

# Polymerization of ethylene with $(C_5Me_5)_2Zr(NMe_2)_2$ cocatalyzed by common alkyl aluminums

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## Abstract

Polymerizations of ethylene have been carried out by using  $Cp_2^*Zr(NMe_2)_2$  ( $Cp^* = C_5Me_5$ ) compound combined with common alkyl aluminums ( $AlR_3$ ) and methylaluminoxane (MAO) as cocatalysts. The  $AlMe_3$  cocatalyzed system showed no activity due to the formation of stable but inactive heterodinuclear  $[Cp_2^*Zr(\mu-Me)_2AlMe_2]^+$  cations; however, the bulkier  $AlR_3$  [ $AlEt_3$ ,  $Al(i-Bu)_3$  and  $Al(i-Bu)_2H$ ] cocatalyzed systems showed very high activities. Especially,  $Cp_2^*Zr(NMe_2)_2/Al(i-Bu)_3$  catalyst showed higher catalytic activity and produced higher molecular weight (MW) polymer than  $Cp_2^*Zr(NMe_2)_2/MAO$  catalyst, demonstrating both MAO and bulky  $AlR_3$  are effective cocatalysts for  $Cp_2^*Zr(NMe_2)_2$  compound.

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**Keywords:** Ethylene polymerization; Metallocene; Alkyl aluminum cocatalyst; Transition metal chemistry

## 1. Introduction

Before the invention of the methylaluminoxane (MAO) as an effective cocatalyst for the olefin polymerizations by metallocene compounds, they have only remained model catalysts for the mechanistic study for the olefin polymerization, because they showed only negligible activity when common alkyl aluminums ( $AlR_3$ ) were used as cocatalysts [1–3]. The continuing commercial interests on the metallocene catalysts are attributed to the outstanding features of MAO to increase the activity of polymerization [4]. However, MAO itself is a formidable obstacle to commercialize the metallocene technology, because excess amount is needed to activate metallocene, increasing the cost of the technology. In addition, the exact structure and the role of MAO have not been fully understood.

The utilization of  $AlR_3$  as a cocatalyst of metallocene compound as in the case of heterogeneous Ziegler–Natta catalysts has been a main issue, since the metallocene compounds was developed, resulting in failure. Various types of cocatalyst such as non-coordinating anions have been developed as a substitute for MAO, leaving the cost

problem unsolved. Because of the low efficiency of  $AlR_3$  as a cocatalyst there have been no detailed reports on the olefin polymerizations by metallocene catalysts cocatalyzed by  $AlR_3$ .

Group 4 *ansa*-metallocene amide compounds have been considered as a new class of stereoselective olefin polymerization catalysts since Jordan et al. reported an efficient synthesis method of *ansa*-metallocene  $^{ch}Cp_2Zr(NR_2)_2$  ( $^{ch}Cp_2Zr =$  chiral *ansa*-metallocene framework) via an amine elimination route [5]. The efficiency of amine elimination route was proven to be exploited because the amide derivatives could be used directly in catalyst formulation in the presence of MAO or  $AlR_3$ /non-coordinating anionic compounds [6].

In this study we investigate an effectiveness of  $AlR_3$  and MAO cocatalysts for the ethylene polymerizations by using a metallocene diamide compound,  $Cp_2^*Zr(NMe_2)_2$  ( $Cp^* = C_5Me_5$ ). The effects of the type and the amount of  $AlR_3$  on the catalytic activity and the properties of polymer are reported.

## 2. Experimental

All reactions were performed under a purified nitrogen atmosphere using standard glove box and Schlenk techniques.

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Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5 Å/13X. Trimethylaluminum ( $\text{AlMe}_3$ ), triethylaluminum ( $\text{AlEt}_3$ ), diethylaluminum chloride ( $\text{AlEt}_2\text{Cl}$ ), triisobutylaluminum ( $\text{Al}(i\text{-Bu})_3$ ), and diisobutylaluminum hydride ( $\text{Al}(i\text{-Bu})_2\text{H}$ ) donated by Korea Petrochemical Co. and were used without further purification. MAO was purchased from Akzo Chemical as 8.4 wt.% total Al (Al in MAO is composed of 81.5 wt.% from MAO and 18.5 wt.% from  $\text{AlMe}_3$ ) solution in toluene. Solvents were distilled from Na/benzophenone and stored over molecular sieves (4 Å). Literature procedures [7] were employed to synthesize  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  complexes.

### 2.1. Polymerization of ethylene

Ethylene polymerizations were performed in a 250 ml round-bottom flask equipped with a magnetic stirrer and a thermometer. In a dry box, the reactor was charged with toluene (80 ml) and a prescribed amount of MAO or alkylaluminum cocatalyst. The reactor was immersed in a constant temperature bath previously set to desired temperature. When the reactor temperature had been equilibrated to the bath temperature, ethylene was introduced into the reactor after removing argon gas under vacuum. When absorption of ethylene into toluene ceased, a prescribed amount of metallocene catalyst dissolved in toluene was injected into the reactor and then the polymerization was started. Polymerization kinetics was determined at every 0.01 s from the rate of consumption, measured by a hot-wire flowmeter (model 5850 D from Brooks Instrument Div.) connected to a personal computer through an ac/dc converter. Polymerization was quenched by the addition of methanol containing HCl (5 vol.%) and then the unreacted monomer was vented. The polymer was washed with an excess amount of methanol and dried in vacuo at 50 °C.

### 2.2. Characterization techniques

Thermal analysis of polymer was carried out by using a dupont differential scanning calorimeter (DSC, model 910) at 10 °C/min heating rate under nitrogen atmosphere. The results of the second scan are reported to eliminate differences in sample history. Infrared spectra were obtained with an ATI Mattson Genesis Series FTIR. Polymer films of 100  $\mu\text{m}$  thickness were prepared for IR examination by using a hot press (Graseby Specac Film Maker) at 150 °C for 30 s. Molecular weight and its distribution ( $M_w/M_n$ ) were determined by gel permeation chromatography (GPC) on a Waters 150-C at 135 °C in 1,2-dichlorobenzene with a data processor, equipped with polystyrene gel columns.  $^1\text{H}$  NMR spectra of compounds were recorded on a Bruker WM-300 spectrometer using tetramethylsilane as an internal standard  $\text{CD}_2\text{Cl}_2$  solvent. Wilmad NMR tube with J Young valve was used for a NMR-scale reaction.

## 3. Results and discussion

### 3.1. Effect of $\text{AlR}_3$ on the ethylene polymerization

Metallocene catalysts for the polymerization of ethylene are almost as old as Ziegler–Natta catalysis itself. In 1957, Natta et al. [8] and independently Breslow and Newburg [3] reported on a soluble, crystalline and isolobal complex from  $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_3$  catalyst which was active towards ethylene polymerization but much slower than a comparative heterogeneous Ziegler–Natta catalyst, e.g.  $\text{TiCl}_4/\text{AlEt}_3$ . Even though there have been tremendous research about and developments on the metallocene catalyst systems, MAO invented by Kaminsky et al. [9] remains the most effective cocatalyst for the metallocene complexes. We revisited the effectiveness of  $\text{AlR}_3$  as a cocatalyst for the metallocene amide compound. Common alkylaluminums such as  $\text{AlMe}_3$ ,  $\text{AlEt}_3$ ,  $\text{AlEt}_2\text{Cl}$ ,  $\text{Al}(i\text{-Bu})_3$ , and  $\text{Al}(i\text{-Bu})_2\text{H}$ , were tested as cocatalysts for  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  complex. The rate of polymerization ( $R_p$ ) obtained by using  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{AlMe}_3$  and  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{AlEt}_2\text{Cl}$  catalysts were too low to detect by our rate monitoring system, as reported earlier. However,  $\text{AlEt}_3$ ,  $\text{Al}(i\text{-Bu})_3$ , and  $\text{Al}(i\text{-Bu})_2\text{H}$  cocatalyzed systems showed unexpectedly high activity in the ethylene polymerizations. Figs. 1–3 illustrate rate profiles of ethylene polymerization obtained by using  $\text{AlEt}_3$ ,  $\text{Al}(i\text{-Bu})_3$ , and  $\text{Al}(i\text{-Bu})_2\text{H}$  as cocatalysts, respectively. Polymerization rate profile obtained by  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{MAO}$  ( $\text{Al}/\text{Zr} = 2000$ ) catalyst is also shown for the comparison in Fig. 1. The  $\text{Al}(i\text{-Bu})_3$  and  $\text{Al}(i\text{-Bu})_2\text{H}$  cocatalyzed systems are characterized by both higher activity and better stability than the

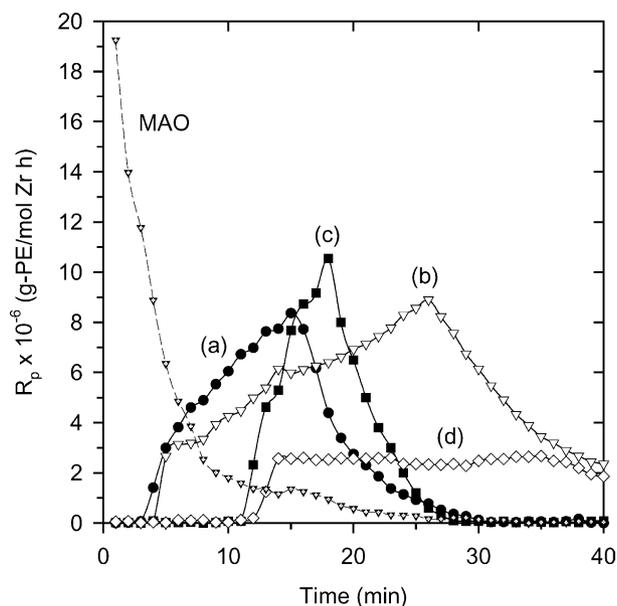


Fig. 1.  $R_p$  vs. time curve obtained by  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{AlEt}_3$  catalyst. Polymerization conditions:  $T_p = 30^\circ\text{C}$ ,  $P_{\text{C}_2\text{H}_4} = 1.3\text{ atm}$ ,  $[\text{Zr}] = 1.275\ \mu\text{M}$ , toluene = 80 ml; and (a)  $[\text{Al}]/[\text{Zr}] = 9$ ; (b) 12; (c) 18; and (d) 27. MAO cocatalyzed system polymerized at the same conditions except  $[\text{Al}]/[\text{Zr}] = 2000$ .

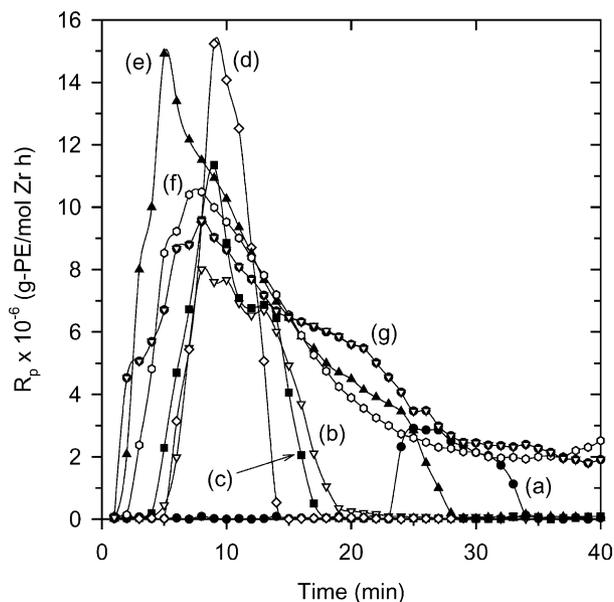


Fig. 2.  $R_p$  vs. time curve obtained by  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{Al}(i\text{-Bu})_3$  catalyst. Polymerization conditions:  $T_p = 30^\circ\text{C}$ ,  $P_{\text{C}_2\text{H}_4} = 1.3$  atm,  $[\text{Zr}] = 1.275 \mu\text{M}$ , toluene = 80 ml; and (a)  $[\text{Al}]/[\text{Zr}] = 24$ ; (b) 48; (c) 72; (d) 96; (e) 167; (f) 238; and (g) 334.

MAO cocatalyzed system. It is interesting to note that all catalyst systems cocatalyzed by common alkyl aluminums have quite long induction periods, about 12 min (Fig. 1(d)). In general, the induction period becomes longer at higher alkyl aluminum concentrations. The MAO cocatalyzed system is characterized by the negligible induction period and rapid deactivation (Fig. 1).

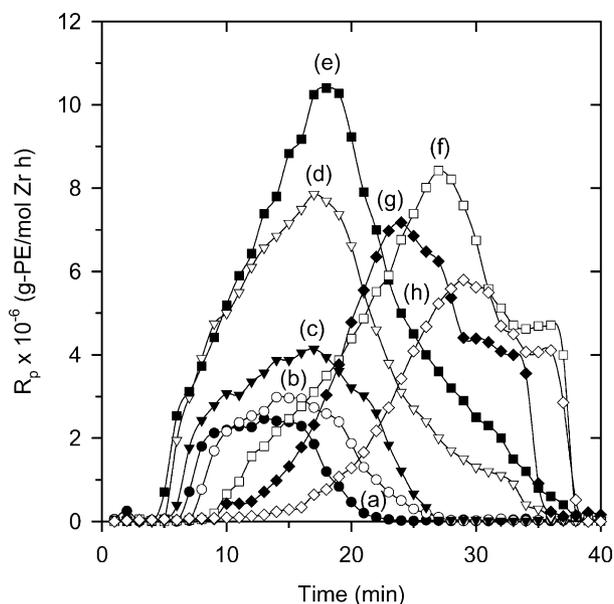
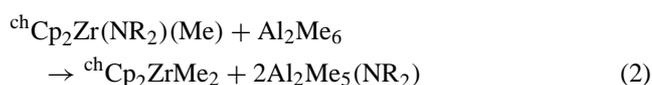
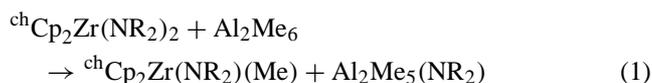


Fig. 3.  $R_p$  vs. time curve obtained by  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{Al}(i\text{-Bu})_2\text{H}$  catalyst. Polymerization conditions:  $T_p = 30^\circ\text{C}$ ,  $P_{\text{C}_2\text{H}_4} = 1.3$  atm,  $[\text{Zr}] = 1.275 \mu\text{M}$ , toluene solvent = 80 ml; and (a)  $[\text{Al}]/[\text{Zr}] = 59$ ; (b) 82; (c) 118; (d) 153; (e) 235; (f) 352; (g) 471; and (h) 588.

The best activity as the average rate of polymerization ( $\bar{R}_p$ ) for  $\text{Al}(i\text{-Bu})_3$  and  $\text{Al}(i\text{-Bu})_2\text{H}$  cocatalyzed systems was recorded when  $[\text{Al}]/[\text{Zr}]$  is around 250; however, the  $\text{AlEt}_3$  cocatalyzed system showed high activity at very narrow  $[\text{Al}]/[\text{Zr}]$  range, demonstrating that the activity of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  complex is very sensitive to the type and the concentration of cocatalyst (Table 1).

In the previous reports [6] we showed that *ansa*-metallocene amide  $^{\text{ch}}\text{Cp}_2\text{Zr}(\text{NR}_2)_2$  is stoichiometrically alkylated by  $\text{AlMe}_3$  to afford  $^{\text{ch}}\text{Cp}_2\text{ZrMe}_2$ .



After alkylating  $^{\text{ch}}\text{Cp}_2\text{Zr}(\text{NR}_2)_2$  by four equivalents of  $\text{AlMe}_3$ , methylzirconium cations ( $[\text{rac}(\text{EBI})\text{ZrMe}]^+$ ) are in situ generated successfully by reacting complexes with ammonium salts (e.g.,  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $[\text{HNMePh}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ , and  $[\text{HNEt}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ ) and alkyl abstraction reagents. The formation of these cationic species which polymerize propylene stereospecifically was also proved by using spectroscopic measurements [6].

Similar NMR-scale reactions of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  with one to four equivalents of  $\text{AlMe}_3$  showed that  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  compound is stoichiometrically alkylated by  $\text{AlMe}_3$  to afford  $\text{Cp}_2^*\text{ZrMe}_2$  [ $\delta(\text{Zr}-\text{Me}) = -1.43$  ppm in  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$  solvent)] compound. Further, addition of  $\text{AlMe}_3$  ( $[\text{Al}]/[\text{Zr}] = 8$ ) led to the formation of heterodinuclear  $[\text{Cp}_2^*\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$  [ $\delta(\mu\text{-Me}) = -0.80$  ppm and  $\delta(\text{Al}-\text{Me}) = -0.59$  ppm in  $^1\text{H}$  NMR spectrum] cations, the adduct of the base-free  $[\text{Cp}_2^*\text{ZrMe}]^+$  cation and  $\text{AlMe}_3$ . These dinuclear species show polymerization activity if they undergo loss or displacement of  $\text{AlMe}_3$  during polymerization, ultimately leading to  $[\text{Cp}_2^*\text{ZrMe}]^+$  cations. However, the dinuclear species remains unchanged even after increasing the amount of  $\text{AlMe}_3$  to  $[\text{Al}]/[\text{Zr}] = 16$ . Addition of small amount of ethylene monomer to the NMR tube containing this mixture yielded no polymer.

Reactions of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  with 10–40 equivalents of MAO (Al in MAO is composed of 81.5 wt.% of MAO and 18.5 wt.%  $\text{AlMe}_3$ ) in an NMR tube showed that  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  compound is alkylated by MAO and/or free  $\text{AlMe}_3$  contained in MAO, followed by activated to give  $[\text{Cp}_2^*\text{ZrMe}]^+[\text{MAO}]^-$  cations [ $\delta(\text{Zr}-\text{Me}) = -0.65$  ppm in  $^1\text{H}$  NMR spectrum], which are very active for the ethylene polymerizations. These results obtained from the reactions of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  with  $\text{AlMe}_3$  and MAO are summarized in Scheme 1. The alkylated  $\text{Cp}_2^*\text{ZrMe}_2$  species react further with MAO to generate cationic alkylzirconium complexes,  $[\text{Cp}_2^*\text{ZrMe}]^+[\text{MAO}]^-$ , which polymerize ethylene. However, in the presence of  $\text{AlMe}_3$  instead of MAO, the alkylated  $\text{Cp}_2^*\text{ZrMe}_2$  species react with  $\text{AlMe}_3$  in excess to form

Table 1  
The effect of cocatalyst on ethylene polymerization by  $\text{Cp}^*_2\text{Zr}(\text{NMe}_2)_2/\text{AlR}_3$  catalysts

Cocatalyst <sup>a</sup>	[Al]/[Zr]	$\bar{R}_p \times 10^{-6b}$	DSC				GPC	
			$T_m$ (°C)	$T_c$ (°C)	$\Delta H_f^c$ (J/g)	$X_c^c$ (%)	$\bar{M}_w \times 10^{-3}$	MWD
AlEt <sub>3</sub>	9	1.70	131.8	115.5	173.9	64.4	37.8	4.8
	12	3.57	131.4	115.1	167.5	62.1	38.7	5.8
	18	1.34	131.4	115.1	154.1	57.1	38.7	5.6
	27	1.23	132.1	115.3	178.1	66.0	23.0	3.2
Al( <i>i</i> -Bu) <sub>3</sub>	24	0.53	132.6	116.2	170.4	63.1	42.3	4.8
	48	1.32	132.9	115.4	195.6	72.5	50.9	3.6
	72	2.02	132.6	114.6	162.5	60.2	35.8	2.9
	96	2.58	133.1	114.7	156.9	58.1	33.4	2.8
	96 <sup>d</sup>	0.69	133.4	117.9	221.1	81.9	3.31	5.6
	96 <sup>e</sup>	4.86	132.9	115.3	160.4	59.4	27.8	2.6
	167	3.45	132.2	115.1	161.3	59.8	30.9	2.8
	238	4.33	132.5	115.4	175.3	64.9	26.2	2.4
	334	3.47	133.1	115.9	158.7	58.8	26.1	2.7
Al( <i>i</i> -Bu) <sub>2</sub> H	59	0.65	132.4	117.7	232.1	86.0	9.6	5.2
	82	0.88	132.0	118.4	213.0	78.9	10.1	4.8
	118	1.43	132.0	118.4	212.7	78.8	8.1	2.9
	153	3.01	132.4	118.1	204.8	75.9	7.8	3.1
	235	4.01	132.8	117.7	181.4	67.2	7.8	2.7
	352	3.27	133.1	116.8	197.9	73.3	7.3	2.6
	471	1.75	132.8	118.8	180.0	66.7	6.7	3.3
	588	1.67	132.3	119.7	181.6	67.3	6.3	3.6
MAO	2000	1.71	131.4	116.6	118.8	44.0	4.2	2.3

Polymerization conditions are the same as those in Figs. 1–3.

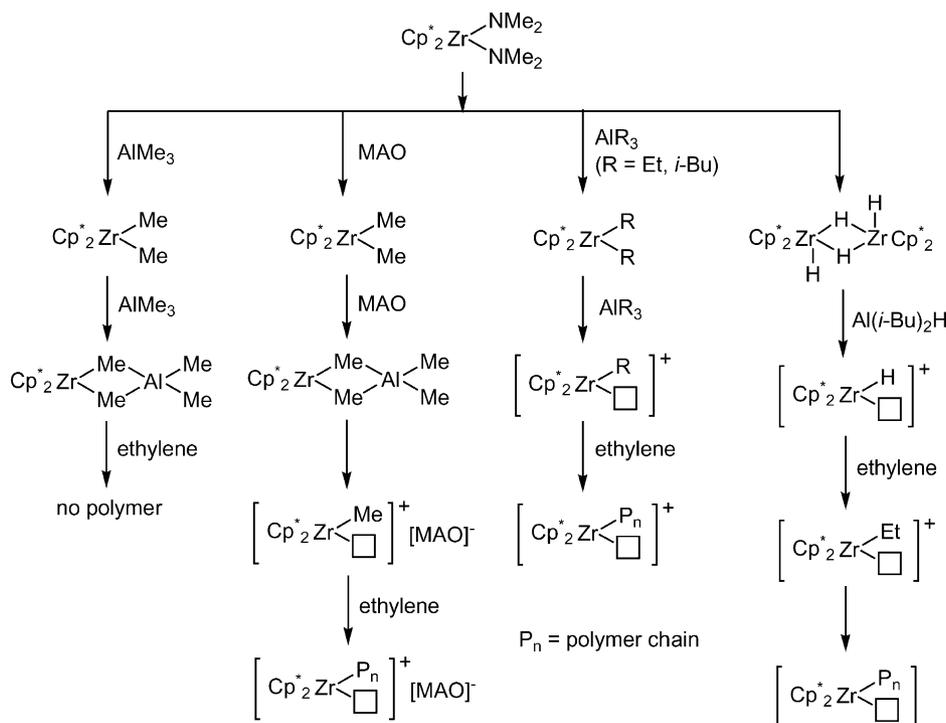
<sup>a</sup> Alkylaluminum cocatalysts such as AlMe<sub>3</sub> and AlEt<sub>2</sub>Cl showed negligible activities.

<sup>b</sup> Unit is g-PE/mol-Zr h.

<sup>c</sup>  $\Delta H_f$  is the heat of fusion and  $X_c$  is the crystallinity calculated from the heat of fusion,  $(\Delta H_f/\Delta H_f^0) \times 100$ , where  $\Delta H_f^0$  is the heat of fusion of folded-chain polyethylene (269.9 J/g) [6].

<sup>d</sup> Polymerization was performed in heptane in the same conditions.

<sup>e</sup> Polymerization was performed in methylene chloride in the same conditions.



Scheme 1.

cationic alkylzirconium species,  $[\text{Cp}_2^*\text{Zr}(\mu\text{-R})_2\text{AlR}_2]^+$ , which are coordinatively saturated and lack a vacant orbital suitable for binding the ethylene monomer. This heterodinuclear complexes reacts further to form  $[\text{Cp}_2^*\text{ZrR}]^+$  cations to be activated for the polymerization. The negligible activity of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{AlMe}_3$  system demonstrates that  $[\text{Cp}_2^*\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$  cations remain inactive due to the stability of the  $\text{AlMe}_3$  adduct.

Similar NMR-scale reactions of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  with  $\text{AlEt}_3$  and  $\text{Al}(i\text{-Bu})_3$  by increasing  $[\text{Al}]/[\text{Zr}]$  ratios from 2 to 8, followed by the addition of small amount of ethylene monomer yielded white precipitates of polymer, indicating the formation of active  $[\text{Cp}_2^*\text{ZrR}]^+$  cations. In these cases no evidence indicating the formation of heterodinuclear  $[\text{Cp}_2^*\text{Zr}(\mu\text{-R})_2\text{AlR}_2]^+$  cations was found. These results mean that  $[\text{Cp}_2^*\text{ZrR}]^+$  [ $\delta(\text{Zr-CH}_2) = 0.35$  ppm for  $\text{R} = \text{Et}$  and  $0.37$  ppm for  $\text{R} = i\text{-Bu}$  in  $^1\text{H}$  NMR spectra] cations are directly formed from corresponding alkylated  $\text{Cp}_2^*\text{ZrR}_2$  species as shown in Scheme 1. NMR-scale reactions of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  with four equivalents of  $\text{Al}(i\text{-Bu})_2\text{H}$  in  $\text{CD}_2\text{Cl}_2$  solvent resulted in homodinuclear  $[\text{Cp}_2^*\text{Zr}(\text{H})(\mu\text{-H})_2\text{Zr}(\text{H})]$  [ $\delta(\mu\text{-H}) = -0.81$  ppm and  $\delta(\text{Zr-H}) = -1.87$  ppm in  $^1\text{H}$  NMR spectrum] species. Addition of four more equivalent of  $\text{Al}(i\text{-Bu})_2\text{H}$  and then small amount of ethylene yielded white precipitates of polymer, indicating the formation of active cationic  $[\text{Cp}_2^*\text{ZrH}]^+$  species which are easily transformed to  $[\text{Cp}_2^*\text{ZrEt}]^+$  by the reaction with ethylene monomer (Scheme 1) [10].

These results indicate that intermediate adducts derived from the reaction of  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  with various alkyl aluminums are different. The bulkier ethyl or isobutyl constituents render the inactive heterodinuclear complexes sterically unfavorable and this could result in a dissociation of the dinuclear or intermediate complexes to the active monomeric  $[\text{Cp}_2^*\text{ZrR}]^+$  species. However, the long induction periods (Figs. 1–3) of the bulky alkyl aluminum cocatalyzed systems demonstrated that the alkylation followed by dissociation is a somewhat slow process. The bulkiness of isobutyl constituents also gives rise to more separate monomeric  $[\text{Cp}_2^*\text{ZrR}]^+$  species, facilitating the access of ethylene monomers to the active sites once the active species form. The rapid rise to the maximum rate (Fig. 2) explains this suggestion.

### 3.2. Characterization of polymers

As summarized in Table 1, the molecular weight (MW) of polymers decreases as the cocatalyst concentration increases. The MW value is the highest in the alkyl aluminum cocatalyzed systems when  $\text{Al}(i\text{-Bu})_3$  is used as a cocatalyst and the lowest when  $\text{Al}(i\text{-Bu})_2\text{H}$  is used. The MAO cocatalyzed system produced polymer of lower MW than alkyl aluminum cocatalyzed systems; however,  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{MAO}$  catalyst showed an ability similar to so-called single site catalyst to produce polymer with narrow molecular weight distribution ( $\text{MWD} = 2.3$ ).

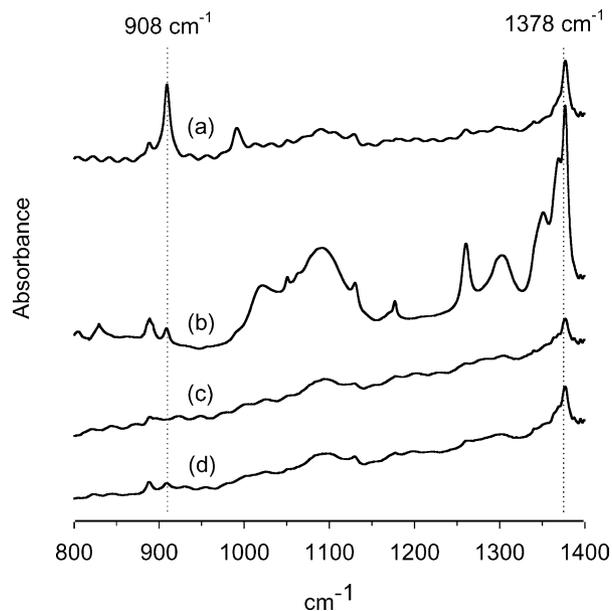


Fig. 4. FTIR analysis of polymer produced by  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2$  combined with (a) MAO (sample in Fig. 1); (b)  $\text{AlEt}_3$  (sample in Fig. 1(c)); (c)  $\text{Al}(i\text{-Bu})_3$  (sample in Fig. 2(e)); and (d)  $\text{Al}(i\text{-Bu})_2\text{H}$  (sample in Fig. 3(d)).

The higher MWD values for alkyl aluminum cocatalyzed systems demonstrate that the active sites generated in  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{AlR}_3$  catalysts are not so uniform as those generated in  $\text{Cp}_2^*\text{Zr}(\text{NMe}_2)_2/\text{MAO}$  catalyst. The broad MWD by alkyl aluminum cocatalyzed systems is most probably due to complicated equilibrium reactions formed during polymerization.

A strong enhancement of the polymerization rate was observed in polar methylene chloride solvent compared to that measured in toluene, while a low activity was observed in heptane solvent, as shown in Table 1. As generally accepted, the active species in the polymerization of olefins with metallocene systems is an ion pair. It is clear that, depending on the polarity of the solvent, the strength of association of the ion pair can change, and hence, an effect on the activity of the catalytic system can be expected. The increase in the activity is explained by an easier ionic dissociation of  $\text{Zr-R-Al}$  bond, which increases the population of the cationic active species and to the low-coordinating power of the methylene chloride molecule. Similar solvent effects were reported for the olefin polymerizations by various metallocene catalysts combined with MAO [11–15].

Where no specific chain transfer agents have been added in metallocene catalyzed polymerization systems, two chain transfer reactions are usually considered:  $\beta$ -hydride elimination and alkylation of the cocatalyst. The  $\beta$ -hydride elimination produces double bonds at the chain end and chain transfer to Al cocatalyst produces alkyl groups. Fig. 4 shows IR spectra of polymers obtained using different cocatalysts. The peaks at  $908$  and  $1378\text{ cm}^{-1}$  are assigned to vinyl and alkyl end groups, respectively. The MAO cocatalyzed polymer shows a strong peak at  $908\text{ cm}^{-1}$  indicating  $\beta$ -hydride

elimination is a main chain transfer process. However, this peak becomes very weak in the alkyl aluminum cocatalyzed systems, especially in the Al(*i*-Bu)<sub>3</sub> cocatalyzed system (Fig. 4(b)). In addition, the peak intensities at 1378 cm<sup>-1</sup> band most probably induced by chain transfer to Al cocatalyst are relatively strong. These results demonstrate that the chain transfer to Al cocatalyst becomes dominant in the alkyl aluminum cocatalyzed systems. Thus, the lower MW value of polymers obtained by Al(*i*-Bu)<sub>2</sub>H cocatalyzed system can be explained by rapid chain transfer reactions to cocatalyst (see Table 1 and Fig. 4(c)).

#### 4. Conclusion

Zirconocene amide complex Cp<sub>2</sub>\*Zr(NMe<sub>2</sub>)<sub>2</sub> showed high activity when combined with either MAO or common alkylaluminum cocatalysts such as AlEt<sub>3</sub>, Al(*i*-Bu)<sub>3</sub>, and Al(*i*-Bu)<sub>2</sub>H. The AlMe<sub>3</sub> cocatalyzed system showed no activity due to the formation of stable and heterodinuclear [Cp<sub>2</sub>\*Zr(μ-Me)<sub>2</sub>AlMe<sub>2</sub>]<sup>+</sup> cations. In Cp<sub>2</sub>\*Zr(NMe<sub>2</sub>)<sub>2</sub>/AlR<sub>3</sub> systems, the easiness of dissociations of inactive AlR<sub>3</sub> adducts to active [Cp<sub>2</sub>\*ZrR]<sup>+</sup> cations determines the catalyst activity. End group analysis of the polymer showed that β-hydride elimination is a main chain transfer process for the MAO cocatalyzed system, while the chain transfer to cocatalyst becomes dominant for the alkyl aluminum cocatalyzed systems.

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