

COPPER(0)-MEDIATED RADICAL POLYMERIZATION OF STYRENE AT ROOM TEMPERATURE*

Xiao-fei Zhang, Yang Wu, Jun Huang, Xue-lang Miao, Zheng-biao Zhang** and Xiu-lin Zhu**
Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

Abstract The “living”/controlled radical polymerization (LRP) of styrene (St) at room temperature is rarely reported. In this work, copper(0) (Cu(0))-mediated radical polymerization of St at room temperature was investigated in detail. Dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) as well as a binary solvent, tetrahydrofuran/1,1,1,3,3,3-hexafluoro-2-propanol were used as the solvents, respectively. Methyl-2-bromopropionate and ethyl 2-bromoisobutyrate were used as the initiators, respectively. The polymerization proceeded smoothly with moderate conversions at room temperature. It was found that DMF was a good solvent with the essential features of LRP, while DMSO was a poor solvent with uncontrollable molecular weights. Besides, the match among the initiator, solvent and molar ratios of reactants can modulate the livingness of the polymerization, and the proper selection of ligand was also crucial to a controlled process. This work provided a first example of Cu(0)-mediated radical polymerization of St at room temperature, which would enrich and strength the LRP technique.

Keywords: Gel permeation chromatography (GPC); Kinetics (polym.); Cu(0)-mediated radical polymerization; Styrene.

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-013-1243-6>.

INTRODUCTION

During the past decades, the development of “living”/controlled radical polymerization (LRP) has made vast progress in the precise synthesis of well-defined polymers with predetermined molecular weights, tailored architectures and functionalities. Following the great discovery of LRP by Otsu in 1982^[1], many powerful LRP techniques have been developed, including stable free radical polymerization (SFRP)^[2, 3], reversible addition-fragmentation transfer polymerization (RAFT)^[4, 5], organotellurium-mediated LRP (TERP), organobismuthine-mediated LRP (BIRP), organostibine-mediated LRP (SBRP)^[6, 7] and metal-catalyzed LRP^[8–11]. The metal-catalyzed LRP mainly included cobalt-mediated LRP^[12, 13], atom transfer radical polymerization (ATRP)^[14–16] and Cu(0)-mediated controlled radical polymerization (also named single-electron transfer mediated LRP, SET-LRP)^[17–22]. Despite of that the mechanism of Cu(0)-mediated controlled radical polymerization is still debated in literatures^[17, 23–25], Cu(0)-mediated controlled radical polymerization with Cu(0) as catalyst has shown its distinct

* The work was financially supported by the National Natural Science Foundation of China (Nos. 20904036 and 21174094), the Nature Science Key Basic Research of Jiangsu Province for High Education (No. 12KJA150007), and Creative Experiment Plan of Soochow University Undergraduates (57315977).

** Corresponding author: Zheng-biao Zhang (张正彪), E-mail: zhangzhengbiao@suda.edu.cn
Xiu-lin Zhu (朱秀林), E-mail: xlzhu@suda.edu.cn

Received August 13, 2012; Revised November 1, 2012; Accepted November 15, 2012
doi: 10.1007/s10118-013-1243-6

advantages over other LRP^[17, 18], including low temperature (room temperature and below), small amount of catalyst, ultrafast polymerization and high molecular weight polymers with narrow molecular weight distributions. Matyjaszewski *et al.*^[23–25] argued that Cu(0)-mediated controlled radical polymerization was a kind of ATRP: activator regenerated by electron transfer-ATRP, in which Cu(0) reduced the excess of Cu(II) to regenerate active Cu(I). Putting aside the mechanism aspect, the use of Cu(0) as the LRP catalyst directly is favorable, since it is cheaper and easier to be handled than Cu(I) or Cu(II) complexes. Besides, Cu(0) is highly active and the polymerization could be conducted at room temperature, which could be seen as a powerful technique to synthesize well-controlled polymers.

It is well-known that St can be easily polymerized by SFRP, ATRP and RAFT with all the elemental characteristics of LRP. The rate constant of St polymerization is relatively low in comparison with that of methyl methacrylate^[26, 27]. Usually, SFRP, ATRP and RAFT of St were conducted at relatively high temperatures, such as 80 °C or above. Recently, Perrier *et al.* reported the Cu(0)-mediated living radical polymerization of St in toluene at 90 °C with well-controlled behavior^[28]. In their communication, the right selection of ligand was very important to the control process. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (PMDETA) was superior to hexamethylene tris(2-aminoethyl)amine (Me₆TREN) and 4,4'-dinonyl-2,2'-bipyridine (diNbpy). It was noteworthy that Me₆TREN and diNbpy were both highly effective ligands in ATRP, implying an intricate process in Cu(0)-mediated polymerization of St. To the best of our knowledge, low-temperature LRP of St was rarely reported. LRP of St at low temperature (such as 25 °C) has merits for both the scientific research and practical applications. In 1999, Sawamoto demonstrated that the rhenium (V) iododioxobis(triphenylphosphine) mediated LRP of St can be performed at 30 °C with narrow polydispersity^[29]. However, there was no detailed data about the polymerization profile in that report. In 2008, Dhamodharan *et al.* reported the polymerization of St by SET initiation, followed by RAFT control at ambient temperature^[20]. Well-controlled polymerization was presented by this method, termed as SET-RAFT. However, the reaction system was complicated and the exact polymerization mechanism was not exactly defined. In this work, we investigated the feasibility and possibility of controlled polymerization of St at room temperature by the utilization of the powerful Cu(0)-mediated controlled radical polymerization. Dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and a binary solvent, tetrahydrofuran (THF)/1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)^[30], were used as solvents, respectively. Methyl-2-bromopropionate and ethyl 2-bromoisobutyrate were used as initiators, respectively.

EXPERIMENTAL

Materials

Styrene (St, > 99%) was purchased from Shanghai Chemical Reagents Co. (Shanghai, China). It was washed three times with an aqueous solution of sodium hydroxide (5 wt%), followed by washing with deionized water until the solution was neutralized. The resulting solution was dried over anhydrous magnesium sulfate, distilled twice at reduced pressure, and stored at –18 °C. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (PMDETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 0.4 nm molecular sieves and distilled under vacuum. Methyl-2-bromopropionate (MBP) (98%) and ethyl 2-bromoisobutyrate (EBiB) (98%) were purchased from Acros and used as received. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Shanghai Dai'shang Chemical Co. (Shanghai, China). Copper (75 μm powder, 99%, Aldrich), dimethyl sulfoxide (DMSO) (99.9%, Shanghai Chemical Reagents Co.) and *N,N*-dimethylformamide (DMF) (99.9%, Shanghai Chemical Reagents Co.) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co. and used as received unless it was mentioned.

Characterization

The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the resulting polymers were determined using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1 (pore size: 10 nm, 100–5000 Da), HR 2 (pore size: 50 nm, 500–20000 Da) and HR 4 (pore size 1000 nm, 50–100000 Da) columns (7.8 × 300 mm, 5 μm beads size) with molecular weights

ranging from 10^2 – 5×10^5 . THF was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. GPC samples were injected using a Waters 717 plus autosampler and calibrated with poly(styrene) (PSt) standards purchased from Waters. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry measurements were performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Both matrix, 4-hydroxy- α -cyanocinnamic acid, and sample were dissolved in 1:1 (V/V) acetonitrile: water with 1% trifluoroacetic acid. This mixture solution (0.5 μ L) was placed on a metal sample plate. The sample was air-dried at ambient temperature. The ^1H -NMR spectrum of the precipitated polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using CDCl_3 as the solvent and tetramethylsilane (TMS) as an internal standard.

Typical Procedures for Cu(0)-mediated Polymerization at 25 °C

The monomer (St, 2.00 mL, 17.4 mmol), solvent (DMF, 1.00 mL), initiator (MBP, 0.0144 g, 0.087 mmol), catalyst (Cu(0), 5.56 mg, 0.0870 mmol) and ligand (PMDETA, 22.0 μ L, 0.0835 mmol) were added to a 5.0 mL-ampoule in the following order: Cu(0), monomer, ligand, solvent and initiator. The solution was deoxygenated by bubbling with argon for 20 min. The ampoule was then flame sealed and placed in a stirred oil bath equipped with a thermostat at (25 ± 0.1) °C. After 12 h, the ampoule was cooled by ice water. Afterwards, the ampoule was opened, and the contents were dissolved in 5.0 mL of THF and passed through a small basic Al_2O_3 chromatographic column to remove any unreacted Cu(0) catalyst and Cu(II) compounds. The resultant solution was precipitated into 150 mL of cold methanol (0 °C) under stirring. The polymer was isolated by filtration and dried under vacuum until a constant weight was recorded at room temperature. The monomer conversion was 17.7% by gravimetric calculation. Samples were dissolved in CDCl_3 for ^1H -NMR spectroscopy. The M_n and M_w/M_n values were determined by GPC with PSt standards ($M_{n,\text{GPC}} = 6.65 \times 10^3$, $M_w/M_n = 1.35$).

Typical Procedures for Chain Extension of PSt Using PSt as Macro-initiator

PSt sample ($M_{n,\text{GPC}} = 6.66 \times 10^3$, $M_w/M_n = 1.21$) obtained by Cu(0)-mediated polymerization was used as the macro-initiator for the chain extension reaction. PSt (0.170 g, 0.0252 mmol) was dissolved in 1.30 mL of fresh St and 0.650 mL of DMF. The catalyst (Cu(0), 1.60 mg, 0.0252 mmol) and ligand (PMDETA, 6.34 μ L, 0.0252 mmol) were then added to this solution. The solution was deoxygenated by bubbling with argon for 20 min. The ampoule was then flame sealed and placed in a stirred oil bath equipped with a thermostat at (25 ± 0.1) °C. After 48 h, the ampoule was cooled by ice water. The rest of the procedure was identical to that described above with initiator replaced by PSt. The monomer conversion was 19.0% by gravimetric calculation. The M_n and M_w/M_n values were determined by GPC with PSt standards ($M_{n,\text{GPC}} = 1.54 \times 10^4$, $M_w/M_n = 1.31$).

RESULTS AND DISCUSSION

Cu(0)-catalyzed polymerizations of St were carried out at 25 °C with DMF, DMSO and binary THF/HFIP as solvents. It was reported that binary mixture of organic solvent can also modulate reaction parameters such as the polymerization rate and molecular weight predictability in Cu(0)-mediated polymerizations^[18]. The binary mixture of THF and HFIP was then used as the solvent of Cu(0)-mediated polymerization of St to examine the polymerization performance. MBP and EBiB were used as the initiators, which were both effective initiators for ATRP and Cu(0)-mediated controlled radical polymerization of acrylates and methacrylates, respectively. The reaction conditions were also modulated at the molar ratios of $[\text{St}]_0:[\text{MBP}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 200:1:1:1$ (Fig. 1) and $[\text{St}]_0:[\text{MBP}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 500:1:1:1$ (Fig. 2). Cu(0) powder with a particle size of less than 75 μm was used as the primary activating species. Figure 1 summarizes the kinetic data for the MBP-initiated Cu(0)-mediated polymerization of St under various conditions. As shown in Fig. 1(a), the polymerization of St can proceed at 25 °C. It was obvious that the rate of Cu(0)-mediated polymerization of St was much slower than that of MA or MMA at 25 °C, due to the low propagating rate constant of St polymerization^[26, 27]. Control experiments, the reaction without both of Cu(0)/PMDETA and initiator, *i.e.*, only St or the mixture of St and solvent, were also performed, and there were no polymers after 144 h in these cases

(Table S1, Supporting Information). These results confirmed that combination of MBP with Cu(0)/PMDETA initiated and catalyzed the polymerization process. The results in Fig. 1(a) further revealed that there was slight difference in the polymerization kinetics among the three solvents. Figure 1(b) describes the number-average molecular weight ($M_{n, GPC}$) and molecular weight distribution (M_w/M_n) as functions of the monomer conversion at various conditions. It was found that these three solvents showed different controllability over the polymerization of St. In the case of $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 200:1:1:1$, the molecular weights increased with monomer conversions by using DMF and DMSO as solvents as presented in Fig. 1(b).

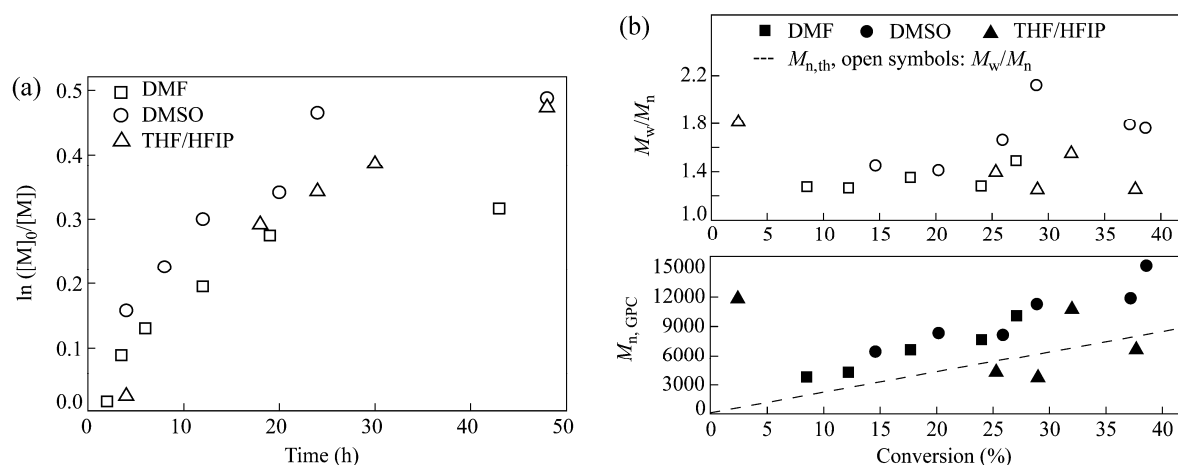


Fig. 1 Polymerization profiles of Cu(0)-mediated polymerization of styrene (St) with different solvents at $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 200:1:1:1$ ($[St]_0 = 6.03$ mol/L, St: 2.0 mL, solvent: 1.0 mL; THF/HFIP as solvent: THF; 0.33 mL, HFIP; 0.67 mL; Temperature = 25 °C) (a) kinetic investigation ($\ln([M]_0/[M])$ versus time) and (b) evolution of the number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(styrene) (PSt) with conversion

Theoretical molecular weight ($M_{n,th}$) = $([St]_0/[MBP]_0) \times M_{St} \times \text{Conversion} + M_{MBP}$, where M_{St} and M_{MBP} represent the molecular weights of St and MBP, respectively.

The polydispersity values of PSt with DMF as solvent increased slightly with time evolution (< 1.50). While the polydispersity values increased remarkably with time (> 1.50) by using DMSO as the solvent, indicating of a poor control. In THF/HFIP binary solvent, the polymerization was uncontrollable, e.g. the molecular weights of the polymers did not increase with monomer conversions and obtained polymers showed high polydispersity values. Similar kinetic results were observed in the case of $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 500:1:1:1$, as shown in Fig. 2(a). The kinetic plots were non-linear in both Fig. 1(a) and Fig. 2(a), indicating a complicated process of Cu(0)-mediated polymerization of St. At $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 500:1:1:1$ (Fig. 2b), with DMF as solvent, the polydispersity values increased moderately with time evolution. Most of the polydispersity values were below 1.30 and were lower than those of Fig. 1(b) with the same solvent, indicating an improved controllability over the polymerization. Similarly, the polydispersity values of the PSt obtained from DMSO system were also reduced remarkably in comparison with those of Fig. 1(b). These results implied that the molar ratio of the reactants not only impacted on the polymerization rates but also the process control. With THF/HFIP as the solvent, the controllability of polymerization was not improved by the change of molar ratio of the reactants (Fig. 2b). From these results, it could be deduced that the solvent had crucial effects on the polymerization process, especially on the living natures^[17, 18]. Also, the effects of the solvent were complicated and cooperative with the molar ratio of reactants. Both in the cases of $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 200:1:1:1$ and $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 500:1:1:1$, DMF showed better control over the molecular weights than other two solvents.

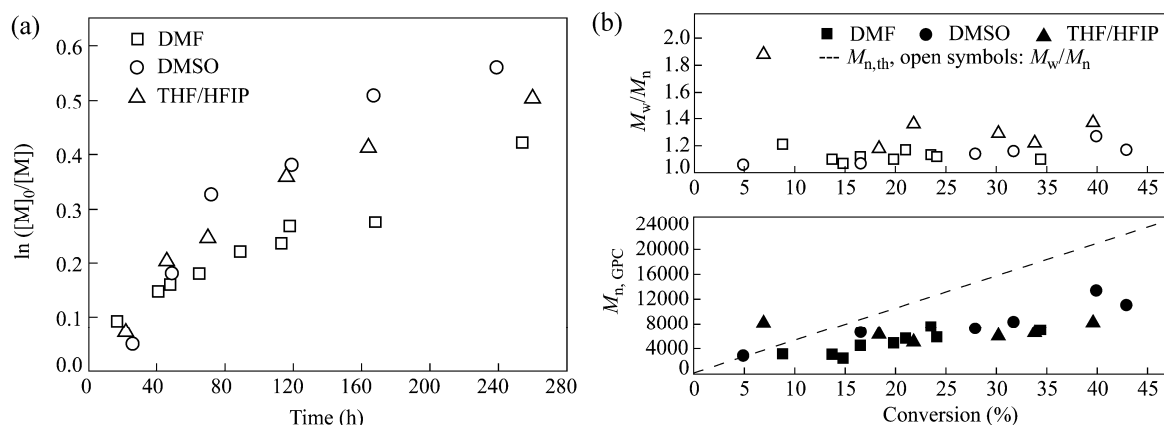


Fig. 2 Polymerization profiles of Cu(0)-mediated polymerization of styrene (St) with different solvents at $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 500:1:1:1$ ($[St]_0 = 6.03$ mol/L, St: 2.0 mL, solvent: 1.0 mL; THF/HFIP as solvent: THF, 0.33 mL, HFIP, 0.67 mL; Temperature = 25 °C) (a) kinetic investigation ($\ln([M]_0/[M])$) versus time and (b) evolution of the number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(styrene) (PSt) with conversion

Theoretical molecular weight ($M_{n,th}$) = $([St]_0/[MBP]_0) \times M_{St} \times \text{Conversion} + M_{MBP}$, where M_{St} and M_{MBP} represent the molecular weights of St and MBP, respectively.

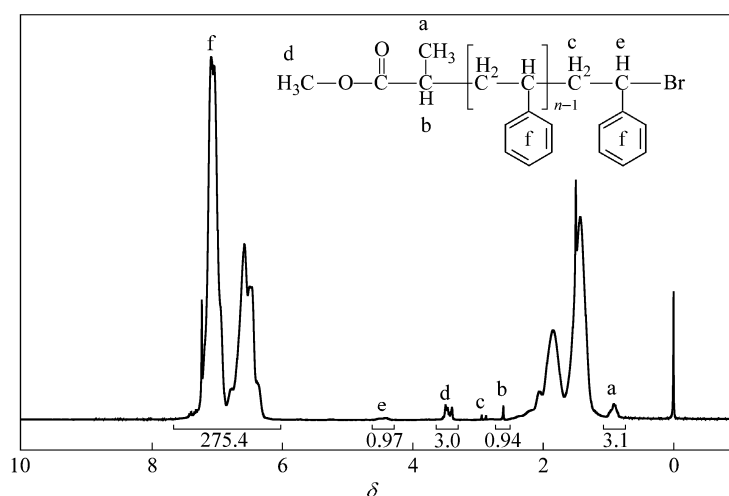


Fig. 3 ^1H -NMR spectrum of poly(styrene) ($M_{n, GPC} = 6.65 \times 10^3$, $M_w/M_n = 1.35$) obtained from the MBP and Cu(0)/PMDETA mediated polymerization with DMF as solvent. CDCl_3 was used as the solvent and tetramethylsilane (TMS) as the internal standard.

To further confirm the livingness of Cu(0)-mediated polymerization of St mediated by DMF, the chain ends structure of the PSt prepared with DMF as solvent was analyzed by ^1H -NMR spectroscopy (Fig. 3). The PSt sample ($M_{n, GPC} = 6.65 \times 10^3$, $M_w/M_n = 1.35$) was obtained at 17.7% conversion from the polymerization with $[St]_0:[MBP]_0:[Cu(0)]_0:[PMDETA]_0 = 200:1:1:1$ (Fig. 1a). The chemical shift at $\delta = 6.4\text{--}7.5$ (f, 5H, integral value = $I_{6.4} = 275.4$) corresponded to the aromatic protons in the phenyl groups of St repeated units. The chemical shifts at $\delta = 2.9$ and $\delta = 4.3$ can be assigned to the methylene (c) and methyne protons (e, 1H, integral value = $I_{4.3} = 0.97$) of the last St unit capped by bromine, respectively. The chemical shifts at $\delta = 3.4\text{--}3.7$ (d, 3H, integral value = $I_{3.4} = 3.0$), $\delta = 2.6$ (b, 1H, integral value = $I_{2.63} = 0.94$) and $\delta = 0.8\text{--}1.06$ (a, 3H, integral value = $I_{0.8} = 3.1$) can be assigned to the methoxyl, methyne and methyl protons arising from MBP moieties,

respectively. From these results, it can be found that the bromo-chain end-functionality of the polymers (e, 1H, integral value = $I_{4.3}$ = 0.97) was close to the MBP derived polymers (b, 1H, integral value = $I_{2.63}$ = 0.94), indicating a living process of the polymerization. Assuming that each polymer chain was captured by an initiator fragment from MBP moiety, the molecular weight ($M_{n, \text{NMR}}$) of PSt can be calculated from the integrals in $^1\text{H-NMR}$, according to Eq. (1):

$$M_{n, \text{NMR}} = (I_{6.4}/5) \times 104.15/(I_{3.4}/3) + 165.9 \quad (1)$$

where, 104.15 and 165.9 are the molecular weights of St and MBP, respectively. The molecular weight of PSt sample calculated from the $^1\text{H-NMR}$ spectrum ($M_{n, \text{NMR}}$) was 5.90×10^3 , which was close to the GPC value (6.65×10^3), indicating that most of the PSt chain ends were captured by MBP.

In both ATRP and Cu(0)-mediated controlled radical polymerization, the different structures of R groups in the initiator (R-X) showed important effects on the controllability of the polymerization^[14, 15, 18]. To verify the effects of initiator, the bromide initiator, EBiB, bearing R group different from that of MBP was used as the initiator. EBiB has been used in Cu(0)/bpy catalyzed LRP of MMA in DMSO^[17], Cu(0)/PMDETA catalyzed LRP of MMA in HFIP^[30] and Cu(0)/Me₆TREN catalyzed LRP of MA in DMSO at 25 °C^[18, 31]. Here, the using EBiB as the initiator was carried out under the identical conditions as in Fig. 1 with EBiB instead of MBP. The results are summarized in Figs. 4 and 5. It could be found that with the molar ratio of $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 200:1:1:1$, there was relatively large difference in the polymerization rates when using different solvents, *e.g.*, DMF, DMSO and THF/HFIP. However, as aforementioned in Fig. 1(a), there was small difference of the polymerization rates with MBP as initiator among these solvents. Whereas, when the molar ratio of $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0$ was changed to 500:1:1:1 (Fig. 5a), the polymerization kinetics showed unobvious difference among the three solvents mediated polymerizations. These results suggested that the effects of the initiators were complicated, and the molar ratio of reactants should be taken into consideration. The evolutions of molecular weights of the polymers with monomer conversion were investigated under different molar ratios of $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0$. The results of $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 200:1:1:1$ and $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 500:1:1:1$ are shown in Figs. 4(b) and 5(b), respectively. In the case of the molar ratio of $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 200:1:1:1$ (Fig. 4b), the molecular weights of the polymers increased with monomer conversion in DMF, DMSO and THF/HFIP systems. Also, the livingness in the case of DMF and THF/HFIP was better than that of DMSO.

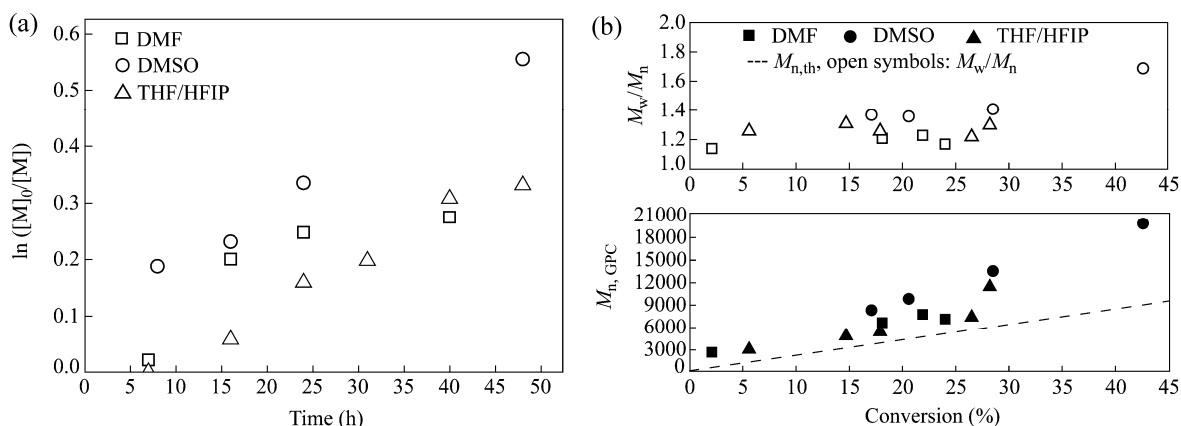


Fig. 4 Polymerization profiles of Cu(0)-mediated polymerization of styrene (St) with different solvents at $[\text{St}]_0:[\text{EBiB}]_0:[\text{Cu}(0)]_0:[\text{PMDETA}]_0 = 200:1:1:1$ ($[\text{St}]_0 = 6.03 \text{ mol/L}$, St: 2.0 mL, solvent: 1.0 mL; THF/HFIP as solvent: THF, 0.33 mL, HFIP, 0.67 mL; Temperature = 25 °C) (a) kinetic investigation ($\ln([M]_0/[M])$) versus time, and (b) evolution of the number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(styrene) (PSt) with conversion
Theoretical molecular weight ($M_{n, \text{th}} = ([\text{St}]_0/[\text{EBiB}]_0) \times M_{\text{St}} \times \text{Conversion} + M_{\text{EBiB}}$, where M_{St} and M_{MBP} represent the molecular weights of St and MBP, respectively.

It should be noted that with MBP as initiator (Fig. 2), the polymerization with THF/HFIP as solvent was uncontrollable. These results implied that the effects of the solvent cannot be evaluated independently; and the initiator and solvent may affect the polymerization behavior synergistically. The GPC measured molecular weights of PSt obtained from DMSO system deviated much from the theoretical values ($M_{n,th}$), and the polydispersity values were relatively high ($M_w/M_n > 1.40$). As the molar ratio of $[St]_0:[EBiB]_0:[Cu(0)]_0:[PMDETA]_0$ was changed to 500:1:1:1 (Fig. 5b), the molecular weight distributions of the polymers obtained in THF/HFIP system were much broader ($M_w/M_n > 1.70$) than that from DMF and DMSO system. Also, DMF was the best solvent from the control over molecular weights and molecular weight distributions.

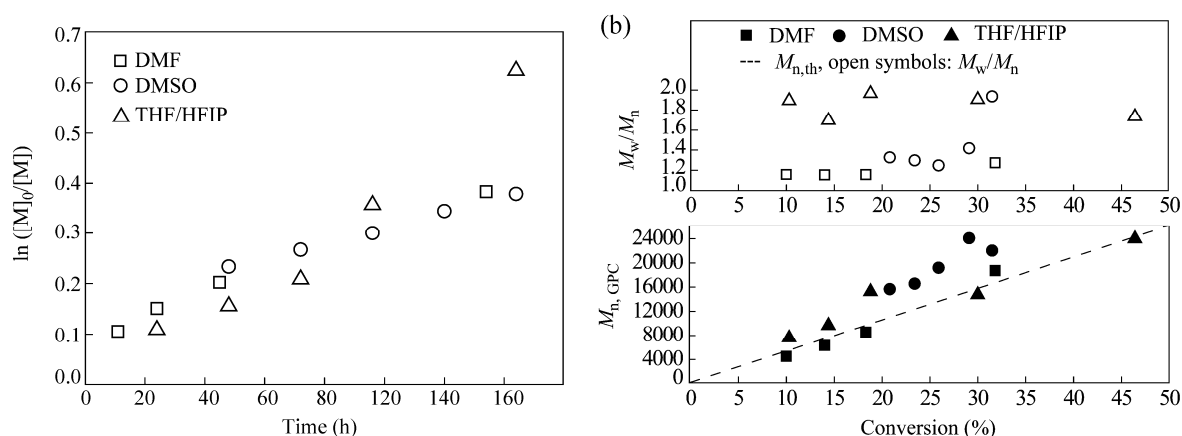


Fig. 5 Polymerization profiles of Cu(0)-mediated polymerization of styrene (St) with different solvents at $[St]_0:[EBiB]_0:[Cu(0)]_0:[PMDETA]_0 = 500:1:1:1$ ($[St]_0 = 6.03$ mol/L, St: 2.0 mL, solvent: 1.0 mL; THF/HFIP as solvent: THF, 0.33 mL, HFIP, 0.67 mL; Temperature = 25 °C) (a) kinetic investigation ($\ln([M]_0/[M])$) versus time, and (b) evolution of the number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(styrene) (PSt) with conversion
Theoretical molecular weight ($M_{n,th}$) = $([St]_0/[EBiB]_0) \times M_{St} \times \text{Conversion} + M_{EBiB}$, where M_{St} and M_{MBP} represent the molecular weights of St and MBP, respectively.

The living feature with DMF as solvent can be also confirmed with the locating of EBiB moieties at the chain ends of PSt from the $^1\text{H-NMR}$ spectrum, as indicated in Fig. 6. Similar with the MBP end-capped PSt in Fig. 3, the chemical shifts at $\delta = 2.9$ (b, 2H, integral value = $I_{2.9} = 1.8$) and $\delta = 4.3$ (d, 1H, integral value = $I_{4.3} = 1.0$) can be assigned to the methylene and methyne protons of the last St unit capped by bromine. The chemical shifts at $\delta = 3.3\text{--}3.5$ and $\delta = 0.8\text{--}1.06$ can be assigned to the methylene (c) and methyl protons (a, 9H, integral value = $I_{0.8} = 9.2$) arising from EBiB moieties, respectively. These results proved that the calculated bromo-chain end-functionality of the polymers (d, 1H, integral value = $I_{4.3} = 1.0$) was close to the EBiB derived polymers (a, 9H, integral value = $I_{0.8} = 9.2$), which was an important evidence of a “living” process.

To further investigate the chain end functionality of PSt, the polymers were characterized by MALDI-TOF mass spectrometry. Figure 7 shows the expanded MS spectrum of a PSt sample obtained at 31.8% conversion from the polymerization at the molar ratio of $[St]_0:[EBiB]_0:[Cu(0)]_0:[PMDETA]_0 = 500:1:1:1$ (Fig. 5a). It can be found from Fig. 7 that there was only one main series of peaks, their interval was regular, *ca.* 104.15, the molar mass of St, and the experimental isotopic mass distribution values in the main peak series of MALDI-TOF spectrum (with the subtraction of m/z value of sodium cation (Na^+)) are in good agreement with the theoretical values in Eq. (2):

$$M_{\text{theo}} = 115.1 + n \times 104.15 + 79.9 \quad (2)$$

M_{theo} refers to the theoretical mass value by Eq. (2). 115.1 and 79.9 refer to the molecular weights of ethyl isobutyrate and bromine species of EBiB, respectively. 104.15 and n are the average mass of St repeated unit and

number of the St unit in the polymer chains. The molecular weight from MALDI-TOF measurement was 1.36×10^4 , $M_w/M_n = 1.01$, slightly lower than $M_{n, \text{GPC}}$ ($M_{n, \text{GPC}} = 1.87 \times 10^4$). The deviation was due to the mass discrimination during the MALDI-TOF measurement process^[32–35]. These results clearly showed that EBiB moieties were attached at polymer chain ends.

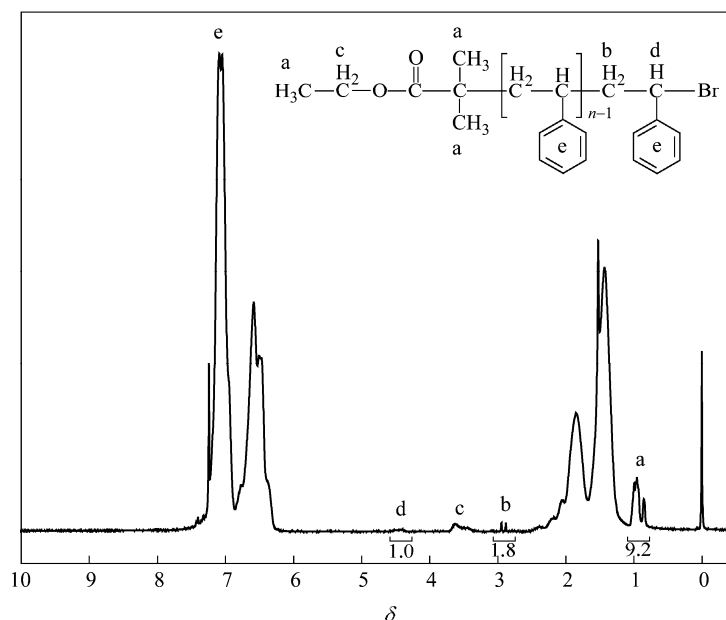


Fig. 6 ¹H-NMR spectrum of poly(styrene) ($M_{n, \text{GPC}} = 6.66 \times 10^3$, $M_w/M_n = 1.21$) obtained from the EBiB and Cu(0)/PMDETA mediated polymerization with DMF as solvent. CDCl_3 was used as the solvent and tetramethylsilane (TMS) as the internal standard.

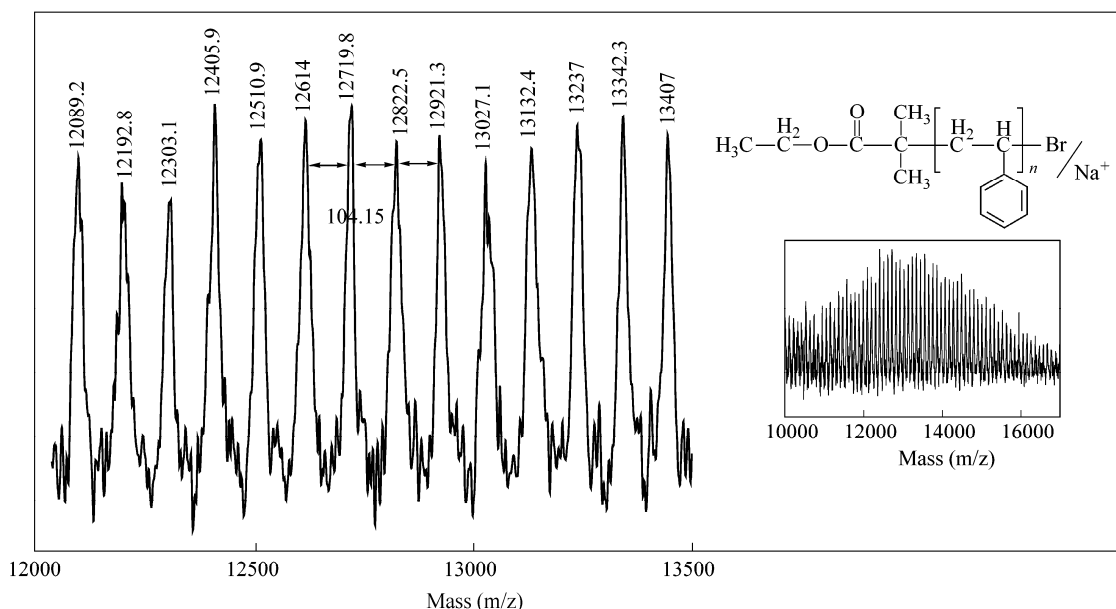


Fig. 7 Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry of poly(styrene) (PSt, $M_{n, \text{GPC}} = 1.87 \times 10^4$, $M_w/M_n = 1.27$) obtained from the EBiB and Cu(0)/PMDETA mediated polymerization with DMF as solvent

The living nature of the polymerization with DMF as solvent was further confirmed by chain extension reaction. PSt sample ($M_{n, \text{GPC}} = 6.66 \times 10^3$, $M_w/M_n = 1.21$) obtained by Cu(0)-mediated polymerization of St in DMF was used as the macro-initiator. The chain extensions were successful at ambient temperature using Cu(0)/PMDETA as a catalyst and DMF as solvent. PSt with much higher molecular weight than that of macro-initiator was obtained, *e.g.* $M_{n, \text{GPC}} = 1.54 \times 10^4$ with $M_w/M_n = 1.31$ showed in Fig. 8. It was clear that with DMF as solvent, most of the obtained bromine end-capped polymers could be reactivated as the macro-initiator.

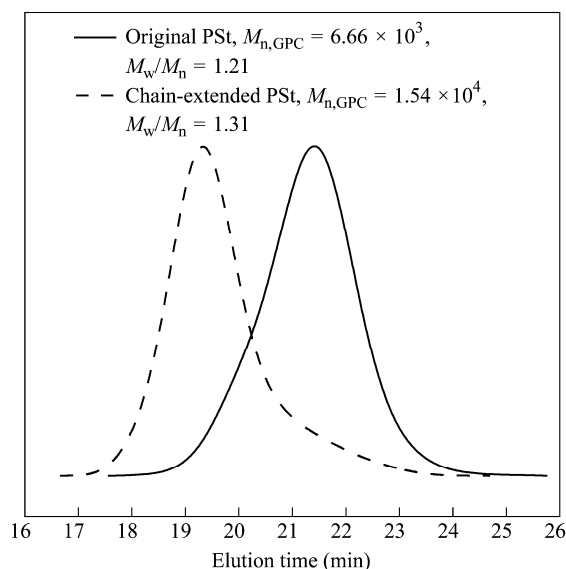


Fig. 8 GPC curves before and after chain extension in DMF with poly(styrene) (PSt) as the macro-initiators in Cu(0)-mediated polymerization at 25 °C ($[\text{St}]_0/[\text{PSt}]_0/[\text{Cu}(0)]_0/[\text{PMDETA}]_0 = 300/1/1/1$, $[\text{St}]_0 = 5.82 \text{ mol/L}$, St: 1.30 mL, St/DMF: 2/1 (V/V), 48 h, 19.0% conversion)

In this work, we also conducted many experiments with Cu(0)/Me₆TREN as the catalyst. The results are summarized in Table 1. The results indicated that the polymerization rates by the catalysis of Cu(0)/Me₆TREN were uniformly lower than those by Cu(0)/PMDETA (Figs. 1 and 4), and the polymerization was poorly controlled with Me₆TREN as ligand. These results agreed with those of Perrier^[28], confirming that Cu(0)-mediated polymerization of styrene is a complicated process. More experiments are now in progress in our lab.

Table 1. Cu(0)-mediated polymerization of St with Me₆TREN as ligand

Entry	Solvent	Time (h)	Con. (%)	$M_{n, \text{GPC}}$	M_w/M_n	$M_{n, \text{th}}$
1	DMSO	18	12.8	7440	2.60	2830
2	DMSO	48	15.4	4220	4.20	3370
3	DMF	18	14.8	8600	1.81	3240
4	DMF	48	17.1	Bimodal	—	—
5	THF/HFIP	18	17.6	7880	1.34	3830
6	THF/HFIP	48	24	10600	1.47	5160
7	DMSO	18	4.8	8400	2.52	1190
8	DMSO	48	7.9	8920	2.54	1840
9	DMF	18	2.7	8710	2.78	760
10	DMF	48	5.5	Bimodal	—	—
11	THF/HFIP	18	12.8	Bimodal	—	—
12	THF/HFIP	48	17.3	18360	2.80	3790

Polymerization temperature = 25 °C; $[\text{St}]_0/[\text{Initiator}]_0/[\text{Cu}(0)]_0/[\text{Me}_6\text{TREN}]_0 = 200:1:1:1$; St: 2 mL, solvent: 1 mL; $M_{n, \text{th}} = ([\text{St}]_0/[\text{Initiator}]_0) \times M_{\text{St}} \times \text{Conversion} + M_{\text{initiator}}$, where M_{St} and $M_{\text{initiator}}$ represent the molecular weights of St and initiator, respectively.

Entries 1–6: initiator, methyl-2-bromopropionate (MBP); Entries 7–12: initiator, ethyl 2-bromoisobutyrate (EBiB)

It can be concluded that in both cases of MBP and EBiB initiated polymerization DMF was a better choice of solvent, which facilitated a well-controlled polymerization of St. DMSO was not a good solvent. However, Cu(0)-mediated polymerization of St was found to be a complicate process from the results of Figs. 1, 2, 4, 5 and Table 1. The effects of initiator, solvent, reactants molar ratios and ligand on the polymerization profiles were found to be cooperative and complicated. The poorly controlled Cu(0)-mediated polymerization of St^[20] may be due to that DMSO was selected as the solvent or an improper combination of initiator, solvent and molar ratios of reactants.

CONCLUSIONS

This work explored the Cu(0)-mediated polymerization of St with variant parameters at room temperature. The results demonstrated that DMF was a good solvent for a well-controlled process, while DMSO was a bad solvent. The control process can be also affected by different initiators and molar ratios of reactants, and the solvent/initiator/molar ratios of reactants showed complicated and cooperative effects on the polymerization process. This work provided the possibility of Cu(0)-mediated polymerization of St with features of LRP at room temperature. The search for the optimal conditions is ongoing in our lab, aiming at both the increase of the polymerization rate and the control over molecular weights.

SUPPORTING INFORMATION GPC traces of Cu(0)-mediated radical polymerization of styrene with DMF as solvent. Cu(0)-mediated radical polymerization of styrene in the presence of various initiators and solvents at the molar ratio of $[St]_0:[initiator]_0:[Cu(0)]_0:[PMDTA]_0 = 1000:1:1:1$.

REFERENCES

- 1 Otsu, T., Yoshida, M. and Tazaki, T., *Makromol. Chem. Rapid Commun.*, 1982, 3(2): 133
- 2 Solomon, D.H., Rizzardo, E. and Cacioli, P. 1985, *Eur. Pat. Appl.*, 135280
- 3 Hawker, C.J., Bosman, A.W. and Harth, E., *Chem. Rev.*, 2001, 101(12): 3661
- 4 Chiefari, J., Chong, Y.K., Ercole, F., Krstina, J., Jeffrey, J., Le, T.P.T., Mayadunne, R.T.A., Meijs, G.F., Moad, C.L., Moad, G., Rizzardo, E. and Thang, S.H., *Macromolecules*, 1998, 31(16): 5559
- 5 Moad, G., Rizzardo, E. and Thang, S.H., *Aust. J. Chem.*, 2012, 65(8): 985
- 6 Yamago, S.J., *Polym. Sci., Part A: Polym. Chem.*, 2006, 44(1): 1
- 7 Yamago, S., *Chem. Rev.*, 2009, 109(11): 5051
- 8 Kato, M., Kamigaito, M., Sawamoto, M. and Higashimura, T., *Macromolecules*, 1995, 28(5): 1721
- 9 Kamaigato, M., Ando, T. and Sawamoto, M., *Chem. Rev.*, 2001, 101(12): 3689
- 10 Makoto, O., Takaya, T. and Mitsuo, S., *Chem. Rev.*, 2009, 109(11): 4963
- 11 Wang, J.S. and Matyjaszewski, K., *Macromolecules*, 1995, 28(23): 7901
- 12 Wayland, B.B., Poszmik, G., Mukerjee, S.L. and Fryd, M.J., *Am. Chem. Soc.*, 1994, 116(17): 7943
- 13 Wayland, B.B., Basickes, L., Mukerjee, S., Wei, M. and Fryd, M., *Macromolecules*, 1997, 30(26): 8109
- 14 Wang, J.S. and Matyjaszewski, K., *J. Am. Chem. Soc.*, 1995, 117(20): 5614
- 15 Matyjaszewski, K. and Xia, J., *Chem. Rev.*, 2001, 101(9): 2921
- 16 di Lena, F. and Matyjaszewski, K., *Prog. Polym. Sci.*, 2010, 35(8): 959
- 17 Percec, V., Guliashvili, T., Ladislav, J.S., Wistrand, A., Stjern Dahl, A., Sienkowska, M.J., Monteiro, M.J. and Sahoo, S., *J. Am. Chem. Soc.*, 2006, 128(43): 14156
- 18 Rosen, B.M. and Percec, V., *Chem. Rev.*, 2009, 109(11): 5069
- 19 Nguyen, N.H., Rosen, B.M., Lligadas, G. and Percec, V., *Macromolecules*, 2009, 42(7): 2379
- 20 Subramanian, S.H., Babu, R.P. and Dhamodharan, R., *Macromolecules*, 2008, 41(1): 262
- 21 Wright, P.M., Mantovani, G. and Haddleton, D.M., *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46(22): 7376

- 22 Levere, M.E., Willoughby, I., O'Donohue, S., Cuendias, A., Grice, A.J., Fidge, C., Becer, C.R. and Haddleton, D.M., *Polym. Chem.*, 2010, 1(7): 1086
- 23 Matyjaszewski, K., Coca, S., Gaynor, S.G., Wei, M.L. and Woodworth, B.E., *Macromolecules*, 1997, 30(23): 7348
- 24 Matyjaszewski, K., Tsarevsky, N.V., Braunecker, W.A., Dong, H., Huang, J., Jakubowski, W., Kwak, Y., Nicolay, R., Tang, W. and Yoon, J.A., *Macromolecules*, 2007, 40(22): 7795
- 25 Lin, C.Y., Coote, M.L., Gennaro, A. and Matyjaszewski, K., *J. Am. Chem. Soc.*, 2008, 130(38): 12762
- 26 Matheson, M.S., Auer, E.E., Bevilacqua, E.B. and Hart, E.J., *J. Am. Chem. Soc.*, 1951, 73(4): 1700
- 27 Deady, M., Mau, A.W.H., Moad, G. and Spurling, T.H., *Makromol. Chem.*, 1993, 194(6): 1691
- 28 Tom, J., Hornby, B., West, A., Harrison, S. and Perrier, S., *Polym. Chem.*, 2010, 1(4): 420
- 29 Kotani, Y., Kamigaito, M. and Sawamoto, M., *Macromolecules*, 1999, 32(8): 2420
- 30 Wang, W.X., Zhang, Z.B., Zhu, J., Zhou, N.C. and Zhu, X.L., *J. Polym. Sci., Part A: Polym. Chem.*, 2009, 47(22): 6316
- 31 Levere, M.E., Nguyen, N.H. and Percec, V., *Macromolecules*, 2012, 45(20): 8267
- 32 Guttman, C.M., Wetzel, S.J. and Flynn, K.M., *Anal. Chem.*, 2005, 77(14): 4539
- 33 Mourey, T.H., Hoteling, A.J. and Balke, S.T., *J. Appl. Polym. Sci.*, 2005, 97(2): 627
- 34 Schriemer, D.C. and Li, L., *Anal. Chem.*, 1997, 69(20): 4169
- 35 Schriemer, D.C. and Li, L., *Anal. Chem.*, 1997, 69(20): 4176