

Electronic Supplementary Information

Basic Ionic Liquids: a New Type of Ligand and Catalyst for the AGET ATRP of Methyl Methacrylate

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Table S1 Bulk AGET ATRP of MMA with TBPBr as the Ligand^a

Entry	Conversion (%)	$M_{n,GPC}$ (g/mol)	$M_{n,th}$ (g/mol)	M_w/M_n
A ^b	8.4	5270	2100	1.29
B ^c	29.8	8100	7460	1.34
C ^c	27.1	7760	6780	1.21
D ^c	24.2	7620	6060	1.18
E ^c	19.9	7950	4980	1.16

^a Polymerization temperature: 60 °C, polymerization time: 60 h, MMA: 2 mL

^b [MMA]₀/[EBiB]₀/[FeCl₃·6H₂O]₀/[TBABr]₀/[VC]₀ = 250/1/1/2/2

^c [MMA]₀/[EBiB]₀/[FeCl₃·6H₂O]₀/[TBABr]₀/[VC]₀/[BILs]₀ = 250/1/1/2/2/10.8;

BILs: (B) [Bmim][OH]; (C) [Bmim][PO₄]; (D) [Bmim][CO₃]; (E) [Bmim][HCO₃]

Table S2 Effect of the ratio of $[[\text{Bmim}][\text{PO}_4]]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0$ on the polymerization of MMA^a

Entry	$[[\text{Bmim}][\text{PO}_4]]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0$	Conversion (%)	$M_{n,\text{GPC}}$ (g/mol)	$M_{n,\text{th}}$ (g/mol)	M_w/M_n
1	2/1	5.9	2440	1480	1.26
2	4/1	10.4	3540	2600	1.34
3	6/1	15.8	4400	3950	1.38
4	10/1	25.8	6620	6460	1.41
5	14/1	44.4	12160	11110	1.51
6	18/1	67.7	19200	16940	1.62

^aPolymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[[\text{Bmim}][\text{PO}_4]]_0/[\text{VC}]_0 = 250/1/1/x/2$

($x = 2, 4, 6, 10, 14, 18$), MMA: 2 mL, temperature: 60 °C, polymerization time: 18 h.

Table S3 Effect of the ratio of $[[\text{Bmim}][\text{CO}_3]]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0$ on the polymerization of MMA^a

Entry	$[[\text{Bmim}][\text{CO}_3]]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0$	Conversion (%)	$M_{n,\text{GPC}}$ (g/mol)	$M_{n,\text{th}}$ (g/mol)	M_w/M_n
1	2/1	4.6	2130	1150	1.26
2	4/1	7.1	2760	1780	1.32
3	6/1	10.2	3900	2550	1.35
4	10/1	20.6	10240	5160	1.39
5	16/1	43.7	17910	10940	1.46
6	22/1	72.5	28360	18140	1.57

^aPolymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[[\text{Bmim}][\text{CO}_3]]_0/[\text{VC}]_0 = 250/1/1/x/2$

($x = 2, 4, 6, 10, 16, 22$), MMA: 2 mL, temperature: 60 °C, polymerization time: 18 h.

Table S4 Effect of the ratio of $[[\text{Bmim}][\text{HCO}_3]]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0$ on the polymerization of MMA^a

Entry	$[[\text{Bmim}][\text{HCO}_3]]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0$	Conversion (%)	$M_{n,\text{GPC}}$ (g/mol)	$M_{n,\text{th}}$ (g/mol)	M_w/M_n
1	2/1	3.1	1960	780	1.22
2	4/1	5.4	2080	1350	1.23
3	8/1	8.6	4230	2150	1.24
4	10/1	14.2	4600	3550	1.37
5	14/1	31.7	12270	7930	1.38
6	18/1	44.5	18370	11140	1.41
7	24/1	76.4	29730	19120	1.54

^aPolymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[[\text{Bmim}][\text{HCO}_3]]_0/[\text{VC}]_0 = 250/1/1/x/2$

($x = 2, 4, 6, 10, 14, 18, 24$), MMA: 2 mL, temperature: 60 °C, polymerization time: 18 h.

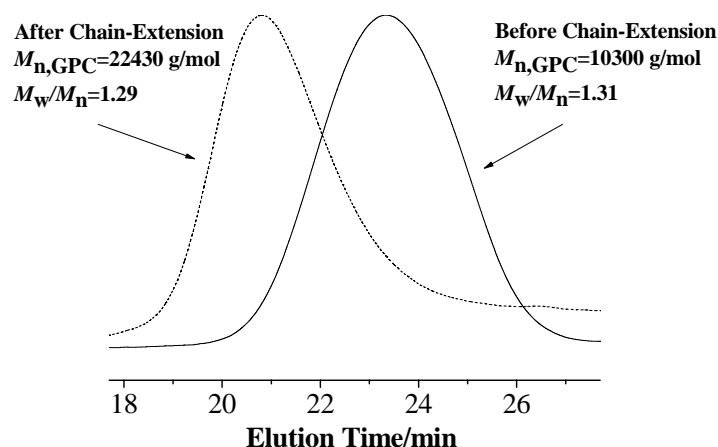


Figure S1. GPC traces of before and after chain extension using PMMA prepared by AGET ATRP of MMA (using $[\text{Bmim}][\text{PO}_4]$ as the ligand) as the macroinitiator. Polymerization conditions for macroinitiator PMMA: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[[\text{Bmim}][\text{PO}_4]]_0/[\text{VC}]_0 = 250/1/1/6/2$, MMA: 2 mL, conversion: 44.2%, time: 82 h, $M_{n,\text{GPC}} = 10300$ g/mol, $M_w/M_n = 1.31$; for chain extension: $[\text{MMA}]_0/[\text{PMMA}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[[\text{Bmim}][\text{PO}_4]]_0/[\text{VC}]_0 = 250/0.25/1/6/2$, MMA: 2 ml, time: 48 h, conversion: 26.6%, temperature: 60 °C.

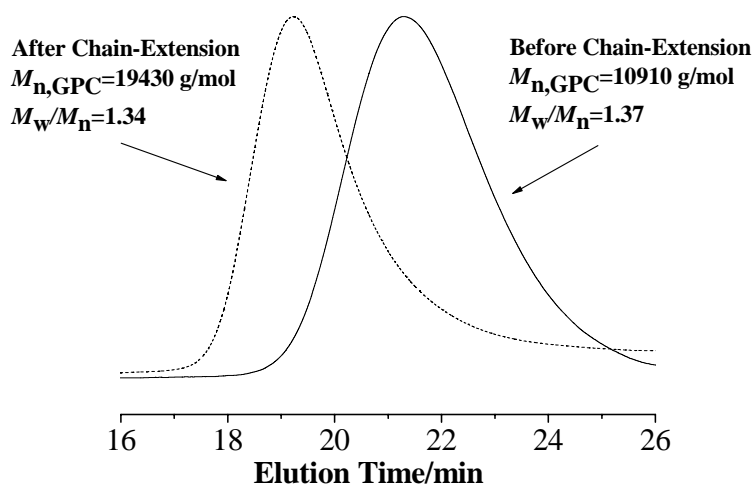


Figure S2. GPC traces of before and after chain extension using PMMA prepared by AGET ATRP of MMA (using [Bmim][CO₃] as the ligand) as the macroinitiator. Polymerization conditions for macroinitiator PMMA: [MMA]₀/[EBiB]₀/[FeCl₃·6H₂O]₀/[[Bmim][CO₃]]₀/[VC]₀ = 250/1/1/6/2, MMA: 2 mL, conversion: 37.4%, time: 86 h, $M_{n, GPC} = 10910$ g/mol, $M_w/M_n = 1.37$; for chain extension: [MMA]₀/[PMMA]₀/[FeCl₃·6H₂O]₀/[[Bmim][CO₃]]₀/[VC]₀ = 250/0.25/1/6/2, MMA: 2 ml, time: 48 h, conversion: 23.6%, temperature: 60 °C.

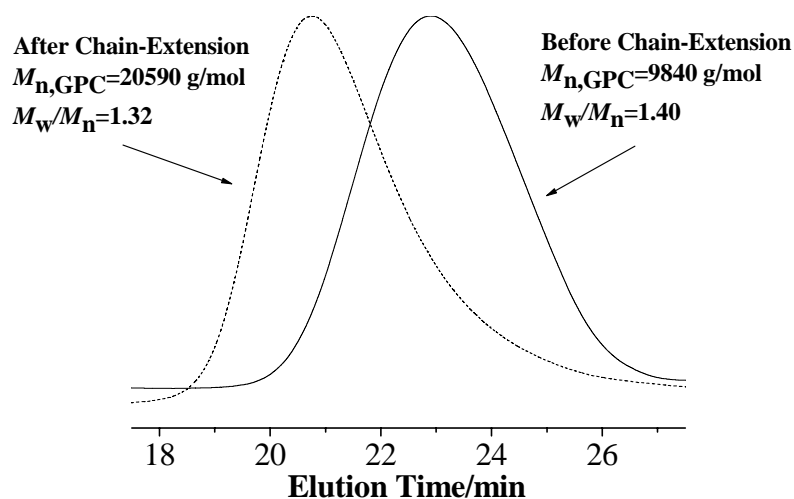


Figure S3. GPC traces of before and after chain extension using PMMA prepared by AGET ATRP of MMA (using [Bmim][HCO₃] as the ligand) as the macroinitiator. Polymerization conditions for macroinitiator PMMA: [MMA]₀/[EBiB]₀/[FeCl₃·6H₂O]₀/[[Bmim][HCO₃]]₀/[VC]₀ = 250/1/1/6/2, MMA: 2 mL, conversion: 40.2%, time: 78 h, $M_{n, GPC} = 9840$ g/mol, $M_w/M_n = 1.40$; for chain extension: [MMA]₀/[PMMA]₀/[FeCl₃·6H₂O]₀/[[Bmim][HCO₃]]₀/[VC]₀ = 250/0.25/1/6/2, MMA: 2 ml, time: 48 h, conversion: 28.7%, temperature: 60 °C.