

Butadiene Polymerization Catalyzed by Tri(aryloxo)aluminum Adduct of Cobalt Acetate

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Tris(2-phenylphenoxy)aluminum ((2-PhC₆H₄O)₃Al) exists as a dimeric form in toluene. When toluene-insoluble anhydrous cobalt acetate is treated with tris(2-phenylphenoxy)aluminum in toluene, the toluene-soluble adduct (2-PhC₆H₄O)₃Al·Co(OAc)₂ is formed. The 2-phenylphenoxy ligand in the adduct can be replaced with another aryloxo ligand to give (aryloxo)(2-PhC₆H₄O)₂Al·Co(OAc)₂ (aryloxo = 2-methylphenoxy, 2-isopropylphenoxy, 4-methylphenoxy, 4-isopropylphenoxy, or 4-*tert*-butylphenoxy). These complexes are active for butadiene polymerization without gel formation when activated with an equivalent amount of (2-PhC₆H₄O)AlEt₂ for 2 h. The highest activity, 175 kg/mol·Co (turnover number, 3200) was achieved with (2-PhC₆H₄O)₃Al·Co(OAc)₂ at 65 °C for 2 h. The microstructure of the polymer chains is mostly *trans*-1,4-configuration (70-75%) with the remaining being 1,2-vinyl. The *cis*-1,4-configuration observed by IR is minimal (1-5%). By replacing the 2-phenylphenoxy with a 4-alkylphenoxy ligand, the amount of 1,4-configuration slightly increases, resulting in increase in the endothermic melting signal at -30~50 °C in the DSC curve. The molecular weights of the polymers are high (*M*_n: 300000~800000) with a fairly narrow molecular weight distribution (*M*_w/*M*_n, 2.0-2.7).

Key Words : Butadiene polymerization, *trans*-1,4-Polybutadiene, Cobalt complexes, Phenoxyaluminum complexes

Introduction

Poly(1,3-butadiene) (PBD) is a material produced industrially in large volumes. 1,3-Butadiene (BD) can be enchain in three ways (*cis*-1,4-, *trans*-1,4-, and 1,2-vinyl) and, hence, a variety of backbone microstructures are possible. Among those, the soft rubbery PBD enriched in *cis*-1,4-configurations and the crystalline PBD enriched in 1,2-syndiotactic configurations are industrially produced.^{1,2} Recently, polymers with other microstructures have become of interest, and several are currently under development.³ A typical example is PBD composed of ~20% 1,2-vinyl and ~80% *trans*-1,4-configurations.⁴ Due to the presence of the hard *trans*-1,4-units, it has some crystalline domains, while the pendant 1,2-vinyl units are useful for cross-linking. This type of high *trans*-1,4-polybutadiene (TPBD) has drawn attention as a candidate to replace natural rubber in some applications.⁵ A characteristic property of the cured TPBD is strain-induced crystallization when highly elongated at room temperature.

Many catalytic systems based on a variety of transition metal have been developed to tune the chain microstructure during BD polymerization.⁶ Recent academic activities have focused on the construction of metal dichloride complexes coordinated by elaborate ligands, which can be activated with methylaluminoxane (MAO) or [Ph₃C]⁺B(C₆F₅)₄⁻, to elucidate the effect of ligand structure on the polymerization reactivity.⁷⁻¹⁹ However, considering the high price of MAO or [Ph₃C]⁺B(C₆F₅)₄⁻ and the cost of constructing the elabo-

rate complexes, these catalytic systems are seldom relevant for commercial use. A simple Ziegler-Natta system composed of an off-the-shelf metal complex and an inexpensive, simple alkylaluminum, such as triethylaluminum (AlEt₃), is more attractive from the perspective of commercial use. In this regard, cobalt-based systems have received the earliest recognition in the commercial production of PBD. For instance, the ternary system of Co(O₂CC₇H₁₅)₂-AlEt₂Cl-H₂O (O₂CC₇H₁₅ = 2-ethylhexanoate) produces a highly *cis*-1,4-PBD.²⁰ The quaternary system of Co(acac)₃-AlEt₃-H₂O-CS₂ produces 1,2-syndiotactic PBD.²¹ TPBD bearing ~80% *trans*-1,4-configuration and ~20% 1,2-vinyl is also produced by a ternary system: Co(O₂CC₇H₁₅)₂-AlEt₃-phenol derivative.⁴ In this kind of multi-component catalytic system, the structure of the active species is still elusive, and some side reactions, such as formation of gels or bad-smelling oligomers are concomitant because of the generation of unwanted other species.²² Mixing the three components generates fine black particles, causing the isolated resin to appear gray.²³ This work represents the results of an endeavor to unveil the active species of the ternary system of Co(O₂CC₇H₁₅)₂-AlEt₃-phenol derivative. The catalyst disclosed in this work is highly active and free from the formation of gels and bad-smelling oligomers.

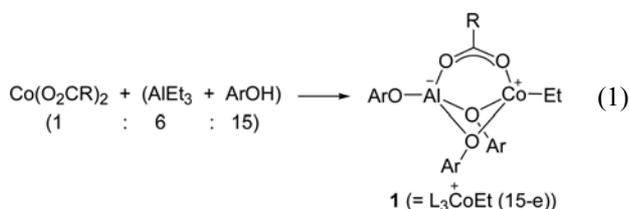
Results and Discussion

Hypothesis for the Active Species. A reported polymerization procedure for the ternary system of Co(O₂CC₇H₁₅)₂-

AlEt₃-phenol is the successive charging of a premixed solution of AlEt₃ and phenol derivative in a 1:2.5 mole ratio and a solution of cobalt(II) 2-ethylhexanoate (Co(II)(O₂CC₇H₁₅)₂). The Al/Co mole ratio is as high as 6; hence, the mole ratio of Co:Al:phenol derivative is 1:6:15. The polymerization is carried out in hexane or cyclohexane. In order to solubilize the catalyst in cyclohexane, Co(II)(O₂CC₇H₁₅)₂, which bears hydrophobic alkyl groups, may be employed instead of the more common Co(OAc)₂. The phenol derivative used is *p*-dodecylphenol, which bears a lipophilic long alkyl chain, or 2-phenylphenol.

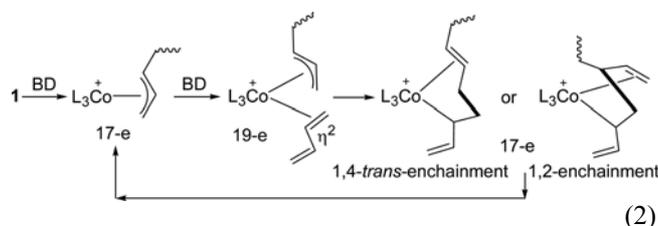
Alkylaluminum frequently acts as a reducing agent, and it can be postulated that the active species may be a cobalt(I) organometallic complex coordinated by an allyl ligand system. The π-allylcobalt(I) complex, (η³-cyclooctenyl)(η²:η²-1,5-cyclooctadiene)cobalt(I), is prepared from cobalt(III) acetylacetonate by the action of AlEt₃ in the presence of 1,5-cyclooctadiene.²⁴ However, this π-allylcobalt(I) complex generates mainly bad-smelling oligomers when BD is added. When AlEt₃ is additionally added, some polymers are generated in small yields, but formation of a significant amount of bad-smelling oligomers is inevitable.

We presume that the active species in Co(O₂CC₇H₁₅)₂-AlEt₃-phenol ternary system may be the cobalt(II) species that is the tri(aryloxo)aluminum adduct of EtCo(O₂CC₇H₁₅) (Eq. 1). EtCo(O₂CC₇H₁₅) was proposed as the active species for the ternary system of Co(O₂CC₇H₁₅)₂-AlEt₂Cl-H₂O, which produces *cis*-1,4-PBD. Only one 2-ethylhexanoate ligand is replaced with an ethyl group, even with excess addition of AlEt₂Cl, leaving the other 2-ethylhexanoate bound to the cobalt as spectator ligands.^{20,25} The replacement of one carboxylate ligand with an ethyl group may occur to give (RCO₂)CoEt by the action of (aryloxo)₂AlEt, which is generated by reacting AlEt₃ and the phenol derivative in a 1:2.5 mole ratio. Another complex that is generated by the reaction of AlEt₃ and the phenol derivative is (aryloxo)₃Al, which may form an adduct with the 11-electron species (RCO₂)CoEt to give the 15-electron species **1** (Eq. 1). Similar type of zwitterionic titanium complex constructed with tris(pyrazoyl)methane was also introduced for ethylene polymerization.²⁶



A plausible polymerization mechanism is shown in Eq. (2). By reacting with BD, the generated cobalt ethyl complex **1** forms an η³-allyl complex, which is a 17-electron species with a paramagnetic cobalt(II) center. BD can coordinate to this species in the η²-mode to give a 19-electron paramagnetic cobalt(II) species. The 17- and 19-electron species are quite acceptable structures for organometallic cobalt(II) complexes. The C-C bond formation in the 19-

electron species occurs by the attack of the allyl-carbon on the η²-BD. Bond formation through an unsubstituted allyl-carbon results in 1,4-enchainment, while that through a substituted allyl-carbon results in 1,2-enchainment. In this mechanism, the more thermodynamically stable *transoid*-η³-allyl species can be an intermediate, resulting in a *trans*-configuration for the 1,4-enchainment.



Formation of Co(OAc)₂ Adduct of Tri(aryloxo)aluminum.

Reaction of 3 equivalents of phenol derivatives with AlEt₃ in toluene quantitatively affords tri(aryloxo)aluminum (Eq. 3). The ¹H NMR spectrum indicates that it exists as a dimer in benzene solution. In the ¹H NMR spectrum of tris(2-phenylphenoxy)aluminum, two signals are observed at 6.67 ppm and 6.36 ppm, isolated from the other collapsed signals at 7.22-6.76 ppm. Analysis of the integration values indicates two sets of 2-phenylphenoxy signals in a 1:2 ratio. One set is assigned to the bridged phenylphenoxy, and the other set is from the terminal phenylphenoxy. In the ¹³C NMR spectra, two sets of phenylphenoxy signals are observed either by formation of dimeric structure. For tri(2-isopropylphenoxy)aluminum, two broad methine isopropyl (Me₂CH-) signals are observed at 3.86 and 3.45 ppm in a 2:1 ratio. For tris(2,6-dimethylphenoxy)aluminum, the two methyl signals are observed at 2.70 and 1.98 ppm in a 2:1 ratio. Tri(aryloxo)aluminum was reported as an adduct of an amine base, indicative of Lewis acidity in the monomeric form.²⁷ The dimeric structure of tris(2-phenylphenoxy)aluminum complex is unambiguously confirmed by X-ray crystallography (Figure 1).

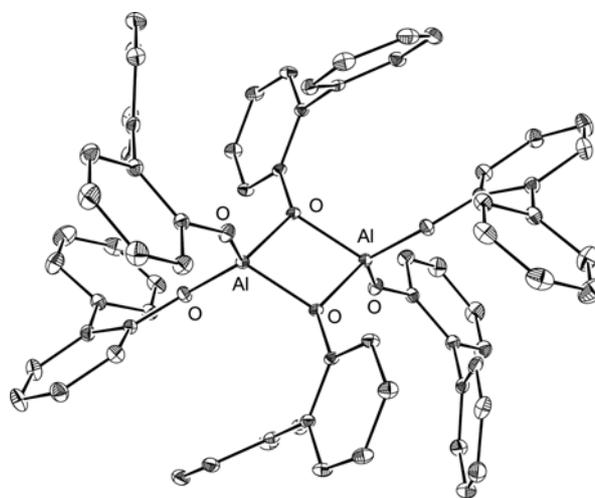
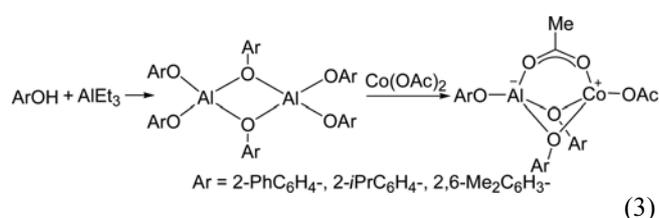


Figure 1. The dimeric structure of tris(2-phenylphenoxy)aluminum revealed by X-ray crystallography.



$\text{Co}(\text{OAc})_2$ is completely insoluble in hydrocarbon solvents such as toluene or benzene, but it becomes soluble when a dispersion of anhydrous $\text{Co}(\text{OAc})_2$ in toluene or benzene is heated in the presence of tri(aryloxo)aluminum. In the ^1H NMR in C_6D_6 , the aryloxo-signals are not observed, even though significant amounts of complexes are dissolved. The formation of an adduct situates the aryloxo-unit in proximity to paramagnetic cobalt center, consequently perturbing the observation of its signals. We presume that the $\text{Co}(\text{OAc})_2$ adduct of tri(aryloxo)aluminum is formed (Eq. 3). Similar types of cobalt complexes ligated by alkoxoaluminum complexes ($\text{Co}\{\text{Al}(\text{OR})_4\}_2$) have been reported.²⁸ The isolated blue solid is very soluble in benzene or toluene but insoluble in cyclohexane or hexane. Recrystallizations were tried in various ways but failed; most often, a powdery solid precipitated in these trials. The adduct is easily destroyed by contact with moisture. When the blue solid is exposed to air, it becomes a pale purple solid. When the solid is redissolved in toluene or benzene, an insoluble portion remains, which may be the water-adduct of $\text{Co}(\text{OAc})_2$. Hydrated cobalt acetate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) does not form such an adduct with tri(aryloxo)aluminum. When a dispersion of anhydrous $\text{Co}(\text{OAc})_2$ is heated in toluene in the presence of 2-phenylphenol, $\text{Co}(\text{OAc})_2$ remains as a solid and blue solution is not formed. When 2-phenylphenol is added to the dimeric form of $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al}$ in benzene, the ^1H NMR spectrum indicates the formation of a monomer complex $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al} \cdot (2\text{-PhC}_6\text{H}_4\text{OH})$. When the dispersion of anhydrous $\text{Co}(\text{OAc})_2$ is treated with $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al} \cdot (2\text{-PhC}_6\text{H}_4\text{OH})$ in toluene, $\text{Co}(\text{OAc})_2$ again remains as a solid instead of forming the blue solution. Both the donating site of the aryloxy unit and the Lewis acidic site of the aluminum center may be required to form such a toluene-soluble bimetallic adduct.

Activation Reaction for Polymerization. When an equimolar amount of AlEt_3 is added to the $\text{Co}(\text{OAc})_2$ adduct of tris(2-phenylphenoxo)aluminum ($(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al} \cdot \text{Co}(\text{OAc})_2$) in toluene, the blue colored solution immediately turns to a dark brown-red. Some amount reduced cobalt metal precipitates as a black solid. When the activated catalyst (19 μmol Co in 0.20 mL toluene) is added to a solution of BD (~4.5 g) in cyclohexane (20 mL) and the resulting solution is stirred for 2 h at 65 $^\circ\text{C}$, a very thick viscous solution is formed, from which 1.21 g of polymer is isolated (entry 1 in Table 1). When the adduct is reacted with Et_3Al for 2 h at room temperature before charging the reactor, a slightly higher amount of polymer is obtained (1.67 g, entry 2).

When the adduct is activated with $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$, the activity nearly doubled and 3.28 g polymer is isolated (entry 3). Addition of at least one equivalent of $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$

is necessary for the activation; negligible amount of polymer is isolated when half equivalent of $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$ is added. The activator $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$ is prepared simply by mixing equimolar amounts of AlEt_3 and 2-phenylphenol. The ^1H and ^{13}C NMR spectra indicate the clean formation of $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$.²⁹ Another advantage of using $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$ as an activator instead of AlEt_3 is that no black precipitate forms. In contrast to the immediate color change by the action of AlEt_3 , when $(2\text{-PhC}_6\text{H}_4\text{O})\text{AlEt}_2$ is employed as an activator, the color of the blue solution starts to change after about 30 minutes, gradually turning to a dark brown-red without the formation of any black precipitate. Charging the blue solution to the reactor immediately after mixing the two components gives a smaller amount of polymer and the formation of a gel (entry 4). The activity of the activated catalyst decreases by half when it is stored for 12 h at room temperature, indicating that the activated species is unstable in toluene solution at room temperature (entry 5). The highest polymer yield occurs at a temperature around 65 $^\circ\text{C}$. At 45 $^\circ\text{C}$, a negligible amount of polymer is obtained (entry 6). At the higher temperatures of 75 and 85 $^\circ\text{C}$, the yields are reduced by almost half (entries 7 and 8). When the polymerization time is shortened from 2.0 h to 1.0 h, the yield dramatically decreases from 3.28 g to 0.40 g (entry 9). This observation implies that some induction time is needed for the activated species to initiate the polymerization. By lengthening the time to 3.0 h, the yield increases slightly to 3.40 g (entry 10), which may be a mechanical limitation of the yield in our polymerization system. The resulting polymerization solution containing 3.28 or 3.40 g dissolved polymer is very thick, viscous, and almost unstirrable with a magnetic stirring bar. The formation of 3.32 g of polymer in 2 h corresponds to a turnover number (TON) of 3200 or an activity of 175 kg/mol-Co.

$(2\text{-PhC}_6\text{H}_4\text{O})\text{Et}_2\text{Al}$ is the best of the surveyed activators. Other (aryloxo) AlEt_2 complexes show worse results. (2-Alkylphenoxo)diethylaluminum complexes ($(2\text{-MeC}_6\text{H}_4\text{O})\text{AlEt}_2$, $(2\text{-}i\text{PrC}_6\text{H}_4\text{O})\text{Et}_2\text{Al}$, $(2\text{-}t\text{BuC}_6\text{H}_4\text{O})\text{Et}_2\text{Al}$) produce lower yields (entries 11-13). With (4-alkylphenoxo)diethylaluminum complexes ($(4\text{-MeC}_6\text{H}_4\text{O})\text{Et}_2\text{Al}$, $(4\text{-}i\text{PrC}_6\text{H}_4\text{O})\text{Et}_2\text{Al}$), some gels are formed despite their high activities (entries 14 and 15). The ternary system prepared from $\text{Co}(\text{O}_2\text{CC}_7\text{H}_{15})_2$ activated with a reaction mixture of 6 equivalents of AlEt_3 and 15 equivalents of 2-phenylphenol also produces a gel at the same polymerization conditions. Using this ternary system, a successful polymerization was reported without the formation of gel when using a more dilute BD solution in cyclohexane (~1/3 BD concentration).

Effect of Structure of Aryloxo Ligand on Polymerization Reactivity. When a toluene solution of $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al} \cdot \text{Co}(\text{OAc})_2$ is stirred for 1 day at 70 $^\circ\text{C}$ after the addition of an equivalent amount of *o*-cresol, exactly the same mole of 2-phenylphenol is liberated, which is extracted with hexane. This result indicates the formation of the adduct $(2\text{-MeC}_6\text{H}_4\text{O})(2\text{-PhC}_6\text{H}_4\text{O})_2\text{Al} \cdot \text{Co}(\text{OAc})_2$. Through the same procedure, 2-phenylphenoxo in $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al} \cdot \text{Co}(\text{OAc})_2$ can be replaced with various phenol derivatives, such as 2-isopropylphenol,

Table 1. Butadiene polymerization results with (2-PhC₆H₄O)₃Al·Co(OAc)₂^a

Entry	Activator	Activation time (h)	Polymerization time (h)	Temp (°C)	Yield (g)	F _{1,4} ^b	M _n ^c × 10 ⁻³	PDI
1	Et ₃ Al	0	2	65	1.21	72	308	2.58
2	Et ₃ Al	2	2	65	1.67	72	394	2.65
3	(2-PhC ₆ H ₄ O)Et ₂ Al	2	2	65	3.28	71	662	2.41
4	(2-PhC ₆ H ₄ O)Et ₂ Al	0	2	65	2.54 (gel)	-	-	-
5	(2-PhC ₆ H ₄ O)Et ₂ Al	12	2	65	1.53	71	362	2.68
6	(2-PhC ₆ H ₄ O)Et ₂ Al	2	2	45	~0	-	-	-
7	(2-PhC ₆ H ₄ O)Et ₂ Al	2	2	75	1.85	72	665	2.19
8	(2-PhC ₆ H ₄ O)Et ₂ Al	2	2	85	1.80	71	657	2.25
9	(2-PhC ₆ H ₄ O)Et ₂ Al	2	1	65	0.40	70	98	2.37
10	(2-PhC ₆ H ₄ O)Et ₂ Al	2	3	65	3.40	71	730	2.20
11	(2-MeC ₆ H ₄ O)Et ₂ Al	2	2	65	2.00	72	456	2.30
12	(2- <i>i</i> PrC ₆ H ₄ O)Et ₂ Al	2	2	65	1.18	71	430	2.19
13	(2- <i>t</i> BuC ₆ H ₄ O)Et ₂ Al	2	2	65	0.85	71	404	2.20
14	(4-MeC ₆ H ₄ O)Et ₂ Al	2	2	65	3.12 (gel)	-	-	-
15	(4- <i>i</i> PrC ₆ H ₄ O)Et ₂ Al	2	2	65	3.29 (gel)	-	-	-
16 ^d	Comp	2	2	65	2.73 (gel)	-	-	-

^aPolymerization condition: (2-PhC₆H₄O)₃Al·Co(OAc)₂ (14 mg, 19 μmol) activated with an equimolar amount of activator in 0.20 mL toluene at rt, butadiene (~4.5 g) in cyclohexane (20 mL). ^bMole fraction of 1,4-units measured via ¹H NMR spectroscopy. ^cMeasured by GPC using polystyrene standards. ^dComparison study with a ternary system of Co(O₂CC₇H₁₃)₂-AlEt₃-2-PhC₆H₄OH (1:6:15 mole ratio, 19 μmol of cobalt).

p-cresol, 4-isopropylphenol, and 4-*t*-butylphenol, resulting in the formation of (2-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, (4-MeC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, (4-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, and (4-*t*BuC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ respectively. The exchange reaction fails with 2-*t*-butylphenol. In this case, the added 2-*t*-butylphenol itself is extracted with hexane. When two equivalents of *o*-cresol are added, two equivalents of 2-phenylphenol are extracted, indicating the formation of (2-MeC₆H₄O)₂(2-PhC₆H₄O)Al·Co(OAc)₂.

When the adduct of (2-MeC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ is activated with (2-PhC₆H₄O)AlEt₂, it is active for BD polymerization, but the activity is reduced by about half compared with (2-PhC₆H₄O)₃Al·Co(OAc)₂ (1.42 g versus 3.28 g, entries 1 and 2 in Table 2). The adduct of (2-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, which bears the bulkier 2-iso-

propylphenoxo group, exhibits a higher activity (2.56 g). The adduct bearing a *para*-alkylphenoxo group shows a lower activity than the adduct bearing the corresponding *ortho*-alkylphenoxo group. The adduct of (4-MeC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ gives 1.08 g of polymer, while (2-MeC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ gives 1.42 g of polymer. The adduct of (4-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ gives 1.40 g of polymer, while (2-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ gives 2.56 g of polymer. Bulkier substituents in the phenoxo groups increase the activity, and (4-*t*BuC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ gives 1.70 g of polymer (entry 6). Multiple 2-phenylphenoxo groups are crucial; the adducts bearing either one or no 2-phenylphenoxo group, ((2-MeC₆H₄O)₂(2-PhC₆H₄O)Al·Co(OAc)₂, (2-MeC₆H₄O)₃Al·Co(OAc)₂, and (2-*i*PrC₆H₄O)₃Al·Co(OAc)₂) show negligible activities under the same activation and polymerization

Table 2. Butadiene polymerization results with Co(OAc)₂ adducts of various tri(aryloxo)aluminum species activated with (2-PhC₆H₄O)AlEt₂^a

Entry	Catalyst	Yield (g)	F _{1,4} ^b (%)	1,4- <i>trans</i> :1,4- <i>cis</i> :1,2-	M _n ^d × 10 ⁻³	PDI
1	(2-PhC ₆ H ₄ O) ₃ Al·Co(OAc) ₂	3.28	71	64 : 1 : 35	662	2.41
2	(2-MeC ₆ H ₄ O)(2-PhC ₆ H ₄ O) ₂ Al·Co(OAc) ₂	1.42	70	60 : 6 : 34	259	2.69
3	(2- <i>i</i> PrC ₆ H ₄ O)(2-PhC ₆ H ₄ O) ₂ Al·Co(OAc) ₂	2.56	73	59 : 5 : 36	785	2.32
4	(4-MeC ₆ H ₄ O)(2-PhC ₆ H ₄ O) ₂ Al·Co(OAc) ₂	1.08	75	69 : 1 : 30	299	2.56
5	(4- <i>i</i> PrC ₆ H ₄ O)(2-PhC ₆ H ₄ O) ₂ Al·Co(OAc) ₂	1.40	74	68 : 2 : 30	454	2.09
6	(4- <i>t</i> BuC ₆ H ₄ O)(2-PhC ₆ H ₄ O) ₂ Al·Co(OAc) ₂	1.70	70	64 : 4 : 32	692	2.04
7	(2-MeC ₆ H ₄ O) ₂ (2-PhC ₆ H ₄ O)Al·Co(OAc) ₂	~0	-	-	-	-
8	(2,6-Me ₂ C ₆ H ₃ O) ₃ Al·Co(OAc) ₂	~0	-	-	-	-
9	(2- <i>i</i> PrC ₆ H ₄ O) ₃ Al·Co(OAc) ₂	~0	-	-	-	-

^aPolymerization condition: Cobalt complex (11 mg, 16 μmol) activated with an equimolar amount of (2-PhC₆H₄O)AlEt₂ in 0.20 mL toluene, butadiene (~6.7 g) in cyclohexane (20 mL). ^bMole fraction of 1,4-units measured by ¹H NMR spectroscopy. ^cMeasured by FT-IR spectroscopy. ^dMeasured by GPC using polystyrene standards.

conditions (entries 7-9).

Characterization of Polymers. In the ^1H NMR spectra, three vinyl signals are observed (Figure 1). A signal at 5.40 ppm is assigned to 1,4-enchainment, while the two signals at 5.56 and 4.96 ppm are assigned to pendant vinyl groups formed by 1,2-enchainment. From the integration of these signals peaks, the mole fraction of 1,4-enchainment ($F_{1,4}$) can be calculated by the equation $F_{1,4} = (I_{5.2-5.8} - I_{4.70-5.20}/2) / \{I_{4.70-5.20} + (I_{5.2-5.8} - I_{4.70-5.20}/2)\}$, where $I_{4.70-5.20}$ and $I_{5.2-5.8}$ are the integration values at 4.70-5.2 ppm and 5.2-5.8 ppm, respectively. All the PBDs generated using $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al}\cdot\text{Co}(\text{OAc})_2$ show nearly identical $F_{1,4}$ values of 70-72% (Table 1 and entry 1 in Table 2). The ^{13}C NMR signals are rather simple in the aliphatic region (Figure 2). The big signal at 32.7 ppm is assigned to methylene ($-\text{CH}_2-$) from successive *trans*-1,4-enchainment, because the same signal is observed in the ^{13}C NMR spectrum of genuine *trans*-1,4-PBD.⁷ Five other signals are observed. Among these, the four signals at 43.5, 38.1, 34.0, and 30.1 ppm (labeled as 1-4) match those observed for *trans*-1,4-PBD containing a small amount (~ 5 mol %) of 1,2-enchainment.¹⁴ Because the polymer chain bears more 1,2-vinyl units (30%), the successive 1,2-enchainment should be considered in the analysis of the signals. The methylene signals labeled as 2' and 3' overlap those observed from the isolated 1,2-enchainment, but the methine carbon labeled as 1' and methylene carbon labeled as x are observed as small signals at around 41 ppm and 38-40 ppm, respectively. The small signals are complicated due to presence of racemic and meso configurations in the successive 1,2-vinyl-enchainment. The signal at 27.4 ppm is assigned to 1,4-*cis*-methylene. The signals in the aromatic region are also assignable to polymer chains of *trans*-1,4-PBD containing a significant amount of 1,2-enchainment. The signals at 142.7 and 114.5 ppm (labeled as a and b) are assigned to the pendant vinyl groups. In the ^{13}C NMR spectrum of *trans*-1,4-PBD containing a small amount of 1,2-enchainment (~ 5 mol %), only two more signals are observed around the big signal at 130 ppm.¹⁴ In the case of *trans*-1,4-PBD containing 30 mol % 1,2-vinyl, the arrangement of the 1,4-units is more complex, and many signals are observed around the big signal at 130 ppm. The polymer chains obtained using the ternary system of $\text{Co}(\text{O}_2\text{CC}_7\text{H}_{15})_2\text{-AlEt}_3\text{-2-PhC}_6\text{H}_4\text{OH}$ were described as having a similar microstructure, composed of 72 mol % 1,4-*trans* and 25 mol % 1,2-vinyl with a negligible amount of *cis*-1,4-configuration

(3 mol %).⁴

The ratio of 1,4-*trans*:1,4-*cis*:1,2-vinyl can also be calculated from FTIR data obtained with a single-reflection ATR accessory. For the sample obtained with $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al}\cdot\text{Co}(\text{OAc})_2$, which shows 71% 1,4-configuration from ^1H NMR spectrum (entry 1 in Table 2), the ratio of 1,4-*trans*:1,4-*cis*:1,2-vinyl is 64:1:35. The $F_{1,4}$ value measured from IR (65%) agrees fairly well with that calculated from the ^1H NMR (71%), and the IR data confirm that most of the 1,4-units are in the *trans*-configuration.

The microstructure of a polymer chain is somewhat dependent on the catalyst structure (Table 2). Substitution of the 2-phenylphenoxy ligand in $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al}\cdot\text{Co}(\text{OAc})_2$ with a 2-alkylphenoxy ligand (2-MeC₆H₄O or 2-*i*PrC₆H₄O) has a negligible effect on the total amount of 1,4-units but marginally increases the number of *cis*-1,4-units at the expense of *trans*-1,4-units (entries 1-3). Substitution with a 4-alkylphenoxy ligand (4-MeC₆H₄O, 2-*i*PrC₆H₄O, or 4-*t*BuC₆H₄O) increases the fraction of 1,4-units from $\sim 65\%$ to $\sim 70\%$ (entries 1, 4-6). For the samples obtained with (4-MeC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ and (4-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, the 1,4-*cis* content is negligible (1-2%), but 4% 1,4-*cis* content is observed for the sample obtained with (4-*t*BuC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂. Due to the increase in crystalline *trans*-1,4-units, a broad endotherm signal is observed at $-30\sim 50$ °C in the DSC curves

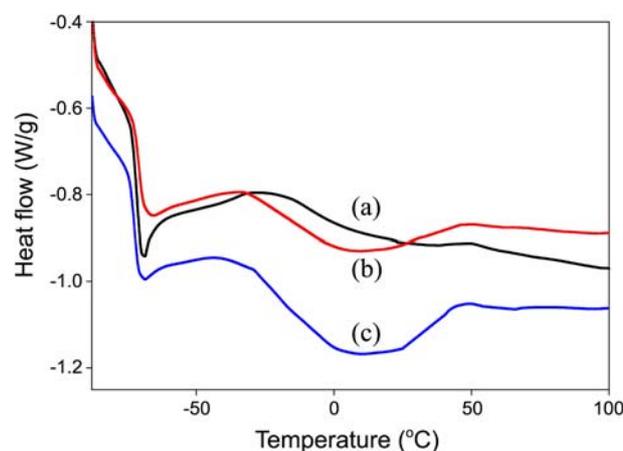


Figure 3. DSC thermograms of PBDs obtained with $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al}\cdot\text{Co}(\text{OAc})_2$ (entry 1 in Table 2) (a), $(4\text{-}i\text{PrC}_6\text{H}_4\text{O})(2\text{-PhC}_6\text{H}_4\text{O})_2\text{Al}\cdot\text{Co}(\text{OAc})_2$ (entry 5 in Table 2) (b), and $(4\text{-MeC}_6\text{H}_4\text{O})(2\text{-PhC}_6\text{H}_4\text{O})_2\text{Al}\cdot\text{Co}(\text{OAc})_2$ (entry 4 in Table 2) (c).

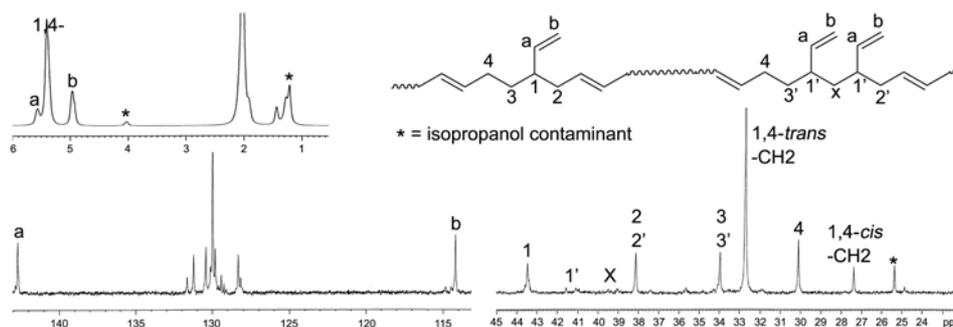


Figure 2. The ^1H NMR and ^{13}C NMR spectra of polybutadiene generated using $(2\text{-PhC}_6\text{H}_4\text{O})_3\text{Al}\cdot\text{Co}(\text{OAc})_2$ (entry 1 in Table 2).

(Figure 3). The molecular weights of the samples are fairly high, with M_n values of 300000-800000, and their polydispersity indices (PDI, M_w/M_n) are in the fairly narrow range of 2.0-2.7, indicating a single active species in the polymerization solution.

Summary. Toluene-soluble cobalt acetate adducts of tri(aryloxo)aluminum ((2-PhC₆H₄O)₃Al·Co(OAc)₂, (2-*i*PrC₆H₄O)₃Al·Co(OAc)₂, and (2,6-Me₂C₆H₃O)₃Al·Co(OAc)₂) are formed when toluene-insoluble anhydrous cobalt acetate is treated with tri(aryloxo)aluminum in toluene for 1 day at 70 °C. The 2-phenylphenoxo ligands in (2-PhC₆H₄O)₃Al·Co(OAc)₂ can be replaced with other 2-alkylphenoxo or 4-alkylphenoxo ligands by stirring with an equivalent amount of 2-alkylphenol or 4-alkylphenol at 70 °C. These complexes are active for butadiene polymerization without gel formation when activated with an equivalent amount of (2-PhC₆H₄O)AlEt₂ for 2 h. The highest activity, 175 kg/mol-Co (turnover number: 3200) is achieved with (2-PhC₆H₄O)₃Al·Co(OAc)₂ by running the polymerization at 65 °C for 2 h. Replacing the 2-phenylphenoxo ligands with other aryloxo ligands results in some reduction in the activity. The microstructure of the polymer chains, as determined from the ¹H NMR spectra, is mostly 1,4-configuration (70-75%), with the remaining being 1,2-vinyl (25-30%). The IR data indicate a minimal amount of *cis*-1,4-configuration (1-5%). By replacing one 2-phenylphenoxo with a 4-alkylphenoxo ligand, the 1,4-configuration slightly increases from 70 to 75%, resulting in an increase in the endothermic melting signal at -30~50 °C in the DSC curves. The molecular weights of the polymers are high (M_n : 300000-800000) with a fairly narrow molecular weight distribution (M_w/M_n : 2.0-2.7).

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. Hexane, toluene, and C₆D₆ were distilled from benzophenone ketyl. Cyclohexane and toluene (anhydrous grade) used for the polymerization reaction were purchased from Aldrich and purified over Na/K alloy. The ¹H NMR (600 MHz) spectra were recorded on a Bruker, Advance 600. Quantitative analyses of *trans*-1,4-, *cis*-1,4-, and 1,2-vinyl units were carried out using an FTIR instrument equipped with a single-reflection ATR accessory according to a procedure given in the Shimadzu application news (No. A321). Gel permeation chromatograms (GPC) were obtained at room temperature in CHCl₃ using a Waters Millennium apparatus with polystyrene standards. DSC (Differential Scanning Calorimetry) thermograms were obtained from a second heating at a heating rate of 10 °C/min with Thermal Analysis Q10 instrument.

A Typical Procedure for Preparation of (Aryloxo)₃Al. To a stirred solution of 2-phenylphenol (1.00 g, 5.87 mmol) in toluene (8 mL) was added a solution of Et₃Al (0.22 g, 1.96 mmol) in toluene (2 mL) and then the solution was stirred for 1 h at room temperature. The compound was used without purification for the next step. NMR data for (2-

PhC₆H₄O)₃Al: ¹H NMR (600 MHz, C₆D₆) δ 7.25-6.75 (m, 48H, CH), 6.67 (t, *J* = 6.4 Hz, 2H, 4-CH [bridge]), 6.36 (d, *J* = 8.0 Hz, 4H, 2-CH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K) δ 153.35, 147.11, 139.88, 135.94, 133.51, 132.47, 132.13, 130.99, 129.87, 129.67, 129.27, 128.80, 128.71, 126.61, 125.63, 122.12, 121.16, 120.63. NMR data for (2,6-DiMeC₆H₄O)₃Al: ¹H NMR (600 MHz, C₆D₆) δ 6.85-6.70 (m, 14H, CH), 6.61 (t, *J* = 8.0 Hz, 4H, 4-CH), 2.70 (s, 12H, CH₃ [bridge]), 1.98 (s, 24H, CH₃). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K) δ 153.20, 148.18, 130.94, 130.02, 129.24, 126.39, 126.36, 120.33, 18.18, 17.62. NMR data for (2-*i*PrC₆H₄O)₃Al: ¹H NMR (C₆D₆) δ 8.00-6.50 (br, 24H, CH), 4.10-3.70 (br, 2H, isopropyl-CH [bridge]), 3.70-3.30 (br, 4H, isopropyl-CH), 1.12 (s, 36H, CH₃). ¹³C{¹H} NMR (100 MHz, C₆D₆, 298 K) δ 153.70, 147.25, 139.57, 138.02, 127.14, 121.28, 119.72, 27.22, 23.63.

A Typical for Preparation of (Aryloxo)₃Al·Co(OAc)₂. To a stirred solution of (2-PhC₆H₄O)₃Al (1.04 g, 1.96 mmol) in toluene (10 mL) was added Co(OAc)₂ (0.347 g, 1.96 mmol), and the mixture was stirred 1 day at 70 °C under a nitrogen atmosphere. The solution was filtered to remove the small amount of solid impurities. After the solvent was removed, the complex was triturated in hexane to obtain a blue solid (1.18 g, 85%).

A Typical Procedure for Substitution of 2-PhC₆H₄O Ligand with Other Aryloxo Ligand. To a solution of (2-PhC₆H₄O)₃Al·Co(OAc)₂ (0.50 g, 0.70 mmol) in toluene (5 mL) was added *o*-cresol (0.075 g, 0.70 mmol), and then the solution was stirred for 1 day at 70 °C under a nitrogen atmosphere. After the solvent was removed, hexane (2.0 mL) was added to the resulting solid. The solid was collected by filtration and washed with additional hexane (2.0 mL × 3). Removal of hexane from the filtrate gave 2-phenylphenol (0.12 g, 0.70 mmol). Other complexes of (2-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, (4-MeC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂, and (4-*i*PrC₆H₄O)(2-PhC₆H₄O)₂Al·Co(OAc)₂ were prepared by the same method and conditions using the corresponding phenol derivatives. The adduct of (2-MeC₆H₄O)₂(2-PhC₆H₄O)Al·Co(OAc)₂ was prepared by the same method and conditions but adding two equivalents of *o*-cresol.

(2-PhC₆H₄O)Et₂Al. 2-Phenylphenol (0.68 g, 3.97 mmol) solution in toluene (8 mL) was added to a solution of Et₃Al (0.45 g, 3.97 mmol) in toluene (2 mL). The compound was used without purification as an activator. ¹H NMR (600 MHz, C₆D₆) δ 7.43 (dd, *J* = 1.6, 8.4 Hz, 2H, CH), 7.28 (dt, *J* = 2.0, 6.8 Hz, 2H, CH), 7.20 (d, *J* = 7.6 Hz, 1H, CH), 7.17 (t, *J* = 4.8 Hz, 1H, CH), 7.11 (dd, *J* = 1.6, 7.6 Hz, 1H, CH), 6.78 (dt, *J* = 2.0, 8.0 Hz, 1H), 6.85 (dt, *J* = 1.2, 7.2 Hz, 1H, CH), 0.96 (t, *J* = 8.0 Hz, 6H, CH₃), -0.03 (q, *J* = 8.0 Hz, 4H, CH₂). ¹³C{¹H} NMR (100 MHz, CD₃OD, 298 K) δ 114.90, 138.02, 134.52, 132.32, 130.16, 129.09, 128.77, 124.94, 122.29, 8.89, 0.48.

A Typical Polymerization Procedure. To a stirred solution of (2-PhC₆H₄O)₃Al·Co(OAc)₂ (56 mg, 79 μmol) in toluene (0.80 mL) was added a solution of (2-PhC₆H₄O)AlEt₂ (20 mg, 80 μmol) in toluene (0.20 mL), and then the solution

was stirred for 2 h at room temperature. A bomb reactor (50 mL) was assembled inside a glove box after charging with the activated catalyst solution (11.3 mg, 15.9 μmol , 0.2 mL) and cyclohexane (20 mL). 1,3-Butadiene (~6.70 g) was added, and then the reactor was stirred at 65 °C for 2 h. 2-Propanol (1.0 phm) and 2,6-di-*tert*-butyl-4-methylphenol (1.0 phm) were added to the solution as stabilizers, and then the solvent was evacuated with a rotary evaporator. The polymer was dried under vacuum.

X-ray Structural Determination. The crystallographic measurements were performed at 100 K using a Bruker APEX II CCD-based diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). The reflection data were collected as multi-scan frames with 0.5°/frame and an exposure time of 10 s/frame. Cell parameters were determined and refined by SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were calculated at idealized positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Crystallographic data for (2-PhC₆H₄O)₃Al: C₃₆H₂₇AlO₃, *M* = 1009.45, triclinic, *a* = 11.0291(3), *b* = 11.0919(3), *c* = 12.9605(4) Å, $\alpha = 75.495(2)$, $\beta = 77.308(2)$, $\gamma = 65.6400(10)^\circ$, *V* = 1386.08(7) Å³, *T* = 100 (2), space group *P*-1, *Z* = 2, 4866 reflections measured, 643 unique. The final *wR*₂ was 0.1151 (all data). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-888641).

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