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ATRP of MMA Catalyzed by $Fe^{II}Br_2$ in the Presence of Triflate Anions

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S Supporting Information

Atom transfer radical polymerization (ATRP)[1−6] was extensively studied during the past decade. Many transition metals, such as Cu, Ru, Fe, Ni, and Os, were successfully employed as ATRP catalysts.[7,8] Fe-based ATRP is a very attractive system because iron has the lowest toxicity and lowest price. The first Fe-based ATRPs, conducted in the presence of phosphines, amine, or pyridine containing ligands, were reported in 1997.[9,10] Later, various Fe-based complexes containing half-metallocene,[11] cyclic amines,[12] diimines,[13] substituted phosphines,[14] carbenes,[15] carboxylic acids,[16,17] or halide ligands forming anionic Fe species[18,19] or ionic liquids[20] were successfully reported to conduct ATRP.

Recently, we reported $Fe^{II}Br_2$-catalyzed ATRP of methyl methacrylate (MMA) in polar solvents without any additional ligand.[21] However, we were unable to conduct the polymerization in nonpolar solvents because $Fe^{II}Br_2$ could not be dissolved. Herein, we present $Fe^{II}Br_2$-catalyzed ATRP of MMA in a nonpolar solvent, anisole, in the presence of tetra(*n*-butyl)ammonium triflate (TBAOTf). TBAOTf helps to dissolve $Fe^{II}Br_2$ in the monomer/solvent mixture but does not coordinate strongly to Fe center. This catalytic system leads to robust control over ATRP of MMA.

Triflate anions are considered as either noncoordinating[22] or weakly coordinating,[23] since their coordination is weak and reversible. Weakly coordinating or noncoordinating anions are those which do not form permanent coordinative bond with the metal and which are weak Lewis bases. Generally, their negative charge is delocalized. The coordination sites occupied by weakly coordinating anions could be considered as "vacant" because they would easily vacate this coordination site in the presence of other ligands.

The polymerization of MMA did not occur in anisole, even after 8 h at 60 °C, in the absence of TBAOTf because $Fe^{II}Br_2$ was not soluble. The triflate anions facilitated $Fe^{II}Br_2$ dissolution and led to a well-controlled polymerization. $Fe^{II}Br_2$/TBAOTf-catalyzed ATRP of MMA was successfully carried out in 33.3% (v/v) anisole at 60 °C with the molar ratio $[MMA]:[EBrPA]:[Fe^{II}Br_2] = 400:1:1$ (EBrPA: ethyl 2-bromo-2-phenylacetate) in the presence of various ratios $[TBAOTf]/[Fe^{II}Br_2]$ (Figure 1). With 0.5 equiv of TBAOTf, the solution was still heterogeneous. As a result, the activity was lower than with 1 equiv of TBAOTf. Conversion of 44% was achieved after 4 h with 0.5 equiv of TBAOTf, while the conversion 57% was reached with 1 equiv of TBAOTf. However, once $Fe^{II}Br_2$ was completely dissolved, the activity did not change with a further increase of [TBAOTf] added. The conversion reached 56%, 57%, and 55% in 4 h with 0.75, 1, and 2 equiv of TBAOTf, respectively. Independently of the excess TBAOTf added, the polymerizations were well controlled, yielding polymers with M_w/M_n values around 1.15 throughout the polymerizations, and resulted in PMMA with molecular weights agreeing with theoretical values. Similar polymerization rates with 0.75, 1, or 2 equiv TBAOTf suggest the reversible weak coordination of triflate anions. Solvent, monomer, and triflate anions likely occupy the "vacant" coordination sites of iron centers, increasing solubility, while they do not significantly influence the catalytic properties and allow the alkyl halides to be activated by the atom transfer process.

These observations were very different from those with tetra(*n*-butyl)ammonium bromide (TBABr). In the presence of 1 equiv of TBABr, the activity was higher (73% conversion in 4 h) than with 1 equiv of TBAOTf, although M_w/M_n values were also higher (1.28 vs 1.17). However, when 2 equiv of TBABr was added, the activity dropped (29% conversion in 4 h) while M_w/M_n values decreased from 1.29 to 1.15. In the presence of 5 equiv of TBABr, the activity was even lower (22% conversion in 4 h) and the M_w/M_n values increased to 1.42−1.59. In all cases, the molecular weights of obtained PMMA agreed with theoretical values. These experiments indicate that triflate anions interact with iron centers weakly and do not significantly affect their catalytic properties but nevertheless facilitate dissolution of $Fe^{II}Br_2$ in less polar media.

$Fe^{II}Br_2$/TBAOTf-catalyzed ATRP of MMA with different targeted degrees of polymerization (DP) was evaluated in 33.3% (v/v) anisole at 60 °C, using the molar ratio $[MMA]:[EBrPA]:[Fe^{II}Br_2]:[TBAOTf] = (100, 200, \text{or } 400):1:1:1$ (Table 1). The polymerizations were well controlled, providing PMMA with $M_w/M_n = 1.14−1.24$, and the molecular weights in good agreement with the theoretical values. The conversion reached 63%, 56%, and 42% after 2 h polymerization for targeted DP = 100, 200, and 400, respectively. Higher conversion could be achieved at longer times. For example, 98% conversion was reached after 16 h with targeted DP = 200. The molecular weight of obtained PMMA was $M_n = 17\,900$ with $M_w/M_n = 1.20$. The polymerization of MMA was also well controlled in bulk and toluene, indicating that anisole was not a specific solvent for $Fe^{II}Br_2$/TBAOTf controlled ATRP of MMA. The rates of polymerization in NMP with or without TBAOTf were both slower (36% and 44% conversion in 2 h, respectively) than that in anisole with TBAOTf (63% conversion in 2 h). The M_w/M_n values in NMP with or without TBAOTf were 1.28−1.29, which were higher than that in anisole (1.19). The influence of NMP solvent was more significant than that of TBAOTf, which further illustrated the weakly coordinating nature of anions.

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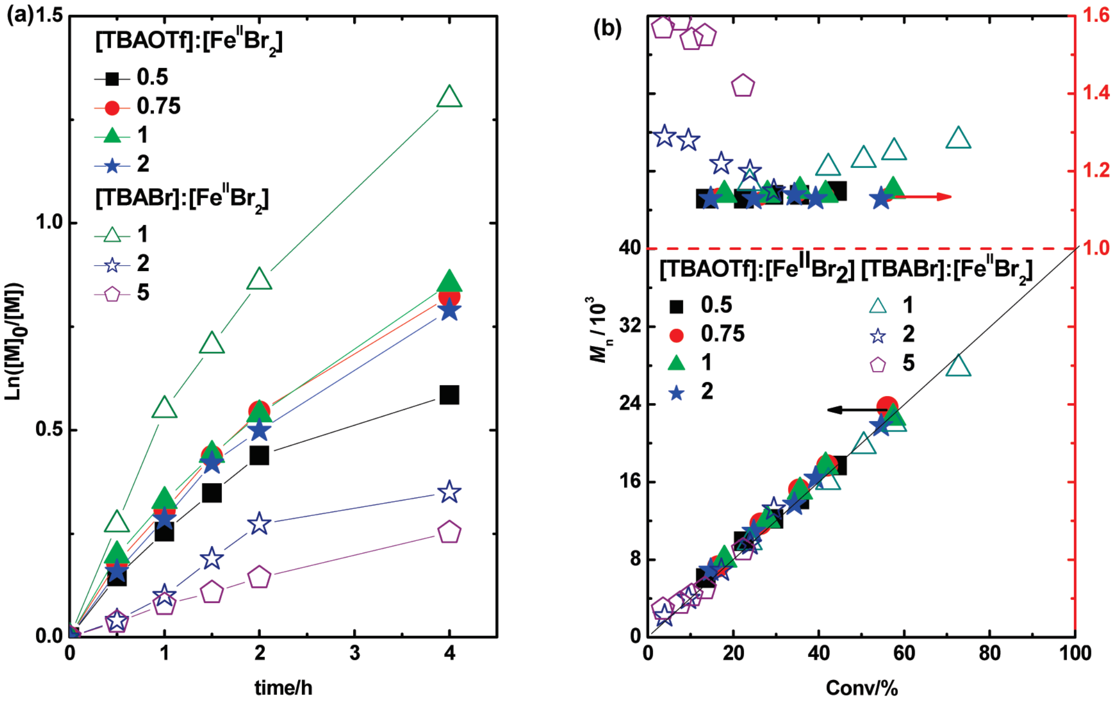

Figure 1. (a) Kinetic plots of ln([M]$_0$/[M]) vs time and (b) plot of number-average molecular weights M_n and M_w/M_n values vs conversion for Fe^{II}Br$_2$/TBAOTf- and Fe^{II}Br$_2$/TBABr-catalyzed ATRP of MMA with different ratio between Fe^{II}Br$_2$ and TBAOTf or TBABr. [MMA]:[EBrPA]:[Fe^{II}Br$_2$]: = 400:1:1 at 60 °C in 33.3% (v/v) anisole.

Table 1. Fe^{II}Br$_2$/TBAOTf ATRP of MMA with Different Targeted Degree of Polymerization and in Different Solvents[a]

solvent	molar ratio[b]	time (h)	conv (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
anisole	100:1:1:1	2	63	6600	6500	1.19
anisole	200:1:1:1	2	56	12400	11400	1.22
anisole	200:1:1:1	4	67	15500	13700	1.24
anisole	200:1:1:1	16	98	17900	19900	1.20
anisole	400:1:1:1	2	42	17600	16900	1.14
anisole	400:1:1:1	8	71	26400	28600	1.14
none	100:1:1:1	2	67	8500	6900	1.19
toluene	100:1:1:1	2	65	7900	6700	1.22
NMP	100:1:1:1	2	36	4400	3800	1.29
NMP	100:1:1:0	2	44	5000	4600	1.28

[a] Monomer/solvent = 2/1 (v/v) or in bulk, at 60 °C. [b] [MMA]$_0$:[EBrPA]$_0$:[Fe^{II}Br$_2$]$_0$:[TBAOTf]$_0$.

Table 2. ATRP of MMA with Different Ratios of Bromide Anions to Fe^{II} Species[a]

entry	Fe^{II} salt	salt (ratio)	Br/Fe^{II}	conv (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
1	Fe^{II}(OTf)$_2$		0	0			
2	Fe^{II}(OTf)$_2$	TBABr (1)	1	43	14900	17400	1.14
3	Fe^{II}(OTf)$_2$	TBABr (2)	2	32	11600	13000	1.14
4	Fe^{II}(OTf)$_2$	TBABr (3)	3	23	11100	9500	1.14
5	Fe^{II}(OTf)$_2$	TBABr (4)	4	17	6300	7100	1.28
6	Fe^{II}Br$_2$	TBAOTf (2)	2	55	21800	22300	1.13
7	Fe^{II}Br$_2$	TBABr (1)	3	73	27700	29400	1.28
8	Fe^{II}Br$_2$	TBABr (2)	4	29	13200	12100	1.15
9	Fe^{II}Br$_2$	TBABF$_4$ (3)	2	7	3600	3000	1.24
10	Fe^{II}Br$_2$	TBAPF$_6$ (3)	2	9	3700	3800	1.23
11	Fe^{II}Br$_2$	TBAClO$_4$ (3)	2	1	1200	600	1.27

[a] [MMA]:[EBrPA]:[Fe^{II}] = 400:1:1; in 33.3% anisole (v/v), at 60 °C, for 4 h polymerization.

The catalytic activity of Fe^{II}(OTf)$_2$ was also studied. Fe^{II}(OTf)$_2$ is soluble in anisole but has very low activity in ATRP without any additional halide ligand (Table 2). When 1 equiv TBABr was added, a well-controlled polymerization was attained, and 43% conversion was reached in 4 h. However, a further increase in the ratio of TBABr decreased the catalytic activity. The control of polymerization was still acceptable even when 3 equiv of TBABr was added, but it decreased with 4 equiv of TBABr. The highest activity was found when the ratio between bromide anions and iron centers was 1:1. Compared to the experiments starting with Fe^{II}Br$_2$ and various ratios of TBABr, the results were slightly different, even when the ratio between bromide anions and iron centers was the same (cf. entry 3 and 6; entry 4 and 7; entry 5 and 8 in Table 2). Probably, the association/exchange process between iron centers and bromide anions could not reach equilibrium, and consequently the activity of the complexes in ATRP was different or some iron species were hydrolyzed.[18,19]

The effect of adding other weakly coordinating anions was also investigated. In the presence of tetra(n-butyl)ammonium perchlorate, TBAClO$_4$, the system was heterogeneous even with the ratio of TBAClO$_4$ to Fe^{II}Br$_2$ 3:1. The polymerization was very slow with low initiation efficiency. Tetra(n-butyl)ammonium with BF$_4$ anion and PF$_6$ anion behaved in a similar way. The activity was much lower with TBABF$_4$ (7% conversion in 4 h) or TBAPF$_6$ (9% conversion in 4 h) than with TBAOTf (55% conversion in 4 h). While the polymerizations were controlled,

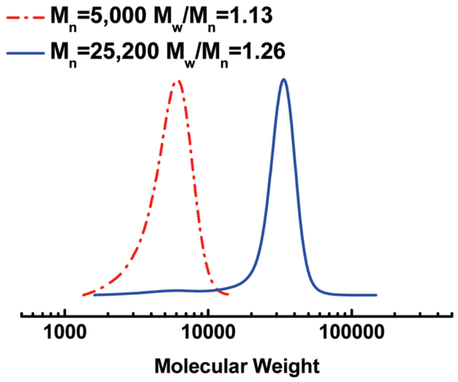

Figure 2. Chain extension of $Fe^{II}Br_2$/TBAOTf-catalyzed ATRP of MMA.

these experiments suggest the activity of the iron halide complexes vary for different weakly (or non-) coordinating anions. $Fe^{II}Br_2$ in the presence of TBAOTf appears to be the best catalytic system of those tested in this study. The role of halide and other noncoordinative anions in Fe-based ATRP is still under investigation.

Polymerization of MMA with $Fe^{II}Cl_2$/TBAOTf was not as well controlled, plausibly due to slower deactivation, as M_w/M_n values were much larger (cf. Supporting Information). Also, ATRP of styrene with ($Fe^{II}Cl_2$ or $Fe^{II}Br_2$)/TBAOTf was not successful, yielding oligomers, most likely formed via cationic oligomerization catalyzed by strong Lewis (FeX_3) or Bronstad acid (traces of triflic acid; cf. Supporting Information).

The chain extension experiment showed the well-preserved chain-end functionality (Figure 2). First, PMMA macroinitiator was synthesized using molar ratio of reagents [MMA]:[EBrPA]:[$Fe^{II}Br_2$]:[$Fe^{III}Br_3$]:[TBAOTf] = 100:1:0.8:0.2:1, in 33.3% (v/v) anisole at 60 °C. The reaction was stopped after 1 h at 41% conversion, yielding PMMA with M_n = 4800 and M_w/M_n = 1.16. The macroinitiator, precipitated in petroleum ether and dried under vacuum, was filtered through an alumina column to remove the catalyst. PMMA was obtained as a white powder with slightly higher molecular weight (M_n = 5000 and M_w/M_n = 1.13). The chain extension experiment was performed using the following molar ratio of reagents: [MMA]:[PMMA-Br]:[$Fe^{II}Br_2$]:[$Fe^{III}Br_3$]:[TBAOTf] = 1000:1:0.8:0.2:1, in 33.3% (v/v) anisole at 60 °C. PMMA with M_n = 25 200 and M_w/M_n = 1.26 was obtained after 2 h polymerization at 20% conversion. A very small amount of dead chains (<10%) was observed after chain extension, indicating well-preserved chain-end functionality.

In summary, $Fe^{II}Br_2$ provided robust control over ATRP of MMA in the presence of TBAOTf in anisole and other nonpolar solvents. The weakly coordinating triflate anions helped dissolve $Fe^{II}Br_2$ in anisole but had little effect on the catalytic reactivity of the iron species. The catalyst activity and the level of control over the polymerization did not change with increasing ratio of TBAOTf, once $Fe^{II}Br_2$ was completely dissolved. The chain-end functionality was well preserved during the polymerization, as shown by successful chain extension experiments.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Results of polymerization of styrene catalyzed by $FeBr_2$/TBAOTf and MMA catalyzed by $FeCl_2$/TBAOTf. This material is available free of charge via the Internet at http://pubs.acs.org.

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