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ATRP of MMA with ppm Levels of Iron Catalyst

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Atom transfer radical polymerization (ATRP) can be conducted with a range of transition metals, such as Cu, Ru, Fe, Ni, and Os, etc., as catalysts.[1−7] ATRP provides a versatile tool to prepare polymeric materials with various architectures including block and graft copolymers, stars, and brushes.[8−11] Recently, effort has focused on the development of more environmentally friendly and lower cost catalyst systems.[3] This has resulted in the development of two procedures that allow an ATRP to be conducted in the presence of ppm amounts of transition metal catalyst, namely, activators regenerated by electron transfer (ARGET)[12−20] and initiators for continuous activator regeneration (ICAR) ATRP.[14,21,22] In ARGET and ICAR ATRP the activator state of the catalyst is continuously regenerated by various reducing agents, thereby overcoming the effect of inevitable radical termination reactions. In addition to organic reducing agents also metallic Cu^0,[23−27] Zn^0, Mg^0, and Fe^0 can be used. It was recently reported that the pure metals can act as supplemental activators and reducing agents (SARA).[28] Iron is a desirable catalyst for ATRP because Fe has both the lowest toxicity of the suitable transition metals and the lowest price. The first Fe-based ATRP conducted in the presence of various phosphines, amine, or pyridine containing ligands was reported in 1997.[29,30] The triphenylphosphine, tributylphosphine, tributylamine, and 4,4′-di(5-nonyl)-2,2′-bipyridine ligands were expanded to include half-metallocene,[31] cyclic amines,[32] diimines,[33] substituted phosphines,[34] carbenes,[35] carboxylic acids,[36,37] or halide ligands forming anionic Fe species[38,39] or ionic liquids.[40] More recently, $FeBr_2$-catalyzed ATRP in polar solvent without any additional ligand[41] or in the presence of a nonpolar solvent and weakly coordinating anions[42] was reported. Activators generated by electron transfer (AGET) and, after this paper was submitted, also ICAR ATRP with Fe catalyst were successfully carried out, allowing the initial use of air stable Fe^{III} salts, instead of Fe^{II}.[43−47] In this Communication, we report ATRP of methyl methacrylate (MMA) with ppm amount of $Fe^{III}Br_3$ or $Fe^{II}Br_2$ catalysts. Either Fe^0 wire or azobis(isobutyronitrile) (AIBN) was employed to form and then regenerate $Fe^{II}Br_2$.

$Fe^{III}Br_3$ is oxidatively stable and soluble in many solvents, such as anisole, toluene, tetrahydrofuran, *N*-methyl-2-pyrrolidone, and MMA. A dark red stock solution of 1% $Fe^{III}Br_3$ in anisole (w/w) was prepared and stored in air for use in the following experiments. The polymerization was well controlled with the ratio of reagents $[MMA]_0$:$[EBrPA]_0$:$[Fe^{III}Br_3]_0$:$[TBABr]_0$ = 200:1:0.02:0.08 (EBrPA: ethyl 2-bromo-2-phenylacetate; TBABr: tetrabutylammonium bromide), with 1 cm Fe^0 wire (d = 0.5 mm), in 50% (v/v) anisole, at 60 °C. The molecular weight of the poly(methyl methacrylate) (PMMA) prepared agreed well with theoretical values. The conversion reached 81% after 30.5 h, giving PMMA with M_n = 17 800 and M_w/M_n = 1.19.

Solid $Fe^{III}Br_3$ does not react with oxygen but can absorb water in air; thus, the $Fe^{III}Br_3$/anisole solution may also contain a small amount of water after being stored for a long time. When water was intentionally added to $Fe^{III}Br_3$/anisole 1% (w/w) solution with the targeted ratio of $[Fe^{III}Br_3]_0$:$[H_2O]_0$ ∼ 1:30, the color of the stock solution became orange and phase separation was observed. After mixing the suspension in ultrasonic bath, a small amount of this $Fe^{III}Br_3$/anisole/H_2O mixture was added to the reaction solution which remained homogeneous. ATRP of MMA with $Fe^{III}Br_3$/anisole/H_2O under identical conditions was slower than in the previous experiment, while the level of control was comparable. The conversion reached 73% after 55 h, yielding PMMA with M_n = 15 200, M_w/M_n = 1.24. Thus, a small amount of water did not interfere with this polymerization system.

The polymerization was also successful solely in the presence of Fe^0 wire, without initially added $Fe^{III}Br_3$, although not as well controlled as with deliberate addition of $Fe^{III}Br_3$ (Figure 2). PMMA with high molecular weight was formed at the beginning of the reaction due to the absence of deactivator. The initial molecular weight was as high as M_n = 17 200 at 8% conversion with M_w/M_n = 1.81. However, after a sufficient amount of $Fe^{III}Br_3$ was generated through radical termination, a well-controlled polymerization occurred. The final molecular weights were slightly higher than theoretical values due to low initiation efficiency (∼84%). The conversion reached 81% after 71 h, providing PMMA with M_n = 19 600 and M_w/M_n = 1.36. In order to obtain better control from the start of the polymerization, the initiator was reacted with Fe^0 wire for 16 h to generate sufficient amount of $Fe^{III}Br_3$, before the addition of MMA. Under these circumstances, the polymerization was better controlled giving PMMA with M_n = 17 000 and M_w/M_n = 1.22 and reached 79% conversion after 64 h.

Because of the limited solubility of $Fe^{II}Br_2$ in anisole/MMA solution, the polymerization of MMA reached only 9% conversion after 48 h in the absence of TBABr with ratio of reagents $[MMA]_0$:$[EBrPA]_0$:$[Fe^{III}Br_3]_0$ = 200:1:0.02, with 1 cm Fe^0 wire (d = 0.5 mm), in 50% (v/v) anisole, at 60 °C (Table 1, entry 1). With initial ratio $[TBABr]_0$:$[Fe^{III}Br_3]_0$ = 1:1, the conversion reached 15% in 21 h; however, the conversion increased to only 16% after 48 h (Table 1, entries 2 and 3). This can be rationalized, since $[Fe^{III}Br_3]$ increases with time due to radical termination and there is less available TBABr to solubilize $Fe^{II}Br_2$. Thus, the

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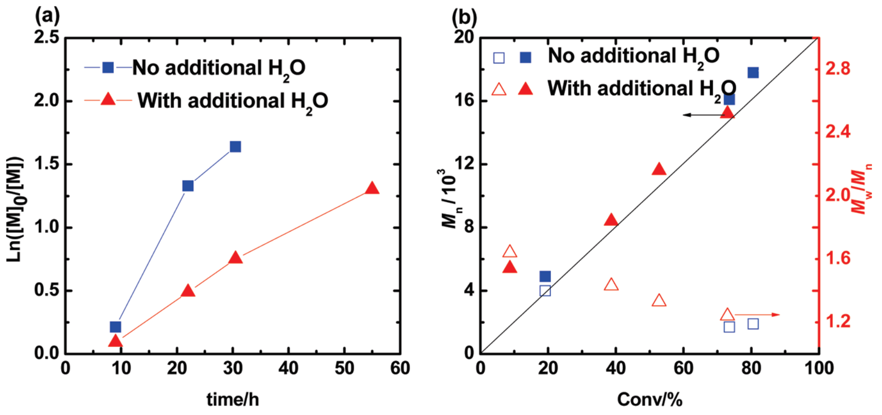

Figure 1. (a) Kinetic plots of ln($[M]_0/[M]$) vs time and (b) plot of number-average molecular weights M_n and M_w/M_n values vs conversion for ATRP of MMA with ppm level of $Fe^{III}Br_3$ as catalyst in the presence of Fe^0 wire (d = 0.5 mm, L = 1). $[MMA]_0$:$[EBrPA]_0$:$[Fe^{III}Br_3]_0$:$[TBABr]_0$ = 200:1:0.02:0.08 at 60 °C in 50% (v/v) anisole with ($[H_2O]_0$:$[Fe^{III}Br_3]_0$ = 30:1) or without additional water.

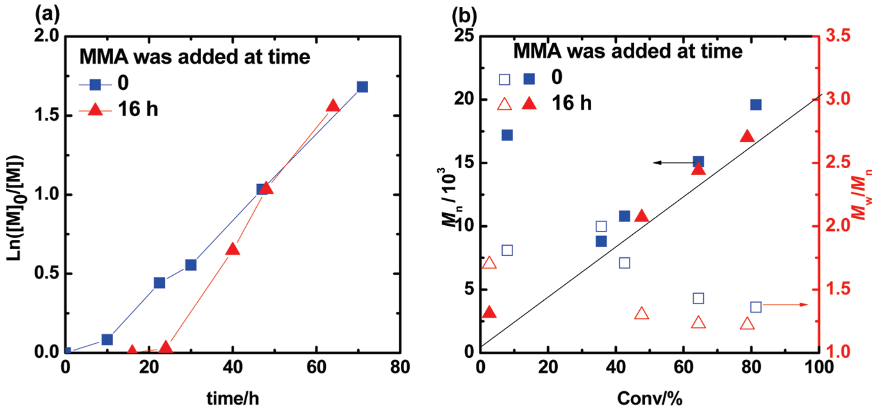

Figure 2. (a) Kinetic plots of ln($[M]_0/[M]$) vs time. (b) Plot of number-average molecular weights M_n and M_w/M_n values vs conversion for ATRP of MMA without initially addition of $Fe^{III}Br_3$ $[MMA]_0$:$[EBrPA]_0$:$[TBABr]_0$ = 200:1:0.08 in the presence of Fe^0 wire (d = 0.5 mm, L = 1), at 60 °C in 50% (v/v) anisole. MMA was added at time = 0 and 16 h.

Table 1. ATRP of MMA with ppm Levels of $Fe^{III}Br_3$/TBABr as Catalyst in the Presence of Fe^0 Wire[a]

entry	[TBABr]: $[Fe^{III}Br_3]$	Fe^0 length (cm)	time (h)	conv (%)	$M_{n,}$ GPC	$M_{n,th}$	M_w/M_n
1	0	1	48	9	2600	2000	1.86
2	1	1	21	15	2900	3200	1.41
3	1	1	48	16	3200	3400	1.39
4	4	1	9	19	4900	4000	1.40
5	4	1	30.5	81	17800	16400	1.19
6	4	0.5	25	45	8500	9200	1.23
7	4	0.5	50	70	12500	14200	1.20

[a] $[MMA]_0$:$[EBrPA]_0$:$[Fe^{III}Br_3]_0$ = 200:1:0.02 at 60 °C in 50% (v/v) anisole with various ratio of TBABr and different length of Fe^0 wire (d = 0.5 mm).

rate of polymerization strongly decreased after reaching certain conversion. A well-controlled polymerization of MMA was achieved by using 4 equiv of TBABr to $Fe^{III}Br_3$. The polymerization was relatively fast, reaching 19% conversion in 9 h and 81% conversion in 30.5 h, yielding PMMA with M_n = 17 800 and M_w/M_n = 1.19 (Table 1, entries 4 and 5). The polymerization was slower when 0.5 cm Fe^0 wire (d = 0.5 mm) was used, and it required 25 h to achieve 45% conversion and 50 h to reach 70% conversion, giving PMMA with M_n = 12 500 and M_w/M_n = 1.20 (Table 1, entries 6 and7).

The polymerization of MMA starting with 100 ppm $Fe^{II}Br_2$ was also well controlled with the ratio of reagents $[MMA]_0$:$[EBrPA]_0$:$[Fe^{II}Br_2]_0$:$[TBABr]_0$ = 200:1:0.02:0.08, with 1 cm Fe^0 wire (d = 0.5 mm), in 50% (v/v) anisole, at 60 °C (Table 2, entry 1). The conversion reached 77% in 48 h, resulting in PMMA with M_n = 14 400 and M_w/M_n = 1.20.

The polymerizations of MMA in the presence of $Fe^{III}Br_3$ and Fe^0 wire were also carried out in other solvents such as THF and toluene with ratio of reagents $[MMA]_0$:$[EBrPA]_0$:$[Fe^{III}Br_3]_0$:$[TBABr]_0$ = 200:1:0.02:0.08, with 1 cm Fe^0 wire (d = 0.5 mm), in 50% (v/v) solvent, at 60 °C (Table 2, entries 2 and 3). The polymerization conducted in THF was faster than in toluene; 97% and 76% conversions were achieved in 45 h in THF and toluene, respectively. Both polymerizations were well controlled with M_w/M_n values around 1.20.

ICAR ATRP with 100 ppm $Fe^{III}Br_3$ and 200 ppm TBABr in 33.3% (v/v) anisole, THF, and toluene was performed with the ratio of reagents $[MMA]_0$:$[EBrPA]_0$:$[Fe^{III}Br_3]_0$:$[TBABr]_0$:

Table 2. ATRP of MMA with ppm Amounts of Iron Halide Catalysts in the Presence of Fe^0 Wire or AIBN in Various Solvents

entry	solvent	iron halide	RA[c]	time (h)	conv (%)	$M_{n,GPC}$	$M_{n,th}$	M_w/M_n
1[a]	anisole	$Fe^{II}Br_2$	Fe^0	48	77	14 400	15 600	1.20
2[a]	THF	$Fe^{III}Br_3$	Fe^0	45	97	18 800	19 600	1.18
3[a]	toluene	$Fe^{III}Br_3$	Fe^0	45	76	16 400	15 400	1.18
4[b]	anisole	$Fe^{III}Br_3$	AIBN	48	51	9 100	10 400	1.38
5[b]	THF	$Fe^{III}Br_3$	AIBN	48	94	18 500	19 000	1.29
6[b]	toluene	$Fe^{III}Br_3$	AIBN	48	61	10 900	12 400	1.68

[a] $[MMA]_0:[EBrPA]_0:[FeBr_x]_0:[TBABr]_0$ = 200:1:0.02:0.08 with 1 cm Fe^0 wire (d = 0.5 mm) in 50% different solvents. [b] $[MMA]_0:[EBrPA]_0:[Fe^{III}Br_3]_0:[TBABr]_0:[AIBN]_0$ = 200:1:0.02:0.04:0.1 at 60 °C in 33.3% (v/v) different solvents. [c] RA: reducing agent.

$[AIBN]_0$ = 200:1:0.02:0.04:0.1 at 60 °C. The conversion reached 51%, 94%, and 61% after 48 h in anisole, THF, and toluene, respectively. The polymerization in THF reached high conversion, and the M_w/M_n value was lower than 1.3. ICAR ATRP in anisole and toluene was slower, and the control was not as good as in THF.

In summary, successful ATRP of MMA was carried out with ppm amount of iron bromide at 60 °C in the presence of Fe^0 as supplemental activator and reducing agent in a SARA-ATRP or AIBN as initiator in an ICAR-ATRP. In both cases well-controlled polymerizations were achieved; $M_w/M_n \sim 1.2$ for ATRP with Fe^0 in anisole, THF, and toluene and ~1.3 for ATRP with AIBN in THF.

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■ REFERENCES

(1) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614–5615.

(2) Matyjaszewski, K.; Xia, J. H. *Chem. Rev.* **2001**, *101*, 2921–2990.

(3) Tsarevsky, N. V.; Matyjaszewski, K. *Chem. Rev.* **2007**, *107*, 2270–2299.

(4) Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93–146.

(5) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.

(6) Ouchi, M.; Terashima, T.; Sawamoto, M. *Chem. Rev.* **2009**, *109*, 4963–5050.

(7) Lena, F.; Matyjaszewski, K. *Prog. Polym. Sci.* **2010**, *35*, 959–1021.

(8) Davis, K. A.; Matyjaszewski, K. *Adv. Polym. Sci.* **2002**, *159*, 1–166.

(9) Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350.

(10) Lee, H.-i.; Pietrasik, J.; Sheiko, S. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2010**, *35*, 24–44.

(11) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Prog. Polym. Sci.* **2008**, *33*, 759–785.

(12) Jakubowski, W.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 4482–4486.

(13) Jakubowski, W.; Min, K.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 39–45.

(14) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J. Y.; Braunecker, W. A.; Tsarevsky, N. V. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15309–15314.

(15) Dong, H. C.; Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 2974–2977.

(16) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. *Langmuir* **2007**, *23*, 4528–4531.

(17) Min, K.; Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 1789–1791.

(18) Pietrasik, J.; Dong, H.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 6384–6390.

(19) Tang, H.; Arulsamy, N.; Radosz, M.; Shen, Y.; Tsarevsky, N. V.; Braunecker, W. A.; Tang, W.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2006**, *128*, 16277–16285.

(20) Gnanou, Y.; Hizal, G. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 351–359.

(21) Zhang, L. F.; Miao, J.; Cheng, Z. P.; Zhu, X. L. *Macromol. Rapid Commun.* **2010**, *31*, 275–280.

(22) Plichta, A.; Li, W. W.; Matyjaszewski, K. *Macromolecules* **2009**, *42*, 2330–2332.

(23) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M. L.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348–7350.

(24) Matyjaszewski, K.; Tsarevsky, N. V.; Braunecker, W. A.; Dong, H.; Huang, J.; Jakubowski, W.; Kwak, Y.; Nicolay, R.; Tang, W.; Yoon, J. A. *Macromolecules* **2007**, *40*, 7795–7806.

(25) Magenau, A. J. D.; Kwak, Y.; Matyjaszewski, K. *Macromolecules* **2011**, *43*, 9682–9689.

(26) Kwak, Y.; Magenau, A. J. D.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 811–819.

(27) Nicolay, R.; Kwak, Y.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 541–544.

(28) Zhang, Y.; Wang, Y.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 683–685.

(29) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507–4510.

(30) Matyjaszewski, K.; Wei, M. L.; Xia, J. H.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161–8164.

(31) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 6877–6880.

(32) Niibayashi, S.; Hayakawa, H.; Jin, R. H.; Nagashima, H. *Chem. Commun.* **2007**, 1855–1857.

(33) Gibson, V. C.; O'Reilly, R. K.; Reed, W.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Chem. Commun* **2002**, 1850–1851.

(34) Xue, Z. G.; Linh, N. T. B.; Noh, S. K.; Lyoo, W. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 6426–6429.

(35) Louie, J.; Grubbs, R. H. *Chem. Commun* **2000**, 1479–1480.

(36) Zhu, S. M.; Yan, D. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4308–4314.

(37) Zhu, S. M.; Yan, D. Y. *Macromolecules* **2000**, *33*, 8233–8238.

(38) Teodorescu, M.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 2335–2339.

(39) Ishio, M.; Katsube, M.; Ouchi, M.; Sawamoto, M.; Inoue, Y. *Macromolecules* **2009**, *42*, 188–193.

(40) Sarbu, T.; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001**, *202*, 3379–3391.

(41) Wang, Y.; Matyjaszewski, K. *Macromolecules* **2010**, *43*, 4003–4005.

(42) Wang, Y.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 1226–1228.

(43) Zhang, L. F.; Cheng, Z. P.; Zhang, Z. B.; Xu, D. Y.; Zhu, X. L. *Polym. Bull.* **2010**, *64*, 233–244.

(44) Zhang, L. F.; Cheng, Z. P.; Lu, Y. T.; Zhu, X. L. *Macromol. Rapid Commun.* **2009**, *30*, 543–547.

(45) Liangjiu Bai; Lifen Zhang; Zhengbiao Zhang; Yingfeng Tu; Nianchen Zhou; Zhenping Cheng; Zhu, X. *Macromolecules* **2010**, *43*, 9283–9290.

(46) Qin, J.; Cheng, Z.; Zhang, L.; Zhang, Z.; Zhu, J.; Zhu, X. *Macromol. Chem. Phys.* **2011**10.1002/macp.201000737.

(47) Zhu, G.; Zhang, L.; Zhang, Z.; Zhu, J.; Tu, Y.; Cheng, Z.; Zhu, X. *Macromolecules* **2011**, *44*, 3233–3239.