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Low temperature effect on ATRP of styrene and substituted styrenes enabled by SaBOX ligand

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HIGHLIGHTS

- Controlled ATRP of styrene type monomers were achieved at low temperatures.
- ATRP of 4-MeOSt provided polymers rather than oligomers.
- Stereospecificity of polystyrene was gradually enhanced by lowering the temperature.
- A series of novel SaBOX ligands exhibited high activity at low temperature.

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ABSTRACT

A series of side-armed bisoxazoline (SaBOX) ligands have been designed and prepared, which exhibited high activity under (SARA) ATRP conditions even at low temperatures. Notably, both polymerization rate and controllability on molecular weight (MW) were significantly improved by using 4-MeOSt as monomer instead of styrene under the conditions in this work, which is significantly different from the previous reports that only oligomers were produced in the conventional ATRP of 4-MeOSt due to the presence of cationic species. Systematic studies indicated that SaBOX ligand enabled the low polymerization temperature, which is necessary to suppress the cationic polymerization process and produce high MW polymers rather than oligomers during the ATRP of 4-MeOSt. Meanwhile, the highly active SaBOX ligand guaranteed the high polymerization rate and good controllability. Moreover, by employing these SaBOX ligands, the controlled ATRP of styrene and substituted styrenes could be successfully achieved at low temperatures (−30 °C–25 °C), producing polymers with molecular weights close to theoretical values and relatively narrow molecular weight distributions (Đs = 1.2–1.5). More notably, the triad syndiotacticity (rr) of polystyrene was gradually enhanced from 48% to 62% by lowering the polymerization temperature, which demonstrated that the stereospecificity could be tuned in ATRP of styrene for the first time. The improved syndiotacticity and the subdued side reactions indicated the superiority and necessity of the polymerization at low temperature for ATRP in some aspects.

1. Introduction

Generally, high reaction temperatures (≥80 °C) are necessary for ATRP of styrene type monomers to maintain a sufficiently large propagation rate. One of the most extensively studied systems is the polymerization of styrene conducted at 110–130 °C with CuX/(dNbpy)$_2$ as the catalyst [1]. The reaction temperature can be lowered to 80–90 °C with the use of a more efficient catalyst, such as CuBr/PMDETA [2]. Under these conventional conditions, the polymerization of styrene and styrene monomers with electron-withdrawing (EW) substituents can proceed well with good controllability. However, for the styrene monomers bearing electron-donating (ED) substituents, the polymerization rate is slow and the controllability is poor [3]. And the polymerization of 4-MeOSt, which contains a strong ED substituent, gave only oligomers under conventional ATRP conditions, probably because of the formation of cationic propagating species via the heterolysis of the dormant C–Br or the oxidation of free radicals by Cu(II) species [4]. On the other hand, higher stereospecificity has been

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achieved in the ATRP for simple monomers such as methacrylates and (meth)acrylamides, via employing specific solvents (bulky fluorinated alcohols) [5], additives (bulky Lewis acids) [6] or catalysts (side-armed bisoxazoline (SaBOX)/copper complex) [7] at relatively low temperatures, while the stereospecific ATRP of styrene type monomers has been seldom reported [8].

ATRP at low temperature would be advantageous and necessary in a few aspects, as thermal crosslinking, chain transfer, thermal self-initiation, as well as other side reactions occurred less readily [9] and higher stereoregular polymers were produced at low temperature [5–7]. Therefore, the highly active and compatible catalytic system for low temperature ATRP has been extensively explored and are very limited. Recently, as an optimized approach of conventional ATRP, Cu (0)-RDRP [10] (Cu(0)-involved reversible deactivation radical polymerization, typically referred to as either single electron transfer (SET) LRP or supplemental activation and reducing agents (SARA) ATRP) was reported for the polymerization of acrylates, methacrylates and vinyl chloride at ambient temperature or lower temperatures, which produced ultrahigh molecular weight and/or highly syndiotactic polymers. Nevertheless, the conventional ATRP or Cu(0)-RDRP of styrene type monomers at low temperatures is still a significant unsolved problem. For instance, Dhamodharan et al. conducted the SET-LRP of styrene mediated by copper catalyst at ambient temperature, however, the polydispersity (PDI) of the resultant polystyrene was broad (around 2.50) [11]. Very recently, Hawker's group reported the controlled polymerization of styrene via (SARA) ATRP. Nevertheless, no conversion of monomer was detected in 36 h when lowering the temperature to 40 °C [12a]. The groups of Coelho and Zhu reported the polymerizations of styrene at room temperature under (ARGET) ATRP and (SARA) ATRP conditions, respectively, in which the polymerizations proceeded slowly furnishing conversions around 10% in 40 h [12b,c]. As we all know, there has been no report about conventional ATRP or Cu(0)-RDRP of styrene and substituted styrenes at ambient temperature and lower temperatures (< 0 °C) to produce polymers with good controllability and improved syndiotacticity so far, probably due to the lack of highly active and compatible catalytic system.

Previously, we developed a kind of SaBOX ligands, which exhibited high activity in (SARA) ATRP of methyl methacrylate (MMA). The polymerization temperature could be lowered to -60 °C and highly syndiotactic PMMA was produced [7a]. As a further study, we have recently explored the low temperature (SARA) ATRP of styrene and some substituted styrenes (Scheme 1) by employing this kind of highly active SaBOX ligands. Very controlled polymerizations were realized at low temperature (-30 °C ~ room temperature), which is necessary to provide polystyrenes with enhanced syndiotacticity and the polymers of 4-MeOSt rather than oligomers for the first time. Herein, we reported the results in details.

2. Results and discussion

2.1. The ATRP of Styrene at Ambient Temperature Employing Various BOX Ligands

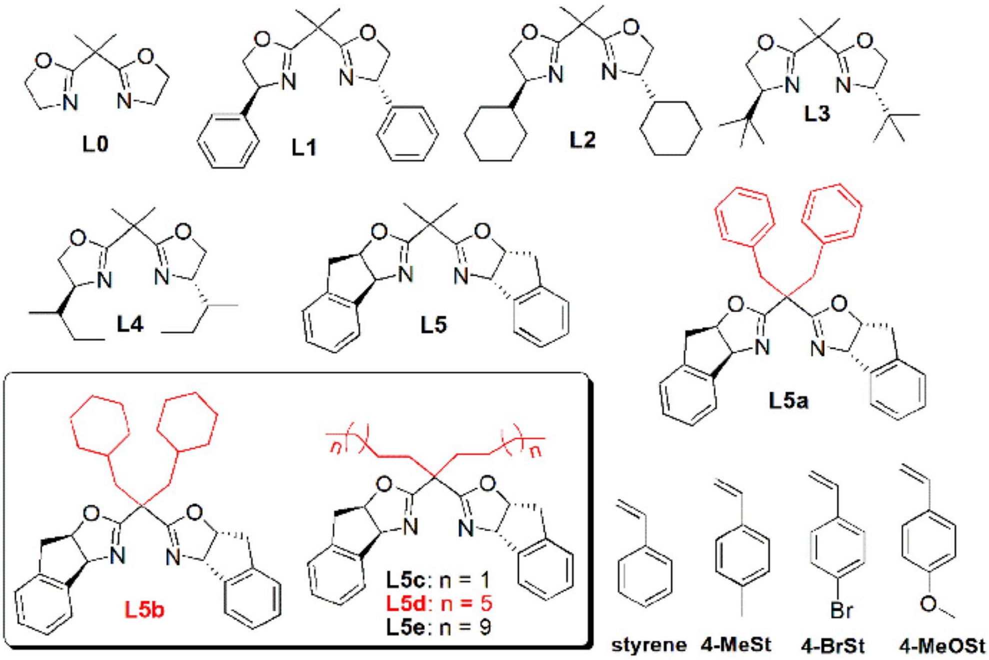
The highly active ligand is the key issue for exploring the low temperature effect on ATRP of styrene type monomers. Thus, we firstly investigated the scaffold effect of common ligands on the ATRP of styrene at ambient temperature (25 ± 2 °C) under the commonly used (SARA) ATRP conditions (elemental copper as the reducing agent, 2-bromopropionitrile (2-BPN) as an initiator and $CuBr_2$/BOX as the catalyst). The results are summarized in Table 1, which clearly showed that the structure of BOX scaffold had a significant influence on the polymerization rate and controllability. All the polymerizations were conducted for 48 h to avoid significant vitrification at high conversion. Employing **L0** as the ligand, the polymerization proceeded mildly, giving a conversion of 38% in 48 h and producing PS with broad MW distribution (Đ = 1.9). The polymerization mediated by **L1** was sluggish, achieving a conversion of 27% in 48 h. **L2** was a more inefficient ligand for the ATRP of styrene. The conversion was only 10% in 48 h and the MW distribution was even broader (Đ = 2.6) by employing **L2** as the ligand. Unexpectedly, the ligands with alkyl substituents **L3** and **L4**, which were not efficient in the ATRP of MMA [7], achieved higher polymerization rate, giving conversions of 40% and 42% in 48 h, respectively. However, the MW distributions of the resultant polymers were still broad (Đ = 1.7–1.9). Mediated by **L5**, the ATRP of styrene exhibited a relatively high rate with a conversion of 41% in 48 h and a better controllability (Đ = 1.4). For comparison, the two commonly-employed ligands with high activity, Me_6TREN and PMDETA were also utilized in the ambient temperature ATRP of styrene (runs 1 and 2). However, the conversions were lower than 20%, and the molecular weights were much higher than theoretical values and the MW distributions were very broad (Đs = 2.0–2.4). Based on above results, the indane-BOX is optimal as the ligand scaffold for ambient temperature ATRP of styrene.

Next, the further study was focused on the side arm strategy to achieve higher polymerization rate and better MW controllability. Firstly, we employed two SaBOX ligands with two pendant phenyl (**L5a**) or cyclohexyl (**L5b**) groups, which were reported before (Scheme 1). Similar with the ATRP of MMA previously reported by our group [7a], there is no obvious change in both polymerization rate and controllability by substituting **L5** with **L5a**. By contrast, both the polymerization rate and MW controllability were improved by using **L5b** as the ligand instead of **L5**. The conversion was 44% in 48 h and the MW distribution was relatively narrow (Đ = 1.3). Besides, the measured M_n closely approximates the theoretical value. The results of styrene polymerizations mediated by **L3** and **L4** indicated that the introduction of alkyl groups to the ligands seemed to be beneficial for the performance. This might be due to that the alkyl group enhanced the solubility of catalysts in a system with weak polarity. Therefore, we designed three new ligands (**L5c**, **L5d** and **L5e**, Scheme 1) by introducing linear alkyl chains with different length as side arms. As shown in Table 1, compared to **L5b**, the newly designed ligands indeed achieved faster polymerization rate and comparable controllability in the polymerizations of styrene. The conversions were 48%, 50% and 50% in 48 h by employing **L5c**, **L5d** and **L5e**, respectively. The MW distributions were 1.4–1.5. A linear first-order kinetic plot and an agreement between experimental and theoretical MW proved a controlled polymerization for the ATRP of styrene that was conducted at room temperature using **L5d** as the ligand (Fig. 1).

2.2. The ATRP of Substituted Styrenes at Ambient Temperature Employing Typical BOX Ligands

As two typical substituted styrene monomers, 4-bromostyrene (4-BrSt) and 4-methylphenylene (4-MeSt) were polymerized by employing ligands **L0**, **L5**, **L5b** and **L5d**, respectively, in order to correlate electronic effect of the monomer with polymerization rate and controllability in the chosen system. Different from the polymerization of styrene, **L5b** was more efficient than **L5d** for the polymerizations of these two substituted styrene monomers, probably due to the varied polarity of the reaction system employing different monomers. When 4-MeSt was used as the monomer instead of styrene, the polymerization rate was slower (achieving a conversion of 45% in 69 h) and the MW distribution was broader (Đ = 1.5) by using **L5b** as the ligand. By contrast, 4-BrSt with an electron-withdrawing (EW) substituent led to a faster polymerization rate and a good controllability compared with styrene, giving a conversion of 53% in 39 h and producing polymers with narrow MW distribution (Đ = 1.3). These results are consistent with the previous reports and due to that an EW substituent increases the energy of the dormant species P-X by destabilizing the partial positive charge of the carbon at the chain end and consequently decreases the bond dissociation energy of C-X [3].

In order to analyze the retained chain ends precisely by MALDI-TOF



Scheme 1. Ligands and Monomers Employed in Current Work.

Table 1
The ATRP of styrene at ambient temperature[a].

Run	Ligand	Conv.[b]	$M_{n,\ theory}$ (10^3)	$M_{n,\ GPC}$[c] (10^3)	Đ[c]
1	Me_6TREN	15	1.70	7.78	2.4
2	PMDETA	18	2.01	15.4	2.0
3	**L0**	38	4.09	9.28	1.9
4	**L1**	27	2.95	47.1	1.8
5	**L2**	10	1.18	34.5	2.6
6	**L3**	40	4.30	7.57	1.9
7	**L4**	42	4.51	9.60	1.7
8	**L5**	41	4.40	7.56	1.4
9	**L5a**	40	4.30	8.22	1.6
10	**L5b**	44	4.72	6.40	1.3
11	**L5c**	48	5.13	7.32	1.5
12	**L5d**	50	5.34	6.74	1.4
13	**L5e**	50	5.34	7.56	1.5

[a] Reaction conditions: $n(M):n(BPN):n(CuBr_2):n(Ligand):n(Cu(0)) = 200:2:1:2:4$, $n(M) = 5$ mmol, at ambient temperature (25 ± 2) °C, THF (0.1 mL) was employed as the solvent to prepare the catalyst solution, 48 h.

[b] Monomer conversion measured by ^1H NMR.

[c] Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, $Đ = M_w/M_n$.

MS and ^1H NMR, polymers with low MWs were prepared using ligand **L5b** or **L5d** (Supplementary Table S1). The ^1H NMR spectra (Fig. 2 and Supplementary Figs. S1–2) of polystyrene, poly(4-MeSt) and poly(4-BrSt) indicated the presence of bromo-terminated chains ($\delta = 4.34–4.64$ ppm for CH(Ph)Br, $\delta = 4.37–4.66$ ppm for CH(4-MePh)Br, $\delta = 4.12–4.52$ ppm for CH(4-BrPh)Br, respectively, in $CDCl_3$) [13], characteristic of chains obtained through an ATRP mechanism. The MALDI-TOF spectrum (Fig. 3) of polystyrene showed three families of peaks. The main and tiny peaks correspond to analytes having the formulas $CH_3CH(CN)(Sty)_nCH = CH(Ph)Ag^+$ and $CH_3CH(CN)(Sty)_{n+1}CH{=}CH(Ph)K^+$, respectively. As vinyl-terminated end-group resonances are not observed in the NMR, it was believed that these species correspond to bromo-terminated chains that have undergone a dehydrobromination process upon contact with the silver salt [13]. The other set of peaks match the molecular formula $CH_3CH(CN)(Sty)_nCH_2CH(Ph)BrK^+$, namely the dormant chains formed during ATRP with the potassium ions. Similarly, the MALDI-TOF spectrum of poly(4-MeSt) shows two families of peaks (Supplementary Fig. S3). The main peaks correspond to the molecular formula $CH_3CH(CN)(4\text{-}MeSt)_nCH = CH(4\text{-}MePh)Ag^+$. The other set of peaks match the species having the molecular formula $CH_3CH(CN)(4\text{-}MeSt)_nCH_2CH(4\text{-}MePh)$

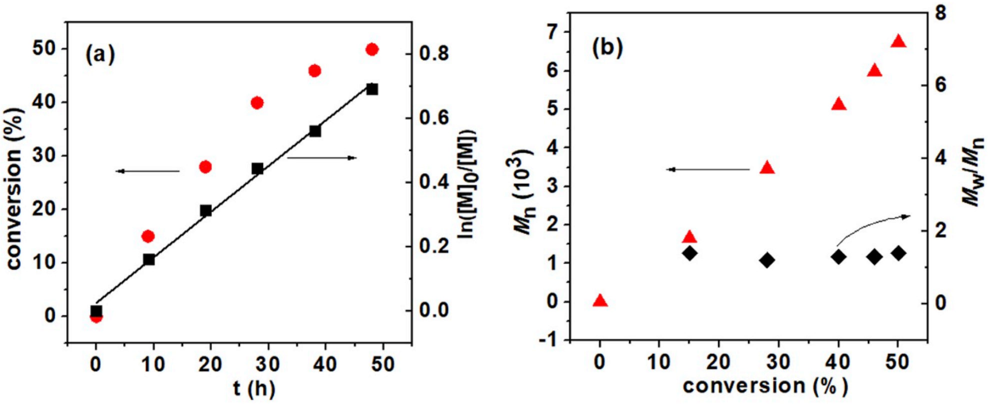


Fig. 1. (a) First-order kinetic plot as well as (b) evolution of MW and Đ (M_w/M_n) as a function of conversion for ATRP of styrene employing **L5d** as the ligand at ambient temperature.

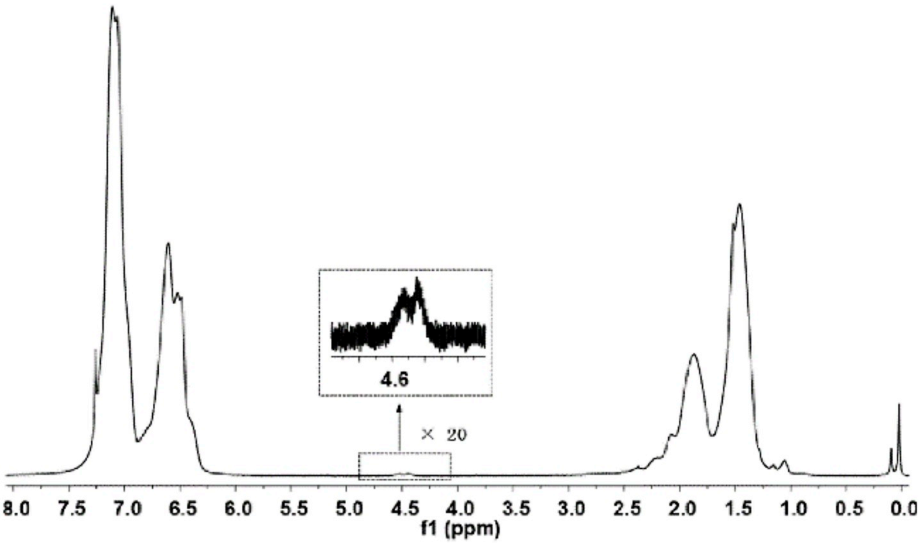


Fig. 2. ^{1}H NMR spectrum (CDCl$_3$, 25 °C) for PS with a low polymerization degree (run 1 in Table S1).

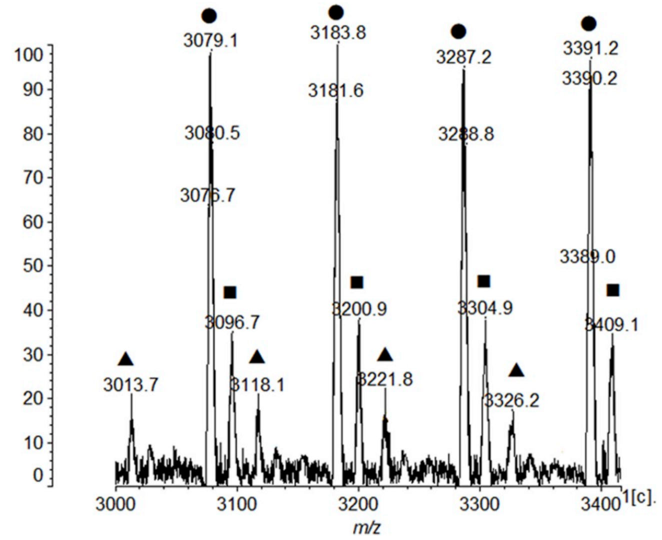


Fig. 3. MALDI-TOF mass spectrum of PS with a low polymerization degree (run 1 in Table S1). ●: $CH_3CH(CN)(Sty)_nCH = CH(Ph)Ag^+$, ■: $CH_3CH(CN)(Sty)_nCH_2CH(Ph)BrK^+$, ▲: $CH_3CH(CN)(Sty)_{n+1}$ $CH{=}CH(Ph)K^+$.

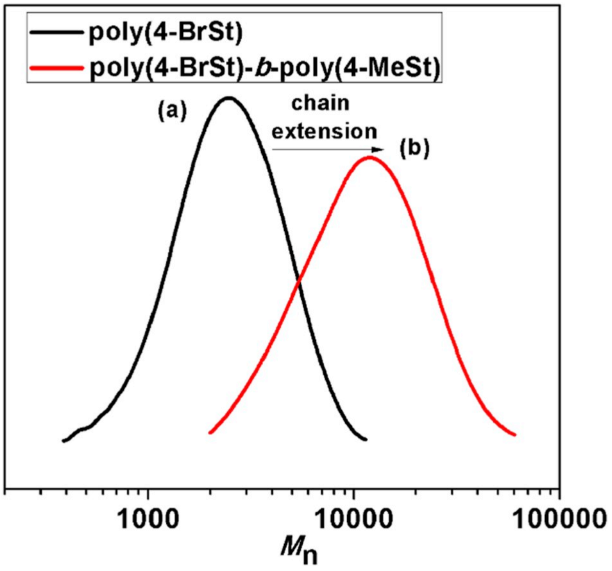


Fig. 4. GPC traces of (a) poly(4-BrSt) homopolymer (M_n = 3370, Đ = 1.5); (b) block copolymer poly(4-BrSt)-*b*-poly(4-MeSt) (M_n = 8227, Đ = 1.4).

BrK^+, namely the dormant chains with the potassium ions. To demonstrate the presence of an active end group, a poly(4-BrSt) homopolymer (M_n = 3370, Đ = 1.5) was employed as macroinitiator for chain extension with 4-MeSt as the monomer at 60 °C under the similar polymerization conditions mentioned above for 42 h. A clear shift in the MW and a final M_n of 8227 as well as a low dispersity value (final Đ = 1.4) were observed by GPC, demonstrating high end group fidelity of the resultant poly(4-BrSt) (Fig. 4). These results manifested that all the polymerizations of styrene, 4-MeSt and 4-BrSt proceeded in ATRP manner.

2.3. The Polymerization of 4-MeOSt under (SARA) ATRP Conditions

According to previous reports, the conventional ATRP of 4-MeOSt, which bears a strong ED substituent on the para-position of styrene monomer, only gave oligomers, probably because of the formation of cationic propagating species via the heterolysis of the dormant C–Br or the oxidation of free radicals by Cu(II) species [4]. To our surprise, the polymerization of 4-MeOSt was very fast and the controllability was good by the $CuBr_2$/**L5b** catalytic system (run 11 in Table 2), giving a high conversion of 61% in 2.5 h and producing polymers with high MW ($M_n = 7.97 \times 10^3$, Đ = 1.2). This seemed that the stability of the secondary radical might have a much more important influence on the activation rate (Scheme 2). Because a possible extra contributing structure, drawn as radical I, provided additional stabilization for the radical generated by dissociation of C-X [14]. Therefore, the polymerization rate was much faster than that for styrene. Another possible reason is that cationic active species existed in the system, and the polymerizations partially proceeded via cationic mechanism. By contrast, Me_6TREN and PMDETA gave much lower conversions of ca. 20% over a much longer period of time, and their control over MW were very poor under the same conditions (runs 13–14).

In order to understand the mechanism for the polymerization of 4-MeOSt, we analyzed the structure of the resultant polymer in details and found the structure of poly(4-MeOSt) was much different from those of the polymers mentioned above. The ^{1}H NMR spectrum of poly(4-MeOSt) indicated the presence of bromo-terminated chains (Supplementary Fig. S4, δ = 4.09–4.37 ppm for CH(4-MeOPh)Br in $CDCl_3$) [13], characteristic of chains obtained through an ATRP

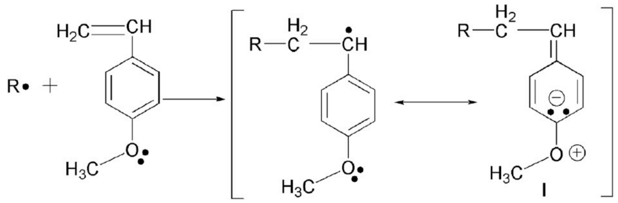
Table 2
The ATRP of substituted styrene monomers at ambient temperature[a].

Run	Monom.	L	t (h)	Conv.[b]	$M_{n,\ theory}$ (10^3)	$M_{n,\ GPC}$[c] (10^3)	Đ[c]
1	4-MeSt	**L0**	69	34	4.15	13.1	1.9
2		**L5**	69	37	4.51	7.15	2.0
3		**L5b**	69	45	5.45	9.56	1.5
4		**L5d**	69	40	4.86	8.57	1.6
5	4-BrSt	**L0**	39	45	8.37	12.9	2.0
6		**L5**	39	47	8.74	11.4	2.4
7		**L5b**	39	53	9.84	10.8	1.3
8		**L5d**	39	47	8.74	9.71	1.5
9	4-MeOSt	**L0**	36	24	3.35	26.4	2.2
10		**L5**	5.0	44	6.04	5.55	1.2
11		**L5b**	2.5	61	8.32	7.97	1.2
12		**L5d**	7.0	50	6.84	5.39	1.2
13		Me_6TREN	116	20	2.82	8.57	1.6
14		PMDETA	67	21	2.95	9.51	1.7

[a] Reaction conditions: $n(M):n(BPN):n(CuBr_2):n(Ligand):n(Cu(0))$ = 200:2:1:2:4, $n(M)$ = 5 mmol, at ambient temperature (25 ± 2) °C, THF (0.1 mL) was employed as the solvent to prepare the catalyst solution.

[b] Monomer conversion measured by ^1H NMR.

[c] Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, $Đ = M_w/M_n$.



Scheme 2. Plausible Mechanism for the Radical Polymerization of 4-MeOSt.

mechanism. However, the signals corresponding to vinyl-terminated end-group were observed at 5.73–6.11 ppm, resulting from transfer reactions [4]. This is characteristic of chains obtained through a cationic polymerization mechanism. We also employed MALDI-TOF to analyze the structure of poly(4-MeOSt). Considering that the initiator BPN has a very similar molecular weight with the monomer 4-MeOSt, we employed EBPA (ethyl α-bromophenylacetate) as the initiator to prepare the sample (M_n = 5433) for an accurate analysis. The MALDI-TOF spectrum (Supplementary Fig. S5) of poly(4-MeOSt) showed three families of peaks. The two main peak groups matched the molecular formulas $CH_3CH_2OOCCH(Ph)(4\text{-}MeOSt)_nCH_2CH(4\text{-}MeOPh)BrK^+$ and $CH_3CH_2OOCCH(Ph)(4\text{-}MeOSt)_{n+1}CH{=}CH(4\text{-}MeOPh)Na^+$, which correspond to polymers produced by the initiation of EBPA. The other peaks correspond to analyte having the formula $H(4\text{-}MeOSt)_{n+2}CH{=}CH(4\text{-}MeOPh)K^+$, confirming that a small amount of polymers were produced via cationic polymerization, namely by the initiation of H^+ formed during chain transfer process.

2.4. *The Temperature Effect on ATRP of Styrene and Substituted Styrene Monomers*

With these highly active ligands in hand, we subsequently investigated the temperature effect on ATRP of styrene type monomers. Firstly, we conducted the polymerizations of 4-MeOSt at different temperatures (−20–60 °C) under the similar conditions mentioned above. As shown in Table 3, using EBPA as the initiator, the polymerization of 4-MeOSt at 60 °C proceeded very quickly and achieved a high conversion of 72% in 0.5 h by the ligand **L5b**. However, the resultant polymer possessed a molecular weight much lower than the theoretical value ($M_n = 5.91 \times 10^3$) and the molecular weight distribution was relatively broad (Đ = 1.6). The ^1H NMR spectrum of the polymer (Supplementary Fig. S6) indicated the conspicuous signals ascribed to vinyl-terminated end-group (5.73–6.11 ppm) but the absence of peaks corresponding to bromo-terminated chains (4.09–4.37 ppm) [13]. Besides, as shown in Fig. 5a, the MALDI-TOF MS spectrum of the polymer showed two set of peaks having the formula $H(4\text{-}MeOSt)_{n+1}CH{=}CH(4\text{-}MeOPh)H^+$ and $H(4\text{-}MeOSt)_nCH = CH(4\text{-}MeOPh)Ag^+$, respectively. These results confirmed that nearly all the polymers were produced via the mechanism of cationic polymerization at 60 °C due to the H^+ transfer process. While, the polymerization of 4-MeOSt at ambient temperature was mild and the conversion reached to 67% in 6.0 h. The molecular weight ($M_n = 9.20 \times 10^3$) was close to the theoretical value and the molecular weight distribution was narrow (Đ = 1.2). As mentioned above, the ^1H NMR and MALDI-TOF MS analysis indicated that at ambient temperature, the poly(4-MeOSt) was mainly produced via ATRP mechanism (Supplementary Figs. S4–5). Further lowering the polymerization temperature to 0 °C, the MALDI-TOF MS and NMR analysis indicated that the poly(4-MeOSt) components produced via cationic polymerization were almost negligible (Supplementary Figs. S7 and S9). The monomer conversion gradually increased with polymerization time and the molecular weight of the polymer gradually rose with the increase of monomer conversion. Moreover, the molecular weight distribution of the polymer remained very narrow (runs 3–6, Table 3). The first-order kinetic plot was linear and the molecular weights agreed with the theoretical values, presenting the characteristics of controllable polymerization (Supplementary Fig. S10). When the polymerization was conducted at −20 °C, the MALDI-TOF MS analysis of the resultant poly(4-MeOSt) (Fig. 5b) showed only one set of peaks matching the molecular formula $CH_3CH_2OOCCH(Ph)(4\text{-}MeOSt)_nCH = CH(4\text{-}MeOPh)K^+$, which correspond to polymers produced by the initiation of EBPA in an ATRP manner. In addition, the ^1H NMR spectrum of the polymer indicated the presence of bromo-terminated chains (Supplementary Fig. S8, δ = 4.09–4.37 ppm for $CH(4\text{-}MeOPh)Br$ in $CDCl_3$) [13], while no signals corresponding to vinyl-terminated end-group were observed (5.73–6.11 ppm), indicating that nearly all the polymers were produced via ATRP mechanism. These results demonstrated that the low polymerization temperature enabled by SaBOX/Copper catalysts is necessary to suppress side reactions, such as transfer reaction and cationic polymerization, during ATRP of 4-MeOSt to produce polymers with controlled MWs.

We also studied the temperature effect on the stereospecificity for the ATRP of styrene. As shown in Table 3 and Fig. 6, the polystyrene produced by **L5d** at 60 °C possesses the rr value of 48%, which was analyzed and calculated according to literature [15], while the polymerization at ambient temperature provided polystyrene with a higher rr value of 51% (Supplementary Fig. S11). Surprisingly, the polymerization temperature for styrene could be lowered to −30 °C by the employment of the novel SaBOX ligand **L5d** and the syndiotacticity was further improved with the rr value gradually increasing to 62% (Fig. 6 and Supplementary Figs. S11–13). At the same time, the molecular weight distribution was narrow (Đ = 1.2), indicative of the excellent controllability of the polymerization. These results were very unusual, as nearly no conversion of styrene was detected in 90 h at 0 °C when Me_6TREN and PMDETA were employed as the ligands (runs 13–14). Different from the previous report [15a], the above results showed that the stereochemistry could be tuned in the radical polymerization of styrene for the first time.

As discussed above, the investigations about the SaBOX ligands enabled low temperature ATRP demonstrated the advantage or necessity in some respects, such as reducing side reactions and improving stereoregularity.

3. Experiments

3.1. *Polymerization*

All polymerizations were set up and performed under an atmosphere of oxygen-free, dry argon using standard Schlenk-line techniques or inside a nitrogen-filled glovebox. In an ampule equipped with a magnetic stirrer bar, a mixture of $CuBr_2$, ligand and Cu(0) powder in solvent was stirred at room temperature for 2 h under the atmosphere of

Table 3
The (SARA) ATRP at different temperatures[a].

Run	Monomer	L	T (°C)	t (h)	Conv.[b] (%)	$M_{n,\ theory}$ (10^3)	$M_{n,\ GPC}$[c] (10^3)	Đ[c]	rr/mr/mm[d] (%)
1	4-MeOSt	**L5b**	60	0.5	72	9.90	5.91	1.6	–
2		**L5b**	25	6.0	67	8.56	9.20	1.2	–
3		**L5b**	0	15	17	2.52	2.87	1.2	–
4		**L5b**	0	25	26	3.73	3.58	1.2	–
5		**L5b**	0	40	39	5.48	5.28	1.2	–
6		**L5b**	0	50	49	6.82	6.51	1.1	–
7[e]		**L5b**	−20	100	21	3.06	3.16	1.2	–
8	St	**L5d**	60	28	89	9.40	9.00	1.3	48/40/12
9		**L5d**	25	48	50	5.34	6.74	1.4	51/40/9
10		**L5d**	0	90	33	3.57	5.61	1.5	54/37/9
11		**L5d**	−20	100	17	1.90	4.85	1.2	56/38/6
12		**L5d**	−30	142	17	1.90	3.51	1.2	62/32/6
13		**Me$_6$TREN**	0	90	trace	–	–	–	–
14		**PMDETA**	0	90	trace	–	–	–	–

[a] Reaction conditions: n(M):n(Initiator):n(CuBr$_2$):n(Ligand):n(Cu(0)) = 200:2:1:2:4, n(M) = 5 mmol, THF (0.1 mL) was employed as the solvent to prepare the catalyst solution, Initiator = BPN for monomer styrene and Initiator = EBPA for monomer 4-MeOSt.

[b] Monomer conversion measured by ^{1}H NMR.

[c] Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, Đ = M_w/M_n.

[d] Tacticity determined by ^{13}C NMR.

[e] THF (0.34 mL) was employed as the solvent.

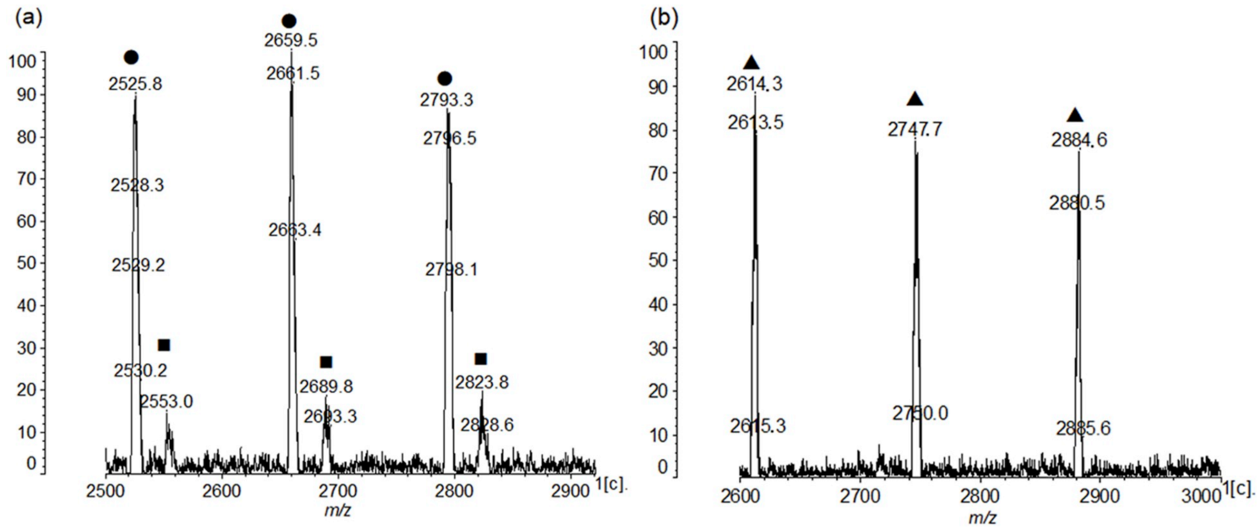


Fig. 5. MALDI-TOF mass spectra of poly(4-MeOSt) produced respectively at 60 °C (a) and −20 °C (b) by **L5d** (runs 1 and 7 in Table 3). ●: H(4-MeOSt)$_n$CH = CH(4-MeOPh)Ag$^+$, ■: H(4-MeOSt)$_{n+1}$ CH=CH(4-MeOPh)H$^+$, ▲: CH$_3$CH$_2$OOCCH(Ph)(4-MeOSt)$_n$CH = CH(4-MeOPh)K$^+$.

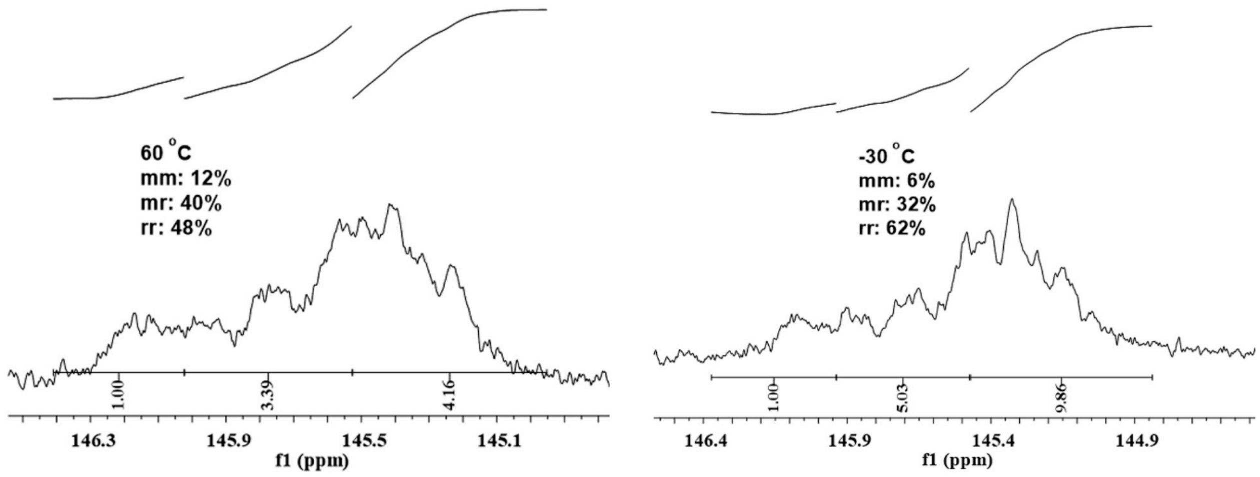


Fig. 6. Quaternary carbon spectral assignments of the polystyrenes produced by **L5d**/copper catalyst at 60 °C and −30 °C (runs 8 and 12 in Table 3), according to the literature [15] (1, 1, 2, 2-Tetrachloroethane-d_2, 80 °C).

nitrogen. Then, the catalyst mixture was cooled to a certain temperature for 20 min if necessary. After that, monomer and initiator were added into the ampule. The ampules were placed at a certain temperature. After stirring for the allotted period of time, an aliquot (0.05 mL) was removed and quenched with $CDCl_3$ (0.5 mL). Conversion was determined by integration of the monomer vs. polymer resonances in the ^1H NMR spectrum of the crude product. After completion of the reaction, the contents of the ampules were dissolved in THF. The solution was filtered through a glass funnel with neutral alumina. The filtrate was concentrated under reduced pressure. The residuals were resolved with 5 mL THF. This solution was added to an approximately 50-fold excess of rapidly stirred methanol. The precipitate that formed was filtered and washed with methanol. The precipitate was dried to constant weight in a vacuum oven at 50 °C.

4. Conclusions

In summary, the current work successfully realized the very controlled ambient temperature (SARA) ATRP of styrene and substituted styrenes, whatever the substituent is strongly electron-withdrawing or electron-donating for the first time by the employment of highly active SaBOX ligand, which was shown to proceed with living characteristics (linear evolution of molecular weight with conversion, relatively narrow molecular weight distribution, and good adherence to expected molecular weight as well as retained active C–Br chain-end functionalities). Under ATRP conditions, the current methods provided polymers of 4-MeOSt rather than commonly produced oligomers, due to the suppressed cationic polymerization process by lowering reaction temperature. Besides, the (SARA) ATRP of styrene could proceed at −30 °C, furnishing polystyrenes exhibiting controlled molecular weights ($Đ = 1.2–1.4$) and enhanced syndiotacticity (with rr value up to 62%). By analyzing and comparing the structure of polymers obtained at high temperature (60 °C) and low temperature (25 °C ∼ −30 °C), it was found that SaBOX enabled low temperature ATRP of styrene and substituted styrenes would be advantageous and necessary in some aspects, as side reactions occurred less readily at lower temperatures and the polymers produced at lower temperatures exhibited higher stereoregularity. Therefore, this work is an attractive and promising supplement for the burgeoning ATRP methodology.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2019.121630.

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