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Reverse Atom Transfer Radical Polymerization of Styrene Initiated by Tetramethylthiuram Disulfide/CuSCN/*N*, *N*, *N*′, *N*″, *N*″-Pentamethyldiethylenetriamine in the Presence of Acetonitrile

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ABSTRACT

A reverse atom transfer radical polymerization of styrene was successfully carried out in acetonitrile (28.6%, v/v), using tetramethylthiuram disulfide (TMTD)/CuSCN/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the initiating system. The polymerizations exhibited first-order rate plots and linear increase of the number-average molecular weight with conversion along with relatively low molecular weight distributions (M_w/M_n). However, induction periods of the polymerization were relatively long. ^{1}H NMR spectra analyses revealed α-$S_2CN(CH_3)_2$ and ω-SCN end groups on the polystyrene chain.

Key Words: Reverse atom transfer radical polymerization; Living polymerization; Tetramethylthiuram disulfide; Styrene; *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

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INTRODUCTION

As one of the most convenient methods to synthesize well-designed polymers with low molecular weight distributions, atom transfer radical polymerization (ATRP) has attracted increasing interest since it was discovered in 1995.[1–5] In ATRP, polymerization is well controlled due to a low steady-state radical concentration which resulted by a fast dynamic equilibrium established between the dormant species and the active species with transition-metal complex acting as reversible halogen atom transfer reagents. Considerable efforts have been made to find new transitional metals and new ligands, because the transitional metal halide/ligand has a deep effect on the activity of ATRP. Several metal complexes, comprised of Cu(I),[1,2] Fe(II),[6,7] Ni(II),[8,9] Ru(II),[10,11] and Rh(III),[12] have been successfully used as catalysts for ATRP, however, the most widely used class of metal complexes are copper based.[13–15] Recently, CuSCN[16,17] was successfully introduced into ATRP and the effect of copper counter ion on polymerization was also studied. As a result, CuSCN could increase the polymerization rate compared with CuBr and CuCl system, especially, CuSCN is relatively more stable and cheaper. In the ligand field, multidentate amines, such as *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetramine were introduced into ATRP by Xia and Matyjaszewski,[18] they found the polymerization rate was faster for Styrene (St) than those using a 2,2′-bipyridine (bpy) ligand. Recently, tetraethylthiuram disulfide (TD), one good iniferter,[19] was introduced into reverse ATRP as a new initiator by Qiu.[20] However, homogeneous reverse ATRP for St initiated by TMTD/CuSCN/PMDETA system has not been reported.

In this article, we described the reverse ATRP of St with tetramethylthiuram disulfide (TMTD) as the initiator and CuSCN/PMDETA as the catalyst. The effects of the catalyst concentration and reaction temperature on the polymerization were also reported.

EXPERIMENTAL

Materials

Styrene (Chemically Pure, Shanghai Chemical Reagent Co. Ltd.) was purified by washing with a 5% sodium hydroxide aqueous solution, followed by washing with water and dried with sodium sulfate anhydrous overnight, and finally distillated over CaH_2 under vacuum before use. Tetramethylthiuram disulfide (99.9%, Zhengjiang Zhengdu Chemical Reagent Factory) was recrystallized from a mixture of ethanol and chloroform. Copper (I) thiocyanate (CuSCN) (98.0%, Yixing Liaoyuan Chemical Co. Ltd.) was purified by washing with acetic acid and acetone, then dried under vacuum. *N*,*N*,*N*′,*N*″,*N*″-PMDETA was dried with a 4 Å molecular sieve and distillated under vacuum. Acetonitrile (CH_3CN) was distillated before use. Tetrahydrofuran (THF) (Analytical Reagent, Shanghai Chemical Reagent Co. Ltd.), hydrochloric acid (HCl) (Analytical Reagent, Jiangsu Jincheng Chemical Reagent Co. Ltd.), and methanol (commercially available) were used as received.

Polymerization

A dry glass tube was filled with CuSCN, TMTD, PMDETA, St, and CH_3CN. Vibrating until the system became a homogeneous solution. After the repetition of a vacuum/nitrogen cycle four times, the tube was sealed under nitrogen and placed in an oil bath thermostat at the desired temperature. At timed intervals of polymerization, the tube was cooled into cold water and the polymerization was stopped. Afterwards, the tube was opened and the contents were dissolved in 20 mL THF, precipitated into a large amount of methanol/HCl (100/0.05, v/v). The monomer conversion was determined gravimetrically.

Characterization

Number-average molecular weights and molecular weight distributions of polymers obtained were measured using Waters 1515 GPC with THF as a mobile phase and with column temperature of 30°C. Polystyrene standards are used to calibrate the columns. ^{1}H NMR spectra were recorded in $CDCl_3$ with an INOVA 400 MHz spectrometer at ambient temperature.

RESULTS AND DISCUSSION

Effect of Concentrations of Catalyst

The results of reverse ATRP of St with TMTD as the initiator catalyzed by CuSCN/PMDETA in acetonitrile at 120°C are shown in Figs. 1–4. The linear dependence of $\ln[M]_0/[M]$ on reaction time observed in Fig. 1 shows that the kinetics are first order and that the living radical concentrations are constant during the polymerization process. From Fig. 2, it can also be seen that the monomer conversion increases with reaction time. However, long induction periods were observed for the reverse ATRP of St initiated by TMTD/CuSCN/PMDETA. The induction periods at $[\text{TMTD}]_0/[\text{CuSCN}]_0 = 1:1$, $1:5$, and $1:10$ are estimated as 16.5, 12.6, and 8.7 h, respectively and become shorter with an increasing ratio of $[\text{CuSCN}]_0/[\text{TMTD}]_0$. The corresponding apparent rate constant (k_p^{app}) at $[\text{CuSCN}]_0/[\text{TMTD}]_0 = 1$, 5, and 10 are about 1.15×10^{-5}, 1.79×10^{-5}, $2.18 \times 10^{-5}\,s^{-1}$, respectively.

Such long induction period was also reported by Hu et al.[21] and Ruckenstein et al.[13] The reasons for it have not been known clearly, one of which may be the residual oxygen. However, such a long induction period remained the same when we repeated it several times. According to the polymerization mechanism proposed by Qiu[20] for reverse ATRP of St initiated with TD/CuBr/bpy, another possible explanation may be the formation of $CuSCN(S_2CN(CH_3)_2)_2$ (Sch. 1) and the establishment of equilibrium, which was indicated by the color changes from green to red brown, then to colorlessness. The long induction period may also be due to the formation of the actual initiating center which resulted from the interaction between the initiator and the catalyst because the copper can coordinate with the initiator (TMTD used in this system) via a Cu–S bond,[22–24] a similar phenomenon was also reported by Ruckenstein.[13]

Figure 3 shows the experimental molecular weights increases linearly with increasing monomer conversion, however, they are a little lower than the theoretical ones, which resulted in the initiator efficiency $(f) > 1.0$, particularly at high conversion. This may

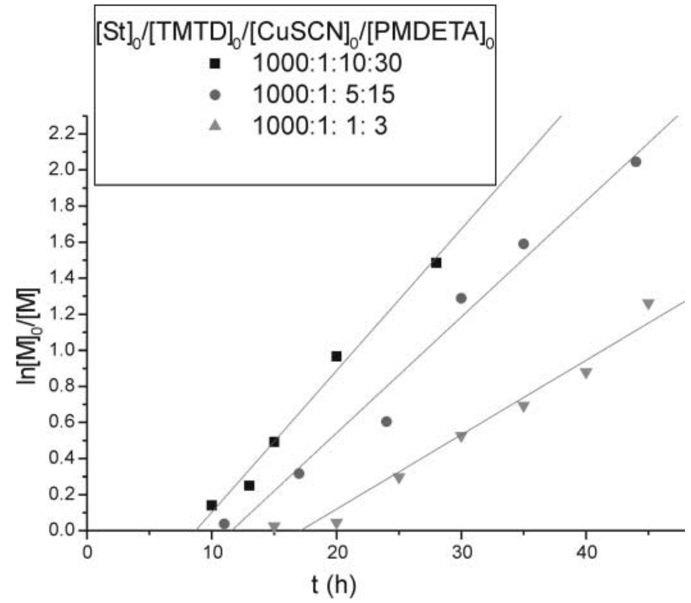

Figure 1. Kinetic plots of $\ln[M]_0/[M]$ vs. reaction time for the solution reverse ATRP of St at 120°C with different catalyst concentrations. Polymerization conditions: $[\mathrm{St}]_0 = 6.22\,\mathrm{mol/L}$; $\mathrm{St/CH_3CN} = 2.5/1$ (v/v).

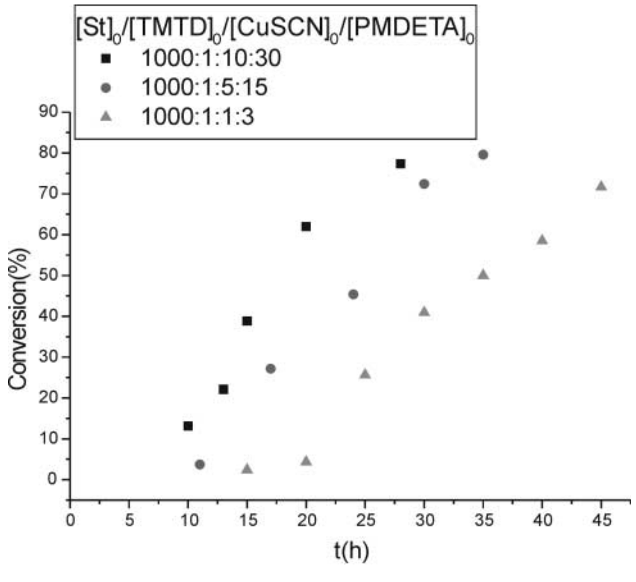

Figure 2. Conversion vs. reaction time for the reverse ATRP of St in acetonitrile at 120°C, polymerization conditions as in Fig. 1.

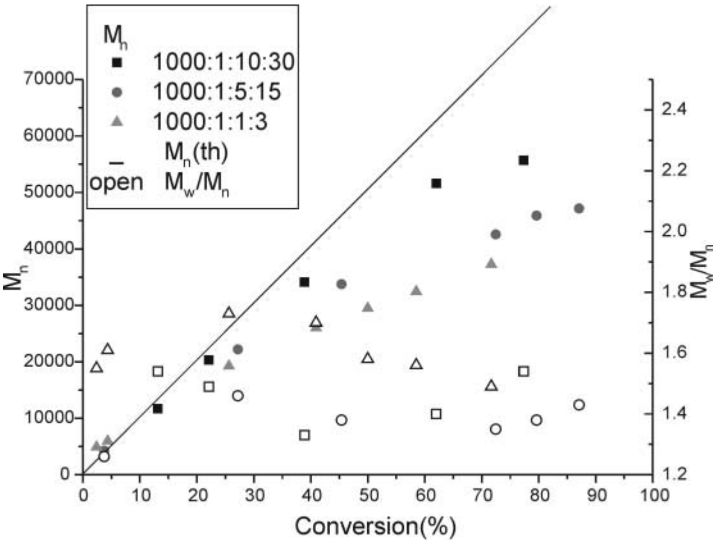

Figure 3. The dependence of the molecular weights and molecular weight distributions on the monomer conversion for the reverse ATRP of St in acetonitrile at 120°C, polymerization conditions as in Fig. 1.

probably be due to auto thermal polymerization of St and self-initiation through the Mayo mechanism[25] and the similar results also appeared in reverse ATRP of AIBN/$FeCl_3$/PPh_3 system reported by Kun-Yuan Qiu et al.[7] and St/PEBr/$Cu(phen)_2Br$ system reported by Shengkang Ying et al.[26] As shown in Fig. 3, when $[St]_0/[TMTD]_0/[CuSCN]_0/[PMDETA]_0 = 1000:1:5:15$ and $1000:1:10:30$, the M_w/M_n of given

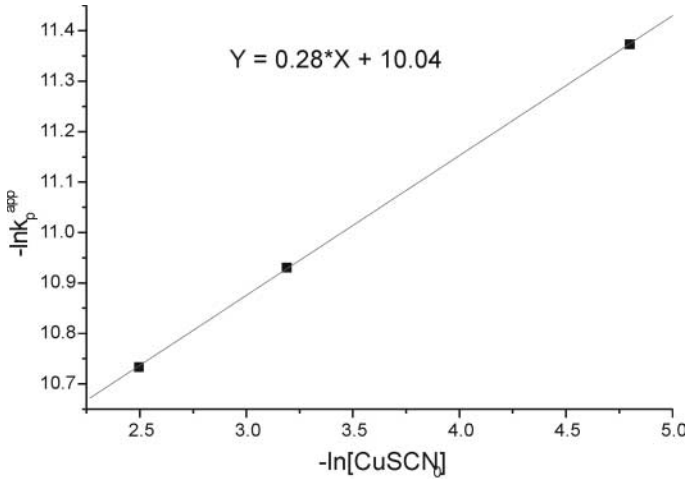

Figure 4. Dependence of k_p^{app} on the concentration of catalyst for the reverse ATRP of St in acetonitrile at 120°C.

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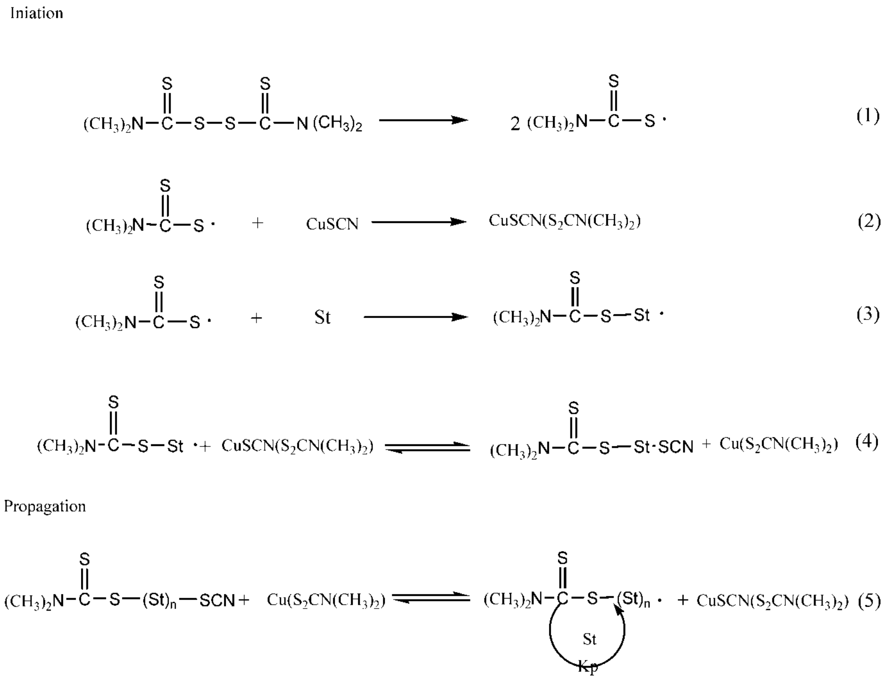

Scheme 1. Mechanism of the reverse ATRP.

polymers are relatively lower. The M_n(th) of PSt can be calculated by the following equation and $f = M_n(\text{th})/M_n$ (GPC):

$$M_n(\text{th}) = \frac{[\text{St}]_0}{[\text{TMTD}]_0} \times \text{MW}_{\text{St}} \times \text{Conversion}$$

where MW_{St} is the molecular weight of St, as formation of $CuSCN(S_2CC_2H_6)$, only one molar concentration of TMTD is included in the above equation, which is similar to St/BPO/CuBr/dNbpy[27]and St/TD/CuBr/bpy system.[20] The plot of $-\ln k_p^{app}$ vs. $-\ln[\text{CuSCN}]_0$ is given in Fig. 4. The slope of the line suggests the reaction order with respect to catalyst concentration is approximately 0.28, which is lower than the expected results by the equation proposed by Matyjaszewski et al.[28] and this result is probably due to formation of the actual initiating center resulting from the interaction between the initiator and the catalyst discussed above.

Effect of Polymerization Temperature on Reverse ATRP of Styrene

In order to shorten the induction period, the effect of the reaction temperature on the rate of polymerization was studied over a temperature range from 110°C to 130°C. Figure 5 shows the induction periods become shorter with an increasing reaction temperature and are estimated as 13.5, 8.7, and 2.6 h, when the polymerization temperatures are 110°C, 120°C, and 130°C, respectively. Figure 5 also shows the first order kinetic plots,

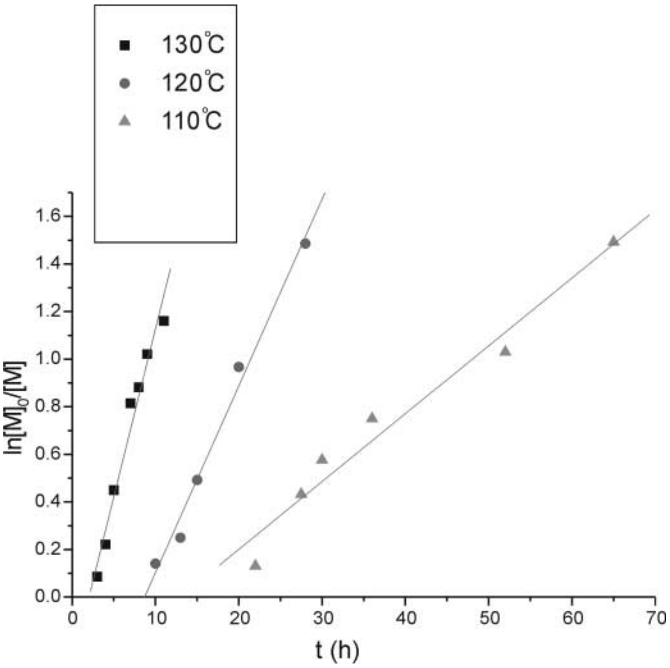

Figure 5. Kinetic plots of ln$[M]_0/[M]$ vs. reaction time for the reverse ATRP of St in acetonitrile at different temperature. Polymerization conditions: $[\mathrm{St}]_0/[\mathrm{TMTD}]_0/[\mathrm{CuSCN}]_0/[\mathrm{PMDETA}]_0 = 1000:1:10:30$; $[\mathrm{St}]_0 = 6.22\,\mathrm{mol/L}$; $\mathrm{St/CH_3CN} = 2.5/1$ (v/v).

suggesting in all cases the radical concentrations remained constant and k_p^{app} increased with the reaction temperature. As can be seen from Fig. 6, the experimental molecular weights increased linearly with increasing monomer conversion over all temperature ranges studied, but were a little lower than theoretical values. The M_w/M_n of the polymers increased with temperature, which was also due to the presence of thermal polymerization of St at a relatively high temperature and long reaction time. Therefore, the polymer obtained at 110°C seemed to give the lowest M_w/M_n values. On the basis of the Arrhenius equation, plot of $-\ln k_p^{app}$ vs. $1/T$ obtained from the experimental results in Fig. 5 was given in Fig. 7. The apparent activation energy was calculated and found to be 103 kJ/mol, which is higher than those reported for the homogeneous CuBr/dNbpy ATRP system (50 kJ/mol)[28] and the heterogeneous $\mathrm{Cu(phen)_2Br}$ ATRP system (75 kJ/mol),[26] which was attributed to the long induction periods in the polymerization process.

Comparison Experiments

Comparison experiments are carried out and results are shown in Table 1. From Table 1, we can see that the addition of TMTD can fasten the polymerization of St and the M_w/M_n of obtained polymers have a little decrease but are also relatively high (2.01) (entries 1 and 2). In the presence of CuSCN/PMDETA, the "living"/controlled radical

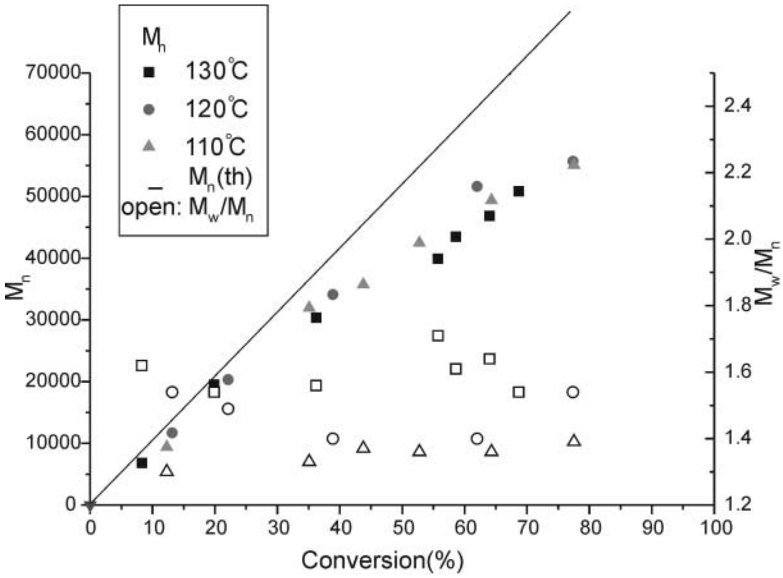

Figure 6. The dependence of the molecular weights and molecular weight distributions on the monomer conversion for the reverse ATRP of St in acetonitrile at different temperature, polymerization conditions as in Fig. 5.

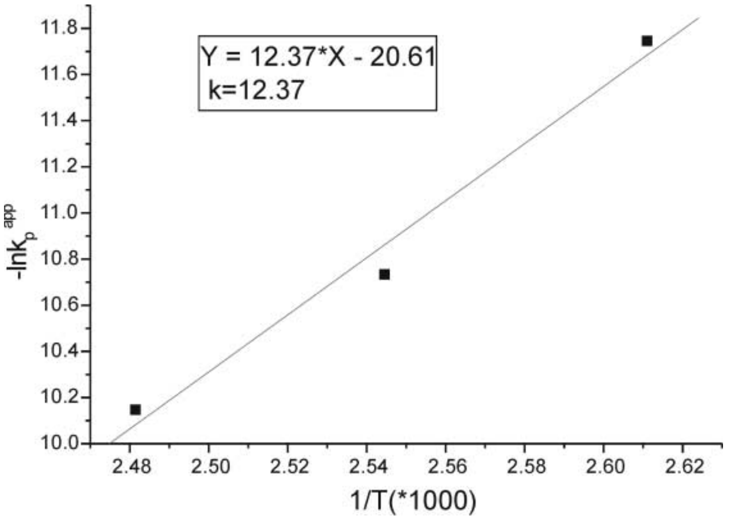

Figure 7. The dependence of k_p^{app} on the reaction temperature for the reverse ATRP of St in acetonitrile. Polymerization conditions as in Fig. 5.

Table 1. The results of comparison experiments for polymerization of St with various initiating system.

Entry	$[St]_0/[TMTD]_0/$ $[CuSCN]_0/[PMDETA]_0$	Time (h)	Conversion (%)	$M_n(GPC) \times 10^{-4}$ $(g\,mol^{-1})$	M_w/M_n
1	1000 : 0 : 0 : 0	8	36.2	14.8	2.19
2	1000 : 1 : 0 : 0	7	38.8	5.1	2.01
3	1000 : 1 : 1 : 3	15	2.4	0.5	1.55
4	1000 : 1 : 1 : 3	35	50.0	2.9	1.58

Note: Polymerization conditions: $[St]_0 = 6.22\,mol/L$; $St/CH_3CN = 2.5/1$ (v/v); 120°C.

polymerization of St can be successfully performed (entries 3, 4, Figs. 1–3) and the M_w/M_n of obtained polymers are relatively lower.

End Group Analysis

As shown in Fig. 8, reverse ATRP of St with an [TMTD]/[CuSCN]/[PMDETA] initiating system was supported by the analyses of the resultant polymer end-groups using

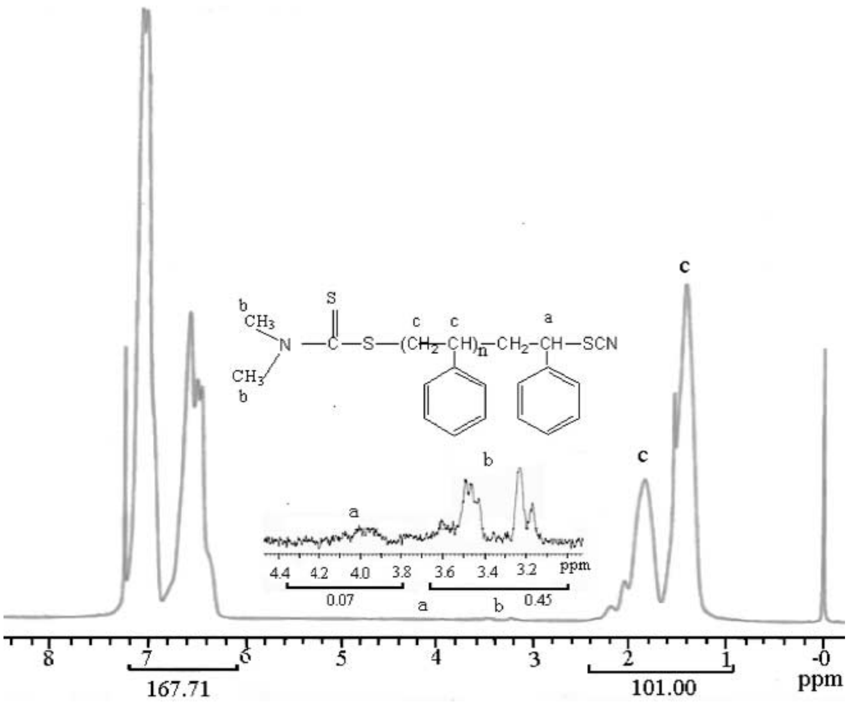

Figure 8. 400 MHz ^1H NMR spectroscopy of the α-$S_2CN(CH_3)_2$ and ω-SCN end groups of PSt initiated with TMTD/CuSCN/PMDETA ($[St]_0/[TMTD]_0/[CuSCN]_0/[PMDETA]_0 = 1000:1:10:30$) at 120°C in acetonitrile (in $CDCl_3$). Sample: $M_{n(PSt\text{-}SCN)} = 33{,}000$, $M_w/M_n = 1.38$.

^{1}H NMR spectroscopy. The peak at around δ 3.8–4.4 ppm (a) was attributed to the methyne proton in the monomer unit adjacent to $-$SCN, $-CH_2C(Ph)H-SCN$. The signals near δ 3.0–3.7 were due to the methyl protons of $-S_2CN(CH_3)$. The ratio of the two absorptions (a)–(b) was about 1 : 6.4, which was well in accordance with the structure of the polymer. However, we find there is a obvious difference between M_n calculated from ^{1}H NMR spectrum [46,000 (b)] and the value measured by GPC (33,000). The measurements were repeated and the results were the same. We think it is due to irreversible termination reactions or the presence of thermal polymerization of St and other side reactions.[29] The similar results were also reported by Shen et al.[30]

Chain Extension Reaction

The functionality of the macroinitiator P_{St-SCN} (M_n (GPC) = 33,000, M_w/M_n = 1.38) prepared via the reverse ATRP with $[St]_0/[TMTD]_0/[CuSCN]_0/[PMDETA]_0$ = 1000 : 1 : 10 : 30 at 120% was proved by its chain extension with fresh St in the case of $[St]_0/[Recovered\text{-}PSt]_0/[CuSCN]_0/[PMDETA]_0$ = 1000 : 1 : 10 : 30 at 120% in acetonitrile (28.6%, v/v). After 15 h, a 11% conversion was reached and the final chain-extended P_{St} has an M_n(GPC) value of 45,000 and a M_w/M_n value of 1.51 was shown in

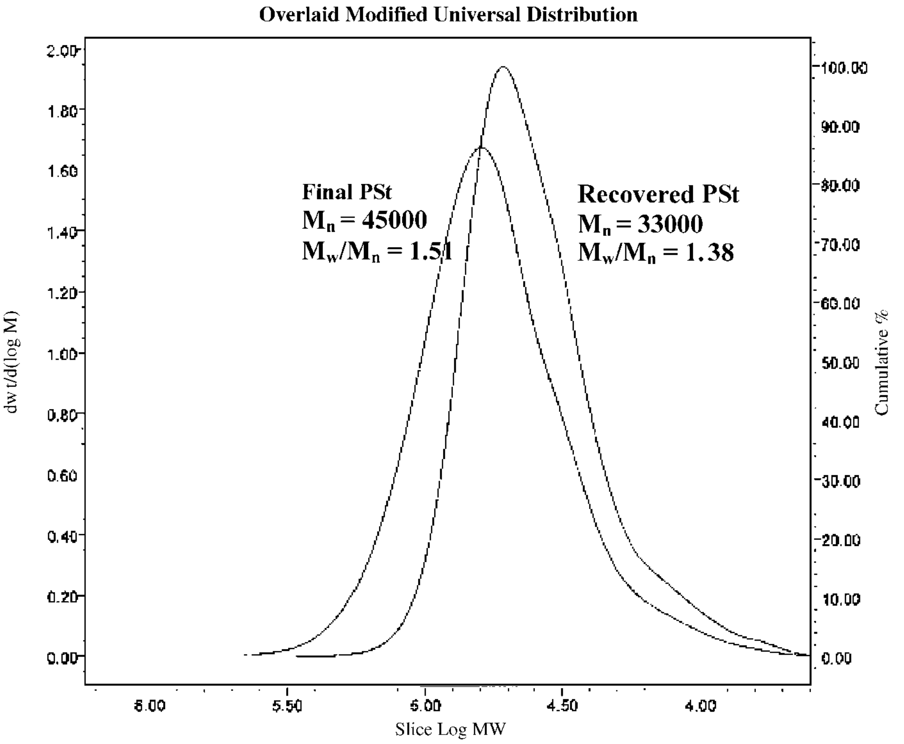

Figure 9. GPC curves of polymers recovered PSt and final PSt chain extension of PSt synthesized by TMTD/CuSCN/PMDETA.

Fig. 9. The increase in the molecular weight indicated that the chain ends of the obtained macroinitiator are functionalized. However, the final PSt has a higher M_w/M_n, which suggest that not all chains are active.

CONCLUSION

In conclusion, the reverse ATRP of St was successfully carried out initiated with TMTD/CuSCN/PMDETA system. The reaction order with respect to catalyst concentration is approximately 0.28 and an apparent activation energy is calculated and found to be 103 kJ/mol. Plots of $\ln[M]_0/[M]$ vs. reaction time and the molecular weights vs. the monomer conversion showed a linear dependence, however, long induction periods appeared in this system.

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