

Polymerization of *t*-Butyl Vinyl Ether Mediated by an Aluminum Lewis Acid–TrF System and Its Complex Structure–Tacticity Correlation

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A variety of aluminum (aryloxide)s were used with triphenylmethyl fluoride (TrF) initiator for the isoselective cationic polymerization of *t*-butyl vinyl ether. This contribution discusses the relationship between polymer tacticity and counteranion structure, which changed according to the bulkiness, strength and chirality of the Lewis acid combined with TrF so as to make the ionic pair more interactive in the polymerization process. Newly developed organoaluminum activators, **15** and **22**, showed *mm* = 55–57%, which is a more than 10% increase in *mm* compared with achiral aluminum compounds.

Sequential 1,3-polyol fragments are often encountered in naturally occurring complex molecules.[1] In both biological systems and material science, stereocontrol of the fundamental structure represented by poly(vinyl alcohol) (PVA) and its behavior in polar media have attracted a great deal of attention in the field of advanced materials.[2] Over the past four decades, methods for synthesizing PVA have focused on radical polymerization of vinyl acetates and have provided efficient routes to syndiotact-rich PVA due to the generally inexpensive monomers, easy conversion of precursors into PVA by saponification, and industrial feasibility.[3] On the other hand, among a myriad of reports on cationic polymerization of alkyl vinyl ethers, we are intrigued about why $Et_2O{\cdot}BF_3$ can best polymerize *t*-butyl vinyl ether in an isoselective manner under optimal conditions.[2,4,5] Early studies by two research groups, Higashimura et al. and Kunitake et al. , concluded that a small ionic radius for the counter anion and use of non-polar solvent enhanced the isotactic index. This trend is somewhat different from that followed by other vinyl ether monomers such as isobutyl vinyl ether.[5] To gain an insight into selective chain-growth and to further improve stereoregularity, we hypothesized that a tightly coordinated ionic pair or reactive dormant species could be achieved by the proper choice of a bridging atom and a Lewis acid, and that the course of carbon–carbon bond propagation would be substantially reflected by the coordination sphere of the Lewis acid component linked with the termini. Very recently, a similar approach has been presented by Sawamoto and co-workers in the polymerization of isobutyl vinyl ether effected by chloride initiator/$(ArO)_2TiCl_2$/2,6-di-*t*-butyl-4-methylpyridine (DTBMP) systems.[6] Herein we discuss the relationship between polymerization activity/tacticity and counter anion structure created by a range of chiral as well as achiral aluminum-based Lewis acids.[7]

Results and Discussion

I. Cationic Polymerization by Achiral Fluorinated Initiator. A. Comparison of Boron- and Aluminum-Based Lewis Acid Activators. First, we investigated the cationic polymerization of *t*-butyl vinyl ether catalyzed by well-established boron and aluminum Lewis acids in the presence of a relatively stable triphenylmethyl halide (TrX) initiator. In the absence of any cation sources, trace contaminants in the reaction vessel and some decomposed fragments originating from the monomer, activators, or their ligand molecules can initiate polymerization. In contrast, a trityl cation can unambiguously function as an efficient initiator for the formation of the first carbon–carbon bond with a monomer.[5] We primarily focused on quite fundamental information such as the appropriate size for a halogen atom to link an oxonium cation and Lewis acid and how bulky Lewis acid activators can relieve complete dissociation of an ionic pair or provide a similar trend of poor stereoregularity, as has been observed in halogenated or polar media.[4b] Polymerization data are shown in Table 1; these results clearly demonstrate that a non-trivial fluorine-stabilizing effect enhances or preserves isotact stereoregularity under the given polymerization conditions (particularly entry 3 vs 4). In the area of homogeneous Ziegler catalysis, Marks and co-workers reported that tris(perfluoroaryl)borane and aluminum activators had a significant counter anion effect on the predominant formation of monomeric or dimeric zirconocenium ions.[8] The strong steric encumbrance for cation–anion interaction exemplified by $B(C_{12}F_9)_3$, ATPH, and ATPH-Br activators decreases *mm* ratios from those seen with $B(C_6F_5)_3$, MAD, and MABR, respectively. Simple organoaluminums such as $AlMe_3$ and Et_2AlF have completely different tendencies with regard to tacticity. The solid-state structures of AlR_3 (R = Me, Et) and fluoride ion were studied by Natta and Atwood on the basis of diffraction analysis. They reported an anionic dinuclear complex structure with colinearity among Al–F–Al atoms (Chart 1).[9] This irregular but interesting counter anion structure can be considered in the case of TrF/$AlMe_3$ and would allow a discrete ionic pair, resulting in active and atactic polymerization. Unlike $AlMe_3$, Et_2AlF is known to exist as a tetrameric complex in solution: due to intrinsic viscosity, the structure is esti-

Table 1. Polymerization of *t*-Butyl Vinyl Ether by Boron or Aluminum-Based Initiator [a)]

Entry	Initiator	Conditions °C, h	Yield[b)] %	*mm*/*mr*/*rr*[c)]
1	$Et_2O{\cdot}BF_3$	−78, 4	90	63:30:7
2	$TrBF_4$	−78, 1	82	65:28:7
3	TrCl-$B(C_6F_5)_3$	−78, 2	92	atactic
4	TrF-$B(C_6F_5)_3$	−78, 0.5	87	44:39:17
5	TrCl-$B(C_{12}F_9)_3$	−78, 0.5	95	atactic
6	MAD	−78, 1	15	atactic
7	MABR	−78, 1	75	atactic
8	TrF-MAD	−78, 0.5	85	43:42:15
9	TrF-MABR	−78, 0.5	93	42:42:16
10	TrF-ATPH	−78–25, 10	29	38:41:21
11	TrF-ATPH-Br	−78, 0.5	90	25:46:29
12	TrF-$AlMe_3$	−78, 1	74	33:44:23
13	TrF-$AlEt_2F$	−78, 0.5	77	49:37:14
14	TrF-$Al(C_6F_5)_3$	−78, 0.5	81	42:44:14

a) All polymerizations were carried out in toluene under an argon atomosphere as follows: solvent 10 mL; initiator = 0.10 mmol; monomer = 10.0 mmol. b) MeOH-insoluble fraction. c) Estimated by ^{13}C NMR measurement.

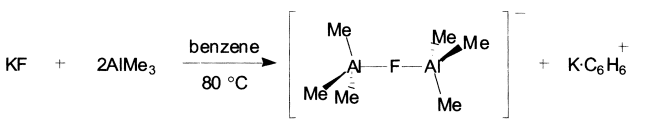


Chart 1.

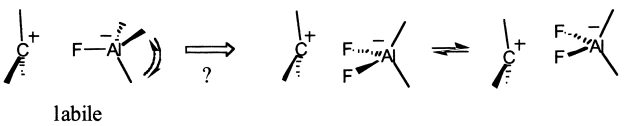


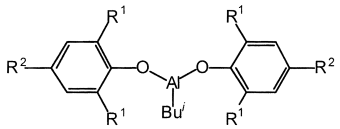
Chart 2.

mated to be polymeric or more crowded than anticipated from the formula.[10] Furthermore, the additional fluorine and possible formation of highly fluorinated aluminums Tr-F-AlF_nEt_{3-n} by disproportionation, in spite of insoluble and almost inactive AlF_3, can play a crucial role in increasing activity and isotacticity, as seen in entries 1 and 2. The fact that a small fluorine atom emerged as the best choice from the high affinity of B-F and Al-F, based on bond-strength data in diatomic molecules, suggests the formation of an active and rather compact ionic pair even with the use of bulkier Lewis acids.[11]

B. Reaction between Bis(aryloxy)aluminum Hydride or Isobutyl and Trityl Fluoride: Cationic Polymerization Mediated by the Resulting Complexes. Next, we examined the modification of an aluminum Lewis acid–TrF system. Olah and co-workers recently reported that some carbocations can be stabilized by apically bound fluoride ions within a distorted trigonal bipyramidal structure.[12,13] The above proposed model of tight coordination between a boron or aluminum metal center and a fluorine atom, and stabilization of the carbocation/oxonium ion by fluorine throughout the polymerization reaction, can be further extended to the generation of difluoroaluminate counter anions, which would hopefully enable divalent equilibration–stabilization toward the counter cation and possibly rotation of the ligand on aluminum (Chart 2).

In light of the slight carbonyl alkylating ability of $(ArO)_2Al$-R,[14] reductive cleavage of the carbon–fluorine bond of TrF should be considered for the formation of $(ArO)_2Al$-F; ideally, 2 molar amounts of TrF could complete the direct production of difluoroaluminates, with a general formula of $Tr^+[\mu\text{-}F_2Al(OAr)_2]^-$. Two types of reducing aluminum precursors, $(ArO)_2AlH$ and $(ArO)_2AlBu^i$, were synthesized according to the methods of Barron, Ittel, and Lehmkuhl[15, 16] and their ^1H NMR data are described in Table 2.

Table 2. ^1H NMR Data of $^iBuAl(OAr)_2$ [a)]



12: $(BHT)_2AlBu^i$
13: $(2,4,6\text{-}^tBu_3C_6H_2O)_2AlBu^i$
14: $(2,6\text{-}Ph_2C_6H_3O)_2AlBu^i$

R_3Al	^iBu group CH_2	CH	CH_3
$^iBu_3Al$	0.25	1.91	0.98
12[b)]	0.47(d)	1.83(m)	0.77(d)
13	0.42(d)	1.77(m)	0.70(d)
14	−1.40(d)	0.62(m)	0.34(d)

a) Measured in C_6D_6 at r.t.; b) Identical with literature data.[16]

NMR-scale reactions of $(BHT)_2AlH{\cdot}OEt_2$ or $(BHT)_2AlBu^i$ with 1 or 2 molar amounts of TrF were performed in C_6D_6 at room temperature. In each case, a colorless solution of aluminum bis(aryloxide) turned to a dark brownish suspension upon the addition of TrF. In a stoichiometric reaction of $(BHT)_2AlH{\cdot}OEt_2$ and TrF, the ^1H NMR spectrum obtained clearly indicated not only resonance peaks reminiscent of $(BHT)_2AlH{\cdot}OEt_2$, and aromatic proton peaks based on a triphenylmethyl group, but also new three peaks at 5.41, 3.26, and

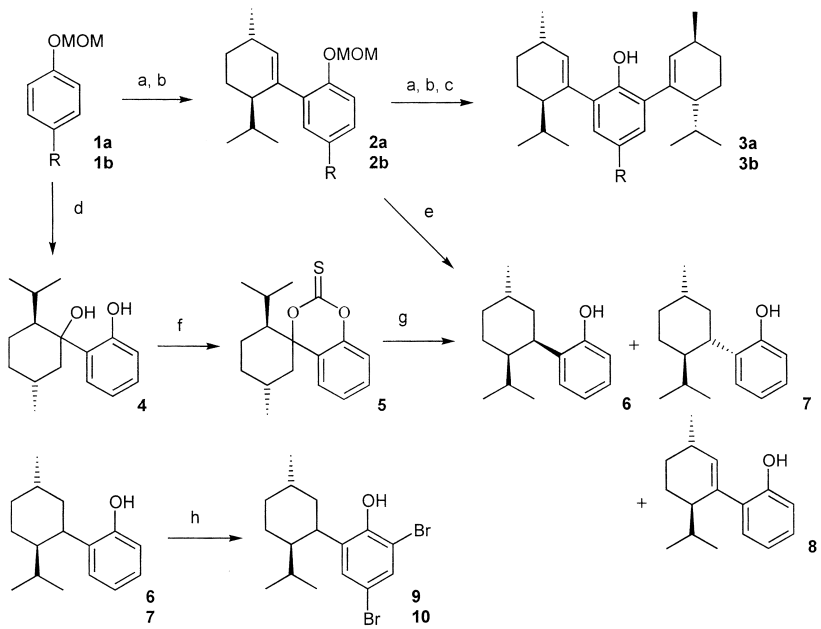
Table 3. Polymerization of *t*-Butyl Vinyl Ether Initiated by TrF-$(ArO)_2AlR$ (2:1) System[a)]

Entry	$(ArO)_2AlR$	Conditions °C, h	Yield[b)] %	M_n[c)] $\times 10^{-4}$	M_w/M_n[c)]	*mm*/*mr*/*rr*[d)]
1	$(BHT)_2AlH{\cdot}OEt_2$	−78, 12	64	7.97	18.3	41:41:18
2		−48, 1	99	6.87	3.94	44:38:18
3	**12**	−78, 0.5	89	4.15	3.56	47:40:13
4	**13**	−78, 0.5	84	3.29	3.78	40:42:18
5	**14**	−78, 0.5	65	3.24	4.17	46:40:14

a) The polymerization was conducted in dry toluene under Ar. TrF:Al:monomer = 2:1:100. b) MeOH insoluble fraction. c) Estimated by GPC using polystyrene standards. d) Determined by ^{13}C NMR analysis.

1.11 ppm, which we assigned to a CH proton of triphenylmethane, CH_2, and CH_3 protons of free ether, respectively, and which were taken as evidence of the expected conversion of TrF to TrH. On the other hand, a 1:2 mixture of aluminum/TrF showed, in addition to the aforementioned resonance signals, some unassignable peaks in the ^1H NMR spectrum. However, regardless of the stoichiometry, the existence of TrF was suggested by ^{19}F NMR measurements; i.e., the original peak (−127.18 ppm) was completely displaced upfield at −163.27 ppm. Similarly, ether-free $(BHT)_2AlBu^i$ was treated with TrF in C_6D_6. Again, the insoluble species was not characterized, but the relatively clean formation of TrH with collapse of the ^{i}Bu group was observed from the ^1H NMR spectra with Al/TrF ratios of both 1:1 and 1:2. As a result of the above spectroscopic data, we predict that the insoluble material in aromatic hydrocarbon solvent includes highly fluorinated aluminate species. In this context, we next examined the polymerization of *t*-butyl vinyl ether using 1:2 mixtures of $(BHT)_2AlH{\cdot}OEt_2$ or various $(ArO)_2AlBu^i$ and TrF. The results of polymerization summarized in Table 3 indicated that, except for entries 1 and 2, the resulting dark solutions of Al/TrF (1:2) display high activity, with *mm* uniformly > 40%. The suppression of decreasing isotacticity can be explained by more efficient cation-stabilization with additional fluorine. These results encouraged us to the use of chiral (aryloxy)aluminums as chiral counter anion components in combination with TrF.

II. Design and Synthesis of New Aluminum Lewis Acids. Binaphthyl-based ligation for the formation of chiral bidentate aluminum Lewis acids is well-documented in organic synthesis.[17] Recent advances in the design of new types of monodentate chiral phenolic ligands have been made with regard to axial chirality of *m*-terphenyl-2′-ols in our laboratory.[18] In this study, we sought to replace *t*-Bu groups with chiral terpenes, represented by menthyl groups. With regard to our synthetic strategy, there are only limited examples of Pd- or Cu-catalyzed cross-coupling between bromopyridine and menthyl Grignard reagent, and these give lower yields.[19] Additionally, as a preliminary experiment, methanesulfonic acid (−)-menthol and (+)-neomenthol esters were exposed to 2-(methoxymethoxy)phenyllithium ether in THF, but no coupling



Scheme 1. a) (1) *n*-BuLi/THF-hexane, 0 °C, (2) $B(OMe)_3$, (3) NH_4Cl aq; b) cat. $[Pd(PPh_3)_4]$, methenyl triflate, Cs_2CO_3/DME–H_2O, 80 °C; c) 3 M HCl aq-THF, reflux; d) (1) *n*-BuLi/THF–hexane, 0 °C, (2) (−)-menthone, −78 °C, (3) 3 M HCl aq-THF, reflux; e) (1) cat. Raney® nickel, H_2 (1 atm)/EtOH, r.t., (2) 3 M HCl aq-THF, reflux; f) 1,1′-thiocarbonyldimidazole/THF, reflux; g) *n*-BuSnH/xylenes, reflux; h) Br_2/CH_2Cl_2, 0 °C–r.t.

products were obtained due to steric hindrance and the lower nucleophilicity relative to anions of cyclopentadiene derivatives.[20] Thus, we began our synthesis of chiral phenols with a menthenyl group at *ortho* positions via repeated Suzuki coupling, as shown in Scheme 1.

Menthenyl triflate, which we chose as a coupling partner due to its physical stability, can be indirectly prepared from (−)-menthone via regioselective formation of the silyl enol ether in an acceptable yield.[21] The triflate was reacted with arylboronic acid at 80 °C in the presence of Cs_2CO_3 base under the influence of catalytic $Pd(PPh_3)_4$ to furnish the desired coupling product **2a**. Furthermore, a boronic acid group was introduced at the 6 position of **2a**, and a second Suzuki coupling was then conducted under the same conditions. Final removal of methoxymethyl (MOM) protection by means of HCl/THF/H_2O gave rise to 2,6-dimenthenylphenol **3a** in an overall yield of 68%. Similarly, the *p*-chloro derivative **3b** was synthesized to be used as a ligand for the chiral counterpart of MABR. Moreover, to obtain new chiral and Lewis acidic aluminum tris(aryloxide)s, dibromophenols **9** and **10** were synthesized via **6** and **7**, respectively. Hydrogenation of **2a** or **8** was carried out using a variety of transition metal catalysts. For **2a**, $Pd(OH)_2$ was the most active, but gave a mixture of neomenthyl and menthyl configurations (86:14). Fortunately, stereoselectivity of $>$ 99% for the neomenthyl configuration was established using a Raney® nickel catalyst, though with lower activity (50% yield; r.t., 96 h). On the other hand, an attempted hydrogenation of **8** was unsuccessful even with promising catalysts: $Pd(OH)_2$, Raney® nickel, PtO_2 and Crabtree's Ir^+. To identify a synthetic route for menthyl stereoselection, we studied the reductive cleavage of **5**, which is simply accessible by anionic coupling of **1a** with (−)-menthone, removal of MOM ether and successive thiocarbonate formation from **4** and 1,1′-thiocarbonyldiimidazole. Dissolving metal-mediated reduction of **5** was highly susceptible to the reaction conditions. For example, Li-naphthalenide was used in THF at −100 °C to give a mixture of **6** and **7** in a yield of 71% (77:23), whereas Li/NH_3, Li/NH_3/*t*-BuOH, and Ba in THF are too active even below at −78 °C and give **4** or **8** as a major product. Our optimization experiments gave moderate menthyl selectivity (62%) attained by *n*-Bu_3SnH reduction in *o*-xylene reflux. The menthyl-major mixture was subjected to recycling preparative HPLC and essentially pure **7** was obtained as a colorless oil. The relatively broad multiple resonance of a benzylic proton at 2.83–2.97 ppm in ^1H NMR would be characteristic of a menthyl configuration, while the benzylic proton of **6** would be observed at 3.52–3.60 ppm. To offset any suspicion regarding the stereochemistry, we obtained a crystal of the *p*-nitrobenzoate ester of stereoisomer **6** and carried out an X-ray diffraction analysis, whereas the ester from **7** is no longer crystalline. Figure 1 shows the ORTEP diagram of dimer molecules of the ester from **6**, which clarifies the absolute configuration and the location of the phenolate moiety axial to the cyclohexane ring.

The reaction of $AlMe_3$ and **3a** was performed in dry hexane or toluene at r.t. under Ar (Scheme 2). The desired air- and

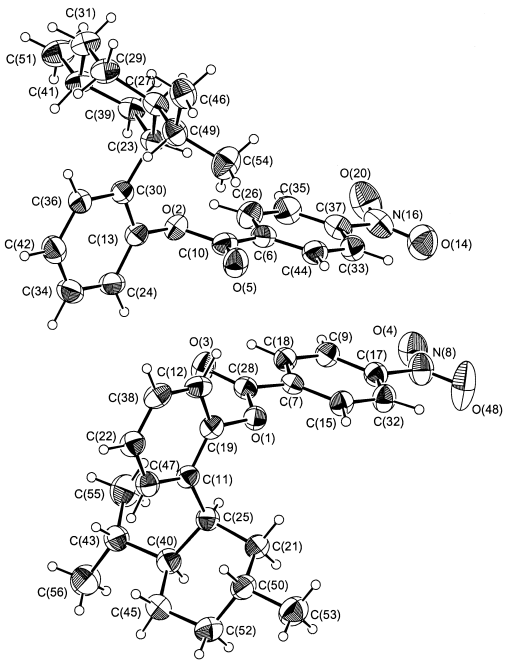
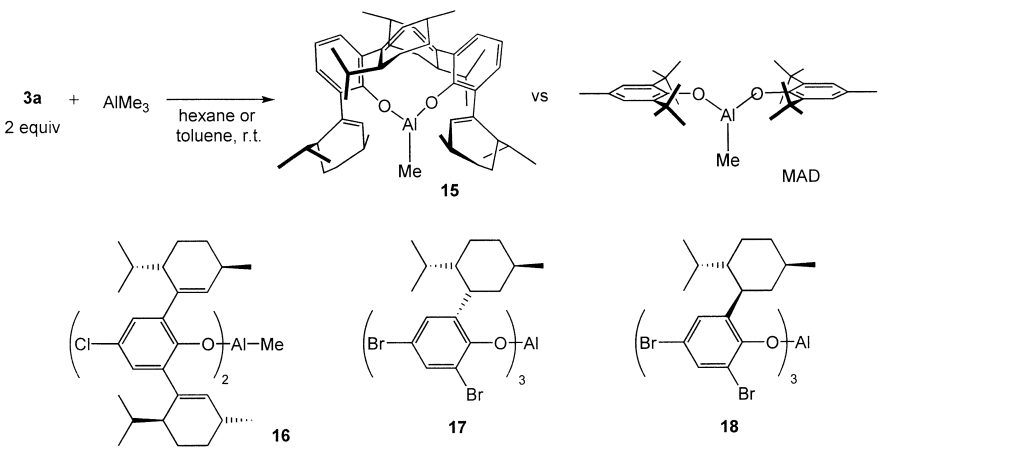


Fig. 1. ORTEP drawing of *o*-neomenthylphenyl *p*-nitrobenzoate derived from **6**.



Scheme 2. New aluminum Lewis acids with chiral aryloxides.

Table 4. Selected Bond Lengths, Bond Angels, and Torsional Angles of **15**

Bond Lengths			
Al(l)–O(2)	1.716(1)	Al(l)–O(0)	1.708(1)
Al(l)–O(26)	1.947(2)	O(2)–C(19)	1.360(2)
O(3)–C(20)	1.365(2)	C(4)–C(7)	1.487(2)
C(8)–C(16)	1.495(2)	C(9)–C(13)	1.488(2)
C(10)–C(11)	1.493(2)	C(4)–C(17)	1.349(2)
C(6)–C(13)	1.339(2)	C(8)–C(27)	1.342(2)
C(10)–C(22)	1.338(2)		
Bond Angels			
O(2)–Al(1)–O(3)	113.6(1)	O(2)–Al(1)–C(26)	123.7(1)
O(3)–Al(1)–C(26)	121.3(1)	Al(1)–O(2)–C(19)	131.0(1)
Al(1)–O(3)–C(20)	132.0(1)	C(7)–C(4)–C(17)	120.2(1)
C(16)–C(8)–C(27)	120.0(2)	C(11)–C(10)–C(22)	120.0(2)
C(6)–C(13)–C(9)	119.1(1)	C(5)–C(4)–C(17)	122.6(1)
C(23)–C(8)–C(27)	123.0(2)	C(22)–C(10)–C(42)	122.5(2)
C(6)–C(13)–C(35)	122.0(1)		
Torsional Angles			
O(3)–Al(1)–O(2)–C(19)	73.9(1)	O(2)–Al(1)–O(3)–C(20)	50.7(1)
C(26)–Al(1)–O(2)–C(19)	−119.3(2)	C(26)–Al(1)–O(3)–C(20)	−116.4(2)
Al(1)–O(2)–C(19)–C(7)	37.5(1)	Al(1)–O(2)–C(19)–C(11)	−144.5(2)
Al(1)–O(3)–C(20)–C(9)	53.0(1)	Al(1)–O(3)–C(20)–C(16)	−128.1(2)
C(17)–C(4)–C(7)–C(19)	−70.2(2)	C(27)–C(8)–C(16)–C(20)	114.2(2)
C(20)–C(9)–C(13)–C(6)	−74.3(2)	C(22)–C(10)–C(11)–C(19)	122.6(2)

a) Bond lengths are given in Å, and angles in °. See Fig. 2 for the numbering.

moisture-sensitive methylaluminum bis(aryloxide) **15** was isolated by recrystallization from saturated hexane solution, and the solid-state structure was characterized by a diffraction study at −80 °C. Selected bond lengths, bond angles, and tortional angles are shown in Table 4. As can be seen in Fig. 2, the characteristic features are as follows: (1) the structure has almost C_2 symmetry in terms of the Al–Me bond, (2) summation of the aluminum bonds indicates coordinative unsaturation of the aluminum center; i.e., aluminum has sp^2 geometry, and (3) all of the menthenyl isopropyl groups are located in the same orientation to each phenolate face, excluding the formation of other isomeric conformers. In comparison with the MAD structure, the steric environment around the aluminum coordination site is fairly sophisticated, with two menthenyl groups in the proximity of the Al–Me bond. Other new aluminum compounds, **16**, **17**, and **18**, were prepared from **3b**, **9**, and **10** in toluene solution, respectively, and used for a polymerization study without any characterization (Scheme 2).

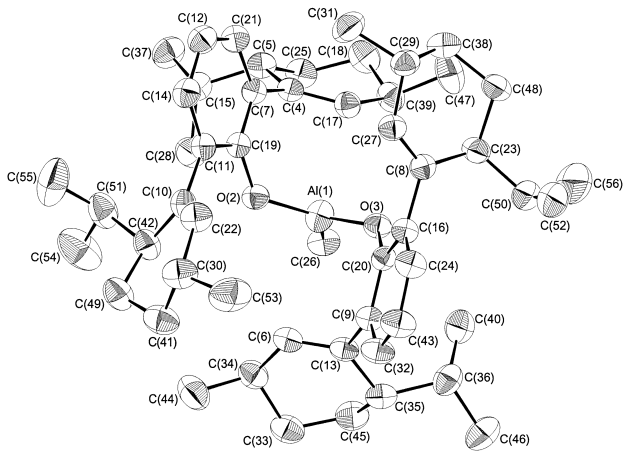
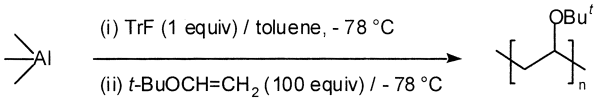


Fig. 2. ORTEP drawing of **15**. All hydrogen atoms are omitted for clarity.

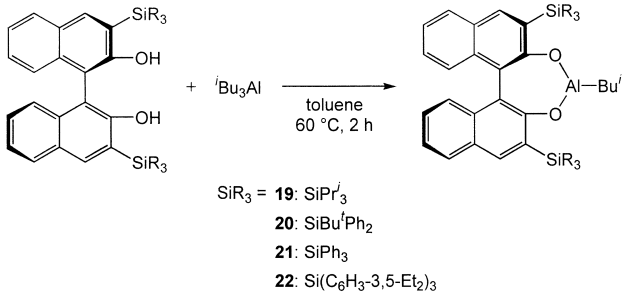
III. Polymerization Using Chiral Aluminum Lewis Acids. A. Polymerization Catalyzed by a Chiral Methylaluminum Bis(aryloxide)–TrF System. As discussed above, we examined chiral aluminum Lewis acids **15**–**18** modified from MAD, MABR, and ATPH-Br with regard to the cationic polymerization. Our preliminary results with methylaluminum binaphtholate derivatives–TrF (1:1) showed that Lewis acids with substantial steric bulk are needed for successful initiation upon activation of C–F bond of the TrF initiator. As shown in Table 1, chiral Lewis acids **15**–**18** were exposed to TrF in dry toluene at −78 °C and the resulting complex was reacted with excess monomer at −78 °C. The results are shown in Table 5. The best *mm* ratio was reproducibly obtained with Entry 1, although the molecular weight distribution was very broad. Other chiral and halogenated Lewis acids **16**–**18** can act as strong activators, to provide atactic polymers. The poly(vinyl ether) obtained in Entry 1 was treated with dry HBr gas in $CHCl_3$ at 0 °C. NMR analysis of the precipitated PVA after neutralization gave similar isotacticity. ^{13}C NMR measurement indicated a high intensity of *mmmm*, as observed

Table 5. Polymerization of *t*-Butyl Vinyl Ether Catalyzed by a Chiral Lewis Acid-TrF[a)]



Entry	Lewis acid	Yield[b)]/%	M_n[c)] $\times 10^{-4}$	M_w/M_n[c)]	*mm*/*mr*/*rr*[d)]
1	**15**	76	9.06	7.56	57:36:7
2	**16**	99	17.40	6.22	32:46:22
3	**17**	97	8.85	2.11	32:44:24
4	**18**	75	9.46	1.79	22:47:31

a) Polymerization was performed at −78 °C for 0.5 h under Ar; b) MeOH insoluble solid; c) Estimated by GPC (polystyrene standards, THF); d) Determined by ^{13}C NMR assay.



Scheme 3. Binaphtholate-based isobutylaluminums.

with $Et_2O{\cdot}BF_3$. At present, no valuable information was obtained from the NMR spectra to elucidate the detailed mechanism of isoselective monomer insertion in the chain-end transition state, but we should consider that the observations in Table 5 are due to the results of chirality matching or mismatching.

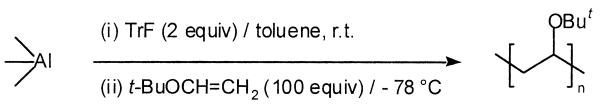
B. Active Cationic Polymerization Mediated by a Binaphthol-Based Isobutylaluminum–TrF (1:2) System. We encountered difficulty in the synthesis and reaction of a chiral isobutyl derivative of **15**. Thus, we attempted to use of isobutylaluminum binaphtholates, which are thought to have more vacant space around aluminum. As for $(BHT)_2AlBu^i$, a variety of 3,3′-disilylated binaphthols were treated with an equimolar amount of $^iBu_3Al$ at 60 °C in toluene to produce **19**–**22** (Scheme 3).

Unlike achiral isobutylaluminums, Lewis acid **20**, for instance, has two unequivalent ^{i}Bu doublet methylene peaks and two singlet methyl peaks in its ^{1}H NMR spectrum. Treatment of Lewis acid solutions with 2 molar amounts of TrF at room temperature followed by the addition of *t*-butyl vinyl ether at −78 °C, resulted in the immediate formation of viscous solutions. After the usual work-up, the desired polymers were isolated and characterized by GPC and ^{13}C NMR analyses. As can be seen in Table 6, Lewis acids **20**–**22** have moderate to good activities, and give isotact-rich polymers with fairly broad M_w/M_n values. It is still unclear why **19** gave only oligomeric material. The higher isotacticity in Entry 4 approaches the result with **15**. The π-electrons of the triarylsilyl groups may play a crucial role in the formation of a sterically more interactive ionic pair within the chain-end (Entry 20 vs 21 and 22).

Conclusion

We have demonstrated that, upon combination with TrF, highly modified/sterically bulky aluminum Lewis acids can enhance isotact-selectivity in the cationic polymerization of *t*-butyl vinyl ether. These results are highly informative for understanding the important roles of fluorine and group 13 Lewis acids, although they somewhat conflict with an earlier finding that larger counteranions tended to decrease the *mm* ratio. Our results indicated that the structure of the whole counteranion as well as the use of a fluoride-based initiator, the number of fluorines and other conditions that are appropriate for minimizing the cation–anion distance, are essential factors in designing highly isoselective activators. Notably, the present results indicated that chiral aluminum Lewis acids, **15** and **22**, are effec-

Table 6. Polymerization of *t*-Butyl Vinyl Ether Mediated by Binaphthol-Based Chiral Alminum Lewis Acid–TrF System[a)]



Entry	Lewis acid	Yield[b)]/%	M_n[c)] $\times 10^{-4}$	M_w/M_n[c)]	*mm*/*mr*/*rr*[d)]
1	**19**	no polym	—	—	—
2	**20**	72	2.84	8.22	44:43:13
3	**21**	74	3.25	11.4	52:37:11
4	**22**	51	4.62	7.40	55:34:11

a) Polymerization was performed at −78 °C for 0.5 h under Ar; b) MeOH insoluble solid; c) Estimated by GPC (polystyrene standards, THF); d) Determined by ^{13}C NMR measurement.

tive activators.

Experimental

All manipulations of oxygen- and moisture-sensitive materials were performed in an argon-filled glovebox or by standard Schlenk techniques unless otherwise specified. Hydrocarbons (pentane, hexane, and toluene), ether solvents, and the monomer (ether, tetrahydrofuran, and *t*-butyl vinyl ether, Aldrich, 98%) were distilled from Na/benzophenone ketyl in the presence or absence of 18-crown-6 before use.

NMR spectra were recorded on either Varian INOVA 500 (FT 500 MHz, ^{1}H; 125 MHz, ^{13}C) or Gemini-300 (FT 300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) instruments. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to internal solvent resonances and are reported relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external $CF_3C_6H_5$ (−64 ppm). Oxygen- and moisture-sensitive NMR samples were prepared in a glovebox and sealed with Teflon caps. Elemental analyses were performed at the School of Agriculture, Nagoya University. For ^{13}C NMR analyses of poly(vinyl ether) microstructures, 100–150 mg of polymer samples were completely dissolved in C_6D_6 (0.6 mL) with a heat gun in a 5-mm NMR tube, and the samples were transferred to the NMR spectrometer with the probehead preequilibrated at 70 °C. A 45° pulse width and 1.30 s acquisition time were used with a pulse delay of 5.0 s. Triad signals were assigned according to literature criteria,[22] and the stereoregularities of some isotact-rich samples were further confirmed by ^{13}C NMR analyses of PVA (10% in DMSO-d_6 at 50 °C with an acquisition time and a pulse delay of 1.64 s and 1.80 s, respectively) obtained after cleavage of ethers.[7b,23] Infrared (IR) spectra were measured on a Shimadzu FTIR-9100 spectrometer. Separation of 2-menthyl- and 2-neomenthylphenols was achieved by recycling preparative HPLC on a Japan Analytical Industry Co., Ltd. LC-908 equipped with an RI-5 detector and a JAIGEL-SIL, s-043-15 column (250 mm length × 20 mm inner diameter). Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. Reaction products of small moisture-insensitive molecules were purified by flash chromatography on silica gel E. Merck 9385 or silica gel 60 extra pure. Analytical thin-layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Gel permeation chromatography (GPC) analyses of polymer samples were carried out with a JASCO PU-980 pump and a JASCO RI-930 detector using Tosoh TSKgel GMH_{HR}-H and TSKgel G3000HHR (300 mm length × 7.8 mm inner diameter) in series. Solutions of polymer samples dissolved in THF were filtered through a Dismic-13JP PTFE 0.5 μm filter. All GPC data were analyzed using JASCO Borwin Ver. 1.21 software. The molecular weight calibration curve was obtained using standard polystyrenes.

Me_3Al, $^iBu_3Al$, Et_2AlF, and $B(C_6F_5)_3$ were provided by Toso-Akzo Chem. Co. Ltd., Japan. $(BHT)_2AlH{\cdot}OEt_2$,[15] $(BHT)_2AlMe$ (MAD),[24] (4-Br-2,6-$^tBu_2C_6H_2O)_2AlMe$ (MABR),[25] $(2,6\text{-}Ph_2C_6H_3O)_3Al$ (ATPH),[26] (4-Br-2,6-$Ph_2C_6H_3O)_3Al$ (ATPH-Br),[27] $(BHT)_2AlBu^i$,[16] $(2,4,6\text{-}^tBu_3C_6H_2O)_2AlBu^i$,[16] $B(C_{12}F_9)_3$,[8a,c] $Al(C_6F_5)_3$,[28] (R)-(+)-3,3′-$(R_3Si)_2$-1,1′-bi-2-naphthol (R = *i*Pr, Ph; R_3Si = ^{t}BuPh_2Si),[29] and (*R*)-(+)-3,3′-bis[tris(3,5-diethylphenyl)silyl]-1,1′-bi-2-naphthol[30] were prepared as described in the literature. All other chemicals were purchased from commercial suppliers.

Preparation of Trityl Fluoride (TrF). Several methods have been reported for the synthesis of TrF,[31] most of which produce much more crystalline triphenylmethanol (TrOH) as a residual starting material or a byproduct; this disturbs the crystallization/purification of TrF. Therefore, dimethylaminosulfer trifluoride (DAST) was used as a fluorinating agent to complete the conversion. To a solution of TrOH (5.0 mmol, 1.3 g) in CH_2Cl_2 (15 mL) was added DAST (5 mmol, 0.66 mL) via a plastic disposable syringe at −78 °C, and the mixture was stirred overnight while being allowed to warm to room temperature. The resulting mixture was poured into a separatory funnel containing water. Extraction with ether and concentration of the organic extract gave a yellowish solid, which was washed with ice water and then dissolved in hot hexane. Analytically pure TrF was obtained by crystallization from decanted hexane solution (1.18 g, 90%). 282 MHz ^{19}F NMR ($CDCl_3$) δ − 127.21 (s).

Preparation of Menthenyl Triflate. Synthesis of the title compound has been reported in the literature, but we could not reproduce the reported good yield.[32] We mainly used the following amine-free procedure.[33] To a THF solution (20 mL) of trimethylsilyl enol ether (17 mmol, 3.9 g) derived from (−)-methone in 87% yield was added a solution of *n*-BuLi (1.6 M in hexane, 12.5 mL) at −78 °C under an argon atmosphere. After this mixture was stirred at −78 °C for 0.5 h and at 0 °C for 1.5 h, a THF solution (15 mL) of *N*-phenyl bis(trifluoromethanesulfoneimide) (20 mmol, 7.15 g) was added dropwise. The reaction was continued overnight, while slowly warming to room temperature, and then quenched by addition of 1 M HCl aq. Extraction with ether, drying of the organic layer, concentration on a rotary evaporator, and chromatographic purification of the residue using hexane as an eluant gave the corresponding enol triflate as a colorless oil (3.99 g, 82%). This material is stereochemically pure and, unlike menthenyl iodide and bromide, is stable at room temperature under light. 300 MHz ^{1}H NMR ($CDCl_3$) δ 5.64 (1H, br s, CH=C), 2.42–2.53 (1H, m, CH), 2.26–2.41 (1H, m, CH), 2.07–2.22 (1H, m, CH), 1.75–1.88 (2H, m, CH,), 1.34–1.50 (1H, m, CH), 1.06–1.25 (1H, m, CH), 1.04 (3H, d, J = 7.2 Hz, CH_3), 0.95 (3H, d, J = 7.2 Hz, CH_3), 0.82 (3H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 151.80, 125.93, 118.58 (J_{C-F} = 320 Hz), 43.08, 30.62, 29.95, 27.30, 22.44, 21.19, 19.78, 16.27; 282 MHz ^{19}F NMR ($CDCl_3$) δ −74.99.

Synthesis of (+)-2-Menthenylphenyl Methoxymethyl Ether (2a). To a solution of **1a** (20 mmol, 2.8 g) in THF (40 mL) was added *n*-BuLi (1.6 M in hexane, 13 mL) at 0 °C under Ar. The suspension was stirred at 0 °C for 2 h. $B(OMe)_3$ (30 mmol, 3.4 mL) was added in one portion and the resulting clear solution was stirred for 1 h, and then for another 1 h after the addition of sat. NH_4Cl aq. The product was extracted with EtOAc (2 times) and the combined extracts were dried over $MgSO_4$. Solvents were removed by evaporation and in vacuo to give a mixture of the desired arylboronic and diarylborinic acids, which can be used without further purification. They should not be allowed to stand longer at ambient temperature because of the slow deprotection of methoxymethyl ether. The mixture was dissolved in DME–H_2O (50 mL/8 mL). Menthenyl triflate (15 mmol, 4.3 g) and Cs_2CO_3 (18 mmol, 5.9 g) were added and the reaction solution was degassed and filled with argon, and [$Pd(PPh_3)_4$] (0.1 mmol, 116 mg) was then added. The mixture was heated at 80 °C for 12 h. After the usual work-up and purification by column chromatography on silica gel (EtOAc/hexane = 1:20), the desired coupling product was obtained (4.1 g, 99.6%). $[\alpha]_D^{29}$ +58.4 (*c* 0.56, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.12–7.20 (2H, m, Ar–H), 6.92–7.04 (2H, m, Ar–H), 5.55 (1H, dd, J = 1.8, 3.6 Hz, C=CH), 5.19 (1H, d, J_{gem} = 6.6 Hz, OC*H*HO), 5.13 (1H, d, J_{gem} = 6.6 Hz, OCH*H*O), 3.48 (3H, s, OCH_3), 2.82–2.91 (1H, m, CHC=C), 2.17–2.32 (1H, m, CHC=C), 1.83–1.93 (1H, m, CH), 1.72–1.83 (1H, m, CH),

1.58–1.69 (1H, m, CH), 1.31–1.46 (1H, m, CH), 1.13–1.30 (1H, m, CH), 0.99 (3H, d, J = 6.9 Hz, CH_3), 0.85 (3H, d, J = 6.9 Hz, CH_3), 0.58 (3H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 154.17, 141.06, 135.52, 133.58, 130.38, 127.41, 121.84, 114.17, 94.42, 55.89, 42.34, 31.58, 31.51, 28.62, 22.11, 21.72, 20.93, 15.75; IR (liquid film) 2955, 1597, 1487, 1244, 1154, 1078, 1005, 924, 864, 752 cm^{-1}; Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55 %. Found: C, 78.92; H, 9.50%.

Synthesis of (+)-2,6-Dimenthenylphenol (3a). A second attempt to introduce a menthenyl group into the 6 position of **2a** was made in the same manner as described above through the formation of boronic and borinic acids followed by Suzuki coupling with menthenyl triflate. The obtained methoxymethyl ether was deprotected in 3 M HCl/THF/H_2O at reflux to give the corresponding phenol (68%). mp 98–101 °C; $[\alpha]_D^{29}$ +91.9 (c 0.53, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 9.46 (2H, d, J = 7.5 Hz, Ar-H), 6.80 (1H, t, J = 7.5 Hz, Ar-H), 5.95 (1H, s, OH), 5.68 (2H, s, C=CH), 2.63–2.76 (2H, m, CH-C=C), 2.20–2.36 (2H, m, CH-C=C), 1.75–1.96 (4H, m, CH), 1.57–1.72 (2H, m, CH), 1.36–1.51 (2H, m, CH), 1.15–1.31 (2H, m, CH), 1.01 (6H, d, J = 6.9 Hz, CH_3), 0.84 (6H, d, J = 6.9 Hz, CH_3), 0.59 (6H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 148.80, 139.48, 135.75, 128.88, 127.16, 119.38, 42.93, 31.31, 28.51, 21.92, 21.78, 20.90, 15.96; IR (KBr) 3499, 2955, 1603, 1439, 1331, 1262, 1225, 1090, 1021, 795, 749 cm^{-1}; Anal. Calcd for $C_{26}H_{38}O$: C, 85.19; H, 10.45%. Found: C, 85.08; H, 10.53%.

Synthesis of (+)-4-Chloro-2,6-dimenthenylphenol (3b). The *p*-chloro analogue was synthesized from **1b** by repeated boronic acid formation followed by a cross-coupling reaction and final removal of a methoxymethyl group in the same manner as shown for **3a** (51%).

4-Chloro-2-menthenylphenyl Methoxymethyl Ether (2b): 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.10–7.14 (2H, m, Ar-H), 6.96 (1H, d, J = 9.3 Hz, Ar-H), 5.57 (1H, br, C=CH), 5.15 (1H, d, J = 6.6 Hz, Ar-O-C*H*H), 5.10 (1H, d, J = 6.6 Hz, Ar-O-CH*H*), 3.46 (3H, s, OCH_3), 2.77–2.88 (1H, m, CH-C(Ar)=C), 2.15–2.30 (1H, m, CH-C=C-Ar), 1.83–1.93 (1H, m, C*H*-C(Me)-C=C), 1.73–1.82 (1H, C*H*H-C-C(Me)-C), 1.53–1.70 (1H, m, $CHMe_2$), 1.30–1.45 (1H, m, CH*H*-C-C(Me)-C), 1.10–1.25 (1H, m, C*H*H-C(Me)-C=C), 1.00 (3H, d, J = 7.2 Hz, C*H*$_3$-CHC=C), 0.86 (3H, d, J = 6.9 Hz, CH_3), 0.59 (3H, d, J = 6.6 Hz, CH_3). **3b**: $[\alpha]_D^{29}$ +101.2 (c 0.57, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 6.92 (2H, s, Ar-H), 5.88 (1H, s, OH), 5.68 (2H, s, C=CH), 2.60–2.71 (2H, m, CH-C=C), 2.18–2.34 (2H, m, CH-C=C), 1.75–1.95 (4H, m, CH), 1.53–1.70 (2H, m, CH), 1.35–1.51 (2H, m, CH), 1.13–1.34 (2H, m, CH), 1.01 (6H, d, J = 6.9 Hz, CH_3), 0.85 (6H, d, J = 6.9 Hz, CH_3), 0.60 (6H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR (C_6D_6) δ 148.94, 139.85, 137.41, 131.75, 127.86, 125.63, 43.79, 32.15, 29.57, 22.69, 22.62, 21.69, 16.87; IR (KBr) 3484, 2959, 1595, 1435, 1325, 1221, 1130, 965, 872, 689 cm^{-1}; Anal. Calcd for $C_{26}H_{37}ClO$: C, 77.87; H, 9.30%. Found: C, 77.87; H, 9.49%.

(+)-Thiocarbonate (5): To a solution of **1a** (10 mmol, 1.3 mL) in THF (20 mL) was added *n*-BuLi (1.6 M in hexane, 6.25 mL) at 0 °C under Ar. The suspension was stirred at 0 °C for 2 h. (−)-Menthone (9.3 mmol, 1.44 mL) was added at −78 °C. After 10 min, the cooling bath was removed to allow the mixture to warm to room temperature. Next, 3 M HCl was added and the resulting mixture was refluxed overnight to complete cleavage of MOM ether. After acidic work-up, the corresponding crude diol **4** was obtained. 300 MHz ^{1}H NMR ($CDCl_3$) δ 9.79 (1H, s, Ar-OH), 7.12 (1H, td, J = 7.5, 1.5 Hz, Ar-H), 6.97 (1H, dd, J = 7.8, 1.5 Hz, Ar-H), 6.77–6.87 (2H, m, 2Ar-H), 2.48 (1H, s, OH), 2.00–2.09 (1H, m, CH), 1.82–1.96 (2H, m, 2CH), 1.64–1.79 (3H, m, 3CH), 1.35–1.58 (2H, m, 2CH), 1.04 (1H, qd, J = 12.6, 3.6 Hz, CH), 0.93 (3H, d, J = 6.3 Hz, CH_3), 0.90 (3H, d, J = 6.9 Hz, CH_3), 0.84 (3H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 156.71, 128.81, 128.14, 125.93, 119.24, 117.67, 83.83, 49.89, 49.69, 34.53, 28.04, 26.64, 23.69, 21.92, 20.70, 18.61. Compound **4** was heated with 1,1′-thiocarbonyldiimidazole in THF overnight. Usual work-up and chromatographic purification (EtOAc/hexane = 1:20) gave the desired cyclic thiocarbonate **5** as a crystalline solid (1.31 g, overall yield: 45%). $[\alpha]_D^{29}$ +2.85 (c 0.57, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.35 (1H, m, Ar-H), 7.24 (1H, m, Ar-H), 7.15 (1H, d, J = 8.4 Hz, Ar-H), 7.09 (1H, d, J = 7.5 Hz, Ar-H), 1.68–2.19 (7H, m, 7CH), 1.30 (1H, dd, J = 14.4, 12.0 Hz, CH), 0.97–1.15 (1H, m, CH), 0.85 (3H, d, J = 6.0 Hz, CH_3), 0.89 (3H, d, J = 6.9 Hz, CH_3), 0.84 (3H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 184.33, 146.79, 129.06, 125.77, 124.13, 123.07, 115.50, 91.32, 48.60, 47.36, 33.77, 26.75, 26.56, 23.24, 21.30, 19.97, 17.14; IR (KBr) 2961, 1489, 1374, 1323, 1283, 1235, 1217, 1128, 911, 770 cm^{-1}; Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64%. Found: C, 70.31; H, 7.55%.

***n*-Bu$_3$SnH Reduction of 5.** To a reflux solution of *n*-Bu_3SnH in *o*-xylene was added an *o*-xylene solution of **5** (0.5 mmol, 145 mg) over 1 h. After the addition of **5**, the reaction was allowed to continue for an additional 30 h. The solution was cooled, washed with ice water and extracted with ether. The organic layer was dried over $MgSO_4$, and filtered through a celite pad. Evaporation of solvents and purification by preparative HPLC (EtOAc/H = 1:100) furnished **6**, **7**, and **8** in respective yields of 53, 32, and 20%. The absolute configurations of **6** and **7** were confirmed by a diffraction study of *p*-nitrobenzoate ester of **6**. The ester was recrystallized from EtOH to give a cubic crystal suitable for X-ray analysis.

(+)-2-Neomenthylphenol (6). $[\alpha]_D^{29}$ +41.2 (c 0.51, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.48 (1H, dd, J = 1.5, 7.5 Hz, Ar-H), 7.06 (1H, td, J = 7.8, 1.5 Hz, Ar-H), 6.83 (1H, t, J = 7.8 Hz, Ar-H), 6.76 (1H, dd, J = 1.5, 7.8 Hz, Ar-H), 4.66 (1H, s, OH), 3.56 (1H, td, J = 5.4, 2.4 Hz, ArCH), 1.81–1.98 (2H, m, 2CH), 1.65–1.77 (2H, m, 2CH), 1.41–1.61 (2H, m, 2CH), 1.23–1.39 (2H, m, 2CH), 1.01 (1H, qd, J = 12.3, 1.5 Hz, CH), 0.89 (3H, d, J = 6.6 Hz, CH_3), 0.80 (3H, d, J = 6.3 Hz, CH_3), 0.72 (3H, d, J = 6.3 Hz, CH_3). 75 MHz ^{13}C NMR ($CDCl_3$) δ 153.21, 131.15, 130.57, 126.30, 119.66, 115.40, 46.72, 41.00, 35.28, 32.88, 29.91, 27.35, 25.88, 22.64, 21.42, 21.13; IR (liquid film) 3100–3800, 2800–3030, 1607, 1586, 1385, 1269, 1098, 936, 820, 750 cm^{-1}; Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%. Found: C, 82.65; H, 10.13%.

(−)-2-Menthylphenol (7). $[\alpha]_D^{29}$ −48.8 (c 0.40, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.14 (1H, d, J = 7.5 Hz, Ar-H), 7.04 (1H, t, J = 7.5 Hz, Ar-H), 6.91 (1H, t, J = 7.5 Hz, Ar-H), 6.74 (1H, d, J = 7.5 Hz, Ar-H), 4.60 (1H, s, OH), 2.90 (1H, m, ArCH), 1.69–1.86 (3H, m, 3CH), 1.40–1.60 (3H, m, 3CH), 0.98–1.28 (3H, m, 3CH), 0.89 (3H, d, J = 6.3 Hz, CH_3), 0.81 (3H, d, J = 6.9 Hz, CH_3), 0.69 (3H, d, J = 6.6 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 152.77, 132.21, 127.41, 126.17, 121.03, 115.25, 46.77, 44.56, 38.19, 35.27, 33.21, 27.53, 24.65, 22.47, 21.62, 15.77; IR (liquid film) 3100-3700, 2800–3030, 1590, 1456, 1370, 1267, 1086, 938, 833, 750 cm^{-1}; Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41%. Found: C, 82.67; H, 9.79%.

2-Menthenylphenol (8). 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.12 (1H, t, J = 7.5 Hz, Ar-H), 7.04 (1H, d, J = 7.5 Hz, Ar-H), 6.92 (1H, d, J = 7.5 Hz, Ar-H), 6.68 (1H, d, J = 7.5 Hz, Ar-H), 5.73 (1H, br s, C=CH), 5.64 (1H, s, OH), 2.50–2.62 (1H, m, C=C-CH),

2.23–2.39 (1H, m, C=C-CH), 1.79–1.98 (2H, m, 2CH), 1.66–1.79 (1H, m, CH), 1.40–1.57 (1H, m, CH), 1.14–1.30 (1H, m, CH), 1.01 (3H, d, J = 7.2 Hz, CH_3), 0.85 (3H, d, J = 6.9 Hz, CH_3), 0.63 (3H, d, J = 6.6 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 152.15, 137.90, 136.70, 128.23, 128.08, 127.68, 119.88, 115.41, 43.39, 31.05, 31.01, 28.39, 21.78, 21.59, 20.95, 16.13

Hydrogenation of 2a. Compound **6** can be stereoselectively obtained by hydrogenation and successive deprotection. A suspension of **2a** (0.52 mmol, 142 mg) and Raney® nickel (H_2O dispersion, 50 mg) in EtOH (10 mL) was stirred at room temperature under hydrogen (1 atm). After being stirred for 96 h, the mixture was filtered through a celite pad. The filtrate was concentrated and the residue was subjected to column chromatography on silica gel (EtOAc/hexane = 1:10) to give the corresponding MOM ether (72 mg, 50%). The stereoselectivity was determined by ^{1}H NMR analysis to be > 99:1. 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.50 (1H, dd, J = 1.2, 7.8 Hz, Ar-H), 7.06–7.16 (2H, m, Ar-H), 6.89 (1H, dt, J = 1.8, 7.2 Hz, Ar-H), 5.22 (1H, d, J = 6.6 Hz, OC*H*HO), 5.19 (1H, d, J = 6.6 Hz, OCH*H*O), 3.71–3.78 (1H, m, Ar-CH), 3.49 (3H, s, OCH_3), 1.81–1.97 (2H, m, CH), 1.22–1.75 (6H, m, 6CH), 1.00 (1H, dq, J = 4.8, 12.9 Hz, CH), 0.88 (3H, d, J = 6.3 Hz, CH_3), 0.78 (3H, d, J = 6.3 Hz, CH_3), 0.70 (3H, d, J = 6.3 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 154.91, 134.12, 130.29, 126.20, 120.36, 113.87, 94.31, 55.84, 46.78, 41.37, 35.38, 32.50, 29.92, 27.34, 25.81, 22.70, 21.40, 21.17

(+)-2,4-Dibromo-6-neomenthylphenol (9). Compound **6** (0.87 mmol, 202 mg) was treated by the dropwise addition of bromine (2.2 mmol, 0.11 mL) in CH_2Cl_2 at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was diluted with ether, poured into a separatory funnel, and washed with brine. The organic extract was then dried over $MgSO_4$. After filtration and evaporation of the solvents, the residue was subjected to chromatographic purification (silica gel, hexane only) to give dibromophenol **9** as a white solid (216 mg, 64%). $[\alpha]_D^{29}$ +27.3 (*c* 0.49, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.53 (1H, d, J = 2.4 Hz, Ar-H), 7.44 (1H, d, J = 2.4 Hz, Ar-H), 5.61 (1H, s, OH), 3.66 (1H, td, J = 5.1, 2.1 Hz, ArCH), 1.82–1.98 (2H, m, CH), 1.62–1.72 (1H, m, CH), 1.22–1.52 (5H, m, CH), 0.90–1.08 (1H, m, CH), 0.90 (3H, d, J = 6.6 Hz, CH_3), 0.81 (3H, d, J = 6.6 Hz, CH_3), 0.70 (3H, d, J = 6.3 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 149.20, 134.80, 132.56, 130.82, 111.43, 111.05, 46.49, 40.45, 35.06, 34.13, 29.80, 27.13, 25.84, 22.50, 21.46, 21.09; IR (KBr) 3513, 2953, 1561, 1453, 1316, 1231, 1171, 1130, 849, 716 cm^{-1}; Anal. Calcd for $C_{16}H_{22}Br_2O$: C, 49.26; H, 5.68%. Found: C, 49.24; H, 5.69 %.

(−)-2,4-Dibromo-6-menthylphenol (10). Compound **7** was brominated in the identical manner as described for **9** to afford the desired phenol as a colorless oil (85%). $[\alpha]_D^{29}$ −37.1 (*c* 0.52, $CHCl_3$); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.41 (1H, d, J = 2.1 Hz, Ar-H), 7.19 (1H, d, J = 2.1 Hz, Ar-H), 5.51 (1H, s, OH), 3.07 (1H, td, J = 11.7, 3.3 Hz, ArCH), 1.69–1.86 (3H, m, CH), 1.34–1.60 (3H, m, CH), 1.08–1.28 (1H, m, CH), 0.88–1.08 (2H, m, CH), 0.89 (3H, d, J = 6.6 Hz, CH_3), 0.83 (3H, d, J = 6.9 Hz, CH_3), 0.69 (3H, d, J = 6.9 Hz, CH_3); 75 MHz ^{13}C NMR ($CDCl_3$) δ 148.90, 136.03, 130.71, 129.88, 112.78, 110.99, 46.96, 44.30, 39.32, 35.09, 33.07, 27.68, 24.49, 22.42, 21.59, 15.78; IR (KBr) 3515, 2953, 1703, 1566, 1321, 1252, 1142, 1001, 853, 696 cm^{-1}; Anal. Calcd for $C_{16}H_{22}Br_2O$: C, 49.26; H, 5.68%. Found: C, 49.26; H, 5.56%.

Synthesis of 15. A magnetic stirrer bar and **3a** (0.20 mmol, 73 mg) were charged in a flame-dried 100 mL Schlenk flask. Dry toluene (10 mL) was condensed at −78 °C under 10^{-4} Torr. To this solution was added a solution of Me_3Al (0.5 M in hexane, 0.20 mL) at room temperature under Ar. After stirring for 1h, a slightly yellow solution of **15** was formed with the extrusion of methane gas. For a polymerization study this solution was used without any special treatment. Compound **15** can also be prepared in dry hexane. Careful concentration and crystallization of the saturated solution at room temperature gave rise to a colorless crystal, which was characterized by X-ray diffraction study because ^{1}H and ^{13}C NMR analyses of **15** in C_6D_6 gave very broad signals.

General Procedure for Polymerization Using a Lewis Acid and TrF (1:1) System. To a solution of a Lewis acid (0.1 mmol) in dry toluene (10 mL) was added TrF (0.1 mmol, 26 mg) at −78 °C under argon. After several minutes, *t*-butyl vinyl ether (10.0 mmol, 1.31 mL) was added via a syringe dropwise. Polymerization was continued under the conditions stated in Tables 1 and 4, and MeOH (0.5 mL) and pyridine (0.2 mL) were then added to quench the reaction. The mixture was poured into MeOH (500 mL) with vigorous stirring. The white precipitate was collected by filtration and dried in vacuo (25 °C/10^{-4} Torr) to give poly(*t*-butyl vinyl ether) as a white powdery solid.

Typical Polymerization Procedure Using a Lewis Acid–TrF (1:2) System. To a solution of a Lewis acid (0.1 mmol) in dry toluene (10 mL) was added TrF (0.2 mmol, 52 mg) at 25 °C under argon. After several minutes, the reaction vessel was cooled at −78 °C and *t*-butyl vinyl ether (10.0 mmol, 1.31 mL) was added via a syringe dropwise. Polymerization was continued under the conditions Tables 3 and 5, and MeOH (0.5 mL) and pyridine (0.2 mL) were then added to quench the reaction. The subsequent procedure is the same as described above.

X-ray Crystallographic Analysis. Crystals of *p*-nitrobenzoic acid ester of **6** and **15** were grown from saturated solution in EtOH and dry hexane, respectively. The former sample was mounted on a glass fiber. The crystal of **15** was carefully handled

Table 7. Crystallographic Data for Ester from **6** and **15**

Compound	ester from **6**	**15**
Formula	$C_{23}H_{27}NO_4$	$C_{53}H_{77}AlO_2$
Formula weight	381.72	773.18
Crystal color, habit	colorless, platy	colorless, cube
Crystal system	Orthorthombic	Orthorthombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	7.5290(2)	12.6330(2)
b/Å	20.4320(15)	17.0840(3)
c/Å	27.8630(21)	22.6770(4)
V/Å^3	4286.2(8)	4894.2(2)
Z	8	5
D_x/Mg m^{-3}	1.53	1.31
F(000)	408	848
μ/mm^{-1}	0.0801	0.0971
T/K	298	193
θ_{max}/^{0}	23.62	24.84
Limiting indices	0 ≤ h ≤ 8	$-15 \le h \le 15$
	0 ≤ k ≤ 23	$-20 \le k \le 20$
	0 ≤ l ≤ 32	$-27 \le l \le 27$
Independent reflections	3323	4563
Observed reflections	2366	4431
R; ωR	0.039, 0.036	0.043, 0.060
S	1.487	2.960

in a glovebox and fixed in a glass capillary tube. X-ray data were collected on a MacScience DIP Image plate diffractometer with $\lambda(\mathrm{MoK}_\alpha) = 0.7107$ Å, and solved by direct methods, followed by full-matrix least squares refinement with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic (Table 7). Reflection data with $|I| > 3\sigma(I)$ were used. The function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$, where $\omega = 1.0/[\sigma^2(F_o) + 0.03[F_c]^2]$. Crystallographic data for the ester of **6** and **15** have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC NO. 154117 and 154118, respectively. The details of structures have been deposited as Document No. 74043 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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References

1 T. Nakata, N. Hata, K. Iida, and T. Oishi, *Tetrahedron Lett.*, **28**, 5661 (1987).

2 a) K. Fujii, *J. Polym. Sci., Macromol. Rev.*, **5**, 431 (1971). b) T. Sato, In "PVA no Sekai," ed by POVAL Committee, Kobunshi Kankokai, Kyoto (1992), Chap. 1.

3 C. A. Finch, "Polyvinyl Alcohol-Developments," John Wiley & Sons, Chichester (1992).

4 a) S. Okamura, T. Kodama, and T. Higashimura, *Makromol. Chem.*, **53**, 180 (1962). b) T. Higashimura, K. Suzuoki, and S. Okamura, *Makromol. Chem.*, **86**, 259 (1965).

5 a) T. Kunitake, *J. Macromol. Sci., Chem.*, **A9**, 797 (1975). b) T. Kunitake and K. Takarabe, *Makromol. Chem.*, **182**, 817 (1981).

6 M. Ouchi, M. Kamigaito, and M. Sawamoto, *Macromolecules*, **32**, 6407 (1999).

7 a) G. Natta, G. Dall' Asta, G. Mazzanti, U. Giannini, and S. Cesca, *Angew. Chem.*, **71**, 205 (1959). b) S. Okamura, T. Higashimura, and T. Watanabe, *Makromol. Chem.*, **50**, 137 (1961). c) H. Yamaguchi, T. Doiuchi, and K. Kawamoto, *Macromolecules*, **18**, 2120 (1985); d) S. Aoshima, K. Shachi, and E. Kobayashi, *Polymer J.*, **26**, 335 (1994).

8 a) Y.-X. Chen, C. L. Stern, S. Yang, and T. J. Marks, *J. Am. Chem. Soc.*, **118**, 12451 (1996). b) Y.-X. Chen, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, **119**, 2582 (1997). c) Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern, and T. J. Marks, *J. Am. Chem. Soc.*, **120**, 6287 (1998).

9 a) G. Natta, G. Allegra, G. Perego, and A. Zambelli, *J. Am. Chem. Soc.*, **83**, 5033 (1961). b) G. Allegra and G. Perego, *Acta Crystallogr.*, **16**, 185 (1963). c) J. L. Atwood and W. R. Newberry III, *J. Organometal. Chem.*, **66**, 15 (1974).

10 a) A. W. Laubengayer and G. F. Lengnick, *Inorg. Chem.*, **1966**, 5. b) J. Weidlein and V. Krieg, *J. Organometal. Chem.*, **11**, 9 (1968). c) G. Gundersen, T. Haugen, and A. Haaland, *J. Organometal. Chem.*, **54**, 77 (1973).

11 J. A. Kerr, in "Handbook of Chemistry and Physics 74th," ed by D. R. Lide, CRC, Boca Raton (1993), pp. 9–123.

12 K. O. Christe, X. Zhang, R. Bau, J. Hegge, G. A. Olah, G. K. S. Prakash, and J. A. Sheehy, *J. Am. Chem. Soc.*, **122**, 481 (2000).

13 a) F. Iwasaki and K.-Y. Akiba, *Acta Crystallogr.*, **B37**, 180 (1981). b) J. Antel, K. Harms, P. G. Jones, R. Mews, G. M. Sheldrick, and A. Waterfeld, *Chem. Ber.*, **118**, 5006 (1985). c) A. D. Allen and T. T. Tidwell, *Adv. Carbocation Chem.*, **1**, 1 (1989). d) M. A. McAllister and T. T. Tidwell, *Croat. Chem. Acta*, **65**, 633 (1992). e) J. Y. Becker, E. Shakkour, and L. Shimoni, *Struct. Chem.*, **4**, 85 (1993).

14 M. D. Healy, M. B. Power, and A. R. Barron, *Coord. Chem. Rev.*, **130**, 63 (1994).

15 M. D. Healy and A. R. Barron, A*ngew. Chem., Int. Ed. Engl.*, **31**, 921 (1992).

16 a) A. P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robbins, and S. D. Ittel, *Organometallics*, **7**, 409 (1988). b) R. Benn, E. Janssen, H. Lehmkuhl, A. Rufinska, K. Angermund, P. Betz, R. Goddard, and C. Krüger, *J. Organomet. Chem.*, **411**, 37 (1991).

17 W. D. Wulff, in "Lewis Acids in Organic Synthesis," ed by H. Yamamoto, Wiley-VCH, Weinheim (2000), Vol. 1, Chap 7.

18 S. Saito, T. Kano, K. Hatanaka, and H. Yamamoto, *J. Org. Chem.*, **62**, 5651 (1997).

19 H. Brunner, R. Störiko, and B. Nuber, *Tetrahedron: Asymmetry*, **9**, 407 (1998).

20 a) E. Cesarotti, H. B. Kagan, R. Goddard, and C. Krüger, *J. Organomet. Chem.*, **162**, 297 (1978). b) R. L. Halterman and K. P. C. Vollhardt, *Organometallics*, **7**, 883 (1988).

21 C. M. Garner, B. C. Mossman, and M. E. Prince, *Tetrahedron Lett.*, **34**, 4273 (1993).

22 K. Hatada, T. Kitayama, N. Matsuo, and H. Yuki, *Polymer J.*, **15**, 719 (1983).

23 a) T. Moritani, I. Kuruma, K. Shibatani, and Y. Fujiwara, *Macromolecules*, **5**, 577 (1977). b) D. W. Ovenall, *Macromolecules*, **17**, 1458 (1984).

24 K. Maruoka, T. Itoh, M. Sakurai, K. Nonoshita, and H. Yamamoto, *J. Am. Chem. Soc.*, **110**, 3588 (1988).

25 T. Ooi, K. Maruoka, and H. Yamamoto, "Org. Synth. Coll. Vol. IX" (1998), p. 356.

26 K. Maruoka, H. Imoto, S. Saito, and H. Yamamoto, *J. Am. Chem. Soc.*, **116**, 4131 (1994).

27 S. Saito, K. Shimada, and H. Yamamoto, *Synlett*, **1996**, 720.

28 G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett, and A. Voigt, *J. Am. Chem. Soc.*, **121**, 4922 (1999).

29 K. Maruoka, T. Itoh, Y. Araki, T. Shirasaka, and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, **61**, 2975 (1988).

30 K. Maruoka, A. B. Concepcion, and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, **65**, 3501 (1992).

31 a) D. P. Cox, J. Terpinski, and W. Lawrynowicz, *J. Org. Chem.*, **49**, 3216 (1984). b) P. S. Bhadury, M. Pandey, and D. K. Jaiswal, *J. Fluorine Chem.*, **73**, 185 (1995).

32 L. A. Paquette, C. S. Ra, and S. D. Edmonson, *J. Org. Chem.*, **55**, 2443 (1990).

33 J. E. McMurry and W. J. Scott, *Tetrahedron Lett.*, **74**, 979 (1983).