

# Fe(2-EHA)<sub>3</sub>/Al(*i*-Bu)<sub>3</sub>/Hydrogen Phosphite Catalyst for Preparing Syndiotactic 1,2-Polybutadiene

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**ABSTRACT:** Polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene with an iron(III) catalyst system has been investigated. Activity of the catalyst was affected by the type of cocatalyst alkylaluminum and the phosphorus compound as an electron donor, molar ratio of catalyst components, and their aging sequence and aging time of the catalyst. The microstructure and configuration of the polymer was decided by the catalyst components, the higher [Al]/[Fe] molar

ratio tending to yield syndiotactic 1,2-polybutadiene, while the higher [P]/[Fe] molar ratio favors the formation of amorphous 1,2-polybutadiene. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4265–4269, 2006

**Key words:** syndiotactic 1,2-polybutadiene; iron-based catalyst; thermoplastic elastomer; stereoselectivity

## INTRODUCTION

Syndiotactic 1,2-polybutadiene, a typical thermoplastic elastomer<sup>1,2</sup>, is widely used in various products such as films, footwear soles, tubes, and hoses.

Conjugated diene polymerization catalysts based on transition metal compounds, such as nickel, cobalt, and titanium compounds, and rare earth compounds have been widely investigated,<sup>3–9</sup> but relatively less attention has been paid to iron-based catalysts because of the latter's low activity and poor stereoselectivity.<sup>10</sup>

The binary system iron-compound/alkylaluminum has very low activity for conjugated diene polymerization,<sup>11</sup> and accordingly, an additional electron donor is needed to achieve reasonable activity. Most of the electron donors used for the iron-based catalyst system are bidentate nitrogen-containing compounds such as phenyl-2-pyridylacetonitrile, 2-cyanopyridine,<sup>12</sup> 1,10-phenanthroline,<sup>13,14</sup> and bipyridine,<sup>15</sup> where in the last case by Porri et al., methylaluminumoxane is used as the cocatalyst.<sup>16</sup>

For most late transition metal-based catalysts, low polymerization temperature, for instance, room temperature or below, is used. At higher temperatures, either the activity is lowered<sup>15</sup> or the stereoselectivity becomes poorer,<sup>13–16</sup> and sometimes the microstruc-

ture of the resulting polymer is changed simultaneously.<sup>13,14</sup>

Recently, we examined iron 2-ethylhexanoate (Fe(2-EHA)<sub>3</sub>)/AlR<sub>3</sub> as the catalyst, using diethyl phosphite (DEP) as an electron donor, for polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene. Some interesting behaviors of this catalyst system, different from that of most other transition metal-based catalyst systems for diene polymerization, are discussed.

## EXPERIMENTAL

### Materials

Fe(2-EHA)<sub>3</sub> was synthesized in this laboratory by extraction of FeCl<sub>3</sub>·6H<sub>2</sub>O with 2-ethyl hexanoate in hexane and diluted to 0.2M. Al(*i*-Bu)<sub>3</sub> was purchased from Aldrich and diluted to 1M in hexane. DEP and 1,3-butadiene were supplied by Jinzhou Petrochemical Co. of PetroChina. DEP was used as 0.1M solution in hexane and 1,3-butadiene was purified by passing through columns of sodium hydroxide and silica gel to remove inhibitor and moisture before use. Triphenyl phosphine, triethyl phosphite, triphenyl phosphite, diphenyl phosphite, diethyl ethyl phosphate, triethyl phosphate, tributyl phosphate, and triphenyl phosphate (Acros Co.) were diluted to 0.1M in toluene.

Analytical grade 99.5% hexane was dried by refluxing for 6 h over sodium diphenyl ketyl and then distilled under nitrogen.

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**TABLE I**  
Effect of Different Phosphorus Compounds on the 1,3-Butadiene Polymerization With Fe(2-EHA)<sub>3</sub>-Al(*i*-Bu)<sub>3</sub> Catalyst

Phosphorus compound		Yield (wt %)	1,2 (mol %)	1,4 (mol %)	<i>T</i> <sub>m</sub> (°C)
Triphenyl phosphine	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	oligomer	—	—	—
Triethyl phosphite	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P	oligomer	—	—	—
Triphenyl phosphite	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P	oligomer	—	—	—
Diethyl phosphite	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)H	85.0	90.9	9.1	177.4
Diphenyl phosphite	(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> P(O)H	75.0	84.8	15.2	180.1
Diethylethyl phosphate	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)C <sub>2</sub> H <sub>5</sub>	oligomer	—	—	—
Triethyl phosphate	(C <sub>2</sub> H <sub>5</sub> O) <sub>3</sub> P(O)	oligomer	—	—	—
Tributyl phosphate	(C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub> P(O)	oligomer	—	—	—
Triphenyl phosphate	(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> P(O)	82.8	95.0	5.0	189.0

Polymerization conditions: in hexane at 50°C for 4 h, [Bd] = 1.85 mol/L, [Fe]/[Bd] = 1.5 × 10<sup>-4</sup>, [Al]/[Fe] = 25, [P]/[Fe] = 4.0 (mol/mol).

### Polymerization

Polymerization of 1,3-butadiene was conducted in a 100 mL reactor sealed with a rubber septum. After purging the reactor with nitrogen, 50 mL of the monomer solution in 1.85M were injected, and then, Fe(2-EHA)<sub>3</sub>, DEP, or other phosphorus compound, and Al(*i*-Bu)<sub>3</sub> in designed molar ratios were added sequentially. Polymerization was performed at 50°C for 4 h and was terminated by the addition of ethanol containing a small amount hydrogen chloride and 1 wt % 2,6-di-*tert*-butyl-4-methylphenol. The resulting polymer was obtained by precipitating in ethanol and was filtrated and washed with ethanol, then it was dried at 40°C in vacuum to constant weight.

### Characterization

The yield of the polymer is the weight percentage of the isolated polymer to the weight of the initially charged 1,3-butadiene. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Varian Unity-400 spectrometer in perdeuterio-*o*-dichlorobenzene at 400 MHz and at 135°C using tetramethylsilane as an internal standard. Number-average molecular weight (*M*<sub>n</sub>) and molecular weight distribution (*M*<sub>w</sub>/*M*<sub>n</sub>) of polymers were determined by GPC in 2,4,6-trichlorobenzene at 135°C (calibrated with polystyrene standards), using a Polymer Laboratory PL 220 equipment. X-ray diffraction powder spectrum was recorded on a D/max 2000PC apparatus with Cu Kα radiation. Melting point was determined under nitrogen by differential scanning calorimetry (Perkin-Elmer-7) at a scanning rate of 10°C/min.

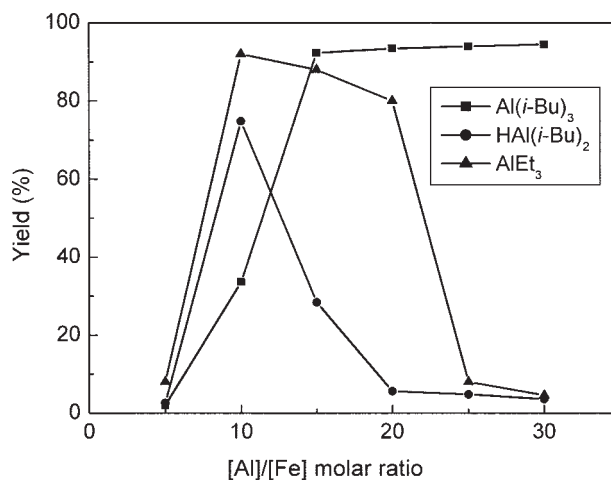
## RESULTS AND DISCUSSION

### Effect of different phosphorus compounds on polymerization

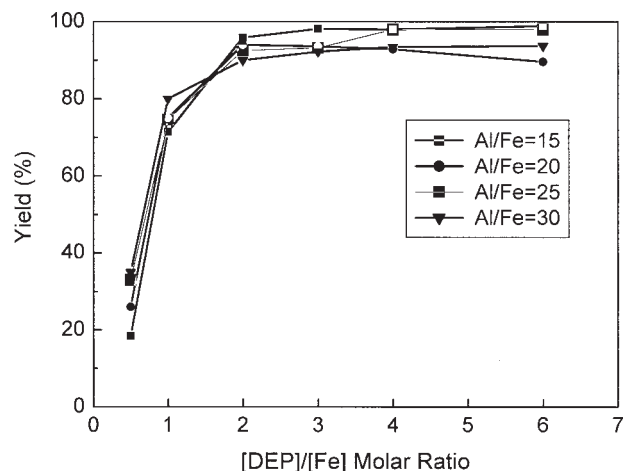
Table I shows the effect of various phosphorus compounds as electron donor with Fe-based catalysts in

1,3-butadiene polymerizations. As can be seen in Table I, only oily oligomers were obtained when the phosphorus compound is a trivalent compound such as triphenyl phosphine, triethyl phosphite, or triphenyl phosphite. Using hydrogen phosphite as the ligand for the iron-based catalyst, not only high catalyst activity but also high 1,2-microstructure content of the polybutadiene were obtained. Diethyl phosphite gave even higher catalyst activity and 1,2-microstructure content than diphenyl phosphite.

Phosphates with flexible alkyls (ethyl, butyl, etc.) behave similar to that of trivalent phosphorus compound systems, yielding oily oligomers. If, however, the alkyl is rigid, high 1,2-microstructure polybutadiene content can be achieved, similar to the case with alkyl phosphite system. So, for alkyl phosphate system, the alkyl is steric hindrance and rigid group and it is benefit to obtaining the high molecular weight polymer. Triphenyl phosphate system is close to diethyl phosphite system in catalyst activity, but the



**Figure 1** Results of butadiene polymerization with iron-based catalysts using different alkyl aluminums. Polymerization conditions: in hexane, 50°C for 4 h, [Fe]/[Bd] = 1.5 × 10<sup>-4</sup>, and [P]/[Fe] = 2.0 (mol/mol).



**Figure 2** Effect of [DEP]/[Fe] molar ratios on polymerization of butadiene. Polymerization conditions: in hexane at 50°C for 4 h, [Bd] = 1.85 mol/L, and [Fe]/[Bd] =  $1.5 \times 10^{-4}$  (mol/mol).

former gives higher 1,2-microstructure content in polybutadiene. Thus, proper phosphorus compound can enhance markedly catalyst activity and stereoselectivity of the polybutadienes.

### Effect of alkylaluminum

Figure 1 shows the effect of different cocatalyst alkylaluminums on 1,3-butadiene polymerization. The activity of the catalyst increases with increasing [Al]/[Fe] ratio, and reaches a maximum at [Al]/[Fe] = 10–15. There are then different trends that follow: (1) for Al(*i*-Bu)<sub>3</sub> system, the activity of catalyst holds unchanged in a broad [Al]/[Fe] range of 15–30; (2) for AlEt<sub>3</sub> or AlH(*i*-Bu)<sub>2</sub> as the cocatalyst, the yield of polymer decreases quickly; and (3) AlEt<sub>3</sub> system

shows comparatively higher catalyst activity within the wide range of [Al]/[Fe] tested.

The reduction ability is believed to be related to the stability of the oxidation state of the iron species. We have shown previously that the active species are Fe<sup>2+</sup>-complexes. The alkylaluminum with stronger reduction ability causes over-reduction of the active Fe<sup>2+</sup>-complexes to the inactive Fe<sup>0</sup>-species so as to reduce the concentration of the active species.

### Effect of [P]/[Fe] and [Al]/[Fe] ratios

In conjugated diene polymerization catalyzed by binary Fe(2-EHA)<sub>3</sub>/Al(*i*-Bu)<sub>3</sub>, only a trace of polymer is described in the literature,<sup>14</sup> no matter how the [Al]/[Fe] molar ratio was changed and how the polymerization time was prolonged. This implies that 2-ethyl hexanoate is not a proper ligand and extra electron donor is required for polymerization of conjugated diene.

With the addition of an appropriate amount of DEP, the polymerization activity was highly promoted. Figure 2 shows the effects of the [P]/[Fe] ratio on 1,3-butadiene polymerization, when the concentrations of Fe(2-EHA)<sub>3</sub> and Al(*i*-Bu)<sub>3</sub> were kept constant. With increments of [P]/[Fe], polymer yield increases to its maximum at [P]/[Fe] = 2, and the high yield is maintained until to a [P]/[Fe] = 6. The results as shown in Figure 2 may imply that the [P]/[Fe] ratio is directly associated with the concentration of the active sites, which increases with increment of [P]/[Fe] ratio until reaching a maximum.

Dependence of polymer yield on [Al]/[Fe] molar ratio is very similar to that on [P]/[Fe] molar ratio as shown in Table II. At constant [P]/[Fe] molar ratio, Fe(2-EHA)<sub>3</sub>/Al(*i*-Bu)<sub>3</sub>/DEP catalyst keeps high catalyst activity in a broad range of [Al]/[Fe] ratio.

**TABLE II**  
Effect of Al/Fe Molar Ratio on the Polymerization of Butadiene

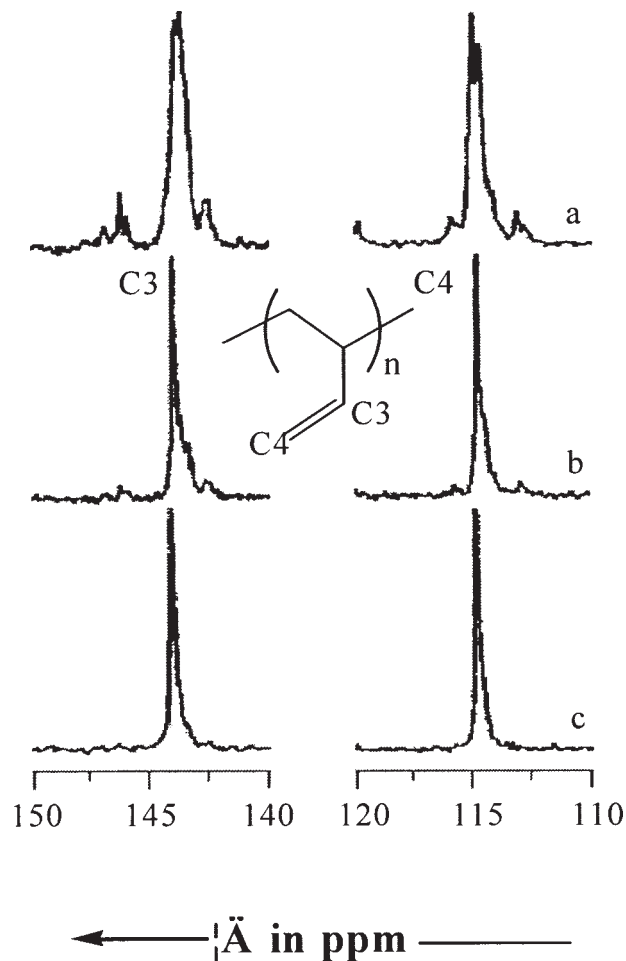
P/Fe	Al/Fe	Yield (wt %)	$M_n \times 10^{-4}$	$M_w/M_n$	Polymer appearance	1,2 (mol %)	1,4 (mol %)	$T_g$ (°C)	$T_m$ (°C)
2.0	10	33.6	n.d. <sup>a</sup>	n.d.	Elastomer	87.9 <sup>b</sup>	12.1 <sup>b</sup>	-26.0	none
	15	95.9	47.5	3.30		87.7 <sup>b</sup>	12.3 <sup>b</sup>	-26.2	none
	20	96.3	n.d.	n.d.		87.4 <sup>b</sup>	12.6 <sup>b</sup>	-26.5	160.7
	25	95.0	n.d.	n.d.	Crystalline material	91.0 <sup>c</sup>	9.0 <sup>c</sup>	none	174.1
	30	90.4	40.0	2.35		91.2 <sup>c</sup>	8.8 <sup>c</sup>	none	175.9
4.0	40	90.0	n.d.	n.d.	Elastomer	91.0 <sup>c</sup>	9.0 <sup>c</sup>	none	179.1
	10	26.0	n.d.	n.d.		86.8 <sup>b</sup>	13.2 <sup>b</sup>	-27.0	none
	15	95.0	47.6	3.11	83.3 <sup>b</sup>	16.7 <sup>b</sup>	-30.2	none	
	20	93.6	n.d.	n.d.	85.1 <sup>b</sup>	14.9 <sup>b</sup>	-28.6	none	
	25	93.2	44.2	2.38	Crystalline material	n.d.	n.d.	-37.1	158.1
	30	92.2	n.d.	n.d.		90.8 <sup>c</sup>	9.2 <sup>c</sup>	none	177.3
	40	89.8	n.d.	n.d.		n.d.	n.d.	none	178.1

Polymerization conditions: in hexane at 50°C for 4 h, [Bd] = 1.85 mol/L, [Fe]/[Bd] =  $1.5 \times 10^{-4}$  (mol/mol).

<sup>a</sup> n.d. denotes not determined.

<sup>b</sup> Estimated by the formula  $T_g = 91V - 106$ .<sup>17</sup>

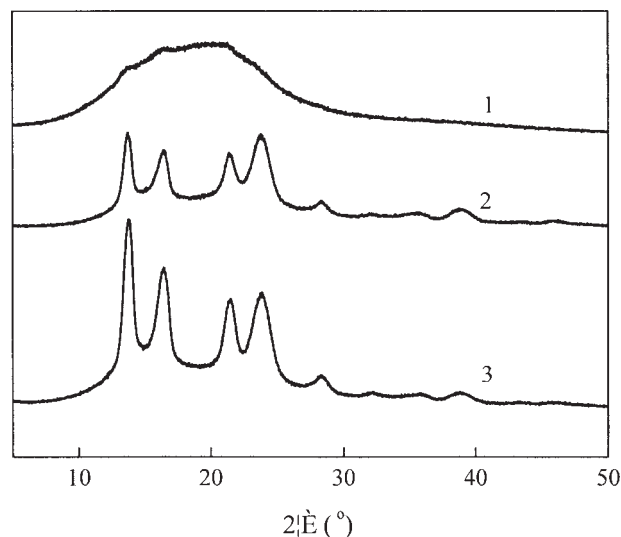
<sup>c</sup> Determined by <sup>1</sup>H NMR.



**Figure 3**  $^{13}\text{C}$  NMR spectra (olefinic region) of polybutadiene obtained with  $\text{Fe}(\text{2-EHA})_3\text{-Al}(\text{i-Bu})_3\text{-DEP}$  catalyst at  $[\text{Al}]/[\text{Fe}] = 10$  (a), 20 (b), and 30 (c) (mol/mol).

An interpretation for the fact is that when  $[\text{Al}]/[\text{Fe}]$  molar ratio is lower than 15,  $\text{Al}(\text{i-Bu})_3$  exists in not enough quantity to activate all the Fe-species, and after it reached about 15–20, the yield keeps high (above 90%), but configuration of the polybutadiene will change from amorphous to crystalline.

Figure 3 shows the  $^{13}\text{C}$  NMR spectra (olefinic region) of polybutadiene. Peaks at 114.5 and 114.0 ppm are assigned to the carbons of syndiotactic and atactic 1,2-microstructures<sup>18</sup> respectively. Along with increase in  $[\text{Al}]/[\text{Fe}]$  ratio from 10 to 30, increase in amount of syndiotactic structure is evident. Figure 4 shows the X-ray spectra of polybutadiene obtained at  $[\text{Al}]/[\text{Fe}]$  ratio, and with  $[\text{Al}]/[\text{Fe}]$  ratio increase, polybutadiene crystallinity increases. Figure 4(a) is the X-ray spectrum of the polymer at  $[\text{Al}]/[\text{Fe}] = 15$ ; the absence of peak of crystalline polymer indicates that polybutadiene is in an amorphous state under these conditions. Figures 4(b) and 4(c) display X-ray diagrams of crystalline polybutadiene polymerized at  $[\text{Al}]/[\text{Fe}] = 20$  and 25 respectively.

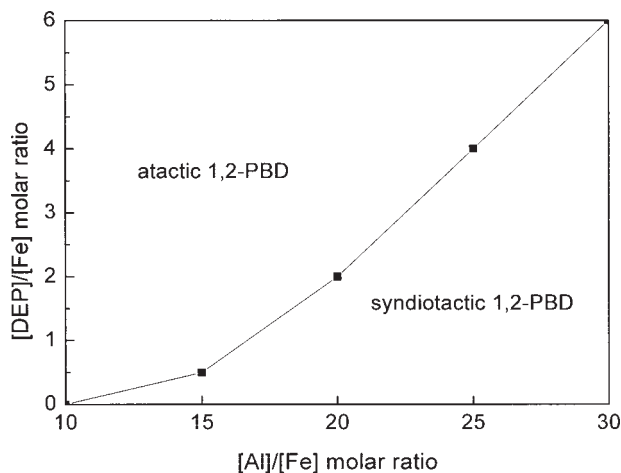


**Figure 4** X-ray spectra of polybutadiene obtained at  $[\text{Al}]/[\text{Fe}] = 10$  (a), 20 (b), and 30 (c) (mol/mol).

With polybutadienes catalyzed by  $\text{Fe}(\text{2-EHA})_3\text{-Al}(\text{i-Bu})_3\text{-DEP}$ ,  $[\text{P}]/[\text{Fe}]$  and  $[\text{Al}]/[\text{Fe}]$  molar ratios have significant effect on stereoregularity. By adjusting catalyst components, both elastomeric and crystalline materials can be obtained. Under otherwise identical conditions, higher  $[\text{Al}]/[\text{Fe}]$  molar ratio tends to yield syndiotactic 1,2-polybutadiene, while higher  $[\text{P}]/[\text{Fe}]$  molar ratio favors formation of amorphous 1,2-polybutadiene (Fig. 5).

#### Effect of aging sequence and aging time on polymerization behaviors

The oxidation state of the active species of iron-based catalysts is normally unstable and as a consequence,



**Figure 5** Correlation between the molar ratios of the catalyst components and configuration of polybutadiene. Polymerization conditions: in hexane at  $50^\circ\text{C}$  for 4 h,  $[\text{Bd}] = 1.85\text{M}$ , and  $[\text{Fe}]/[\text{Bd}] = 1.5 \times 10^{-4}$  (mol/mol).

**TABLE III**  
Effects of Aging Sequence and Aging Time of the Catalyst Components on Butadiene Polymerization

Addition sequence	Aging time (mm)	Yield (%)
Bd + (Fe + Al) + DEP	1	26.8
	15	12.8
Bd+(Fe + DEP) + Al	1	97
	15	96
Bd + (Al +DEP) + Fe	1	26.8
	15	trace

Polymerization were carried out at 50°C with hexane as solvent; [Bd] = 3.0M, [Fe] = 0.75 mM, [DEP]/ [Fe] = 2.0, and [Al]/[Fe] = 20.

low polymerization temperature is required. Fe<sup>2+</sup>-complex has been proved to be the only active species in diene polymerization.<sup>11</sup> In a binary catalyst system iron-compound/AlR<sub>3</sub>, inactive Fe<sup>0</sup>-species is more easily produced than the formation of active Fe<sup>2+</sup>-species due to over-reduction by aluminum compound as stated above, leading to very low catalytic activity.<sup>19</sup> And this is probably one of the reasons why extra electron donor, such as dialkyl phosphite, which is assumed to stabilize Fe<sup>2+</sup>-species, is a prerequisite for the system.

As set forth above, the active species of the current catalyst is particularly stable. Dialkyl phosphite as an electron donor is believed to be decisive to stabilization of the active species. Data in Table III demonstrate the importance of formation of Fe-DEP complex in catalyst activity. Fe(2-EHA)<sub>3</sub> and DEP first aged together give the best activity. Aging time gives almost no difference in activity, indicating that Fe-DEP complex has been quickly formed. While Fe(2-EHA)<sub>3</sub> and Al(*i*-Bu)<sub>3</sub> aged first gives much lower activity, the activity becomes even lower with longer aging time, and as expected, no activity is observed without the use of DEP. The results confirms that DEP as an electron donor is effective to stabilize the active species from over-reduction by the formation of Fe-DEP complex.

### CONCLUSIONS

When polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene with an iron(III) catalyst system,

using Al(*i*-Bu)<sub>3</sub> as a cocatalyst, addition of an appropriate phosphorus compound markedly enhance the catalyst activity and the stereoselectivity, the activity being high and constant in a broad range of [Al]/[Fe]. Fe(2-EHA)<sub>3</sub>/Al(*i*-Bu)<sub>3</sub>/DEP catalyst keeps high catalyst activity in a broad range of [P]/[Fe] and [Al]/[Fe] ratios. Aging Fe(2-EHA)<sub>3</sub> and DEP together first gives the best activity, aging time having almost no difference in activity. Different [Al]/[Fe] and [P]/[Fe] ratios lead to polymers of different stereoregularity. While higher [Al]/[Fe] molar ratio tends to yield syndiotactic polymers, higher [P]/[Fe] molar ratio favors amorphous polymers.

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