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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis of a Well-Defined Naphthalene-Labeled Polystyrene via Atom Transfer Radical Polymerization

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**To cite this Article** Cheng, Zhenping , Zhu, Xiulin , Zhu, Jian , Lu, Jianmei and Yu, Jianhui(2005) 'Synthesis of a Well-Defined Naphthalene-Labeled Polystyrene via Atom Transfer Radical Polymerization', Journal of Macromolecular Science, Part A, 42: 3, 341 – 349

**To link to this Article:** DOI: 10.1081/MA-200050467

**URL:** <http://dx.doi.org/10.1081/MA-200050467>

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## Synthesis of a Well-Defined Naphthalene-Labeled Polystyrene via Atom Transfer Radical Polymerization

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*The atom transfer radical polymerization of styrene (St) in bulk using 1-(chloromethyl)naphthalene (1-CMN) as an initiator in the presence of CuCl/N,N,N',N''-pentamethyldiethylenetriamine (PMDETA) was investigated at 125°C. The results showed that 1-CMN was an effective initiator with higher initiation efficiency in ATRP of St. The molecular weights of the obtained polystyrene (PS) increased linearly with monomer conversion and the corresponding polydispersity index of polymers remained relatively narrow (1.17–1.30), indicative of well controlled polymerization of St in the presence of 1-CMN/CuCl/PMDETA. The end functionalized PS with naphthalene-label exhibited fluorescence in N,N-dimethylformamide (DMF).*

**Keywords** 1-(chloromethyl)naphthalene, atom transfer radical polymerization, styrene, fluorescence

### Introduction

The polymer with high sensitivity fluorescent probes have been widely used not only in the field of biochemistry (1), but also in synthetic polymer chemistry (2, 3). The luminescent techniques have been applied to study structural, conformational, and dynamic properties of polymer molecules (4–6), surface characterization (7), polymer relaxation processes (8), and diffusion in polymer systems including gels (9) and polymer miscibility (10).

Many processes have been used to synthesize fluorescent polymers. Valeur (11) and Sasaki et al. (12) independently synthesized narrow polydispersity polymers labeled with an anthracene chromophore in the middle of the main chain by living anionic polymerization and studied local chain motions of the polymers. Free radical polymerization has also been employed for the preparation of anthracene-labeled polymers (13, 14). Although the free radical polymerization is relatively easy to perform and the reaction conditions are not stringent, the resulting polymers are normally obtained as a mixture of different structures (14). Furthermore, this method lacks the control of molecular

Received February 2004; Accepted July 2004

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weight, molecular architecture and content of anthracene units. Recently, the atom transfer radical polymerization (ATRP) technique (15–18) has been exploited to overcome these shortcomings, and can obtain good control over molecular weight and structure.

Kim et al. (19) synthesized anthracene-labeled poly(methyl methacrylate) via ATRP. Ohno et al. (20) obtained a well-defined anthracene-labeled PS with 9,10-bis(1-bromoethyl-carbalkoxymethyl) anthracene (ANTDBr) as a bifunctional initiator and cuprous bromide complex Cu(I)Br/4,4'-di-n-heptyl-2,2'-bipyridine as a catalyst. Recently, Moon et al. (21) synthesized fluorescently labeled phthalic anhydride (PA) functionalized polymers and Klok et al. (22) synthesized fluorescent star-shaped PS by ATRP.

Karin Schillén (23) synthesized naphthalene-labeled poly(acrylic acid) by polymer-analogous amidation of a single commercial PAA sample. In this work, we report synthesis of end functionalized PS with naphthalene labeled, using 1-(chloromethyl)-naphthalene (1-CMN) as an initiator in the presence of CuCl/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA).

## Experimental

### Materials

Styrene (St) (chemically pure; Shanghai Chemical Reagent Co., Ltd., China) was purified by extracting with a 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with sodium sulfate anhydrous overnight, and finally distilled over CaH<sub>2</sub> under vacuum before use. Copper chloride (CuCl) (analytical reagent; Shanghai Zhenxin Chemical Reagent Factory, China) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol absolute, dried under vacuum. 1-(chloromethyl)naphthalene (1-CMN) (99%; Changzhou Wujin Linchuan Chemical Factory, China), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (98%; Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4 Å molecular sieve and distilled under vacuum. N,N-dimethylformamide (DMF) (analytical reagent; Shanghai No.1 Chemical Reagent Factory, China), tetrahydrofuran (THF) (analytical reagent; Shanghai Chemical Reagent Co., Ltd., China), hydrochloric acid (HCl) (analytical reagent; Jiangsu Jincheng Chemical Reagent Co., Ltd., China), and methanol (commercially available) were used as received.

### Polymerization

A typical polymerization is as follows: A dry glass tube (10 mL) was filled with CuCl (5.8 mg, 0.058 mmol), PMDETA (36 µL, 0.174 mmol), 1-CMN (10.3 mg, 0.058 mmol), and St (4.0 mL, 34.6 mmol). Then, it was degassed under vacuum and charged with N<sub>2</sub> (5 times), sealed under vacuum, and placed in an oil bath held by a thermostat at 125°C for polymerization. After the reaction was carried out for a prescribed time, the tube was rapidly cooled to room temperature with ice water. Afterward, the tube was opened, and contents were dissolved in THF, precipitated into a large amount of methanol. The dried polymer was then characterized gravimetrically.

### Characterizations

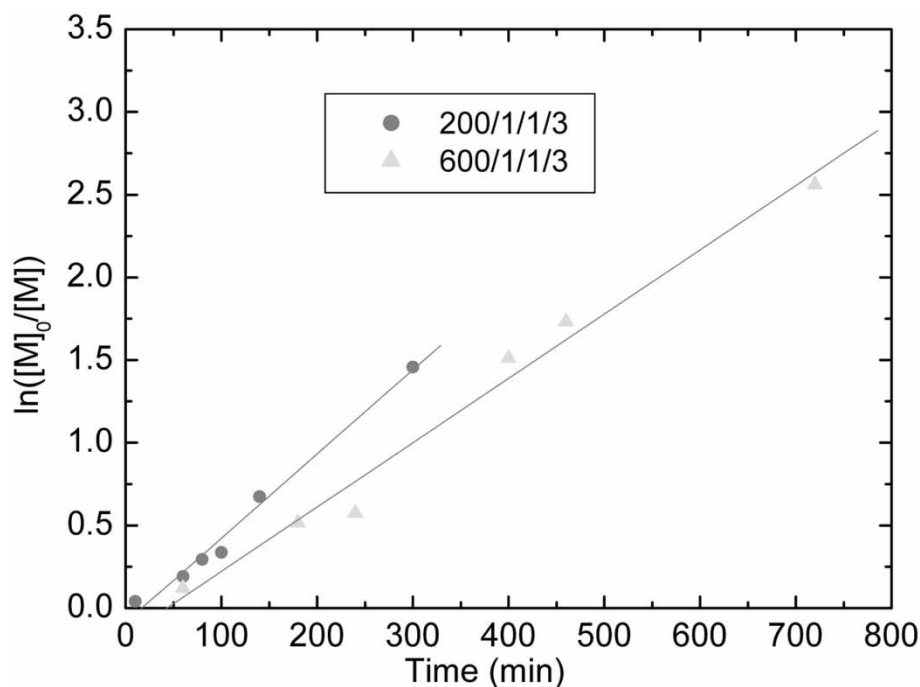
The monomer conversion was determined by gravimetry. The molecular weights and molecular weight distributions were determined with a Waters 1515 gel permeation

chromatograph (Milford, MA) equipped with refractive index detector, using HR<sub>1</sub>, HR<sub>3</sub> and HR<sub>4</sub> columns with a molecular weight range 100–50,000 calibrated with PS standard samples. THF was used as a mobile phase at a flow rate of 1.0 mL/min operated at 30°C. <sup>1</sup>H NMR spectrum was recorded in CDCl<sub>3</sub> with an Inova 400 MHz spectrometer (Palo Alto, CA) at ambient temperature. Fluorescence emission spectrum was obtained on a Perkin–Elmer LS-50B fluorescence spectrophotometer with DMF as solvent. The excitation wavelength was 340 nm.

## Results and Discussion

### *Kinetics of ATRP of St in the Presence of 1-CMN/CuCl/PMDETA*

The ATRP of St was carried out using 1-CMN as an initiator. Figure 1 shows the plots of  $\ln([M]_0/[M])$  against polymerization time  $t$  at different mole ratios of  $[St]_0/[1-CMN]_0/[CuCl]_0/[PMDETA]_0$  (200/1/1/3, 600/1/1/3), where  $[M]$  represents the monomer concentration and the subscript zero denotes the initial state ( $t = 0$ ). All the polymerizations of St show linear first-order rate plots, indicating that the radical concentration stays constant throughout the course of the polymerizations. At the same time, it can be seen that increasing the mole ratio (from 200/1/1/3 to 600/1/1/3) decreased the polymerization rate as predicted. This was due to a decreasing of the concentration of the initiator (1-CMN). It can also be seen from Fig. 1, that an induction period of polymerization at all mole ratios is observed, and the induction period becomes short as the mole ratios



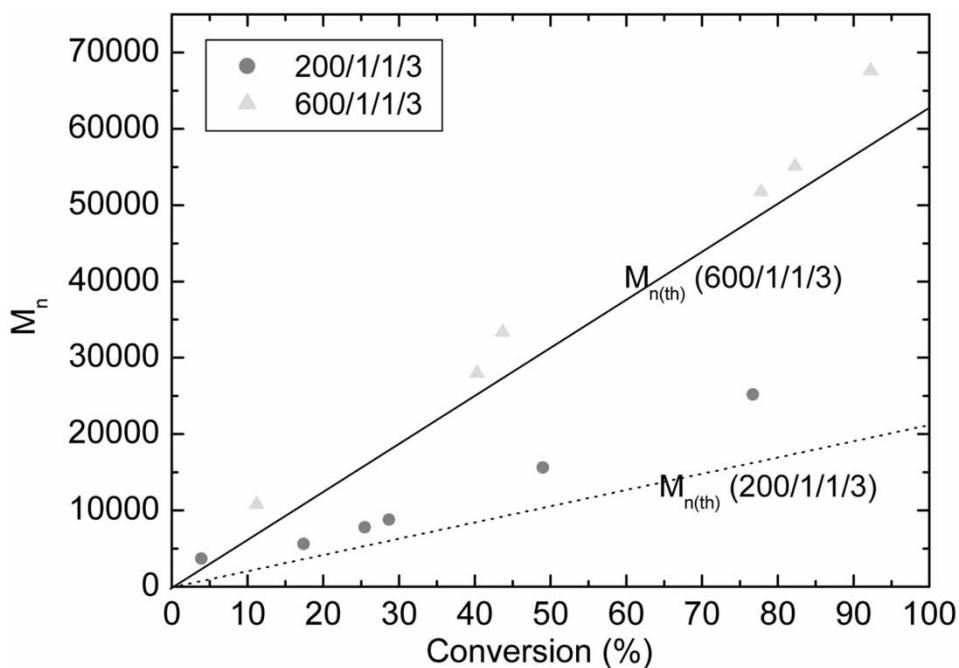
**Figure 1.** Kinetics of ATRP of St in bulk with different mole ratios of  $[St]_0/[1-CMN]_0/[CuCl]_0/[PMDETA]_0$  at 125°C.

are decreased. The induction period may be attributed to the establishment of equilibrium before ATRP may proceed or the consumption of residual oxygen.

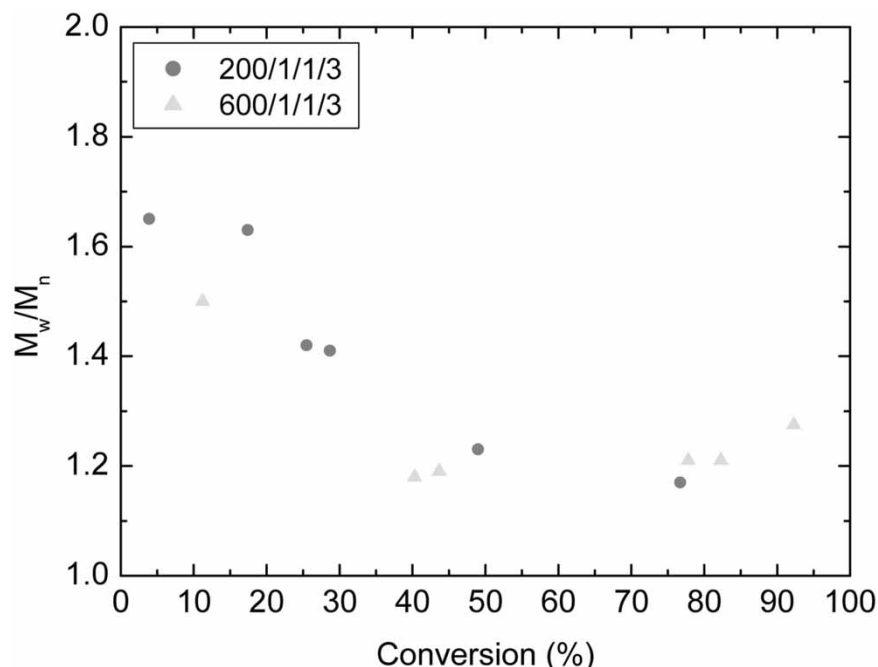
Figure 2 shows the number-average molecular weight ( $M_n$ ) of the produced polymers as a function of conversion. It can be seen that  $M_n$  linearly increases with conversion at all mole ratios; moreover the corresponding  $M_w/M_n$  (Fig. 3) decreases with conversion and stays remarkably small (around 1.2) when conversion is more than 30%. Together with the straight kinetic plot in Fig. 1, these results confirm that the polymerization proceeds in a "living" fashion with negligible contribution from transfer and termination reactions. From Fig. 2, it can be seen that the values of  $M_n$  from GPC deviate the corresponding theoretical one,  $M_{n(th)}$ , calculated from the degree of polymerization as predicted by the initial ratio of monomer : initiator at lower mole ratio (200/1/1/3). However,  $M_n$ s agree well with  $M_{n(th)}$  as increasing the mole ratio (600/1/1/3), indicative that well-defined PS can be obtained at a higher mole ratio of  $[St]_0/[1-CMN]_0/[CuCl]_0/[PMDTA]_0$ . This can be contributed to the termination reaction of initial radicals generated by 1-CMN at higher initiator concentration.

#### Effect of the Monomer Concentration on ATRP of St

The effect of the monomer concentration on ATRP of St in DMF has been investigated, and all results are listed in Table 1. In Table 1, it can be seen that conversion increases with the monomer concentration, from 47.9% to 99.0% when the concentration of monomer from 3.9 M increases to 8.6 M, indicative of increasing the polymerization rate with a concentration of monomer as predicted by mechanism of conventional free radical polymerization.



**Figure 2.** Effects of molecular weight ( $M_n$ ) on monomer conversion at different mole ratios of  $[St]_0/[1-CMN]_0/[CuCl]_0/[PMDTA]_0$ . Conditions: in bulk; temperature = 125°C.



**Figure 3.** Effects of molecular weight distribution ( $M_w/M_n$ ) on monomer conversion at different mole ratios of  $[St]_0/[1-CMN]_0/[CuCl]_0/[PMDETA]_0$ . Conditions: in bulk; temperature = 125°C.

### Fluorescence of Resulting PS and End Group Analysis

Figure 4 shows the fluorescence emission spectrum of naphthalene-labeled PS in DMF with excitation wavelength 340 nm at room temperature. The spectrum shows that the naphthalene-labeled PS exhibits a strong fluorescence emission in a short wavelength region, and the fluorescence maximum wavelengths are 438 nm.

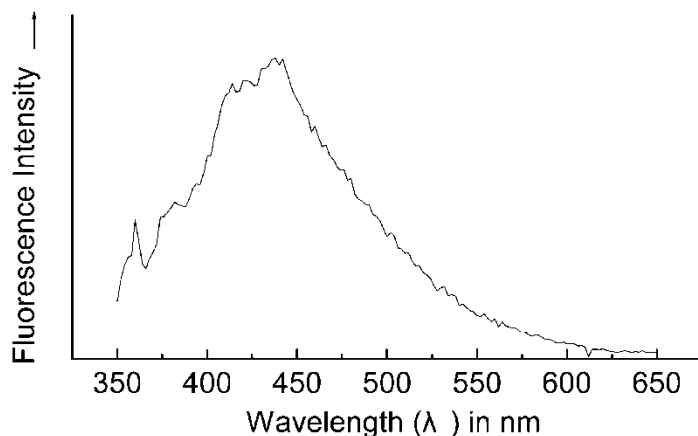
In order to further verify the fact that the naphthalene unit is definitely attached onto the end of polymeric chains according to the mechanism of ATRP, the end group analysis of the resultant PS is carried out by  $^1H$  NMR spectroscopy, as shown in Fig. 5. The naphthalene protons that are derived from 1-CMN are seen at 7.408–7.793 ppm (*a* in

**Table 1**  
Effect of solvent on polymerization of St

Entry	Concentration of monomer (M)	Conversion (%)	$M_{n(GPC)}$	$M_{n(th)}^a$	$M_w/M_n$
1	8.6 (bulk)	99.0	41,800	10,470	1.23
2	7.2	96.3	38,490	10,190	1.25
3	4.5	64.8	33,000	6910	1.39
4	3.9	47.9	28,440	5150	1.45

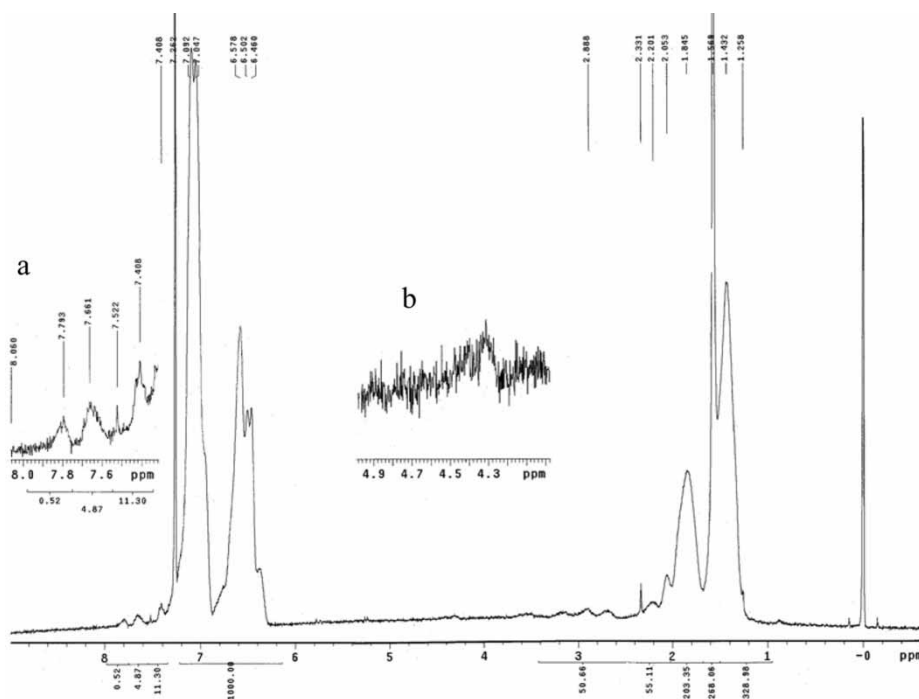
Polymerization conditions:  $[St]_0/[1-CMN]_0/[CuCl]_0/[PMDETA]_0 = 100/1/1/3$ ; time = 14 h; temperature = 125°C; solvent = DMF.

$$^aM_{n(th)} = [St]_0/[1-CMN]_0 \times 104 \times \text{conversion} + M_{W(1-CMN)}.$$



**Figure 4.** Fluorescence emission spectrum of naphthalene-labeled PS in DMF. The polymer concentration in DMF was  $1.0 \times 10^{-5}$  mol/L; Excitation wavelength was 340 nm; Sample:  $M_n(\text{GPC}) = 8750$ ,  $M_w/M_n = 1.41$ .

Fig. 4). Signals (24–26) at 4.313 ppm (**b** in Fig. 4) correspond to methylene protons in the PS-end due to a  $\omega$ -chlorine group. Both of these results indicate that the end functionalized PS with a fluorescent naphthalene-labeled from initiator of 1-CMN and a  $\omega$ -chlorine group from catalyst obtained from 1-CMN/CuCl/PMDETA initiating system. In Fig. 5, the



**Figure 5.**  $^1\text{H}$  NMR spectrum of polymer synthesized by ATRP of styrene with 1-CMN as an initiator. Sample:  $M_n(\text{GPC}) = 8750$ ,  $M_w/M_n = 1.41$ .

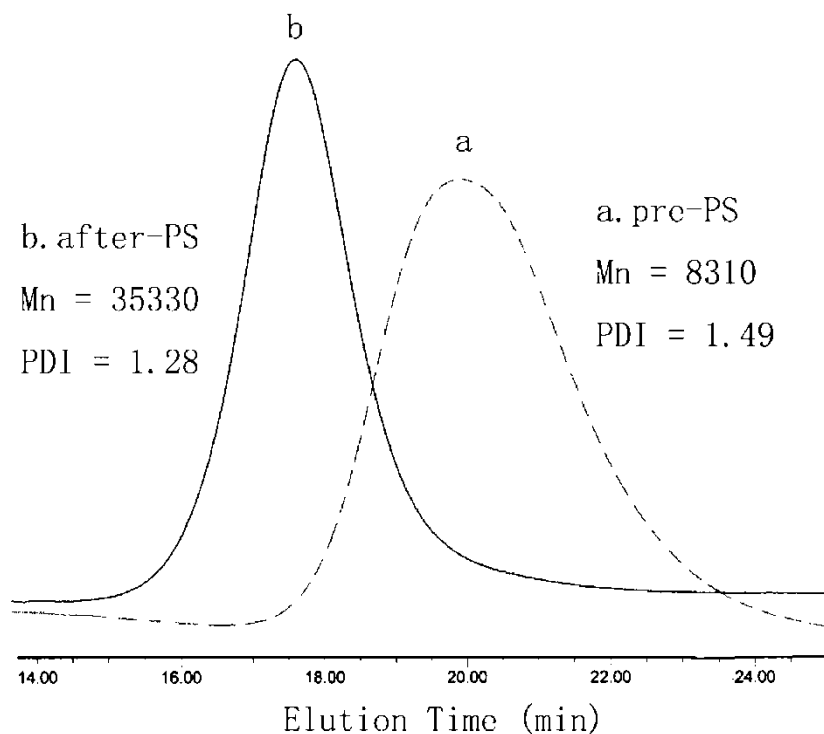
molecular weight determined from the  $^1\text{H}$  NMR spectrum ( $M_{n,\text{NMR}} = 8890$ ) is calculated from the peak intensity ratios between the naphthalene groups (**a**) and the phenyl groups in main chain, which agrees well with that obtained from GPC ( $M_{n,\text{GPC}} = 8750$ ).

### Chain Extension

To further investigate the living nature of the polymerization, the chain extension polymerizations of St were carried out in bulk at  $95^\circ\text{C}$  with a PS obtained by ATRP of St in the presence of 1-CMN/CuCl/PMDETA as catalyst via the conventional ATRP. The  $M_n$  of the resulting PS increases from 8310 up to 35330, and the polydispersity index decreases from 1.49 to 1.28, which can be essentially demonstrated by the GPC curves shown in Fig. 6. This result further confirms the presence of a chlorine atom at the  $\omega$ -chain end of the original PS that can serve as a macroinitiator.

### Conclusions

1-(Chloromethyl)naphthalene can be successfully used as an effective initiator in the atom transfer radical polymerization of St in bulk in the presence of CuCl/PMDETA, and a well-defined fluorescent naphthalene-labeled PS was obtained. Chain extension and  $^1\text{H}$



**Figure 6.** GPC curves of PS (a) before obtained via ATRP of St with 1-CMN/CuCl/PMDETA as an initiating system and (b) after the chain extension reaction. Chain extension conditions:  $[\text{St}]_0/[\text{macroinitiator}]_0/[\text{CuCl}]_0/[\text{PMDETA}]_0 = 400/1/1/2$ ; temperature =  $95^\circ\text{C}$ ; in bulk; time = 9 h; conversion = 66%.



NMR of the resulting PS were performed to further confirm the “living”/controlled nature of the polymerization process.

### Acknowledgment

We gratefully acknowledge the National Nature Science Foundation of China (No.20176033) for support for this work.

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