Neutral Olefin Polymerization Activators as Highly Active Catalysts for ROP of Heterocyclic Monomers and for Polymerization of Styrene

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Potent olefin polymerization activators[1] for metallocene and related precatalysts are typically group 13 based aluminum and boron compounds such as methylaluminoxane (MAO),[2] $B(C_6F_5)_3$ (**1**),[3] $Al(C_6F_5)_3$ (**2**),[4,5] $[Ph_3C]^+[B(C_6F_5)_4]^-$,[6] and $[HNRR'_2]^+[B(C_6F_5)_4]^-$,[7] capable of generating highly active, single-site homogeneous olefin polymerization catalysts.[8] In particular, strong organo-Lewis acids **1** and **2** have attracted increasing attention because the real polymerization catalysts (the activated forms) are usually isolable and X-ray crystallographically characterizable cationic complexes, and studies of such isolated complexes have provided valuable insight into the molecular basis of polymerization catalysis.[1,3−5,8,9] In combination with suitable cationic initiators, borates $[RB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$ have also been used as weakly coordinating counteranions[10] in carbocationic polymerization.[11]

We are interested in using these strong Lewis acids to directly initiate polymerization processes. In this work, we found that **1**, **2**, and $Al(OC_6F_5)_3$ (**3**)[12,13] are exceptional catalysts for ring-opening polymerization (ROP) of heterocyclic monomers such as cyclohexene oxide (CHO). More significantly, **2** and **3** are found to be highly active for styrene polymerization in the absence of a transition-metal catalyst and without cocatalysis with adventitious moisture.

Compound **3** was synthesized by reacting C_6F_5OH (3 equiv) and $AlMe_3$ in toluene at room temperature for 3 h, followed by heating under mild reflux conditions for 12 h, and finally under vigorous reflux for 3 h.[14] ^{19}F NMR spectra[15] reveal a dimeric structure in solution which is consistent with the structure in the solid state as confirmed by X-ray diffraction studies,[16] featuring two $-OC_6F_5$ groups symmetrically bridging two Al centers (Figure 1).

Initial polymerization studies using **3** as activator for metallocene-catalyzed olefin polymerization yielded disappointing results. For example, activating C_2-symmetric $Et(Ind)_2ZrMe_2$[17] with **3** produced an isotactic polypropylene catalyst with very low activity (1.3×10^3 g of PP/(mol of Zr·atm·h)), although the isotacticity is high ([*mmmm*] = 98%). NMR reaction studies of various dimethylzirconocenes having different symmetries (L_2 = Cp_2,[18] C_{2v}; $Et(Ind)_2$, C_2, $Me_2C(Cp)(Flu)$,[19] C_s) with **3** have yielded the same conclusion: facile $-OC_6F_5$ group transfer to Zr[20] forming inactive species $L_2ZrMe(OC_6F_5)$ and $L_2Zr(OC_6F_5)_2$,[13b,14b,20] thereby diminishing catalytic activities of the systems derived from **3** (eq 1).

$$2L_2ZrMe_2 + 2Al(OC_6F_5)_3 \rightarrow L_2ZrMe(OC_6F_5) + L_2Zr(OC_6F_5)_2 + Me_xAl(OC_6F_5)_{3-x}\ (x = 1, 2) \quad (1)$$

To avoid decomposition of the activated catalyst derived from **3**, styrene polymerization was then attempted by first adding the activator **3** to styrene monomer followed by addition of a syndiospecific styrene polymerization precatalyst Cp^*TiMe_3.[21] Unexpectedly, rapid polymerization was initiated by **3** alone, and all monomer was consumed even before adding the precatalyst Cp^*TiMe_3. This surprising result is in sharp contrast to the polymerizations using other aluminum species such as $AlMe_3$ and $Al(O^iPr)_3$ and the borane **1**, none of which produced an isolable amount of polymer in 2 h (entries 1−3, Table 1). On the other hand, **3** initiates very rapid styrene polymerization, consuming all monomer within 5 min in a [M]/[I] ratio of 1000 giving TONs of 11 640 at 23 °C, although polymerizations at 0 and −78 °C are slower (entries 4−6). Remarkably, **2** initiates even more rapid polymerization of styrene with TONs reaching 22 800 at −78 °C, corresponding to an activity of 1.4×10^8 g of PS/(mol_{Al}·mol_S·h) (entry 8). Lewis acids (**1**−**3**) are also exceptional catalysts for ROP of CHO (entries 9−14), with **2** exhibiting the highest activity having TONs of 158 000 (entries 10, 11), which corresponds to an activity of 3.1×10^9 g of P(CHO)//(mol_{Al}·mol_{CHO}·h). The structurally related aluminum alkoxy, alkyl, and zinc alkyl initiators exhibit none or very low activity in polymerization of CHO as reported in the literature (entries 15−18).[22,23]

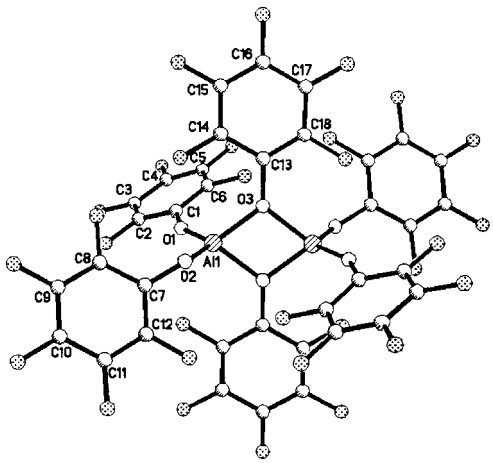

Figure 1. Crystallographic structure of **3**. Selected bond lengths and angles (Å, deg): Al1−O1 = 1.663(3); Al1−O2 = 1.684(2); Al1−O3 = 1.837(3); O1−Al1−O2 = 118.5(2); O1−Al1−O3 = 118.9(1); O2− Al1−O3 = 108.5(1).

In cationic polymerization of styrene or other electron-rich olefins, Lewis acids usually act as co-initiator or catalyst, and direct initiation by a Lewis acid is rare and usually slow.[24] Evidence that the styrene polymerization by **2** (toluene solvate or unsolvate form) is not caused by cocatalysis with adventitious moisture derives from several lines. First, solvents were extensively dried over activated alumina, Q-5 catalyst, and finally Na/K alloy or distilled over tri(*n*-octyl)aluminum, and styrene monomer was distilled over CaH_2 and tri(*n*-octyl)-aluminum. Polymerizations were performed with rigorous exclusion of oxygen and moisture in an Ar-filled glovebox (<0.5 ppm of O_2 and moisture) or interfaced to a high-vacuum line (10^{-6}−10^{-7} Torr). Second, strong Lewis acid **1** was inactive in our system, indicating a stringently dry condition of the current system.[10c] Third, addition of a stoichiometric amount of water to the styrene polymerization initiated by **2** completely shuts

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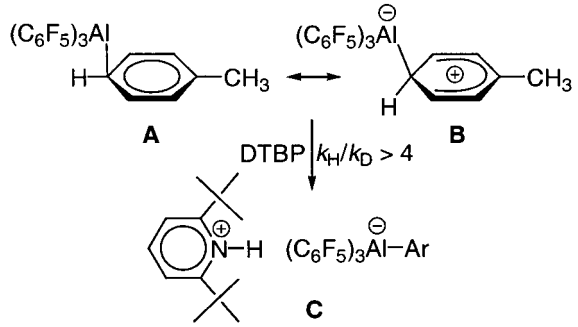
Table 1. Results for Styrene (S) Polymerization and ROP of Cyclohexene Oxide (CHO)[a]

entry	initiator	monomer	[M]/[I] ratio	T_p (°C)	t_p (min)	yield (%)	TON[b] (h^{-1})	M_w[c]	M_w/M_n[c]
1	$AlMe_3$	S	1000	23 (or 0)	120	trace	0		
2	$Al(O^iPr)_3$	S	1000	23 (or 0)	120	trace	0		
3	$B(C_6F_5)_3$ (**1**)	S	1000	23 (or 0)	120	trace	0		
4	$Al(OC_6F_5)_3$ (**3**)	S	1000	23	5.0	97	11600	4060	9.55
5	$Al(OC_6F_5)_3$ (**3**)	S	1000	0	7.0	89	7630	8440	5.03
6	$Al(OC_6F_5)_3$ (**3**)	S	500	−78	31	95	920	8360	6.26
7	$Al(C_6F_5)_3$ (**2**)	S	1000	0	5.0	96	11500	6780	5.03
8	$Al(C_6F_5)_3$ (**2**)	S	1000	−78	2.0	76	22800	9480	3.90
9	$B(C_6F_5)_3$ (**1**)	CHO	500	0	0.25	100	120000	29000	8.97
10	$Al(C_6F_5)_3$ (**2**)	CHO	500	0	0.17	88	158000	20700	8.77
11	$Al(C_6F_5)_3$ (**2**)	CHO	500	−78	0.17	88	158000	27000	6.89
12	$Al(OC_6F_5)_3$ (**3**)	CHO	500	23	1.0	96	28800	58800	4.47
13	$Al(OC_6F_5)_3$ (**3**)	CHO	500	0	1.67	97	17400	56200	3.65
14	$Al(OC_6F_5)_3$ (**3**)	CHO	500	−78	38.8	27	210	95200	3.81
15	$Al(O^iPr)_3$	CHO	500	23	60	trace	0		
16[d]	$AlMe_3$	CHO	250	−20	1440	trace	0		
17[d]	$AlEt_3$	CHO	250	−20	1440	87	9	36200	4.91
18[e]	$ZnEt_2$	CHO	100	80	1440	47	2		

[a] Conditions for styrene polymerization: 17.4 μmol of initiator (I); 2.0 mL of styrene (17.4 mmol); [M]/[I] = 1000 except for run 6 where the ratio is 500; 5 mL of toluene. Conditions for cyclohexene oxide polymerization: 9.88 μmol of initiator; 0.5 mL of CHO (4.94 mmol); [M]/[I] = 500; 2 mL of toluene. [b] Turnover numbers in moles of monomer (S or CHO) consumed per mole of aluminum per hour. [c] Determined by GPC relative to polystyrene standards. [d] Date from ref 22. [e] Data from ref 23.

Scheme 1

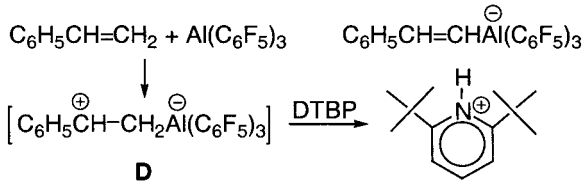


down the polymerization. Fourth, addition of solid **2** (toluene solvate or unsolvate form) to neat, extensively dried styrene causes a violent polymerization reaction.

From the crystal structure,[4a] the **2**·toluene complex can be viewed as two canonical forms, **A** and **B** (Scheme 1). Therefore, it is possible that the activated toluene could serve as a protogen that actually initiates the polymerization (if not all the polymerization). Indeed, reaction of **2**·toluene with 2,6-di-*tert*-butylpyridine (DTBP),[25] commonly used as a proton trap,[26] affords formation of $DTBPH^+$ paired with aluminate anions (**C**).[27] When using unsolvate **2** and C_7D_8, the same reaction reveals a large primary isotope effect of $k_H/k_D \sim 4.9$ at 23 °C. Accordingly, in the presence of 1 equiv of DTBP, the styrene polymerization by **2** is substantially retarded, resulting in a low monomer conversion under otherwise identical conditions. However, the polymerization is never completely shut down, and polymer yield is kept constant upon addition of excess of DTBP, suggesting a second initiation pathway other than by protons (vide infra).

Interestingly, in the absence of toluene, addition of unsolvate **2** to neat styrene also causes very rapid polymerization, whereas addition of DTBP traps the protons to form $DTBPH^+$ and aluminates and thus substantially retards the polymerization. Again, the polymerization is not completely shut down, which is attributable to the direct initiation by zwitterion **D** (Scheme 2). Obviously, for polymerizations in nonpolar media and in the absence of proton traps, initiations via proton transfer from both activated toluene and styrene dominate the polymerization.

Scheme 2



In summary, we have synthesized and structurally characterized the new initiator **3** and found that **2** and **3** are highly active for polymerization of styrene as well as for ring-opening polymerization of CHO. Three different initiation pathways in styrene polymerization by **2** have been identified; they are proton transfer from the alane-activated toluene, proton transfer from the zwitterionic adduct of styrene and **2**, and direct initiation by the zwitterionic adduct. The observed broad molecular weight distributions of the resulting polymers reflect these diverse initiations in the system. Further studies are underway to better control the polymerization by this novel initiator system.

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Supporting Information Available: Crystallographic data for **3** and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) One paper[13a] briefly mentioned in-situ generation of "**3**" by mixing C_6F_5OH and $AlMe_3$ in toluene at room temperature, and another paper[13b] described isolation of "**3**" from the reaction in hexane which gave spectroscopic data completely different from ours.[15] In our hands, using toluene and reflux conditions for greater than 12 h are required to produce **3.** Otherwise, different species, likely the methyl-bridging dimers, are produced.

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(14) (a) Anal. Calcd for $C_{36}Al_2F_{30}O_6 \cdot {}^1/_2C_7H_8$: C, 39.58; H, 0.34. Found: C, 39.61; H, 0.36. (b) See Supporting Information for details.

(15) ^{19}F NMR (C_7D_8, 23 °C): δ −154.93 (t, $^3J_{F-F}$ = 21.2 Hz, 2 F, *p*-F-bridging), −158.11 (t, $^3J_{F-F}$ = 21.5 Hz, 4 F, *p*-F-terminal), −159.01 (d, $^3J_{F-F}$ = 21.5 Hz, 4 F, *o*-F-bridging), −163.54 (m, 8 F, *o*-F-terminal + *m*-F-terminal), −166.39 (pent, 4 F, *m*-F-bridging).^{19}F NMR (C_6D_6, 23 °C): δ −155.33, −158.60 (t), −159.80 (d), −164.08 (t), −164.36 (d), −166.87 (t).

(16) Crystallographic data for **3**: triclinic, space group $P\bar{1}$; a = 10.258(4) Å, b = 10.478(4) Å, c = 11.205(4) Å, α = 99.320-(7)°, β = 107.210(7)°, γ = 104.419(7)° at 173(2) K; V = 1077.5(7) Å^3; Z = 1; D_{calc} = 1.905 mg/m^3, absorption coefficient = 0.250 mm^{-1}, $F(000)$ = 602, number of reflections collected = 4003, number of independent reflections = 3469, R_1 = 0.0430 ($I > 2\sigma(I)$), wR_2 = 0.1035.

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(27) ^{1}H NMR (C_6D_6, 23 °C) for DTBP: δ 7.18 (t, 1H, Ar), 6.89 (d, 2H, Ar), 1.38 (s, 18H, *t*Bu); in C_6D_5Br: 1.32 (*t*-Bu). ^{1}H NMR (C_6D_6, 23 °C) for $DTBPH^+$: δ 7.10 (t, 1H, Ar), 6.51 (d, 2H, Ar), 0.66 (s, 18H, *t*-Bu); in C_6D_5Br: 1.00 (*t*-Bu). ^{19}F NMR (C_6D_6, 23 °C) for $[(C_6F_5)_3AlAr]^-$ anion: −123.20 (m, 6 F, *o*-F), −154.21 (t, 3 F, *p*-F), −162.20 (m, 6 F, *m*-F). Two other minor aluminate species are also seen in the ^{19}F NMR.

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