

# Effects of Aluminum Alkyls on Ethylene/1-Hexene Polymerization with Supported Metallocene/MAO Catalysts in the Gas Phase

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**ABSTRACT:** The effects of aluminum alkyls on the gas-phase ethylene homopolymerization and ethylene/1-hexene copolymerization over polymer-supported metallocene/methylaluminoxane [(*n*-BuCp)<sub>2</sub>ZrCl<sub>2</sub>/MAO] catalysts were investigated. Results with triisobutyl aluminum (TIBA), triethyl aluminum (TEA), and tri-*n*-octyl aluminum (TNOA) showed that both the type and the amount of aluminum alkyl influenced the polymerization activity profiles and to a lesser extent the polymer molar masses. The response to aluminum alkyls depended on the morphology and the Al : Zr ratio of the catalyst. Addition of TIBA and TEA to supported catalysts with Al : Zr >200 reduced the initial activity but at times resulted in higher average activities due to broadening of the kinetic profiles, i.e., alkyls can be used to

control the shape of the activity profiles. A catalyst with Al : Zr = 110 exhibited relatively low activity when the amount of TIBA added was <0.4 mmol, but the activity increased fivefold by increasing the TIBA amount to 0.6 mmol. The effectiveness of the aluminum alkyls in inhibiting the initial polymerization activity is in the following order: TEA > TIBA >> TNOA. A 2-L semibatch reactor, typically run at 80°C and 1.4 MPa ethylene pressure for 1 to 5 h was used for the gas-phase polymerization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3549–3560, 2004

**Key words:** polyethylene; aluminum alkyls; metallocene catalysts; gas-phase polymerization; morphology

## INTRODUCTION

Kaminsky's group first discovered the metallocene/methylaluminoxane (MAO) catalyst system over 25 years ago.<sup>1</sup> These single-site catalysts have the unique ability to catalyze the polymerization of ethylene and  $\alpha$ -olefins to polyolefins with tailored microstructures at high polymerization activities.<sup>2</sup> Despite this potential, metallocene/MAO catalysts are still not widely commercialized; an excessive amount of MAO is required in homogeneous phase processes to realize the high polymerization activity potential of metallocene catalysts.<sup>3</sup> MAO is both expensive and hazardous. In addition, homogeneous phase polymerization processes are associated with poor product morphology, reactor fouling, and the handling of a large inventory of hazardous solvents. Demand for metallocene-based linear low-density polyethylene, (mLLDPE) is expected to grow at the rate of 15–20% per year in the next few years if the current production and processing problems are solved.<sup>4</sup>

Several researchers<sup>5–7</sup> have successfully supported metallocene/MAO catalysts on solid carriers (for use in gas-phase and slurry polymerizations) to overcome the problems associated with homogeneous systems.

Aluminum alkyls are often added to the reactor during slurry or gas-phase polymerization with supported metallocene/MAO and conventional Ziegler-Natta catalysts to scavenge impurities; in conventional Ziegler-Natta systems, aluminum alkyls also serve as cocatalysts responsible for the generation of active sites. There are also numerous reports on the use of aluminum alkyls as cocatalyst in the polymerization of ethylene and  $\alpha$ -olefins using supported metallocene catalysts.<sup>5–8</sup> The overwhelming majority of these studies paid attention only to the effect of the aluminum alkyls on the polymer molar mass and on the overall (i.e., averaged) activity of the catalytic systems. The effect of aluminum alkyls on activity profiles received little attention, even though this is of crucial importance to the successful design and operation of industrial gas-phase processes, and most of the new mLLDPE production is expected to come from gas-phase processes.<sup>9</sup> Furthermore, the detailed investigations of the effects of aluminum alkyls on activity profiles of olefin polymerization systems focused either on conventional Ziegler-Natta catalysts (for example, see Lynch et al.<sup>10</sup> for gas-phase and Nooijen<sup>11</sup> for slurry phase) or homogeneous and slurry metallocene-based systems.<sup>12–16</sup>

Harlan et al.<sup>17</sup> reported the formation of the Lewis acid–base complex Cp<sub>2</sub>Zr(X)[ $\mu$ -XAl(<sup>*t*</sup>Bu)<sub>3</sub>] between triisobutyl aluminum (TIBA) and Cp<sub>2</sub>ZrX<sub>2</sub> (where X = CH<sub>3</sub><sup>-</sup> or Cl<sup>-</sup>). At sufficiently high aluminum alkyl concentration, this can render the metallocene inactive

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TABLE I  
Description of Polymer-Supported Metallocene/MAO Catalysts

Catalyst	Support <sup>a</sup>	Amount of support used, (g)	Amount of MAO added <sup>b</sup> (mL)	Zr content		Al : Zr ratio
				Mass %	$\mu\text{mol/g cat}$	
CAT1	Poly(DVB/HEMA)	2.01	17.8	0.18	20	380
CAT2	Poly(DVB/HEMA)	1.00	15.0	0.24	26	215
CAT3	Poly(DVB/NVP)	1.51	11.0	0.16	18	230
CAT4	Poly(DVB)	2.00	4.9	0.11	12	110
CAT5	Poly(EGDM)	1.51	10.0	0.13	14	285
CAT6	Poly(DVB/HEMA)	1.50	5.0	0.06	7	375

<sup>a</sup> DVB, divinyl benzene; HEMA, 2-hydroxyethyl methacrylate; NVP, *n*-vinyl-2-pyrrolidinone; EGDM, ethylene glycol dimethacrylate.

<sup>b</sup> Volume of MAO solution (10 mass % in toluene); MMAO-4 solution in toluene (6.92 mass % Al) used for CAT1.

in olefin polymerization.<sup>18</sup> Therefore, an optimum amount of aluminum alkyl is desired in the polymerization reactor, i.e., an amount that is sufficient to scavenge impurities but not excessive to substantially inhibit the catalytic activity. Aluminum alkyls affect polymerization systems differently depending on the catalyst used and the polymerization conditions. Satyanarayana and Sivaram<sup>15</sup> reported a steady increase in polyethylene molar mass with increasing Al(TIBA) : Ti ratio for MgCl<sub>2</sub>-supported Cp<sub>2</sub>TiCl<sub>2</sub> catalyst. Increasing the TIBA concentration was reported to increase<sup>19</sup> as well as decrease<sup>20</sup> the molar masses of polypropylenes produced with metallocene catalysts. Chien and Wang<sup>21</sup> partly replaced the MAO in a homogeneous Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO system with TMA and observed negligible change in polymerization behavior below a TMA : MAO ratio of 10. However, at higher TMA : MAO ratios of about 100, the kinetic profile changed from the maximum initial activity to the gradually increasing (i.e., induction) type. This could be explained with the reversible complexation reactions between metallocene, MAO, and the aluminum alkyl.<sup>22</sup>

The undesirable aluminum alkyl–metallocene interaction can be avoided in laboratory gas-phase polymerization by venting and/or evacuating the excess aluminum alkyl after scavenging impurities.<sup>23</sup> This procedure is not possible with the continuous industrial (gas-phase and slurry) processes. Therefore, the objective of our work was to investigate the effects of aluminum alkyls on the kinetic behavior and polyolefin properties for gas-phase ethylene and ethylene/1-hexene polymerization with supported (*n*-BuCp)<sub>2</sub>ZrCl<sub>2</sub>/MAO.

## EXPERIMENTAL

### Materials

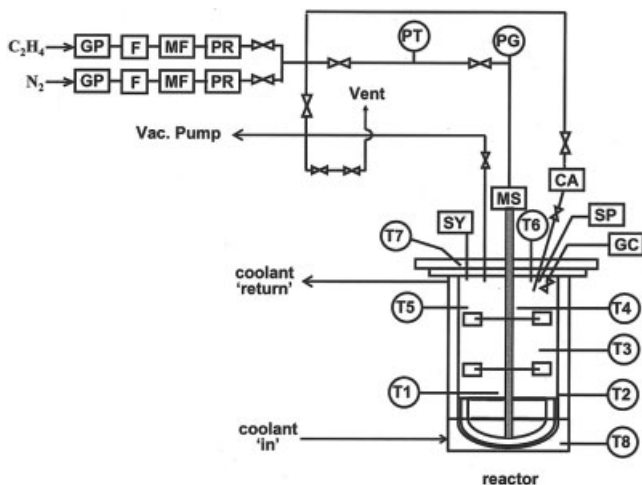
MAO (10 wt % in toluene) and modified MAO type-4 (MMAO-4; in toluene, 6.92 wt % Al) were purchased from Sigma-Aldrich and used as received. Neat triethyl aluminum (TEA), neat TIBA, and neat tri-*n*-octyl aluminum (TNOA) from Texas Alkyls were stored in

a glove box and used without further purification. Porous organic supports were either purchased from HayeSep Separations (Deerfield, IL) or made in our laboratory as previously described.<sup>24</sup> Anhydrous toluene was purchased from Sigma-Aldrich and used as received. Ultra-high purity nitrogen and polymerization grade ethylene were purchased from Praxair (Edmonton, Alberta, Canada). Ethylene was further purified in All-Tech (Deerfield, IL) columns before entering the reactor. Metallocene (*n*-BuCp)<sub>2</sub>ZrCl<sub>2</sub> and 1-hexene were donated by NOVA Chemicals and used as received.

### Catalyst

Catalysts were typically prepared by placing the desired amount of organic support in a three-neck flask and heating (at  $\sim 75^\circ\text{C}$ ) while evacuating for about 16 h. The evacuated support was suspended in 5–10 mL anhydrous toluene followed by the addition of a predetermined amount of the MAO solution. The support/MAO suspension was left on a shaker (200 rpm) at room temperature for 2–3 h followed by the addition of the metallocene solution that was prepared by dissolving the desired amount of (*n*-BuCp)<sub>2</sub>ZrCl<sub>2</sub> in 5 mL anhydrous toluene. The suspension was allowed to react for 1–2 h on the shaker at room temperature and then dried by solvent evacuation at room temperature.

Six different catalysts, described in Table I, were prepared by varying the support material, cocatalyst, precursor loading, and Al : Zr ratio. CAT1 was prepared using the modified MAO (MMAO-4) cocatalyst. The support used for CAT2 and CAT6 was synthesized in our laboratory; this support was soft and highly friable with broad pore- and particle-size distributions. In comparison, the other supports, obtained from HayeSep Separations, were hard. Catalysts CAT2 and CAT6 were made from the same support batch and they both had Al : Zr >200; however, CAT2 had considerably higher aluminum and zirconium loadings. The Al and Zr contents of the catalysts were measured by neutron activation analysis.



**Figure 1** Schematic diagram of reactor system. CA, catalyst injector; GC, gas chromatograph; GP, gas purifiers; F 7- $\mu$ m filter; MF, mass flow meter; MS, MagneDrive stirrer; PG, pressure gauge; PR, pressure regulator; PT, pressure transducer; SP, syringe pump; SY, syringe injection port; T1 to T8, thermocouples.

### Gas-phase polymerization

A 2-L stainless steel reactor equipped with gas purification, temperature control, and data acquisition systems was used for the polymerizations. A schematic diagram of the reactor system is shown in Figure 1; a detailed description of the reactor and of the polymerization procedure have been given elsewhere.<sup>25</sup> In a typical run, the desired amount of supported catalyst was loaded into the catalyst holder inside the glove box, and a 500- $\mu$ L gas-tight Hamilton syringe, also inside the glove box, was filled with the desired type and amount of aluminum alkyl. The catalyst holder was connected, under flowing ultra-high purity nitrogen, to the reactor which had been prepurified by heating to  $\sim 90^\circ\text{C}$  and overnight evacuation to  $<1$  Pa. The reactor, containing a seedbed of 80 g NaCl, was pressure tested with ultra-high purity nitrogen; this was followed by evacuation, filling with ethylene to about 1 bar, and injection of the desired amount of aluminum alkyl. The ethylene pressure in the reactor was then increased to about 7 bar and the reactor contents were stirred for 20–30 min at 450 rpm to allow scavenging of the impurities by the aluminum alkyl. During this scavenging, the reactor was gradually cooled to the polymerization temperature of  $80^\circ\text{C}$ . Catalyst was injected with flowing ethylene, at 1.4 MPa, and the reactor pressure was maintained at 1.4 MPa by continuous ethylene feed to replenish the amount consumed in the reactor. In some of the runs with TIBA, the reactor was vented to about 1 bar or evacuated to  $<10$  Pa before the catalyst was injected. This evacuation or venting removed most of the residual TIBA. Less than  $0.1 \mu\text{mol}$  of TIBA would have

been left in the reactor after the evacuation or venting if all the injected TIBA was in the vapor before the evacuation or venting. The amount of TIBA in the reactor for these runs will be referred to as “trace.” In some runs the catalyst was contacted with TIBA before being exposed to ethylene. In such runs, the catalysts were injected using ultra-high purity nitrogen at 3.5 bar; the nitrogen remained in the reactor for the duration of the run.

### RESULTS AND DISCUSSION

Two sets of polymerization runs were made: the first set, described in Table II, used catalysts CAT1, CAT2, CAT3, and CAT4 to investigate how the amount and type of aluminum alkyl affect the activity profiles of these catalysts in ethylene homopolymerization and ethylene/1-hexene copolymerization. The second set of experiments, with catalysts CAT5 and CAT6, summarized in Table III, were used to investigate the effects of TIBA concentration and order of contact between catalyst, TIBA, and ethylene on homopolymerization activity profiles. The polymerization runs were not done in the order presented in Tables II and III. The average gas-phase temperatures, as measured by thermocouple T1 (see Fig. 1), for each run are given in Tables II and III; however, these average values alone are not good indicators of the thermal history of the runs. Hence, the temperature profiles of all runs are shown in the panels below the activity profiles (e.g., Fig. 2). Temperature is an important parameter, which not only affects polymerization rates, but also affects catalyst activation and deactivation behavior and molar masses of produced polymers. The output from thermocouple T1 was used for temperature control; it is located in the reaction zone and always indicates the maximum temperature of all the thermocouples. The temperatures of the growing polymer particles may be significantly higher than the surrounding gas temperature, especially if the gas temperature is higher than the set-point temperature of  $80^\circ\text{C}$ .

#### Effect of alkyl aluminum type and concentration

The effect of TIBA concentration on ethylene homopolymerization activity profiles for CAT1 is shown in Figure 2. No TIBA was used in Run 1 or in Run 2; the reactor was vented and evacuated to  $<10$  Pa after scavenging with 0.3 mmol TIBA for 30 min. The partial pressure of TIBA in the reactor after evacuation would have been very low, probably  $<5$  mPa, because there was about 7 bar of  $\text{N}_2$  in the reactor during the scavenging. Comparison of Run 1 and Run 2 shows that the activity for Run 2 was about 10% higher than the activity for Run 1. The lower activity observed for Run 1 was likely due to deactivation of some of the catalyst by the residual impurities in the reactor. The

TABLE II  
Description of Polymerization Runs (Total Pressure = 1.4 MPa for All Runs)

Catalyst	Al alkyl used <sup>a</sup>	Run number	Materials charged to reactor			Gas Temp. <sup>c</sup> (°C)	Activity (g PE/(g cat · h))		$t_{Rmax}^d$ (h)
			Catalyst <sup>b</sup> (mg)	Al alkyl (mmol)	1-C <sub>6</sub> H <sub>12</sub> (mL)		Average	Max	
CAT1	None	1	103	None	0	86	347	494	0.21
	TIBA	2	103	Trace <sup>e</sup>	0	88	413	545	0.30
	TIBA	3	104	0.20	0	86	300	365	0.75
	TIBA	4	107	0.39	0	85	266	327	1.47
	TIBA	5	103	0.79	0	83	149	227	3.65
	TIBA	6	105	1.18	0	82	10	—	>5
CAT2	TIBA	7	60.0	Trace <sup>e</sup>	0	80	236	1594	0.04
	TIBA	8	61.4	0.20	0	80	389	1034	0.32
	TIBA	9	60.6	Trace <sup>e</sup>	4.45	80	691	750	0.45
	TIBA	10	60.3	0.20	4.50	80	836	1305	0.50
	TEA	11	60.3	0.26	4.25	80	955	1557	0.63
CAT3	TIBA	12	76.3	Trace <sup>e</sup>	2.30	80	497	635	0.51
	TIBA	13	76.9	Trace <sup>e</sup>	4.72	80	549	727	0.65
	TIBA	14	77.7	0.12	4.28	80	365	441	0.48
	TIBA	15	78.7	0.28	4.32	80	284	323	1.35
	TEA	16	80.2	0.29	4.25	80	144	247	2.18
CAT4	TNOA	17	76.3	0.22	4.32	80	456	632	0.88
	TIBA	18	89.6	Trace <sup>e</sup>	4.60	80	70	89	0.50
	TIBA	19	86.7	0.20	4.72	80	147	175	0.71
	TIBA	20	87.5	0.35	4.88	80	145	184	0.47
	TIBA	21	88.7	0.59	4.85	80	734	933	0.70
	TIBA	22	88.6	0.79	4.80	80	607	962	0.75

<sup>a</sup> TIBA, triisobutyl aluminum; TEA, triethyl aluminum; TNOA, tri-*n*-octyl aluminum.

<sup>b</sup> Total mass of supported catalyst (see Table I for composition).

<sup>c</sup> Average temperature measured by thermocouples T1 (see Fig. 1).

<sup>d</sup>  $t_{Rmax}$ , time required after catalyst injection to attain maximum polymerization activity.

<sup>e</sup> TIBA was removed from reactor by venting or evacuation before catalyst addition (see text).

close similarity of the activity profiles of these two runs supports the argument that evacuation essentially removed all the TIBA from the reactor.

Comparing Runs 2 to 6 in Figure 2 reveals that increasing the amount of TIBA in the reactor system-

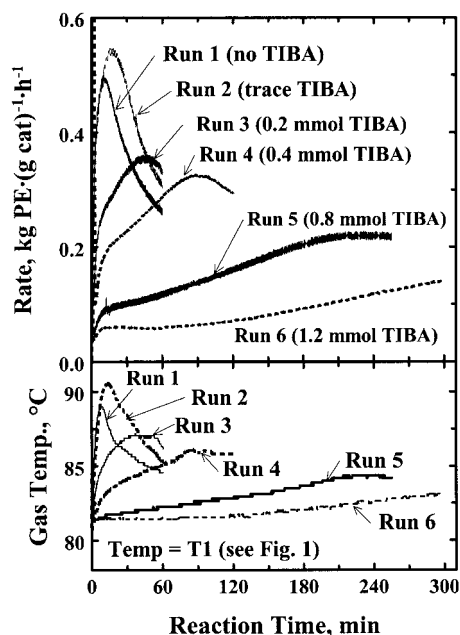
atically decreased the maximum activity value and increased the time,  $t_{Rmax}$ , required to reach the maximum polymerization activity;  $t_{Rmax}$  increased from 0.3 h for Run 2 to over 5 h for Run 6. This broadening of activity profile by TIBA was also recently observed

TABLE III  
Description of Ethylene Homopolymerization Runs Showing Effects of Contact Order and TIBA Concentration

Catalyst	Run number	Materials in reactor		Pressure (MPa)		$t_{mix}^a$ (min)	$t_{Rmax}^b$ (h)	Activity (g PE/(g cat · h))	
		Catalyst <sup>b</sup> (mg)	Al alkyl (mmol)	N <sub>2</sub>	Total			Average	Max
CAT5	23	80.4	Trace	0.00	1.38	0.0	0.36	243	316
	24	87.9	Trace	0.35	1.73	1.0	0.11	84	117
	25	84.6	Trace	0.35	1.73	0.0	0.47	263	289
	26	84.5	0.28	0.35	1.73	0.0	0.96	223	318
	27	85.7	0.28	0.35	1.73	0.0	1.09	235	359
	28	92.0	0.28	0.35	1.73	1.0	0.10	42	74
CAT6	29	49.9	0.59	0.00	1.38	0.0	0.45	1,287	1,735
	30	50.1	0.59	0.35	1.73	0.0	0.61	971	1,167
	31	49.8	0.59	0.35	1.73	3.0	0.53	759	1,001
	32	50.2	Trace	0.35	1.73	0.0	0.07	370	1,506
	33	50.0	Trace	0.35	1.73	3.0	0.07	328	1,160

<sup>a</sup>  $t_{mix}$ , time catalyst was in reactor (at 80°C and 450 rpm) before starting ethylene feed.

<sup>b</sup>  $t_{Rmax}$ , time required to attain maximum polymerization rate after starting ethylene feed.



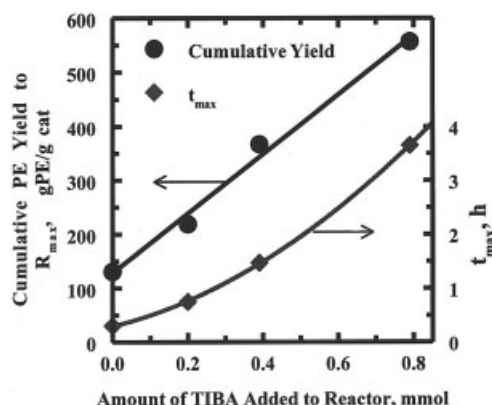
**Figure 2** Effect of the amount of TIBA added to reactor on the activity profile for ethylene homopolymerization (CAT1).

by Kumkaew et al.<sup>26</sup> with a silica-supported catalyst (Al : Zr ratio = 110). The effect of TIBA was more pronounced with the silica-supported catalyst; using 1.0 mmol TIBA in their reactor resulted in long induction periods.

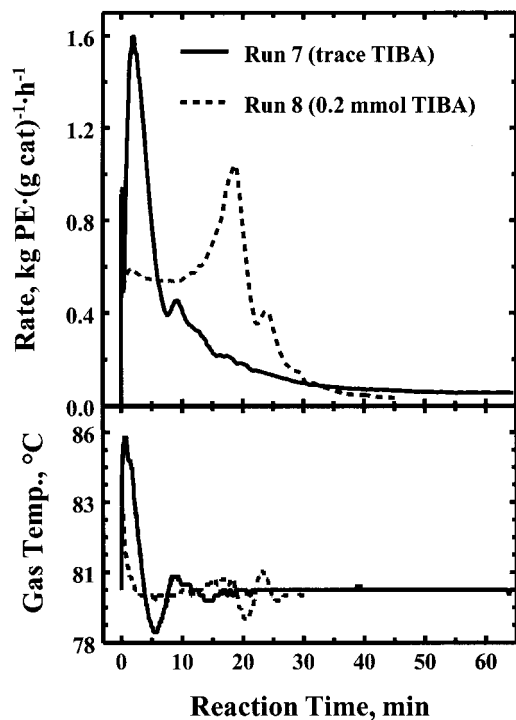
The above trend suggests that injecting the catalyst into the ethylene/TIBA environment results in competitive adsorption on the vacant coordination sites of the catalyst. Sites on which TIBA is adsorbed are probably inactive (dormant) since the results in Figure 2 show that TIBA reduced the activity and delayed the rate of activation. These dormant sites appear to gradually be reactivated probably as the result of aluminum alkyl depletion. Bochman and Lancaster<sup>22</sup> have presented experimental evidence that active metallocenium species react reversibly with residual and external TMA to form a dormant hetero-dinuclear cation  $[(Cp_2Zr-Me) \cdot Me_3Al]^+$ . Equilibrium between similar dormant and active sites was also proposed for propylene polymerization catalyzed by a metallocene/MAO system.<sup>27</sup> TIBA depletion in the reactor may be due to reaction with impurities, chain transfer to aluminum, and thermal decomposition. The cumulative amount of product produced up to the maximum activity as a function of the amount of TIBA added to the reactor is shown in Figure 3. For Runs 2 to 5, the PE yield increased with increasing amount of TIBA added even though the maximum activity decreased; Run 6 is not included in Figure 3 because the rate had not reached a maximum in the 5 h of polymerization. It is interesting to note that the PE yield shown in Figure 3 increases linearly with the amount of TIBA

added to the reactor. The broader activity profiles at higher TIBA concentrations made temperature control easier. The time required to reach the maximum activity is also shown in Figure 3. For large commercial reactors the alkyl content can be adjusted for temperature control, and the average residence time can be optimized to maximize yield.

The effect of TIBA concentration on homopolymerization activity profiles for CAT2 is shown in Figure 4. The maximum activity for Run 7 (trace TIBA) was higher than the maximum activity for Run 8 (0.2 mmol TIBA). However, the average activity for Run 8 was higher than the average activity for Run 7. The rate increased very rapidly at the beginning of the run, reaching a maximum activity of 1.6 kg PE/(g cat · h) in 2 min. This rapid increase in the rate resulted in a 6°C increase in the gas temperature, which was probably accompanied by a much larger increase in the internal temperature of growing polymer particles. It is difficult to control the gas temperature for such rapidly increasing rates. The rapid deactivation after the 2-min reaction time was probably the result of overheating. Deactivation rates of metallocene catalysts were found to increase with increasing temperature.<sup>26, 28, 29</sup> The activity profile of Run 8 was relatively flat at about 0.6 kg/(g cat · h) for the first 10 min before increasing to the maximum value. It is likely that the residual TIBA in Run 8 was consumed in the first 10 min, which was followed by an increase in activity. This later increase in activity was not as sharp as Run 7, resulting in better control of the gas temperature (see lower panel in Fig. 4). The large polymer particles, due to the growth during the first 10 min, also would result in a smaller increase in the internal polymer particle temperature. The difference in the observed response of CAT1 and CAT2 to TIBA may be related to the morphology and/or compositions of these catalysts. Additional investigations on the effects of support structure and composition on catalytic activity are required.



**Figure 3** Effect of amount of TIBA on time to achieve maximum activity and yield up to maximum activity (CAT1).



**Figure 4** Effect of amount of TIBA on homopolymerization activity for CAT2.

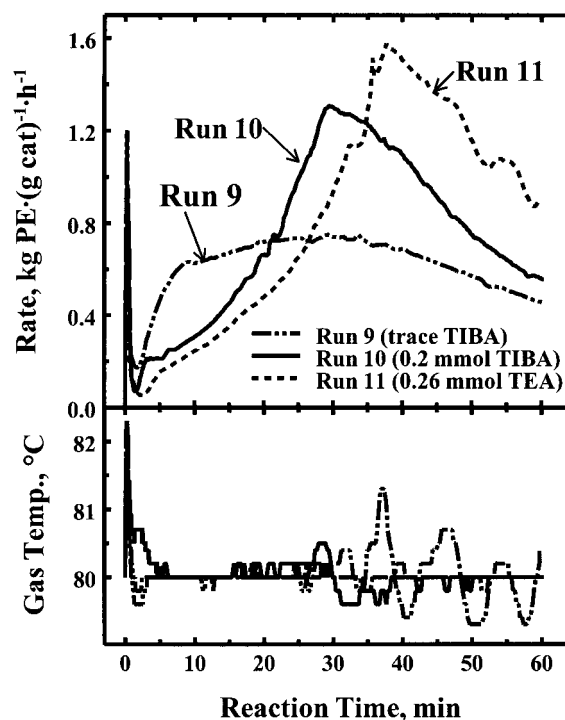
Activity profiles for ethylene/1-hexene copolymerization with CAT2 and TIBA and TEA are shown in Figure 5. The copolymerization activity profile differed remarkably from those for homopolymerization (cf. Runs 7 and 9, Table II). The maximum copolymerization rate for Run 9 was less than half the homopolymerization rate for Run 7, but the copolymerization activity profile was nearly flat, leading to a three times higher copolymer yield than homopolymer yield during the 1-h polymerization runs. The presence of residual TIBA and TEA suppressed the initial copolymerization activities. The effect of TEA was more pronounced than that of TIBA; TEA suppressed the initial activity to a lower value for a longer period. All three copolymerization runs had higher average activity than the homopolymerization run with the same catalyst.

The above comonomer enhancement is widely observed for both conventional Ziegler-Natta and metallocene catalysts.<sup>26,30</sup> This phenomenon has been attributed to enhanced accessibility of the active sites by the monomer molecules<sup>31</sup>; diffusion through the short-chain-branched LLDPE is faster than through the linear HDPE around the active site. The comonomer enhancement has also been attributed to chemical activation of certain types of sites by the 1-hexene<sup>32</sup>; however, this is more feasible in the multisite conventional Ziegler-Natta systems than the metallocene systems. TEA had a stronger effect because it is more reactive and diffuses faster than TIBA; hence, it com-

petes more favorably with ethylene in adsorbing to the vacant site on the active metallocene center.

The effects of TEA, TIBA, and TNOA on the copolymerization behavior were further investigated with CAT3. The activity profiles for Runs 12 and 13 in Figure 6, with trace TIBA, show the effect of increasing the amount of 1-hexene from 2.3 to 4.7 mL. Doubling the 1-hexene resulted in a moderate increase in the maximum polymerization rate and the average activity (see Table II). This catalyst had very low homopolymerization activity [average activity of 0.04 kg PE/(g cat · h) during a 1 h run]; the reasons for the low homopolymerization activity of this catalyst are being investigated. Increasing the amount of TIBA from a trace to 0.12 and 0.28 mmol (Runs 13 to 15), with about the same initial concentration of 1-hexene, decreased the maximum activities and broadened the profiles (see Fig. 6); this behavior is similar to that observed with CAT1.

The effect of the type of aluminum alkyl on activity profiles is shown in Figure 7. Runs 15–17 had similar amounts of 1-hexene but different aluminum alkyls at approximately the same molar concentration. The activity profiles of these runs again show that the lower molar mass TEA suppressed the activity the most, delaying the occurrence of the maximum activity to more than 2 h after catalyst injection. TEA also exhibited an induction period of more than 10 min during which no ethylene flow into the reactor was observed. On the other hand, the higher molar mass TNOA



**Figure 5** Effect of TIBA and TEA on copolymerization activity for CAT2.

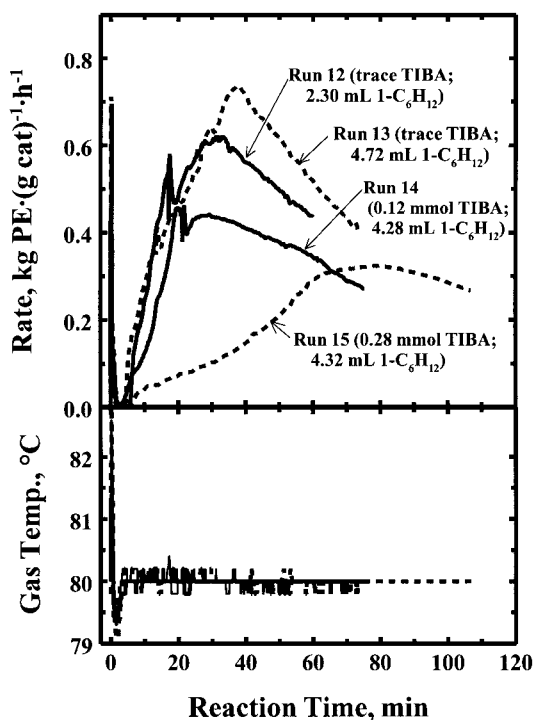


Figure 6 Effect of amount of TIBA and amount of 1-hexene on activity for CAT3.

caused only a small delay in the attainment of maximum activity;  $t_{R_{max}}$  for Run 17 with TNOA was 0.88 h compared to 0.56 h for Run 13 with a trace of TIBA. The average and maximum activities for Run 17 were about 15% less than those for Run 13. The delay in  $t_{R_{max}}$  for TIBA and TEA, and the similarity in activity profiles and average activity for TNOA and trace TIBA runs, supports the reactivity and/or diffusivity effects mentioned earlier.

Nooijen<sup>11</sup> reported a strong effect of cocatalyst (TEA, TIBA, TNOA, and IPRA) diffusion on the rate of activation of  $MgCl_2$ -supported Ziegler-Natta catalyst in slurry polymerization. At constant cocatalyst to catalyst ratio, the maximum activity was directly dependent on the reactivity of the cocatalyst. Note that the aluminum alkyl effects observed by Nooijen<sup>11</sup> with conventional Ziegler-Natta catalysts was the opposite of that shown in Figures 5 and 6. This is expected because the aluminum alkyls act as cocatalysts in the conventional Ziegler-Natta catalysts. The slowly diffusing high molar mass alkyl aluminums in the slurry become less effective cocatalysts. On the contrary, the trend observed by Lynch et al.<sup>10</sup> for  $SiO_2/MgCl_2$ -supported  $TiCl_4$  catalyst in the gas-phase was similar to ours, i.e., increasing the size of the aluminum alkyl increased the polymerization activity. Diffusion in the gas is much more rapid than in liquid present in slurry polymerizations.

The effect of TIBA concentration on a catalyst with a lower Al : Zr ratio, CAT4, was examined in Runs

18–22; CAT4 had an Al : Zr ratio of 110 compared to Al : Zr ratios  $>210$  for the previous three catalysts. Activity profiles for TIBA from trace amounts to 0.79 mmol are shown in Figure 8. The activity profiles in Figure 8 show a different effect of increasing TIBA concentration than that observed with the previous three catalysts. The activity of CAT4 was very low with trace amounts of TIBA (Run 18) and the activity only increased slightly with an increase in TIBA to 0.2 mmol (Run 19) and 0.35 mmol (Run 20). Increasing the amount of TIBA in the reactor to 0.59 mmol resulted in a large increase in the polymerization activity; average and maximum activities increased more than fivefold. There appears to be a threshold amount of TIBA below which the activity remained low.

The above behavior can be explained in terms of the formation of dormant metallocene complexes. Zurek and Ziegler<sup>33</sup> concluded (through density functional theory calculations for  $Cp_2ZrMe_2/MAO$  in solution) that Al : Zr ratio  $\geq 275$  ensures the disappearance of free  $Cp_2ZrMe_2$ , the homo-dinuclear  $[Cp_2ZrMe-(\mu-Me)-ZrMeCp_2]^+[MeMAO]^-$ , and the weak  $Cp_2ZrMe_2 \cdot MAO$  complex. The homo-dinuclear cation is inactive in olefin polymerization and high metallocene concentration favors the formation of these species<sup>22</sup> [see eq. (1)].

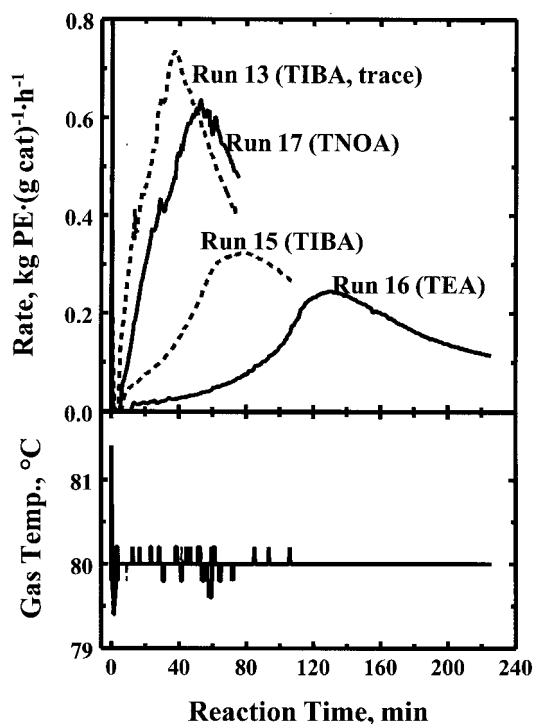
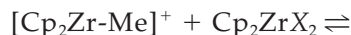
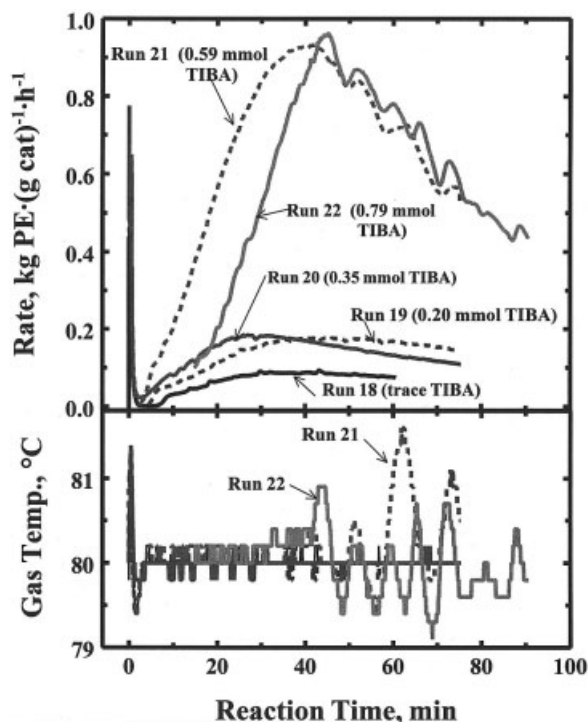
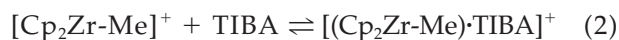


Figure 7 Effect of alkyl type on copolymerization activity for CAT3.



**Figure 8** Effect of amount of TIBA on copolymerization activity for CAT4.

The last step in our catalyst preparation was evaporation of the catalyst suspension to dryness. During this step, the metallocene/MAO solution was concentrated in the catalyst pores. If an Al : Zr ratio of 110 is not high enough to prevent interaction between the metallocene molecules, it is possible that the inactive homo-dinuclear species  $[\text{Cp}_2\text{Zr}(\text{X})-\mu\text{X}-\text{Zr}(\text{X})\text{Cp}_2]^+$  was formed. Note that the poly(DVB) support used to make CAT4 has no functional groups that would chemically react with MAO. The support merely acts as a container for the catalyst precursors; hence, the catalyst would bear some similarity with the homogeneous one. Increasing TIBA concentration in the reactor favors the formation of the dormant metallocenium-ion/TIBA complex [eq. (2)] at the expense of the formation of the inactive homodinuclear complex in eq. (1). The dormant complex reactivates as the polymerization proceeds (i.e., as TIBA is depleted).



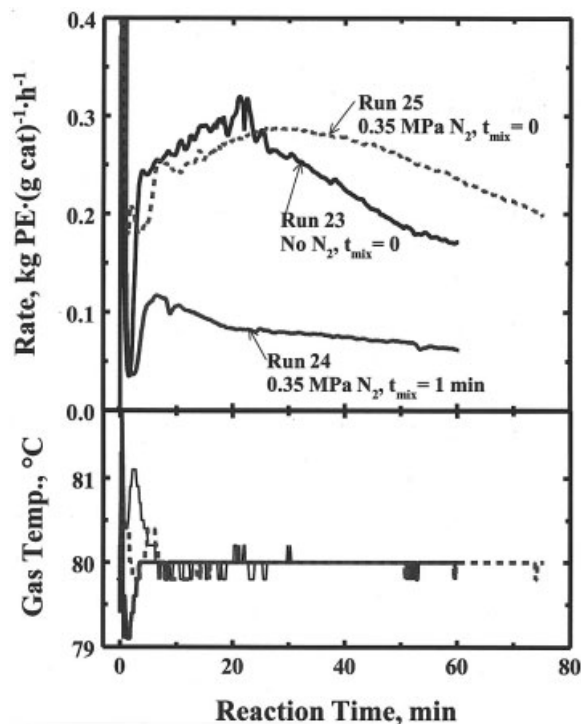
Among all the catalysts used in this work, only catalyst CAT4 had an Al : Zr ratio significantly lower than the 275 range reported by Zurek and Ziegler.<sup>33</sup>

#### Effect of contact mode of catalyst with TIBA

The last set of polymerization experiments consisted of 11 runs, 6 with CAT5 and the remaining 5 with

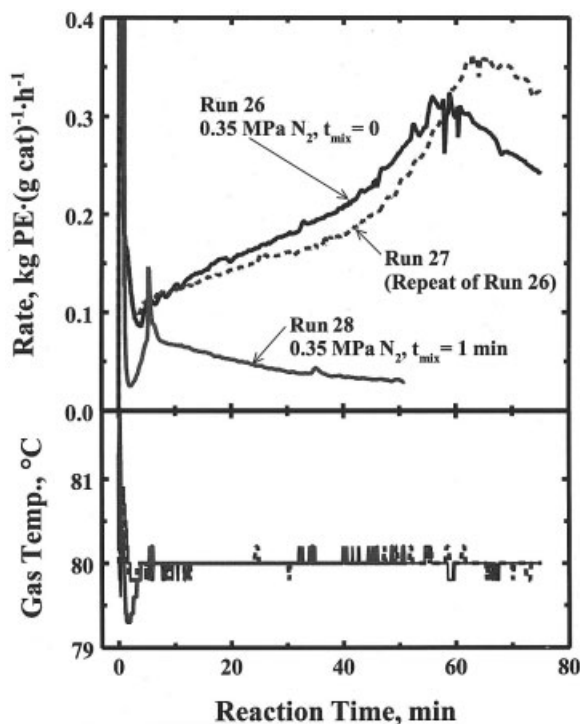
CAT6. CAT5 was made from a different type of support (no DVB component). In all runs in which the catalysts were contacted with TIBA in the reactor before introducing ethylene, 0.35-MPa nitrogen was used to inject the catalysts. Comparative runs were also conducted with the same nitrogen partial pressure in the reactor. The effect of nitrogen was examined in homopolymerization Runs 23 and 25. No nitrogen was used in Run 23 and 0.35 MPa nitrogen were present in Run 25; the ethylene pressure was 1.4 MPa in both runs. This catalyst had moderate ethylene homopolymerization activity and relatively flat activity profiles as shown in Figure 9. The addition of nitrogen to the reactor did not have a significant effect on the activity profile and the average activity of the two runs was within 10%.

Exposing CAT5 to nitrogen and a low concentration (trace) of TIBA, while stirring at 80°C, for 1 min before introducing ethylene resulted in an over threefold decrease in average catalytic activity (cf. Runs 24 and 25). Runs 26 to 28 are similar to Runs 24 and 25 except that a larger concentration of TIBA was used for these runs; Runs 26 and 27 are repeat runs. The activity profiles in Figure 10 show that the reproducibility is good. Again, exposing CAT5 to nitrogen and TIBA for 1 min before introducing ethylene resulted in a large decrease in activity; this time an over fivefold decrease (cf. Runs 26 and 27 with Run 28). Comparison of Run 28 to Runs 26 and 27 (Figure 10 and Table III) reveals



**Figure 9** Effect of presence of nitrogen and exposure of catalyst to TIBA (trace) in the absence of ethylene on homopolymerization activity for CAT5.





**Figure 10** Effect of exposure of catalyst to nitrogen and TIBA (0.28 mmol) in the absence of ethylene on homopolymerization activity for CAT5.

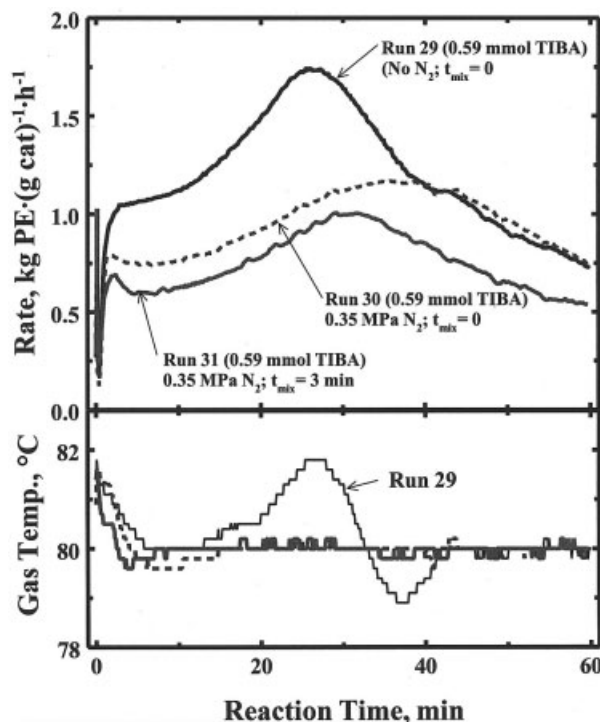
a dramatic reduction of activity. The deactivation due to the exposure of CAT5 to nitrogen and TIBA in the absence of ethylene is irreversible since no increases in activities of the deactivated catalyst were observed. TIBA must play a role in this deactivation since CAT 5 is stable when stored under nitrogen for extended periods of time.

Experiments similar to those done with CAT5 were repeated for CAT6, a catalyst with much higher homopolymerization activity than CAT5. Runs 29 and 30 were made to determine the effect of nitrogen in the reaction mixture on the polymerization activity. The activity profiles for these two runs are shown in Figure 11 (Note: The only difference between these two runs was the presence of 0.35 MPa of nitrogen in Run 30). The presence of nitrogen resulted in an over 30% decrease in the maximum activity and a 25% decrease in average activity (see Table III). No such effect was observed with CAT5 in Runs 23 and 24; for these runs the presence of nitrogen resulted in a decrease in the maximum activity by <10% and the average activity for the first hour of polymerization was about 10% higher in the presence of nitrogen. The reason for this different effect of nitrogen is probably due to the much higher activity of CAT6.

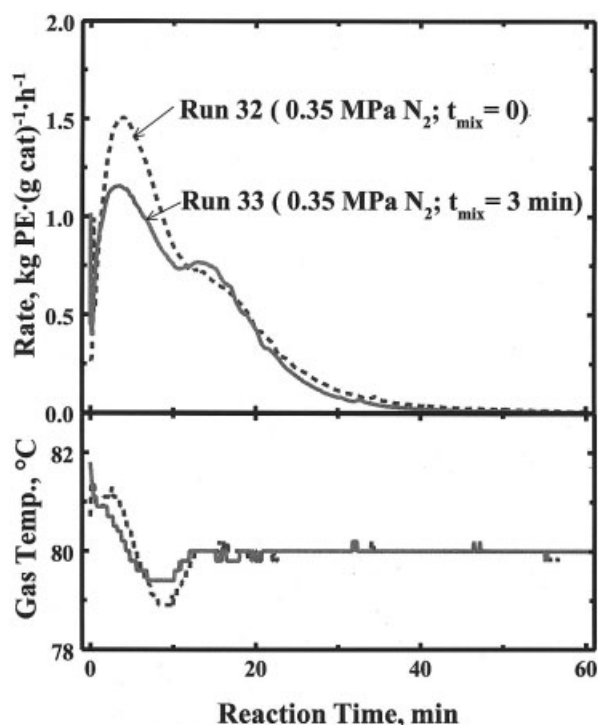
Weickert et al.<sup>34</sup> predicted a nonlinear decrease in activity in the presence of inert components (gas or liquid) in a polymerization reactor due to an "enrichment effect" of the inerts. At high polymerization

activities in the gas-phase, the monomer molecules get into the porous polymerizing particle largely by convective flow, contrary to the widely assumed diffusive transport in the models describing the growth of polymer particles.<sup>35</sup> Veera et al.<sup>36</sup>, and Kittilsen et al.<sup>37</sup> have modeled this convective monomer transport during olefin polymerization. High ethylene consumption rate inside the polymerizing particles creates a pressure differential between the inside of the catalyst particles and the bulk gas. This pressure difference causes flow of both ethylene and nitrogen into the growing polymer particles. The inert nitrogen exits the particles only by diffusion. The net partial pressure of nitrogen in the particle will, therefore, be determined by the difference between the rates of convection and diffusion. In Runs 23 and 25 with CAT5 the maximum polymerization rates were lower by over a factor of four compared to Runs 29 and 30 with CAT6; hence, the presence of nitrogen was much more significant for CAT6 than for CAT5.

Runs 30 and 31 (Fig. 11) show that contacting CAT6 with TIBA for 3 min in the reactor containing 0.59 mmol TIBA prior to ethylene feed resulted in a moderate, about 20%, reduction in the average polymerization activity while the shape of the activity profiles remained essentially the same. The similarity in the activity profiles of these two runs suggests either a single site type or all the different sites were uniformly affected by the TIBA. The activity profiles for homopo-



**Figure 11** Effect of exposure of catalyst to nitrogen and TIBA (0.59 mmol) in the absence of ethylene on homopolymerization activity for CAT6.



**Figure 12** Effect of presence of nitrogen and exposure of catalyst to TIBA (trace) in the absence of ethylene on homopolymerization activity for CAT6.

lymerization with CAT6 with only traces of TIBA were different from those with 0.59 mmol TIBA (compare Fig. 11 and 12). The higher amounts of TIBA (Fig. 11) resulted in slower activation than the trace amount of TIBA (Fig. 12). Stirring the catalyst in the reactor for 3 min in the presence of nitrogen and the absence of ethylene resulted in an 11% reduction in average activity for the 1-h runs (cf. Runs 32 and 33). All the loss in activity occurred in the first 12 min of polymerization; the activity profiles were essentially the same after the first 12 min. The difference in the maximum activity in the early stage of polymerization may be due to the exposure to TIBA in the absence of ethylene or the difference may be due to irreproducibilities, most likely due to temperature variations of the growing polymer particles. We frequently observe 10 to 20% variations in activities for runs with high initial activities. Regardless of the cause, the decrease in activity caused by the exposure of CAT6 to nitrogen and TIBA in the absence of ethylene was small compared to similar exposures for CAT5. The different behavior of CAT5 and CAT6 may be due to the difference in the supports used or the differences in the Zr loadings.

### Polymer properties

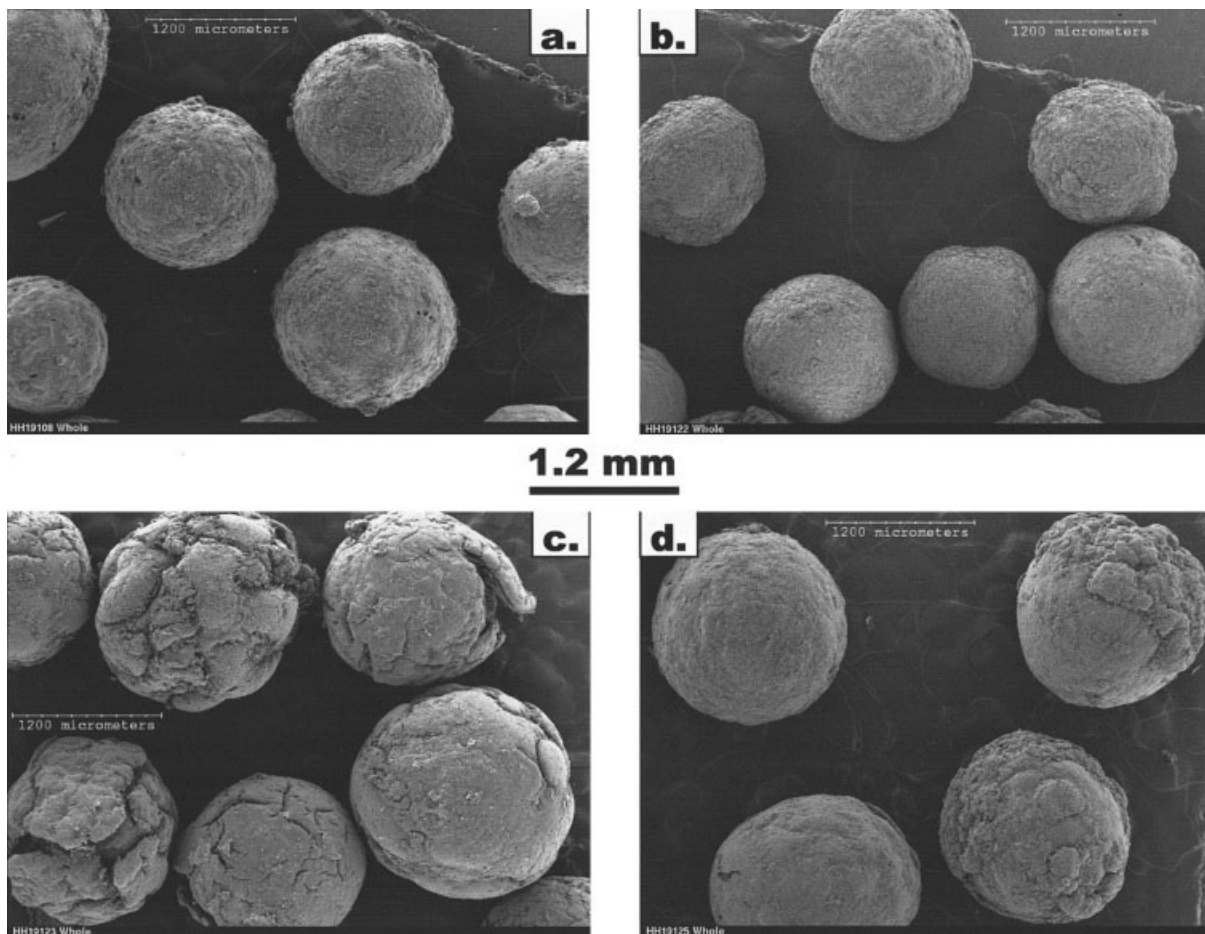
In addition to the roles discussed above, aluminum alkyls also participate in the termination of growing

polymer chains (i.e., act as chain transfer agents) and/or reactivation of dormant sites.<sup>38</sup> Molar masses for the products from the various runs are listed in Table IV. The molar masses and polydispersities were affected by the concentration of TIBA, the presence of 1-hexene, and the type of catalyst. The influence of TIBA on molar masses differed for different catalysts. For homopolymerization with CAT1, increases in TIBA concentration resulted in decreases in  $M_w$ , while an increase in TIBA concentration resulted in increases in  $M_w$  for homopolymerization with CAT2 (cf. Runs 7 and 8) and CAT5 (cf. Run 25 with Runs 26 and 27). The TIBA concentration did not have a significant effect on molar masses of products made with CAT6. The TIBA concentration also did not have a large influence on  $M_w$  during copolymerization with CAT3, but for

**TABLE IV**  
Molar Masses of Products

Catalyst	Run no.	$M_w$ , ( $\times 10^{-3}$ )	Polydispersity ( $M_w/M_n$ )
CAT1	1	180.9	2.9
	2	186.1	2.6
	3	181.9	2.4
	4	169.4	2.3
	5	159.4	2.5
	6	143.4	2.8
			2.55 (0.23) <sup>a</sup>
CAT2	7	185.1	2.3
	8	230.6	2.0
	9	89.4	2.4
	10	73.4	2.5
	11	90.7	2.4
			2.30 (0.19)
CAT3	12	86.3	2.5
	13	87.05	2.5
	14	88.3	2.5
	15	89.9	2.8
	16	90.4	2.5
	17	88.2	2.4
CAT4	18	102.2	3.2
	19	94.5	2.7
	20	91.5	3.0
	21	81.7	2.4
	22	80.2	2.3
CAT5	23	149.5	2.7
	24	148.8	2.8
	25	144.9	2.6
	26	180.0	2.3
	27	181.4	2.4
	28	139.6	2.7
CAT6	29	164.0	2.1
	30	168.8	2.1
	31	162.2	2.1
	32	150.3	2.1
	33	178.4	2.0

<sup>a</sup> Average polydispersity with standard deviation in parentheses.



**Figure 13** Scanning electron micrographs of product particles produced with CAT3; (a) Run 13; (b) Run 15; (c) Run 16; (d) Run 17 (see Table II for polymerization conditions).

CAT4,  $M_w$  decreased with increasing TIBA concentration. The type of aluminum alkyl did not have a significant effect on molar masses for CAT2 and CAT4. Using TEA resulted in slightly higher  $M_w$  values (cf. Run 10 with 11 and Run 15 with 16) and TNOA resulted in about the same  $M_w$  as TIBA (cf. Runs 15 and 17). The polydispersities of products made in the presence of TEA and TNOA were somewhat lower than those made with TIBA. The exposure of the catalyst to TIBA without the presence of ethylene did not have significant effects on the molar masses (Runs 23 to 33), even though exposure of the catalyst to TIBA affected the activity, especially for CAT5.

The presence of 1-hexene resulted in a decrease in molar masses; homopolymers had  $M_w$  values ranging from 143,400 to 230,600 while copolymers had  $M_w$  values ranging from 73,400 to 102,200. The average polydispersity of the homopolymers was 2.37 (Runs 1–8 and 23–33), while the copolymers had an average polydispersity of 2.58 (Runs 9–22). The homopolymers made with CAT1 (Runs 1–6) and CAT5 (Runs 23–28) had higher polydispersities and standard deviations than the homopolymers made with CAT2

(Runs 7 and 8) and CAT6 (Runs 29–33). The variations in polydispersity for the products with CAT1 can be ascribed, in part, to the variations in temperature profiles (see Fig. 2). Note that particle temperature could be considerably higher than the bulk-gas temperature.<sup>39</sup> Kumkaew et al.<sup>26</sup> reported a decrease in polymer molar mass with increasing polymerization temperature. The zirconocene loading and the Al : Zr ratios influenced the polydispersity; CAT6 with the lowest Zr loading and Al : Zr ratio of 375 produced products with polydispersities of about 2.1 while other catalysts with similar Al : Zr ratios, but higher Zr loading, produced products with polydispersities of about 2.5. CAT4, which has the lowest Al : Zr ratio, produced the product with the highest polydispersities; however, increasing the TIBA concentrations for CAT4 decreased the polydispersities from over 3 to 2.3 (see Table IV).

All the polymerization runs described in this work produced spherical polyolefin particles. Figure 13 shows typical product particles obtained with CAT3. The spherical shape is due to the direct replication of the catalyst particle morphology, i.e., the porous

spherical polymer support beads resulted in spherical supported catalyst particles and the replication of the catalyst particle morphology produced polyethylene particles that were spherical, free flowing, and easy to handle. Several polymer-supported catalysts prepared in our laboratory over the past few years produced polymer particles with good replication of catalyst morphology.<sup>24</sup>

## CONCLUSIONS

High-activity supported  $(n\text{-BuCp})_2\text{ZrCl}_2/\text{MAO}$  and  $(n\text{-BuCp})_2\text{ZrCl}_2/\text{MMAO-4}$  were prepared using different porous polymeric supports. The catalysts were active in gas-phase ethylene homopolymerization and ethylene/1-hexene copolymerization. Activities were generally higher for copolymerization than homopolymerization due to the comonomer synergism. Excellent catalyst particle to product particle replication was observed.

Residual aluminum alkyls in the reactor significantly suppressed the initial polymerization activity. However, the broadening of the activity profiles due to the presence of aluminum alkyls frequently led to higher average activities for 1-h runs. The effectiveness of the aluminum alkyls in inhibiting the initial polymerization activity decreases with increasing size of the alkyl group, i.e., TEA > TIBA > TNOA. The growing polymer particles probably had significantly higher internal temperatures than the surrounding gas phase for runs in which the activity increased rapidly during the initial stages of polymerization. This overheating was the probable cause for the rapid deactivation; the overheating probably affected the molar masses as well. Rapid changes in catalyst activity are undesirable, in laboratory as well as in industrial reactors, because they make temperature control difficult. The results presented in this study show that such undesirable activity profiles can be modified by controlling the aluminum alkyl concentration without a loss in average polymerization activity.

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