

# Copolymerization of Styrene and Ethylene with Mononuclear and Dinuclear Half-Titanocenes

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**ABSTRACT:** With mononuclear half-titanocenes such as CpTiCl<sub>3</sub>, IndTiCl<sub>3</sub>, and Me<sub>5</sub>Cp-TiCl<sub>3</sub>, as well as the constrained geometry catalyst (CGC) and a new dinuclear hexamethyltrisiloxanediylbis(cyclopentadienyltitanium trichloride) (TSDT), the copolymerization of styrene and ethylene was examined. The thermal properties and structure of copolymerization products were investigated with differential scanning calorimetry and <sup>13</sup>C-nuclear magnetic resonance. In addition, the raw polymer was separated into homopolymer and copolymer with an extraction method and cross fractionation chromatography. With the above analysis, it was concluded that the raw polymer obtained with CpTiCl<sub>3</sub> and IndTiCl<sub>3</sub> was a mixture of syndiotactic polystyrene and polyethylene homopolymers with 10–30 wt % copolymer, whereas that produced by Me<sub>5</sub>CpTiCl<sub>3</sub> and TSDT was a homopolymer mixture with a negligible amount of copolymer. Only CGC produced the copolymer of styrene and ethylene perfectly. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2187–2198, 1998

**Key words:** styrene/ethylene copolymerization; half-titanocene; constrained geometry catalyst; analysis of copolymerization products

## INTRODUCTION

The copolymerization of styrene (S) and ethylene (E) has been achieved with Ziegler-Natta catalyst by several authors.<sup>1–3</sup> However, for many Ziegler-Natta catalyst systems, the S content in the copolymer is less than 1 mol %.<sup>1,2</sup> The reported polymers comprise a mixture of homopolymers and copolymer due to the difference of catalytic active centers.

The product of S/E copolymerization catalyzed with homogeneous titanocene and zirconocene

was also found to be a mixture of homopolymers and copolymer.<sup>4–6</sup> It was reported<sup>4</sup> that a catalyst based on 2,2'-thiobis(4-methyl-6-*t*-butylphenoxy)-titanium dichloride and methylaluminoxane (MAO) affords a mixture of syndiotactic polystyrene (sPS) and alternating S/E copolymer. It was also announced<sup>3,7,8</sup> that CpTiCl<sub>3</sub>-MAO catalyst system produces homopolymers and S/E copolymer.

Later, the patent literature<sup>9</sup> reported the copolymerization of S and E promoted by dimethylsilyl(phenylamido)(tetramethylcyclopentadienyl)titanium dichloride and MAO. The obtained copolymer was called "pseudorandom" because the S content in the copolymer was always less than 50 mol %.

Recently we found that a dinuclear titanocene, hexamethyltrisiloxanediylbis(cyclopentadienyltitanium trichloride), can catalyze the polymerizations of S as well as E.<sup>10,11</sup>

Dedicated to Prof. Tae-oan Ahn on his retirement from Seoul National University in August, 1997.

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In this paper, the copolymerization of S and E catalyzed with mononuclear<sup>7,8</sup> and dinuclear<sup>10</sup> half-titanocenes which are known to be active in the homopolymerization of both S and E monomers was examined in detail to study the effect of titanocene structure on product structure. The thermal properties and structure of the obtained copolymerization products were investigated by using differential scanning calorimetry (DSC) and <sup>13</sup>C-nuclear magnetic resonance (<sup>13</sup>C-NMR). The fractionation of raw polymer was carried out with the extraction method and cross fractionation chromatography to estimate the components and their content. For comparison, Dow's constrained geometry catalyst [CGC, dimethylsilyl(*t*-butylamido)(tetramethylcyclopentadienyl)titanium dichloride] was also examined because CGC was announced<sup>9,12</sup> to produce S/E copolymer without any published data.

## EXPERIMENTAL

### Materials

Cyclopentadienyltitanium trichloride (CpTiCl<sub>3</sub>; Strem Chemical, Newburyport, MA), pentamethylcyclopentadienyltitanium trichloride (Me<sub>5</sub>Cp-TiCl<sub>3</sub>, Strem Chemical), and modified methylaluminoxane (MMAO-4, 7.6 wt % Al; Akzo Nobel, Deer Park, TX) were used as received. Styrene (Junsei Chem. Co., Tokyo, Japan) was distilled from calcium hydride and stored at 0°C under nitrogen in darkness. Ethylene (Polymerization grade, 99.5% purity; Korea Petrochemical Ind. Co., Ulsan, Korea) was purified with the usual methods.<sup>13</sup> Toluene and tetrahydrofuran (Duksan Pharm. Co., Ansan, Korea) were purified by refluxing with sodium-benzophenone complex.

### Preparation of Mononuclear and Dinuclear Half-Titanocenes

Indenyltitanium trichloride (IndTiCl<sub>3</sub>)<sup>14</sup> and dimethylsilyl(*t*-butylamido)(tetramethylcyclopentadienyl)titanium dichloride<sup>9</sup> were prepared with the published procedures. The trisiloxane-bridged dinuclear half-titanocene, hexamethyltrisiloxanediylbis(cyclopentadienyltitanium trichloride) (TSDT), Cl<sub>3</sub>TiCp—(CH<sub>3</sub>)<sub>2</sub>Si—O—Si(CH<sub>3</sub>)<sub>2</sub>—O—Si(CH<sub>3</sub>)<sub>2</sub>—CpTiCl<sub>3</sub>, was prepared by the reaction of disodium salt of 1,5-dicyclopentadienylhexamethyltrisiloxane with 2 equivalents of TiCl<sub>4</sub> so-

lution at -78°C.<sup>10,11</sup> The resulting solution was heated to room temperature and stirred for 5 h. Recrystallization from ether gave a pale green, solid product.

### Polymerization and Characterization of Polymer

Into a 400-mL glass reactor were introduced sequentially the proper amounts of toluene, MMAO solution, and S, followed by saturation with E at atmosphere pressure. With continuous flow of E, the polymerization was initiated by injecting the required amount of titanocene catalysts. The polymerization was terminated by the addition of acidified methanol. The polymer was coagulated with 5% HCl in methanol, recovered by filtration, washed with fresh methanol, and dried under vacuum.

The syndiotactic index was estimated from the weight of residual polymer after extraction of raw polymer with boiling methylethylketone for 10 h. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) (Waters 150 C and 150 CV, Milford, MA) in 1,2,4-trichlorobenzene at 135°C and data were analyzed using PS calibration curves. The fractionation of polymers was recorded on cross fractionation chromatography (CFC T-150A; Mitsubishi Petrochemical Co., Tokyo, Japan) in *o*-dichlorobenzene.<sup>15</sup> Approximately 4 mg of polymer (0.4 wt % in *o*-dichlorobenzene) was loaded onto a column of inert packing by slow cooling, followed by stepwise elution from the column at 40 to 145°C with a flow rate of 1 mL/min. Each eluted polymer solution was automatically sent to the size-exclusion chromatography system equipped with an infrared detector. The melting temperature (*T<sub>m</sub>*) and the crystallization temperature (*T<sub>c</sub>*) of the obtained polymer were measured by DSC (Dupont TA 2000, Wilmington, DE) at 20°C/min. The structure of the polymer was examined with <sup>13</sup>C-NMR (Bruker ARX 300, Germany and Varian Unity 300 Plus, Palo Alto, CA) at 135°C in 1,2,4-trichlorobenzene/benzene-*d*<sub>6</sub> (9/1 vol %).

## RESULTS AND DISCUSSION

### Catalyst Activity and Thermal Properties of the Polymer

The copolymerization of S and E was carried out with mononuclear titanocenes such as CpTiCl<sub>3</sub>, IndTiCl<sub>3</sub>, and Me<sub>5</sub>CpTiCl<sub>3</sub>, and the results are

**Table I** Effect of [S]/[E] Feed Ratio on the Catalyst Activity and Transition Temperatures of the Polymer for Mononuclear Titanocenes and CGC

Catalyst	[S]/[E] <sup>a</sup>	Polymer	Activity <sup>b</sup>	$T_m$ (°C)		$T_c$ (°C)	
CpTiCl <sub>3</sub>	none/0.61	HE-1	6.9	132	—	114	—
	0.09/0.61	ES-1	17.2	125	248	107	207
	0.35/0.61	ES-2	22.5	126	250	108	210
	0.35/none	HS-1 <sup>c</sup>	36.8	—	254	—	218
IndTiCl <sub>3</sub>	none/0.61	HE-2	7.2	131	—	114	—
	0.09/0.61	ES-3	20.1	122	261	100	226
	0.35/0.61	ES-4	42.0	123	262	106	231
	0.35/none	HS-2 <sup>d</sup>	87.0	—	267	—	235
Me <sub>5</sub> CpTiCl <sub>3</sub>	none/0.61	HE-3	2.4	126	—	108	—
	0.09/0.61	ES-5	1.8	124	265	110	235
	0.35/0.61	ES-6	3.2	124	269	103	235
	0.35/none	HS-3 <sup>e</sup>	32.9	—	271	—	236
CGC	none/0.61	HE-4	112.2	132	—	115	—
	0.09/0.61	ES-7	175.5	87	—	69	—
	0.35/0.61	ES-8	178.2	82	—	65	—
	0.35/none	HS-4 <sup>f</sup>	1.4	—	263	—	219

Copolymerization conditions: [Ti] = 3.2 ~ 4.8 × 10<sup>-6</sup> mol/L, [Al]/[Ti] = 1000, 40°C, 2 h.

<sup>a</sup> Feed ratio: (mol/L)/(mol/L).

<sup>b</sup> Activity: (kg polymer)/(mol Ti h).

<sup>c</sup> [rr] = 0.883, SI = 89.0 wt %.

<sup>d</sup> [rr] = 0.979, SI = 93.3 wt %.

<sup>e</sup> [rr] = 0.985, SI = 96.7 wt %.

<sup>f</sup> [rr] not measured, SI = 91.7 wt %.

shown in Table I. The  $T_m$  and  $T_c$  of the products were also measured. The result of the CGC was also included.

As shown in Table I, E had lower reactivity than S for CpTiCl<sub>3</sub> and IndTiCl<sub>3</sub> as well as Me<sub>5</sub>CpTiCl<sub>3</sub>, and the catalyst activity of mononuclear titanocenes increased steadily with addition of S although the Me<sub>5</sub>CpTiCl<sub>3</sub>-MMAO catalyst system gave a minimum activity with a small amount of S. Me<sub>5</sub>CpTiCl<sub>3</sub> had lower activity than CpTiCl<sub>3</sub> and IndTiCl<sub>3</sub> for homopolymerization of E. The catalyst activity of CGC for S was much lower than that of half-titanocenes but was enhanced to a great extent by addition of E.

As reported,<sup>16,17</sup> the stereoregularity of mononuclear titanocenes expressed by [rr] triads as well as syndiotactic index (SI) for S homopolymerization is given in the footnote of Table I, and decreased as follows; Me<sub>5</sub>CpTiCl<sub>3</sub> > IndTiCl<sub>3</sub> > CGC ≧ CpTiCl<sub>3</sub>.

The DSC thermograms of ES-1, ES-3, ES-5, and ES-7 which were produced by CpTiCl<sub>3</sub>, In-

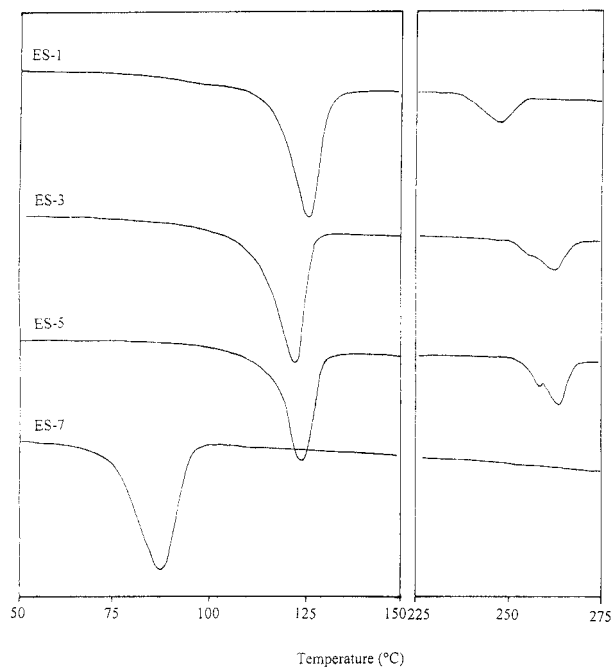
dTiCl<sub>3</sub>, Me<sub>5</sub>CpTiCl<sub>3</sub>, and CGC, respectively, for a constant feed ratio ([S]/[E] = 0.09/0.61) are shown in Figure 1.

As expected, the raw polymers (ES-1, ES-3, ES-5) obtained with mononuclear titanocenes had clearly two  $T_m$ s and  $T_c$ s, the values of which are slightly lower than those of the homopolymers polyethylene (PE) and sPS. On the other hand, the raw polymer (ES-7) produced by CGC had one  $T_m$  and  $T_c$  which were lower than those of PE and sPS.

The copolymerization of S and E catalyzed with dinuclear titanocene TSdT, and MMAO cocatalyst was carried out for various comonomer feed ratios and the results are shown in Table II.

As can be seen in Table II, the dinuclear titanocene TSdT had less activity for E than that for S and the catalyst activity increased continuously with the addition of S.

The syndiotacticity of sPS produced by TSdT was [rr] = 0.956, SI = 93.2 wt %, comparable with that by IndTiCl<sub>3</sub>.

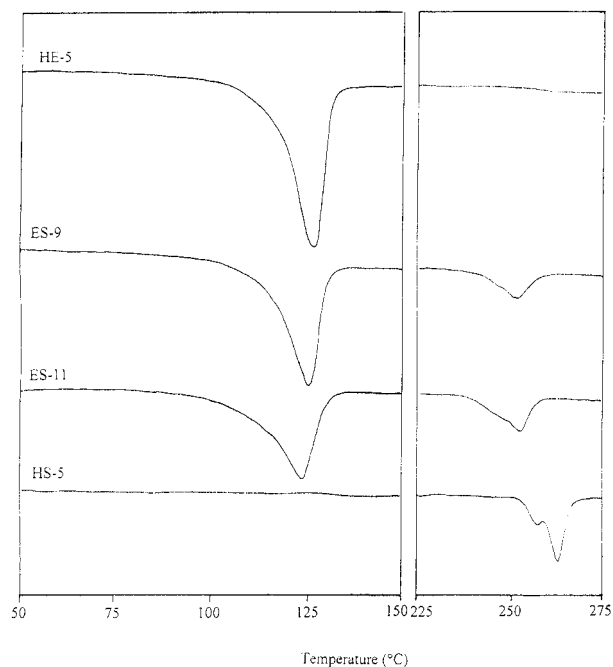


**Figure 1** DSC thermograms of ES-1, ES-3, ES-5, and ES-7.

The DSC thermograms of the produced raw polymers are shown in Figure 2.

The copolymerization products clearly exhibited two  $T_m$ s and  $T_c$ s, the values of which are slightly lower than those of the homopolymers. The transition temperatures of PE decreased steadily whereas those of sPS increased continuously with the addition of S.

From the thermal analysis, it was considered that the copolymerization products obtained with the mononuclear and dinuclear half-titanocenes such as CpTiCl<sub>3</sub>, IndTiCl<sub>3</sub>, Me<sub>5</sub>CpTiCl<sub>3</sub>, and TSdT



**Figure 2** DSC thermograms of HE-5, ES-9, ES-11, and HS-5.

are mainly mixtures of PE and sPS. To the contrary, the CGC-MMAO catalyst system produced S/E copolymer as already announced.<sup>9,12</sup>

#### Extraction of the Polymer

To separate the copolymerization product into the homopolymers and S/E copolymer, the raw polymer obtained with CpTiCl<sub>3</sub>, IndTiCl<sub>3</sub>, CGC, and TSdT was extracted with boiling toluene and methylethylketone (MEK). The content and transition temperatures of soluble and insoluble parts

**Table II** Effect of [S]/[E] Feed Ratio on the Catalyst Activity and Transition Temperatures of the Polymer for Dinuclear Titanocene TSdT

Polymer	[S]/[E] <sup>a</sup>	Activity <sup>b</sup>	$T_m$ (°C)		$T_c$ (°C)	
HE-5	none/0.61	2.4	131	—	115	—
ES-9	0.09/0.61	5.1	130	254	115	217
ES-10	0.35/0.61	7.2	130	255	115	218
ES-11	0.52/0.61	9.8	128	261	114	217
ES-12	1.04/0.61	12.4	125	264	113	225
HS-5 <sup>c</sup>	1.04/none	16.4	—	265	—	231

Copolymerization conditions: [Ti] =  $3.4 \times 10^{-6}$  mol/L, [Al]/[Ti] = 1000, 40°C, 3 h.

<sup>a</sup> Feed ratio: (mol/L)/(mol/L).

<sup>b</sup> Activity: (kg polymer/mol Ti h).

<sup>c</sup> [rr] = 0.956, SI = 93.2 wt %.

**Table III Content and Transition Temperature of Toluene Soluble and Insoluble Parts in the Copolymerization Products Obtained with Mononuclear and Dinuclear Half-Titanocenes**

Polymer	Soluble Part					Insoluble Part				
	Content (wt %)	$T_m$ (°C)		$T_c$ (°C)		Content (wt %)	$T_m$ (°C)		$T_c$ (°C)	
ES-1	17	121	243	104	n.d.	83	133	259	115	223
ES-2	10	122	246	107	203	90	133	260	115	224
ES-3	25	122	254	101	n.d.	75	133	270	115	235
ES-4	15	125	251	103	213	85	133	271	115	236
ES-7	100	87		69		0	—		—	
ES-9	8	126	248	113	211	92	131	264	116	232
ES-10	4	128	250	113	214	96	130	264	116	233

n.d., not detected.

for toluene and MEK are given in Tables III and IV, respectively.

The soluble content in raw polymer extracted with toluene was larger than that with MEK because toluene has higher solubility than MEK for PE and sPS. In addition, ES-7 which was obtained with CGC dissolved completely in boiling toluene while only 13 wt % of ES-7 was extracted by boiling MEK.

The soluble contents of ES-1, ES-3, and ES-9 which were obtained at lower [S]/[E] feed ratio were higher than those of ES-2, ES-4, and ES-10 at higher feed ratio. It might be considered that

S/E copolymer is easily obtained at low concentration of S as reported.<sup>7</sup>

Unexpectedly, the soluble part of ES-1, ES-3, and ES-9 also had two  $T_m$ s and  $T_c$ s which were lower than those of the raw polymers because some homopolymers of low molecular weight (MW) might be extracted<sup>17</sup> with toluene and MEK. On the other hand,  $T_m$  and  $T_c$  of the insoluble part were slightly higher than those of the raw polymers.

From the above results, it was concluded that the extraction method of copolymerization products with boiling toluene and MEK is less suitable

**Table IV Content and Transition Temperature of MEK Soluble and Insoluble Parts in the Copolymerization Products Obtained with Mononuclear and Dinuclear Half-Titanocenes**

Polymer	Soluble Part					Insoluble Part				
	Content (wt %)	$T_m$ (°C)		$T_c$ (°C)		Content (wt %)	$T_m$ (°C)		$T_c$ (°C)	
ES-1	11	120	n.d.	104	n.d.	89	133	259	114	222
ES-2	6	122	243	106	196	94	134	262	115	224
ES-3	18	119	249	101	n.d.	82	132	268	114	230
ES-4	9	123	251	103	211	91	133	270	115	231
ES-7	13	n.d.		n.d.		87	89		70	
ES-9	5	123	244	111	n.d.	95	131	260	114	229
ES-10	2	126	248	113	n.d.	98	130	262	115	230

n.d., not detected.

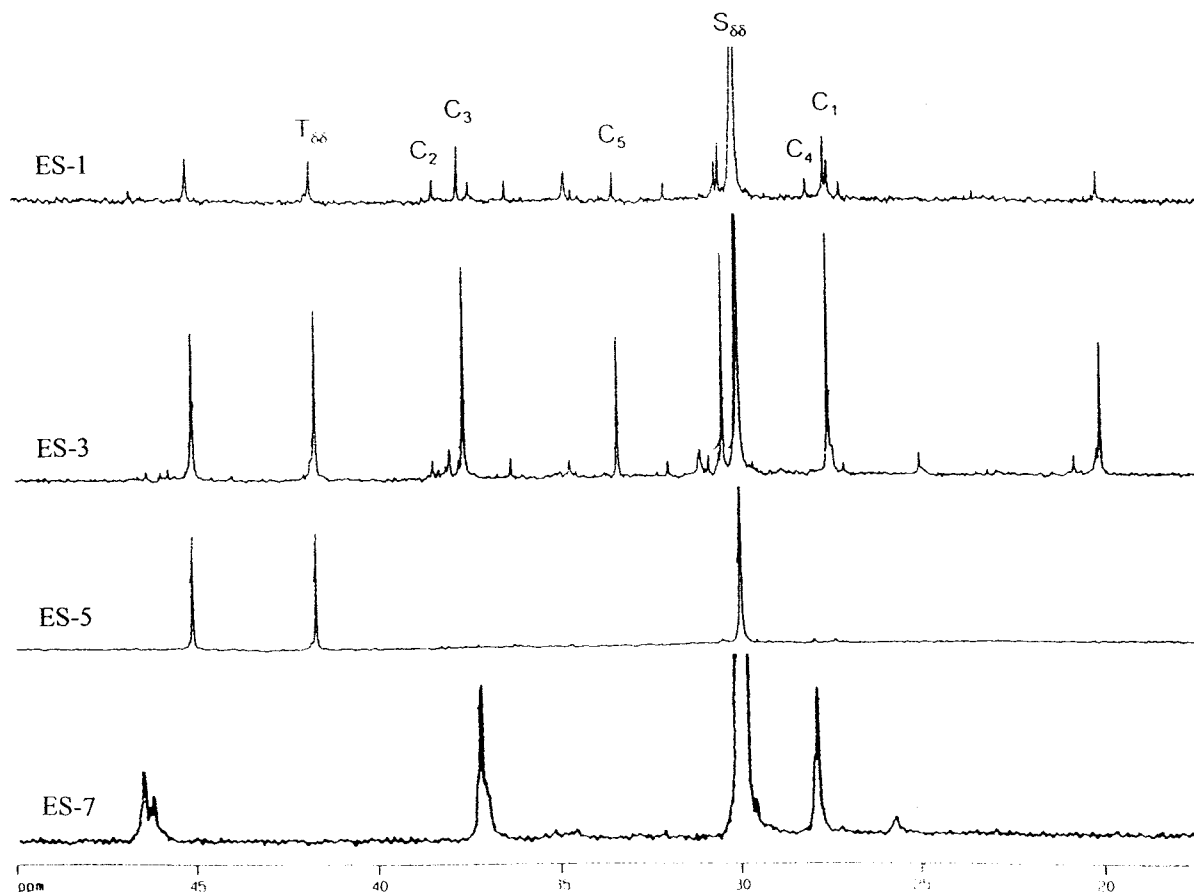


Figure 3  $^{13}\text{C}$ -NMR spectra of ES-1, ES-3, ES-5, and ES-7.

to separate the product into the homopolymers and copolymer.

### $^{13}\text{C}$ -NMR Analysis of the Polymer

It is well known that  $^{13}\text{C}$ -NMR analysis is efficient in determining the structure of S/E copolymerization products.<sup>2</sup>

To analyze the content of homopolymers and copolymer in the raw polymers, the  $^{13}\text{C}$ -NMR spectra of products prepared with  $\text{CpTiCl}_3$ ,  $\text{IndTiCl}_3$ ,  $\text{Me}_5\text{CpTiCl}_3$ , and CGC at constant feed ratio of  $[\text{S}]/[\text{E}]$  were obtained and are shown in Figure 3.

In the spectra of ES-1 and ES-3, three main peaks were observed at 45.0, 41.6, and 30.0 ppm. The peak at 30.0 ppm is due to the methylene group of PE, and the peaks at 45.0 and 41.6 ppm are designated  $-\text{CH}_2-$  and  $-\text{CH}-$  in sPS, respectively.<sup>6</sup> In addition, peaks were also observed at 46.2, 38.2, 37.5, 34.0 ~ 34.6, 27.0 ~ 27.5, and

20.0 ppm. The peaks at 38.2 and 27.0 ppm were correspondent to SES sequences<sup>4</sup> and the peaks at 37.5 and 27.5 ppm to ESE sequences.<sup>5</sup> The peak at 46.2 ppm appeared due to the  $-\text{CH}-$  of SES sequences and the peak at 20.0 ppm due to the unsaturated chain end groups.<sup>4</sup> The presence of such unsaturated chain end groups is indicative of secondary insertion of S into metal-E bonds followed by  $\beta$ -hydrogen elimination.<sup>4</sup>

The low intensity resonances detected at 34.0 ~ 34.6 ppm could arise either from tail-to-tail arranged S units or from E units bridging head-to-head arranged S units.<sup>6</sup> These resonances are probably due to traces of atactic PS produced together with copolymer.<sup>6</sup>

From the above  $^{13}\text{C}$ -NMR spectra of ES-1 and ES-3, it was confirmed that the copolymerization product produced by  $\text{CpTiCl}_3$  and  $\text{IndTiCl}_3$  is composed of homopolymers and copolymer.

In the spectra of ES-5, only three peaks were observed at 45.0, 41.6, and 30.0 ppm which are

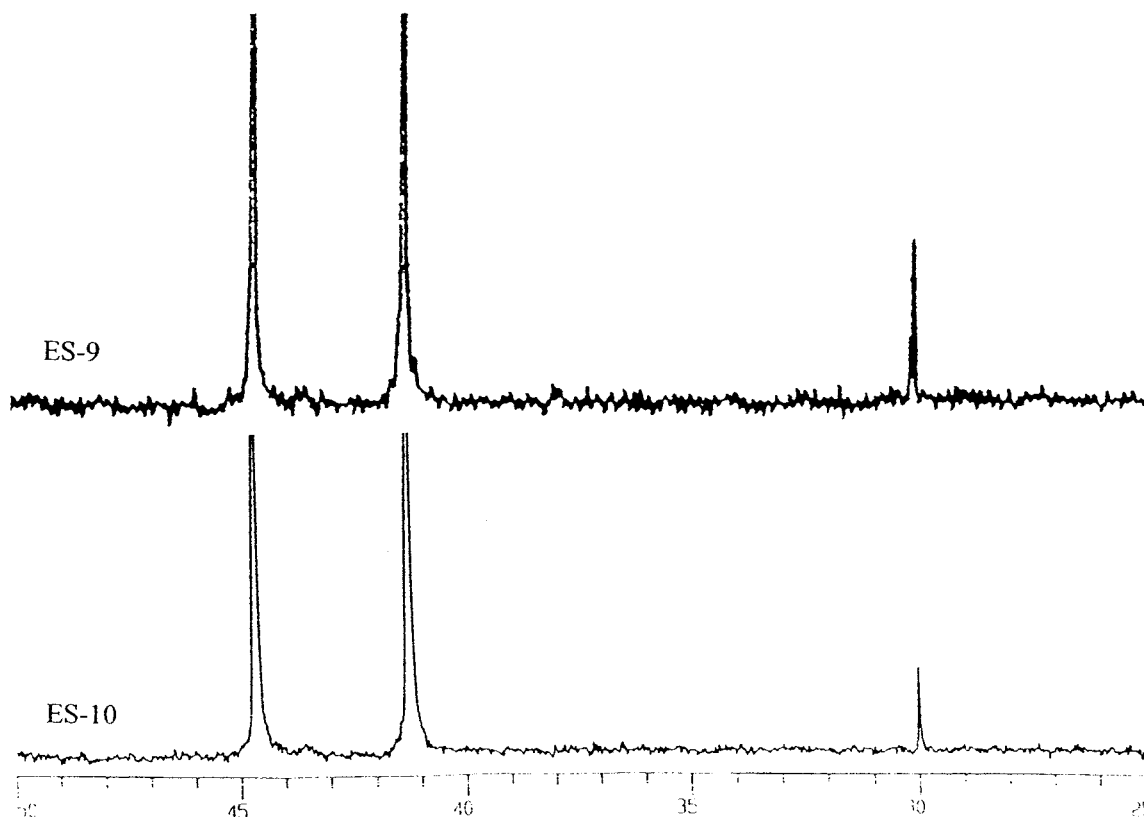


Figure 4  $^{13}\text{C}$ -NMR spectra of ES-9 and ES-11.

correspondent to PE and sPS homopolymers. In other words,  $\text{Me}_5\text{CpTiCl}_3$  could hardly initiate the copolymerization of S and E.

In the spectrum of ES-7, the peaks were observed at 46.2, 37.5, 30.0, 27.6, and 27.0 ppm. The peaks at 37.5 and 27.6 ppm corresponded to the ESE sequence. The peaks at 45.0 and 41.6 ppm as well as 30.0 ppm corresponding to sPS and PE could hardly be observed, which suggested that ES-7 prepared with CGC was a copolymer without any homopolymer. The S content<sup>8</sup> of ES-7 was estimated from the  $-\text{CH}_2-$  peak at 30.0 ppm and the phenyl  $\text{C}_1$  peak at 145.5 ppm to be 11.2 mol %.

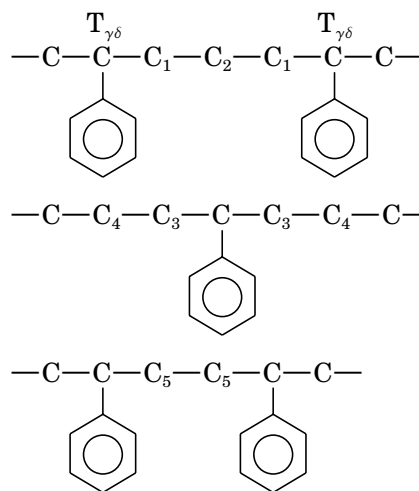
The structure of ES-9 and ES-10 obtained with TSDT was investigated by using  $^{13}\text{C}$ -NMR and the spectra are shown in Figure 4.

In the spectra of ES-9 and ES-10, only three sharp peaks at 45.0, 41.6, and 30.0 ppm were observed, which correspond to the  $-\text{CH}_2-$  and  $-\text{CH}-$  in sPS and the methylene group of PE, respectively. The peaks of ESE and SES sequences corresponding to copolymer could hardly be observed, as in the case of ES-5.

The relative abundance of the aliphatic carbons and the copolymer content in the raw polymers

were estimated from the above  $^{13}\text{C}$ -NMR spectra and are shown in Table V.

The carbon species of the aliphatic region in Table V were assigned as shown below:



In Table V, ES-5 and ES-9 obtained with  $\text{Me}_5\text{CpTiCl}_3$  and TSDT, respectively, had only two carbons ( $\text{S}_{\delta\delta} = 30.0$  ppm and  $\text{T}_{\delta\delta} = 41.6$  ppm) which

**Table V** Chemical Shift of  $^{13}\text{C}$ -NMR Spectra and Copolymer Content (mol %) in the Copolymerization Products Obtained with Mononuclear and Dinuclear Half-Titanocenes

$\delta$ (ppm)	Carbon	Sequence	ES-1	ES-3	ES-5	ES-7	ES-9
27.0	C <sub>1</sub>		0.015	0.010	—	0.044	—
27.2 ~ 27.6	C <sub>4</sub>		0.050	0.102	—	0.079	—
29.8 ~ 30.3	S <sub><math>\delta\delta</math></sub>		0.827	0.626	0.217	0.724	0.393
34.0 ~ 34.6	C <sub>5</sub>		0.030	0.044	—	—	—
37.2 ~ 37.6	C <sub>3</sub>		0.035	0.085	—	0.093	—
38.0 ~ 38.2	C <sub>2</sub>		0.014	0.033	—	—	—
41.6	T <sub><math>\delta\delta</math></sub>		0.028	0.087	0.783	—	0.606
46.2	T <sub><math>\gamma\delta</math></sub>		0.004	0.014	—	0.059	—
		EEE	0.852 (0.651) <sup>a</sup>	0.761 (0.519)	0.217 (0.069)	0.724 (0.525)	0.393 (0.147) <sup>a</sup>
		ESE + SES	0.072 (0.131)	0.139 (0.222)	—	0.276 (0.475)	—
		SSS	0.076 (0.218)	0.100 (0.256)	0.783 (0.931)	—	0.607 (0.853)

<sup>a</sup> Weight percent.

correspond to EEE and SSS sequences. The copolymer content in the products was calculated from the peak area of ESE and SES sequences divided by total peak area. The copolymer content of ES-1 obtained with CpTiCl<sub>3</sub> (7.2 mol %) was lower than that of ES-3 with IndTiCl<sub>3</sub> (13.9 mol %).

From the above  $^{13}\text{C}$ -NMR analysis, it was concluded that the copolymerization product obtained with dinuclear titanocene is a mixture of PE and sPS, and S/E copolymer is less produced by TSdT.

On the other hand, ES-7 obtained with CGC exhibited no T <sub>$\delta\delta$</sub> , which indicates that ES-7 is a copolymer.

### CFC Analysis of the Polymer

A heterogeneous copolymer such as linear low-density PE which is produced by a Ziegler–Natta catalyst could be fractionated by on-line temperature-rising elution fractionation (TREF) to check the uniformity of the copolymer.<sup>15</sup> Therefore, the raw polymer which was obtained by copolymerization of S and E with mononuclear and dinuclear half-titanocenes was analyzed by CFC.

The CFC chromatograms (TREF, differential-type, and contour-type diagrams) of ES-1, ES-3, ES-5, ES-7, and ES-9 obtained with CpTiCl<sub>3</sub>, IndTiCl<sub>3</sub>, Me<sub>5</sub>CpTiCl<sub>3</sub>, CGC, and TSdT, respectively, are shown in Figure 5.

With a general observation of Figure 5, it was noticed that the TREF diagrams for ES-1, ES-3,

and ES-5 can be divided into three regions, whereas ES-7 exhibited one region with a more uniform shape. The three regions could also be distinguished in the differential-type diagrams and the contour-type diagrams for ES-1, ES-3, and ES-5. On the other hand, the diagram for ES-9 was too sharp to divide.

From the TREF diagram for ES-1, it was considered that ES-1 was composed of three kinds of polymers which correspond to the above three regions; the first polymer was extracted below 83°C, the second from 83 to 98°C, and the third was dissolved above 98°C.

The three kinds of polymers were fractionated below 85°C, from 85 to 99°C, and above 99°C for ES-3; below 83°C, from 83 to 98°C, and above 98°C for ES-5.

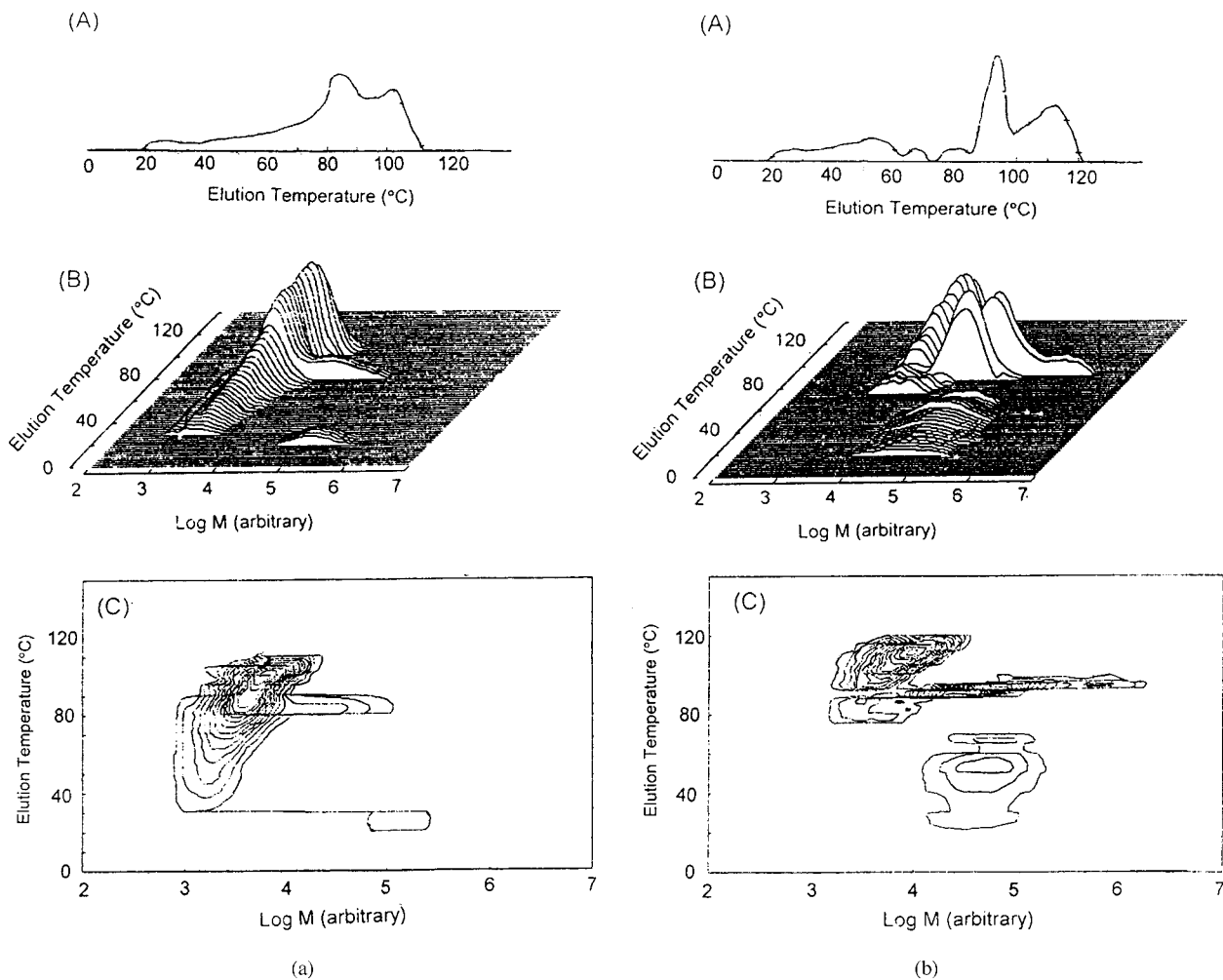
ES-7, which was previously confirmed to be S/E copolymer, was fractionated below 80°C. The shape of the diagram in Figure 5(A) was unimodal whereas diagrams in Figure 5(B) and (C) were very uniform.

Most of ES-9 were fractionated above 90°C with a small amount of polymer dissolved below 90°C.

In addition, it was found that PE was eluted at 85–100°C and sPS at 90–110°C from the authentic analysis with CFC.

From the above results it was considered that, as components of the raw polymer, S/E copolymer was fractionated below 85°C, PE from 85 to 95°C, and sPS above 95°C.





**Figure 5** CFC chromatograms of (a) ES-1, (b) ES-3, (c) ES-5, (d) ES-7, and (e) ES-9: (A) TREF, (B) differential-type, and (C) contour-type diagrams.

The content of S/E copolymer, PE, and sPS homopolymers in the produced raw polymers was calculated from TREF diagrams of the CFC chromatogram, and the results are given in Table VI.

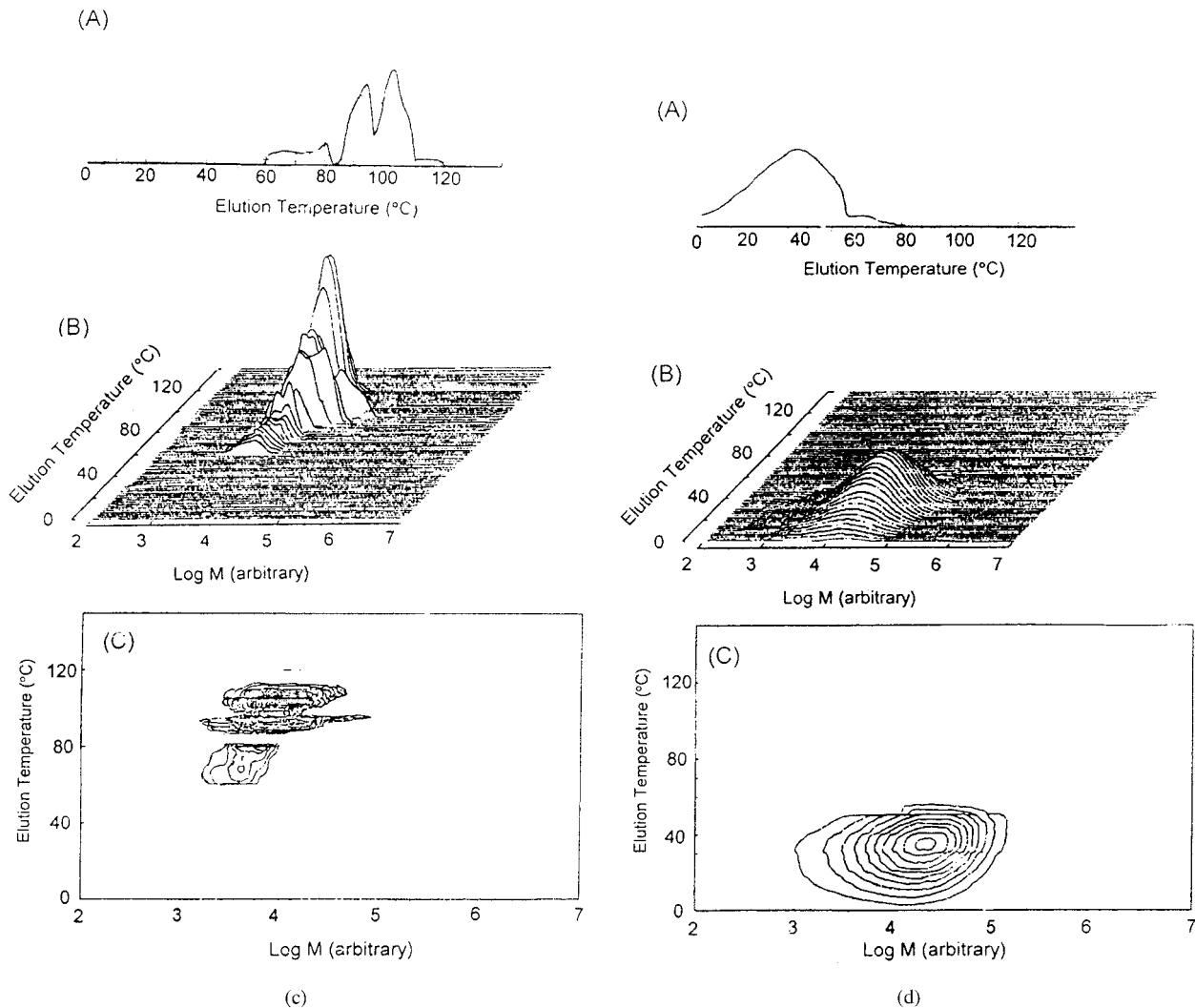
The S/E copolymer content in the raw polymers prepared with various titanocenes decreased in the following order; CGC  $\gg$  IndTiCl<sub>3</sub> > CpTiCl<sub>3</sub>  $\gg$  Me<sub>5</sub>CpTiCl<sub>3</sub> > TSDT. The S/E copolymer content was smaller than that of the soluble part in toluene (Table III) and larger than that in MEK (Table IV). On the other hand, the copolymer content calculated with CFC results was much larger than that estimated with <sup>13</sup>C-NMR analysis because low MW homopolymers might be extracted with rising temperature. The sPS content of ES-5 and ES-9 obtained with highly syndiospecific

titanocenes, Me<sub>5</sub>CpTiCl<sub>3</sub> and TSDT, was much higher than that of the others, which corresponded to the <sup>13</sup>C-NMR results.

From the above results, it was concluded that the raw polymers produced by mononuclear and dinuclear half-titanocenes are composed of homopolymers and copolymer. Only CGC produced S/E copolymer perfectly. The copolymer content of the raw polymer obtained with IndTiCl<sub>3</sub> was much higher than that of the others.

To examine the MW difference, the GPC curves of PE, sPS, and the raw polymer obtained with TSDT are shown in Figure 6 and the raw polymer produced by IndTiCl<sub>3</sub> was included.

The GPC curve of PE [Fig. 6(A)] was asymmetrical with broad molecular weight distribution



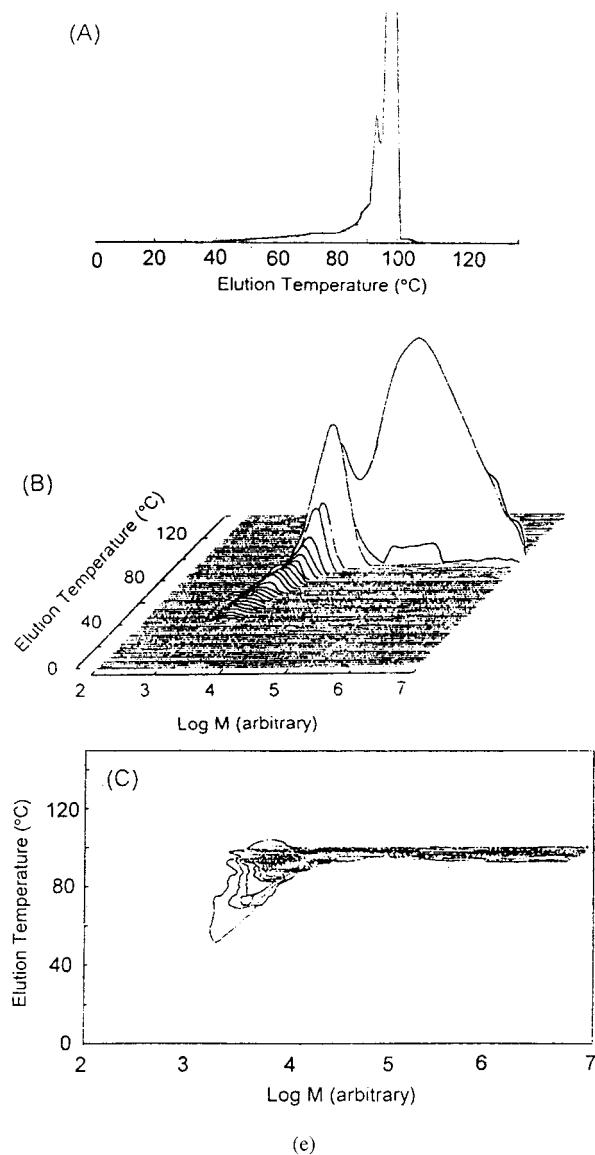
**Figure 5** (Continued from the previous page)

(MWD), whereas the curve of sPS [Fig. 6(B)] was symmetrical with very narrow MWD. The weight-average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) were 425,000 and 8.2 for PE and 84,000 and 2.7 for sPS, respectively. On the other hand, the copolymerization product obtained with TSdT exhibited a bimodal MWD [Fig. 6(C)], and its  $M_w$  and  $M_w/M_n$  were 128,000 and 12.4, respectively. The two maximum peaks corresponded to those of PE and sPS homopolymers. In Figure 6(D), the curve of the copolymerization product prepared with  $\text{IndTiCl}_3$  ( $M_w = 84,000$ ;  $M_w/M_n = 19.5$ ) exhibited the clear trimodal MWD with three peaks which corresponded to those of PE, sPS, and copolymer. The latest elution peak was correspondent to the S/E copolymer.

From these CFC and GPC results, it was concluded that the raw polymer prepared with the half-titanocenes was a mixture of homopolymers and copolymer.  $\text{IndTiCl}_3$  was more favorable to an incorporation of S into the PE chain than  $\text{CpTiCl}_3$ . On the other hand, the highly syndiospecific titanocenes such as  $\text{Me}_5\text{CpTiCl}_3$  and TSdT could hardly initiate copolymerization of S and E. Only CGC produced S/E copolymer perfectly.

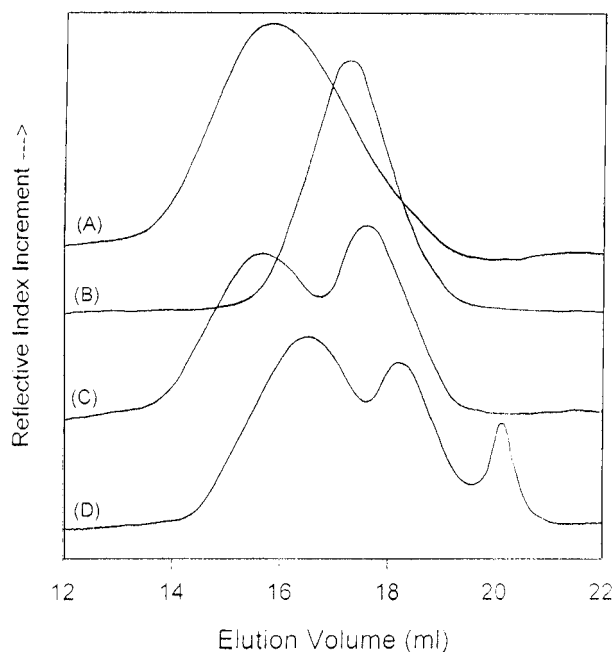
## CONCLUSIONS

The copolymerization of S and E was conducted with mononuclear half-titanocenes,  $\text{CpTiCl}_3$ ,  $\text{IndTiCl}_3$ ,  $\text{Me}_5\text{CpTiCl}_3$ , and dinuclear titanocene



**Figure 5** (Continued from the previous page)

TSDT as well as CGC. The thermal properties and the structure of the copolymerization products were investigated with DSC and  $^{13}\text{C}$ -NMR. From



**Figure 6** Gel permeation chromatograms of (A) PE obtained with TSDT, (B) PS with TSDT, (C) copolymerization product with TSDT, and (D) copolymerization product with  $\text{IndTiCl}_3$ .

DSC and  $^{13}\text{C}$ -NMR analysis, it was found that the raw polymer obtained with  $\text{CpTiCl}_3$  and  $\text{IndTiCl}_3$  was a mixture of sPS and PE homopolymers with copolymer (with  $^{13}\text{C}$ -NMR: 7.2 mol %, 13.1 wt % for  $\text{CpTiCl}_3$ ; 13.9 mol %, 22.2 wt % for  $\text{IndTiCl}_3$ ), whereas that produced by  $\text{Me}_5\text{CpTiCl}_3$  and TSDT was a homopolymer mixture with a negligible amount of copolymer. Only CGC produced copolymer of S and E perfectly. With an extraction method and CFC, the raw polymer could be separated into homopolymer and copolymer although the copolymer content (with CFC: 14.3 wt % for  $\text{CpTiCl}_3$ ; 27.2 wt % for  $\text{IndTiCl}_3$ ; 7.6 wt % for  $\text{Me}_5\text{CpTiCl}_3$ ; 6.5 wt % for TSDT) was slightly

**Table VI** Content (wt %) of S/E Copolymer, PE and sPS Homopolymers in Copolymerization Products Measured with CFC

Product	ES-1	ES-3	ES-5	ES-7	ES-9
Catalyst	$\text{CpTiCl}_3$	$\text{IndTiCl}_3$	$\text{Me}_5\text{CpTiCl}_3$	CGC	TSDT
S/E Copolymer	14.3	27.2	7.6	100	6.5
PE	48.6	48.0	25.9	—	33.2
PS	37.1	24.8	66.5	—	60.3

[S]/[E] feed ratio: 0.09/0.61 [(mol/L)/(mol/L)].

larger than that estimated from  $^{13}\text{C}$ -NMR because low MW homopolymer could also be extracted.

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