

Ambient Temperature Living Radical Copolymerization of Styrene and Methyl Methacrylate with Sodium Hypophosphite as Reducing Agent^{*}

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Abstract A facile, safe and economical reducing agent, sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), has been successfully employed for ambient temperature living radical copolymerization of styrene (St) and methyl methacrylate (MMA). Such effective reducing agent significantly improved the reactivity of low reactive St monomers during the copolymerization, where the reactivity ratios of St and MMA were determined to be 0.50 and 0.36 by Finemann-Ross method. Thus the copolymerizations proceeded fast and showed typical living/controlled features, as evidenced by pseudo first-order kinetics of polymerization, linear increase in molecular weight versus monomer conversion, and low polydispersity index values. Effects of the concentration of reducing agent and the monomer feed ratio on the copolymerization were investigated in detail. Furthermore, gel permeation chromatography and ^1H -NMR analyses as well as chain extension experiments confirmed the high chain-end functionality of the resultant copolymer.

Keywords: Controlled/living radical copolymerization; Sodium hypophosphite; Ambient temperature; Methyl methacrylate; Styrene.

INTRODUCTION

Atom transfer radical polymerization (ATRP) has received great attention in the past decades because it is applicable to a wide range of monomers under mild reaction conditions and can produce numerous complex polymer architectures^[1–5]. Originally, the normal ATRP technique employs a low oxidation state metal catalyst. However, the catalyst is unstable and sensitive to air. Therefore, the desire for exploiting novel ATRP techniques continues by utilizing more stable and facile metal catalysts, *e.g.*, the combination of high oxidation state metal (Cu(II)X_2) and various reducing agents (tin(II) 2-ethylhexanoate, glucose, ascorbic acid, phenylhydrazine, phenol, alcohols, nitrogen-containing ligands, monomers, radical initiator and *etc.*)^[6–13], and zero-valence copper (Cu(0))^[14, 15]. Particularly, Cu(0) -mediated living radical polymerization (Cu(0) -LRP), also coined as single electron transfer-living radical polymerization (SET-LRP), has been demonstrated to be robust and efficient for synthesis of well-defined polymers, although its mechanism is still debated in the literature. Percec and his coworkers propose that the methodology undergoes a very low activation energy outer-sphere SET process. Consequently, Cu(0) -LRP can be carried out at ambient temperature and involves fast activation and

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deactivation steps and negligible bimolecular termination due to a low polymerization temperature.

To date, Cu(0)-LRP was successfully extended to methyl methacrylate (MMA) and derivatives^[14–20]. In contrast, the homopolymerizations of styrene (St) *via* Cu(0)-LRP proceeded very slowly and were out of control^[21–23]. This is possibly due to sluggish initiation and low reactivity at ambient temperature. Recently, Percec's, Haddleton's, Huang's and Zhu's groups reported that nascent Cu(0) nanoparticles considerably enhanced rates of polymerizations because of greater surface size^[24–28]. Thus, we reason that by utilizing an effective reducing agent and a high oxidation state metal (the compound Cu(II)Br₂), the *in situ* generated Cu(0) nanoparticles can provide a facile route to the ambient temperature radical polymerization of St. On the other hand, the high reactive and suitable monomer for ambient temperature Cu(0)-LRP, MMA, is chosen as the comonomer, targeting the controlled St polymers with high monomer conversions. Following this issue, we note a strong and safe reducing agent, sodium hypophosphite (NaH₂PO₂·H₂O), which can efficiently reduces Cu(II) to Cu(0) nanoparticles^[29–32]. However, to the best of our knowledge, there is no report on the living radical polymerization of vinyl monomers by using a combination of NaH₂PO₂·H₂O and a high oxidation state metal at ambient temperature, particular low reactive St monomer. Therefore, the aim of this paper is to detailedly investigate the NaH₂PO₂·H₂O/Cu(II)Br₂-mediated living radical copolymerization of St and MMA and to synthesize well-defined copolymer. Gel permeation chromatography (GPC) and ¹H-NMR analyses as well as chain extension experiments were used to detect the polymerization kinetics and the living radical polymerization characteristics.

EXPERIMENTAL

Materials

St and MMA (> 99%) were washed with 5% NaOH solution followed by deionized water, distilled under reduced pressure before use. Ethyl 2-bromoisobutyrate (EBiB, 98%, Aladdin), PMDETA (99%, Aladdin), NaH₂PO₂·H₂O, and CuBr₂ were used as received. Dimethyl sulfoxide (DMSO, 99%) was distilled under reduced pressure before use.

Polymerization

St, MMA, CuBr₂, PMDETA, DMSO, EBiB and NaH₂PO₂·H₂O were added to a dry Schlenk tube in sequence. The mixture was degassed by five freeze-pump-thaw technique cycles before the tube was sealed with a rubber septum. The tube was then placed in an oil bath at 25 °C under stirring. After a desire reaction time, the mixture was cooled by liquid nitrogen and exposed to air, and then dissolved with appropriate amount of CHCl₃ and precipitated by an excess of methanol/HCl (*V/V*, 100/0.1). The final product was separated by filtration and dried under vacuum at 30 °C until a constant weight. The monomer conversions were determined by gravimetry.

Characterization

¹H-NMR spectra of the copolymer samples were recorded on a Bruker 300 MHz Spectrometer using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. The number-average molecular weight ($M_{n, GPC}$) and polydispersity index (PDI) were determined by gel permeation chromatography (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 THF at a flow rate of 1.0 mL/min. The universal calibration was utilized to correct the molecular weights.

RESULTS AND DISCUSSION

Sodium Hypophosphite/Cupric Bromide Catalyzed Living Radical Copolymerization of St and MMA at Ambient Temperature

The preliminary experiments show that the copolymerization of St and MMA at ambient temperature in absence of sodium hypophosphite (NaH₂PO₂·H₂O) did not occur. The NaH₂PO₂·H₂O/cupric bromide (CuBr₂) catalyzed radical copolymerization of St and MMA was first investigated with a [MMA]₀/[St]₀/[EBiB]₀/[CuBr₂]₀/[PMDETA]₀ value of 100:100:1:0.1:1 in DMSO at 25 °C (Fig. 1). Clearly, an induction period of ~5 h was

observed. It was perhaps originated from a large amount of deactivator species Cu(II) at the start stage of the copolymerization or residual traces of oxygen remained in the initial mixture despite of five freeze-pump-thaw cycles^[33–35]. Moreover, the kinetics plot exhibits a linear semilogarithmic curve, suggesting that the number of macromolecular chains formed from biradical termination reactions was negligible^[36–42]. Importantly, the monomer conversions reached 88% after 33 h, indicating a higher rate of copolymerization.

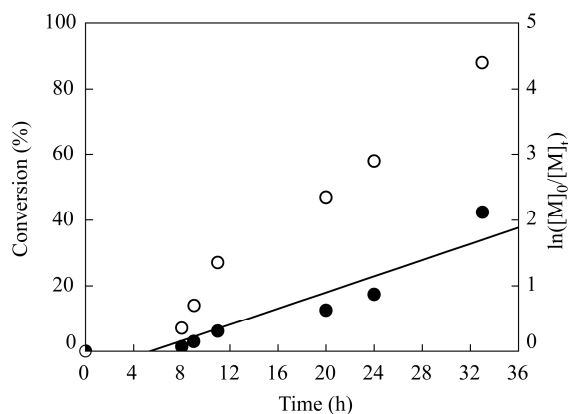


Fig. 1 Kinetic plots of conversion (○) and $\ln([M]_0/[M])$ (●) versus reaction time for living radical copolymerization of St and MMA using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent ($[\text{MMA}]_0/[\text{St}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 100:100:1:0.1:1$, $\text{MMA}/\text{DMSO} = 1:0.2$ (V/V), $\text{MMA} = 1 \text{ mL}$, $T = 25^\circ\text{C}$.)

Figure 2 shows the dependence of molecular weight and PDI results on monomer conversion. Obviously, the molecular weight values do increase with monomer conversions. However, the evolution was not a linear plot, suggesting that the active species concentration does not remain unchanged particularly at lower monomer conversions. PDI (GPC) values were low throughout the copolymerization, keeping in a range of 1.21–1.35. The phenomena were clearly reflected in the corresponding GPC curves (Fig. 3). They are almost symmetrical and shift clearly, confirming the increase of the molecular weight values with monomer conversions. Therefore, the above results suggest that the $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuBr}_2$ catalyzed radical copolymerization of St and MMA proceeded in a controlled/living fashion^[43].

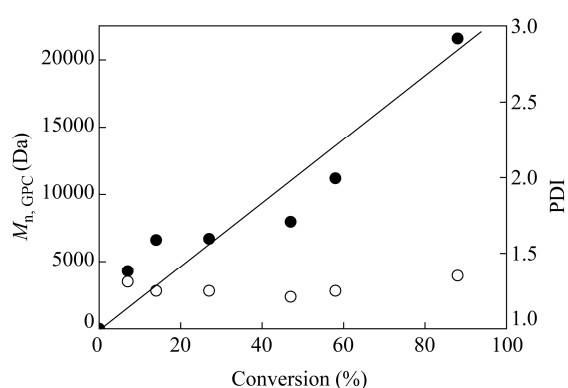


Fig. 2 Dependence of experimental M_n (●) and PDI (○) on the monomer conversion for living radical copolymerization of St and MMA using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent ($[\text{MMA}]_0/[\text{St}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 100:100:1:0.1:1$, $\text{MMA}/\text{DMSO} = 1:0.2$ (V/V), $\text{MMA} = 1 \text{ mL}$, $T = 25^\circ\text{C}$.)

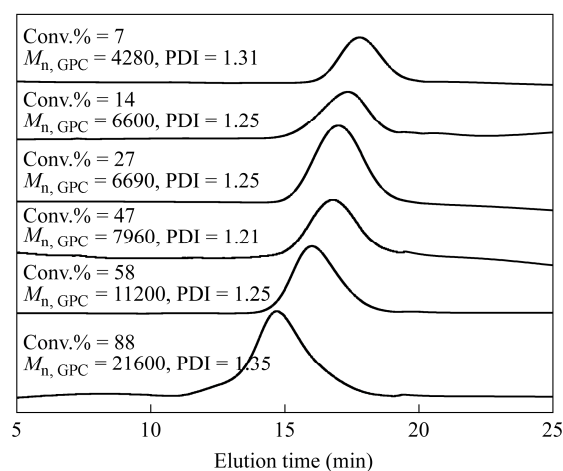


Fig. 3 GPC traces for living radical copolymerization of St and MMA using $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ as reducing agent ($[\text{MMA}]_0/[\text{St}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 100:100:1:0.1:1$, MMA/DMSO = 1:0.2 (V/V), MMA = 1 mL, $T = 25^\circ\text{C}$.)

Determination of Monomer Reactivity Ratio

The monomer reactivity ratio is the most important parameter for the copolymerization reaction, reflecting the relative reactivities of two monomers. The copolymerizations with varied monomer ratios ($[\text{MMA}]_0/[\text{St}]_0 = 180:20, 160:40, 140:60, 120:80, 100:100, 60:140$ and $40:160$) were respectively conducted, while the monomer conversions were limited to 10% by modulating the polymerization durations (Table 1). The monomer reactivity ratios were calculated by the Finemann-Ross method^[44, 45]:

$$\frac{\rho - 1}{R} = r_{\text{St}} - r_{\text{MMA}} \frac{\rho}{R^2}$$

where ρ and R refer to $[\text{St}]/[\text{MMA}]$ and $[\text{St}]_0/[\text{MMA}]_0$, respectively. $[\text{St}]$ and $[\text{MMA}]$ correspond to the copolymer compositions of St and MMA, whilst $[\text{St}]_0$ and $[\text{MMA}]_0$ correspond to the initial feed compositions of St and MMA. The r_{St} and r_{MMA} values can be obtained from the plot of $(\rho - 1)/R$ versus ρ/R^2 . That is, r_{St} is the intercept of the curve, and r_{MMA} is the negative slope.

Table 1. Data for determining reactivity ratios of St and MMA^a

Entry	$[\text{MMA}]_0/[\text{St}]_0$	R^b	ρ^c	$(\rho - 1)/R$	ρ/R^2
1	180:20	0.111	0.252	-6.739	20.453
2	160:40	0.250	0.45	-2.2	7.2
3	140:60	0.429	0.606	-0.918	3.293
4	120:80	0.667	0.834	-0.249	1.875
5	100:100	1	1.2	0.2	1.2
6	60:140	2.333	2.178	0.505	0.4
7	40:160	4	3.018	0.505	0.189

^a $[\text{MMA}]_0 + [\text{St}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0/[\text{PMDETA}]_0 = 200:1:0.1:1:1$, MMA/DMSO = 1:0.2 (V/V), MMA = 1 mL, $T = 25^\circ\text{C}$; ^b $R = [\text{St}]_0/[\text{MMA}]_0$. $[\text{St}]_0$ and $[\text{MMA}]_0$ correspond to the feed compositions of St and MMA, respectively.

^c $\rho = [\text{St}]/[\text{MMA}]$. $[\text{St}]$ and $[\text{MMA}]$ correspond to the copolymer compositions of St and MMA, respectively.

The copolymer compositions of St and MMA were acquired from ^1H -NMR analyses (Fig. 4). The characteristic peaks of St and MMA units were clearly observed in the spectrum. Particularly, compared with the spectra of the homopolymers of St and MMA, the peaks of the copolymer show obviously broadening and multi-splitting at $\delta = 0\text{--}3.7$. Thus, the resultant product was random copolymers of the two monomers. The copolymer compositions of St and MMA can be obtained by comparing integral value of peak c derived from phenyl group of St ($I_{6.5\text{--}7.2}$) unit with that of peak f derived from methoxy group of MMA unit ($I_{2.6\text{--}3.7}$), i.e., $\rho = [\text{St}]/[\text{MMA}] = (I_{6.5\text{--}7.2}/5)/(I_{2.6\text{--}3.7}/3)$.

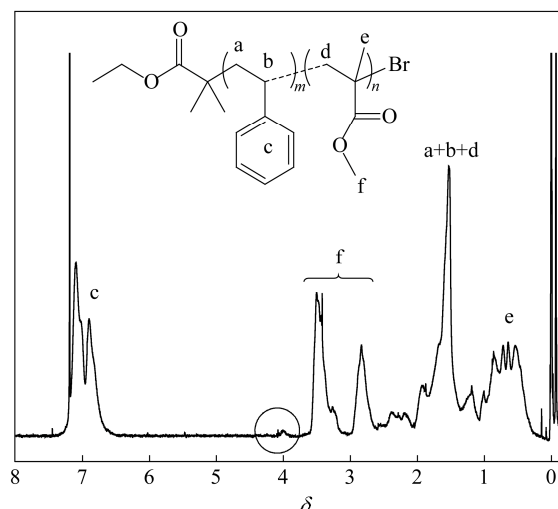


Fig. 4 ^1H -NMR spectrum of the copolymer obtained from the living radical copolymerization of St and MMA using $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ as reducing agent ($[\text{MMA}]_0/[\text{St}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 140:60:1:0.1:1$, $\text{MMA}/\text{DMSO} = 1:0.2$ (V/V), $\text{MMA} = 1$ mL, $T = 25$ °C.)

The reactivity ratio values for St and MMA determined by the Finemann-Ross method are 0.497 and 0.358, respectively (Fig. 5), which are verified by the Kelen-Tudos method (r_{St} and r_{MMA} are 0.597 and 0.392, respectively)^[46]. Thus, the results obtained by two methods can be reliable, which are in accord with their conventional radical copolymerization results^[47–52]. Obviously, the reactivity of St is far higher than that of MMA during the copolymerization. Therefore, benefited from $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}/\text{CuBr}_2/\text{PMDETA}$ catalytic system, the increased reactivity of St contributed to higher rates of copolymerization. Since the product values of reactivity ratios (r_{St} , r_{MMA}) for St and MMA are less than the correct one, the behavior of the current copolymerization reaction belongs to random copolymerization.

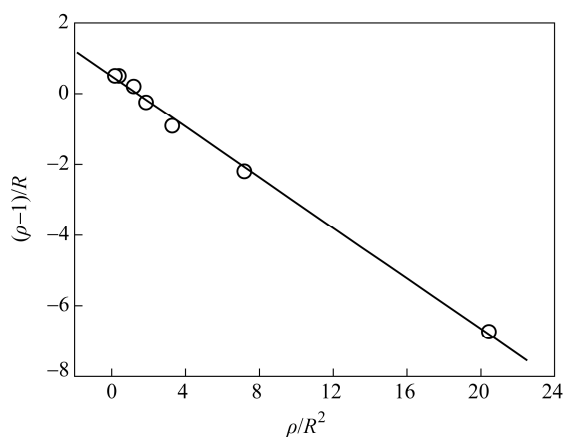


Fig. 5 Plot of $(\rho-1)/R$ versus ρ/R^2 for the living radical copolymerization of St and MMA using $\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$ as reducing agent

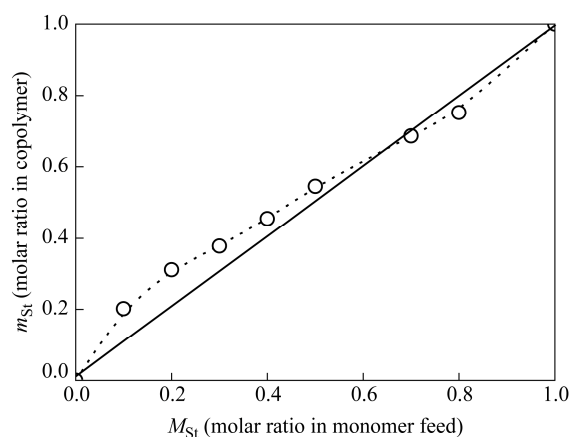


Fig. 6 Plot of copolymer composition (m_{St}) versus monomer feed (M_{St}) for the living radical copolymerization of St and MMA

The compositions of the generated copolymer versus monomer feed are plotted in Fig. 6. Clearly, the copolymer composition (m_{St}) increased with monomer feed (M_{St}), and they are very close. Therefore the predetermined copolymer composition can be obtained by varying monomer feed.

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

To access a higher rate of copolymerization and an ideal controlled/living feature, it is important to optimize the amount of reducing agent (Table 2). Clearly, the rate of copolymerization increased with the increase of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuBr}_2$ molar ratio. For example, at a lower $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuBr}_2$ molar ratio of 0.1:0.1, the monomer conversion only reached 10% after 33 h (entry 1). In Contrast, at a higher $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuBr}_2$ molar ratio of 5:0.1, the monomer conversion reached 97% after the identical polymerization duration (entry 6). In case of molecular weights, they increased with the according monomer conversions. Moreover, the PDI values enhanced with an increase in the $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ concentration. Therefore, in consideration of the effect of reducing agent on rate of polymerization, molecular weight and PDI, a $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuBr}_2$ molar ratio of 1:0.1 is selected for the radical copolymerization of St and MMA at ambient temperature.

Table 2. Effect of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ concentrations on the living radical copolymerizations of St and MMA^a

Entry	$[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0/[\text{CuBr}_2]_0$	Conv. (%)	$M_{n,\text{GPC}}$ (Da)	PDI
1	0.1:0.1	10	5940	1.12
2	0.2:0.1	24	6030	1.19
3	0.5:0.1	32	8925	1.25
4	1:0.1	88	21600	1.35
5	2:0.1	90	23600	1.36
6	5:0.1	97	26600	1.39

^a $[\text{MMA}]_0/[\text{St}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 100:100:1:0.1:1$, $\text{MMA}/\text{DMSO} = 1:0.2$ (V/V), $\text{MMA} = 1$ mL, $T = 25$ °C, time = 33 h.

Effect of Monomer Feed Ratio

The effect of monomer feed ratio on $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}/\text{CuBr}_2$ mediated radical copolymerization of St and MMA was also examined (Table 3). Obviously, the monomer conversions lowered with the increase of initial loading of St. For example, the polymerization for a $[\text{MMA}]_0/[\text{St}]_0$ ratio of 40:160 only reached 27% conversion after 20 h (entry 5), whereas the polymerization for a $[\text{MMA}]_0/[\text{St}]_0$ ratio of 180:20 reached 97% conversion under similar conditions (entry 1). The decrease of rate of copolymerization may be attributed to the fact that the reactivity of St lowered with consumption of MMA when the polymerizations were carried out at a lower amount of MMA.

Chain-end Structure and Possible Polymerization Mechanism

The most important characteristic of controlled/living polymerization is to prepare well-defined polymer with high chain-end functionality. As clearly shown in ¹H-NMR spectrum (Fig. 4), the proton from EBiB or monomer adjacent to the bromine atom at the ω -end was observed at about $\delta = 4$ ^[21]. It strongly proves that the copolymerization proceeded *via* the mechanism of the metal-catalyzed living radical polymerization. An additional evidence for verifying high chain-end functionality of the copolymer is that the chain extension experiment with St using the copolymer as the macroinitiator was successfully performed. As shown in Fig. 7, the obvious peak shift from the original random copolymer (M_n (GPC) = 6030, PDI (GPC) = 1.19) to the resulted block copolymer P(St-*co*-MMA)-block-PSt (M_n (GPC) = 28900, PDI (GPC) = 1.38) was observed. The monomodal GPC curve and low PDI value of the block copolymer suggest the successful chain extension reaction. The results prove the living nature of the copolymerization.

Table 3. Effect of monomer feed ratios on the living radical copolymerizations of St and MMA^a

Entry	$[\text{MMA}]_0/[\text{St}]_0$	Conv. (%)	$M_{n,\text{GPC}}$ (Da)	PDI
1	180:20	97	15600	1.38
2	140:60	55	12900	1.19
3	100:100	47	11200	1.25
4	60:140	33	6730	1.27
5	40:160	27	5260	1.24

^a $([\text{MMA}]_0 + [\text{St}]_0)/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}]_0/[\text{PMDETA}]_0 = 200:1:0.1:1:1$, $\text{MMA}/\text{DMSO} = 1:0.2$ (V/V), $\text{MMA} = 1$ mL, $T = 25$ °C, time = 20 h.

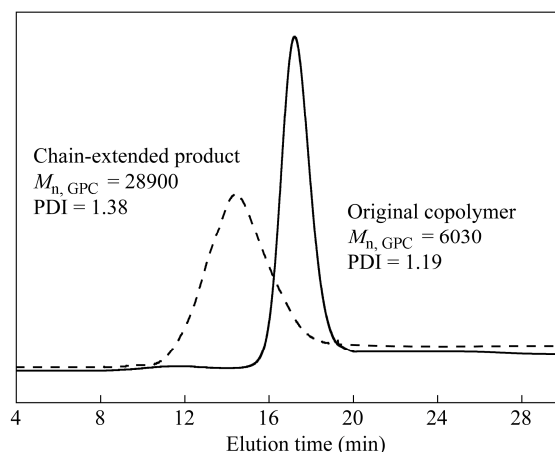
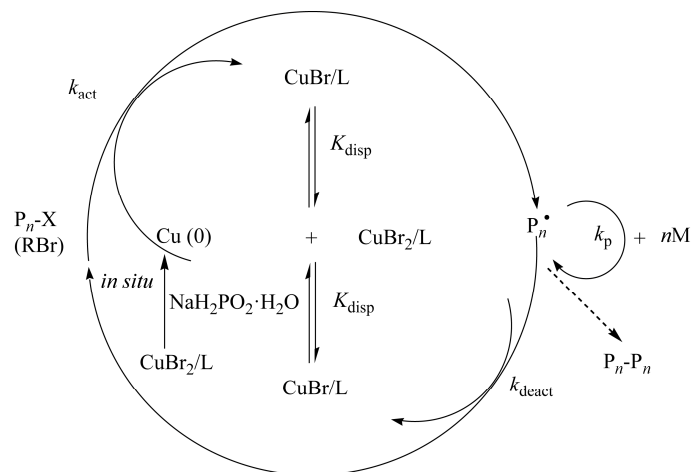


Fig. 7 GPC curve for the chain reaction of the resultant copolymer with St
 Conditions for the synthesis of original macroinitiator: [MMA/St] = 100/100/[EBiB]₀/[NaH₂PO₂·H₂O]₀/[CuSO₄·5H₂O]₀/[PMDETA]₀ = 200:1:0.2:0.1:1, St/DMSO = 2:1 (V/V), *T* = 25 °C, time = 33 h, monomer conversion = 24%; Chain extension conditions: [St]₀/[P(MMA-*co*-St)-Br]₀/[NaH₂PO₂·H₂O]₀/[CuSO₄·5H₂O]₀/[PMDETA]₀ = 400:1:1:0.1:1, St/DMSO = 2:1 (V/V), *T* = 25 °C, time = 236 h, monomer conversion = 83%.

A possible mechanism is proposed to explain NaH₂PO₂·H₂O/CuBr₂ mediated ambient temperature radical copolymerization of St and MMA^[29–32]. Many reports have demonstrated that NaH₂PO₂·H₂O can efficiently reduce Cu(II) to Cu(0) nanoparticles. The phenomenon was also observed from our experiments. Therefore, the radical copolymerizations of St and MMA with NaH₂PO₂·H₂O as reducing agent were actually controlled by *in situ* generated Cu(0)-mediated living radical polymerization (Scheme 1). Though the mechanism of Cu(0)-mediated living radical polymerization is still debated in the literature, this methodology has received great attention since its emergency in 2006 because it is a vigorous technique for synthesizing polymeric materials with a predetermined molecular weight, a low PDI and high chain end functionality^[14–20, 23–26, 53–55].



Scheme 1 Proposed mechanism of living radical copolymerization of St and MMA with NaH₂PO₂·H₂O as reducing agent (the start components are shown as the italic text)

CONCLUSIONS

The ambient temperature living radical copolymerization of St and MMA was successfully performed by using a facile, safe, and economical reducing agent, *i.e.*, sodium hypophosphite (NaH₂PO₂·H₂O). The reactivity ratios of St and MMA were determined to be 0.50 and 0.36, respectively, indicating that the reactivity of low reactive St

monomer was considerably increased during the copolymerization. The copolymerization reaction exhibits controlled/living characteristics, as evidenced by pseudo first-order kinetics of polymerization, linear increase of molecular weights with monomer conversions, and low PDI values within a range of 1.2 to 1.4. Dependences of the copolymerization on the concentration of reducing agent and the monomer feed ratio were investigated in more detail. An increase in the concentration of reducing agent induces an increased rate of copolymerization. In contrast, an increase in the initial loading of St leads to the decrease in rate of copolymerization. Furthermore, the high chain-end functionality of the resultant copolymer was confirmed by a combination of gel permeation chromatography and ^1H -NMR analyses as well as chain extension reaction.

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