

# Butadiene Polymerization with Nickel Compounds: Effect of Cocatalysts

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## SYNOPSIS

The preparation of a high *cis*-1,4-polybutadiene, using a novel ternary catalyst system composed of triethylaluminum, a soluble nickel compound, and boron trifluoride diethyl etherate has been reported in the literature. The present paper reports the polymerization results obtained when the triethylaluminum was replaced with other alkylaluminums and the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was replaced with other  $\text{BF}_3$  complexes or  $\text{HF} \cdot \text{Et}_2\text{O}$ . When utilizing  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , both the polymerization rate and the polymer DSV decreased significantly as the length of the alkyl group in the alkylaluminum increased from  $\text{C}_1$  to  $\text{C}_6$ . However, the length and nature of the alkyl group had virtually no effect when utilizing  $\text{BF}_3 \cdot \text{phenolate}$  ( $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$ ) and only a small effect with  $\text{HF} \cdot \text{Et}_2\text{O}$ ; although the length of the alkyl group had no significant effect when using  $\text{BF}_3$  complexes of aromatic aldehydes, the branched alkyl groups gave greater polymerization rates than did the corresponding *n*-alkyls. In summary, the strongly acidic complexes,  $\text{BF}_3 \cdot \text{phenolate}$  and  $\text{HF} \cdot \text{etherate}$ , promoted rapid polymerization when employed with any of the alkylaluminums. However, with other  $\text{BF}_3$  complexes, the alkylaluminum selected had an important influence upon either the conversion and/or the polymer DSV.

## INTRODUCTION

Nickel-containing catalysts for the production of very high *cis*-1,4-polybutadiene elastomers were reported first by Ueda and co-workers.<sup>1-3</sup> Although they investigated the use of several metal alkyls and metal halides (Lewis acids), most of their published results utilized only a triethylaluminum (TEAL)–nickel carboxylate–boron trifluoride diethyl etherate ( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) catalyst system, and Ohnishi<sup>2</sup> stated that  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was the best Lewis acid to use with nickel and that boron appeared to be essential.

Dixon and co-workers<sup>4</sup> also reported the preparation of high *cis*-1,4-polybutadiene using a nickel salt and  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , but employing either butyllithium or lithium tetrabutyl boron rather than TEAL. They studied a range of metal halides and metal halide complexes and concluded that  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  gave by far the best results.

The present author<sup>5</sup> described another catalyst system—namely, the complex reaction product of HF, a nickel compound and trialkylaluminums—for producing very high *cis*-1,4-polybutadiene. The HF-containing system readily produced a high molecular weight polymer, which was suitable for oil extension, and high polymerization rates were obtained when using either TEAL or triisobutylaluminum (TIBAL).

The present paper compares the polymerization results obtained when nine different trialkylaluminums ( $\text{R}_3\text{Al}$ ) or dialkylaluminum hydrides ( $\text{R}_2\text{AlH}$ ) were utilized as cocatalysts and when the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was replaced with other  $\text{BF}_3$  complexes<sup>6</sup> or  $\text{HF} \cdot \text{Et}_2\text{O}$ .<sup>7</sup>

## EXPERIMENTAL

The  $\text{BF}_3$  etherate, phenolate, and hydrate complexes were obtained from Allied Chemical Company; the  $\text{BF}_3 \cdot \text{phosphoric acid}$  complex was supplied by Harshaw Chemical Company; the other  $\text{BF}_3$  complexes and the  $\text{HF} \cdot \text{etherate}$  were prepared by bubbling  $\text{BF}_3$

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or HF into the complexing agent. All were approximately 1 : 1 mol ratio complexes except  $\text{BF}_3$  phenolate, which was  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$ . The  $\text{BF}_3$  and HF were purchased from The Matheson Company. The source and analyses of the aluminum alkyls ( $\text{R}_1\text{R}_2\text{Al}$ ) have been reported previously.<sup>8</sup> Nickel octanoate (NiOct) was obtained from The Shepherd Chemical Company.

The polymerization procedure has been described previously.<sup>5b</sup> Duplicate series of polymerizations were terminated after 1, 2, 4, and 19 h. The dilute solution viscosities (DSV) reported herein were determined on polymers that had reached at least 60% conversion so that DSV would not be a function of conversion level.<sup>3a</sup> The polymer microstructures were determined from infrared spectra.<sup>9</sup>

## RESULTS

### Effect of Different Aluminum Alkyls with $\text{BF}_3 \cdot \text{Et}_2\text{O}$

As the length of the alkyl chain in the aluminum alkyls ( $\text{R}_1\text{R}_2\text{Al}$ ) increased from  $\text{C}_1$  to  $\text{C}_6$ , both the polymerization rate and the DSV of the polymers were sharply lower when using  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . The data in the middle column of Table I and the lower curve in Figure 1 show the polymer yields obtained during

**Table I** Effect of  $\text{R}_1\text{R}_2\text{Al}$  with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$

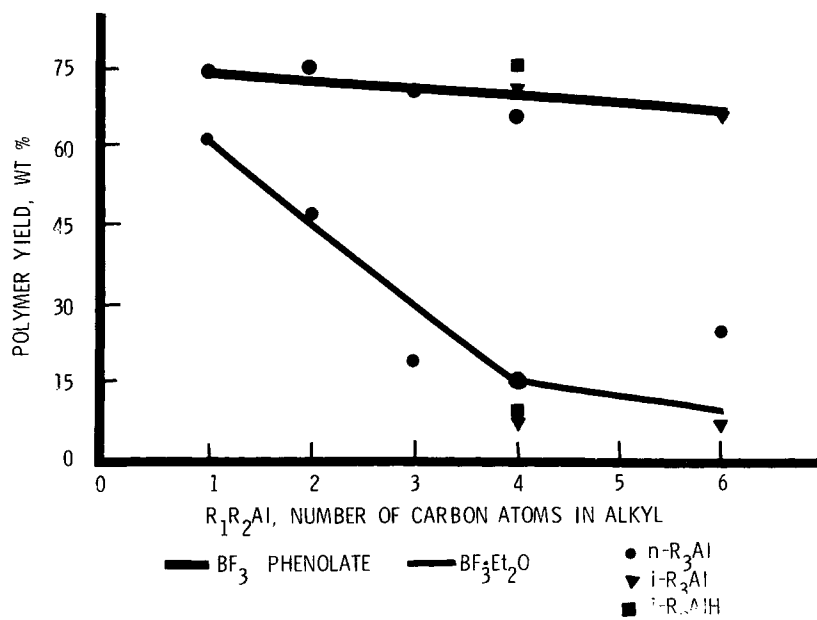
Alkyl in $\text{R}_1\text{R}_2\text{Al}$	Polymer Yield (wt %)	Polymer DSV (dL/g) <sup>a</sup>
$\text{C}_1$	61	2.8
$\text{C}_2$	46	2.8
<i>n</i> - $\text{C}_3$	18	2.4
<i>n</i> - $\text{C}_4$	14	2.5
<i>i</i> - $\text{C}_4$	7	1.5
<i>i</i> - $\text{C}_4$ -H	8	2.2
<i>n</i> - $\text{C}_6$	24	2.6
<i>i</i> - $\text{C}_6$	6	2.0

Polymerization conditions: 1.85 molar solution of butadiene in benzene. "In situ" catalyst addition, TEAL : NiOct :  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  = 0.7 : 0.05 : 0.75 mmhg (millimole per 100 g monomer). Temperature = 50°C; time = 1 h.

<sup>a</sup> DSVs were on duplicate polymers allowed to go to at least 60% conversion (Ref. 3a).

1 h of polymerization with various  $\text{R}_1\text{R}_2\text{Al}$ 's ranging from trimethylaluminum to triisohexylaluminum. Increasing the alkyl from  $\text{C}_1$  to  $\text{C}_4$  appeared to cause most of the decrease in polymer yield.

Duplicate series of polymerizations, which were terminated after 2 and 4 h rather than 1 h, also produced lower polymer yields as the length of the alkyl chain increased, but after 19 h of polymerization, all yields were at least 94% regardless of the size of the alkyl groups.



**Figure 1** Effect of number of carbon atoms in alkylaluminum upon polymer yield. Polymerization conditions: 1.85 M solution of butadiene in benzene  $\text{R}_1\text{R}_2\text{Al} : \text{NiOct} : \text{BF}_3$  complex = 0.7 : 0.075 : 0.75 mmhg for 1 h at 50°C.

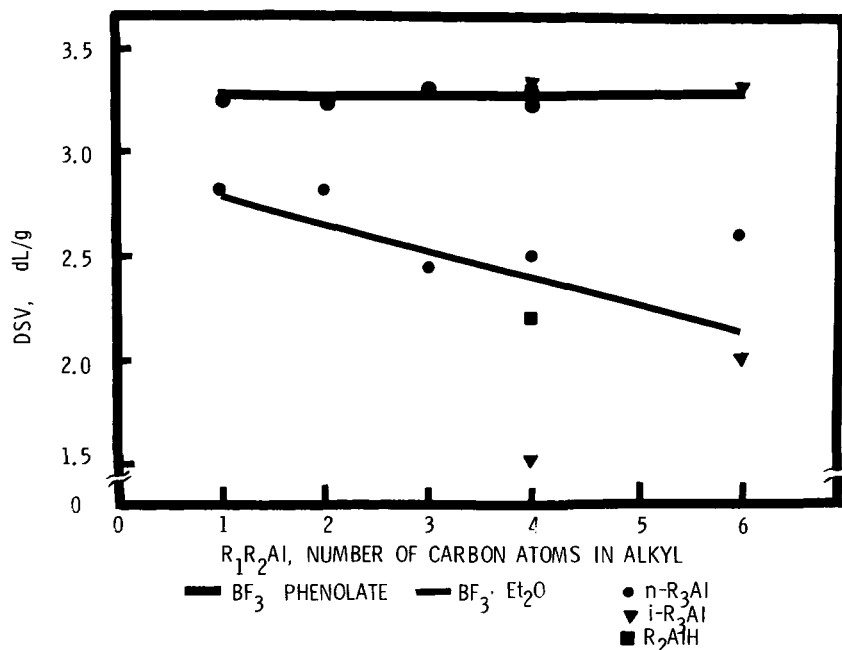


Figure 2 Effect of number of carbon atoms in alkylaluminum compounds upon DSV.

Since the DSVs of the polymers were a function of the percentage of conversion,<sup>3a</sup> increasing rapidly between zero and about 40% conversion and thereafter reaching an almost constant value for a particular set of conditions, the DSVs reported herein were determined on polymers that had reached at least 60% conversion. The data in the right-hand column of Table I and in the lower portion of Figure 2, despite considerable scattering, show that the DSVs declined as the length of the alkyl increased. The iso-C<sub>4</sub>- and iso-C<sub>6</sub>-alkyls produced polymers having lower DSVs than did their straight chain counterparts.

#### BF<sub>3</sub> Ester and Aliphatic Aldehyde Complexes

BF<sub>3</sub> ester and aliphatic aldehyde and ketone complexes acted similarly to BF<sub>3</sub>·Et<sub>2</sub>O in that an increase in the size of the alkyl group on the R<sub>1</sub>R<sub>2</sub>Al

resulted in both a lower polymer yield and lower DSV. This is summarized briefly in Table II.

#### BF<sub>3</sub> Phenolate with Aluminum Alkyls

When BF<sub>3</sub> phenolate was used instead of BF<sub>3</sub>·Et<sub>2</sub>O, the rate of polymerization of butadiene was increased twofold or more. Thus, the polymer yields obtained with TEAL and BF<sub>3</sub> phenolate after 0.5 and 1 h at 50°C were 49 and 75%, respectively, whereas the yield after 1 h with BF<sub>3</sub>·Et<sub>2</sub>O was only 46%. Based upon the 1 h yields, the reaction rate constant,  $k$  h<sup>-1</sup>, with BF<sub>3</sub> phenolate was 1.38 vs. 0.6 with BF<sub>3</sub>·Et<sub>2</sub>O.

Furthermore, with BF<sub>3</sub> phenolate, neither the length and/or branching of the alkyl nor the presence of hydride in the R<sub>1</sub>R<sub>2</sub>Al's had an appreciable effect upon either the polymerization rate or polymer DSV, as shown by the upper lines in Figures 1 and 2.

Table II Comparison of Various BF<sub>3</sub> Complexes

BF <sub>3</sub> Complex	Polymer Yield (%)		DSV	
	TEAL	TIBAL	TEAL	TIBAL
Et <sub>2</sub> O	46	7	2.8	1.5
Ethylbenzoate	45	34	3.3	1.7
Butyraldehyde	44	20	3.6	2.3

#### Comparison of Hydroxyl Containing BF<sub>3</sub> Complexes

BF<sub>3</sub> alcoholates, BF<sub>3</sub> hydrate, and BF<sub>3</sub> phosphoric acid complex were evaluated with TEAL and with tri-(*n*-propyl)-aluminum (TNPA). The results, together with two control experiments, are summarized in Table III. It is pointed out that the butadiene used in this series of experiments contained

**Table III Hydroxyl Containing BF<sub>3</sub> Complexes**

BF <sub>3</sub> Complex	Polymer Yield (%)		DSV	
	TEAL	TNPA	TEAL	TNPA
Et <sub>2</sub> O	25	15	2.5	2.0
-(BF <sub>3</sub> gas)	45	28	2.9	2.6
CH <sub>3</sub> OH	42	49	2.4	2.0
C <sub>2</sub> H <sub>5</sub> OH	53	48	2.8	2.5
2 Phenol	72	—	2.6	—
H <sub>2</sub> O	—	76	—	2.8
H <sub>3</sub> PO <sub>4</sub>	71	72	2.9	—

more vinyl acetylene as an impurity than was present in the other experiments discussed in this report (about 200 ppm vs. 50 ppm of vinyl acetylene) and that acetylenes cause an induction period when using BF<sub>3</sub> · Et<sub>2</sub>O.<sup>3b,4a</sup>

Both the BF<sub>3</sub> methanol and BF<sub>3</sub> ethanol complexes promoted polymerization and/or shortened the induction period significantly more rapidly than did BF<sub>3</sub> · Et<sub>2</sub>O. With either TEAL or TNPA, these BF<sub>3</sub> alcoholates produced approximately 50% yields of polybutadiene in 1 h vs. a 25% yield obtained with TEAL plus BF<sub>3</sub> · Et<sub>2</sub>O. However, the polymers prepared with TNPA and the alcoholates appeared to have somewhat lower DSVs than did those prepared with TEAL.

The BF<sub>3</sub> hydrate and the phosphoric acid complexes produced 76 and 72% yields of polybutadiene, respectively, which were equivalent to the yield produced by BF<sub>3</sub> phenolate. With these complexes, TEAL and TNPA produced approximately equivalent yields of polymers, which appeared to have approximately equivalent DSVs. It is pointed out

that the BF<sub>3</sub> hydrate and H<sub>3</sub>PO<sub>4</sub> complexes (and to a lesser extent the BF<sub>3</sub> alcoholates) have the disadvantage that they are so polar that they are insoluble in benzene and in the butadiene premix. Furthermore, the polybutadienes prepared with BF<sub>3</sub> · H<sub>3</sub>PO<sub>4</sub> contained about 5% of gel, while gel was virtually absent in all the other polymers.

#### Effect of Different Aluminum Alkyls with BF<sub>3</sub> Benzaldehyde

BF<sub>3</sub> benzaldehyde complex was evaluated with each of nine different R<sub>1</sub>R<sub>2</sub>Al's, and the polymer yields obtained during 2 h are presented in Table IV where they may be compared with data for BF<sub>3</sub> · Et<sub>2</sub>O.

The R<sub>1</sub>R<sub>2</sub>Al's containing branched alkyl groups produced significantly higher polymer yields than did the straight-chain R<sub>1</sub>R<sub>2</sub>Al's with BF<sub>3</sub> benzaldehyde; the respective 2 h yields were about 78 vs. 56%. The length of the alkyl group in R<sub>1</sub>R<sub>2</sub>Al had no effect when used with BF<sub>3</sub> benzaldehyde, although the length of the alkyl was very important in combination with BF<sub>3</sub> · Et<sub>2</sub>O.

Other BF<sub>3</sub> aromatic aldehyde complexes gave results similar to those reported for BF<sub>3</sub> benzaldehyde. Table V shows results obtained with BF<sub>3</sub> tolualdehyde and *m*-NO<sub>2</sub>- and *p*-NO<sub>2</sub>-benzaldehyde used with TEAL and with TIBAL.

#### Comparison of Different Aluminum Alkyls Plus HF · Et<sub>2</sub>O

The use of HF · Et<sub>2</sub>O in combination with any of the R<sub>1</sub>R<sub>2</sub>Al's rapidly polymerized butadiene, regardless of the length or the branching of the alkyl group or the presence of hydride. TIBAL gave a slightly

**Table IV Comparison of BF<sub>3</sub> · Et<sub>2</sub>O and BF<sub>3</sub> · C<sub>6</sub>H<sub>5</sub>CHO**

Alkyl	Yield (wt %)		DSV	
	BF <sub>3</sub> · Et <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHO	Et <sub>2</sub> O	C <sub>6</sub> H <sub>5</sub> CHO
C <sub>1</sub>	86	56	2.8	3.3
C <sub>2</sub>	74	58	2.8	2.6
C <sub>2</sub> —H	—	52	—	2.3
C <sub>3</sub>	42	63	2.4	2.5
<i>n</i> -C <sub>4</sub>	34	56	2.5	2.4
<i>n</i> -C <sub>6</sub>	51	53	2.6	2.7
<i>i</i> -C <sub>4</sub>	29	75	1.5	2.6
<i>i</i> -C <sub>4</sub> —H	23	84	2.2	2.2
<i>i</i> -C <sub>6</sub>	13	78	2.0	2.0

Time = 2 h.

**Table V Other BF<sub>3</sub> Aromatic Aldehydes**

BF <sub>3</sub> Complex	Yield (wt %)		DSV	
	TEAL	TIBAL	TEAL	TIBAL
Et <sub>2</sub> O	74	29	2.8	1.5
Benzaldehyde	58	75	2.6	2.6
<i>p</i> -Tolualdehyde	54	76	2.5	2.3
<i>m</i> -NO <sub>2</sub> —benzaldehyde	68	81	2.3	2.5
<i>p</i> -NO <sub>2</sub> —benzaldehyde	31	72	—	2.7

Time = 2 h.

higher rate than did TEAL. Thus, at R<sub>3</sub>Al : NiOct : HF · Et<sub>2</sub>O = 1.0 : 0.075 : 2.5 mmol/100 g butadiene, and 1 h polymerization time at 50°C, TIBAL produced an 88% polymer yield vs. an 81% yield with TEAL, resulting in reaction rate constants,  $k$  h<sup>-1</sup>, of 2.1 vs. 1.66, respectively.

Table VI presents both DSV and Mooney viscosity data on a series of four polymers prepared using TEAL, TNPA, TIBAL, and DIBA-H. The Mooney viscosities averaged 76 ± 2 and thus showed no significant trend. The DSVs of the polymers prepared with both TIBAL and DIBA-H were marginally lower than were the others.

### Polybutadiene Microstructures

The microstructures of the polymers prepared with nickel catalyst systems were unaffected by variations in the size or branching of the alkyl, or the presence of hydride in the R<sub>1</sub>R<sub>2</sub>Al, as shown by infrared analyses presented in Table VII. Replacement of BF<sub>3</sub> · Et<sub>2</sub>O with BF<sub>3</sub> aldehydes, esters, ketones, or phenolates, or with HF · Et<sub>2</sub>O, did not affect the microstructure of the resulting polymers. BF<sub>3</sub> acrylonitrile complex was an exception since it resulted in the content of *trans*-1,4-polybutadiene increasing from about 1.5 to 7.5%.

**Table VI Evaluation of R<sub>1</sub>R<sub>2</sub>Al's with HF · Et<sub>2</sub>O**

Alkyl	Yield (%)	DSV	ML-4
C <sub>2</sub>	92	4.7	74
<i>n</i> -C <sub>3</sub>	92	5.0	76
<i>i</i> -C <sub>4</sub>	91	4.4	78
<i>i</i> -C <sub>4</sub> —H	91	4.3	74

R<sub>1</sub>R<sub>2</sub>Al : NiOct : HF · Et<sub>2</sub>O = 1 : 0.075 : 3 mmol 50°C, 3 h, in benzene.

### DISCUSSION

Since the polymerization rate when using BF<sub>3</sub> · Et<sub>2</sub>O is influenced by the size of the alkyl groups on the aluminum alkyls, it appears that a steric effect is involved. It is believed<sup>2,5,10</sup> that normally an exchange of alkyl groups and fluorine atoms occurs between the R<sub>3</sub>Al and BF<sub>3</sub>. Large alkyl groups probably hinder this exchange and so become one factor in lowering the polymerization rate. Chain transfer occurs<sup>3</sup> in this system. If the chain transfer rate is not altered, more transfers could occur when the polymerization rate is low, and so polymer having a lower DSV could be formed.

It is not known yet how the BF<sub>3</sub> phenolate, alcoholates, and hydrate promote more rapid polymerization of butadiene than does BF<sub>3</sub> · Et<sub>2</sub>O, but these are strong acids (e.g., the acidity function,  $H_0$ , of BF<sub>3</sub> · H<sub>2</sub>O is reported<sup>11</sup> to be -11.2 and BF<sub>3</sub> phenolate as greater than that of concentrated H<sub>2</sub>SO<sub>4</sub> = -6.5). It is proposed that the strongly ionic (acidic) character of BF<sub>3</sub> phenolate and hydrate is a key factor in their promotion of rapid polymerization rates.

**Table VII PBD Microstructure**

Catalyst		cis-	trans-	1,2-
Alkyl Al	BF <sub>3</sub> Complex			
C <sub>1</sub>	Et <sub>2</sub> O	97.2	1.2	1.6
<i>n</i> -C <sub>6</sub>	Et <sub>2</sub> O	97.1	1.6	1.3
C <sub>2</sub>	Butyraldehyde	97.4	1.2	1.4
C <sub>1</sub>	2 Phenol	97.3	1.3	1.4
<i>i</i> -C <sub>4</sub> —H	2 Phenol	97.1	1.1	1.8
C <sub>2</sub>	Benzaldehyde	97.2	1.7	1.1
<i>i</i> -C <sub>4</sub>	<i>p</i> -NO <sub>2</sub> —benzaldehyde	97.6	1.0	1.4
C <sub>2</sub>	Benzonitrile	98.0	1.2	0.8
C <sub>2</sub>	Acrylonitrile	91.8	7.5	0.7
<i>i</i> -C <sub>4</sub>	HF · Et <sub>2</sub> O	97.5	1.4	1.1

HF is a rather strong acid, and it has about 60% ionic character. The  $\text{HF} \cdot \text{Et}_2\text{O}$  is also a strong acid and should be capable of being a proton donor. Both the  $\text{BF}_3$  phenolate and the  $\text{HF} \cdot \text{Et}_2\text{O}$  probably enhance the formation of strong ion pairs, which may promote rapid polymerization. However, HF causes less chain transfer than does  $\text{BF}_3$  and so produces polymers having higher DSVs. The average number of polymer chains formed per nickel atom using  $\text{HF} \cdot \text{Et}_2\text{O}$  and the  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  with TEAL catalyst systems, based upon number average molecular weights,  $\bar{M}_n$ , of about 220,000 and 100,000 and the nickel concentrations in Tables I and VI, are calculated to be about 6 and 20, respectively.

## CONCLUSIONS

When utilizing  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  and a nickel salt with butadiene in benzene premix, both the polymerization rate and the polymer DSV decrease significantly as the size of the alkyl group in the aluminum alkyls ( $\text{R}_3\text{Al}$ ) increases; the only  $\text{R}_3\text{Al}$  for practical use with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  is triethylaluminum.

$\text{BF}_3$  phenolate (or other hydroxyl-containing complexes) helps to promote much more rapid polymerization than does  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ; any available  $\text{R}_1\text{R}_2\text{Al}$  may be used since the size of the alkyl is almost immaterial with the phenolate.

With  $\text{BF}_3$  complexes of aromatic aldehydes, branched alkyls in  $\text{R}_3\text{Al}$  give significantly greater polymerization rates than do straight chain alkyls, but the length of the alkyl has no effect; the preferred  $\text{R}_3\text{Al}$  is triisobutylaluminum (TIBAL).

$\text{HF} \cdot \text{Et}_2\text{O}$  promotes both more rapid polymerization and greater polymer molecular weight than the  $\text{BF}_3$  complexes do, and the nature of the alkyl group in  $\text{R}_3\text{Al}$  has only a small effect; TIBAL is preferred.

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