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Jieai Li[a]; Xiulin Zhu[a]; Jian Zhu[a]; Zhenping Cheng[a]
[a] Key Lab. of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, P. R. China

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Imidazoline Nitroxide-Mediated Radical Polymerization of Styrene

JIEAI LI, XIULIN ZHU, JIAN ZHU, and ZHENPING CHENG

Key Lab. of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou, P. R. China

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Nitroxide-mediated radical bulk polymerizations of styrene were successfully performed using imidazoline nitroxide as mediator. The polymerizations proceeded in a controlled manner. The obtained polymers showed an increase in molecular weight with conversion and narrow molecular weight distributions. The structure of the imidazoline nitroxide, molar ratio of $[\text{styrene}]_0/[\text{BPO}]_0/[\text{nitroxide}]_0$ and the temperature had a considerable effect on the polymerization. The ^{1}H-NMR was used to characterize the obtained polystyrene. The living nature of the polymer was confirmed by successful chain extension reaction of the resulting polystyrene.

Keywords: imidazoline nitroxide; kinetics; living polymerization; nitroxide-mediated radical polymerization (NMRP); polystyrene

1 Introduction

Along with the development of living/controlled free radical polymerization techniques, nitroxide-mediated radical polymerization (NMRP) has attracted considerable interest in recent years (1–3). In NMRP process, both the initiating radicals and the propagating polymeric radicals can be reversibly terminated by the stable nitroxide free radical, (i.e., 2,2,6, 6,-teramethyl-1-piperidinyloxy (TEMPO)), to form a dormant chain. As a result, the concentration of propagating polymer chains in the reaction medium is reduced. Consequently, the rate of bimolecular termination is low and does not lead to a broadening of the molecular weight distributions. Because the dormant chains are thermally labile, especially at high temperature, they can be extended by combining further monomers.

In the NMRP systems, TEMPO and its derivatives were widely used as nitroxide, in conjunction with this process (4–10). In order to enrich the mediator family for NMRP, great effort has been made and a variety of nitroxides, such as di-tert-butyl nitroxide (11, 12), 1,1,3,3-tetraethyl-1,3-dihydroisoindol-2-yloxyl (13), 2,2,5,5-tetrasubstituted pyrrolidinyl-N-oxyl (14–16), oxazolidinyl-N-oxyl (14), morpholine and morpholone type nitroxide (17), imidazolidinone nitroxide (18, 19), and seven- or eight-membered cyclic nitroxides (20), have been introduced in nitroxide-mediated polymerization. The most significant breakthrough in the design of improved nitroxide was the use of alicyclic nitroxides with a hydrogen atom on one of the α-carbons including N-tert-butyl-N-(1-diethylphosphono-(2,2-dimethylpropyl)) nitroxide, (21–24), N-tert-Butyl-N-(1-tert-butyl-2-ethylsulfinyl)propyl nitroxide (25, 26), nitrone (27) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (28–30).

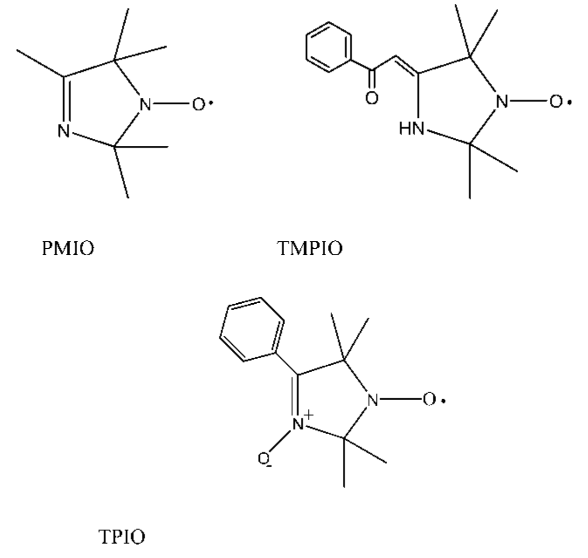
Most of nitroxides are inclined to undergo side reactions (e.g., disproportionation of propagating polymeric radical with nitroxide or chain transfer to nitroxide) (18). Five-membered ring nitroxides are subject to fewer side reactions and they are involatile, which provides an advantage over some commonly used nitroxides (i.e., TEMPO and di-tert-butyl nitroxide). Encouraged by the advantages associated with the use of five-membered ring nitroxides, in this article, we first report the use of five-membered ring imidazoline nitroxides (Scheme 1) on controlled radical polymerization of styrene.

2 Experimental

2.1 Materials

Styrene (St) (Chemically pure, Shanghai Chemical Reagent Co. Ltd., China) was washed with 5% sodium hydroxide solution, and deionized water until neutralization, then dried with sodium sulfate anhydrous overnight, and finally distilled under vacuum before use. Benzoyl peroxide (BPO) (Chemically pure, Shanghai Zhong Li Chemical Co., China) was recrystallized from chloroform and petroleum ether twice.

Address correspondence to: Xiulin Zhu, Key Lab. of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, P. R. China. Fax: 86-512-65112796; E-mail: xlzhu@suda.edu.cn



Sch. 1. Chemical structures of imidazoline nitroxides. 2,2,4,5,5-pentamethyl-3-imidazoline-1-oxyl (PMIO) 2,2,5,5-tetramethyl-4-phenacetyliden-imidazolidine-1-oxyl (TMPIO) 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl (TPIO).

2,2,4,5,5-Pentamethyl-3-imidazoline-1-oxyl (PMIO) (98%, ACROS), 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl (TPIO) (98%, ACROS) and 2,2,5,5-tetramethyl-4-phenacetyliden-imidazolidine-1-oxyl (TMPIO) (98%, ACROS) were used as received.

2.2 Polymerizations

A series of polymerizations of styrene using BPO as an initiator in conjunction with imidazoline nitroxide were performed. A typical polymerization procedure for PMIO-mediated system was as follows: styrene (1 mL, 8.71 mmol) was added to a dry ampoule tube containing the solid mixture of BPO (10.6 mg, 0.0438 mmol) and PMIO (14.3 mg, 0.092 mmol). The ampoule was degassed under vacuum and charged with argon (5 times). Then the ampoule was flame-sealed, and placed in an oil bath held by a thermostat at the desired temperature for polymerization. After the desired polymerization time, the ampoule was quenched in ice water to stop the polymerization and opened. The contents were dissolved in tetrahydrofuran (4 mL) and precipitated into a large amount of methanol (about 300 mL). The polystyrene was dried until constant weight achieved.

For TMPIO-mediated system, styrene (1 mL, 8.71 mmol) was added to a dry ampoule tube containing the solid mixture of BPO (10.6 mg, 0.0438 mmol) and TMPIO (23.8 mg, 0.092 mmol). The other procedures were the same as the PMIO-mediated system.

For the TPIO-mediated system, styrene (1 mL, 8.71 mmol) was added to a dry ampoule tube containing the solid mixture of BPO (10.6 mg, 0.0438 mmol) and TPIO (21.4 mg, 0.092 mmol). The other procedures were the same as the PMIO-mediated system.

2.3 Chain Extension Polymerization

St was added to a dry ampoule containing the obtained polystyrene (PS) (0.1 g) which was capped by PMIO ($[St]_0/[PS]_0 = 100:1$). The ampoule was degassed under vacuum and charged with argon (5 times), and ampoule was flame-sealed and then placed in an oil bath held by a thermostat at 135°C to perform chain extension polymerization. After 15 h, the ampoule was cooled using ice water. The other procedures were the same as above.

2.4 Characterizations

The monomer conversion of the polymerization was determined gravimetrically. The molecular weights (M_n) and molecular weight distributions (M_w/M_n) of the polymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with a refractive index detector, using HR 1, HR 2, and HR 4 column with molecular weight range $100 \sim 500{,}000$ calibrated with polystyrene standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min operated at 30°C. ^{1}H-NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as the internal standard. Semiempirical molecular orbital calculations (AM1) (31) were performed using the Mopac150 program. Glass-transition temperature (T_g) of the obtained PS was measured by Pyris Diamond DSC.

3 Results and Discussion

3.1 Effect of Different Imidazoline Nitroxide on Polymerization

Figure 1 shows the kinetic plots of $\ln([M]_0/[M])$ vs. polymerization time for the nitroxide-mediated radical polymerizations of styrene. As shown in Figure 1, the

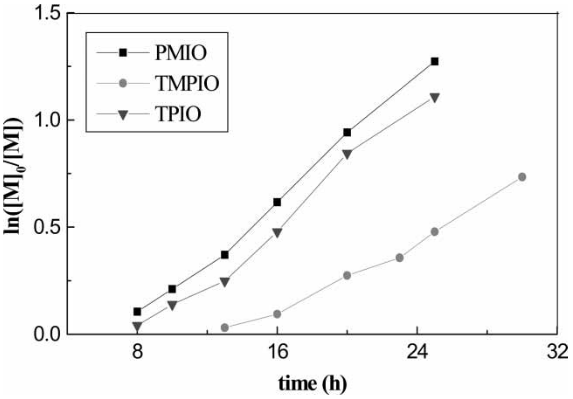


Fig. 1. Kinetic plots of $\ln([M]_0/[M])$ vs. reaction time for nitroxide-mediated polymerization of styrene in the cases of different imidazoline nitroxides. Conditions: temperature $= 125°C$; $[styrene]_0 = 8.71$ M; $[BPO]_0 = 0.0438$ M; $[imidazoline\ nitroxide]_0 = 0.092$ M.

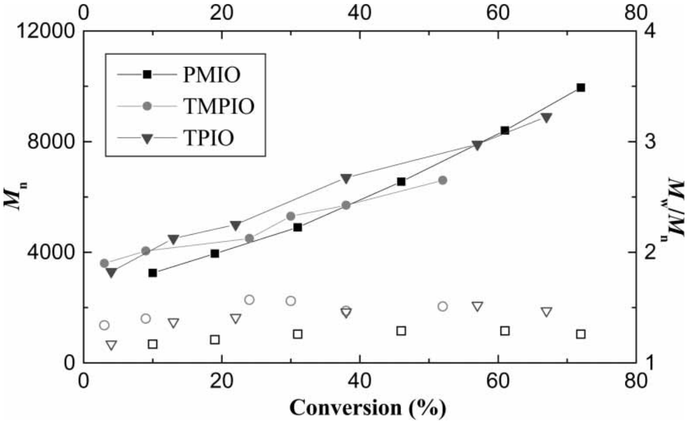


Fig. 2. Dependence of M_n and M_w/M_n on monomer conversions for nitroxide-mediated polymerization of styrene in the cases of different imidazoline nitroxides. Other conditions are the same as in Figure 1.

kinetic plots presented approximate first-order kinetics with respect to the monomer concentration in all cases. Under the conditions employed, the PMIO-mediated polymerization rate was highest among these experimented imidazoline nitroxide systems. Dependence of M_n and M_w/M_n on monomer conversions is illustrated in Figure 2. The M_ns increased linearly with monomer conversion and there was little difference among three imidazoline nitroxide-mediated systems. Use of PMIO provided narrower molecular weight distributions (<1.3) than did other nitroxide tested during this investigation. TMPIO and TPIO used were found to give broad M_w/M_n (about 1.5), except at the beginning of the polymerization. The rate constants and equilibrium constant associated with C-O bond homolysis and reformation are known to be of critical importance (32). The rate constants for C-O bond homolysis are strongly dependent on the structure of the nitroxide (and the carbon-centered radical) formed (33). Therefore, the effect of varying the imidazoline nitroxide structure on the C-O bond length was also examined. Theoretical calculations are presented in Table 1. C-O bond homolysis become easier with the increase of C-O bond length. Compared with PMIO, TMPIO and TPIO have a shorter bond length (C-O) of derived alkoxyamines, which correspondingly affected reverse coupling reaction (between nitroxide and the carbon-centered radical) and account for broad M_w/M_n.

Table 1. Bond length (C-O) of derived alkoxyamines estimated from AM1 molecular orbital calculations

Nitroxide	PMIO	TMPIO	TPIO	TEMPO
Bond length (Å)	1.4442	1.4431	1.4433	1.4489

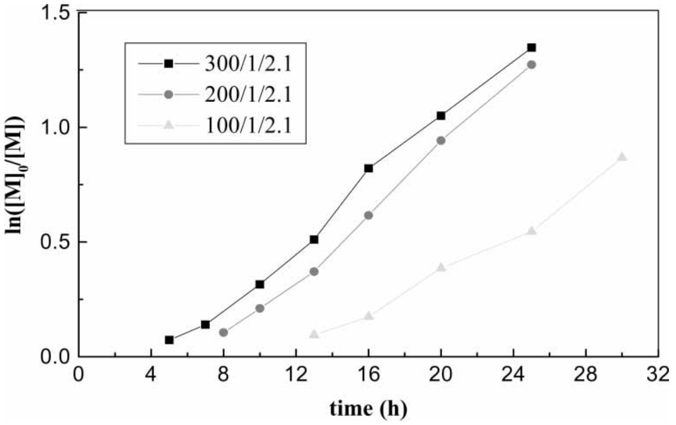


Fig. 3. Kinetic plots of $\ln([M]_0/[M])$ vs. reaction time at different $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ for nitroxide-mediated polymerization of styrene. Conditions: temperature $= 125°\text{C}$; $[\text{styrene}]_0 = 8.71$ M.

3.2 *Effect of Ratios of [Styrene]$_0$/[BPO]$_0$/[PMIO]$_0$ on Polymerization*

The effects of a different ratio of $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ on polymerization of styrene has also been investigated. Kinetic plots of the polymerization are presented in Figure 3. The kinetic plots of $\ln([M]_0/[M])$ vs. reaction time were linear in all cases. The molar ratio of $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ clearly showed an effect on the induction time and the rate of polymerization. These effects are reflected in the increase of the polymerization rate and the trend for induction time to decrease with the increase in the ratio of $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ can be observed. As shown in Figure 4, a linear increase of M_n with monomer conversion and relatively low M_w/M_n in all cases were observed. All these results illustrated the living characteristic of the

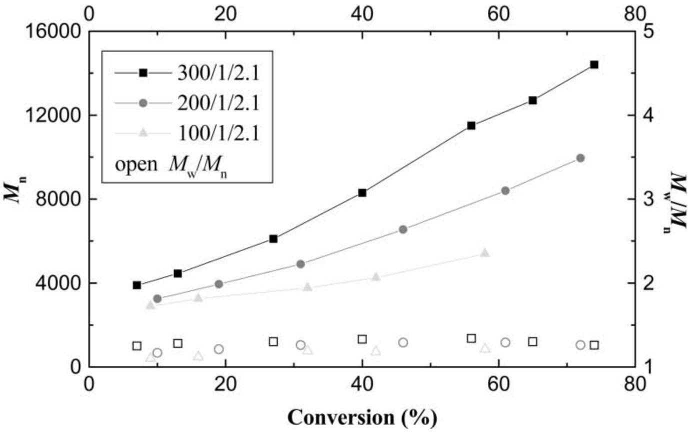


Fig. 4. Dependence of M_n and M_w/M_n on monomer conversions at different $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ for nitroxide-mediated polymerization of styrene. Other conditions are the same as in Figure 3.

polymerizations. The M_ns of obtained polymers with $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0 = 100/1/2.1$ were increased slowly with monomer conversion. An increase in the $[\text{styrene}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ resulted in an larger M_n at equivalent conversion.

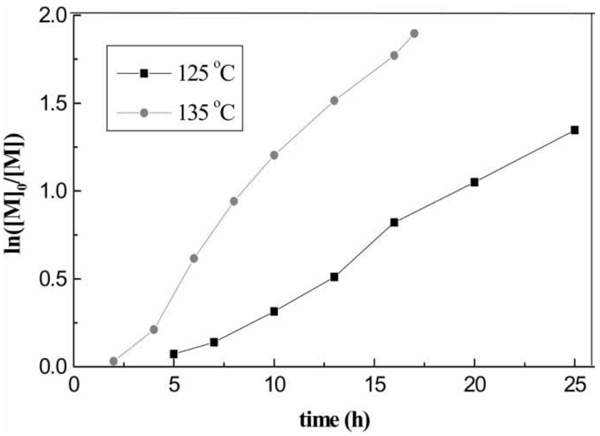


Fig. 5. Kinetic plots of $\ln([M]_0/[M])$ vs. reaction time at different temperatures for nitroxide-mediated polymerization of styrene. Conditions: $[\text{styrene}]_0 = 8.71$ M; $[\text{BPO}]_0 = 0.029$ M; $[\text{PMIO}]_0 = 0.061$ M.

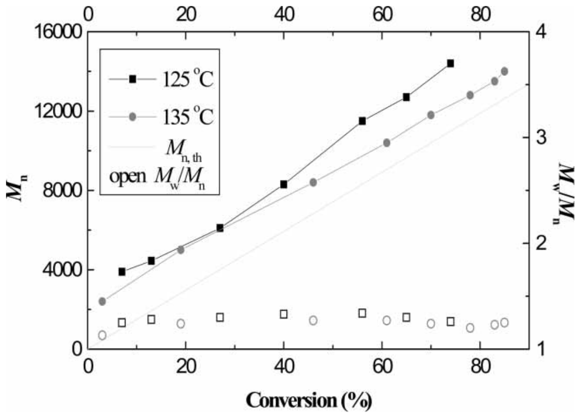


Fig. 6. Dependence of M_n and M_w/M_n on monomer conversions at different temperature for nitroxide-mediated polymerization of styrene. Other conditions are the same as in Figure 5.

3.3 *Effect of Temperature on Polymerization*

The five-membered nitroxides should be anticipated to be less effective than a similarly substituted piperidin-*N*-oxyl (e.g., TEMPO) (18). As shown in Table 1, bond length (C-O) of alkoxyamines based on imidazoline nitroxide was shorter than that of TEMPO-derived alkoxyamine. The energy for C-O homolysis was increased with the decrease of bond length (C-O). Therefore, it is beneficial to increase temperature for imidazoline nitroxide-mediated polymerization of styrene.

Figure 5 shows the kinetic plots of $\ln([M]_0/[M])$ vs. polymerization time for the imidazoline nitroxide-mediated radical polymerizations of styrene at two different temperatures. The polymerization of styrene started after an induction time and the kinetic plots presented approximate first-order kinetics with respect to the monomer concentration in both cases, indicating that the propagating radical concentration was constant and no significant termination reactions occurred during the polymerization. Temperature has a considerable effect on the rate of polymerization. The polymerization rate increased significantly with the increase of the temperature. For example, the monomer conversion was approximately 70% after 10 h at 135°C, however, only 27% at 125°C. The dependence of molecular weights and their distributions of the polymers on monomer conversion are presented in Figure 6. The M_ns increased linearly with monomer conversion. The M_w/M_n in case of 135°C remained relatively narrow (<1.3) or even lower than that at 125°C.

The nitroxide-mediated polymerization of styrene were also conducted under high $[\text{St}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$ at different

Table 2. Experimental results for the effect of temperature on nitroxide-mediated polymerization of styrene

Ratio[a]	T (°C)	t (h)	Conv. (%)	M_n	M_w/M_n	T_g (C)
100/1/2.1	125	13	9	2900	1.10	—
100/1/2.1	135	13	56	5400	1.21	—
200/1/2.1	125	10	19	3950	1.21	89.4
200/1/2.1	125	13	31	4900	1.26	93.3
200/1/2.1	125	16	46	6550	1.29	95.1
200/1/2.1	125	20	61	8400	1.29	97.4
200/1/2.1	125	25	72	9950	1.26	98.6
200/1/2.1	135	13	75	11100	1.19	98.9
300/1/2.1	125	13	40	8300	1.33	—
300/1/2.1	135	13	78	12800	1.20	—
500/1/2.1	125	8	23	8200	1.46	—
500/1/2.1	135	8	73	18000	1.29	102.5
1000/1/2.1	125	8	43	20400	1.62	—
1000/1/2.1	135	8	80	29400	1.32	104.3

[a] $[\text{St}]_0/[\text{BPO}]_0/[\text{PMIO}]_0$.

temperatures. The effect of the temperature on M_n and M_w/M_n was increased clearly with the increase of $[St]_0/[BPO]_0/[PMIO]_0$ (see Table 2). At 135°C, in the case of a high ratio of $[St]_0/[BPO]_0/[PMIO]_0$ (1000/1/2.1), the conversion reached 80% after 8 h, the M_n of obtained polymer reached 29400, and M_w/M_n also remained relatively narrow (1.32). However, using the same conditions, only 43% conversion was obtained, M_w/M_n became broad and reached 1.62 at 125°C. The glass-transition temperature (T_g) of the obtained PS were also measured. As shown in Table 2, only one single T_g was observed for each sample. The different molecular weight was probably responsible for the difference of the T_g and T_g was increased with the increase of molecular weight.

3.4 Chain Extension Polymerization

According to the nitroxide-mediated radical polymerization mechanism, the polymer obtained could be used as a unimolecular initiator for nitroxide-mediated polymerization of styrene. The GPC curves of PS before and after chain extension are shown in Figure 7.

The sample with $M_n = 8300$ ($M_w/M_n = 1.33$) was used as macroinitiator for polymerization of styrene and the resulting polystyrene with $M_n = 16100$ ($M_w/M_n = 1.31$) was obtained, which indicated that alkoxylamine functionality was present at the chain end of the polymer. Figure 8 shows the ^{1}H-NMR spectrum of the polystyrene obtained by using PMIO as mediator. The chemical shifts at $\delta = 0.2-1.2$ ppm (a) are assigned to five methyl resonances of PMIO. The chemical shifts at $\delta = 7.3-7.9$ ppm (b) correspond to phenyl resonances of BPO. All of the chemical shifts indicate the existence of imidazoline nitroxide and the fragment of BPO in the polymeric chain.

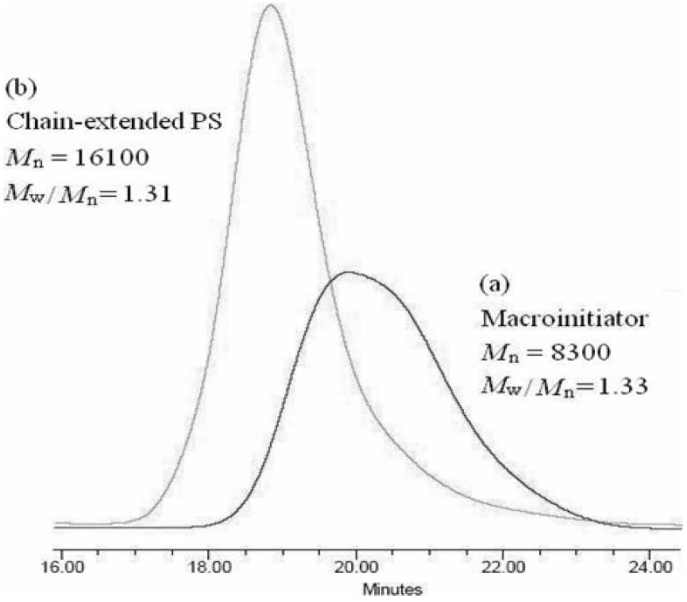


Fig. 7. GPC curves of PS before (a) and after (b) chain extension. Conditions: temperature = 135°C; Time = 15 h; Conversion = 79%; $[St]_0/[PS]_0 = 100: 1$.

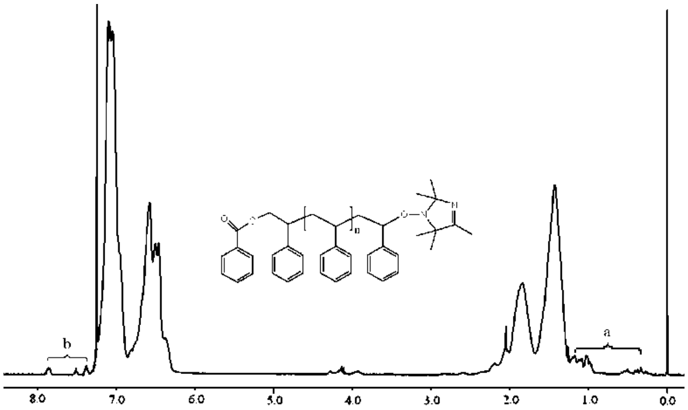


Fig. 8. 400 MHz ^{1}H NMR spectroscopy of polystyrene. Polystyrene: $M_n = 4200$, $M_w/M_n = 1.18$.

4 Conclusions

Well-defined polystyrene could be obtained by using PMIO as the mediator. The structure of the imidazoline nitroxide had an effect on bond length (C-O) of derived alkoxyamine, which affected nitroxide-mediated polymerization of styrene. The increase of polymerization rate and M_n of obtained polymer were observed with the increase of $[styrene]_0/[BPO]_0/[PMIO]_0$. At 135°C, the use of the imidazoline nitroxide, PMIO, maintained living character of polymerization even at high ratio of $[St]_0/[BPO]_0/[PMIO]_0$ (1000/1/2.1).

5 Acknowledgments

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