## **Electronic Supporting Information**

## **An** atom transfer radical polymerization system: catalyzed by iron catalyst in PEG-400

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Entry	t (h)	Conv. (%)	$M_{ m n,th}$ (g·mol <sup>-1</sup> )	$M_{n,GPC}$ (g·mol <sup>-1</sup> )	$M_{ m w}/M_{ m n}$
1	24	trace	NA	NA	NA
2	24	trace	NA	NA	NA
3	4	60.6	12100	24000	1.13
4	4	47.9	9600	18100	1.13

Table S1. Normal ATRP with FeCl<sub>2</sub> using PEG-400 as both solvent and ligand

Polymerization conditions: For Entries 1 and 2,  $[MMA]_0$ :  $[EBrPA]_0$ :  $[FeCl_2]_0$ :  $[FeCl_3.6H_2O]_0 = 200$ : 1: 1: 0. For Entries 3 and 4,  $[MMA]_0$ :  $[EBrPA]_0$ :  $[FeCl_2]_0$ :  $[FeCl_3.6H_2O]_0 = 200$ : 1: 4: 0 and 200: 1: 4: 0.5, respectively, T = 90 °C,  $V_{PEG-400} = V_{MMA} = 1.0$  mL (For Entry 1,  $V_{PEG-400} = 0.2$  mL).

Entry		t (b)	Conv.	$M_{ m n,th}$	M <sub>n,GPC</sub>	
	Х	t (n)	(%)	$(g \cdot mol^{-1})$	(g·mol <sup>-1</sup> )	$M_{\rm W}/M_{\rm n}$
1	2	2	63.4	12700	24000	1.17
2	1	2	66.4	13300	22500	1.14
3	0.5	12	17.8	3600	13700	1.16
4	0.25	24	trace	NA	NA	NA

 Table S2. Effect of catalyst concentration on AGET ATRP in PEG-400 without

 additional ligand

Polymerization conditions:  $[MMA]_0$ :  $[EBrPA]_0$ :  $[FeCl_3.6H_2O]$  :  $[AsAc-Na]_0 = 200$ : 1: x: x, T = 90 °C,  $V_{PEG-400} = V_{MMA} = 1.0$  mL.



Figure S1.  $\ln([M]_0/[M])$  as a function of time (a) and evolution of number-average molecular weight ( $M_{n,GPC}$ ) and molecular weight distribution ( $M_w/M_n$ ) versus

conversion (b) for AGET ATRP of MMA with two different initiators in PEG-400 without additional ligand. Polymerization conditions:  $[MMA]_0$ :  $[initiator]_0$ :  $[FeCl_3 \cdot 6H_2O]_0$ :  $[AsAc-Na]_0 = 400$ : 1: 1: 1,  $V_{MMA} = V_{PEG-400} = 1.0$  mL, T = 90 °C.



**Figure S2.** GPC curves for AGET ATRP of MMA with BPN as the initiator in PEG-400 without additional ligand. Polymerization conditions:  $[MMA]_0$ :  $[BPN]_0$ :  $[FeCl_3 \cdot 6H_2O]_0$ :  $[AsAc-Na]_0 = 400$ : 1: 1: 1, T = 90 °C,  $V_{MMA} = V_{PEG-400} = 1.0$  mL.



**Figure S3.**  $\ln([M]_0/[M])$  as a function of time (a) and evolution of number-average molecular weight  $(M_{n,GPC})$  and molecular weight distribution  $(M_w/M_n)$  versus conversion for AGET ATRP of MMA in two different types of PEG without additional ligand. Polymerization conditions:  $[MMA]_0$ :  $[EBrPA]_0$ :  $[FeCl_3 \cdot 6H_2O]_0$  :  $[AsAc-Na]_0 = 200$ : 1: 1: 1, T = 90 °C.  $V_{MMA} = V_{PEG} = 1.0$  mL.



**Figure S4.** GPC curves for AGET ATRP of MMA in MPEG-750 without additional ligand. Polymerization conditions:  $[MMA]_0$ :  $[EBrPA]_0$ :  $[FeCl_3 \cdot 6H_2O]_0$ :  $[AsAc-Na]_0 = 200$ : 1: 1: 1, T = 90 °C.  $V_{MMA} = V_{MPEG-750} = 1.0$  mL.



**Figure S5.** Infrared Spectroscopy for the obtained PMMA ( $M_{n,GPC} = 11000$  g/mol,  $M_w/M_n = 1.12$ ).

In FT-IR analysis, we can find the wave number at 1700 cm<sup>-1</sup> was attributed to the characteristic absorption peak of the ester carbonyl group from MMA, while that at 1400 cm<sup>-1</sup> was the characteristic absorption peak of phenyl group from EBrPA.



**Figure S6.** MALDI-TOF-MS in the linear mode of PMMA-Br ( $M_{n,GPC} = 9200$  g/mol,  $M_w/M_n = 1.11$ ) and enlargement of the MALDI-TOF-MS from *m/z* 6700 to 7500 of PMMA-Cl.

The MALDI-TOF-MS of PMMA-Cl ranging from 2000 to 12000 is shown in Fig. S6a. Enlargement of the 6700-7500 range is shown in Fig. S6b. Importantly, the series of main peaks is separated by an interval corresponding to a MMA repeating unit (100.1 mass units). This main series is attributed to a polymer chain  $[R-(MMA)_n-Cl + Na]^+$  (6730.5 = 164.2 + 65× 100.12 + 35.5 + 22.99, where 243.1, 100.12 and 22.99 correspond to the molar mass of correspond to the molar mass of EBrPA without bromine chain end, MMA, Cl and Na<sup>+</sup> respectively). Therefore, the obtained

PMAM-Cl has a relatively well-defined structure. The series of less intensive peaks (Fig. S6b) series is attributed a possible structural defects in polymer chain. This we deduce mainly caused by some side reactions during polymerization, or probably due to the occurrence of the fragmentation during ionization in the MALDI-TOF-MS analysis.