COCATALYTIC ACTIVITIES OF METHYLALUMINOXANE PREPARED BY DIRECT WATER ADDITION METHOD IN ETHYLENE POLYMERIZATION OVER Cp$_2$ZrCl$_2$

Taek Kyu Han*, Tae Seok Seo, Hong Ki Choi and Seong Ihl Woo[†]

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1,
Kusong-dong, Yusong-gu, Taejon 305-701, Korea

Abstract–The characterization of ethylene polymerization behaviors catalyzed over Cp$_2$ZrCl$_2$/MAO homogeneous system using methylaluminoxanes prepared by the direct hydrolysis of AlMe$_3$ (Me=methyl) were reported. The MAO was prepared at the ratio of [H$_2$O]/[Al]=1 and 0.5 and at three different temperatures, i.e., –40, –60 and –80 °C. The polymerization rate was not decreased with polymerization time when the MAO prepared at the ratio of [H$_2$O]/[AlMe$_3$]=1 at –60 °C was used as a cocatalyst regardless of the ratio of Al/Zr and the polymerization temperature. The polymerization rate drastically decreased with polymerization time above 60 °C in case of using MAO prepared at the ratio of [H$_2$O]/[AlMe$_3$]=1 at –80 °C. However, in case of the MAO prepared at the ratio of [H$_2$O]/[AlMe$_3$]=0.5 at –80 °C, the rate continuously increased with polymerization time at the polymerization temperature of 70 °C and 80 °C. The amount of MAO needed to activate Cp$_2$ZrCl$_2$ was larger than that of MAO prepared at the ratio of [H$_2$O]/[Al]=1. The viscosity molecular weight of polyethylene (PE) cocatalyzed with MAO prepared at the ratio of [H$_2$O]/[Al]=0.5 was lower than that of polyethylene obtained with MAO prepared at the ratio of [H$_2$O]/[Al]=1.

Key words : MAO, Cp$_2$ZrCl$_2$, Metallocene, PE, Polymerization

INTRODUCTION

Alkyl aluminoxanes have been found to be an effective co-catalyst in the olefin polymerization catalyzed over metallocenes. Especially, methylaluminoxane (MAO) was found to be a best cocatalyst. The suspected formation of MAO synthesized by partial hydrolysis of AlMe$_3$ was subsequently supported by its direct synthesis and characterization as a mixture of oligomers of approximate composition -(-MeAl-O-)-$_n$. However, the exact composition and structure are still not entirely clear although quite a number of investigations by cryoscopy, UV, vibrational and NMR spectroscopy, chromatography, and other means [Kaminsky, 1983; Sinn et al., 1988; Pasynkiewicz, 1990; Brintzinger et al., 1995] have been carried out. When the hydrolysis of AlMe$_3$, which is highly exothermic (and indeed potentially dangerous), is conducted under controlled conditions, it appears to generate mostly oligomers Me$_2$Al-[-O-AlMe-]$_n$-OAlMe$_2$ with n=5-20. Residual AlMe$_3$ in MAO solutions [Resconi et al., 1990] seems to participate in equilibria that interconvert different MAO oligomers [Cam et al., 1990; Pasynkiewicz, 1990; Cam and Giannini, 1992] and possibly also cyclic and branched oligomers [Sinn et al., 1988; Pasynkiewicz, 1990; Kaminsky et al., 1992].

Here, we report for the first time the influence of the hydrolysis temperature and the molar ratio of AlMe$_3$ to water on the ethylene polymerization catalyzed over Cp$_2$ZrCl$_2$ cocatalyzed by MAO's prepared by the direct hydrolysis of AlMe$_3$. The exact composition and structure of MAO effectively being able to cocatalyze a homogeneous olefin polymerization system has not been adequately understood so far. However, adequate Lewis acidity are certainly present in MAO prepared by direct hydrolysis of AlMe$_3$.

EXPERIMENTAL SECTIONS

1. Synthesis of Methylaluminoxane (MAO-x(y) ; x=[H$_2$O]/[AlMe$_3$], y=hydrolysis temperature)

In case of the synthesis of MAO-1(-40), 300 ml of AlMe$_3$ (2 M in toluene) was cooled at –40 °C in 1,000-ml flask equipped with a magnetic stirrer, nitrogen inlet and the syringe adapter to control the addition rate of water. 10.8 ml (0.6 mol) of water was added dropwise for 2 h. The mixture was warmed slowly to room temperature and stirred for 24 h. The product was separated by filtration and the filtrate was distilled at 40 °C under reduced pressure until all volatiles were removed. The other MAO's were synthesized in the same route except the ratio of water to AlMe$_3$ and the temperature of water addition. These conditions are shown in Table 1. The average molecular weight of MAO was determined by a freezing point depression method using benzene as a solvent [Shugar, 1990]. First, using a test tube under nitrogen atmosphere, 1 g of MAO was dissolved in 25 ml of benzene. The solution was allowed to cool in ice/acetone bath and the freezing point of the solution was recorded using a Beckman thermometer. The average molecular weight M$_2$

[†]To whom correspondence should be addressed.
E-mail : wsi@convex.kaist.ac.kr
*Present address : Daeduk R & D Center, Yu-Kong Limited Co., 140-1 Wonchon-dong, Yusong-gu, Taejon 305-370

Table 1. The ratio of [H₂O]/[AlMe₃] and the temperature of water addition in the preparation of methylaluminoxane by the direct hydrolysis of Al(CH₃)₃ with water and the average molecular weight of the synthesized MAO's

MAO	[H₂O]/ [Al(CH₃)₃]	Temperature (°C)	Molecular weight
MAO-1(-40)	1	-40	1,165
MAO-1(-60)	1	-60	1,015
MAO-1(-80)	1	-80	597
MAO-0.5(-80)	0.5	-80	-

of MAO was calculated by the equation;

$$M_2 = \frac{10^3 \cdot w_2 \cdot k_f}{w_1 \cdot \Delta T}$$

where, ΔT is the depression of the melting point in °C, w_1 weight of solvent, w_2 weight of solute, k_f the cryoscopic constant, (5.12 for benzene) and M_2 molecular weight of solute.

2. Polymerization

Solution polymerizations in toluene were carried out using a Teflon magnetic stirrer for agitation at the total pressure of 1.1 atm in a 500-ml glass reactor. Toluene (200 ml) was introduced into the reactor, the temperature was increased to polymerization temperature, and then toluene was saturated with ethylene. A prepared MAO and Cp₂ZrCl₂ dissolved in toluene were injected into the reactor by a tuberculin syringe, and then the polymerization was started. The polymerization rate was determined every 0.01 sec from the rate of monomer consumption measured with a hot-wire flowmeter (model 5850D from Brooks Instrument Div.) connected to a personal computer through a A/D converter. Polymerization productivity was calculated by integrating the consumption rate of monomer recorded in computer as well as from the polymer yield. Results agreed within ±5 % with the actual yield of polymer after polymerization. All the runs were stopped by injecting ethanol to kill the active polymerization sites. The polymers were precipitated by the addition of an excess of acidified methanol. The precipitated polymer was recovered by filtration, washed with fresh ethanol and dried in vacuo.

3. Analytical Procedures

Intrinsic viscosity, [η], of the polymer in decalin was determined using a modified Ubbelohde viscometer at 135±0.1 °C by one-point intrinsic viscosity [Elliott et al., 1970].

$$[\eta] \cdot C = (2 \cdot \eta_{sp} - 2 \cdot \ln \eta_{rel})^{0.5}$$

where [η] is intrinsic viscosity, C is the concentration of polymer in decalin solution (g/dL), η_{sp} is specific viscosity, and η_{rel} is relative viscosity. Viscosity average molecular weight (M_v) of polyethylene was calculated from the equation; [η]=2.3× 10⁻⁴×M_v^{0.82} [Chiang, 1958; Kissinger and Hughes, 1959].

RESULTS AND DISCUSSION

Fig. 1 shows the polymerization rate curves at three differ-

ent concentrations of MAO at 25 °C using MAO-1(-40) as a cocatalyst. Fig. 2 also shows polymerization behaviors at two different concentrations of cocatalyst using MAO-1(-80). In case of these two MAO's, the time to reach the maximum polymerization rate, t_{max}, did not change much and after reaching maximum rate, the polymerization rate decreased. However, in case of MAO-1(-60), the polymerization behavior was different. The initial activation did not occur at Al/Zr ratio of 250,000 during first 5 min (Fig. 3). After reaching the maximum rate, the polymerization rates were not deactivated much regardless of the concentration of MAO. From these results of polymerization behaviors, it can be proposed that the structure of MAO is very different according to the hydrolysis tem-
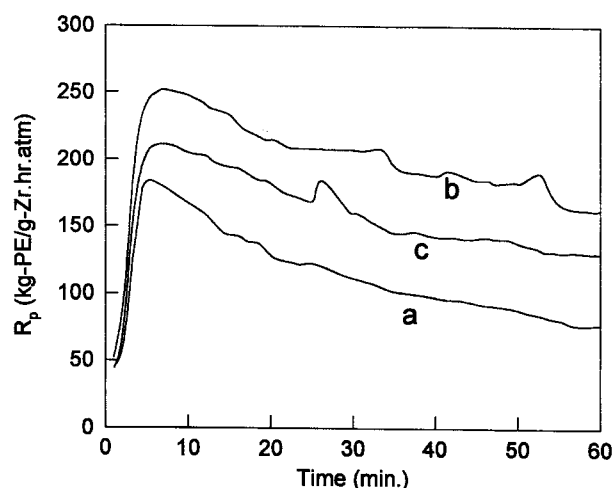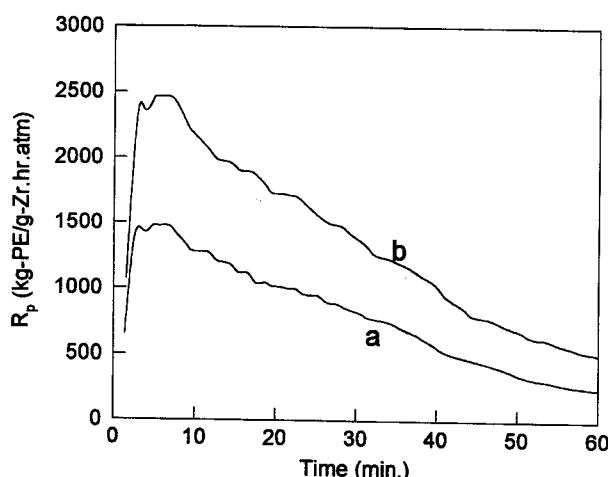

Fig. 1. The effect of [Al]/[Zr] ratio on the rate profiles in ethylene polymerizations catalyzed over Cp₂ZrCl₂ cocatalyzed by MAO-1(-40).
Polymerization conditions : total pressure=1.1 atm ; solvent= toluene (100 cc) ; [Cp₂ZrCl₂]=6.0×10⁻⁷ mol/L ; 30 °C ; [Al]/ [Zr]=(a) 350,000, (b) 620,000, (c) 1,000,000.
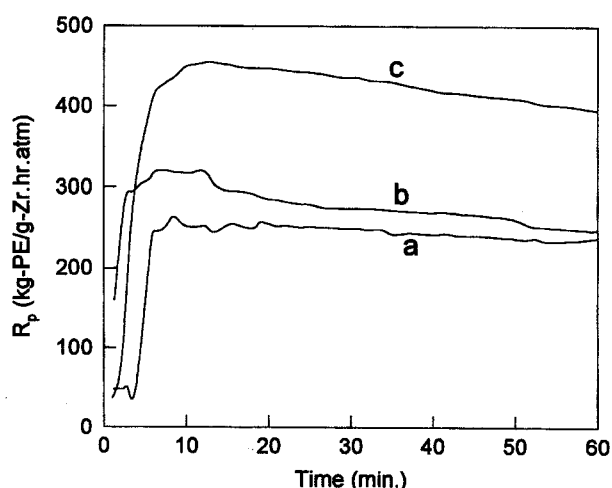

Fig. 2. The effect of [Al]/[Zr] ratio on the rate profiles in ethylene polymerizations catalyzed over Cp₂ZrCl₂ cocatalyzed by MAO-1(-80).
Polymerization conditions : total pressure=1.1 atm ; solvent= toluene (100 cc) ; [Cp₂ZrCl₂]=6.0×10⁻⁷ mol/L ; 60 °C ; [Al]/ [Zr]=(a) 430,000 and (b) 860,000.

Fig. 3. The effect of [Al]/[Zr] ratio on the rate profiles in ethylene polymerizations catalyzed over Cp₂ZrCl₂ cocatalyzed by MAO-1(-60).

Polymerization conditions : total pressure = 1.1 atm ; solvent = toluene (100 cc) ; [Cp₂ZrCl₂] = 6.0×10⁻⁷ mol/L ; 30 ℃ ; [Al]/[Zr] = (a) 250,000, (b) 620,000 and (c) 870,000.

perature of AlMe₃. The hydrolysis reaction rapidly occurs at relatively high temperature and highly exothermic so the structure of products might be very heterogeneous. Some oligomeric molecules might be hydrated so much that it contains a greater number of Al-O structures. The molar ratio of CH₃/Al in MAO prepared at −40 ℃ must be smaller than that of CH₃/Al in MAO prepared at −60 and −80 ℃. On the other hand, MAO-1(-40) contains the unreacted AlMe₃ because the hydrolysis reaction occurs instantaneously to form Al(OH)₃ or Al₂O₃ when an AlMe₃ contacts with H₂O and the AlMe₃ far from water molecules keeps unreacted. On the contrary, if the hydrolysis reaction temperature of AlMe₃ is decreased, the reaction will be slowly progressed. Therefore, the structure of products is more homogeneous and the amount of unreacted AlMe₃ decreases. The catalytic activity and stability are influenced by the ratio of CH₃/Al-O and the amount of AlMe₃ contained in MAO [Kaminsky et al., 1992]. The cocatalytic activities of two MAO's were compared according to the ratio

Table 2. The comparison of two hydrolyzed MAO's in the activity of ethylene polymerization catalyzed over Cp₂ZrCl₂/MAO and the physical properties of produced polyethylene according to the variation of the Al/Zr ratio

MAO	[Al]ᵃ/[Zr]	Activity (kg-PE/g-Zr·hr·atm)	Viscosity (dL/g)	Mv (×10⁻⁵)
MAO-1(-40)	350,000	124	8.51	3.7
	620,000	201	6.60	2.7
	1,000,000	162	6.94	2.9
MAO-1(-60)	250,000	240	5.76	2.3
	620,000	300	7.02	2.9
	870,000	370	7.42	3.1

Other conditions : total pressure=1.1 atm, polymerization temperature=30 ℃, solvent=toluene (100 cc), [Al]ᵃ=the concentration of Al in MAO (I), [Cp₂ZrCl₂]= 6.0×10⁻⁷ mol/L.

of Al/Zr in Table 2. The activity was the maximum at 620,000 of [Al]/[Zr] molar ratio when MAO-1(-40) was used as the cocatalyst. However, it increased with the increase of MAO concentration in case of MAO-1(-60). The molecular weight of the produced polyethylene did not vary much with the concentration of MAO in case of both MAO's. The activity is larger when MAO-1(-60) is used as cocatalyst than in case of MAO-1(-40). The molecular weight of the PE's were similar. This might be due to the fact that MAO-1(-40) contains more Al-O and less methyl group than MAO-1(-60). As shown in Table 1, the molecular weight of MAO-1(-40) is largest so MAO-1(-40) contains the smallest amount of the terminal methyl group. If MAO contains Al-O too much, MAO's will be less effective to activate Cp₂ZrCl₂ through dechlorination and
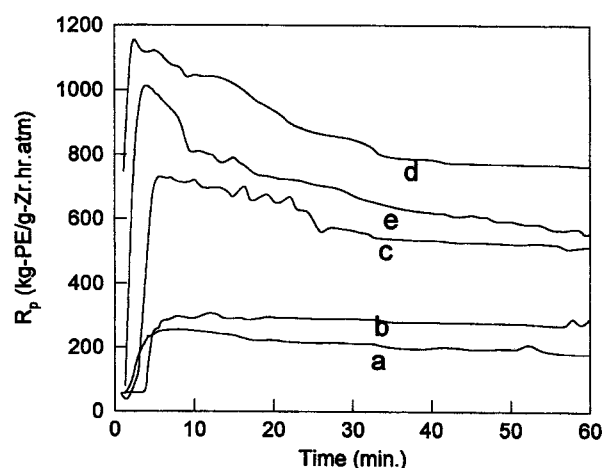

Fig. 4. The effect of polymerization temperature on the rate profiles in ethylene polymerizations catalyzed over Cp₂ZrCl₂ cocatalyzed by MAO-1(-40).

Polymerization conditions : total pressure = 1.1 atm ; solvent = toluene (100 cc) ; [Cp₂ZrCl₂] = 6.0×10⁻⁷ mol/L ; [Al]/[Zr] = 620,000 ; Polymerization temperature = (a) 25 ℃, (b) 40 ℃, (c) 60 ℃, (d) 70 ℃ and (e) 80 ℃.
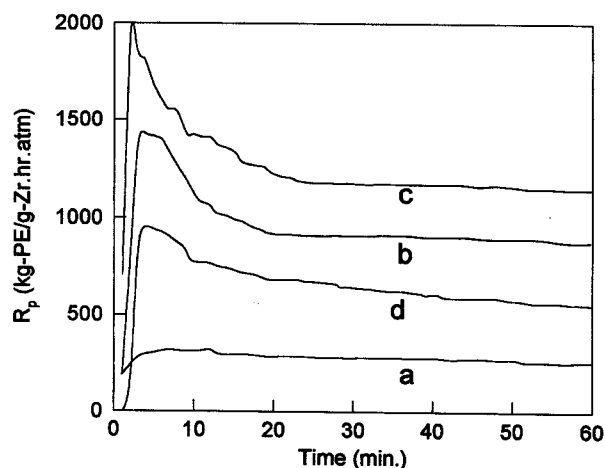

Fig. 5. The effect of polymerization temperature on the rate profiles in ethylene polymerizations catalyzed over Cp₂ZrCl₂ cocatalyzed by MAO-1(-60).

Polymerization conditions : total pressure = 1.1 atm ; solvent = toluene (100 cc) ; [Cp₂ZrCl₂] = 6.0×10⁻⁷ mol/L ; [Al]/[Zr] = 620,000 ; Polymerization temperature = (a) 30 ℃, (b) 50 ℃, (c) 70 ℃ and (d) 80 ℃.
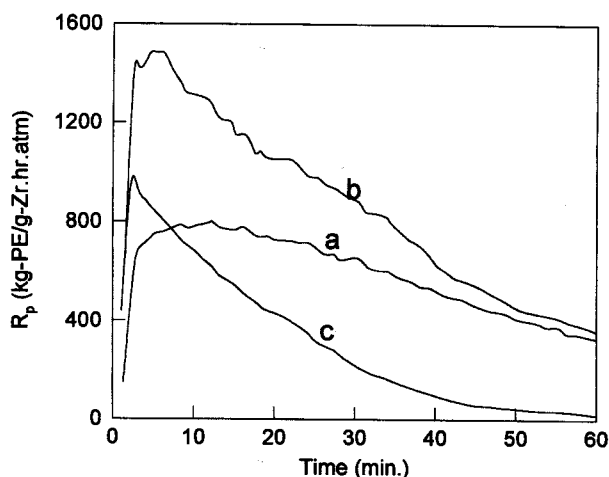
Fig. 6. The effect of polymerization temperature on the rate profiles in ethylene polymerizations catalyzed over Cp_2ZrCl_2 cocatalyzed by MAO-1(-80).

Polymerization conditions : total pressure=1.1 atm ; solvent= toluene (100 cc) ; $[Cp_2ZrCl_2] = 6.0\times10^{-7}$ mol/L ; $[Al]/[Zr] = 430,000$; Polymerization temperature (a) 50 °C, (b) 60 °C and (c) 70 °C.

Table 3. The comparison of two hydrolyzed MAO's in the activity of ethylene polymerization catalyzed over $Cp_2ZrCl_2/$ MAO and the physical properties of produced polyethylene according to the variation of the polymerization temperature

MAO	Polymerization temperature (°C)	Activity (kg-PE/ g-Zr·hr·atm)	Viscosity (dL/g)	Mv ($\times10^{-5}$)
MAO-1(-40)	30	201	6.60	2.7
	40	270	6.38	2.6
	60	595	4.59	1.8
	70	988	4.48	1.7
	80	863	3.44	1.2
MAO-1(-60)	30	300	7.02	2.9
	50	1,100	5.76	2.3
	70	1,300	3.69	1.3
	80	860	2.51	0.8

Other conditions : total pressure=1.1 atm, solvent=toluene (100 cc), $[Al]/[Ti] = 620,000$ where [Al]=the concentration of Al in MAO, $[Cp_2ZrCl_2]=6.0\times10^{-7}$ mol/L.

ethylation to form cationic species, Cp_2ZrMe^+.

The dependence of polymerization rate behavior on polymerization temperature is shown in Fig. 4, 5 and 6, respectively. The initial activation was fast and the decay rate of polymerization was samll at low polymerization temperature and became higher at higher temperature in case of MAO-1(-40) and MAO-1(-60). However, in case of MAO-1(-80) (Fig. 6), polymerization rate drastically decreased above 60 °C. These results are arising from the higher content of unreacted $AlMe_3$ and digomer of low molecular weight, i.e., $Me_2Al-O-AlMe_2$. $AlMe_3$ and $Me_2Al-O-AlMe_2$ will reduce Cp_2-$ZrCl_2$ to inactive dimeric species such as $Cp_2Zr-\mu^2-Me_2AlMe_2$ instead of the formation of cationic active species.

The effect of polymerization temperature on the average activity and molecular weight of PE polymerized over Cp_2ZrCl_2 cocatalyzed by MAO-1(-40) and MAO-1(-60) are shown in Table 3. In both MAO's, the average activity was maximum at 70 °C. The molecular weight of the produced PE was decreased with the increase of temperature.

Fig. 7 shows the polymerization rate profiles when ethylene was polymerized with Cp_2ZrCl_2 cocatalyzed by MAO-0.5(-80) at two different MAO concentrations. The induction time was about 5 min. The deactivation did not occur even though the MAO concentration was very high. Fig. 8 shows the influence of the polymerization temperature on polymerization rate profiles. The rate continuosly increased at 70 °C and 80 °C. This
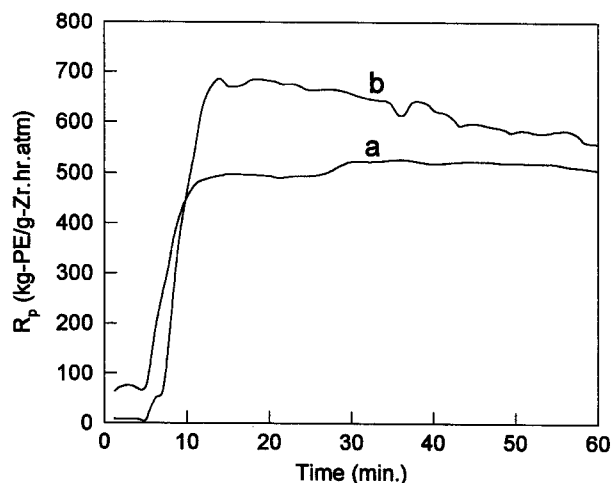

Fig. 7. The effect of [Al]/[Zr] ratio on the rate profiles in ethylene polymerizations catalyzed over Cp_2ZrCl_2 cocatalyzed by MAO-0.5(-80).

Polymerization conditions : total pressure=1.1 atm ; solvent=toluene (100 cc); $[Cp_2ZrCl_2]=6.0\times10^{-7}$ mol/L ; 50 °C ; $[Al]/[Zr]=$(a) 620,000 and (b) 1,600,000.
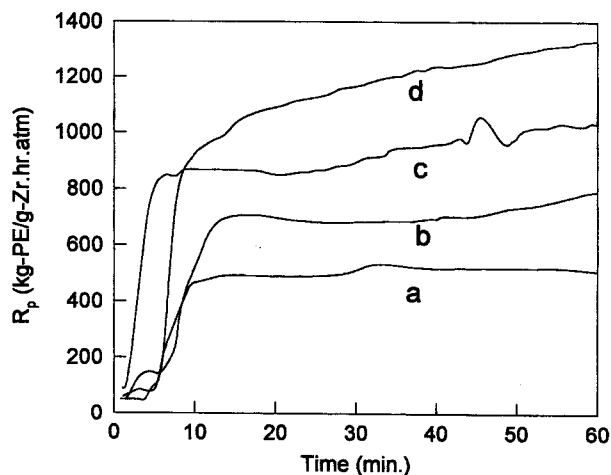

Fig. 8. The effect of polymerization temperature on the rate profiles in ethylene polymerizations catalyzed over Cp_2ZrCl_2 cocatalyzed by MAO-0.5(-80).

Polymerization conditions : total pressure=1.1 atm ; solvent= toluene (100 cc) ; $[Cp_2ZrCl_2]=6.0\times10^{-7}$ mol/L ; $[Al]/[Zr]=$ 620,000 ; Polymerization temperature (a) 50 °C, (b) 60 °C, (c) 70 °C and (d) 80 °C.

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Table 4. The activity of ethylene polymerization catalyzed over Cp₂ZrCl₂ cocatalyzed by MAO-0.5(-80) and the molecular weight of the produced polyethylene's according to the variation of the polymerization temperature and the [Cp₂ZrCl₂]/[MAO] ratio

$[Al]^a/[Zr]$	Polymerization temperature (°C)	Activity (kg-PE/ g-Zr·hr·atm)	Viscosity (dL/g)	Mv ($\times 10^{-5}$)
620,000	50	460	3.21	1.1
1,600,000	50	560	3.46	1.2
620,000	60	650	3.01	1.0
620,000	70	910	2.33	0.8
620,000	80	1,100	1.90	0.6

Other conditions : total pressure=1.1 atm, solvent=toluene (100 cc), $[Al]^a$=the concentration of Al in MAO (I), $[Cp_2ZrCl_2]$=6.0×10⁻⁷ mol/L

behavior is different from the case of the MAO's prepared with the ratio of $[H_2O]/[AlMe_3]$=1, in which the polymerization rate decreased above 70 °C as shown in Fig. 4, 5 and 6. MAO will contain more methyl group or unreacted $AlMe_3$ molecules when $[H_2O]/[AlMe_3]$ is 0.5 than when $[H_2O]/[AlMe_3]$ is 1. This will decrease the polymerization rate. Hence, the increase in the polymerization rate above 70 °C might be due to the unknown structure of MAO prepared at the rate of $[H_2O]/[AlMe_3]$ of 0.5 and 80 °C. The cocatalytic activity of this MAO increased with increase in polymerization temperature as shown in Table 4. The viscosity molecular weight obtained by MAO prepared at the ratio of $[H_2O]/[AlMe_3]$=0.5 is lower than that of polyethylene obtained by MAO's synthesized at the ratio of $[H_2O]/[Al]$=1. This result suggests that MAO synthesized at the ratio of $[H_2O]/[Al]$=0.5 contains much more CH_3 group at the end of MAO which plays a role as a chain transfrer agent.

CONCLUSION

The characterization of ethylene polymerization behaviors catalyzed over Cp_2ZrCl_2/MAO homogeneous system using methylaluminoxanes prepared by the direct hydrolysis of $AlMe_3$ were very different according to the hydrolysis temperature and the ratio of $[H_2O]/[AlMe_3]$. The polymerization rate was not decreased with polymerization time when the MAO prepared at the ratio of $[H_2O]/[AlMe_3]$=1 at −60 °C was used as a cocatalyst regardless of the ratio of Al/Zr and the polymerization temperature. The polymerization rate drastically decreased with polymerization time above 60 °C in case of using MAO prepared at the ratio of $[H_2O]/[AlMe_3]$=1 at −80 °C. However, in case of the MAO prepared at the ratio of $[H_2O]/[AlMe_3]$=0.5 at −80 °C, the rate continuously increased with polymerization time at the polymerization temperature of 70 °C and 80 °C. The ammount of MAO to activate Cp_2ZrCl_2

into ethylene polymerization centers was larger than MAO hydrolyzed at the ratio of $[H_2O]/[AlMe_3]$=1. Conclusively, the optimum condition to synthesize the MAO being able to co-catalyze a homogeneous polymerization system must be sought according to the polymerization conditions.

ACKNOWLEDGMENT

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