

# Influence of Cocatalyst on the Structure and Properties of Polypropylene/Poly (ethylene-*co*-propylene) In-Reactor Alloys Prepared by MgCl<sub>2</sub>/TiCl<sub>4</sub>/Diester Type Ziegler-Natta Catalyst

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**ABSTRACT:** In this work, a series of polypropylene/poly(ethylene-*co*-propylene) (iPP/EPR) in-reactor alloys were prepared by MgCl<sub>2</sub>/TiCl<sub>4</sub>/diester type Ziegler-Natta catalyst with triethylaluminum/triisobutylaluminum (TEA/TIBA) mixture as cocatalyst. The influence of cocatalyst and external electron donor, e.g., diphenyldimethoxysilane (DDS) or dicyclopentyldimethoxysilane (D-donor), on the structure and mechanical properties of iPP/EPR in-reactor alloys were studied and discussed. According to the characterization results, PP/EPR was mainly composed of random poly(ethylene-*co*-propylene), segmented poly(ethylene-*co*-propylene), and high isotactic PP. Using TEA/TIBA mixture as cocatalyst and DDS as external elec-

tron donor, as TEA/TIBA ratio increased, the impact strength of iPP/EPR in-reactor alloys had an increasing trend. Using TEA/TIBA mixture as cocatalyst and D-donor as external electron donor, the impact strength of iPP/EPR in-reactor alloy were dramatically improved. In this case, the iPP/EPR in-reactor alloy prepared at TEA: TIBA = 4 : 1 was the toughest. The influence of cocatalyst and external electron donor on the flexural modulus and flexural strength could be ignored. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5154–5164, 2012

**Key words:** copolymerization; polyolefins; structure; mechanical properties; alloys

## INTRODUCTION

Because of the excellent mechanical properties and easy-getting monomer, isotactic polypropylene (iPP) is a widely used thermoplastic material. However, the shortcoming of brittleness at low-temperature limits its application. To improve the impact properties of iPP, some types of elastomer such as ethylene/propylene copolymer (EPR) is usually incorporated into the iPP matrix, forming heterophase impact polypropylene blends with acceptable loss of stiffness.<sup>1–5</sup> Comparing to the high energy consumption of physical blending iPP with EPR, recently iPP/EPR in-reactor alloys without further blending process have drawn more and more attention in both science and industry. This kind of alloy is now

mainly produced by a two-step sequential polymerization process, in which the first step is propylene homopolymerization and the second step is ethylene-propylene copolymerization. The product is a heterophasic material with iPP as the continuous phase and EPR as the dispersed phase. By fractionation of the alloys, it has also been found that considerable amount of segmented copolymer fractions exist in iPP/EPR in-reactor alloys.<sup>6–10</sup> These segmented copolymers are believed to be miscible with both iPP and EPR components and can thus act as the compatibilizer.<sup>11,12</sup> It can help to decrease the size of the dispersed EPR phase and improve the toughness of alloy. Therefore, regulating the microstructure of ethylene-propylene copolymer in iPP/EPR alloys has strong influences on the mechanical and physical performance of the materials.

Since the development of Ziegler-Natta catalysts in the 1950s, intensive efforts have been devoted to studies of ethylene-propylene copolymerization by titanium-based heterogeneous catalysts, including TiCl<sub>3</sub>/AlR<sub>3</sub> systems and supported Ti/Mg systems.<sup>13–17</sup> Comparing to EPR synthesized with homogeneous catalyst systems like VOCl<sub>3</sub>-Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>, a common feature of the copolymers produced with heterogeneous catalysts is their extremely broad

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composition distribution.<sup>15,18</sup> In general the product can be considered a mixture of two types of copolymers: random ethylene-propylene copolymers with close to ideally random sequence distribution and segmented copolymers. The actual composition distribution depends to a large extent on the catalyst system and operating conditions of the copolymerization. In our previous work,<sup>18,19</sup> it was found that the composition of ethylene-propylene copolymerization product synthesized by supported Ti catalysts is strongly affected by the type of cocatalyst. To regulate the amount of EPR (disperse phase) and segmented ethylene-propylene copolymers (compatibilizer) in iPP/EPR in-reactor alloys, mixtures of triethylaluminium (TEA) and triisobutylaluminium (TIBA) were used as cocatalysts to prepare iPP/EPR in-reactor alloys in this article. The influence of cocatalyst on composition distribution and chain structure of EPR and segmented ethylene-propylene copolymer in the iPP/EPR in-reactor alloys synthesized by MgCl<sub>2</sub>/TiCl<sub>4</sub>/diester type Ziegler-Natta catalyst were investigated.

## EXPERIMENTAL

### Synthesis of the iPP/EPR in-reactor alloys

The iPP/EPR in-reactor alloy was synthesized in a multistage subsequential polymerization process. In the first stage, or the prepolymerization stage, the slurry polymerization of propylene was conducted in a 0.8 L stainless steel jacketed autoclave for 15 min. A high yield Ziegler-Natta catalyst, TiCl<sub>4</sub>/MgCl<sub>2</sub>/diester, kindly donated by Aoda, SINOPEC (Beijing, China), was used in the polymerization. The catalyst had a Ti content of 2.9 wt %. Triethylaluminium (TEA, Albermarle), triisobutylaluminium (TIBA, Albermarle) or TEA/TIBA mixtures of different molar ratio was used as the cocatalyst (Al/Ti = 100). Diphenyldimethoxysilane (DDS, Huabang Chemistry, Hubei, China) or dicyclopentyldimethoxysilane (D-donor, Huabang Chemistry, Hubei, China) was used as the external electron donor (Si/Ti = 5). *n*-Heptane was used as the solvent. Propylene (contained 6.25 mol % H<sub>2</sub>) pressure in the prepolymerization stage was 1 atm and the temperature was 25°C. The mechanical stir speed is about 300 rpm. After the prepolymerization, propylene (contained 1 mol % H<sub>2</sub>) was introduced into the autoclave to 0.6 MPa. Propylene homopolymerization was carried out for 2 h at 75°C. During this period, the mechanical stir speed was adjusted to 100 rpm after the homopolymerization of propylene being performed for 10 min. At the end of this stage, propylene and solvent were removed by evacuation to 5 mmHg for 5 min, and the copolymerization of ethylene and propylene started. The gaseous ethylene and propyl-

ene had been completely mixed in a container in the molar ratio of 1 : 2 (ethylene : propylene) in advance, contained 1 mol % H<sub>2</sub>. The ethylene/propylene mixture of a constant pressure (0.3 MPa) was continuously supplied to the autoclave through an inlet pipe in the bottom of the autoclave. Meanwhile, the ethylene/propylene mixture was discharged by a vent-pipe on the cover of the autoclave to make the mixture composition constant. After being copolymerized for 20 min at 75°C, the copolymerization was terminated by pouring the resulting polymer into an excess of ethanol containing 5% HCl, filtering and washing the solid product with ethanol for three times. Subsequently, the copolymer was dried in vacuum at 60°C for 12 h.

### Homopolymerization of propylene

Homopolypropylene was prepared by two-stage polymerization process. In the prepolymerization and homopolymerization stage, the slurry polymerization of propylene was the same as preparation of the iPP/EPR in-reactor alloy. At the end of homopolymerization, propylene and solvent were removed by vacuum, pouring the resulting polymer into an excess of ethanol containing 5% HCl, filtering and washing the solid product with ethanol for three times. Subsequently, PP was dried in vacuum at 60°C for 12 h.

### Determination of the isotacticity index of PP

About 1 g PP was dissolved in 250 mL boiling *n*-heptane and then heated under reflux for 12 h. The solution was cooled to 25°C. The crystallized PP was collected and weighted. The isotacticity index of PP equaled to the weight percentage between the crystallized PP and nascent PP.

### Fractionation of the iPP/EPR in-reactor alloys

About 2 g of iPP/EPR in-reactor alloy was heated under reflux in 200 mL of *n*-octane for 2 h, then cooled to room temperature (25°C) and kept at 25°C for 24 h. The suspension was separated into solution and solid by centrifuging. The solid was dried in vacuum and called as octane insoluble part (C8-insol.). The solution was distilled to remove *n*-octane and then dried in vacuum. The corresponding solid was called as *n*-octane soluble part (C8-sol.). C8-insol. was extracted with boiling *n*-heptane for 12 h by a modified Kumagawa extractor.<sup>20</sup> Then the *n*-heptane soluble part (C7-sol.) was recovered by rotating evaporation. Both the *n*-heptane soluble part and the *n*-heptane insoluble part (C7-insol.) were dried in vacuum.

### Thermal analysis of the fractions

The DSC measurements were carried out on a Perkin–Elmer Pyris-1 calorimeter. About 5 mg of each sample was sealed in an aluminum sample cell, melted at 180°C for 5 min, and then successively annealed at 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, and 50°C, respectively, for 12 h at each temperature. Finally the samples were cooled down to room temperature. Stepwise crystallization was conducted under nitrogen atmosphere to avoid oxidation. Then the melting endotherm of the sample was recorded at a heating rate of 10°C min<sup>-1</sup> from 40 to 200°C.

### <sup>13</sup>C NMR analysis of the fractions

<sup>13</sup>C NMR spectra of the fractions were measured on a Varian Mercury Plus 300 NMR spectrometer at 75 MHz. *o*-Dichlorobenzene-*d*<sub>4</sub> was used as a solvent, and the concentration of the polymer solution was 10 wt %. The spectra were recorded at 120°C with hexamethyldisiloxane as an internal reference. Chromium triacetylacetonate (4–5 mg) was added to each sample to shorten the relaxation time and ensure the quantitative results. Broadband decoupling with a pulse delay of 3 s was employed. Typically, 5000 transients were collected.

### Measurement of the molecular weight

The molecular weights and molecular weight distributions of the fractions were measured by gel permeation chromatography (GPC) in a PL 220 GPC instrument (Polymer Laboratories) at 150°C in 1,2,4-trichlorobenzene with 0.0125% bibutyl hydroxy toluene (BHT). Three PL mixed B columns (500–10<sup>7</sup>) were used. Universal calibration against narrow polystyrene standards was adopted.

### Measurement of the mechanical and physical properties

The notched Charpy impact strength of the polymer sample was measured on a Pendulum Impact Testing Machine, ZBC1251-2 Model (Shenzhen SANS Testing Machine, China) according to ASTM D256. The flexural modulus was measured following ASTM D790 on an Electromechanical Universal Testing Machine, CMT4104 Model (Shenzhen SANS Testing Machine, China). The polymer granules were heat-molded at 180°C into sheets, which were then cut into pieces, put into a 280 × 280 × 4 mm<sup>3</sup> mold, and pressed under 20 MPa at 180°C for 5 min. The sample plates were then slowly cooled to room temperature in the mold. Sample strips for the tests were cut from the plate following ASTM D256. For each test point, five parallel measurements were made and the average values were adopted.

### Morphology analysis

The morphology and dispersion state of EPR phase in the iPP/EPR in-reactor alloys were investigated using a scanning electron microscope (HITACHI, S-4800). The SEM samples were prepared as follows: strips of the polymer were prepared as described in the section above, and were fractured in liquid nitrogen. The fractured surface was dipped into toluene at room temperature and etched by toluene under ultrasonic for 5 min. Then the fractured surface was coated with platinum and observed by SEM.

## RESULTS AND DISCUSSION

### Homopolymerization of propylene

In iPP/EPR in-reactor alloys, PP is matrix. PP can be isotactic, syndiotactic, or atactic, depending on the orientation of the pendant methyl groups attached to alternate carbon atoms. Because of its structure, isotactic PP has the highest crystallinity, resulting in good mechanical properties such as stiffness and tensile strength. Syndiotactic PP is less stiff than isotactic but has better impact strength and clarity. Because of its irregular structure, the atactic form has low crystallinity, resulting in a sticky, amorphous material used mainly for adhesives and roofing tars.<sup>21,22</sup> Increasing the amount of atactic PP in a predominantly isotactic formulation increases the room temperature impact resistance and stretchability but decreases the stiffness, haze, and color quality.<sup>23</sup> Triethylaluminum (TEA) and triisobutylaluminum (TIBA) are the most frequently used cocatalysts for activating titanium-based Ziegler–Natta catalysts. In industrial propylene polymerization catalyzed by MgCl<sub>2</sub>/TiCl<sub>4</sub>/diester type high-yield catalyst, TEA is the first choice of cocatalyst, as it gives PP of higher isotacticity than TIBA.<sup>19</sup> Electron donors are major components in propylene polymerization catalyst system, where a high stereospecificity is required to produce the isotactic PP. In this article, two silanes, namely diphenyldimethoxysilane (DDS) and dicyclopentyldimethoxysilane (D-donor), were used as external electron donors. First, homopolymerizations of propylene were performed with DDS and D-donor, respectively. The influence of external electron donors on propylene polymerization were listed in Table I. PP-1, PP-2 were homopolypropylene prepared by using DDS or D-donor as external electron donor, respectively. According to Table I, the isotacticity index and the content of C7-insoluble of PP-2 (prepared by the catalyst system using D-donor as external electron donor) were a little higher than that of PP-1. Using *n*-heptane as solvent, nascent PP could be divided into two parts, namely *n*-heptane soluble part (PP-C7-sol.) and *n*-

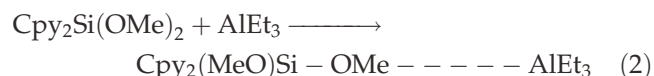
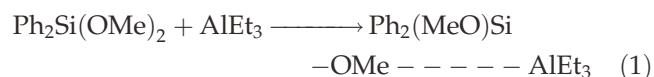
TABLE I  
Influence of External Electron Donors on Propylene Polymerization<sup>a</sup>

Entry	Alkylaluminium	Silane	Activity (kg PP/g cat-h)	I.I. <sup>b</sup> (wt %)	C8-sol. (wt %)	C7-sol. (wt %)	C7-insol. (wt %)
PP-1	TEA	DDS	0.94	98.3	0.9	4.1	95.0
PP-2	TEA	D-donor	0.87	99.2	0.6	2.5	96.9

<sup>a</sup> Al/Ti = 100, Si/Ti = 5.

<sup>b</sup> Isotacticity index: weight percent of insoluble PP in boiling n-heptane.

heptane insoluble part (PP-C7-insol.).<sup>24</sup> The former contained mainly atactic PP and/or low isotactic PP. The latter was mainly isotactic PP. The molecular weights of these two parts were listed in Table II. The molecular weight of nascent PP-2 was much higher than that of nascent PP-1. The molecular weight of PP-C7-insol. in PP-2 was also much higher than that in PP-1. However, the molecular weights of the PP-C7-sol. in PP-1 and PP-2 were similar to each other. Data in Tables I and II indicated that D-donor could not only increase the isotacticity index of PP but also increase the molecular weight of isotactic PP. For alkoxy silanes (R<sub>2</sub>(CH<sub>3</sub>O)<sub>2</sub>Si, R = Cpy, Ph etc.), cyclopentyl (Cpy) was more bulky than phenyl (Ph). The steric hindrance of organoaluminum containing Cpy was higher than that of organoaluminum containing Ph. The higher isotacticity index showed that the presence of large alkoxy groups made the alkoxy silane more effective in selective poisoning and activating the isospecific centers.<sup>24</sup> Cpy<sub>2</sub>(MeO)Si-OMe----AlEt<sub>3</sub> in eq. (2) had higher hindrance than Ph<sub>2</sub>(MeO)Si-OMe----AlEt<sub>3</sub> in eq. (1). Triisobutylaluminium acted as a chain transfer agents. There was more triisobutylaluminium in DDS system than in D-donor system. As it was shown by the high molecular weight produced by Cpy<sub>2</sub>(MeO)<sub>2</sub>Si.



To further investigate the composition of the nascent PPs, PP-1 and PP-2 were divided into three parts, namely C8-soluble, C7-soluble, and C7-insoluble, by fractionation using *n*-octane and *n*-heptane as solvent. Measured by DSC, there was no melting peak on the DSC curves of C8-soluble which indicated that this part was atactic PP. On the DSC curves of C7-soluble there were broad melting peaks in the field of 120–150°C (as show in Fig. 1). Since the melting point of this part was much lower than that of isotactic PP, this part should be PP with relatively lower isotacticity. Hence nascent PP com-

prised three parts: atactic PP (aPP), PP with relatively lower isotacticity (LiPP) and isotactic PP (iPP).

The molecular weights of these three parts were compared in Table III. The molecular weights of aPP in PP-1 and PP-2 were about the same. The molecular weights of LiPP in PP-1 and PP-2 were about the same too. The molecular weight of iPP in PP-2 was much higher than that in PP-1. The toughness of a grade of PP is directly related to molecular weight: higher molecular weights provide greater toughness. As a result, higher molecular weight PP have greater impact resistance and elongation and less brittleness.<sup>25–27</sup> This would further affect the mechanical properties of iPP/EPR in-reactor alloys. The molecular weight and isotacticity of homopolypropylene prepared by using DDS or D-donor as external donor were high enough for polypropylene to act as stiff matrix in PP/EPR. By fractionation, DSC, and GPC, the composition of every fraction was disclosed.

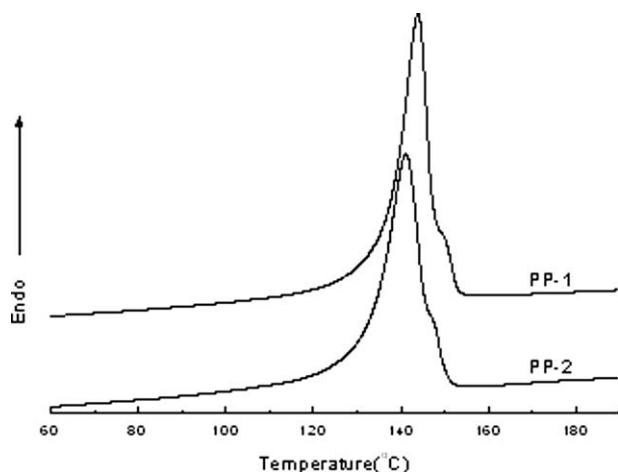
#### Composition of iPP/EPR in-reactor alloys synthesized with mixed cocatalyst

Al-alkyls are well known cocatalysts for Ziegler-Natta olefin polymerization. They affect the activity of the catalyst system, the molecular weight of the copolymer and the microstructure of the copolymer.<sup>28,29</sup>

The iPP/EPR in-reactor alloys prepared with TEA/TIBA mixture were shown in Table IV. These alloys were also fractionated into three parts, namely C8-soluble, C7-soluble, and C7-insoluble. These three parts were treated by stepwise annealing, respectively, and then measured by DSC. Figure 2 showed the DSC heating curves of the stepwise-annealed samples. There was no melting peak on the heating curves of C8-soluble parts [Fig. 2(a)]. In Figure 2(b)

TABLE II  
Molecular Weight of PP, *n*-Heptane Soluble Part and *n*-Heptane Insoluble Part

Sample	Nascent PP		PP-C7-sol.		PP-C7-insol.	
	PP-1	PP-2	PP-1	PP-2	PP-1	PP-2
$\bar{M}_n (\times 10^3)$	38.4	63.6	2.6	2.7	35.9	56.1
$\bar{M}_w/\bar{M}_n$	4.9	4.7	2.0	2.1	4.2	4.2



**Figure 1** DSC melting traces of C7-soluble fraction in PP-1 and PP-2.

there were multiple melting peaks appeared. The peaks at 60–130°C corresponded to PE or PP segments existing along the same polymer chain. The peaks at 130–160°C should be the melting peaks of PP with relatively lower isotacticity (LiPP) by comparing with Figure 1. In Figure 2(c) there were broad melting peaks existed in the range of 150–180°C which should arise from iPP. According to the fractionation results of homopolypropylene, C8-soluble parts was the mixture of random poly(ethylene-*co*-propylene) and aPP, C7-soluble parts was the mixture of segmented poly(ethylene-*co*-propylene) and LiPP.

The content of random and segmented poly(ethylene-*co*-propylene) in the iPP/EPR alloys could be estimated by the equations as followed:

$$C_R = C_8 - \frac{W_{iPP}}{W'_{iPP}} \times C'_R$$

$$C_S = C_7 - \frac{W_{iPP}}{W'_{iPP}} \times C'_S$$

where  $C_R$  was the weight percentage of random poly(ethylene-*co*-propylene) in the iPP/EPR alloys;

**TABLE III**  
Molecular Weight of Fractionations of PP

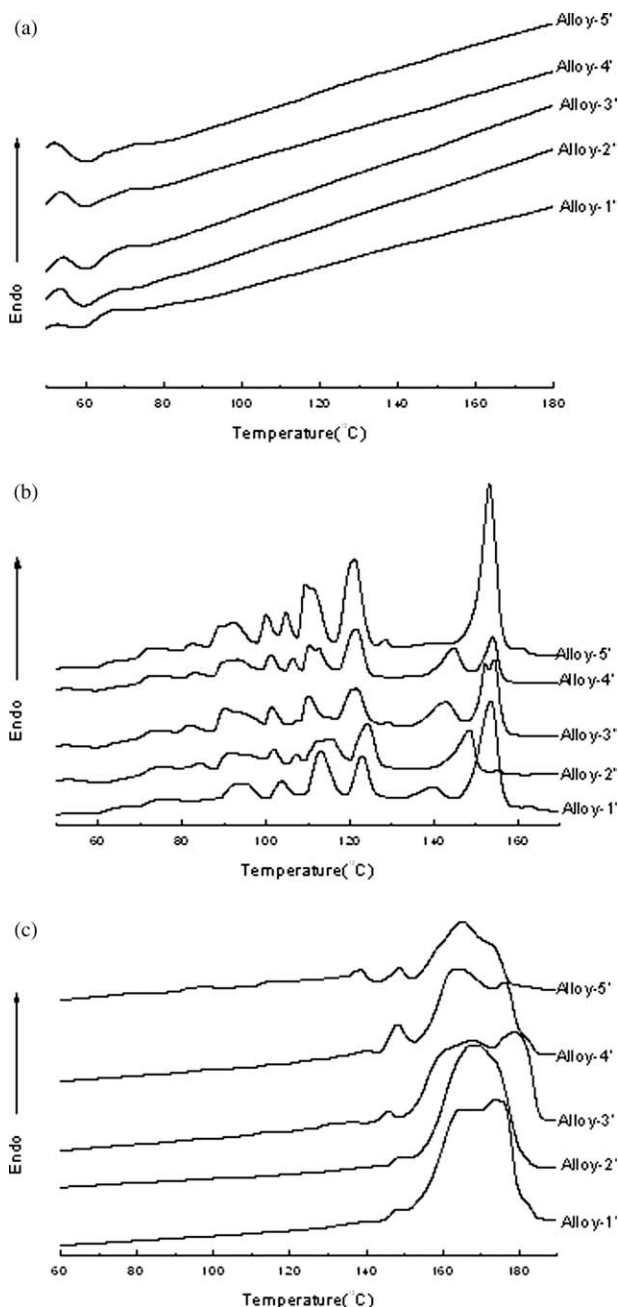
Fractionations	aPP (C8-sol.)		LiPP (C7-sol.)		iPP (C7-insol.)	
	PP-1	PP-2	PP-1	PP-2	PP-1	PP-2
$\overline{M}_n (\times 10^3)$	13.0	13.7	4.1	3.8	43.9	60.1
$\overline{M}_w/\overline{M}_n$	3.2	3.1	2.2	2.3	4.3	4.6

$C_8$  was the weight percentage of C8-soluble parts in the iPP/EPR alloys;  $W_{iPP}$  was the weight percentage of iPP in the iPP/EPR alloys,  $W'_{iPP}$  was the weight percentage of iPP in homopolypropylene;  $C'_R$  was the weight percentage of aPP in homopolypropylene;  $C'_S$  was the weight percentage of segmented poly(ethylene-*co*-propylene) in the iPP/EPR alloys;  $C_7$  was the weight percentage of C7-soluble parts in the iPP/EPR alloys;  $C'_S$  was the weight percentage of LiPP in homopolypropylene.

The calculation results were summarized in Table V. Compared with Table IV, most of C7-sol. was LiPP. Titanium catalysts contain two kinds of active polymerization species, of which  $Ti^{2+}$  species are active only for ethylene and  $Ti^{3+}$  species are normally active for both ethylene and propylene.<sup>30,31</sup> If the growing polymer chain end is an ethylene unit, the  $Ti^{2+}$  species can also effect the addition of propylene.<sup>32</sup> TEA has higher Lewis acidity and lower steric hindrance than TIBA, making its association with the active sites easier. TEA has higher reduction power than TIBA. So the Ti species reacting with TEA may have more  $Ti^{2+}$  species than with TIBA. Therefore, in the copolymerization of propylene and ethylene with high activity Ziegler-Natta catalyst, when TIBA was used, a slight increase of catalytic activity with respect to TEA was noticed.<sup>29</sup> As shown in Table V, as TEA/TIBA ratio in the catalyst systems increased, contents of PP in the iPP/EPR alloys decreased, and contents of poly(ethylene-*co*-propylene) (including random and segmented

**TABLE IV**  
Synthesis of iPP/EPR In-Reactor Alloys with TEA/TIBA Mixture

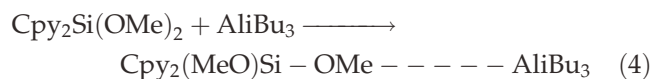
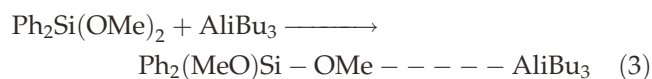
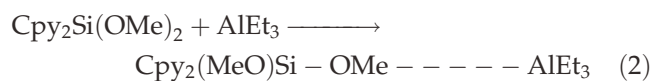
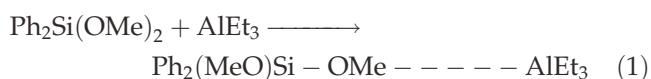
Entry	Alkylaluminium	Silane	Activity (kgPP/EPR/gcat-h)	C8-sol. (wt %)	C7-sol. (wt %)	C7-insol. (wt %)
Alloy-1	TEA	DDS	0.90	9.5	4.7	85.8
Alloy-2	TEA : TIBA(4 : 1)	DDS	0.97	13.1	6.4	80.5
Alloy-3	TEA : TIBA(4 : 2)	DDS	1.03	9.8	5.3	84.9
Alloy-4	TEA : TIBA(4 : 3)	DDS	0.84	13.2	7.1	79.7
Alloy-5	TEA : TIBA(4 : 4)	DDS	1.01	14.4	6.7	78.9
Alloy-1'	TEA	D-donor	0.93	10.0	3.4	86.5
Alloy-2'	TEA : TIBA(4 : 1)	D-donor	1.15	17.4	4.2	78.4
Alloy-3'	TEA : TIBA(4 : 2)	D-donor	1.02	15.1	4.0	81.0
Alloy-4'	TEA : TIBA(4 : 3)	D-donor	0.91	17.6	3.7	78.8
Alloy-5'	TEA : TIBA(4 : 4)	D-donor	0.95	19.0	3.5	77.5



**Figure 2** DSC melting traces of (a) C8-soluble, (b) C7-soluble and (c) C7-insoluble.

poly(ethylene-*co*-propylene)) increased dramatically in both Alloy 1–5 series and Alloy 1'–5' series.

Organoaluminum compounds interact with the organosilane compounds. Detailed  $^{13}\text{C}$  NMR,  $^{29}\text{Si}$  NMR, and IR studies of  $\text{Ph}_x\text{Si}(\text{OMe})_{4-x}\text{-AlEt}_3$  and  $\text{R}_x\text{Si}(\text{OMe})_{4-x}\text{-AlEt}_3$  mixtures ( $x = 0\text{--}3$ ) showed complexity of these interactions.<sup>33,34</sup> Once DDS or D-donor reacted with TEA or TIBA, four complexes would yield as followed (Cpy = cyclopentyl):



Since the bulkiness of Cpy and iBu were higher than that of Ph and Et, respectively, the product yielded in eq. (4) had the highest hindrance among those four products when they reacted with Ti species. Thus in the catalyst system using TIBA and D-donor as cocatalyst and external electron donor, respectively, the reduction powder of organoaluminum was weakened. There were the most  $\text{Ti}^{3+}$  species in this catalyst system that resulted in the highest content of poly(ethylene-*co*-propylene).<sup>28</sup> Therefore, in Alloy 1'–5' series the contents of poly(ethylene-*co*-propylene) was a little higher than that in Alloy 1–5 series. Meanwhile, as TEA/TIBA ratio in the catalyst systems increased, the content of both random and segmented poly(ethylene-*co*-propylene) in Alloy 1–5 series increased. However, in Alloy 1'–5' series, the content of random poly(ethylene-*co*-propylene) increased slightly, but the content of segmented poly(ethylene-*co*-propylene) in Alloy 2' was the highest and then dropped to some extent from Alloy 3' to Alloy 5'. This may be due to group exchanges among various organoaluminum. In our previous work,<sup>19</sup> it was found that using TEA/TIBA (molar ratio = 1 : 1) mixture as cocatalyst the random fraction of poly(ethylene-*co*-propylene) became blockier than the TEA or TIBA activated systems. When TEA, TIBA and D-donor coexist in the catalysis system, group exchanges among TEA, TIBA and the products yield in eqs. (3) and (4) must happen, forming new types of organoaluminums like  $\text{AlEt}_2(\text{i-Bu})$ ,  $\text{AlEt}(\text{i-Bu})_2$ ,  $\text{Cpy}_2(\text{MeO})\text{Si}(\text{OMe}) \cdots \text{Al}(\text{Et})_2\text{iBu}$ ,  $\text{Cpy}_2(\text{MeO})\text{Si}(\text{OMe}) \cdots \text{Al}(\text{iBu})_2\text{Et}$  and so on. It was assumed that two groups of active sites in the catalyst, one group of sites (Sites-R) produce random copolymer, and the other (Site-S) produce segmented copolymer. The Sites-R may become more active when they combine with the alkyl aluminum compounds, so TEA can help the production of random copolymers, as it has stronger ability to combine with the active sites. TIBA may be not so effective in activating Sites-R, but it seems to be able to turn a part of Sites-R into Sites-S, producing segmented poly(ethylene-*co*-propylene). When TEA/TIBA/D-donor mixture was introduced into the catalyst system, the newly formed organoaluminum compounds as well as TEA and TIBA will compete with each other,

TABLE V  
Compositions of iPP/EPR In-Reactor Alloys

Entry	Alkylaluminium	Silane	Random EP <sup>a</sup> (wt %)	Segmented EP (wt %)	PP (wt %)
Alloy-1	TEA	DDS	8.7	1.0	90.3
Alloy-2	TEA : TIBA(4 : 1)	DDS	12.3	2.9	84.8
Alloy-3	TEA : TIBA(4 : 2)	DDS	9.0	1.6	89.4
Alloy-4	TEA : TIBA(4 : 3)	DDS	12.4	3.7	83.9
Alloy-5	TEA : TIBA(4 : 4)	DDS	13.6	3.3	83.1
Alloy-1'	TEA	D-donor	9.5	1.2	89.3
Alloy-2'	TEA : TIBA(4 : 1)	D-donor	16.9	2.2	80.9
Alloy-3'	TEA : TIBA(4 : 2)	D-donor	14.6	1.9	83.5
Alloy-4'	TEA : TIBA(4 : 3)	D-donor	17.1	1.7	81.2
Alloy-5'	TEA : TIBA(4 : 4)	D-donor	18.5	1.5	80.0

Random EP = random poly(ethylene-*co*-propylene); Segmented EP = segmented poly(ethylene-*co*-propylene).

making the active sites oscillating between different states, and resulting in the formation of more segmented copolymers. Because the steric hindrance of organoaluminum containing Cpy was higher than that of organoaluminum containing Ph, the former was more stable than the latter. The homogenization of different organoaluminums in the catalyst system contained TEA/TIBA/D-donor mixture could be pressed to some extent. TEA/TIBA/D-donor complex could be a more efficient "chain shuttling" agent than TEA/TIBA/DDS complex. The former could produce random poly(ethylene-*co*-propylene) with more segmented copolymer existing along the same polymer chain. As TEA/TIBA ratio increased in Alloy 1'–5' series, the amount of TIBA/D-donor complex increased. Since the steric hindrance of TIBA/D-donor complex was higher than that of TEA/D-donor complex, there were more random poly(ethylene-*co*-propylene) with more segmented copolymer existing along the same polymer chain yielded. However, because PE or PP segments in those segmented copolymer was too short to crystallize, the random poly(ethylene-*co*-propylene) with segmented copolymer existing along the same polymer chain could be dissolved by *n*-octane and then

was included in C8-sol. That was the reason for increment in C8-sol. and reduction in C7-sol. in Alloy 1'–5' series.

#### Structure of iPP/EPR in-reactor alloys synthesized with mixed cocatalyst

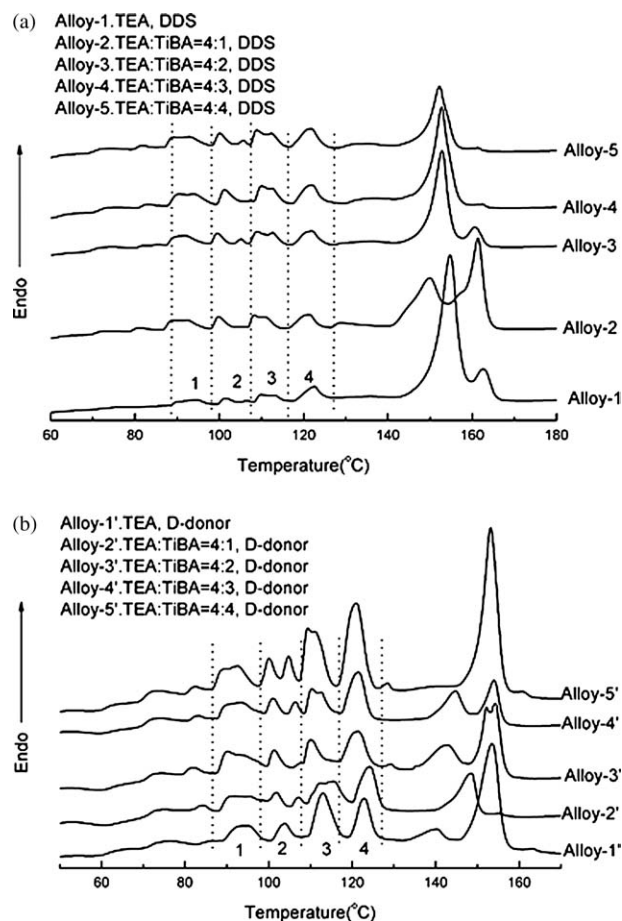
The C8-sol. parts of iPP/EPR in-reactor alloys were measured by <sup>13</sup>C NMR. The results were summarized in Table VI. The random index was seen to decrease when TEA/TIBA ratio increased. This was in good correlation with the other studies where random copolymers were obtained when overreduction of titanium was prevented moderately.<sup>35</sup>

The annealed C7-sol. parts of Alloy 1–5 and Alloy 1'–5' were measured by DSC. The results were shown in Figure 3. The melting peaks at the temperature higher than 130°C should come from LiPP. The multiple peaks at the range of 80–130°C were approximately divided into four parts (as shown in Fig. 3). The enthalpies of fusion and peak melting temperatures of annealed C7-sol. in iPP/EPR in-reactor alloys were shown in Table VII. From Alloy-1 to Alloy-5, as TEA/TIBA ratio increased, the enthalpy of fusion calculated from every independent

TABLE VI  
<sup>13</sup>C NMR Results of C8-sol. in iPP/EPR In-Reactor Alloys

Entry	Ethylene content (mol %)	Monomer triad (mol %)						Random index <sup>a</sup> (mol %)
		EEE	EEP	PEP	EPE	PPE	PPP	
Alloy-1	42.80	13.12	16.11	13.57	7.83	24.64	24.73	62.15
Alloy-2	42.38	16.35	15.98	10.05	7.39	29.20	21.03	62.62
Alloy-3	41.06	15.64	14.72	10.70	7.13	26.83	24.98	59.38
Alloy-4	44.06	17.58	16.75	9.73	8.97	19.93	27.04	55.38
Alloy-5	46.27	17.90	17.95	10.42	8.55	18.27	26.91	55.19
Alloy-1'	48.41	15.59	20.34	12.48	9.96	23.82	17.81	66.60
Alloy-2'	42.18	14.36	15.72	12.10	10.81	23.97	23.04	62.60
Alloy-3'	41.28	13.44	15.80	12.04	8.96	32.09	17.67	68.89
Alloy-4'	49.16	17.88	16.93	14.35	9.57	15.24	26.03	56.09
Alloy-5'	36.26	9.45	15.02	11.79	10.41	28.71	24.62	65.93

<sup>a</sup> Random index = (EEP + EPE + PEP + PPE)/(EEP + EPE + PEP + PPE + EEE + PPP).



**Figure 3** DSC melting traces of C7-soluble in (a) Alloy-1-5 and (b) Alloy-1'-5'.

peak increased gradually. However, as TEA/TIBA ratio increased, the peak melting temperatures of every peak were no much difference among 80–130°C. It was said the lamella thickness of the crystals in C7-sol. parts were almost similar to each other, but their crystallinity increased slightly as TEA/TIBA ratio increased. The same situation could be seen in Alloy-1'-5' series. Furthermore, the enthalpies of fusion of C7-sol. in Alloy-1'-5' were universally

higher than that of C7-sol. in Alloy-1-5. These phenomena further verified that TEA/TIBA/D-donor complex could produce more segmented poly(ethylene-co-propylene).

The molecular weight and its distribution of every fraction of iPP/EPR in-reactor alloys were measured by GPC. The results were summarized in Table VIII. The molecular weights of C8-sol. (most was random poly(ethylene-co-propylene)) both in Alloy-1-5 series and Alloy-1'-5' series first decreased and then increased as TEA/TIBA ratio increased. The molecular weight distributions of these parts first broadened and then narrowed as TEA/TIBA ratio increased. This phenomenon was probably the sum of many parameters and could not be explained by the influence of TIBA alone.

Aluminum alkyls with shorter alkyl groups more eagerly act as a chain transfer agents than aluminum alkyls with longer groups. Evidently the longer group prevents the free cocatalyst molecule from getting close to the active polymer chain end.<sup>28</sup> As a result, the molecular weights of both C7-sol. (most was LiPP) and C7-insol. (most was iPP) in Alloy-1-5 series increased as TEA/TIBA ratio increased. Universally, the molecular weights of C8-sol., C7-sol., and C7-insol. in Alloy-1'-5' series were much higher than that of the counter parts in Alloy-1-5 series. This might be due to the higher steric hindrance of D-donor. When D-donor reacted with aluminum alkyls, aluminum alkyls/D-donor complex whose steric hindrance was higher than that of aluminum alkyls/DDS complex would form. The former could more efficiently prevent free cocatalyst from acting as a chain transfer agents and produce polymer with higher molecular weight. However, in Alloy-1'-5' series, the molecular weights of both C7-sol. and C7-insol. firstly increased and then decreased. The molecular weights of C7-sol. and C7-insol. in Alloy-2' were the highest one among the counter parts, respectively. The reactions of aluminum alkyls with alkylalkoxy silanes are not very fast under typical

**TABLE VII**  
Enthalpies of Fusion and Peak Melting Temperatures of Annealed C7-sol. in iPP/EPR In-Reactor Alloys

Entry	1		2		3		4	
	$\Delta H$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H$ (J g <sup>-1</sup> )	$T_m$ (°C)	$\Delta H$ (J g <sup>-1</sup> )	$T_m$ (°C)
Alloy-1	1.65	94.3	0.77	101.3	1.76	109.9	2.80	122.4
Alloy-2	3.18	89.0	1.57	99.7	2.87	108.3	3.10	121.2
Alloy-3	2.57	91.3	1.55	99.5	3.33	108.9	3.05	122.0
Alloy-4	3.77	90.3	1.79	101.2	3.30	110.1	3.87	121.8
Alloy-5	3.51	89.1	1.71	100.0	3.76	108.9	4.36	121.8
Alloy-1'	2.22	89.3	1.15	103.6	4.36	109.8	3.35	122.8
Alloy-2'	1.96	90.6	0.97	102.1	3.51	115.4	4.09	120.4
Alloy-3'	3.06	89.9	0.97	101.2	1.73	108.4	3.55	117.3
Alloy-4'	2.43	92.3	1.47	101.0	2.62	110.4	4.60	117.7
Alloy-5'	3.22	92.4	2.25	98.3	5.76	109.3	8.49	121.0



TABLE VIII  
GPC Results of Every Fraction in iPP/EPR In-Reactor Alloys Using DDS or D-Donor as External Electron Donor

Entry	C8-sol.		C7-sol.		C7-insol.	
	$\bar{M}_n (\times 10^3)$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n (\times 10^3)$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n (\times 10^3)$	$\bar{M}_w/\bar{M}_n$
Alloy-1	21.6	3.8	6.2	6.7	35.8	5.6
Alloy-2	20.7	3.8	8.8	6.3	39.6	4.6
Alloy-3	17.3	5.3	11.5	5.9	50.7	4.0
Alloy-4	12.6	5.4	9.7	6.6	55.6	5.4
Alloy-5	16.0	5.2	14.9	5.3	56.4	3.9
Alloy-1'	51.5	3.9	9.7	7.9	49.3	7.1
Alloy-2'	41.5	3.7	20.5	4.9	78.0	5.4
Alloy-3'	34.5	5.1	12.8	7.9	77.5	3.5
Alloy-4'	32.6	4.9	13.9	6.5	70.8	4.4
Alloy-5'	47.8	3.7	12.7	6.2	63.6	5.5

polymerization conditions.<sup>36</sup> When TEA/TIBA ratio was relatively low, e.g., TEA : TIBA = 4 : 1, most of aluminum alkyls could react with D-donor and formed aluminum alkyls/D-donor complex. This complex had higher steric hindrance than TEA or TIBA did. Thus the chain transfer reaction could be inhibited. Since the steric hindrance of *t*-butyl was higher than that of ethyl, the reaction between D-donor and TIBA was relatively slower. As TEA/TIBA ratio further increased, there were more and more free TIBA remained in the catalyst systems. Those free TIBA would act as chain transfer agents and made polymers with relatively lower molecular weight.

Figure 4 displays the typical SEM photographs of the cryogenically fractured surface of iPP/EPR in-reactor alloy strips etched by toluene. In these pictures, biphasic structure could be clearly seen. Different preparation conditions led to different morphology in iPP/EPR in-reactor alloys. In Alloy-1 [Fig. 4(a)], the size of small cavities was not uniform. In Alloy-2' [Fig. 4(b)], the size of cavities was smaller than that in Alloy-1, with an average cavity diameter less than 1  $\mu\text{m}$ . Meanwhile, the dispersion of cavities was rather uniform than that in Alloy-1.

#### Mechanical properties of iPP/EPR in-reactor alloys

The mechanical properties of iPP/EPR in-reactor alloys were measured and summarized in Table IX. In Alloy-1–5 series, as TEA/TIBA ratio increased, the impact strength increased gradually which was higher than that of a conventional iPP ( $\sim 4 \text{ kJ m}^{-2}$ ). The flexural modulus and flexural strength almost remain constant which was a little lower than that of iPP (flexural modulus = ca. 1600 MPa). As shown in Table V, as TEA/TIBA ratio increased, the content of both random poly(ethylene-*co*-propylene) and segmented poly(ethylene-*co*-propylene) increased gradually. In iPP/EPR in-reactor alloys segmented poly(ethylene-*co*-propylene) acted as compatibilizer

between iPP and random poly(ethylene-*co*-propylene).<sup>3</sup> The more segmented poly(ethylene-*co*-propylene)s, the more homogeneously random poly(ethylene-*co*-propylene) could dispersed into iPP matrix with smaller particle diameter, and thereby, the more tough the iPP/EPR in-reactor alloy was. Random poly(ethylene-*co*-propylene) was elastomer. The

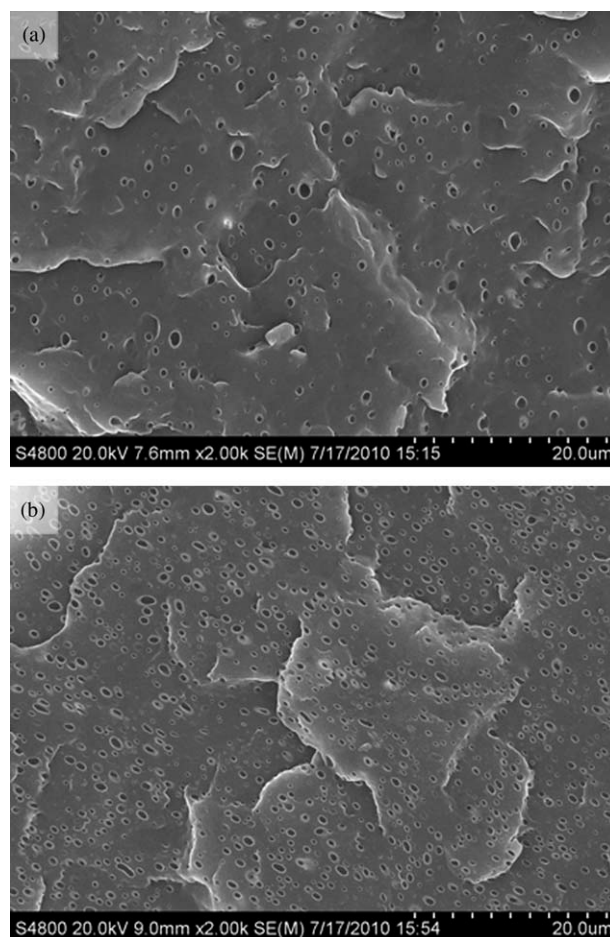


Figure 4 SEM photographs of fractured surface of the iPP/EPR in-reactor alloys etched by toluene at 50°C: (a) Alloy-1; (b) Alloy-2'.

**TABLE IX**  
**Mechanical Properties of the iPP/EPR In-Reactor Alloys**

Entry	Impact strength (kJ m <sup>-2</sup> )	Flexural modulus (MPa)	Flexural strength (MPa)
Alloy-1	4.6	1071.9	43.5
Alloy-2	6.2	1046.5	38.9
Alloy-3	6.3	1084.7	41.7
Alloy-4	4.9	1102.7	39.6
Alloy-5	7.8	1057.8	35.7
Alloy-1'	9.2	1026.5	44.3
Alloy-2'	55.0	1030.8	34.7
Alloy-3'	36.1	1029.2	36.9
Alloy-4'	37.2	985.3	35.7
Alloy-5'	41.7	1092.1	37.4

more random poly(ethylene-*co*-propylene) dispersed properly into iPP matrix, the more tough the iPP/EPR in-reactor alloy was. Universally, the impact strength of Alloy-1'-5' was much higher than that of Alloy-1-5. This might be arose from better morphology in Alloy-1'-5' (as shown in Fig. 4) and higher molecular weight (as shown in Table VIII) of Alloy-1'-5'. However, the improved morphology in Alloy-1'-5' was relative to the higher content of random poly(ethylene-*co*-propylene) (as shown in Table V). The flexural modulus and flexural strength of Alloy-1'-5' were similar to that of Alloy-1-5. However, the impact strength of Alloy-2' was the highest among Alloy-1'-5' series. On one hand, as shown in Table VIII, the molecular weights of C7-sol. and C7-insol. were the highest one among the counter parts. As mentioned above, C7-sol. and C7-insol. were mainly PP. This higher molecular weight PP provided greater impact resistance. On the other hand, the content of segmented poly(ethylene-*co*-propylene) in Alloy-2' was the highest (as shown in Table V) among Alloy-1'-5'. Although the content of random poly(ethylene-*co*-propylene) in Alloy-5' was the highest among Alloy-1'-5', the content of segmented poly(ethylene-*co*-propylene) was just 1.5 wt % which was lower than that in Alloy-2'. This might result in relatively poor compatibility between iPP and random poly(ethylene-*co*-propylene). It indicated that to attain high impact PP the content of random poly(ethylene-*co*-propylene) and segmented poly(ethylene-*co*-propylene) should be high enough and the ratio between them should be proper.

## CONCLUSIONS

In conclusion, strong cocatalyst effects were found in preparation of iPP/EPR in-reactor alloy with MgCl<sub>2</sub>/TiCl<sub>4</sub>/diester type Ziegler-Natta catalyst by multistage sequential polymerization process. Meanwhile, the structure and mechanical properties of iPP/EPR in-reactor alloy were strongly influenced

by external electron donor. Using TEA/TIBA mixture as cocatalyst and DDS as external electron donor, as TEA/TIBA ratio increased, the content of random poly(ethylene-*co*-propylene) and segmented poly(ethylene-*co*-propylene) increased, the molecular weight of PP in the alloys increased too. This resulted in the increase in the impact strength. Using TEA/TIBA mixture as cocatalyst and D-donor as external electron donor, the content of poly(ethylene-*co*-propylene), the molecular weight and impact strength of iPP/EPR in-reactor alloy were dramatically improved. There was an optimum feed ratio between TEA and TIBA, e.g., TEA : TIBA = 4 : 1 (Al/Ti = 100). The iPP/EPR in-reactor alloy prepared under this condition was the most tough, since the content of segmented poly(ethylene-*co*-propylene) and the molecular weight of this alloy were the highest. The influence of cocatalyst and external electron donor on the flexural modulus and flexural strength could be ignored.

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