

The Architecture of Hydroxy-Functionalized aPS-b-Random Copolymer-b-PE via One-Pot Strategy Combining Living Free Radical Polymerization with Coordination Polymerization

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ABSTRACT: The copolymerization of styrene with ethylene was promoted by CpTiCl₃/BDGE/Zn/MAO catalyst system combining free radical polymerization with coordination polymerization via sequential monomer addition strategy in one-pot. The effect of polymerization conditions such as temperature, time, ethylene pressure, and Al/Ti molar ratio on the polymerization performance was investigated. The hydroxy-functionalized aPS-b-random copolymer-b-PE triblock copolymer was obtained by solvent extraction and determined by GPC, DSC, WAXD, and ¹³C-NMR. The DSC result indicated that the aPS-b-random copolymer-b-PE had a T_g at 87°C and a T_m at 119°C which attributed to the T_g of aPS segment and the

T_m of PE segment, respectively. The microstructure of the hydroxy-functionalized aPS-b-random copolymer-b-PE was further confirmed by WAXD, ¹³C-NMR, and ¹H-NMR analysis; and these results demonstrated that the obtained block copolymer consisted of aPS segment, S-E random copolymer segment, and crystalline PE segment. The connection polymerization of the hydroxy-functionalized aPS with random copolymer-b-PE was revealed by GPC results. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3171–3179, 2011

Key words: radical polymerization; coordination polymerization; block copolymer

INTRODUCTION

Over the past few decades, styrene-ethylene (S-E) copolymers have received great attention due to their impressive viscoelastic behavior, mechanical properties, and compatibilities with other polymeric materials.¹ Copolymerization of styrene with ethylene promoted by Ziegler-Natta catalysts have been reported.^{2–4} Because of low activity for styrene polymerization, the classic heterogeneous Ziegler-Natta

catalysts only incorporate small amounts of comonomer, primarily as isolated units.⁵ These catalysts commonly used in the synthesis of isotactic poly- α -olefins are not generally suitable for the synthesis of S-E copolymers.⁶

S-E copolymer was obtained for the first time based on stereorigid *ansa*-zirconocenes and half-sandwich group 4 metal metallocenes following coordination polymerization in one-pot.^{7–11} The efficient copolymerization of ethylene with styrene has become possible and been widely investigated by both academic and industrial researchers.^{12–19} Kakugo et al.²⁰ reported the synthesis of isotactic poly(styrene-*alt*-ethylene) with a melting point of 145°C catalyzed by 2,2'-thio-bis(6-*tert*-butyl-4-methylphenoxy)titanium dichloride/MAO catalyst system. Subsequently, the isotactic alternating S-E copolymers have been obtained by several researchers with metallocene catalyst system such as ethylenebis(1-indenyl) zirconium dichloride/MAO,²¹ *rac*-(ethylene)bis(1-indenyl)zirconium dichloride/MAO,^{22,23} (η^1 : η^5 -C₁₃H₈SiMe₂NCMe₃)TiMe₂ with 1 equiv of [Ph₃C][B(C₆F₅)₄],²⁴ *rac*-[Methylene(3-*tert*-butyl-1-indenyl)₂ZrCl₂]/MAO.²⁵ Particularly, Oliva et al.²⁶ synthesized high-

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molecular weight isotactic alternating S-E copolymers that could be stretched into fibers by *rac*-isopropylidenebis(1-indenyl)zirconium dimethyldiamide/MAO catalytic system. Syndiotactic S-E copolymers were also reported. Chu et al.²⁷ obtained syndiotactic polystyrene/polyethylene block copolymers by CpTiCl₃. Grassi et al.⁶ obtained styrene-butadiene block copolymers (sPS-PB) using MAO-activated CpTiCl₃ and converted them into sPS-B samples consisting of styrene-1-butene-ethylene units through the selective hydrogenation of the unsaturated polybutadiene segments. Zhang and Nomura¹¹ reported the living copolymerization of syndiotactic polystyrene/polyethylene block copolymers by a half-titanocene C₅Me₅TiCl₂(N = C^tBu₂). Hou and coworkers²⁸ reported syndiotactic styrene-styrene sequences in S-E copolymer via the scandium half-metallocene complex [Sc(η⁵-C₅Me₄SiMe₃)(CH₂SiMe₃)₂(THF)], in combination with 1 equiv of [Ph₃C][B(C₆F₅)₄].

Frank and coworkers²⁹ reviewed the methodology to form PE(iPP)-b-aPS copolymer combining coordination polymerization with anionic polymerization or coordination polymerization with living radical polymerization by two-pot strategy.

Ye and coworkers³⁰ reported the synthesis of block copolymer of ethylene with styrene via a new two-step strategy combining living coordination polymerization of ethylene with ATRP of styrene catalyzed by a functionalized Pd-diimine catalyst.

Recently, living radical polymerization of styrene promoted by metallocene/epoxide/metal catalyst system was investigated by Asandei et al.^{31–33} In the literature, Asandei et al. described in detail the polymerization mechanism and the role of each component of the catalyst system for the polymerization. Metallocene complex was reduced by metals to form metallocene complex radical. Subsequent opening of the epoxide ring by metallocene complex radical gave a carbon-centered free radical which initiated the propagation of the monomer. The metallocene complex radical reversibly terminated the growing chain as persistent radical (dormant species) and the number-average molecular weight (M_n) and the molecular weight distribution (MWD) of the obtained polymer could thus be controlled. Asandei et al. also reported the effect of different reducing agents (metals),³⁴ initiator,^{31,35} ligands of metallocene complexes,³⁶ solvents and additives³⁷ on the reaction. Herein, based on both Asandei and Chen³¹ results and coordination polymerization, we introduced the synthesis of the hydroxy-functionalized aPS-b-random copolymer-b-PE triblock copolymer catalyzed by CpTiCl₃/BDGE/Zn/MAO combining living radical polymerization with coordination polymerization in one-pot. The effect of conditions such as temperature, time, pressure of ethylene, Al/Ti molar

ratio on the polymerization performance was investigated.

EXPERIMENTAL

General procedures and materials

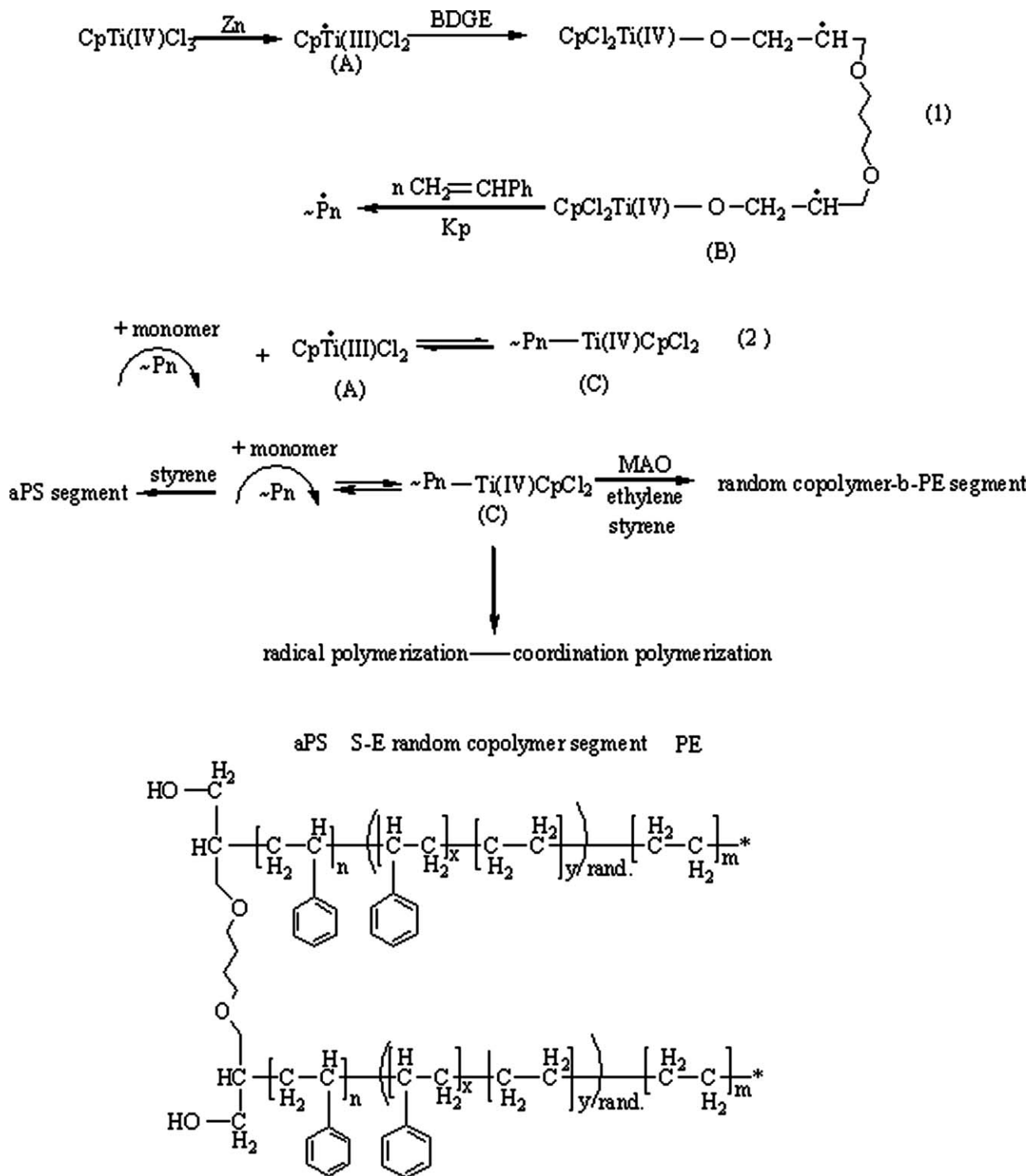
Polymerization-grade ethylene was not further purified; styrene was stirred overnight with sodium hydroxide, dried over calcium hydride for 8 h, distilled under reduced pressure, and stored under argon at –25°C; toluene was refluxed over metallic sodium/benzophenone for 48 h and distilled under a nitrogen atmosphere before use; dicyclopentadiene, *n*-butyl lithium (1.6M solution in hexane) and 1,4-butanediol diglycidyl ether (BDGE) were purchased from Acros; TiCl₄, dichloromethane, chloroform, and Zn powder were purchased from Beijing Chemical Agency at Daxing District; methylalumoxane (MAO) was purchased from Albemarle with 10 wt % solution in toluene.

Synthetic procedure of metallocene complexes

CpTiCl₃ and Cp₂TiCl₂ were prepared according to the literature³⁸ by adding the stoichiometric amount of dicyclopentadiene to an organolithium reagent followed by the reaction with TiCl₄ in tetrahydrofuran. Elemental analysis for CpTiCl₃ (219.4, yield 70.2%): Calcd. C: 27.5, H: 2.28; Found C: 27.3, H: 2.33. ¹H resonances (δ in ppm, CDCl₃, 25°C): 6.50 (5H, s, C₅H₅). Elemental analysis for Cp₂TiCl₂ (248.9, yield: 74.6%), Calcd. C: 48.4, H: 4.02. Found: C: 48.3, H: 4.06. ¹H resonances (δ in ppm, CDCl₃, 25°C): 6.46 (10H, s, C₁₀H₁₀).

Copolymerization

Calculated amount of metallocene complex CpTiCl₃ (0.04 g, 0.18 mmol), Zn (0.018 g, 0.27 mmol) and solvent (1, 4-dioxane, 10 mL) were added to an autoclave (300 mL) which was degassed and was filled with argon. The reduction occurred in less than 10 min at r.t. A mixture of initiator (BDGE 0.05 mL, 0.045 mmol) and monomer (styrene, 3 mL) was injected into the autoclave by an air-tight syringe. The reactor was heated up to 90°C and stirred for 2.5 h*. Then cooled to 50°C, 70 mL of toluene and 31.5 mL of MAO (10 wt % in toluene, ratio of Al/Ti was 300 in mol) was introduced, and the mixture was stirred for 10 min. Ethylene with desired pressure was charged in and stirred to desired time. The polymerization was terminated by excess amount of methanol/HCl (100/10 in v/v) solution. The resultant copolymer was filtered and washed with fresh methanol and water and dried by vacuum at 50°C.



Scheme 1 The course of the styrene/ethylene copolymerization catalyzed by CpTiCl₃/BDGE/Zn/MAO catalyst system.

Solvent extraction

Selective solvent fraction to remove homopolymer was carried out using a Soxhlet extractor. The crude product was placed in a cellulose thimble and extracted successively with boiling butanone for 12 h to remove the soluble atactic polystyrene. The residue was extracted with boiling tetrahydrofuran

(THF) for 12 h to remove S-E random copolymer. The THF-insoluble fraction was extracted with boiling CHCl₃ for 12 h to remove the insoluble sPS and PE homopolymer.^{11,39-43} The CHCl₃-soluble fraction (aPS-b-random copolymer-b-PE) was isolated by evaporation of solvent, dried under vacuum at 50°C, weighed, and analyzed by DSC, WAXD, GPC, ¹³C-NMR, and ¹H-NMR spectroscopy.

Characterization

GPC analysis was performed at 150°C on a PL-GPC200, using trichlorobenzene as eluent, linear polystyrene as standard. The glass transition temperature and melting temperature were determined with a Perkin–Elmer DSC-2 system at 10°C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 300°C for 5 min, cooling at 10°C/min to room temperature then recording the second DSC scan. WAXD was recorded with a Ricon D/Max-3A diffraction system. The radiation source was nickel filtered Cu K α radiation ($\lambda = 1.5405 \times 10^{-10}$ m). The samples were scanned over a 2θ range of 5–40° at a scan rate of 0.02°/s. ^{13}C -NMR and ^1H -NMR (125 MHz for ^{13}C -NMR, TMS as internal standard) spectra was recorded on an INOVA500 spectrometer at 150°C in *o*-dichlorobenzene (d_4).

RESULTS AND DISCUSSION

Synthesis of the block copolymer

The course of the styrene/ethylene copolymerization catalyzed by CpTiCl₃/BDGE/Zn/MAO catalyst system was described in Scheme 1. The initiating radicals(B) was generated from a redox reaction of BDGE with CpTi[•](III)Cl₂ which was formed by the room temperature Zn reduction of CpTi(IV)Cl₃ [eq. (1)]. CpTiCl₃ was reduced by metallic Zn to form radical CpTi[•](III)Cl₂. Subsequent opening of the epoxide ring from BDGE by CpTi[•](III)Cl₂ gave a carbon-centered free radical which initiates propagation of the monomer (styrene). CpTi[•](III)Cl₂(A) was reversibly combined with the polymeric growing chain $\sim\text{Pn}$ to form dormant species $\sim\text{Pn-Ti(IV)CpCl}_2\text{(C)}$ [eq. (2)]. The living characteristic of the styrene radical polymerization was provided by the reversible end-capping of the propagating chain end by a second equivalent of CpTi(III)Cl₂ (A).³¹ Then, the dormant species (C) obtained was activated by MAO to yield the Ti(IV) species which promoted the successive coordination polymerization of olefins. Following, the single species mechanism was confirmed by the GPC result of the hydroxy-functionalized aPS-*b*-random copolymer-*b*-PE triblock copolymer.

To isolate the goal block copolymer, hydroxy-functionalized aPS-*b*-random copolymer-*b*-PE triblock copolymer, from the crude product, selective solvent extraction was carried out successively with boiling butanone, THF, and CHCl₃ solvents. It was found that butanone was a good solvent for atactic polystyrene, and THF was poor solvent for syndiotactic PS and PE homopolymer but good for S-E random copolymers. The amount of THF-soluble fraction

was negligible ($\leq 1\%$), but the amount of THF-insoluble fraction was over 99%, indicating the absence of S-E random copolymer.^{11,44} The CHCl₃ was a poor solvent for sPS and PE.^{11,44,45} The amount of CHCl₃-insoluble fraction was trace indicating that the metallocene CpTiCl₃ or Cp₂TiCl₂ was completely consumed by the room temperature Zn reduction before the living radical polymerization of styrene. The generation of stable dormant species $\sim\text{Pn-Ti(IV)CpCl}_2$ was confirmed during the living radical polymerization of styrene.³¹ The Ti(IV)-C bond formed by alkylation of Ziegler-Natta catalyst with cocatalyst is the active center for the coordination polymerization of olefins.⁴⁶ Kaminsky and his co-workers found that MAO, as cocatalyst throughout the coordination polymerization course, is the integrant component with respect to metallocene catalytic systems for olefin polymerization. In this study, after the living radical polymerization of styrene, the dormant species $\sim\text{Pn-Ti(IV)CpCl}_2$ was used as a living growing chain for the successive coordination polymerization of the olefins in the presence of MAO to form hydroxy-functionalized aPS-*b*-random copolymer-*b*-PE by the coming monomer (ethylene or styrene) inserted into the Ti(IV)-C bond of the dormant species (Scheme 1). The effect of polymerization conditions such as temperature, Al/Ti molar ratio, pressure of ethylene and time on the performance were summarized in Table I.

From runs 1 and 2 in Table I, it can be noticed that the yield of copolymer increased with the increasing of reaction temperature from 40 to 50°C. The molecular weight distribution (MWD) of the obtained copolymer kept in a narrow range (1.74–1.77). These results indicated that the catalytic active center was stable, and the propagation rate was enhanced as temperature increase; it was also found that the copolymerization performance was not in the living manner, but that it exhibited single site mechanism. However, the M_n of the copolymer decreased and its MWD became broader when the polymerization temperature was over 50°C (runs 2–4 in Table I). It was possible that the side reactions increased and the concentration of ethylene decreased while the deactivation rate of the active species increasing at higher temperature. The effect of polymerization time on the copolymerization behavior was shown in Table I (runs 5, 2, 6, and 7). The M_n and MWD of the copolymer increased with increasing of reaction time. These MWD results also indicated that the polymerization manner was not living. The effect of ethylene pressure on the polymerization performance was investigated when the temperature was kept constant at 50°C (runs 8, 2, and 9 in Table I). With increasing of ethylene pressure from 0.1 to 0.4 MPa, the yield, M_n and MWD of the copolymer increased.

TABLE I
Effect of Conditions on the Copolymerization

Run	Ethylene (MPa)	T (°C)	Al/Ti (mol)	Time (min)	Yield ^a (g)	M_n^b ($\times 10^{-4}$)	MWD ^b	T_m^c (°C)	Effici. ^d	(wt %) ^e
1	0.3	40	300	10	3.25	10.52	1.74	119	0.52	91.8
2	0.3	50	300	10	3.71	9.61	1.77	119	0.65	94.7
3	0.3	60	300	10	3.08	8.64	1.88	116	0.60	92.6
4	0.3	70	300	10	2.52	7.85	2.11	113	0.54	90.0
5	0.3	50	300	5	2.25	5.83	1.75	114	0.65	91.2
6	0.3	50	300	20	4.85	12.56	1.79	120	0.65	95.7
7	0.3	50	300	30	5.92	15.33	1.83	124	0.65	96.5
8	0.1	50	300	10	2.08	5.39	1.70	113	0.65	90.6
9	0.4	50	300	10	5.30	13.72	1.81	121	0.65	96.1
10	0.3	50	250	10	2.83	9.52	1.72	117	0.50	90.3
11	0.3	50	350	10	2.13	7.97	1.85	115	0.45	86.4
12 ^f	0.3	50	300	10	3.61	10.11	1.75	118	0.62	94.0
13 ^g	0.3	50	–	30	–	–	–	–	–	–

Reaction conditions: CpTiCl₃/Zn/BDGE/St = 8/12/1/300; monomer: Styrene (3 mL); radical polymerization of styrene was carried out at 90°C for 2.5 h in 1,4-dioxane. Solvent for the coordination polymerization: toluene (70 mL).

^a The CHCl₃ soluble fraction.

^b Number average molecular weight of the copolymer determined by GPC.

^c Melting point of the copolymer determined by DSC.

^d Ratio of the MAO activated Ti(IV) species for coordination polymerization, Effici. = [BDGE]_{measured}/[BDGE]_{cal.}, [BDGE]_{measured} = Yield/ M_n , [BDGE]_{cal.} = [BDGE]_{orig.} \times 0.7.

^e Ratio of CHCl₃ soluble extract in the crude product.

^f Catalyst system: Cp₂TiCl₂/Zn/BDGE/St = 8/12/1/300.

^g without MAO.

MAO was used as a cocatalyst for alkylation agent, chain-transfer agent, deimpurifier, and reducing agent. The catalytic activity of the metallocene catalyst depended upon the amount of MAO used. From Table I (runs 2, 10, and 11), it could be found that the yield and M_n of the copolymer increased with the increasing of Al/Ti molar ratio from 250 to 300. However, with the increase of the Al/Ti ratio from 300 to 350, the yield and M_n of the copolymer decreased. MWD became broader with increasing of Al/Ti molar ratio. The result revealed that MAO as chain transfer took place to some extent. It also implied that the dormant species \sim Pn-Ti(IV)CpCl₂ produced during the living radical polymerization of styrene directly promoted the coming monomer coordination polymerization, MAO in the mixture might take the roles of chain-transfer agent, reducing agent and deimpurifier. Generally, high molar ratio of Al/Ti (Al/Ti = 1000) was required for olefin polymerization by CpTiCl₃/MAO.⁴⁷ Besides other roles mentioned earlier, cocatalyst might also surround the active species to make a positive environment for olefin coordination polymerization. Larger amount of cocatalyst is necessary to promote the polymerization smoothly. However, without adding MAO in the polymerization, the copolymer (aPS-b-random copolymer-b-PE) soluble in CHCl₃ and the S-E random copolymer soluble in THF were not observed (run 13 in Table I). The result confirmed that the cocatalyst MAO takes the roles of deimpurifier and making a positive environment for olefin

coordination polymerization besides alkylation, chain-transfer and reducing agent.

Compared to the CpTiCl₃/Zn/BDGE/MAO catalyst system, the Cp₂TiCl₂/Zn/BDGE/MAO catalyst system was also good for the copolymerization of styrene with ethylene to prepared hydroxy-functionalized aPS-b-random copolymer-b-PE with higher M_n (10.11×10^4 g/mol) in yield (3.61 g) under the same polymerization conditions (run 12 in Table I).

Characterization of the block copolymer

The thermal property of aPS (butanone-soluble fraction) and PE ($M_n = 15.2 \times 10^4$ g/mol, MWD = 1.9) synthesized by CpTiCl₃/MAO in our lab, and the hydroxy-functionalized aPS-b-random copolymer-b-PE (run 2 in Table I) were determined by DSC (Fig. 1).

From Figure 1, it was obvious that the T_g (87°C) of aPS-b-random copolymer-b-PE was lower than that of aPS homopolymer (91°C) (curve a and b in Fig. 1). It was possibly that the PE segment embedded into the aPS phase that affected the thermal property of aPS. Comparing with PE homopolymer ($T_m = 132^\circ\text{C}$), the melting point of hydroxy-functionalized aPS-b-random copolymer-b-PE was much lower (119°C) (curve b and c in Fig. 1). It is probable that the aPS segment of the copolymer moved into PE phase, which affected the crystallinity of PE resulting in the T_m of PE phase shifted to lower temperature. The melting point (119°C) and crystallinity were attributed to a unique blocky microstructure which

offered enough consecutive sequences of comonomer ethylene units in the copolymer backbone to form a crystalline phase. However, the glass transition peak (87°C) was attributed to the aPS phase. These results indicated that the hydroxy-functionalized aPS-b-random copolymer-b-PE included both PE segment resulting in crystalline phase and aPS segment. For curve b in Figure 1 no signal was found from 200 to 270°C, which suggested that long syndiotactic polystyrene sequence was excluded. So the active species activated by MAO was favorable for ethylene coordination polymerization. In our previous work,⁴⁸ Ti(IV) active center of metallocene catalyst was also confirmed for ethylene polymerization favorably.

The relationship between thermal property of the hydroxy-functionalized aPS-b-random copolymer-b-PE and polymerization conditions was also summarized in Table I. The melting point (T_m) of the copolymer decreased with increasing polymerization temperature at the range of 40–70°C (runs 1–4 in Table I). However, it increased with increasing of ethylene pressure (runs 8, 2, and 9 in Table I) and polymerization time (runs 5, 2, 6, and 7 in Table I). These results implied that the length of PE segment of the copolymer was relative to ethylene concentration and polymerization time.

The WAXD patterns of the hydroxy-functionalized aPS-b-random copolymer-b-PE and PE homopolymer were shown in Figure 2. It was found that two typical peaks of PE at $2\theta = 21.5^\circ$ and 23.9° were observed in both curve a and curve b which attributed to crystallization domain of PE segment.²¹ The broad peaks at $2\theta = 10\text{--}15^\circ$ and $18\text{--}22.5^\circ$ attributed to aPS segment. These results suggested that the goal copolymer had both crystalline PE segment and aPS segment.

¹³C-NMR analysis of CHCl₃-soluble fraction was shown in Figure 3. From Figure 3, multiplets at δ

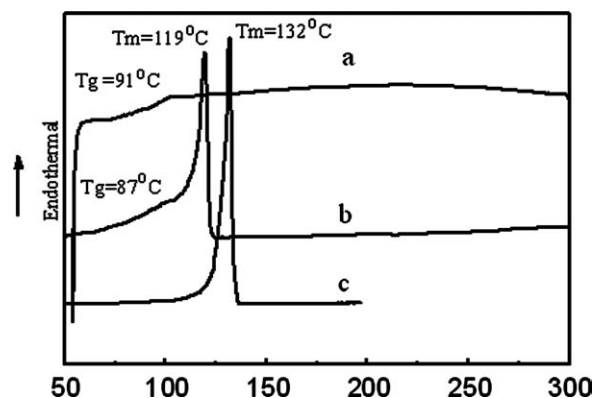


Figure 1 The DSC curves of boiling butanone-soluble fraction aPS (a), CHCl₃-soluble fraction hydroxy-functionalized aPS-b-random copolymer-b-PE (b) from run 2 in Table I and PE (synthesized in our lab via coordination polymerization by metallocene/MAO; $M_n = 15.2 \times 10^4$ g/mol, MWD = 1.9) (c).

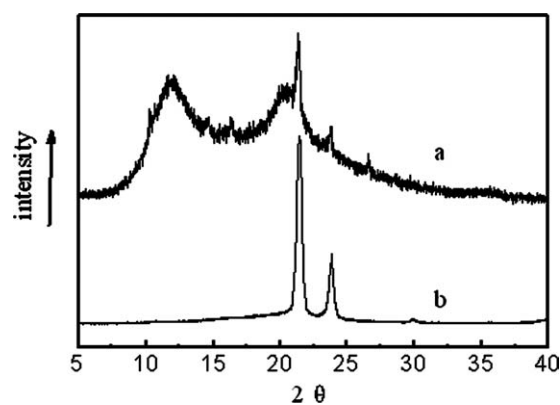


Figure 2 WAXD spectra of CHCl₃-soluble fraction hydroxy-functionalized aPS-b-random copolymer-b-PE (a) from run 2 in Table I and PE (which is synthesized in our lab via coordination polymerization by metallocene/MAO; $M_n = 15.2 \times 10^4$ g/mol, MWD = 1.9) (b).

145.5–146.8 ppm assigned to the C-1 of phenyl ring from aPS and the peaks at δ 44.20 and 41.87 ppm assigned to methylene and methyl carbon in the backbone of aPS. The peak at δ 30 ppm assigned to $S_{\delta\delta}$ from ethylene sequence. These results indicated that the aPS-b-random copolymer-b-PE embraced both aPS segment and PE segment. Other resonance peaks at δ 27.73 and 45.85 ppm in the aliphatic region assigned to $S_{\beta\delta}$ and $T_{\delta\delta}$ from the copolymer sequence, respectively. These patterns of resonances were diagnostic of an S-E copolymer containing ESE, SEE, and SES sequence which attributed to a transitional S-E random segment within the copolymer backbone.

The ¹H-NMR spectrum of aPS sample* catalyzed by CpTiCl₃/Zn/BDGE was shown in Figure 4(a). The peaks at δ 6.4–7.2 ppm was 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) in Scheme 2. Where I_a and I_{OH} was defined as the integrated intensities of the aromatic ring and —OH peaks, respectively; n stood for the polymerization degree.

According to the polymerization course (Scheme 1), the radical ring-opening reaction of two epoxy functional group in BDGE would generate two C radical species (B in Scheme 1). The aPS chain

Catalyst system: CpTiCl₃/Zn/BDGE/St = 8/12/1/300; monomer: Styrene (3 mL); radical polymerization of styrene was carried out at 90 °C for 2.5 h in 1, 4-dioxane (IE = 0.70, $M_n = 1.0 \times 10^4$, MWD = 1.30). When the experiment was performed in a 300-mL Schlenk following the literature,^{31,39–43} the mixture color was changed into lime-green, demonstrating the formation of metallocene complex radical CpTi(III)Cl₂. FTIR result confirmed that the opening of the epoxide ring of BDGE by metallocene complex radical CpTi*(III)Cl₂ took place by entire disappearing of the signal at 910.4 cm⁻¹ attributed to epoxy group

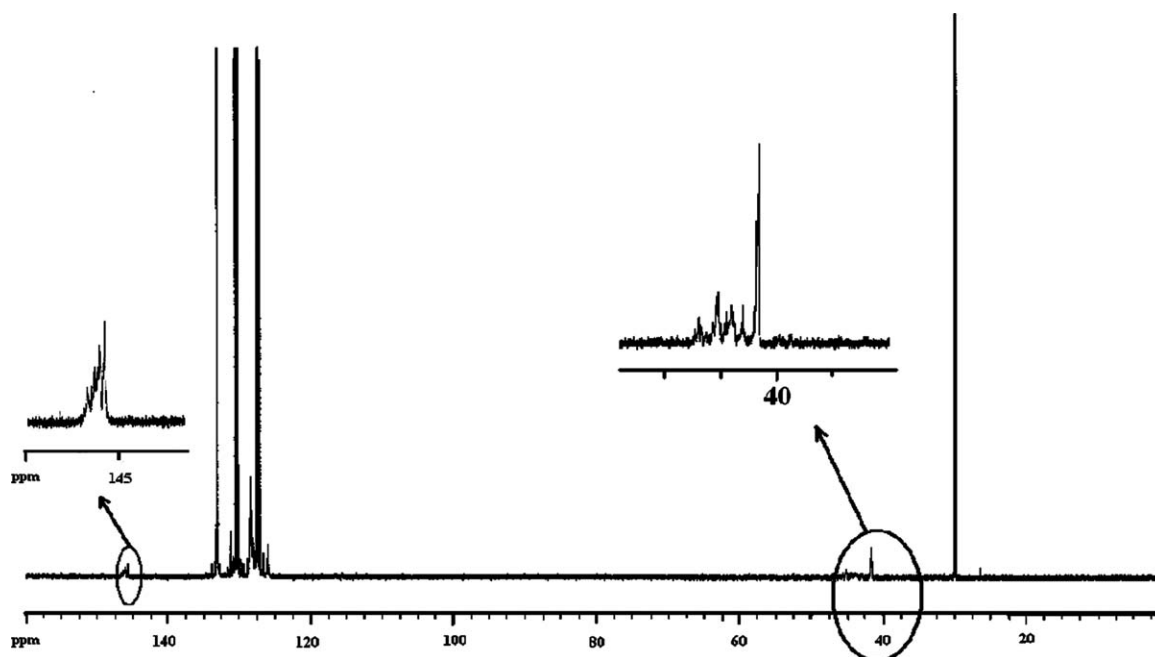


Figure 3 ^{13}C -NMR spectrum of CHCl_3 -soluble fraction hydroxy-functionalized aPS-b-random copolymer-b-PE sample from run 2 in Table I.

propagated towards two directions, respectively. The value of M_{nr} for each direction of aPS chain was calculated from the value of n according to eq. (2) in Scheme 2. Where M_{nr} was defined as the number average of the molecular weight of aPS propagated in one direction. M_s was defined as the molecular weight of styrene monomer ($M_s = 104$).

The number of functional groups (r) was given by eq. (3) in Scheme 2. Where M_n was the number average molecular weight of aPS determined by GPC and the value M_i ($= 128$) arose from the contribution of the initiator (BDGE) to the molecular weight of the polymer.

The number of functional groups for one molecule of aPS (r) calculated by ^1H -NMR result was in good agreement with the number of epoxide groups of BDGE (Fig. 4).

However, the relative proton integral concentration of the hydroxyl group of hydroxy-functionalized aPS-b-random copolymer-b-PE was neglectable because of enough high molecular weight of the copolymer.

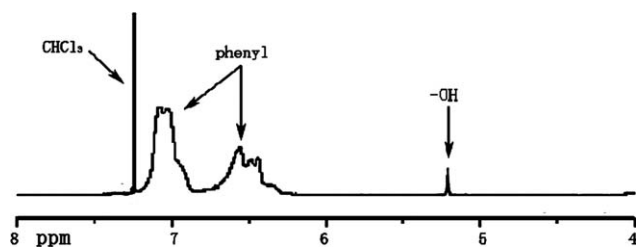


Figure 4 ^1H -NMR spectrum of butanone-soluble fraction aPS sample.

Taking into account the results of DSC, WAXD, ^{13}C -NMR, and ^1H -NMR, the microstructure of the obtained copolymer was hydroxy-functionalized aPS-b-random copolymer-b-PE.

The connecting reaction of the hydroxy-functionalized aPS initiated by living radical polymerization with random copolymer-b-PE catalyzed by coordination polymerization was confirmed by GPC (Fig. 5). The experiment was carried out in a 200-mL glass schlenk flask. Ethylene pressure was kept at 0.12 MPa. Other conditions were the same as the experiment*. The samples for GPC analysis were obtained by a syringe from the polymerization mixture at 10 min (curve b in Fig. 5), 20 min (curve c in Fig. 5), and 30 min (curve d in Fig. 5) starting from the coordination polymerization. The living radical polymerization of styrene was performed in solution. After that, some white copolymer solid was precipitated from the mixture when ethylene was charged. From Figure 5, it was found that the elution time was decreased with increasing of polymerization time, which demonstrated that the molecular weight of the copolymer was increased and larger than that of

Catalyst system: $\text{CpTiCl}_3/\text{Zn}/\text{BDGE}/\text{St} = 8/12/1/300$; monomer: Styrene (3 mL); radical polymerization of styrene was carried out at 90°C for 2.5 h in 1, 4-dioxane ($\text{IE} = 0.70$, $M_n = 1.0 \times 10^4$, $\text{MWD} = 1.30$). When the experiment was performed in a 300-mL Schlenk following the literature,^{31,39-43} the mixture color was changed into lime-green, demonstrating the formation of metallocene complex radical $\text{CpTi}^(\text{III})\text{Cl}_2$. FTIR result confirmed that the opening of the epoxide ring of BDGE by metallocene complex radical $\text{CpTi}^*(\text{III})\text{Cl}_2$ took place by entire disappearing of the signal at 910.4 cm^{-1} attributed to epoxy group

$$n = \frac{I_a / I_{OH}}{5/1} = \frac{235/1}{5/1} = 47 \quad (1)$$

$$Mn_r = n \times Ms = 47 \times 104 = 4888 \quad (2)$$

$$r = \frac{Mn - M_i}{Mn_r} = \frac{10000 - 128}{4888} = 2.02 \quad (3)$$

Scheme 2 The equations for the calculation of the arms of the resultant copolymer.

the dormant species (Scheme 1C). If the dormant species was terminated, hydroxy-functionalized atactic polystyrene was formed (curve a in Fig. 5). The shoulder signals placed at the right side of the GPC curves of the copolymers were not observed, it also confirmed that the goal copolymer was precipitated from the mixture, the fraction of the atactic homopolystyrene formed by the living radical polymerization and inactivated by MAO was removed by filtration. The hydroxy-functionalized atactic polystyrene labeled by curve a in Figure 5 featured $M_n = 1.0 \times 10^4$ and $MWD = 1.30$, implied the polymerization in living manner. However, the copolymers labeled by curve b, c, and d, their $M_n = 5.59 \times 10^4$, 7.32×10^4 and 9.12×10^4 , and $MWD = 1.77$, 1.79 , and 1.83 , respectively. The result showed that the copolymerization, i.e., the coordination polymerization follows the single-site mechanism. The average molecular weight and molecular weight distribution was performed by PL-GPC200 instrument using standard polystyrene as reference and 1,2,4-trichlorobenzene as solvent at 150°C .

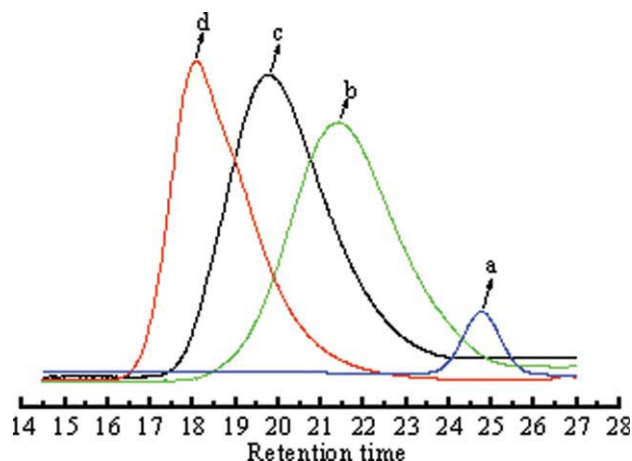


Figure 5 GPC curves of aPS (a), at 10 min (b), 20 min (c), and 30 min (d) starting from the coordination polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

CONCLUSIONS

The Titanocene/Zn/BDGE/MAO catalyst system was able to promote the copolymerization of styrene and ethylene, depending upon the polymerization conditions (temperature, ethylene pressure, Al/Ti mole ratio, and time). For the S-E copolymerization, an active species, $\sim\text{Pn-Ti(IV)CpCl}_2$ generated from radical ring opening reaction of BDGE by Ti(III) complex was responsible for promoting styrene atactic-specific polymerization, with the sequential introduction of MAO and ethylene, the dormant species $\sim\text{Pn-Ti(IV)CpCl}_2$ activated by MAO was favorable for promoting ethylene coordination polymerization. Overall, the catalyst system was able to promote the copolymerization of styrene and ethylene via one-pot strategy combining free radical polymerization with coordination polymerization mechanism.

The copolymerization by Titanocene/Zn/BDGE/MAO catalyst produced both a CHCl_3 -soluble fraction which was hydroxy-functionalized aPS-b-random copolymer-b-PE copolymer and a butanone-soluble fraction which was aPS homopolymer. As investigated by $^{13}\text{C-NMR}$, $^1\text{H-NMR}$, GPC, DSC, and WAXD, the hydroxy-functionalized copolymer was confirmed to feature blocky microstructure with one single glass transition (T_g) and one melting point (T_m).

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