Supporting information

# Pushing the limits of robust and eco-friendly ATRP processes: untreated water as the solvent

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## 1. Water analyses

**Table S1.** pH, EC and pE of the different sources of water investigated for the SARA ATRP.

| Water source | pH | EC (µS/cm) | pE |
|---|---|---|---|
| Deionized water | 6.0 | 1.7 | 9.92 |
| Mondego river | 7.2 | 125 | 7.45 |
| Miranda stream | 7.2 | 78 | 7.45 |
| Sea | 7.5 | 52800 | 6.90 |
| Rain | 6.9 | 32 | 7.89 |
| Leiria spring | 6.7 | 141 | 8.18 |

**Table S2.** Ion concentration for deionized water and untreated waters used as polymerization solvent in ATRP reactions.

| | | Water source | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Deionized water** | **Mondego river** | **Miranda stream** | **Sea** | **Rain (µmol/L)*** | **Leiria spring** |
| **[Ion] (mmol/L)** | $Ca^{2+}$ | < 0.007 | 0.162 | 0.10 | 9.18 | 43/40 | 0.077 |
| | $Mg^{2+}$ | < 0.004 | 0.123 | 0.082 | 51.47 | 28/20 | 0.119 |
| | $K^{+}$ | < 0.003 | 0.049 | 0.021 | 10.18 | 7/40 | 0.010 |
| | $Na^{+}$ | < 0.013 | 0.387 | 0.318 | 507.1 | 109/150 | 0.783 |
| | $Li^{+}$ | < 0.007 | < 0.007 | < 0.007 | < 0.07 | -/- | < 0.007 |
| | $NH_4^{+}$ | < 0.003 | < 0.003 | 0.009 | < 0.02 | -/250 | < 0.003 |
| | $F^{-}$ | < 0.011 | < 0.011 | < 0.011 | < 0.11 | -/- | < 0.011 |
| | $Cl^{-}$ | < 0.056 | 0.330 | 0.243 | 528.21 | 90/170 | 0.649 |
| | $NO_3^{-}$ | < 0.016 | 0.076 | 0.044 | < 0.16 | -/20 | 0.077 |
| | $SO_4^{2-}$ | < 0.021 | 0.107 | 0.056 | 27.59 | 55/50 | 0.036 |
| | $Br^{-}$ | < 0.001 | 0.001 | < 0.001 | 0.60 | -/- | 0.005 |
| | $PO_4^{3-}$ | < 0.002 | < 0.002 | < 0.002 | < 0.002 | -/- | < 0.002 |

*Values obtained in the literature and expressed in µmol/L [1, 2]

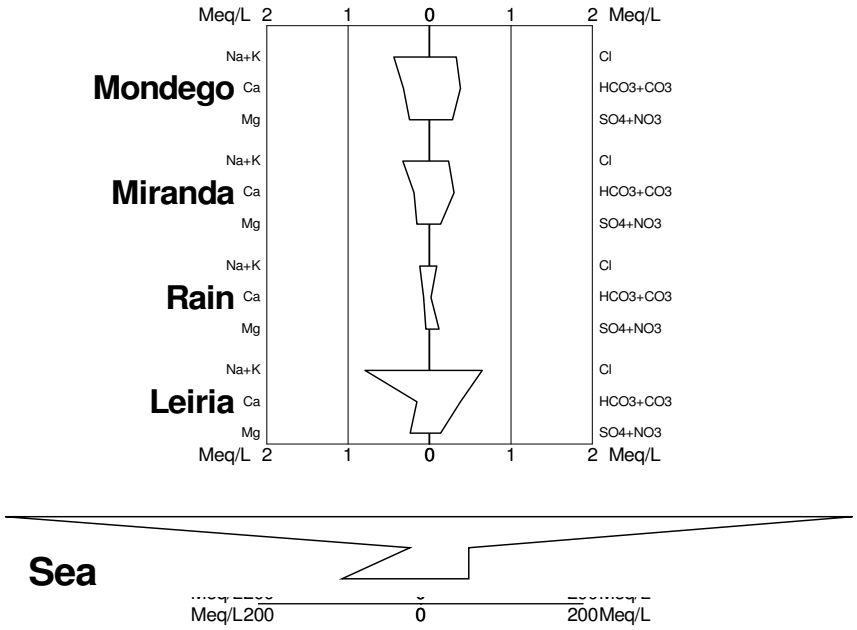


**Fig. S1.** Stiff diagrams of the untreated waters used for the SARA ATRP of AMPTMA.

## 2. Characterization of polymers

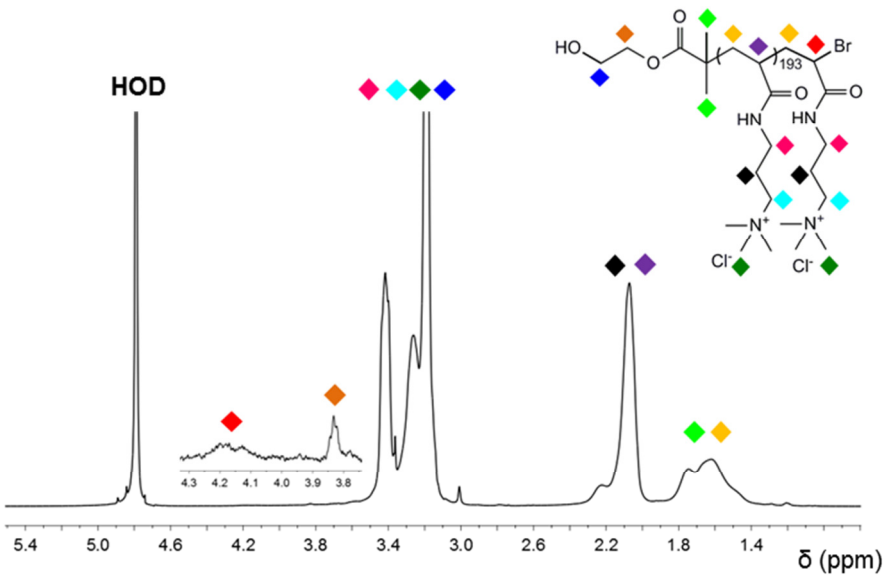


**Fig. S2.** 400 MHz $^{1}$H NMR spectrum, in $D_2O$, of a pure PAMPTMA-Br ($M_n^{SEC}$ = 42.3 x $10^3$; $Đ$ = 1.10) prepared by Cu(0)-catalyzed SARA ATRP in water from the Mondego river.

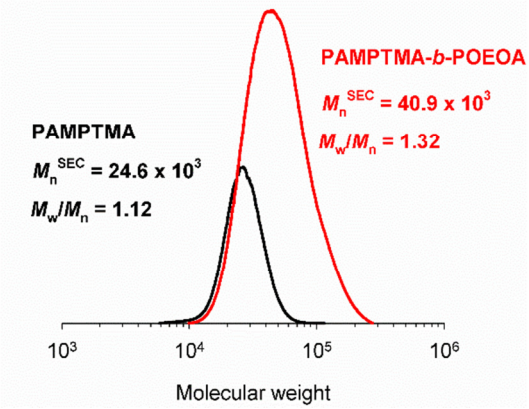


**Fig. S3.** Molecular weight distribution of PAMPTMA macroinitiator (conv.$_{AMPTMA}$ = 99%; $M_n^{th}{}_{macroinitiator}$ = 20.1 x $10^3$) and PAMPMTA$_{96}$-*b*-POEOA$_{78}$ (conv.$_{OEOA480}$ = 98%; $M_n^{th}{}_{copolymer}$ = 57.7 x $10^3$) obtained after "one-pot" chain extension by SARA ATRP in water from the Mondego river.

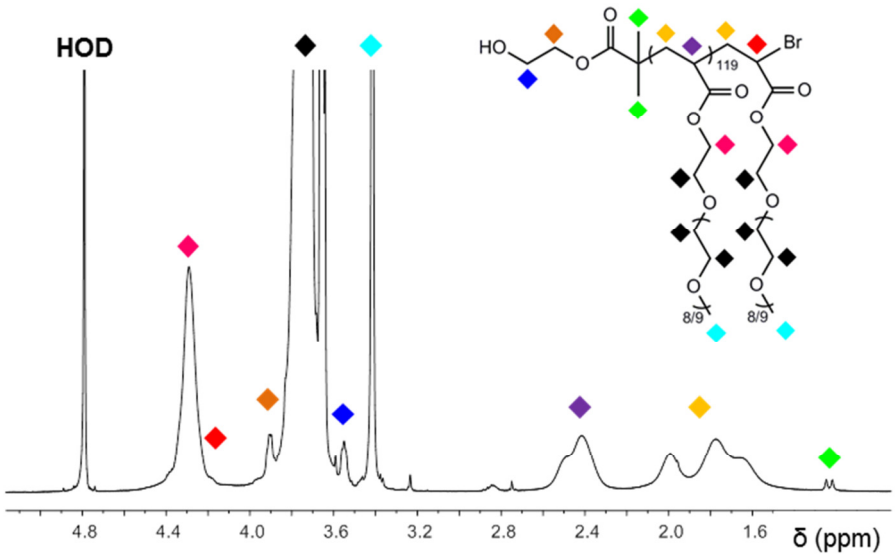


**Fig. S4.** 400 MHz $^1$H NMR spectrum, in $D_2O$, of a pure POEOA-Br ($M_n^{SEC}$ = 65.5 x $10^3$; $Đ$ = 1.20) prepared by $Na_2S_2O_4$-catalyzed SARA ATRP in water from the Mondego river.

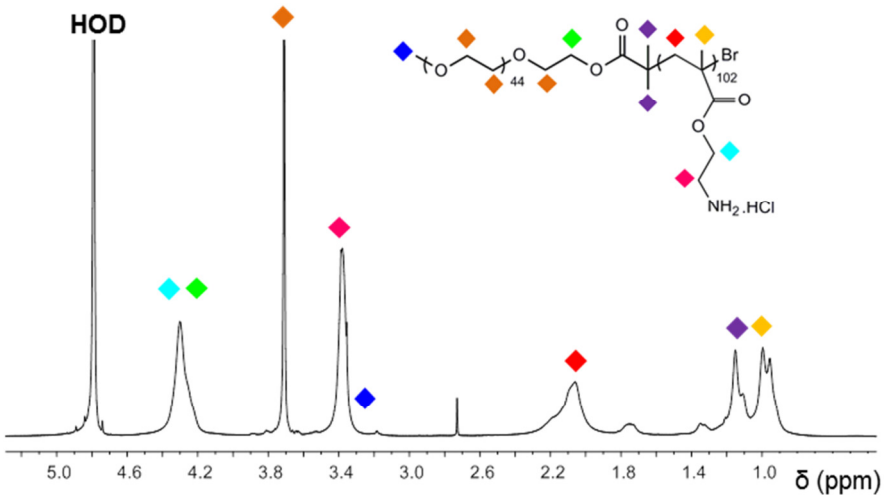


**Fig. S5.** 400 MHz $^{1}$H NMR spectrum, in $D_2O$, of a pure PEG-*b*-PAMA ($M_n^{SEC}$ = 21.3 x $10^3$; $Đ$ = 1.16) prepared by ARGET ATRP in water from the Mondego river.

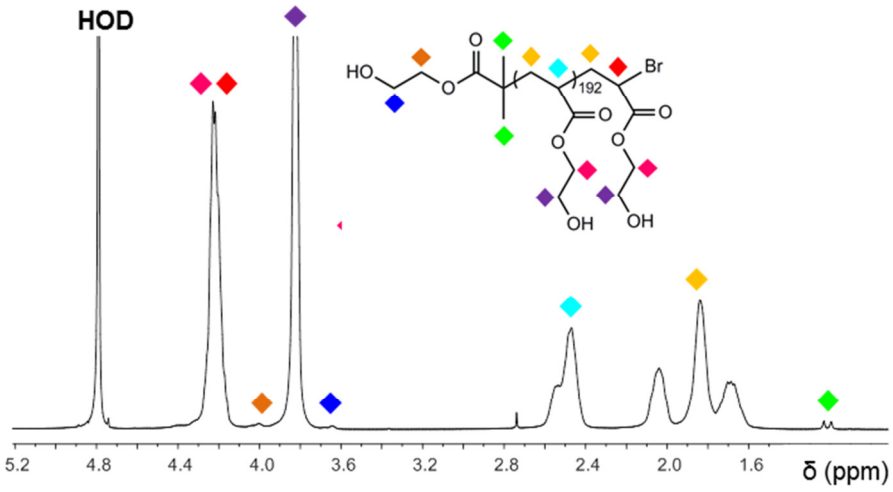


**Fig. S6.** 400 MHz $^{1}$H NMR spectrum, in $D_2O$, of a pure PHEA-Br ($M_n^{SEC}$ = 26.9 x $10^3$; $Đ$ = 1.19) prepared by Cu(0)-catalyzed SARA ATRP in water from the Mondego river.

## References

1. M. T. C. de Melo, M. A. M. da Silva and W. M. Edmunds, *Phys. Chem. Earth PT B*, 1999, **24**, 331-336.
2. A. Vázquez, M. Costoya, R. M. Peña, S. García and C. Herrero, *Chemosphere*, 2003, **51**, 375-386.