

# C<sub>2</sub>-Symmetry Dimethylated Zirconocenes Activated with Triisobutyl Aluminum as Effective Homogeneous Catalysts for Copolymerization of Olefins

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Received 24 February 2010; accepted 14 April 2010

DOI: 10.1002/pola.24074

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** We investigated the catalytic performance of both bridged unsubstituted [*rac*-EtInd<sub>2</sub>ZrMe<sub>2</sub>, *rac*-Me<sub>2</sub>SiInd<sub>2</sub>ZrMe<sub>2</sub>] and 2-substituted [*rac*-Et(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub>, *rac*-Me<sub>2</sub>Si(2-MeInd)<sub>2</sub>ZrMe<sub>2</sub>] dimethylbisindenylzirconocenes activated with triisobutyl aluminum (TIBA) as a single activator in (a) homopolymerizations of ethylene and propylene, (b) copolymerization of ethylene with propylene and hexene-1, and (c) copolymerization of propylene with hexene-1 (at Al<sub>TIBA</sub>/Zr = 100–300 mol/mol). Unsubstituted catalysts were inactive in homopolymerizations of ethylene and propylene and copolymerization of propylene with hexene-1 but exhibited high activity in copolymerizations of ethylene with propylene and hexene-1. 2-Substituted zirconocenes activated with TIBA were active in homopolymerizations of ethylene and propyl-

ene and exhibited high activity in copolymerization of ethylene with propylene and hexene-1, and in copolymerization of propylene with hexene-1. Comparative microstructural analysis of ethylene-propylene copolymers prepared over *rac*-Me<sub>2</sub>SiInd<sub>2</sub>ZrMe<sub>2</sub> activated with TIBA or Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> has shown that the copolymers formed upon activation with TIBA are statistical in nature with some tendency to alternation, whereas those with borate activated system show a tendency to formation of comonomer blocks. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 2934–2941, 2010

**KEYWORDS:** activation; copolymerization; dimethylated bisindenylzirconocenes; polymerization; triisobutyl aluminum

**INTRODUCTION** Group IVB metallocenes represent a unique class of catalysts for synthesis of various polyolefins. In contrast to multisite character of Ti–Mg catalysts widely used in industry, the single site nature of active sites in metallocenes ensures better compositional, fractional, and structural homogeneity of synthesized polymers.

Metallocene-containing catalytic systems are normally being activated with polymethylalumoxane (MAO), perfluorophenyl borates, or boranes, see for example, reviews.<sup>1–4</sup> However, practical implementation of metallocene-based catalytic systems is restricted by some drawbacks of the above activators. Whereas the very high cost of MAO as cocatalyst, due to large molar excess of it to precatalyst needed for an efficient activation, makes sometimes the system prohibitively expensive making the heterogenization of borate is problematic.

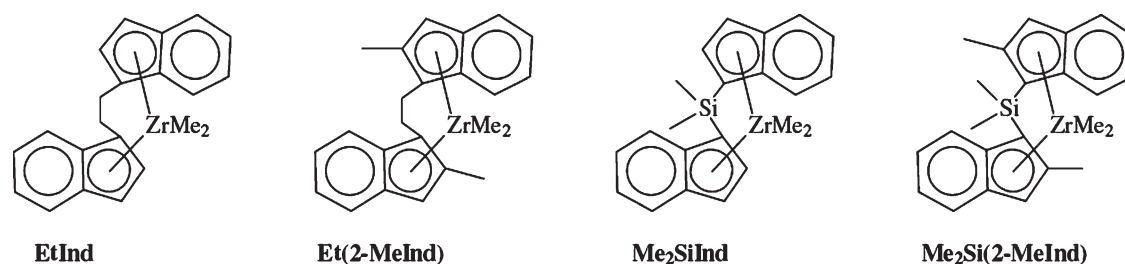
There are literature indications that triisobutyl aluminum (TIBA) may be useful as a component of catalytic system. Thus, partial replacement of MAO by TIBA can considerably increase the activity of metallocene catalysts,<sup>5–10</sup> promote incorporation of comonomer,<sup>7,10</sup> and afford polymerizations in aliphatic solvents due to a higher solubility of the MAO

modified with TIBA.<sup>7,9</sup> The effect was explained<sup>6,11</sup> by passivation of trimethyl aluminum (TMA) that is present in commercially available MAO in amounts of up to 30–40 mol %. TMA is known to block cationic active sites via formation of L<sub>2</sub>M<sup>+</sup>Me(μ-Me)AlMe<sub>2</sub> complexes. Exchange of TMA methyl groups by TIBA isobutyl groups leads to formation of Al<sub>2</sub>(<sup>t</sup>Bu)<sub>6-x</sub>(Me)<sub>x</sub> dimers and elimination of TMA from reactions.

Effective activation of metallocene and “postmetallocene” catalysts with preliminary preactivation with MAO at low Al<sub>MAO</sub>/M molar ratios (not enough for activation with TIBA) was further reported for polymerization of ethylene and propylene.<sup>12–16</sup> ESR and <sup>1</sup>H NMR analysis of products formed in reaction between MAO and TIBA and in the catalytic system *rac*-Me<sub>2</sub>SiInd<sub>2</sub>ZrCl<sub>2</sub>/MAO/TIBA have shown<sup>15</sup> that a higher catalytic activity is due to the formation of mixed alkylalumoxane clusters (such as AlMe<sub>1+2x-y</sub>Bu<sub>y</sub>O<sub>(1-x)n</sub>) and <sup>t</sup>Bu<sub>2</sub>Al(μ-Me)<sub>2</sub>Al<sup>t</sup>Bu<sub>2</sub> dimers. On activation, the former ones yield weaker bound (compared with MAO) counterions, whereas the latter ones become less active in blocking active sites via strong coordination with the cation.

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*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 48, 2934–2941 (2010) © 2010 Wiley Periodicals, Inc.



**SCHEME 1** The zirconocenes used in the study.

TIBA is sometimes used as a scavenging agent for moisture and other polar impurities or as an alkylating agent for dichloride precatalysts based both on metallocene<sup>17–22</sup> and “postmetallocene”<sup>23–28</sup> under their activation with  $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ . However, instability of borate in the presence of TIBA and different routes of activation/deactivation reactions depending on the type of catalyst and molar ratio of components<sup>18–20</sup> should be mentioned for these systems.

Although the cationic nature of active species in the homogeneous system  $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_2\text{Cl}$  catalyzing ethylene polymerization had been proposed by Shilov and coworkers<sup>29,30</sup> in the early 1960s, up to now there have been little literature evidences for the effective activation of metallocene complexes with organoaluminum compounds such as perfluorophenylaluminates<sup>1,31–33</sup> or combination of alkylaluminum compounds,  $\text{AlMe}_3/\text{AlMe}_2\text{F}$ .<sup>34</sup>

Previously,<sup>35,36</sup> we have shown that some dimethylated zirconocenes, containing a substituent in position 2 of the indenyl ligand, can be readily activated with TIBA as a single activator for homopolymerizations of ethylene and propylene. The performance of the 2-substituted catalysts activated with TIBA was found to be comparable (and even better) compared with that of catalytic systems activated with MAO. The activity, stability, and stereospecificity (in case of propylene polymerization) of the above catalysts were close to those of zirconocene dichlorides activated with MAO, as well as molecular weights of synthesized polymers. Recently, the use of TIBA as an individual activator for some chelate-like complexes of IVB and VIII Groups transition metals was reported in refs.<sup>37–39</sup>

In this article, we report on the catalytic performance of some bridged dimethylated bisindenylzirconocenes (Scheme 1) activated with TIBA (as a single activator) in copolymerizations of (a) ethylene with propylene and hexene-1 and (b) propylene with hexene-1. In experiments, we used bridged zirconocenes *rac*- $\text{EtInd}_2\text{ZrMe}_2$ , *rac*- $\text{Me}_2\text{SiInd}_2\text{ZrMe}_2$ , and their 2-Me-substituted derivatives.

## RESULTS AND DISCUSSION

The catalytic performance of dimethylated zirconocenes **EtInd**, **Me<sub>2</sub>SiInd**, **Et(2-Me)Ind**, and **Me<sub>2</sub>Si(2-Me)Ind** activated with TIBA ( $\text{Al}_{\text{TIBA}}/\text{Zr} = 100\text{--}300$  mol/mol) in homopoly-

merizations and copolymerizations of olefins (along with molecular weight data) are characterized in Table 1.

### Polymerization of Ethylene and Propylene

As is seen in Table 1, unsubstituted dimethylated zirconocene **EtInd** and **Me<sub>2</sub>SiInd** are inactive (experiment numbers 1 and 2) in homopolymerization of ethylene (E). 2-Me-substituted derivatives activated with TIBA led to formation of polyethylene (PE) (experiment numbers 3, 5, 6) and polypropylene (PP) (experiment number 4) at specific productivities of 1550, 1760, 1640, and 883 kg polymer/(mol Zr h [monomer]), respectively. The polymerization of propylene (P) over **Et(2-Me)Ind** proceeds at a lower specific rate (curve 2, Fig. 1) than that of ethylene (curve 1, Fig. 1). However, in homopolymerization TIBA is a less effective activator than MAO for this precatalyst. The overall activity in propylene polymerization was one order of magnitude lower than that with MAO as activator.<sup>40</sup> The reproducibility of ethylene polymerization over **Me<sub>2</sub>Si(2-Me)Ind**/TIBA can be illustrated by the fact of actual coincidence between curves 3 and 4 in Figure 1.

Polymers formed over TIBA-activated catalysts exhibited relatively high molecular weight and a polydispersity close to that of the polymers prepared over single-site catalysts. Synthesized PE showed high melting points  $T_m$  [141 °C,  $\Delta H = 118$  J/g (experiment number 3 in Table 1); 143 °C,  $\Delta H = 145$  J/g (experiment number 6)]. Note that the values of  $T_m$  are about similar level after the second heating of PE samples: 141 °C in experiment number 3 and 141 °C in experiment number 6. The isotactic PP formed over **Et(2-Me)Ind**/TIBA showed a macro tacticity index of  $D_{998}/D_{973} = 0.91$  and  $T_m = 148$  °C ( $\Delta H = 52$  J/g).

### Copolymerization of Ethylene with Propylene

In contrast to homopolymerization, both unsubstituted zirconocenes, **EtInd** and **Me<sub>2</sub>SiInd**, exhibited high catalytic activity in copolymerization (experiment numbers 7 and 8). Rough estimates for the activity of **EtInd**, **Et(2-Me)Ind**, and **Me<sub>2</sub>Si(2-Me)Ind** catalysts (at  $E/P = 0.7/1$  mol/mol) gave the values of 32,000, 50,000, and 53,000 kg copolymer/(mol Zr h  $\Sigma[\text{monomer}]$ ), respectively. In copolymerization, the activity of 2-Me-substituted zirconocenes was 10- to 30-folds higher than that in separate homopolymerizations of E and P. Much higher activity of the catalysts in copolymerization can be associated only with the presence of comonomer.

**TABLE 1** Homo- and Copolymerization of Olefins Over Dimethylated Zirconocenes with TIBA as an Activator<sup>a</sup>

Experiment Number	Catalyst	Ol. <sup>b</sup>	Zr·10 <sup>6</sup> (mol)	Al/Zr <sup>c</sup> (mol/mol)	P <sup>d</sup> (atm)	t <sup>e</sup> (min)	Y <sup>f</sup> (g)	Com. <sup>g</sup> (mol %)	M <sub>n</sub>	M <sub>w</sub> /M <sub>n</sub>
1	EtInd <sub>2</sub> ZrMe <sub>2</sub>	E <sup>h</sup>	4.8	250	12.0	60	Tr. <sup>i</sup>			
2	Me <sub>2</sub> SiInd <sub>2</sub> ZrMe <sub>2</sub>	E	5.2	250	12.0	60	Tr.			
3	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E	5.1	300	12.0	18.0	3.4		125,600	2.71
4	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	P <sup>j</sup>	4.1	100	5.8	10	2.1		76,400	2.11
5	Me <sub>2</sub> Si(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E	4.4	300	8.4	38	4.0		64,400	3.49
6	Me <sub>2</sub> Si(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E	4.6	300	9.0	31	4.9		88,000	3.00
7	EtInd <sub>2</sub> ZrMe <sub>2</sub>	E/P	5.0	100	12.0	4.5	17.2	9	22,200	3.02
8	Me <sub>2</sub> SiInd <sub>2</sub> ZrMe <sub>2</sub> <sup>k</sup>	E/P	10.2	80	12.0	4.8	17.5	8	21,000	2.57
9	Me <sub>2</sub> SiInd <sub>2</sub> ZrMe <sub>2</sub> (B) <sup>l</sup>	E/P	4.4	100	12.0	2.4	19.2	13	11,000	6.10
10	Me <sub>2</sub> SiInd <sub>2</sub> ZrMe <sub>2</sub> (B) <sup>m</sup>	E/P	8.2	100	12.0	2.7	18.7	17	16,300	3.27
11	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E/P	5.2	100	12.0	1.9	11.1	10	37,000	3.12
12	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E/P	3.1	200	12.0	4.0	14.6	n/d <sup>n</sup>	62,200	2.07
13	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E/P	3.6	400	12.0	4.5	15.3	n/d	29,160	2.75
14	Me <sub>2</sub> Si(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E/P	3.0	100	12.0	2.9	11.0	13	6300	3.68
15	EtInd <sub>2</sub> ZrMe <sub>2</sub>	E/H <sup>o</sup>	4.9	100	12.0	15.3	12.8	7	40,300	2.42
16	Me <sub>2</sub> SiInd <sub>2</sub> ZrMe <sub>2</sub>	E/H	4.9	100	12.0	33.1	5.2	6	69,300	2.38
17	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E/H	4.6	100	12.0	2.0	11.6	5	27,200	4.18
18	Me <sub>2</sub> Si(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	E/H	3.4	130	12.0	2.2	13.2	9	57,000	2.61
19	EtInd <sub>2</sub> ZrMe <sub>2</sub>	H/P	4.1	100	5.8	60.0	Tr.			
20	Me <sub>2</sub> SiInd <sub>2</sub> ZrMe <sub>2</sub>	H/P	3.7	100	5.8	60.0	Tr.			
21	Et(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	H/P	4.7	100	5.8	20.8	5.1	10	22,500	2.24
22	Me <sub>2</sub> Si(2-MeInd) <sub>2</sub> ZrMe <sub>2</sub>	H/P	2.5	180	5.8	21.0	3.5	12	94,400	2.47
23	EtInd <sub>2</sub> ZrMe <sub>2</sub>	H/P/E	4.1	100	12.0	5.0	7.2	8 <sub>H</sub> /28 <sub>P</sub> <sup>p</sup>		

<sup>a</sup> Polymerization conditions: 30 °C, 60 mL toluene, com.1/com.2 = 0.7/1 mol/mol.

<sup>b</sup> The olefin or olefins in the feed.

<sup>c</sup> Mole ratio Al<sub>TIBA</sub>/Zr.

<sup>d</sup> Monomer pressure.

<sup>e</sup> Polymerization time.

<sup>f</sup> Yield of polymer.

<sup>g</sup> Comonomer content in copolymer.

<sup>h</sup> E, ethylene.

<sup>i</sup> Traces of polymer.

<sup>j</sup> P means propylene.

<sup>k</sup> E/P = 0.2 mol/mol.

<sup>l</sup> Activator Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>/TIBA (B/Zr = 1.2 mol/mol), E/P = 0.4/1 mol/mol.

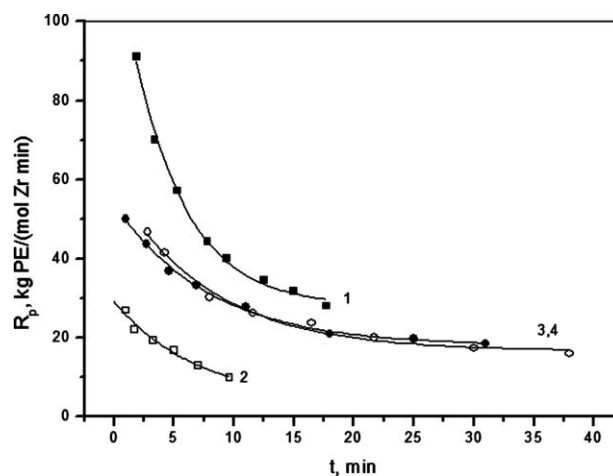
<sup>m</sup> As in Ex. 9 but E/P = 0.7/1 mol/mol.

<sup>n</sup> Not determined.

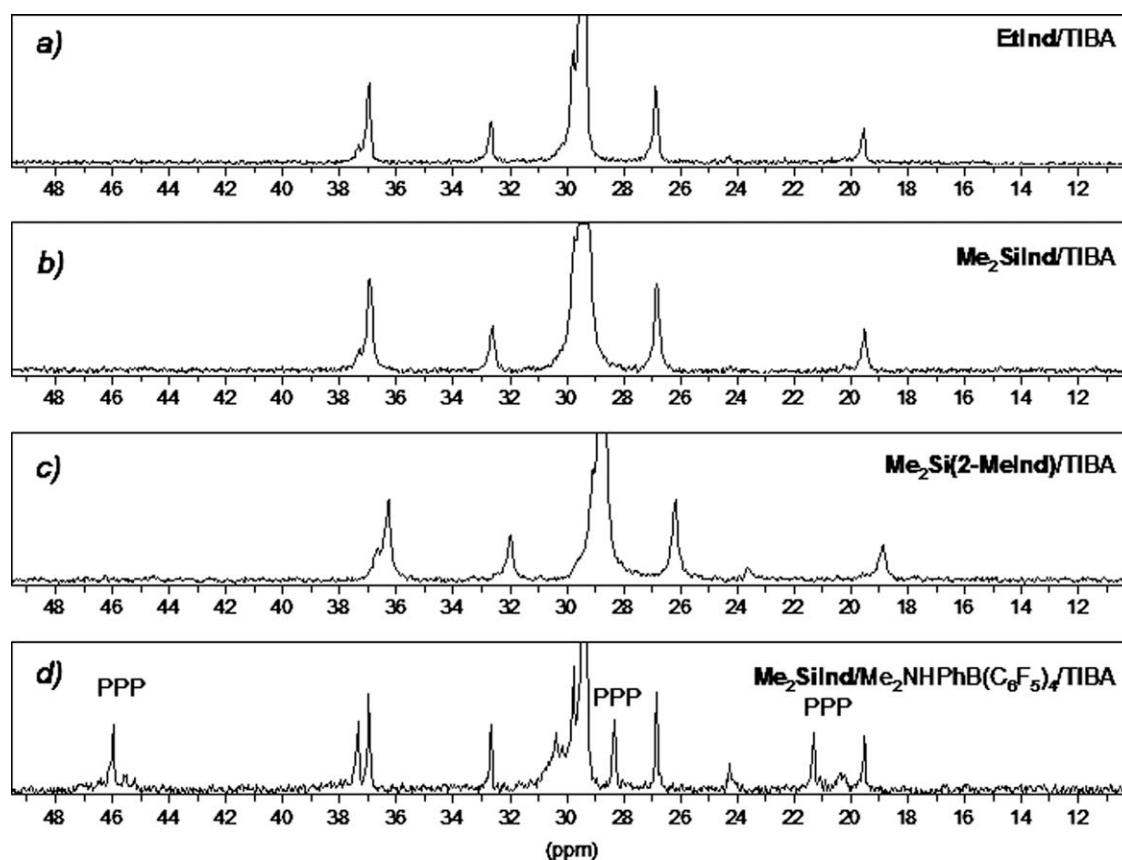
<sup>o</sup> H means hexene-1.

<sup>p</sup> The contents of corresponding comonomers specified in subscript.

Specific character of TIBA as a cocatalyst may be demonstrated by considering the microstructure of the copolymers formed. We compared the microstructure of the E-P copolymers prepared over zirconocenes activated with TIBA and the copolymers synthesized over the **Me<sub>2</sub>Si(2-MeInd)** catalyst activated with Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>. Figure 2 shows the <sup>13</sup>C NMR spectra of E-P copolymers prepared over (a) **EtInd**/TIBA (9 mol % P in copolymer), (b) **Me<sub>2</sub>SiInd**/TIBA (8 mol % P in copolymer), (c) **Me<sub>2</sub>Si(2-MeInd)**/TIBA (13 mol % P in copolymer), and (d) **Me<sub>2</sub>SiInd**/Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (17 mol % P in copolymer). The spectrum of the copolymer formed over borate-activated catalyst [Fig. 2(d)] is seen to contain signals (at 45.96, 28.32, and 20–22 ppm) from carbon atoms corresponding to PPP sequences. Such signals are not exhibited by the copolymers synthesized over TIBA-activated catalysts, even at a close P content of copolymer [Fig. 2(c)].



**FIGURE 1** Time dependence of specific polymerization rate,  $R_p$ , for ethylene (1, 3, 4) and propylene (2) over **Et(2-MeInd)**/TIBA (1, 2) and **Me<sub>2</sub>Si(2-MeInd)**/TIBA (3, 4): experiment numbers 3–6 in Table 1.



**FIGURE 2**  $^{13}\text{C}$  NMR spectra of ethylene-propylene copolymers prepared over (a) **EtInd/TIBA** (9 mol % propylene in copolymer), (b) **Me<sub>2</sub>SiInd/TIBA** (8 mol % propylene in copolymer), (c) **Me<sub>2</sub>Si(2-MeInd)/TIBA** (13 mol % propylene in copolymer), and (d) **Me<sub>2</sub>SiInd/Me<sub>2</sub>NHPb(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>/TIBA** (17 mol % propylene in copolymer): experiment numbers 7, 8, 14, and 10 in Table 1, respectively.

The sequence distribution and composition of binary copolymers (as derived from  $^{13}\text{C}$  NMR data) are presented in Table 2. It follows that the E-P copolymers obtained with TIBA do not contain PPP and even EPP sequences (experiment numbers 7, 8, and 14). The amount of P units in the copolymer attains a value of 9, 8, and 13 mol %, respectively. Copolymer with a higher P content was obtained in case of the **Me<sub>2</sub>Si(2-MeInd)** catalyst. The average sequence lengths for this copolymer (estimated according to ref. 41) were found to be  $n_E = 10.7$ ,  $n_P = 1$  (experiment number 7) and  $n_E = 6.4$ ,  $n_P = 1$  (experiment number 14). In other words, short blocks of E units are separated by single P units. An increase in the P content of copolymers obtained over the catalysts activated with TIBA is accompanied by a relative growth of signals from PEP sequences at 24.24 ppm and a decrease in the content of EEE triads. The triad distribution of the E-P copolymer obtained with borate activator is quite different. Total content of PPP and PPE triads reaches 12%, whereas the content of PEE and EPE triads is considerably lower than in the E-P copolymer obtained with TIBA. The average sequence lengths in the “borate” copolymer were found to be  $n_E \sim 15$  and  $n_P \sim 3$ , respectively. In other words, the catalyst with borate counterions promotes serial insertions of P

while that with TIBA, only single ones followed by multiple E insertions. As a consequence, the former copolymer shows blocky-like structure, whereas the latter ones are statistical and prone to alternating. It should also be kept in mind that the borate copolymer may exhibit fractional inhomogeneity (mixture of two copolymers) because the catalyst can be activated by both borate and TIBA (added as an impurity scavenger). In this case, part of the copolymer formed upon activation with borate might contain a larger amount of P blocks of higher length than that for nascent polymer (experiment number 10 in Table 2). The amount of PPP triads in the borate copolymer (10 mol %) is greater than that of EPP triads (2 mol %), which indicates the presence of lengthy propylene blocks.

A difference in the microstructure of copolymers obtained over different catalysts can be illustrated by the IR spectra of polymer films. Figure 3 shows the IR spectra of E-P copolymers prepared over (1) **Me<sub>2</sub>Si(2-MeInd)/TIBA** (13 mol % P in copolymer) and (2) **Me<sub>2</sub>SiInd/Me<sub>2</sub>NHPb(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>** (17 mol % P in copolymer): experiment numbers 14 and 10 in Table 1. The absorption band at  $998\text{ cm}^{-1}$  corresponding to sequence lengths of 11–12 repeat units in crystalline regions of isotactic PP reveals the presence of isotactic P

**TABLE 2** Microstructure of Binary Copolymers (According to  $^{13}\text{C}$  NMR Data)

Copolymer <sup>a</sup>	XXX	YXX + XXY	YXY	XYX	XYY + YYX	YYY	X	Y
X = E, Y = P (7)	0.75	0.15	0.01	0.09	0	0	0.91	0.09
X = E, Y = P (8)	0.74	0.18	0.01	0.08	0	0	0.92	0.08
X = E, Y = P (10)	0.75	0.05	0.03	0.05	0.02	0.10	0.83	0.17
X = E, Y = P (14)	0.65	0.17	0.05	0.13	0	0	0.87	0.13
X = E, Y = H (15)	0.78	0.14	0.01	0.07	0	0	0.93	0.07
X = E, Y = H (16)	0.82	0.11	0.01	0.06	0	0	0.94	0.06
X = E, Y = H (17)	0.84	0.11	0	0.05	0	0	0.95	0.05
X = E, Y = H (18)	0.72	0.14	0.05	0.09	0	0	0.91	0.09
X = P, Y = H (21)	0.69	0.21	0	0.10	0	0	0.90	0.10
X = P, Y = H (22)	0.82	0.11	0.01	0.06	0	0	0.94	0.06

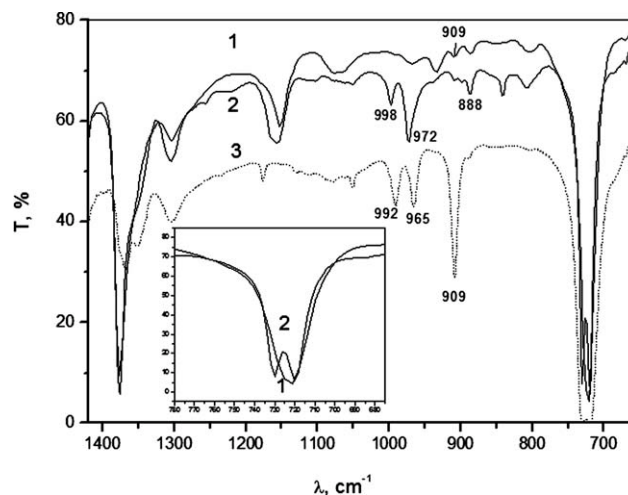
<sup>a</sup> Values in parentheses indicate experiment numbers in Table 1.

blocks in the copolymer obtained over the borate-activated catalyst, which is in agreement with NMR data. The band at  $720\text{ cm}^{-1}$  (rock vibrations of  $\text{CH}_2$  groups) belonging to E sequences in the copolymers split into two bands in case of “borate” copolymer and do not split in case of the copolymer obtained with TIBA. The above splitting is typical of crystalline PE and it is absent in PE melts and solutions.<sup>43</sup> The “borate” copolymer demonstrates the presence of crystalline phase even in a melted film, whereas the “TIBA” copolymer is amorphous.

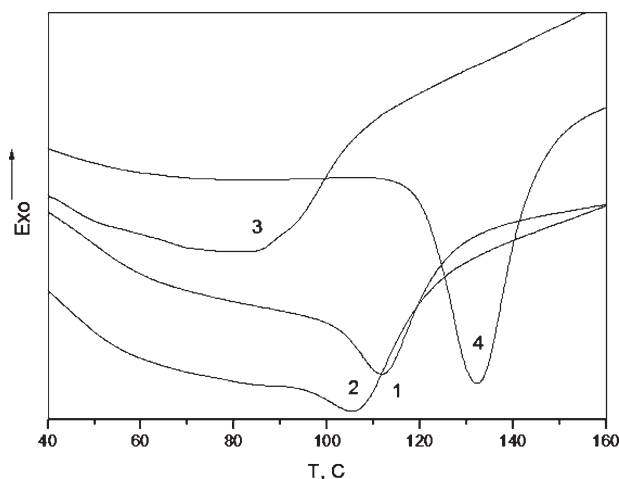
Thermophysical properties of synthesized copolymers were also found to correlate with their microstructure. Figure 4 presents the DSC thermograms of copolymers prepared over different catalytic systems. The copolymers obtained over TIBA-containing catalysts (curves 1–3) exhibit broad, vaguely pronounced melting peaks, whereas the copolymers with a “block” microstructure (curve 4) exhibit a well pronounced peak ( $T_m = 132\text{ }^\circ\text{C}$ ,  $\Delta H = 81.3\text{ J/g}$ ).

The molecular weight (MW) of E–P copolymers is markedly lower than that of homopolymers. Along with much higher catalysts activity in copolymerization, this is indicative of higher chain transfer during copolymerization, which either can be associated with  $\beta$ -hydride shift (to transition metal or monomer) or chain transfer to TIBA. Comparatively high MW of copolymers makes it difficult to detect signals from terminal groups in  $^{13}\text{C}$  NMR spectra. However,  $\beta$ -hydride elimination is not the main chain release process for the TIBA-activated system. In the IR spectra, the band intensities at  $909\text{ cm}^{-1}$  and  $992\text{ cm}^{-1}$  (CH wag vibrations in terminal vinyl groups formed upon  $\beta$ -H transfer after the last ethylene insertion) are low even for a copolymer with a minimal MW (Fig. 3, spectrum 1). For comparison, the fragment of IR spectrum of PE (with nearly the same molecular weight:  $M_n = 13,000$ ,  $M_w/M_n = 2.8$ ) obtained with catalytic system  $\text{Me}_2\text{SiCp}^*\text{ZrMe}_2/\text{TIBA}/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$  is also presented in Figure 3 (spectrum 3). Chain transfer to monomer was shown to be the main chain release reaction for the latter catalyst giving rise to terminal vinyl groups.<sup>42</sup> The band at  $965\text{ cm}^{-1}$  corresponds to the terminal *trans*-vinylene groups

formed upon coordination and following isomerization of macromonomer. The intensities of all these end groups are minor for E–P copolymers obtained with TIBA-activated catalysts.  $\beta$ -H transfer after primary insertion of propylene is also inessential, so that the intensity of the band related to CH wag vibrations in vinylidene end groups ( $888\text{ cm}^{-1}$ ) is also small. The intensity of the later band is somewhat higher in the E–P copolymer obtained with borate activator (spectrum 2). As follows from Figure 5, with increasing [TIBA], the MW gradually shifts toward lower values, which evidences the participation of TIBA in the reaction of chain transfer.



**FIGURE 3** IR spectra of ethylene-propylene copolymers prepared over (1)  $\text{Me}_2\text{Si}(2\text{-MeInd})/\text{TIBA}$  and (2)  $\text{Me}_2\text{SiInd}/\text{Me}_2\text{NHPb}(\text{C}_6\text{F}_5)_4$  (13 mol % propylene in copolymer); experiment numbers 14 and 9 in Table 1. Fragment of the IR spectrum (3) of the PE ( $M_n = 13,000$ ,  $M_w/M_n = 2.8$ ) obtained over the catalytic system  $\text{Me}_2\text{SiCp}^*\text{ZrMe}_2/\text{TIBA}/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$  is presented for comparison (dotted curve). Chain transfer to monomer was shown to be a main chain release reaction for this catalyst in ethylene polymerization.<sup>42</sup>



**FIGURE 4** DSC thermograms of ethylene-propylene copolymers prepared over (1) **EtInd**/TIBA (9 mol % propylene in copolymer), (2) **Et(2-MeInd)**/TIBA (10 mol % propylene in copolymer), (3) **Me<sub>2</sub>Si(2-MeInd)**/TIBA (13 mol % propylene in copolymer), and (4) **Me<sub>2</sub>SiInd**/Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> (17 mol % propylene in copolymer): experiment numbers 7, 11, 14, and 10, respectively (see Table 1).

The above differences in the activity of catalysts and structure/properties of copolymers can be attributed to different nature of active sites. As is known<sup>1</sup>, the borate counterion B<sup>-</sup>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> is weaker bound with L<sub>2</sub>Zr<sup>+</sup>Me...X<sup>-</sup> than MeMAO<sup>-</sup>. It can be assumed that the addition of TIBA leads to formation of stronger bound ion pairs L<sub>2</sub>Zr<sup>+</sup>Me...MeAl<sup>-</sup>iBu<sub>3</sub>. 2-Me substituent in the indenyl ligand weakens the bond and thus facilitates initiation under the action of incoming olefin. The process of the displacement of counterion into the outer coordination sphere becomes still more effective with participation of  $\alpha$ -olefins with a higher (compared with ethylene) basicity. In case of noncoordinating borate counterion, possible is incorporation of several P molecules bulkier than E. When counterions are formed in the presence of TIBA, after catalyst initiation single inclusions of P are followed by a much longer sequence of E insertions. In the latter case, active sites can come to “dormant” state due to reversible coordination of TIBA counterion until the oncoming act of dissociation.

#### Copolymerization of Ethylene with Hexene-1

The catalytic activity of 2-Me-substituted zirconocenes in copolymerizations of E with hexene-1 (H) was found to be close to that in copolymerization with P. For unsubstituted complexes it was markedly lower. At other equal conditions (see Table 1), the activity of examined zirconocenes decreases in the order: **Me<sub>2</sub>Si(2-MeInd)** (75000) > **Et(2-MeInd)** (53000) > **EtInd** (7200) > **Me<sub>2</sub>SiInd** {1400 kg polymer/(mol Zr h  $\Sigma$ [monomer])}. Note that unsubstituted dimethylated zirconocenes are also active in E-H copolymerizations. These data suggest that the initiation of a precatalyst requires the involvement of a second monomer with a higher (compared with E) basicity.

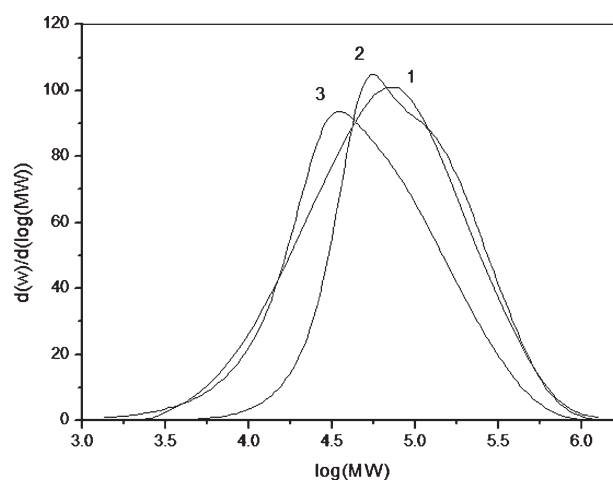
The microstructure of E-H copolymers is characterized in Table 2 (experiment numbers 15–18). The amount of H units in E-H copolymers is somewhat lower than that of P units in E-P copolymers (at other equal conditions). As follows from Table 2, E-H copolymers are formed by sequences of E blocks separated by single H units ( $n_E \sim 12, 12, 14,$  and 7 for experiment numbers 15–18, respectively).

Generally, the MWs of E-H copolymers are higher than those of E-P copolymers. Polydispersity factor for the copolymers is close to 2.0 (except for experiment number 17). Just as in case of E-P copolymers, both the IR and <sup>13</sup>C NMR spectra showed no bands belonging to unsaturated terminal groups. A higher MW of E-H copolymers can be explained by higher steric hindrance for the approach of TIBA, a major chain propagation agent, to Zr<sup>+</sup>-(E)<sub>n</sub>-R-Pol active sites caused by a higher size of R in case of hexene compared with propylene.

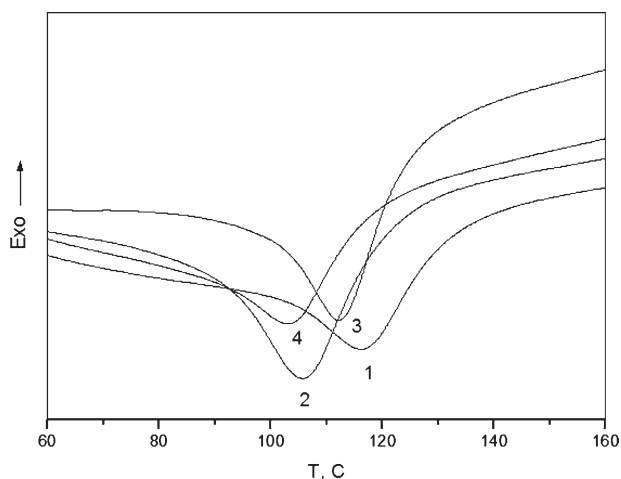
E-H copolymers exhibit a low extent of crystallinity (Fig. 6) and relatively high  $T_m$  values: 117, 106, 113, and 103 °C (experiment numbers 15–18).

#### Copolymerization of Propylene with Hexene-1

Unsubstituted zirconocenes activated with TIBA were inactive in P-H copolymerizations (experiment numbers 19 and 20). Meanwhile, TIBA-activated 2-substituted dimethylated zirconocenes (Al<sub>TIBA</sub>/Zr = 100–200 mol/mol) showed the catalytic activity in these copolymerizations close to that in P polymerization: 530 and 680 kg/(mol Zr h [comonomer]), respectively (cf. experiment numbers 4 and 21 and 22). The catalytic performance of these systems is close to that of unsubstituted dichloro analogs of **EtInd** and **Me<sub>2</sub>SiInd** in the P-H copolymerization activated with MAO at Al<sub>MAO</sub>/Zr  $\approx 10^3$  mol/mol.<sup>9,44</sup>



**FIGURE 5** GPC profiles of ethylene-propylene copolymers prepared over **Et(2-MeInd)**/TIBA at [TIBA] = (1) 8.7 (Al<sub>TIBA</sub>/Zr = 100 mol/mol), (2) 12.0, (Al<sub>TIBA</sub>/Zr = 200 mol/mol), and (3) 24.0  $\times 10^{-3}$  M (Al<sub>TIBA</sub>/Zr = 400 mol/mol): experiment numbers 11–13 in Table 1.



**FIGURE 6** DSC thermograms of ethylene-hexene-1 copolymers prepared over (1) **EtInd**/TIBA (7 mol % hexene-1 in copolymer), (2) **Me<sub>2</sub>SiInd**/TIBA (6 mol % hexene-1 in copolymer), (3) **Et(2-Me)Ind**/TIBA (5 mol % hexene-1 in copolymer), and (4) **Me<sub>2</sub>Si(2-Me)Ind**/TIBA (9 mol % hexene-1 in copolymer): experiment numbers 15–18, respectively (see Table 1).

The H content of copolymers is about 10 mol %. The distribution of triads (Table 2) was calculated using <sup>13</sup>C NMR spectra of copolymers according to the work.<sup>45</sup> As follows from Table 2, P–H copolymers are formed by sequences of P blocks ( $n_p \sim 10$ ) separated by single H units. These copolymers are amorphous elastomeric materials.

#### Ternary Ethylene/Propylene/Hexene-1 Copolymer

Unsubstituted **EtInd** (inactive in both homo-P and P–H copolymerization) exhibited high activity {3300 kg copolymer/(mol Zr h Σ[comonomer])} in ternary reaction with E (experiment number 23) yielding ternary E–P–H copolymer (relative amount of comonomers 64, 28, and 8 mol %, respectively). The triad composition of the copolymer (calculated according to the work in ref. 46) is presented in Table 3. It follows that macromolecules contain no HPH triads and the amount of HEH sequences is only about 2 mol %.

#### CONCLUSIONS

TIBA was found to act as an effective activator for dimethylated bisindenylzirconocenes in homopolymerization and copolymerization of olefins at low  $Al_{TIBA}/Zr$  ratios (100–300 mol/mol). Inactive in homopolymerization of ethylene and propylene, unsubstituted zirconocenes **EtInd**

and **Me<sub>2</sub>SiInd** upon activation with TIBA showed high activity in copolymerizations of ethylene with propylene and hexene-1. As compared with the borate cocatalyst, **Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>**, forming ionic pairs with weakly coordinated counterion, TIBA does not admit successive incorporation of two and more  $\alpha$ -olefin molecules into a copolymer chain, thus restricting the formation of XXX, XXE, and XEX triads (here E = ethylene and X = propylene or hexene-1). As a result, these copolymers exhibit lower crystallinity and melting point. 2-Substituted **Et(2-Me)Ind** and **Me<sub>2</sub>Si(2-Me)Ind** activated with TIBA show better catalytic performance in copolymerizations. In the **Et(2-Me)Ind**/TIBA/hexene-1 system, chain transfer proceeds mainly via TIBA.

#### EXPERIMENTAL

All manipulations with air- and moisture-sensitive materials were performed inside of a helium glove box or using Schlenk line techniques. Homopolymerization and copolymerization procedures were essentially the same as described elsewhere.<sup>35</sup>  $Al^iBu_3$  (TIBA) as a 1 M solution in toluene was purchased from Aldrich. Dimethylanilinium tetrakis(pentafluorophenyl)borate **Me<sub>2</sub>NHPhB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>** was purchased from Boulder Scientific.

The dimethyl derivatives **EtInd**, **Me<sub>2</sub>SiInd**, **Et(2-Me)Ind**, and **Me<sub>2</sub>Si(2-Me)Ind** were synthesized from the respective dichloride complexes (Boulder Scientific) according to a published procedure.<sup>47,48</sup>

MW and MW characteristics of polymers ( $M_w$ ,  $M_n$ ,  $M_w/M_n$ ) were measured by gel permeation chromatography (GPC) using a Waters GPCV-2000 device (PLgel columns, eluent 1,2,4-trichlorobenzene, 135 °C). GPC columns were calibrated using commercially available polystyrene standards.

Melting points ( $T_m$ ) of polymers were measured (under Ar) by differential scanning calorimetry (DSC) on a STA 409 PC analyzer at a heating rate of 10 degree/min.

<sup>13</sup>C NMR spectra of polymer solutions (10 wt %) in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> were taken (at 130 °C) with a Bruker AC-200 spectrometer. Chemical shifts were determined using a signal of residual protons from deuteriochloroethane as a reference [ $\delta = 73.78$  ppm (3)].

The financial support from Russian Federal Agency of Sciences and Innovations (Contract N 0646) and partial financial support from Total Petrochem. Res. are acknowledged.

**TABLE 3** Microstructure of Ternary Ethylene–Propylene–Hexene-1 Copolymer Obtained Over **EtInd**/TIBA (Experiment Number 23 in Table 1)

EEE	EEP + PEE	PEP	EEH + HEE	HEH	EPE	EPP + PPE	PPP	HPP + PPH
0.25	0.28	0.07	0.02	0.02	0.13	0.06	0.09	0
HPH	PHP	HHH	HHP + PHH	EHE	EHH + HHE	P	H	E
0	0	0	0	0.08	0	28	8	64

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