Living/Controlled Radical Polymerization of Styrene with a New Initiating System: DCDPS/$FeCl_3$/PPh_3

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ABSTRACT: The living/controlled radical polymerization of styrene was investigated with a new initiating system, DCDPS/$FeCl_3$/PPh_3, in which diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS) was a hexa-substituted ethane thermal iniferter. The polymerization mechanism belonged to a reverse atom transfer radical polymerization (ATRP) process. The polymerization was controlled closely in bulk (at 100 °C) or in solution (at 110 °C) with a high molecular weight and quite narrow polydispersity (M_w/M_n = 1.18 ~ 1.28). End-group analysis results by ^{1}H NMR spectroscopy showed that the polymer was ω-functionalized by a chlorine atom, which also was confirmed by the result of a chain-extension reaction in the presence of a $FeCl_2$/PPh_3 or CuCl/bipy (2,2′-bipyridine) catalyst via a conventional ATRP process. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 101–107, 2000

Keywords: living/controlled radical polymerization; reverse atom transfer radical polymerization; diethyl 2,3-dicyano-2,3-diphenylsuccinate; styrene

INTRODUCTION

Radical polymerization processes are important for the industrial production of commodity polymers, but they are not living polymerization, and the molecular weight and molecular weight distribution are very difficult to control because of the irreversible termination reactions between two propagating radicals by coupling and disportionation.[1] To develop living radical polymerization, efforts have focused on minimizing termination or transfer of propagating chains through a sufficiently low concentration of radicals by reversible deactivation of radicals to the dormant species.[2]

Georges et al.[3,4] reported a living/controlled radical polymerization of styrene (St) in bulk using 2,2′-azo-bis-iso-butyronitrile (AIBN) as the initiator and the stable counter-radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Later, Sawamoto et al.[5] and Wang and Matyjaszewski[6] described a new living radical polymerization technique, atom transfer radical polymerization (ATRP), that uses alkyl halide species, RX, as initiators and transition-metal compounds at a lower oxidation state complexed with suitable ligands, M_t^n/LX, as catalysts. A wide variety of monomers such as St,[1,2,6–8] methyl methacrylate (MMA),[8,9] methyl acrylate (MA),[10] acrylonitrile,[11] and *n*-butyl acrylate[12] have been polymerized successfully by this method, and it exhibits some characteristics of living polymerization. Percec et al.[13,14] reported the living radical polymerization of St with arenesulfonyl chloride catalyzed by copper-based complexes in heterogeneous and homogeneous conditions. Matyjaszewski et al.[1,2,6,15] described the living/controlled radical polymerization of St with copper-based catalyst systems, RX/CuCl/bipy (2,2′-bipyridine) or 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dTbipy) or 4,4′-di-(5-nonyl)-2,2′-bipyridyl (dN-bipy) as ligands. A living/controlled radical process in which polystyrenes (PSts) with predetermined molecular weights up

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to 10^5 and polydispersities as narrow as 1.05 have been obtained with a CuCl/dNbipy catalyst system.[1]

The living/controlled radical polymerization of MMA can be carried out by ATRP with iron-based catalyst systems such as RX/$FeCl_2$/PPh_3,[16] RX/$FeBr_2$/dNbipy, or N(nBu)$_3$.[8] The living/controlled radical polymerization of St also can be carried out by ATRP with iron-based catalyst systems such as RX/$FeBr_2$/N(nBu)$_3$, RX/$FeBr_2$/dNbipy, and RX/$FeBr_2$/P(nBu)$_3$,[8] but Matyjaszewski et al.[8] reported that the ATRP of St with PPh_3 as a ligand in an iron-based system such as 1-phenylethyl bromide/$FeBr_2$/PPh_3 was controlled poorly, with a slow polymerization rate and a high polydispersity (M_w/M_n = 1.76).

This type of ATRP, however, has two major problems: the toxicity of the halide species RX and the oxidation of the catalyst M_t^n/LX by the oxygen in the air.[17] To overcome the drawbacks, "reverse" and "alternative" ATRPs recently were promoted by Matyjaszewski et al.[18,19] and Teyssié et al.,[17] respectively. Wang and Matyjaszewski[18] reported the living/controlled radical polymerization of St via a reverse ATRP under heterogeneous conditions with AIBN/$CuCl_2$/bipy as the initiating system, but it was uncontrolled for both MMA and MA. Shortly thereafter, by using a alkyl-substituted bipyridine ligand such as dNbipy as a ligand instead of bipy, Xia and Matyjaszewski[19] described reverse ATRP under homogeneous conditions in which the living/controlled polymerization of St, MMA, and MA all were carried out successfully. More recently, Teyssié et al.[17] reported that the AIBN/$FeCl_3$/PPh_3 system could be used for the synthesis of well-defined poly(methyl methacrylate) (PMMA) in bulk and solution polymerization of MMA at 85 °C. The PMMA obtained was α-functionalized by an isobutyronitrile group and ω-functionalized by a chlorine group.

In our lab, we studied a carbon—carbon bond thermal iniferter, diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), to initiate the polymerization of MMA, and the results revealed that the polymerization exhibited some living characteristics.[20] We thought it would be interesting to introduce the iniferter to the reverse ATRP system and study its polymerization nature. Therefore, we exploited DCDPS into the reverse ATRP initiating system DCDPS/$FeCl_3$/PPh_3 to produce a new initiating system. A well-defined PSt with a high molecular weight and quite narrow polydispersity was obtained through the polymerization of St by this process. End-group analysis showed that the PSt obtained was ω-functionalized by a chlorine group that was confirmed by the extension of PSt in the presence of $FeCl_2$/PPh_3 or CuCl/bipy and fresh St via a conventional ATRP process.

EXPERIMENTAL

Materials

$FeCl_3 \cdot 6H_2O$ was dehydrated by reactions with thionyl chloride,[21] and $FeCl_2 \cdot 4H_2O$ (Aldrich) was used as received. CuCl was purified by stirring in acetic acid, filtered, washed with ethanol, and dried. 2,2′-Bipyridine (bipy) was recrystallized from acetone. St was dried over CaH_2 and then distilled under vacuum. Triphenylphosphine was recrystallized from ethanol to eliminate triphenylphosphine oxide.[17] DCDPS was prepared according to the reported procedure.[20,22]

Polymerization

The polymerization was carried out in a sealed tube equipped with a three-way stopcock under vacuum. After the reaction components were charged into a dry glass tube, the tube was sealed under a vacuum performing with three-pump-thaw cycles and immersed in an oil bath thermostated at the desired temperature. At certain time intervals, the glass tubes were taken out and broken. The resultant polymers were dissolved in tetrahydrofuran (THF), precipitated in methanol,

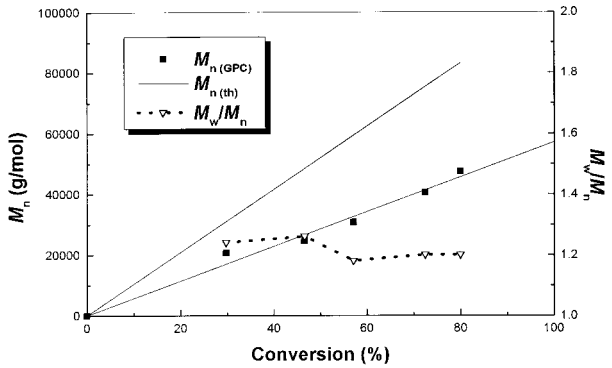


Figure 1. Dependence of the number-average molecular weight and molecular weight distribution of PSt on conversion at 100 °C in the bulk polymerization of St. The conditions were $[St]_0 = 8.75\ mol \cdot L^{-1}$, $[FeCl_3]_0 = 17.5 \times 10^{-3}\ mol \cdot L^{-1}$, $[PPh_3]_0 = 52.6 \times 10^{-3}\ mol \cdot L^{-1}$, and $[DCDPS]_0 = 4.4 \times 10^{-3}\ mol \cdot L^{-1}$.

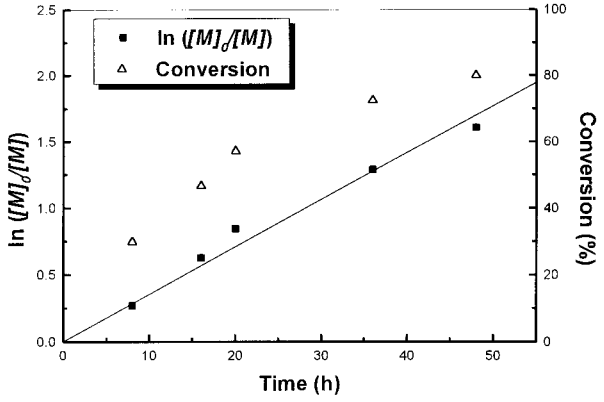


Figure 2. Time dependence of $\ln([M]_0/[M])$ and conversion at 100 °C in the bulk polymerization of St. The conditions were $[St]_0 = 8.75\ mol \cdot L^{-1}$, $[FeCl_3]_0 = 17.5 \times 10^{-3}\ mol \cdot L^{-1}$, $[PPh_3]_0 = 52.6 \times 10^{-3}\ mol \cdot L^{-1}$, and $[DCDPS]_0 = 4.4 \times 10^{-3}\ mol \cdot L^{-1}$.

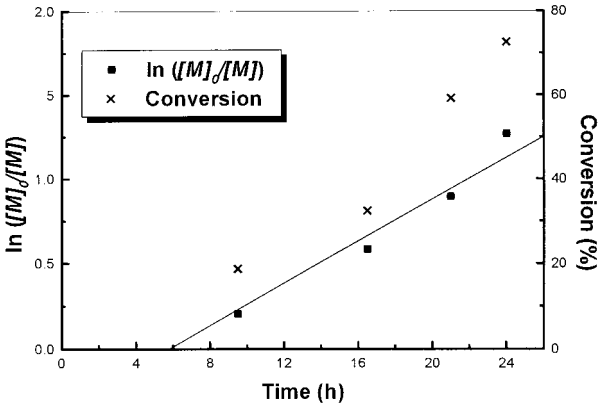


Figure 3. Time dependence of $\ln([M]_0/[M])$ and conversion at 110 °C in the solution polymerization of St. The conditions (in toluene) were $[St]_0 = 5.83\ mol \cdot L^{-1}$, $[FeCl_3]_0 = 11.66 \times 10^{-3}\ mol \cdot L^{-1}$, $[PPh_3]_0 = 34.98 \times 10^{-3}\ mol \cdot L^{-1}$, and $[DCDPS]_0 = 2.9 \times 10^{-3}\ mol \cdot L^{-1}$.

and dried. The conversion of polymerization was determined gravimetrically.

Polymer Characterization

The number-average molecular weight (M_n) and molecular weight distribution or polydispersity index (M_w/M_n) of the polymers were determined at 35 °C with gel permeation chromatography (GPC; Waters Associates Model HPLC/GPC 515 liquid chromatography equipped with a refractive index detector and HT2 + HT3 + HT4 μ-Styragel columns and calibrated with standard PSt) with THF as the eluent and a flow rate of 1.0 mL/min. ^{1}H NMR spectra were taken at 25 °C with a Brucker ARX400 (400 MHz) spectrometer with $CDCl_3$ and tetramethylsilane as the solvent and internal reference, respectively.

RESULTS AND DISCUSSION

The radical polymerization of St was carried out in bulk with the DCDPS/$FeCl_3$/PPh_3 initiating system ($[St]_0$: $[DCDPS]_0$: $[FeCl_3]_0$: $[PPh_3]_0$ = 2000 : 1 : 4 : 12) at 100 °C; the results are shown in Figures 1 and 2. From Figure 1, we can see that the number-average molecular weight (GPC) of PSt increased linearly with the conversion increasing from 20,600 to 47,400, although the increase was less than the calculated values, assuming that one molecule of DCDPS generated two living polymer chains. The molecular weight distribution remained quite narrow (1.18 ~ 1.26) during the whole course of the polymerization. In a comparison experiment, the bulk polymerization of St initiated by DCDPS alone ([DCDPS]

Table I. Results of Styrene Polymerization in Toluene at 110 °C[a]

Entry	Time (h)	Conversion (%)	M_n (GPC)[b]	M_n (th)[c]	M_w/M_n
1	9.5	18.7	14,000	19,400	1.23
2	16.5	32.4	26,900	33,700	1.26
3	21.0	59.2	39,400	61,500	1.23
4	24.0	72.6	42,300	75,500	1.28

[a] Conditions: $[St]_0 = 5.83\ mol \cdot L^{-1}$; $[FeCl_3]_0 = 11.66 \times 10^{-3}\ mol \cdot L^{-1}$; $[PPh_3]_0 = 34.98 \times 10^{-3}\ mol \cdot L^{-1}$; $[DCDPS]_0 = 2.9 \times 10^{-3}\ mol \cdot L^{-1}$.

[b] GPC calibrated with PS standards.

[c] M_n (th) = $([St]_0/2[DCDPS]_0) \times MW_{St} \times$ Conversion, where M_n (th) and MW_{St} represent theoretical molecular weight and the molecular weight of St, respectively.

Table II. Kinetic Data and Estimated Concentration of Growing Radicals for Bulk[a] and Solution[b] Polymerization of Styrene with the DCDPS/$FeCl_3$/PPh_3 Initiating System

	Bulk	Solution
Temperature (°C)	100	110
$[M]_0$ (mol · L^{-1})	8.75	5.83
k_p^{app} (10^5 s^{-1})	1.09	1.94
k_p. (10^{-3}L mol^{-1} s^{-1})	1.05[c]	1.34[c]
[P·] (10^8 mol · L^{-1})	1.04	1.45

[a] Conditions: $[St]_0 = 8.75$ mol · L^{-1}; $[FeCl_3]_0 = 17.5 \times 10^{-3}$ mol · L^{-1}; $[PPh_3]_0 = 52.6 \times 10^{-3}$ mol · L^{-1}; $[DCDPS]_0 = 4.4 \times 10^{-3}$ mol · L^{-1}.

[b] Conditions (in toluene): $[St]_0 = 5.83$ mol · L^{-1}; $[FeCl_3]_0 = 11.66 \times 10^{-3}$ mol · L^{-1}; $[PPh_3]_0 = 34.98 \times 10^{-3}$ mol · L^{-1}; $[DCDPS]_0 = 2.9 \times 10^{-3}$ mol · L^{-1}.

[c] Values extrapolated from the 30 to 90 °C range to 110 °C. See Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. Macromolecules 1993, 26, 6410.

$= 4.4 \times 10^{-3}$ mol · L) was carried out at 100 °C; a 46.9% conversion was obtained only after 1 h. The molecular weight and polydispersity index of the resulting PSt were 123,700 and 1.55, respectively. A logarithmic plot of $\ln([M]_0/[M])$ versus time t is shown in Figure 2; a straight line passes through the origin, showing that the kinetics was of the first order in the monomer and the concentrations of the growing species were constant during the polymerization. Both of these results suggested that the polymerization of St with the DCDPS/$FeCl_3$/PPh_3 initiating system exhibited some living/controlled polymerization characteristics.

The solution polymerization of St with the same initiating system was carried out in toluene at 110 °C, and the results were compiled in Table I. The M_n (GPC) of PSt increased with the increasing conversion, and the polydispersity indices were narrow ($M_w/M_n < 1.28$). Also, a linear plot for $\ln([M]_0/[M])$ versus time t can be observed in Figure 3, but there is a long induction period. The reason may be that the lower concentration of DCDPS caused the slower decomposition of the initiator and, at the same time, $FeCl_3$ was in great excess compared to the radical generated. Therefore, the polymerization was inhibited. From the slopes of the straight kinetic plots in Figures 2 and 3, we calculated the apparent propagation rate constants (k_p^{app}). Assuming propagation occurs via "normal" free radicals, we estimated the stationary concentration of radicals, [P·], from the ratio of the apparent rate constants, k_p^{app}, and the rate constants of radical propagation, k_p., available;[6,23] that is, $[P\cdot] = k_p^{app}/k_p$.. Table II shows the kinetic data and estimated concentrations of the growing radicals in the polymerization of St with the DCDPS/$FeCl_3$/PPh_3 initiating system. The concentrations of the growing radicals in bulk and solution polymerization were low enough to minimize the termination or transfer of the propagating radicals, which also were confirmed by the results of the low polydispersity indices of the resultant PSt.

However, some deviation from the theoretical molecular weight was observed with this DCDPS/$FeCl_3$/PPh_3 initiating system, as shown in Figure 1 and Table I. Similar deviation results were reported by Sawamoto et al.[5] and Teyssié et al.[24] with CCl_4/$RuCl_2(PPh_3)_2$/MeAl(ODBP)$_2$ and CCl_4/Ni(NCN′)Br initiating systems, respectively.

To gain a better understanding of the reverse ATRP mechanism, we studied the effect of various concentrations of initiator on the level of the control of polymerization. As seen from Table III,

Table III. Data of Polystyrene Initiated with the DCDPS/$FeCl_3$/PPh_3 System at Various Concentrations of the Initiator[a]

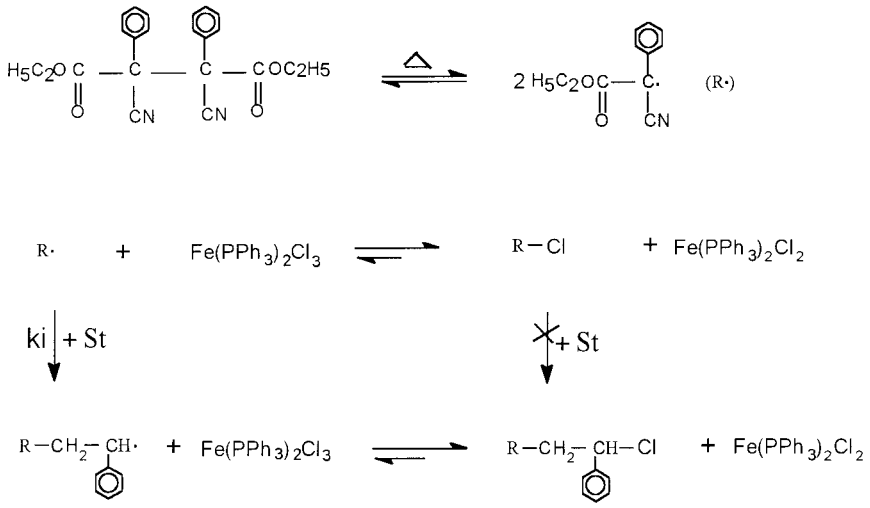
Entry	$[DCDPS]_0$ (10^{-3} mol · L^{-1})	Time (h)	Conversion (%)	M_n (GPC) (g mol^{-1})[b]	M_n (th) (g mol^{-1})[c]	M_w/M_n
1	17.50	24	74.9	8,600	18,700	1.19
2	8.75	24	73.0	22,100	36,500	1.18
3	4.37	24	63.8	35,600	66,300	1.20
4	2.91	24	61.6	42,800	92,400	1.19

[a] Conditions: $[St]_0 = 8.75$ mol · L^{-1}; [DCDPS]/[$FeCl_3$]/[PPh_3] = 1/4/12 (constant ratio); temperature = 100 °C.

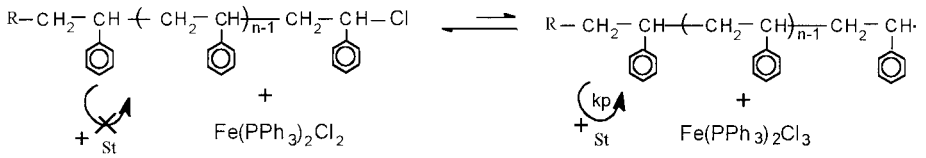
[b] GPC calibrated with PS standards.

[c] M_n(th) ($[St]_0/2[DCDPS]_0$) × MW_{St} × Conversion, where M_n (th) amd MW_{St} represent theoretical molecular weight and the molecular weight of St, respectively.

Initiation:



Propagation:



Scheme 1.

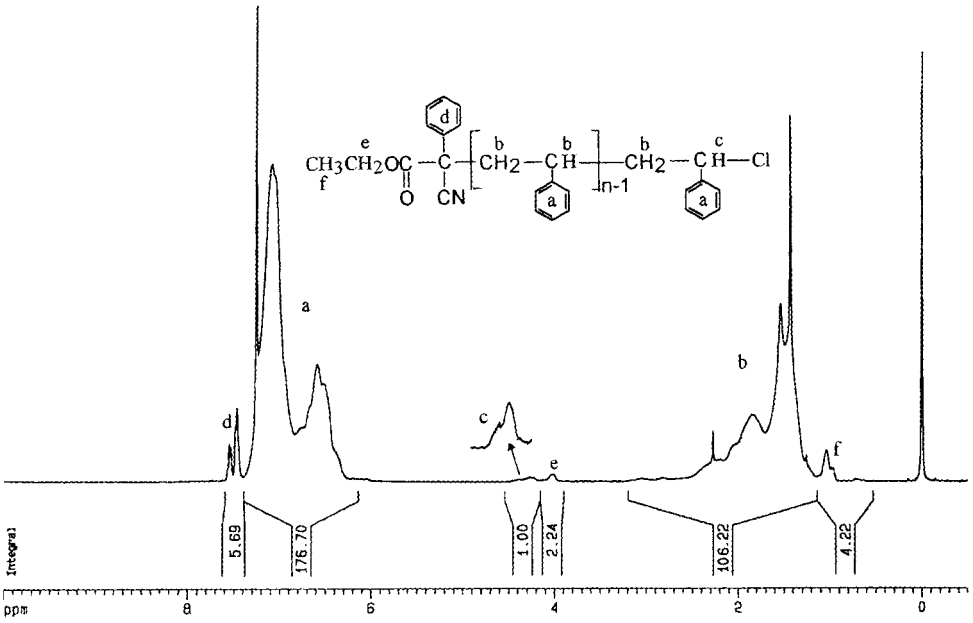


Figure 4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of PSt (M_n = 3550, M_w/M_n = 1.37) prepared with St/DCDPS/$FeCl_3$/PPh_3 (200/1/4/12) in bulk at 100 °C.

the molecular weight increased with the decreasing DCDPS concentrations in the same experimental conditions, whereas the polydispersity indices were essentially the same. Therefore, in this system there appears to have been no significant effect of $[DCDPS]_0$ on the polydispersity indices. Indeed, even in a very low concentration of the initiator ($[St]_0/[DCDPS]_0 = 3000/1$), the polymerization of St went well and over a wide range of DCDPS concentrations, $[St]_0/[DCDPS]_0$, changing from 500 to 3000; the polydispersity remained quite low ($M_w/M_n \approx 1.20$).

Polymerization Mechanism

A polymerization mechanism is proposed as depicted in Scheme 1. In the initiation step, it consists of the homolytic decomposition of DCDPS to form the primary radicals (R·) and the addition of R· radicals with the monomer. Then, the activated monomer radicals react with $Fe(PPh_3)_2Cl_3$ by abstracting the chlorine atom from it and generate the lower oxidation state metal complex $Fe(PPh_3)_2Cl_2$. The radicals formed can react with the monomer to create propagating chains or directly react with the catalyst to form the reduced species M_T^n and the dormant species. Finally, the polymer propagates exactly via a conventional ATRP process.

End-Group Analysis

According to ^1H NMR spectroscopy, the PSts produced by this initiating system were polymers end-functionalized with an α-(carbethoxy-cyano-phenyl)-methyl and an ω-chloride group,[25] as shown in Figure 4. The broad signal at about 4.39 ppm was responding to the ω end-group, that is, —$CH_2C(Ph)H$—Cl, which similarly was observed by Wang and Matyjaszewski.[18] The signals at 1.12 ppm, 4.02 ppm, and 7.35 ~ 7.52 ppm were attributed to the protons of methyl (f), methylene (e), and the phenyl groups (d), respectively, at the α chain end that came from the fragments of DCDPS. The molecular weight determined from the NMR spectrum [M_n (NMR) ≈ 3,690] was close to the one obtained from GPC [M_n (GPC) ≈ 3,550]. Accordingly, the end-functionalized PSt with an α-(carbethoxy-cyano-phenyl)-methyl group from the DCDPS fragments and an ω-chlorine atom group from the catalyst was obtained by this initiating system.

To investigate the living nature of the polymerization, the chain-extension polymerization of St was carried out in bulk at 100 °C with PSt (M_n = 14,800; M_w/M_n = 1.24) in the presence of $FeCl_2/PPh_3$ as the catalyst via a conventional ATRP. The number-average molecular weight of the resulting PSt increased to 60,800, and the polydispersity index slightly decreased to 1.19, which essentially was demonstrated by the GPC curves shown in Figure 5(a). With CuCl/bipy as the catalyst (in bulk at 130 °C), the number-average molecular weight of the final PSt increased from 14,800 to 103,600 (M_w/M_n = 1.55), as shown in Figure 5(b). The results confirmed the presence of a chlorine atom at the ω chain end of the original PSt that served as a macroinitiator. These results indicated that the $DCDPS/FeCl_3/PPh_3$ initiating

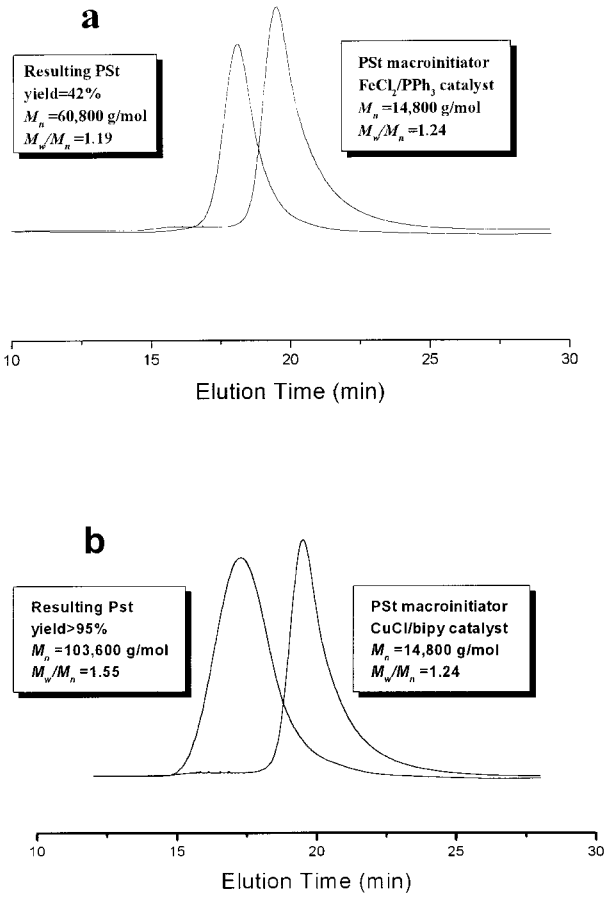


Figure 5. GPC curves of PSt before and after a chain-extension reaction in the presence of (a) the $FeCl_2/PPh_3$ system at 100 °C (Conditions: t = 22 h, $[St]_0$ = 8.75 mol · L^{-1}, $[PSt]_0 = 4.38 \times 10^{-3}$ mol · L^{-1}, $[FeCl_2] = 17.5 \times 10^{-3}$ mol · L^{-1}, and $[PPh_3]_0 = 52.6 \times 10^{-3}$ mol · L^{-1}) and (b) the CuCl/bipy system at 130 °C (Conditions: t = 10 h, $[St]_0$ = 8.75 mol · L^{-1}, $[PSt]_0 = 5.68 \times 10^{-3}$ mol · L^{-1}, [CuCl] = 5.68×10^{-3} mol · L^{-1}, and $[bipy]_0 = 17.04 \times 10^{-3}$ mol · L^{-1}).

system induced living polymerization via reverse ATRP.

CONCLUSIONS

The new initiating system, DCDPS/$FeCl_3$/PPh_3, was used in the living/controlled radical polymerization of St. A well-defined PSt with a high molecular weight (up to 47,400) and quite narrow polydispersity index (M_w/M_n = 1.20) was obtained from the polymerization of St in bulk or in toluene with the DCDPS/$FeCl_3$/PPh_3 initiating system. The mechanism of polymerization belonged to a reverse ATRP. The number-average molecular weights of the polymers increased with the increasing monomer conversion, and first-order plots were conducted from which the concentrations of the growing radicals were estimated. The chain-extension reaction and ^{1}H NMR results confirmed the PSt obtained could act as a macroinitiator.

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25. Recently in our lab, Chen and Qiu (Chen, X. P.; Qiu, K. Y. J Macromol Sci Pure Appl Chem, submitted.) investigated the radical polymerization of St with an AIBN/$FeCl_3$/PPh_3 initiating system. In this work, a similar end-group analysis by ^{1}H NMR was carried out. The ω-$CH_2C(Ph)H$—Cl end-group (a signal at 4.4 ppm) and α-$(CH_3)_2CCN$ end-group (a signal at 1.1 ppm) were found via ^{1}H NMR spectroscopy.