Electron-Transfer-Induced Iron-Based Atom Transfer Radical Polymerization of Styrene Derivatives and Copolymerization of Styrene and Methyl Methacrylate

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Introduction

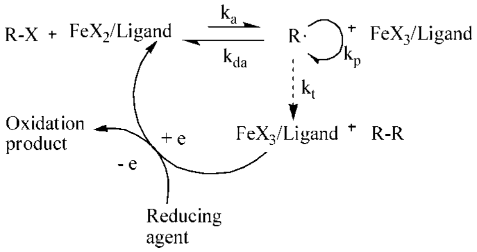
In the past decade, controlled radical polymerization (CRP) has emerged as a powerful technique for the synthesis of previously unattainable well-defined polymeric materials.[1] As one of the most important CRP techniques, atom transfer radical polymerization (ATRP) is based on the reversible reaction between a low oxidation state metal complex with an alkyl halide, which yields a high oxidation state metal complex and a radical.[2] This equilibrium results in a low radical concentration at any given time, thereby minimizing bimolecular termination reactions and allowing the synthesis of polymers with predetermined molecular weights and narrow molecular weight distributions as well as desired composition and architecture.[3–5]

Normal ATRP usually involves a combination of a relatively unstable lower oxidation state metal complex (e.g., Cu(I) or Fe(II)) and an alkyl halide.[6] Reverse ATRP, using more stable metal species (Cu(II) or Fe(III)) and a radical source such as azobis(isobutyronitrile) (AIBN), is generally more convenient.[7] However, reverse ATRP rarely allows the synthesis of pure block copolymers since the products are always contaminated with homopolymers formed by direct initiation from the free radical initiator.[8,9]

Recently, Matyjaszewski reported a new procedure for initiating ATRP whereby the active metal catalyst is generated by electron transfer (AGET) ATRP.[10–13] Specifically, active Cu(I) species is generated in situ from oxidatively stable Cu(II) via one-electron reduction by benign reducing agents such as tin 2-ethylhexanoate ($Sn(EH)_2$)[12] or vitamin C (ascorbic acid).[14] In view of the known toxicity of copper compounds, we have sought to develop a more environmentally friendly AGET-ATRP system.

In this paper, we report the first iron-based AGET-ATRP of styrene derivatives. Similar to copper-based AGET-ATRP, active Fe(II) species were generated by reducing air-stable Fe(III) bromide by FDA-approved $Sn(EH)_2$ or D-glucose (Scheme 1.) This redox reaction does not yield any other initiating radicals (Scheme 2.) Controlled polymerizations of styrene, 4-methylstyrene, 4-*tert*-butylstyrene, 4-acetoxystyrene, and methyl 4-vinylbenzoate were successfully achieved by using 1-bromoethylbenzne as the initiator and $FeBr_3$/tributylamine/$Sn(EH)_2$ as the catalyst. Well-defined block copolymers were obtained by chain extension of polystyrene macroinitiators. Well-defined copolymers of styrene and methyl methacrylate (MMA) with adjustable content were also synthesized using this methodology.

Scheme 1. Proposed Mechanism for Activator Generated by Electron Transfer for Atom Transfer Radical Polymerization (AGET-ATRP)



Scheme 2. Reduction of Fe(III) to Fe(II) by Tin(II) 2-Ethylhexanoate

$$Sn(EH)_2 + 2\,FeBr_3/ligand \xrightleftharpoons{K_{eq}} Sn(EH)_2Br_2 + 2\,FeBr_2/ligand$$

Experimental Section

Materials. All chemicals and reagents were obtained from Aldrich unless otherwise stated. Styrene (99%), 4-methylstyrene (96%), 4-*tert*-butylstyrene (93%), 4-acetoxystyrene (96%), and methyl methacrylate (99%) were passed through basic alumina and dried over calcium hydride before use. Methyl 4-vinylbenzoate (97%), 1-bromoethylbenzene (97%), iron(III) bromide (98%), tin(II) 2-ethylhexanoate ($Sn(EH)_2$) (95%), tributylamine (98.5%), and D-glucose (99%) were used as received.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded using a Bruker 300-DPX spectrometer at ambient temperature (^1H NMR, 300 MHz; ^{13}C NMR, 75 MHz). Chemical shifts are referenced to $CDCl_3$. Molecular weights and polydispersities were determined on a Shimadzu gel permeation chromatography (GPC) chromatograph containing a three-column bed (styragel HR 7.8 × 300 mm columns with 5 μm beads size; 100−5000, 500−30 000, and 2000−4 × 10^6 Da), a Shimadzu RDI-10A differential refractometer, and a Shimadzu SPD-10A tunable absorbance detector (254 nm). GPC samples were run in tetrahydrofuran at a flow rate of 1 mL/min at 35 °C and calibrated against polystyrene standards. Analysis was done using EZSTART 7.2 software. Gas chromatography (GC) analysis was performed on an Agilent 5890 Series II instrument with a FID detector and 95% dimethylpolysiloxane and 5% diphenylpolysiloxane column. The samples were heated from 40 to 100 °C at a ramp rate of 4 °C/min.

Kinetics of AGET-ATRP of Styrene Derivatives. In a N_2-filled drybox, a round-bottom flask equipped with a magnetic stir bar was charged with degassed styrene (2.08 g, 0.02 mol), $FeBr_3$ (29.5 mg, 0.1 mmol), $Sn(EH)_2$ (40.5 mg, 0.1 mmol), tributylamine (18.5 mg, 0.1 mmol), internal standard tetrachloroethane (TCE, 0.05 g), and toluene (5 mL). The mixture was stirred for 10 min before 1-bromoethylbenzene (18.5 mg, 0.1 mmol) was added to initiate the polymerization. After the initial sample was taken, the flask was sealed and placed in an oil bath at 110 °C. Samples were taken at specific time intervals using a syringe and analyzed by GC. The conversion of styrene was calculated from the integration of styrene peak with respect to TCE peak. The molecular weight was measured by GPC.

General Procedure for AGET-ATRP of Styrene Derivatives. In a N_2-filled drybox, a round-bottom flask equipped with a magnetic stir bar was charged with degassed styrene (2.08 g, 0.02 mol), $FeBr_3$ (29.5 mg, 0.1 mmol), $Sn(EH)_2$ (40.5 mg, 0.1 mmol), tributylamine (18.5 mg, 0.1 mmol), and toluene (1 mL). The mixture was stirred for 10 min before 1-bromoethylbenzene (18.5 mg, 0.1 mmol) was added to initiate the polymerization. The flask was sealed and placed in an oil bath at 110 °C for 2 h. At the end of this period, the polymer was precipitated with a large excess of

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Table 1. Electron Transfer Induced Iron-Catalyzed Atom Transfer Radical Polymerization (ATRP) of Styrene Derivatives[a]

entry	monomer	monomer (g)	M/I[b]/$FeBr_3$/Sn(EH)$_2$/L[b]	conv (%)	$M_{n,exp}$[c] × 10^{-4}	$M_{n,theo}$[d] × 10^{-4}	PDI[c]
1	4-*tert*-butylstyrene	1.60	100/1/1/1/1	51	1.19	0.82	1.33
2	4-*tert*-butylstyrene	3.20	200/1/1/1/1	57	2.08	1.82	1.47
3	4-methylstyrene	2.36	200/1/1/1/1	61	1.28	1.44	1.38
4	4-methylstyrene	4.72	400/1/1/1/1	59	2.67	2.76	1.44
5	styrene	2.08	200/1/1/1/1	61	1.92	1.26	1.35
6	styrene	2.08	200/1/1/0.5/1	53	1.13	1.10	1.21
7	styrene	4.16	400/1/1/1/1	68	2.67	2.83	1.20
8[e]	styrene	2.08	200/1/1/1/1	65	1.67	1.35	1.27
9[e]	styrene	4.16	400/1/1/1/1	57	2.23	2.37	1.13
10[f]	styrene	2.08	200/1/1/1[f]	32	0.68	0.66	1.20
11	4-acetoxystyrene	1.62	100/1/1/1/1	85	1.36	1.38	1.32
12	4-acetoxylstyrene	3.24	200/1/1/1/1	78	2.67	2.52	1.33
13	methyl 4-vinylbenzoate	1.62	100/1/1/1/1	93	1.93	1.51	1.34
14	methyl 4-vinylbenzoate	1.62	200/1/1/1/1	93	3.15	3.01	1.29

[a] Conditions: toluene, 1 mL; 110 °C, 2 h. [b] I: 1-bromoethylbenzene; L: tributylamine. [c] By GPC using polystyrene standards. [d] $M_{n,theo} = M_{monomer\ molar\ mass} \times ([M]_0/[I]) \times$ conversion. [e] Reactions in presence of limited amount of air. [f] Reaction using $FeBr_2$ as catalyst, M/I/$FeBr_2$/L = 200/1/1/1.

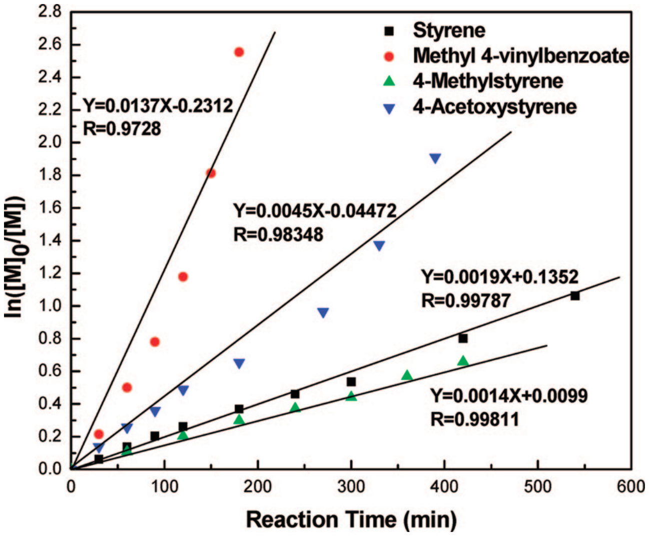

Figure 1. Kinetics for electron-transfer-induced iron-catalyzed atom transfer radical polymerization of styrene derivatives. Conditions: monomer, 0.02 mol; [M]/[1-bromoethylbenzene]/[$FeBr_3$]/[Sn(EH)$_2$]/[tributylamine] = 200/1/1/1/1; toluene, 5 mL; tetrachloroethane, 0.05 g as internal standard; 110 °C.

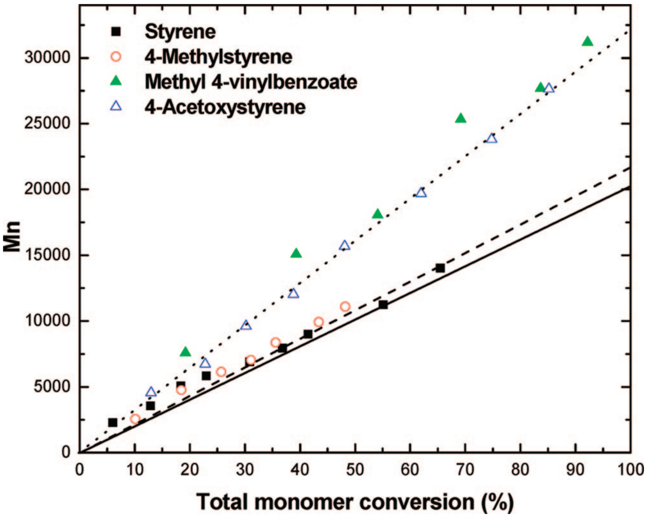

Figure 2. Molecular weight dependence on total monomer conversion for electron-transfer-induced iron-catalyzed atom transfer radical polymerization of styrene derivatives. Conditions: monomer, 0.02 mol; [M]/[1-bromoethylbenzene]/[$FeBr_3$]/[Sn(EH)$_2$]/[tributylamine] = 200/1/1/1/1; toluene, 5 mL; tetrachloroethane, 0.05 g as internal standard; 110 °C.

hexane and washed with methanol. The polymer was collected by filtration and dried under high vacuum for 24 h. Yield, 1.27 g; M_n, 1.26 × 10^4 g/mol; PDI, 1.35.

General Procedure for Block Copolymer Formation: Preparation of Poly(4-methylstyrene)-*b*-polystyrene. In a N_2-filled drybox, a polystyrene macroinitiator (M_n, 714; PDI, 1.32) (71 mg, 0.1 mmol) prepared by AGET-ATRP was dissolved in 4-methylstyrene (2.36 g, 0.02 mol) in a round-bottom flask. The flask was then charged with $FeBr_3$ (29.5 mg, 0.1 mmol), Sn(EH)$_2$ (40.5 mg, 0.1 mmol), tributylamine (18.5 mg, 0.1 mmol), and toluene (1 mL). The mixture was stirred for 10 min before 1-bromoethylbenzene (18.5 mg, 0.1 mmol) was added to initiate the polymerization. The flask was sealed and placed in an oil bath at 110 °C for 4 h. At the end of this period, the polymer was precipitated with a large excess of hexane and washed with methanol. The polymer was collected by filtration and dried under high vacuum for 24 h. Yield, 1.18 g; M_n, 13 031; PDI, 1.25.

General Procedure for AGET-ATRP of Styrene in Limited Amount of Air. In a N_2-filled drybox, a round-bottom flask equipped with a magnetic stir bar was charged with degassed styrene (2.08 g, 0.02 mol), $FeBr_3$ (29.5 mg, 0.1 mmol), Sn(EH)$_2$ (40.5 mg, 0.1 mmol), tributylamine (18.5 mg, 0.1 mmol), and toluene (1 mL). The mixture was stirred for 10 min before 1-bromoethylbenzene (18.5 mg, 0.1 mmol) was added to initiate the polymerization. The contents of the flask were exposed to air for 5 min and then sealed and placed in an oil bath at 110 °C for 2 h. At the end of this period, the polymer was precipitated with a large excess of hexane and washed with methanol. The polymer was collected by filtration and dried under high vacuum for 24 h. Yield, 1.35 g; M_n, 1.35 × 10^4 g/mol; PDI, 1.27.

General Procedure for AGET-ATRP of Styrene in the Presence of Glucose as Reducing Agent. In a N_2-filled drybox, a round-bottom flask equipped with a magnetic stir bar was charged with degassed styrene (2.08 g, 0.02 mol), $FeBr_3$ (29.5 mg, 0.1 mmol), D-glucose (18.0 mg, 0.1 mmol), tributylamine (18.5 mg, 0.1 mmol), and toluene (1 mL). The mixture was stirred for 10 min before 1-bromoethylbenzene (18.5 mg, 0.1 mmol) was added to initiate the polymerization. The flask was sealed and placed in an oil bath at 110 °C for 2 h. At the end of this period, the polymer was precipitated with a large excess of hexane and washed with methanol. The polymer was collected by filtration and dried under high vacuum for 24 h. Yield, 0.50 g; M_n, 5.6 × 10^3 g/mol; PDI, 1.19.

General Procedure for AGET-ATRP Copolymerization of Styrene and Methyl Methacrylate. In a N_2-filled drybox, a round-bottom flask equipped with a magnetic stir bar was charged with degassed styrene (1.04 g, 0.01 mol), methyl methacrylate (1.00 g, 0.01 mol), $FeBr_3$ (14.8 mg, 0.05 mmol), Sn(EH)$_2$ (20.3 mg, 0.05 mmol), tributylamine (9.3 mg, 0.05 mmol), and toluene (1 mL). The mixture was stirred for 10 min before 1-bromoethylbenzene (9.3 mg, 0.05 mmol) was added to initiate the polymerization. The flask was sealed and placed in an oil bath at 110 °C for 2 h. At the

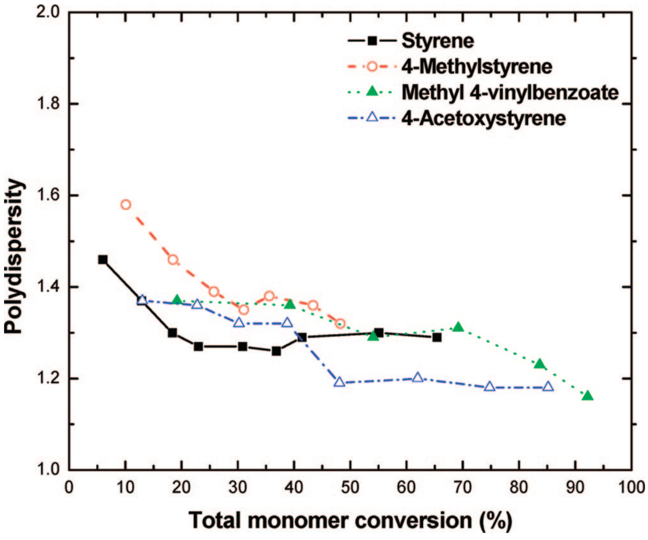

Figure 3. Polydispersity vs total monomer conversion for electron-transfer-induced iron-catalyzed atom transfer radical polymerization of styrene derivatives. Conditions: monomer, 0.02 mol; [M]/[1-bromoethylbenzene]/[$FeBr_3$]/[$Sn(EH)_2$]/[tributylamine] = 200/1/1/1/1; toluene, 5 mL; tetrachloroethane, 0.05 g as internal standard; 110 °C.

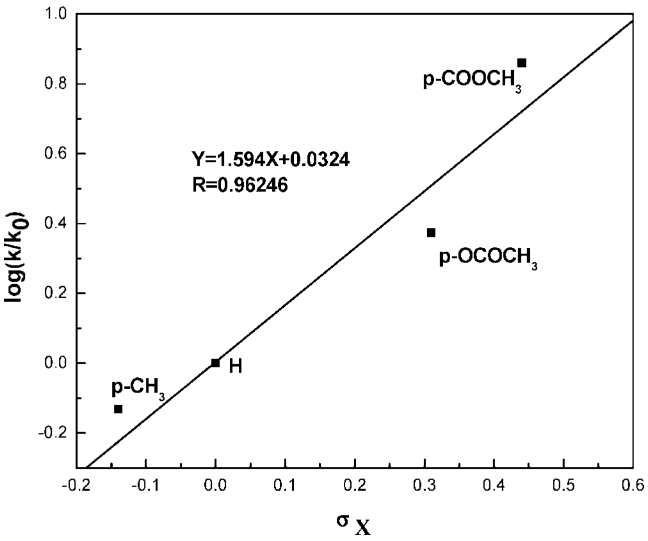

Figure 4. Hammett plot for $k_{p(app)}$ in electron-transfer-induced iron-catalyzed atom transfer radical polymerization of styrene derivatives. Conditions: monomer, 0.02 mol; [M]/[1-bromoethylbenzene]/[$FeBr_3$]/[$Sn(EH)_2$]/[tributylamine] = 200/1/1/1/1; toluene, 5 mL; tetrachloroethane, 0.05 g as internal standard; 110 °C.

end of this period, the polymer was precipitated with a large excess of hexane and washed with methanol. The polymer was collected by filtration and dried under high vacuum for 24 h. Yield, 1.03 g; M_n, 2.42 × 10^4 g/mol, PDI, 1.38.

Results and Discussion

AGET-ATRP of Styrene Derivatives. A series of styrene derivatives were polymerized by the novel iron-based AGET-ATRP technique (Table 1). The results show controlled polymerization for all the styrene derivatives examined. The apparent polymerization rate is the first order with respect to monomer concentration (Figure 1), and molecular weight increases linearly with respect to total monomer conversion (Figure 2). The obtained M_n values are in good agreement with theoretical numbers, and the polydispersities are relatively low (less than 1.5, Figure 3). For comparison, normal Fe(II)-catalyzed ATRP proceeds significantly more slowly (entry 10, Table 1). A comparison of entries 5 and 6 in Table 1 indicates that decreasing the amount of reducing agent results in decreased monomer conversion and a narrower PDI. Presumably this is because the concentration of the deactivating Fe(III) species is higher in the presence of less reducing agent, and this leads to a lower concentration of the propagating radical (see Scheme 1).

Table 3. Electron-Transfer-Induced Iron-Catalyzed Atom Transfer Radical Polymerization of Styrene in the Presence of D-Glucose as Reducing Agent[a]

entry	styrene (g)	M/I[b]/$FeBr_3$/ glucose/L[b]	conv (%)	$M_{n,exp}$[c] × 10^{-4}	$M_{n,theo}$[d] × 10^{-4}	PDI[c]
1	2.08	200/1/1/1/1	24	0.56	0.50	1.19
2	4.16	400/1/1/1/1	29	1.04	1.21	1.23

[a] Conditions: toluene, 1 mL; 110 °C, 2 h. [b] I: 1-bromoethylbenzene; L: tributylamine. [c] By GPC using polystyrene standards. [d] $M_{n,theo} = M_{monomer\ molar\ mass}$ × ($[M]_0$/[I]) × conversion.

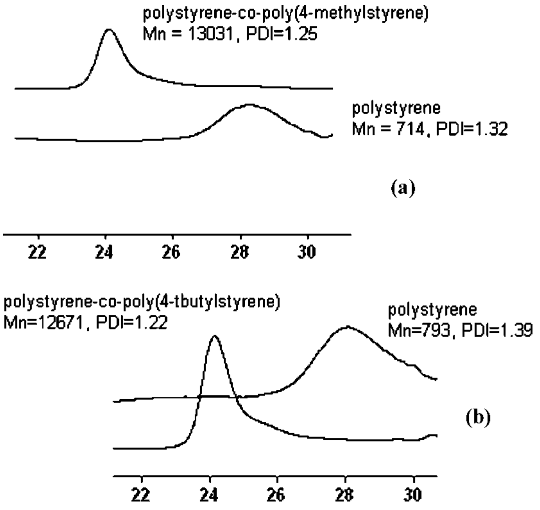

Figure 5. Chain extension of polystyrene macroinitiator prepared by electron-transfer-induced iron-catalyzed atom transfer radical polymerization with (a) poly(4-methylstyrene) and (b) poly(4-*tert*-butylstyrene).

Styrene Polymerization in the Presence of Limited Amount of Air. As shown by entries 8 and 9 in Table 1, the polymerizations remains well controlled even in the presence of a small amount of air. Presumably, the reducing agent maintains a steady concentration of the active Fe(II) species.

Substituent Effects on Polymerization Rate: Hammett Plot. As shown by Figure 1, monomers with electron-withdrawing substituents polymerize faster than those having electron-

Table 2. Effect of Iron Concentration on Electron-Transfer-Induced Atom Transfer Radical Polymerization of Styrene[a]

entry	molar ratioSt/I[b]/$FeBr_3$/ $Sn(EH)_2$/L[b]	iron (mmol)	time (h)	conv (%)	$M_{n,theo}$[c] × 10^{-4}	$M_{n,expt}$[d] × 10^{-4}	PDI[d]
1	200/1/1/1/1	0.1	3	80.2	1.67	1.52	1.18
2	200/1/0.5/0.5/0.5	0.05	3	77.9	1.62	1.53	1.26
3	200/1/0.1/0.1/0.1	0.01	3	44.2	0.92	1.05	1.28
4	200/1/0.1/0.1/0.1	0.01	17	87.4	1.82	2.03	1.23

[a] Conditions: styrene, 2.08 g (0.02 mol); toluene, 1 mL; 110 °C. [b] I: 1-bromoethylbenzene; L: tributylamine. [c] $M_{n,theo} = M_{monomer\ molar\ mass}$ × ($[M]_0$/[I]) × conversion. [d] By GPC using polystyrene standards.

Table 4. Copolymerization of Styrene and Methyl Methacrylate Using Electron-Transfer-Induced Iron-Catalyzed Atom Transfer Radical Polymerization[a]

entry	MMA (g)	[styrene]/[MMA] (molar ratio)	yield (%)	MMA incorp (%)	$M_{n,exp}{}^{b} \times 10^{-4}$	$M_{n,theo}{}^{c} \times 10^{-4}$	PDI[b]
1[d]	2.00	0	54.5	100	1.73	2.18	1.98
2[d]	1.33	1:2	55.8	63.7	2.60	2.26	1.48
3[d]	1.00	1:1	50.4	47.6	2.42	2.06	1.38
4[d]	0.67	2:1	53.4	37.3	2.33	2.19	1.20
5[e]	1.00	1:1	11.7	54.9	0.30	0.48	1.28
6[e]	0.67	2:1	22.2	29.5	0.67	0.74	1.21

[a] Conditions: [M]/[1-bromoethylbenzene]/[$FeBr_3$]/[L]/[reducing agent] = 400/1/1/1/1, toluene, 1 mL; 110 °C, 2 h. [b] By GPC using polystyrene standards. [c] $M_{n,theo} = M_{monomer\ molar\ mass} \times ([M]_0/[I]) \times$ conversion. [d] Coplymerizations using $Sn(EH)_2$ as reducing agent. [e] Copolymerizations using D-glucose as reducing agent.

donating substituents. These results are in agreement with those from conventional radical polymerizations[15] as well as previously reported controlled radical polymerizations.[16] The Hammett plot (Figure 4) gives a linear relationship between the apparent rate constant and Hammett constants σ for different para substituents. A ρ value of 1.59 was obtained for the iron-based AGET-ATRP, which is in good agreement with the ρ of 1.51 for copper-based ATRP reported by Matyjaszewski.[16] One possible explanation involves the effect of the substituent on the stability of the polystyryl halide. The partially positive carbon of the polarized C−X bond will be stabilized by electron-donating substituents, thereby lowering the ground-state energy of the dormant species.

Effects of Varying Iron Concentration. Table 2 summarizes a series of experiments in which styrene was polymerized in presence of different concentration of the iron-based catalyst. The amount of iron varied from 0.1 mmol to as low as 0.01 mmol. According to Table 2, the polymerization rate decreased with the reduction in the concentration of iron species. With 0.1 mmol of iron (entry 1), 80.2% conversion was obtained after 3 h reaction, while with 0.01 mmol of iron (entry 3), only 44.2% conversion was obtained. However, the system remained well-controlled at all iron concentrations. Figure S1 shows the first-order polymerization kinetics, and Figure S2 shows good control over the molecular weight and polydispersity using only 0.01 mmol of iron catalyst.

Decreasing the amount of iron catalyst has the advantage of decreasing the metal residue in the final product; e.g., the product from entry 1 is an orange powder while the products from entries 3 and 4 are white.

Styrene Polymerization in the Presence of Glucose as Reducing Agent. AGET-ATRP of styrene was also carried out in the presence of D-glucose as the reducing agent (Table 3). Although the monomer conversion for the same time period was lower than that in the presence of $Sn(EH)_2$, a stronger reducing agent, the system is well controlled.

Extension of Polystyrene Macroinitiator by AGET-ATRP. The "living" nature of this iron-based AGET-ATRP system was further confirmed by treating the macroinitiator made by this technique with a different monomer for chain extension using similar conditions. For example, an bromo-functionalized polystyrene macroinitiator (M_n, 714; PDI, 1.32) (71 mg, 0.1 mmol) prepared by AGET-ATRP was employed to polymerize 4-methylstyrene (2.36 g) using 0.1 mmol of Fe catalyst at 110 °C. The GPC analysis of the resulting block copolymer revealed the expected increased molecular weight (M_n, 13 031; PDI, 1.25) and no detectable amount of unreacted starting block (Figure 5a). Similarly, a block copolymer of styrene and 4-*tert*-butylstyrene was synthesized through this method (Figure 5b).

Copolymerization of Styrene and Methyl Methacrylate (MMA). Copolymerization of styrene and methyl methacrylate was carried out with the same methodology using either $Sn(EH)_2$ and D-glucose as the reducing agent (Table 4). The copolymer compositions were determined by ^1H NMR integration of the aliphatic proton vs the aromatic protons (Figure S3). The gel permeation chromatography showed only one peak with both refractive index (RI) and UV detector, which indicates a true copolymer over the entire molecular weight distribution range. The homopolymerization of MMA was not controlled with polydispersity of 1.98, as were the copolymerizations with high MMA/styrene feed ratios. However, higher amounts of styrene in the feed led to well-controlled polymerizations with low polydispersities, suggesting higher selectivity of the iron-based catalyst for the polystyryl radical. As with styrene homopolymerization, the use of the weaker reducing agent, D-glucose, resulted in lower yields, but the polymerizations remained well-controlled.

Summary

The first oxidatively stable and environmentally friendly iron-based AGET-ATRP system for styrene derivatives has been reported. Similar to previously reported copper-based system, the reducing agents $Sn(EH)_2$ and D-glucose were employed to generate the active Fe(II) species in situ. Monomers with electron-withdrawing substituents polymerize faster than those having electron-donating substituents. The amount of iron catalyst could be reduced to as a low as 0.01 mmol while retaining sufficient activity to impart control. Well-defined copolymers of styrene and MMA were also synthesized through this method.

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Supporting Information Available: (a) Kinetics for electron-transfer-induced atom transfer radical polymerization of styrene at low iron concentration; (b) molecular weight and polydispersity dependence on total monomer conversion for electron-transfer-induced atom transfer radical polymerization of styrene at low iron concentration; (c) ^1H NMR spectrum of styrene/methyl methacrylate copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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