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Iron-mediated AGET ATRP of Styrene and Methyl Methacrylate Using Ascorbic Acid Sodium Salt as Reducing Agent[*]

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Abstract Atom transfer radical polymerization of styrene (St) and methyl methacrylate (MMA) in bulk and in different solvents using activators generated by electron transfer (AGET ATRP) were investigated in the presence of a limited amount of air using $FeCl_3\cdot 6H_2O$ as the catalyst, ascorbic acid sodium salt (AsAc-Na) as the reducing agent, and a cheap and commercially available tetrabutylammonium bromide (TBABr) as the ligand. It was found that polymerization in THF resulted in shorter induction period than that in bulk and in toluene for AGET ATRP of St, while referring to AGET ATRP of MMA, polymerization in THF showed three advantages compared with that in bulk and toluene: 1) shortening the induction period, 2) enhancing the polymerization rate and 3) having better controllability. The living features of the obtained polymers were verified by chain end analysis and chain-extension experiments.

Keywords: Atom transfer radical polymerization (ATRP); AGET ATRP; Iron catalyst; Kinetics (polym.).

INTRODUCTION

Atom transfer radical polymerization (ATRP), as one of the most widely used “living” radical polymerizations (LRPs), provides a facile way to synthesize well-defined polymers with designable architectures, predetermined molecular weights and narrow molecular weight distributions[1–8]. However, it has been found that there are some disadvantages for normal ATRP processes, such as that the catalyst used is sensitive to air and humidity, which does not facilitate the handling of ATRP catalyst. The advent of activators generated by electron transfer (AGET) ATRP[9–11] developed by Matyjaszewski's group gives answers for solving the problem mentioned above, and the mechanism is outlined in Scheme 1. Here, a higher oxidation state catalyst (*e.g.*, Cu(II) or Fe(III) salts) is used instead of the lower oxidation state one (*e.g.*, Cu(I) or Fe(II) salts), and the activators (lower oxidation state catalyst) are produced by an *in situ* reduction of the former with a reducing agent added into the polymerization system[12]. AGET ATRP has all the advantages of normal ATRP as well as additional benefits of facile preparation, storing, and reducing amount of catalyst. Furthermore, it remains tolerant of air during the polymerization due to the presence of reducing agents.

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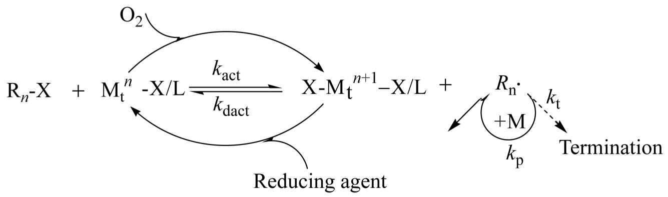

Scheme 1 Mechanism of AGET ATRP in the presence of a limited amount of air

Actually, catalytic system always plays a key role in ATRP techniques. To date, many transition metal complexes such as copper[13, 14], iron[15–24], ruthenium[25, 26] and other transition metals[27, 28] have been used to catalyze an ATRP process solely or by combination both of them[29]. Among these ATRP metal catalysts, iron salt as AGET ATRP metal catalyst was widely used owing to its distinct advantages, such as low toxic, biocompatible, abundant, environmentally friendly and cost-effective. Iron catalyst has been one of the most favorite ATRP catalysts and may be used in industry in future[30, 31]. Like other metal complexes, ligands such as triphenylphosphine[32], half-metallocene[33, 34], organic acid[35–37] and onium salts[38–41], also affect the catalytic performance of iron complexes in activity and controllability over polymerization, which provide appropriate solubility and an adjustable redox potential to the metal complexes.

In addition, a typical feature of ATRP is the existence of equilibrium between active and dormant species to keep the concentration of radicals low enough to minimize termination. As a result, compared with the conventional radical polymerization, ATRP needs a longer reaction time, which limits the usefulness of this reaction for industrial applications. To overcome the key drawback, there have been some methods to enhance the polymerization rate of ATRP, such as increasing polymerization temperature[42] or adding additives such as Lewis acids[43, 44] and catalytic amounts of base[40, 45]. Recently, our group reported AGET ATRP of MMA using a new environmentally benign ascorbic acid sodium salt (AsAc-Na) as the reducing agent and tris-(3,6-diox a-heptyl) amine (TDA-1) as the ligand. The polymerization rate was enhanced significantly compared with that using ascorbic acid (AsAc) as the reducing agent before[46]. In this work, we built an rate-enhanced AGET ATRP of MMA and St using $FeCl_3\cdot 6H_2O$ as the catalyst, cheap and commercially available tetrabutylammonium bromide (TBABr) or tetra-*n*-butylphosphonium bromide (TBPBr) as the ligand, ethyl 2-bromoisobutyrate (EBiB) and (1-bromoethyl)benzene (PEBr) as the initiator, and AsAc-Na as the reducing agent. The effect of reducing agent (acid and acid sodium salt) for both MMA and St were investigated. Furthermore, it is found that solvents have significant influence not only on the polymerization rate but also the controllability over molecular weights and molecular weight distributions for AGET ATRP of MMA and St. All the polymerizations were conducted in the presence of limited amounts of air.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) (+99%) and styrene (St) (+99%) were purchased from Shanghai Chemical Reagents (Shanghai, China). The monomers were purified by passing through a column filled with neutral aluminum oxide before use. Ethyl 2-bromoisobutyrate (EBiB) (98%) and (1-bromoethyl)benzene (PEBr) (97%) was purchased from Acros and used as received. Tetrabutylammonium bromide (TBABr) (99%, Shanghai Chemical Reagents) and tetra-*n*-butylphosphonium bromide (TBPBr) (99%, Shanghai Chemical Reagents) were used as received. Iron(III) chloride hexahydrate ($FeCl_3\cdot 6H_2O$) (+99%), ascorbic acid (AsAc) (+99.7%), ascorbic acid sodium salt (AsAc-Na) (+99%) were purchased from Shanghai Chemical Reagents (Shanghai, China) and used as received. Tetrahydrofuran (THF) (99.9%, Shanghai Chemical Reagents), toluene (+99.9% Shanghai Chemical Reagents) and methanol (99.9%, Shanghai Chemical Reagents) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents and used as received unless mentioned.

General Procedure for AGET ATRP of MMA and St

A typical bulk polymerization procedure with the molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 500/1/1/2/2$ in the presence of a limited amount of air is as follows: A mixture was obtained by adding $FeCl_3 \cdot 6H_2O$ (10.2 mg, 0.0376 mmol), TBABr (24.3 mg, 0.0753 mmol), EBiB (5.7 μL, 0.0376 mmol), MMA (2.0 mL, 18.8 mmol) and AsAc-Na (14.9 mg, 0.0752 mmol) to a dried ampoule with a stir bar. The ampoule was flame sealed and then transferred into an oil bath held by a thermostat at the desired temperature (90 °C) for polymeration under stirring. $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L based on the reaction solution (2.0 mL) was calculated from the residual volume (air volume, 6.3 mL) of ampoule after adding the reaction mixture. After the desired polymerization time, the ampoule was cooled by immersing into ice water. Afterward, the ampoule was opened and the contents were dissolved in THF (≈ 2 mL) and the solution was precipitated into a large amount of methanol (≈ 200 mL) with stirring. The polymer obtained by filtration was dried under vacuum until constant weight at 50 °C. The monomer conversion was determined gravimetrically. General procedure for AGET ATRP of styrene was similar to that of MMA, but the polymerizations were carried out at 110 °C.

Typical Procedures for Chain Extension Using PS as Macroinitiator

A predetermined quantity of PS sample (obtained by polymerization of St in the presence of air, $M_{n,\,GPC}$ = 6330 g/mol, $M_w/M_n = 1.38$) was used as the macroinitiator and dissolved in 1.0 mL of St in a dried ampoule. The predetermined quantity of $FeCl_3 \cdot 6H_2O$, TBABr and AsAc-Na were added successively. The rest of the procedures was the same as the general procedure for AGET ATRP of St described above. The chain-extension polymerization was conducted under stirring at 110 °C. The monomer conversion was 18.5% after 9 h. The M_n and M_w/M_n values were determined by GPC with PS standards ($M_{n,\,GPC}$ = 20300 g/mol, $M_w/M_n = 1.39$).

Characterization

The number-average molecular weight ($M_{n,\ GPC}$) and molecular weight distribution (M_w/M_n) values of the resultant 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, 100–5000 Da), HR 2 (pore size: 500, 500–20000 Da), and HR 4 (pore size 10000, 50–100000 Da) columns (7.8 mm × 300 mm, 5 μm beads size) with measurable molecular weights ranging from 10^2 to 5×10^5 g/mol. 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 or PMMA standards purchased from Waters. ^{1}H-NMR spectrum of the obtained polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard.

RESULTS AND DISCUSSION

Effect of Reducing Agent on AGET ATRP of MMA and St in Bulk

The polymerizations of St and MMA in the presence of air were first studied using AsAc-Na and AsAc as the reducing agent, respectively. All results show the possibility to synthesize well-defined polymers with controlled molecular weights and narrow molecular weight distributions *via* iron-mediated AGET ATRP. From entries 1 to 6 in Table 1, the resultant PSs and PMMAs are with controlled molecular weight distributions ($M_w/M_n < 1.46$). By comparison of entry 1 with entry 2 in the case of TBABr as the ligand, it can be seen that polymerization rate of St using AsAc-Na as the reducing agent is faster than that of using AsAc as the reducing agent, 61.1% of monomer conversion in 29 h (entry 1) versus 74.1% of monomer conversion in 61 h (entry 2). When TBPBr was used as the ligand, a monomer conversion of 73.4% in 44 h (entry 3) and 63.9% in 46 h (entry 4) were obtained, respectively, in the case of AsAc-Na and AsAc. If MMA was used as the monomer, the results listed in entries 5 and 6 indicate that using AsAc-Na as the reducing agent not only increases the polymerization rate significantly but also enhances controllability of the polymerization; 86.9% of monomer conversion in 15 h, $M_w/M_n = 1.24$ (entry 5) versus 17.6% of monomer conversion in 96 h, $M_w/M_n = 1.45$ (entry 6). In summary, AGET ATRP using sodium salts as the reducing agent shows faster polymerization rate and better controllability than that with acids as the reducing agent, which can be further confirmed by the results in entries 7–9. No polymers occured (entry 7) versus 18.8% of monomer conversion (entry 9) in 90 h for using Ph-OH versus Ph-ONa as the reducing agent, respectively. The fact that the basicity of sodium salts[45–47] and ascorbate anions could be ‘‘dragged’’ into the solution by the ligand onium ions and the amount of available reducing agent in solution was increased correspondingly[39], may result in the enhancement of rate and controllability of the polymerization for the iron-mediated AGET ATRP of MMA and St.

Table 1. Effect of ligand and reducing agent on AGET ATRP of St and MMA in the presence of a limited amount of air

Entry	Monomer	Time (h)	Conv. (%)	$M_{n,\,th}$ (g/mol)	$M_{n,\,GPC}$ (g/mol)	M_w/M_n	Ligand/RA
1[a]	St	29	61.1	12500	13300	1.33	TBABr/AsAc-Na
2[a]	St	61	74.1	15100	9000	1.19	TBABr/AsAc
3[b]	St	44	73.4	15300	19200	1.23	TBPBr/AsAc-Na
4[b]	St	46	63.9	13300	8000	1.24	TBPBr/AsAc
5[c]	MMA	15	86.9	43500	56800	1.24	TBABr/AsAc-Na
6[c]	MMA	96	17.6	8800	15400	1.45	TBABr/AsAc
7[d]	St	90	0	0	–	–	TBABr/Ph-OH
8[d]	St	70	7.3	1500	5600	1.18	TBABr/Ph-ONa
9[d]	St	90	18.8	3900	9600	1.24	TBABr/Ph-ONa

[a] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3\cdot 6H_2O]_0/[Ligand]_0/[RA]_0 = 200/1/1/2/2$, $V_{St} = 2.0$ mL, in bulk, temperature = 110 °C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L; [b] Polymerization conditions: $[St]_0/[PEBr]_0/ [FeCl_3\cdot 6H_2O]_0/[Ligand]_0/[RA]_0 = 500/1/1/2/1$, $V_{St} = 2.0$ mL, in bulk, temperature = 110 °C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L; [c] Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3\cdot 6H_2O]_0/[TBABr]_0/[RA]_0 = 500:1:1:2:2$, $V_{MMA} = 2.0$ mL, in bulk, temperature = 90°C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L; [d] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3\cdot 6H_2O]_0/[TBABr]_0/[RA]_0 = 200/1/1/2/2$, $V_{St} = 2.0$ mL, in bulk, temperature = 110, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L.

Effect of Solvent on AGET ATRP of MMA and St

A weakly polar solvent toluene and a strongly polar solvent THF were selected in the reaction systems to investigate the effect of solvent on AGET ATRP of MMA and St using AsAc-Na as the reducing agent. All results in Table 2 show the possibility to synthesize well-defined polymers with controlled molecular weights and narrow molecular weight distributions *via* iron-mediated AGET ATRP in different solvents. From entries 1–6, the resultant PSs and PMMAs are with controlled molecular weight distributions ($M_w/M_n < 1.32$). The polymerization rate of AGET ATRP using AsAc-Na as the reducing agent in solvents follows this order: THF > bulk > toluene. For example, 32.7% of monomer (St) conversion is achieved in toluene after 24 h (entry 1), 48.3% of monomer conversion is obtained in bulk after 23 h (entry 2) while 57.6% monomer conversion is achieved in THF after 20 h (entry 3). This order can be confirmed by the results of AGET ATRP of MMA with 51.6% of monomer conversion in 15 h, 68.4% of monomer conversion in 10 h and 80.9% monomer conversion in 4.5 h for polymerization in toluene, bulk and THF, respectively. This is because polar solvent facilitates dissolving the basic reducing agent AsAc-Na in the polymerization system[39].

Table 2. Effect of solvent on AGET ATRP of St and MMA in the presence of a limited amount of air

Entry	Monomer	Time (h)	Conv. (%)	$M_{n,\,th}$ (g/mol)	$M_{n,\,GPC}$ (g/mol)	M_w/M_n	Solvent
1[a]	St	24	32.7	6800	8400	1.19	toluene
2[a]	St	23	48.3	10000	12000	1.25	bulk
3[a]	St	20	57.6	12000	16800	1.20	THF
4[b]	MMA	15	51.6	25800	38100	1.23	toluene
5[b]	MMA	10	68.4	34200	43000	1.30	bulk
6[b]	MMA	4.5	80.9	40500	34900	1.31	THF

[a] Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3\cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 200/1/1/2/2$, $V_{St} = 2.0$ mL, temperature = 110 °C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L for bulk polymerization, $[O_2]_0 = 1.7 \times 10^{-2}$ mol/L for solution polymerization ($V_{solvent} = 1.0$ mL); [b] Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3\cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 500/1/1/2/2$, $V_{MMA} = 2.0$ mL, temperature = 90 °C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L for bulk polymerization, $[O_2]_0 = 1.7 \times 10^{-2}$ mol/L for solution polymerization ($V_{solvent} = 1.0$ mL).

Kinetics of AGET ATRP of St in Bulk and in Solvents in the Presence of Air

In order to further investigate the polymerization behavior, the polymerization kinetics of St was studied in different solvents (THF, toluene) and in bulk. Figure 1(a) shows the kinetics of AGET ATRP of St in the presence of limited amounts of air under the same molar ratio of $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 200/1/1/2/2$ in different solvents at 110 °C, respectively. From Fig. 1(a), it can be seen that all the kinetics show linear plots, indicating that the polymerizations were approximately first order with respect to the monomer concentration and that the number of active species remains constant throughout the polymerization up to 83% monomer conversion. As shown in Fig. 1(b), the $M_{n,\,GPC}$ values of the resultant polymers increase with the monomer conversion and are close to their corresponding theoretical ones, at the same time, the molecular weight distributions of the polymers keep low ($M_w/M_n < 1.45$), which indicate a well-controlled process of AGET ATRP of St. In addition, from Fig. 1(a), the apparent rate constants of propagation k_p^{app} ($R_p = -d[M]/dt = k_p[P_n\cdot]\,[M] = k_p^{app}\,[M]$), as determined from the polymerization kinetic slopes) are 1.44×10^{-5} s^{-1} and 1.20×10^{-5} s^{-1} for solvents being THF and toluene, 1.42×10^{-5} s^{-1} for polymerization in bulk, respectively. However, in the earlier stage of the polymerizations, the induction periods of 5 h for THF, 8 h in bulk and 12 h for toluene, are observed, respectively, which indicate that the polymerization in THF has a shorter induction period due to better solubility of polar solvent THF for the reducing agent AsAc-Na.

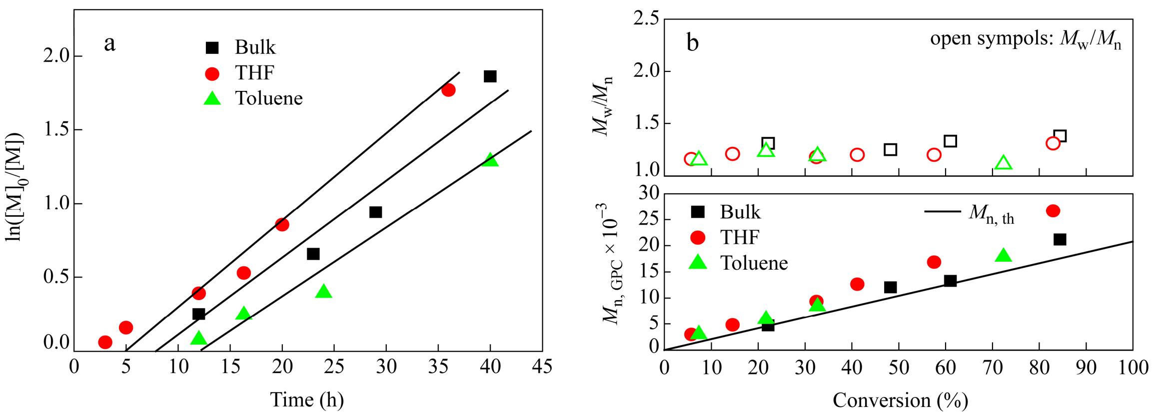

Fig. 1 $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,\,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for AGET ATRP of St using TBABr as the ligand
Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 200/1/1/2/2$, $V_{St} = 2.0$ mL, temperature = 110 °C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L for bulk polymerization and $[O_2]_0 = 1.7 \times 10^{-2}$ mol/L for solution polymerization ($V_{solvent} = 1.0$ mL).

Kinetics of AGET ATRP of MMA in Bulk and in Solvents in the Presence of Air

AGET ATRP of MMA was also conducted with the same molar ratio of $[MMA]_0/[EBiB]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 500/1/1/2/2$ in different solvents (THF, toluene) and in bulk. Figure 2(a) shows the kinetics of AGET ATRP of MMA in the presence of a limited amount of air. From Fig. 2(a), it can be seen that the polymerization kinetics in the three cases shows linear plots, indicating that the polymerizations are also approximately first-order with respect to the monomer concentration. Figure 2(b) describes the number-average molecular weight ($M_{n,\,GPC}$) and molecular weight distribution (M_w/M_n) as functions of the monomer conversion. It is found that the $M_{n,\,GPC}$ values of the polymers, being close to the corresponding theoretical ones, increase linearly with monomer conversion while keeping low M_w/M_n values. Moreover, the conversion could be higher than 94.5% while M_w/M_n values can keep lower than 1.17. In addition, the apparent rate constants of propagation k_p^{app} are 9.00×10^{-5} s^{-1} for THF and 3.05×10^{-5} s^{-1} for toluene, 3.88×10^{-5} s^{-1} in bulk, respectively, which keep the same polymerization rate order as shown in Table 2. At the same time, the induction periods are about 0 h, 8.9 h and 1 h for THF, toluene and in bulk, respectively. Therefore, THF as a solvent not only enhances the polymerization rate but also shortens the induction period for AGET ATRP of

MMA in the presence of a limited amount of air. In addition, $M_{n,\,GPC}$ values of the resultant PMMAs in THF are almost consistent with their corresponding theoretical ones while keeping narrow polydispersity, which indicates a better controllable polymerization in THF.

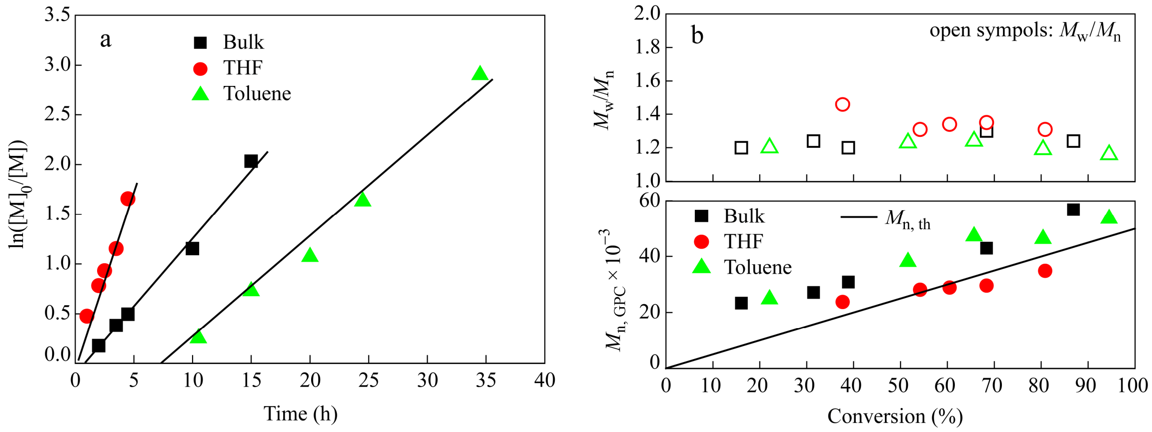

Fig. 2 ln($[M]_0$/[M]) as a function of time (a) and number-average molecular weight ($M_{n,\,GPC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for AGET ATRP of MMA using TBABr as the ligand
Polymerization conditions: $[MMA]_0/[EBiB]_0/[FeCl_3\cdot6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 500/1/1/2/2$, $V_{MMA} = 2.0$ mL, temperature = 110 °C, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L for bulk polymerization, $[O_2]_0 = 1.7 \times 10^{-2}$ mol/L for solution polymerization ($V_{solvent} = 1.0$ mL).

Analysis of Chain End and Chain Extension

The chain end of the PS ($M_{n,\,GPC} = 21000$ g/mol, $M_{n,\,NMR} = 19430$ g/mol) obtained by AGET ATRP of St in the presence of limited amounts of air was analyzed by ^{1}H-NMR spectroscopy, as shown in Fig. 3. The chemical shifts at $\delta = 6.35$–7.50 (**a** in Fig. 3) are attributed to the aromatic protons in the PEBr initiator moieties and PS main chains. The chemical shift at $\delta = 1.03$ (**b** in Fig. 3) are attributable to the methyl protons in the initiator PEBr, which indicates that the initiator PEBr moieties were successfully attached to the polymer chain ends.

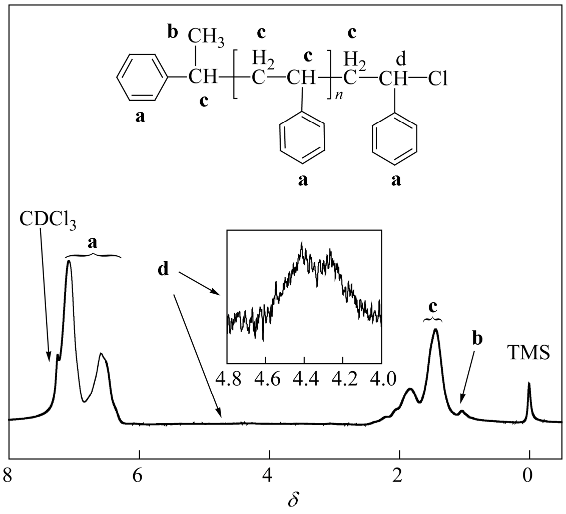

Fig. 3 ^{1}H-NMR spectrum of PS ($M_{n,\,GPC} = 21000$ g/mol, $M_{n,\,NMR} = 19430$ g/mol), [$M_{n,\,NMR} = (932.3/5) \times 104 + 36.5$], $M_w/M_n = 1.18$) obtained in the presence of air with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Polymerization conditions: $[St]_0/[PEBr]_0/[FeCl_3\cdot6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0 = 200/1/1/2/2$; $V_{St} = 2.0$ mL, $V_{THF} = 1.0$ mL, $[O_2]_0 = 1.7 \times 10^{-2}$ mol/L, time = 19 h, conversion = 71.5%, temperature = 110 °C.

The chemical shifts at $\delta = 1.40–2.15$ (**c** in Fig. 3) are assigned to the methylene and methyne protons in the PS main chains. The chemical shifts at $\delta = 4.2–4.6$ (**d** in Fig. 3) are assigned to the methyne protons in the chain ends of PS because of the electron-attracting function of ω-Cl atom[39, 49]. In addition, the percentage of chain-end functionality f ($f = 95.0\%$) 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).

As discussed above, the obtained PS could be used as a macroinitiator to conduct a chain-extension reaction due to the "living" chain end. Therefore, the PS ($M_{n, GPC}$ = 6330 g/mol, PDI = 1.38) obtained by AGET ATRP was used as the predecessor in chain extension experiments to confirm its "living" feature. As shown in Fig. 4, there was a peak shift from the macroinitiator to the chain-extended PS ($M_{n, GPC}$ = 20300 g/mol, PDI = 1.39). The successful chain-extension reaction further verified the features of controlled/''living'' free-radical polymerization of St in this system.

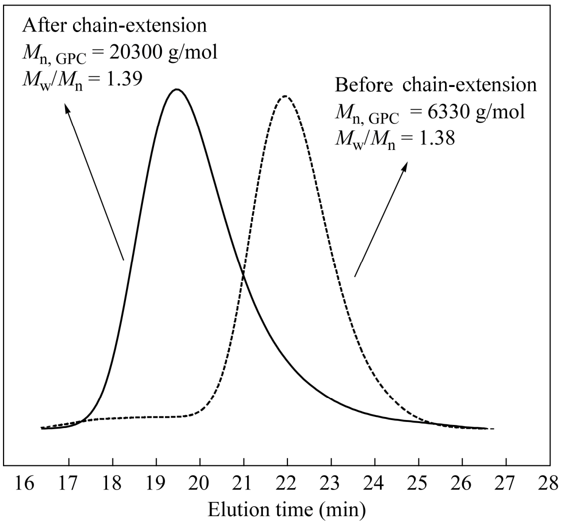

Fig. 4 GPC traces of before and after chain extension using PS prepared by AGET ATRP of St as the macroinitiator. Before chain extension: $[St]_0/[PEBr]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0$ = 200/1/1/2/2, V_{St} = 2.0 mL, $[O_2]_0 = 3.0 \times 10^{-2}$ mol/L, in bulk, temperature = 110 °C; time = 19 h, conversion = 26.9%, $M_{n, GPC}$ = 6330 g/mol, M_w/M_n = 1.38; After chain extension: $[St]_0/[PS]_0/[FeCl_3 \cdot 6H_2O]_0/[TBABr]_0/[AsAc\text{-}Na]_0$ = 100/0.1/1/2/2, V_{St} = 1.0 mL, $[O_2]_0 = 6.8 \times 10^{-2}$ mol/L, in bulk, temperature = 110 °C, time = 9 h, conversion = 18.5%, $M_{n, GPC}$ = 20300 g/mol, M_w/M_n = 1.39.

CONCLUSIONS

In this work, the Fe(III)-mediated AGET ATRP of St and MMA with a cheap and commercially available TBABr as the ligand was demonstrated. Rate of polymerization using AsAc-Na as the reducing agent was faster than that using AsAc. The polymerization can be successfully carried out in different solvents in the presence of limited air and showed characters of "living"/controlled free-radical polymerization. In addition, polymerization in THF resulted in shorter induction period than that in bulk and in toluene for AGET ATRP of St, while referring to AGET ATRP of MMA, polymerization in THF showed three advantages compared with that in bulk and toluene: 1) shorting the induction period, 2) enhancing the polymerization rate and 3) having better controllability.

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