Ethylene Polymerization under Mild Conditions Using Simple Aluminum Alkyls and Chloro Activators

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Methylaluminum sesquichloride ($Al_2Cl_3Me_3$, MAS), in the presence of ethyl trichloroacetate (ETAC), is found to be an effective catalyst for the production of polyethylene. Optimal catalyst productivities are obtained for a MAS:ETAC ratio of 1:1 at a reaction temperature of 75 °C. The polymerization is first order in both ethylene and MAS/ETAC concentration. NMR studies indicate that a 1:1 adduct is formed between binuclear MAS and ETAC, which is postulated to be a direct precursor to the active species. The productivity at elevated temperatures is limited by a radical decomposition process. Screening of various additives revealed that many halogenated organic reagents can act as activators, including carbon tetrachloride and *p*-toluene sulfonyl chloride. Improved productivities are obtained using sulfonyl chloride activators due to circumvention of radical decomposition pathways.

Introduction

Aluminum complexes play an essential role in a vast array of catalytic and polymerization reactions. In particular, haloaluminum alkyl species of the type AlX_nR_{3-n}, $n = 1-3$, are known catalysts for carbocationic,[1,2] anionic,[3,4] ring-opening,[5] and radical[6] polymerization and are widely used as Lewis acids in Friedel−Crafts and Diels−Alder reactions.[7] One of their most important commercial applications has been as cocatalysts in the polymerization of ethylene and other α-olefins using homogeneous transition metal complexes.[8,9] Extremely high levels of Al, with Al:M ratios ranging from 50:1 up to 15000:1, are often required to achieve optimal productivities. These cocatalysts are thought to play several roles in the formation and stabilization of active polymerization catalysts including the following: (i) alkylation of metal chloride precursors, (ii) alkyl ligand abstraction to afford cationic transition metal species, (iii) scavenging of impurities present in the solvent and gas feeds, and (iv) prevention of bimetallic decomposition reactions. The precise role of aluminum in these systems, as well as the necessity for such high concentrations of cocatalyst, has been a topic of intense research and debate. Over the past decade, attracted by the potential for eliminating the need for the relatively expensive and often more toxic transition metal component, interest has grown in exploring the use of aluminum compounds themselves as ethylene polymerization catalysts.

Cationic aluminum alkyl complexes supported by anilinotropone,[10] pyridylaminoamido,[11] Schiff base,[12] aminotroponiminate,[13] and amidinate[14] ligands have all been shown to produce polyethylene but with low productivities. Although well-defined neutral and cationic aluminum alkyl complexes have been isolated and characterized, it is still unclear if they are directly responsible for the observed catalytic activity. Theoretical[15−17] and experimental[13] studies imply that β-H-transfer reactions dominate relative to propagation in cationic aluminum alkyl species, suggesting that more complex structures for the active species may be involved. It has even been suggested that part per billion concentrations of transition metals in these systems may be significantly affecting the results and that aluminum-based ethylene polymerization is unlikely, if not impossible.[17]

Nevertheless, the viability of simple aluminum alkyls to insert ethylene was clearly established over 50 years ago by Ziegler's seminal studies on the *Aufbaureaktion* for aluminum alkyls,[18,19] where a stepwise insertion of ethylene into the aluminum−carbon bonds of trialkylaluminums was found to generate long-chain aluminum trialkyls. For this insertion to occur, an ethylene pressure of 50−300 bar has to be maintained at a temperature of 100−120 °C. The production of polyethylene by exposure of heptane solutions of trialkylaluminums to high pressures of ethylene at lower temperatures over several days[20,21] has suggested that the synthesis of high molecular weight polyethylene using aluminum catalysts may be possible.

In this paper we describe an ethylene polymerization reaction mediated by an aluminum catalyst/chloro-activator combination.

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Table 1. Ethylene Polymerization by MAS/ETAC Mixtures

entry[a]	MAS (mmol)	ETAC (mmol)	time (h)	pressure (bar)	yield (g)	productivity[b]	M_w [c] (Da)	M_n [c] (Da)	PDI
1	1.0	1.0	1.0	4.0	2.09	538	716 660	292 149	2.45
2	2.0	2.0	1.0	5.0	4.88	488	723 314	287 059	2.52
3	2.0	2.0	1.0	4.0	4.04	505	735 899	284 489	2.59
4	2.0	2.0	1.0	3.0	3.15	525	637 055	269 731	2.36
5	2.0	2.0	1.0	2.0	2.08	520	563 200	210 625	2.41
6	2.0	2.0	1.0	1.5	1.59	530	507 680	161 773	3.14
7	2.0	2.0	0.1	4.0	0.24	300	657 288	260 021	2.53
8	1.0	0.0	1.0	4.0	trace	n/a	n/a	n/a	n/a
9	1.0	0.1	1.0	4.0	0.08	10	n/a	n/a	n/a
10	1.0	0.5	1.0	4.0	1.33	332	996 025	387 062	2.57
11	1.0	1.5	1.0	4.0	1.57	393	753 036	274 655	2.74
12	1.0	2.0	1.0	4.0	1.22	305	391 281	155 653	2.51
13	1.0	5.0	1.0	4.0	0.20	50	139 557	58 378	2.39

[a] Reaction conditions: Fischer−Porter glass reactor, 200 mL toluene, 80 °C. [b] Productivities given relative to MAS in g of PE mol^{-1} h^{-1} bar^{-1}. [c] Molecular weights determined by GPC at 130 °C.

While the productivities do not compete with classical transition metal based catalysts, this work highlights the importance of gaining further understanding of the role of high concentrations of alkylaluminum species in transition metal mediated olefin polymerization as well as the necessity for careful control experiments.

Results and Discussion

Ethylene Polymerization Using Methylaluminum Sesquichloride/Ethyl Trichloroacetate Mixtures. Traditional transition metal based catalysts for ethylene polymerization are often screened for activity with a variety of alkylaluminum reagents as cocatalysts. Initial studies with iron precatalysts activated by methylaluminum sesquichloride (MAS) and ethyl trichloroacetate (ETAC) showed excellent productivities. However, these productivities were maintained in control experiments in the absence of the transition metal “precatalyst”, suggesting that the polymerization was actually being mediated by an aluminum-based polymerization catalyst.

Productivity values and polymer data for MAS/ETAC catalyzed ethylene polymerizations are collected in Table 1. First, it has to be recognized that the productivity of the MAS/ETAC system (entry 1, 538 g of polyethylene (PE) mol^{-1} h^{-1} bar^{-1}) is low compared to reported productivities in transition metal mediated ethylene polymerizations. Often in these systems, however, thousands of equivalents of alkylaluminum reagents are added as cocatalysts. This system generates comparable quantities of polymer; the reactor is invariably filled. The resultant polymer was found to be highly linear by ^{13}C NMR spectroscopy, with molecular weights in the range of $(2-3) \times 10^5$ Da. Quite narrow polydispersity indices of ca. 2.5 are suggestive of single-site behavior. The polymerization is first order in ethylene pressure (Table 1, entries 2−6; Figure 1), with changes to pressure having minimal effect on molecular weight. In addition, molecular weights were unaffected by reaction times; molecular weight values for a 6 min polymerization run remained high (entry 7; $M_n = 260\ 021$). These observations are indicative of an extremely fast propagation rate, leading to polymer precipitation from solution. Quenching the reaction with acidified methanol generated fully saturated polyethylene, implying that the chains are bonded to aluminum.

While every precaution to exclude transition metal impurities from the Fischer−Porter reactors is taken, polymerizations were repeated in all-glass vessels at lower pressures (1.0 bar) under stringent conditions. Slightly lower productivities were observed, but this may be attributed to inefficient stirring (ca. 400 g of PE mol^{-1} h^{-1} bar^{-1}; $M_n = 229\ 214$, M_w/M_n (PDI) = 2.47).

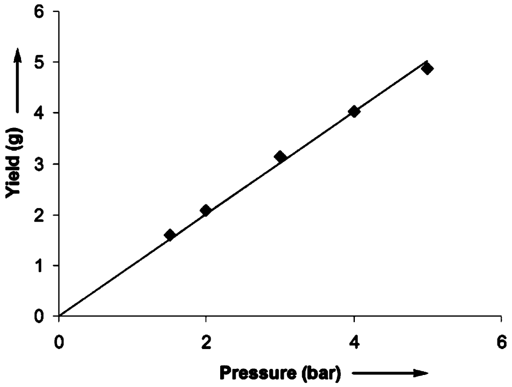

Figure 1. Pressure dependence of polymerization of ethylene by MAS/ETAC.

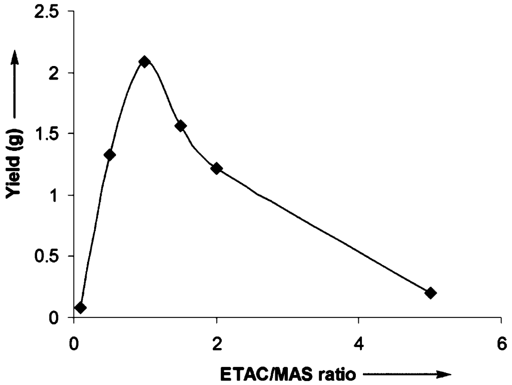

Figure 2. Variation in polymer yield versus ETAC/MAS ratio.

Varying the amount of ETAC added to the polymerization run showed an optimal ratio of 1:1 equivalents of MAS to ETAC (Table 1, entries 1, 8−13; Figure 2). Interestingly, no polymer is observed in the absence of ETAC (entry 8), implying an important role for this reagent as a catalyst activator. The optimal 1:1 ratio implies the formation of an active species with two aluminum metal centers per molecule of ethyl trichloroacetate. There is an approximate first-order dependence on ETAC concentration up to 1.0 equiv; at higher concentrations the productivity falls, implying that excess chloro reagent suppresses the polymerization and potentially competes with ethylene for active sites. The molecular weight of the resultant PE is also lowered at higher ETAC concentrations, as are the number of active chains, suggesting that high ETAC levels can poison the active sites. Addition of 5 mmol of ETAC to 1 mmol of MAS generates polyethylene with molecular weights lowered from ca. 290 000 to ca. 58 000 Da.

Table 2. Variation of MAS/ETAC Concentration and Polymerization Temperature[a]

Entry	MAS (mmol)	ETAC (mmol)	temp (°C)	yield (g)	productivity[b]
1	3.0	3.0	80	5.36	446
2	2.0	2.0	80	4.04	505
3	1.5	1.5	80	3.12	520
4	1.0	1.0	80	2.09	538
5	0.5	0.5	80	0.88	440
6	0.2	0.2	80	0	0
7	1.0	1.0	25	0.96	240
8	1.0	1.0	40	1.05	263
9	1.0	1.0	60	1.29	323
10	1.0	1.0	70	2.06	515
11	1.0	1.0	75	2.38	595
12	1.0	1.0	80	2.09	523
13	1.0	1.0	90	0.05	12

[a] Reaction conditions: Fischer−Porter glass reactor, 200 mL of toluene, 1.0 h, 4.0 bar ethylene. [b] Productivities given relative to MAS in g of PE mol^{-1} h^{-1} bar^{-1}.

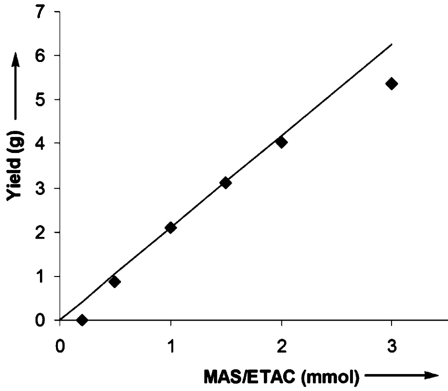

Figure 3. Dependence of polymer yield and productivity on MAS/ETAC loading.

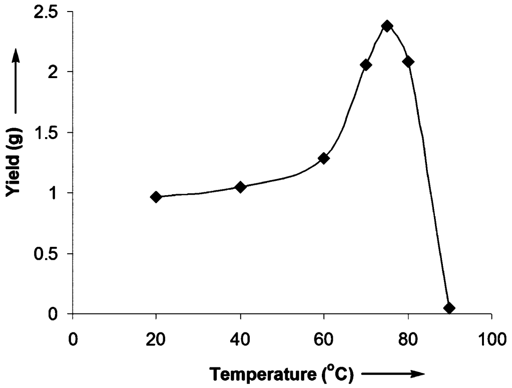

Figure 4. Temperature dependence of MAS/ETAC polymerization of ethylene.

Table 3. Selected NMR Data for Reaction of MAS and ETAC

MAS (μmol)	ETAC (μmol)	^{13}CCl$_3$ (ppm)	O^{13}CH$_2$ (ppm)	^{27}Al (ppm)
0.0	1.0	90.6	65.3	n/a
1.0	0.0			177, 135
1.0	0.1	87.8	76.4	177, 135, 95
1.0	0.3	87.8	76.1	177, 135, 95
1.0	0.5	87.8	76.1	177, 135, 95
1.0	1.0	88.1	74.7	128
1.0	2.0	89.1	70.7	128
1.0[a]	1.0[a]		63.3	124, 95, 89
1.0[b]	1.0[b]			101, 4, −18

[a] Spectra recorded after 5.0 min at 80 °C. [b] Spectra recorded after 1.0 h at 80 °C.

Ethylene polymerizations were conducted to confirm that a MAS/ETAC complex was the active species. Productivity values and polymer characteristics are collected in Table 2 (entries 1−6); a plot of yield vs concentration of MAS/ETAC is shown in Figure 3. A general first-order dependence of the polymer yield on MAS/ETAC concentration is apparent, but the trend deviates significantly at high and low catalyst loadings. At high catalyst loadings, mass transport problems were encountered due to filling of the reactor with swollen polymer, thus lowering the polymer yield and productivity. At low catalyst loadings, the added alkylaluminum is acting primarily as a scavenger, lowering the actual concentration of MAS in solution and lowering the observed productivity. This is most apparent with the addition of 0.2 mmol of catalyst and activator; the MAS is entirely consumed by scavenging trace impurities in the reactor, and no polyethylene is observed.

Figure 4 (Table 2, entries 7−13) shows a temperature profile for the polymerization of ethylene by MAS/ETAC. Productivity drops off rapidly at temperatures higher than 80 °C. This decrease in reactivity is concomitant with consumption of the MAS, observed by a lack of reaction when quenching the polymerization with methanol. The optimal temperature of 75 °C gave a productivity of ca. 600 g of PE mol^{-1} h^{-1} bar^{-1}. Molecular weights increased significantly upon lowering the temperature (75 °C, $M_n = 293\,548$, PDI = 2.49; 60 °C, $M_n = 521\,169$, PDI = 2.94; 40 °C, $M_n = 733\,165$, PDI = 2.98), potentially due to decreased radical-induced decomposition and higher ethylene solubility. Attempts to expand the scope of this reaction to α-olefins as monomers or co-monomers have been unsuccessful. Polypropylene or poly(isobutylene), for example, are not formed under these conditions as the reactions favor the Friedel−Crafts alkylation of toluene.

Interaction between Methylaluminum Sesquichloride and Ethyl Trichloroacetate. To investigate the nature of the active species in this polymerization, MAS/ETAC mixtures were monitored by ^{1}H, ^{13}C, and ^{27}Al NMR spectroscopy. Mixtures of MAS and ETAC in the ratios of 1:0.1, 1:0.3, 1:0.5, 1:1, and 1:2 in toluene-d_8 were analyzed first at room temperature and subsequently at the polymerization temperature of 80 °C. Key results are collected in Table 3.

An upfield shift in the ^{13}C resonance for the -CCl$_3$ group from δ 91 to ca. δ 88 is in accord with Cl coordination, shielding the carbon center. A shift to lower field, from ca. δ 65 to δ 76, is observed for the OCH$_2$−^{13}C resonance. If ligation of ETAC to aluminum were to occur, constrained rotation and steric crowding of the OCH$_2$ site may result in a downfield shift. When the ratio of MAS:ETAC is 1:2, however, both the CCl$_3$ and OCH$_2$ resonances shift toward that of free ETAC (δ 89 and 70.7 ppm, respectively). This is again in agreement with a 1:1 MAS/ETAC complex being preferred; at high ETAC loadings, the coordinated and uncoordinated activators are in equilibrium. On the NMR time scale, they appear at averaged chemical shifts.

For aluminum-containing compounds, ^{27}Al NMR is a valuable tool in following chemical transformations and determining the coordination number of these species in solution.[22−24] Spectra of methylaluminum sesquichloride, expected to exist in solution as a chloro-bridged dimer,[25] show two broad resonances, at δ 177 and δ 135, in the region of four-coordinate aluminum

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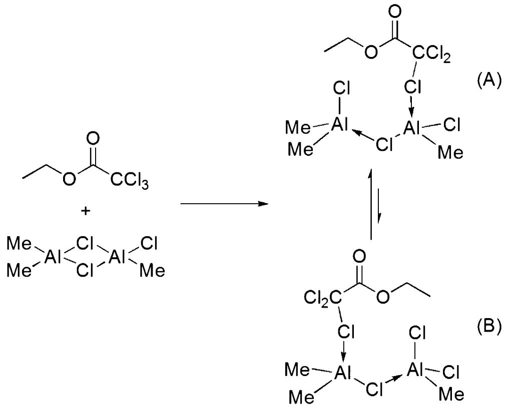
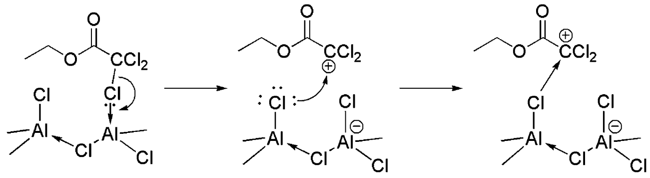
species, which correspond to the two nonequivalent aluminum centers in $Al_2Cl_3Me_3$. Upon addition of small quantities of ETAC to MAS, the starting materials continue to dominate the spectra, with a small signal appearing at δ 95 and a shoulder appearing on the upfield side of the broad δ 135 resonance. Upon reaching a 1:1 ratio, however, a spectrum containing a single major resonance at δ 128 is obtained. This implies that the two aluminum environments are made equivalent (presumably by rapid exchange process), further supported by the appearance of only a single Al−CH_3 resonance in the ^{1}H NMR spectrum. These observations are consistent with a binuclear aluminum species persisting upon coordination of ETAC, a factor which may minimize decomposition reactions and facilitate catalyst formation. At higher ETAC loadings the ^{27}Al spectrum remains unchanged. Compound **A** (eq 1) is postulated as a static structure for this adduct, though there is the potential for an equilibrium with a second species **B**. It might be expected that the equilibrium will lie in favor of structure **A** in which the CCl_3 unit forms a dative covalent interaction with the more Lewis acidic aluminum center.



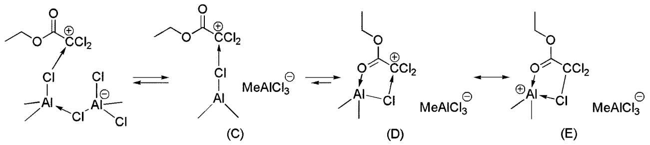
(1)

The most active polymerizations, however, occur at temperatures of 70−80 °C. Heating MAS/ETAC solutions (0.1 M, toluene-d_8) to 80 °C results in a palpable change in the NMR spectra. New signals appear in the ^{27}Al spectrum at δ 124, δ 95, and δ 89, while ^{1}H and ^{13}C NMR spectra become complicated with the formation of multiple products. The ^{13}C signal for the *C*Cl_3 group is no longer present, implying that a chlorine transfer to aluminum may have occurred. Halide transfer to main group metal centers is known to give trihalomethyl cations.[26] A similar chloride transfer to aluminum centers is proposed as an initiation step in the carbocationic polymerization of isobutylene and propylene.[27−29] The high dimerization energies coupled with high Lewis acidity of active alkylaluminum reagents could more readily facilitate this chloride transfer and suggests the possible formation of an ionic active species, possibly by the halide abstraction pathway shown in Scheme 1.

Scheme 1. Proposed Zwitterionic Precatalyst for MAS/ ETAC Ethylene Polymerization



Scheme 2. Formation of Electrophilic Active Species in MAS/ETAC Ethylene Polymerization



It is instructive to examine more closely the components of this zwitterionic species. Notably, “coordination” of an aluminate anion invokes parallels to the type of species that have been proposed upon activation of titanium halides with chloroaluminum alkyl reagents. Analogously, the aluminate anion could dissociate to give a product **C** of the type shown in Scheme 2. Chelation of the carbonyl oxygen to the three-coordinate Al center might be anticipated under these circumstances, lending stability to the system and affording a product of type **D**. Compound **D** can be alternatively represented as canonical form **E**, which has a formal positive charge at Al and may explain the enhanced reactivity of the Al−C bond toward olefin insertion.

These solutions are not thermally stable, however. Leaving relatively concentrated solutions of MAS/ETAC at elevated temperatures for 1 h promotes decomposition of the mixture via a radical mechanism. While halide exchange dominates the observed reactivity at lower concentrations and with less reactive substrates,[30] aluminum alkyls and polyhalogenated organics are known to undergo vigorous radical decomposition reactions at elevated temperatures.[31−33] In this case, new resonances in the ^{27}Al spectra at δ 3 and δ −18 support the formation of decomposition species with high coordination numbers. Both NMR and GC/MS studies confirmed the consumption of MAS and ETAC and the concomitant generation of radical decomposition products, processes observed previously in reactions of CCl_4 with alkylaluminum reagents.[33]

These decomposition reactions imply that the aging of MAS/ ETAC solutions should be important in influencing polymerization productivity. Aging a dilute (0.001 M) solution of MAS/ ETAC at 80 °C for 30 min prior to commencing the polymerization gave an improved productivity of 800 g mol^{-1} h^{-1} bar^{-1} (conditions as in Table 1, entry 1, M_n = 316 572, PDI = 3.01). However, aging solutions at either higher concentrations (0.1−1.0 M) or for longer periods of time gave decreased polymer yields. Radical decomposition of MAS/ ETAC solutions generate product mixtures which are inactive for ethylene polymerization. The formation of the proposed cation−anion pair could potentially be stabilized by utilizing a polar solvent such as bromobenzene. Polymerization and ^{27}Al NMR studies indicate that an interaction between the halobenzene solvent and alkylaluminum reagent may prevent the formation of the active species and promote the formation of a new species that is deep red in color. Reactions conducted in bromobenzene produced negligible polymer, while polymerizations in 75:25 toluene:bromobenzene mixtures gave lowered productivities (110 g of PE mol^{-1} h^{-1} bar^{-1}).

Polymerization of Ethylene with Various Aluminum Alkyls and Activators. To further probe the scope of the

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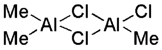
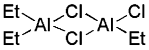
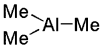
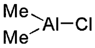
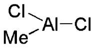
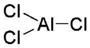
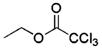
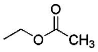
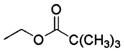
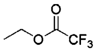
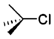
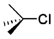
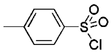
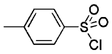
Table 4. Effect of Alkylaluminum Reagent[a]

Entry	Alkyl aluminum	Yield (g)	Productivity[b]
1		2.09	269
2		0.30	38
3		*trace*	*n/a*
4		0.09	11
5		1.31	164
6		*trace*	*n/a*
7	MAO	*trace*	*n/a*

[a] Reaction conditions: 1.0 mmol of alkylaluminum reagent, 1.0 mmol of ETAC, 4.0 bar ethylene, 1.0 h, Fischer−Porter glass reactor, 200 mL of toluene, 80 °C. [b] Productivities given relative to Al in g mol^{-1} h^{-1} bar^{-1}.

Table 5. Effect of Activator on Polyethylene Productivity[a]

Entry	Activator	Temp (°C)	Yield (g)	Productivity[b]	M_w (Da)[c]	M_n (Da)[c]	PDI[c]
1		80	2.09	538	716660	292149	2.45
2		80	*trace*	*n/a*	*n/a*	*n/a*	*n/a*
3		80	*trace*	*n/a*	*n/a*	*n/a*	*n/a*
4		80	0.95	238	284864	97690	2.92
5	CCl_4	80	0.06	15	*n/a*	*n/a*	*n/a*
6	CCl_4	30	1.09	273	2178717	792623	2.75
7		80	*trace*	*n/a*	*n/a*	*n/a*	*n/a*
8		30	0.11	28	266354	58526	4.55
9	$(^nBu)_4N^+Cl^-$	80	*trace*	*n/a*	*n/a*	*n/a*	*n/a*
10	$(^nBu)_4N^+Cl^-$	30	0.19	48	1354834	265560	5.10
11	$(^nOct)_4N^+Cl^-$	80	*trace*	*n/a*	*n/a*	*n/a*	*n/a*
12	$(^nOct)_4N^+Cl^-$	30	*trace*	*n/a*	*n/a*	*n/a*	*n/a*
13		80	1.93	483	649309	239690	2.71
14		30	0.25	63	*n/a*	*n/a*	*n/a*

[a] Reaction conditions: 1.0 mmol of MAS, 1.0 mmol of activator, 1.0 h, 4.0 bar ethylene, Fischer−Porter glass reactor, 200 mL of toluene, 80 °C. [b] Productivities given relative to MAS in g of PE mol^{-1} h^{-1} bar^{-1}. [c] Molecular weights determined by GPC at 130 °C.

aluminum/chloro-activator polymerization system, screening studies were conducted with a series of alkylaluminum reagents, as summarized in Table 4. Interestingly, trimethylaluminum and dimethylaluminum chloride were both poor catalysts for the polymerization of ethylene in the absence of transition metal catalysts when activated with ETAC. Since $AlMe_3$, $AlEt_3$, and Me_2AlCl are among the more common alkylaluminum reagents utilized in industry and academia, this may explain why aluminum-centered polymerization processes have remained largely unnoticed. It was only when more Lewis acidic methylaluminum dichloride was combined with ETAC that substantial productivities, and polymer characteristics (Table 4, entry 5) similar to those of the MAS/ETAC system, were observed. These results suggest that two factors are important for catalyst productivity. First, the aluminum reagent must be highly Lewis acidic, since only $MeAlCl_2$ and $Al_2Cl_3Me_3$ reagents gave active catalysts. Second, the formation of a strongly associated bimetallic aluminum system appears to be important. The dimerization enthalpy for methylaluminum sesquichloride is calculated to be 19.4 kcal/mol, higher than the dimerization enthalpy for either Me_2AlCl or $MeAlCl_2$.[25,29] This observation concurs with recent theoretical[34] and experimental[35] studies which have suggested that dinuclear species may promote higher productivities. Changing the alkyl substituent from methyl- to ethylaluminum sesquichloride resulted in a 7-fold decrease in productivity (Table 4, entry 2). The greater steric hindrance of the ethyl species, affording a lower dimerization enthalpy, may account for its inferior performance relative to MAS. This is also supported by the observation of low productivities when $EtAlCl_2$ and $^nBuAlCl_2$ are employed (14 and 8 g of PE mol^{-1} h^{-1} bar^{-1}, respectively). MAO/ETAC mixtures also gave only trace amounts of polyethylene.

To provide further support for aluminum-based polymerization catalysis, it is useful to compare the productivities of entry 1 to entries 4 and 5. Methylaluminum sesquichloride is readily prepared from the reaction of methylaluminum dichloride ($MeAlCl_2$) and dimethylaluminum chloride (Me_2AlCl). If the observed productivity is due to a transition metal contaminant in the alkylaluminum reagents, then an average productivity of Me_2AlCl and $MeAlCl_2$ should be observed. However, a much improved productivity is found for MAS, suggesting that an intrinsic property of the MAS/ETAC combination is responsible for the superior productivity.

Polymerizations conducted using MAS with various activators were also revealing (Table 5). The necessity for chloro-containing activators is apparent. As there is potential for ETAC simply binding to aluminum through its oxygen functionalities and effectively acting as a ligand, entries 1−4 tested ethyl acetate derivatives. A halogen source is necessary to activate these systems, with ethyl acetate and ethyl trimethylacetate showing no productivity. The trifluoro derivative showed moderate productivity; molecular weights were decreased to ca. 97 000 Da. This lowered productivity may be due to the hard-donor properties of fluorine and stronger C−F bond in these systems.

The strong indication of a chlorine source being necessary for productivity led us to investigate simple alkyl chlorides as activators. When a dilute MAS solution under ethylene at 80 °C was treated with CCl_4 (Table 5, entry 5), the solution immediately turned deep red and very little polymer was formed. A radical reaction dominates at these temperatures, even at low concentrations,[33] killing the polymerization. Reducing the temperature helped control these decomposition reactions; a productivity of 273 g of PE mol^{-1} h^{-1} bar^{-1} was observed at 30 °C (Table 5, entry 6). The lifetime of the catalyst was short, however, since even at these lower temperatures, decomposition limited catalyst productivity. Switching activators to less reactive or more ionic chlorine sources met with limited success (Table 5, entries 7−12). Tosyl chloride, ($CH_3C_6H_4SO_2Cl$, TosCl; Table 5, entries 13 and 14) proved to be a much improved activator for ethylene polymerization. As was the case with ETAC, higher temperatures led to enhanced productivities. Molecular weights

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(34) Talarico, G.; Budzelaar, P. H. M. *Organometallics* **2002**, *21*, 34.

(35) Cavell, R. G.; Aparna, K.; Kamalesh Babu, R. P.; Wang, Q. *J. Mol. Catal. A: Chem.* **2002**, *189*, 137.

and polydispersities were similar to ETAC, again pointing to a halogen transfer activation process, rather than a ligand effect.

^{27}Al NMR studies were used to investigate the activation of MAS by TosCl. Room-temperature spectra indicated the formation of a new peak at δ 96 along with a broad shoulder obscured by a resonance of unreacted MAS. At low TosCl loadings the spectra appear strikingly similar to resonances observed in MAS/ETAC studies. At 1:1 catalyst:activator ratios only two peaks are present in ^{27}Al spectra, at δ 131 and δ 97. At higher TosCl loadings, peaks at δ 96 and δ 82 dominate the spectrum. Surprisingly, however, no evidence of decomposition is observed at elevated temperatures. Spectra of concentrated MAS/TosCl solutions in toluene-d_8 were heated at 80 °C in toluene for 24 h with only minor deviations to the recorded spectra.

Gratifyingly, this observation correlates with improved catalyst stability in the polymerization reactor. Longer reaction lifetimes are possible, with no drop in productivity observed over a 2 h run. A productivity of approximately 1000 g of PE mol^{-1} h^{-1} bar^{-1} ($M_n = 254\,443$, PDI = 2.65) was obtained at 80 °C with a catalyst loading of 0.2 mmol of MAS/0.2 mmol of TosCl. The MAS/TosCl catalyst system can also be operated in heptane; the productivity remained high (502 g of PE mol^{-1} h^{-1} bar^{-1} compared to 483 g of PE mol^{-1} h^{-1} bar^{-1} in toluene), while molecular weights decreased slightly. Current efforts are being directed toward optimizing the MAS/TosCl polymerization conditions and investigating substituent effects for the sulfonyl chloride activator.

Conclusions

The results reported in this paper show that simple aluminum alkyl reagents can function as catalysts for the homogeneous polymerization of ethylene to high molecular weight linear polyethylene under conditions (T, P) comparable to those utilized in homogeneous transition metal catalyzed ethylene polymerizations. Key to the formation of an active catalyst is a combination of a relatively Lewis acidic aluminum alkyl reagent such as methylaluminum sesquichoride with a chlorine-containing activator. The active species is an intimate combination of these two reagents and shows single-site behavior. Control over the molecular weight of the resultant PE proved possible by changes to the reaction temperature, catalyst loadings, and the nature of the aluminum and chloro-activator reagents. By comparison to traditional homogeneous transition metal ethylene polymerization systems, which often require complex ligand syntheses and relatively expensive transition metal components along with, in many cases, a massive excess of alkylaluminum reagent, the results described here highlight the potential of simple aluminum compounds as viable ethylene polymerization catalysts under relatively mild conditions.

Experimental Section

General Methods. Air-sensitive reactions were performed using standard Schlenk and vacuum line techniques. Toluene was dried by passing it through a cylinder filled with commercially available Q-5 catalyst (13% copper(II) oxide on Al_2O_3). NMR spectra were recorded on a Bruker DRX400 operating at 400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 104.3 MHz for ^{27}Al. GC analyses of organic products were carried out on a HP-5890 gas chromatograph. Gel permeation chromatographs (GPCs) were obtained using a Waters 150CV and Shodex 807, 806, and 804 columns. Neat quantities of methylaluminum sesquichloride were purchased from Aldrich Chemical Co. and used as received. Solutions of methylaluminum sesquichloride (1.0 M, hexanes) were synthesized according to literature procedures[29] or prepared as stock solutions from commercial sources of pure compound. Trimethylaluminum, dimethylaluminum chloride, methylaluminum dichloride, ethylaluminum sesquichloride, and trichloroaluminum were purchased from Aldrich as 1.0 M solutions in hexanes and used as received. Ethyl trichloroacetate, ethyl acetate, ethyl trimethylacetate, ethyl trifluoroacetate, carbon tetrachloride, and *tert*-butyl chloride were purchased from Aldrich and freshly distilled from CaH_2 under an inert atmosphere prior to use. Tetrabutylammonium chloride, tetraoctylammonium chloride, and *p*-toluene sulfonyl chloride were purchased from Aldrich and dried rigorously prior to use. Standardized solutions of all reagents were prepared under nitrogen in a glovebox using freshly dried and degassed toluene.

Ethylene Polymerization Procedure. A standard procedure is outlined below; conditions and reagent volumes were changed as appropriate. A 400 mL Fischer−Porter reactor, equipped with a mechanical stirrer and ethylene inlet, was charged with toluene (200 mL) and flushed with ethylene for 15 min. Methylaluminum sesquichloride (0.5 M in toluene, 2.0 mL, 1.0 mmol) was injected into the reactor, followed by injection of ethyl trichloroacetate (0.5 M in toluene, 2.0 mL, 1.0 mmol). The reactor was pressurized to 4.0 bar. The reactions were carried out at 80 °C for 1.0 h. Each reaction was terminated by disconnecting the reactor from the ethylene line, releasing the pressure and quenching the reaction with acidified (5%) methanol. The reaction mixture was combined with 300 mL of methanol, and the precipitated solid was filtered, washed with methanol, and dried under vacuum at 60 °C until reaching constant weight.

NMR Experiments. NMR experiments were conducted in Wilmad 400 MHz NMR tubes fitted with a J-Young valve. Methylaluminum sesquichloride (50.0 μL, 0.280 mmol) was added to each tube, followed by 0.7 mL of toluene-d_8. Ethyl trichloroacetate or *p*-toluene sulfonyl chloride was added to each tube via microsyringe in the ratio of 0.1, 0.3, 0.5, 1.0, and 2.0 equiv of activator to methylaluminum sesquichloride. Tubes were sealed and kept at 0 °C until the run. ^{1}H, ^{13}C, and ^{27}Al spectra were recorded at 20 and 80 °C. For some samples, the tubes were removed from the spectrometer and heated at 80 °C in an oil bath for 1 h and spectra recollected.

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Supporting Information Available: ^{27}Al NMR spectra on the MAS/ETAC system. This material is available free of charge via the Internet at http://pubs.acs.org.

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