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ORIGINAL PAPER

Stable free radical polymerization of styrene with 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl as mediators

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Abstract The stable free radical polymerizations of styrene were investigated with five 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl stable radicals as mediators and benzoyl peroxide (BPO) as initiators at 125 °C. The results indicated that the polymerizations proceeded in a "living"/controlled manner, i.e., the polymerization rates were first-order with respect to the monomer concentrations, molecular weights increased linearly with conversions and the molecular weight distributions were relatively low ($M_w/M_n = 1.2–1.4$), ^{1}H NMR analysis of the polymer chain-ends and successful chain extensions. The polymerization rates were faster than that of 4-hydroxyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl (OH-TEMPO) mediated ones. The effects of steric interference of different substitute groups at four-position of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), the molar ratios of stable radical to BPO and the temperature on the polymerizations were investigated.

Keywords Nitroxide-mediated polymerization · Styrene ·
Gel permeation chromatographer (GPC) ·
4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl

Introduction

"Living"/controlled radical polymerization (LCRP) has been widely conducted in research laboratories for the synthesis of a wide variety of polymeric materials. Up

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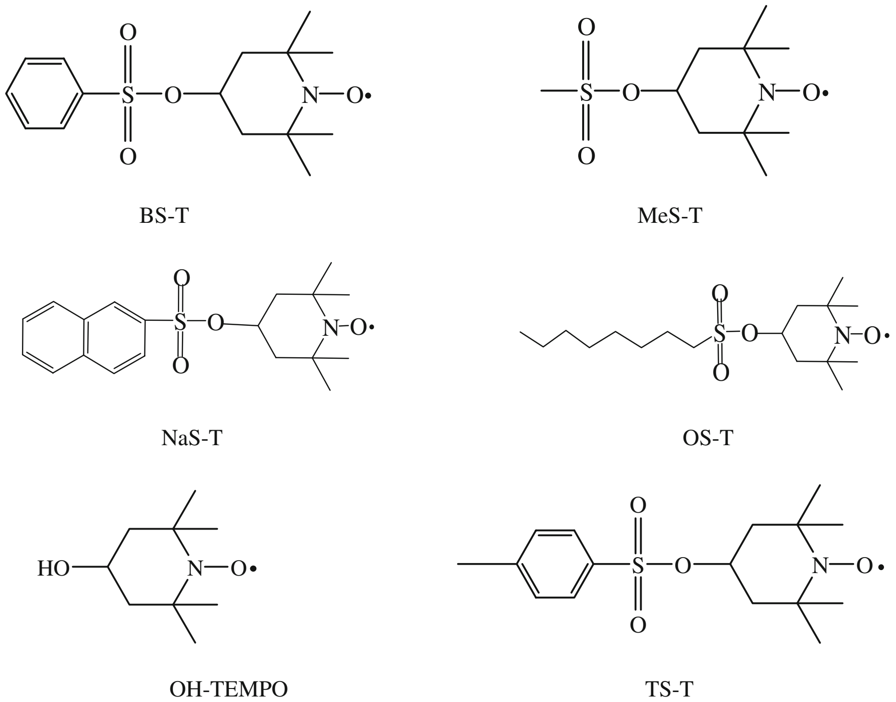
to now, several methods, such as atom transfer radical polymerization (ATRP) [1, 2], nitroxide-mediated polymerization (NMP) [3, 4], reversible addition-fragmentation transfer polymerization (RAFT) [5, 6], have been developed to synthesize well-defined polymers. The success of LCRP relies on the robustness of radical chemistry and the capacity to control the polymer structure, such as predetermined molecular weight, narrow molecular weight distribution, well-defined end groups and architectures, under milder experimental conditions than the living ionic polymerization [7, 8]. Among them, the NMP is an attractive LCRP system because it is metal free and effective in the polymerization of a broad range of monomers with various functionalities. Particularly, NMP provides colorless and odorless polymers with no demanding purification. The control of the NMP process depends on the reversible termination of the growing polymeric radical by the stable nitroxide free radical to give a dormant or inactive species in which the nitroxide moiety is covalently bound to the polymer chain end at high temperature [9–11]. Whenever this equilibrium is shifted toward the dormant form, the stationary concentration of the active species is low and the irreversible chain termination is limited. NMP has witnessed an important advance with the development of a new generation of acyclic nitroxides bearing a hydrogen atom on the α-carbon [9]. These novel nitroxides were able to control the polymerization of not only styrene but also alkyl acrylates, acrylamides, and dienes [12–15].

However, one of the most important disadvantages of NMP is the slow polymerization rate under relatively high polymerization temperature (125–145 °C). In the past years, great efforts have been carried out toward the increase of polymerization rates. One approach to increase polymerization rate is the addition of additives, such as camphorsulfonic acid (CSA) [16], 2-fluoro-1-methylpyridinium *p*-toluenesulfonate [17] and acetic anhydride [18]. Georges et al. [16] demonstrated that the addition of CSA to a BPO-initiated, TEMPO mediated polymerization of styrene increased both the molecular weight and monomer conversion. They deduced that the addition of CSA increased the consumption of TEMPO which could build up during the polymerization, resulting in the rate enhancement. The removal of the excess nitroxide shifts the equilibrium back to the side of the active polymer radical, thus accelerates the polymerization rate. Another approach is using thermal instable nitroxide derivatives to enhance the rate of polymerization, such as 4-acetamido-TEMPO, 4-oxo-TEMPO [19]. It was reported that the structural properties of the nitroxide moiety, including H bonding [20], polar [21], and steric effects [22], could influence the equilibrium constant between nitroxide-capped polymer and free radicals. Hence, the design of nitroxide structure allows the equilibrium constant K shifting toward the free radical species. That is, the reversible deactivation of the growing radicals can be influenced by the type of the nitroxide.

In this work, we first used five nitroxides (Scheme 1) bearing various sulfonate groups, including 4-benzenesulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-methanesulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-(2′-naphthalenesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-(octanesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-(4′-toluenesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, to mediate NMP of styrene. Since sulphonate is similar with CSA in structure, it can be supposed to incorporate into the nitroxide molecular and used as an accelerator.



Scheme 1 Chemical structures of the STNO and OH-TEMPO (*BS-T* 4-benzenesulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl, *MeS-T* 4-methanesulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl. *NaS-T* 4-(2′-naphthalenesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, *OS-T* 4-(octanesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, *OH-TEMPO* 4-hydroxyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl, *TS-T* 4-(4′-toluenesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl)

The nitroxide molecular bearing a sulphonate moiety was expected to control and accelerate the polymerization, simultaneously. Meanwhile, the NMP of styrene mediated with these stable radicals were systemically investigated to examine the steric and bulky effects of the different four-substitute TEMPO-based nitroxides on the polymerization profiles, including the polymerization rate and "living"/controlled features.

Experimental

Materials

Styrene (St. Shanghai Chemical Reagent Co., China, chemically pure) was washed with 5% sodium hydroxide aqueous solution and deionized water until neutralization, then dried with anhydrous sodium sulfate overnight, and finally distilled under vacuum before use. 4-Hydroxyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl (OH-TEMPO) (Wuxi Fu An Chemical Co., China, 97%) was recrystallized from hexane and ethanol. BPO (Shanghai Zhong Li Chemical Co., China, chemically pure) was recrystallized from chloroform and petroleum ether. Toluene sulphonyl chloride (Shanghai She Shan Chemical Plant, China, chemical pure) was recrystallized from petroleum ether. Benzene sulphonyl (Shanghai Ting Xin Chemical Plant, China, chemically pure), methanesulphonyl chloride (Shanghai Chemical Reagent Co., China, chemically pure), 2-naphthalenesulfonyl chloride (ACROS, 97%) and octanesulfonyl chloride (ACROS, 96%) were used without further purification.

Synthesis of 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl [23]

The synthesis of 4-(4′-toluenesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl (TS-T) was a typical procedure. Toluene sulphonyl chloride was added to a stirred solution of OH-TEMPO in dry pyridine at 0–10 °C, and stirring was continued at this temperature overnight. The mixture was then poured into crushed ice. Insoluble TS-T was collected by suction filtration and washed by ice water, then dried in vacuum at room temperature for 48 h, anal. calcd.: C, 58.89; H, 7.36; N, 4.29. Found: C, 58.91; H, 7.56; N, 4.33. Similar procedures are used for BS-T, anal. calcd.: C, 57.67; H, 7.10; N, 4.48. Found: C, 57.95; H, 7.08; N, 4.48, MeS-T, anal. calcd.: C, 47.98; H, 8.05; N, 5.59. Found: C, 47.89; H, 8.36; N, 5.53, NaS-T, anal. calcd.: C, 62.96; H, 6.67; N, 3.86. Found: C, 63.34; H, 6.30; N, 3.97. For the synthesis of liquid OS-T, the liquid mixture was washed with deionized water several times and evaporated under reduced pressure, then dried in vacuum at room temperature for 48 h, anal. calcd.: C, 58.59; H, 9.83; N, 4.02. Found: C, 58.20; H, 9.96; N, 4.00.

Polymerization

A series of polymerizations of styrene using BPO as an initiator in conjunction with OH-TEMPO or 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl were performed. A typical polymerization procedure was as follows: styrene (2.0 mL, 17.4 mmol) was added to a dry ampule tube containing the solid mixture of BPO (14.7 mg, 0.0609 mmol) and OH-TEMPO (12.6 mg, 0.0731 mmol). The contents were purged with nitrogen (N_2) to eliminate oxygen for approximately 10 min, and flame sealed. Then the ampules were firstly placed in an oil bath held by a thermostat at 95 °C for 3 h, then switched to the oil bath of 125 °C to polymerize which was regarded as the beginning of the polymerization. After desired polymerization time, the ampule was put into ice water to stop the polymerization and opened. The contents were dissolved in tetrahydrofuran (about 4 mL) and precipitated into a large amount of methanol (about 300 mL). The obtained polymer was dried in vacuum until constant weight achieved.

Chain extension polymerization

St was added to a flask containing the obtained polystyrene (PSt) (1.0 g) with the 500/1 molar ratio of $[St]_0$ to $[PSt]_0$. The flask was degassed under vacuum and charged with N_2 three times, sealed under N_2 and then heated to 125 °C with magnetic stirring. After 1.5 h, the flask was cooled using cold water. The other procedures were the same as above.

Characterizations

The monomer conversion of the polymerization was determined gravimetrically. The number-average 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 columns with a molecular weight range of 100–500,000 and calibrated with polystyrene standard samples. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min at 30 °C. The elemental analyses for C, H and N were performed on a MOD. 1106 elemental analyzer. ^{1}H NMR spectra of the polymers were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard.

Results and discussion

Effect of different 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl (STNO) on polymerization

The NMPs of styrene in bulk were performed with BPO as an initiator in the presence of the 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl radicals, which is referred to STNO for convenience. In the context, 4-benzenesulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-methanesulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-(2′-naphthalenesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-(octanesulphonate)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-hydroxyl-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-(4′-toluenesulphonate)-2,2,6,6-tetramethylpip eridine-*N*-oxyl are referred to BS-T, MeS-T, NaS-T, OS-T, OH-TEMPO and TS-T, respectively. In this work, the effects of different STNO on the polymerization were studied. For the comparison purpose, the control experiments of styrene polymerization with OH-TEMPO as the stable radical were also carried out. The experimental results are concluded in Figs. 1 and 2.

As shown in the Figs. 1 and 2, the kinetics presented approximately first-order plots for STNO/BPO system, indicating a steady state for propagating radicals. It was also obviously shown in Figs. 1 and 2, that the polymerization had an induction time of 2 h for OH-TEMPO/BPO system. The use of STNO as nitroxide stable free radicals almost eliminated the induction period in BS-T, NaS-T and TS-T medicated systems (Fig. 1), or shortened the induction time in OS-T and MeS-T systems. In addition, the STNO mediated polymerizations were much faster than that mediated by OH-TEMPO/BPO system (Figs. 1, 2). The monomer conversion was close to or greater than 80% after 8 h at 125 °C in the cases of STNO/BPO system, which was 42% only for OH-TEMPO/BPO system.

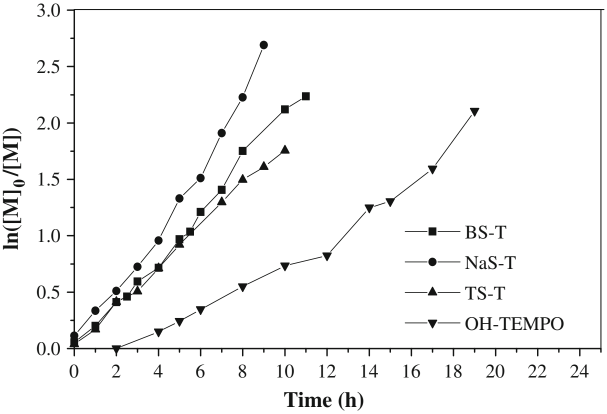


Fig. 1 Kinetic plots of ln($[M]_0/[M]$) versus reaction time for bulk polymerizations of styrene at 125 °C in the cases of different 4-aryl substitute groups of 2,2,6,6-tetramethylpiperidine-*N*-oxyl ($[\mathrm{St}]_0 = 8.71$ M, $[\mathrm{BPO}]_0 = 0.0305$ M, $[\mathrm{STNO}]_0 = 0.0366$ M, $[\mathrm{OH\text{-}TEMPO}]_0 = 0.0366$ M)

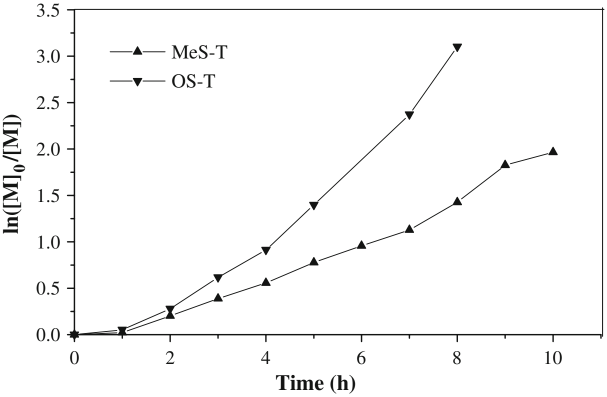


Fig. 2 Kinetic plots of ln($[M]_0/[M]$) versus reaction time for bulk polymerizations of styrene at 125 °C in the cases of different chain length of four-substitute groups of 2,2,6,6-tetramethylpiperidine-*N*-oxyl ($[\mathrm{St}]_0 = 8.71$ M, $[\mathrm{BPO}]_0 = 0.0305$ M, $[\mathrm{STNO}]_0 = 0.0397$ M)

In the Figs. 1 and 2, it also could be seen that different groups at the four position of 2,2,6,6-tetramethylpiperidine-*N*-oxyl had considerable effects on the rate of polymerization. For the substitutional aryl groups, NaS-T had the greatest polymerization rate, and there were no obvious difference in polymerization rate between 4-benzenesulphonate (BS-T) and 4-toluenesulphonate substitute (TS-T) substitutional STNO. Furthermore, it can be found that the polymerization rate increase with the chain length. As shown in Fig. 2, the polymerization rate of 4-octanesulphonate substitutional STNO (OS-T) was much higher than that of 4-methanesulphonate substitutional STNO (MeS-T). When the bulk of substitutional group of four position increased, the rate constant of recombination in the equilibrium (Scheme 2) decreased due to the steric hindrance. As the consequence,

$$P_n\cdot + T\cdot \rightleftharpoons P_n\text{-}T$$

Scheme 2 Equilibrium between dormant ($P_n - T$) and active species ($P_n\cdot$) in nitroxide-mediated polymerization

the stable nitroxide radical and the propagating radicals increased, which promoted the polymerization rate. However, the concomitant was the increased side reactions which broader molecular weight distributions of the polymer as shown in the Figs. 3 and 4. When the OH-TEMPO was used in the control experiment, the equilibrium (Scheme 2) shifted to right side, and the concentrations of radicals were decreased, reflecting in the slower polymerization rate and the less side reactions. Therefore, the values of M_w/M_n for OH-TEMPO mediated system was a litter lower than the STNO/BPO systems. Figures 3 and 4 showed the evolutions of molecular weights and molecular weight distributions with monomer conversions. The M_n increased with monomer conversion linearly independent which kind of STNO was used. It can be also found that the TS-T/BPO system was superior to other STNO mediated

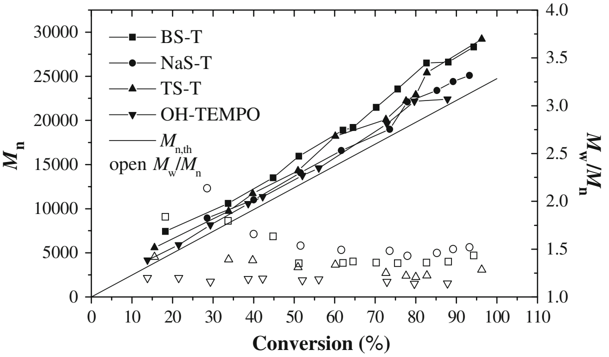


Fig. 3 Dependence of M_n and M_w/M_n on monomer conversion in the cases of different 4-aryl groups of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (other conditions are the same as in Fig. 1)

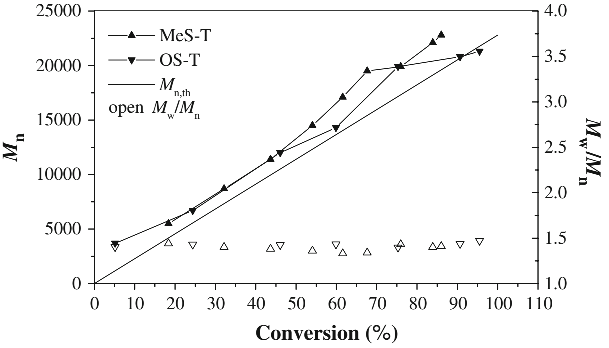


Fig. 4 Dependence of M_n and M_w/M_n on monomer conversion in the cases of different chain length of four-substitute groups of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (other conditions are the same as in Fig. 2)

systems for the mildly lower molecular weight distributions. In all the polymerization systems, the M_ns were greater than the theoretical molecular weights ($M_{n,th}$) due to the termination reactions by recombination of the free radicals. $M_{n,th}$ can be calculated by Eq. 1

$$M_{n,th} = [St]_0 \times M_{WSt} \times \text{ Conversion } /[T\cdot]_0, \tag{1}$$

where $[St]_0$ and $[T\cdot]_0$ are the initial concentration of styrene and stable nitroxide free radical, respectively, M_{WSt} is the molecular weight of styrene.

Effect of $[TS\text{-}T]_0/[BPO]_0$ molar ratio on polymerization

Since the TS-T/BPO combination had a better controllability over the polymerization than other STNO, the effects of molar ratios of TS-T and BPO on the polymerizations were further investigated. The kinetic plots at various molar ratios of TS-T to BPO are shown in Fig. 5. The molar ratios of TS-T to BPO clearly showed some effects on the induction time and the rate of polymerization. At low molar ratio ($[TS\text{-}T]_0/[BPO]_0 = 1.2/1$), almost no induction period can be observed. While it appeared at higher molar ratios of TS-T/BPO such as $[TS\text{-}T]_0/[BPO]_0 = 1.3/1$ and 1.5/1. The induction time was attributed to the excess of nitroxide [24] at the beginning of the polymerization. The effective starting of the polymerization was only after the reduction of the amount of nitroxide by the radicals arising from the BPO decomposition and self-initiation of styrene. As a consequence, the molar ratios of TS-T to BPO played some roles on the rate of polymerization. The higher molar ratio of $[TS\text{-}T]_0$ to $[BPO]_0$ ($[TS\text{-}T]_0/[BPO]_0 = 1.5/1$) caused the slowest polymerization as shown in Fig. 5. As shown in the Fig. 6, for the TS-T mediated systems, M_ns increased with monomer conversions and the values of M_w/M_n maintained relatively low. In all the molar ratios of TS-T to BPO in the polymerizations, "living"/controlled features were observed.

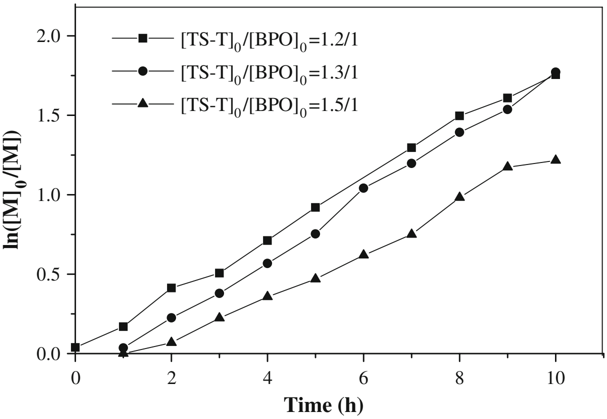


Fig. 5 Kinetic plots of $\ln([M]_0/[M])$ versus reaction time at different $[TS\text{-}T]_0/[BPO]_0$ molar ratios for bulk polymerizations of styrene at 125 °C ($[St]_0 = 8.71$ M; $[BPO]_0 = 0.0305$ M)

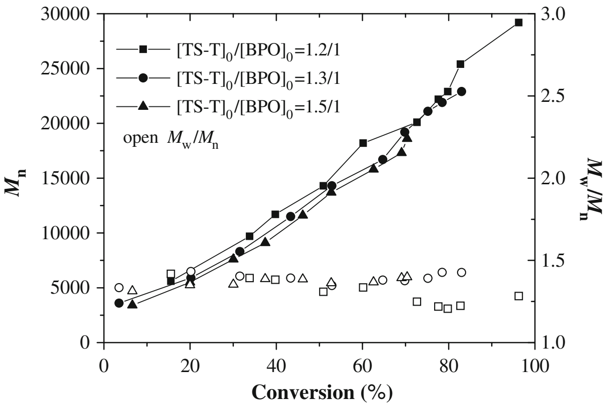


Fig. 6 Dependence of M_n and M_w/M_n on monomer conversion at different [TS-T]$_0$/[BPO]$_0$ molar ratios for bulk polymerizations of styrene at 125 °C (other conditions are the same as in Fig. 5)

Effect of temperature on polymerization

The effect of the temperature on the rate of TS-T-mediated polymerization was also investigated, and the results are shown in Figs. 7 and 8. The conversion increased obviously with the polymerization temperature. For example, with the temperature increasing from 125 to 135 °C, the conversion increased from 62 to 80% after 8 h. However, M_n and M_w/M_n were changing in a narrow range. The rate of polymerization increased significantly with the increase of polymerization temperature, which could be attributed to the fact that BPO decomposed slower at a lower temperature while its decomposition was faster at higher temperature. Besides, the thermal initiation of styrene also increased with the increase of polymerization temperature.

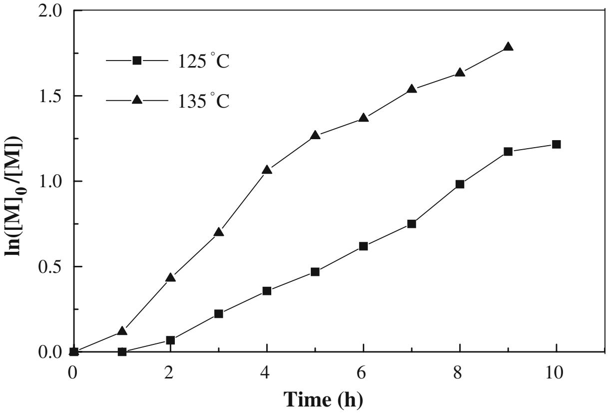


Fig. 7 Kinetic plots of ln([M]$_0$/[M]) versus reaction time at different temperatures for bulk polymerizations of styrene ($[St]_0 = 8.71$ M, $[BPO]_0 = 0.0305$ M, $[TS\text{-}T]_0 = 0.0458$ M)

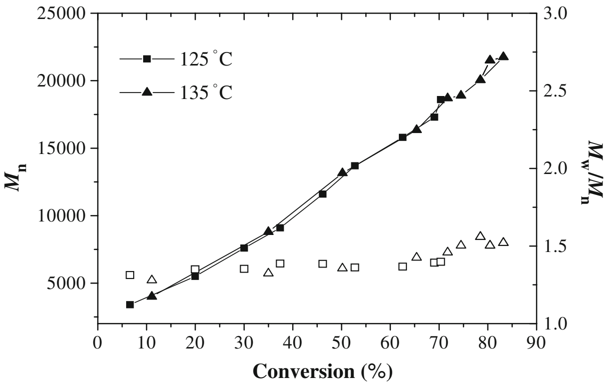


Fig. 8 Dependence of M_n and M_w/M_n on monomer conversion at different temperatures for bulk polymerizations of St (Other conditions are the same as in Fig. 7)

Chain extension reaction

According to the mechanism of NMP, the obtained polymer could be used as a unimolecular initiator for nitroxide-mediated polymerization of styrene. The chain extension polymerization with PSt (TS-T mediated system, $M_n = 23{,}000$ g/mol, $M_w/M_n = 1.29$) as the macroinitiator was also successfully performed by the addition of fresh St. As shown in Fig. 9, the M_n of the original PSt shifted from 23,000 to 33,200 g/mol after the chain extension reaction. The M_w/M_n of the chain-extended polymer was 1.44, which was a little higher than the original PSt. This result indicated that there was a small fraction of dead polymer chains in macroinitiator [25]. The chain-extension results demonstrated that most of the PSt

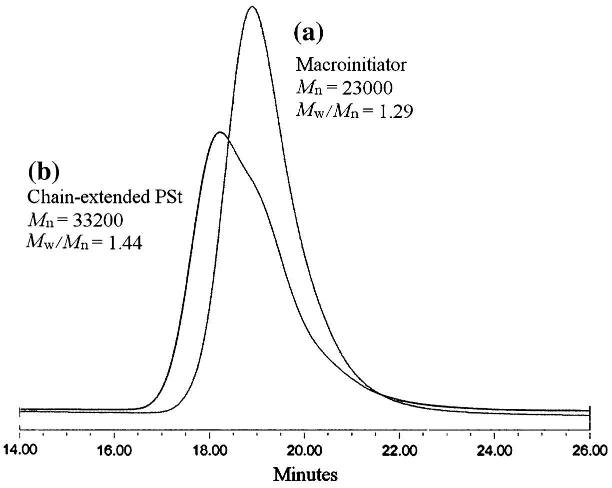


Fig. 9 GPC curves of PSt before (**a**) and after (**b**) chain extension (temperature = 125 °C, time = 1.5 h, conversion = 49%, $[St]_0/[PSt]_0 = 500/1$)

polymer chains were living, and the TS-T mediated polymerizations complied with the classical NMP.

^{1}H NMR spectra of the PSt mediated by the five STNO radicals

Figure 10 shows the ^{1}H-NMR spectra of the PSt arising from the polymerizations with different STNO as mediator. A series of peaks could be found between 0.1 and 1.2 ppm (a), which were assigned to the four piperidinyloxy methyl resonances of STNO bonded to PSt and have also been confirmed by Georges et al. [26]. Other characteristic chemical shifts are also shown in Fig. 10. These peaks indicated the existence of the STNO moiety in the end of polymeric chain.

Conclusions

In conclusion, the controlled free radical polymerizations of styrene initiated with BPO in the presence of five 4-sulphonate-2,2,6,6-tetramethylpiperidine-*N*-oxyl

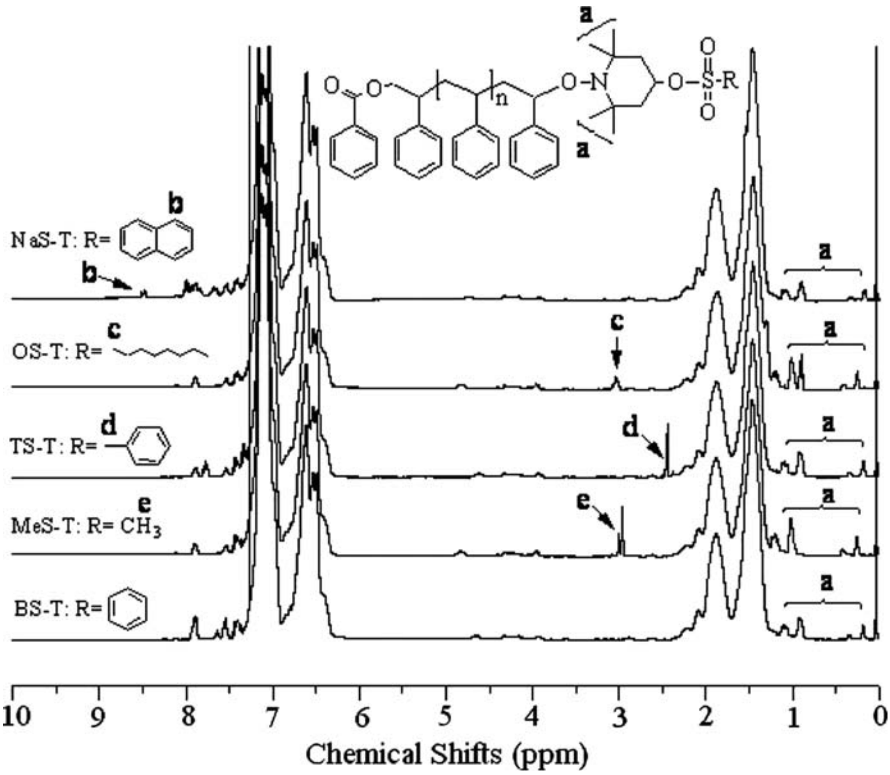


Fig. 10 400 MHz ^{1}H NMR spectra of polystyrene mediated by STNO (NaS-T: $M_n = 6{,}700$, $M_w/M_n = 1.39$. OS-T: $M_n = 5{,}300$, $M_w/M_n = 1.41$. TS-T: $M_n = 5{,}500$, $M_w/M_n = 1.35$. MeS-T: $M_n = 5{,}100$, $M_w/M_n = 1.35$. BS-T: $M_n = 5{,}700$, $M_w/M_n = 1.43$)

(STNO) radicals were successfully carried out. The polymerizations were well controlled in terms of linear kinetic plots, linear increase of M_n of the polymers with increasing conversion, ^{1}H NMR spectra of the PSt and successful chain extension reactions. Most of the M_w/M_n of the obtained polymers remained relatively low. The rates of polymerization mediated by these STNO were accelerated in comparison with the OH-TEMPO/BPO system. Different four-substitute groups of TEMPO as well as the $[STNO]_0/[BPO]_0$ molar ratios had considerable effects on the rate of the polymerization.

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