# Asymmetric Polymer Synthesis by Repetitive *Sakurai–Hosomi* Allylation Reaction of Compounds Possessing Both Formyl and Allylsilane Functions

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Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

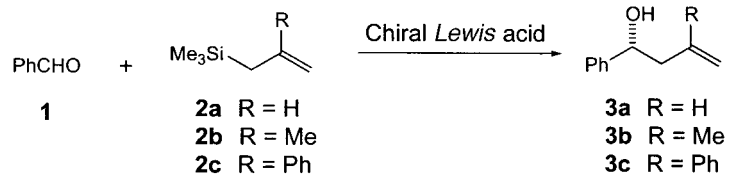
Trialkylallylsilanes generally react with aldehydes in the presence of a *Lewis* acid to the corresponding homoallylic alcohols. Chiral *Lewis* acids promote the same reaction to yield the enantiomerically-enriched homoallylalcohols. We have prepared four compounds (**7**–**10**) that possess both formyl and allylsilane functions. *Lewis* acids initiated self-polyaddition reactions of these compounds by means of repetitive allylation. The use of chiral *Lewis* acids resulted in the formation of optically active polymers that possess *exo*-methylene and secondary OH functions in their main chain. The optical purity of these chiral polymers was estimated based on the results of model asymmetric reactions between benzaldehyde and $\beta$-substituted allylsilanes and by controlled degradation.

**1. Introduction.** – Reaction between aldehydes and allylsilanes readily takes place in the presence of *Lewis* acids to afford homoallylalcohols, a transformation known as the *Sakurai–Hosomi* allylation reaction [1]. When chiral *Lewis* acids are used, enantiomerically-enriched homoallylalcohols are produced (*Scheme 1*) [2]. Since the *Sakurai–Hosomi* allylation smoothly proceeds without any side reaction, such transformations are suited for polymerization reactions. We recently reported that the polymerization by means of repetitive allylation between bis($\beta$-allylsilane) and dialdehydes yields polymers with a unique main-chain structure composed of *exo*-methylene and secondary alcohol repeating units [3–5]. By employing a chiral *Lewis* acid as a catalyst, the two-component polyaddition smoothly occurred with these monomers and yielded optically active polymers. Repetitive asymmetric reaction of achiral monomers belongs to the most promising methods to synthesize optically active polymers[1]). Since allylsilanes are inert to aldehydes in the absence of *Lewis* acids, compounds that incorporate both functions (A-B monomers) can be synthesized and utilized in the asymmetric allylation polymerization procedure in a one-component self-polyaddition manner. In this paper, we will discuss the synthesis of (A-B)-type monomers and their polymerization behavior.

In asymmetric polymerization reactions, it is sometimes difficult to determine the optical purity of the produced materials due to the large number of stereogenic centers on the polymer main chain. We estimated the degree of asymmetric induction during

[1]) We recently reported asymmetric polymerizations based on repetitive *Diels–Alder* [6] and *Mukaiyama* aldol reactions [7].

*Scheme 1*




polymerization based on the results of model asymmetric reactions. Furthermore, some optically active polymers were degraded to the corresponding chiral low-molecular-weight compounds, which were analyzed by high-performance liquid chromatography (HPLC) using chiral stationary phase columns. Hence, the optical purity of such polymers can be accurately determined by determining the enantiomeric excess (ee) of the degraded chiral units. In the present paper, we describe and summarize the results obtained with asymmetric allylation polymerizations of A-B monomers.

**2. Results and Discussion.** – *Addition of β-Substituted Allylsilanes to Benzaldehyde.* To apply a C–C bond-forming reaction for the polymerization of monomers, very clean and fast transformations are required. Although *Sakurai–Hosomi* reactions are ideal candidates for polymer synthesis from this point of view [1], no such study on the allylation polymerization has been reported to date. We, therefore, examined model reactions of the β-substituted trialkyl allylsilanes **2a–c** with benzaldehyde (**1**). Since one of the most efficient catalysts for the allylation of aldehydes is $Sc(OTf)_3$[2]), as reported by *Aggarwal* [8], we first tested this catalyst for the reaction between β-substituted allylsilanes and benzaldehyde. Interestingly, the allylation with $Sc(OTf)_3$ is highly solvent-dependent. The use of $CH_2Cl_2$, DMF (*N*,*N*-dimethylformamide), and toluene led to basically no reaction. However, a dramatic effect was observed in propionitrile (EtCN) (*Table 1*, *Entry 1*). Starting from equimolar amounts of the two substrates and 2 mol-% of $Sc(OTf)_3$, the corresponding racemic alcohols **3a–c** were obtained in quantitative yield (*Entries 1*, *2*). MeCN and $MeNO_2$ also gave rise to high yields (86 and 87%, resp.) in this reaction. However, EtCN was certainly the solvent of choice for the planned polymer synthesis.

There are various reports on chiral *Lewis*-acid catalyst for enantioselective C–C bond forming reactions [9]. We focused on chiral acyloxyboranes, which are efficient catalyst for such reactions, including allylations. As a model reaction, we examined the enantioselective addition of the allylsilanes **2a–c** to benzaldehyde in the presence of **4**, a chiral oxazaborolidinone derived from L-valine, which is an excellent catalyst for the ring cleavage of chiral acetals present as silyl enol ethers [10]. In the presence of **4**, allylation of benzaldehyde with **2b** took place at −78° in EtCN and gave **3b** in 79% yield, with an enantiomeric excess of 34% (*Entry 3*). A lower enantioselectivity was observed in $CH_2Cl_2$ (*Entry 4*). In the case of **2c**, even lower ee values were obtained (*Entries 5*, *6*).

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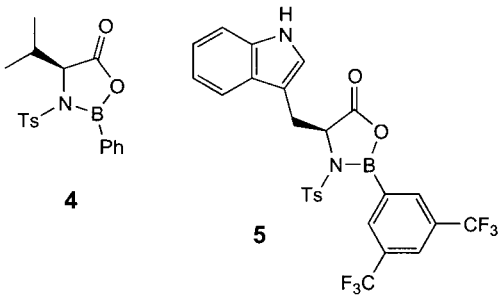
[2]) Tf stands for (trifluoromethyl)sulfonyl.

Table 1. *Addition of β-Substituted Allylsilanes to Benzaldehyde as a Model Reaction for Asymmetric Polymerization in EtCN*

| *Entry* | Allylsilane | Catalyst | *T* [°] | Time [h] | Yield[a]) [%] | ee[b]) [%] | Config. |
|---|---|---|---|---|---|---|---|
| *1*[c]) | **2b** | $Sc(OTf)_3$ | rt | 12 | 99 | – | – |
| *2* | **2c** | $Sc(OTf)_3$ | rt | 12 | 99 | – | – |
| *3* | **2b** | **4** | −78 | 24 | 79 | 34 | (*R*) |
| *4*[d]) | **2b** | **4** | −78 | 24 | 70 | 11 | (*R*) |
| *5* | **2c** | **4** | −78 | 48 | 79 | 22 | (*R*) |
| *6*[d]) | **2c** | **4** | −78 | 48 | 67 | 0 | – |
| *7* | **2a** | **5** | −78 | 6 | 0 | – | – |
| *8* | Allyltributyltin | **5** | −78 | 6 | 0 | – | – |
| *9* | **2b** | **5** | −78 | 1 | 93 | 77 | (*R*) |
| *10* | **2b** | **6a** | −20 | 12 | 0 | – | – |
| *11* | **2b** | **6b** | −20 | 1 | 99 | 75 | (*R*) |
| *12*[e]) | **2b** | **6b** | −78 | 2 | 99 | 89 | (*R*) |
| *13* | **2c** | **6b** | −78 | 0.5[f]) | 99 | 79 | (*R*) |

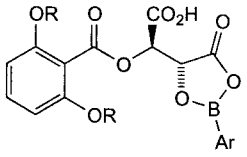
[a]) After purification. [b]) Enantiomeric excess, determined by HPLC using a chiral column (*Chiralpac AD*). [c]) High yields were also obtained when MeCN (86%) and $MeNO_2$ (87%) were used. The use of $CH_2Cl_2$, DMF, toluene, and $EtNO_2$ gave no product. THF was polymerized in the presence of $Sc(OTf)_3$. [d]) $CH_2Cl_2$ was used. [e]) Reported in the literature [13]. [f]) After 5 min, no more starting material (**2c**) could be detected.




**4**




**5**




**6a** R = Me, Ar = Ph
**6b** R = $^{i}$Pr,
Ar = 3,5-bis(trifluoromethyl)phenyl
**6c** R = $^{i}$Pr, Ar = pentafluorophenyl

Next, we examined the oxazaborolidinone **5** derived from L-tryptophan as another chiral acyloxyborane. This compound is a highly effective catalyst for asymmetric transformations, *e.g.*, the *Mukaiyama* aldol reaction of aldehydes with silyl enol ethers [11], as well as the *Diels–Alder* reaction of α-substituted α,β-enals with dienes [12]. Although no application of this catalyst to the *Sakurai–Hosomi* allylation has been reported, we decided to examine the catalytic activity of **5** in asymmetric allylation reactions. Unfortunately, the reaction between benzaldehyde and allyl(trimethyl)silane in the presence of **5** failed at −78° (*Table 1*, *Entry 7*). Allyl(tributyl)tin was also ineffective under these conditions (*Entry 8*). However, we found that **2b** smoothly reacted to the homoallylic alcohol **3b**, with 77% ee (*Entry 9*).

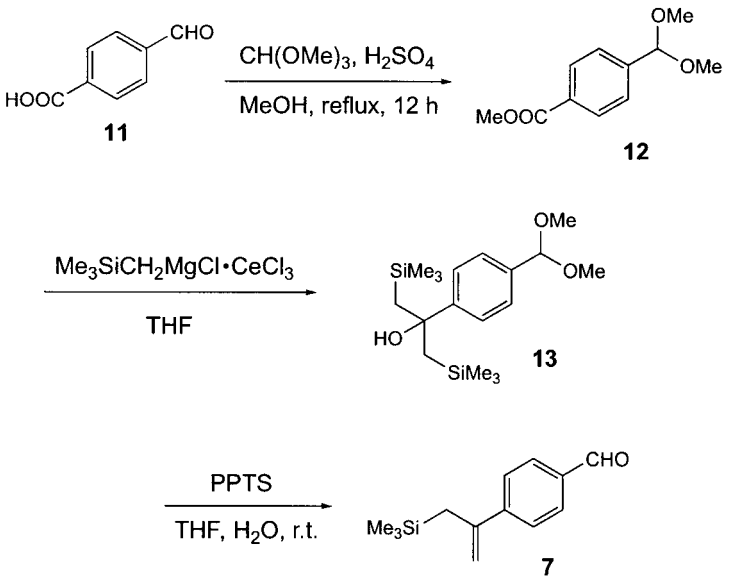
Chiral acyloxyborane catalysts derived from tartaric acid are known to be highly effective for allylations of aldehydes [13]. We, thus, examined compounds of type **6** in the above model reaction. Catalyst **6a** induced no reaction at −20°. Compound **6b**, however, with its electron-withdrawing groups on the aromatic ring attached to B, gave rise to quantitative yields of the corresponding homoallylalcohols (*Entries 11–13*),

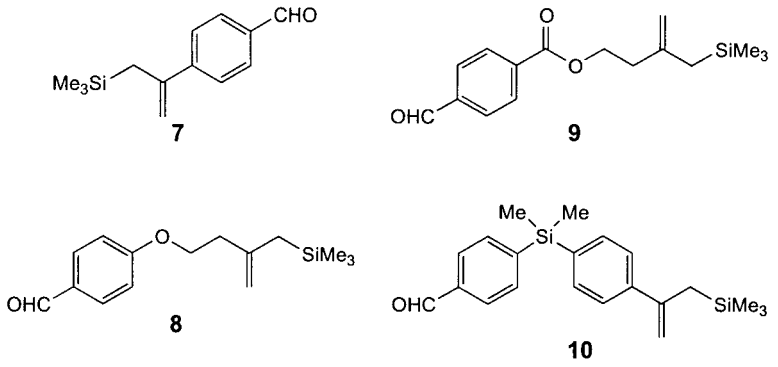
highest enantioselectivities being observed at $-78°$. The reactivity of the $\beta$-phenyl-substituted allylsilane **2c** was also quite high. Even at $-78°$, **2c** was completely consumed within 5 min. These findings prompted us to prepare monomers that possess $\beta$-substituted allylsilane moieties.

*Preparation of Monomers.* Based on the results presented in *Scheme 1* and *Table 1*, we designed the (A-B)-type monomers **7**–**10**, which possess both $\beta$-substituted allylsilyl moieties and formyl groups suitable for self-polyaddition reactions. One useful method to create allylsilanes is the reaction between an ester and a silylmethyl *Grignard* · $CeCl_3$ reagent followed by desilylation through *Peterson* olefination [14]. We have reported the preparation of various kinds of bis(allylsilane)s according to this procedure [3]. In *Scheme 2*, the synthesis of **7** is shown. 4-Formylbenzoic acid (**11**) was reacted with trimethyl orthoformate to the ester **12**, which smoothly reacted with an excess of $Me_3SiCH_2Mg \cdot CeCl_3$ to the alcoholic intermediate **13**. The latter was treated with pyridinium *p*-toluenesulfonate (PPTS) in THF/$H_2O$, leading to both acetal cleavage and elimination of $Me_3SiOH$ in one step. Thereby, PPTS was found to be the most effective reagent for the one-pot transformation of **13** to **7**. Acidic workup with aqueous 1N HCl solution also led to the corresponding monomer **7**, but contaminated with a desilylated side product that was difficult to remove.

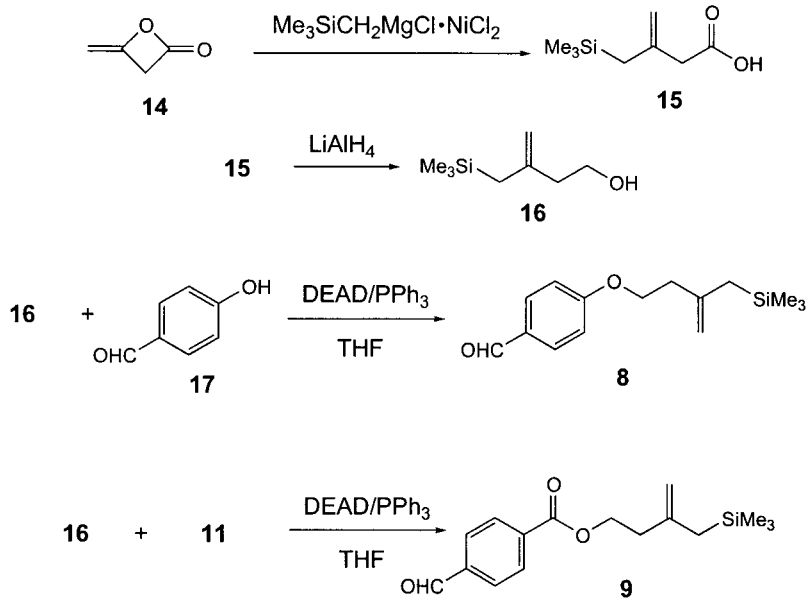
Allylsilyl moieties can also be made from diketene **14**, which is a but-3-enoic acid synthon (*Scheme 3*). *Itoh* reported an excellent method to prepare 4-[(trimethylsilyl)-methyl]but-3-enoic acid (**15**) in this way by employing a trimethylsilylmethyl *Grignard* reagent in the presence of catalytic amounts of $NiCl_2$. After reduction of the COOH group of **15** with $LiAlH_4$, the intermediate **16** was coupled with *p*-hydroxybenzalde-

*Scheme 2*






*Scheme 3*

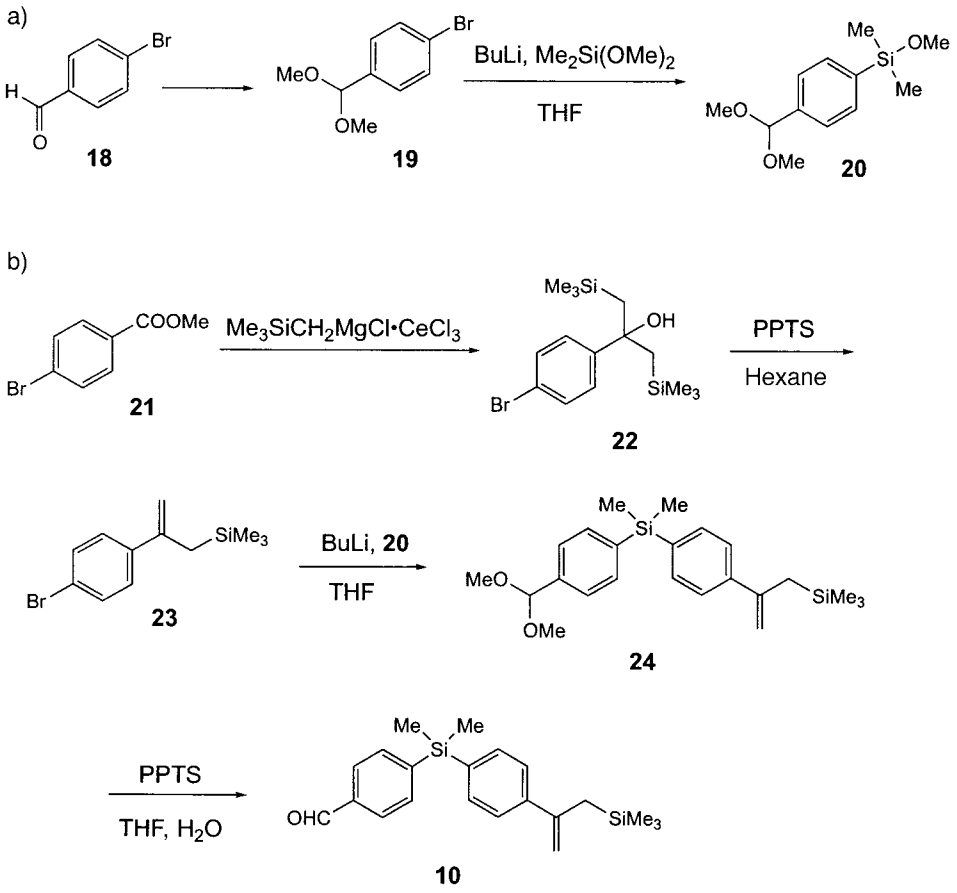



DEAD: Diethyl 4,4′-azodicarboxylate

hyde (**17**) or 4-formylbenzoic acid (**11**) under *Mitsunobu* conditions. Two kinds of A-B monomers, **8** and **9**, were obtained by this procedure.

Another interesting monomer is **10**, which contains a silyl bridge between the allylsilane and the CHO functions (*Scheme 4*). The allylsilyl moiety of **10** was constructed according to *Narayanan*'s method presented in *Scheme 2*. Starting from methyl *p*-bromobenzoate (**21**) (*Scheme 4, b*), the *β*-substituted allylsilane **23** was prepared. Lithiation of **23** followed by coupling with methoxysilane **20**, prepared from **18** and **19** according to *Scheme 4, a*, led to the precursor **24**, which, upon treatment with PPTS, afforded the desired monomer **10**.

*Scheme 4*




*Asymmetric Allylation Polymerization*. The (A-B)-type monomers **7**–**10** are quite stable compounds, that can be kept for several months without any decomposition. Upon adding selected *Lewis* acids to a solution of the above monomers, repetitive allylation occurred, and polymeric materials were generated. The results of allylation polymerizations with **7** are summarized in *Table 2*. For example, upon addition of $TiCl_4$ to a solution of **7** in EtCN, polymerization occurred immediately. Unfortunately, this polymeric product was completely insoluble in common organic solvents, such as THF, DMF, $CHCl_3$, and toluene (*Table 2*, *Entry 1*). However, when $TiCl_4$ was replaced by $Sc(OTf)_3$, THF-soluble polymers were obtained in high yield (*Entry 2*). Size-exclusion chromatography (SEC) measurements suggested an average molecular weight $M_w$ of 8700. NMR Spectra of the polymer confirmed the expected main-chain structure composed of *exo*-methylene and secondary alcohol repeating units, a unique backbone that would be difficult to prepare by other methods.

Table 2. *Asymmetric Allylation Polymerization of* **7** *in EtCN*

| *Entry* | *Lewis* Acid | *T* [°] | Time [h] | Yield [%] | $M_w$ [a]) | $M_w/M_n$ [a]) | $[\Phi]_{405}$ [b]) |
|---|---|---|---|---|---|---|---|
| *1* | $TiCl_4$ | 0 | 2 | 99 | – | – | – |
| *2* | $Sc(OTf)_3$ | 23 | 6 | 94 | 8700 | 3.0 | – |
| *3* | L-**6b** | 23 | 5 | 66 | 7200 | 3.1 | −298 |
| *4* | L-**6b** | −20 | 2 | 88 | 7300 | 2.8 | −525 |
| *5* | L-**6b** | −78 | 8 | 99 | 16000 | 2.6 | −667 |
| *6* | D-**6b** [c]) | −78 | 8 | 91 | 15000 | 2.2 | +627 |
| *7* | L-**6c** | −78 | 8 | 56 | 10000 | 2.0 | −580 |

[a]) Estimated by SEC with polystyrene standards. [b]) Molar optical rotation ($c = 1.0$, THF).

Next, we studied the polymerization of **7** catalyzed by chiral *Lewis* acids. At room temperature, **6b** nicely promoted the asymmetric allylation polymerization of **7** and afforded the corresponding chiral polymer **25** in 66% yield (*Table 2*, *Entry 3*, and *Scheme 5, a*). Compound **25** exhibited optical activity with a negative sign of rotation. At lower temperature, the polymerization still smoothly occurred, but the optically active product displayed higher rotation values (*Entries 4*, *5*), indicating a higher degree of asymmetric induction. When D-**6b** instead of L-**6b** was used as a catalyst, a similar optical rotation with opposite sign was observed (*Entry 6*). We found that the pentafluoro derivative **6c** also acts as a catalyst. The optical rotation of the corresponding polymer was somewhat lower, though (*Entry 7*).

The next A-B monomer we tried to polymerize was **8**, which contains an ether linkage between the allylsilane and the CHO functions. Polymerization with **6b** at −20° in EtCN produced an insoluble material that escaped NMR characterization and SEC measurement (*Table 3*, *Entry 1*). At −78°, the monomer was not reactive enough to form a polymer (*Entry 2*). Monomer **9**, however, exhibited a much higher reactivity and yielded the polymeric product **26** in high yields, even at low temperature (*Table 3*, *Entries 3*, *4*, and *Scheme 5, b*).

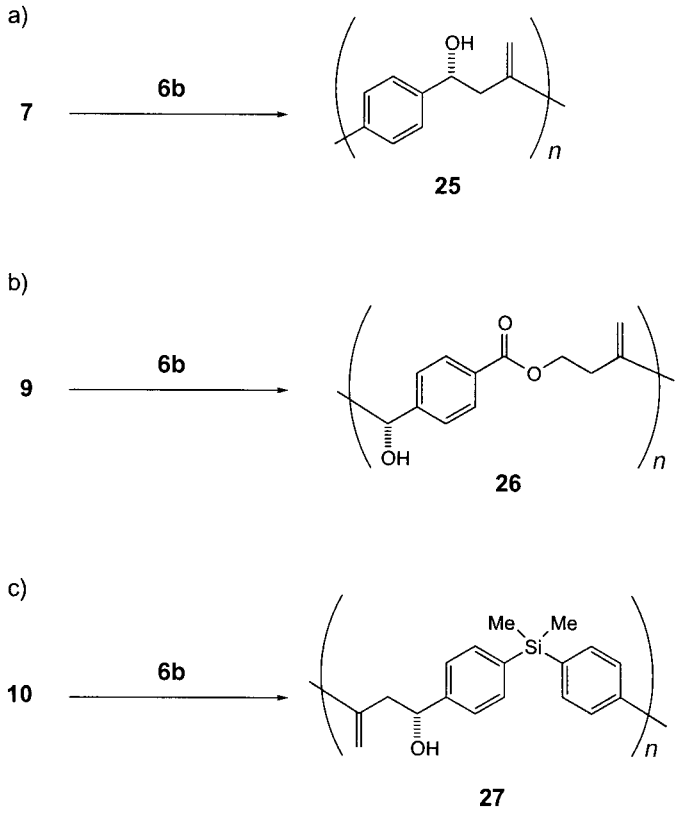
Table 3. *Asymmetric Allylation Polymerization of Monomers* **8** *and* **9** *Containing Ether or Ester Linkages in the Presence of* **6b** *in EtCN*

| *Entry* | Monomer | *T* [°] | Time [h] | Yield [%] | $M_w$ [a]) | $M_w/M_n$ [a]) | $[\Phi]_{405}$ [b]) |
|---|---|---|---|---|---|---|---|
| *1* | **8** | −20 | 20 | 67 [c]) | – | – | – |
| *2* | **8** | −78 | 48 | 0 | – | – | – |
| *3* | **9** | −20 | 6 | 75 | 35000 | 4.6 | +23.0 |
| *4* | **9** | −78 | 6 | 88 | 19000 | 4.1 | +57.5 |

[a]) Estimated by SEC with polystyrene standards. [b]) Molar optical rotation ($c = 1.0$, THF). [c]) Insoluble in THF.

One method to determine the optical purity of chiral polymers is controlled degradation into low-molecular-weight chiral molecules that can be easily analyzed by, *e.g.*, chromatographic techniques. Unfortunately, the attempted degradation of the

*Scheme 5*




chiral polymer **26**, with its ester linkages in the main chain, was unsuccessful and produced complex mixtures that could not be purified.

We then turned our attention to monomer **10**, which contains readily degradable phenyl–Si bonds. The optical purity of such chiral polymers can be evaluated by analyzing the chiral repeating unit obtained from degradation[3]). Asymmetric polymerization of **10** with **6b** in EtCN afforded the optically active polymer **27** in high yield (*Table 4* and *Scheme 5, c*). Compounds **10** and **27** are quite stable under standard workup conditions and can be stored for at least several months. We have then examined the degradation of **27**. Phenyl–Si bonds are known to be cleavable by treatment with $F^-$ [18]. Exposure of **27** to $Bu_4NF$ (TBAF) produced the chiral unit **3c**, which was already known from our model reaction study (*cf. Scheme 1*). Degradation and analysis of **3c** revealed that 78% ee was attained at $-78°$ (*Table 4*, *Entry 1*), which is comparable to the result obtained in the model reaction (*Table 1*, *Entry 13*). The ee values decreased with an increase in reaction temperature, as expected (*Entries 2*, *3*). Molar rotation values of the chiral polymers were also found to be temperature-

[3]) See, *e.g.*, [16][17].

dependent. It is, therefore, tangible that there is a linear agreement between the overall molar rotation of the polymer and the enantiomeric excess of the monomers, which defines the optical purity of these materials. While the chiral catalyst L-**6b**, derived from L-tartaric acid, led to polymers that display negative rotation values, the same catalyst made from D-tartaric acid gave rise to polymers characterized by an opposite sense of rotation (*Entries 4–6*).

Table 4. *Asymmetric Allylation Polymerization of Monomer* **10** *in EtCN*

| *Entry* | Catalyst | Yield [%] | *T* [°] | Time [h] | $M_w$[a]) | $M_w/M_n$[a]) | $[\Phi]_{405}$[b]) | ee [%][c]) | Config. |
|---|---|---|---|---|---|---|---|---|---|
| *1* | L-**6b** | 89 | −78 | 12 | 11000 | 2.5 | −596 | 78 | (*R*) |
| *2* | L-**6b** | 95 | −20 | 1 | 16000 | 2.4 | −213 | 58 | (*R*) |
| *3* | L-**6b** | 92 | 0 | 1 | 15000 | 2.4 | −116 | 46 | (*R*) |
| *4* | D-**6b** | 91 | −78 | 12 | 11000 | 2.6 | +611 | 75 | (*S*) |
| *5* | D-**6b** | 91 | −20 | 1 | 17000 | 2.3 | +218 | 59 | (*S*) |
| *6* | D-**6b** | 96 | 0 | 1 | 14000 | 2.7 | +114 | 45 | (*S*) |

[a]) Estimated by size exclusion chromatography (SEC) with polystyrene standards. [b]) Molar optical rotation ($c = 1.0$, THF). [c]) Determined by HPLC using a chiral column (*Chiralpac AD*).

**3. Conclusion.** – We have presented a new way to prepare optically active polymers with chiral main-chain structures by means of repetitive asymmetric allylation. (A-B)-type monomers that incorporate both allylsilane and CHO groups were successfully prepared. Different *Lewis* acids could initiate a new type of polyaddition reaction, which we term 'allylation polymerization'. The use of chiral acyloxyborane *Lewis* acid catalysts made it possible to perform asymmetric allylation polymerization. Thereby, the degree of asymmetric induction was estimated from model reactions and, in the case of polymer **27**, by controlled degradation. In the meantime, we have also successfully prepared optically active materials by asymmetric *Diels–Alder* [6] and aldol polymerization [7] based on repetitive asymmetric C,C bond-forming reactions to establish the general applicability of our new approach to optically active polymers.

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## Experimental Part

*General*. Reagents: Commercially available chemicals used were of *Guaranteed Reagent* (*GR*) quality, or purified and dried according to standard methods. TLC: precoated silica gel *60 $F_{254}$* (*Merck*); visualization by irradiation with UV light or detection by phosphomolybdic acid (20% soln. in EtOH). Flash chromatography (FC) was performed on $SiO_2$ (*Wakogel C-200*, 100–200 mesh). M.p.: *Yanaco* micro melting point apparatus, uncorrected. Optical rotations: *JASCO DIP-140* digital polarimeter with a 10-cm thermostated microcell. IR Spectra: *JEOL JIR-7000* FT-IR spectrometer, in $cm^{-1}$. $^1H$- (300 MHz) and $^{13}C$-NMR (75 MHz) spectra were recorded on *Varian Mercury 300* spectrometer, $\delta$ in ppm rel. to $SiMe_4$ as an internal standard, *J* in Hz. Elemental analyses were performed by the Microanalytical Center of the Kyoto University. HPLC Analyses were performed in hexane/$^i$PrOH, with a *JASCO* HPLC system composed of 3-Line Degasser *DG-980-50*, HPLC pump *PV-980*, column oven *CO-965* equipped with a *Chiralpac AD* column (*Daicel*) and a UV detector (*JASCO UV-975*). Size exclusion chromatography (SEC) for molecular weight determination and distribution

was conducted at 40° in THF, with a *JASCO PU-980* pump, a *JASCO UVDEC-100-III* UV detector, and *Shodex A-802* (pore size: 20 Å) or A-803 (pore size: 100 Å) columns at a flow rate of 1.0 ml/min. A molecular weight calibration curve was obtained by using a series of polystyrene standards (*Tosoh Co.*, Japan).

*Methyl 4-(1,1-Dimethoxymethyl)benzoate* (**12**). A soln. of 4-formylbenzoic acid (**11**) (7.5 g, 50 mmol) in MeOH (50 ml) was treated with $HC(OMe)_3$ (11.0 ml, 100 mmol) and conc. $H_2SO_4$ (2 g). After stirring for 12 h at 80°, the mixture was concentrated and poured into 10% aq. $NaHCO_3$ soln. The org. layer was extracted with $Et_2O$, washed with sat. aq. NaCl soln., dried ($MgSO_4$), and evaporated. The oily residue was purified by distillation (92–93°, 2 mm) to give **12** as a colorless oil (9.45 g, 90%). $^1$H-NMR (300 MHz): 8.05 (*d*, *J* = 8.5, 2 arom. H); 8.03 (*d*, *J* = 8.5, 2 arom. H); 5.44 (*s*, C*H*(OMe)$_2$); 3.92 (*s*, $CO_2$Me); 3.33 (*s*, CH(O*Me*)$_2$). $^{13}$C-NMR (75 MHz): 167.1; 143.2; 130.4; 129.8; 127.1; 102.6; 52.9; 52.4. Anal. calc. for $C_{11}H_{14}O_4$ (210.23): C 62.85, H 6.71; found: C 62.75, H 6.74.

*4-{1-[(Trimethylsilyl)methyl]ethenyl}benzaldehyde* (**7**). Powdered $CeCl_3 \cdot 7\,H_2O$ (12 g, 45 mmol) was dried at 140° for 4 h under reduced pressure (1 mm). Under an argon atmosphere, anh. THF (100 ml) was added, and the resulting suspension was stirred for 12 h at r.t. The white slurry obtained was cooled to −78° and dropwise treated with $Me_3SiCH_2SiCl$ (prepared from $Me_3SiCH_2Cl$ (7.0 ml, 50 mmol) and Mg (1.5 g, 70 mmol) in $Et_2O$ (30 ml)). The creamy-colored suspension was stirred at −78° for 1 h, treated with **12** (2.1 g, 10 mmol), and stirred for an additional 2 h. The mixture was allowed to warm to r.t., stirred for 12 h, cooled to 0°, and slowly quenched by dropwise addition of $H_2O$. The mixture was extracted with $Et_2O$, washed with brine, and dried ($MgSO_4$). Evaporation of the solvent *in vacuo* led to crude **13**, which was dissolved in THF (90 ml) and aq. pyridinium *p*-toluenesulfonate (PPTS) soln. (1M, 10 ml). The mixture was stirred for 3 h at r.t., washed with brine, and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the crude product was purified by CC (hexane) to yield **7** (58%) as a colorless oil. IR (neat): 2954, 1701, 1605, 1250, 842. $^1$H-NMR (300 MHz): 9.99 (*s*, CHO); 7.82 (*d*, *J* = 8.3, 2 arom. H); 7.52 (*d*, *J* = 8.3, 2 arom. H); 5.24 (*s*, 1 H, C=C$H_2$); 5.00 (*s*, 1 H, C=C$H_2$); 2.04 (*s*, SiC$H_2$); −0.10 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz): 192.1; 149.3; 146.1; 135.6; 130.0; 127.2; 113.1; 26.3; −1.1. Anal. calc. for $C_{13}H_{18}OSi$ (218.37): C 71.50, H 8.31; found: C 71.47, H 8.22.

*4-{3-[(Trimethylsilyl)methyl]but-3-enyloxy}benzaldehyde* (**8**). To an iced soln. of **16** (1.68 g, 10.6 mmol), *p*-hydroxybenzaldehyde **17** (1.34 g, 11.0 mmol), and $Ph_3P$ (3.01 g, 11.4 mmol) in THF (40 ml) was added a toluene soln. of diethyl 4,4′-azodicarboxylate (DEAD) (40%, 5.0 g, 11.5 mmol) diluted with THF (15 ml). The mixture was stirred at r.t. for 2 h. The solvent was evaporated, the residue was dissolved in hexane/AcOEt 3:1 and filtered. The filtrate was concentrated, and the crude product was purified by FC (hexane/AcOEt 3:1) to yield **8** (1.67 g, 60%) as a colorless oil. IR (neat): 3060, 1682, 1251, 1159. $^1$H-NMR (300 MHz): 9.87 (*s*, CHO); 7.82 (*d*, *J* = 8.8, 2 arom. H); 6.99 (*d*, *J* = 8.8, 2 arom. H); 4.69 (*s*, 1 H, C=C$H_2$); 4.66 (*s*, 1 H, C=C$H_2$); 4.15 (*t*, *J* = 6.98, $CH_2O$); 2.47 (*t*, *J* = 6.98, C=CC$H_2$CH$_2$); 1.6 (*s*, $CH_2Si$); 0.05 ($SiMe_3$). $^{13}$C-NMR (75 MHz): 191.1; 164.3; 143.6; 132.3; 130.2; 115.1; 109.4; 67.4; 37.6; 27.6; −1.0. Anal. calc. for $C_{15}H_{22}O_2Si$ (262.14): C 68.65, H 8.45; found: C 68.60, H 8.48.

*3-[(Trimethylsilyl)methyl]but-3-enyl 4-Formylbenzoate* (**9**). This compound was prepared from **16** (1.58 g, 10 mmol), **11** (2.61 g, 11.0 mmol), $Ph_3P$ (3.01 g, 11.4 mmol), and DEAD (40%, 5.0 g, 11.5 mmol) according to the procedure described for the synthesis of **8**. IR (neat): 2957, 1715, 1635, 1273, 1108. $^1$H-NMR (300 MHz): 10.01 (*s*, CHO); 8.19 (*d*, *J* = 8.7, 2 arom. H); 7.95 (*d*, *J* = 8.7, 2 arom. H); 4.72 (*s*, 1 H, C=C$H_2$); 4.65 (*s*, 1 H, C=C$H_2$); 4.47 (*t*, *J* = 6.87, $CH_2O$); 2.44 (*t*, *J* = 6.87, C=CC$H_2$CH$_2$); 1.60 (*s*, $CH_2Si$); 0.05 ($SiMe_3$). $^{13}$C-NMR (75 MHz): 192.0; 164.3; 143.4; 139.4; 136.6; 130.5; 129.8; 109.7; 64.1; 37.4; 27.2; −1.0. Anal. calc. for $C_{15}H_{22}O_3Si$ (290.43): C 66.17, H 7.64; found: C 66.15, H 7.68.

*{4-[(Dimethoxymethyl)phenyl]}(methoxy)dimethylsilane* (**20**). To 1-bromo-4-(dimethoxymethyl)benzene (**19**) (3.70 g, 16 mmol) in THF (80 ml) was slowly added BuLi (1.6M in hexane, 16 mmol, 10 ml) at −78° over 30 min. Stirring was continued for 1 h at −78°, and $(MeO)_2SiMe_2$ (2.73 ml, 20 mmol) was added to the above suspension. The resulting mixture was stirred for 1 h at −78°, allowed to warm to r.t., and stirred for 12 h. The mixture was concentrated *in vacuo*, diluted with anh. $Et_2O$ (40 ml), filtered through *Celite*, and concentrated *in vacuo*. The crude product was purified by distillation to yield **20** (2.23 g, 58%) as a colorless oil. B.p. 90–92° (2 mm Hg). IR (neat): 2954, 2830, 1450, 1353, 1254, 1190, 1098, 1056, 984, 828, 784. $^1$H-NMR (300 MHz): 7.58 (*d*, *J* = 7.0, 2 arom. H); 7.47 (*d*, *J* = 7.0, 2 arom. H); 5.39 (*s*, C*H*(OMe)$_2$); 3.43 (*s*, SiOMe); 3.34 (*s*, CH(O*Me*)$_2$); 0.38 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz): 139.7; 138.0; 133.7; 126.5; 103.5; 53.1; 51.0; −2.0. Anal. calc. for $C_{12}H_{20}O_3Si$ (240.37): C 59.96, H 8.39; found: C 59.91, H 8.35.

*[2-(4-Bromophenyl)prop-2-enyl]trimethylsilane* (**23**). Powdered $CeCl_3 \cdot 7\,H_2O$ (33.5 g, 90 mmol) was dried at 140° for 4 h under reduced pressure (1 mm). Under an argon atmosphere, anh. THF (160 ml) was added at r.t. and the resulting suspension was stirred for 12 h. The white slurry obtained was cooled to −78°. $Me_3SiCH_2MgCl$ (prepared from $Me_3SiCH_2Cl$ (12.7 g, 100 mmol) and Mg (2.7 g, 110 mmol) in $Et_2O$ (50 ml)) was

added slowly. The creamy suspension was stirred at −78° for 1 h. Then, *methyl 4-bromobenzoate* (**21**) (6.45 g, 30 mmol) was added. The mixture was stirred for 2 h at −78°, allowed to warm to r.t., and stirred for an additional 12 h. The iced mixture was quenched carefully by dropwise addition of $H_2O$, extracted with $Et_2O$, washed with brine, and dried ($MgSO_4$). Evaporation of the solvent *in vacuo* led to the crude intermediate **22**, which was dissolved in THF (150 ml) and pyridinium *p*-toluenesulfonate soln. (THF/$H_2O$ 9:1, 1.0M, 30 ml). The mixture was stirred for 3 h at r.t., washed with brine, and dried ($MgSO_4$). Evaporation of the solvent *in vacuo* and purification by CC (hexane) yielded **23** (68%) as a colorless oil. IR (neat): 3084, 2954, 1616, 1249, 1100, 852. $^1$H-NMR (300 MHz): 7.43 (*d*, *J* = 8.4, 2 arom. H); 7.28 (*d*, *J* = 8.4, 2 arom. H); 5.13 (*s*, 1 H, C=$CH_2$); 4.90 (*s*, 1 H, C=$CH_2$); 2.00 (*s*, $CH_2$Si); −0.8 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz): 145.8; 142.0; 131.5; 128.3; 121.4; 111.0; 26.3; −1.1. Anal. calc. for $C_{12}H_{17}BrSi$ (269.25): C 53.53, H 6.36; found: C 53.55, H 6.31.

*4-[4-([1-[(Trimethylsilyl)methyl]ethenyl]phenyl)dimethylsilyl]benzaldehyde* (**10**). Allylsilane **23** (2.96 g, 11 mmol) was dissolved in THF (80 ml) and cooled to −78°. BuLi (1.6M in hexane, 10 ml, 16 mmol) was added dropwise over 30 min, and the mixture was stirred for 1 h at this temperature. A soln. of **20** (2.16 g, 9 mmol) in THF was added to the suspension, which was stirred for 1 h at −78° and then allowed to warm to r.t. After being stirred for 12 h at r.t., the mixture was poured into sat. aq. $NaHCO_3$ soln. and extracted with $Et_2O$. The combined org. layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated to yield the acetal **24**, which was taken up in THF/$H_2O$ 9:1 (100 ml) containing PPTS (1M). The mixture was stirred for 12 h at r.t. and extracted with $Et_2O$. The combined org. extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by CC (hexane/AcOEt 19:1) to yield monomer **10** (58%) as a colorless oil. IR (neat): 3066, 3021, 2956, 2898, 2736, 1704, 1598, 1386, 1252, 1105, 835. $^1$H-NMR (300 MHz): 10.02 (*s*, CHO); 7.83 (*d*, *J* = 8.0, 2 arom. H); 7.68 (*d*, *J* = 8.0, 2 arom. H); 7.47–7.39 (*m*, 4 arom. H); 5.18 (*s*, 1 H, C=$CH_2$); 4.89 (*s*, 1 H, C=$CH_2$); 2.02 (*s*, $CH_2$Si); 0.59 (*s*, $Ph_2SiMe_2$); −0.08 (*s*, $SiMe_3$). $^{13}$C-NMR (75 MHz): 192.9; 147.6; 146.7; 136.9; 135.8; 135.0; 134.3; 129.0; 126.2; 110.9; 26.2; −1.05; −2.26. Anal. calc. for $C_{21}H_{28}OSi_2$ (352.62): C 71.53, H 8.00; found: C 71.55, H 7.99.

*Polymerization of Monomer* **7** *Promoted by Sc(OTf)$_3$.* Compound **7** (436 mg, 2.0 mmol) was dissolved in anh. EtCN (2 ml) at r.t., and $Sc(OTf)_3$ (20 mg, 0.04 mmol) was added. The soln. was stirred at r.t. for 6 h. Then, 1N aq. HCl (2 ml) was added and the mixture was poured into MeOH/$H_2O$ (2:1), whereupon polymer **25** precipitated. It was filtered off, washed with MeOH/$H_2O$ (2:1), and dried *in vacuo* to yield a white solid (275 mg, 94%). $^1$H-NMR (300 MHz): 7.55–7.30 (*m*, $C_6H_4$); 5.46, 5.19 (2 br. *s*, C=$CH_2$), 4.75–4.70 (*m*, C*H*−OH); 3.04–2.76 (*m*, $CH_2$); 2.10 (br. *s*, OH); 0.56 (*s*, $SiMe_2$).

*Asymmetric Polymerization of Monomer* **7**. An anh. soln. of **6b** (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)) in EtCN was added to a soln. of **7** (218 mg, 1 mmol) in EtCN (2 ml) at −78°. The mixture was stirred for 8 h at this temp., quenched with 2N aqueous HCl (1 ml), poured into MeOH/$H_2O$ (2:1), filtered, and dried *in vacuo* to yield the chiral polymer **25** (145 mg, 99%) as a white solid. $M_w$ = 16000. $M_w/M_n$ = 2.6. $[\Phi]_{405}$ = −667 (*c* = 1.0, THF). IR (KBr): 3388, 1566, 1405. $^1$H-NMR (300 MHz): 7.55–7.30 (*m*, $C_6H_4$); 5.46, 5.19 (2 br. *s*, C=$CH_2$), 4.75–4.70 (*m*, C*H*−OH); 3.04–2.76 (*m*, $CH_2$); 2.10 (br. *s*, OH); 0.56 (*s*, $SiMe_2$). $^{13}$C-NMR (75 MHz): 145.7; 145.2; 139.6; 126.6; 126.3; 115.0; 71.6; 45.8.

*Asymmetric Polymerization of* **9**. From monomer **9**, under the conditions described for the asymmetric polymerization of **7**, the chiral polymer **26** (88%) was obtained as a white solid. $M_w$ = 19000. $M_w/M_n$ = 4.1. $[\Phi]_{405}$ = +57.5 (*c* = 1.0, THF). $^1$H-NMR (300 MHz): 7.98–7.85, 7.45–7.32 ($C_6H_4$); 5.03, 4.98 (2 br. *s*, C=$CH_2$); 4.50–4.38 ($OCH_2$); 2.60–2.40 ($OCH_2CH_2$). $^{13}$C-NMR (75 MHz): 166.7; 149.6; 142.0; 129.6; 129.5; 126.0; 115.8; 71.8; 63.4; 46.6; 35.2.

*Asymmetric Polymerization of* **10**. From monomer **10**, under the conditions described for the asymmetric polymerization of **7**, the chiral polymer **27** (89%) was obtained as a white solid. $M_w$ = 11000. $M_w/M_n$ = 2.5. $[\Phi]_{405}$ = −596 (*c* = 1.0, THF). IR (KBr): 3419, 2952, 1597, 1251, 814. $^1$H-NMR (300 MHz): 7.55–7.30 (*m*, $C_6H_4$); 5.46, 5.19 (2 br. *s*, C=$CH_2$); 4.75–4.70 (*m*, C*H*−OH); 3.04–2.76 (*m*, $CH_2$); 2.10 (br. *s*, OH); 0.56 (*s*, $SiMe_2$). $^{13}$C-NMR (75 MHz): 145.2; 141.1; 138.2; 137.6; 129.0; 125.9; 125.6; 72.3; 46.0; −2.0.

*Degradation of the Chiral Polymer* **27**. Compound **27** was dissolved in $Me_4NF$ soln. (1.0M, 3 ml, in THF) and heated at 60° for 24 h. The mixture was diluted with $Et_2O$ (50 ml), washed with 2N aq. HCl and brine, dried ($MgSO_4$), and concentrated. The crude product was purified by FC (hexane/AcOEt 4:1) to yield **3c** (87%). The ee was determined by HPLC with a chiral stationary phase (*Daicel Chiralpak AD* column) and hexane/$^i$PrOH 30:1 at a flow rate of 0.5 ml/min. The retention times for the degradation products (*R*)-**3c** and (*S*)-**3c** were 34.1 and 38.2 min, resp.

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