

# Efficient Control of Molecular Weight with Trialkylaluminum in Ethylene–Norbornene Copolymerization by $[\text{Ph}_2\text{C}(\text{Flu})(3\text{-MeCp})]\text{ZrCl}_2$ –Methylaluminoxane Catalyst

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**ABSTRACT:** Ethylene–norbornene (E–N) copolymerizations were conducted with  $C_1$ –symmetric  $[\text{Ph}_2\text{C}(\text{Flu})(3\text{-RCp})]\text{ZrCl}_2$  [R: Me (**1**) or  $\text{Me}_3\text{Si}$  (**2**)], which give alternating E–N copolymer, activated by methylaluminoxane (MAO) in the absence or presence of  $\text{R}_3\text{Al}$  [R: Me, Et, *i*Bu, "Oct]. The activity of **1** in the absence of  $\text{R}_3\text{Al}$  was approximately double of that of **2** and became two– to fourfold by the addition of  $\text{R}_3\text{Al}$  depending on the amount and R of  $\text{R}_3\text{Al}$ .  $\text{Et}_3\text{Al}$  increased the activity most effectively and the number–average molecular weight ( $M_n$ ) of the produced polymer was decreased from 100,000 g/mol to 25,000 g/mol according to the amount of  $\text{Et}_3\text{Al}$  added. On the other hand, the  $M_n$  value was increased by the addition of *i*Bu<sub>3</sub>Al from 100,000 g/mol to 209,000 g/mol accompanied by the increase of the activity with approximately 2.5–fold. Consequently, **1** was found to be one of the most promising complexes for synthesis of alternating E–N copolymers, of which  $M_n$  value is widely controlled by the kind and the amount of  $\text{R}_3\text{Al}$  added accompanied by the increase in the copolymerization activity.

**Keywords:** chain transfer; copolymerization; ethylene; metallocene catalysts; norbornene; polyolefins; synthesis

## INTRODUCTION

Polymers with precisely controlled molecular weight are highly requested in industrial and academic fields. How to control chain transfer reactions is a key to control the molecular weight of polymers in addition polymerization. In usual olefin polymerization with Ziegler–Natta catalysts, three types of chain transfer reactions are present<sup>[1]</sup>: 1)  $\beta$ –hydrogen transfer to monomer, 2)  $\beta$ –hydrogen transfer to an active

center, 3) transmetallation of propagation chain with organometallic compound. The chain transfer of types 1 and 2 should be controlled by the design of catalyst, whereas the chain transfer of type 3 can be controlled by just selecting a suitable organometallic compound added.

Compared with hydrogen which is generally used as a chain transfer reagent, the chain transfer reaction of type 3 has a privilege to give metal-terminated polymers, which can be applied to chain-end functionalization and block-copolymer synthesis.<sup>[2]</sup>  $R_3Al$  are commercially available and strong Lewis acidity, and for these features they have been frequently used as cocatalyst and/or chain transfer reagent in olefin polymerization with Ziegler-Natta catalysts.

Cycloolefin copolymers such as poly(ethylene-co-norbornene) have attracted a lot of attention recently because of their original characteristic properties. As far as we know, however, there is only one report on the effect of  $R_3Al$  in E-N copolymerization: Brintzinger and Fink et al. investigated the effects of  $R_3Al$  or dialkylzincs with  $[Me_2C(Ind)(Cp)]ZrCl_2$  and *rac*- $[C_2H_4(2-^iBuMe_2SiO-Ind)_2]ZrCl_2$  activated by MAO and found that high molecular weight copolymers were obtained by addition of a certain amount of  $^iBu_3Al$ .<sup>[3]</sup>

On the other hand, the reaction behavior of  $[Me_2C(Flu)(3-RCp)]ZrCl_2$  complex is significantly dependent on the bulkiness of the substituent at 3-position on Cp ring. In alternating E-N copolymerization with  $[Me_2C(Flu)(3-RCp)]ZrCl_2$  [R: Me,  $^iPr$ ,  $^iBu$ ], the activity showed maximum when R =  $^iPr$ .<sup>[4]</sup> The effects of  $R_3Al$  as a chain transfer reagent should also depend on the substituent at 3-position of *ansa*-(Flu)(Cp)-type metallocene.

We therefore conducted E-N copolymerization with  $[Ph_2C(Flu)(3-RCp)]ZrCl_2$  [R: Me (**1**) or  $Me_3Si$  (**2**)] as shown in Scheme 1 in the presence of a series of  $R_3Al$  and found that **1** combined with MAO is one of the promising catalysts to synthesize alternating E-N copolymers, where the  $M_n$  value was widely controlled by the kind and the amount of  $R_3Al$  added with keeping the high copolymerization activity.

## EXPERIMENTAL

### Materials

Because of air and moisture sensitivity of organometallic compounds, all the manipulations were carried out under an atmosphere of pure and dry nitrogen, using standard Schlenk techniques. **1** and **2** were synthesized according to literature.<sup>[5]</sup> MAO in toluene solution, and  $Me_3Al$ ,  $Et_3Al$ ,  $^iBu_3Al$ ,  $^nOct_3Al$  were provided by Tosoh Finechem Co. and used without any treatment. Norbornene (Tokyo Chemical Ind.

Co.) was purified by stirring it over calcium hydride at 60 °C for 5 h and then distilled. The stock solution of norbornene was prepared in toluene (7 M). Research grade ethylene (Sumitomo Seika Chemicals Co.) was purified by passing it through a Gasclean and a Drycolumn (Nikka Seiko Co.). All solvents were commercially obtained and dried by standard methods.

### General Procedure of E–N Copolymerization

Polymerizations were performed in a 100 mL glass reactor equipped with a seal septum and a magnetic stirrer under nitrogen atmosphere. Firstly, the reactor was charged with toluene, the stock solution of norbornene, and MAO with a syringe under nitrogen gas flow. After the solution was saturated with gaseous ethylene under atmospheric pressure, polymerization was started by the addition of solution of complex. Polymerization was conducted for 30 min and terminated with acidic methanol. The obtained polymers were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

### Copolymer Characterization

The  $^{13}\text{C}$  NMR spectra of the copolymers were measured at 130 °C on a JEOL Lambda 500 or a GSX 500 spectrometers operated at 125 MHz in the pulse Fourier transform mode using 1,1,2,2-tetrachloroethane- $d_2$ , and the central peak of the solvent (74.47 ppm) was used as reference. Molecular weight and molecular weight distribution of the copolymers were determined by gel permeation chromatography (GPC) with a Waters 150 CV at 135 °C using 1,2-dichlorobenzene as a solvent and calibrated by polystyrene standards.

## RESULTS

### Effects of $\text{R}_3\text{Al}$ addition

In the absence or presence of  $\text{R}_3\text{Al}$ , E–N copolymerizations were conducted with **1** and **2** combined with MAO (Table 1). As reported previously,<sup>[4,6]</sup> alternating E–N copolymers were obtained from these catalyst systems and **1** showed approximately twofold activity of **2** (Figure 1). In addition, the effects of bulkiness of  $\text{R}_3\text{Al}$  added and the substituent at 3-position of *ansa*–(Flu)(Cp)–type metallocene on norbornene content seemed to be negligible under the present reaction conditions (Table 1).

All the copolymerizations in the presence of  $\text{R}_3\text{Al}$  proceeded to give alternating copolymers with higher activities than those in the absence of  $\text{R}_3\text{Al}$ , and the activity enhancement of **1** was more significant than that of **2**. The activity of **1** was increased

more than double by the addition of  $i\text{Bu}_3\text{Al}$  and  $^n\text{Oct}_3\text{Al}$ , and copolymers with higher  $M_n$  were obtained. On the other hand, it is worth to note that the activity of **1** was increased approximately fourfold by the addition of  $\text{Et}_3\text{Al}$  accompanied by the decrease in the  $M_n$  of the copolymer. Although several papers reported that the activity of metallocene catalysts was decreased by the addition of less hindered  $\text{R}_3\text{Al}$  like  $\text{Me}_3\text{Al}$ ,<sup>[3,7]</sup> the activities of **1** and **2** were increased even by the addition of  $\text{Me}_3\text{Al}$ .

The observation that the activity of **1** was effectively enhanced by the addition of  $\text{R}_3\text{Al}$  accompanied by the increase or decrease of the  $M_n$  values encouraged us to control the molecular weight with  $\text{R}_3\text{Al}$  efficiently.

### Effects of $i\text{Bu}_3\text{Al}$ addition

The addition of  $i\text{Bu}_3\text{Al}$  and  $^n\text{Oct}_3\text{Al}$  increased both the copolymerization activity and the  $M_n$  value of the produced copolymer. We investigated the effect of the amount of  $i\text{Bu}_3\text{Al}$  because  $i\text{Bu}_3\text{Al}$  is more common and inexpensive compared with  $^n\text{Oct}_3\text{Al}$  (Table 2). The increase in the amount of  $i\text{Bu}_3\text{Al}$  added improved the activity of **1** accompanied by the increase in the  $M_n$  value of the copolymer to reach up to 209,000 g/mol with 3 mmol of  $i\text{Bu}_3\text{Al}$ , and the polymerization of entry 4 was terminated in 20 min due to the difficulty in homogeneous stirring.

Then we conducted the same experiment using **2** for comparison. In the absence of  $i\text{Bu}_3\text{Al}$ , the activity of **2** is about half of that of **1**, whereas the molecular weights of the obtained polymers were almost the same. The addition of  $i\text{Bu}_3\text{Al}$  gradually increased the  $M_n$  values of the polymers accompanied by the increase in the activity also in the case of **2**. The effects were however less significant compared with **1**.

### Effects of $\text{Et}_3\text{Al}$ addition

The activity increased with increasing the amount of  $\text{Et}_3\text{Al}$  added and showed the maximum with fourfold of the original activity by the addition of 1 mmol of  $\text{Et}_3\text{Al}$  (Table 2). Further addition of  $\text{Et}_3\text{Al}$  caused a slight decrease in the activity.

On the other hand, the  $M_n$  value was monotonously decreased by the increment of  $\text{Et}_3\text{Al}$ . Consequently, the copolymer with low  $M_n$  of 25,000 g/mol was obtained in high yield in the presence of 3 mmol of  $\text{Et}_3\text{Al}$ . The number of polymer chain ( $N$ ) was calculated from the polymer yield and the  $M_n$  value determined by GPC and are shown in Table 2. The  $N$  value was also increased with increasing the amount of  $\text{Et}_3\text{Al}$ . The results indicate that  $\text{Et}_3\text{Al}$  was an efficient chain transfer reagent in the **1** system.

Then we conducted the same experiment using **2**. We observed similar tendency also in the activity which showed maximum with a certain  $\text{Et}_3\text{Al}$  amount, although the

enhancement of the activity was less than double. On the other hand, 1 mmol of Et<sub>3</sub>Al made the  $M_n$  value approximately half but further addition hardly changed it.

## DISCUSSION

The active species of zirconocene–MAO is a coordinative–unsaturated cationic Zr(IV)–alkyl species which is generated by the abstraction of the anionic ligand by MAO. Hence the MAO derived anion is present as a counter anion (Scheme 2, **A**). Lewis acidic R<sub>3</sub>Al can react with **A** in two ways: one is the formation of heterobinuclear species with the cationic Zr species (**B**)<sup>[3,8]</sup> and the other is the coordination to the MAO–derived counter anion (**D**). The former should depress the activity but the latter should enhance it. If unstable **B** can be formed as an intermediate, chain transfer reaction occurs without the depression of the activity (**C**). These effects should be strongly depending on the zirconocene ligand as well as R in R<sub>3</sub>Al used.

### 1) Effects of R<sub>3</sub>Al addition on activity

The relative values of activity,  $M_n$  and  $N$  in the presence of R<sub>3</sub>Al to those in the absence of R<sub>3</sub>Al are calculated from the data in Table 1 and summarized in Table 3. The activities of **1** and **2** were increased by the addition of R<sub>3</sub>Al in all cases and the highest activity was observed by the addition of Et<sub>3</sub>Al. This result suggests that the substituent on Cp ring should prevent the formation of stable **B** regardless of R in R<sub>3</sub>Al, and hence R<sub>3</sub>Al can selectively coordinate to the counter anion to enhance the activity. However, the activity enhancement observed in **2** was significantly smaller than that in **1**, because the bulky Me<sub>3</sub>Si group sterically prohibits the coordination of the counter anion in the more hindered **2** to originally give the loosely–bounded ion pair. The lower activity of **2** in the absence of R<sub>3</sub>Al despite the formation of loosely–bounded ion pair should be ascribed to the steric hindrance of the coordination site caused by the bulky Me<sub>3</sub>Si group.

### 2) Effects of R<sub>3</sub>Al addition on $M_n$ and $N$ values

The effects of R<sub>3</sub>Al on the  $M_n$  and the  $N$  values can also be interpreted according to Scheme 2, especially by the formation and the stability of **B**. The addition of Et<sub>3</sub>Al decreased the  $M_n$  value and increased the  $N$  value in both catalyst systems, and the increasing ratio of the  $N$  value decreased in the following order; **1** (9.56) > **2** (2.80). This order can be explained by the easier access of Et<sub>3</sub>Al to the **1**–derived zirconium cation compared with the more hindered **2**–derived one to cause the chain transfer reaction via **B**. The effects of Et<sub>3</sub>Al concentration shown in Table 2 support this

interpretation. The increase in the amount of Et<sub>3</sub>Al monotonously decreased the  $M_n$  value and synchronously increased the  $N$  value of the polymer obtained with **1**, whereas the  $M_n$  value of the polymers obtained with **2** was almost independent of the amount of Et<sub>3</sub>Al.

In contrast to Et<sub>3</sub>Al, the addition of <sup>i</sup>Bu<sub>3</sub>Al and <sup>n</sup>Oct<sub>3</sub>Al increased the  $M_n$  value accompanied by the considerable increase of the activity especially in the **1** system. The increasing ratios of the activities in both **1** and **2** systems are higher than those of the  $N$  values, indicating that the addition of <sup>i</sup>Bu<sub>3</sub>Al and <sup>n</sup>Oct<sub>3</sub>Al enhances the propagation rate more than the chain transfer rate. The  $N$  values shown in Table 2 indicate that the chain transfer reaction by <sup>i</sup>Bu<sub>3</sub>Al proceeded in the **1** system but not in the **2** system. The bulky Me<sub>3</sub>Si group at 3-position on Cp ring in **2** should prevent the formation of heterobinuclear species B with <sup>i</sup>Bu<sub>3</sub>Al.

## CONCLUSION

We found that the activity of [Ph<sub>2</sub>C(Flu)(3-MeCp)]ZrCl<sub>2</sub> (**1**) was enhanced effectively by the addition of <sup>i</sup>Bu<sub>3</sub>Al or Et<sub>3</sub>Al accompanied with increasing or decreasing the  $M_n$  value of the produced copolymer, respectively, in E-N copolymerization. Thus the **1**-MAO combined with R<sub>3</sub>Al was proved to be one of the most promising catalytic systems for the synthesis of alternating E-N copolymers with controlled  $M_n$  values in high yields.

## REFERENCES

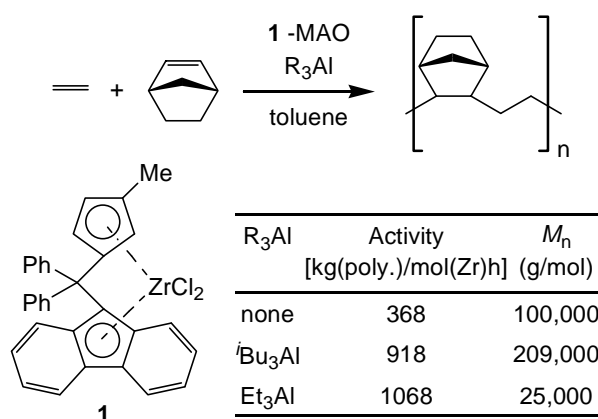
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Text for the ‘Table of Contents’

**Only by choosing the amount of *i*Bu<sub>3</sub>Al or Et<sub>3</sub>Al added, the *M<sub>n</sub>* values of alternating ethylene/norbornene (E–N) copolymers were widely controlled from 25,000 g/mol to 209,000 g/mol accompanied with the increase in the polymer yields by the use of [Ph<sub>2</sub>C(Flu)(3–MeCp)]ZrCl<sub>2</sub> (**1**) combined with methylaluminoxane (MAO) in toluene.**

Graphic for the ‘Table of Contents’



Scheme 1: C<sub>1</sub>-symmetric metallocenes for ethylene–norbornene copolymerization [R: Me (**1**) or Me<sub>3</sub>Si (**2**)]

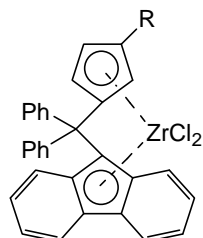


Table 1. E–N Copolymerizations with **1** and **2** activated by MAO in the absence or presence of R<sub>3</sub>Al<sup>a</sup>.

Entry	Complex	R <sub>3</sub> Al	Yield (g)	Activity <sup>b</sup>	<i>M<sub>n</sub></i> (x 10 <sup>4</sup> ) <sup>c</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>c</sup>	N content	N conv. (%) <sup>e</sup>	<i>N</i> (μmol) <sup>f</sup>
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							in			
							copoly.			
							(mol%) <sup>d</sup>			
1	<b>1</b>	-	0.92	368	10.0	1.72	40	10	9	
2	<b>1</b>	Me <sub>3</sub> Al	1.57	628	13.6	1.40	-	-	12	
3	<b>1</b>	Et <sub>3</sub> Al	3.19	1276	3.7	1.93	41	36	86	
4	<b>1</b>	<sup>i</sup> Bu <sub>3</sub> Al	1.98	792	12.3	1.84	39	21	16	
5	<b>1</b>	<sup>n</sup> Oct <sub>3</sub> Al	2.15	860	11.0	1.79	-	-	20	
6	<b>2</b>	-	0.43	172	9.5	1.47	39	5	5	
7	<b>2</b>	Me <sub>3</sub> Al	0.50	200	9.3	1.55	-	-	5	
8	<b>2</b>	Et <sub>3</sub> Al	0.73	292	5.4	1.97	40	8	14	
9	<b>2</b>	<sup>i</sup> Bu <sub>3</sub> Al	0.63	252	12.2	1.76	38	7	5	
10	<b>2</b>	<sup>n</sup> Oct <sub>3</sub> Al	0.69	276	12.2	1.81	-	-	6	

<sup>a</sup> Polymerization conditions: Zr = 5  $\mu$ mol, Al (MAO)/Zr = 2000, R<sub>3</sub>Al = 1 mmol, solvent = toluene, total volume = 30 mL, [N] = 1.0 M, ethylene = 1 atm, time = 30 min., temperature = 40 °C.

<sup>b</sup> Activity = kg(poly) mol<sup>-1</sup>(Zr) h<sup>-1</sup>.

<sup>c</sup> Molecular weight and molecular weight distributions were measured by GPC using polystyrene standard.

<sup>d</sup> Norbornene content in copolymer calculated from the <sup>13</sup>C NMR spectrum of copolymer.

<sup>e</sup> Norbornene conversion calculated from norbornene content in copolymer and yield.

<sup>f</sup> Number of polymer chains calculated from yield and  $M_n$ .

Table 2. Effect of <sup>i</sup>Bu<sub>3</sub>Al and Et<sub>3</sub>Al amount on E–N Copolymerizations with **1** and **2** activated by MAO<sup>a</sup>.

Entry	Comple x	<sup>i</sup> Bu <sub>3</sub> Al (mmol)	Et <sub>3</sub> Al (mmol)	Yield (g)	Activity <sup>b</sup>	$M_n$ (x 10 <sup>4</sup> ) <sup>c</sup>	$M_w/M_n$ <sup>c</sup>	$N$ ( $\mu$ mol) <sup>d</sup>
1 <sup>e</sup>	<b>1</b>	–	–	0.92	368	10.0	1.72	9
2	<b>1</b>	1	–	1.98	792	12.3	1.84	16
3	<b>1</b>	2	–	1.98	792	15.0	1.88	13
4 <sup>f</sup>	<b>1</b>	3	–	1.53	918	20.9	1.59	7
5	<b>1</b>	–	0.1	2.02	808	6.1	1.63	33
6	<b>1</b>	–	0.5	2.05	820	4.0	1.95	51
7	<b>1</b>	–	1	3.19	1276	3.7	1.93	86
8	<b>1</b>	–	2	3.05	1220	3.5	1.86	87



9	<b>1</b>	–	3	2.67	1068	2.5	1.94	107
10 <sup>e</sup>	<b>2</b>	–	–	0.43	172	9.5	1.47	5
11	<b>2</b>	1	–	0.63	252	12.2	1.76	5
12	<b>2</b>	2	–	0.52	208	14.3	1.71	4
13	<b>2</b>	3	–	0.61	244	15.6	1.67	4
14	<b>2</b>	–	0.1	0.55	220	6.5	1.65	9
15	<b>2</b>	–	0.5	0.79	316	5.8	2.08	14
16	<b>2</b>	–	1	0.73	292	5.4	1.97	14
17	<b>2</b>	–	2	0.66	264	5.7	2.04	12
18	<b>2</b>	–	3	0.47	188	5.0	2.05	9

<sup>a</sup> Polymerization conditions: Zr = 5  $\mu$ mol, Al (MAO)/Zr = 2000, solvent = toluene, total volume = 30 mL, [N] = 1.0 M, ethylene = 1 atm, time = 30 min, temperature = 40 °C.

<sup>b</sup> Activity = kg(poly) mol<sup>-1</sup>(Zr) h<sup>-1</sup>.

<sup>c</sup> Molecular weight and molecular weight distributions were measured by GPC using polystyrene standard.

<sup>d</sup> Number of polymer chains calculated from yield and  $M_n$ .

<sup>e</sup> In the absence of alkylaluminum.

<sup>f</sup> Time = 20 min.

Table 3. Relative values of activity,  $M_n$  and  $N$  calculated from the data in Table 1.

Entry	Complex	R <sub>3</sub> Al	Relative value		
			Activity	$M_n$	$N$
1	<b>1</b>	–	1.00	1.00	1.00
2	<b>1</b>	Me <sub>3</sub> Al	1.71	1.36	1.33
3	<b>1</b>	Et <sub>3</sub> Al	3.47	0.37	9.56
4	<b>1</b>	<sup>i</sup> Bu <sub>3</sub> Al	2.15	1.23	1.78
5	<b>1</b>	<sup>n</sup> Oct <sub>3</sub> Al	2.34	1.10	2.22
6	<b>2</b>	–	1.00	1.00	1.00
7	<b>2</b>	Me <sub>3</sub> Al	1.16	0.98	1.00
8	<b>2</b>	Et <sub>3</sub> Al	1.70	0.57	2.80
9	<b>2</b>	<sup>i</sup> Bu <sub>3</sub> Al	1.47	1.28	1.00
10	<b>2</b>	<sup>n</sup> Oct <sub>3</sub> Al	1.60	1.28	1.20

Scheme 2. Plausible interactions between zirconium cation and R<sub>3</sub>Al

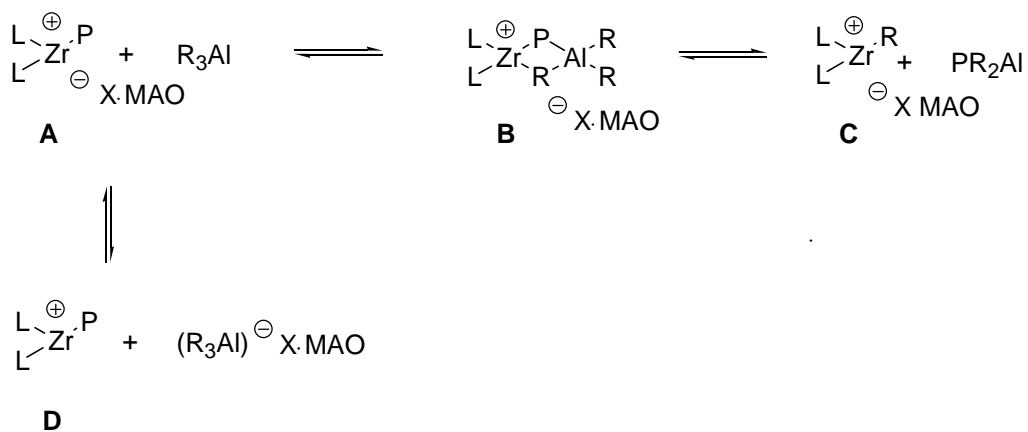


Figure 1.  $^{13}\text{C}$  NMR spectra of E–N copolymers obtained in Table 1 in the absence or presence of  $\text{Et}_3\text{Al}$ .

