Ethylene Oxide Polymerization Catalyzed by Aluminum Complexes of Sulfur-Bridged Polyphenols

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ABSTRACT: The products derived from the reaction of sterically hindered sulfur-bridged bisphenols with aluminum trialkyls enable the efficient polymerization of ethylene oxide. The activity of the catalyst is largely determined by the structure of the bisphenol ligand and the size of the aluminum alkyl groups. Bonds of sulfur to aluminum are a common feature of the solid-state structures of compounds examined to this point. In solution, precatalysts of the formula  $(3-t-Bu-5-Me-2-OAlEt_2-C_6H_2)_2S$  are fluxional, and two processes appear to contribute to the equilibration of all ethyl substituents. The addition of a hindered monomer, 1,2-epoxyhexane, causes the initial formation of solvation complexes with the aluminum precatalysts and effects the disproportionation of the initial dialuminum complex of the bisphenol. One of the polymer end groups appears to be easily replaced by a halide atom during acid workup.

## Introduction

High-molecular-weight poly(ethylene oxide) (MW > $1 \times 10^5$  Da) is a water-soluble polymer which finds application in such areas as flocculation, rheological modification of aqueous solutions, drug release, and polymeric electrolytes.<sup>1</sup> A large proportion of the substances reported to catalyze the polymerization of EO to high MW are inorganic solids, whose mechanisms for polymerization can best be characterized as heterogeneous.<sup>2</sup> Given the large discrepancy observed in such polymerizations between the number of metal atoms contained in the catalyst charged to the reactor and the number-average MW of the polymer produced, one may conclude that only a small fraction of the metal centers present in the system are involved in the initiation and propagation of polymerization at any one time. These factors make the elucidation of the structure of the catalyst active site extremely difficult. To better understand the chemical steps involved in EO polymerization and therefore to improve the catalysis of this process through rational design, researchers have turned to the synthesis of well-defined catalyst precursors.

Trivalent aluminum complexes have a combination of properties that makes them predisposed to catalyze polymerization of energetic monomers such as ethylene oxide (EO). Bearing basic groups such as alkyl or alkoxide fragments, these species are quite reactive toward electrophilic carbon atoms, while the open coordination site forms strong associations with Lewis basic atoms. Aluminum compounds are also known to undergo ligand-exchange reactions. Therefore, it has been possible to construct mechanisms for oxirane ring opening which involve the activation of the epoxide ring by one aluminum atom while another aluminum atom contributes the alkoxide which attacks this ring. This reaction path, which may include the concomitant exchange of a charge-balancing ligand between the two aluminum centers, was postulated by Vandenberg as early as 1960 to be the route taken by aluminum-based epoxide-polymerization catalysts.<sup>3</sup>

Although many classes of compounds catalyze the ring-opening polymerization of oxiranes, aluminum aryloxide complexes have received recent attention as catalysts<sup>4</sup> and cocatalysts<sup>5</sup> for this reaction, as well as for the polymerization of styrene and methyl acrylate<sup>6</sup> and lactones.7 There are two clear reasons for this interest. First, the catalysts form homogeneous solutions, allowing detailed in-situ analysis of their structures. Second, the catalytic behavior reflects the structure of the precursor's ligand environment, enabling correlations to be made between ligand structure and polymer microstructure. It appears that bulky phenolate ligands confer a degree of resistance to alkyl- or alkoxide-bridged aluminum cluster formation and influence the tacticity and regiospecificity of epoxide polymerization.8

We wish to extend the general body of knowledge about this class of catalysts by including our recent studies of a specific family of aluminum phenoxide catalysts for EO polymerization. Our work with aluminum phenoxide catalysts has shown<sup>9</sup> that some of these systems, namely those bearing sulfur bridges between the phenolate groups, are highly active toward the production of high-MW poly(ethylene oxide) and copolymers of EO with other oxiranes. Ligand structure has a profound influence on catalyst behavior, leading us to investigate the role of the ligand in the steps leading to polymerization. The work presented herein deals with experiments designed to shed light on three important aspects of catalysis: (a) the structure of catalyst precursors in the solid state and in solution; (b) the changes

Table 1. Productivity of Catalysts in Ethylene Oxide Homopolymerizations Run at 25 °C in Hexane (See Experimental Section for Details of Run Procedure)

alkyl- aluminum	ligand	ligand:Al	productivity g(PEO)/ mmol(Al)	<i>M</i> <sub>w</sub> /1000	$M_{ m w}/M_{ m n}$
AlEt <sub>3</sub>	[none]		0.7		
	1	1:1	1.1		
	2a	1:2	0.4	213.0	4.6
	2b	1:2	0.3		
	3	1:2	0.8	97.3	6.0
	4a	1:2	3.4	49.0	5.6
$Al(i-Bu)_3$	4a	1:2	6.0	23.1	1.3
	<b>4b</b>	1:2	5.2	23.8	1.1
	<b>4c</b>	1:2	2.2	32.4	1.1
	5a	1:1	15	103.7	1.2
	5b	1.2:1	13	62.8	1.1
	5b	1:1	11	66.8	1.2
	<b>5c</b>	1:1	9.8	95.3	1.2
	5d	1:2	4.4		
	6	1:1	4.3		
	7	1:4	7.3	78.3	1.3
	8	1:2	1.0		
	9	1:1	3.1	29.0	1.2

in structure effected by the introduction of monomer; and (c) the initiation of polymerization. The sulfur atom of the ligand appears to play an important role in each of these three phases of catalyst formation.

#### **Results and Discussion**

**Ethylene oxide polymerizations.** In our initial screen for catalytic activity, a number of combinations of trialkylaluminum compounds with phenols were evaluated in their ability to produce poly(EO) at room temperature in hexane (Table 1). Under our conditions, triethylaluminum (TEAl) performed poorly.<sup>10</sup> By contrast, mixtures of certain phenols with trialkylaluminum compounds, especially with triisobutylaluminum (TiBA), gave fairly high productivity. In particular, those ligands belonging to structure families **4**, **5**, and

7 (see Scheme 1) enabled polymerization to proceed with productivity ranging from 2.2 (4c) to 15 (5a) g/mmol(Al) with TiBA. Among these ligands is a thiacalixarene (7), which indicates that oligomeric analogues of sulfidebridged bisphenols may also display high activity when combined with aluminum alkyls. The ligands associated with high productivity share a structural motif: an o-sulfide bridge between two phenol rings, with sterically demanding *t*-butyl groups flanking the hydroxyl groups at the remaining ortho positions. This commonality suggests that a divalent sulfur atom may have an important role in determining the structure and reactivity of the catalyst precursor and the active site. The dependence of activity upon the oxidation state of sulfur is not easy to predict on the basis of known chemistry. Ohba and co-workers, studying the Lewisacid-catalyzed rearrangement of aromatic epoxides to ketones by aluminum complexes, found that sulfoxide-, sulfone-,<sup>11</sup> and trisulfido-bridged<sup>12</sup> biphenol ligands all support high activity for this reaction.

Focusing on structural details within groups 4 and **5**, we see that alkylation of one of the hydroxyl groups dramatically increases productivity. Within ligand family 5, the smallest capping group ( $R_1 = Me, 5a$ ) imparts the highest productivity. It is worth remarking that, whereas the conversion of one of the OH groups to an alkyl or silyl ether increases activity, elimination of one of the oxygenated groups lowers activity: note that the productivity of TiBA/9 is only half that of TiBA/4a. Also interesting is the preservation of moderate activity in the TiBA complex of ligand 6 (which has no OH groups) compared with that for TiBA alone.<sup>10</sup> The surprising persistence of catalytic activity upon mono- and dialkylation of a supporting bisphenolate ligand was also observed in the area of Meerwein-Ponndorf-Verley transfer hydrogenation by Nguyen and co-workers.<sup>13</sup> No significant change in productivity is observed upon

compound	10	11	12
empirical formula	$C_{30}H_{48}Al_2O_2S$	$C_{25}H_{37}AlO_2S$	C <sub>28</sub> H <sub>43</sub> AlO <sub>3</sub> S
formula weight	526.70	428.59	486.66
temperature (K)	223(2)	173(2)	223(2)
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_{1}/c$	$P2_1/n$	Pbca
a (Å)	16.925(2)	9.9515(10)	17.632(3)
b (Å)	9.924(2)	9.0271(9)	16.211(2)
c (Å)	19.268(3)	27.670(3)	20.041(3)
$\alpha$ (deg)	90	90	90
$\beta$ (deg)	92.85(1)	94.909(2)	90
$\gamma$ (deg)	90	90	90
volume (Å <sup>3</sup> )	3232.3(9)	2476.5(4)	5728.3(14)
Z	4	4	8
density (calcd, g/cm <sup>3</sup> )	1.082	1.149	1.129
absorption coeff $(cm^{-1})$	1.77	1.84	1.69
F(000)	1144	928	2112
crystal size (mm)	0.22 imes 0.36 imes 0.38	0.28 imes 0.11 imes 0.06	0.25 imes 0.30 imes 0.42
$\Theta$ range (deg)	2.12 - 22.50	3.72 - 25.01	1.99 - 27.49
index ranges	$0 \le h \le 18$	$-6 \le h \le 11$	$-22 \le h \le 22$
	$-1 \le k \le 10$	$-10 \le k \le 10$	$-20 \le k \le 20$
	$-20 \le l \le 20$	$-32 \le l \le 32$	$-25 \le l \le 23$
reflections collected	4335	10655	38768
independent reflections	4172	4211	6550
R(int)	0.0595	0.0545	0.0678
GOF on $F^2$	0.976	1.032	1.036
final R indices $[I > 2\sigma(I)]$			
$R_1{}^b$	0.0749	0.0537	0.0566
$wR_{2}^{c}$	0.1074	0.1182	0.1414

Table 2. X-ray<sup>a</sup> Crystallographic Parameters for Compounds 10, 11, and 12

<sup>*a*</sup> Obtained with monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Refinement method: full-matrix least-squares on  $F^2$ . <sup>*b*</sup>  $R1 = \sum (||F_o| - |F_c||)/\sum |F_o|$ . <sup>*c*</sup>  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2]]$ . <sup>*l*</sup>



 Table 3. Selected Bond Distances (Å) and Angles (deg)
 for Compound 10

		-		
Bond Distances				
S-Al(1)	2.453(3)	Al(1)-C(25)	1.936(7)	
S-C(13)	1.770(8)	Al(2)-O(2)	1.765(5)	
S-C(2)	1.799(6)	Al(2)-C(29)	1.975(10)	
Al(1)-C(23)	1.954(8)	O(1) - C(1)	1.404(7)	
Al(2) - O(1)	1.946(5)	O(2)-C(12)	1.354(8)	
Al(2)-C(27)	1.948(9)	C(1) - C(2)	1.378(8)	
Al(1)-O(1)	1.855(4)	C(12)-C(13)	1.383(9)	
Bond Angles				
C(13) - S - C(2)	107.6(3)	C(12)-C(13)-S	121.1(7)	
C(2)-S-Al(1)	87.8(3)	C(13) - S - Al(1)	114.5(3)	
O(1)-Al(1)-C(23)	109.2(3)	O(1) - Al(1) - C(25)	118.6(3)	
O(1) - Al(1) - S	84.6(2)	C(25)-Al(1)-C(23)	118.6(3)	
C(23)-Al(1)-S	98.0(3)	C(25) - Al(1) - S	121.6(2)	
O(2)-Al(2)-C(27)	115.6(6)	O(1) - Al(2) - O(2)	96.3(2)	
O(2) - Al(2) - C(29)	105.7(5)	O(1) - Al(2) - C(27)	111.1(5)	
O(1) - Al(2) - C(29)	103.8(4)	C(27)-Al(2)-C(29)	121.0(6)	
C(1) - O(1) - Al(1)	111.1(4)	C(1) - O(1) - Al(2)	113.4(4)	
Al(1) - O(1) - Al(2)	112.5(2)	C(12) - O(2) - Al(2)	134.8(5)	
C(2) - C(1) - O(1)	117.5(6)	C(1)-C(2)-S	118.6(6)	

replacing the methyl groups para to the oxygen atoms in **4a** with *t*-butyl groups (compare productivities of **4a**/ TiBA with **4b**/TiBA).

In addition to high productivity, catalyst combinations of TiBA and polyphenolic ligands show fairly narrow molecular-weight distributions  $(1.1 \le M_w/M_n \le 1.25)$ . This implies that catalyst initiation is relatively fast relative to propagation and also that chain termination and transfer pathways are much slower than propagation, but it cannot tell us about the homogeneity of catalyst structure. From a comparison between number-average MW ( $M_n$ ) and catalyst productivity, one can estimate the number of polymer chains produced per metal atom. Given that this number—ca. 0.2–0.4 for mixtures of TiBA and ligand groups 4 and 5—is substantially less than one, it is possible that initiation of polymerization may involve multiple metal centers.

 Table 4. Selected Bond Distances (Å) and Angles (deg)

 for Compound 11

Bond Distances				
S-C(1)	1.780(3)	O(1) - C(2)	1.339(3)	
S-C(7)	1.798(2)	O(2) - C(8)	1.393(3)	
S-Al	2.4926(11)	O(2) - C(20)	1.446(3)	
Al-O(1)	1.768(2)	C(1) - C(6)	1.392(4)	
Al-C(13)	1.940(3)	C(1) - C(2)	1.399(4)	
Al-C(14)	1.948(3)			
Bond Angles				
C(1) - S - C(7)	105.50(12)	C(13)-Al-S	123.08(10)	
C(1)-S-Al	91.35(9)	C(14)-Al-S	96.56(11)	
C(7)-S-Al	105.49(9)	C(2)-O(1)-Al	125.45(18)	
O(1) - Al - C(13)	109.16(12)	C(8) - O(2) - C(20)	113.9(2)	
O(1) - Al - C(14)	115.93(13)	C(2)-C(1)-S	116.7(2)	
C(13) - Al - C(14)	121.91(14)	O(1) - C(2) - C(1)	120.5(2)	
O(1)-Al-S	84.39(7)			

**X-Ray Structural Analysis.** To better understand the relationship between ligand constituents and catalyst behavior, combinations of aluminum alkyl compounds with representatives of the two most productive ligand families were subjected to crystallographic analysis. The reaction of two equiv of TEAl with the bisphenol **4a** produces **10**, whose crystal structure is shown in Figure 1. Both aluminum atoms are each covalently bound to two alkyl groups and one phenoxide. Clearly, a reaction of the type

$$ArOH + AlR_3 \rightarrow ArOAlR_2 + R - H$$

has occurred at both sides of **4a**. The coordination environments of the two tetrahedral Al centers are different. Although both Al atoms have two ethyl substituents, Al(1) is bound to one phenoxide oxygen, O(1), and the bridging sulfur, S, whereas Al(2) is bonded to both phenoxide oxygens, O(1) and O(2). Similar oxygen sharing is observed in the structures of 2,2'methylenebis(6-*t*-butyl-4-methylphenoxy)aluminum me-



**Figure 1.** X-ray crystal structure of **10**. The thermal ellipsoids were scaled to enclose 30% probability. Carbons C(27), C(28) and C(29), C(30) suffer from a two-site (80:20) disorder; only the major conformer is depicted.

 Table 5. Selected Bond Distances (Å) and Angles (deg)
 for Compound 12

	Bond Dis	stances		
S(1) - C(17)	1.775(2)	O(1) - C(1)	1.348(3)	
S(1) - C(6)	1.776(2)	O(2) - C(12)	1.345(3)	
S(1)-Al(1)	2.6603(10)	C(1)-C(6)	1.403(3)	
Al(1) - O(2)	1.7584(17)	C(12) - C(17)	1.396(3)	
Al(1) - O(1)	1.7594(18)	C(23)-C(24)	1.472(6)	
Al(1)-C(23)	1.961(3)	O(3)-C(25)	1.461(3)	
Al(1)-O(3)	1.969(2)	O(3)-C(27)	1.466(6)	
Bond Angles				
C(17) - S(1) - C(6)	104.03(11)	O(1) - Al(1) - S(1)	81.04(6)	
C(17) - S(1) - Al(1)	88.58(8)	C(23) - Al(1) - S(1)	92.65(12)	
C(6)-S(1)-Al(1)	89.95(8)	O(3) - Al(1) - S(1)	168.45(7)	
O(2) - Al(1) - O(1)	115.03(9)	C(1) - O(1) - Al(1)	130.12(15)	
O(2)-Al(1)-C(23)	123.25(14)	C(12) - O(2) - Al(1)	127.68(15)	
O(1)-Al(1)-C(23)	119.31(14)	O(1) - C(1) - C(6)	120.4(2)	
O(2)-Al(1)-O(3)	93.00(8)	C(1)-C(6)-S(1)	118.22(18)	
O(1) - Al(1) - O(3)	93.34(8)	O(2) - C(12) - C(17)	120.5(2)	
C(23)-Al(1)-O(3)	98.90(14)	C(12)-C(17)-S(1)	117.71(18)	
O(2) - Al(1) - S(1)	80.43(6)	C(25)-O(3)-C(27)	114.9(3)	
O(2) $AI(1)$ $O(1)$	00.40(0)	O(20) O(3) O(21)	114.3(3)	

thide.<sup>14</sup> No other Al–Al bridging interactions, whether intra- or intermolecular, are observed. Some disorder is present which affects the methyl carbons of the ethyl groups, but this has no meaningful impact on the structure.

Compound 11, prepared from the reaction of equimolar quantities of trimethylaluminum<sup>15</sup> and ligand **5a**, presents a simpler geometry (Figure 2). In this case, the aluminum atom's tetrahedral ligand environment consists of one phenoxide oxygen, two methyl groups, and the bridging sulfur atom. Again, no intermolecular bridging interactions are noted. The monomeric nature of **11** shows this sulfur bridge to be a ligand of sufficient binding energy to compete effectively with solvation by an aluminum-bound methyl group from another molecule of **11**. A similar effect was observed by Dagorne et al.<sup>4g</sup> in complexes of aluminum with monophenolate ligands to which are appended *o*-dialkylaminomethyl groups, these compounds being monomeric in the solid state.

The fact that the structure of 11 is as simple as it is raises two interesting questions. First, although one might be tempted to attribute the high activity of complexes of the type 10 to the fact that two aluminum centers lie in close proximity to each other,<sup>16</sup> this



Figure 2. X-ray crystal structure of 11.



Figure 3. The proton NMR spectrum of 10 as a function of temperature.

situation does not exist for the even more active catalysts related to monomeric 11. During EO polymerization, do both aluminum atoms on structures akin to **10** participate in the creation of a single PEO chain? Second, the methoxy group in 11 does not participate in either inter- or intramolecular bonding to aluminum. The literature contains examples of methyl ethers binding to aluminum, as in the complex LAIMe ( $LH_2 =$ 25,27-dimethoxy-26,28-dihydroxy-p-t-butylcalix[4]arene), wherein both aryl methyl ether groups coordinate to the aluminum atom.<sup>17</sup> However, in another case, a phenoxyaluminum complex active for the polymerization of  $\epsilon$ -caprolactone, bearing a 4-methoxyphenyl group attached to the biphenol bridge, shows no bonding interaction between ether function and aluminum.<sup>18</sup> If the methoxy group of 5a does not bind to the active center of the catalyst, why then is the productivity of 5a/TiBA so much higher than that of 9/TiBA, a complex lacking this methoxy group?

**Proton NMR Analysis of Catalyst Solutions.** The variable-temperature <sup>1</sup>H NMR spectra of **10** in toluene $d_8$ , shown in Figure 3, reveal the existence of rapid interconversion of structures. As the temperature is lowered from 50 to  $-80^{\circ}$  C, the ethylaluminum portion of the spectrum appears to pass through three regimes. From about 50 down to 10° C, the metal alkyl resonances take the form of two very broad resonances at 0.4 and 1.2 ppm, respectively. From 10 to  $-50^{\circ}$  C, these signals decoalesce and form a well-defined pattern with <sup>1</sup>H<sup>-1</sup>H coupling. Below  $-50^{\circ}$  C, some of the peaks



broaden or disappear, although the triplets at both 1.8 and 0.65 ppm remain fairly well-resolved. At  $-40^{\circ}$  C, where the peaks are best resolved, two-dimensional analysis (COSY) reveals that there are three coupled sets of resonances associated with the methyl and methylene groups of the two diethylaluminum moieties which exist in a 1:2:1 ratio (Figure 4).One explanation



**Figure 4.** The aluminum alkyl region of the proton NMR spectrum of **10**, observed at -40 °C, showing the three sets of methyl and methylene resonances associated with ethylaluminum groups as revealed by two-dimensional NMR spectroscopy (COSY). The protons in these sets are in a 1:2:1 intensity ratio (A:B:C).

for this behavior is that there are two processes which interconvert the environments of the aluminum alkyl groups with activation barriers of different magnitude. Using the crystal structure of 10 as the basis for the discussion of exchange pathways, three possible routes for the equilibration of all ethyl signals can be proposed (Scheme 2). In the first process (A), rupture of the Al-S donor interaction permits the rotation of the diethylalumino group about the Al-O bond axis. A similar process, **B**, interconverts the other two ethylaluminum groups through the cleavage of the Al-O donor interaction. Both paths work with both enantiomers of the initial complex. However, neither A, B, nor the combination of both suffices to equilibrate all the ethyl groups. A third process, C, in which the two donor atomaluminum interactions are exchanged, is required. Since

two Al–Et groups exchange rapidly at  $-40^{\circ}$  C, it is reasonable to postulate that either A or B (but not both) is fast relative to the NMR time scale at that temperature, whereas process C begins to affect the spectrum only around 10 °C. The existence of other exchange mechanisms, such as inter- or intramolecular Al–C bond metathesis, cannot be ruled out, but no other scheme seems able to offer as simple an explanation for the observations.

In addressing the question of structural change upon addition of monomer to the catalyst solution, we were obliged to work with more sterically demanding monomers, as the addition of even propylene oxide caused changes in the spectrum which were too rapid to be followed by NMR. 1,2-Epoxyhexane (EH) was chosen because, in this case, an initial monomer-catalyst complex could be studied at room temperature, and the disappearance of monomer was not complete for several hours. The <sup>1</sup>H NMR spectra of mixtures of EH and **10** measured prior to the onset of oligomerization are remarkably dependent upon the EH:Al ratio (Figure 5).



**Figure 5.** Proton NMR spectra of **10** with varying levels of EH: (a) EH/Al = 0.27; (b) EH/Al = 0.5; (c) EH/Al = 1.1; (d) EH/Al = 1.6; and (e) EH/Al = 5. Dotted lines indicate the shifts in peak positions for the three protons on carbons 1 and 2 of EH.

As EH:Al is raised from 0.27:1 to 5:1, the three resonances associated with the three oxirane C-H bonds of EH first move downfield, then upfield. Although they



Figure 6. Comparison of proton NMR spectra for (a)  $\rm EH$  + 10 (EH/Al = 2.2); (b)  $\rm EH$  + triethylaluminum; and (c)  $\rm EH$  alone.

remain broad at EH/Al = 5, these three signals are fairly close to their positions in spectra of EH alone. At lower ratios, the average magnetic environments of the three oxirane protons are significantly altered, this effect being most pronounced at EH/Al  $\approx$  1. The aluminum alkyl portion of the spectrum is also quite dependent upon the relative amount of EH. To varying degrees, the broad signals that characterized solutions of 10 alone at ambient temperature (Figure 3) have collapsed into well-resolved methyl and methylene patterns. It appears that reversible coordination of oxirane to aluminum accounts for both the broadened EH patterns and the suppression of the exchange processes which interconvert the aluminum alkyl groups in complex 10.

The ethylaluminum peaks in the proton NMR spectrum of 10 + 2.2 equiv of EH (Figure 5c) show two methylene quartets at 0.45 and 0.10 ppm in a 1:2.7 intensity ratio. This reflects the existence of two distinct aluminum centers, one with three ethyl groups and one with a single alkyl group. By comparing this spectrum with that for the complex formed between triethylaluminum and one equivalent of EH (Figure 6c), one can reasonably attribute the methylene signals centered at 0.1 ppm and the associated methyl triplet at 1.36 ppm to Et<sub>3</sub>Al·EH. The remaining ethylaluminum peaks can then be assigned to the EH-solvate of the disproportionation product 2,2'-thiobis(6-t-butyl-4-methylphenoxy)-(ethyl)aluminum. Further support for this hypothesis can be found in the spectrum of the diethyl ether solvate of the disproportionation adduct 12 which shows a quartet at 0.4 ppm. The crystal structure of **12** (Figure 7) features a pentacoordinate aluminum atom having donor-acceptor interactions with both the sulfur bridge and the diethyl ether molecule. Okuda has also found that 4a can act as a tridentate OSO ligand, adopting a facial geometry when bound to Ti(IV).<sup>19</sup>

At EH:Al ratios less than 1:1 (Figure 5a and b) the combination of **10** with EH yields a more complicated spectrum with one very distinct feature: a complex multiplet centered at -0.76 ppm. The appearance of this multiplet, expanded in Figure 8, in the region associated with the methylene group attached to aluminum, indicates a diastereotopic environment for the methylene protons. On the basis of spectroscopy of a similar compound reported by Taden et al.,<sup>7c</sup> one can represent this complex as in Scheme 3, in which dimerization of the monoethyl complex through one oxygen of each diphenoxyaluminum molecule leads to a loss of symmetry.



**Figure 7.** X-ray crystal structure of **12**. Atoms C(27) and C(28) suffer from a 70:30 two-site disorder; only the major conformer is depicted.



**Figure 8.** Expansion of complex multiplet centered at -0.76 ppm observed in the proton NMR spectrum of **10** in the presence of 1.0 equiv EH (upper) along with simulation (lower), generated using parameters described in the text and a line width of 0.75 Hz. Asterisks denote peaks excluded from simulation.



This pattern is adequately simulated<sup>20</sup> by a model that has the absolute value of the  ${}^{1}\text{H}{-}{}^{1}\text{H}$  coupling constant between the geminal methylene protons equal to 14.8 Hz, all the coupling constants between methyl and methylene protons equal to 8.2 Hz, and the two chemical shifts for the methylene protons equal to -0.738 and -0.778 ppm.

The initial reactions which occur when EH is added to **10** can now be described (see Scheme 4). At substoichiometric levels, the EH causes the disproportionation of **10** into an epoxide solvate of the trialkylaluminum and an alkylaluminum bis(phenoxide), the latter possibly existing as a dimer. As the level of EH rises to molar equivalence to Al, the bisphenoxyaluminum



compound(s) are solvated by epoxide to form a welldefined structure similar to that of **12**. Interestingly, although AlEt<sub>3</sub>·EH is preferentially formed over the EH solvate of the bisphenoxyaluminum species, the oxirane protons of EH are more perturbed by coordination to the latter than to the trialkylaluminum, as judged by the relative deviations from the spectrum of free EH (Figure 6). This may indicate that the oxirane ring is more predisposed to opening in when bound to the monoaluminum bisphenoxide. At high levels of EH, epoxide coordinated to both aluminum compounds exchanges with free epoxide.

If we turn to the coordination chemistry of the aluminum complex of the monoalkylated bisphenol, we see more subtle changes than are observed with 10. In this case, we are dealing with complex 13, the reaction product of ligand 5a with one equivalent of triethylaluminum. The proton spectra of 13 and 13 + 1 equiv of EH (Figure 9) are fairly similar, in that no new



of EH.

ethylaluminum resonances appear and the original peaks are only slightly shifted upon EH addition. That EH is coordinated to aluminum is clear by the position of the oxirane proton resonances, which are shifted by up to 0.5 ppm downfield from their positions in the spectrum of free EH (Figure 6c).<sup>21</sup> Perhaps most surprising is that the singlet for the protons of the methoxy substituent moves 0.2 ppm downfield from its original position at 3.7 ppm when EH is added, returning to approximately the same position found in the spectrum of the unreacted ligand (4.0 ppm). Although not conclusive, this evidence suggests that, in solution, the methyl aryl ether group of ligand **5a** interacts in some fashion with the aluminum atom and that this interaction (whether intra- or intermolecular) is disrupted by the addition of a donor molecule. The participation of the methoxy group in the coordination environment of 13, though not apparent in the crystal structure of related complex **11**, may help explain the unusually high epoxide polymerization activity of adducts of ligands in its family (5) with trialkylaluminum compounds. Perhaps this weak donor interaction between the methoxy group and an aluminum center acts as a placeholder for incoming monomer, preventing the formation of stronger bridging interactions between aluminum centers which would slow polymerization.

Polymer End-Group Analysis. To fully understand how catalyst structure affects polymerization behavior, one must know the mechanism of initiation. Unfortunately, EH, though it is useful for the study of coordination to aluminum compounds, initiates very slowly compared with propagation, leading to very high-MW poly(EH) ( $M_w > 1 \times 10^5$ ) even at very low EH:Al. Thus, no useful information regarding the initial ring-opening step can be gleaned from the system. End-group analysis of samples of low-MW poly(ethylene oxide) produced by adducts of ligands 4a and 5a with TiBA, however, may help us identify the initiating group. For the 4a/ 2TiBA catalyst, the end-group analysis has not been fruitful: samples quenched with HCl show a number of possible end groups by <sup>13</sup>C NMR analysis, along with free ligand; the MALDI-TOF results of the polymer are also unsatisfactory, with several trains of peaks separated by the mass of EO.

In contrast, the corresponding analysis of the polymer produced by **5a**/TiBA is more straightforward. In the <sup>13</sup>C NMR spectrum (Figure 10) of the sample quenched by HCl, both free ligand **5a** and chloride-terminated polymer are observed. The analogous NMR spectrum for the HBr-quenched material is nearly identical, except the peak associated with the carbon of the CH<sub>2</sub>-Cl group at 42.6 ppm is missing and a new peak appears



**Figure 10.** <sup>13</sup>C NMR spectrum of poly(ethylene oxide) produced by the catalyst **5a**/TiBA quenched by HCl/MeOH, with assignments; peaks for neutralized ligand **5a** are marked L.

at 33.3 ppm attributable to the  $CH_2Br$  group. Integration of the haloethyl chain end peaks finds them to be roughly equal in intensity to the corresponding  $CH_2$ -OH ends. A reasonable conclusion from the data is that the hydroxyl-bearing chain ends result from the reaction of acid with the growing chain end of structure  $-CH_2O$ -[Al], while the haloethyl end group results from the displacement of the original initiating group from the polymer.

By GPC, the two polymer samples have low molecular weights and narrow molecular-weight distributions:  $M_{\rm n}$ = 11 000 (HCl-quenched);  $M_n = 13$  000 (HBr-quenched);  $M_w/M_n = 1.07$  in both cases. This indicates that the reaction of HCl or HBr with the polymer does not involve the cleavage of C-O bonds randomly along the polymer chain, as this would cause the value of  $M_{\rm w}/M_{\rm n}$ to approach the value of 2.0 as the proportion of chain termini derived from chain scission increases.<sup>22</sup> Molecular-weight analysis also finds the number of polymer molecules in these two samples to be approximately half the number of molecules of 5a/TiBA complex introduced to the reactor. Again, the narrowness of the polymer molecular-weight distributions argues against the idea that those aluminum atoms in excess of the number of polymer molecules failed to initiate polymerization due to a prolonged induction period. It is more likely that the structure responsible for polymer propagation involves one growing polymer chain, two phenoxide ligands, and two aluminum atoms.

MALDI-TOF spectrometry (Figure 11) confirms the existence of halide-terminated poly(ethylene oxide), which not only contributes sequences of mass peaks (separated by 44 daltons) as predicted for such structures but also yields characteristic isotopic distributions at the parent ion for each oligomer, corresponding to the calculated isotopic distributions (Figure 12). However, in addition to these sequences, a major series of mass peaks is observed which is identical for both HCland HBr-quenched polymer samples; this mass sequence and its isotopic distributions correspond exactly to those predicted for a poly(ethylene oxide) structure with one end group composed of ligand **5a** (Figure 13). This structure appears to be somewhat unstable; a second sample of HCl-quenched polymer prepared in the same way yielded only the chloroethyl-terminated polymer mass sequence in the MALDI-TOF spectrum and



**Figure 11.** MALDI-TOF spectrum of poly(ethylene oxide) produced by the catalyst **5a**/TiBA, quenched with HCl/MeOH. Mass series **a**: ligand-terminated poly(ethylene oxide); mass series **b**: chloride-terminated poly(ethylene oxide).



**Figure 12.** A portion of the MALDI-TOF spectrum of HClquenched poly(ethylene oxide) prepared from **5a**/TiBA, showing experimental signal and, below it, the calculated isotopic distribution for the ligand-terminated polymer with formula  $C_{97}H_{180}O_{39}SNa$ .



**Figure 13.** A portion of the MALDI-TOF spectrum of HClquenched poly(ethylene oxide) prepared from **5a**/TiBA, showing experimental signal and, below it, the calculated isotopic distribution for the chloride-terminated polymer with formula  $C_{116}H_{233}O_{58}ClNa$ .

an NMR spectrum similar to that shown in Figure 10. This instability could explain why ligand-terminated polymer is not observed as a major component in the  $^{13}$ C NMR spectra.

Given our current state of knowledge, we cannot determine the actual structure of the ligand-terminated chain end. However, if it is easily converted by the methyl



Figure 14. Spectra obtained from 2-D NMR experiment (DEPT) on poly(propylene oxide) made with catalyst 4a/TiBA (1:2), showing the assignments based on ref 4e.

action of HX (X = Cl, Br) into a haloethyl chain end, it may be that the initiating group is the sulfur atom, rather than the oxygen atom of the phenoxy moiety. The reaction of thioethers with ethylene oxide has been postulated to lead to addition products with sulfonium structures.<sup>23</sup>

Poly(Propylene Oxide) Analysis. Poly(propylene oxide) (PPO) produced by catalyst **4a**/TiBA (molar ratio 1:2) was examined by DEPT NMR analysis to probe the regiochemistry of insertion. Using the assignments of Antelmann et al.,<sup>4e</sup> the methylene and methine portions of the <sup>13</sup>C spectrum, shown in Figure 14, can be broken down into those carbons associated with the hydroxyl end groups and those associated with the bulk polyether. The fact that both methylene and methine carbons are bound to hydroxyl groups is strong evidence that the initial insertion is not regioselective. Similarly, the level of head-to-head and tail-to-tail insertion is roughly that of head-to-tail insertion, indicating a polymerization operating essentially without regiochemical control. We did not attempt to reproduce the elegant analysis of Antelmann et al.4e to determine the stereospecificity of the various ring-opening events and so cannot distinguish our polymerization mechanism from the one employed by simple Lewis acid catalysts such as BF<sub>3</sub>. However, the PPO described in our work bears a strong resemblance to that made by  $[(C_{30}H_{44}O_2)-$ AlCl]<sub>2</sub>, the catalyst used in theirs.

### Conclusions

The reaction of sulfur-bridged bis(phenol) compounds with trialkylaluminum species yields highly active catalysts for EO polymerization. The sulfur atom binds to aluminum in the solid-state structures of these catalyst precursors. Greater steric bulk at the ortho positions of the phenols and in the aluminum alkyl groups increases catalyst productivity. Alkylation of one of the phenol oxygens causes a large increase in catalytic activity. In solution, donor-aluminum interactions in the compound (3-t-Bu-5-Me-2-OAlEt<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>S are fluxional, and interconvert via at least two distinct pathways. Upon addition of monomer, these species react differently depending on ligand structure. Addition of an epoxide to one dialuminum bis(phenoxide) complex causes its disproportionation to the epoxide solvates of both trialkylaluminum species and monoaluminum bis-(phenoxide). Thus, it is unlikely that a bisphenol adduct comprising two phenoxyaluminum moieties represents

the active site structure in this chemistry. The adduct of a singly capped bis(phenol) does not disproportionate upon making an epoxide donor complex. Coordination of 1,2-epoxyhexane to aluminum species induces substantial shifts in the oxirane proton NMR positions, shifts which are most pronounced for the solvate of an ethylaluminum thiobis(phenoxide) compound. Competition for oxirane initially favors triethylaluminum, formed along with this ethylaluminum thiobis(phenoxide) through disproportionation, despite the greater perturbation of the oxirane coordinated to the latter. The first ring-opening reaction for catalysts containing the singly capped bisphenol ligand seems to involve the attack of a group easily cleaved from the polymer by hydrochloric acid. Propylene oxide polymerization proceeds with low regioselectivity. The sulfur atom of the ligands appears to prevent the clustering of aluminum-containing species by providing an intramolecular Lewis base and may also be involved in the first ring-opening event.

### **Experimental Section**

Materials. Unless otherwise specified, all chemical reactions were performed under nitrogen. Toluene, diethyl ether, and tetrahydrofuran were passed through a deoxo/sieves train before use, while hexanes were passed through molecular sieves. Triethylaluminum (1.56 mol/L solution in heptane) and triisobutylaluminum (0.865 mol/L solution in hexanes) were obtained from Akzo Nobel. Trimethylaluminum was obtained from Aldrich as a 2 mol/L solution in hexane. m-Xylene-2sulfenyl chloride was prepared in a manner analogous to that for 2-mesitylenesulfenyl chloride reported by Hicks et al.<sup>24</sup> 2,6-Di-t-butylphenol (1), sulfur dichloride (80%), sodium hydride (95%), ethyl p-toluenesulfonate (98%) and methyl p-toluenesulfonate (98%) were used as received from Aldrich. Sodium t-butoxide (98%) was used as received from Alfa Aesar. 2.4-Di-t-butylphenol (97%) was used as received from Acros Organics. 2,2'-Methylenebis(6-t-butyl-4-methylphenol) (2a) was obtained from R. T. Vanderbilt Company, Inc. 2,2'-Ethylidenebis(4,6-di-t-butylphenol) (2b) and 2,2'-thiobis(6-t-butyl-4-methylphenol) (4a) were obtained from Ciba Specialty Chemicals. 4,4'-Thiobis(2-t-butyl-5-methylphenol) (3) was obtained from Monsanto. Syntheses of 2,2'-thiobis(4,6-dimeth $ylphenol)^{25}$  (4c) and 2-t-butyl-6-[(3-t-butyl-2-methoxy-5-methylphenyl)thio]-4-methylphenol<sup>26</sup> (5a) were similar to reported preparations.

2,2'-Thiobis(4,6-di-t-butylphenol) (4b).27 To a solution of 33.18 g of 2,4-di-t-butylphenol (161 mmol) in 175 mL of hexanes was added dropwise a solution of 4.8 mL of sulfur dichloride (76 mmol, 0.47 equiv) in 55 mL of hexanes at room temperature over a period of 45 min, with some gas evolution. The yellow solution was brought to reflux, which was maintained overnight. The organic fraction was dried with anhydrous sodium sulfate, filtered, and reduced by rotary evaporation to a yellow oil. Crystals were obtained by dissolution in 100 mL of acetonitrile and chilling to 0 °C. After filtration and drying in vacuo overnight at room temperature, we obtained 19.999 g of slightly yellow crystals which contained, by NMR, 0.5 equiv of acetonitrile. Correcting for this, the yield is 57% based on SCl<sub>2</sub>. (The sample used in the preparation of polymerization catalysts was purified by column chromatography (7:1 hexanes/toluene), which resulted in poorer yield but no MeCN impurity; the samples are otherwise spectroscopically indistinguishable.) <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 7.29 (d, J = 2.4 Hz), 2H, Ar-H; 7.18 (d, J = 2.4 Hz), 2H, Ar-H; 6.50 (s), 2H, OH; 2.03 (s), 1.6 H, (MeCN); 1.43 (s), 18H, t-Bu; 1.24 (s) 18H, *t*-Bu. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>), δ (ppm): 151.8, 143.0, 136.0, 127.8, 125.2, 118.9, 35.2, 34.3, 31.4, 29.5.

2-t-Butyl-6-[(3-t-butyl-2-ethoxy-5-methylphenyl)thio]-4-methylphenol (5b). To a solution of 10.036 g 4a (28.0 mmol) in 100 mL of THF was added 0.685 g of sodium hydride (28.5 mmol, 1.02 equiv), and the mixture was refluxed for 2 h. While the reaction mixture was still refluxing, a solution of 5.595 g of ethyl p-toluenesulfonate (27.9 mmol, 1 equiv) was added over a period of 3 h. (During this period, an additional 50 mL of THF were injected into the flask to make up for solvent apparently lost to a leaky joint.) The thick blue-green slurry with white precipitate was refluxed overnight. Next, the slurry was quenched with 200 mL of water and mixed with 200 mL of diethyl ether to extract the reaction product. The aqueous phase was washed with a further 50 mL of diethyl ether. The combined organic fractions were dried over anhydrous sodium sulfate, filtered, and reduced to a viscous yellow fluid by rotary evaporation. The material was purified first by column chromatography in hexanes/toluene at a volume ratio of 40:1, with one less-pure fraction recrystallized from ethanol. Three crops were recovered, with a total weight of 5.36 g (50%). M.p. 116.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.22 (d, J = 2.0 Hz), 1H, Ar-H; 7.17 (s), 1H, OH; 7.11 (d, J = 2.0Hz), 1H, Ar-H; 6.93 (d, J = 2.0 Hz), 1H, Ar-H; 6.50 (d, J = 2.0), 1H, Ar-H; 4.15 (q, J = 7.0 Hz), 2H, CH<sub>2</sub>CH<sub>3</sub>; 2.24 (s), 3H, Ar-CH<sub>3</sub>; 2.12 (s), Ar-CH<sub>3</sub>; 1.52 (t, J = 7.0 Hz), CH<sub>2</sub>CH<sub>3</sub>; 1.36 (s), t-Bu. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 154.3, 153.7, 143.4, 136.3, 134.5, 133.9, 130.4, 129.2, 128.2, 127.2, 117.3, 70.3, 35.4, 35.2, 31.3, 29.5, 21.4, 20.9, 15.4. IR (cm<sup>-1</sup>): 3386 (br), 2958, 1437, 1238, 1220, 1030. MS (m/z): 387 (M + 1), 404 (M + 18) (calcd 386.23). Calcd for  $C_{24}H_{34}O_2S$  (%): C, 74.56; H, 8.86; O, 8.28; found: C, 74.19; H, 9.22; O, 8.31.

2-t-Butyl-6-([3-t-butyl-5-methyl-2-(trimethylsilyloxy)phenyl]thio)-4-methylphenol (5c). A round-bottom flask was charged with a stirbar, 10.035 g of 4a (28.0 mmol), 5 mL of triethylamine (36 mmol, 1.3 equiv), and 100 mL of hexanes. The flask was immersed in an ice-water bath. To this solution was added dropwise a solution of 4.6 mL of chlorotrimethylsilane (36 mmol, 1.3 equiv) in 50 mL of hexanes, with the formation of a white precipitate. The slurry was allowed to reach ambient temperature and stirred for 3 days. The slurry was then filtered twice through a medium glass frit then washed with 125 mL of water. The aqueous solution was then washed with 75 mL of hexanes, and the combined organic fractions were dried over anhydrous magnesium sulfate. After filtering, the organic phase was reduced by rotary evaporation to 10.39 g of white powder (86%). M.p. 103.29 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.14 (m), 2H, Ar-H; 6.90 (s) 1H, Ar-H; 6.73 (s), 1H, OH; 6.31 (m), 1H, Ar-H; 2.25 (s), 3H, Ar-CH<sub>3</sub>; 2.08, 3H, Ar-CH<sub>3</sub>; 1.37, 1.38 (two s), 18H, t-Bu; 0.47, 9H, Si-CH<sub>3</sub>.  $^{13}C{^{1}H}$  NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 151.1, 146.5, 137.9, 133.6, 131.4, 128.3, 127.5, 126.7, 124.0, 123.8, 123.5, 114.4, 32.4, 32.3, 27.8, 26.8., 18.4, 18.1, 0.0. IR (cm<sup>-1</sup>): 3402 (br), 2956, 1434, 1241, 904, 849. MS (m/z): 431 (M + 1), 448 (M + 18) (calcd 430.24). Calcd for C<sub>25</sub>H<sub>38</sub>O<sub>2</sub>SSi (%): C, 69.71; H, 8.89; found: C, 69.79; H, 9.16.

2,4-Di-t-butyl-6-[(3,5-di-t-butyl-2-methoxyphenyl)thio]phenol (5d). To a slurry of 2.17 g of sodium *t*-butoxide (22.6 mmol) in 50 mL of THF was added a solution of 10.023 g of 4b.0.5 MeCN (21.6 mmol) in 45 mL of THF over a period of 17 min while the mixture was heated to reflux. To the resulting clear solution was added a solution of 4.06 g of methyl p-toluenesulfonate (21.8 mmol) dropwise over 1 h followed by overnight stirring with continued reflux. The resulting thick, vellow slurry was allowed to cool and then was taken up with 200 mL of diethyl ether and 200 mL of water. The organic fraction was separated and washed twice with water, while the aqueous fraction was washed twice with ether after the addition of 4.8 g of NaCl to facilitate separation. The organic fractions were combined and dried over anhydrous sodium sulfate, filtered, and reduced in vacuo to a deep golden oil. Hexanes (150 mL) were added and quickly removed in vacuo to complete the removal of polar solvent. Crystals were obtained by the addition of ethanol (50 mL) and standing at 0 °C. After drying in air, 7.147 g (72%) were obtained. M.p. 100.24 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  (ppm): 7.46 (m), 2H, Ar-H; 7.19 (m) 1H, Ar-H; 7.11 (s), 1H, OH; 6.59 (m), 1H, Ar-H; 4.04 (s), 3H, O-CH<sub>3</sub>; 1.43, 18H, t-Bu; 1.32, 9H, t-Bu; 1.12, 9H, t-Bu. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>), δ (ppm): 154.2, 154.0, 146.7, 143.0, 142.6, 135.9, 131.5, 130.1, 126.8, 123.2, 122.6, 116.0, 61.9, 35.7, 35.5, 34.7, 31.8, 31.4, 31.4, 29.7. IR (cm<sup>-1</sup>): 3395 (br); 2961, 1468, 1442, 1362, 1244, 1105. MS (m/z): 457 (M + 1), 474 (M

+ 18) (calcd 456.31). Calcd for  $C_{29}H_{44}O_2S$  (%): C, 76.26; H, 9.71; O, 7.01; found: C, 76.15; H, 10.06; O, 7.19.

Bis(3-t-butyl-2-methoxy-5-methylphenyl)sulfide (6).<sup>26</sup> To a refluxing mixture of 1.569 g of sodium hydride (65.4 mmol) and 40 mL of THF was added a solution of 9.992 g of 4a (27.9 mmol) in 15 mL of THF dropwise over a period of 5 h. The reaction mixture was refluxed for 3 days. To the slurry was then added a solution of 12.990 g of methyl p-toluenesulfonate (69.75 mmol) in 25 mL of THF over a period of 2.5 h. This reaction was continued under reflux for 17 h then allowed to cool. The slurry was poured into a mixture of ice and sodium chloride and then brought to a pH of 3 with the addition of hydrochloric acid. The mixture was poured into a separatory funnel, and extracted with one 100 mL portion and two 65 mL portions of hexanes. The combined organic fractions were dried over anhydrous sodium sulfate, filtered, and reduced to an off-white solid by rotary evaporation. The pure compound was recovered by recrystallization from ethanol. Yield: 8.72 g (81% based on 4a). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 7.00 (d, J = 2.2 Hz), 2H, Ar–H; 6.74 (d, J = 2.2 Hz), 2H, Ar– H; 3.92 (s), 6H, OCH<sub>3</sub>; 2.17 (s), 6H, Ar-CH<sub>3</sub>; 1.38 (s), 18H, *t*-Bu. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>), δ (ppm): 156.4, 143.2, 133.2, 130.8, 128.7, 127.2, 61.4, 35.1, 30.9, 21.0.

t-Butylthiacalix[4]arene (7).28 A 250 mL round-bottom flask was charged with a stirbar, 63.42 g of 4-t-butylphenol (422 mmol). 26.50 g of elemental sulfur (827 mmol atomic sulfur), 19 mL of tetraethylene glycol dimethyl ether, and 8.60 g of sodium hydroxide (215 mmol). A nitrogen stream flowed over the surface of the slurry to help remove hydrogen sulfide, and the effluent gas was bubbled through a concentrated solution of sodium hypochlorite. The reaction temperature was slowly raised to 200 °C over about 4 h, heated at 210–240 °C for an additional 6 h, and then allowed to cool slowly. The very dark red solid was broken up in a mixture of toluene and ether at a volume ratio of 1:1. To the slurry was then added 350 mL of an 0.5 mol/L solution of sulfuric acid in water. The organic fraction was separated and the aqueous portion washed with 100 mL of a toluene/ether mixture of a volume ratio of 1:1. The combined organic fractions were reduced by rotary evaporation and vacuum pump to a thick, dark red liquid, to which were added 150 mL of hexanes. This precipitated a cream-colored powder, which was filtered on medium glass frit and air-dried, yielding 10.6 g (14% based on sulfur). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 9.58 (s), 4H, OH; 7.62 (s), 8H, Ar-H; 1.21 (s), 36H, t-Bu. MS (m/z): 720 (M - 1).

**Bis(3-t-butyl-2-hydroxy-5-methylphenyl)sulfoxide (8).** Compound **8** was prepared by the reaction of **4a** with 1 equiv of 3-chloroperbenzoic acid according to literature procedures.<sup>29</sup>

2,4-Bis-t-butyl-6-[(2,6-dimethylphenyl)thio]phenol (9). Under N<sub>2</sub>, 2.225 g of *m*-xylene-2-sulfenyl chloride (12.9 mmol) was dissolved in 25 mL of hexanes. Under air, a 100 mL threenecked round-bottom flask was charged with a stirbar and 2.64 g of 2,4-di-t-butylphenol (12.8 mmol); then, a reflux condenser with vacuum adapter and addition funnel were attached. The phenol was dried in vacuo for 20 min, placed under N<sub>2</sub>, and immersed in an oil bath set at 100 °C. The solution of m-xylene-2-sulfenyl chloride was then added via addition funnel, and the reaction mixture was refluxed overnight. Solvent had evaporated by morning, probably through a leaky joint. The resulting brown solid was ground up in a mortar and pestle and recrystallized from ethanol, yielding 2.170 g of cream-colored solid that melted at 101–102 °C. A second, somewhat darker crop of 0.434 g was recovered from the mother liquor. Combined yield: 59% (based on 2,4-di-tbutylphenol). M.p. 81.67 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.07-7.13 (m), 4H, Ar-H; 6.82 (d, J = 2.4 Hz), 1H, Ar-H; 6.28 (s), 1H, OH; 2.41 (s), 6H, CH<sub>3</sub>; 1.38 (s), 9H, t-Bu; 1.13 (s), 9H, t-Bu. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>), δ (ppm): 151.2, 143.6, 142.8, 142.6, 135.5, 129.5, 128.8, 128.3, 126.1, 123.5, 35.3, 34.4, 31.6, 29.7 22.2, 21.7. IR (cm<sup>-1</sup>): 3413 (br), 2959, 1461, 1440, 771. MS (m/z): 343 (M + 1), 360 (M + 18) (calcd 342.20). Calcd for  $C_{22}H_{30}OS\;(\%):\ C,\;77.14;\;H,\;8.83;\;O,\;4.67;\;found:\ C,\;73.99;\;H,$ 8.14; 0, 3.74.

Bis(3-t-butyl-2-(diethylaluminoxy)-5-methylphenyl)sulfide (10). An exemplary synthesis is described. Under nitrogen, 2.03 g of **4a** (5.4 mmol) was dissolved in 15 mL of dry hexanes. To this solution was slowly added 7 mL of triethylaluminum solution (10.8 mmol); the resulting solution was allowed to stir at ambient temperature overnight. Clear, colorless crystals suitable for X-ray analysis were obtained by slow evaporation of solvent over an extended period at ambient temperature. <sup>1</sup>H NMR (toluene- $d_8$ ),  $\delta$  (ppm): 7.23 (d), 2H, Ar-H; 7.16 (d), 2H, Ar-H; 2.09 (s), 6H, Ar-CH<sub>3</sub>; 1.44 (s), 18H, *t*-Bu; 1.21 (br s), 6H; 0.9 (br s), 6H; 0.26 (br s); 8H. <sup>13</sup>C{<sup>1</sup>H} NMR (toluene- $d_8$ ),  $\delta$  (ppm): 156.5, 142.0, 133.9, 133.5, 131.7, 121.4, 36.2, 20.9, 9.4, 1.6; the last two peaks being ~0.5 ppm fwhm. Calcd for C<sub>30</sub>H<sub>48</sub>Al<sub>2</sub>O<sub>2</sub>S (%): C, 68.41; H, 9.18; found: C, 67.09; H, 9.34.

(3-t-Butyl-2-diethylalumino-5-methylphenyl)(3-t-butyl-2-methoxy-5-methylphenyl)sulfide (11). To a solution of 2.008 g (5.4 mmol) of 5a in 15 mL of dry hexanes was added dropwise a hexane solution of trimethylaluminum (5.4 mmol) in hexane (8 mL). After being stirred for 2 h at ambient temperature, all volatiles were removed. Colorless crystals were obtained by storage of a toluene/pentane solution at -25to -30 °C. The NMR spectrum revealed the presence of one equivalent of toluene as the solvent of crystallization. The crystal structure of this compound lacked this solvent, however. <sup>1</sup>H NMR (toluene- $d_8$ ),  $\delta$  (ppm): 7.21 (s), 1H, Ar-H (phenolic); 7.15 (s), Ar-H (phenolic); 7.06 (t), 2H, J = 7.2 Hz, Ar-H (toluene); 6.98 (d), 1H, J = 7.2 Hz, Ar-H (toluene); 6.94 (t), 1H, J = 7.6 Hz, Ar-H (toluene); 6.89 (s), 1H, Ar-H (phenolic); 6.82 (s), 1H, Ar-H (phenolic); 3.62 (s), 3H, OCH<sub>3</sub>; 2.11 (s), 3H, Ar-CH<sub>3</sub>; 2.09 (s), 3H, Ar-CH<sub>3</sub>; 1.72 (s), 3H, Ar-CH<sub>3</sub>; 1.45 (s), 9H, t-Bu; 1.29 (s), 9H, t-Bu; -0.41 (s), 6H, Al-CH<sub>3</sub>. <sup>13</sup>C{<sup>1</sup>H} NMR (toluene- $d_8$ ),  $\delta$  (ppm): 159.9, 154.5, 142.7, 139.8, 137.7, 132.7, 131.2, 131.1, 129.6, 129.2, 128.4, 125.6, 65.1, 35.5, 35.4, 31.5, 29.6, 22.7, 20.8, 14.2, -9.0. Calcd for C<sub>25</sub>H<sub>37</sub>AlO<sub>2</sub>S (%): C, 70.06; H, 8.70; found: C, 68.44; H, 8.66.

2,2'-Thiobis (6-t-butyl-4-methylphenoxy) (ethyl) a lumi-bis (big the second snum Diethyl Etherate (12). To a solution of 2.018 g of 4a in 40 mL of dry diethyl ether was slowly added 3.65 mL of triethylaluminum solution (5.62 mmol) at ambient temperature. After stirring overnight, the volume was reduced by evaporation to about 10 mL. Clear, colorless crystals were obtained by cooling a mixture of this solution with pentane at -25 to -30 °C. The NMR of this compound showed a slight excess of diethyl ether. <sup>1</sup>H NMR (toluene- $d_8$ ),  $\delta$  (ppm): 7.45 (d), 2H, J = 2.0 Hz, Ar-H; 7.07 (d), 2H, J = 2.0 Hz, Ar-H; 3.91 (br q), 5H, CH<sub>3</sub>CH<sub>2</sub>O; 2.10 (s), 6H, Ar-CH<sub>3</sub>; 1.45 (s), 18H, *t*-Bu; 1.39 (t), 3H, J = 8.0 Hz, CH<sub>3</sub>CH<sub>2</sub>Al; 1.05 (t), 8H, J = 7.2Hz, CH<sub>3</sub>CH<sub>2</sub>O; 0.41 (q), 2H, J = 8.0 Hz, CH<sub>3</sub>CH<sub>2</sub>Al. <sup>13</sup>C{<sup>1</sup>H} NMR (toluene- $d_8$ ),  $\delta$  (ppm): 137.8, 133.1, 130.0, 126.8, 123.4, 65.6, 35.2, 29.7, 13.9, 9.9. Calcd for C<sub>28</sub>H<sub>43</sub>AlO<sub>3</sub>S (%): C, 69.10; H, 8.91; found: C, 68.73; H, 9.15.

**EO Polymerizations.** Polymerizations were carried out in a glass slurry reactor composed of a jacketed reactor kettle fitted with an air-powered mechanical stirrer, thermometer, jacketed addition funnel, coldfinger condenser, and gas-dispersion tube. A generalized description of the polymerization procedure is as follows. To a dry, N<sub>2</sub>-flushed reactor was charged 275 mL of hexane. A hexane solution of catalyst was injected via oven dried syringe followed by condensation/ addition of 50–100 mL of EO to the jacketed addition funnel. The polymerization was initiated by addition of 3 mL of EO, followed by dropwise addition over 2 h. The reaction was stopped after 3–6 h total reaction time by addition of 2-propanol to inactivate the catalyst and removal of excess EO to scrubbers under positive  $CO_2$  pressure. The polymer was discharged, washed with hexane, and dried in vacuo overnight.

To prepare the EO oligomers whose analyses are presented in Figures 10–13, the above general procedure was followed, with the following specific conditions. The catalyst was prepared by mixing 3.7 g (10 mmol) of **5a** with 10 mmol of TiBA (solution in hexane) overnight with additional hexane. The catalyst solution was added to ca. 300 mL of hexanes in the jacketed glass reactor. EO (50 mL) was added over a period of 1 h, and the reaction was allowed to proceed for 4.25 h. The reaction temperature was kept at 27–30 °C for 4 h, at the end of which period, a mixture of 5 mL of 37% hydrochloric acid/ water and 50 mL of methanol was added. After removal of residual monomer by nitrogen sparge, the polymer slurry was collected and dried in a vacuum oven at 50 °C. Yield: 27.2 g. A similar procedure, only quenched with a mixture of 5 mL of 48% hydrobromic acid/water and 50 mL of methanol, yielded 43.5 g of polymer.

**PO** Homopolymerization. The PPO oligomer was prepared using the same apparatus as in the EO polymerizations. In this case, the catalyst was a hexane solution containing a mixture of ligand 4a (5 mmol) and TiBA (10 mmol). PO (20 mL) was added in one portion to ca. 300 mL of hexanes followed by the catalyst solution. The reaction was maintained at 29–30 °C for 2h, at the end of which period, a mixture of 5 mL of 37% hydrochloric acid/water and 50 mL of methanol was added. After removal of residual monomer by nitrogen sparge, the polymer slurry was collected and allowed to airdry, and 5.5 g of a viscous, deep yellow polymer was recovered.

**Crystallography.** Data tables are presented in the body of the paper, while the details of data collection and analysis are to be found in the Supporting Information.

**NMR Spectroscopy.** Ligand analyses were done using a Bruker AMX-300 (300 MHz) spectrometer. Catalyst and polymer NMR spectra were obtained on a 400 MHz instrument (Varian). Catalysts and mixtures of catalysts with 1,2-epoxyhexane were prepared in toluene- $d_8$  (vacuum distilled from sodium-potassium alloy) after first removing any proteated solvents used in catalyst synthesis. The poly(ethylene oxide) samples were dissolved in CDCl<sub>3</sub> and analyzed by <sup>13</sup>C NMR.

**Gel-Permeation Chromatography (GPC).** The numberaverage and weight-average molecular weights were measured using a Polymer Liquids PL Aquagel-OH, 16 mm column using 0.05% NaN<sub>3</sub> as the mobile phase, at a rate of 0.8 mL/min and an injection size of 200 mL. A Water 590 HPLC isocratic pump was used together with a Waters 717Plus Autosampler and dual detection on a Wyatt Technology Dawn DSP Laser Photometer and a Water 2410 refractive index detector. The results were interpreted by use of WTC-Astra 4.72 software.

**Mass Spectrometry.** Spectra of compounds **5b**, **5c**, **5d**, and **9** were collected using a Finnigan TSQ-7000 mass spectrometer with a headpressure of 1 psi, a source temperature of 150 °C, an emission current of 800  $\mu$ A, an electron lens voltage of 130, and an electron multiplier at 1300 eV. Ammonia was used as the chemical ionization gas and caused the appearance of M + 18 peaks in addition to those identifiable as M + 1. Compound **7** was analyzed by electron impact using a solids probe. This sample was dissolved in *o*-dichlorobenzene, and a small amount was transferred to a probe crucible and inserted into the probe, which was then inserted into the source of the spectrometer. The probe was then heated at 20 °C/min to 300 °C.

MALDI-TOF mass spectrometry on polymeric samples was performed on a Bruker Biflex III time-of-flight mass spectrometer, operated in the linear and reflectron modes. The matrix was 10% water in THF saturated with 2-(4-hydroxyphenylazo)-benzoic acid (HABA). Samples were prepared as approximately 2000 ppm solutions in 10% water/THF. Sample and matrix solutions were combined 1:1 and briefly vortex-mixed. Approximately 1  $\mu$ L of this preparation was spotted directly onto a stainless-steel target disk. Spectra were acquired by averaging a few hundred laser shots. Mass calibration was performed using oligomer peaks from poly(ethylene glycol) (PEG) 3350 and 8000 in the same matrix. Parent ions were mainly M·Na<sup>+</sup> cations, formed from sodium salt in the matrix.

**FT-IR Spectroscopy.** Spectra were collected on a Nicolet Magna 750 FT-IR spectrometer via transmission. The samples were prepared as thin films cast from a methylene chloride solution. Resolution was set at 4 cm<sup>-1</sup>, and 128 scans were collected. Spectra were processed with triangular apodization.

**Differential Scanning Calorimetry.** Melting points were obtained on a TA Instruments DSC 2920, heating from 30 to 180 °C in air at a rate of 5 °C/min.

**Elemental Analysis.** Analyses were performed by Quantitative Technologies, Inc., Whitehouse, NJ except for that of compound **10**, which was analyzed by Complete Analysis Laboratories, Inc., Parsippany, NJ.

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Supporting Information Available: Tables of crystallographic data for 10, 11, and 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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