

Article

## Synthesis of Ethylene or Propylene/1,3-Butadiene Copolymers Possessing Pendant Vinyl Groups with Virtually No Internal Olefins

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**Abstract:** In general, ethylene/1,3-butadiene copolymerizations provides copolymers possessing both pendant vinyls and vinylenes as olefinic moieties. We, at MCI, studied the substituent effects of *C*<sub>2</sub>-symmetric zirconocene complexes, *rac*-[Me<sub>2</sub>Si(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub> (Indenyl' = generic substituted indenyl), after activation on the ratio of the pendant vinyls and vinylenes of the resultant copolymers. Complexes examined in this study were *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride (**1**), *rac*-dimethylsilyl-bis[1-(2-methyl-4,5-benzindenyl)] zirconium dichloride (**2**), *rac*-dimethylsilyl-bis[1-(2-methyl-4-phenylindenyl)]zirconium dichloride (**3**), *rac*-dimethylsilyl-bis(2-ethyl-4-phenylindenyl) zirconium dichloride (**4**), *rac*-dimethylsilyl-bis[1-(2-*n*-propyl-4-(1-naphthyl)indenyl)]zirconium dichloride (**5**), *rac*-dimethylsilyl-[1-(2-ethyl-4-(5-(2,2-dimethyl-2,3-dihydro-1*H*-cyclopenta [a]naphthalenyl)indenyl))][1-(2-*n*-propyl-4-(5-(2,2-dimethyl-2,3-dihydro-1*H*-cyclopenta[a] naphthalenyl)indenyl))]zirconium dichloride (**6**), *rac*-dimethylsilyl-bis[1-(2-ethyl-4-(9-phenanthryl)indenyl)]zirconium dichloride (**7**), and *rac*-dimethylsilyl-bis[1-(2-*n*-propyl-4-(9-phenanthryl)indenyl)]zirconium dichloride (**8**). We found that the ratio of the pendant vinyls and vinylenes is strongly affected by the bulkiness of the substituent on the complexes examined. The vinyl content increased linearly in the following order, **8** > **7** > **6** > **5** > **4** > **3** > **2** > **1**. Notably, complex **8**/DMAO formed ethylene/1,3-butadiene copolymers possessing predominant vinyl groups, which can be

crucial precursors for functionalized polyolefins. Likewise, complex **8**/DMAO afforded propylene/1,3-butadiene copolymers with predominant vinyl groups.

**Keywords:** 1,3-butadiene;  $C_2$ -symmetric zirconocene; insertion mode; vinyl groups; internal olefins; vinylenes

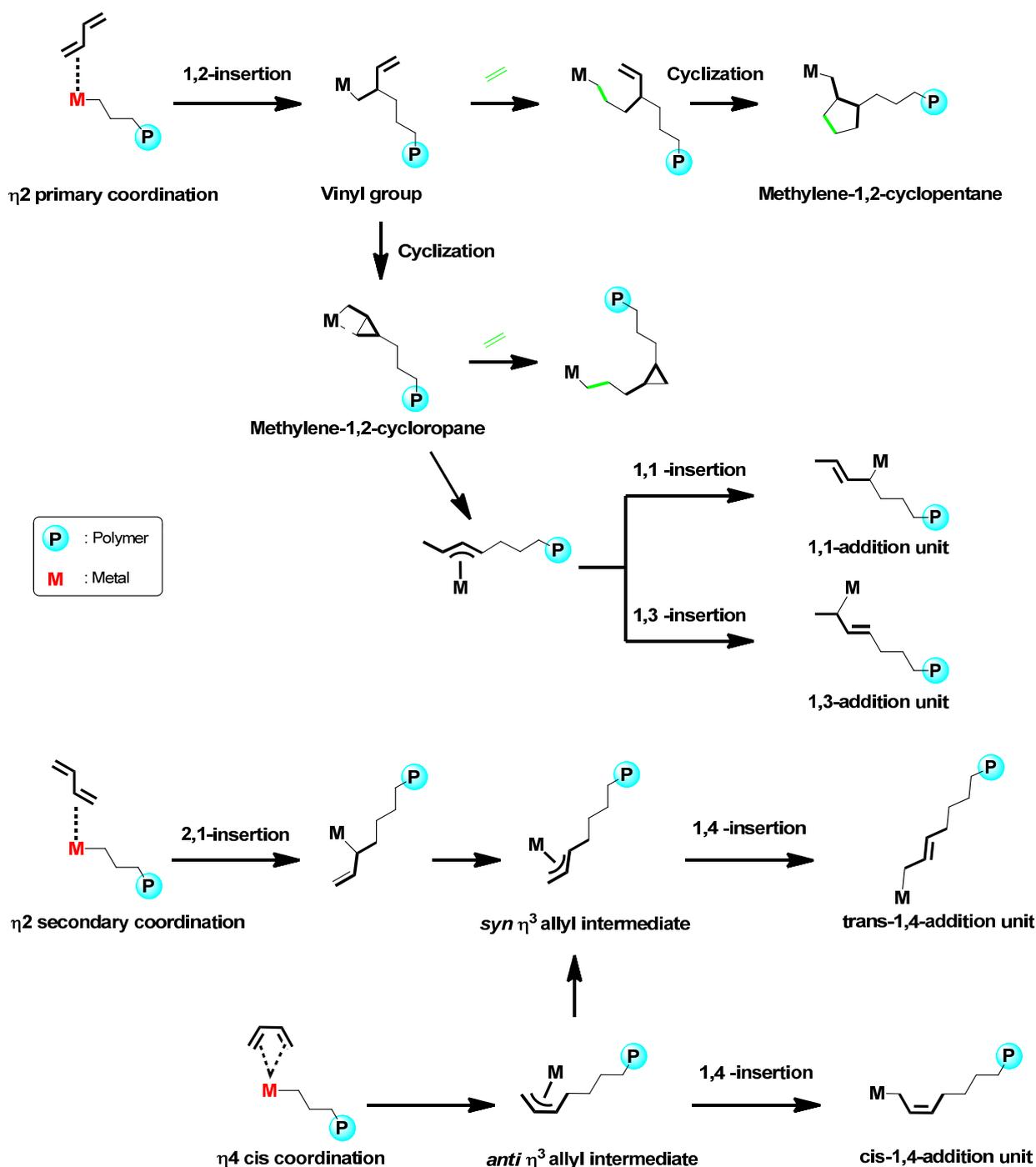
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## 1. Introduction

Polyolefins, represented by polyethylene, polypropylene, and amorphous ethylene/ $\alpha$ -olefin copolymers, can display useful mechanical properties (high impact strength, hardness/softness, durability), chemical stability (low reactivity, oil resistance, weathering resistance), thermal stability (heat/cold resistance), processability, lightweight, cost-effectiveness, and recyclability. However, due to their non-polar nature, they show poor affinity for polar materials such as polar organic polymers, glasses, and metals. To overcome this drawback, several attempts have been made in an effort to introduce polar groups into polyolefins, which include copolymerization of ethylene with polar monomers via a high pressure radical polymerization and the modification of polyolefins by a radical reaction [1]. However, these methods have disadvantages to control over polymer architecture (e.g., contents and distributions of polar groups, product molecular weights, molecular weight distributions, and branching extent) due to inherently poor reaction selectivity and unfavorable side reactions. Conversely, the direct synthesis of functionalized polyolefins by the anionic insertion copolymerization of olefins and polar  $CH_2=CHX$  monomers ( $X$  = polar groups) using organometallic complexes has extensively been investigated [1]. Although these investigations have made an impact on polymer synthesis, these are far from being of practical use because of low productivity and a low degree of polar monomer incorporation.

In this study, we focused on the copolymerization of butadiene with olefins for the purpose of creating new functionalized polyolefinic materials using cost-competitive feedstocks. Because butadiene is a conventional monomer, yet it is able to generate a vinyl group onto the polymer backbone. The pendant vinyl group can be converted to functional groups, or utilized by itself. Thus it is that we explored catalysts that can copolymerize butadiene with olefin(s), where the insertion reaction of the butadiene proceeds preferentially via a 1,2-insertion without the accompanying subsequent cyclization, since the formation of the internal olefin, the cause of the degradation of the polymer generated by the 1,4-insertion, is unfavorable.

However, upon copolymerizing butadiene with olefins, several kinds of reaction pathways are possible (Scheme 1) [2–5].  $\eta^2$  primary coordination of butadiene leads to formation of vinyl groups or rings through a primary vinyl insertion, whereas  $\eta^2$  secondary and  $\eta^4$ -cis coordination of butadiene leads to trans and cis 1,4-butadiene units through the formation of a syn- $\eta^3$ -coordinated growing chain and an anti- $\eta^3$ -coordinated growing chain, respectively [6–9]. Until now, reports on olefin/butadiene copolymerization, where the insertion reaction of the 1,3-butadiene proceeds via 1,2-insertion preferentially to form a vinyl group, are scarce.



**Scheme 1.** Reaction pathways of ethylene/1,3-butadiene copolymerization.

A rare example of such polymerization is propylene/butadiene copolymerization using *rac*-[Me<sub>2</sub>Si (2-methyl-4-phenylindenyl)<sub>2</sub>]ZrCl<sub>2</sub> in the presence of hydrogen [10,11]. However, while this method provides a copolymer having pendant vinyl groups in the main chain with a minimal number of internal olefins, there is still room for investigation regarding the substituent effects on the number of both internal olefins and vinyl groups.

Thus, we preliminary investigated a wide variety of catalysts including metallocene and post-metallocene catalysts to find catalysts that are capable of generating copolymers with predominant pendant vinyl groups in ethylene/butadiene copolymerization [12]. As a result, we found a qualitative correlation

between the catalyst structure and the insertion mode of butadiene. As a general rule, catalysts incorporating  $\alpha$ -olefins with 1,2-insertion favor the 1,2-insertion of butadiene. On the other hand, catalysts incorporating  $\alpha$ -olefins with 2,1-insertion prefer the 1,4-insertion of butadiene. Namely, the catalysts inserting  $\alpha$ -olefins by the 1,2-insertion tend to produce olefin/butadiene copolymers having pendant vinyl groups. This tendency is, in general, pronounced when steric regulation becomes significant. From our preliminary results obtained through the screening study,  $C_2$ -symmetric zirconocene,  $rac$ -[Me<sub>2</sub>Si(2-methyl-4-phenylindenyl)<sub>2</sub>]ZrCl<sub>2</sub> [10,11] was an especially efficient catalyst to incorporate butadiene by 1,2-insertion to obtain the desired polymer structure of an ethylene/butadiene copolymer.

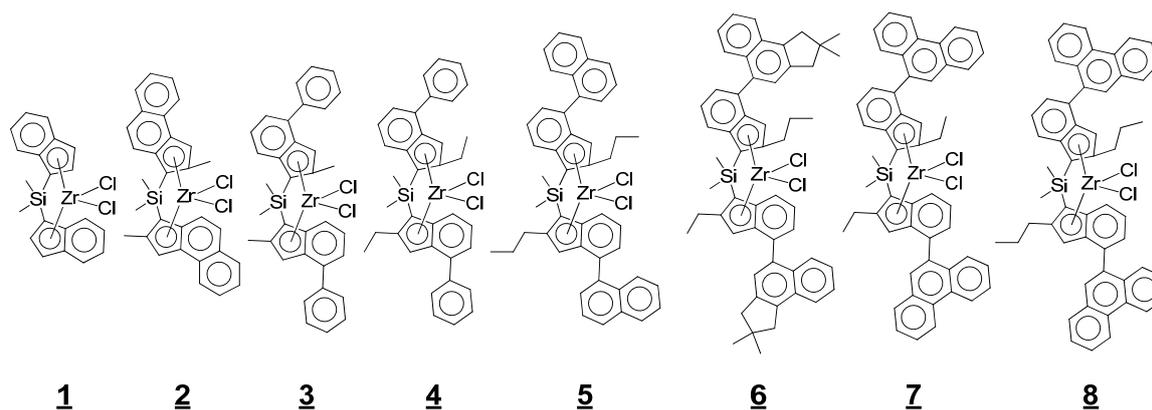
Interestingly, this phenomenon is supported by molecular modeling calculations for an analogous  $C_2$ -symmetric zirconocene,  $rac$ -[H<sub>2</sub>C(3-R-1-indenyl)<sub>2</sub>]ZrCl<sub>2</sub> catalyst system (R = H, Me, Et, <sup>*i*</sup>Pr, <sup>*t*</sup>Bu) in that  $\eta^2$  primary coordination of butadiene is energetically favorable compared to  $\eta^2$  secondary coordination and the  $\eta^4$ -cis coordination of butadiene [8]. In addition, the relative amount of constitutional monomer units derived from butadiene are affected by the bulkiness of the substituent. To that end, we have anticipated that tuning the steric property of the  $rac$ -[R<sub>2</sub>Si(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub> (Indenyl' = generic substituted indenyl) would lead to a further increase in the pendant vinyl group while keeping the internal olefins at a negligible level. Herein we describe studies on a series of  $rac$ -[SiMe<sub>2</sub>(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub> catalysts with diverse steric properties to clarify factors that control the insertion mode of butadiene, and investigated methods to prepare copolymers that contain predominant pendant vinyl groups and are substantially free of internal olefins (derived from 1,4- or 1,3-addition units).

## 2. Results and Discussion

### 2.1. Ethylene/Butadiene Copolymerization by $rac$ -[SiMe<sub>2</sub>(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub>

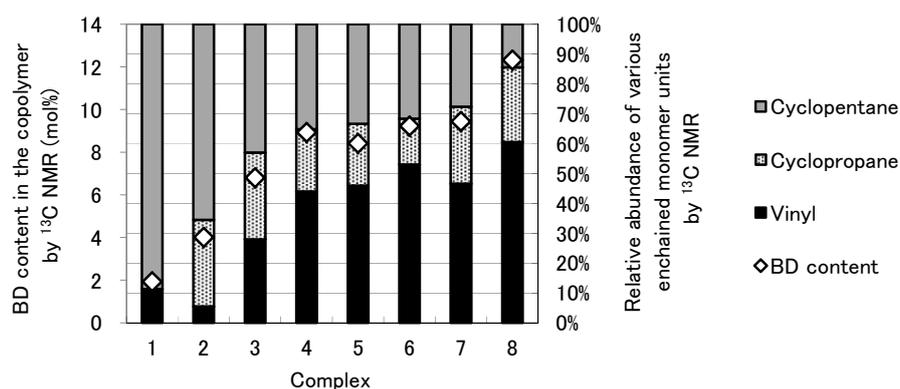
#### Influence of Substituent on Insertion Mode of Butadiene in Ethylene/Butadiene Copolymerization

We evaluated eight  $C_2$ -symmetric zirconocene complexes,  $rac$ -[SiMe<sub>2</sub>(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub> (Figure 1);  $rac$ -dimethylsilylbis(1-indenyl)zirconium dichloride (**1**),  $rac$ -dimethylsilyl-bis[1-(2-methyl-4,5-benzindenyl)] zirconium dichloride (**2**),  $rac$ -dimethylsilyl-bis[1-(2-methyl-4-phenylindenyl)] zirconium dichloride (**3**),  $rac$ -dimethylsilyl-bis(2-ethyl-4-phenylindenyl)zirconium dichloride (**4**),  $rac$ -dimethylsilyl-bis[1-(2-*n*-propyl-4-(1-naphthyl)indenyl)]zirconium dichloride (**5**),  $rac$ -dimethylsilyl-[1-(2-ethyl-4-(5-(2,2-dimethyl-2,3-dihydro-1H-cyclopenta[a]naphthalenyl)indenyl))][1-(2-*n*-propyl-4-(5-(2,2-dimethyl-2,3-dihydro-1H-cyclopenta[a]naphthalenyl)indenyl))]zirconium dichloride (**6**),  $rac$ -dimethylsilyl-bis[1-(2-ethyl-4-(9-phenanthryl)indenyl)]zirconium dichloride (**7**), and  $rac$ -dimethylsilyl-bis[1-(2-*n*-propyl-4-(9-phenanthryl)indenyl)]zirconium dichloride (**8**) for ethylene or propylene/butadiene copolymerization in the presence of hydrogen under identical conditions. The resultant copolymers were analyzed by <sup>13</sup>C-NMR, and the butadiene content and relative abundance of various enchainment monomer units were determined. The copolymers were also analyzed by <sup>1</sup>H-NMR to determine the quantity of the double bonds (vinyl groups and internal olefins) more accurately, because by <sup>13</sup>C-NMR analysis, the polymer is exposed to harsh conditions such as 140 °C for 12 h, so that the consumption of double bonds, especially the consumption of internal olefins during an analysis is anticipated.



**Figure 1.** Ansa-zirconocene catalysts employed in this study.

Ethylene/butadiene copolymerization results are summarized in Table 1. In the case of complex **1** /*i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, although activity was significantly high, butadiene was hardly incorporated into the resultant polymer, and the majority of butadiene units formed a five-membered ring (Table 1, run 1; Figure 2). However, a strong correlation between the microstructure of the copolymer and the bulkiness of the substituent on *rac*-[SiMe<sub>2</sub>(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub> was observed; as bulkiness of the substituent increases, a relative abundance of rings relative to all the structural units derived from butadiene decreased and conversely, that of the vinyl groups increased (Table 1, run 1–8; Figure 2). Surprisingly, complex **8**, which has the most bulky substituent generated 18 times as much vinyl groups compared to uncrowded complex **1**. These results suggest that, steric hindrance on *rac*-[SiMe<sub>2</sub>(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub> is effective to generate pendant vinyl groups by hampering the formation of sterically demanding cyclopropane and the cyclopentane rings. The amount of internal olefins was negligible for all cases regardless of the type of substituent, even according to sensitive <sup>1</sup>H-NMR analysis (Figures 3 and 4).

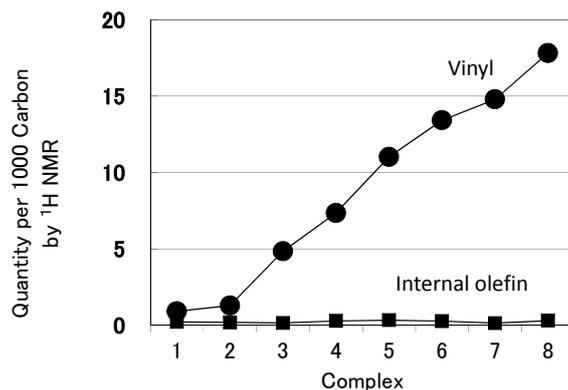


**Figure 2.** Butadiene content and relative abundance of various enchainment units (mol % calculated by <sup>13</sup>C-NMR) in ethylene/butadiene copolymerization by complexes **1–8** /*i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>. Polymerization conditions refer to entries **1–8** in Table 1.

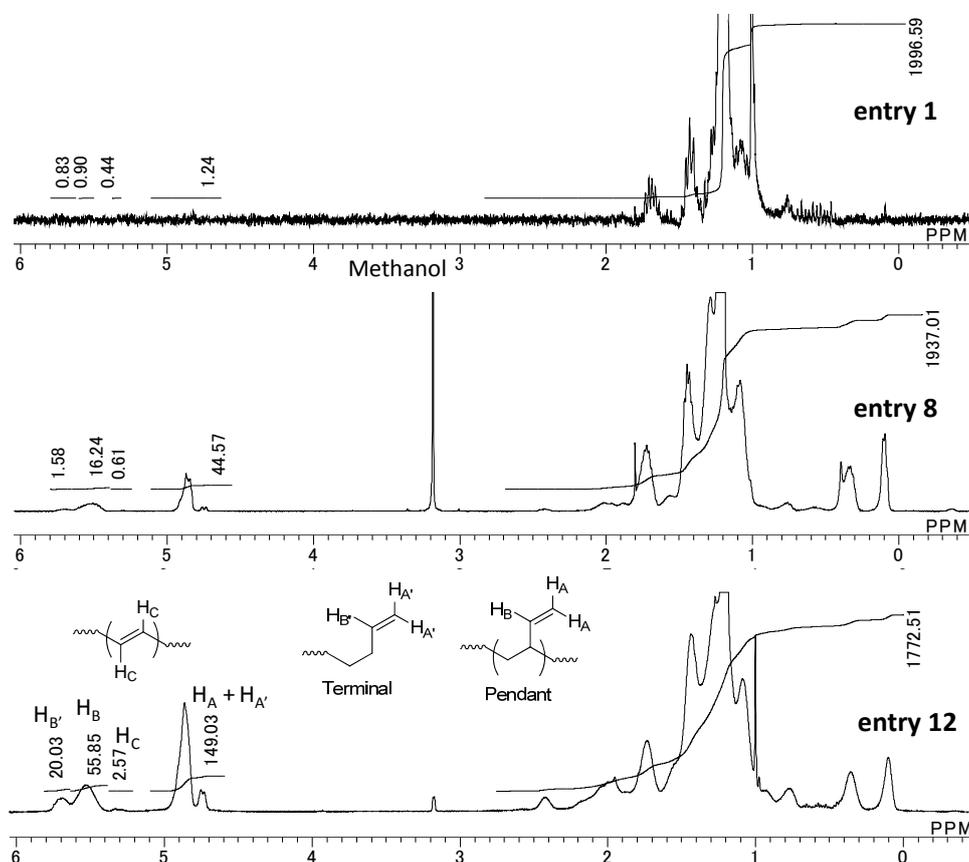
**Table 1.** Ethylene/butadiene copolymerization results for complexes 1–8 <sup>a</sup>.

Entry	Cat	A <sup>b</sup>	$M_w^c$ (10 <sup>3</sup> )	$M_w/M_n$	BD in Polym. <sup>d</sup> (mol %)	Mole Fraction <sup>e</sup>		Quantity per 1000 Carbon <sup>f</sup>		$T_g$ (°C)	$T_m$ (°C)
						1,2-addition units $f_w/f_{cycPro}/f_{cycPen}$	Internal olefins <sup>g</sup>	Vinyl groups <sup>h</sup>	Internal olefins <sup>g</sup>		
1	1	371.2	91.9	2.0	2	11/0/89	0	1	0.2	-	113
2	2	44.9	156.6	3.2	4	5/29/66	0	1	0.2	-	100
3	3	14.1	89.2	2.4	7	28/29/43	0	5	0.1	-33	71/117
4	4	6.2	37.7	2.4	9	44/21/35	0	7	0.3	-39	52/114
5	5	6.8	71.1	2.0	8	46/21/33	0	11	0.3	-32	55
6	6	5.3	50.5	2.1	9	53/15/32	0	13	0.3	-33	45
7	7	2.4	77.9	3.8	9	47/26/28	0	15	0.1	-32	52/113
8	8	3.6	77.9	2.9	12	61/25/14	0	18	0.3	-33	33/105
9 <sup>i</sup>	8	4.4	114.0	2.8	10	49/27/23	0	18	0.1	-31	37
10 <sup>j</sup>	8	4.5	132.5	2.9	12	72/14/14	0	41	0.0	-23	-
11 <sup>k</sup>	8	1.9	35.7	3.1	10	79/5/16	0	49	0.2	-14	-
12 <sup>l</sup>	8	1.3	39.3	3.9	16	95/0/5	0	76	1.3	-10	-

<sup>a</sup> Conditions: hexane 250 mL, butadiene 25 g, ethylene 0.51 MPa (partial pressure at 60 °C), H<sub>2</sub> 372 mL (volume under atmospheric pressure at 20 °C), Zr 0.002 mmol, <sup>i</sup>Bu<sub>3</sub>Al 0.5 mmol, Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> 0.012 mmol, polymerization time 20 min, 60 °C, total pressure 0.78 MPa; <sup>b</sup> Activity based on polymer yield; unit: kg-polymer/(mmol-Zr hr); <sup>c</sup> Weight average molecular weight determined by GPC using polystyrene calibration; <sup>d</sup> Butadiene content in the copolymer determined by <sup>13</sup>C-NMR; <sup>e</sup> Relative abundance of various enchainment units relative to all the structural units derived from butadiene determined by <sup>13</sup>C-NMR; <sup>f</sup> determined by <sup>1</sup>H-NMR; <sup>g</sup> The total amount of  $f_{1,4}$  and  $f_{1,3}$ ; <sup>h</sup> The total amount of pendant vinyl groups and terminal vinyl groups; <sup>i</sup> hexane 1000 mL, butadiene 100 g, ethylene 0.55 MPa (partial pressure at 60 °C), H<sub>2</sub> 620 mL (volume under atmospheric pressure at 20 °C), Zr 0.004 mmol, <sup>i</sup>Bu<sub>3</sub>Al 2.0 mmol, Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> 0.024 mmol; <sup>j</sup> hexane 1000 mL, butadiene 100 g, ethylene 0.55 MPa (partial pressure at 60 °C), H<sub>2</sub> 620 mL (volume under atmospheric pressure at 20 °C), Zr 0.004 mmol, DMAO 11.2 mmol as Al; <sup>k</sup> hexane 1000 mL, butadiene 300 g, ethylene 0.42 MPa (partial pressure at 60 °C), H<sub>2</sub> 620 mL (volume under atmospheric pressure at 20 °C), Zr 0.004 mmol, DMAO 11.2 mmol as Al; <sup>l</sup> hexane 2000 mL, butadiene 190 g, ethylene 0.17 MPa (partial pressure at 70 °C), H<sub>2</sub> 990 mL (volume under atmospheric pressure at 20 °C), Zr 0.008 mmol, DMAO 22.4 mmol as Al, 70 °C.



**Figure 3.** Quantity of vinyl groups and internal olefins (per 1000 carbon calculated by  $^1\text{H-NMR}$ ) in ethylene/butadiene copolymerization by complexes **1–8**/ $i\text{Bu}_3\text{Al/Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ . Polymerization conditions refer to entries **1–8** in Table 1.



**Figure 4.**  $^1\text{H-NMR}$  spectra of the ethylene/butadiene copolymers obtained from entries **1**, **8**, and **12** of Table 1.

Interestingly, DMAO is more efficient than  $i\text{Bu}_3\text{Al/Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  for generating vinyl groups (Table 1, entries 9 and 10). As part of an effort to increase the number of vinyl groups, the butadiene/ethylene ratio in the feed was increased at DMAO activation conditions. As a result, we succeeded in synthesizing ethylene/butadiene copolymers which are dominated by vinyl groups ( $f_v = 79$  mol %; Table 1, entry 11). Further increase in butadiene/ethylene feed ratio [13] led to formation of ethylene/butadiene copolymers whose structural units derived from butadiene are mostly vinyl groups ( $f_v = 95$  mol %; Table 1, entry

12). Notably, the quantity of vinyl groups per 1000 carbon reached 76 for this condition (Table 1, entry 12; Figure 4). Although the formation of internal olefins accompanied this condition (1.3 per 1000 Carbon; Table 1, entry 12), it is a quantity far too low compared to that of the vinyl groups. The remaining internal olefins will be eliminated by introducing a higher amount of hydrogen [10,11].

## 2.2. Propylene/Butadiene Copolymerization by Complexes 3 and 8

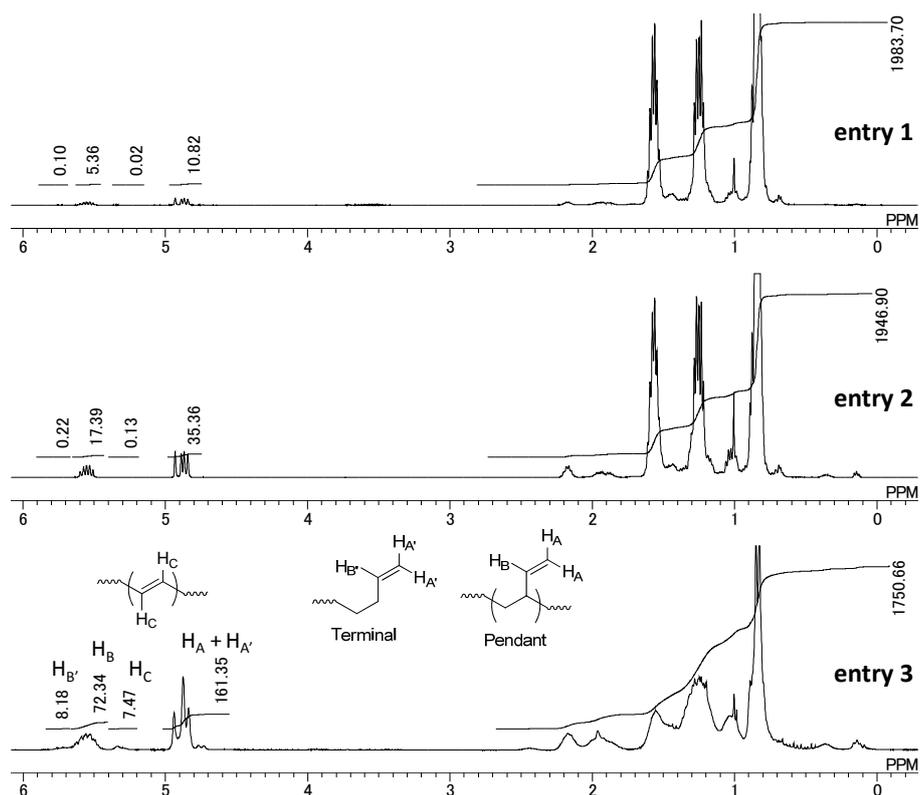
Following the ethylene/butadiene copolymerization, propylene/butadiene copolymerization was conducted using complexes 3 and 8 combined in activation with MMAO so as to compare with the previous study [10,11]. As with the results obtained by the ethylene/butadiene copolymerization, a similar substituent effect on the vinyl content was observed. Therefore, in this case again, we succeeded in synthesizing a propylene/butadiene copolymer possessing predominant vinyl groups (Table 2; Figure 5; Figure 6). Notably, the vinyl content obtained by complex 8 overwhelmed that by the previously reported complex 3 [10,11].

**Table 2.** Propylene/butadiene copolymerization results using complexes 1–8 <sup>a</sup>.

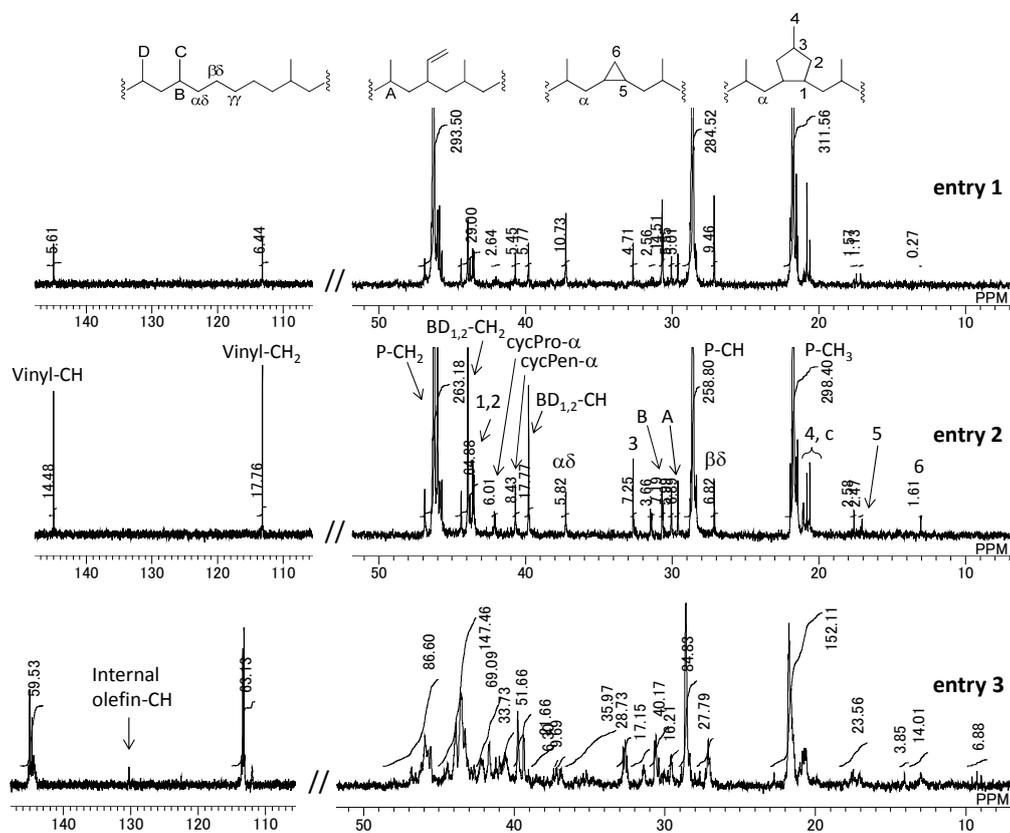
Entry	Cat	A <sup>b</sup>	$M_w^c$ (10 <sup>3</sup> )	$M_w$ / $M_n$	BD in Polym. <sup>d</sup> (mol %)	Mole Fraction <sup>e</sup>			Quantity per 1000 Carbon <sup>f</sup>		$T_g$ (°C)	$T_m$ (°C)	
						1,2-addition units		Internal olefins <sup>g</sup>	$f_{H-1,4}$	Vinyl groups <sup>h</sup>			Internal olefins <sup>g</sup>
						$f_{1,4}^i$	$f_{1,3}^i$						
						$f_{1,4}^i/f_{1,3}^i$							
1	3	16.6	99.6	2.4	5	38/2/28	0	32	6	0	6	122	
2	8	25.4	257.0	3.0	9	60/5/25	0	10	17	0	-15.3/3.9	102	
3 <sup>i</sup>	8	0.7	37.6	2.6	37	58/13/26	0	3	86	3.7	-24	-	

<sup>a</sup> Conditions: hexane 500 mL, butadiene 20 g, propylene 0.63 MPa (partial pressure at 60 °C), H<sub>2</sub> 124 mL (volume under atmospheric pressure at 20 °C), Zr 0.002 mmol, MMAO 5.6 mmol as Al, Polymerization time 20 min, 60 °C, total pressure 0.78 MPa; <sup>b</sup> Activity based on polymer yield; unit: kg-polymer/(mmol-Zr hr); <sup>c</sup> Weight average molecular weight determined by GPC using polystyrene calibration; <sup>d</sup> Butadiene content in the copolymer determined by <sup>13</sup>C-NMR; <sup>e</sup> Relative abundance of various enchainment units relative to all the structural units derived from butadiene determined by <sup>13</sup>C-NMR; <sup>f</sup> determined by <sup>1</sup>H-NMR; <sup>g</sup> The total amount of  $f_{1,4}$  and  $f_{1,3}$ ; <sup>h</sup> The total amount of pendant vinyl groups and terminal vinyl groups; <sup>i</sup> butadiene 200 g, propylene 0.26 MPa (partial pressure at 60 °C).

Likewise, increasing the butadiene concentration in the feed led to the formation of propylene/butadiene copolymers abundant with vinyl groups (quantity of vinyl groups = 86 per 1000 carbon; Table 2, entry 3; Figure 5). Although an extremely high butadiene/propylene feed ratio entails the formation of a small amount of internal olefins (quantity of internal olefins = 3.7 per 1000 carbon; Table 2, entry 3; Figure 5), the quantity is still far too low compared to that of the vinyl group. The remaining internal olefins will be eliminated by introducing a higher amount of hydrogen, as mentioned above [10,11].



**Figure 5.**  $^1\text{H}$ -NMR spectra of the propylene/butadiene copolymers obtained from the runs 1, 2, and 3 of Table 2.



**Figure 6.**  $^{13}\text{C}$ -NMR spectra of the propylene/butadiene copolymers obtained from the runs 1, 2, and 3 of Table 2.

### 3. Experimental Section

#### 3.1. General

All manipulations were performed using dry box techniques under a purified N<sub>2</sub> atmosphere or Schlenk techniques under N<sub>2</sub> atmosphere, or on a high-vacuum line, unless otherwise indicated.

#### 3.2. Materials

Hexane employed as a polymerization solvent (Kanto Chemical Co., Inc., Tokyo, Japan) was dried over Al<sub>2</sub>O<sub>3</sub> and degassed by the bubbling with nitrogen gas. Toluene used for dissolving pre-catalysts was purified by passage through columns of activated alumina and a BASF R3-11 oxygen scavenger (BASF, Ludwigshafen, Germany). Ethylene and propylene were obtained from Sumitomo Seika Co., Tokyo, Japan. Triisobutylaluminium (<sup>i</sup>Bu<sub>3</sub>Al) and Methyl-isobutylalumoxane (modified methylalumoxane, MMAO) were purchased from Tosoh Finechem Corp., Yamaguchi, Japan and used as received. Dried methylaluminoxane (DMAO) was prepared by concentrating MAO (1.2 M in toluene, Albemarle, Baton Rouge, LA, USA) in vacuo to remove the remaining trimethylaluminum, providing a solid white powder; the white powder was dissolved in dried toluene prior to use. Triphenylcarbenium tetrakis(pentafluorophenyl)borate ([Ph<sub>3</sub>C]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>) was purchased from Asahi Glass Corp., Tokyo, Japan and used as received. *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride (**1**) was purchased from Strem Chemicals Inc., Newburyport, MA, USA. Ansa-zirconocene catalysts **2–8** employed in this study (Figure 1) were prepared according to the methods described in our previous papers: *rac*-dimethylsilyl-bis[1-(2-methyl-4,5-benzoindenyl)]zirconium dichloride (**2**) [14], *rac*-dimethylsilyl-bis[1-(2-methyl-4-phenylindenyl)]zirconium dichloride (**3**) [14], *rac*-diniethylsilyl-bis(2-ethyl-4-phenylindenyl)zirconium dichloride (**4**) [15], *rac*-dimethylsilyl-bis[1-(2-*n*-propyl-4-(1-naphthyl)indenyl)]zirconium dichloride (**5**) [15], *rac*-dimethylsilyl-[1-(2-ethyl-4-(5-(2,2-dimethyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalenyl)indenyl))][1-(2-*n*-propyl-4-(5-(2,2-dimethyl-2,3-dihydro-1H-cyclopenta[*a*]naphthalenyl)indenyl)]zirconium dichloride (**6**) [16], *rac*-dimethylsilyl-bis[1-(2-ethyl-4-(9-phenanthryl)indenyl)]zirconium dichloride (**7**) [15], *rac*-dimethylsilyl-bis[1-(2-*n*-propyl-4-(9-phenanthryl)indenyl)]zirconium dichloride (**8**) [15]. [η<sup>1</sup>: η<sup>5</sup>-tert-butyl(dimethylfluorenylsilyl)-amido]dimethyltitanium ([*t*-BuNSiMe<sub>2</sub>Flu]TiMe<sub>2</sub>) was synthesized according to the methods described in the literature [17].

#### 3.3. Polymerization Procedure

##### 3.3.1. Ethylene/Butadiene Copolymerization (Table 1)

A prescribed amount of hexane was introduced into a SUS autoclave (1000 mL; entry 1–8, 4000 mL; entry 9–12) equipped with two propeller-like stirrers under nitrogen at an atmospheric pressure of 25 °C. A toluene solution of DMAO or <sup>i</sup>Bu<sub>3</sub>Al was loaded. Then a prescribed amount of butadiene was charged. Subsequently, the mixture was heated to a prescribed polymerization temperature, and a prescribed amount of hydrogen (the volume under atmospheric pressure at 20 °C) was added, then ethylene was introduced into the reactor up to the polymerization pressure (0.78MPa). For runs in which <sup>i</sup>Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> was employed as a co-catalyst, Zr complex/toluene, <sup>i</sup>Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>/toluene, and toluene wash (2 mL) were sequentially injected into the reactor to start the reaction. For runs in which

the DMAO was employed as a co-catalyst, Zr complex/toluene and toluene wash (2 mL) were injected sequentially into the reactor to start the reaction. The pressure was kept constant at 0.78 MPa by feeding ethylene on demand. After the reaction was performed at a prescribed polymerization temperature for 20 min, the polymerization was terminated by adding a small amount of methanol. The resulting mixture was poured into a large excess of methanol containing hydrochloric acid to precipitate the polymer. The polymer was separated by filtration, and admixed with a stabilizing agent, 0.1 wt % of antioxidant (SUMILIZER® GS(F): 2-[1-(2-Hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, sumitomo chemical co. ltd, Tokyo, Japan), then dried under reduced pressure at 20 °C for 24 h.

### 3.3.2. Propylene/Butadiene Copolymerization (Table 2)

A prescribed amount of hexane was introduced into a SUS autoclave (1000 mL) equipped with two propeller-like stirrers under nitrogen at an atmospheric pressure of 25 °C. A toluene solution of MMAO was loaded, then a prescribed amount of butadiene was charged. Subsequently, the mixture was heated to a prescribed polymerization temperature, and a prescribed amount of hydrogen (the volume under atmospheric pressure at 20 °C) was added. Then, propylene was introduced into the reactor up to the polymerization pressure (0.78 MPa). Zr complex/toluene and toluene wash (2 mL) were injected sequentially into the reactor to start the reaction. The pressure was kept constant at 0.78 MPa by feeding propylene on demand. After the reaction was performed at 60 °C for 20 min, the polymerization was terminated by adding a small amount of methanol. The work-up procedure for the propylene/butadiene copolymer was identical to that for the ethylene/butadiene copolymerization.

## 3.4. Polymer Characterization

### 3.4.1. Microstructure Analysis of Ethylene/Butadiene Copolymer by <sup>13</sup>C-NMR

<sup>13</sup>C-NMR spectra of the ethylene/butadiene copolymers were recorded on an ECA500 spectrometer (125 MHz) from Japan Electron Optics Laboratory Co. Ltd. (JEOL, Tokyo, Japan), using 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> as a solvent at 140 °C. Chemical shifts were referenced to the residual solvent peak ( $\delta_{13C} = 72.4$  ppm). The spectrum was analyzed with reference to the chemical shifts of the signals assigned to the vinyl groups, the cyclopropane skeleton, the cyclopentane skeleton, the 1,4-addition units and the 1,3-addition units in the ethylene/butadiene copolymers which were described in previous papers [8,18]. The determination of the butadiene content (1) and the vinyl groups content (2); the cyclopropane skeleton content (3); the cyclopentane skeleton content (4); the 1,4-addition units content (5) and the 1,3-addition units content (6) relative to all the butadiene-derived structural units was performed in accordance with the following Equations (1) to (6).

Proportion of structural units derived from butadiene relative to all the monomer units in the copolymer is given by Equation (1).

$$\text{BD content (mol \%)} = 100 \times (A + B + C + D + E) / \{(A + B + C + D + E) + [(1000 - (A + B + C + D + E) \times 4)]/2\} \quad (1)$$

Fraction of vinyl groups ( $f_v$ ), cyclopropane rings ( $f_{\text{cycPro}}$ ), cyclopentane rings ( $f_{\text{cycPen}}$ ), 1,4-addition units ( $f_{1,4}$ ), and 1,3-addition units ( $f_{1,3}$ ) relative to all the structural units derived from butadiene is given by Equations (2)–(6), respectively.

$$f_v (\text{mol } \%) = 100 \times A / (A + B + C + D + E) \quad (2)$$

$$f_{\text{cycPro}} (\text{mol } \%) = 100 \times B / (A + B + C + D + E) \quad (3)$$

$$f_{\text{cycPen}} (\text{mol } \%) = 100 \times C / (A + B + C + D + E) \quad (4)$$

$$f_{1,4} (\text{mol } \%) = 100 \times D / (A + B + C + D + E) \quad (5)$$

$$f_{1,3} (\text{mol } \%) = 100 \times E / (A + B + C + D + E) \quad (6)$$

The letters A to E indicate the respective integrated values per one carbon of the structural units derived from the structures illustrated below, based on the total integrated value, 1000, of all the peaks in the  $^{13}\text{C}$ -NMR spectrum of the ethylene/butadiene copolymers.

A: (Integrated value per one carbon of the vinyl groups) = integrated value of the peak at 113.8 ppm ( $\text{R}^1\text{-CH}(\text{HC}=\text{CH}_2)\text{-R}^2$ )

B: (Integrated value per one carbon of the cyclopropane skeleton) = [(integrated value of the peak at 17.2 ppm (cis CH in Chemical Formula ( $\alpha$ ))) + (integrated value of the peak at 19.2 ppm (trans CH in Chemical Formula ( $\alpha$ )))]/2



C: (Integrated value per one carbon of the cyclopentane skeleton) = [(integrated value of the peak at 43.1 ppm (cis CH in Chemical Formula ( $\beta$ ))) + (integrated value of the peak at 46.3 ppm (trans CH in Chemical Formula ( $\beta$ )))]/2



D: (Integrated value per one carbon of the 1,4-addition units) = [integrated value of the peaks at 131–130 ppm ( $\text{R}^1\text{-HC}=\text{CH-R}^2$ )]/2

E: (Integrated value per one carbon of the 1,3-addition units) = [integrated value of the peak at 137.3 ppm ( $\text{R}^1\text{-HC}=\text{CH-CH}(\text{Me})\text{-R}^2$ )]

### 3.4.2. Microstructure Analysis of Ethylene/Butadiene Copolymers by $^1\text{H}$ -NMR

$^1\text{H}$ -NMR spectra of the ethylene/butadiene copolymers were recorded on a JEOL270 spectrometer (270 MHz) from Japan Electron Optics Laboratory Co. Ltd. (JEOL, Tokyo, Japan), using *o*-dichlorobenzene- $d_4$  as a solvent at 120 °C. Chemical shifts were referenced to the residual solvent peak ( $\delta_{\text{1H}} = 7.15$  ppm). Quantity of the vinyl groups Equation (7) and the internal olefins Equation (8) in ethylene/butadiene copolymers were quantified as per 1000 Carbon in accordance with the following Equations (7) and (8), respectively.

$$\text{Quantity of vinyl groups per 1000 Carbon} = F + G \quad (7)$$

$$\text{Quantity of internal olefins per 1000 Carbon} = H \quad (8)$$

The letters F to H indicate the respective integrated values per one proton of the structural units derived from the structures illustrated below, based on the total integrated value, 2000, of all the peaks in the  $^1\text{H-NMR}$  spectrum of the ethylene/butadiene copolymer.

F: (Integrated value per one proton of the pendant vinyl groups) = integrated value of the peak at 5.4–5.6 ppm ( $\text{R}^1\text{-CH}(\underline{\text{H}}\text{C}=\text{CH}_2)\text{-R}^2$ )

G: (Integrated value per one proton of the terminal vinyl groups) = integrated value of the peak at 5.6–5.8 ppm ( $\text{R}^1\text{-(}\underline{\text{H}}\text{C}=\text{CH}_2)$ )

H: (Integrated value per one proton of the internal olefins) = [integrated value of the peaks at 5.2–5.4 ppm ( $\text{R}^1\text{-}\underline{\text{H}}\text{C}=\underline{\text{C}}\text{H-R}^2$ )]/2

### 3.4.3. Microstructure Analysis of Propylene/Butadiene Copolymer by $^{13}\text{C-NMR}$

$^{13}\text{C-NMR}$  spectra of the propylene/butadiene copolymers were recorded on an ECA500 spectrometer (125 MHz) from Japan Electron Optics Laboratory Co. Ltd. (JEOL, Tokyo, Japan), using 1,1,2,2-tetrachloroethane- $d_2$  as a solvent at 140 °C. Chemical shifts were referenced to the residual solvent peak ( $\delta_{13\text{C}} = 72.4$  ppm). The spectrum was analyzed with reference to the chemical shifts of the signals assigned to the vinyl groups, the cyclopropane skeleton, the methylcyclopentane skeleton [19], the 1,4-addition units and the 1,3-addition units in the propylene/butadiene copolymers which were described in previous papers [8,10,11]. The determination of the butadiene content (Equation (9)) and the vinyl groups content (Equation (10)), the cyclopropane skeleton content (Equation (11)), the methylcyclopentane skeleton content (Equation (12)), the 1,4-addition units content (Equation (13)), the 1,3-addition units content (Equation (14)), and the hydrogenated 1,4-addition units content (Equation (15)) relative to all the butadiene-derived structural units was performed in accordance with the following Equations (9) to (15).

Proportion of structural units derived from butadiene relative to all the monomer units in the copolymer is given by Equation (9).

$$\text{BD content (mol \%)} = 100 \times (I + J + K + L + M + N) / \{ (I + J + K + L + M + N) + [(1000 - (I + J + K + L + M + N) \times 4)] / 3 \} \quad (9)$$

Fraction of vinyl groups ( $f_v$ ), cyclopropane rings ( $f_{\text{cycPro}}$ ), cyclopentene rings ( $f_{\text{cycPen}}$ ), 1,4-addition units ( $f_{1,4}$ ), 1,3-addition units ( $f_{1,3}$ ), and hydrogenated 1,4-addition units ( $f_{\text{H-1,4}}$ ) relative to all the structural units derived from butadiene is given by Equations (10)–(15), respectively.

$$f_v \text{ (mol \%)} = 100 \times I / (I + J + K + L + M + N) \quad (10)$$

$$f_{\text{cycPro}} \text{ (mol \%)} = 100 \times J / (I + J + K + L + M + N) \quad (11)$$

$$f_{\text{MecycPen}} \text{ (mol \%)} = 100 \times K / (I + J + K + L + M + N) \quad (12)$$

$$f_{1,4} \text{ (mol \%)} = 100 \times L / (I + J + K + L + M + N) \quad (13)$$

$$f_{1,3} \text{ (mol \%)} = 100 \times M / (I + J + K + L + M + N) \quad (14)$$

$$f_{\text{H-1,4}} \text{ (mol \%)} = 100 \times N / (I + J + K + L + M + N) \quad (15)$$

The letters I to N indicate the respective integrated values per one carbon of the structural units derived from the structures illustrated below, based on the total integrated value, 1000, of all the peaks in the  $^{13}\text{C}$ -NMR spectrum of the propylene/butadiene copolymers.

I: (Integrated value per one carbon of the vinyl groups) = integrated value of the peak at 113.2 ppm ( $\text{R}^1\text{-CH(HC}=\underline{\text{C}}\text{H}_2\text{)-R}^2$ )

J: (Integrated value per one carbon of the cyclopropane skeleton) = [(integrated value of the peak at 12.9 ppm ( $\text{CH}_2$  in Chemical Formula ( $\alpha'$ ))



K: (Integrated value per one carbon of the methylcyclopentane skeleton) = integrated value of the peak at 32.5 ppm ( $\text{CH}$  in Chemical Formula ( $\beta'$ ))



L: (Integrated value per one carbon of the 1,4-addition units) = [integrated value of the peaks at 128–133 ppm ( $\text{R}^1\text{-HC}=\underline{\text{C}}\text{H-R}^2$ )]/2

M: (Integrated value per one carbon of the 1,3-addition units) = [integrated value of the peak at 134–136 ppm ( $\text{R}^1\text{-HC}=\underline{\text{C}}\text{H-CH(Me)-R}^2$ )]

N: (Integrated value per one carbon of the hydrogenated 1,4-addition units) = [integrated value of the peaks at 37.1 ppm ( $\text{CH}_2$  in Chemical Formula ( $\gamma'$ ))]/2



#### 3.4.4. Microstructure Analysis of Propylene/Butadiene Copolymer by $^1\text{H}$ -NMR

$^1\text{H}$ -NMR spectra of the propylene/butadiene copolymers were recorded on a JEOL270 spectrometer (270 MHz) from Japan Electron Optics Laboratory Co. Ltd. (JEOL, Tokyo, Japan), using *o*-dichlorobenzene- $d_4$  as a solvent at 120 °C. Chemical shifts were referenced to the residual solvent peak ( $\delta_{\text{1H}} = 7.15$  ppm). The number of vinyl groups (Equation (16)) and the internal olefins (Equation (17)) in propylene/butadiene copolymers were quantified as per 1000 Carbon in accordance with the following Equations (16) and (17), respectively.

$$\text{Quantity of vinyl groups per 1000 Carbon} = \text{O} \quad (16)$$

$$\text{Quantity of internal olefins per 1000 Carbon} = \text{P} \quad (17)$$

The letters O and P indicate the respective integrated values per one proton of the structural units derived from the structures illustrated below, based on the total integrated value, 2000, of all the peaks in the  $^1\text{H}$ -NMR spectrum of the propylene/butadiene copolymers.

O: (Integrated value per one proton of the vinyl groups) = [integrated value of the peak at 4.7–5.0 ppm ( $R^1\text{-CH}(\text{HC}=\underline{\text{C}}\text{H}_2)\text{-R}^2$ ) + integrated value of the peak at 5.4–5.8 ppm ( $R^1\text{-CH}(\underline{\text{H}}\text{C}=\text{CH}_2)\text{-R}^2$ )]/3

P: (Integrated value per one proton of the internal olefins) = [integrated value of the peaks at 5.2–5.4 ppm ( $R^1\text{-}\underline{\text{H}}\text{C}=\underline{\text{C}}\text{H}\text{-R}^2$ )]/2

#### 3.4.5. GPC Analysis

Molecular weights ( $M_w$  and  $M_n$ ) and molecular weight distributions (MWDs) of the polymers were determined using a Waters GPC2000 gel permeation chromatograph (Waters, Milford, MA, USA) equipped with four TSKgel columns (two sets of TSKgel GMH6-HT and two sets of TSKgel GMH6-HTL) at 140 °C using PS calibration. *o*-Dichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min.

#### 3.4.6. DSC Analysis

The glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) of the polymers were determined by differential scanning calorimetry (DSC) with a Shimadzu DSC-60 instrument (Shimadzu Corporation, Kyoto, Japan). In a  $N_2$  (nitrogen) atmosphere, the polymer was heated from ordinary temperature to 200 °C at a temperature increasing rate of 50 °C/min, held at the temperature for 5 min, cooled to –100 °C at a temperature decreasing rate of 10 °C/min, and held at the temperature for 5 min. The temperature was again increased to 200 °C at a temperature increasing rate of 10 °C/min. The  $T_g$  and the  $T_m$  were obtained from an endothermic curve recorded during the second scanning.

### 4. Conclusions

In this study, we investigated the substituent effects of  $C_2$ -symmetric zirconocene complexes **1–8**, *rac*-[Me<sub>2</sub>Si(Indenyl')<sub>2</sub>]ZrCl<sub>2</sub>, after activation, on the structures of the resultant copolymers in the copolymerization of ethylene or propylene with butadiene. As a result, we can reveal a larger steric hindrance on the complex tends to suppress the formation of cyclopropyl and cyclopentyl moieties in the copolymer. Additionally, we have found that the steric hindrance exercises a great influence on the ratio of the pendant vinyls and vinylenes (internal olefins), and complex **8** having the largest steric hindrance provides copolymers having predominant pendant vinyl groups with virtually no internal olefins. These results indicate that the steric hindrance on the zirconocene complex employed can control the insertion mode of butadiene and, moreover, mitigate the cyclization process leading to the generation of cyclopropyl and cyclopentyl moieties. The copolymers can be transformed into functionalized copolymers using procedures from the literature. The functionalized copolymers we obtained will have a wide variety of applications covering various fields.

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## Author Contributions

Terunori Fujita, Makoto Mitani and Kenji Michiue conceived and designed the experiments; Kenji Michiue performed the experiments; Makoto Mitani and Kenji Michiue analyzed the data; Kenji Michiue wrote the paper; All the authors discussed the results and improved the final text of the paper.

## Conflicts of Interest

The authors declare no conflict of interest.

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