

'Living' radical polymerization of styrene with AIBN/FeCl₃/PPh₃ initiating system via a reverse atom transfer radical polymerization process

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Abstract: Well-defined polystyrenes with an α -C(CH₃)₂(CN) and an ω -chlorine atom end-groups, and narrow polydispersity ($M_n = 3000$ – 4000 g mol^{-1} , $M_w/M_n = 1.3$ – 1.4) have been synthesized by a radical polymerization process using 2,2'-azobisisobutyronitrile (AIBN)/FeCl₃/PPh₃ initiating system. When the ratio of [St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀ is 200:1:4:12 at 110 °C, the radical polymerization is 'living', but the molecular weight of the polymers is not well-controlled. The polymerization mechanism belongs to a reverse atom transfer radical polymerization (ATRP). Because the polymer obtained is end-functionalized by a chlorine atom, it can then be used as a macroinitiator to perform a chain extension polymerization in the presence of CuCl/2,2'-bipyridine catalyst system via a conventional ATRP process. The presence of a chlorine atom as an end-group was determined by ¹HNMR spectroscopy.

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Keywords: reverse atom transfer radical polymerization; living radical polymerization; styrene; AIBN/FeCl₃/PPh₃ initiating system

INTRODUCTION

Although, in contrast to ionic processes, radical polymerization is suitable for producing polymers from a wide range of monomers under relatively mild reaction conditions, it is not well-controlled because of facile coupling and disproportionation terminations between the propagating species during the polymerization. Sawamoto and co-workers^{1,2} and Matyjaszewski and co-workers^{3,4} reported an efficient way to carry out radical polymerization in a 'living'/controlled manner based on transition-metal catalyst. Matyjaszewski and co-workers^{3,4} named the process atom transfer radical polymerization (ATRP). In ATRP, alkyl halides are often used as initiators; transition metal compounds in their lower oxidation state are used as catalysts (eg Cu(I),^{4–10} Fe(II),^{11,12} Ru(II),² Ni(II),¹³ Rh(I),¹⁴ Pa(II)¹⁵; and electron-donating compounds such as 2,2'-bipyridine (bipy) or triphenylphosphine (PPh₃) as metal complex ligands. Styrene (St), methyl methacrylate (MMA), methyl acrylate, acrylonitrile and 2-hydroxyethyl acrylate, etc. were polymerized via ATRP.^{4–10,16,17}

So far, it has been reported that iron-based catalyst systems, such as organic halides RX/FeCl₂/PPh₃,¹¹ RX/FeBr₂/dNbipy (4,4'-bis(5-nonyl)-2,2'-bipyridine) or N(nBu)₃ systems,¹² can be used for 'living'/controlled radical polymerization of MMA by the ATRP technique, and 'living'/controlled radical polymerization of St can be carried out by ATRP with iron-

based catalyst systems such as RX/FeBr₂/N(nBu)₃, RX/FeBr₂/dNbipy or RX/FeBr₂/P(nBu)₃ systems.¹² However, it has been reported that ATRP of St using an iron-based catalyst system such as 1-phenylethyl bromide/FeBr₂/PPh₃ was poorly controlled, with a slow polymerization rate and high polydispersity (reaction time 15 h, conversion = 47%, $M_{n(\text{GPC})} = 4200 \text{ g mol}^{-1}$, $M_w/M_n = 1.76$).¹²

Reverse ATRP has been explored^{18–21} since 1995, and 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 a lower oxidation state Mt^n/L_x (easily oxidized by oxygen) and halide species RX (usually toxic), respectively. The reverse ATRP initiating systems, ie 2,2'-azo-bisobutyronitrile (AIBN)/CuCl₂ (or CuBr₂)/bipy,^{19–21} AIBN/FeCl₃/PPh₃,¹⁸ have been reported in the literature.

Recently, we have synthesized well-defined PMMA and PSt with an α -hydrogen atom and an ω -chlorine atom as end-groups, respectively, and with high molecular weight and quite narrow polydispersity, using a 1,1,2,2-tetraphenyl-1,2-ethanediol/FeCl₃/PPh₃ initiation system.^{22,23} Well-defined PSt with narrow polydispersity can be synthesized with other iron-based initiating system such as a diethyl 2,3-dicyano-2,3-diphenyl succinate (DCDPS)/FeCl₃/PPh₃ initiating system.²⁴

In this paper, the synthesis of well-defined PSt with

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(Received 24 February 2000; revised version received 28 April 2000; accepted 22 June 2000)

α -isobutyronitrile and ω -chlorine end-groups, together with the radical polymerization behaviour of St with an AIBN/FeCl₃/PPh₃ initiating system are described.

EXPERIMENTAL

Materials

FeCl₃ (anhydrous) was prepared by dehydration of FeCl₃·6H₂O with thionyl chloride according to the method of Bryant and Fernelius.²⁵ AIBN was recrystallized from ethanol. St was dried over CaH₂ and distilled under vacuum. Triphenylphosphine (Aldrich) was recrystallized from ethanol to eliminate triphenylphosphine oxide.

Polymerization

In a typical run, the monomer was added to a dry glass tube with the solid components. Three freeze–vacuum–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, heterogeneous polymerization was stopped by cooling the tube in an ice water bath. After the polymerization product had been dissolved in THF, the PSt was precipitated in methanol and dried. The polymerization yield was determined gravimetrically.

Measurements

Molecular weights and molecular weight distributions of polymer samples were measured by gel permeation chromatography using a Waters 515 GPC with Styragel columns (HT2+HT3+HT4) at 35 °C, THF as eluent (1.0 ml min⁻¹), polystyrene samples as calibration standards, and Waters Millennium 32 as data processing software. ¹H NMR spectra were taken with a Bruker ARX400 (400 MHz) spectrometer in CDCl₃ at 25 °C, using tetramethylsilane (TMS) as internal reference.

RESULTS AND DISCUSSION

Polymerization

Radical polymerization of St was carried out in bulk with an AIBN/FeCl₃/PPh₃ system ([St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀ = 200:1:4:12) at 110 °C, and the correlations of conversion and ln([M]₀/[M]) with time, respectively, are shown as curves (a) in Fig 1. It can be seen that the plot of ln([M]₀/[M]) versus time gives an almost straight line and passes through the origin. When the [St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀ ratio is 200:1:10:30 and other conditions are identical, the plot of ln([M]₀/[M]) versus time also gives a straight line and passes through the origin for conversions up to 64.4%, as observed from curves (b) in Fig 1. This means that the concentration of growing radicals is constant during the polymerization, indicating that the kinetics is first order in monomer concentration in the polymerization system at 110 °C. For [St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀ = 200:1:4:12, the GPC curves of the PSt obtained are shown in Fig 2,

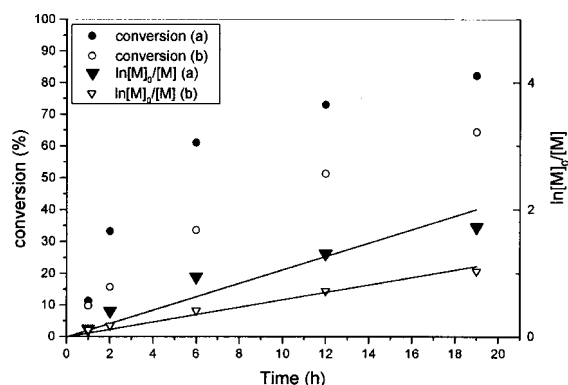


Figure 1. Time dependence of $\ln[M]_0/[M]$ and conversion at 110 °C where $[M]_0$ and $[M]$ are the styrene concentration at times 0 and t , respectively. Conditions: $[St]_0 = 8.74 \text{ mol l}^{-1}$, $[AIBN]_0 = 4.43 \times 10^{-2} \text{ mol l}^{-1}$; (a) $[FeCl_3]_0 = 17.72 \times 10^{-2} \text{ mol l}^{-1}$, $[PPh_3]_0 = 53.15 \times 10^{-2} \text{ mol l}^{-1}$; (b) $[FeCl_3]_0 = 4.43 \times 10^{-1} \text{ mol l}^{-1}$, $[PPh_3]_0 = 1.33 \text{ mol l}^{-1}$.

from which it can be seen that the polydispersity indices are narrow ($M_w/M_n = 1.33$ – 1.39) when the corresponding conversions range from 33.2 to 82.2%. These results reveal that the polymerization of St with an AIBN/FeCl₃/PPh₃ initiation system at 110 °C exhibits ‘living’ radical polymerization characteristics.

Figure 3 shows that the average number molecular weight $M_n(\text{GPC})$ of PSt (measured by GPC) increases linearly with increasing conversion, although the data points are scattered. When the conversion is 11.3%, $M_n(\text{GPC})$ is higher than $M_{n(\text{th})}$ the theoretical number-average molecular weight, computed from $M_{n(\text{th})} = ([St]_0/2[AIBN]_0) \times MW_{St} \times \text{conversion}$, and

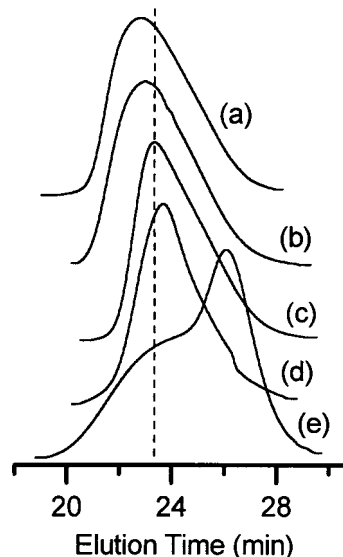


Figure 2. GPC curves of polystyrene prepared in bulk with AIBN/FeCl₃/PPh₃ at 110 °C. Conditions: $[St]_0 = 8.74 \text{ mol l}^{-1}$, $[AIBN]_0 = 4.43 \times 10^{-2} \text{ mol l}^{-1}$, $[FeCl_3]_0 = 17.72 \times 10^{-2} \text{ mol l}^{-1}$, $[PPh_3]_0 = 53.15 \times 10^{-2} \text{ mol l}^{-1}$. (a) $M_n(\text{GPC}) = 4000 \text{ g mol}^{-1}$, $M_w/M_n = 1.39$, conversion = 82.2%, $f = 2.05$; (b) $M_n(\text{GPC}) = 3900 \text{ g mol}^{-1}$, $M_w/M_n = 1.38$, conversion = 73%, $f = 1.87$; (c) $M_n(\text{GPC}) = 3800 \text{ g mol}^{-1}$, $M_w/M_n = 1.33$, conversion = 61%, $f = 1.61$; (d) $M_n(\text{GPC}) = 3100 \text{ g mol}^{-1}$, $M_w/M_n = 1.33$, conversion = 33.2%, $f = 1.06$; (e) $M_n(\text{GPC}) = 2100 \text{ g mol}^{-1}$, $M_w/M_n = 1.81$, conversion = 11.3%, $f = 0.52$.

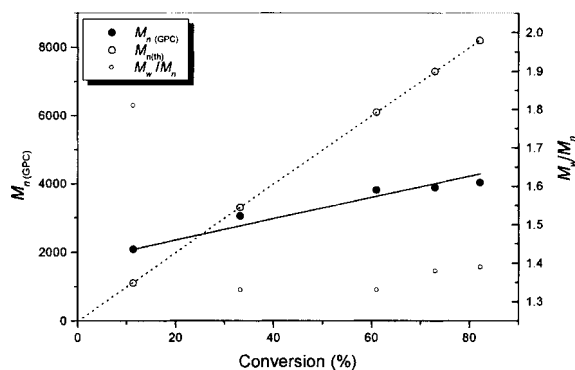


Figure 3. Dependence of polystyrene molecular weight and polydispersity on monomer conversion at 110 °C. Conditions: [St]₀=8.74 mol l⁻¹, [AIBN]₀=4.43 × 10⁻² mol l⁻¹, [FeCl₃]₀=17.72 × 10⁻² mol l⁻¹, [PPh₃]₀=53.15 × 10⁻² mol l⁻¹.

quite a broad polydispersity index ($M_w/M_n=1.81$) is obtained. This may stem from conventional radical polymerization of St during the initial polymerization step. In other words, reverse ATRP starts with higher conversion, eg 33.2%.

The initiator efficiency f (calculated from $f=M_{n(th)}/M_{n(GPC)}$) increases with the reaction time from 0.52 to 2.05 when the conversion increases from 11.3 to 82.2% (Fig 2). As shown in Fig 3, the two straight lines of $M_{n(GPC)}$ and $M_{n(th)}$ versus conversion intersect each other. We think that auto thermal polymerization of St takes place at higher temperature after a longer reaction time, resulting in $f > 1$. Moreover, after longer reaction times, larger f values are obtained. So, reverse ATRP for St with the AIBN/FeCl₃/PPh₃ system is not well-controlled, although good controlled results were obtained by Teyssié and co-workers¹⁸ when using the same initiation system for MMA.

When polymerization was carried out at 120 °C under different [St]₀/[AIBN]₀ ratios keeping the [AIBN]₀: [FeCl₃]₀: [PPh₃]₀ ratio at 1:4:12, the results compiled in Table 1 were obtained. It can be seen that as the initial concentration ratio of monomer St to initiator AIBN changes from 200:1 to 500:1, the polydispersity index becomes broader, increasing from 1.41 to 1.56, and the molecular weight becomes higher. It is also apparent that the polymerization is not very well-controlled.

The results for bulk polymerization of St initiated with AIBN/FeCl₃/PPh₃ ([St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀=200:1:4:12) at different temperatures (110, 120 and 130 °C) are compiled in Table 2. Entries 1 and 2 indicate that the conversion increases with increasing reaction temperature, and the polydispersity index is practically unchanged (being 1.39 and 1.41, respectively) when the reaction temperature rises from 110 to 120 °C. At 130 °C, however, it becomes quite large ($M_w/M_n=1.81$) although the conversion (85.6%) is nearly equal to that of Entries 1 and 2, as shown in Entry 3. From the results of Entries 3–5, it can be seen that the polydispersity of the polymer becomes larger, increasing from 1.39 to 1.81 when the reaction time increases from 1.5 to 12 h. This is attributed to the presence of thermal polymerization of St at higher reaction temperature (130 °C) and longer polymerization period. In addition, at lower reaction temperature such as 90 °C, only a trace of polymer was obtained after 20 h because of the very slow rate of polymerization.

From the above results, it can be observed that well-defined PSt with narrow polydispersities and high conversion can be synthesized using an AIBN/FeCl₃/PPh₃ initiating system ([St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀=200:1:4:12) at 110 °C. However, the mol-

Table 1. Results of bulk polymerization of styrene initiated with AIBN/FeCl₃/PPh₃ at 120 °C^a

Entry no	C ^b	Reaction time (h)	Conversion (%)	M _{n(th)} ^c (g mol ⁻¹)	M _{n(GPC)} (g mol ⁻¹)	M _w /M _n
1	500	19	91.6	23800	6300	1.56
2	330	19	89.4	15300	5400	1.44
3	250	19	86.2	11200	3800	1.43
4	200	19	85.3	8900	3600	1.41

^a Conditions: [St]₀=8.74 mol/l⁻¹, [AIBN]₀: [FeCl₃]₀: [PPh₃]₀=1:4:12.

^b C = [St]₀: [AIBN]₀.

^c M_{n(th)} = 104 × ([St]₀/2[AIBN]₀) × conversion.

Table 2. Results of bulk polymerization of styrene initiated with AIBN/FeCl₃/PPh₃ at different temperatures^a

Entry no	Temperature (°C)	Time (h)	Conversion (%)	M _{n(th)} ^b (g mol ⁻¹)	M _{n(GPC)} (g mol ⁻¹)	M _w /M _n
1	110	19	82.2	8500	4000	1.39
2	120	19	85.3	8900	3600	1.41
3	130	12	85.6	8900	8000	1.81
4	130	8	59.3	6200	3100	1.50
5	130	1.5	18.9	2000	2500	1.39

^a Conditions: [St]₀=8.74 mol l⁻¹, [St]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀=200:1:4:12.

^b M_{n(th)} = 104 × ([St]₀/2[AIBN]₀) × conversion.

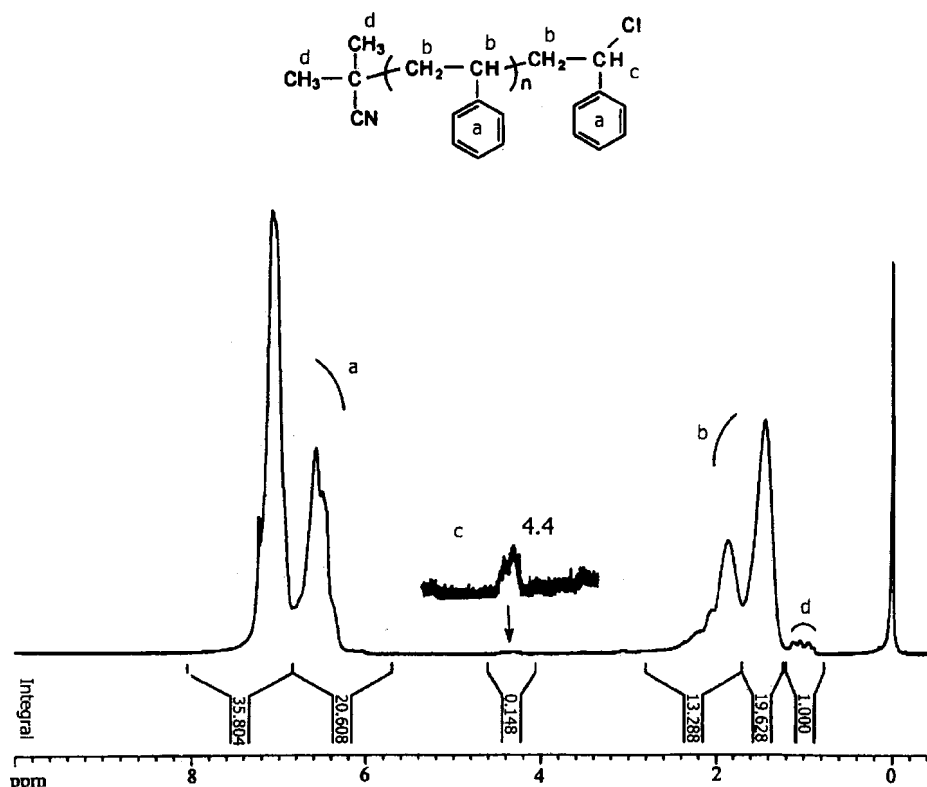


Figure 4. ^1H NMR of polystyrene obtained from bulk polymerization of styrene with the AIBN/ FeCl_3 / PPh_3 (1:4:12) initiating system after 19h at 120°C .

ecular weights of the obtained polymers are not very well-controlled.

End-group analysis

Reverse ATRP of St with an AIBN/ FeCl_3 / PPh_3 initiating system is supported by the analysis of the end-groups of the resultant polymer using ^1H NMR spectroscopy, as shown in Fig 4.

Signal *c* at 4.4 ppm is assigned to the proton of one end-group, that is to $-\text{CH}_2\text{C}(\text{Ph})\text{H}-\text{Cl}$ as mentioned in the literature.¹⁹ Therefore, an ω -chlorine atom is present as an end-group. From the integration of the signals of *d* (α - $(\text{CH}_3)_2\text{CCN}$ end-group) and that of *c* (ω -end-group), the ratio of the two groups is calculated to be 1.13, showing that the number of α - $(\text{CH}_3)_2\text{C}(\text{CN})$ groups is higher than that of ω - PhCHCl groups. That is to say, coupling termination between the propagating species may take place during polymerization. In addition, $M_n(\text{NMR})$ is about 6900 g mol^{-1} , which is close to $M_n(\text{GPC})$ (6300 g mol^{-1}). This supports the hypothesis that the reaction proceeds via reverse ATRP. Therefore, PSt synthesized by an AIBN/ FeCl_3 / PPh_3 initiating system bears α - $(\text{CH}_3)_2\text{CCN}$ and ω -chlorine atom end-groups.

Mechanism of polymerization

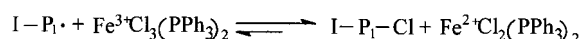
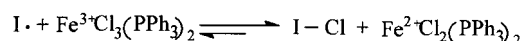
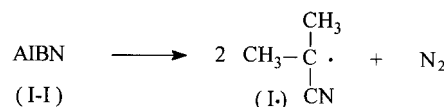
We propose the mechanism of St polymerization with an AIBN/ FeCl_3 / PPh_3 initiating system which is depicted in Scheme 1. The mechanism is reverse ATRP, as proposed by Matyjaszewski and co-workers¹⁹ and Teyssié and co-workers.¹⁸ As illustrated in Scheme 1, in the initiation step, the primary radical $\text{I}\cdot$ or the propagating chain active species $\text{I}-\text{P}_1\cdot$

abstracts a Cl atom from the highly oxidized transition-metal species $\text{FeCl}_3(\text{PPh}_3)_2$, to produce the reduced transition-metal species $\text{FeCl}_2(\text{PPh}_3)_2$ and the dormant species $\text{I}-\text{Cl}$ or $\text{I}-\text{P}_1-\text{Cl}$. The subsequent propagating steps then follow conventional ATRP.

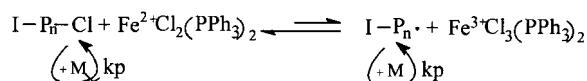
Chain extension polymerization of styrene

^1H NMR analysis of the PSt obtained reveals that an ω -chlorine atom is present as an end-group of the PSt

Initiation:



Propagation:



Scheme 1

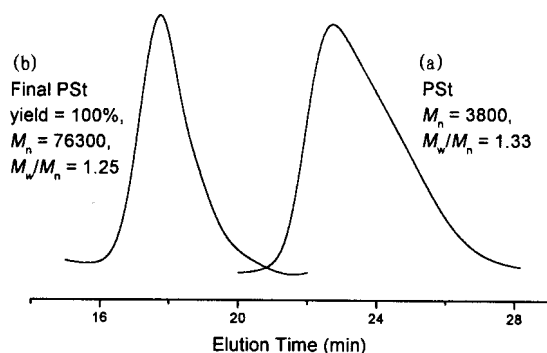


Figure 5. GPC curves of polystyrene (a) before and (b) after chain extension polymerization with styrene in bulk at 130 °C. Conditions: $[St]_0 = 8.24 \text{ mol l}^{-1}$, $[PSt]_0 = 1.52 \times 10^{-2} \text{ mol l}^{-1}$, $[CuCl]_0 = 1.52 \times 10^{-2} \text{ mol l}^{-1}$, $[2,2'\text{-bipyridine}]_0 = 4.56 \times 10^{-2} \text{ mol l}^{-1}$.

chain; therefore, this PSt can act as a macroinitiator for extension polymerization of St.

Extension polymerization of St was carried out in bulk at 130 °C with PSt ($M_n = 3800 \text{ g mol}^{-1}$, $M_w/M_n = 1.33$) in the presence of a CuCl/bipy ATRP catalyst system. When $[St]_0 = 8.24 \text{ mol l}^{-1}$, $[PSt]_0 = 1.52 \times 10^{-2} \text{ mol l}^{-1}$, $[CuCl]_0 = 1.52 \times 10^{-2} \text{ mol l}^{-1}$, $[bipy]_0 = 4.56 \times 10^{-2} \text{ mol l}^{-1}$, $t = 10 \text{ h}$, the conversion is higher than 95%. The M_n of the final PSt increases up to 76300 g mol^{-1} and the polydispersity index is essentially the same as that of the macroinitiator PSt (about 1.25) as shown in Fig 5. The initiation efficiency f ($f = M_{n(\text{th})}/M_{n(\text{GPC})}$; $M_{n(\text{th})} = M_{n(\text{PSt})} + 104 \times ([St]_0/[PSt]_0) \times \text{conversion}$) of the extension polymerization is 0.75.

CONCLUSIONS

Well-defined PSt samples with $\alpha\text{-C}(\text{CH}_3)_2(\text{CN})$ and ω -chlorine atom end-groups, narrow polydispersity ($M_n = 3000\text{--}4000 \text{ g mol}^{-1}$, $M_w/M_n = 1.3\text{--}1.4$) and high conversion have been synthesized by a radical polymerization process with an AIBN/FeCl₃/PPh₃ initiation system. When the ratio of $[St]_0:[AIBN]_0:[FeCl_3]_0:[PPh_3]_0$ is 200:1:4:12 at 110 °C, the reverse ATRP of St with an iron-based initiating system using PPh₃ as the ligand exhibited 'living' radical polymerization characteristics, with low polydispersity of the

polymers. However, the molecular weight of the polymers was not well-controlled. Because the polymer obtained is end-functionalized by a chlorine atom, it can then be used as a macroinitiator to perform extension polymerization in the presence of a CuCl/bipy catalyst system via an ATRP process.

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