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Asymmetric allylation polymerization of bis(allylsilane) and dialdehyde containing Si–phenyl linkage

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Abstract—Repetitive Sakurai–Hosomi allylation between dialdehyde and bis(allylsilane) yielded a polymer having stereogenic carbons in its main chain. In the presence of an enantiopure Lewis acid catalyst such as chiral (acyloxy)borane (CAB), the allylation polymerization proceeded in a stereoselective manner to give optically active polymers. We have prepared new monomers containing Si–phenyl linkages for the asymmetric allylation polymerization. After polymerization, the Si–phenyl linkages in the main chain could be cleaved easily to give the corresponding chiral homoallylic alcohol. The enantiomeric purity of the chiral polymer was then evaluated by chiral HPLC analysis of the alcohol obtained from the degradation.

1. Introduction

The synthesis of optically active polymers having main chain configurational chirality is an important technology, which is essential for the molecular design of the next generation polymeric materials.[1–3] A great number of methods for enantioselective transformations including C–C bond forming reactions have been extensively studied.[4,5] If an asymmetric C–C bond forming reaction proceeds in quantitative conversion without any side reactions, it can be used for optically active polymer synthesis. During our study on asymmetric polymerization based on C–C bond forming reactions,[6,7] we have found that the enantioselective addition of allylsilane to an aldehyde (Sakurai–Hosomi allylation[8]) is a suitable reaction for the synthesis of optically active polymers. Repetitive Sakurai–Hosomi allylation between bis(allylsilane) and dialdehyde produced a polymer having a chiral homoallylic alcohol unit structure. When a chirally modified Lewis acid catalyst was used, optically active polymer having main chain configurational chirality was obtained.[9] This is the first example of asymmetric allylation polymerization. However, a drawback of this type of asymmetric polymerization is the difficulty in the evaluation of the degree of asymmetric induction during the polymerization. Since it is difficult to determine the enantiomeric purity of chiral polymers by direct analysis, only a few reports have discussed the degree of asymmetric induction in such systems.[10] A precise model reaction study is an important approach to gain such information. Another persuasive and reliable method to understand the asymmetric induction is the analysis of the low-molecular-weight chiral compounds derived from degradation of the chiral polymer. In order for this strategy to succeed, we have designed a new monomer structure suitable for degradation analysis. We report herein the preparation of new monomers possessing Si–phenyl linkages and their asymmetric allylation polymerization. The obtained optically active polymers were degraded to the low-molecular-weight chiral compound, which was analyzed by chiral HPLC to evaluate the degree of asymmetric induction. The corresponding model reactions have been also studied.

2. Results and discussion

2.1. Monomer synthesis

It is well known that the bond between Si and an aryl group can be cleaved easily by means of treatment with fluoride anion.[11] We have prepared new monomers (**4**, **7**, **12** and **15**) containing Si–phenyl bonds, as shown in Schemes 1–4. After asymmetric polymerization, the Si–phenyl linkages in the main chain of the chiral polymer may be cleaved readily. Silyl containing dialdehyde **4** was prepared by coupling of *para*-lithiobenz-

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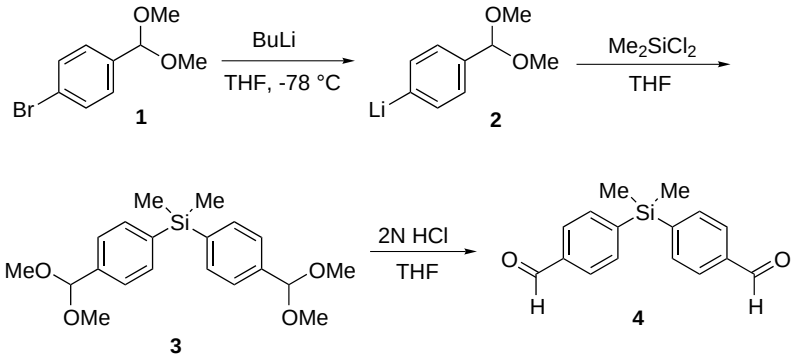
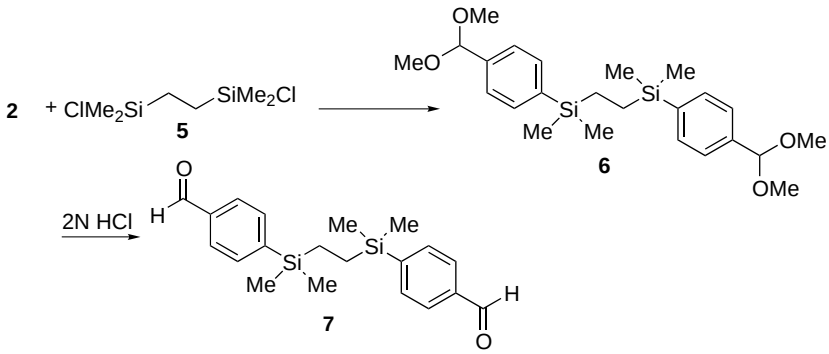
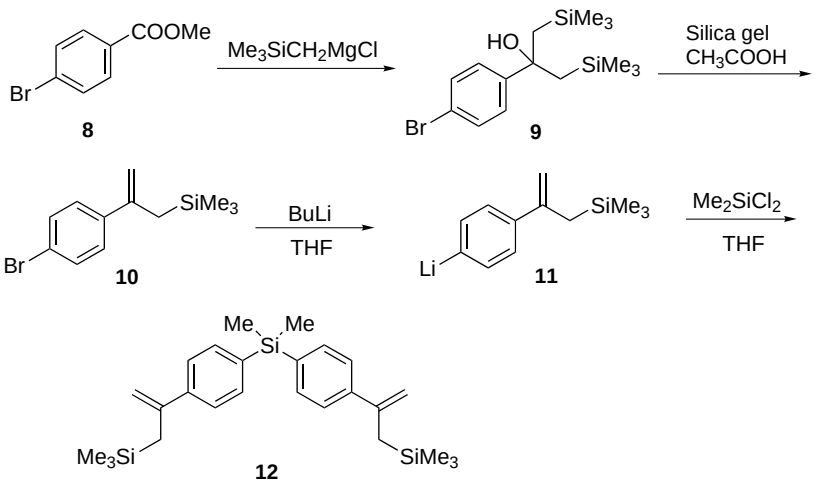


Scheme 1.

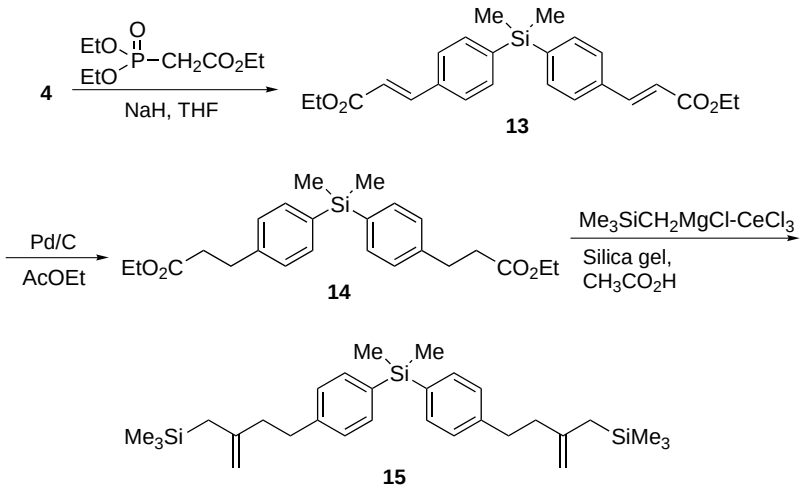


Scheme 2.



Scheme 3.

aldehyde dimethylacetal **2** with dichlorodimethylsilane, followed by deprotection of the acetal moiety. Si–phenyl linkage was stable enough under the acidic conditions used for acetal deprotection to isolate the desired dialdehyde **4** (Scheme 1). The use of 1,2-bis-(chlorodimethylsilyl)ethane as the silylating agent gave another dialdehyde **7** (Scheme 2). Bis(allylsilane)s containing the Si–phenyl linkage were then prepared by coupling of lithiated β-phenylallylsilane **11** and silylating agent (Schemes 3 and 4). One of the most convenient methods to construct β-substituted allylsilane structures is Narayanan's method[12] based on the Peterson olefination reaction. The allylsilane moiety of **10** was formed using this method from **8** as a starting material. Careful lithiation of **10** with *n*-BuLi at −78°C followed by coupling with dichlorodimethylsilane led to **12** in good yield (Scheme 3). Another bis(allylsilane) **15** was prepared as shown in Scheme 4. Diester **14** was prepared from dialdehyde **4** using the Horner–Emmons reaction,[13] followed by hydrogenation. The ester moiety was then readily converted into the allylsilane using the above method. These monomers are all stable enough to be purified by standard silica gel column chromatography.



Scheme 4.

2.2. Asymmetric allylation polymerization

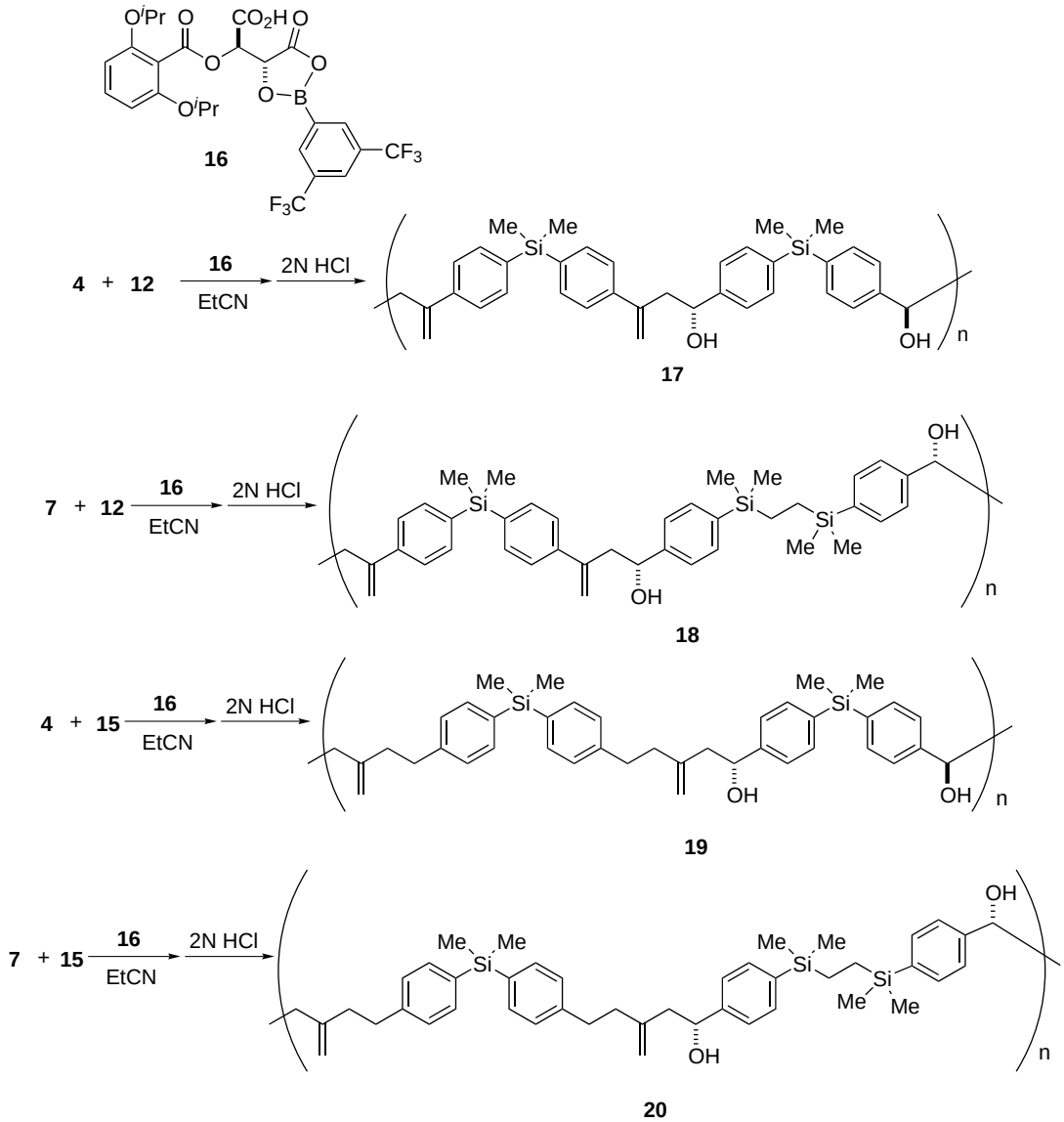
We have examined the asymmetric polymerization of dialdehyde and bis(allylsilane) monomers mentioned above. Without catalyst no reaction occurred between the monomers. Chirally modified Lewis acid catalyst is required to initiate the asymmetric polymerization. Although several enantioselective catalysts effective for the allylation reaction have been reported, one of the most efficient and reliable catalyst is the chiral (acyloxy)borane (CAB) developed by Yamamoto.[14] This is the only reported catalyst that has been used for the enantioselective addition of β-substituted allylsilanes. We chose this catalyst for the asymmetric allylation polymerization. In the presence of CAB **16** asymmetric polymerization of **4** and **12** occurred smoothly to give the corresponding chiral polymer **17** (Scheme 5). After the separation of **16** the polymer was isolated as a white powder whose THF solution showed optical activity. At 0°C monomers were consumed completely within 30 min to give an optically active polymer **17** having M_w of 46000 (Table 1, run 1). The structure of polymer **17** was confirmed by NMR spectroscopy, which shows the unique main chain structure containing *exo* methylene, secondary alcohol, and silicon, as shown in Scheme 5, and may be difficult to prepare by other polymerization methods. Lowering the temperature resulted in the chiral polymer having higher optical rotation value (entries 1–3). Even at −78°C, the polymerization reaction proceeded in homogeneous system with a complete consumption of the monomers to give the chiral polymer. This is a new type of synthetic chiral polymer containing silicon atoms in the main chain. All other combinations of the monomers were subjected to the asymmetric polymerization. The corresponding optically active polymers **17**, **18**, **19** and **20** were obtained in high yields in all cases.

2.3. Model reaction

In order to estimate the degree of asymmetric induction during the polymerization, we investigated the enantioselective addition of β-substituted allylsilanes **21** and **24** with benzaldehyde using **16** as a catalyst (Scheme 6). In these reactions quantitative conversion was attained within a few hours to give the homoallylic alcohol products **23** and **25**. Enantiopurities of the products were determined by chiral HPLC analysis. Another model reaction of bis(allylsilane) **26** and benzaldehyde (Scheme 7) also took place smoothly at −78°C to give **27**. Chiral HPLC analysis of **27** resulted in a 80.7:17.8:1.5 ratio of stereoisomers (*R*,*R*)-**27**:(*R*,*S*)-**27**:(*S*,*S*)-**27**. This stereoselectivity is similar to the model reactions in Scheme 6. These model reactions show that the asymmetric allylation polymerization should proceed in a stereoselective manner with asymmetric induction similar to those of model reactions.

2.4. Degradation of chiral polymer

Although the model reaction study gives important information of stereoselectivity during polymerization, the enantiomeric purity of the chiral polymers is still unknown. We have tried to cleave Si–phenyl linkages in the polymer main chain. Although the Si–phenyl linkage of the chiral polymer is quite stable under standard workup conditions, the polymer could be degraded readily by treatment with tetrabutylammonium fluoride (TBAF). A THF solution of **17** was thus treated with TBAF at 60°C for 24 h (Scheme 8). The chiral polymer **17** was completely degraded under these conditions to give the corresponding low-molecular-weight chiral compound **23**, which is identical with the product of the model reaction (Scheme 6). The other chiral polymers were similarly degraded to **23** and **25**. The e.e. of the degraded product can then be determined by using chiral HPLC analysis. For example, chiral HPLC analysis of the degraded product **23** from chiral polymer **17** (obtained from the asymmetric polymerization of **4** and **12** at 0°C) had 57% e.e. (Table 1, entry 1). This selectivity is the same as that attained in the model reaction of Scheme 6 at the same temperature. The same level of enantioselectivity obtained at −20°C is predictable from the model reaction at this temperature (entry 2). At −78°C, higher enantioselectivities were achieved in the asymmetric polymerization. The use of D-CAB, which was prepared from commercially avail-



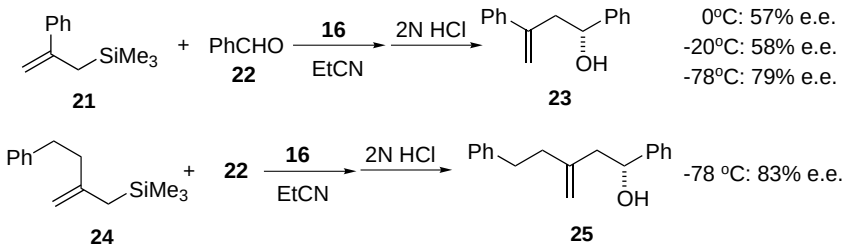
Scheme 5.

Table 1. Asymmetric allylation polymerization of bis(allylsilane) and dialdehyde using CAB[a] catalyst in propionitrile

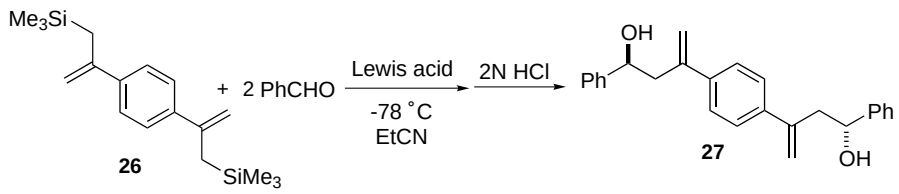
Entry	Monomer	Temp. (°C)	Time (h)	Yield (%)	M_w[b]	M_w/M_n[b]	$[\Phi]_{405}$[c]	E.e.[d] (%)
1	**4**+**12**	0	0.5	93	46000	5.7	−821.7	57
2	**4**+**12**	−20	1	89	32000	4.6	−881.4	58
3	**4**+**12**	−78	10	95	57000	6.9	−990.0	72
4[e]	**4**+**12**	−20	1	93	30000	4.2	+772.9	58
5	**4**+**15**	−78	12	98	11000	3.7	−21.1	80
6	**7**+**15**	−78	12	96	22000	4.5	−36.6	72
7	**7**+**12**	−78	12	95	32000	4.9	−859.8	74

[a] CAB derived from L-tartaric acid was used unless otherwise stated.
[b] Estimated by size exclusion chromatography (SEC) with polystyrene standards.
[c] Molar optical rotation was measured as THF solution (*c* 1.0, THF).
[d] Determined by HPLC using a chiral column (Chiralpac AD).
[e] CAB derived from D-tartaric acid was used.

able D-tartaric acid, afforded the same polymer having opposite main chain configuration (entry 4). Degradation of **19** and **20** yielded **25**, which was also analyzed by chiral HPLC to determine the enantiopurity. From the polymerization of **4** and **15**, the obtained chiral polymer **19** had e.e. of 80% (entry 5), which, to our knowledge, is the highest asymmetric induction achieved in asymmetric polyaddition.

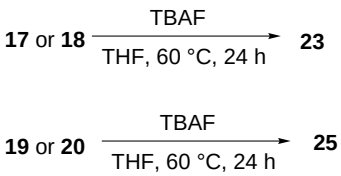


Scheme 6.



Lewis acid	(*R*,*R*):(*R*,*S*):(*S*:*S*)
$BF_3 \cdot OEt_2$	24.4 : 51.0 : 24.6
16	80.7 : 17.8 : 1.5

Scheme 7.



Scheme 8.

3. Conclusions

In conclusion, we have shown that silicon containing dialdehydes **4** and **7** and bis(allylsilane)s **12** and **15** prepared in this study are useful monomers for asymmetric allylation polymerization using chiral (acyloxy)borane **16** as a catalyst to give chiral polymers **17**–**20**, having unique main chain structure, in high yield. These chiral polymers could be degraded easily by treatment with TBAF to give the corresponding enantioenriched homoallylic alcohols **23** and **25**. Chiral HPLC analysis of the alcohol revealed that the asymmetric polymerization occurred with a high level of asymmetric induction. This was also confirmed by the corresponding model reactions. The above mentioned methodology can be applied to other asymmetric polymerization systems.

4. Experimental

4.1. General

Melting points were determined on a Yanaco micro melting apparatus and were uncorrected. Optical rotations were measured on a JASCO DIP-140 digital polarimeter using a 10 cm thermostated microcell. Both ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and were reported in reciprocal centimeter (cm^{-1}). Elemental analyses were performed by the Microanalytical Center of Kyoto University. HPLC analyses were performed with a JASCO HPLC system composed of 3-Line Degasser DG-980-50, HPLC pump PV-980, Column oven CO-965, equipped with a chiral column (Chiralpac AD, Daicel) using hexane/propan-2-ol as an eluent. UV detector JASCO UV-975 was used for the peak detection. Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution was conducted at 40°C with JASCO PU-980 as a pump, JASCO UVDEC-100-III as a UV detector and Shodex column A-802 (pore size: 20 Å) and A-803 (pore size: 100 Å) as columns. The eluent was THF and flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained by using a series of polystyrene standards (Tosoh Co., Japan). All reagents and solvents were purified and dried as necessary according to standard procedures.

4.2. Monomer synthesis

4.2.1. Dialdehyde 4. 4-Bromobenzaldehyde dimethyl acetal **1** (7.40 g, 32 mmol) was dissolved in THF (120 mL) under nitrogen. *n*-BuLi/hexane solution (1.6 M, 32 mmol, 20 mL) was added slowly at −78°C over 30 min. After stirring the mixture for 1 h at −78°C, dichlorodimethylsilane (1.52 mL, 12.5 mmol) was added to the above suspension. The reaction mixture was then stirred for 1 h at −78°C, allowed to warm to room temperature and was stirred for 12 h. The reaction mixture was quenched with 2N HCl and extracted

with ether. The organic phase was washed with brine and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave the crude acetal/aldehyde mixture. To the crude mixture acetic acid (10 mL) and H_2O (3 mL) were added and stirred for 3 h at room temperature. The reaction mixture was poured into a saturated aqueous solution of $NaHCO_3$ and extracted with ether. The combined extract was washed with brine, dried ($MgSO_4$), filtered and concentrated. The crude product was purified by column chromatography (hexane:AcOEt, 4:1) and/or recrystallization (hexane/AcOEt) to give dialdehyde **4** as a white solid (2.18 g, 8.1 mmol, 65%); mp 78–80°C, ^{1}H NMR ($CDCl_3$): δ 10.02 (s, 2H, C*H*O), 7.85 (d, $J=8.0$ Hz, 4H, Ph-*H*), 7.68 (d, $J=8.0$ Hz, 4H, Ph-*H*), 0.64 (s, 6H, SiCH_3); ^{13}C NMR ($CDCl_3$): δ 192.8, 146.0, 137.2, 135.0, 129.1, −2.5; IR (KBr): 3024, 2853, 1699, 1592, 1209, 806 cm^{-1}. Anal. calcd for $C_{16}H_{16}O_2Si$: C, 71.60; H, 6.01. Found: C, 70.94; H, 6.04%.

4.2.2. Dialdehyde 7. Prepared as above, Mp 85–87°C; ^{1}H NMR ($CDCl_3$): δ 10.02 (s, 2H, C*H*O), 7.84–7.62 (m, 8H, Ph-*H*), 0.65 (s, 4H, SiCH_3), 0.28 (s, 12H, SiCH_2CH_2Si); ^{13}C NMR ($CDCl_3$): δ 193.0, 148.3, 136.8, 134.5, 129.0, 7.91, −3.49; IR (KBr): 3029, 2833, 2827, 1701, 1592, 1209, 806 cm^{-1}. Anal. calcd for $C_{16}H_{16}O_2Si$: C, 67.74; H, 7.39. Found: C, 67.72; H, 7.41%.

4.2.3. 2-(4-Bromophenyl)-3-trimethylsilyl-1-propene 10. Powdered $CeCl_3\cdot 7H_2O$ (33.5 g, 90 mmol) was dried at 140°C/1 mmHg for 4 h. Under an argon atmosphere, dry THF (160 mL) was added at room temperature and the resulting suspension of $CeCl_3$ was stirred for 12 h. The white slurry obtained was then cooled to −78°C, and trimethylsilylmethylmagnesium chloride/ether solution [prepared from chloromethyltrimethylsilane (12.7 g, 100 mmol), magnesium (2.7 g, 110 mmol), and ether (50 mL)] was added slowly. The cream-colored suspension was stirred at −78°C for 1 h and 4-bromobenzoic acid methyl ester **8** (6.45 g, 30 mmol) was added. The reaction mixture was stirred for 2 h at −78°C, allowed to warm to room temperature and stirred for additional 12 h. After cooling to 0°C, the reaction was quenched carefully with dropwise addition of water. The mixture was extracted with ether, washed with brine and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave the crude alcohol intermediate **9**. Silica gel (column chromatography grade, 25 g) was added to a hexane (100 mL) solution of **9** and acetic acid (1.0 mL) was then added to the mixture. Stirring was continued for 30 min, and silica gel was removed by filtration. After addition of a saturated aqueous solution of $NaHCO_3$, the aqueous layer was extracted with ether. The organic layer was washed with brine and dried ($MgSO_4$). Chromatographic purification of the crude mixture (hexane) afforded allylsilane **10** as a colorless oil (5.25 g, 19.5 mmol, 65%); ^{1}H NMR ($CDCl_3$): δ 7.43 (d, $J=8.4$ Hz, 2H, Ph-*H*), 7.28 (d, $J=8.4$ Hz, 2H, Ph-*H*), 5.13 (s, 1H, C=CH_2), 4.90 (s, 1H, C=CH_2), 2.00 (s, 2H, CH_2Si), −0.08 (s, 9H, SiCH_3); ^{13}C NMR ($CDCl_3$): δ 145.8, 142.0, 131.5, 128.3, 121.4, 111.0, 26.3, −1.1; IR (film): 3084, 2954, 1616, 1249, 1100, 852 cm^{-1}. Anal. calcd for $C_{12}H_{17}BrSi$: C, 53.53; H, 6.36. Found: C, 53.55; H, 6.31%.

4.2.4. Bis(allylsilane) 12. Allylsilane **10** (5.25 g, 19.5 mmol) was dissolved in THF (80 mL) and cooled to −78°C. A *n*-BuLi/hexane solution (1.6 M, 20 mmol, 12.5 mL) was added dropwise over 30 min, and stirred for 1 h at this temperature. The solution became yellow and then dichlorodimethylsilane (0.85 mL, 7 mmol) was added slowly. The reaction mixture was stirred for 1 h at −78°C, allowed to warm to room temperature and stirred for 12 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ether. The combined extract was washed with brine, dried ($MgSO_4$), filtered and concentrated. The crude product was purified by column chromatography (hexane) to give bis(allylsilane) **12** as colorless oil in 87% yield. ^{1}H NMR ($CDCl_3$): δ 7.45 (d, $J=8.2$ Hz, 4H, Ph-*H*), 7.38 (d, $J=8.2$ Hz, 4H, Ph-*H*), 5.16 (s, 2H, C=CH_2), 4.87 (s, 2H, C=CH_2), 2.01 (s, 4H, CH_2Si), 0.54 (s, 6H, Ph-SiCH_3), −0.08 (s, 9H, CH_2-Si-CH_3); ^{13}C NMR ($CDCl_3$): δ 146.8, 143.7, 137.3, 126.0, 110.6, 26.3, −1.0, −1.9; IR (film): 3064, 2956, 1614, 1251, 852 cm^{-1}. Anal. calcd for $C_{26}H_{40}Si_3$: C, 71.48; H, 9.23. Found: C, 71.68; H, 9.27%.

4.2.5. Diester 13. A solution of triethyl phosphonoacetate (5.4 g, 24 mmol) in THF (10 mL) was added to a suspension of NaH (0.24 g, 24 mmol) in THF (20 mL) at 0°C. After stirring for 30 min at 0°C, a THF (10 mL) solution of dialdehyde **4** (10 mmol) was added and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with water and extracted with ether. The combined organic layer was dried ($MgSO_4$), filtered and concentrated. The crude product was purified by recrystallization (hexane) to give diester **13** as a white solid in 90% yield. Mp 87–88°C; ^{1}H NMR ($CDCl_3$): δ 7.67 (d, $J=15.9$ Hz, 2H, Ph-C*H*=CH) 7.55–7.45 (m, 8H, Ph-*H*), 6.46 (d, 2H, $J=15.9$ Hz, Ph-CH=C*H*), 4.26 (q, $J=7.0$ Hz, 4H, COOCH_2CH$_3$), 1.34 (t, $J=7.0$ Hz, 6H, COOCH$_2$CH_3), 0.57 (s, 6H, Ph-SiCH_3); ^{13}C NMR ($CDCl_3$): δ 144.8, 141.0, 135.5, 135.0, 119.0, 60.9, 14.7, −2.3; IR (film): 2983, 1707, 1637, 1312, 1254, 1176, 815 cm^{-1}. Anal. calcd for $C_{26}H_{40}Si_3$: C, 70.56; H, 6.91. Found: C, 70.45; H, 7.02%.

4.2.6. Diester 14. α,β-Unsaturated diester **13** (8 mmol) was dissolved in AcOEt (20 mL) and 10% Pd/C powder (0.25 g) was added. The reaction mixture was stirred for 12 h under a H_2 atmosphere. The mixture was filtered through a Celite pad and the filtrate was concentrated in vacuo to give diester **14** as a colorless oil in 98% yield. ^{1}H NMR ($CDCl_3$): δ 7.34 (d, $J=8.1$ Hz, 4H, Ph-*H*), 7.08 (d, $J=8.1$ Hz, 4H, Ph-*H*), 3.98 (q, $J=7.0$ Hz, 4H, COOCH_2CH$_3$), 2.83 (t, $J=8.0$ Hz, 2H, Ph-CH_2CH$_2$), 2.50 (t, $J=8.0$ Hz, 2H, Ph-CH$_2$CH_2), 1.11 (t, $J=7.0$ Hz, 6H, COOCH$_2$CH_3), 0.41 (s, 6H, Ph-SiCH_3); ^{13}C NMR ($CDCl_3$): δ 173.0, 141.7, 136.0, 136.0, 134.6, 128.0, 60.6, 35.9, 31.1, 14.4, −2.1; IR (film): 2979, 1733, 1372, 1251, 1176, 811 cm^{-1}. Anal. calcd for $C_{26}H_{40}Si_3$: C, 69.86; H, 7.82. Found: C, 69.90; H, 7.90%.

4.2.7. Bis(allylsilane) 15. Powdered $CeCl_3 \cdot 7H_2O$ (29.8 g, 80 mmol) was dried at 140°C/1 mmHg for 4 h. Under an argon atmosphere, dry THF (160 mL) was added at room temperature and the resulting suspension of $CeCl_3$ was stirred for 12 h. The white slurry obtained was then cooled to −78°C and trimethylsilylmethylmagnesium chloride/ether solution, prepared from chloromethyltrimethylsilane (12.7 g, 100 mmol), magnesium (2.7 g, 110 mmol) and ether (50 mL) was added slowly. The cream-colored suspension was stirred at −78°C for 1 h and diester **14** (12 mmol) was added. The reaction mixture was stirred for 2 h at −78°C, allowed to warm to room temperature and stirred for 12 h. After cooling to 0°C, the reaction was quenched carefully with dropwise addition of water, and then diluted with ether, washed with brine and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave the crude diol intermediate. Silica gel (column chromatography grade, 25 g) was added to a hexane (100 mL) solution of the intermediate and acetic acid (1.0 mL) was then added. Stirring was continued for 30 min and silica gel was removed by filtration. After addition of a saturated aqueous solution of $NaHCO_3$, the aqueous layer was extracted with ether. The combined extract was washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by column chromatography (hexane) to give bis(allylsilane) **15** in 55% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, J=7.9 Hz, 4H, Ph-*H*), 7.45 (d, J=7.9 Hz, 4H, Ph-*H*), 4.93 (s, 2H, C=CH_2), 4.84 (s, 2H, C=CH_2), 3.01 (m, 2H, Ph-CH_2CH$_2$), 2.51 (m, 2H, Ph-CH$_2$CH_2), 1.85 (s, 4H, CH_2Si), 0.80 (s, 6H, Ph-SiCH_3), 0.03 (s, 18H, Si-CH_3); ^{13}C NMR ($CDCl_3$): δ 147.5, 143.6, 135.6, 134.6, 128.2, 107.5, 40.4, 34.9, 27.4, 0.9, −1.86; IR (film): 3011, 2953, 1633, 1250, 849 cm^{-1}. Anal. calcd for $C_{14}H_{30}Si_2$: C, 73.09; H, 9.81. Found: C, 73.30; H, 10.00%.

4.3. Typical procedure for asymmetric allylation reaction promoted by chiral (acyloxy)borane catalyst

A solution of (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl)-tartaric acid (74 mg, 0.2 mmol) and 3,5-bis(trifluoromethyl)phenylboronic acid (51 mg, 0.2 mmol) in dry propionitrile (1 mL) was stirred for 30 min at room temperature under argon to form chiral (acyloxy)-borane. After the above solution was cooled to −78°C, benzaldehyde (106 mg, 1 mmol) and allylsilane (1 mmol) were added and stirred for 2 h. The reaction mixture was then quenched with 2N aqueous HCl (1 mL) and extracted with ether, dried ($MgSO_4$) and concentrated. The crude product was purified by flash column chromatography to give homoallyl alcohol. The enantioselectivity was determined by HPLC analysis using a chiral stationary-phase column.

4.3.1. Homoallyl alcohol 23. ^{1}H NMR ($CDCl_3$): δ 7.49–7.29 (m, 10H, Ph-*H*), 5.44 (br s, 1H, =CH_2), 5.19 (br s, 1H, =CH_2), 4.75 (m, 1H, C*H*OH), 3.05 (m, 2H, CH$_2$=C-CH_2), 2.19 (s, 1H, O*H*); ^{13}H NMR ($CDCl_3$): δ 145.3, 144.2, 140.6, 128.8, 127.8, 126.6, 126.1, 116.1, 72.3, 46.2; IR (film): 3220, 2940, 1627 cm^{-1}. E.e.=79%. Conditions for HPLC analysis of the enantiomers of **23** are as follows. Daicel Chiralpak AD, hexane:propan-2-ol=30:1 (v/v), flow rate=0.5 mL/min, t_R=34.1 min (*R*), 38.2 min (*S*). The homoallyl alcohol **23** obtained from the model reaction using **16** was converted to the known compound (3-hydroxy-1,3-diphenylpropan-1-one) by Lemieux–von Rudloff oxidation and the absolute configuration was determined to be *R* by comparison of the specific rotation of the corresponding hydroxyketone with the literature value.[15]

4.3.2. Homoallyl alcohol 25. ^{1}H NMR ($CDCl_3$): δ 7.38–7.27 (m, 10H, Ph-*H*), 5.00 (s, 1H, =CH_2), 4.97 (s, 1H, =CH_2), 4.81 (m, 1H, C*H*OH), 2.80 (m, 2H, Ph-CH_2CH$_2$), 2.48 (m, 4H, CH$_2$=C-CH_2, Ph-CH$_2$CH_2), 2.15 (s, 1H, O*H*); ^{13}H NMR ($CDCl_3$): δ 146, 144, 142, 129, 128, 126, 114, 72, 47, 38, 35; IR (film): 3397, 3027, 2932, 1644 cm^{-1}. E.e.=83%. Conditions for HPLC analysis of the enantiomers of **25** are as follows. Daicel Chiralpak AD, hexane:propan-2-ol=30:1 (v/v), flow rate=0.4 mL/min, t_R=37.0 min (*R*), 39.7 min (*S*). The absolute configuration of **25** was assigned on the assumption that the asymmetric induction occurred in the same sense as the reaction of **21** and **22**.

4.3.3. Homoallyl alcohol 27. ^{1}H NMR ($CDCl_3$): δ 7.45–7.27 (m, 14H, Ph-*H*), 5.47 (br s, 2H, =CH_2), 5.19 (br s, 2H, =CH_2), 4.75 (m, 2H, C*H*OH), 3.05 (m, 4H, Ph-CH_2CH$_2$), 2.19 (s, 2H, CHO*H*); ^{13}H NMR ($CDCl_3$): δ 145, 144, 140, 129, 128, 127, 126, 116, 72, 46; IR (film): 3399, 2940, 1623 cm^{-1}. Anal. calcd for $C_{26}H_{26}Si_2$: C, 84.29; H, 7.07. Found: C, 84.21; H, 7.13. (*R*,*R*)-**27**:(*R*,*S*)-**27**:(*S*,*S*)-**27**=80.7:17.8:1.5. Conditions for HPLC analysis of the stereoisomers of **27** are as follows. Daicel Chiralpak AD, hexane:propan-2-ol=3:1 (v/v), flow rate=0.5 mL/min, t_R=25.0 min (*R*,*R*), 34.0 min (*R*,*S*), 39.3 min (*S*,*S*). The absolute configuration of **27** was assigned on the assumption that the asymmetric induction occurred in the same sense as the reaction of **21** and **22**.

4.4. Asymmetric allylation polymerization promoted by chiral (acyloxy)borane catalyst

4.4.1. Polymerization of 12 and 4. A dry propionitrile (1 mL) solution of chiral (acyloxy)borane **16** prepared from (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl) tartrate (74 mg, 0.2 mmol) and 3,5-bis(trifluoromethyl)phenylboronic acid (51 mg, 0.2 mmol) was added to a solution of bis(allylsilane) **12** (219 mg, 0.5 mmol) and dialdehyde **4** (134 mg, 0.5 mmol) in propionitrile (1 mL) at −78°C. The mixture was stirred at −78°C for 10 h and quenched with 2N HCl (1 mL). The mixture was poured into MeOH/H_2O (2:1), filtered and dried under vacuum to yield a white solid (266 mg, 95%); M_w=57000, M_w/M_n=6.93, $[\Phi]_{405}$ −990.0 (*c* 1.0, THF), ^{1}H NMR ($CDCl_3$): δ 7.54–7.31 (m, 16H, Ph-*H*), 5.46 (b, 2H, C=CH_2), 5.19 (b, 2H, C=CH_2), 4.70 (m, 2H, C*H*OH), 2.90 (m, 4H, CH$_2$=C-CH_2), 2.10 (b, 2H, O*H*), 0.57 (b, 6H, Ph-SiCH_3), 0.53 (b, 6H, Ph-SiCH_3); ^{13}C NMR ($CDCl_3$): δ 145, 141, 138, 135, 116, 72, 46, −2.0; IR (film): 3395, 3013, 2953, 1597, 1250, 811 cm^{-1}.

4.4.2. Polymer 19. ^{1}H NMR ($CDCl_3$): δ 7.51–7.18 (m, 16H, Ph-*H*), 4.99 (b, 2H, C=CH_2), 4.96 (b, 2H, C=CH_2), 4.77 (m, 2H, C*H*OH), 2.76 (m, 4H, Ph-CH_2CH$_2$), 2.45 (m, 8H, CH$_2$=C-CH_2, Ph-CH$_2$CH_2), 2.10 (b, 2H, O*H*), 0.52 (b, 12H, Ph-SiCH_3)); IR (film) 3393, 3011, 2925, 1643, 1249, 804 cm^{-1}.

4.4.3. Polymer 20. ^{1}H NMR ($CDCl_3$): δ 7.44–7.32 (m, 16H, Ph-*H*), 5.00 (b, 2H, C=CH_2), 4.99 (b, 2H, C=CH_2), 4.77 (m, 2H, C*H*OH), 2.76 (m, 4H, Ph-CH_2CH$_2$), 2.45 (m, 8H, CH$_2$=C-CH_2, Ph-CH$_2$CH_2), 2.10 (b, 2H, O*H*), 0.64 (b, 4H, SiCH_2CH_2Si), 0.53 (b, 6H, CH$_2$CH$_2$SiCH_3), 0.23 (b, 6H, Ph-SiCH_3); IR (film): 3402, 3014, 2951, 1644, 1250, 828 cm^{-1}.

4.4.4. Polymer 18. ^{1}H NMR ($CDCl_3$): δ 7.55–7.17 (m, 16H, Ph-*H*), 5.46 (b, 2H, C=CH_2), 5.20 (b, 2H, C=CH_2), 4.71 (m, 2H, C*H*OH), 2.79 (m, 4H, CH$_2$=C-CH_2), 2.18 (b, 2H, O*H*), 0.64 (b, 4H, SiCH_2CH_2Si), 0.58 (b, 6H, CH$_2$CH$_2$SiCH_3), 0.23 (b, 6H, Ph-SiCH_3) IR (film) 3404, 3015, 2952, 1596, 1248, 812 cm^{-1}.

4.5. Cleavage of allylation polymer

The allylation polymer (100 mg) was dissolved in TBAF/THF solution (1.0 M, 3 mL) and heated at 60°C for 24 h. The reaction mixture was diluted with ether (50 mL) and washed with 2N aqueous HCl and brine, dried over $MgSO_4$ and concentrated. The crude product was purified by flash column chromatography to give homoallyl alcohol. The enantioselectivity was determined by HPLC analysis using a chiral stationary-phase column. Isolated yields of homoallyl alcohol were 80–85% in all cases.

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