Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Mechanism and Application of Surface-Initiated, Zn^0-Mediated ATRP

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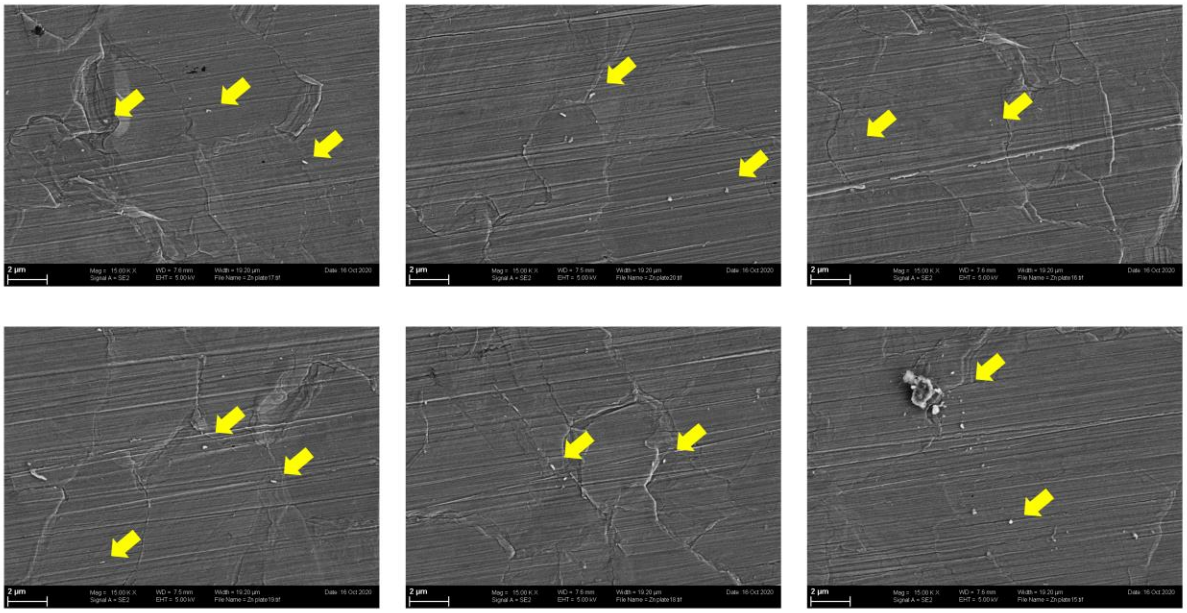

Figure S1. Scanning electron micrographs (SEM) highlighting the formation of Zn^0 nano/microparticles after the polishing process.

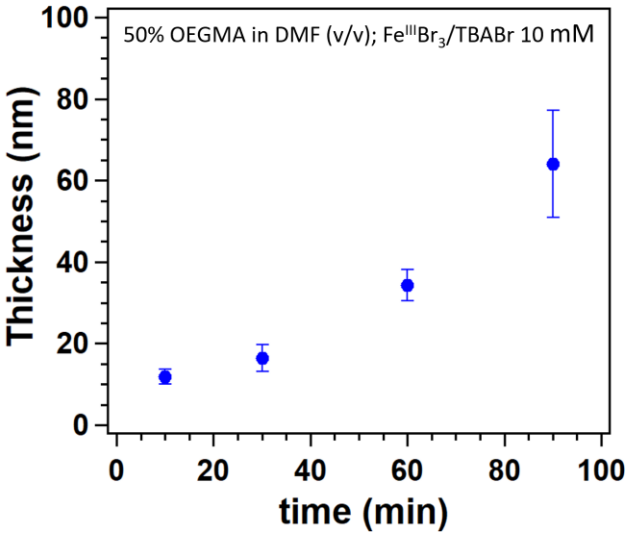

Figure S2. SI-Zn^0-ATRP of OEGMA using Fe-based catalyst. $Fe^{III}Br_3$/tertbutylammonium bromide (TBABr) is readily reduced to $Fe^{II}Br_2$/TBABr activators by the Zn^0 surface, triggering the growth of more than 30 nm-thick POEGMA brushes in just 60 min of reaction.

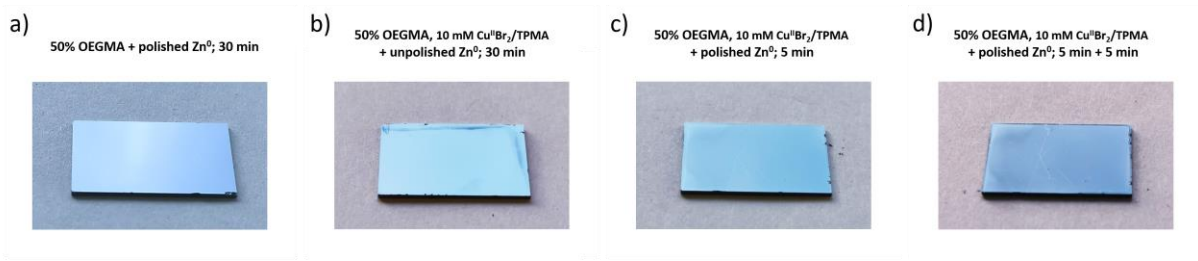

Figure S3. (a) When SI-Zn^0-ATRP was performed in the absence of $Cu^{II}Br_2$ and ligand, by sandwiching a 50% OEGMA in DMF (v/v) between an initiator-bearing substrate (reported in the picture) and a polished Zn^0 plate, no appreciable growth of brushes was recorded, with the dry thickness of polymer layer < 5 nm. (b) When SI-Zn^0-ATRP was carried out using 50% OEGMA in DMF (v/v) and 10 mM $Cu^{II}Br_2$/TPMA but without polishing the Zn^0 plate a relevant brush growth was not recorded, with average polymer thickness < 5 nm, and just few areas presenting very inhomogeneous growth. (c,d) Re-initiation efficiency was demonstrated by first growing a 18 ± 2 nm-thick POEGMA brush (c), using 50% OEGMA in DMF + 10 mM $Cu^{II}Br_2$/TPMA and carrying out the polymerization for 5 min. Later on, the same substrate was subjected to a freshly prepared reaction solution (50% OEGMA in DMF + 10 mM $Cu^{II}Br_2$/TPMA) while carrying out polymerization for further 5 min (d). The final POEGMA brush-thickness resulted 35 ± 3 nm, reaching nearly twice the value recorded for the first "brush block".