Highly Active Catalysts for the Ring-Opening Polymerization of Ethylene Oxide and Propylene Oxide Based on Products of Alkylaluminum Compounds with Bulky Tetraphenol Ligands

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ABSTRACT: Mixtures of hindered (poly)phenols and alkylaluminum compounds have been evaluated as catalysts for the polymerization of ethylene oxide (EO) and propylene oxide (PO). Certain ligands bearing four phenol groups form particularly active catalysts when combined with triisobutylaluminum (2 equiv) and triethylamine (1 equiv) as initiator. Productivities of >100 g/mmol Al have been achieved in both EO and PO polymerizations by use of a dibenzothiophene-bridged tetraphenol. In general, catalyst activity increases with the increasing bulk of the substituents *ortho* to the phenol hydroxyl groups. Mechanistic investigations support a dinuclear insertion process. Chain transfer to alcohol (2-propanol or benzyl alcohol) has been demonstrated. Poly(propylene oxide) produced in this manner is atactic and highly regioirregular.

Introduction

High molecular weight poly(ethylene oxide) (PEO) is a useful water-soluble polymer. Its unique binding, thickening, lubricity, water retention, and film formation properties find a variety of applications, such as in personal care, building materials, mining, papermaking, drug delivery, tablet binders, and polymeric electrolytes. Most systems that catalyze the polymerization of ethylene oxide (EO) are heterogeneous,[1] but homogeneous catalysts have also drawn attention for decades.[2] Vandenberg[3] first demonstrated that a combination of trialkylaluminum species with water, ether, or 2,4-pentanedione is an effective catalyst for the ring-opening polymerization of EO and substituted oxiranes. He proposed a bimetallic mechanism for the oxirane ring opening that involved the growing chain shifting from one Al atom to an adjacent Al atom bearing a coordinating activated epoxide.[3] It was also found that addition of less than 1 equiv of Lewis base per aluminum atom could significantly increase the activity of trialkylaluminum compounds in EO polymerization.[4] Recently, a variation on the AlR_3/NR'_3 polyoxirane catalyst, in which the amine was replaced by an alkoxide salt, has been developed by Deffieux and co-workers for propylene oxide (PO) polymerization.[5]

Recent years have seen increasing attention paid to aluminum alkoxides as homogeneous catalysts (or cocatalysts[6]) for the polymerization of EO,[7] PO,[8] and cyclohexene oxide,[8a,9] lactones and lactides,[8b,10] and other oxygenates.[11] While almost all of these catalysts are aluminum phenoxides, chelating aluminum 2,2′-methylenebisphenoxides and their derivatives have been particularly extensively studied.[8b,c,9,10,11b] Okuda has presented[12] evidence that, in PO polymerization, the dinuclear mechanism for epoxide polymerization originally advanced by Vandenberg[3] holds for aluminum complexes in this family. However, from the standpoint of practical synthesis of high-molecular weight PEO, the work on these chelating systems is wanting in two regards: (1) it has mostly focused on the polymerization of monomers other than EO; (2) the metal-based productivities (i.e., g polymer/mmol Al) of these catalytic systems are still low. In 2005, we reported that aluminum complexes of sterically hindered sulfur-bridged bisphenols can be efficient catalysts for EO polymerization.[13] In the present contribution we further show aluminum tetraphenoxides to be especially highly active catalysts during ring-opening polymerization of both EO and PO in the presence of Lewis bases.

Results and Discussion

The ligands investigated in this work included both bisphenols and tetraphenols (Scheme 1). Cottone and Scott have reported[14] the synthesis of a number of tetraphenols of the type shown, including compounds **4**, **5**, and **8**, and have characterized the complexes formed upon their reactions with alkylaluminum species. Like Scott et al.,[15] as well as other investigators,[16] we have an interest in testing complexes based on ligands that support multiple metal atoms in the hope that bimolecular catalysis mechanisms, such as those described by Vandenberg[3] and Okuda,[12] may be facilitated.

Initiation by Lewis Base. A Symyx Parallel Pressure Reactor (PPR)[17] equipped with 48 cells that are run simultaneously was used to screen catalytic activity during EO and PO polymerization. The catalysts were generated in situ from a number of combinations of aluminum precursors and phenol ligands. Under our experimental conditions, triisobutylaluminum (TiBA) with 0.5 equiv of triethylamine[18] was found to be very active (productivity = 40.4 g PEO/mmol Al) in polymerizing EO. Aluminum bisphenoxide generated from ligand **1** is known to polymerize PO[8c] and EO,[13] although the Al-based productivities are low. In the PPR, we again found **1**/TiBA (1:1) performed poorly (0.5 g PEO/mmol Al) during EO polymerization. However, addition of 0.5 equiv of triethylamine significantly improved its productivity to 14.4 g/mmol (Table 1). Similar

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Scheme 1

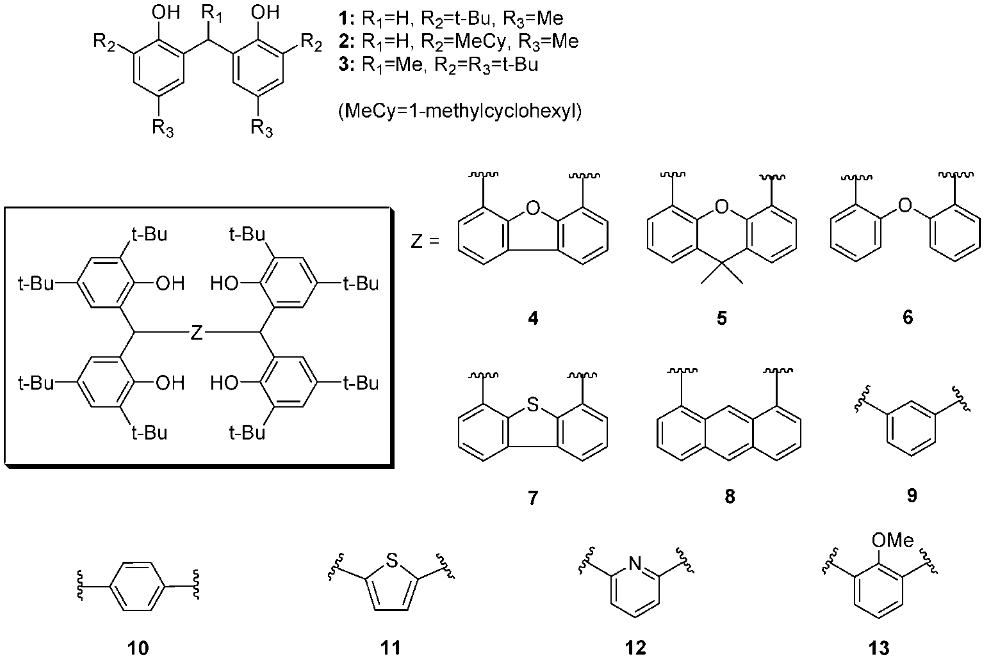


Table 1. PEO Productivity of 1/Al(i-Bu)$_3$ Catalysts with Various Lewis Bases[a]

Lewis base	base:Al	productivity g (PEO)/mmol (Al)
NEt_3	0:1	0.5
NEt_3	0.5:1	14.4
NEt_3	1:1	5.4
NEt_3	2:1	1.9
pyridine	0.5:1	14.2
DBU[b]	0.5:1	13.1

[a] Conditions: 2 h reaction at 40 °C, in hexane, 20 μmol Al(i-Bu)$_3$, 20 μmol **1**; data are averages of at least two cells. [b] DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene.

activities were observed when 0.5 equiv of pyridine or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used. Excess base ($>$0.5 equiv) resulted in loss of productivity.

Initiation by amine in the TiBA/amine system is suggested by the early work of Kutner and Vandenberg.[4] The analogous mechanism by which a bisphenoxide/amine catalyst is believed to initiate and propagate the coordinative anionic polymerization of oxiranes is illustrated for the catalyst **3**/TiBA/NEt_3 in Scheme 2. Attack of amine upon the back side of an EO molecule coordinated to an aluminum atom generates a Zwitterionic tetracoordinate "ate" complex which then transfers the growing chain to a neutral aluminum complex to which a molecule of monomer is already bound. This mechanism explains the loss of productivity as the amine/Al ratio increases beyond 1:2, since the active catalyst is a 1:1 mixture of zwitterion and neutral aluminum complexes. Repeated chain-exchange reactions among aluminum complexes (though not necessarily confined to unchanging pairs of aluminum species) eventually generate high MW polymer. To shed light on this hypothesis, PEO of low MW produced under conditions of low EO/Al by the bisphenol-based system **3**/TiBA/NEt_3 was analyzed by MALDI-TOF mass spectroscopy. The resulting spectrum (Figure 1) shows that indeed ring-opening by trialkylamine is the predominant initiation pathway.

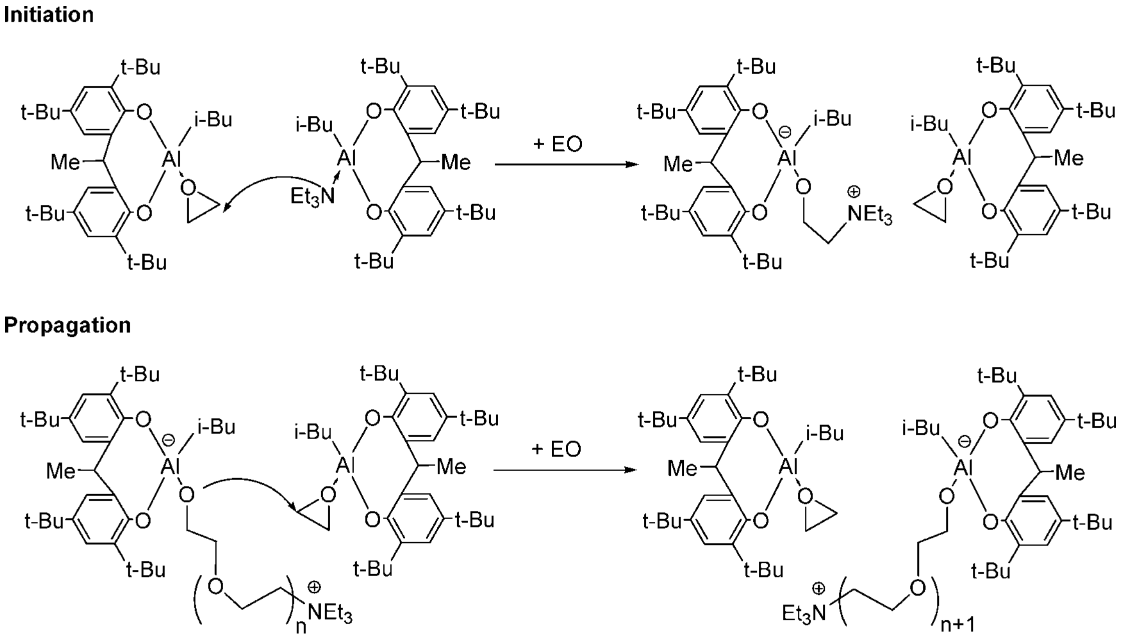
Screening of Various Catalytic Systems. In Table 2 are shown the Al-based productivities of different catalysts run at various levels of aluminum precursor, but with a fixed ratio of TiBA:NEt_3 = 2:1 and a ratio of phenol OH group to Al = 2:1. All bisphenols showed moderate activity. Comparison of the productivities for **1** and **2** suggests that increasing the steric bulk on the *ortho*-positions results in an increase of catalytic activity. Catalysts with certain tetraphenol ligands (**5**, **6**, and **8**) displayed poorer PEO productivities than those of bisphenol analogues run under similar conditions. Other tetraphenols (**7**, **10**, and **13**) gave rise to catalysts with activity equal to or higher than that of the ligand-free case. These ligands do not appear to share any particular structural feature that can account for the difference in catalyst performance.

A comparison of catalyst productivities at different catalyst charges reveals an interesting trend. Clearly the bisphenol-based catalysts tend to lose activity precipitously at low catalyst charge. This could be explained either by the sensitivity of these catalysts to poisons (either adventitious or of their own making) or to the fact that the mechanism is bimolecular in catalyst. By contrast, the ligand-free catalyst and the most active tetraphenol-based systems maintained high activity at lower levels of catalyst ($\leq$10 μmol Al). For some of these catalysts (e.g., catalyst **7**/TiBA), productivity is lowest at high catalyst level. This is an artifact of the way the run was conducted: catalytic activity is underestimated at high catalyst charge because most EO is consumed during the run, leading to relative monomer starvation in these cases.

Diethylaluminum chloride (DEAC) will generate a complex lacking Al−C bonds upon reaction with 2 equiv of hindered phenol. One would therefore expect DEAC-based complexes to behave quite differently from analogues made from trialkylaluminum reagents. Indeed, we found DEAC/NEt_3 and the bisphenol complex formed from **1**/DEAC to be essentially inactive for PEO (see Table 3). However, the productivity of **7**/DEAC/NEt_3 was comparable to that of its TiBA analogue at the same concentrations. The origin of the loss in catalyst activity seen in the replacement of the isobutyl groups with chlorine atoms is not known, but it may lie in the greater tendency to form tight Al−X−Al bridges when X = Cl. Perhaps in the case of dialuminum species prepared from tetraphenols such as ligand **7**, the formation of these bridges is made more difficult by steric congestion.

Alcohols as Chain Transfer Agent (CTAs). Chain transfer represents a more practical way to control MW in the reactor than other methods, for example, changing the catalyst charge

Scheme 2



or initiator ratio, due to a combination of economic and product quality issues. Inoue and co-workers[6a] discovered that alcohols led to the expected reduction of polymer MW during the polymerization of PO catalyzed by a porphinatoaluminum catalyst and a diphenoxyaluminum cocatalyst. We have tested 2-propanol (*i*-PrOH) and benzyl alcohol (BzOH) as potential CTAs for several active catalysts. Both were considered to have enough steric bulk to disfavor the formation of strong alkoxide bridges between aluminum atoms.

In the absence of alcohol, the PEO obtained from the ligand-free TiBA catalyst had a narrow polydispersity ($M_W/M_N = 1.3$) and a small polymer/Al ratio (~0.5), which would be expected if the only initiator is triethylamine (Al/NEt$_3$ = 2:1). However, PEO obtained from ligand/TiBA systems had broader MW distributions (with $M_W/M_N = 2-3$) and higher molar polymer/Al ratios (close to 1) without added CTA, which suggests that the ligand/TiBA system is sensitive to some species, either an impurity or the ligand itself, that tends to broaden the MW distribution.

Addition of the alcohols resulted in complete loss of activity for the ligand-free TiBA catalyst as well as for the analogue based on **1**. Surprisingly, both **7**/TiBA and **7**/DEAC maintained high activity in the presence of 3 equiv of alcohol. Addition of up to 3 equiv (to Al precursor) of *i*-PrOH lowered MW but did not broaden the MWD, which suggested an effective chain transfer. As expected, the molar polymer/Al ratio increased with the addition of *i*-PrOH. BzOH was found to be a worse CTA than *i*-PrOH, because not only did it reduce productivity more significantly, but its chain transfer efficiency (molar polymer/Al ratio) was lower than that of *i*-PrOH.

Dibenzothiophene-Bridged Ligands: Bisphenol vs Tetraphenol. It is possible that the unusually high activity of **7**/TiBA derives from the nature of the bridging dibenzothiophene group

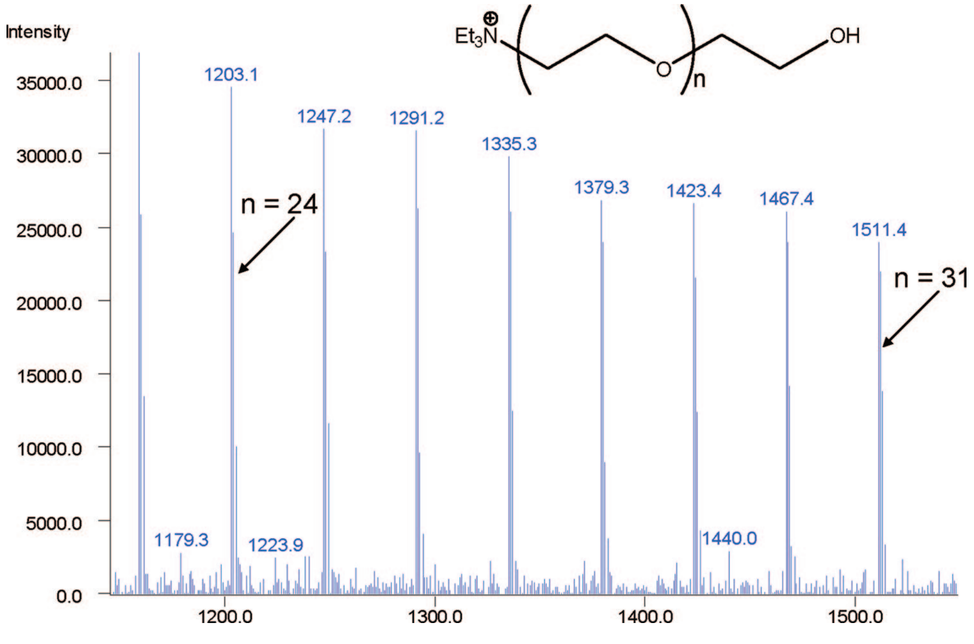


Figure 1. Portion of the MALDI-TOF mass spectrum of PEO made by **3**/Al(i-Bu)$_3$/NEt$_3$ (0.2/0.2/0.1 mmol) with 0.2 mL EO at 40 °C in hexane/toluene (total volume 4.5 mL) for 30 min (GPC/M_N = 2520, M_W/M_N = 1.29).

Table 2. PEO Productivity of Ligand/Al(i-Bu)$_3$/NEt$_3$ Catalysts[a]

ligand	L, μmol	Al(i-Bu)$_3$, μmol	yield,[b] g	prod.,[c] g (PEO)/mmol (Al)
none	0	20	0.807	40.4
none	0	10	0.598	59.8
none	0	5	0.176	35.3
1	20	20	0.288	14.4
1	10	10	0.070	7.0
1	5	5	0.008	1.5
2	20	20	0.467	23.3
2	10	10	0.092	9.2
2	5	5	0.008	1.6
3	20	20	0.356	17.8
3	10	10	0.084	8.4
3	5	5	0.001	0.2
4	10	20	0.651	32.5
4	5	10	0.283	28.3
4	2.5	5	0.009	1.9
5	10	20	0.026	1.3
6	10	20	0.191	9.5
7	10	20	0.765	38.2
7	5	10	0.676	67.6
7	2.5	5	0.379	75.7
8	5	10	0.013	1.4
9	10	20	0.381	19.0
9	5	10	0.192	19.2
10	10	20	0.492	24.7
10	5	10	0.574	56.9
11	5	10	0.101	10.1
11	2.5	5	0.024	4.8
12	2.5	5	0.018	3.7
13	2.5	5	0.623	124.5

[a] A 2 h reaction at 40 °C, in hexane, Al:N = 2:1; data are averaged results from at least two reactor cells. [b] Yield of PEO was corrected by taking into account catalyst residues. [c] Calculated by dividing yield by amount of Al precursor.

(e.g., the presence of a sulfur atom), rather than the fact that the bridge supports two bisphenol fragments. To resolve this question the bisphenol analogue of **7**, denoted **14**, was prepared and tested with TiBA for EO polymerization both as sole ligand and in combination with another bisphenol, **3**. This study essentially considers the implications of severing one of the C−C bonds that holds **7** together, as shown in Scheme 3. Polymerization performance by the bisphenols, both individually or combined, is strikingly poor relative to that of **7** (Table 4). This finding is consistent with the proposition that the high activity for catalysts based on **7** lies in the constrained environment created by the ligand, which increases the rate for a dinuclear polymerization process.

Highly-Active Catalysts Based on Dibenzothiophene-Bridged Tetraphenols. A series of variants on ligand **7** was prepared in which the *ortho*- and *para*-substituents of the phenol groups were altered to maximize catalyst productivity. These ligands (Scheme 4) were tested in polymerizations of EO under generally comparable conditions, the results of which are shown in Table 5. The highest productivities and polymer MW were obtained at low catalyst concentration and longer polymerization time; an effect of catalyst preparation conditions (with the mixture of ligand and TiBA allowed to react either overnight at ambient temperature or for 1 h at 60 °C) was not clearly apparent. Ligands with methyl groups at the *ortho*-positions were associated with very poor productivity, while increases in steric bulk beyond that of *t*-butyl generally led to higher activity than that of **7**/TiBA. This effect can be explained conventionally as the result of a reduction in the propensity of the catalyst to form inactive polynuclear clusters upon increase in the bulk of the ligands. An alternative suggested by a reviewer is that large groups ortho to the phenoxide oxygen atoms prevent these atoms from being alkylated by monomer, an event that would greatly perturb the structure of the active site. The activity of catalysts made from **7a**, however, which has methyl groups in place of the *para*-*t*-butyl groups found on **7**, is somewhat higher than those of analogous catalysts based on **7**, while **7d**, with ethyl groups in these positions, gives (perhaps fortuitously) intermediate results. No correlation of MW distribution with ligand structure was discovered. Number-average MW generally correlated with productivity, with approximately one polymer chain generated per aluminum atom. It should be noted that, in the absence of CTA, the polymer chain/Al ratio for a mechanism such as the one in Scheme 2 would be expected to be 1:2 rather than 1:1. The source of this discrepancy could be initiation or chain-transfer events not anticipated by this scheme, such as initiation at one of the phenoxide groups or chain-transfer to adventitious protic impurities such as water.

The more productive ligands in the dibenzothiophene family, as well as ligand **13**, were tested with Et$_2$Al(OEt) and Me$_2$Al(O-*i*-Pr) as metallating agents in addition to TiBA and DEAC. The results, graphically displayed in Figure 2, indicate that catalysts based on ligands with *t*-butyl *ortho*-groups have activities that do not strongly depend on the nature of the organometallic component. However, as the size of the *ortho*-groups increases, the activities for catalysts made from dialkylaluminum alkoxide precursors begin to drop off significantly. A similar, though less dramatic, trend is observed with DEAC versus TiBA.[19] This loss in polymerization activity could derive from a slowing down in the rate of catalyst formation from ligand and alkylaluminum compound as the bulk of the ligand grows. Corroborating evidence for the impact of catalyst formation rate upon catalyst productivity can be found in the pressure traces for these runs. In Figure 3 are shown three curves of pressure versus time for three catalyst systems based on ligand **7a**, with TiBA, DEAC, and Me$_2$Al(O-*i*-Pr) as the aluminum components. All other variables were held constant. The polymer yields (corrected for catalyst residues) were 0.675, 0.357, and 0.641 g, respectively. It is clear from this graph that the uptake of EO, as evidenced by pressure decrease, begins immediately after injection for the TiBA- and DEAC-based systems, while it is delayed in the case of Me$_2$Al(O-*i*-Pr). Ligand **7a** was chosen for this comparison because the yields for the catalysts based on TiBA and Me$_2$Al(O-*i*-Pr) are similar, so that the difference between the two curves could not be accounted for by a catalyst activity discrepancy alone. However, one can appreciate that if the onset of activity were to be delayed much further, polymer yield would decrease.

X-ray Crystallography. Catalysts based on ligand **7** were the first ones in our investigation to show a combination of high productivity for PEO as well as relative insensitivity to both the metallating agent and 2-propanol. An investigation of the structures of both the ligand and its complexes with aluminum followed. A crystal structure of ligand **7** (Figure 4) shows a coordination pocket formed by the four hydroxyl groups bounded by the *ortho*-*t*-butyl groups. The bridging dibenzothiophene group is essentially flat, with no atom in it lying more than 0.011 Å from the plane formed by this fragment. Suitable crystals of aluminum complexes of ligands in the dibenzothiophene-bridged family were difficult to obtain as the compounds are quite air-sensitive and appear to undergo irreversible reactions with darkening upon removal of solvents and warming even in the absence of air. However, a structure of the complex (Figure 5) formed from the reaction of 2 equiv of AlMe$_3$ with ligand **7a** was obtained under conditions in which a small amount of diethyl ether (present as a minor impurity in the ligand) caused the preferential crystallization of crystals of **15**, the dietherate complex, with 2 equiv of dichloromethane as solvent of crystallization (see Tables 6 and 7; a sample of this solvate was later prepared by the intentional addition of 2 equiv of ether prior to reaction with AlMe$_3$ and its NMR spectra and elemental analysis are reported in the Experimental Section). The central dibenzothiophene group is slightly twisted, with an angle of 2.7° between the planes defined by its two C6 rings.

Table 3. Effect of Precursor on Catalyst Activity and Sensitivity to Chain-Transfer Agents[a]

catalyst	L:Al, μmol	CTA	CTA, μmol	prod, g (PEO)/ mmol (Al)	M_N/1000	M_W/M_N	polymer/Al[b]
Al(*i*-Bu)$_3$	0:20	none	0	38.9	64.2	1.3	0.51
Al(*i*-Bu)$_3$	0:10	*i*-PrOH	10	<0.2			
Et$_2$AlCl	0:20	none	0	0.5			
1/Al(*i*-Bu)$_3$	20:20	none	0	12.4	14.3	2.4	0.86
1/Al(*i*-Bu)$_3$	20:20	BzOH	20	0.4			
1/Et$_2$AlCl	20:20	none	0	1.0			
7/Al(*i*-Bu)$_3$	5:10	none	0	77.1	78.5	3.8	0.98
7/Al(*i*-Bu)$_3$	5:10	*i*-PrOH	30	68.1	20.9	2.5	3.26
7/Al(*i*-Bu)$_3$	5:10	BzOH	40	6.7	3.2	2.4	2.12
7/Et$_2$AlCl	5:10	none	0	77.9	52.2	3.0	1.49
7/Et$_2$AlCl	5:10	*i*-PrOH	30	66.6	15.6	1.5	4.26

[a] A 2 h reaction at 40 °C, in hexane, Al:NEt$_3$ = 2:1; data from representative cells. [b] Molar ratio, calculated by dividing the productivity by M_N/1000.

Scheme 3

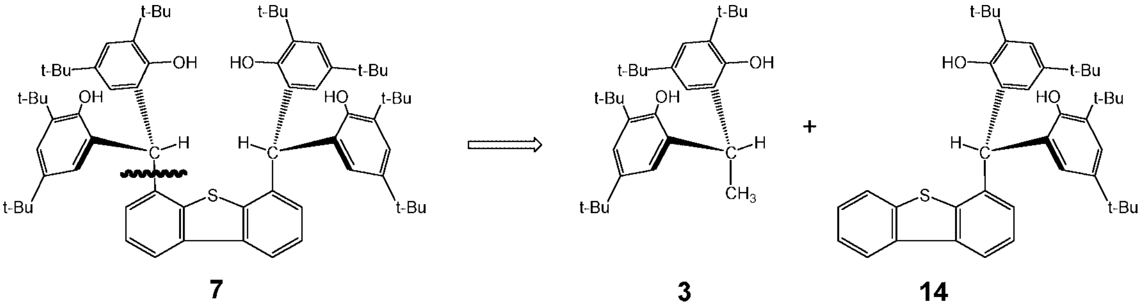


Table 4. PEO Productivity Comparison:[a] **Tetraphenol Ligand 7 vs Bisphenols**

ligand	precursor	yield, [b]g	prod., g/mmol
3	Al(*i*-Bu)$_3$	0.084	8.4
3	Et$_2$AlCl	0.005	0.5
14	Al(*i*-Bu)$_3$	0.038	3.8
14	Et$_2$AlCl	0.007	0.7
3 + **14** (1:1)	Al(*i*-Bu)$_3$	0.129	12.9
3 + **14** (1:1)	Et$_2$AlCl	0.002	0.2
7	Al(*i*-Bu)$_3$	0.715	71.5
7	Et$_2$AlCl	0.745	74.5

[a] Conditions: 1 mL EO; NEt$_3$ as initiator; 10 μmol Al; ArOH:Al:N = 4:2:1 molar ratio; 2 h reaction; T = 40 °C; catalysts prepared in situ in 1 h incubation at 60 °C; data are averages of at least two cells. [b] Yield of PEO was corrected by taking into account catalyst residues.

The coordination of two ether molecules shows that a dinuclear catalyst of this structure would be able to accommodate a molecule of EO and a growing polymer chain and perform the mechanism of Scheme 2. On the other hand, in this crystal structure the coordination spheres of the two aluminum centers lie on opposite sides of the plane defined by the dibenzothiophene fragment, with the torsional angle created by the two Al−O (ether) bonds being 129.4° and the distance between one Al atom and the oxygen atom of the ether molecule attached to the other Al center being about 7.6 Å. Thus large-amplitude motions would be required for this mechanism to function.

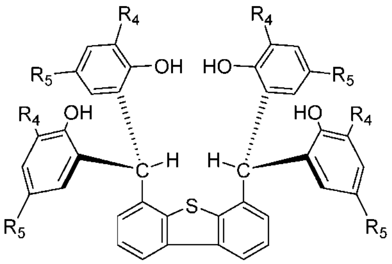
PO Polymerization. Various catalysts were also studied for the polymerization of PO: in addition to testing with no ligand, TiBA was employed as precursor with ligands **3**, **7**, **7a**, and **13**. The results (Table 8) show that tetraphenols greatly enhance the PO polymerization activities of aluminum alkyl/Lewis base mixtures, since TiBA/NEt$_3$ and **3**/TiBA/NEt$_3$ are quite poor by comparison. What activity the ligand-free system does have is extinguished by the addition of 3 equiv 2-propanol, while the activity of the tetraphenol-based catalysts is not curtailed as severely by chain-transfer agent. The MW of poly(propylene oxide) (PPO) produced in the presence of *i*-PrOH decreases more than one would expect from simply the loss in productivity (as seen in an increase in the ratio of polymer molecules to Al), suggesting the participation of the alcohol in chain-transfer events.

A comparison of the $^{13}C\{^1H\}$ NMR spectra for TiBA/NEt$_3$ and **7**/TiBA/NEt$_3$ is presented in Figures 6 and 7 (NMR analysis of PPO was guided by the assignments made by Chisholm and Navarro-Llobet[20]). For PPO made by TiBA/NEt$_3$, the methine carbon resonances in Figure 6 (74.5−76.5 ppm region) appear as four signals of equal intensity, which are assigned to the triads ***mm***, ***mr***+***rm***, and ***rr***. The methylene carbon resonances (72.5−74.5 ppm region) split into eight peaks of equal intensity, which are assigned to the tetrads ***mmm***, ***rmm***, ***mmr***, ***rmr*** for the left four peaks and ***mrm***, ***mrr***, ***rrm***, ***rrr*** for the right four peaks. The methyl carbon resonances show a simple doublet in Figure 7 (17−18 ppm region), which is assigned to dyads ***m*** and ***r***. Based on these assignments, the polymer produced by TiBA/NEt$_3$ is found to contain ***m*** and ***r*** dyads in a (51 ± 2)/(49 ± 2) ratio, while that produced by **7**/TiBA/NEt$_3$ has a ratio of ***m***/***r*** = (45 ± 3)/(55 ± 3).

In comparison with the TiBA/NEt$_3$ catalyst, the catalyst formed from ligand **7** with TiBA and NEt$_3$ makes PPO with a considerable amount of regioirregularities (only 62% head-to-tail linkages vs 94% for the ligand-free system), although the polymer in both cases is essentially atactic. The low level of regiospecificity for ring opening displayed by the **7**/TiBA/NEt$_3$ catalyst, comparable to that observed by Antelmann et al.[21] in PPO produced by hindered phenoxyaluminum compounds, may indicate a higher level of charge separation or Lewis acidity compared with the ligand-free system. It is also conceivable that the mechanism of polymerization is not as is shown in Scheme 2 but cationic in nature, involving the nucleophilic attack of monomer upon oxonium species, since cationic initiation is associated with nearly equal proportions of regular and inverted regiochemistry. The possibility of multiple polymerization mechanisms operating concurrently cannot be ruled out, either.

In summary, a series of aluminum phenoxides were screened using a parallel reactor system as catalysts for ring-opening polymerization of both EO and PO in the presence of Lewis bases. MALDI-TOF shows that triethylamine is likely to be the predominant initiator in this family of catalysts. Dibenzothiophene-

Scheme 4



	R_4	R_5
7	t-Bu	t-Bu
7a	t-Bu	Me
7b	Me	Me
7c	Me	t-Bu
7d	t-Bu	Et
7e	MeCy	Me
7f	1-adamantyl	Me
7g	$C(Me)_2CH_2CMe_3$	Me
7h	$C(Me)_2Ph$	$C(Me)_2Ph$

Table 5. Productivity of Tetraphenol/Triisobutylaluminum/Triethylamine Catalysts Based on Dibenzothiophene-bridged Ligands[a]

ligand	Al(*i*-Bu)$_3$, μmol	reaction time, h	prod., g/mmol	M_N/1000	M_W/M_N	polymer/Al[b]
7	5	2	76.2	71	2.13	1.1
7	2[c]	3	169.6	132	2.03	1.3
7a	2	2	65.1			
7a	2[c]	2	108.1	110	1.88	1.0
7a	2[c]	3	245.6	162	2.07	1.5
7b	10	2	4.1			
7c	5	2	12.5			
7d	5	2	108.7	83	2.52	1.3
7e	5	2	73.4	100	2.36	0.7
7e	2[c]	3	236.7	175	1.97	1.4
7f	5	2	117.7	137	2.16	0.9
7g	5	2	131.4	164	2.13	0.8
7h	5	2	142.4	70	1.50	2.0
7h	2[c]	2	197.9	187	2.05	1.1
7h	2[c]	3	346.6	227	2.27	1.5

[a] Data from representative cells; conditions: 1 mL EO; L:Al:N = 1:2:1; reaction temperature 40 °C. [b] Molar ratio, calculated by dividing the productivity by M_N/1000. [c] Catalyst prepared by mixing ligand and Al(i-Bu)$_3$ overnight at room temperature (normal procedure: incubation of ligand and Al(*i*-Bu)$_3$ for 1 h at 60 °C).

bridged tetraphenol ligands were found to be very active when combined with TiBA or DEAC. High activity was also obtained from a tetraphenol bridged by a 2-methoxy-1,3-phenylene group. The polymerization results, including those comparing one tetraphenol ligand with two bisphenol fragments of the same, are not inconsistent with a dinuclear mechanism enhanced in rate by immobilization of two metal centers in the same molecule. The structure of a dialuminum dietherate complex based on a tetraphenol ligand indicates that this mechanism is possible.

Experimental Section

General. Unless otherwise specified, all chemical reactions were performed under nitrogen. Ethylene oxide (EO, 99.99%) and propylene oxide (PO, 99.99%) were purchased from Airgas Great Lakes who obtained it from ARC Specialty Products, a division of Balchem Corporation and used as received. Anhydrous toluene (99.8%) and anhydrous hexanes (≥99%) were purchased from Aldrich and further purified by passage through columns under dry nitrogen containing activated A204 alumina (available from LaRoche Inc.) and Q5 catalyst (originally available from Engelhard Chemicals Inc., now BASF). Prior to use, the alumina was activated at 375 °C in a stream of dry nitrogen and the Q5 was activated at 200 °C in a stream of 5% hydrogen in nitrogen. All other materials obtained from commercial sources were used without further purification. 2,2′-Methylenebis(6-*t*-butyl-4-methylphenol) (**1**; 99%) and 2,2′-methylenebis(6-(1-methylcyclohexyl)-4-methylphenol) (**2**; 90%) were purchased from TCI America, while 2,2′-ethylidenebis(4,6-di-*t*-butylphenol) (**3**; 99%) was obtained from Sigma-Aldrich. 4,6- Dibenzothiophenedicarbaldehyde was prepared according to the method of Skar and Svendsen.[22] Syntheses of 2,2′,2″,2‴-(4,6-dibenzofurandiyldimethylidyne)tetrakis(4,6-di-*t*-butylphenol) (**4**), 2,2′,2″,2‴-[(9,9-dimethyl-9*H*-xanthene-4,5-diyl)dimethylidyne]tetrakis(4,6-di-*t*-butylphenol) (**5**), and 2,2′,2″,2‴-(anthracene-1,8-diyldimethylidyne)tetrakis[4,6-di-*t*-butyl-phenol] (**8**) were similar to literature[14b] procedures. Synthesis and characterization of compounds **7a**−**h** is documented in the Supporting Information. NMR spectra (nonpolymer) were collected using a Varian Inova 400 MHz NMR spectrometer. Elemental analyses were provided by Quantitative Technologies, Inc., Whitehouse, NJ. High-resolution LC-MS spectra were obtained in ESI mode on a Waters Alliance 2795 Ternary gradient LC system coupled to a LCT-Premier TOF-MS system and equipped with a Z-spray source. Even though formic acid was employed as ionizing aid, ammonium ions were often associated with the ligands in the MS due to the presence of a small impurity of ammonium acetate.

Melting Point. Melting points were determined in all cases by differential scanning calorimetry (DSC). The DSC samples, sealed in aluminum pans, were run on a TA Instruments DSC Q100 (compounds **8**, **11**, **12**, and **13**) or TA Instruments DSC 2920 (all others) equipped with liquid N_2 for cooling. The cell was purged with N_2. Temperature reliability was ±1 °C; heat of fusion accuracy was ±1%. Samples were ramped from 30 to 180 °C, back down to 30 °C, and heated again to 180 °C, all at 5 °C/min. Reported MPs were taken at the minima of the melting endotherms. In those cases where the sample did not decompose during the first heat, only the first heat MP was recorded herein.

Synthesis of 2,2′,2″,2‴-[Oxybis(2,1-phenylenemethylidyne)]tetrakis(4,6-di-*t*-butylphenol) (6). A mixture of 1.0 g (4.4 mmol) of bis(2-formylphenyl)ether, 18 g (88 mmol) of 2,4-di-*t*-butylphenol was heated for 1 h at 96 °C, after which 1.5 mL of 12 N HCl solution was added and the mixture was stirred for 12 h. Precipitate was obtained by adding 40 mL of acetonitrile and 10 mL of water and stirring the mixture at room temperature overnight. The product was collected, recrystallized from acetonitrile/water (4:1), washed with acetonitrile/water (4:1), followed by cold acetonitrile, and dried to yield 2.0 g white solid (45%). Elem. anal. Calcd. for $C_{70}H_{94}O_5$ (%): C, 82.79; H, 9.33. Found: C, 82.65; H, 9.35. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 4H, aryl-*H*), 7.03, (m, 2H, spacer aryl-*H*), 6.96 (br, 4H, spacer aryl-*H*), 6.76 (s, 4H, aryl-*H*), 6.17 (d, 2H, spacer aryl-*H*, J = 6.4 Hz), 6.10 (s, 2H, *CH*), 4.87 (s, 4H, *OH*), 1.31 (s, 36H, *t*-Bu), 1.16 (s, 36H, *t*-Bu). ^{13}C NMR ($CDCl_3$): 155.57, 150.34, 142.31, 136.56, 132.53, 129.67, 128.39, 126.99, 124.63, 123.71, 122.70, 119.04, 39.90, 34.86, 34.28, 31.51, 29.90. Mp = 104.5 °C (decomposed). Mass spec.: 1032.74 $(M + NH_4)^+$; theor. accurate mass: 1014.71.

Synthesis of 2,2′,2″,2‴-(4,6-Dibenzothiophenediyldimethylidyne)-tetrakis(4,6-di-*t*-butylphenol) (7). A mixture of 0.6 g (2.5 mmol) of 4,6-dibenzothiophenedicarbaldehyde and 10.3 g (50 mmol) of 2,4-di-*t*-butylphenol was heated at 96 °C under nitrogen. After stirring for 1 h, 0.8 mL of 12 N HCl solution was added, and the mixture was stirred for 18 h. The brown homogeneous solution was allowed to cool to room temperature. A total of 20 mL of acetonitrile and 5 mL of water was added, and the mixture was stirred at room temperature overnight. The product was collected, recrystallized from acetonitrile/water (4:1), washed with acetonitrile/water (4:1), followed by cold acetonitrile, and dried to yield 1.85 g white solid (72%). Elem. anal. Calcd. for $C_{70}H_{92}O_4S$ (%): C, 81.66; H, 9.01. Found: C, 81.64; H, 9.05. ^{1}H NMR ($CDCl_3$): δ 8.15 (d, 2H, dibenzothiophene-*H*, J = 7.2 Hz), 7.46 (t, 2H, dibenzothiophene-*H*, J = 7.6 Hz), 7.24 (s, 4H, aryl-*H*), 7.12 (d, 2H,

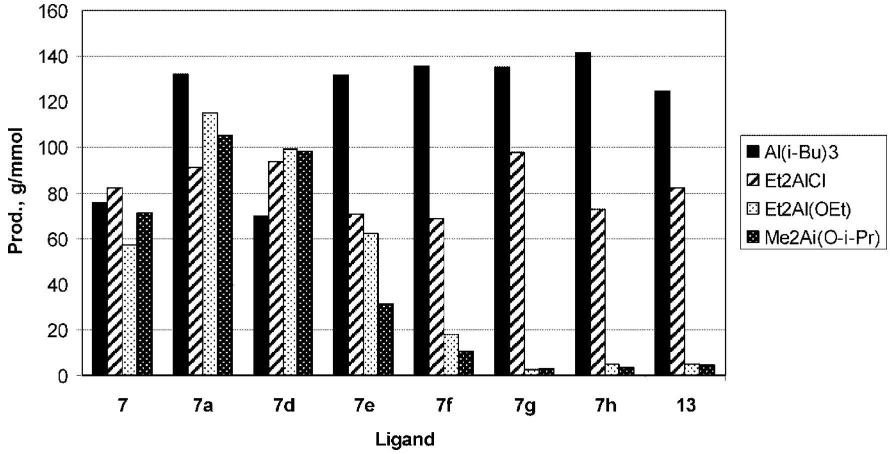


Figure 2. Productivities for PEO catalysts based on tetraphenols and alkylaluminum precursors (5 μmol Al, L:Al:NEt_3 = 1:2:1).

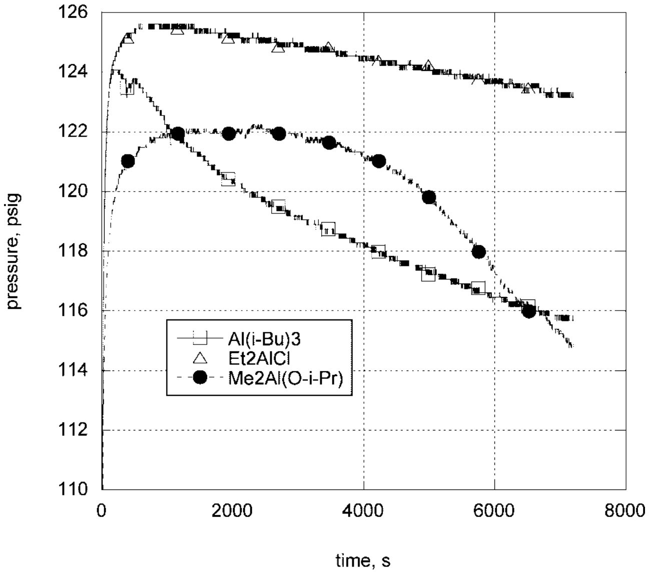


Figure 3. Evolution of reactor pressure over time for three EO polymerization runs (40 °C) based on ligand **7a**. In each case, the charges of aluminum reagent, ligand, and triethylamine were 5, 2.5, and 2.5 μmol, respectively.

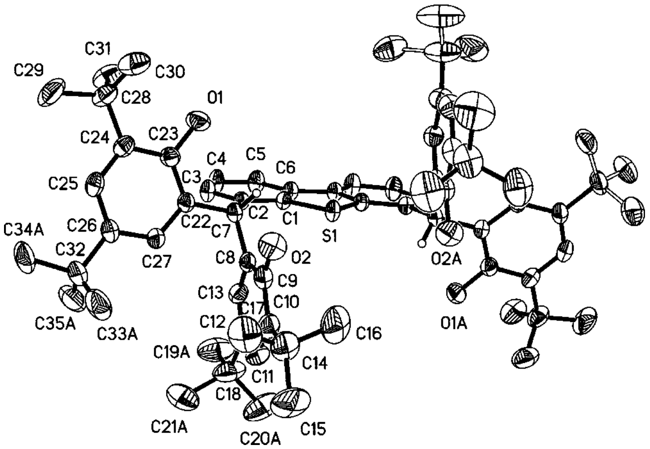


Figure 4. Crystal structure of ligand **7** with ellipsoids showing 50% probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

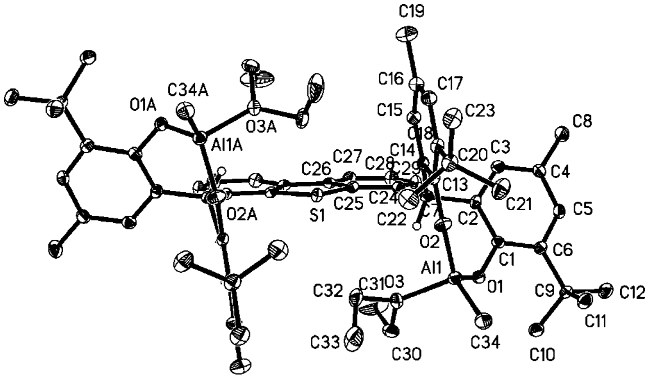


Figure 5. Crystal structure of compound **15** with ellipsoids showing 50% probability. Hydrogen atoms and molecules of dichloromethane have been omitted for clarity.

Table 6. X-ray Diffraction of Compounds 7 and 15: Structural Parameters

	7•4THF	$15 \cdot 2CH_2Cl_2$
empirical formula	C86 H120 Al0 O8 S	C70 H94 Al2 Cl4 O6 S
formula weight	1313.88	1259.27
temperature, K	200(2)	100(2)
wavelength, Å	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a (Å)	24.8232(12)	20.498(2)
b (Å)	15.9962(8)	18.837(2)
c (Å)	20.8462(10)	18.260(2)
β (deg)	97.642(1)	104.904(2)
volume ($Å^3$)	8204.0(7)	6813.5(14)
Z	4	4
θ_{max} (deg)	28.32	28.28
reflections collected	42971	8392
independent reflections	10196	8392
R (int)	0.0264	0.0000
goodness-of-fit on F^2	1.016	1.002
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0645$ $wR_2 = 0.1702$	$R_1 = 0.0591$ $wR_2 = 0.1156$
R indices (all data)	$R_1 = 0.0830$ $wR_2 = 0.1798$	$R_1 = 0.1236$ $wR_2 = 0.1390$
largest diff. peak, hole (e $Å^{-3}$)	0.495, −0.302	0.364, −0.344

dibenzothiophene-*H*, *J* = 7.6 Hz), 6.72 (s, 4H, aryl-*H*), 5.78 (s, 2H, *CH*), 4.67 (s, 4H, *OH*), 1.35 (s, 36H, *t*-Bu), 1.10 (s, 36H, *t*-Bu). ^{13}C NMR ($CDCl_3$): 151.0, 142.8, 140.1, 136.7, 135.5, 127.4, 125.9, 125.3, 124.4, 123.4, 121.1, 47.0, 35.0, 34.4, 31.6, 30.0. Mp = 142.3 °C (decomposed). Mass spec.: 1046.70 $(M + NH_4)^+$; theor. accurate mass: 1028.67. A sample suitable for single-crystal X-ray diffraction was obtained from a failed attempt to obtain crystals of the reaction product of **7** with $Et_2Al(OEt)$; the workup yielded a solid which was recrystallized from tetrahydrofuran and contained four molecules of this solvent per molecule of **7**.

Synthesis of α,α,α′,α′-Tetrakis(3,5-di-*t*-butyl-2-hydroxyphenyl)-*m*-xylene (9). A 100 mL round-bottomed flask was charged with 19.87 g 2,4-di-*t*-butylphenol (96.3 mmol) and 0.649 g isophthala-

Table 7. Key Interatomic Distances (Å) and Angles (deg) from the Crystal Structure of 15•2CH$_2$Cl$_2$

Al(1)−O(2)	1.7121(18)	O(2)−Al(1)−O(1)	116.24(9)
Al(1)−O(1)	1.7344(18)	O(2)−Al(1)−O(3)	104.10(9)
Al(1)−O(3)	1.8838(19)	O(1)−Al(1)−O(3)	98.52(9)
Al(1)−C(34)	1.942(3)	O(2)−Al(1)−C(34)	110.38(11)
Al(1)−Al(1A)	8.397(2)	O(1)−Al(1)−C(34)	117.27(11)
Al(1)−O(3A)	7.583(2)	O(3)−Al(1)−C(34)	108.42(11)
O(1)−C(1)	1.367(3)	C(1)−O(1)−Al(1)	127.63(16)
O(2)−C(13)	1.359(3)	C(13)−O(2)−Al(1)	150.08(17)
O(3)−C(32)	1.468(3)	C(32)−O(3)−C(30)	114.9(2)
O(3)−C(30)	1.476(3)	C(32)−O(3)−Al(1)	120.77(17)
S(1)−C(25)	1.773(2)	C(30)−O(3)−Al(1)	122.88(15)
C(1)−C(2)	1.404(3)	C(25)−S(1)−C(25)#1	91.94(16)
C(2)−C(7)	1.534(3)		
C(7)−C(24)	1.533(3)		
C(24)−C(25)	1.415(3)		

Table 8. Polymerization of PO by Selected Catalysts[a]

ligand	Al(*i*-Bu)$_3$, μmol	*i*-PrOH, μmol	prod., g (PPO)/mmol	M_N/1000	M_W/M_N	polymer/Al[b]
none	20.0	0	11.7	13.9	2.1	0.9
none	20.0	60	<0.2			
3	20.0	0	0.3			
7	5.0	0	121.9	74.2	2.8	1.7
7	10.0	0	79.8	34.9	2.2	2.3
7	10.0	30	34.8	9.4	3.2	3.8
7a	10.0	0	46.3	30.1	4.3	1.6
7a	10.0	30	9.4	3.9	5.6	2.6
13	10.0	0	31.7			
13	10.0	30	14.7			

[a] Conditions: NEt$_3$ as initiator; TiBA as precursor; L:Al:N = 1:2:1 (if ligand present). [b] Molar ratio, calculated by dividing the productivity by M_N/1000.

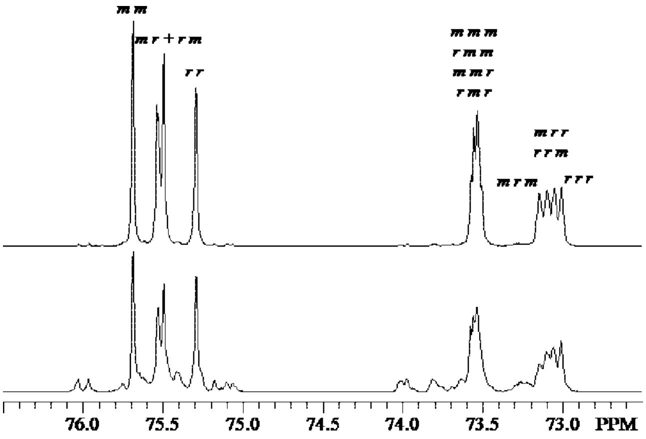


Figure 6. ^{13}C{^{1}H} NMR spectra for the methine and methylene carbons of PPO prepared by Al(*i*-Bu)$_3$/NEt$_3$ (upper trace) and **7**/Al(*i*-Bu)$_3$/NEt$_3$ (upper, lower trace).

ldehyde (4.84 mmol; OH/CHO = 10.0) and heated until the solids melted together. The mixture was stirred under nitrogen for 1 h, then 1.5 mL concentrated HCl was added. The slightly darkened mixture was stirred for 13 h at 95 °C, then allowed to cool to about 65 °C. To the solution were then added 40 mL acetonitrile and 10 mL water. Upon cooling to 33 °C with vigorous stirring, a solid precipitated which was then filtered, washed with acetonitrile, dried, and then recrystallized from ethanol. Yield: 2.623 g cream-colored powder (59%). Elem. anal. Calcd. for C$_{64}$H$_{90}$O$_4$ (%): C, 83.25; H, 9.82. Found: C, 83.04; H, 9.78. ^{1}H NMR (CDCl$_3$): δ 7.37 (t, J = 7.4 Hz, 1H, aryl-*H*), 7.24−7.27 (m, 4H, aryl-*H*), 7.12−7.15 (m, 3H, aryl-*H*), 6.64 (s, 4H, aryl-*H*), 5.57 (s, 2H, *CH*), 4.72 (s, 4H, *OH*), 1.36 (s, 36H, *t*-Bu), 1.15 (s, 36H, *t*-Bu). Mp = 125.4 °C (decomposed). Mass spec.: 940.71 (M + NH$_4$)$^+$; theor. accurate mass: 922.68.

Synthesis of α,α,α′,α′-Tetrakis(3,5-di-*t*-butyl-2-hydroxyphenyl)-*p*-xylene (10). A 100 mL round-bottomed flask was charged with 20.43 g 2,4-di-*t*-butylphenol (97%, 99.0 mmol) and 0.674 g terephthalaldehyde (5.03 mmol; OH/CHO = 9.8) and heated until the solids melted together. The mixture was stirred under nitrogen at 88 °C for 1 h, then 1.5 mL of concentrated HCl was added. The slightly darkened mixture was stirred for 13 h at 92−5 °C, then allowed to cool to about 65 °C. Brown crystals were observed in the mixture within the first hour after the addition of acid. To the slurry were then added 40 mL of acetonitrile and 10 mL of water. After cooling, the solid was filtered, washed with acetonitrile, dried, and then recrystallized from ethanol/toluene. Yield: 3.152 g ivory-colored powder (68%). Elem. anal. Calcd. for C$_{64}$H$_{90}$O$_4$ (%): C, 83.25; H, 9.82. Found: C, 82.54; H, 9.85. ^{1}H NMR (CDCl$_3$): δ 7.21−7.27 (m, 8H, aryl-*H*), 6.67 (s, 4H, aryl-*H*), 5.64 (s, 2H, *CH*), 4.74 (s, 4H, *OH*), 1.38 (s, 36H, *t*-Bu), 1.16 (s, 36H, *t*-Bu). Mp = 77.1 °C (decomposed). Mass spec.: 940.71 (M + NH$_4$)$^+$; theor. accurate mass: 922.68.

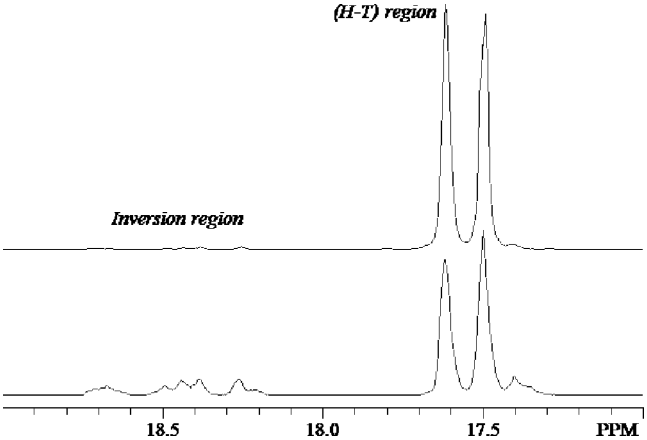


Figure 7. ^{13}C{^{1}H} NMR spectra for the methyl carbons of PPO prepared by Al(*i*-Bu)$_3$/NEt$_3$ (upper trace) and **7**/Al(*i*-Bu)$_3$/NEt$_3$ (upper, lower trace).

Synthesis of 2,2′,2′′,2′′′-(Thiophene-2,5-diyldimethylidyne)tetrakis[4,6-di-*t*-butyl-phenol] (11). The reaction was carried out in the glovebox under nitrogen. 2,4-Di-*t*-butylphenol (1.55 g, 7.5 mmol) was dissolved in 15 mL of anhydrous diethyl ether. The mixture was cooled to 0 °C. Methylmagnesium bromide (2.5 mL, 3 M in ether) was added slowly. The reaction mixture was warmed up to 25 °C and stirred for 1 h, after which the ether was evaporated under vacuum. The solid was redissolved in 15 mL of anhydrous toluene. Thiophene-2,5-dialdehyde (0.25 g, 1.8 mmol) in toluene/THF was added slowly. After the mixture was stirred at 25 °C overnight, HPLC analysis indicated the reaction was not complete. The mixture was stirred at 65−75 °C overnight. After cooling to room temperature, the mixture was diluted with toluene and treated with 1 N HCl. The organic layer was washed with NaCl/H$_2$O, and dried over MgSO$_4$. The solvent was evaporated off. The crude product was solidified by stirring in acetonitrile/ethanol/H$_2$O. After filtration, the solid was further purified by column chromatography (silica gel, hexanes/ethyl acetate 50:1 as eluent), and recrystallization from ethanol/H$_2$O. Finally, 0.37 g (22% yield) of **11** was obtained as white solid. Elem. anal. Calcd. for C$_{62}$H$_{88}$O$_4$S (%): C, 80.12; H, 9.54. Found: C, 78.76; H, 9.70. ^{1}H NMR (CDCl$_3$): δ 7.2 (4H), 6.8 (4H), 6.7 (2H), 5.8 (2H), 5.0 (4H), 1.4 (36H), 1.21 (36H). ^{13}C NMR: 150.1, 145.3, 142.9, 136.6, 127.9, 127.4, 123.7, 123.1, 42.3, 34.9, 34.3, 31.5, 29.9. Mp = 153.1 °C (decomposed). Mass spec.: 927.64 (M − H)$^+$; theor. accurate mass: 928.64.

Synthesis of 2,2′,2′′,2′′′-(pyridine-2,6-diyldimethylidyne)-tetrakis[4,6-di-*t*-butyl-phenol] (12). Pyridine-2,6-dicarbaldehyde (0.27 g, 2 mmol), and 2,4-di-*t*-butylphenol (10.32 g, 50 mmol) were charged into a 50 mL single-neck flask equipped with a mechanical stirrer. After purging with nitrogen, the mixture was heated to 96 °C for 1 h, followed by the addition of concentrated HCl (0.7 mL). The reaction mixture was stirred overnight at 96 °C, allowed to cool and was then stirred with ethanol/H$_2$O/acetonitrile. A solid precipitated from the mixture. After filtration, the crude product was recrystallized from acetonitrile/ethanol. A white solid (1.35 g, 73% yield) was obtained. Elem. anal. Calcd. for $C_{63}H_{89}NO_4$ (%): C, 81.86; H, 9.70; N, 1.52. Found: C, 77.79; H, 9.71; N, 1.39. ^{1}H NMR ($CDCl_3$): δ 8.1 (1H), 7.4 (2H), 7.2 (5H, overlapped with residual of $CHCl_3$ from solvent), 6.9 (2H), 6.7 (4H), 6.4 (4H), 1.4 (36H), 1.1 (36H). ^{13}C NMR: 160.6, 150.2, 143.7, 143.3, 139.6, 127.5, 124.2, 123.3, 123.1, 42.9, 35.0, 34.4, 31.5, 30.1. Mp = 124.5 °C (decomposed). Mass spec.: 922.67 $(M - H)^+$; theor. accurate mass: 923.68.

Synthesis of 2-Methoxy-1,3-benzenedicarboxaldehyde. 2-Hydroxy-1,3-benzenedicarboxaldehyde (1.05 g, 7 mmol), dimethyl sulfate (1.06 g, 8.4 mmol), and 55 mL of acetonitrile were charged into a single-necked flask equipped with a mechanical stirrer. Potassium carbonate (1.45 g, 10.5 mmol) was added at room temperature under nitrogen. The mixture was stirred at 75 °C until GC-MS indicated that the reaction was complete. The reaction mixture was cooled to ambient temperature, diluted with diethyl ether, washed with NaCl/H_2O, and dried over $MgSO_4$. After removal of volatiles, the crude product was recrystallized from diethyl ether. A pale yellow solid (0.62 g, 54% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 10.4 (2H), 8.1 (2H), 7.4 (1H), 4.1 (3H).

Synthesis of 2,2′,2″,2‴-(2-Methoxybenzene-1,3-diyldimethylidyne)tetrakis[4,6-di-*t*-butyl-phenol] (13). 2-Methoxy-1,3-benzenedicarboxaldehyde (0.29 g, 1.8 mmol) and 2,4-di-*t*-butylphenol (9.28 g, 45 mmol) were charged into a 50 mL single-neck flask equipped with a mechanical stirrer. After purging with nitrogen, the mixture was heated to 96 °C for 1 h, followed by the addition of concentrated HCl (0.65 mL). The reaction mixture was stirred overnight at 96 °C, allowed to cool and was then stirred with ethanol/H_2O. A solid precipitated from the mixture. After filtration, the crude product was recrystallized from acetonitrile. A white solid (0.94 g, 55% yield) was obtained. Elem. anal. Calcd. for $C_{65}H_{92}O_5$ (%): C, 81.88; H, 9.73. Found: C, 81.76; H, 9.54. ^{1}H NMR ($CDCl_3$): δ 7.2 (6H, overlapped with residual of $CHCl_3$ from solvent), 7.1 (1H), 7.0 (2H), 6.8 (4H), 5.9 (2H), 5.0 (4H), 3.4 (3H), 1.4 (36H), 1.2 (36H). ^{13}C NMR: 154.6, 150.6, 142.4, 136.7, 134.4, 130.6, 127.0, 125.5, 123.5, 123.0, 62.9, 39.8, 35.0, 34.3, 31.5, 29.8. Mp = 158.5 °C (decomposed). Mass spec.: 951.69 $(M - H)^+$; theor. accurate mass: 952.69.

Synthesis of 4-Dibenzothiophenecarbaldehyde. To a solution of dibenzothiophene (2.76 g, 15 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (2.5 mL, 16.7 mmol) in 75 mL of hexane was slowly added 10.7 mL (15 mmol) of *sec*-BuLi (1.4 M solution in cyclohexane) at −78 °C. Once the addition is completed, the yellow milky reaction mixture was heated at 60 °C for 30 min, followed by cooling to −78 °C again. Upon a slow addition of 3 mL of *N*,*N*-dimethylformamide, the mixture was warmed to room temperature and kept stirring overnight. The mixture was poured into 100 mL of 1 M HCl aqueous solution at 0 °C, and ethyl acetate was added. The two phases were separated, and the water phase was extracted by ethyl acetate twice. The combined organic phase was washed with water and brine, dried over $MgSO_4$. Yellow solid was obtained after filtration and evaporation of solvent. The crude product was purified by a silica gel column chromatography (acetone/hexane, 1:4) to yield 1.6 g of yellow solid (50%). ^{1}H and ^{13}C NMR were in accordance with a literature report.[23]

Synthesis of 2,2′-(4-Dibenzothiophenylmethylidyne)bis(4,6-di-*t*-butylphenol) (14). A mixture of 1.06 g (5 mmol) of 4-dibenzothiophenecarbaldehyde, 2.06 g (10 mmol) of 2,4-di-*t*-butylphenol, and 0.20 g of toluene sulfonic acid monohydrate in 30 mL of hexane was refluxed for 6 h. The solvent was removed under vacuum and the residue was dissolved into 80 mL of toluene. The resulting solution was neutralized by 20 mL of 0.1 N aqueous NaOH solution and washed with water (3 × 50 mL). Sticky yellow solid was recovered after removal of toluene. Recrystallization of the crude product from ethanol/water (4:1) twice gave 1.1 g of pale yellow solid (36%). Elem. anal. Calcd. for $C_{41}H_{50}O_2S$ (%): C, 81.14; H, 8.30. Found: C, 79.55; H, 8.59. ^{1}H NMR ($CDCl_3$): δ 8.15 (m, 2H, dibenzothiophene-*H*), 7.78 (d, 1H, dibenzothiophene-*H*, J = 6.8 Hz), 7.44 (m, 3H, dibenzothiophene-*H*), 7.28 (s, 2H, aryl-*H*), 7.12 (d, 1H, dibenzothiophene-*H*, J = 6.8 Hz), 6.74 (s, 2H, aryl-*H*), 5.90 (s, 1H, *CH*), 4.73 (s, 2H, *OH*), 1.39 (s, 18H, *t*-Bu), 1.20 (s, 18H, *t*-Bu). ^{13}C NMR ($CDCl_3$): 150.96, 142.92, 140.26, 139.73, 136.76, 136.47, 135.87, 135.43, 126.93, 126.15, 125.25, 124.56, 124.52, 123.36, 123.01, 121.85, 120.94, 46.86, 35.04, 34.43, 31.58, 30.07. Mp = 180.6 °C (decomposed). Mass spec.: 624.39 $(M + NH_4)^+$; theor. accurate mass: 606.35.

Synthesis of 15. To a solution of 0.171 g **7a** (0.199 mmol) in 10.88 g toluene, chilled to −25 °C, was added 50 μL diethyl ether (0.476 mmol, 2.4 equiv) and, slowly, 0.210 mL of a 2 mol/L solution of trimethylaluminum in hexanes (2.2 equiv). After stirring at ambient temperature overnight, the volatiles were removed in vacuo and hexane was added and stripped by vacuum distillation twice. Hexanes were added to the solid, and the slurry was filtered, washed, and dried under vacuum to yield 0.114 g off-white powder. After correction for residual hexane, the calculated yield is 48%. Complete characterization of this compound was hampered by its sensitivity to air and moisture. Elem. anal. Calcd. for $C_{68}H_{90}Al_2O_6S$ (%): C, 74.97; H, 8.33. Found: C, 71.52; H, 7.82. ^{1}H NMR (toluene-d_8): δ 7.90 (d, 2H, dibenzothiophene-*H*, J = 7.6 Hz), 7.79 (d, 2H, dibenzothiophene-*H*, J = 6.8 Hz), 6.7−7.4 (broad, Ar-*H*, ∼10H), 6.40 (s, 2H, Ar_3CH), 3.4−4.0 (broad, 8H, OCH_2), 1.9−2.3 (broad, ∼12H, CH_3), 1.2−1.8 (broad, ∼36H, *t*-Bu), 1.0 (br m, ∼12H, OCH_2CH_3), −0.17 (s, 6H, Al−CH_3). ^{13}C NMR (C_6D_6; toluene-d_8): 139.6, 138.4, 137.5, 130.4, 129.0, 127.8, 126.6, 125.6, 120.9, 70.1, 43.9, 35.5 (br), 32.4, 30.6 (br), 23.5, 21.6, 14.9, 14.7, −10.0.

MALDI-TOF Mass Spectrometry. The experiments were performed on a Bruker Biflex III time-of-flight mass spectrometer, operated in the reflectron mode. The matrix was acetone saturated with 2-(4-hydroxyphenylazo)benzoic acid (HABA). Samples were made up as approximately 2000 ppm solutions in acetone with 10% water. Sample and matrix solution were combined 1:1 and briefly vortex-mixed. Approximately 1 μL of this preparation was spotted directly onto a stainless steel target disk. Spectra were acquired over a mass range of 538−7000 Da by averaging 600−750 laser shots. Mass calibration was performed using oligomer peaks from polyethylene glycol (PEG) 600 in the same matrix. Mass resolving power was 2600−3600.

^{13}C NMR of Poly(propylene oxide). Polymer samples were examined in chloroform-*d* at a concentration of 0.10 g/mL and at 28 °C. NMR experiments were carried out with a Varian Unity spectrometer operating at a proton Larmor frequency of 400 MHz. Inverse-gated ^{13}C{^{1}H} NMR and distortionless enhancement by polarization transfer (DEPT) experiments were performed. In these experiments, a ^{13}C−^{1}H coupling constant (J_{CH}) of 130 Hz and a delay time (d_1) of 8 s were used. The deconvolution of ^{13}C NMR spectra was done using the NMR utility transform software (NUTS).

Polymerization Screening Procedure. A Symyx PPR[17] reactor system, modified to handle ethylene oxide (EO) and propylene oxide (PO), was used for all the polymerization runs. An ISCO syringe pump (Teledyne Isco Inc.) and a dedicated robotically controlled needle and compressible gas injector valve were used to deliver the EO or PO during each requested injection. The experimental designs for each 48-cell PPR library were arranged so that each cell was mirrored by a second cell with complementary address (A1 ↔ H6, B2 ↔ G5, etc.) such that each condition was run in duplicate. This ensured that each reaction condition would be run in two cells with run times approximately averaging the same value as for the other 23 conditions. All manipulations were carried out in a glovebox under an inert nitrogen atmosphere.

Glass inserts, which were previously weighed and dried in a vacuum oven at 125 °C, were manually loaded into the reaction modules and PEEK stir paddles, also weighed and dried in a vacuum oven at 125 °C, were inserted into the collets of the reactor heads. The module heads were sealed to the module bodies and a continuous purge-vent cycle run for 60 min prior to each run. The reactor was heated to 60 °C and each cell was charged with the amount of solvent (hexane or toluene) calculated to give a total reaction volume of 4.5 mL after all additions were complete. Under standard run conditions, each cell was then charged with a discrete amount of ligand solution followed by a discrete amount of metal precursor solution. After the ligand and precursor additions were complete, the cells were incubated at 60 °C for 1 h with stirring.

During the incubation period, the ISCO syringe pump was filled with the necessary amount of ethylene oxide or propylene oxide and the delivery system was primed. After the incubation period, the cells were allowed cool to 40 °C and then pressurized to ∼100 psi with nitrogen. In special cases (see Table 5) the cells were charged with mixtures of ligand and precursor that had been allowed to stir overnight at ambient temperature. Each cell was then charged with a discrete amount of Lewis base solution and/or a discrete amount of chain transfer agent solution. Each cell was then charged with 1.0 mL of EO or PO and the cell contents were stirred at 40 °C for 2 h. After the 2 h reaction time, the cells were alternately vented and purged with nitrogen for ∼20 min with stirring to remove any unreacted EO or PO prior to opening the reactors. The glass inserts with their associated stir paddles were removed from the reactor wells and dried in a Genevac centrifugal evaporator for 3 h under vacuum at 30 °C. Polyethylene oxide (PEO) yield weights were then obtained by difference. The yields were corrected by subtracting the weights of ligand and initiator, with the estimate for residues derived from the organometallic component based on the following (g/mol): 62.4 (Et_2AlCl, as AlCl), 44.0 ($Al(i\text{-}Bu)_3$, as AlOH), 72.0 (Et_2AlOEt, as AlOEt), 86.1 ($Me_2Al(O\text{-}i\text{-}Pr)$, as $Al(O\text{-}i\text{-}Pr)$).

Supporting Information Available: Synthesis and characterization of compounds **7a**−**h**. Atomic coordinates for the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The ratio of productivities for TiBA- and DEAC-based catalysts based on bulky ligands such as **7e** is probably even larger than is shown in Figure 2 because the runs were made at 5 μmol Al. At this catalyst concentration, the productivities of TiBA-based catalysts with very bulky ligands are underestimated, as can be seen in Table 5.

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