

Living/Controlled Radical Autopolymerization of Styrene in the Presence of CuCl_2 and 2,2'-Bipyridine

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Received 22 August 2002; accepted 11 December 2002

ABSTRACT: The bulk autopolymerization of styrene (St) was successfully conducted in the presence of CuCl_2 and 2,2'-bipyridine (bpy) at 110 and 130°C. We found that this polymerization was a living/controlled radical polymerization at a $[\text{St}]_0/[\text{CuCl}_2]_0/[\text{bpy}]_0$ ratio of 54:1:2.5. The resulting number-average molecular weights linearly increased with conversion, and the polydispersity indices were very narrow (<1.5). The polymerization rate increased with temperature. Increasing the ratios (i.e., 129:1:2.5, 259:1:2.5, and 386:1:2.5) led to a decrease in the ability to control the autopolymer-

ization of St, even uncontrolled polymerization (i.e., 643:1:2.5). The analysis of end groups by $^1\text{H-NMR}$ indicated that the spontaneous generation of radicals from St were generated by a Mayo-type process, and this living/controlled radical polymerization might have undergone a reverse atom-transfer radical polymerization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1532–1538, 2003

Key words: living polymerization; atom transfer radical polymerization (ATRP); radical polymerization

INTRODUCTION

The field of living radical polymerization has flourished in recent years¹ on the expectation that this process might be an alternative to living ionic polymerization, which requires very drastic experimental conditions (e.g., low temperature, the thorough elimination of moisture and impurities). Indeed, this technique has the advantage of being easily conducted because the only essential purification is the elimination of oxygen. In particular, both stable free-radical polymerization^{2–7} and atom-transfer radical polymerization (ATRP)^{8–11} have generated great interest in industry and academia. In both cases, the approach to achieving livingness is based on the equilibrium between the active macromolecular radical and a dormant species.

Typically, living radical polymerizations are conducted in the bulk by the simple heating of a mixture of the monomer and initiator at a higher temperature (e.g., 125 and 130°C) for extended periods of time. However, for styrene (St)-based monomers, the elevated temperatures and long reaction times may lead to the formation of additional radical species by autopolymerization.¹² These radicals could

be captured with added persistent species, e.g., 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) to give *in situ* unimolecular initiators. It may, therefore, be possible to conduct living radical polymerization in the absence of added initiating systems by reliance only on added persistent species to mediate the polymerization. Studies on the autopolymerization of St in the presence of TEMPO have been reported by Hawker and coworkers,⁷ Georges et al.,¹³ Matyjaszewski and coworkers,^{6,14–16} and other authors.^{17–19}

In this article, we report the autopolymerization of St in the presence of CuCl_2 and 2,2'-bipyridine (bpy).

EXPERIMENTAL

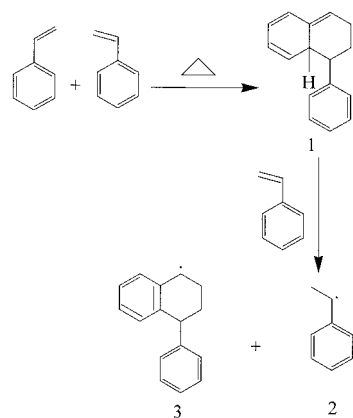
Materials

St (chemically pure; Shanghai Chemical Reagent Co., Ltd., China) was purified by extraction with a 5% sodium hydroxide aqueous solution, followed by washing with water and drying with sodium sulfate anhydrous overnight, and finally distillation over CaH_2 *in vacuo* before use. Copper(I) chloride (CuCl ; analytical reagent; Shanghai Zhenxin Chemical Reagent Factory) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with ethanol anhydrous, and dried *in vacuo*. Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; analytical reagent; Shanghai Chemical Reagent Co., Ltd.), bpy (analytical reagent; Shanghai No.1 Chemical Reagent Factory), tetrahydrofuran (THF; analytical reagent; Jiangsu Changshu Yangyuan Chemical Reagent Factory, Suzhou, China), hydrochloric acid (an-

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 20176033.

Contract grant sponsor: Nature Science Foundation of Jiangsu Province; contract grant number: BK2001141.



Scheme 1

alytical reagent; Jiangsu Jincheng Chemical Reagent Co., Ltd., Changzhou, China), and methanol (commercially available) were used as received.

General polymerization procedures

The typical procedures were as follows. A dry glass tube was filled with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (83.1 mg, 0.487 mmol), bpy (190.0 mg, 1.216 mmol), and St (3.0 mL, 26.135 mmol). Then, it was degassed *in vacuo* and charged with N_2 (five times), sealed *in vacuo*, and placed in a thermostated oil bath. At timed intervals, we stopped the polymerization by cooling the tube in cold water. Afterward, the tube was opened, and the contents were dissolved in THF and precipitated into a large amount of methanol. The dried polymer was then characterized by gravimetry.

Characterization

Conversions of the monomer were determined gravimetrically. The molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatograph (Milford, MA) with THF as the mobile phase and with a column temperature of 30°C . Polystyrene (PSt) standards were used to calibrate the columns. $^1\text{H-NMR}$ spectra were recorded in CDCl_3 with an INOVA 400-MHz spectrometer (Palo Alto, CA) at ambient temperature.

RESULTS AND DISCUSSION

Effect of the polymerization temperature

The thermal autopolymerization of St has been known since 1839 and is still a source of much controversy and research.¹² The most widely accepted mechanism for the spontaneous generation of radicals from St was first proposed by Mayo in 1968 and involves an initial [4 + 2] Diels–Alder reaction between two molecules of St.²⁰ This gives the monaromatized Mayo adduct **1**, which cannot undergo a thermal 1,3-sigmatropic shift because of symmetry considerations and, therefore, undergoes a molecularly assisted homolysis reaction with another molecule of St to give the aromatized radical **2** and the radical **3** derived from St (Scheme 1). Under normal thermal polymerization conditions, **2** and **3** give uncontrolled polymerization, leading to high-molecular-weight and wide-polydispersity PSt. In the presence of the CuCl_2/bpy complex, however, the opportunity exists to control this autopolymerization by the trapping of **2** and **3** to establish an equilibrium between the active species and a dormant species and, further, to control the polymerization.

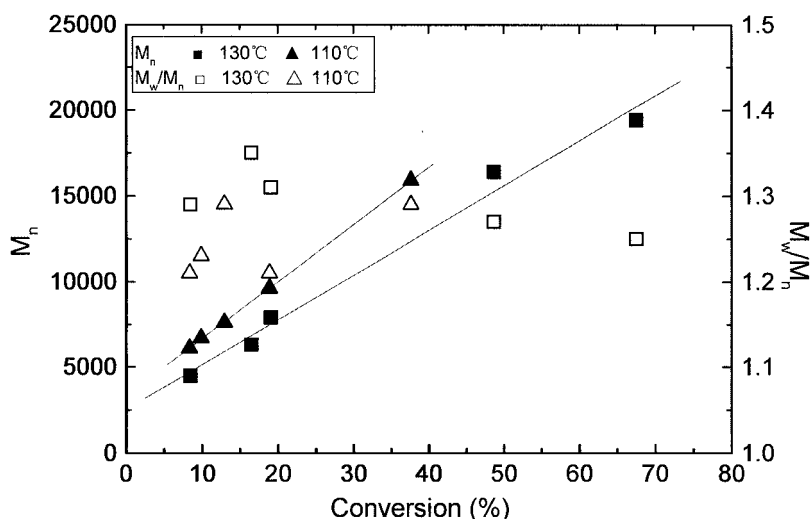


Figure 1 Dependence of M_n and M_w/M_n on the monomer conversion in the thermally initiated bulk polymerization of St at different temperatures ($[\text{St}]_0/[\text{CuCl}_2]_0/[\text{bpy}]_0 = 54/1/2.5$).

TABLE I
Thermal Autopolymerization of St in the Absence of
CuCl₂ and bpy *In Vacuo*

Temperature (°C)	Time (h)	Conversion (%)	M_n (GPC)	M_w/M_n
70	5.3	9.2	334,500	2.04
	16.0	18.3	327,500	1.95
	48.0	58.0	321,900	2.12
90	3	13.4	180,200	2.01
	6	27.7	155,100	1.99
	7.3	43.2	180,200	2.01
120	9.8	56.2	156,800	2.19
	0.8	13.1	114,300	1.96
	2.3	44.4	104,800	2.13
	4.8	90.0	145,800	2.00
	7.0	98.0	134,800	2.28

The dependence of the number-average molecular weight (M_n) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] on conversion in the bulk thermal autopolymerization of St in the presence of CuCl₂ and bpy at different temperatures is plotted in Figure 1. Interestingly, as shown in Figure 1, at a ratio of $[St]_0/[CuCl_2]_0/[bpy]_0$ of 54:1:2.5, the M_n values increased linearly with conversion at both 130 and 110°C (e.g., M_n increased to 19,400 from 4500 at 130°C), and the M_w/M_n values of the resulting polymer were very narrow (1.21–1.35) in both cases. It was obvious that the system fully showed characteristics of a living/controlled radical polymerization. Besides, as also shown in Figure 1, the higher the temperature was, the

smaller the M_n values for the same conversion were. This could be attributed to the fact that the higher the temperature was, the larger the amount of growing radicals were generated by thermal self-initiation from St, leading to the decrease in M_n values.

To verify the function of CuCl₂ and bpy in the thermal polymerization of St, a series of thermal self-initiation polymerizations of St in the absence of CuCl₂ and bpy were conducted, and the results are listed in Table I. As shown in Table I, the M_n values almost stayed constant with increasing conversion at all three temperatures (70, 90, and 120°C), and the corresponding M_w/M_n values were almost more than 2.0. In addition, the M_n values decreased with increasing temperature (i.e., $M_n \approx 320,000$ at 70°C, $M_n \approx 160,000$ at 90°C, and $M_n \approx 120,000$ at 120°C). These results demonstrate the characteristics of a conventional radical polymerization of St. In comparison with the two processes of thermal autopolymerization of St in the presence or absence of CuCl₂ and bpy, we concluded that a conventional radical polymerization could be transferred into a living radical polymerization by the addition of appropriate amounts of CuCl₂ and bpy to the conventional autopolymerization system of St.

To further confirm the living characteristics of the polymers synthesized by the autopolymerization of St in the presence of CuCl₂ and bpy, we conducted a reaction of chain extension, with the polymer as a macroinitiator in the presence of CuCl and bpy. Figure 2 shows the gel permeation chromatography (GPC)

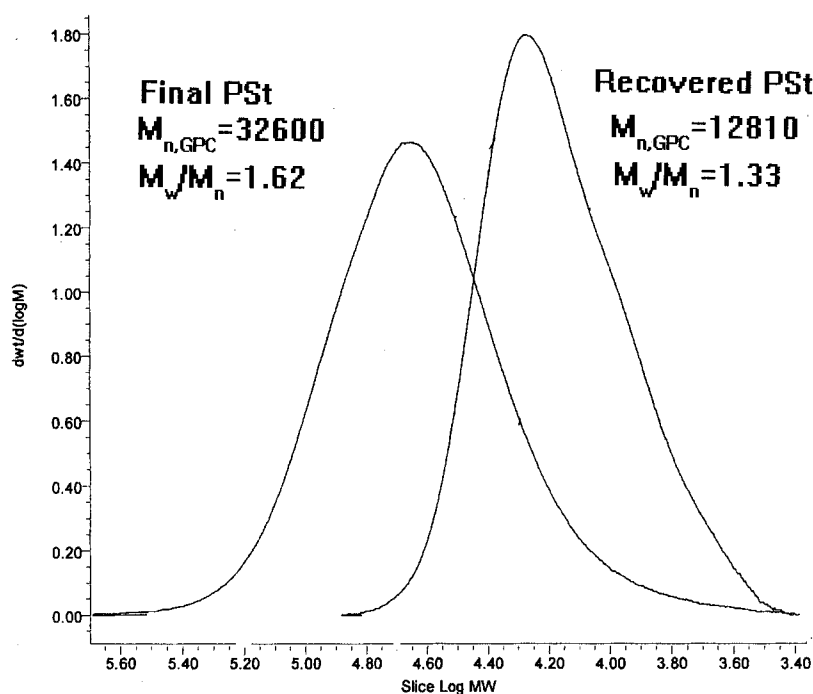


Figure 2 GPC curves of the recovered PSt used as an initiator and the final polymer after precipitation in methanol (temperature = 130°C; time = 6 h; $[St]_0 = 8.7 \text{ mol L}^{-1}$; $[\text{macroinitiator}]_0 = [CuCl]_0 = [bpy]_0/3 = 3.36 \times 10^{-2} \text{ mol L}^{-1}$).

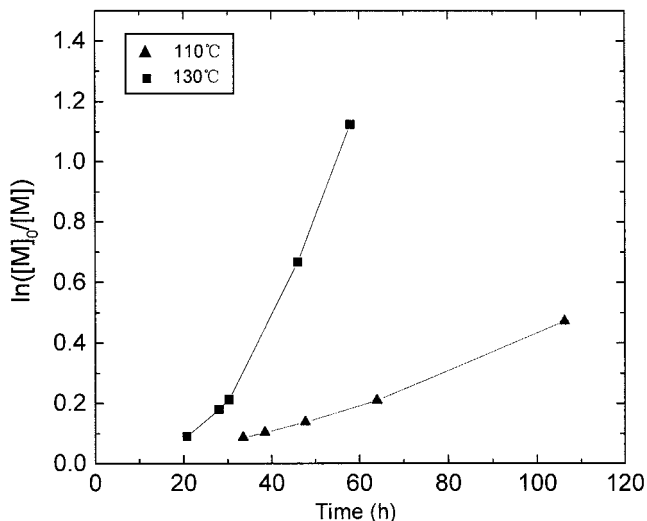


Figure 3 Kinetic plot of $\ln([M]_0/[M])$ (where M is the monomer) versus time in the thermally initiated bulk polymerization of St at different temperatures ($[St]_0/[CuCl_2]_0/[bpy]_0 = 54/1/2.5$).

curves of the macroinitiator and the final polymer obtained after 46.9% conversion of an additional crop of the monomer St. M_w/M_n of the final polymer (1.62) was a little broader than that of the macroinitiator (1.33), but the M_n value increased to 32,600 from 12,810. The success of the chain extension further proved the characteristics of living polymerization in this system of the autopolymerization of St in the presence of $CuCl_2$ and bpy.

The kinetics of the bulk autopolymerization of St in the presence of $CuCl_2$ and bpy at 130 and 110°C are shown in Figure 3. As predicted, the polymerization rate increased with the temperature. At the same time,

an induction period was observed in this polymerization system as observed by Wang and Matyjaszewski,⁶ Hawker and coworkers,⁷ Boutevin and Bertin,¹⁸ and Koda and coworkers¹⁹ in the TEMPO/St polymerization system. With the increase in polymerization temperature, the induction periods decreased. A possible reason for this observed behavior was that the radicals generated spontaneously by autopolymerization were trapped by the $CuCl_2/bpy$ complex in the initial stages of the reaction to give *in situ* initiators. In the presence of excess $CuCl_2/bpy$ complex, these initiators did not result in significant amounts of polymerization, and an induction period was observed. However, as the reaction proceeded, the dynamic equilibrium between active species and dormant species was established, and at this point, the polymerization reaction effectively started.

Effect of the $[St]_0/[CuCl_2]_0$ molar ratio

We examined further the ability to control the molecular weight and its distribution by heating St with various amount of $CuCl_2$ and bpy at 110°C. As shown in Figure 4, the M_n values of polymers synthesized at different ratios increased with conversion; however, at ratios of 129:1 and 259:1, as compared with 54:1, a poor linearity was observed, presumably indicating some contribution of the conventional autopolymerization of St. As shown in Figure 5, the M_w/M_n values increased with the $[St]_0/[CuCl_2]_0$ ratio (i.e., $M_w/M_n = 1.21-1.33$ for 54:1, $M_w/M_n = 1.33-1.51$ for 129:1, and $M_w/M_n = 1.36-1.64$ for 259:1), indicating a decrease in the ability to control this polymerization system. The results listed in Table II further confirmed this trend. When the ratio was 54:1, this system showed good

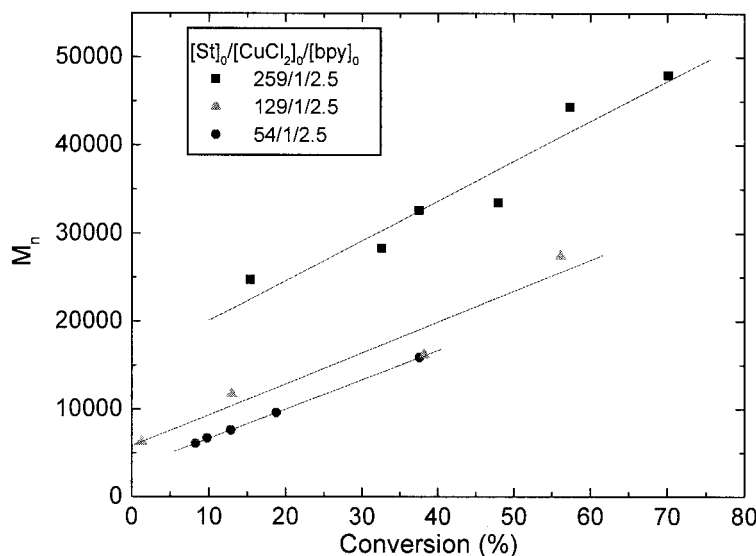


Figure 4 Dependence of M_n on the monomer conversion in the thermally initiated bulk polymerization of St at different molar ratios ($[St]_0/[CuCl_2]_0/[bpy]_0$) at 110°C.

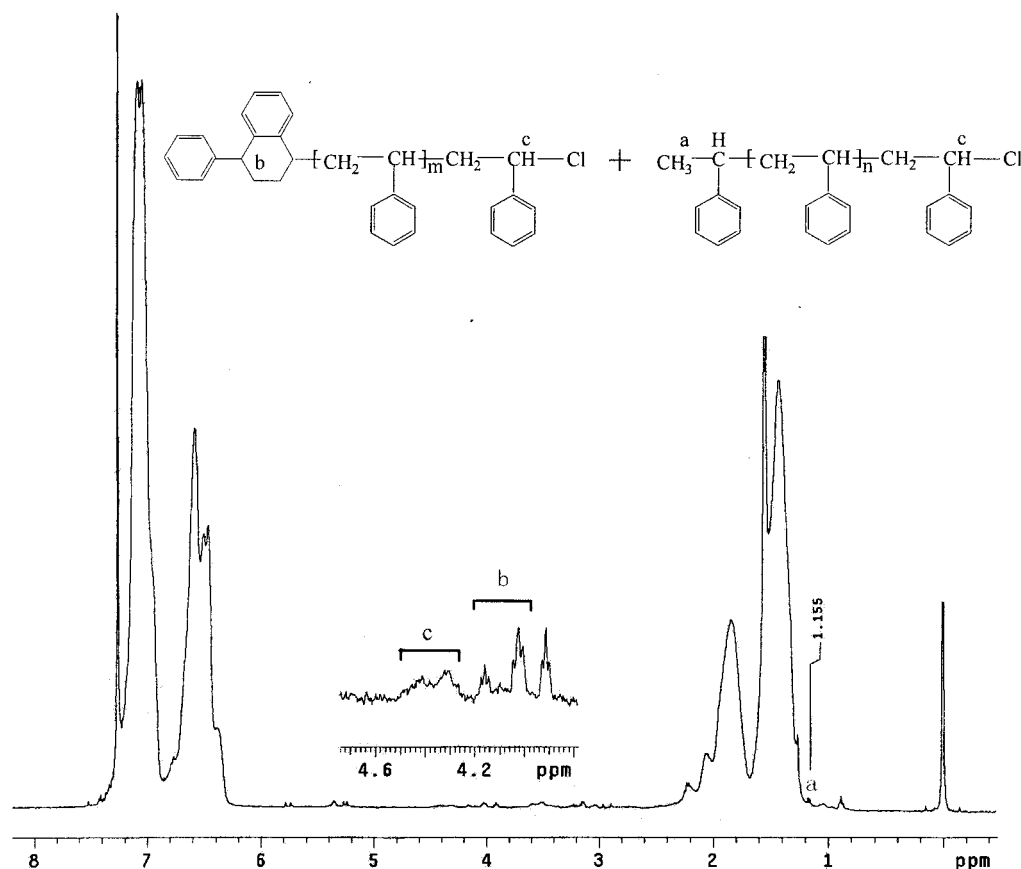


Figure 6 $^1\text{H-NMR}$ spectra of the polymer synthesized by the autopolymerization of St in the presence of CuCl_2 and bpy [M_n (GPC) = 16,400; $M_w/M_n = 1.27$; temperature = 130°C ; $[\text{St}]_0/[\text{CuCl}_2]_0/[\text{bpy}]_0 = 54/1/2.5$].

lower oxidation state transition metal catalyst (i.e., CuCl) are generated *in situ*. The mechanism for reverse ATRP is shown in Scheme 2.

In the comparison of the autopolymerization with reverse ATRP, the only difference lies in the original radical (generated by AIBN decomposition in reverse ATRP and generated by the autopolymerization of St in this case); therefore, the discussion mechanism may be consistent with that of the reverse ATRP as shown in Scheme 2, where $\text{I}\cdot$ is the original radical generated by the autopolymerization of St at higher temperatures. Under our experimental conditions, given the spontaneous generation of radicals from St by a Mayo-type process, $\text{I}\cdot$ (Scheme 2) could be **2** and **3** (Scheme 1). According to the hypotheses mentioned previously, the resulting polymers should contain the 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl, 1-phenyl ethyl, and atom Cl end groups.

Figure 6 shows the $^1\text{H-NMR}$ spectra of the resulting polymer of the autopolymerization of St in the presence of CuCl_2 and bpy. In addition to the signals of the PSt backbone, some signals were observed that were due to these end groups. The signals at 4.02–4.16 ppm were well known from the literature^{37,38} and corresponded to the 4-phenyl-1,2,3,4-tetrahydro-1-naph-

thyl proton in position b; the signals^{31,39–41} at 4.2–4.5 ppm corresponded to the PSt end group (in position c) due to the presence of $\omega\text{-Cl}$. The signal^{9,42} at 1.15 ppm corresponded to the methyl end groups due to the 1-phenyl ethyl in position a. These, including the success of chain extension in the ATRP initiating system (Fig. 2), thus confirmed that the polymer obtained had the end-group moieties of 4-phenyl-1,2,3,4-tetrahydro-1-naphthyl, 1-phenyl ethyl, and $\omega\text{-Cl}$ and that the polymerization should have undergone a reverse ATRP process.

CONCLUSIONS

A conventional radical polymerization was transferred into a living radical polymerization by the addition of appropriate amounts of CuCl_2 and bpy (i.e., $[\text{St}]_0/[\text{CuCl}_2]_0/[\text{bpy}]_0 = 54:1:2.5$) to the conventional autopolymerization system of St at higher temperatures (i.e., 110 and 130°C). The resulting M_n 's linearly increased with conversion, and the polydispersity indices were very narrow (<1.5). The analysis of end groups indicated that the spontaneous generation of radicals from St by a Mayo-type process and this

living/controlled radical polymerization may have undergone a reverse ATRP process.

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