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Alkylaluminophosphonate-catalyzed ring-opening homopolymerization of epichlorohydrin and propylene oxide

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Abstract

Reactions of an aluminum alkyl, AlR_3 (R = Me, Et, ^{i}Bu, ^{t}Bu), with a phosphonic acid, $R'P(O)(OH)_2$ (R′ = H, Me, ^{t}Bu, Ph), in molar ratios of 3:1, 2:1, and 1:1 were conducted in toluene–THF. Resulting aluminophosphonate solutions were screened for catalytic activity for the ring-opening homopolymerization of epichlorohydrin (ECH) and propylene oxide (PO). A highly active catalyst solution, **3a**, was obtained from reaction of $^{t}Bu_3Al$ with $MeP(O)(OH)_2$ in a 2:1 molar ratio in toluene–THF. A more active catalyst, **3b**, was obtained by removing volatiles, specifically THF, from solutions of **3a** and reconstituting with toluene. Catalyst **3a** polymerized ECH at 60°C in 1–3 h to an elastomer with molecular weight, M_n, of 103 000 and polydispersity, M_w/M_n, of 1.9. Catalyst **3b** yielded poly-ECH with M_n of 130 000 and M_w/M_n of 1.9 within 15 min. Catalysts **3a** and **3b** polymerized PO to oily oligomers with M_n of 3588 and 4046 and M_w/M_n of 1.1 and 1.2, respectively. Known dimeric and tetrameric aluminophosphonates such as $[^{t}Bu_2AlO_2P(OSiMe_3)Ph]_2$ and $[RAlO_3PR']_4$ (R = Me, R′ = Me; R = ^{t}Bu, R′ = Me, Ph) do not account for the observed activity of the catalyst solutions. Comparisons of catalytic activity with that for well-defined catalysts and a structural analogy of alkylaluminophosphonates to cyclic and cage *tert*-butylaluminoxanes are presented.

Keywords: Catalysis; Epoxide; Polymerization; Aluminum; Phosphonate; Polyether

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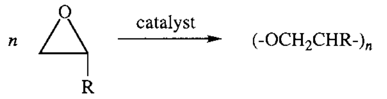
1. Introduction

Polyether elastomers continue to find use in automotive and industrial applications that require materials with low gas permeability, retention of flexibility at both low and high temperatures, and stability upon extended exposure to heat, hydrocarbons, and ozone [1]. The commercially important elastomers are amorphous homopolymers of epichlorohydrin (ECH), as well as copolymers and terpolymers of ECH, ethylene oxide (EO), propylene oxide (PO), and allyl glycidyl ether (AGE).



R = H (EO), CH_3 (PO), CH_2Cl (ECH), $CH_2OCH_2CH{=}CH_2$ (AGE) (1)

A variety of reagents will catalyze the ring-opening oligomerization or polymerization of epoxides (Eq. (1)) [2], including metal alkoxides [3], tin reagents [4], hydrolyzed zinc and cadmium alkyls [5], heterometallic cyanide complexes (e.g. $Zn_3Co(CN)_6$) [6], calcium amide–alkoxides [7], and neutral and cationic aluminum complexes supported by chelating ligands such as porphyrins [8], salen [9,10], diamidoamines [11], biphenolates [12], and others [13]. The disadvantages of many of these catalysts include high cost, poor polymerization activity, and production of polymers with low molecular weight or with crystallinity too excessive for elastomer applications. The preferred commercial catalysts for the synthesis of high-molecular-weight amorphous polyethers are based on trialkylaluminum and water combinations, often with additional components such as acetylacetone (acac) [1,14,15]. These aluminoxane-based 'Vandenberg catalysts' [15] also have several drawbacks, including cost, limited control over

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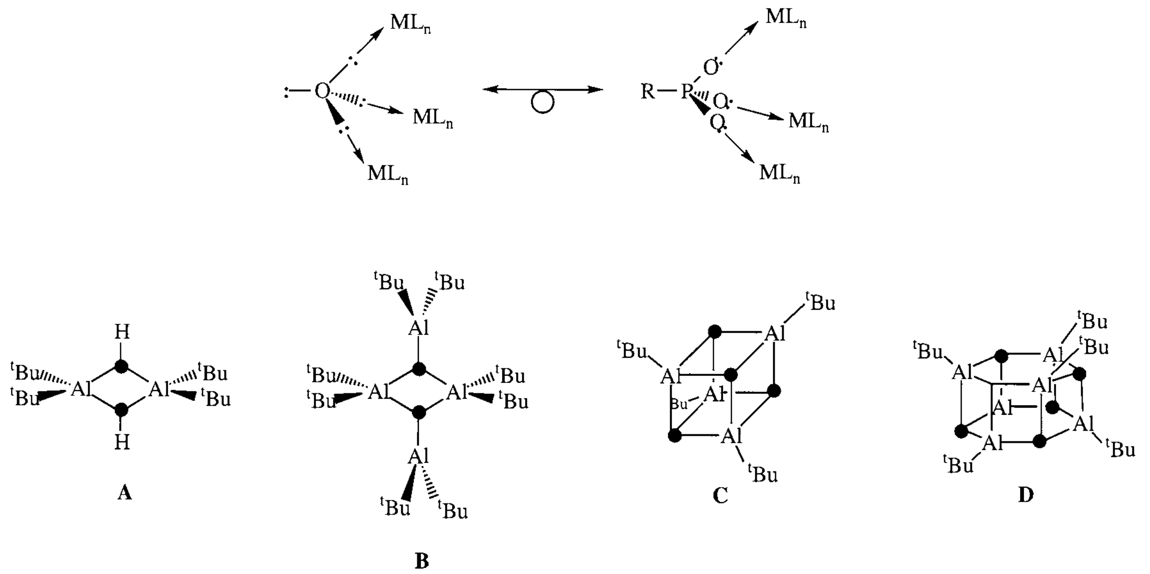

Fig. 1. Structural relationship of alkylaluminophosphonates and *tert*-butylaluminoxanes; ● represents μ_3-R′PO$_3^{2-}$ and μ_3-O^{2-}, respectively.

molecular weights and polydispersities of the resulting polymers, and a dearth of information concerning the catalyst active site(s), polymerization mechanism(s), and the role of additives such as acac. A clearer understanding of the structure, solution dynamics, and reactivity of aluminoxane-based catalysts is desirable for rational improvements to the catalysts, but only a limited understanding of these reagents has emerged despite extensive research on aluminoxane structure and reactivity over the past three decades [16–18].

One approach to alternate epoxide polymerization catalysts is the development of structurally well-defined alkylaluminoxane analogues that exhibit industrially useful catalytic activity. We hypothesized that potential analogues might include molecular alkylaluminophosphonates, since they are structurally similar to the well-studied *tert*-butylaluminoxanes [17,19] based on an isolobal relationship of μ_3-O^{2-} and μ_3-RPO$_3^{2-}$ groups as illustrated in Fig. 1. The *tert*-butylaluminoxanes **A**, **B**, and **D** are known and structurally characterized, as are the phosphonate tetramers **C**, hexamers **D**, and trimethylsilyl derivatives of dimeric **A** [20,21]. The tetrameric ($n = 4$) aluminoxane **C** of formula (^{t}BuAlO)$_n$ is not known, presumably due to strain introduced by the 90° bond angles at oxygen [22], but the tetramer may still be considered the parent compound of the series, three of which ($n = 6$, 8, 9) are stable and have been characterized by X-ray crystallography [17]. Phosphonate dimers **B**, believed to be formed in 2:1 reaction mixtures of aluminum alkyls and phosphonic acids, have not been isolated, but the analogous gallophosphonate [(^{t}Bu$_2$Ga)$_2$O$_3$PPh]$_2$ has been isolated and fully characterized [23].

Structural rearrangements and the presence of numerous equilibria in solution have been proposed to partially account for the complexity of alkylaluminoxane solutions [16]. Similarly, intermolecular exchange reactions have been observed in crossover experiments with tetrameric alkylgallophosphonates and tetrameric alkylaluminophosphonates (**C**) [20,24]. Although the cyclic and cage alkylaluminophosphonates do not possess the ring strain nor, presumably, the resulting latent Lewis acidity proposed for the *tert*-butylaluminoxanes [18], the similarities in structures and solution dynamics justified exploration of these compounds as alkylaluminoxane analogues and as catalysts for the polymerization of epoxides. In planning the present study, we were also cognizant that products of methylphosphonic acid and aluminum alkyls were claimed as epoxide polymerization catalysts in a patent by Vandenberg [25], although no details have been reported. Herein, we report results of our initial screening of alkylaluminophosphonates as catalysts for the homopolymerization of ECH and PO.

2. Experimental

2.1. General procedures

All reactions were performed under an atmosphere of purified nitrogen using standard inert-atmosphere techniques. Tetrahydrofuran, diethyl ether, and pentane were distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from sodium. Benzene-d_6 and dimethylsulfoxide-d_6 were dried by storage over activated molecular sieves. Compounds **12**–**15** [20], **16** [26], [^{t}Bu$_2$AlO^{t}Bu]$_2$ [27], and ^{t}Bu$_3$Al [28] were prepared as previously described. Epichlorohydrin, propylene oxide, and triisobutylaluminum were provided by Zeon Chemicals and used as received. Phosphonic acids and trimethylaluminum were purchased from Aldrich and used without further purification. Solution NMR spectra were recorded on Bruker AMX-500 and Varian Inova 300 spectrometers using a deuterated solvent as the internal lock. Chemical shifts are reported relative to TMS. Gas chromatography (GC) was performed on a Gow Mac Series 69-750P gas chromatograph equipped with a flame ionization detector, a Spectra Physics SP 4270 integrator, and a packed (15% carbowax) Alltech column of dimensions 10′ 1/8″ × 0.85″. GC analyses were performed with an injection temperature of 250°C and an initial column temperature of 110°C ramped 18°C min^{-1} to the final column temperature of 180°C. Gel permeation chromatography (GPC) was performed at Zeon Chemicals Technical Center on a Waters 600E solvent delivery system equipped with 10^6, 10^5, 10^4 and 10^3 Å Ultrasyragel columns, 700 WISP autosampler, and model 410 refractive index detector. THF was used as the eluent at a flow rate of 0.8 ml min^{-1}. Polymer solutions in THF were filtered through a 0.45 μm syringe filter prior to analysis to remove high-molecular-weight insoluble polymer and microgels, which can plug the GPC columns. Although the amount of material removed by filtration in this work was minimal, for some polyethers the insoluble fraction is very significant. Thus, molecular weights of polyether elastomers based on GPC data must be interpreted with caution. Molecular weights were determined by comparison with calibration curves based on polystyrene standards in THF.

2.2. Preparation of catalyst solutions ***1–11***

A solution of methylphosphonic acid (0.270 g, 2.81 mmol) in 5.0 ml of THF was added dropwise to a toluene (10.0 ml) solution of ^{t}Bu$_3$Al (1.08 g, 5.47 mmol) at 0°C. After the addition was complete, the reaction flask was warmed to room temperature and the resulting solution was stirred an additional 12 h. This solution was used as catalyst **3a** for polymerization of ECH and PO. Analogous procedures were used for preparation of catalyst solutions **1**, **2**, and **4**–**11**. Molar ratios of aluminum alkyl and phosphonic acid, substituents, and solvents for catalyst solutions **1**–**11** are identified in Table 1.

A modified procedure was used for the preparation of catalysts **3b** and **5b**. The addition of methylphosphonic acid to ^{t}Bu$_3$Al was performed as described above and the resulting solution was warmed to r.t. The warm solution was stirred an additional hour. Volatiles were removed in vacuo and the remaining residue was redissolved with a volume of pure toluene equal to the original volume of toluene. This reconstituted sample was used as catalyst **3b**. Catalyst **5b** was prepared analogously from *tert*-butylphosphonic acid and ^{t}Bu$_3$Al (Table 1).

2.2.1. General polymerization procedure using aluminophosphonate catalysts ***1–11***

Epoxide (1.5–2.0 g) and toluene (10.0 ml) were injected into a capped 20 ml pressure bottle which had been purged and pressurized to 10 psi with purified

Table 1
Representative data for polymerization of ECH [a]

Catalyst [b]	R,R′	[Al]/[P]	Solvent	$[ECH]_0/[Al]_0$	Time	% Conversion [c]
1	^{t}Bu, H	2:1	Toluene–THF	145	1.5 h	45
2	^{t}Bu, Me	1:1	Toluene–THF	123	1.5 h	22
3a	^{t}Bu, Me	2:1	Toluene–THF	101	1.5 h	94 [d]
3b	^{t}Bu, Me	2:1	Toluene	99	15 min	100 [e]
4	^{t}Bu, Me	3:1	Toluene–THF	100	7 h	37
5a	^{t}Bu, ^{t}Bu	2:1	Toluene–THF	68	12 h	82
5b	^{t}Bu, ^{t}Bu	2:1	Toluene	52	15 min	100
6	^{t}Bu, Ph	2:1	Toluene–THF	227	1.5 h	11
7	^{i}Bu, H	2:1	Toluene–THF	72	3.75 h	19
8	^{i}Bu, Me	2:1	Toluene–THF	76	1h	23
9	^{i}Bu, ^{t}Bu	2:1	Toluene–THF	81	3.5 h	29
10	^{i}Bu, Ph	2:1	Toluene–THF	129	12 h	32
11	Me, Me	2:1	Toluene–THF	12	1.5 h	38

[a] All polymerizations were performed at 60°C in toluene unless otherwise indicated.

[b] Prepared by reaction of R_3Al with $R'P(O)(OH)_2$ in the molar ratio and solvent specified. Catalysts **3b** and **5b** were prepared from **3a** and **5a**, respectively, by removal of volatiles in vacuo and reconstitution with toluene.

[c] Conversion calculated from GC integration of epoxide.

[d] Coagulated and isolated. $M_n = 103\,000$; $M_w/M_n = 1.9$.

[e] Coagulated and isolated. $M_n = 130\,000$; $M_w/M_n = 1.9$.

nitrogen. A solution of catalyst was added via syringe at r.t. and the reaction flask was immersed horizontally in a 60°C shaker bath and agitated. The volume of catalyst solution added was chosen to give the desired monomer to catalyst ratio. Since the catalyst structures are unknown, monomer to catalyst ratio refers to the molar ratio of epoxide to aluminum. Epoxide concentration was monitored by gas chromatography prior to catalyst addition and at reaction times of 15 min and 1 h. Additional monitoring was performed on sluggish reaction solutions. For polymerization performed as part of the initial mass screening, conversions were calculated from epoxide concentration as determined by GC integration. For the most active catalysts with high conversions, the pressure cap was removed and the viscous reaction solution transferred into a beaker of water. The polymer was coagulated by boiling the aqueous suspension and the product was isolated by decantation. Alternatively, the viscous reaction solution was poured into a crystallizing dish and volatiles were evaporated in air. This latter procedure was particularly useful for the oily oligomers obtained from the PO polymerizations. Products were dried in air, in vacuo, or in a forced air oven. Data for two representative examples are given below.

*2.2.2. ECH polymerization with catalyst **3b***

Polymerization of ECH (1.62 g, 17.5 mmol) catalyzed by **3b** (0.191 mmol of Al) at 60°C was complete within 15 min as determined by GC. Coagulation of the product in boiling water yielded 1.56 g (16.9 mmol, 96%) of poly-ECH. $^{13}C\{^1H\}$-NMR (DMSO-d_6, 25°C, 75.4 MHz): δ 78.24 (s, CH), 78.08 (s, CH), 68.83 (s, CH_2O), 68.65 (s, CH_2O), 44.23 (s, CH_2Cl).

*2.2.3. PO polymerization with catalyst **3b***

Polymerization of PO (1.68 g, 28.9 mmol) catalyzed by **3b** (0.274 mmol of Al) at 60°C was complete within 45 min as determined by GC. Coagulation of the product by solvent evaporation in air and drying in vacuo yielded 1.38 g (23.8 mmol, 82%) of poly-PO as a viscous oil. $^{13}C\{^1H\}$-NMR (DMSO-d_6, 25°C, 75.4 MHz): δ 76.6–75.9 (m, CHO), 75.0–73.8 (m, CH_2O), 71.5–70.0 (m, CHOH), 67.0 (m, CHOH), 19.4–17.1 (m, CH_3).

2.3. General polymerization procedure for well-defined catalyst precursors

Since solubilities of the well-characterized molecules **12**–**16** varied considerably, the polymerization procedure was slightly altered. The solid catalyst precursor was weighed into a 20 ml pressure bottle in the glovebox and the bottle was subsequently capped and pressurized to 10 psi with purified nitrogen. A solution of epoxide (2.0 g) in toluene (10.0 ml) was added via syringe. All subsequent procedures were the same as given in Section 2.3 except that the first GC analyses were performed immediately after the addition of epoxide and toluene rather than prior to catalyst addition. The well-defined catalyst precursors showed no appreciable activity for the polymerization of ECH.

3. Results and discussion

A series of polymerization experiments were conducted to screen combinations of aluminum alkyls and phosphonic acids for catalytic activity in the ring-opening homopolymerization of epichlorohydrin. Reactions of an aluminum alkyl, AlR_3 (R = Me, Et, ^{i}Bu, ^{t}Bu), with a phosphonic acid, $R'P(O)(OH)_2$ (R′ = H, Me, ^{t}Bu, Ph), in molar ratios of 3:1, 2:1, and 1:1 were performed in toluene–THF. Aliquots of the resulting aluminophosphonate solutions were used to polymerize ECH at 60°C in toluene with monomer to catalyst ratios, [epoxide]/[Al], of approximately 100. Lower ratios were employed for evaluating some of the less-active catalysts. Selected data from these screening experiments are presented in Table 1.

All of the catalysts screened showed at least modest activity for the polymerization of ECH, but in general, the most active solutions resulted from reaction of an aluminum alkyl and a phosphonic acid in a 2:1 molar ratio with a reaction time of 12 h. Reaction times of only 1–3 h gave less active catalysts. Comparisons of conversion and reaction time (Table 1) for catalysts obtained from ^{t}Bu$_3$Al and $MeP(O)(OH)_2$ in molar ratios of 1:1 (**2**), 2:1 (**3a**), and 3:1 (**4**) clearly show **3a** to be the most active. For catalysts obtained from reaction of R_3Al and $R'P(O)(OH)_2$ in a 2:1 molar ratio, catalyst **3a** (R = ^{t}Bu, R′ = Me) is clearly superior to catalysts **1**, **5a**, and **6**–**11**. Catalyst **3a** routinely gave conversions exceeding 92% in less than 2 h for a monomer to catalyst ratio of ca. 100.

Coagulation of products from the screening experiments yielded polymers with rubber-like consistency[1]. The ^{13}C-NMR spectrum of a representative sample of elastomeric poly-ECH prepared from catalyst **3a** exhibits CH, CH_2O, and CH_2Cl resonances at 79.0, 69.6, and 43.5 ppm, respectively. Backbone methine and methylene resonances show tacticity splitting whereas the chloromethyl resonance does not. There are no additional resonances that could be assigned to end groups such as CHOH as previously identified for low-molecular-weight oligomers of ECH [9]. The ^{13}C-NMR data are very comparable to those reported by Cheng [29] for high-molecular-weight poly-ECH prepared using

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[1] We note that it is common industrial practice to add antioxidants during coagulation to stabilize polyether elastomers against attack by oxygen, which results in chain scission [1]. Antioxidants were not added to our polymers since polymer characterization was completed before appreciable chain scission could occur.

Table 2
Representative data for polymerization of PO [a]

Entry	Catalyst [b]	[Al]/[P]	Solvent	$[\text{PO}]_0/[\text{Al}]_0$	Time	% Conversion [c]
1	**3a**	2:1	Toluene–THF	105	1 h	99 [d]
2	**3a**	2:1	Toluene–THF	93	12 h	97 [e]
3	**3a**	2:1	Toluene–THF	135	2 h	79 [f]
4	**3b**	2:1	Toluene	103	15 min	98 [g]
5	**3b**	2:1	Toluene	120	15 min	88 [e]
6	**3b**	2:1	Toluene	120	12 h	100 [e]
7	**4**	3:1	Toluene–THF	87	1 h	22

[a] All polymerizations were performed at 60°C in toluene unless otherwise indicated.

[b] Prepared by reaction of $^t\text{Bu}_3\text{Al}$ with MeP(O)(OH)_2 in the molar ratio and solvent specified. Catalysts **3b** was prepared from **3a** by removal of volatiles in vacuo and reconstitution with toluene.

[c] Conversion calculated from GC integration of epoxide.

[d] Coagulated and isolated. $M_n = 3588$; $M_w/M_n = 1.1$.

[e] Polymerization conducted at 23°C.

[f] Catalyst aged under an inert atmosphere for 5 days at r.t.

[g] Coagulated and isolated. $M_n = 4046$; $M_w/M_n = 1.2$.

Vandenberg catalysts. The absence of end groups in the NMR data for poly-ECH prepared using **3a** is consistent with GPC measurements, which show M_n of 103 000 and M_w/M_n of 1.9.

Catalyst **3a** also oligomerized PO at 60°C with a monomer to catalyst ratio of ca. 100 and with near quantitative conversion in an hour (Table 2, entry 1). Excellent conversion was also obtained at r.t. when the reaction time was extended to 12 h (Table 2, entry 2), and the catalyst retained its activity upon storage under an inert atmosphere for 5 days (Table 2, entry 3).

In contrast to the rubber-like poly-ECH obtained with catalyst **3a**, polymerization of PO yielded oily low-molecular-weight oligomers. The ^{13}C-NMR spectrum of a representative oil exhibits numerous resonances in the regions of 76.2, 74.2, and 17.1–19.4 ppm assignable to methine, methylene, and methyl carbons, respectively [8,9,11]. Additional resonances in the vicinity of 67 and 71 ppm may be assigned to CHOH end groups, suggesting the products to be low-molecular-weight oligomers. This is verified by GPC data which shows M_n of 3588 and M_w/M_n of 1.1.

Monitoring of the polymerization solutions by GC made it apparent that small quantities of THF were sometimes consumed, suggesting possible THF incorporation in the polymers. Since we, as had Vandenberg [15], previously observed THF polymerization or copolymerization in related alkylaluminoxane-based catalysts, and since THF may also compete with epoxide for coordination sites on the catalyst, we opted to prepare two additional catalysts, **3b** and **5b**, which were essentially free of THF[2]. Catalysts **3b** and **5b** were prepared from **3a** and **5a**, respectively, by removal of volatiles in vacuo and reconstitution of the remaining residues with fresh toluene. This procedure removed essentially all THF except for traces, which undoubtedly remained coordinated to some aluminum sites. The resulting increase in activity was substantial. Whereas catalysts **3a** polymerized ECH with greater than 93% conversion in less than 2 h, **3b** yielded essentially quantitative conversion in only 15 min (Table 1). Similarly, **5a** required 12 h to achieve an 82% conversion of ECH to poly-ECH, but the same catalyst, stripped of volatiles and reconstituted with fresh toluene (**5b**) quantitatively converted ECH to polymer in only 15 min. Comparison of entries 1 and 4 in Table 2 shows catalyst **3b** is also more active than **3a** for the oligomerization of PO. This increase is further evident by comparison of PO oligomerization by **3a** and **3b** at r.t. (Table 2, entries 2, 5). In addition to the increase in the rate of polymerization upon removal of THF, GPC data shows that removal of THF from the catalyst solutions also results in an increase in molecular weight of the resulting polymer. M_n for poly-ECH increased from 103 000 to 130 000 and for poly-PO M_n increased from 3588 to 4046 for samples prepared using **3a** and **3b**, respectively. We propose no explanation for this observation, but do note that an increase in activity of the catalyst upon removal of volatiles and reconstitution with fresh toluene was not observed in all catalyst samples.

Comparison of epoxide polymerization activity of **3a** and **3b** with that of recently reported well-defined catalysts shows the alkylaluminophosphonates to be of comparable or superior activity to all but the 'high-speed living polymerization' catalysts developed by Inoue and co-workers [8]. Data presented in Table 3 show catalysts **3a** and **3b** to give greater conversions of PO to oligomers with greater M_n in less time than achieved with neutral and cationic Schiff-base, diamidoamine, and porphyrin complexes of aluminum. Whereas cata-

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[2] THF was initially used to solubilize the phosphonic acids for the preparation of catalysts **1**–**11**. We viewed homogeneity of the catalyst reaction solutions highly important for reproducibility based on the known dependence of alkylaluminoxane composition and activity on synthesis conditions [16,17].

Table 3
Comparison of PO polymerization data for several aluminum catalysts

Entry	Catalyst [a]	$[PO]_0/[Al]_0$	Time	Temperature (°C)	Conversions (%)	M_n	References
1	$[Al(Salen)(MeOH)_2][BPh_4]$	315	12 h	25	[b]	750–1000	[10d]
2	$[Al\{Salpen(^tBu)\}]_2[GaCl_4]_2$	477	12 h	25	[b]	2000–3000	[10a]
3	$[Al(L_3H)][AlCl_4]$	16	48 h	80	58	2158	[11]
4	Al(Salen)Cl	100	480 h	80	74	2450	[9b]
5	Al(TPP)Cl	200	7 h	25	20	3300	[8c]
6	**3a**	105	1 h	60	99	3588	This work
7	**3b**	103	15 min	60	98	4046	This work
8	Al(TPP)Cl–Lewis acid	200	3 min	25	86	11 900	[8c]
9	IBAO–PO	50	48 h	80	7	90 000	[14a]

[a] H_2Salen = *N*,*N*′-ethylenebis(2-hydroxyphenyleneimine); H_2Salpen(^{t}Bu) = *N*,*N*′-propylenebis(2-hydroxy-3,5-di-*tert*-butylphenyleneimine); L_3H_3 = *N*,*N*′,*N*″-tris(trimethylsilyl)diethylenetriamine; TPP = tetraphenylporphyrinato; Lewis acid was methylaluminum bis(2,4,6-tri-*tert*-butylphenolate); IBAO = isobutylaluminoxane.

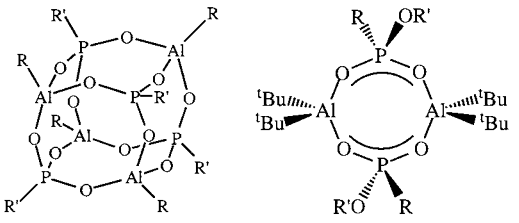
[b] Not reported.

lysts **3a** and **3b** yield PO oligomers with M_n of 3500–4000 in nearly quantitative conversion in as little as 15 min, Al(TPP)Cl polymerizes PO to oligomers with M_n of 3300 in 7 h with only 20% conversion at a monomer to catalyst ratio of 200. The Schiff-base complexes are less active, achieving M_n values of only 500–3000 even with reaction times as long as 480 h. However, addition of the bulky Lewis acid methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) to a solution of Al(TPP)Cl yields a 'high-speed living polymerization' catalyst that produces poly-PO with M_n of 11 900 in 86% yield within minutes. Although structurally ill defined, the isobutylaluminoxane adduct of PO (IBAO–PO) is also noteworthy here since it yields crystalline poly-PO with molecular weights as high as 90 000 [14a]. Conversion, however, is less than 10% in 48 h at a monomer to catalyst ratio of only 50.

Catalytic activity of **3b** approaches that of the Vandenberg catalysts, which yield poly-ECH with M_n in the hundreds of thousands range and possible exceeding a million [15]. Catalyst **3b** gives poly-ECH with M_n of 130 000 within 15 min and with nearly quantitative conversion at a monomer to catalyst ratio of 100. This activity has not been matched by well-defined aluminum complexes based on the limited published data. Inoue and co-workers have reported porphyrin complexes of aluminum to be much less active for the polymerization of ECH than for PO [8e]. Al(TPP)Cl polymerizes ECH with 80% conversion at a monomer to catalyst ratio of 400, but reaction time was three days and molecular weight data for the resulting polymer was not reported [8g]. Similarly, Spassky and coworkers has oligomerized ECH in bulk using Schiff-base complexes of aluminum. Starting with a monomer to catalyst ratio of only 20, oligoethers of ECH with M_n of 930 were obtained in an hour at 60°C with a conversion of 93% [9]. Results for polymerizations with larger initial monomer to catalyst ratios have not been reported, nor have results for the polymerization of ECH by the Schiff-base and diamidoamine aluminum complexes studied by the groups of Atwood [10] and Bertrand [11] or the IBAO–PO catalyst of Barron and co-workers [14a].

Having established that reaction solutions of an aluminum alkyl and a phosphonic acid exhibit moderate activity for the oligomerization of PO and excellent activity for the polymerization of ECH to high-molecular-weight polymers, the catalytic components of these alkylaluminophosphonate solutions need to be determined. The identity of the active component(s) is of particular interest when considering the poly-ECH results. If all aluminum sites in **3a** and **3b** were active for the polymerization of ECH, M_n can be predicted to be 9250 for a monodisperse polymer obtained at an initial monomer to catalyst ratio of 100. The isolation of poly-ECH with M_n of 103 000–130 000 indicates that less than 10% of the aluminum sites are active for producing high molecular weight polymer and may suggest that multiple aluminum atoms (i.e. cluster formation) are required to form an active site. It is noteworthy that Vandenberg has proposed that active sites for epoxide polymerization in alkylaluminoxane catalysts require a minimum of two oxo-bridged aluminum atoms in close proximity to facilitate backside attack on the epoxide and to account for the observed inversion of configuration in the polymer backbone [15].

Control reactions reveal that ^{t}Bu$_3$Al and its aerial oxidation product, [^{t}Bu$_2$AlO^{t}Bu]$_2$ [27], do not actively polymerize ECH. Lack of activity for ^{t}Bu$_3$Al not only eliminates ^{t}Bu$_3$Al as the active catalyst, but also precludes *tert*-butylaluminoxanes, which are potentially accessible by hydrolysis with adventitious water, as the active species. Protic acid initiated cationic polymerization is unlikely as POH groups react rapidly in the presence of excess aluminum alkyl. Catalyst solutions were evaluated by ^{31}P-NMR spectroscopy in an attempt to identify known components. Solutions of **3a** stirred at room temperature for an hour show a multi-



12 R = R' = Me
13 R = ^{t}Bu; R' = Me
14 R = ^{t}Bu; R' = Ph
15 R = Ph; R' = SiMe$_3$
16 R = OPh; R' = Ph

Fig. 2. Molecular alkylaluminophosphonates tested for epoxide polymerization activity.

tude of ^{31}P-NMR resonances in the region from 0.0 to 10.0 ppm. After stirring for 3 h, the spectrum simplifies to intense resonances at 1.2 and 0.8 ppm with less intense resonances at 7.5, 6.8, 4.2, 2.6, and 2.5 ppm. There is no evidence in the spectrum for [^{t}BuAlO$_3$PMe]$_4$ (**13**, δ 10.8), but the resonance at 6.8 ppm is consistent with the presence of small quantities of [^{t}BuAlO$_3$PMe]$_6$ (Fig. 1, structure **D**) [20c]. The intense resonances at 1.2 and 0.8 ppm could indicate the formation of *cis* and *trans* isomers of [^{t}Bu$_2$AlO$_2$P(OAl^{t}Bu$_2$)Me]$_2$ as might be anticipated for the molar ratio of reactants in the preparation of **3a** and as observed in the related gallium chemistry, [^{t}Bu$_2$GaO$_2$P(OR)Ph]$_2$ (R = H, SiMe$_3$, Ga^{t}Bu$_2$) [23,24]. However, we have thus far been unable to isolate and fully characterize the components that give rise to these resonances. Nonetheless, well-defined cyclic and cage alkylaluminophosphonates (Fig. 2) that might mimic structural motifs in these catalyst solutions were tested for the polymerization of ECH. Unfortunately, compounds **12**–**16** exhibited negligible activity and clearly are not representative of the active components in the crude alkylaluminophosphonate solutions **1**–**11**. Thus, the identity of the active species in these solutions remains a mystery. Further research into the isolation and structural characterization of the active components of these alkylaluminophosphonate solutions is ongoing.

4. Supplementary material

Additional data from the screening of alkylaluminophosphonate reaction solutions for ECH and PO polymerization activity are available on request from the authors.

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