

Novel Aluminum-Based, Transition Metal-Free, Catalytic Systems for Homo- and Copolymerization of Alkenes

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Since the initial reports by Ziegler¹ on the “aufbau” reaction, or stepwise insertion of ethene into the aluminum–carbon bond of alkylaluminum compounds, it has been widely believed that because of the accompanying displacement reaction the products of this reaction were limited to oligoethenes, with few reports of the preparation of high molecular weight polyethene at an aluminum center. Martin has described the preparation of polyethene by exposing ethene to a heptane solution of either bis-(dichloroaluminum)ethane or trialkylaluminum over several days.² Recently, Jordan and Gibson have reported the polymerization of ethene using chelated alkylaluminum complexes activated by a Lewis acid.³ On the other hand, the polymerization of higher alkenes, such as propene, by an aluminum-based system has *never* been reported. Herein, we report that high molecular weight, linear homo- and copolymers of ethene and propene can be prepared, in the absence of any transition metal species, via a catalyst system consisting of simple alkylaluminum compounds activated by Lewis acids.

The homo- and copolymerization of ethene and propene were carried out in 125 mL glass-lined reactors and our results are summarized in Tables 1–3. As can be seen, several systems based on the combination of an alkylaluminum compound and a Lewis acid are effective. Of note is the observation that methylaluminoxane (MAO) can act as either one of the two components (presumably because of the presence of small amounts of trimethylaluminum in the commercial sample). Several features of these systems are of interest. First, the molecular weights are high and ¹H and ¹³C NMR spectroscopy indicates that the polymers are highly linear. The linearity of the polyethene formed was further supported by its high melting point (*T*_m > 135 °C). The polypropene is atactic. For the ethene–propene copolymer, the melting point was found to decrease with increasing propene content in the copolymer.

Narrow polydispersities (approximately 2) were observed for the polyethene and polypropene formed, suggesting a single-site catalyst. Finally, in the polymerization of ethene, the polymer molecular weight was found to increase with increasing reaction time (first entry in Table 1), indicating some degree of “livingness” to the system. This *may* be due to the lack of d-orbitals on aluminum that are necessary for chain transfer through facile β-hydrogen abstraction (β-hydrogen abstraction from neutral aluminum alkyls occurs only at elevated temperatures). The transfer of a growing polymer chain from a transition metal center to aluminum to form a stable aluminum-terminated polymer has been reported.⁴

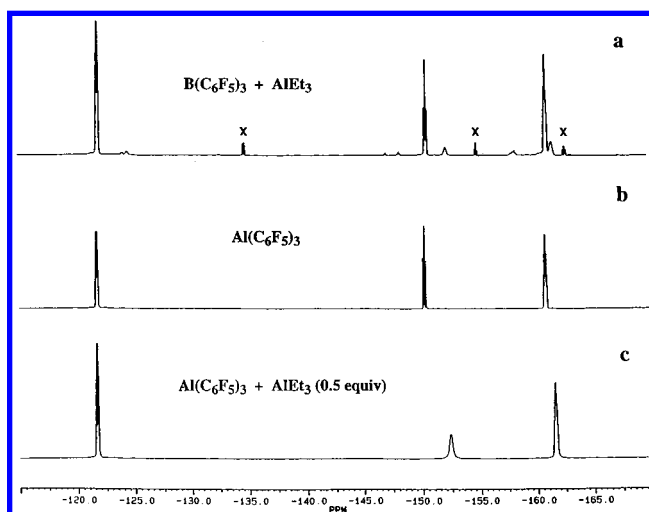


Figure 1. ¹⁹F NMR spectra (C₆D₅Cl) of (a) AlEt₃ + B(C₆F₅)₃, (b) Al(C₆F₅)₃, and (c) Al(C₆F₅)₃ + 0.5AlEt₃. The resonances marked with X correspond to C₆F₅–Et. The resonances are referenced against CF₃COOH at –78.5 ppm.

A critically important issue that must be addressed for all transition metal-free polymerization systems is whether trace amounts of transition metal impurities are actually responsible for the polymerization. For reasons given below, this appears to be unlikely for the present systems. First, the two components used in our systems were analyzed for Ti, Zr, and V by AA spectroscopy and were found at levels less than the detection limit (<20 ppm). Second, any one of the components, when used alone, showed no polymerization activity (as anticipated slight polymerization activity was exhibited by MAO). Third, haloaluminum alkyl compounds, such as AlEt₂Cl and AlEtCl₂, showed no activity when used either alone or with an activator such as MAO or B(C₆F₅)₃. Were the alkylaluminum compound simply activating a trace metal impurity, it seems likely that these compounds would show some activity. Fourth, single-site catalysts do not result from the combination of most transition metal salts and alkylaluminum compounds.

To probe the nature of the active species, the reactions of several trialkylaluminum compounds with B(C₆F₅)₃ were monitored by NMR spectroscopy (C₆D₅Cl).⁵ In the ¹H NMR spectrum of tri-*n*-octylaluminum, the α-CH₂ attached to the aluminum appeared as a triplet at 0.7 ppm, the β-CH₂ appeared as a broad multiplet at 1.7 ppm, the terminal CH₃ appeared as a triplet at 1.1 ppm, and the remainder of the CH₂ units appeared as a broad resonance at 1.5 ppm. Following the addition of 1 equiv of B(C₆F₅)₃, the most significant change in the spectrum involved the shift of the α-CH₂ resonance from 0.7 to 1.8 ppm. The spectrum now corresponded to that of tri-*n*-octylboron as confirmed by its independent synthesis from BH₃·THF and 1-octene! Thus, as reported earlier,⁵ a near-quantitative exchange of organic groups had occurred between aluminum and boron to form trialkylboron and Al(C₆F₅)₃. The same conclusion was also reached from an examination of the ¹³C NMR spectrum of the reaction mixture. Very similar results were also obtained with triethylaluminum. Moreover, neither the combinations, triethylboron and B(C₆F₅)₃ (1:1) or triethylboron and triethylaluminum (1:1), nor Al(C₆F₅)₃ alone catalyzed the polymerization of ethene.

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Table 1. Polymerization of Ethene

catalyst components (mmol)		solvent	yield (g)	activity (kg/mol·h) ^e	M_n^f ($\times 10^{-3}$)	M_w^f ($\times 10^{-3}$)
AlEt ₃ (0.3)	MAO (0.3)	C ₆ H ₅ Cl	3.9 ^a	3.25	40 (111) ^b	98 (263) ^b
AlEt ₃ (0.3)	MAO (0.3)	toluene	0.6 ^a	0.50		
MAO (0.3)	B(C ₆ F ₅) ₃ (0.3)	C ₆ H ₅ Cl	0.4 ^a	0.35	262	485
AlEt ₃ (0.3)	B(C ₆ F ₅) ₃ (0.3)	C ₆ H ₅ Cl	1.0 ^a	0.85		
AlEt ₃ (0.3)	Trityl FAB (0.3)	C ₆ H ₅ Cl	2.8 ^a	2.33		
AlMe ₃ (0.3)	MAO (0.3)	C ₆ H ₅ Cl	1.5 ^a	1.25		
(i-Bu) ₂ AlH (0.3)	B(C ₆ F ₅) ₃ (0.3)	C ₆ H ₅ Cl	0.6 ^a	0.50		
(i-Bu) ₂ AlH (0.3)	An. FAB (0.3)	C ₆ H ₅ Cl	0.5 ^a	0.41		
AlEt ₃ (0.08)	An. FAB (0.08)	C ₆ H ₅ Cl	1.1 ^c	13.75		
Al(i-Bu) ₃ (0.12)	An. FAB (0.06)	C ₆ H ₅ Cl	0.4 ^d	2.22		

^a 20 mL of solvent, 800 psi of ethene, 50 °C, 4 h. ^b 20 h. ^c 10 mL of solvent, 800 psi of ethene, 50 °C, 1 h. ^d 10 mL of solvent, 800 psi of ethene, 50 °C, 1.5 h. ^e Relative to Al (first component). ^f Relative to polystyrene standards. MAO: methylaluminoxane. Trityl FAB: [(C₆H₅)₃C][B(C₆F₅)₄]. An. FAB: [(C₆H₅)N(CH₃)₂H][B(C₆F₅)₄].

Table 2. Polymerization of Propene^a

catalyst components		solvent	yield (g)	activity (kg/mol·h) ^b	M_n^c ($\times 10^{-3}$)	M_w^c ($\times 10^{-3}$)
AlEt ₃	B(C ₆ F ₅) ₃	C ₆ H ₅ Cl	0.71	0.12	74	140
MAO	B(C ₆ F ₅) ₃	toluene	0.95	0.16	112	229
AlMe ₃	B(C ₆ F ₅) ₃	C ₆ H ₅ Cl	0.20	0.03		

^a Reaction Conditions: 0.3 mmol of each catalyst component, 10 mL of solvent, 5 g of propene, 50 °C, 20 h. ^b Relative to Al (first component). ^c Relative to polystyrene standards. MAO: methylaluminoxane.

Table 3. Copolymerization of Ethene and Propene^a

ethene (psi)	propene (psi)	time (h)	yield (g)	propene incorporation (%)	T_m (°C)
700	0	1.5	1.84	0	135.9
400	100	5	4.39	4.67	121.6
300	100	5	2.50	5.40	115.5
150	100	5	0.70	5.88	108.5
50	100	5	0.05	16.9	53.4

^a Reaction conditions for each run: 0.1 mmol each of AlEt₃ and [(C₆H₅)N(CH₃)₂H][B(C₆F₅)₄], 10 mL of C₆H₅Cl, single charge of monomers, 60 °C.

Clearly, the search for the active catalyst formed from triethylaluminum and B(C₆F₅)₃ must lie elsewhere.

The ¹⁹F NMR spectrum of a 1:1 mixture of triethylaluminum and B(C₆F₅)₃ was dominated by resonances due to Al(C₆F₅)₃ (Figure 1a,b). However, there was a second (minor) set of C₆F₅ resonances (Figure 1a). The *p*- and *m*-fluorines resonated at −154.5 (br) and −163.0 ppm (br). The resonance due to *o*-fluorine

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Table 4. Polymerization of Ethene as a Function of Al(C₆F₅)₃·0.5Toluene:AlEt₃ Ratio^a

Al(C ₆ F ₅) ₃ ·0.5 toluene (μmol)	AlEt ₃ (equiv)	yield (g)	activity ^b (kg/mol·h)
80	0.3	0.27	3.4
80	0.5	0.87	10.9
80	0.9	0.08	1.0
80	1.2	0.20	2.5
80	2.0	0.14	1.8

^a Reaction conditions: 15 mL of C₆H₅Cl, 700 psi of ethene, 60 °C, 1 h. ^b Based on Al(C₆F₅)₃·0.5 toluene.

atoms overlapped with the peak from the *o*-fluorine atoms of Al(C₆F₅)₃. **Only the resonances corresponding to the second species was obtained when Al(C₆F₅)₃·0.5 toluene was combined with 0.5 equiv of triethylaluminum in C₆D₅Cl (Figure 1c).** While the exact nature of this species remains uncertain, it is clearly a mixed alkyl, perfluorophenyl complex of aluminum, [(Et)(C₆F₅)₂Al]_x.⁶ Moreover, as shown in Table 4, when ethene was polymerized using varying ratios of Al(C₆F₅)₃·0.5 toluene and AlEt₃, the highest activity was observed for a 1:0.5 ratio of the two components suggesting that [(Et)(C₆F₅)₂Al]_x is the actual catalyst or its direct precursor.

In conclusion, we have demonstrated that simple alkylaluminum compounds, when activated by suitable Lewis acids, are capable of catalyzing the homo- and copolymerization of ethene and propene to high molecular weight polymers with narrow polydispersities.

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