

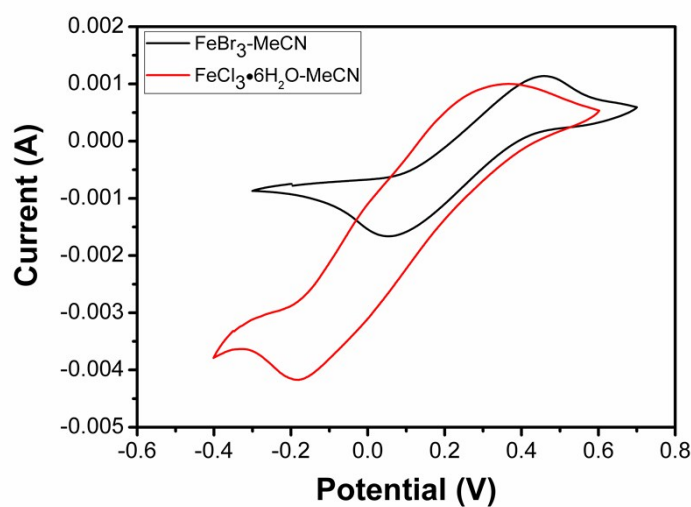
## Supporting Information for

### Ligand-free iron-based electrochemically mediated atom transfer radical polymerization of methyl methacrylate

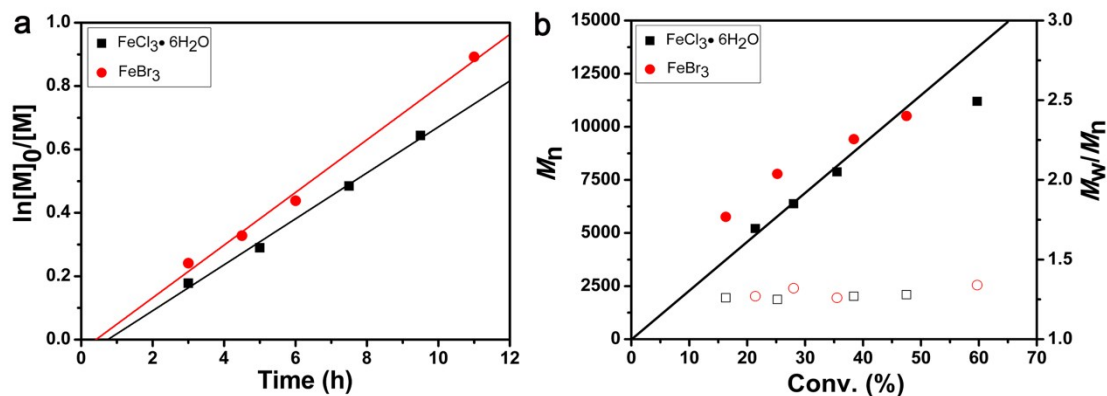
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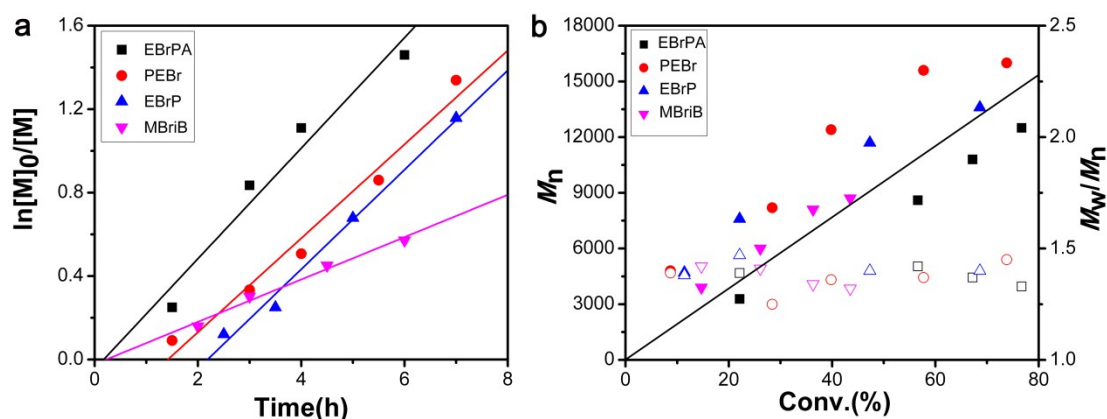
#### Polymerization Data:



**Figure S1.** CV of 10mM FeCl<sub>3</sub>·6H<sub>2</sub>O (red) and FeBr<sub>3</sub> (black) in MeCN containing 0.1 M Et<sub>4</sub>NBF<sub>4</sub> recorded at a scan rate (v) of 50 mV/s.



**Figure S2.** Effect of different types of catalyst on seATRP: (a) First-order kinetic plots of  $\ln([M]_0/[M])$  versus time; (b) plots of  $M_n$  (filled symbols) and  $M_w/M_n$  (open symbols) values versus conversion. Reaction conditions:  $[MMA]_0/[EBPA]_0/[catalysts]_0 = 200:1:1$ ,  $[MMA]_0/[MeCN]_0 = 3:1$  (v/v), 0.1 M  $\text{Et}_4\text{NBF}_4$ ,  $T = 95^\circ\text{C}$ ,  $E_{\text{app}} = -0.59\text{V}$ .



**Figure S3.** Kinetic of iron-catalyzed seATRP using different types of initiators: First-order kinetic plots of  $\ln([M]_0/[M])$  versus time; (B) plots of  $M_n$  (filled symbols) and  $M_w/M_n$  (open symbols) values versus conversion. Reaction conditions:  $[MMA]_0/[initiator]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0 = 200:1:1$ ,  $[MMA]_0/[\text{NMP}]_0 = 3:1$  (v/v), 0.1 M  $\text{Et}_4\text{NBF}_4$ ,  $T = 95^\circ\text{C}$ .

**Table S1.** Iron-mediated seATRP of MMA exposed in air.

<b>Entry</b>	<b>Time (h)</b>	<b>Conv. (%)</b>	<b><math>M_{n,th}</math> (g/mol)</b>	<b><math>M_{n,GPC}</math> (g/mol)</b>	<b><math>M_w/M_n</math></b>
1	2.5	10.2	2290	2190	1.22
2	4.0	17.9	3830	4800	1.48
3	6.0	45.2	9300	11600	1.39
4	9.0	75.6	15380	15400	1.30