

## ORIGINAL ARTICLE

# Synthesis of ethylene–styrene copolymer containing syndiotactic polystyrene sequence by trivalent titanium catalyst

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We describe the synthesis of a styrene–ethylene copolymer using a trivalent titanium-based polymerization catalyst system, *tris*(acetylacetonate)titanium (Ti(acac)<sub>3</sub>), combined with triisobutylaluminum-modified methylaluminoxane. Gel-permeation chromatography measurement revealed that copolymerization using the above-mentioned catalyst system yielded a mixture of two different polymers. <sup>13</sup>C nuclear magnetic resonance (NMR) analysis of the Soxhlet-extracted fractions indicated that the insoluble part contained a long ethylene–ethylene sequence and an isolated styrene unit, whereas the soluble part contained a syndiotactic styrene–styrene sequence with ethylene units adjacent to continuous styrene units. The ratio of the styrene–styrene sequence to the styrene–ethylene joint part of the Soxhlet-soluble fraction, estimated from the NMR resonances, increased with the styrene content. The melting temperature of the Soxhlet-soluble fraction also increased with the (styrene–styrene)/(styrene–ethylene) ratio of the polymers. These two results together indicate that a block-like copolymer was produced that contained long syndiotactic polystyrene portions separated by ethylene units.

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## INTRODUCTION

Since the development of efficient catalyst systems for the syndio-specific polymerization of styrene, for example, trichlorocyclopentadienyltitanium/methylaluminoxane (CpTiCl<sub>3</sub>/MAO), syndiotactic polystyrene (SPS) has been hailed as a new-age engineering plastic.<sup>1–5</sup> SPS exhibits rapid crystallization behavior and a high melting point (~270 °C); it also has a high heat resistance, a high chemical resistance, a low density, a high modulus of elasticity and a low dielectric constant.<sup>6</sup> However, the brittleness of SPS must be reduced for it to be of practical use.

Copolymerization of styrene and an olefinic monomer (for instance, ethylene or propylene) is expected to be a good modification of SPS to improve its toughness. It has been reported that the typical SPS catalyst system, similar to the CpTiCl<sub>3</sub>/MAO system, is inadequate for the copolymerization protocol; the copolymerization of ethylene and styrene by the CpTiCl<sub>3</sub>/MAO catalyst system results in the production of a mixture of SPS and polyethylene (PE) or a mixture of SPS, PE and copolymer.<sup>7,8</sup> Recently, several researchers have reported the development of more efficient catalysts for the copolymerization of ethylene and styrene: a half-titanocene featuring an aryloxy-type ligand, a titanium complex having a pendant-type cyclopentadienyl ligand and a rare-earth metal-based catalyst.<sup>9–17</sup>

However, there have been only limited reports on the synthesis of copolymers containing long syndiotactic styrene–styrene sequences. Hou and co-workers<sup>18</sup> have reported that rare-earth metal-based catalyst systems promote not only the syndiotactic homopolymerization of styrene, but also copolymerization with ethylene, in which the Cp'Sc(CH<sub>2</sub>SiTMS)<sub>2</sub>/Ph<sub>3</sub>C·B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> [Cp' = C<sub>5</sub>Me<sub>4</sub>(CH<sub>2</sub>TMS)] catalyst system produces a multi-block copolymer consisting of a crystalline SPS part and an ethylene-rich part. Carpentier and co-workers<sup>19</sup> have also reported an ansa-lanthanidocene catalyst that can synthesize a copolymer containing long syndiotactic styrene–styrene sequences separated by a single or a few ethylene units. Meanwhile, it has been previously reported that the copolymeric fraction separated from the mixture obtained by the CpTiCl<sub>3</sub>/MAO system contains a similar long syndiotactic styrene–styrene sequence.<sup>8</sup>

Problems associated with the copolymerization of styrene and ethylene by a titanium catalyst appear to arise from a difference of active species (and also propagation mechanisms). It has been traditionally believed that a trivalent titanium (Ti<sup>3+</sup>) species is the predominant active species for the syndiotactic polymerization of styrene by the CpTiCl<sub>3</sub>/MAO type catalysts.<sup>20–26</sup> However, recent studies have indicated that a tetravalent titanium (Ti<sup>4+</sup>) species is also generated and can similarly promote styrene polymerization in the CpTiCl<sub>3</sub>/MAO type catalyst system, independent of the Ti<sup>3+</sup>

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active species.<sup>27–31</sup> An analogous  $Ti^{4+}$  species is believed to be the active species in olefin polymerization by metallocene-type catalyst systems (such as  $Cp_2TiCl_2/MAO$ ).<sup>32</sup> Nomura and others<sup>12,33</sup> have reported that a half-titanocene catalyst, which has an aryloxy-type ligand, conducts the copolymerization of ethylene and styrene, resulting in effective synthesis of the random copolymer. They noted that the active species of this catalyst system might be the  $Ti^{4+}$  species, similar to olefin polymerization.

In addition to syndiotactic poly(ethylene-*co*-styrene), several papers have described copolymers containing a long styrene–styrene sequence. Okuda and co-workers<sup>34</sup> reported the synthesis of poly(propylene-*co*-styrene) that consisted of isotactic styrene–styrene blocks and amorphous propylene blocks; this was synthesized by means of copolymerization with a post-metallocene-type catalyst. Additionally, Longo and co-workers<sup>35</sup> reported the blocky stereospecific copolymerization of styrene and 1,3-butadiene by the half-titanocene-type catalyst.

We inferred from these studies that the  $Ti^{3+}$  in the titanium-based catalyst system is essential for the formation of the SPS structure and is also able to promote the incorporation of ethylene into the polystyrene backbone. Therefore, the trivalent titanium complex shows promise as a precursor of the copolymerization catalyst. In this paper, we report our study of the copolymerization of styrene and ethylene by a trivalent titanium complex-based catalyst system, *tris*(acetylacetonato)titanium ( $Ti(acac)_3/MAO$ ), and we also report the characterization of the obtained polymer.

## EXPERIMENTAL PROCEDURE

### Materials

The methylaluminoxane (triisobutylaluminum-modified methylaluminoxane; MMAO) was provided by Tosoh-Finechem (Shunan, Japan) and used without further purification. Commercially obtained research-grade toluene was purified according to conventional procedures. Research-grade styrene was dried by calcium hydride and then distilled under reduced pressure before polymerization. Commercially available ethylene, provided by Japan Fine Products (Kawasaki, Japan), was dried in a dry column DC-A4 (Nikka Seiko, Tokyo, Japan). The  $Ti(acac)_3$  was synthesized by the reaction of trichlorotitanium and lithium acetylacetonate in the tetrahydrofuran and then recrystallized from distilled toluene. Other solvents and reagents were commercially obtained and used without further purification.

### Polymerization

**Ethylene polymerization.** Prescribed amounts of toluene, the  $Ti(acac)_3$ /toluene solution and the MMAO were added to a 100-ml stainless steel autoclave equipped with a magnetic stirrer. After the contents of the reactor were degassed by vacuum, a prescribed amount of gaseous ethylene was introduced at  $-196^\circ C$  (controlled by a liquid nitrogen bath). The batch-wise polymerization was initiated by increasing the temperature to  $25^\circ C$  (controlled by a water bath equipped with a thermo controller). The polymerization was stopped by the addition of 2-propanol after the reactor was degassed. Then the reaction products were poured into a dilute HCl/methanol solution. The precipitated polymer was filtered and washed with methanol and then dried under vacuum at  $60^\circ C$  for 6 h.

**Styrene polymerization.** Prescribed amounts of toluene, the MMAO and the distilled styrene were added to a 100-ml three-necked round-bottom glass flask equipped with a magnetic stirrer. Polymerization was initiated by addition of the  $Ti(acac)_3$ /toluene solution at  $25^\circ C$ , then stopped by addition of 2-propanol. The reaction products were then poured into a dilute HCl/methanol solution. The precipitated polymer was filtered and washed with methanol and then dried under vacuum at  $60^\circ C$  for 6 h.

**Ethylene/styrene copolymerization.** Prescribed amounts of toluene, the distilled styrene and the MMAO were added to a 100-ml stainless steel autoclave

equipped with a magnetic stirrer. Next, the prescribed amount of the  $Ti(acac)_3$ /toluene solution was added at  $-196^\circ C$  (controlled by a liquid nitrogen bath). Gaseous ethylene was also introduced at  $-196^\circ C$  after the reactor was degassed by vacuum. The batch-wise polymerization was started by increasing the temperature to a predefined value (controlled by a water bath equipped with a thermo controller). The polymerization was stopped by the addition of 2-propanol after the reactor was degassed. The reaction products were then poured into a dilute HCl/methanol solution. The precipitated polymer was filtered and washed with methanol and then dried under vacuum at  $60^\circ C$  for 6 h. The resultant polymer was Soxhlet extracted for 6 h with boiling solvent as appropriate. The soluble portion extracted was precipitated by methanol and then filtered and dried.

### Polymer analysis

The number-average molecular weights ( $M_n$ ) and the weight-average molecular weights ( $M_w$ ) of the polymers were measured by gel-permeation chromatography (GPC) at  $140^\circ C$  on a Polymer Laboratories PL GPC-220 (Polymer Laboratories, Santa Clara, CA, USA) equipped with refractive index detector, using 1,2,4-trichlorobenzene as a solvent. Calibration was done by Polymer Laboratories detector software Cirrus with a polystyrene standard. The  $^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR) spectra of the polymers were recorded at  $120^\circ C$  on a JEOL JNM-LA600 spectrometer (JEOL, Tokyo, Japan) operating at 600 and 150 MHz, respectively, in the pulse Fourier transform mode. Sample solutions were made in tetrachloroethane- $d_2$  up to 10% by weight. The resonances of the tetrachloroethane- $d_2$  ( $^1H=5.91$  p.p.m.,  $^{13}C$  central peak= $74.47$  p.p.m.) were used as internal references. The melting points ( $T_m$ ) and the heats of fusion ( $\Delta H$ ) were measured using a SII DSC6200 (SII, Chiba, Japan). The samples were encapsulated in aluminum pans and scanned at  $10^\circ C\ min^{-1}$  up to  $300^\circ C$ . The first heating data were used for the analysis in order to avoid the influence of heat degradation. The decomposition point of 5% weight loss was determined using a SII TG/DTA6200 (SII).

## RESULTS AND DISCUSSION

Table 1 shows the results of homo- and copolymerization of styrene and/or ethylene by the  $Ti(acac)_3/MAO$  catalyst system. The  $Ti(acac)_3$ , trivalent titanium complex has been reported as a good precursor of the catalyst for the syndiospecific styrene polymerization,<sup>36</sup> as shown in Run 1. Ethylene polymerization by the same catalyst system produced PE with appreciably lower activity in comparison with a typical metallocene catalyst system such as the  $Cp_2ZrCl_2/MAO$ . The PE obtained was revealed to be the linear type PE by  $^{13}C$  NMR analysis (see Supplementary Information).

The copolymerization of styrene and ethylene gave a powdered polymer with moderate activity similar to the styrene homopolymerization product.  $^1H$  NMR analysis of the crude product revealed that both the ethylene and the styrene units were incorporated (see Supplementary Information), regardless of whether it was a homogeneous copolymer or a mixture of the homopolymer. The styrene/ethylene ratio in the crude product was influenced by the polymerization conditions. Runs 3 and 4 indicated dependence on the MMAO concentration when the amount of Ti was fixed at 0.01 mmol. The styrene content of the crude product approximately doubled from 8.6 to 16.5 mol% by using double the amount of MMAO (2000 mmol instead of 1000 mmol), whereas the yield increased slightly from 0.24 to 0.30 g. Runs 5–9 showed a dependence on the amount of  $Ti(acac)_3$  with a fixed amount of MMAO. The yield increased correspondingly with increased amounts of  $Ti(acac)_3$ , although the activity decreased slightly, perhaps due to the decreased Al/Ti ratio. The styrene content also increased by increasing the amount of  $Ti(acac)_3$ , meaning that the consumption of styrene increased by considerably more than the ethylene consumption.

Table 2 shows the dependence on the polymerization temperature in the copolymerization, under the same conditions of 0.02 mmol of

**Table 1** Homo- and copolymerization of ethylene and styrene by Ti(acac)<sub>3</sub>/MMAO catalyst system<sup>a</sup>

Run	Styrene (mmol)	Ethylene (mmol)	Catalyst (mmol)	MMAO (mmol Al)	[Al]/[Ti] (mol mol <sup>-1</sup> )	Time (min)	Yield (g)	Activity (kg mol <sup>-1</sup> Ti h)	St content <sup>b</sup> (mol%)
1	29	0	0.05	25	500	12	0.41	41.0	100
2	0	58	0.01	20	2000	60	0.81	81.0	0
3	29	58	0.01	10	1000	60	0.24	24.0	8.6
4	29	58	0.01	20	2000	60	0.30	30.0	16.5
5	29	29	0.02	20	1000	120	0.46	11.5	31.2
6	29	29	0.05	20	400	120	0.81	8.1	44.9
7	29	29	0.10	20	200	120	1.83	9.2	59.7
8	29	29	0.15	20	133	120	1.72	5.7	58.0
9	29	29	0.20	20	100	120	1.55	3.9	56.0
10	29	29	0.10	25	250	120	1.45	7.3	80.0
11	29	143	0.10	25	250	60	0.74	7.4	26.4
12 <sup>c</sup>	29	29	0.02	20	1000	120	2.14	53.5	83.3

Abbreviations: MMAO, triisobutylaluminum-modified methylaluminoxane; Ti(acac)<sub>3</sub>, tris(acetylacetonate)titanium.<sup>a</sup>Conditions: temperature=25 °C, time=2 h, solvent=toluene (total vol.=30 ml).<sup>b</sup>Styrene (St) content in the clued polymer determined by <sup>1</sup>H nuclear magnetic resonance.<sup>c</sup>Trichlorocyclopentadienyltitanium was used instead of Ti(acac)<sub>3</sub>.**Table 2** Dependence on the polymerization temperature in the copolymerization of ethylene and styrene by Ti(acac)<sub>3</sub>/MMAO catalyst system<sup>a</sup>

Run	Styrene (mmol)	Ethylene (mmol)	Temp. (°C)	Yield (g)	Activity (kg mol <sup>-1</sup> Ti h)	St content <sup>b</sup> (mol%)
13	29	29	-20	0.03	0.8	21.2
14	29	29	0	0.11	2.8	26.8
15	29	29	20	0.29	7.3	13.6
16	29	29	30	0.92	23.0	44.0
17	29	29	40	1.69	42.3	66.6
18	29	29	50	2.80	70.0	78.5

Abbreviations: MMAO, triisobutylaluminum-modified methylaluminoxane; Temp., temperature; Ti(acac)<sub>3</sub>, tris(acetylacetonate)titanium.<sup>a</sup>Conditions: Ti(acac)<sub>3</sub>=0.02 mmol, MMAO=20 mmol Al, time=120 min, solvent=toluene (total vol.=30 ml).<sup>b</sup>Styrene (St) content in the clued polymer determined by <sup>1</sup>H nuclear magnetic resonance.

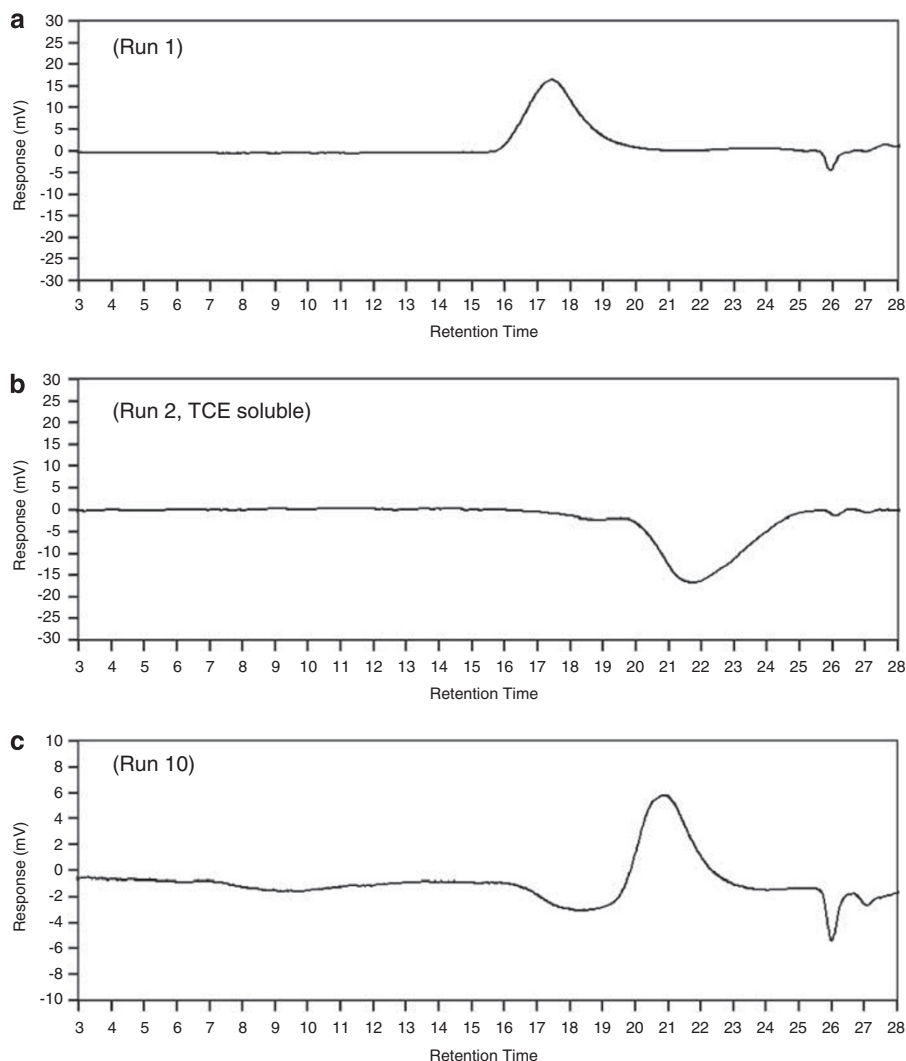
Ti(acac)<sub>3</sub> and 20 mmol of MMAO for 120 min. At temperatures <20 °C, the activity was relatively low, <10 kg mol<sup>-1</sup>·Ti·h, and the styrene content of the crude product was not significantly influenced by the temperature (Runs 13–15). At temperatures >20 °C, however, the yield increased rapidly with temperature, and the styrene content also increased significantly (Runs 16–18), up to 78.5 mol% at 50 °C. The results indicate that the increase in temperature influenced the consumption of styrene more strongly than that of ethylene, resulting in the production of a highly styrene-rich crude product at higher temperatures.

To determine the polymer that comprised the crude product, GPC analysis was performed at 140 °C using 1,2,4-trichlorobenzene as a solvent. The GPC curve of homopolystyrene (Run 1) was obtained as shown in Figure 1a. However, the homo-PE (Run 2) could not be analyzed because the GPC column was blocked, perhaps due to the super-high molecular weight. The boiling 1,1,2,2-tetrachloroethane (TCE)-soluble fraction of the PE (Run 2) was measured and is shown in Figure 1b; in contrast to the polystyrene, this represents the downside peak, due to the difference in refractive indices. As shown in Figure 1c, the crude product of the copolymerization (Run 10) exhibited a bimodal distribution located at opposite sides of the baseline. This implies the existence of binary polymers: one is styrene-rich and has a lower molecular weight, and the other is ethylene-rich and has a higher molecular weight.

The above results indicate that at least two polymerization mechanisms exist in the Ti(acac)<sub>3</sub>/MMAO catalyst system. Traditional belief

holds that the syndiospecific styrene polymerization proceeds with the trivalent Ti<sup>3+</sup> species in a typical catalyst system such as the CpTiCl<sub>3</sub>/MAO.<sup>26–30</sup> However, several papers have now reported that tetravalent Ti<sup>4+</sup> active species are valid for the random copolymerization of styrene and an olefinic monomer in a number of titanium catalysts; for example, the group 4 metallocene system.<sup>12,34</sup> Although the precise mechanism is not clear at present, it is plausible that the titanium of the Ti(acac)<sub>3</sub>/MMAO catalyst system adopts multiple oxidation states during polymerization, with these states promoting the propagation of different polymers.

We attempted to separate these components by Soxhlet extraction using a number of solvents: *o*-dichlorobenzene, TCE, xylene (mixture), methylethylketone and *n*-heptane. The high boiling *o*-dichlorobenzene largely dissolved the crude product in many cases. By contrast, a large part of the crude product was insoluble in the low boiling methylethylketone and *n*-heptane. TCE and the xylene proved suitable for separating the products. The GPC and <sup>1</sup>H NMR analysis of the extracted fraction were carried out and are summarized in Figure 2 and Table 3. The GPC curves of the soluble and insoluble fractions of the product (Run 11) in the boiling TCE are shown in Figure 2a. The insoluble fraction was revealed to consist primarily of the ethylene-rich high-molecular weight polymer, whereas the soluble fraction mainly consisted of the styrene-rich low-molecular weight polymer, although the soluble fraction also contained the ethylene-rich low-molecular weight polymer as observed in Figure 1b. The boiling xylene extraction of the crude product (Run 7) resulted



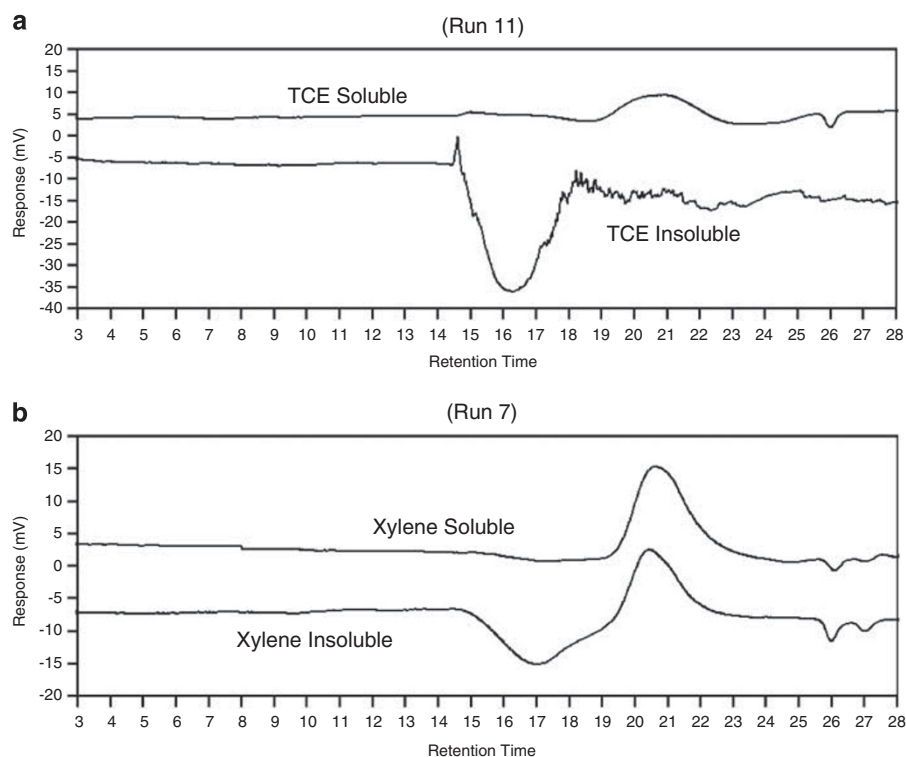
**Figure 1** Gel-permeation chromatography curves of the crude polymers obtained using the *tris*(acetylacetonate)titanium/triisobutylaluminum-modified methylaluminoxane catalyst system. (a) Polystyrene (Run 1), (b) polyethylene (Run 2, boiling 1,1,2,2-tetrachloroethane (TCE)-soluble part), (c) poly(ethylene-co-styrene; Run 10).

in similar separation, as shown in Figure 2b. The xylene-soluble fraction mainly consisted of styrene-rich low-molecular weight polymer, whereas the insoluble fraction consisted of the ethylene-rich high-molecular weight polymer and a considerable amount of styrene-rich polymer.

The microstructure of these extracted fractions, the ethylene-rich polymer and the styrene-rich polymer were investigated by  $^{13}\text{C}$  NMR analysis. Assignments of the resonances of the copolymer were carried out according to the previous reports.<sup>8,18,20–25</sup> The spectrum of the insoluble part, obtained by TCE extraction of the crude product in Run 11, is shown in Figure 3. In addition to continuous homogeneous monomer sequences consisting of ethylene–ethylene (30.1 p.p.m.) and a small amount of styrene–styrene (41.7 and 44.9 p.p.m.), the isolated styrene unit in the PE backbone was observed at 46.6, 37.2 and 28.0 p.p.m. This indicates that the insoluble part is mainly composed of the random copolymer of ethylene and styrene. The spectrum of the soluble part, obtained by xylene extraction of the crude product in Run 7, is shown in Figure 4. This spectrum illustrates the strong SPS backbone, along with the resonances (44.3, 45.3, 43.9, 37.7 and

27.6 p.p.m.) assignable to the specific ethylene–styrene sequences that can be attributed to the connection between the continuous styrene–styrene sequence and the ethylene monomer units (at least 2 units). The resonances assignable to the ethylene–styrene random copolymer were also weakly observable. By comparison, the traditional catalyst system,  $\text{CpTiCl}_3/\text{MMAO}$ , produced only a mixture of PE and SPS under similar polymerization conditions (Run 12, see Supplementary Information).

Table 4 lists the sequence ratio of the Soxhlet-soluble fractions, which were determined by the intensities of  $^{13}\text{C}$  NMR resonances. The ratio between the SPS backbone and the joint part (continuous styrene–styrene sequence adjacent to the ethylene unit),  $[\text{SSS}]/[\text{SSE}]$ , was determined from the methylene carbon of the styrene unit observed at 41.7 and 43.9 p.p.m. Concerning the ethylene part,  $[\text{EEE}]/[\text{ESE}]/[\text{SSE}]$  was similarly determined from the methylene carbon at 30.1, 37.2 and 37.7 p.p.m. The ratio of the SPS backbone to the joint part can be considered as a fraction of the length of the SPS block if the block-type copolymer was formed, and can be expected to correlate with the styrene content or the properties of



**Figure 2** Gel-permeation chromatography curves of the fraction obtained by Soxhlet extraction. (a) The soluble and the insoluble portions in boiling 1,1,2,2-tetrachloroethane (TCE; Run 11). (b) The soluble and the insoluble part in boiling xylene (Run 7).

**Table 3** GPC and  $^1\text{H}$  NMR data for the fractions of Soxhlet extraction<sup>a</sup>

Run	Solvent	Insoluble				Soluble			
		(wt%)	$M_n^b$ ( $\times 10^{-4}$ )	$M_w/M_n^b$	St content <sup>c</sup> (mol%)	(wt%)	$M_n^b$ ( $\times 10^{-4}$ )	$M_w/M_n^b$	St content <sup>c</sup> (mol%)
1 <sup>d</sup>	—	—	144.5	1.99	100	—	—	—	—
2	TCE	63.3	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>	36.7	0.71	2.62	0
7	Xylene	16.1 <sup>f</sup>	177.8/3.3	1.83/1.77	54.1	83.9	2.5	1.35	62.5
7	TCE	3.6	321.7	1.40	7.6	96.4 <sup>f</sup>	219.2/2.5	1.53/2.17	74.1
8	Xylene	13.6 <sup>f</sup>	86.6/3.8	1.94/1.39	— <sup>e</sup>	86.4	2.5	2.14	64.5
9	Xylene	11.8	182.2/3.4	1.78/1.57	28.2	88.2	102.2/2.9	1.84/1.80	61.5
11	TCE	65.7	272.6	1.60	3.3	34.3	3.4	2.00	29.2
16	Xylene	Trace	—	—	—	99 <sup>g</sup>	109.7/2.3	1.98/1.75	52.6
17	Xylene	6.1 <sup>f</sup>	118.7/2.1	2.15/1.72	66.6	93.9	1.4	2.17	67.8
18	Xylene	7.9	— <sup>e</sup>	— <sup>e</sup>	— <sup>e</sup>	92.1	1.3	2.77	75.5
12	Xylene	Trace	—	—	—	99 <sup>g</sup>	0.81 (0.64) <sup>h</sup>	1.82	82.4

Abbreviations: GPC, gel-permeation chromatography; NMR, nuclear magnetic resonance; TCE, 1,1,2,2-tetrachloroethane.

<sup>a</sup>Soxhlet extraction was conducted by boiling the solvent for 6 h.

<sup>b</sup>Number-average molecular weight and polydispersity determined by GPC using PS standard.

<sup>c</sup>Styrene (St) content of the fraction determined by  $^1\text{H}$  NMR in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $120^\circ\text{C}$ .

<sup>d</sup>Raw polymer.

<sup>e</sup>Not determined.

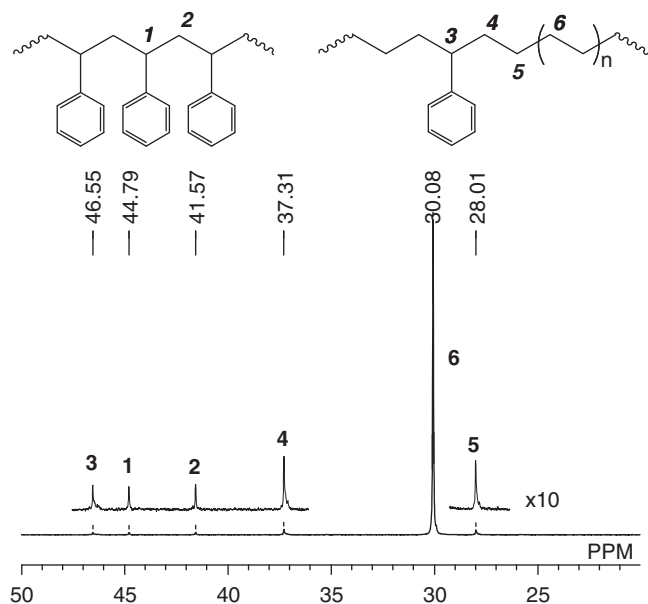
<sup>f</sup>Mixture of the two fractions.

<sup>g</sup>Molecular weight of the homo-syndiotactic polystyrene determined by the intensity of resonances of methane carbon in the  $^{13}\text{C}$  NMR.

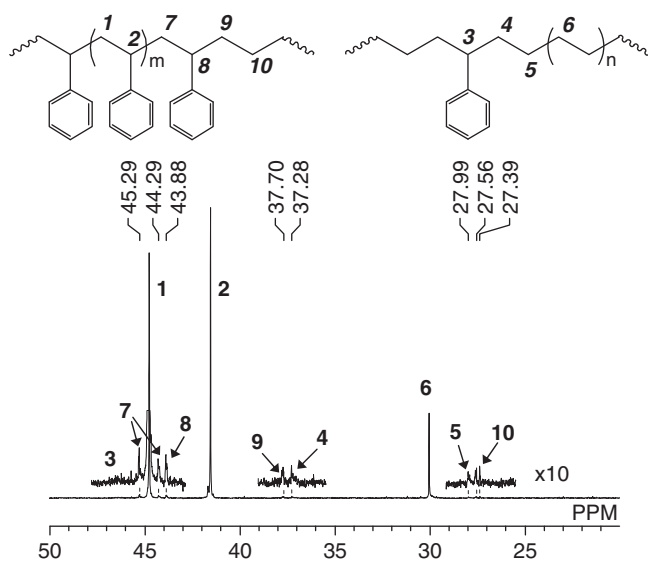
the soluble fraction. Figure 5a shows the relation between  $[\text{SSS}]/[\text{SSE}]$  and the styrene content of the Soxhlet-soluble fraction, plausibly indicating that the length of the styrene–styrene sequence proportionally increases with the styrene content of the copolymers.

The thermal properties of the extracted fractions were investigated by differential scanning calorimeter (DSC) and are listed in Table 5. For analysis of the melting point ( $T_m$ ) and the heat of fusion ( $\Delta H$ ), the first heating data of DSC was used in order to avoid the influence of

heat degradation. Figure 6 shows the DSC curves of SPS (Run 1), PE (Run 2) and the xylene-soluble fraction of the copolymerization product (Run 7). The values of  $T_m$  (and  $\Delta H$ ) of the PE and the SPS were  $126.2^\circ\text{C}$  ( $167.7\text{mJmg}^{-1}$ ) and  $271.5^\circ\text{C}$  ( $32.9\text{mJmg}^{-1}$ ), respectively. The xylene-soluble fraction exhibited a sufficiently high  $T_m$  of approximately  $260^\circ\text{C}$ , which is slightly less than pure SPS, whereas the lower peak was observed at  $\sim 115^\circ\text{C}$ . Figure 5b shows the relation between the  $T_m$  and the  $[\text{SSS}]/[\text{SSE}]$  of the



**Figure 3**  $^{13}\text{C}$  nuclear magnetic resonance spectrum of the insoluble fraction in boiling 1,1,2,2-tetrachloroethane (Run 11).



**Figure 4**  $^{13}\text{C}$  nuclear magnetic resonance spectrum of the soluble fraction in boiling xylene (Run 7).

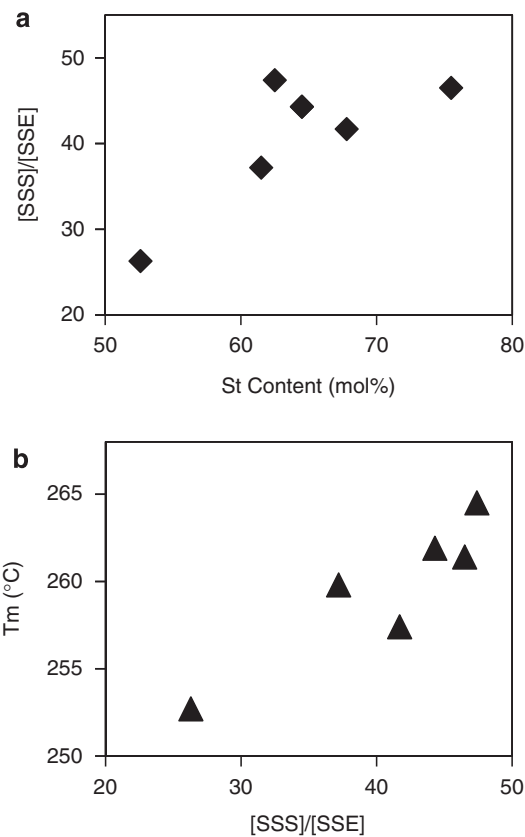
**Table 4** Sequences of the soluble fractions of Soxhlet extraction

Run	Fraction	Sequences <sup>a</sup>	
		[SSS]/[SSE] <sup>b</sup>	[EEE]:[ESE]:[SSE] <sup>c</sup>
7	Xylene soluble	47.4	14.0:0.9:1
8	Xylene soluble	44.3	7.8:1.0:1
9	Xylene soluble	37.2	17.9:1.0:1
16	Xylene soluble	26.3	27.8:5.1:1
17	Xylene soluble	41.7	17.0:3.6:1
18	Xylene soluble	46.5	10.5:1.5:1

<sup>a</sup>Ratio of the intensities of the resonances observed in  $^{13}\text{C}$  nuclear magnetic resonance.

<sup>b</sup>Determined by the methine carbon at 41.7 and 43.9 p.p.m.

<sup>c</sup>Determined by the methylene carbon at 30.1, 37.2 and 37.7 p.p.m.



**Figure 5** Relation of the ratio between the syndiotactic polystyrene backbone and the continuous styrene–styrene sequence adjacent to the ethylene unit, [SSS]/[SSE], and (a) the styrene content, (b) the  $T_m$  of the Soxhlet-soluble fraction.

**Table 5** DSC and  $^{13}\text{C}$  NMR analysis data for the fractions of Soxhlet extraction

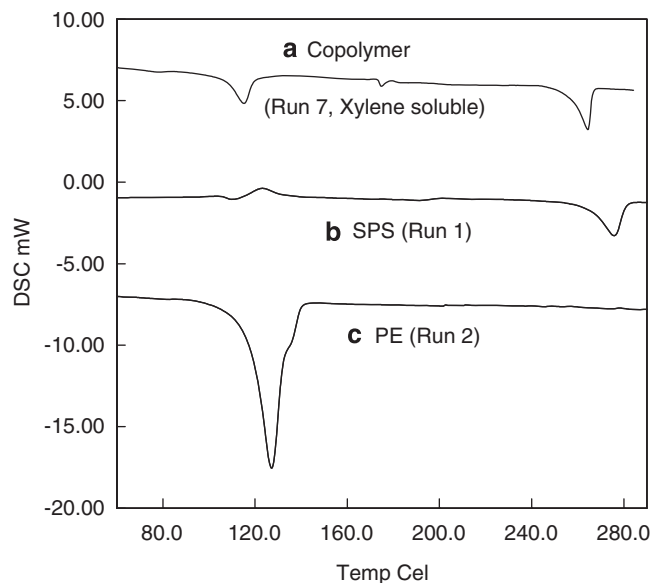
Run	Fraction	St-part		E-part		$T_{d5}^b$ (°C)
		$T_m^a$ (°C)	$\Delta H^a$ ( $\text{mJ mg}^{-1}$ )	$T_m^a$ (°C)	$\Delta H^a$ ( $\text{mJ mg}^{-1}$ )	
1	Raw polymer	271.5	32.9	—	—	271.5
2	Raw polymer	—	—	126.2	167.7	401.6
7	TCE soluble	255.6	23.5	113.8	26.9	— <sup>c</sup>
7	TCE insoluble	— <sup>c</sup>	— <sup>c</sup>	123.0	200.3	— <sup>c</sup>
7	Xylene soluble	264.5	29.9	115.3	24.0	— <sup>c</sup>
8	Xylene soluble	261.9	22.9	114.9	25.4	398.2
8	Xylene insoluble	261.3	13.9	118.7	75.9	— <sup>c</sup>
9	Xylene soluble	259.8	28.1	117.3	19.4	— <sup>c</sup>
11	TCE soluble	262.2	15.8	122.6	35.8	— <sup>c</sup>
16	Xylene soluble	252.7	27.8	117.4	32.9	— <sup>c</sup>
17	Xylene soluble	257.4	24.0	115.0	5.8	— <sup>c</sup>
18	Xylene soluble	261.4	33.8	121.8	5.4	400.6

Abbreviations: DSC, differential scanning calorimeter; DTA, differential thermal analysis; E, ethylene; NMR, nuclear magnetic resonance; St, styrene; TCE, 1,1,2,2-tetrachloroethane; TG, thermogravimetric.

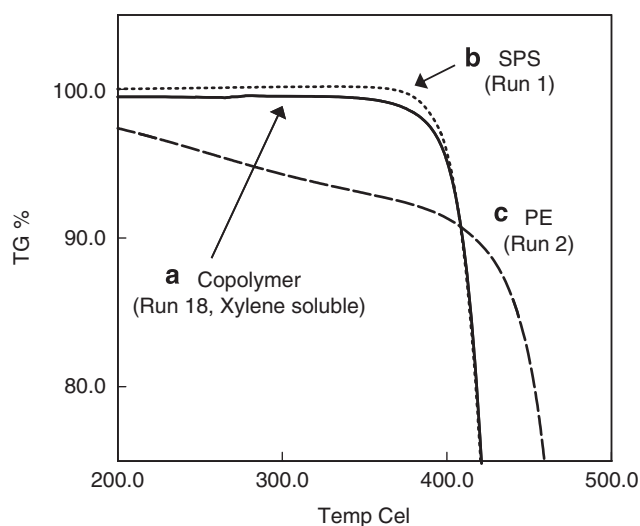
<sup>a</sup>Melting point and heat of fusion determined by DSC.

<sup>b</sup>Decomposition point of 5% weight loss determined by TG/DTA.

<sup>c</sup>Not determined.



**Figure 6** Differential scanning calorimeter curves of the polymers obtained by the *tris*(acetylacetonate)titanium/*triisobutylaluminum*-modified methylaluminoxane catalyst system. (a) Copolymer of styrene and ethylene (Run 7, the soluble fraction in boiling xylene), (b) polystyrene (Run 1) and (c) polyethylene (Run 2).



**Figure 7** Thermogravimetric (TG) curves of the polymers obtained by the *tris*(acetylacetonate)titanium/*triisobutylaluminum*-modified methylaluminoxane catalyst system. (a) Copolymer of styrene and ethylene (Run 18, the soluble fraction in boiling xylene), (b) polystyrene (Run 1) and (c) polyethylene (PE, Run 2). SPS, syndiotactic polystyrene.

Soxhlet-soluble fraction. It reveals that the  $T_m$  increases proportionally with the length of the continuous styrene sequence, which is similar to the relation between  $[SSS]/[SSE]$  and styrene content. These correlations imply that the soluble part is expected to be the block-like copolymer, which consists of the long syndiotactic styrene–styrene sequence divided by the ethylene-based section. The correlation between

the length of the ethylene–ethylene sequence and the  $T_m$  seems ambiguous; however, this may be because this part contains the isolated styrene unit, or it may be because of the contamination of the other random copolymer influences in the NMR or DSC analysis.

Figure 7 shows the results of thermogravimetric/differential thermal analysis of the SPS, the PE and the copolymer extracted by xylene (Run 18). The SPS rapidly degraded at  $\sim 400^\circ\text{C}$ . The decomposition point of 5% weight loss ( $T_{d5}$ ) of the SPS was  $401.6^\circ\text{C}$ . The PE gradually decomposed from under  $200^\circ\text{C}$ , with a  $T_{d5}$  of  $271.5^\circ\text{C}$ . The copolymer exhibited a high  $T_{d5}$  value ( $398.2^\circ\text{C}$ ), with rapid degradation around  $T_{d5}$ , which was reasonably close to that of pure SPS. This indicates that the SPS-based copolymer has a high thermal stability, comparable with pure SPS.

## CONCLUSIONS

We investigated the copolymerization of styrene and ethylene by a trivalent titanium complex-based catalyst system. GPC measurement revealed that the resultant polymer is a mixture of two different copolymers.  $^{13}\text{C}$  NMR analysis of the Soxhlet-extracted fractions of the product implied that the insoluble fractions consist of a random copolymer of ethylene and styrene, whereas the soluble parts consist of a long syndiotactic styrene–styrene sequence and an ethylene-based section. In the Soxhlet-soluble fraction, the ratio of the continuous styrene–styrene sequence to the styrene–ethylene joint sequence increased with the styrene content. The  $T_m$  of the Soxhlet-soluble fraction also increased with the  $[\text{styrene–styrene}]/[\text{styrene–ethylene}]$  ratio. These results together indicate that a block-like copolymer, which contains long SPS portions separated by an ethylene–ethylene sequence, was produced. DSC and thermogravimetric/differential thermal analysis measurements show that the SPS-based copolymer has high thermal stability comparable with pure SPS.

These results indicate that the trivalent titanium catalyst offers promising prospects for the creation of an SPS-based block copolymer. This SPS-based copolymer can be expected to show good performance in industrial applications, although further research into its physical properties, such as mechanical strength, impact strength and viscoelasticity, is necessary. We expect that further investigation toward the refinement of the catalyst system and the evaluation of mechanical properties to develop a tough SPS-based copolymer will be reported in due course.

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