Atom Transfer Radical Polymerization of Styrene Using Multifunctional Iniferter Reagents as Initiators

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Summary: Two multifunctional iniferters, 1,4-bis-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (BDCIB) and 1,3,5-tris-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (TDCIB), were successfully synthesized and used as initiators to initiate the polymerization of styrene in the presence of a CuBr/PMDETA complex. The polymerization results demonstrated that the kinetic plots in all cases were first-order to the monomer, the molecular weight of the polymers increased linearly with the monomer conversion; meanwhile, the molecular weight distribution of the polymer was kept to a very low value ($M_w/M_n \leq 1.35$). Furthermore, the measured molecular weights were very close to the calculated values, which indicated the high efficiency of the initiator for the polymerization of styrene. The effect of catalyst concentration and initiator concentration was not obvious and the influence of polymerization temperature was apparent, and the polymerization rate increased with the polymerization temperature. The results of chain-extension and ^{1}H NMR analysis proved that the polymer obtained was capped with diethylthiocarbamoylthiy (DC) group.

Keywords: atom transfer radical polymerization (ATRP); diethylthiocarbamoylthiy (DC); iniferter; living polymerization; styrene (St)

Introduction

As one of the powerful living free radical polymerization (LFRP) methods, atom transfer radical polymerization (ATRP) is well developed and versatile, has good compatibility with a wide range of functional monomers, and allows excellent control over the polymer architecture.[1–4] As a multicomponent system, the initiator is considered as a very important component in the ATRP system, because it will give rise to initiating radical specie, determines the structure of the polymer end group obtained. So far, most of the initiators for successful ATRP systems are organic halides with a potentially active carbon–halogen bond. Furthermore, the polymer obtained usually ends with the halide group, which limits the functionality of the polymer.[1,2]

Most recently, Qiu et al.[5–8] and our group[9–12] reported that the *N,N*-diethyldithiocarbamate (DC) group can be transferred by mediating the dormant–active species equilibrium during the ATRP process. Meanwhile, in our study, we found that the polymers prepared using this kind of iniferter reagent as initiator via the ATRP technique always captured the DC groups in the end of the polymer chains.[10,11] Moreover, as one of typical phenomenology, polymerization kinetics is very important. Up to now, in the kinetic investigation of ATRP systems, most polymerizations are initiated by common initiators, such as alkyl halides and sulfonyl halides.[13–17] However, no kinetic investigation was reported toward this novel kind of initiators.

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In this work, two multifunctional iniferter reagents, 1,4-bis-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (BDCIB) and 1,3,5-tris-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (TDCIB), were synthesized and used as the initiators to initiate the ATRP of styrene (St). The kinetic investigation in the presence of CuBr/PMDETA using BDCIB as initiator was conducted in detail.

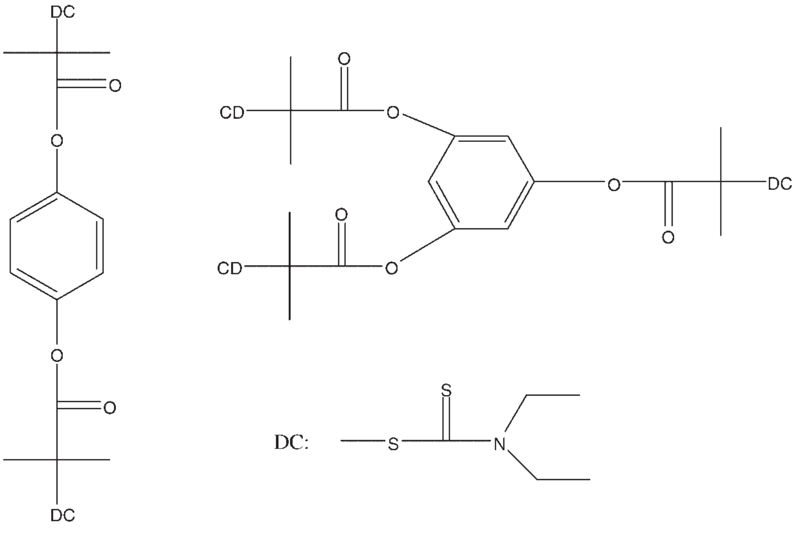
Experimental Part

Materials

Styrene (St) (98%; Chemically Pure, from Shanghai Chemical Reagent Co., China) was washed with 5% sodium hydroxide aqueous solution, and then with deionized water until neutralization. After being dried with anhydrous sodium sulfate overnight, it was finally distilled under reduced pressure and kept in a refrigerator under 0 °C before use. *N,N,N′,N′,N′*-Pentamethyldiethylenetriamine (PMDETA) (98%; Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China) was dried with 4 Å molecular sieves and distilled under vacuum. Copper bromide (98%; Aldrich) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried under vacuum. 1,4-Bis-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (BDCIB) and 1,3,5-tris-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (TDCIB), as shown in Scheme 1, were synthesized according to ref.[10] Other reagents were purchased from Shanghai Chemical Reagent Co. Ltd., China and were used as received.

Characterization

^{1}H NMR spectra were recorded on an INOVA 400 MHz nuclear magnetic resonance (NMR) instrument, using tetramethylsilane (TMS) as the internal standard. The molecular weights and molecular weight distributions of the polymers were determined by gel permeation chromatography (GPC) with a Waters 1515 gel permeation chromatograph equipped with a refractive index detector, using HR1, HR3, and HR4 columns with the molecular weight range 100–500 000 calibrated with polystyrene standard samples. Tetrahydrofuran



1,4-bis-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene(BDCIB)

1,3,5-tris-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene(TDCIB)

Scheme 1.
The structures of multifunctional initiators.

(THF) was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C.

General Procedures of Polymerization

A typical recipe of the ATRP procedure is described as follows: The solution of St (2 mL, 17.4 mmol) and BDCIB (0.1022 g, 0.174 mmol) was added to a dry glass tube filled with CuBr (0.0251 g, 0.174 mmol), and PMDETA (0.11 mL, 0.522 mmol) with a predetermined molar ratio ($[St]_0/[EDDCB]_0/[CuBr]_0/[PMDETA]_0 = 100{:}1{:}1{:}3$). The mixture was then degassed under vacuum and charged with argon five times. The glass tube was sealed under argon atmosphere and placed into an oil bath held by a thermostat at a desired temperature. At timed intervals, the tube was cooled in ice water to stop the polymerization. Afterwards, the tube was opened and the contents were dissolved in about 20 mL of tetrahydrofuran (THF), and then precipitated into a large amount of methanol. The samples were dried to constant weight at 50 °C. The conversion of the monomer was determined by gravimetry. Part of polymer (10 mg) was then dissolved in THF (10 mL) and the solution was used to determine the molecular weight and molecular weight distribution.

Results and Discussion

Kinetic Analyses of the Polymerization

The difunctional iniferter reagent, 1,4-bis-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (BDCIB), was used as the initiator to conduct a kinetic investigation of the ATRP of styrene (St). Figure 1 and 2 present the results of ATRP of St in the cases of different concentration of catalyst complex. From Figure 1, we can see that the plots all show an approximately first-order rate to the monomer under different initiator concentrations, which indicated the propagating radical concentrations were constant during the process of polymerization. However, it is interesting to find that the catalyst concentration almost had no obvious effect on the polymerization rate of St. When the concentration of catalyst varied from 1 to 0.25 equiv. with respect to BDCIB, the apparent rate constants (K_{app}), that is, the slopes of the kinetic plots of $\ln([M]_0/[M])$ versus reaction time (t), are nearly equal for all catalyst concentrations ($K_{app} = 4.8 \times 10^{-5}$, 4.6×10^{-5}, and 4.0×10^{-5} s^{-1} for the ATRP systems with $[CuBr]_0/[EBIB]_0 = 1$, 0.5, and 0.25, respectively), which demonstrates that the polymerization is zero order with

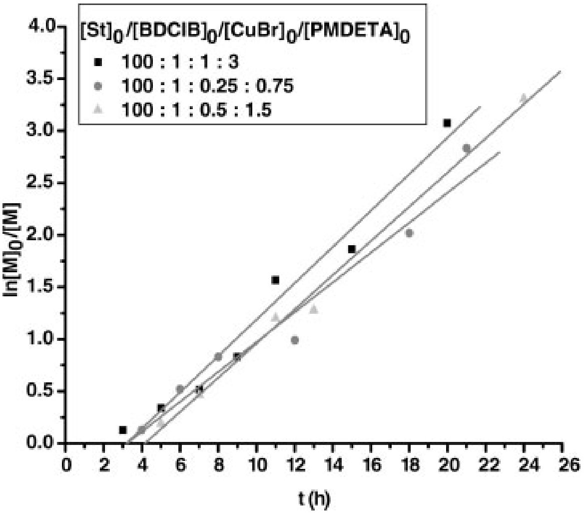


Figure 1.
Kinetic plots of the bulk ATRP of St at 115 °C. Polymerization conditions: $[St]_0/[BDCIB]_0/[CuBr]_0/[PMDETA]_0 = 100{:}1{:}\ n{:}\ 3n$ ($n = 1$, 0.50, .25).

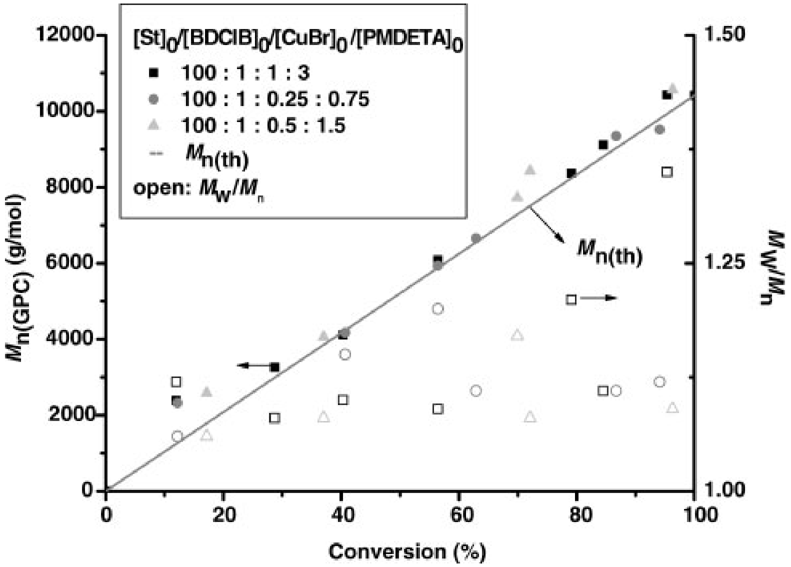


Figure 2.
Dependence of $M_{n(GPC)}$ and M_w/M_n on the monomer conversion for the bulk ATRP of St. Polymerization conditions are same as in Figure 1.

respect to the catalyst. The effect of initiator concentration on the polymerization rate was also negligible as shown in Figure 1 and 3. Interestingly, we found the polymerization rate was much slower in the cases of no initiator or catalyst. So the zero-order dependence is a phenomenon in the specific region of *n* that we studied. The ATRPs of styrene with a reaction order of zero either for the initiator[18] or for the

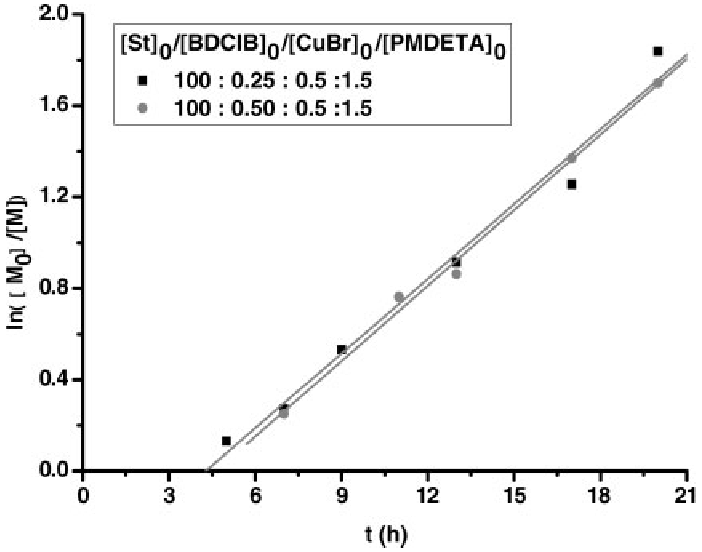


Figure 3.
Kinetic plots of the bulk ATRP of St at 115 °C. Polymerization conditions: $[St]_0/[BDCIB]_0/[CuBr]_0/[PMDETA]_0 = 100$: *n*: 0.5:1.5 ($n = 0.25, 0.50$).

catalyst[19,20] have previously been reported, respectively. Zhang et al.[21] reported the first polymerization system to show zero order with respect to both the initiator and the catalyst. As to the similar studied system, this results may be due to the constant [CuBr]/[CuBr(DC)] and [Initiator]/[CuBr(DC)] ratios following the addition of different amounts of the catalyst and initiator; that is, the concentration of CuBr(DC) formed through self-regulation is proportional to the initial CuBr and initiator concentrations.[22,23] Meanwhile, Figure 1, 3, 5, and 7 also show some considerable induction period (4–6 h). The cause of this phenomenon is not very clear yet, which may be due to the formation of the actual initiating center that results from the establishment of an equilibrium and the consumption of residual oxygen in the polymerization system. In our previous report, we also found the existence of an induction period when using tetramethylthiuram disulfide (TMTD) as an initiator for the ATRP of styrene,[24] and a similar phenomenon was also observed by Ruckenstein.[25] Figure 2 and 4 show the dependence of the molecular weights ($M_{n(GPC)}$s) and molecular weight distributions (M_w/M_n) of the polymers on monomer conversions. $M_{n(GPC)}$ increased linearly with monomer conversion and was close to the theoretical value ($M_{n(th)}$) with relatively narrow molecular weight distribution ($M_w/M_n < 1.35$), which demonstrated that the polymerization was well-controlled and the initiator efficiency was close to 1.0 in most cases. In addition, the concentration of the catalyst had little influence on the molecular weights ($M_{n(GPC)}$s) and molecular weight distributions (M_w/M_n) of the polymers. However, the initiator concentration had the obvious effect on the molecular weights ($M_{n(GPC)}$s) of the polymers, which resulted from the relative high concentration of active species with the relative high concentration of initiator.

From Figure 1, 5, and 6, we can see that the polymerization rate increased with the polymerization temperature. The molecular weight of the polymer was not influenced by the reaction temperature. It increased linearly with monomer conversion at 110 and 120 °C, respectively, and was also close to the theoretical value while keeping the narrow molecular weight

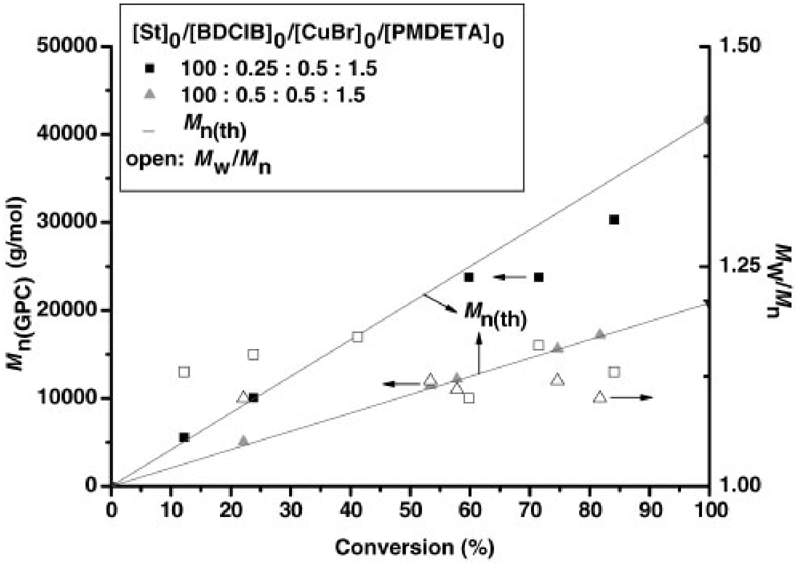


Figure 4.
Dependence of $M_{n(GPC)}$ and M_w/M_n on the monomer conversion for the bulk ATRP of St. Polymerization conditions are same as in Figure 3.

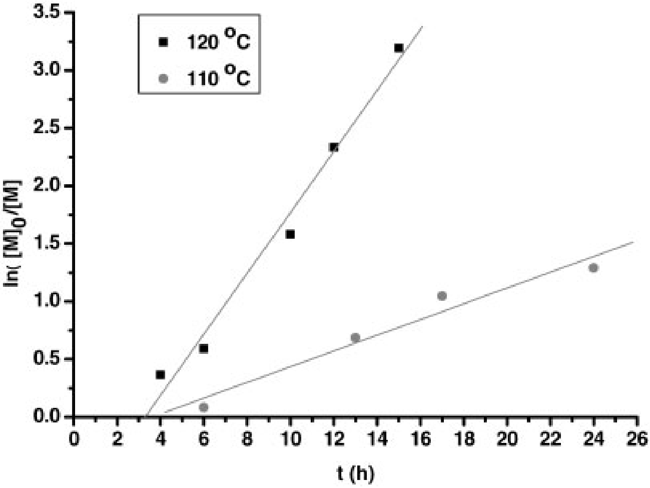


Figure 5.
Kinetic plots of the bulk ATRP of St at 110 and 120 °C. Polymerization conditions: $[St]_0/[BDCIB]_0/[CuBr]_0/[PMDETA]_0 = 100{:}1{:}0.5{:}1.5$.

distribution. The trifunctional iniferter, 1,3,5-tris-(α-*N,N*-diethyldithiocarbamyl-isobutyryloxy)-benzene (TDCIB), was also used as the initiator to conduct the ATRP of St and the results are presented in Figure 7 and 8, respectively. The linear dependence of $\ln([M]_0/[M])$ on reaction time indicated that the concentration of the growing radicals was constant. The $M_{n(\mathrm{GPC})}$ increased linearly with monomer conversion up to a maximum of 99.7% with quite narrow molecular weight distribution

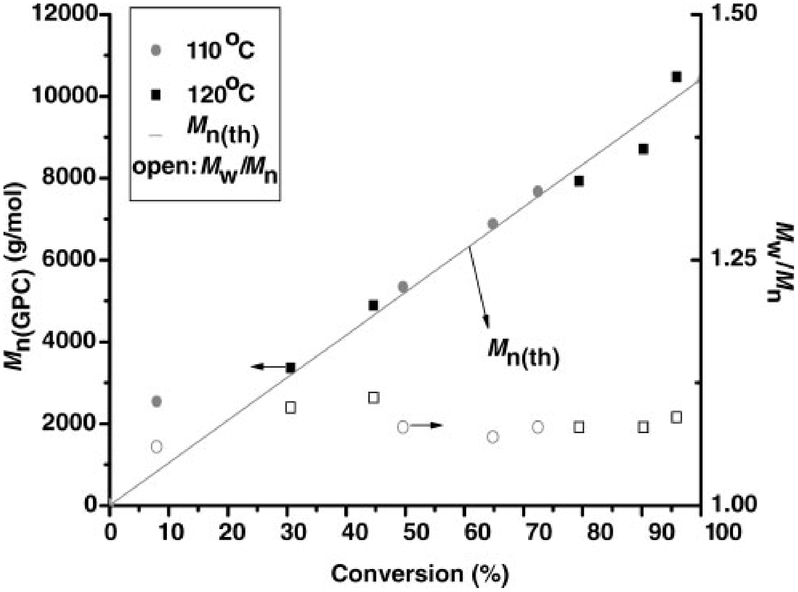


Figure 6.
Dependence of $M_{n(GPC)}$ and M_w/M_n on the monomer conversion for the bulk ATRP of St. Polymerization conditions are same as in Figure 5.

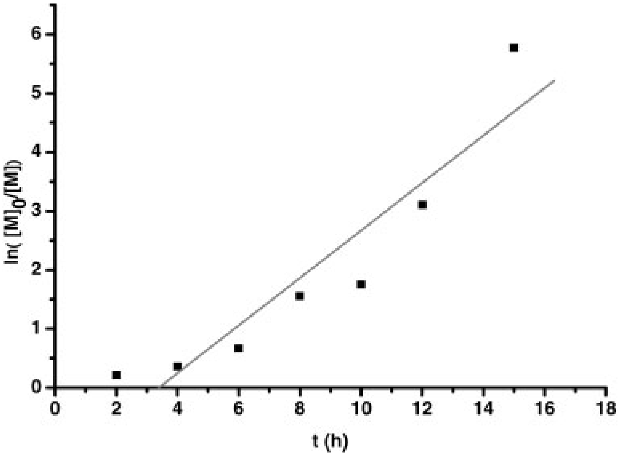


Figure 7.
Kinetic plot of the bulk ATRP of St at 115 °C. Polymerization conditions: $[St]_o/[TDCIB]_o/[CuBr]_o/[PMDETA]_o = 100:1:1:3$.

($M_w/M_n = 1.22$). Furthermore, the $M_{n(GPC)}$ was also close to the $M_{n(th)}$, which demonstrated the relatively high initiator efficiency.

End Group Analysis and Chain Extension

In order to prove the presence of the DC group at the end of the polymer chain, ^1H NMR spectroscopy was used to analyze the structure of the PS obtained. As shown in Figure 9, the corresponding signals at $\delta = 3.40–4.20$ ppm (b) could be assigned to the methylene protons of diethylthiocarbamoylthiyl group, $-S_2CN(CH_2CH_3)$. The chemical shifts at $\delta = 4.60–5.21$ ppm (a) could be ascribed to the St unit adjacent to the terminal DC group, which departed from the repeated units in the main chain due to the proximity to the ω-DC

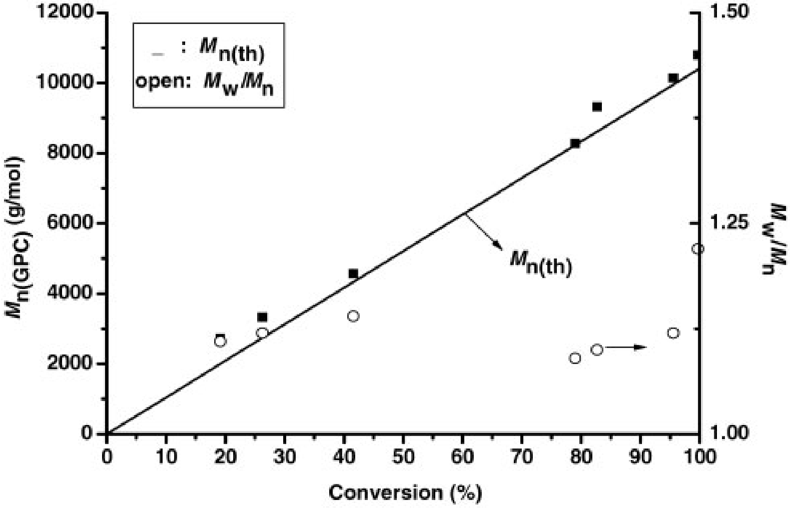


Figure 8.
Dependence of $M_{n(GPC)}$ and M_w/M_n on the monomer conversion for the bulk ATRP of St. Polymerization conditions are same as in Figure 7.

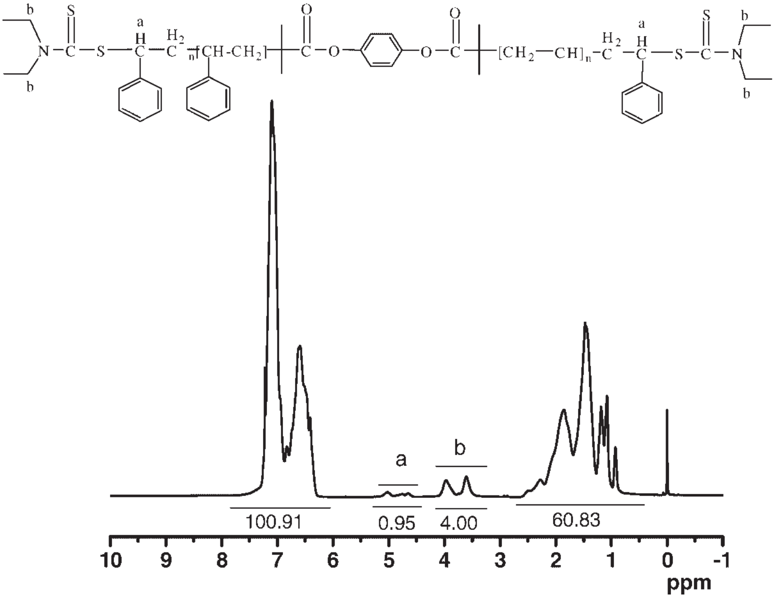


Figure 9.
400 MHz ^{1}H NMR spectrum of the PS prepared using BDCIB/CuBr/PMDETA system in bulk ($[St]_0/[BDBB]_0/[CuBr]_0/[PMDETA]_0 = 100:1:1:3$) at 115 °C ($CDCl_3$). Sample: $M_{n(GPC)} = 4100$ g · mol^{-1}, $M_w/M_n = 1.10$.

end group. Furthermore, the $M_{n(GPC)}$ ($M_{n(GPC)} = 4800$ g · mol^{-1}) was very close to the value calculated from Figure 9 ($M_{n(NMR)} = 4400$ g · mol^{-1}) and $M_{n(th)}$ ($M_{n(th)} = 4200$ g · mol^{-1}), which indicated the efficiency of BDCIB was high. The resulting PS, with the ω-DC group at the chain end, can be used as a macroinitiator for chain extension by an ATRP process. The chain extension was carried out in bulk at 115 °C with a DC-terminated PS ($M_{n(GPC)} = 4100$ g · mol^{-1}, $M_w/M_n = 1.10$) in the presence of CuBr/PMDETA. After 13 h, the $M_{n(GPC)}$ of PS increased to

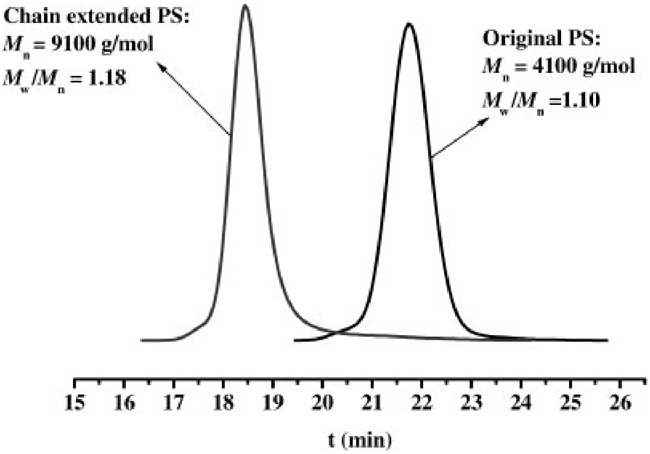


Figure 10.
GPC curves of original PS and chain extended PS. Chain extension conditions via ATRP: $[St]_0/[Macroinitiator]_0/[CuBr]_0/[PMDETA]_0 = 100:1:1:3$, St/DMF = 1:1 (v/v), 115 °C, 13 h, conversion(%) = 40.7%.

$9100\ \mathrm{g \cdot mol^{-1}}$ ($M_w/M_n = 1.18$) as shown in Figure 10. These results indicated that the PS ended with a DC group and was 'living'.

Conclusion

It is desirable to achieve multifunctionalized PS chains with DC groups via ATRP method using two multifunctional iniferters, BDCIB and TDCIB, as initiators. The effect of concentrations of the initiator and catalyst on the polymerization rate was almost negligible and the reaction temperature had a positive effect on the polymerization rate when using BDCIB as the initiator. The efficiencies of these two initiators were both high.

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