Synthesis of Well-Defined Polystyrene by Radical Polymerization Using 1,1,2,2-Tetraphenyl-1,2-ethanediol/FeCl₃/PPh₃ Initiation System

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ABSTRACT: Well-defined polystyrenes with an α-hydrogen atom and an ω-chlorine atom end groups and narrow polydispersity ($M_n = 2500-4200$, $M_w/M_n = 1.29-1.48$) have been synthesized by a free radical polymerization process using a 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)/FeCl₃/PPh₃ initiation system. The end groups were monitored by ^{1}H nuclear magnetic resonance spectroscopy. When the polymerization of styrenes in bulk carried out at 120°C and the ratio of $[St]_0 : [TPED]_0 : [FeCl_3]_0 : [PPh_3]_0$ was 200 : 1 : 4 : 12, the polymerization exhibited some living/controlled radical polymerization characteristics. The polymerization mechanism was proposed proceeding via a reverse atom transfer radical polymerization (ATRP). Because the polymers obtained were end-functionalized by chlorine atoms, they were used as macroinitiators to proceed chain extension polymerization in the presence of CuCl/2,2′-bipyridine catalyst system via a conventional ATRP process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1607–1613, 2000

Key words: well-defined polystyre; 1,1,2,2-tetraphenyl-1,2-ethanediol/FeCl₃/PPh₃; living/controlled radical polymerization; reverse ATRP

INTRODUCTION

A variety of monomers can proceed radical polymerization and copolymerization under relatively mild experimental conditions in contrast to ionic processes, but it often yield polymers with ill-controlled molecular weights and broad polydispersity indices due to the facile coupling and disproportion reactions between the propagating radicals during the polymerization. Gaining control over radical polymerization has been one of the most important topics in contemporary polymer chemistry. Since the pioneering work by Otsu[1] on iniferters, many polymer chemists have devoted efforts to developing "living" radical polymerization processes. Gerorges et al.[2,3] have successfully carried out a living/controlled radical polymerization of styrene (St) by using TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as an organic stable counter radical to limit the undesired coupling and disproportion reaction. Sawamoto[4,5] and Matyjaszewski et al.[6,7] have reported a living/controlled radical polymerization with transition metal catalysts and Matyjaszewski[6,7] named the process atom transfer radical polymerization (ATRP). In this process, active alkyl halides act as initiators, transition metal compounds in their lower oxidation state as catalysts, for example, Cu(I),[7–13] Fe(II),[14,15] Ru(II),[5] Ni(II),[16] Rh(I),[17] Pa(II),[18] and electron-donating compounds such as 2,2′-bipyridine (bipy) or triphenylphosphine as metal complex ligands. Besides St, methyl methacrylate (MMA), methyl acrylate, acrylonitrile, and 2-hydroxyethyl acrylate were polymer-

ized via ATRP.[7–13,19,20] Well-defined poly(methyl methacrylate) (PMMA) and polystyrene (PSt) with α-hydrogen and ω-chlorine end groups were synthesized via ATRP processes using dimethyl 2-chloro-2,4,4-trimethylglutarate/RuCl$_2$/PPh$_3$/Al(OiPr)$_3$[21] and 1-phenylethyl chloride/CuCl/bipy systems,[6] respectively.

Some articles reported that living/controlled radical polymerization of MMA can be carried out by ATRP with iron-based catalyst systems such as RX/FeCl$_2$/PPh$_3$,[14] RX/FeBr$_2$/dNbipy [4,4′-bis(5-nonyl)-2,2′-bipyridine] or N(nBu)$_3$[15] and living/controlled radical polymerization of St can also be carried out by ATRP with iron-based catalyst systems: RX/FeBr$_2$/N(nBu)$_3$, RX/FeBr$_2$/dNbipy and RX/FeBr$_2$/P(nBu)$_3$.[15] However, the ATRP of St in the iron-based system using PPh$_3$ as a ligand, such as 1-phenylethyl bromide/FeBr$_2$/PPh$_3$, was poorly controlled, with a slow polymerization rate and high polydispersity index (the reaction time = 15 h, the conversion = 47%, $M_{n(GPC)}$ = 4200, M_w/M_n = 1.76).[15] More recently, well-defined PSt with very narrow polydispersity indices (M_n = 4300–12,800, M_w/M_n = 1.06–1.09) were synthesized with a novel initiating system based on Fe^{2+} complex and an alkyl iodide initiator, Fe((η^5-C$_5$H$_5$)(CO)$_2$I)/RI.[22]

Because the initiation system for ATRP process has two potential problems: the organic halide RX is usually toxic and the catalyst Mt^n/L$_X$ is easily oxidized by the oxygen in air, a so-called reverse ATRP recently was explored.[23–26] In this new process, a higher oxidation state transition-metal species Mt^{n+1}X/L$_x$ and a conventional radical initiator were used instead of lower oxidation state Mt^n/L$_x$ and organic halide species, respectively. So far, two types of efficient reverse ATRP–initiating systems for living/controlled radical polymerization have been reported, that is, 2,2′-azo-bisisobutyronitrile (AIBN)/CuCl$_2$ (or CuBr$_2$)/bipy for MMA, MA, St polymerization[24,25] and AIBN/FeCl$_3$/PPh$_3$ for MMA polymerization.[23] Recently, we have successfully synthesized well-defined PMMA with an α-hydrogen atom and an ω-chlorine atom as the end groups by bulk polymerization of MMA at 95°C using a new initiation system, 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)/FeCl$_3$/PPh$_3$. The conversion of polymerization reached to ~100%. The molecular weight of PMMA obtained was high, and the polydispersity index was quite narrow (e.g., M_n = 171,800, M_w/M_n = 1.13).[26]

Braun et al.[27–29] reported that TPED could be used as an initiator for common radical polymer-ization and copolymerization of vinyl monomers. The polymers obtained are with α-hydrogen atoms end groups because the activated monomer radicals are produced via a hydrogen transfer addition reaction in the initiation step. However, the conventional radical polymerization is not well controlled, with broad polydispersities. We have investigated the radical polymerization of St with the TPED/FeCl$_3$/PPh$_3$ initiating system. This article describes the synthesis of well-defined PSt, with an α-hydrogen and an ω-chlorine atoms end groups and with narrow polydispersity using the TPED/FeCl$_3$/PPh$_3$ initiating system via a reverse ATRP process. The polymerization exhibited some living/controlled polymerization characteristics, and the resultant PSt with a chlorine-capped end group can be used as a macroinitiator.

EXPERIMENTAL

Materials

FeCl$_3$ (anhydrous) was prepared from FeCl$_3$ · 6H$_2$O treated with thionyl chloride according to reference procedure.[30] TPED was prepared[31] from benzophenone and 2-propanol. St was dried over CaH$_2$ and distilled under vacuum. Triphenylphosphine (Aldrich, Milwaukee, WI) was purified by recrystallization from ethanol to eliminate triphenylphosphine oxide.

Polymerization of Styrene

The monomer was added in a dry glass tube with a magnetic stirring bar and solid components, TPED, FeCl$_3$, and PPh$_3$. Three freeze-pump-thaw cycles were performed. The tube was sealed under vacuum and placed in an oil bath held at the desired temperature by a thermostat. At timed intervals, the heterogeneous polymerization was stopped by cooling the tube in ice water. After the polymerization product was dissolved in THF, the PSt was precipitated in methanol, and dried. The conversion of polymerization was determined gravimetrically.

Characterizations

Molecular weights and molecular weight distributions of polymer samples were measured by gel permeation chromatography (GPC) using a Waters 515 GPC with Styragel Columns (HT2 + HT3 + HT4) at 35°C, THF as eluent (1.0 mL/min), PSt
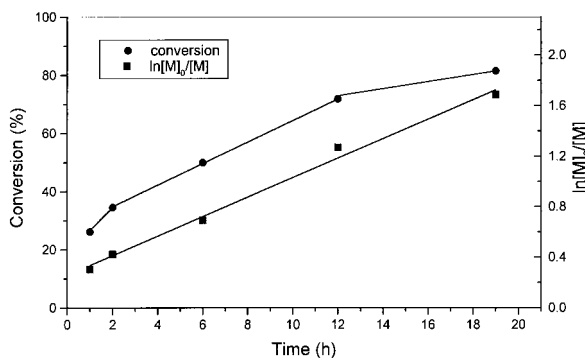
Figure 1 Time dependence of $\ln[M]_0/[M]$ and conversion at 120°C, where $[M]_0$ and $[M]$ are the St concentration at times 0 and t, respectively. Conditions: $[St]_0$ = 8.74 mol/L, $[TPED]_0$ = 4.43 × 10^{-2} mol/L, $[FeCl_3]_0$ = 17.72 × 10^{-2} mol/L, $[PPh_3]_0$ = 53.15 × 10^{-2} mol/L.

as calibration standards, and Waters Millennium 32 as data processing software (Milford, MA). ^{1}H nuclear magnetic resonance (NMR) spectra were taken with a Brucker ARX400 (400 MHz; Billerica, MA) spectrometer in CDCl$_3$ at 25°C, using tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

Polymerization of St with the TPED/FeCl$_3$/PPh$_3$ Initiating System

Radical polymerization of St was carried out in bulk with the TPED/FeCl$_3$/PPh$_3$ system ($[St]_0$: $[TPED]_0$: $[FeCl_3]_0$: $[PPh_3]_0$ = 200 : 1 : 4 : 12) at 120°C, and the results are shown in Figure 1. The plot of $\ln([M]_0/[M])$ versus time appears a straight line and indicates that the kinetics is first order in monomer concentration. This means that the concentration of propagating radicals is constant during the polymerization. The results of GPC curves of the PSts obtained are shown in Figure 2. The polydispersity indices are narrow (M_w/M_n = 1.29–1.48, M_n = 2500–4200) when the conversion is from 34.6 to 81.5%. However, when the conversion is 26.2%, a broader polydispersity index (M_w/M_n = 1.69) is obtained. This suggests that the conventional radical polymerization takes place during the initial polymerization in the reaction system. In other words, the reverse ATRP system will set up at higher conversion, for example, 34.6%. Figure 3 represents the average number molecular weight $M_{n(GPC)}$ of PSt (measured by GPC) increases linearly with increasing of the conversion. These results convincingly re-
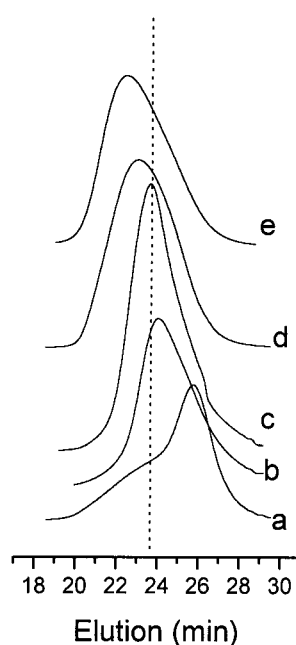

Figure 2 GPC curves of PSt obtained in bulk polymerization with TPED/FeCl$_3$/PPh$_3$ at 120°C. Conditions: $[St]_0$ = 8.74 mol/L, $[TPED]_0$ = 4.43 × 10^{-2} mol/L, $[FeCl_3]_0$ = 17.72 × 10^{-2} mol/L, $[PPh_3]_0$ = 53.15 × 10^{-2} mol/L. (a) M_n = 2100, M_w/M_n = 1.69, conversion = 26.2%, (b) M_n = 2500, M_w/M_n = 1.29, conversion = 34.6%, (c) M_n = 3100, M_w/M_n = 1.30, conversion = 50.0%, (d) M_n = 4100, M_w/M_n = 1.44, conversion = 71.9%, (e) M_n = 4500, M_w/M_n = 1.48, conversion = 81.5%.

veal that the polymerization of St with the TPED/FeCl$_3$/PPh$_3$ initiation system at 120°C is a living/controlled radical polymerization process. Although the St polymerization is initiated with
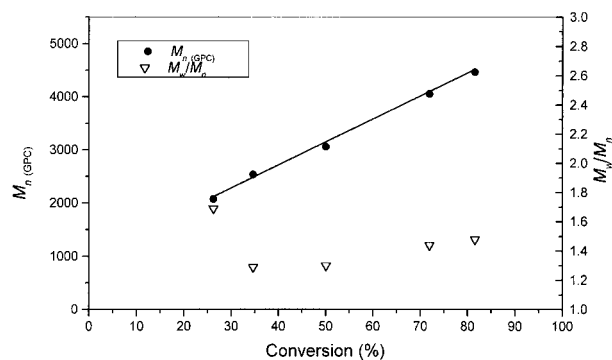

Figure 3 Dependence of the molecular weight and polydispersity of PSt on the monomer conversion with $[St]_0$: $[TPED]_0$: $[FeCl_3]_0$: $[PPh_3]_0$ = 200 : 1 : 4 : 12 at 120°C. Conditions: $[St]_0$ = 8.74 mol/L, $[TPED]_0$ = 4.43 × 10^{-2} mol/L.

Table I   Bulk Polymerization of Styrene Initiated with TPED/FeCl₃/PPh₃ on Different Initial Molar Ratio of Monomer to the Initiator at 120°C

No.	C^a	Time (h)	Conversion (%)	$M_{n(\text{th})}{}^b$	$M_{n(\text{GPC})}$	M_w/M_n
1	500	19	87.0	22600	6000	1.71
2	330	19	84.4	14600	4800	1.63
3	250	19	83.6	10900	4600	1.56
4	200	19	81.5	8500	4500	1.48

Conditions: $[St]_0 = 8.74$ mol/L, $[TPED]_0 : [FeCl_3]_0 : [PPh_3]_0 = 1 : 4 : 12$.
[a] $C = [St]_0 : [TPED]_0$.
[b] $M_{n(\text{th})} = ([St]_0/2[TPED]_0) \times MW_{St} \times$ conversion.

TPED alone at 120°C, the polydispersity index is 2.81 at >95% conversion (see F in Table II).

When the polymerization is carried out at 120°C under different ratios of $[St]_0/[TPED]_0$ and keep the ratio of $[TPED]_0 : [FeCl_3]_0 : [PPh_3]_0 = 1 : 4 : 12$, the results are compiled in Table I. From this table we can see that as the initial concentration ratio of the monomer St to the initiator TPED varied from 200 : 1 to 500 : 1, the polydispersity index of the polymer became broader, from 1.48 to 1.71 with higher molecular weight. It reveals that the polymerization is not completely controlled.

The results of bulk polymerization of St initiated with TPED/FeCl₃/PPh₃ at 110, 120, and 130°C, respectively, are compiled in Table II.

When the molar ratio of the initial concentrations of St, TPED, FeCl₃, and PPh₃ in the poly-

merization system is fixed at 200 : 1 : 10 : 30 or 200 : 1 : 4 : 12, the higher the reaction temperature, the faster rate of polymerization. When the polymerizations are performed at the same reaction temperature and the initial molar ratio of the monomer St to the initiator TPED are identical, lower conversions are observed with higher concentration of FeCl₃. For example, when the temperature is 120°C and the reaction time is 2 h, the conversion for 200 : 1 : 4 : 12 is 34.6% (see E-1 in Table II), which is higher than that of 200 : 1 : 10 : 30 (21.5%, see B-1 in Table II). This suggests that the propagating chain radicals are effectively deactivated to dormant species by FeCl₃.

Though the polydispersity index of the PSt obtained is low ($M_w/M_n = 1.34$, $M_n = 2700$) at low conversion, 21.2% at 130°C ($[St]_0 : [TPED]_0 : [FeCl_3]_0 : [PPh_3]_0 = 200 : 1 : 10 : 30$), it becomes

Table II   Results of Polymerization of Styrene Initiated with TPED/FeCl₃/PPh₃ at 110, 120, and 130°C, respectively

No.	T (°C)	C^a	Time (h)	Conversion (%)	$M_{n(\text{th})}{}^b$	$M_{n(\text{GPC})}$	M_w/M_n
A-1	130	1 : 10 : 30	0.5	21.2	3000	2700	1.34
A-2	130	1 : 10 : 30	2	31.5	3300	2900	1.47
A-3	130	1 : 10 : 30	12	57.6	6000	3400	1.94
B-1	120	1 : 10 : 30	2	21.5	2200	2800	1.32
B-2	120	1 : 10 : 30	12	40.5	4200	3100	1.58
C-1	110	1 : 10 : 30	2	16.1	1700	1800	1.51
C-2	110	1 : 10 : 30	19	34.2	3600	2600	1.72
D-1	110	1 : 4 : 12	2	29.0	3000	2100	1.44
D-2	110	1 : 4 : 12	19	78.0	8100	4300	1.49
E-1	120	1 : 4 : 12	2	34.6	3600	2500	1.29
E-2	120	1 : 4 : 12	12	71.9	7500	4100	1.44
E-3	120	1 : 4 : 12	19	81.5	8500	4500	1.48
F^c	120	—	5	~ 100	10400	31900	2.81

Conditions: $[St]_0 = 8.74$ mol/L, $[TPED]_0 = 4.43 \times 10^{-2}$ mol/L.
[a] $C = [TPED]_0 : [FeCl_3]_0 : [PPh_3]_0$.
[b] $M_{n(\text{th})} = ([St]_0/2[TPED]_0) \times MW_{St} \times$ conversion.
[c] Polymerization initiated only with TPED.

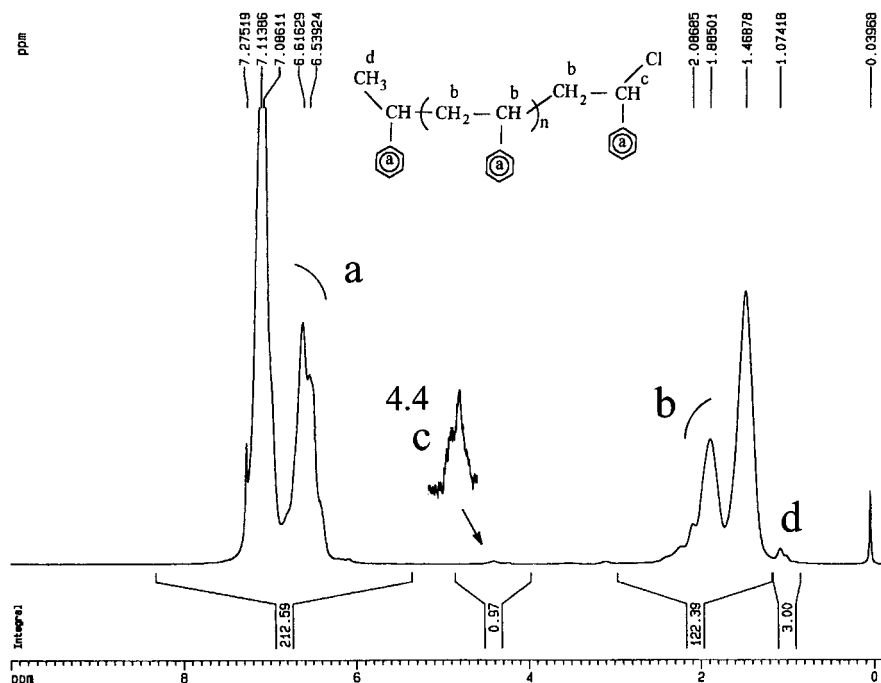**Figure 4** ^{1}H-NMR spectrum of PSt obtained in bulk polymerization with TPED/FeCl$_3$/PPh$_3$ (1 : 4 : 12) at 120°C ($M_{n(GPC)}$ = 4100, M_w/M_n = 1.44).

broader (M_w/M_n = 1.94, M_n = 3400) at higher conversion, 57.6%. The disadvantage of the reverse ATRP at high reaction temperature (130°C) and long polymerization period may be due to the presence of thermal polymerization of St.

From the results mentioned above, it can be seen that the radical polymerization of St using the TPED/FeCl$_3$/PPh$_3$ initiating system, with [St]$_0$: [TPED]$_0$: [FeCl$_3$]$_0$: [PPh$_3$]$_0$ = 200 : 1 : 4 : 12 at 120°C, exhibits some living/controlled characteristics.

Well-Defined Structure of Resultant PSt and End Group Analysis

According to the initiation mechanism of TPED[27–29] and the mechanism polymerization of reverse ATRP using AIBN/FeCl$_3$/PPh$_3$ systems,[23] well-defined PSt with α-hydrogen atom and ω-chlorine atom end groups will be obtained in the polymerization of St using TPED/FeCl$_3$/PPh$_3$ system. The end groups can be monitored by ^{1}H-NMR spectroscopy. Figure 4 shows the ^{1}H-NMR spectrum of a sample of the PSt with M_n = 4100, M_w/M_n = 1.44.

The signal of c at 4.4 ppm is responding to the one end group, that is, CH$_2$C(Ph)H-Cl, as mentioned in literature by Wang and Matyjasze-

wski,[24] that is, an ω-chlorine atom is an end group. The peak at 1.1 ppm, attributed to the chemical shift of d, shows that a methyl group is just at the other end group, CH_3-CH(Ph), as reported in literature also by Wang and Matyjaszewski.[32] Thus, an α-hydrogen atom is another end group.
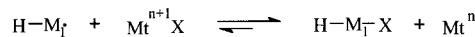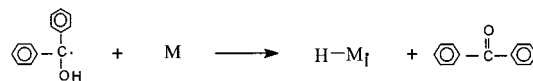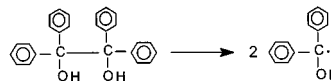
Scheme 1.

The intensity ratio of the peaks d against c in Figure 4 is 3.00 : 0.97, close to 3 : 1; the value is almost equal to the ratio of the hydrogens of the two end groups. Moreover, $M_{n(NMR)}$ (4250) is close to $M_{n(GPC)}$ (4100). These results indicate that all the polymer chains have chlorine ends, supporting that the polymerization with the TPED/FeCl$_3$/PPh$_3$ system proceeds via a reverse ATRP process. Additionally, our results further support the initiation mechanism of TPED is via a hydrogen transfer addition reaction of diphenylhydroxymethyl radicals with monomer, as proposed by Braun et al.[27–29]

Mechanism of Polymerization

Based on end group analysis, we propose the mechanism of St polymerization with the new TPED/FeCl$_3$/PPh$_3$ initiating system, as shown in Scheme 1.

In the initiation reaction step, the initiator TPED firstly cleaves to primary radicals, which then form activated monomer radicals (H–M$_1 \cdot$) via a hydrogen transfer addition. The monomer radical abstracts the chlorine atom (X) from the high oxidized transition-metal species, Mt^{n+1}X, to form the reduced transition-metal species, Mt^n, and the dormant species, H–M$_1$–X. The subsequent propagation steps proceed via an ATPR process.

Chain Extension of PSt

The ^{1}H-NMR analysis of the PSt revealed that an ω-chlorine atom presented as an end group of the PSt chain. Therefore, the PSt can act as a macroinitiator for the extension polymerization. The extension polymerization of PSt (M_n = 4100, M_w/M_n = 1.44) with St was carried out in bulk at 130°C in the presence of the CuCl/bipy catalyst system. When $[St]_0$ = 7.65 mol/L, $[PSt]_0$ = 1.14 × 10^{-2} mol/L, $[CuCl]_0$ = 1.14 × 10^{-2} mol/L, $[bipy]_0$ = 3.42 × 10^{-2} mol/L, t = 12 h, the conversion was >95%. The PSt obtained was with M_n = 82,100, M_w/M_n = 1.33, as shown in Figure 5. It clearly demonstrates the chain extension of PSt takes place, and the initiation efficiency f of the extension polymerization is calculated from f = $M_{n(th)}/M_{n(GPC)}$ [$M_{n\ (th)}$ = 4100 + 104 ($[St]_0$/$[PSt]_0$) × conversion] to be 0.90.

CONCLUSIONS

A well-defined PSt with an α-hydrogen atom and an ω-chlorine atom end groups and narrow poly-

the final PSt
M_n = 82100,
M_w/M_n = 1.33,
conversion = 100%

PSt
M_n = 4100,
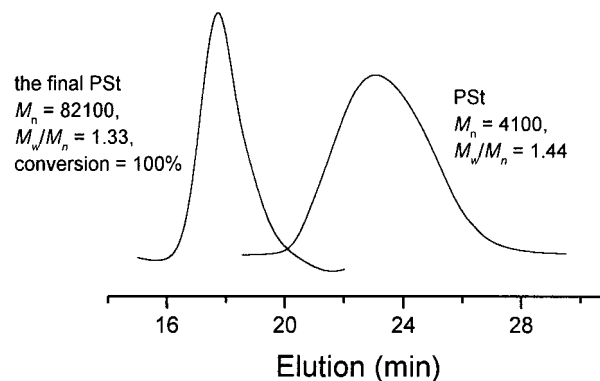M_w/M_n = 1.44

Elution (min)

Figure 5 The GPC curves of PSt before and after chain extension polymerization with St in bulk at 130°C.

dispersity has been synthesized. When the ratio of $[St]_0$: $[TPED]_0$: $[FeCl_3]_0$: $[PPh_3]_0$ is 200 : 1 : 4 : 12 at 120°C, the bulk polymerization exhibits some living/controlled radical polymerization characteristics. The polymers with low polydispersity indices (M_w/M_n = 1.29–1.48) are obtained. The presence of an α-hydrogen atom and an ω-chlorine end group was monitored by ^{1}H-NMR spectrum analysis. The polymerization mechanism was proposed to belong to a reverse ATRP process. Because the PSt obtained is end-functionalized by a chlorine atom, it can be used as a macroinitiator to produce chain extension polymerization in the presence of CuCl/bipy catalyst system via an ATRP process.

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