Synthesis of Well-Defined Comblike Hydroxy-Functionalized Atactic Polystyrene Promoted by Metallocene/Tin/Poly(phenyl glycidyl ether)-*co*-Formaldehyde

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ABSTRACT: Well-defined comblike atactic polystyrene functionalized with hydroxyl groups was synthesized via living/controlling radical polymerization promoted by metallocene complexes in the presence of poly(phenyl glycidyl ether)-*co*-formaldehyde as the initiator and Sn as a reducing agent. The effect of the polymerization conditions, such as the ratio of initiator to monomer, temperature, and polymerization time, and the structure of the metallocene complex on the polymerization process were investigated. The resulting polymers were characterized by gel permeation chromatography, multiangle laser light scattering, ^{1}H-NMR, and ^{13}C-NMR. The results show that the polymer had a narrow molecular weight distribution in the range 1.1–1.4 and the number-average molecular weight of the polymer linearly depended on the monomer conversion within the polymerization timescale, which confirmed that living radical polymerization characteristics prevailed in the polymerization process. Both the number of arms and the number of hydroxyl groups in each polymer molecule were about four, which suggested that they arose from the epoxy functional groups of the initiator. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1574–1580, 2010

Key words: metallocene catalysts; radical polymerization; polystyrene

INTRODUCTION

Polymers with comblike architecture have attracted considerable attention because of their interesting physical properties, such as their viscosities in solution and melt states.[1–3] In general, synthesis of these comblike polymers is accomplished by grafting-onto processes[4–8] (the attachment of side chains to the backbone) or grafting-from processes[9–12] (the grafting of side chains from the backbone). Living free-radical polymerization (LRP) is the preferred route for the synthesis of a variety of well-defined comblike polymers with precisely controlled architecture

because successful atom transfer radical polymerization protocols often require the presence of activated halides along the polymer backbone.[13–16] The LRP of styrene (St) in the presence of epoxides and metals (Zn) in the catalyst system was reported for the first time by Asandei and coworkers,[17–19] and the effects of different reducing agents,[20] ligands,[21] solvents, and additives[22] on the reaction were investigated.

Recently, Asandei and Saha[23] described the synthesis of graft copolymers initiated by an epoxide radical ring-opening reaction with a grafting-from route. Poly(glycidyl methacrylate) as the epoxide macroinitiator was formed via atom transfer radical polymerization. The macroinitiator generated reactive radicals as a result of radical ring opening catalyzed by Cp_2TiCl_2/Zn and formed the copolymers of polystyrene grafted onto poly(alkyl methacrylate) from poly(glycidyl methacrylate); this resulted from the copolymers of glycidyl methacrylate with methyl methacrylate and St initiated by CuBr/2,2′-bipyridyl (bpy).

Herein, we reported that an initiator system, the metallocene complex/poly(phenyl glycidyl ether)-*co*-formaldehyde (I_s)/Sn, was used to produce comblike atactic polystyrene (aPS) functionalized by hydroxyl groups through a LRP strategy. The process was based on a macroinitiator (I_s) containing suitable initiating groups along the backbone; this allowed the
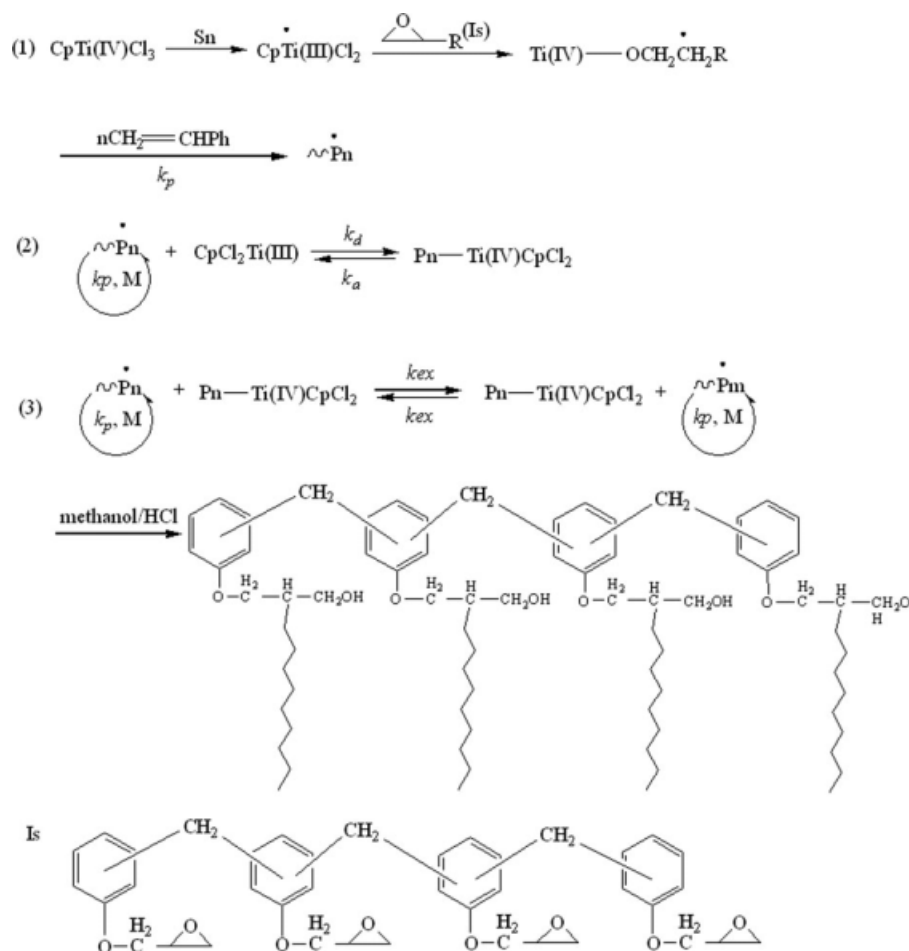
Scheme 1 Polymerization mechanism and structure of the initiator (I_s). Cp is cyclopentadienyl; K_p is the chain growing constant.; M is the monomer; P_n is the polymer; K_d is the constant to form the dormant; K_a is the constant to form the radical species (active species) from the dormant; K_{ex} is reversible homolysis constant.

polymer to be made in one step. A Ti-mediated LRP system was used. CpTiCl$_3$ was reduced by metallic Sn to form radical CpTi(III)Cl$_2$. The subsequent opening of the epoxide ring by CpTi(III)Cl$_2$ gave a carbon-centered free-radical, which initiated the propagation of the monomer. The CpTi(III)Cl$_2$ reversibly terminated the growing chains as persistent radicals, and the number-average molecular weight (M_n) and molecular weight distribution (MWD) could thus be controlled.[17]

EXPERIMENTAL

Materials

All manipulations involving air- and moisture-sensitive compounds were performed under a dry argon atmosphere with Schlenk techniques.

Tetrahydrofuran (THF) and 1,4-dioxane were refluxed overnight in the presence of sodium/benzophenone and distilled before use. Dicyclopentadiene, n-butyl lithium (a 1.6M solution in hexane), indene, and dichlorodimethylsilane were used as received

from Acros (Beijing, China); TiCl$_4$, CH$_2$Cl$_2$, St, and Sn were purchased from Beijing Chemical Agency at Daxing District; I_s was purchased from Aldrich. St was stirred overnight with sodium hydroxide, dried over calcium hydride for 8 h, distilled under reduced pressure, and stored under argon at $-25°C$.
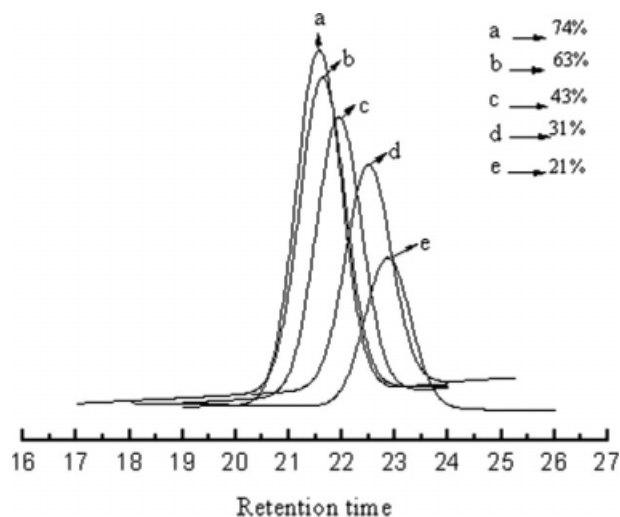
Synthesis of the catalysts

CpTiCl$_3$, (n-BuCp)$_2$TiCl$_2$, and SiMe$_2$(Ind)$_2$TiCl$_2$ were prepared according to the literature[24] by the addition of a stoichiometric amount of diene to an organolithium reagent followed by reaction with the metal halide in THF.

ANAL. Calcd for CpTiCl$_3$ (219, yield = 70.2%): C, 27.4%; H, 2.28%; Ti, 21.8%; Cl, 48.5%. Found: C, 27.3%; H, 2.13%; Ti, 22.1%; Cl, 48.4%. ^{1}H-NMR (CDCl$_3$, δ): 6.50 (s, 5H).

ANAL. Calcd for (n-BuCp)$_2$TiCl$_2$ (361, yield = 65.8%): C, 59.9%; H, 7.26%; Ti, 13.2%; Cl, 19.6%. Found: C, 60.4%; H, 6.69%; Ti, 13.2%; Cl, 19.7%. ^{1}H-NMR (CDCl$_3$, δ): 4.6 (t, 8H), 1.1 (t, 6H), 1.7–1.9 (m, 12H).

ANAL. Calcd for SiMe$_2$(Ind)$_2$TiCl$_2$ (425, yield = 63.6%): C, 56.5%; H, 8.94%; Si, 6.61%; Ti, 11.3%; Cl,

Figure 1 Evolution of the GPC traces of the resulting polymer.

16.7%. Found: C, 56.4%; H, 8.93%; Si, 6.72%; Ti, 11.2%; Cl, 16.7%. ^{1}H-NMR (CDCl$_3$, δ): 0.21 (s, 6H), 6.75–6.81 (m, 8H), 7.30 (d, 4H), 7.26 (d, 4H), 6.08 (d, 4H), 6.60 (d, 4H).

Synthesis of the comblike polymer

Stoichiometric amounts of CpTiCl$_3$ catalyst (0.16 g, 0.73 mmol) and Sn (0.12 g, 1.01 mmol) were added to a 200-mL Schlenk tube, which was degassed and filled with argon. The solvent (1,4-dioxane, 5 mL) was then introduced, and the reaction was allowed to proceed at room temperature for 5 min before the mixture was cooled to −80°C by liquid nitrogen. The initiator (I$_s$, 0.02 g, 0.031 mmol) and monomer (St, 5 mL) were added to the reactor, which was degassed by several freeze–pump–thaw cycles, filled with argon, and finally heated to 90°C in an oil bath. The solution slowly turned orange. After the desired time, the reaction was terminated by the addition of a dilute hydrochloric acid solution in methanol. The mixture was filtered, purified by flash column chromatography on acidic Al$_2$O$_3$, precipitated in methanol, washed by water, and dried *in vacuo* at 60°C to give a white powder. The structure of the initiator (I$_s$) and the polymerization mechanism are shown in Scheme 1.

Characterization

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Inova 600-MHz spectrometer in CDCl$_3$ solution at 25°C. Chemical shifts were referenced with the residual solvent resonance and are reported relative to tetramethylsilane. The molecular weight and MWD of the polymers were determined by gel permeation chromatography (GPC) with a dual detector system consisting of a Waters 2410 differential re-

fractometer and a multiangle laser light scattering (MALLS) device, which was calibrated with polystyrene standards; THF was used as an eluent. The monomer conversion was defined in terms of the amount of product formed relative to the amount of St charged initially.

RESULTS AND DISCUSSION

GPC and MALLS

The effect of the reaction time and temperature on the synthesis of the comblike polymer was investigated when the CpTiCl$_3$/Sn/I$_S$/St ratio was 8 : 12 : 1 : 500. When the reaction was carried out at 90°C for different polymerization times, the GPC curves of the resulting polymer (Fig. 1) shifted to lower retention time as the reaction time increased, which showed that the molecular weight of the polymer increased with increasing monomer conversion. As shown in Figure 2, M_n of the polymer increased as a linear function of monomer conversion up to a molecular mass of 1.2×10^5 g/mol at a monomer conversion of 74%. Throughout the polymerization course, the MWD of the polymer remained in a narrow range of 1.1–1.4 and decreased with increasing monomer conversion. These results indicate that living behavior prevailed in the polymerization process.[25]

Polymerization conditions

The effect of the ratio of initiator (I$_s$) to St on the polymerization process, with the CpTiCl$_3$/Sn/I$_s$ ratio kept constant, is shown in Figure 3. For ratios of initiator to monomer in the range 1 : 250 to 1 : 750, a linear dependence of M_n on the monomer conversion was observed in each case, and M_n of the polymer increased as the ratio of initiator to monomer
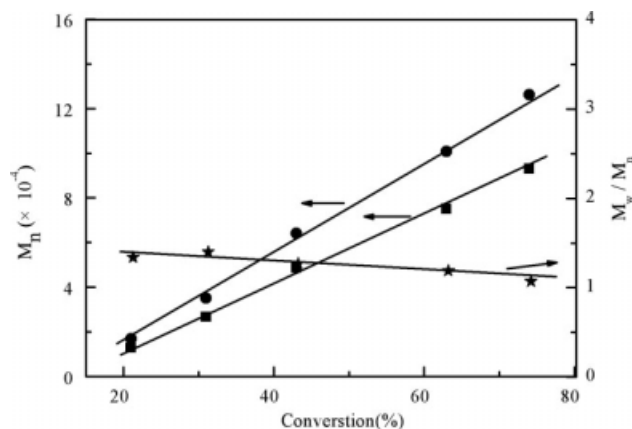
Figure 2 Variation of the molecular weights and MWDs of the resulting polymer with monomer conversion: (●) M_n determined by MALLS and (■) calculated M_n. Reaction conditions: CpTiCl$_3$/Sn/I$_s$/St = 8 : 12 : 1 : 500, monomer = St (5 mL), and solvent = 1,4-dioxane (5 mL). M_n and weight-average molecular weight (M_w)/M_n were determined by MALLS.
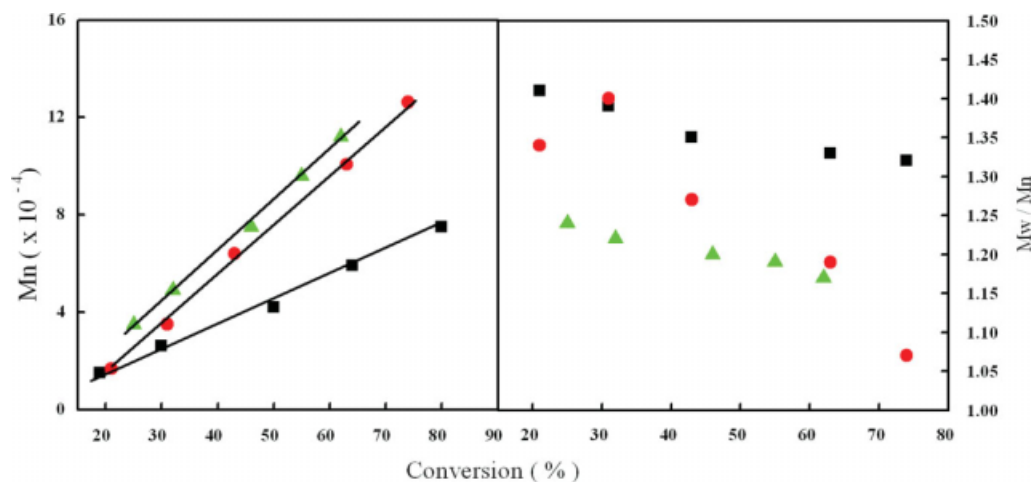
Figure 3 Effect of the ratio of the initiator to monomer on the polymerization. Reaction conditions: CpTiCl$_3$/Sn/Is/St: (■) 8 : 12 : 1 : 250, (●) 8 : 12 : 1 : 500, and (▲) 8 : 12 : 1 : 750. Solvent = 1,4-dioxane (5 mL). M_n and M_w/M_n were determined by MALLS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decreased. MWD of the obtained polymer in each case was within the narrow range 1.1–1.4. The calculated M_n for all cases had the same trend. M_n was linear with the monomer conversion (or time). However, the calculated values M_n were all less than the M_n values found by MALLS.

The effects of the polymerization temperature and time on the polymerization performance are summarized in Table I. From the data for runs 1–4, we observed that the molecular weight of the polymer increased with increasing reaction temperature from 60 to 90°C. MWD of the polymer basically remained constant within the temperature scope, whereas M_n of the polymer increased with increasing temperature. This indicated that the catalytic active center was stable within the temperature range, and the propagation rate increased with temperature. At higher temperatures, for example, at 110°C, however, the molecular weight of the polymer showed a decrease; this suggested that the active species was becoming

deactivated.[26] MWD of the obtained polymer under this condition became broad, which might have resulted from an increased incidence of side reactions and a shift of the reversible dissociation equilibrium toward the active species.[27] When the temperature was kept constant at 90°C (runs 3 and 5–8 in Table I), the plot of ln [([M]$_0$/[M]); where [M]$_0$ is the monomer starting concentration, [M] is the monomer immediately concentration during the polymerization course] versus time (shown in Fig. 4) was linear. This result indicated that the reaction was first order with respect to monomer concentration. It also implied that the concentration of the active species remained constant throughout the polymerization course.

Titanocene complexes

The effect of the structure of the titanocene complexes on the polymerization of St is shown in Table II. M_n of the obtained polymer and monomer conversion

TABLE I
Effect of the Conditions on the Polymerization of St Catalyzed by a CpTiCl$_3$/Sn/I$_s$ Catalyst System

Run	T_p (°C)	Time (h)	$M_n \times 10^{-4a}$	$M_n \times 10^{-4b}$	M_w/M_n^b	$M_n \times 10^{-4c}$	Conversion (%)	IE^d
1	60	18	0.44	0.95	1.08	0.32	23	0.463
2	80	18	4.42	7.01	1.13	1.80	51	0.630
3	90	18	9.30	12.63	1.07	2.56	74	0.736
4	110	18	7.71	7.36	1.62	2.04	80	–
5	90	6	1.28	1.68	1.34	0.56	21	0.762
6	90	8	2.66	3.50	1.40	0.70	31	0.760
7	90	10	4.86	6.40	1.27	1.78	43	0.759
8	90	16	7.50	10.07	1.19	2.88	63	0.745

Reaction conditions: CpTiCl$_3$/Sn/I$_s$/St = 8 : 12 : 1 : 500, monomer = St (5 mL), and solvent = 1,4-dioxane (5 mL).
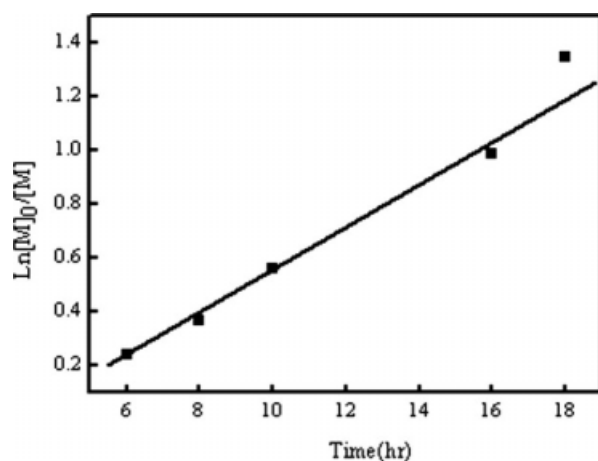^{a} Calculated molecular weight.
^{b} Determined by MALLS.
^{c} Determined by GPC.
^{d} IE = initiation efficiency determined by calculated M_n/M_n by MALLS.
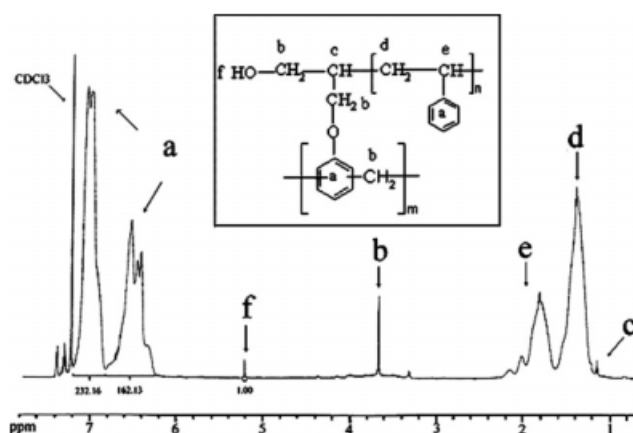T_p is the polymerization temperature.

Figure 4 First-order kinetics plot of $\ln([M]_0/[M])$ versus time. Reaction conditions: $CpTiCl_3/Sn/I_s/St = 8 : 12 : 1 : 500$, monomer = St (5 mL), solvent = 1,4-dioxane (5 mL), and temperature = 90°C.

Figure 5 ^{1}H-NMR spectrum of the polymer sample (run 6 in Table I). Reaction conditions: catalyst/Sn/I_s/St = 8 : 12 : 1 : 500, monomer = St (5 mL), solvent = 1,4-dioxane (5 mL), temperature = 90°C, and time = 8 h.

showed significant differences. These could be attributed to the very different electron releasing effects and steric demands of the ligands used.[28] Both the electron-donating ability and the steric demand of the ligands decreased in the order $SiMe_2(Ind)_2TiCl_2 > (n\text{-}BuCp)_2TiCl_2 > CpTiCl_3$. The C—Ti bond strength of the dormant species decreased in the same order, which resulted in the dormant species [reactions (2) and (3) in Scheme 1] being less stable and having a shorter lifetime. This resulted in the ease of insertion of the monomers into the propagated chains and the overall rate of propagation increase in the order $SiMe_2(Ind)_2TiCl_2 < (n\text{-}BuCp)_2TiCl_2 < CpTiCl_3$, which resulted in the monomer conversion and the molecular weight of the resulting polymer increasing in the same order. So $CpTiCl_3/Sn/I_s$ was the best catalyst system for St polymerization.

As shown in Tables I and II, the data of the obtained polymers M_n determined by GPC and MALLS were considerably different. The value determined by MALLS was dramatically larger than that determined by GPC. It is possible that the size of a polymer molecule changes as the polymer topology changes. A multiarmed, dendritic, or hyperbranched polymer will be more compact than a linear polymer.[29,30] So MALLS is reasonable for testing M_n of a topological polymer. As also shown in Tables I and II, the calculated M_n was lower than the M_n determined by MALLS, which indicated that the initiation efficiency was less than 1. For the experiments carried out at 90°C, the initiation efficiency was 0.736. The initiation efficiency for the polymerization depended on the temperature and the metallocene structure. It became lower with decreasing temperature and more bulk ligand. For example, the initiation efficiencies for $CpTiCl_3$ were 0.736 and 0.463 at 90 and 60°C, respectively. For $SiMe_2(Ind)_2TiCl_2$, the initiation efficiency was 0.412 at 90°C. However, if the temperature was over 90°C, for example, 110°C, the initiation efficiency was conflicting. This may have been due to the side reactions. The initiation efficiency changed slightly within the polymerization timescale, which implied that the active species was stable. The calculated M_n of the obtained polymer polymerized at 90°C was linear with the monomer conversion (Fig. 2).

Calculation of the arm number (*r*) of the polymer

The structure of the initiator (I_s) is shown in Scheme 1; its M_n was 570 g/mol. The number of epoxy

TABLE II
Effect of Metallocene Complexes on the Polymerization of St

Run	Catalyst	$M_n \times 10^{-4a}$	$M_n \times 10^{-4b}$	$M_w/M_n{}^b$	$M_n \times 10^{-4c}$	Conversion (%)	IE^d
3	$CpTiCl_3$	9.30	12.63	1.07	2.56	74	0.736
9	$(n\text{-}BuCp)_2TiCl_2$	5.23	10.36	1.21	2.10	42	0.504
10	$SiMe_2(Ind)_2TiCl_2$	3.54	8.58	1.28	1.73	36	0.412

Reaction conditions: catalyst/Sn/I_s/St = 8 : 12 : 1 : 500, monomer = St (5 mL), solvent = 1,4-dioxane (5 mL), temperature = 90°C, time = 18 h.
^{a} Calculated molecular weight.
^{b} Determined by MALLS.
^{c} Determined by GPC.
^{d} IE = initiation efficiency determined by calculated M_n/M_n by MALLS.

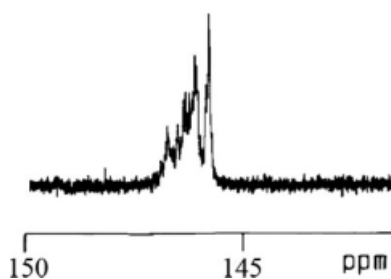**Figure 6** ^{13}C-NMR spectrum of the phenyl ring quaternary carbon region for the polymer sample (run 6 in Table I). Reaction conditions: catalyst/Sn/I$_s$/St = 8 : 12 : 1 : 500, monomer = St (5 mL), solvent = 1,4-dioxane (5 mL), temperature = 90°C, and time = 8 h.

functional groups (m) in I$_s$ was estimated to be about 3.5 (i.e., 570/163). The ^{1}H-NMR spectrum of the polymer sample from a reaction (run 6 in Table I) catalyzed by CpTiCl$_3$/Sn/I$_s$ is shown in Figure 5. The peaks at δ 6.4–7.2 ppm were attributed to the aromatic protons (5H) of the polystyrene, and the signal at 5.24 ppm was attributed to the functional group ─OH. The polymerization degree (n) of the polymer was calculated from the relative integrated intensities according to eq. (1):

$$n = \frac{I_a/I_{OH}}{5/1} = \frac{394/1}{5/1} = 79 \tag{1}$$

where I_a and I_{OH} stand for the integrated intensities of the aromatic ring and ─OH peaks, respectively.

The number-average molecular weight of each arm segment of the polymer (M_{nr}) was calculated from the value of n according to eq. (2):

$$M_{nr} = nM_s + M_i = 79 \times 104 + 159.5 = 8375.5 \tag{2}$$

where M_s is the molecular weight of the St monomer ($M_s = 104$), and the value M_i [(163 × 4 − 14)/4 = 159.5] arises from the contribution of the initiator (I$_s$) to the molecular weight of each arm of the polymer. r of the polymer is given by eq. (3):

$$r = M_n/M_{nr} = 35,000/8375.5 = 4.2 \tag{3}$$

where M_n is the number-average molecular weight of the polymer as determined by MALLS.

The r value of the polymer was consistent with the m value of the initiator. This result indicates that r of the comblike polymer was controlled by the number of epoxy functional groups in the initiator.

^{13}C-NMR spectrum

The ^{13}C-NMR spectrum of the same sample (run 6 in Table I) is shown in Figure 6. The presence of multiple peaks in the range δ 145.9–146.9 ppm,

expected for the quaternary carbon in a phenyl ring, confirmed that the polymer was aPS.

CONCLUSIONS

Well-defined comblike aPS functionalized by ─OH groups was synthesized with metallocene complexes. The molecular weight of the resulting polymer showed a linear dependence on the monomer conversion in all cases within the range of [I$_s$]/[M] from 1 : 250 to 1 : 750; from 60 to 90°C, a linear dependence of M_n of the polymer on the monomer conversion and a linear increase in ln[M]$_0$/[M] with time were also observed. These results suggest that the polymerization behavior had living characteristics. The catalyst system CpTiCl$_3$/Sn/I$_s$ was the most effective for St polymerization. The number of arms and functional groups of the comblike polymer depended on the number of epoxy functional groups of the initiator. The resulting polymer was shown to be aPS by ^{13}C-NMR.

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