Supporting Information

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

Carlos M. R. Abreu, Arménio C. Serra, Anatoliy V. Popov, Krzysztof Matyjaszewski, Tamaz Guliashvili and Jorge F.J. Coelho

*Department of Chemical Engineering, University of Coimbra, Polo II, Rua Silvio Lima, 3030-790 Coimbra, Portugal. Fax: +351 239 798 703; Tel:+351 239 798 764; E-mail: jcoelho@eq.uc.pt
bDepartment of Radiology, University of Pennsylvania, Philadelphia, PA19104, United States.
cDepartment of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States. E-mail: km3b@andrew.cmu.edu
dHome Address: 1761 Foster Street, F5B, Philadelphia PA 191116, United States. E-mail: tamazguliasvili@yahoo.com

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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 (\(M_n,\text{GPC}\)) and dispersity (\(M_w/M_n\)) vs. theoretical number-average molecular weights (\(M_{n,\text{th}}\)) (b) for ATRP of MMA catalyzed with \(\text{Na}_2\text{S}_2\text{O}_4\) in the presence of \(\text{Cu(II)}\text{Br}_2/\text{Me}_6\text{TREN}\) at 30 °C in DMSO. Conditions: \([\text{MMA}]_0/[\text{DMSO}] = 2/1\) (v/v); \([\text{MMA}]_0/[	ext{EBiB}]_0/[	ext{Na}_2\text{S}_2\text{O}_4]_0/[	ext{Cu(II)}\text{Br}_2]_0/[	ext{Me}_6\text{TREN}]_0 = 222/1/1/0.1/0.1.

\(^1\text{H} \text{NMR and MALDI-TOF-MS analyses}\)

The structure of PMA-Br obtained (\(M_{n,\text{GPC}} = 4400, M_w/M_n = 1.04\)) using the catalytic system [\(\text{Na}_2\text{S}_2\text{O}_4]/[\text{Cu(II)}\text{Br}_2]/[\text{Me}_6\text{TREN}\) in EtOH/H\(_2\)O [90/10 (v/v)] was studied by \(^1\text{H}-\text{NMR}\) (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: \(\% \text{ functionality} = [I(g)/(I(c)/6)] \times 100\%\); where I(g) is the integral of the PMA terminal bromo chain-end \(\text{–CH}_2\text{–CH}_2\text{Br(CO}_2\text{Me) at 4.24 ppm and I(c) is the}\)
integral of the initiator fragment $\text{--CH(CH}_3\text{)}_2\text{CO}_2\text{Et}$ at 1.10 and 1.15 ppm. The PMA NMR molar mass was calculated using the equation $M_{n,NMR} = \{[I(e)/(I(g))] + 1\} \times MW_{\text{MA}} + MW_{\text{EBiB}}$, where $I(e)$ is the integral of the PMA main chain C-H proton $\text{--CH}_2\text{--CH}_2\text{--}(\text{CO}_2\text{Me})$ at 2.3 ppm and $I(g)$ is the integral of the active chain end $\text{--CH}_2\text{Br}$ at 4.24 ppm).

Fig. S2 The $^1$H NMR spectrum of PMA-Br obtained at high conversion ($M_{n,GPC} = 4400; M_w/M_n = 1.04; M_{n,NMR} = 4410; \text{active chain-end functionality} = 99 \%$). The PMA is atactic: $[d_r] = [d_m] = 0.5$. 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 $[R-(\text{MA})_n\text{-Br + Na}]^+$ where R-Br is the initiator EBiB (4178.2 = 195.05 + 46 x 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 ($M_n,_{GPC} = 4400$, $M_w/M_n = 1.04$); (b) Enlargement of the MALDI-TOF-MS from $m/z$ 4150 to 47500 of PMA-Br.

The structure of four arm star PMA-Br$_4$ obtained ($M_n,_{GPC} = 37200$, $M_w/M_n = 1.05$) using the catalytic system [Na$_2$S$_2$O$_4$]/[Cu(II)Br$_2$]/[Me$_6$TREN] in EtOH/H$_2$O [90/10 (v/v)] was studied by $^1$H-NMR (Fig. S4).
The $^1$H NMR spectrum of four arm star PMA-Br$_4$ obtained at high conversion ($M_{n, GPC} = 37200$; $M_n/M_n = 1.05$; $M_n, NMR = 43085$; active chain-end functionality = 99 %). The PMA is atactic: [dr] = [dm] = 0.5. The solvent is CDCl$_3$.

The $^1$H NMR spectrum of four arm star PMA-Br$_4$ is presented in Fig. S4.\textsuperscript{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.\textsuperscript{1,9} There are also traces of THF (resonances at 1.84 and 3.73 ppm)\textsuperscript{9,14} and hexanes (resonances 0.8-0.9 and 1.2-1.3 ppm),\textsuperscript{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.\textsuperscript{5-8} The percentage of the chain-end functionality was calculated as follows: % functionality = [I(g)/(I(c)/6)] x 100%; where I(g) is the integral of the PMA terminal bromo chain-end –CH$_2$–CH$_2$Br(CO$_2$Me) at 4.24 ppm and I(c) is the integral of the initiator fragment –CH(CH$_3$)$_2$CO$_2$Et at 1.13 ppm.\textsuperscript{1} The PMA NMR molar mass was calculated using the equation $M_{n, NMR} = [([I(e)/(I(g)/4)] + 4) \times MW_{MA} + MW_{4f-BiB}$, where I(e) is the
integral of the PMA main chain C-H proton –CH$_2$-CH$_4$(CO$_2$Me)- at 2.3 ppm and I(g) is the integral of the active chain end ---CH$_g$Br at 4.24 ppm).

References