

Rapid ambient temperature living radical polymerization of methyl methacrylate and styrene utilizing sodium hypophosphite as reducing agent

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ABSTRACT: A facile, safe, and inexpensive reducing agent, sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), has been successfully used to perform ambient temperature living radical polymerizations of methyl methacrylate (MMA) and styrene (St). The rapid radical polymerizations were readily obtained at 25°C , i.e., MMA reached a conversion of ca 90% after 2.5 h, and St reached a conversion of ca 80% after 40 h. The polymerizations of MMA and St exhibited excellent living/controlled nature, as evidenced by pseudo first-order kinetics of polymerization, linear evolution of molecular weights with increasing monomer conversions, and narrow molecular weight distributions. The various experimental parameters—ligand, solvent, and molar ratio of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ —were varied to improve the control of polymerization, molecular weight, and molecular weight distribution. ^1H NMR analyses and chain-extension reactions confirm the high chain-end functionality of the resultant poly(methyl methacrylate) and polystyrene. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42123.

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INTRODUCTION

An important living radical polymerization (LRP) technique, atom transfer radical polymerization (ATRP), has received great attention over the past decades because it can provide good control over polymer structure.^{1–7} The methodology is based on a dynamic equilibrium between a small amount of active radicals and a large amount of dormant species by using a reversible redox reaction between a low-oxidation-state metal compound (CuBr) and an organic halide (RBr). A normal ATRP system usually uses low-valence metal catalyst which is subject to oxidation.^{8,9} Therefore, many novel techniques are developed by using reducing agent to transform a high-oxidation-state metal compound (the deactivator, CuBr_2) into a low oxidation state one (the activator, CuBr). The employed reducing agents include organic or inorganic compounds (activators (re)generated by electron transfer (A(R)GET) ATRP),^{10–13} zerovalent metals (supplemental activator and reducing agent ATRP),^{14,15} conventional thermal radical initiators (initiators for continuous activator regeneration ATRP),^{16–20} electrical current (electrochemically mediated ATRP),^{21,22} and so on. However, the use of facile, safe, and inexpensive inorganic salts as reducing agents is scarce. Matyjaszewski and his coworkers reported that various inorganic sulfites can offer a good control over the radical polymerizations of methyl acrylate (MA) and styrene (St).²³ Notably, the used catalytic

system is a highly reactive ligand (Me_6TREN) together with CuBr_2 . Reaction duration of 10–40 h for MA was required at 30°C . Particularly, for St, a longer reaction duration (100 h) and a higher reaction temperature (60°C) were required to reach an ideal monomer conversion of ca 80%. In this regard, it is important to explore more efficient inorganic reducing agent to realize rapid ambient temperature LRP of vinyl monomers, particularly St.

Following this aim, we note a facile, inexpensive, and safe reducing agent, i.e., sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$). Compared with sulfites, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ is a stronger reducing agent, which can efficiently reduce higher valence copper compound to lower valence one at ambient temperature. Therefore, this article reports the first utilization of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent, combing with an inexpensive catalytic system—cupric sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)/ N,N,N',N',N' -pentamethyldiethylenetriamine (PMDETA) to conduct rapid controlled/LRP of MMA and St. Gel permeation chromatography (GPC) and ^1H NMR analyses as well as chain extension confirmed living/controlled nature.

EXPERIMENTAL

Materials

MMA and St (>99%) were washed with 5% NaOH solution followed by deionized water, distilled under reduced pressure,

Table I. Radical Polymerizations of MMA^a and St^b Catalyzed with CuSO₄·5H₂O/NaH₂PO₂·H₂O

Entry	Monomer	[M] ₀ /[EBiB] ₀ /[NaH ₂ PO ₂ ·H ₂ O] ₀ / [CuSO ₄ ·5H ₂ O] ₀ /[PMDETA] ₀	Time (h)	Conv. (%)	M _{n,th} (Da)	M _{n,GPC} (Da)	PDI
1	MMA	200 : 0 : 0 : 1 : 0.1 : 0.1	13	9	1800	20,000	2.20
2	MMA	200 : 1 : 1 : 0 : 0	13	79	16,000	51,000	1.89
3	St	200 : 0 : 5 : 0.1 : 1	24	0	/	/	/
4	St	200 : 1 : 5 : 0 : 0	24	11	2480	86,700	1.90

^a Entries 1 and 2 for MMA. MMA/DMSO = 2 : 1 (v/v), [MMA]₀ = 6.29 mol/L, T = 25°C.

^b Entries 3 and 4 for St. St/DMSO = 5 : 1 (v/v), [St]₀ = 7.26 mol/L, time = 24 h, T = 25°C.

and stored at -20°C prior to use. Ethyl 2-bromoisobutyrate (EBiB, 98%, Aladdin), PMDETA (99%, Aladdin), NaH₂PO₂·H₂O, and CuSO₄·5H₂O were used as received. N,N-dimethylformamide (DMF, 98%), toluene (98%), and dimethyl sulfoxide (DMSO, 99%) were distilled under reduced pressure before use.

Polymerization

A dry Schlenk tube was charged with monomer, CuSO₄·5H₂O, PMDETA, solvent, EBiB, and NaH₂PO₂·H₂O. The mixture was degassed by using conventional freeze-pump-thaw technique. The tube was then sealed with a rubber septum, and was placed in an oil bath at 25°C under stirring. After a predetermined reaction time, the mixture was cooled by liquid nitrogen, exposed to air, and diluted with an appropriate amount of chloroform. When the mixture becomes a homogenous solution, an excess of methanol/hydrochloric acid (v/v, 100/0.1) was added to precipitate the polymer. The resultant polymer was filtered and dried at 30°C *in vacuo*.

Characterization

The monomer conversions were determined gravimetrically. ¹H NMR spectra of PMMA and PSt samples were recorded on a Bruker 300 MHz Spectrometer using CDCl₃ as the solvent and tetramethylsilane as the internal standard. The number-average molecular weight (M_{n,GPC}) and polydispersity index (PDI) were determined by GPC. The GPC system was equipped with a Waters 510 HPLC pump and Waters 2414 RI detector using three Waters Ultrastaygel columns (500, 10³, and 10⁵) in tetrahydrofuran at a flow rate of 1.0 mL/min. The universal calibration was utilized to correct the molecular weights.

RESULTS AND DISCUSSION

Rapid Ambient Temperature LRP of MMA and St with NaH₂PO₂·H₂O as Reducing Agent

We first conducted various control polymerizations of MMA and St at 25°C (Table I). The polymerization of MMA in presence of NaH₂PO₂·H₂O/CuSO₄·5H₂O/PMDETA reached a low polymer yield after 13 h (9%, entry 1). The result indicates that a small amount of radicals may be produced from the dissociation of hypophosphite anion. The polymerization in presence of ATRP initiator (EBiB) and NaH₂PO₂·H₂O reached a higher polymer yield after the identical reaction time (79%, entry 2). It powerfully indicates that NaH₂PO₂·H₂O can activate EBiB and produce the radicals. In contrast, the polymerization of St in presence of NaH₂PO₂·H₂O/CuSO₄·5H₂O/PMDETA did not occur (entry 3). The polymerization in presence of NaH₂PO₂·H₂O/EBiB reached 11% conversion after 24 h (entry 4). Clearly, the control polymerizations of MMA and St differ greatly. Moreover, it must be kept in mind that these polymerizations were loss of control, as evidenced by far higher molecular weights than theoretical ones and broad molecular weight distributions. Therefore, to obtain well-controlled/livingness, the radical polymerizations of MMA and St were further investigated under various conditions, and the representative results are summarized in Table II.

As NaH₂PO₂·H₂O does not dissolve in organic solvent, the reaction mixture was a heterogeneous polymerization system. Thus, it is important to choose a suitable solvent for the current study. Solvent significantly influenced the polymerization of MMA initiated with EBiB/NaH₂PO₂·H₂O/CuSO₄·5H₂O/

Table II. Radical Polymerizations of MMA^a and St^b Catalyzed with CuSO₄·5H₂O/NaH₂PO₂·H₂O

Entry	Monomer	Solvent	Ligand	Conv. (%)	M _{n,th} (Da)	M _{n,GPC} (Da)	PDI
1	MMA	None	PMDETA	74	15,000	26,000	1.68
2	MMA	Toluene	PMDETA	33	6790	8500	1.39
3	MMA	DMF	PMDETA	57	11,600	10,800	1.20
4	MMA	DMSO	PMDETA	77	15,600	15,500	1.18
5	St	DMSO	Bpy	0	/	/	/
6	St	DMSO	Me ₆ TREN	15	3310	2450	1.11
7	St	DMSO	PMDETA	65	13,700	11,200	1.26

^a [MMA]₀/[EBiB]₀/[NaH₂PO₂·H₂O]₀/[CuSO₄·5H₂O]₀/[PMDETA]₀ = 200 : 1 : 1 : 0.1 : 0.1, MMA/Solvent = 2 : 1 (v/v), [MMA]₀ = 6.29 mol/L, T = 25°C, time = 2 h.

^b [St]₀/[EBiB]₀/[NaH₂PO₂·H₂O]₀/[CuSO₄·5H₂O]₀/[PMDETA]₀ = 200 : 1 : 5 : 0.1 : 1, St/DMSO = 5 : 1 (v/v), [St]₀ = 7.26 mol/L, T = 25°C, time = 24 h.

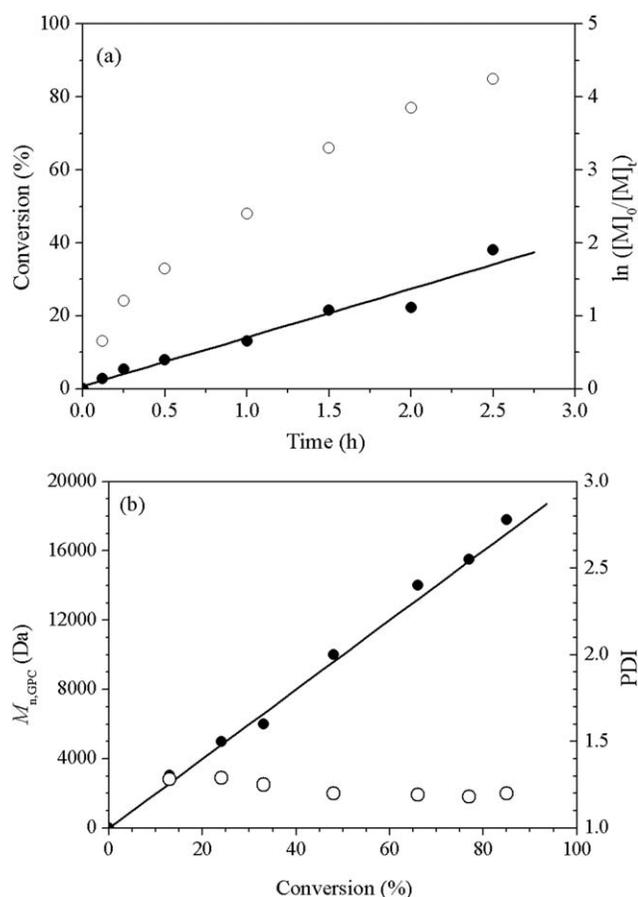


Figure 1. Kinetic plots of (a) conversion (○) and $\ln([M]_0/[M])$ (●) versus reaction time and (b) dependence of experimental M_n (●, theoretical) and PDI (○) on the monomer conversion for radical polymerization of MMA using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent. $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0/[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0/[\text{PMDETA}]_0 = 200 : 1 : 1 : 0.1 : 0.1$, $\text{MMA}/\text{DMSO} = 2 : 1$ (v/v), $[\text{MMA}]_0 = 6.29$ mol/L, $T = 25^\circ\text{C}$.

PMDETA at ambient temperature under similar reaction conditions.²⁴ DMF and nonpolar toluene exhibited lower rates of polymerizations (57% and 33% conversions corresponding to entries 2 and 3, respectively). Contrarily, the bulk polymerization and the solution polymerization in DMSO exhibited higher rates of polymerizations (74% and 77% conversions corresponding to entries 1 and 4, respectively). Importantly, only DMSO system provided the lowest PDI value of 1.18 and controlled molecular weight close to theoretical one (entry 4). The results strongly indicate that the ambient temperature polymerization of MMA in DMSO can produce the best controlled/living characteristics.

Furthermore, the influences of varied ligands (bpy, Me_6TREN , and PMDETA) on the St polymerizations catalyzed with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in DMSO were investigated. With PMDETA, the fastest rate of polymerization was achieved (65% conversion after 24 h, entry 7), which implies that the ratio of activation/deactivation rate (i.e., the equilibrium constant $K = k_a/k_{da}$)²⁵ is the highest for this initiating system. With bpy or Me_6TREN , the polymerizations did not occur or proceeded sluggishly (entries 5 and 6). Importantly, PMDETA was effective

for controlling molecular weight and molecular weight distribution.

To further follow the polymerization kinetics as well as the evolutions of the molecular weight and molecular weight distributions, the polymerizations of MMA and St mediated by $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in DMSO at 25°C were investigated in more detail (Figures 1 and 2). Obviously, the polymerization kinetics curves of MMA (Figure 1a) and St (Figure 2a) are of first order in monomer conversions, implying the constant radical concentration throughout the polymerization.^{26–30} Moreover, the reactions display rapid rates of polymerizations. For example, for MMA, 85% conversion was reached after 2.5 h; for St, 78% conversion was reached after 40 h. Concerning the molecular weights, the linear increases with monomer conversions are observed in two cases (Figures 1b and 2b). Additionally, the molecular weight values are in excellent agreement with ones predicted by the ratio of the consumed monomer to initiator, indicating the negligible number of chains formed from the biradical termination.^{31–33} As shown in Figure 2b, the linear slope based on the experimental data was lower

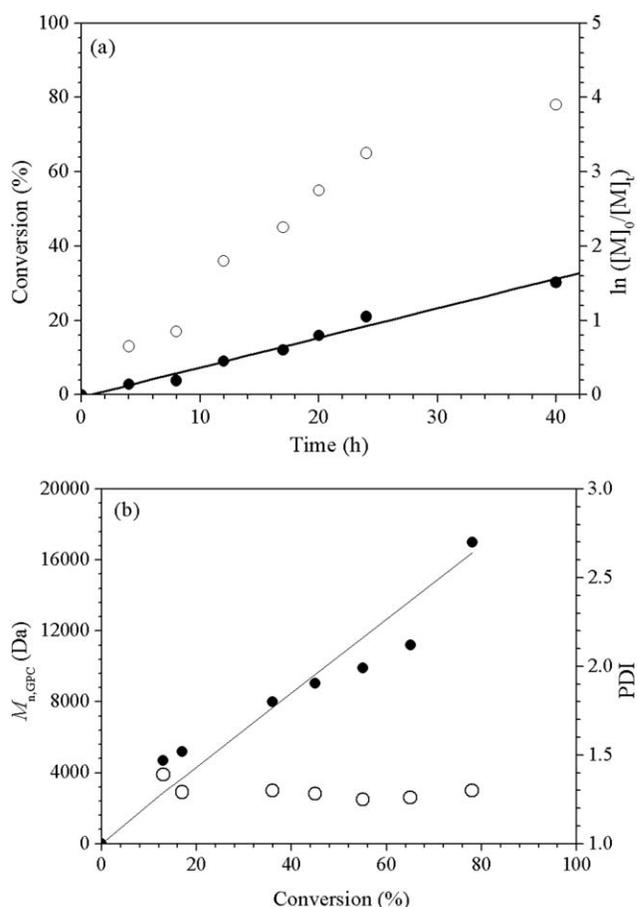


Figure 2. Kinetic plots of (a) conversion (○) and $\ln([M]_0/[M])$ (●) versus reaction time and (b) dependence of experimental M_n (●, theoretical) and PDI (○) on the monomer conversion for radical polymerization of St using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent. $[\text{St}]_0/[\text{EBiB}]_0/[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0/[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0/[\text{PMDETA}]_0 = 200 : 1 : 5 : 0.1 : 1$, $\text{St}/\text{DMSO} = 5 : 1$ (v/v), $[\text{St}]_0 = 7.26$ mol/L, $T = 25^\circ\text{C}$.

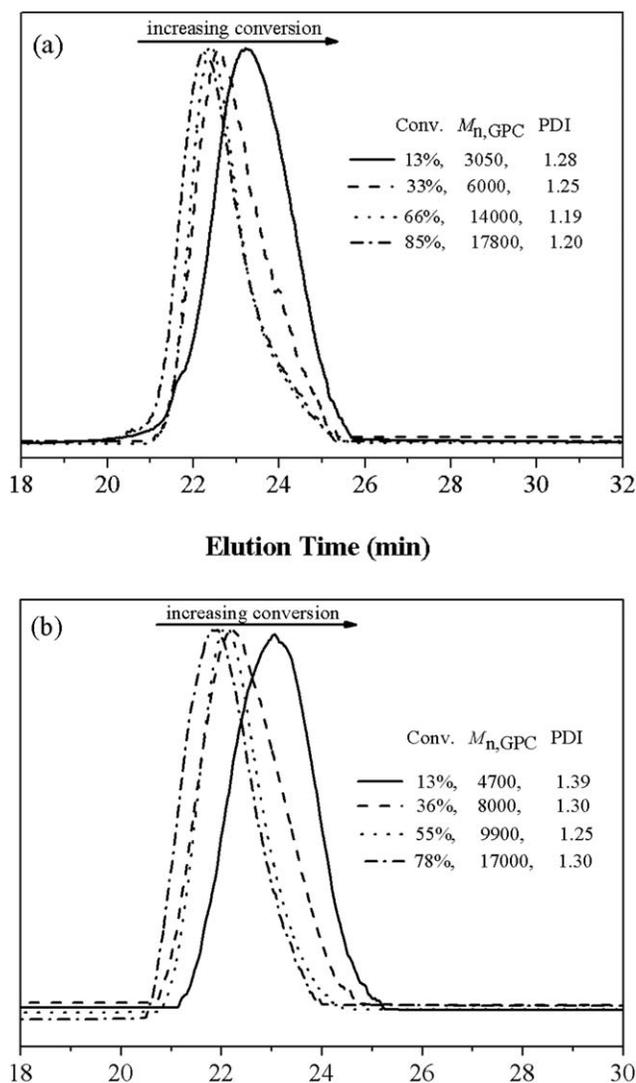


Figure 3. Evolution of GPC traces for radical polymerizations of (a) MMA and (b) St using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent at different monomer conversions. The conditions are as the same as shown in Figures 1 and 2.

Table III. Effect of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ Content on Radical Polymerizations of MMA^a and St^b

Entry	Monomer	$[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0 / [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0$	Conv. (%)	$M_{n,th}$ (Da)	$M_{n,GPC}$ (Da)	PDI
1	MMA	0.1 : 0.1	24	4990	6700	1.35
2	MMA	0.2 : 0.1	48	9790	12,000	1.29
3	MMA	0.5 : 0.1	61	12,400	14,500	1.20
4	MMA	1 : 0.1	77	15,600	15,500	1.18
5	MMA	2 : 0.1	79	16,000	17,600	1.20
6	MMA	3 : 0.1	96	19,400	23,100	1.18
7	St	1 : 0.1	39	8310	6100	1.25
8	St	2 : 0.1	52	11,000	8790	1.31
9	St	3 : 0.1	59	12,500	12,100	1.24
10	St	5 : 0.1	65	13,700	11,200	1.26
11	St	8 : 0.1	67	14,100	10,000	1.23

^a $[\text{MMA}]_0 / [\text{EBiB}]_0 / [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0 / [\text{PMDETA}]_0 = 200 : 1 : 0.1 : 0.1$, $\text{MMA}/\text{DMSO} = 2 : 1$ (v/v), $[\text{MMA}]_0 = 6.29$ mol/L, $T = 25^\circ\text{C}$, time = 2 h.

^b $[\text{St}]_0 / [\text{EBiB}]_0 / [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0 / [\text{PMDETA}]_0 = 200 : 1 : 0.1 : 1$, $\text{St}/\text{DMSO} = 5 : 1$ (v/v), $[\text{St}]_0 = 7.26$ mol/L, $T = 25^\circ\text{C}$, time = 24 h.

than that in theoretical calculation. It may be due to that the number of the generating active radicals shows a low-to-high rule. First, due to low rate of polymerization and nonpolar nature of St, the number of active radicals was less than that as expected when the conversion was lower, also leading to the obviously too high molecular weight of the obtained polystyrene at this stage. With the polymerization proceeding, the reaction heat is continuously produced, which would promote the dissociation of hypophosphite anion or the activation of EBiB by $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, thus forming a large amount of active radicals. The molecular weight distributions remained narrow throughout the polymerization and were all < 1.3 . The similar results are visually reflected in the evolutions of GPC traces, as shown in Figure 3. The GPC traces are monomodal and symmetrical, and display narrow molecular weight distribution results. In addition, they shift cleanly and completely, implying the increase of the molecular weights with monomer conversions. Therefore, the results suggest that the radical polymerization of MMA and St catalyzed with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} / \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ well possess the controlled/living polymerization characteristics.¹⁻⁷

Influence of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ Concentration

The reducing agent, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, is a vital component for the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ -mediated radical polymerizations of MMA and St at ambient temperature. Thus it is necessary to exploit the influence of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ amount on the polymerization (Table III). For MMA, a series of experiments were conducted with different $[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0 / [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0$ ratios ranging from 0.1 : 0.1 to 3 : 0.1 while the $[\text{MMA}]_0 / [\text{EBiB}]_0 / [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0 / [\text{PMDETA}]_0$ ratio was kept unchanged (entries 1-6). It was clear that the monomer conversions enhanced with an increase in the $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ concentration. When a $[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0 / [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]_0$ ratio of 0.1 : 0.1 was used, the monomer conversion reached only 24% after 2 h (entry 1). In contrast, the conversion reached 96% after the identical reaction duration for a ratio of 3 : 0.1 (entry 6). The strong increase of rate of polymerization can be ascribed to the generation of a high concentration of the metal activator.^{34,35} However, an

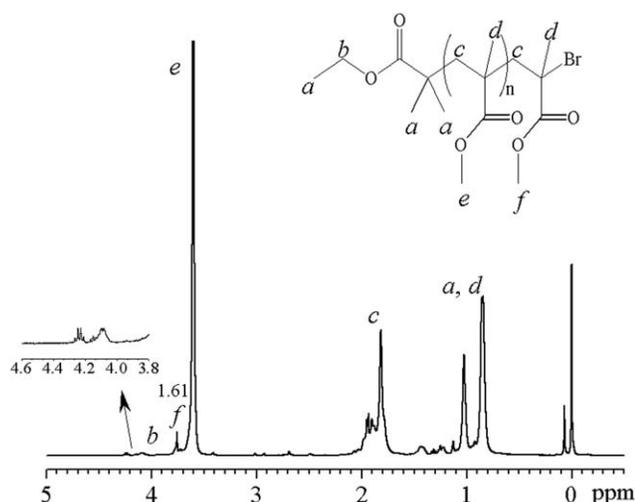


Figure 4. ^1H NMR of PMMA obtained by radical polymerization of MMA using $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ as reducing agent. $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}]_0/[\text{CuSO}_4\cdot 5\text{H}_2\text{O}]_0/[\text{PMDETA}]_0 = 200 : 1 : 1 : 0.1 : 0.1$, $\text{MMA}/\text{DMSO} = 2 : 1$ (v/v), $[\text{MMA}]_0 = 6.29$ mol/L, $T = 25^\circ\text{C}$, monomer conversion = 13%, $M_{n,\text{th}} = 2790$, $M_{n,\text{NMR}} = 3360$.

overestimated concentration of $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ led to a departure of molecular weight value from theoretical one (entry 6). As a result, a $[\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}]_0/[\text{CuSO}_4\cdot 5\text{H}_2\text{O}]_0$ ratio of 1 : 0.1 is enough to provide the controlled/living polymerization of MMA at 25°C .

The similar rule was also observed in the polymerization of St initiated with $\text{EBiB}/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}/\text{CuSO}_4\cdot 5\text{H}_2\text{O}/\text{PMDETA}$. Specially, due to its lower rate of polymerization at ambient temperature, higher levels of $[\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}]_0/[\text{CuSO}_4\cdot 5\text{H}_2\text{O}]_0$ ratio = 5 : 0.1 and $[\text{PMDETA}]_0/[\text{CuSO}_4\cdot 5\text{H}_2\text{O}]_0 = 1 : 0.1$ were required. Even so, compared with the previous works,^{22,36,37} the present work has been provided the fastest and well-controlled polymerization of St at ambient temperature.

Chain-End Functionality

The chain-end structures of PMMA and PSt obtained from $\text{EBiB}/\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}/\text{CuSO}_4\cdot 5\text{H}_2\text{O}/\text{PMDETA}$ system were first analyzed by ^1H NMR technique. As shown in Figures 4 and 5, the protons derived from the ATRP initiator EBiB were clearly observed. In particular, the protons of MMA or St unit adjacent to the bromine atom at the ω -end can be definitely assigned to peak f (Figure 4) or peak g (Figure 5). Thus the results demonstrate that the EBiB moieties were successfully attached to the chain ends of PMMA or PSt.³⁸ Moreover, the ^1H NMR data can be applied to calculate the molecular weight value of the resultant polymers according to the equation as follows:

$$M_{n,\text{NMR}} = \frac{I_M/n}{I_b/2} \times M_M + M_{\text{EBiB}}$$

where I_M is the integration value of the characteristic proton in the main chain of PMMA or PSt, and n corresponds to the number of the proton, such as the methylene protons of MMA unit (peak c in Figure 4, $n = 2$) or the aromatic protons of St unit (peak f in Figure 5, $n = 5$). I_b is the integration value of

the methylene protons of the ethyl ester unit derived from the initiator EBiB (peak b in Figure 4 or 5). M_M and M_{EBiB} are the molecular weights of the monomer (MMA or St) and EBiB , respectively. The obtained $M_{n,\text{NMR}}$ value of PMMA was very close to the theoretical one, implying that the EBiB moieties were successfully attached to the PMMA or PSt chain end and the generated polymers possessed high chain-group fidelity.

Another important method for analyzing chain-end functionality of the resultant PMMA or PSt is to perform chain-extension reaction. Figure 6 shows the GPC traces of the original PMMA, and PSt, and the chain-extended samples obtained via the same polymerization technique, i.e., the radical polymerizations mediated with $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}/\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ in DMSO-Br ($M_{n,\text{GPC}} = 10,000$, $\text{PDI} = 1.35$) to the chain-extended PMMA ($M_{n,\text{GPC}} = 28,500$, $\text{PDI} = 1.30$) was observed (Figure 6a). Likewise, there is an obvious peak shift from the original PSt-Br macroinitiator ($M_{n,\text{GPC}} = 9900$, $\text{PDI} = 1.25$) to the chain-extended PSt ($M_{n,\text{GPC}} = 24,000$, $\text{PDI} = 1.32$) (Figure 6b). The narrow molecular weight distribution and the unimodal shape of the GPC trace of the final product prove that the chain extension reaction is successful. These results indicate that the polymerizations of MMA and St proceed in controlled/living manners.

CONCLUSIONS

The ambient temperature radical polymerizations of MMA and St catalyzed with $\text{CuSO}_4\cdot 5\text{H}_2\text{O}/\text{PMDETA}$ were investigated in detail. The key to success is ascribed to that $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ was adopted as a reducing agent, producing ideal controlled/LRP characteristics as evidenced by pseudo first-order kinetics, linear evolution of molecular weights with increasing monomer conversions, and low PDI values within a range of 1.10–1.30. The polymerizations proceeded fast, for example, MMA reached a

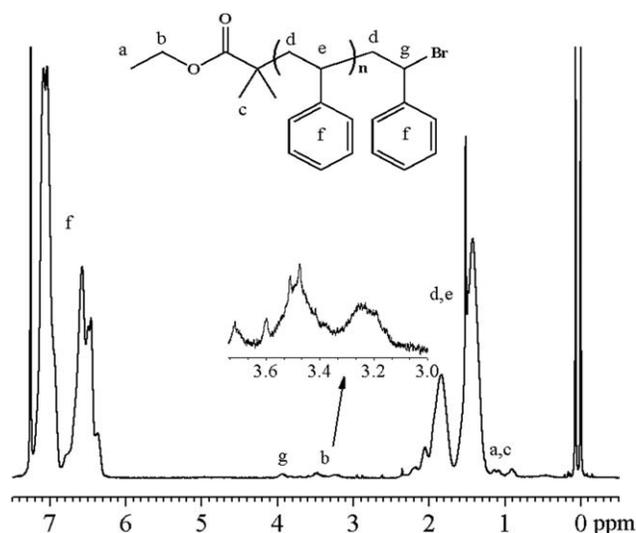


Figure 5. ^1H NMR of PSt obtained by radical polymerization of St using $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ as reducing agent. $[\text{St}]_0/[\text{EBiB}]_0/[\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}]_0/[\text{CuSO}_4\cdot 5\text{H}_2\text{O}]_0/[\text{PMDETA}]_0 = 200 : 1 : 5 : 0.1 : 1$, $\text{St}/\text{DMSO} = 5 : 1$ (v/v), $[\text{St}]_0 = 7.26$ mol/L, $T = 25^\circ\text{C}$, monomer conversion = 17%. $M_{n,\text{th}} = 3730$, $M_{n,\text{NMR}} = 4130$.

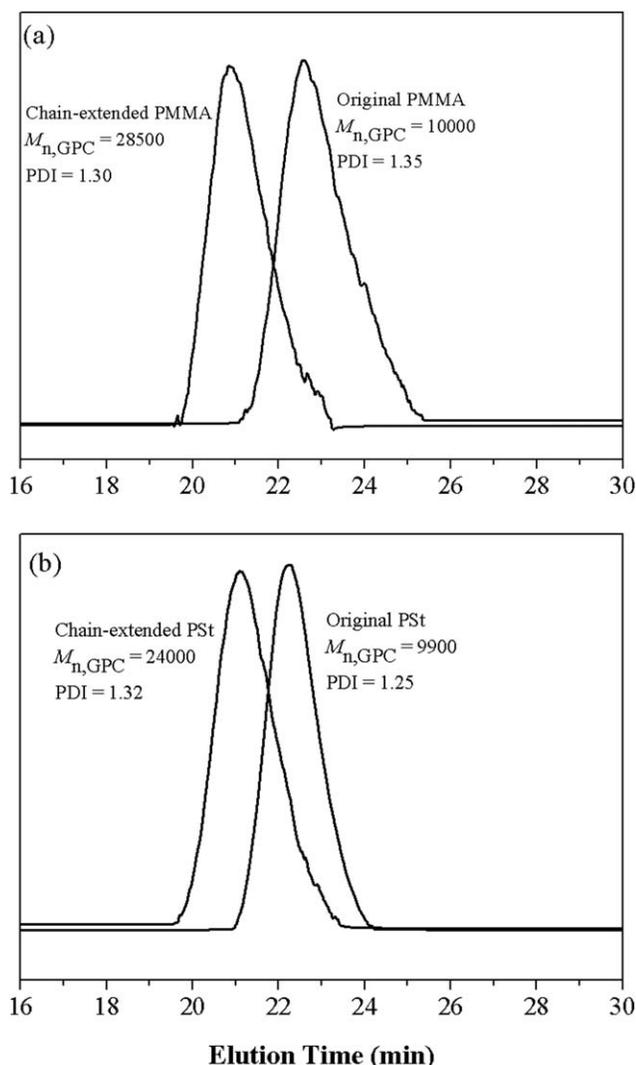


Figure 6. (a) GPC curve for the chain reaction of PMMA-Br with MMA. $[MMA]_0/[PMMA-Br]_0/[NaH_2PO_2 \cdot H_2O]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200 : 1 : 1 : 0.1 : 0.1$, MMA/DMSO = 2 : 1 (v/v), $[MMA]_0 = 6.29$ mol/L, $T = 25^\circ C$, time = 3 h, monomer conversion = 90%. (b) GPC curve for the chain reaction of PSt-Br with St. $[St]_0/[PSt-Br]_0/[NaH_2PO_2 \cdot H_2O]_0/[CuSO_4 \cdot 5H_2O]_0/[PMDETA]_0 = 200 : 1 : 5 : 0.1 : 1$, St/DMSO = 5 : 1 (v/v), $[St]_0 = 7.26$ mol/L, $T = 25^\circ C$, time = 24 h, monomer conversion = 70%.

conversion of ca 90% after 2.5 h, and St reached a conversion of ca 80% after 40 h. Furthermore, the control of the polymerization was investigated in terms of solvent, ligand, and the concentration of reducing agent. The optimized conditions were found to be a combination of DMSO, PMDETA, and molar ratio values of $NaH_2PO_2 \cdot H_2O$ to $CuSO_4 \cdot 5H_2O = 1 : 0.1$ for MMA and 5 : 0.1 for St. Finally, the very high chain-end functionalities of the PMMA and PSt obtained were confirmed by 1H NMR analyses and chain-extension experiments.

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REFERENCES

- Ouchi, M.; Terashima, T.; Sawamoto, M. *Chem. Rev.* **2009**, *109*, 4963.
- Rosen, B. M.; Percec, V. *Chem. Rev.* **2009**, *109*, 5069.
- Braunecker, W. A.; Matyjaszewski, K. *Prog. Polym. Sci.* **2007**, *32*, 93.
- Lena, F. D.; Matyjaszewski, K. *Prog. Polym. Sci.* **2010**, *35*, 959.
- Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015.
- Wu, D. C.; Sun, B.; He, R. W.; Matyjaszewski, K. *Chem. Rev.* **2012**, *112*, 3959.
- Sieglwart, D. J.; Oh, J. K.; Matyjaszewski, K. *Prog. Polym. Sci.* **2012**, *37*, 18.
- Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
- Mitsuru, K.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
- Min, K.; Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 1789.
- Bai, L. J.; Zhang, L. F.; Cheng, Z. P.; Zhu, X. L. *Polym. Chem.* **2012**, *3*, 2685.
- Yu, Y. H.; Liu, X. H.; Jia, D.; Cheng, B. W.; Ren, Y. L.; Zhang, F. J.; Li, H. N.; Chen, P.; Xie, S. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1690.
- Yu, Y. H.; Liu, X. H.; Jia, D.; Cheng, B. W.; Zhang, F. J.; Chen, P.; Xie, S. *Polymer* **2013**, *54*, 148.
- Zhang, Y.; Wang, Y.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 683.
- Visnevskij, C.; Makuska, R. *Macromolecules* **2013**, *46*, 4764.
- Konkolewicz, D.; Magenau, A. J. D.; Averick, S. E.; Simakova, A.; He, H. K.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 4461.
- Guo, T.; Zhang, L. F.; Pan, X. Q.; Li, X. H.; Cheng, Z. P.; Zhu, X. L. *Polym. Chem.* **2013**, *4*, 3725.
- Liu, X. H.; Wang, J.; Yang, J. S.; An, S. L.; Ren, Y. L.; Yu, Y. H.; Chen, P. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1933.
- Liu, X. H.; Wang, J.; Zhang, F. J.; An, S. L.; Ren, Y. L.; Yu, Y. H.; Chen, P.; Xie, S. *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4358.
- Zhang, F. J.; Liu, X. H. *Chinese J. Polym. Sci.* **2013**, *31*, 1613.
- Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81.
- Li, B.; Yu, B.; Huck, W. T. S.; Liu, W. M.; Zhou, F. *J. Am. Chem. Soc.* **2013**, *135*, 1708.
- Abreu, C. M. R.; Mendonça, V.; Serra, A. C.; Matyjaszewski, K.; Guliashvili, T.; Coelho, J. F. J. *ACS Macro Lett.* **2012**, *1*, 1308.
- Markus, H.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 3350.
- Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
- Liu, X. H.; Yu, Y. H.; Jia, D.; Cheng, B. W.; Zhang, F. J.; Li, H. N.; Chen, P.; Xie, S. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1559.

27. Yu, Y. H.; Liu, X. H.; Jia, D.; Cheng, B. W.; Zhang, F. J.; Li, H. N.; Chen, P.; Xie, S. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 1468.
28. Liu, X. H.; Zhang, G. B.; Li, B. X.; Bai, Y. G.; Li, Y. S. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5439.
29. Wang, Y. X.; Li, X. L.; Du, F. F.; Yu, H. S.; Jin, B. K.; Bai, R. K. *Chem. Commun.* **2012**, *48*, 2800.
30. Dong, Y. Q.; Tong, Y. Y.; Dong, B. T.; Du, F. S.; Li, Z. C. *Macromolecules* **2009**, *42*, 2940.
31. Jiang, J. S.; Zhang, Y.; Guo, X. Z.; Zhang, H. Q. *Macromolecules* **2009**, *44*, 5893.
32. Zhai, S. J.; Song, X. M.; Yang, D.; Chen, W. L.; Hu, J. H.; Lu, G. L.; Huang, X. Y. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 4055.
33. Jing, R. K.; Wang, G. W.; Zhang, Y. N.; Huang, J. L. *Macromolecules* **2011**, *44*, 805.
34. Wang, Y.; Soerensen, N.; Zhong, M. J.; Schroeder, H.; Buback, M.; Matyjaszewski, K. *Macromolecules* **2013**, *46*, 683.
35. Pintauer, T.; Matyjaszewski, K. *Chem. Soc. Rev.* **2008**, *37*, 1087.
36. Subramanian, S. H.; Babu, R. P.; Dhamodharan, R. *Macromolecules* **2008**, *41*, 262.
37. Zhang, X. F.; Wu, Y.; Huang, J.; Miao, X. L.; Zhang, Z. B.; Zhu, X. L. *Chinese J. Polym. Sci.* **2013**, *31*, 702.
38. Wang, Y.; Zhong, M. J.; Zhang, Y. Z.; Magenau, A. J. D.; Matyjaszewski, K. *Macromolecules* **2012**, *45*, 8929.