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Reverse atom transfer radical polymerization of styrene in the presence of tetraethylthiuram disulfide

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Abstract

Reverse atom transfer radical polymerization (ATRP) of styrene initiated with tetraethylthiuram disulfide (TD)/cuprous bromide (CuBr)/2,2′-bipyridine (bpy) has been successfully carried out at 120 °C. The kinetic plot was first order in monomer. The measured number-average molecular weight was in good accordance with the theoretical one. Radical scavenger 1,1-diphenyl-2-picrylhydrazyl (DPPH) immediately terminated the reaction, which supported the radical essence of this polymerization. ^{1}H NMR and UV spectra analyses revealed α-S_2CNEt_2 and ω-Br end groups on the polystyrene chain. Conventional ATRP of methyl methacrylate could progress with the obtained polymer acting as the macroinitiator and CuBr/bpy or CuCl/bpy as the catalyst. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Reverse atom transfer radical polymerization; Tetraethylthiuram disulfide; Styrene

1. Introduction

Radical polymerization is a potentially powerful process for the synthesis of high molecular weight vinyl polymers. Relatively simple experimental conditions that the polymerization only requires the absence of oxygen, but can be performed in the medium of water and in a large temperature region make it suitable for the largest variety of monomers compared with other polymerization methods. But it has difficulty in controlling unavoidable termination and transfer reactions of radicals. Fortunately, with the discovery of atom transfer reaction in radical organic chemistry, 'living'/controlled radical polymerization has developed [1]. Originally, iniferter method was used [2], but the obtained polymers were ill controlled with high molecular weight distributions. Following were stable free radicals such as TEMPO [3], various organometallic species [4], degenerative transfer [5], atom transfer radical polymerization (ATRP) [6–8], and reversible addition–fragmentation chain transfer (RAFT) [9].

Using an alkyl halide, R–X, as the initiator and a cuprous halide complex as the catalyst, Wang and Matyjaszewski [6] first discovered ATRP of styrene (St) with predetermined number-average molecular weight (M_n) up to 10^5 and narrow molecular weight distribution, M_w/M_n, down to around 1.10. Percec et al. [8,10] utilized arenesulfonyl chloride as the initiator for ATRP of St under heterogeneous and homogeneous conditions. Xia and Matyjaszewski [11] introduced multidentate ligands, such as tridentate *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) and tetradentate 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) into ATRP. As a result, the polymerization rate was faster for St than those using 2,2′-bipyridine (bpy) ligand. Matyjaszewski et al. [12] demonstrated that the radical polymerization of St initiated with alkyl halide could also be controlled by iron (II) complexes.

Considering the toxic alkyl halide and the easy oxidized transition metal complex in a low oxidation state, Wang and Matyjaszewski [13] discovered reverse ATRP of St, using a traditional radical initiator, 2,2′-azobisisobutyronitrile (AIBN), catalyzed with $CuCl_2$/bpy under heterogeneous conditions. Large amount of the catalyst was needed to gain good control on the polymerization. Otherwise, the polymerization of methyl acrylate (MA) and methyl methacrylate (MMA) were uncontrolled with the same initiation system. Using alkyl substituted bipyridine ligands, Xia and Matyjaszewski [14] realized homogeneous reverse ATRP of St, MA and MMA with AIBN. Then Teyssié et al. [15] introduced 'alternative ATRP'. By utilizing AIBN and $FeCl_3$ complexed by triphenylphosphine, well-controlled PMMA was obtained. Reverse ATRP differs from conventional ATRP in the initiation step that the active radical

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abstracts a halogen atom from the catalyst and forms the dormant halide species and the reduced transition metal species activator. Xia and Matyjaszewski [16] reported a reverse ATRP of St with benzoyl peroxide (BPO) initiator. The presence of $CuBr_2$ could not control the radical polymerization of St. However, catalyzed by CuBr, the living radical polymerization went smoothly. Due to the side reaction, the measured number-average molecular weight was only a half of the calculated one. Qiu et al. [17,18] introduced C–C bond thermal iniferter into the reverse ATRP system of St. Recently, reverse ATRP of St free from halide catalysts has been reported in the literatures [19,20]. Employing metal diethyldithiocarbamates as the catalyst, the controlled radical polymerization of St could be progressed under the initiation of AIBN and diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), respectively.

It is well known that tetraalkylthiuram disulfide is valuable as 'iniferter' in living radical polymerization. However, so far, reverse ATRP initiated with tetraalkylthiuram disulfide has not been reported yet. This article is to introduce a reverse ATRP of St with tetraethylthiuram disulfide (TD) as an initiator and CuBr/bpy complex as a catalyst.

2. Experimental

2.1. Materials

TD was synthesized at 4–7 °C according to the reference method [21] and recrystallized from ethanol, m.p. 73–74 °C. After passing through a column of silica to remove the inhibitor, St (98%) was purified by vacuum distillation. MMA (98%) was dried over CaH_2, filtered and distilled under vacuum. Cuprous bromide (CuBr) and cuprous chloride (CuCl) were synthesized from $CuBr_2$ (analytical reagent (AR)) and $CuCl_2 \cdot 2H_2O$ (AR), respectively, purified by washing with glacial acetic acid and ethanol, and dried under reduced pressure [22]. 2,2′-Bipyridine (AR) was recrystallized twice from ethanol. 1,1-Diphenyl-2-picrylhydrazyl (Pure, Kanto Chemical Co., Inc.) and methanol (AR) were used as received.

2.2. Polymerization

In a representative polymerization, styrene (2.1 g) was added to a dry glass tube containing the solid mixture of TD (9.0 mg), CuBr (4.2 mg) and bpy (14.2 mg). After three cycles of vacuum/nitrogen process, the tube was sealed under vacuum. Then the tube was placed in an oil bath thermostat at the desired temperature 120 °C. After 6 h, the tube was withdrawn from the oil bath and the polymerization was quenched in an ice–salt bath. The reaction content was dissolved in 20 ml tetrahydrofuran (THF). The solution was filtered, followed by precipitation in about 200 ml methanol. The obtained polymer was dried until constant weight. The monomer conversion (31%) of the polymerization was determined gravimetrically.

2.3. Characterization

Molecular weights and molecular weight distributions of obtained polymers were analyzed in THF with a flow rate of 1.0 ml min^{-1} on Waters 515 gel permeation chromatography (GPC) instrument equipped with Styragel Columns (10^1, 10^2, and 10^3 nm pore sizes) operating at 35 °C. Polystyrene (PSt) standards were used for calibration, and Waters millennium 32 was used for data processing. The analyses of the end groups in the resulting products were performed on a Bruker ARX400 400 MHz NMR spectrometer in $CDCl_3$ at 25 °C, using tetramethylsilane as internal reference. Ultraviolet absorption of the polymers was measured in cyclohexane solutions [23] with an Ultraviolet Cary-1E instrument. Glass transition temperatures were recorded at a heat rate of 10 °C min^{-1} and under nitrogen flow, using a Perkin–Elmer 7 differential scanning calorimeter (DSC).

3. Results and discussion

3.1. Polymerization of St initiated by TD/CuBr/bpy

St was polymerized in bulk with TD as the initiator catalyzed by CuBr/bpy at 120 °C ($[St]_0 : [TD]_0 : [CuBr]_0 : [bpy]_0 = 1000 : 1 : 1 : 3$). The results are displayed in Figs. 1 and 2. The plot of $\ln([M]_0/[M])$ versus time is shown in Fig. 1. A straight line through the origin is observed, indicating that the kinetics is first order in monomer and that the concentration of propagating radicals remains constant during the polymerization. It can also be seen that the monomer conversion increases with reaction time in about 40 h. In Fig. 2, the number-average molecular weight measured by GPC, $M_{n(GPC)}$, of the resulting PSt, rises from 35,000 up

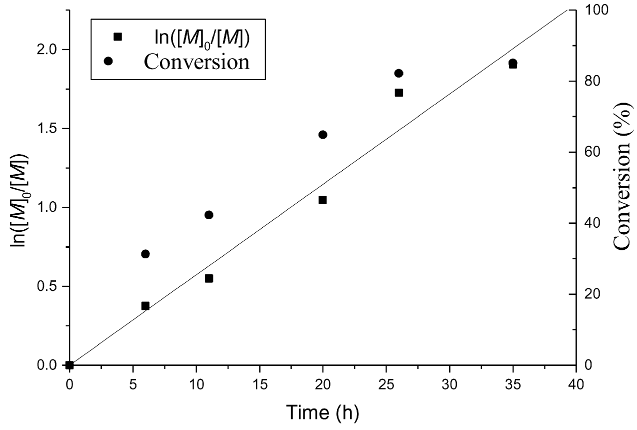


Fig. 1. Kinetic plot for St polymerization initiated with TD/CuBr/bpy in bulk at 120 °C. Conditions: $[St]_0:[TD]_0:[CuBr]_0:[bpy]_0 = 1000:1:1:3$, $[St]_0 = 8.7$ mol l^{-1}.

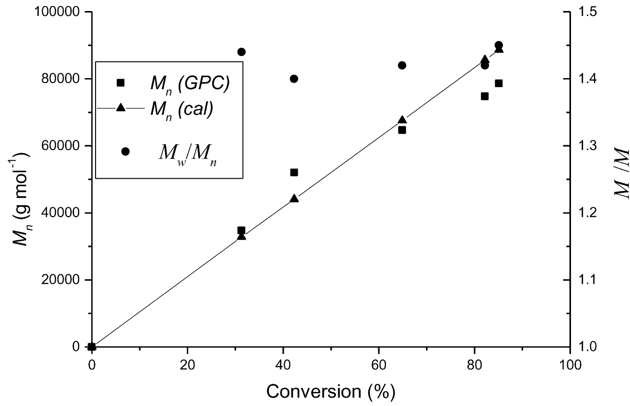


Fig. 2. Dependence of M_n and M_w/M_n on monomer conversion of St polymerization initiated with TD/CuBr/bpy in bulk at 120 °C. See Fig. 1 for conditions.

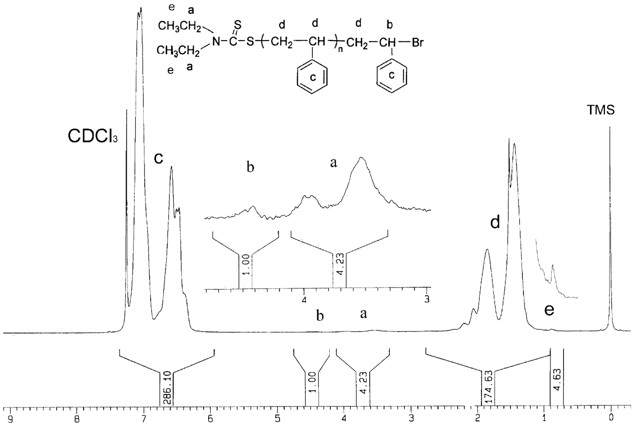


Fig. 3. 400 MHz ^{1}H NMR spectroscopy of the α-dtc, ω-Br end groups of PSt initiated with TD/CuBr/bpy ($[St]_0:[TD]_0:[CuBr]_0:[bpy]_0 = 200:1:1:3$) at 120 °C in bulk (in $CDCl_3$). Sample: $M_{n(PSt-Br)} = 5700$ g mol^{-1}, $M_w/M_n = 1.58$.

to 75,000 proportionally with increasing monomer conversion from 31 to 82%. $M_{n(GPC)}$ is almost equal to the calculated number-average molecular weight, $M_{n(cal)}$ which is computed according to $M_{n(cal)} = ([St]_0/[TD]_0) \times MW_{St} \times$ Conversion (MW_{St}, i.e. the molecular weight of styrene), resulting in f, the initiator efficiency, calculated from $f = M_{n(cal)}/M_{n(GPC)}$ being around 1.0 (as shown in Table 1). Moreover, the molecular weight distributions (M_w/M_n) are demonstrated as low as 1.4.

On the basis of the mentioned results, it can be seen that the controlled radical polymerization of St can be carried out with TD/CuBr/bpy initiating system.

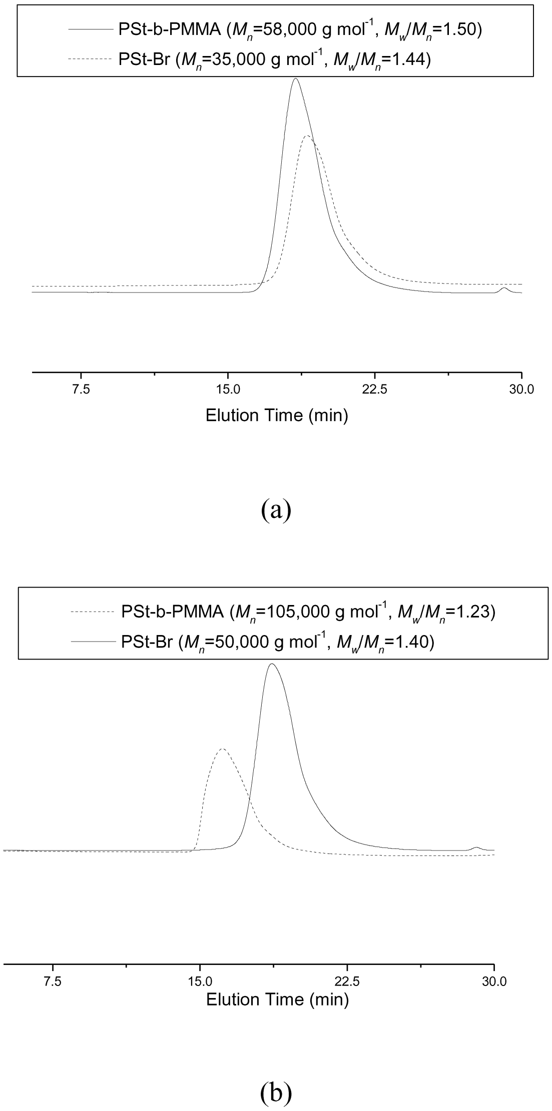
^{1}H NMR spectroscopy of the resulting PSt is shown in Fig. 3. The signals at around δ 3.5–4.0 ppm (a) and δ 0.8–1.1 ppm (e) are assigned to the methylene and methyl protons, respectively, of diethylthiocarbamoylthiyl (dtc) group, $-S_2CN(CH_2CH_3)_2$. The peak at around δ 4.3–4.6 ppm (b) corresponds to the methyne proton in the monomer unit adjacent to bromine, $-CH_2C(Ph)H-Br$. The ratio of the two absorptions (a) and (b) is about 4:1, which is in accordance with the structure of the polymer. Furthermore, the signals at around δ 1.0–2.2 ppm (d) and δ 6.3–7.2 ppm (c) are attributed to the repeat unit of styrene. Signal (e) is partly overlapped by (d), so the integral 4.63 is not so proper (theoretically 6.0). UV spectroscopy analysis of the polymer reveals that there is 0.9 dtc group in per polymer chain [24]. These results show that there are α-dtc and ω-Br end groups in the polymer chain.

The polymerizations of MMA in bulk with the obtained polystyrene bearing bromine terminal group (PSt–Br) acting as a macroinitiator catalyzed by CuBr/bpy ($[MMA]_0:[PSt-Br]_0:[CuBr]_0:[bpy]_0 = 433:1:1:3$) and CuCl/bpy complex ($[MMA]_0 : [PSt-Br]_0 : [CuCl]_0 : [bpy]_0 = 1340 : 1 : 1 : 3$) were performed at 100 °C. GPC plots (Fig. 4(a) and (b)) explicitly illustrates the changes in M_n and M_w/M_n before and after the polymerization. When catalyzed by CuBr/bpy, M_n went from 35,000 up to 58,000, and M_w/M_n changed slightly, from 1.44 to 1.50. From Fig. 4(a), it is demonstrated that the curve of block polymer is tailing. In order to improve the molecular weight

Table 1
The results of comparison experiments for bulk polymerization of styrene with various initiating systems

Entry	Additive	$[TD]_0$[a]/$[CuBr]_0$/ $[bpy]_0$/$[Additive]_0$	Time (h)	Conv. (%)	$M_{n(GPC)}$[b] × 10^{-4} (g mol^{-1})	$M_{n(cal)}$[c] × 10^{-4} (g mol^{-1})	PDI[d]	f[e]
1[f]	–	1000:1:0:0:0	3.3	33	4.4	3.4	1.61	0.8
2[f]	–	1000:1:0:0:0	7.5	56	6.1	5.8	1.70	0.9
3[g]	–	1000:1:1:0:0	42	0	–	–	–	–
4[g]	–	1000:1:1:3:0	6	31	3.5	3.3	1.44	0.9
5[g]	–	1000:1:1:3:0	26	82	7.5	8.6	1.42	1.1
6[g]	DPPH	1000:1:1:3:2	42	0	–	–	–	–
7[g]	MeOH	1000:1:1:3:20	25	73.8	7.9	7.7	1.42	1.0

[a] $[TD]_0 = 8.7$ mmol l^{-1}.
[b] GPC: calibrated by PSt standards.
[c] $M_{n(cal)}$: calculated from $M_{n(cal)} = ([St]_0/[TD]_0) \times MW_{St} \times$ (Conversion/100).
[d] PDI: molecular weight distribution is calculated from M_w/M_n.
[e] f: initiator efficiency calculated from $f = M_{n(cal)}/M_{n(GPC)}$.
[f] At 100 °C.
[g] At 120 °C.



(a)

(b)

Fig. 4. GPC curves of PSt–Br and PSt-*b*-PMMA initiated with PSt–Br catalyzed by CuBr (a) and CuCl (b) in bulk at 100 °C. Conditions: (a) $[MMA]_0 = 9.32$ mol l^{-1}, $M_{n(PSt-Br)} = 35{,}000$ g mol^{-1}, $M_w/M_n = 1.44$, $[MMA]_0:[PSt-Br]_0:[CuBr]_0:[bpy]_0 = 433:1:1:3$; (b) $[MMA]_0 = 9.32$ mol l^{-1}, $M_{n(PSt-Br)} = 50{,}000$ g mol^{-1}, $M_w/M_n = 1.40$, $[MMA]_0:[PSt-Br]_0:[CuCl]_0:[bpy]_0 = 1340:1:1:3$.

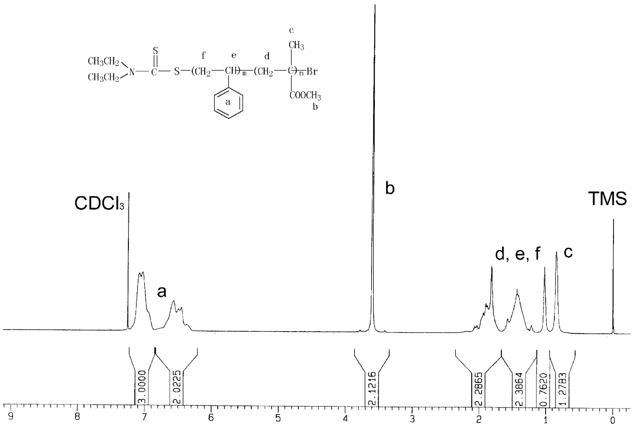


Fig. 5. 400 MHz ^{1}H NMR spectroscopy of PSt-*b*-PMMA initiated with the obtained PSt–Br/CuBr/bpy (in $CDCl_3$). Sample: $M_{n(PSt\text{-}b\text{-}PMMA)} = 58{,}000$ g mol^{-1}, $M_w/M_n = 1.50$.

distribution of the block polymer, we employed CuCl/bpy as the catalyst. As a result of halide exchange [25], the block polymer had narrow polydispersity, 1.23. It is shown in Fig. 4(b) that the curve is symmetric without tailing. ^{1}H NMR analysis for the structure of the block polymer is shown in Fig. 5. The absorption of methyl ester group, $-CH_2C(CH_3)(COOCH_3)-$ of MMA repeat units is at δ 3.6 ppm, and the signals at around δ 6.2–7.2 ppm are ascribed to the phenyl group in the repeat unit of styrene. Two glass transition temperatures 107.0, 124.5 °C assigned to PSt and PMMA segments, respectively, are observed in DSC trace (Fig. 6). Although both temperatures are a little higher than the documented ones, 100 and 105 °C [26], they are in consistent with what Teyssié et al. [27] and Qiu et al. [28–30] have reported. These data show that both PSt and PMMA segments are present in the chain.

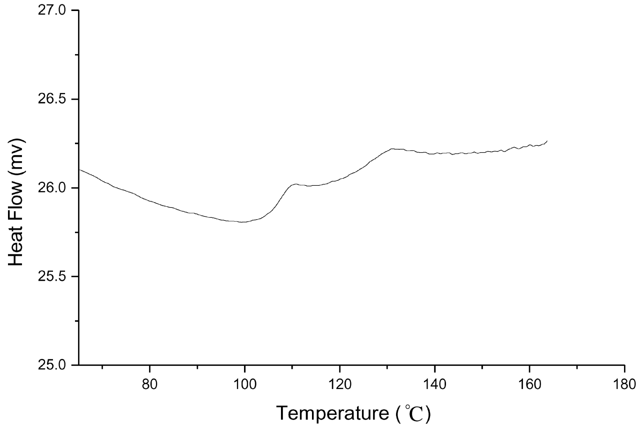
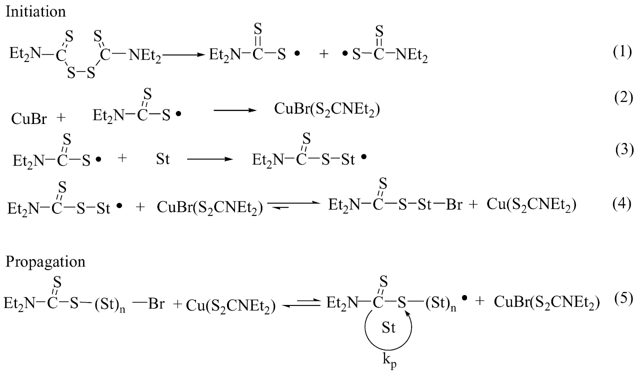


Fig. 6. DSC trace of PSt-*b*-PMMA initiated with PSt–Br/CuBr/bpy at 100 °C. See Fig. 5 for sample.

3.2. Polymerization mechanism

Comparison experiments were carried out to investigate the radical essence of the St polymerization initiated with TD/CuBr/bpy, and the results are summarized in Table 1. It is known that TD is a useful iniferter and that the polymer obtained by the use of iniferter is ill controlled with high molecular weight distributions. The polymerization of St initiated by TD alone at 100 °C did show some characteristics of iniferter (entries 1 and 2). When the monomer conversion reached 33% at 3.3 h, M_n was 44,000 and M_w/M_n was 1.61. After 7.5 h, the conversion rose to 56%, M_n and M_w/M_n were 61,000 and 1.70, respectively. In the presence of CuBr, no polymerization was observed until 42 h (entry 3). This is consistent with the literature [31]. It can also be seen that autopolymerization of styrene was inhibited by this initiating system. Only with the three components acting as the initiating system,



Scheme 1. Proposed mechanism for the polymerization of styrene initiated with TD/CuBr/bpy at 120 °C.

'living'/controlled radical polymerization of St could be successfully performed (entries 4 and 5). The conversion increased from 31 to 82% in 36 h. $M_{n(GPC)}$ was in good agreement with the theoretical one $M_{n(cal)}$ with f about 1.0. Moreover, M_w/M_n was almost unchanged, from 1.44 to 1.42. With the addition of 1,1-diphenyl-2-picrylhydrazyl (DPPH), an effective radical scavenger for St polymerization [32], whose molar concentration was two times to the one of the active radical, the characteristic pink color of DPPH disappeared immediately at the reaction temperature. Until 42 h, no polymer was obtained, which demonstrated that all the active radicals were consumed by DPPH (entry 6). However, with the addition of methanol, an effective terminator for ionic polymerization, being twenty-fold molar excess over TD, the reaction was not affected with 73.8% conversion at 25 h, $M_{n(GPC)}$ 79,000 and M_w/M_n 1.42 (entry 7). These results were identical to those in the absence of methanol.

All above data revealed the radical characteristics of St polymerization initiated with TD/CuBr/bpy, so we propose the mechanism as described in Scheme 1 (Ligand bpy is omitted for simplification).

TD dissociates at the weak S–S bond (bond energy 100 kJ mol^{-1} [33]) at 120 °C and two diethylthiocarbamoylthiyl radicals, $Et_2NCS_2^{\cdot}$, are produced. Active CuBr consumes one radical forming the relatively stable cupric species $CuBr(S_2CNEt_2)$ [34]. Thus CuBr induces the decomposition of TD at 120 °C and produces one active radical $Et_2NCS_2^{\cdot}$ and the deactivator $CuBr(S_2CNEt_2)$ (Eqs. (1) and (2)). The active radical attacks St monomer and produces the activated monomer radical which can be deactivated by $CuBr(S_2CNEt_2)$. Therefore, the dormant chain Et_2NCS_2–St–Br and activator $Cu(S_2CNEt_2)$ [35] are generated (Eqs. (3) and (4)). The bond length of Cu–S, 2.30 Å is shorter than the one of bond Cu–Br, 2.40 Å [36,37]. The greater bond length of Cu–Br corresponds to the lower bond energy, resulting in the easier broken bond. So Eq. (4) is driven into the direction of Et_2NCS_2–St–Br plus $Cu(S_2CNEt_2)$ because of the lower bond energy of Cu–Br than that of Cu–S. The subsequent propagation of styrene is the same as in a conventional ATRP process (Eq. (5)). With the catalyst $Cu(S_2CNEt_2)$, the reverse equilibrium was established between the active radical and the dormant species. Because CuBr consumes an active radical $Et_2NCS_2^{\cdot}$ generating the stable cupric species $CuBr(S_2CNEt_2)$, only one molar concentration of TD is included in the calculation of $M_{n(cal)}$. This calculation is similar to Ref. [16] which reported ATRP of St initiated with BPO/CuBr/dNbpy.

4. Conclusions

The 'living'/controlled radical polymerization of styrene was successfully performed in the presence of TD as the initiator and CuBr/bpy as the catalyst. Linear first-order kinetic plot was observed. Well-controlled polystyrene was obtained with rather low molecular weight distribution ($M_w/M_n = 1.40$). ^{1}H NMR and UV spectra analyses revealed the structure of the resulting polystyrene with α-S_2CNEt_2 and ω-Br end groups. MMA can be polymerized with the resulting PSt–Br as the initiator and CuBr/bpy or CuCl/bpy as the catalyst through a conventional ATRP mechanism. GPC, ^{1}H NMR and DSC analyses demonstrated the block structure of the obtained PSt-*b*-PMMA polymer. The radical nature of St polymerization with TD/CuBr/bpy was illustrated through the comparison experiments with the presence of radical scavenger DPPH and terminator for ionic polymerization, methanol. DPPH terminated the polymerization, while methanol did not affect the progress of monomer consumption.

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