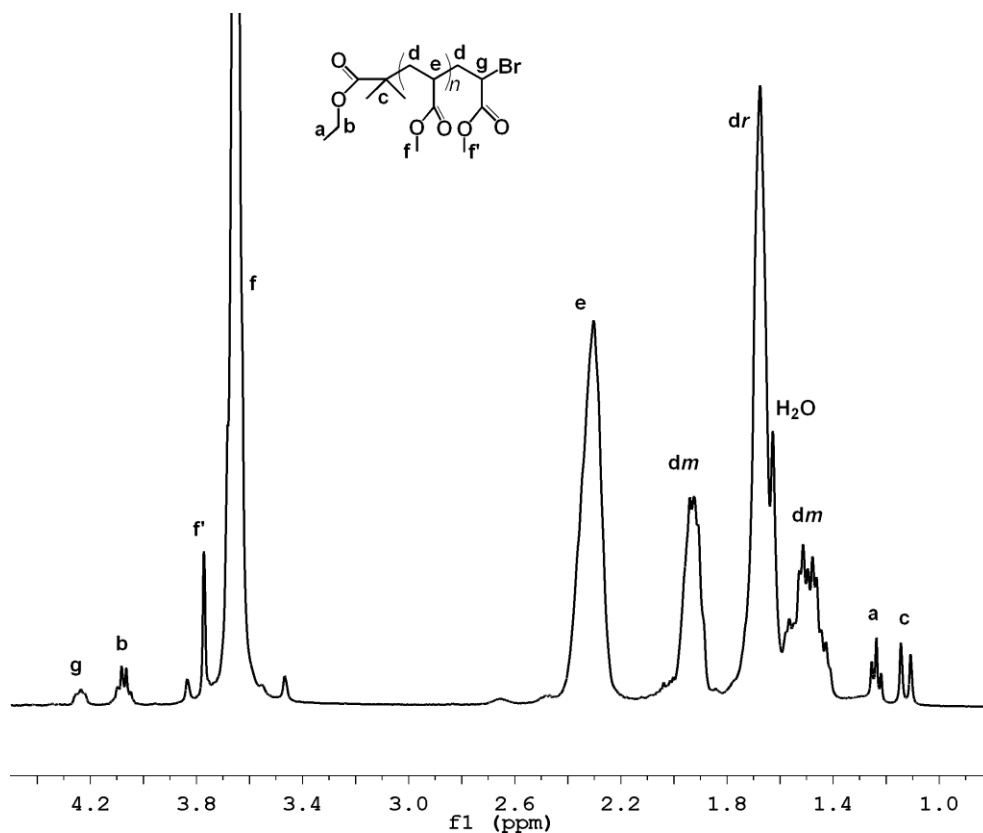
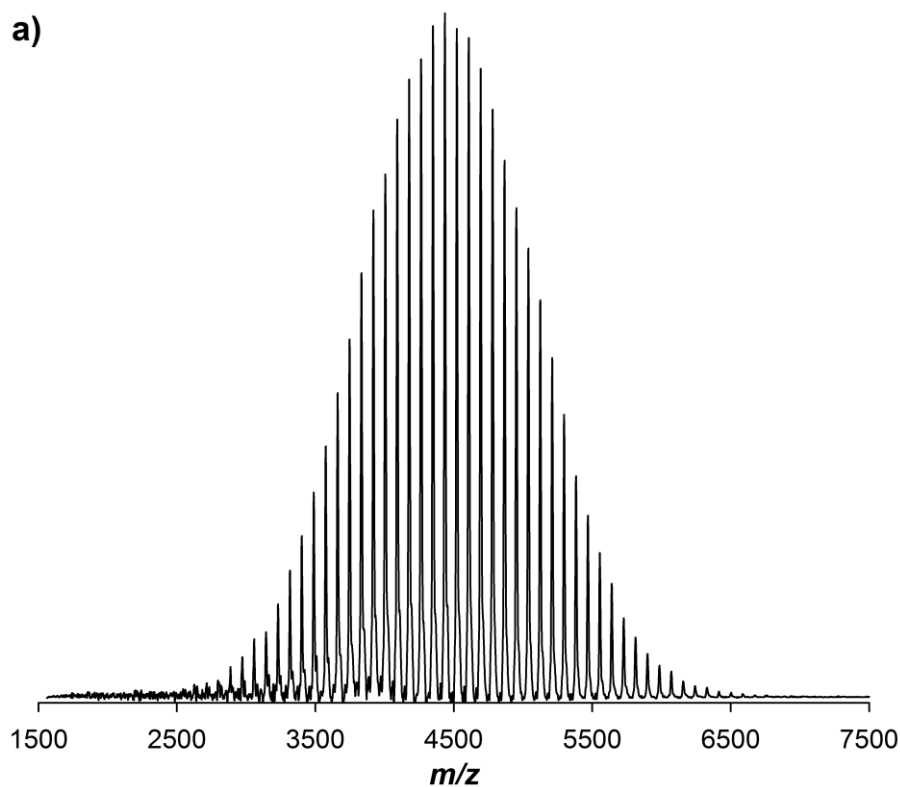


Fig. S2 The ¹H NMR spectrum of PMA-Br obtained at high conversion ($M_{n,\text{GPC}} = 4400$; $M_w/M_n = 1.04$; $M_{n,\text{NMR}} = 4410$; active chain-end functionality = 99 %). The PMA is atactic: $[\text{dr}] = [\text{dm}] = 0.5$. The solvent is CDCl_3 .

In MALDI-TOF-MS experiments, two types of matrices, DHB and HABA were tested, but only the former gave a clearly resolved spectrum (Fig. S3). The MALDI-TOF-MS of PMA-Br ranging from 1500 to 7500 is shown in Fig. S3a. Enlargement of the 4150-4750 range is shown in Fig. S3b. Importantly, the series of main peaks is separated by an interval corresponding to a MA repeating unit (86.1 mass units). This main series is attributed to a polymer chain $[\text{R}-(\text{MA})_n\text{-Br} + \text{Na}]^+$ where R-Br is the initiator EBiB ($4178.2 = 195.05 + 46 \times 86.09 + 22.99$, where 195.05, 86.09 and 22.99 correspond to

the molar mass of EBiB, MA and Na^+ respectively). Therefore, the obtained PMA-Br has a well-defined structure (i.e., without any detectable structural defects). The presence of possible structural defects would cause a deviation of m/z values of distribution. The series of less intensive peaks (Fig. S3b) cannot be ascribed to any chain-end structures expected. The presence of these peaks is probably due to the occurrence of the fragmentation during ionization in the MALDI-TOF-MS analysis, as reported by other authors.¹⁰⁻¹³



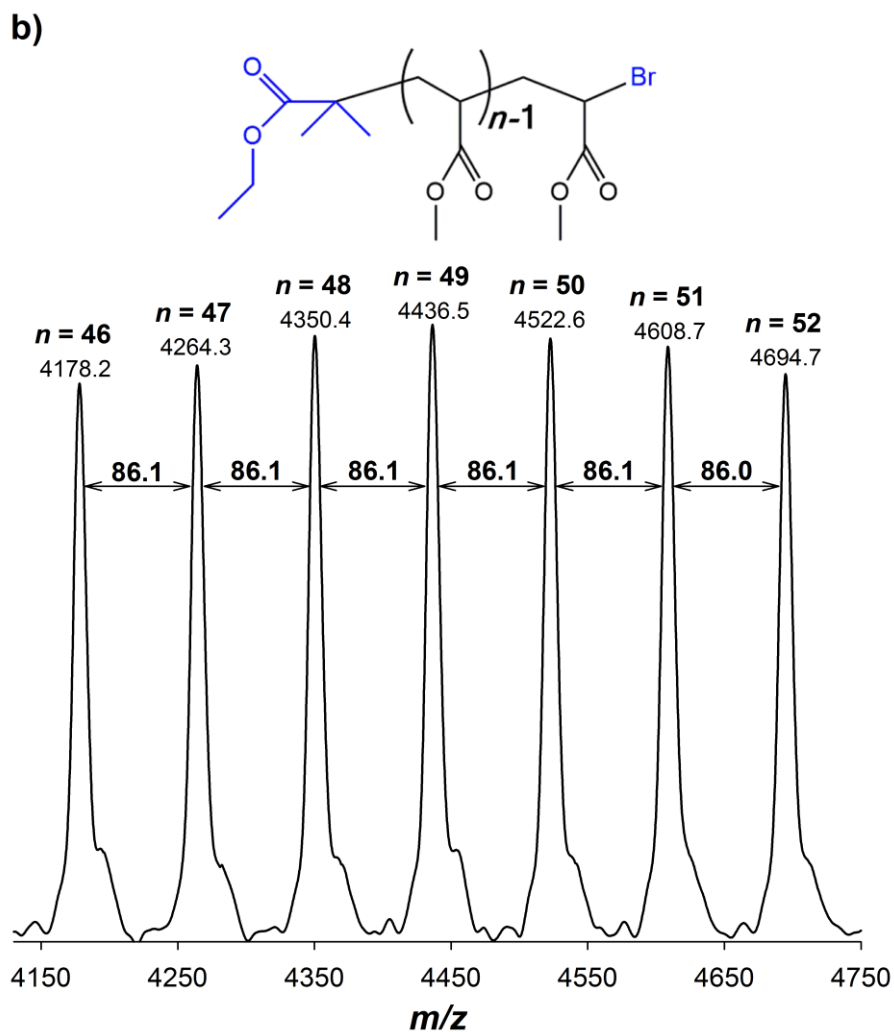


Fig. S3 MALDI-TOF-MS (a) in the linear mode (using DHB as matrix) of PMA-Br ($M_{n, \text{GPC}} = 4400$, $M_w/M_n = 1.04$); (b) Enlargement of the MALDI-TOF-MS from m/z 4150 to 47500 of PMA-Br.

The structure of four arm star PMA-Br₄ obtained ($M_{n, \text{GPC}} = 37200$, $M_w/M_n = 1.05$) using the catalytic system $[\text{Na}_2\text{S}_2\text{O}_4]/[\text{Cu}(\text{II})\text{Br}_2]/[\text{Me}_6\text{TREN}]$ in EtOH/H₂O [90/10 (v/v)] was studied by ¹H-NMR (Fig. S4).

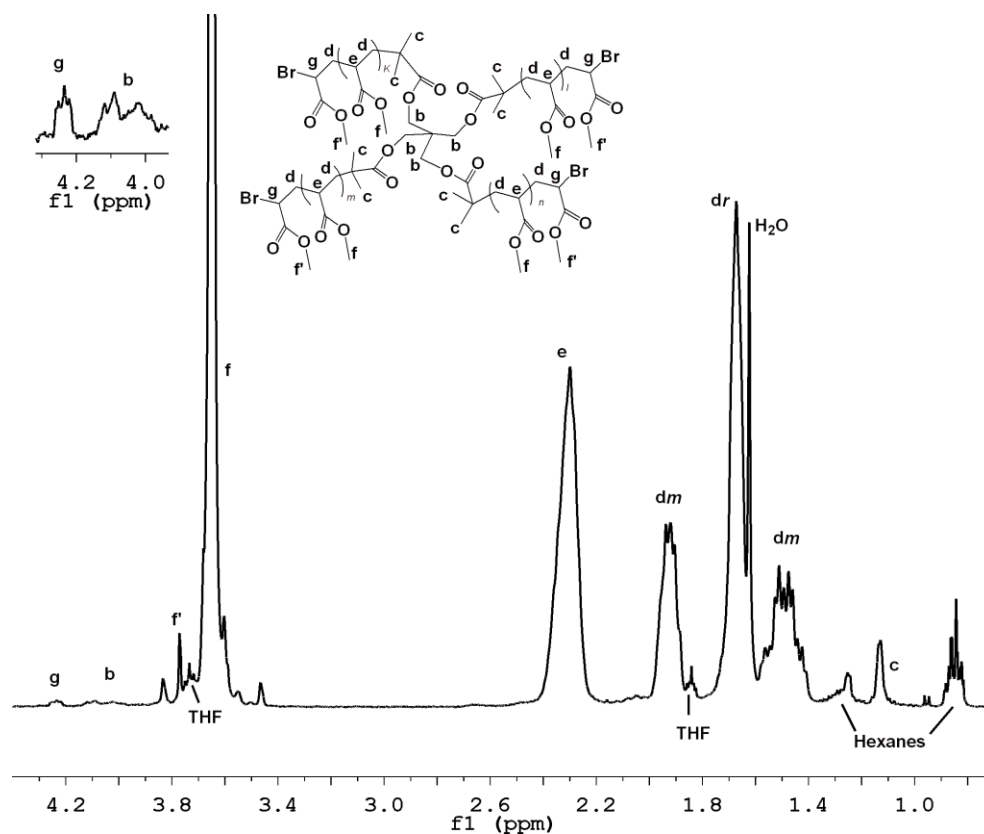


Fig. S4 The ^1H NMR spectrum of four arm star PMA- Br_4 obtained at high conversion ($M_{n,\text{GPC}} = 37200$; $M_w/M_n = 1.05$; $M_{n,\text{NMR}} = 43085$; active chain-end functionality = 99 %). The PMA is atactic: $[\text{dr}] = [\text{dm}] = 0.5$. The solvent is CDCl_3 .

The ^1H NMR spectrum of four arm star PMA- Br_4 is presented in Fig. S4.^{1,5-8} The signal of protons **dr** at 1.67 ppm is partially overlapped with the signal of water trace in CDCl_3 at 1.62 ppm.^{1,9} There are also traces of THF (resonances at 1.84 and 3.73 ppm)^{9,14} and hexanes (resonances 0.8-0.9 and 1.2-1.3 ppm),¹⁴ which were used for PMA purification. The fractions of syndiotactic and isotactic diads (**dr** and **dm** respectively) were obtained by measuring the integrals of signals **dm** and **dr**.⁵⁻⁸ The percentage of the chain-end functionality was calculated as follows: % functionality = $[\text{I}(\mathbf{g})/(\text{I}(\mathbf{c})/6)] \times 100\%$; where $\text{I}(\mathbf{g})$ is the integral of the PMA terminal bromo chain-end $-\text{CH}_2-\text{CH}_g\text{Br}(\text{CO}_2\text{Me})$ at 4.24 ppm and $\text{I}(\mathbf{c})$ is the integral of the initiator fragment $-\text{CH}(\text{CH}_3)_2\text{CO}_2\text{Et}$ at 1.13 ppm.¹ The PMA NMR molar mass was calculated using the equation $M_{n,\text{NMR}} = \{[\text{I}(\mathbf{e})/(\text{I}(\mathbf{g})/4)] + 4\} \times \text{MW}_{\text{MA}} + \text{MW}_{4\text{-BiB}}$, where $\text{I}(\mathbf{e})$ is the

integral of the PMA main chain C-H proton $-\text{CH}_2-\text{CH}_e(\text{CO}_2\text{Me})-$ at 2.3 ppm and $I(\mathbf{g})$ is the integral of the active chain end $---\text{CH}_g\text{Br}$ at 4.24 ppm).

References

1. P. V. Mendonça, A. C. Serra, J. F. J. Coelho, A. V. Popov and T. Guliashvili, *European Polymer Journal*, 2011, **47**, 1460-1466.
2. G. Lligadas, J. S. Ladislaw, T. Guliashvili and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 278-288.
3. V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro and S. Sahoo, *J. Am. Chem. Soc.*, 2006, **128**, 14156-14165.
4. A. Hasneen, S. J. Kim and H.-j. Paik, *Macromol. Res.*, 2007, **15**, 541-546.
5. J. F. J. Coelho, J. Gois, A. C. Fonseca, R. A. Carvalho, A. V. Popov, V. Percec and M. H. Gil, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 4454-4463.
6. J. F. J. Coelho, E. Y. Carvalho, D. S. Marques, A. V. Popov, V. Percec, P. M. F. O. Goncalves and M. H. Gil, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **46**, 421-432.
7. J. F. J. Coelho, E. Y. Carvalho, D. S. Marques, A. V. Popov, P. M. Goncalves and M. H. Gil, *Macromol. Chem. Phys.*, 2007, **208**, 1218-1227.
8. M. Tabuchi, T. Kawauchi, T. Kitayama and K. Hatada, *Polymer*, 2002, **43**, 7185-7190.
9. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.
10. C. M. R. Abreu, P. V. Mendonça, A. C. Serra, J. F. J. Coelho, A. V. Popov, G. Gryn'ova, M. L. Coote and T. Guliashvili, *Macromolecules*, 2012, **45**, 2200-2208.
11. C. Schilli, M. G. Lanzendörfer and A. H. E. Müller, *Macromolecules*, 2002, **35**, 6819-6827.
12. S. Coca, C. B. Jasieczek, K. L. Beers and K. Matyjaszewski, *Journal of Polymer Science Part A: Polymer Chemistry*, 1998, **36**, 1417-1424.
13. E. Beyou, P. Chaumont, F. Chauvin, C. Devaux and N. Zydowicz, *Macromolecules*, 1998, **31**, 6828-6835.
14. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.