Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 9283–9290 **9283**
DOI: 10.1021/ma1013594

Iron-Mediated AGET ATRP of Styrene in the Presence of Catalytic Amounts of Base

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Received June 18, 2010; Revised Manuscript Received September 20, 2010

ABSTRACT: The first example of atom tramsfer radical polymerization using activators generated by electron transfer (AGET ATRP) of styrene in bulk and solution was investigated in the presence of catalytic amounts of NaOH or $Fe(OH)_3$, using $FeCl_3 \cdot 6H_2O$ as the catalyst, (1-bromoethyl)benzene (PEBr) as the initiator, vitamin C (VC) as the reducing agent, and a cheap and commercially available tetrabutylammonium bromide (TBABr) or tetra-*n*-butylphosphonium bromide (TBPBr) as the ligand. It was found that both the polymerization rate and controllability over molecular weights and molecular weight distributions (~1.2) of the resultant polymers could be enhanced in the presence of the catalytic amounts of base as compared with those without base. For example, the polymerization rate of bulk AGET ATRP with a molar ratio of $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/1.5$ using NaOH as the additive was much faster than that without NaOH. The former was 3.5 times the latter. Furthermore, the polymerization of styrene could be successfully carried out even in the conditions when the amount of iron salts, $FeCl_3 \cdot 6H_2O$ as the catalyst, reduced to ppm level.

Introduction

The advent of atom transfer radical polymerization (ATRP) provides a simple way to synthesize well-defined polymers with controlled molecular weights and narrow molecular weight distributions.[1−5] Up to now, several new ATRP techniques, including simultaneous reverse and normal initiation (SR&NI) ATRP or initiators for continuous activator regeneration (ICAR) ATRP,[6−9] activators generated by electron transfer (AGET) ATRP,[10−16] and activators regenerated by electron transfer (ARGET) ATRP,[17−20] have been developed to reduce the amount of catalyst. In the AGET ATRP process, a reducing agent is used to react with the higher oxidation state catalyst (i.e., Cu(II) complex) selectively and to generate the lower oxidation state catalyst such as Cu(I) complex in situ, while an alkyl halide is also used as the initiator for the AGET ATRP system. Thus, AGET ATRP has all the advantages of normal ATRP and reverse ATRP as well as additional benefits of facile preparation, storage, and handing of ATRP catalysts.

The catalyst plays a key role in an ATRP process. Many researchers have made a great deal of efforts to investigate the effect of various transition metal complexes on polymerization, such as copper,[21,22] iron,[23−40] ruthenium,[1,41] and other transition metals.[42,43] Among these ATRP metal catalysts, iron has attracted extensive attentions owing to their low toxicity, readily abundance, and biocompatibility although iron complexes were generally considered to be inferior to copper or ruthenium complexes for the control of polymerization.

It is well-known that the ligand in the ATRP catalyst system provides appropriate solubility and an adjustable redox potential to the metal complexes. Therefore, the selection of ligand is extremely important to achieve high activity for the catalyst.[45] As for the iron-mediated ATRP, these ligands such as organic acid, triphenylphosphine, and onium salts are usually used.[29,37,38] It is noted that the onium salt ligands are much more appreciated due to its commercial availability, low cost, and easy removal from the polymerization system.

On the basis of both the advantages of AGET ATRP and iron catalyst discussed above, we focused our study on the iron-mediated AGET ATRP using conventional onium salts (i.e., tetrabutylammonium bromide or tetra-*n*-butylphosphonium bromide) as the ligands. Actually, there have been some excellent iron-mediated ATRP works using conventional onium salts as the ligands reported by Matyjaszewski, Sawamoto, and other groups.[29,33,40] The obtained polymers had controllable molecular weights and narrow molecular weight distributions. However, the corresponding polymerization rates were relatively slow. As we know, there have been some methods to enhance the polymerization rate of ATRP, such as increasing polymerization temperature[46] or adding additives such as Lewis acid. There have been a number of excellent works on rate enhancement in the presence of Lewis acid.[47−54] Actually, additives are sometimes essential for a successful ATRP. For example, a Lewis acid, such as aluminum alkoxides, is needed for the controlled polymerization of MMA catalyzed by $RuCl_2/(PPh_3)_3$ or other systems. No or very slow polymerization rate was observed in the absence of the Lewis acid.[1,55,56] Besides Lewis acid, Lewis base has also been used to enhance the rate of different chemical reactions, such as cationic polymerization[57,58] and organic reaction.[59,60] However, can the base take effect in the living radical polymerization systems? In this work, we demonstrate that iron-mediated AGET ATRP of styrene using the cheap and commercially available onium salts as ligands can greatly enhance both the polymerization rate and controllability over molecular weights of the obtained polymers in the presence of catalytic amounts of NaOH or $Fe(OH)_3$ for the first time. The effect of the amount of base on the AGET ATRP and the corresponding polymerization kinetics were investigated. The polymerization of styrene could be successfully carried out even in the conditions when the amount of iron salts, $FeCl_3 \cdot 6H_2O$ as the catalyst, reduced to ppm level.

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Experimental Section

Materials. Monomer styrene (St) (>99%) was purchased from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China). The monomer was washed three times with an aqueous solution of sodium hydroxide (NaOH) (5 wt %), followed by washing with deionized water until the solution was neutralized. The resulting solution was then dried over anhydrous magnesium sulfate, distilled twice at reduced pressure, and stored at −18 °C. (1-Bromoethyl)benzene (PEBr) (97%) was purchased from Acros and used as received. Tetrabutylammonium bromide (TBABr) (99%, Shanghai Chemical Reagents Co. Ltd.) and tetra-*n*-butylphosphonium bromide (TBPBr) (99%, Shanghai Chemical Reagents Co. Ltd.) were used as received. Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (>99%), vitamin C (VC) (>99.7%), NaOH (>99%), and $Fe(OH)_3$ (>99%) were purchased from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China) and used as received. Tetrabutylammonium perchlorate (Bu_4NClO_4) was purchased from Tokyo Kasei Kogyo Co. Ltd., and ferrocene (97%) was purchased from Acros Co. Ltd. Tetrahydrofuran (THF) (99.9%, Shanghai Chemical Reagents Co.) and methanol (99.9%, Shanghai Chemical Reagents Co.) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd. and used as received unless mentioned.

General Procedure for AGET ATRP of St. A typical bulk polymerization procedure with the molar ratio of $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/1.5$ is as follows. A mixture was obtained by adding $FeCl_3 \cdot 6H_2O$ (18.6 mg, 0.069 mmol), TBABr (44.6 mg, 0.138 mmol), St (2.0 mL, 17.31 mmol), PEBr (9.8 μL, 0.069 mmol), NaOH (4.2 mg, 0.104 mmol), and VC (24.4 mg, 0.138 mmol) to a dried ampule with a stir bar. The mixture was thoroughly bubbled with argon for 20 min to eliminate the dissolved oxygen. The ampule was flame-sealed and then transferred into an oil bath held by a thermostat at the desired temperature (110 °C) to polymerize under stirring. After the desired polymerization time, the ampule was cooled by immersing into iced water. Afterward, it was opened, and the contents were dissolved in THF (~2 mL) and precipitated into a large amount of methanol (~200 mL). The polymer obtained by filtration was dried under vacuum until constant weight at 50 °C. The monomer conversion was determined gravimetrically.

Typical Procedures for Chain Extension Using PS as Macroinitiator. The PS sample ($M_{n,GPC} = 5250$ g/mol, $M_w/M_n = 1.20$) obtained with the molar ratio of $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/1.5$ in the presence of air was used as the macroinitiator for the chain extension reaction at the molar ratio of $[St]_0/[PS]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/0.5/2/4/4/3$. The polymerization procedure is as follows: PS (90.8 mg, 0.017 mmol) was dissolved in 1.0 mL (0.9 g, 8.66 mmol) of fresh St, and then the predetermined quantity of $FeCl_3 \cdot 6H_2O$ (18.6 mg, 0.069 mmol), TBABr (44.4 mg, 0.138 mmol), VC (24.3 mg, 0.138 mmol), and NaOH (4.1 mg, 0.10 mmol) were added in the presence of air. The rest of the procedure was the same as the procedure described above. The chain-extension reaction was carried out in bulk under stirring at 110 °C. The monomer conversion was 41% by gravimetrical calculation after 21 h. The M_n and M_w/M_n values were determined by GPC with PS standards ($M_{n,GPC} = 23\,500$ g/mol, $M_w/M_n = 1.21$).

Characterization. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1 (pore size: 100 Å, 100−5000 Da), HR 2 (pore size: 500 Å, 500−20 000 Da), and HR 4 (pore size 10 000 Å, 50−100 000 Da) columns (7.8 × 300 mm, 5 μm beads size) with molecular weights ranging from 10^2 to 5×10^5 g/mol. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with polystyrene standards purchased from Waters. The ^1H NMR spectrum of the obtained polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Cyclic voltammetry (CV) experiments were performed at a scanning rate of 50 mV/s with a RST5200 electrochemical system (Zhengzhou Shirui Si Technology Co. Ltd., China) at room temperature, using a Ag counter electrode, Pt working electrode, and a Ag/AgCl reference electrode with Bu_4NClO_4 (0.1 M) as an electrolyte (sweep rate: 50 mV/s). The ferrocene(II)/(III) couple ($E_{1/2} = 450$ mV and $\Delta E_p = 280$ mV) was utilized as a benchmarked redox couple.

Table 1. Effect of the Amount of NaOH on the Bulk AGET ATRP of St[a]

entry	$[NaOH]_0/[Fe(III)]_0$	conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	0/1	0	NA	NA	NA
2	0.75/1	5.6	1450	2500	1.11
3	1.5/1	7.8	2000	2900	1.13
4	3/1	29.4	7640	8740	1.32
5	3.8/1	33.3	8700	12500	1.65
6	7.5/1	46.1	12000	38380	2.20
7	18.3/1	98.3	25600	66380	3.69

[a] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/x$ (x = 0, 0.75, 1.5,3, 3.8, 7.5, 18.3), St = 2 mL, temperature = 110 °C, polymerization time = 7 h.

Results and Discussion

Polymerization of St in the Presence of NaOH. The iron-mediated AGET ATRPs of St in the absence/presence of different amounts of NaOH were first investigated using TBABr as the ligand. The results are listed in Table 1. From entry 1 in Table 1, it can be seen that no polymer was obtained after 7 h when no NaOH was added into the reaction system. As shown in entries 2−7 in Table 1, the conversion of St increased with amount of added NaOH, from 5.6% to 98.3% when the ratio of $[NaOH]_0/[Fe(III)]_0$ increasing from 0.75/1 to 18.3/1, indicating that NaOH can enhance the polymerization rate markedly. At the same time, it can also be seen that the controllability over molecular weights and molecular weight distribution became poor with increasing amount of added NaOH (i.e., M_w/M_n values were 1.11, 1.13, 1.32, 1.65, 2.2, and 3.69 in the cases of $[NaOH]_0/[Fe(III)]_0$ being 0.75/1, 1.5/1, 3.0/1, 3.8/1, 7.5/1, and 18.3/1, respectively), which indicated that a suitable amount of NaOH should be needed for a well-controlled polymerization process.

In order to further investigate the rate enhancement of polymerization with adding NaOH in detail, the kinetics were studied in the presence of catalytic amounts of NaOH using PEBr as the initiator, $FeCl_3 \cdot 6H_2O$ as the catalyst, TBABr as the ligand, and VC as the reducing agent in bulk or in THF solution. Figure 1a shows the kinetics of bulk and solution AGET ATRP of St with a molar ratio of $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/1.5$. At the same time, in order to compare it with the results in the case without NaOH, the kinetics of bulk AGET ATRP of St is also shown in Figure 1a. All the kinetics showed linear plots, indicating that the polymerizations were approximately first order with respect to the monomer concentration and that the number of active species remained constant during the polymerization process. However, the polymerization rates for the solution and bulk AGET ATRPs using NaOH as the additives were much faster than that without NaOH. By calculating the apparent rate constant of polymerization, k_p^{app} ($R_p = -d[M]/dt = k_p[P_n \cdot][M] = k_p^{app}[M]$), as determined from the kinetic slopes, a k_p^{app} of 1.10×10^{-5} s^{-1} for the bulk polymerization and 2.53×10^{-5} s^{-1} for the solution polymerization in the

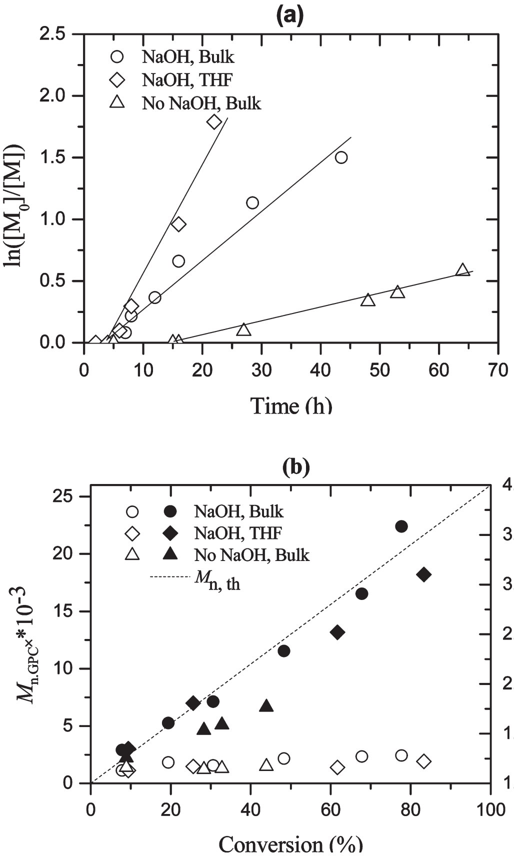

Figure 1. Plots of $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk AGET ATRP of St using TBABr as the ligand. Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/x$ ($x = 0, 1.5$); St = 2 mL; THF = 1 mL only for solution polymerization; temperature = 110 °C.

presence of catalytic amount of NaOH and k_p^{app} of $3.14 \times 10^{-6}\ s^{-1}$ in the absence of NaOH were obtained. The k_p^{app} values of polymerization with NaOH in bulk and solution were 3.5 and 8.1 times that without NaOH, respectively. It is noted that the rate enhancement in THF solution was larger than that in bulk. This was contributed to the fact that THF facilitates the dissolving of the added NaOH in the reaction system. Figure 1b shows the evolution of the number-average molecular weight ($M_{n,GPC}$) values of PS and molecular weight distribution (M_w/M_n) values on the conversion for the bulk AGET ATRP of St at 110 °C. As shown in Figure 1b, the $M_{n,GPC}$ values of the polymers with/without NaOH increased linearly with monomer conversion while keeping low M_w/M_n values ($M_w/M_n = 1.11-1.28$). The experimental molecular weights were somewhat lower than their corresponding theoretical ones for the AGET ATRP without added NaOH while consistent with the corresponding theoretical ones in the case of added NaOH. These results indicated that the bulk AGET ATRP of St in the presence of catalytic amounts of NaOH was a better controlled/"living" radical polymerization process.

Another onium salt ligand TBPBr was also used to evaluate the iron-mediated AGET ATRP of St in the presence of catalytic amounts of NaOH. Three kinetic plots under different polymerization conditions (without NaOH, with NaOH, as well as with both NaOH and THF, respectively) are shown in Figure 2a. Similarly, the polymerization rate in the presence of NaOH was faster than that without NaOH. It is interesting that the polymerization rate with NaOH in THF was fastest among the three cases. The corresponding k_p^{app} was $9.28 \times 10^{-6}\ s^{-1}$ in the case of without NaOH, $1.71 \times 10^{-5}\ s^{-1}$ in the case of with NaOH, and $2.62 \times 10^{-5}\ s^{-1}$ in the case of with NaOH and THF solution. The last one was 2.8 times the first. In addition, in the case of without NaOH, a longer induction period (~16.0 h) was observed as compared with that (~9.5 h) in the case of NaOH and THF. As similar to that using TBABr as the ligand, the $M_{n,GPC}$ values of the obtained PS using TBPBr as the ligand with/without NaOH increased linearly with monomer conversion while keeping low M_w/M_n values ($M_w/M_n = 1.08-1.25$). Experimental molecular weights were lower than their corresponding theoretical ones for the AGET ATRP without added NaOH. The $M_{n,GPC}$ values were consistent with the corresponding theoretical ones in the case of added NaOH. All these results indicated that the AGET ATRP of St using TBPBr or TBABr as the ligand in the presence of catalytic amounts of NaOH not only increased the polymerization rate but also enhanced the controllability over the molecular weights and molecular weight distributions.

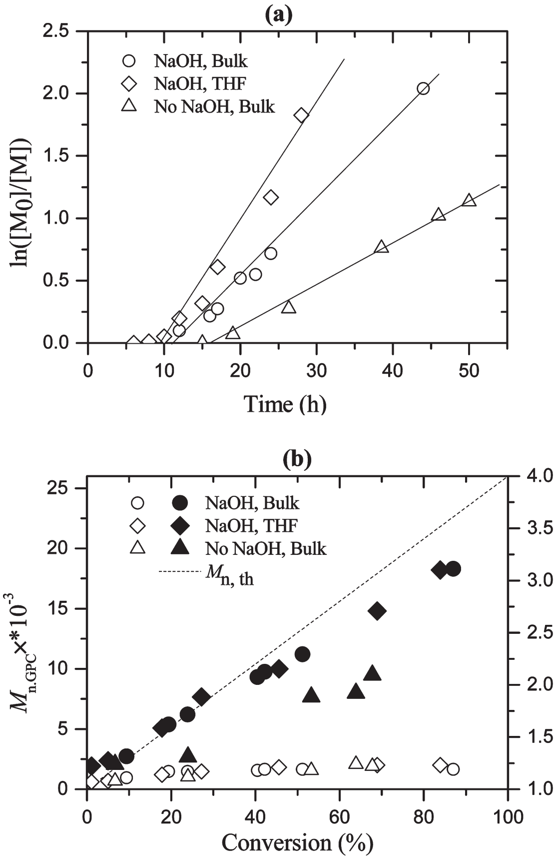

Figure 2. Plots of $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk or solution AGET ATRP of St using TBPBr as the ligand. Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBPBr]_0/[VC]_0/[NaOH]_0 = 250/1/1/2/2/x$ ($x = 0, 1.5$); St = 2 mL; THF = 1 mL only for solution polymerization; temperature = 110 °C.

Polymerization of St in the Presence of $Fe(OH)_3$. It is well-known that the catalyst $FeCl_3 \cdot 6H_2O$ is easy to form $Fe(OH)_3$ in the presence of NaOH, as shown by eq 1. From eq 1, it can be concluded that 3 equiv of NaOH can react with 1 equiv of $FeCl_3$ to produce 1 equiv of $Fe(OH)_3$. Thus, for the polymerization conditions in Figures 1 and 2 in the presence of catalytic amounts of NaOH, the same molar ratio of

$FeCl_3$ and $Fe(OH)_3$ coexisted in the reaction system since $[NaOH]_0/[FeCl_3 \cdot 6H_2O]_0 = 1.5/1$ was used.

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl \qquad (1)$$

In order to investigate whether $Fe(OH)_3$ play a key role in the enhancement of the rate and controllability for the iron-mediated AGET ATRP as discussed above, reference experiments using $Fe(OH)_3$ instead of NaOH were conducted. The results are shown in Figure 3. From Figure 3a, a linear kinetic plot was obtained as shown in Figure 3a. The corresponding k_p^{app} was 1.66×10^{-5} s^{-1}, being 5.3 times the rate enhancement as compared with that in the absence of any additives. In Figure 3b, the $M_{n,GPC}$ values increased linearly with the monomer conversion. At the same time, the M_w/M_n values remained low level ($M_w/M_n = 1.13-1.28$), indicating "living" characteristics of the reaction system in the presence of $Fe(OH)_3$.

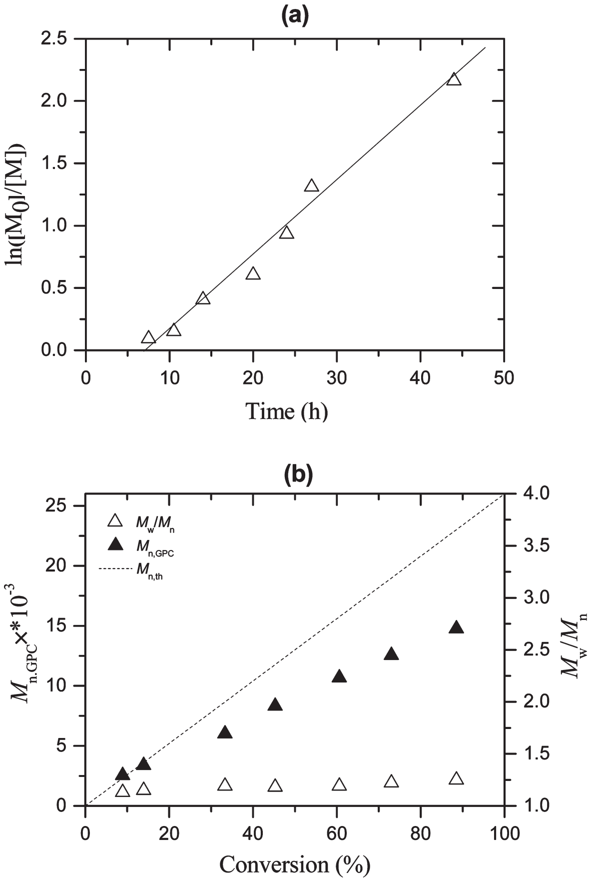

Figure 3. Plots of ln($[M]_0/[M]$) as a function of time (a) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk AGET ATRP of St using TBABr as the ligand. Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[Fe(OH)_3]_0 = 250/1/1/2/2/0.5$; St = 2 mL; temperature = 110 °C.

Table 2 shows the effect of the amount of $FeCl_3 \cdot 6H_2O$ on the bulk AGET ATRP of St in the presence of different amounts of $Fe(OH)_3$ ($Fe(OH)_3$ = 320 or 1060 ppm). From Table 2, it can be seen that the polymerization rate increased with the decreasing of the amounts of $FeCl_3 \cdot 6H_2O$, and even if at 5 ppm level (entry 10) of $FeCl_3 \cdot 6H_2O$, the polymerization was yet well controlled in the presence of $Fe(OH)_3$. It should be noted that the polymerization of St could be carried out rapidly in the presence of $Fe(OH)_3$ ($Fe(OH)_3$ = 1060 ppm) when no $FeCl_3 \cdot 6H_2O$ was added in the reaction system, as shown in entry 11 in Table 2. However, the obtained corresponding PS had broad molecular weight distribution ($M_w/M_n = 1.67$), indicating poor controllability over the polymerization. In order to confirm whether $Fe(OH)_3$ can be used as catalyst to control the polymerization of St, the kinetic experiments were further investigated with a molar ratio of $[St]_0/[PEBr]_0/[Fe(OH)_3]_0/[TBABr]_0/[VC]_0 = 250/1/0.5/2/2$. The results (see Supporting Information Figure S1) showed that the M_w/M_n values were larger than 1.5 although the molecular weights increased with the monomer conversion. Therefore, it should be necessary to remain a limited amount of $FeCl_3 \cdot 6H_2O$ for a well-controlled polymerization system. In addition, by comparison of the results in the cases of $Fe(OH)_3$ = 320 and 1060 ppm, it can be found that the polymerization rate increased with the amount of $Fe(OH)_3$. For example, when 100 ppm of $FeCl_3 \cdot 6H_2O$ was used, a conversion of 78.9% was obtained in 24 h for 320 ppm of $Fe(OH)_3$ system (entry 4 in Table 2), while 74.4% of conversion could be reached in 9.5 h for 1060 ppm of $Fe(OH)_3$ system (entry 8 in Table 2).

Figure 4 further shows the kinetic plots and the evolution of $M_{n,GPC}$ values of PS and M_w/M_n values in the conversion for the bulk AGET ATRP of St at 10 ppm of $FeCl_3 \cdot 6H_2O$ concentration ($Fe(OH)_3$ = 320 ppm). A first-order kinetic plot was observed up to 89% of conversion in Figure 4a, which indicated that the propagating free-radical concentration was stationary during the polymerization. However, an induction period (3.0 h) was observed in Figure 4a, as observed in Figures 1−3. This phenomenon was also observed in our previous works.[61−64] From Figure 4b, the $M_{n,GPC}$ values of the polymers increased linearly with conversion and were close to their corresponding theoretical ones; meanwhile, the M_w/M_n values of the obtained PS remained low (less than 1.5), although a very low $FeCl_3 \cdot 6H_2O$ concentration (10 ppm Fe catalyst) was used. However, as shown in Table 3, at such low concentration of $FeCl_3 \cdot 6H_2O$,

Table 2. Effect of the Amount of $FeCl_3 \cdot 6H_2O$ on the Bulk AGET ATRP of St in the Presence of $Fe(OH)_3$

entry		$FeCl_3 \cdot 6H_2O$ (ppm)	conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
$Fe(OH)_3$ = 320 ppm, polymerization time = 24 h	1[a]	1000	46.7	12 140	9 100	1.28
	2[a]	500	69.4	18 040	14 520	1.46
	3[a]	250	74.4	19 340	17 880	1.36
	4[a]	100	78.9	20 510	20 350	1.37
	5[a]	10	82.2	21 370	19 600	1.42
$Fe(OH)_3$ = 1060 ppm, polymerization time = 9.5 h	6[b]	2000	13.9	3 610	3 370	1.15
	7[b]	200	67.8	17 600	19 100	1.29
	8[b]	100	71.7	18 640	23 240	1.47
	9[b]	50	72.8	18 930	24 870	1.39
	10[b]	5	74.4	19 340	24 560	1.34
	11[b]	0	78.9	20 500	27 800	1.67

[a] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[Fe(OH)_3]_0 = 250/1/x/2/2/0.15$ (x = 0.5, 0.25, 0.125, 0.05, 0.005). [b] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[Fe(OH)_3]_0 = 250/1/x/2/2/0.5$ (x = 1, 0.1, 0.05, 0.025, 0.005, 0); St = 2 mL, temperature = 110 °C.

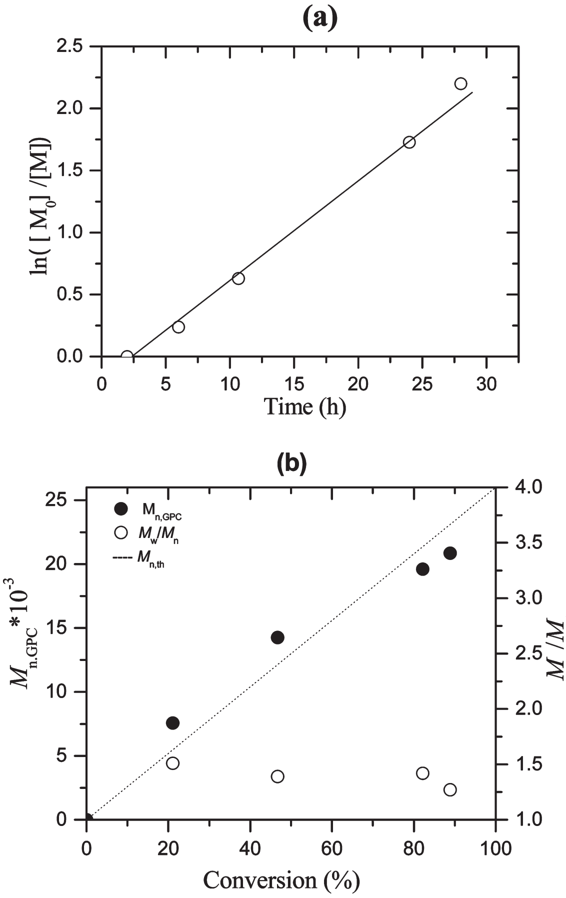

Figure 4. Plots of $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk AGET ATRP of St using TBABr as the ligand. Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[Fe(OH)_3]_0$ = 250/1/0.005/2/2/0.15; St = 2 mL; temperature = 110 °C. The amount of Fe catalyst in $FeCl_3 \cdot 6H_2O$ = 10 ppm.

the polymerization was uncontrolled; M_w/M_n was 1.93 (entry 1 in Table 3) for 10 ppm Fe catalyst and 1.91 (entry 2 in Table 3) for 35 ppm Fe catalyst when NaOH was used instead of $Fe(OH)_3$. When 70 ppm Fe catalyst was used, the polymerization became somewhat controlled (M_w/M_n = 1.47, entry 3 in Table 3). These results indicated that $Fe(OH)_3$ may play bifunctional role in the polymerization process, enhancing the polymerization rate and improving the controllability over the polymerization.

Table 3. Effect of the Amount of Iron Catalyst on the Solution AGET ATRP of St in THF[a]

entry	Fe catalyst (ppm)	conversion (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	10	22.2	5770	6020	1.93
2	35	27.2	7070	6500	1.91
3	70	35.0	9100	8050	1.47

[a] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0$ = 250/1/x/2/2/0.035 (x = 0.006, 0.025, 0.05), St = 2 mL, THF = 1 mL; temperature = 110 °C, polymerization time = 32 h.

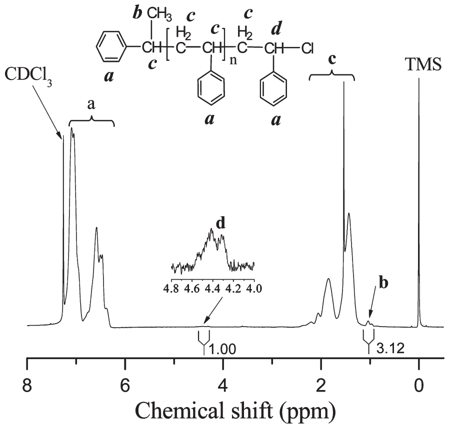

Figure 5. ^{1}H NMR spectrum of PS ($M_{n,GPC}$ = 16 530 g/mol, M_w/M_n = 1.27) obtained by AGET ATRP of St using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0$ = 250/1/1/2/2/1.5; St = 2 mL; time = 28.5 h; conversion = 67.8%; temperature = 110 °C.

Analysis of Chain End and Chain Extension. The chain end of the PS ($M_{n,GPC}$ = 16 530 g/mol, M_w/M_n = 1.27) obtained by AGET ATRP of St in the presence of catalytic amounts of NaOH was analyzed by ^{1}H NMR spectroscopy, as shown in Figure 5. The chemical shifts at δ = 6.37−7.08 ppm (*a* in Figure 5) are attributed to the aromatic protons in the PEBr initiator moieties and PS main chains. The chemical shift at δ = 1.03 ppm (*b* in Figure 5) corresponded to the methyl protons in the initiator PEBr, which indicates that the initiator PEBr moieties were successfully attached to the polymer chain ends. The chemical shifts at 1.42−2.06 ppm (*c* in Figure 5) are assigned to the methylene and methyne protons in the PS main chains. The chemical shifts at 4.2−4.6 ppm (*d* in Figure 5) are assigned to the methyne protons in the chain ends of PSs because of the electron-attracting function of ω-Cl atom.[62,65] In addition, the percentage of chain-end functionality f (f = 96.1%) can be estimated by a comparison of the integrals of the peaks H_b (protons corresponding to the initiator CH_3−CH groups) and H_d (proton CH located in the α-position of the chlorine chain end). Therefore, the obtained PS can be used as macroinitiators to conduct chain-extension reaction. The PS ($M_{n,GPC}$ = 5250 g/mol, M_w/M_n = 1.20) obtained in the presence of NaOH was used as the predecessor in chain-extension experiment. There was a peak shift from the macroinitiator to the chain-extended PS with $M_{n,GPC}$ = 23 500 g/mol and M_w/M_n = 1.21 (Figure 6). The successful chain-extension reaction further verified the features of controlled/"living" free-radical polymerization of St in the presence of NaOH. In addition, the PS obtained using TBPBr as the ligand in the presence of catalytic amounts of NaOH or using TBABr as the ligand in the presence of catalytic amounts of $Fe(OH)_3$ can also be used as macroinitiator to conduct chain-extension reaction (see Supporting Information Figures S2 and S3, respectively).

Cyclic Voltammetry. The redox behavior of catalysts has often supported the catalytic ability in metal-mediated living radical polymerization because it undergoes one-electron redox by reversibly activating the carbon−halogen bond. Therefore, CV for the $FeCl_3$/TBABr complexes under different amounts of NaOH was first measured in methanol solution. The redox peaks and CV data are shown in Figure 7 and Table 4, respectively. For the $FeCl_3$/TBABr complexes with molar ratio of $[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[NaOH]_0$ = 1/2/x (x = 0, 1, and 1.5, respectively), clear oxidation/reduction peaks, which was likely to be assigned to one-electron redox between Fe(II) and Fe(III), were observed as shown in Figure 7a−c. However, when the molar ratio of $[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[NaOH]_0$ was changed into 1/2/3, the complex showed a reduction wave around 0.067 V, but almost no oxidation wave (Figure 7d) was observed, which indicated irreversible oxidation/reduction process. According to eq 1, $FeCl_3$ was likely to be converted into $Fe(OH)_3$ completely at this molar ratio. Such a CV result suggested that $Fe(OH)_3$/TBABr alone was not a good catalyst for the

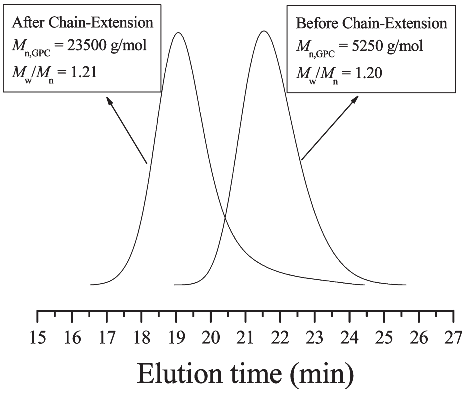

Figure 6. GPC traces of before and after chain extension using PS prepared by AGET ATRP of St as the macroinitiator. Polymerization conditions: $[St]_0/[PS]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[NaOH]_0$ = 250/0.5/2/4/4/3, St = 1 mL, time = 21 h, conversion = 41%, temperature = 110 °C.

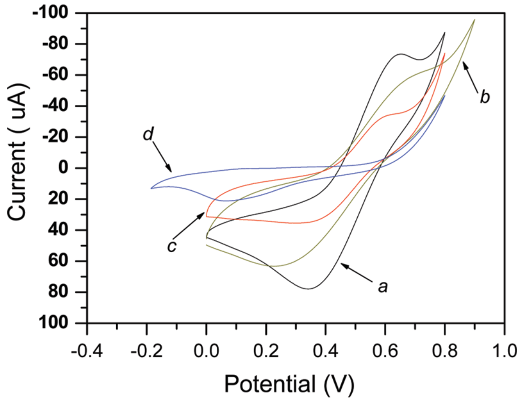

Figure 7. Cyclic voltammograms (50 mV/s) of $FeCl_3 \cdot 6H_2O$/TBABr complexes (10 mM) under different amounts of NaOH in methanol at room temperature. $[Bu_4ClO_4]$ = 100 mM (supporting electrolyte). $[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[NaOH]_0 = 1/2/x$; (a) $x = 0$, (b) $x = 1$, (c) $x = 1.5$, and (d) $x = 3$.

Table 4. Redox Potentials of Fe Complexes Measured in Methanol Corresponding to Those in Figure 7

x^a	E_{pc} (V)	E_{pa} (V)	ΔE_P (V)	$E_{1/2}$ (V)
0	0.342	0.652	0.31	0.497
1	0.227	0.699	0.472	0.463
1.5	0.296	0.600	0.304	0.448
3	0.067	NA	NA	irreversible

[a] $[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[NaOH]_0 = 1/2/x$. E_{pa} and E_{pc} are the peak potentials of the oxidation and reduction waves, respectively. $\Delta E_p = E_{pa} - E_{pc}$. $E_{1/2} = (E_{pa} + E_{pc})/2$.

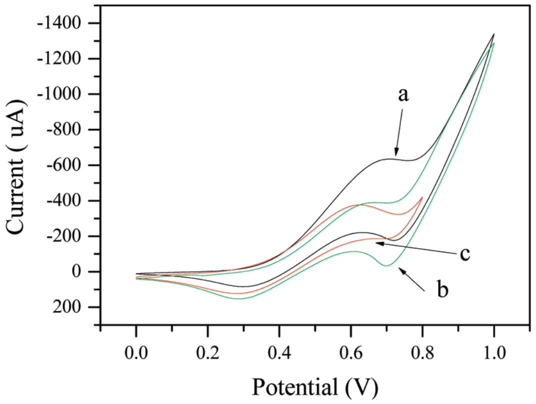

Figure 8. Cyclic voltammograms (50 mV/s) of $FeCl_3 \cdot 6H_2O$/TBABr complexes (10 mM) under different additives in methanol at room temperature. $[Bu_4ClO_4]$ = 100 mM (supporting electrolyte). $[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[additive]_0 = 1/2/2/x$; (a) no additive, $x = 0$; (b) additive = $Fe(OH)_3$, $x = 1$; and (c) additive = NaOH, $x = 1.5$.

Table 5. Redox Potentials of Fe Complexes Measured in Methanol Corresponding to Those in Figure 8

additive/x^a	E_{pc} (V)	E_{pa} (V)	ΔE_P (V)	$E_{1/2}$ (V)
none/0	0.299	0.705	0.406	0.502
$Fe(OH)_3$/1	0.283	0.666	0.383	0.475
NaOH/1.5	0.281	0.623	0.342	0.452

[a] $[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[VC]_0/[additive]_0 = 1/2/2/x$. E_{pa} and E_{pc} are the peak potentials of the oxidation and reduction waves, respectively. $\Delta E_p = E_{pa} - E_{pc}$. $E_{1/2} = (E_{pa} + E_{pc})/2$.

ATRP polymerization, which was consistent with the polymerization results listed in entry 11 of Table 2 and Figure S1 in the Supporting Information. In addition, from Table 4, it can be seen that the redox potential ($E_{1/2}$) of the $FeCl_3$/TBABr complex was 0.497 V (entry 1), 0.463 V (entry 2), and 0.448 V (entry 3) for $x = 0$ (without NaOH), $x = 1$, and $x = 1.5$, respectively. This is contributed to that pH of the reaction system increased with the increase of the amount of the added base NaOH and that $E_{1/2}$ usually decreases with the increase of pH as reported in ref 66. Similarly, from Figure 8 and Table 5, it can also be seen that the $FeCl_3$/TBABr complex in the presence of both a reducing agent VC and additives (NaOH or $Fe(OH)_3$) shown lower $E_{1/2}$, 0.475 V (entry 2 in Table 5) for $Fe(OH)_3$ and 0.452 V (entry 3 in Table 5) for NaOH, by comparison with no additive (0.502 V, entry 1 in Table 5). These CV results were consistent with the polymerization results where the $FeCl_3$/TBABr complexes lead to a fast "living" free-radical polymerization in the presence of NaOH (Figure 1) or $Fe(OH)_3$ (Figure 3). It should be noted that the redox potentials using VC as the reducing agent (0.502 eV, entry 1 in Table 5) was somewhat higher than that (0.497 eV, entry 1 in Table 4) without reducing agent. By comparison of Figures 7 and 8, it can be seen that the oxidation current was higher than the reduction one in Figure 8, which indicated that parts of iron(II) complexes were produced in situ in the presence of the reducing agent VC. In addition, Matyjaszewski et al. reported copper(I) and copper(II) with a same ligand had different $E_{1/2}$, which may be caused by copper(I) complexes and copper(II) complexes with different coordination constants.[44,67,68] Similarly, in this work, when the reducing agent VC was added into iron(III) complexes, the iron(III) complexes with a part of iron(II) complexes produced in situ should show different peak potentials from only iron(III) complexes (without reducing agent). Jorgensen and Skibsted reported that different reducing agents influenced the redox behavior of MbFe(IV)═O and gave different values of redox potential under similar experimental conditions.[69]

As discussed above, $FeCl_3$ together with the added suitable amounts of $Fe(OH)_3$ (for NaOH system, $Fe(OH)_3$ formed in situ by the reaction between $FeCl_3$ and NaOH) probably formed a new complex with the ligand and then stabilized Fe(III) or Fe(II) species at the redox process, At the same time, the basicity of the added NaOH or $Fe(OH)_3$ resulted in the decrease of the values of $E_{1/2}$, The lower redox potentials induced a faster reversible cleavage (activation) of a carbon−halogen terminal and, in turn, generated more radical species, which contributed to the enhancement of rate and controllability of the polymerization for the iron-mediated AGET ATRP process. Thus, CV analysis showed a valuable information on the iron complexes, although the interaction between the $FeCl_3$ and/or $Fe(OH)_3$ complexes was not fully clarified yet.

Conclusions

In this work, the Fe(III)-mediated AGET ATRP of St using a cheap and commercially available TBABr or TBPBr as the ligand was demonstrated. The polymerization can be successfully carried out in the presence of catalytic amounts of NaOH or $Fe(OH)_3$, and the polymerizations showed characters of "living"/controlled free-radical polymerization. The catalytic amounts of base could enhance both the polymerization rate and controllability over molecular weights and molecular weight distributions of the resultant polymers.

Acknowledgment. The financial support from the National Natural Science Foundation of China (Nos. 20874069, 50803044, 20974071, and 20904036), the Specialized Research Fund for the Doctoral Program of Higher Education contract grant (No. 200802850005), and the Qing Lan Project and the Program of Innovative Research Team of Soochow University is gratefully acknowledged.

Supporting Information Available: Results of the kinetic experiments with a molar ratio of $[St]_0/[PEBr]_0/[Fe(OH)_3]_0/[TBABr]_0/[VC]_0 = 250/1/0.5/2/2$; GPC traces of chain extension using TBPBr as the ligand in the presence of catalytic amounts of NaOH and using TBABr as the ligand in the presence of catalytic amounts of $Fe(OH)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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