Enantioselective Synthesis of Chiral Homoallyl Alcohols and Homoallylamines by Nucleophilic Addition of an Allylboron Reagent Modified by a Polymer-Supported Chiral Ligand

Shinichi Itsuno,* Katsuhiro Watanabe,[a] Ashraf A. El-Shehawy[b]

Department of Materials Science, Toyohashi University of Technology, Toyohashi 441-8580 Japan
Fax: +81-05 32-44-68 13; e-mail: itsuno@tutms.tut.ac.jp
[a] Permanent address: Chemistry Department, Kurume National College of Technology, Kutume 830-8555, Japan
[b] Permanent address: Chemistry Department, Faculty of Education, Tanta University, Kafr El-Sheikh, Egypt

Received June 26, 2000; Accepted September 11, 2000

Keywords: asymmetric synthesis; polymer-support; aldehydes; *N*-silylimine; polymers; allylborons

Abstract: Crosslinked polymer-supported chiral *N*-sulfonylamino alcohols **5**–**8** have been prepared by suspension polymerization of enantiopure *N*-sulfonylamino alcohol monomers **1**–**4** with styrene and divinylbenzene. Polymer-supported chiral allylboron reagents were prepared from the polymeric chiral ligands. Enantioselective additions of the polymer-supported allylboron reagents to aldehydes and *N*-(trimethylsilyl)imines have been successfully carried out in the heterogeneous system. The corresponding optically active homoallyl alcohols and homoallylamines were obtained in high yields with high enantioselectivities (up to 95% ee) which are almost the same as those obtained from homogeneous analogues. The polymer-supported chiral ligands used were recovered easily and can be reused without any loss of activity.

Introduction

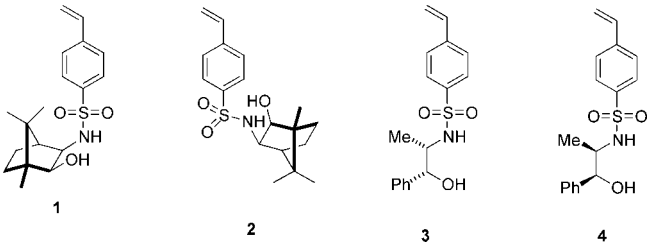
Asymmetric synthesis using polymer-supported reagents and catalysts is a subject of intense research activity.[1] In this context, polymer-supports based on crosslinked polystyrene have been utilized for many asymmetric reactions, since they are easy to prepare and are stable under the various reaction conditions.[2] They also offer various advantages over the homogeneous system, including easy separation and recycle use of the immobilized chiral ligands.[3] Moreover, the synthesis of chiral compound libraries by using combinatorial technique requires polymeric chiral reagents which show high levels of reactivity and stereoselectivity.[4] We have found that enantiopure *N*-sulfonylamino alcohols were excellent chiral ligands for the asymmetric allylboration of aldehydes and imines.[5–10] Allylboron reagents modified by such *N*-sulfonylamino alcohols reacted smoothly with aldehydes and imines to give the corresponding homoallylic alcohols and amines, respectively. We noticed that the *N*-sulfonylamino alcohols were easily immobilized in the polymer-support and could be used as polymeric chiral ligands. A number of chiral allylboron reagents has been so far reported for the asymmetric allylboration of aldehydes, some of which gave high enantioselectivities.[11] However, their application to the polymer-support seems to be difficult in most cases. In this paper we describe the synthesis of the polymer-supported chiral *N*-sulfonylamino alcohols as chiral ligands and their use in the asymmetric allylboration of aldehydes and *N*-silylimines. The recycleability of the polymeric chiral ligands has been also demonstrated.

Results and Discussion

In our previous study, among the various chiral ligands tested in the enantioselective addition of allylboron reagents, *N*-sulfonylamino alcohols derived from D-camphor and norephedrine appeared to be suitable for the allylboration of both aldehydes[7] and *N*-silylimines.[5,6] There are two methods to obtain the polymer-supported chiral *N*-sulfonylamino alcohol ligand, namely a chemical modification method and a polymerization method. The chemical modification method involves attachment of chiral amino alcohol to the partly chlorosulfonylated polystyrene resin.[12] However, our previous research on asym-

  1615-4150/01/34301-89–94 $ 17.50-.50/0

metric reactions using polymer-supported chiral *N*-sulfonylamino acids showed that the chemical modification method always resulted in decreased enantioselectivities.[12] We have thus decided to employ the polymerization method, that is the polymerization of a chiral monomer with styrene and a crosslinking agent, to obtain the polymer-supported chiral ligand. The chiral monomers **1**–**4** were readily prepared from the reaction of *p*-styrenesulfonyl chloride with the enantiopure amino alcohols.



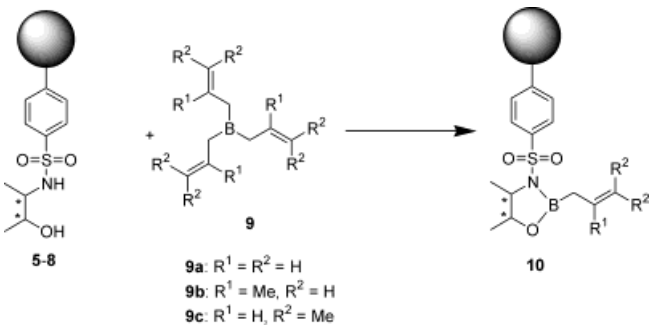
The monomers were then subjected to polymerization with styrene and divinylbenzene under suspension polymerization conditions to give the polymer-supported *N*-sulfonylamino alcohols **5**–**8** in good yield (Scheme 1). Loading of the chiral *N*-sulfonylamino alcohol residues and the degree of crosslinking could be controlled easily by the polymerization method. From (1*R*,2*S*)-norephedrine, we have prepared several polymers **7 a**–**7 e** having various loading and crosslinking degrees. Loading of *N*-sulfonylamino alcohol residues was calculated from elemental analysis. Table 1 shows the polymer yields and their loading and crosslinking degrees.

The polymer-supported *N*-sulfonylamino alcohols prepared above were then allowed to react with triallylborane **9a** in THF to afford the polymeric chiral allylboron reagent **10 a** (Scheme 2). In the preparation of the polymer-supported reagents and their use in asymmetric allylboration, we have used a special flask equipped with a glass sinter and a stopcock, which permitted rapid filtration and washing of the polymer beads under a nitrogen atmosphere.

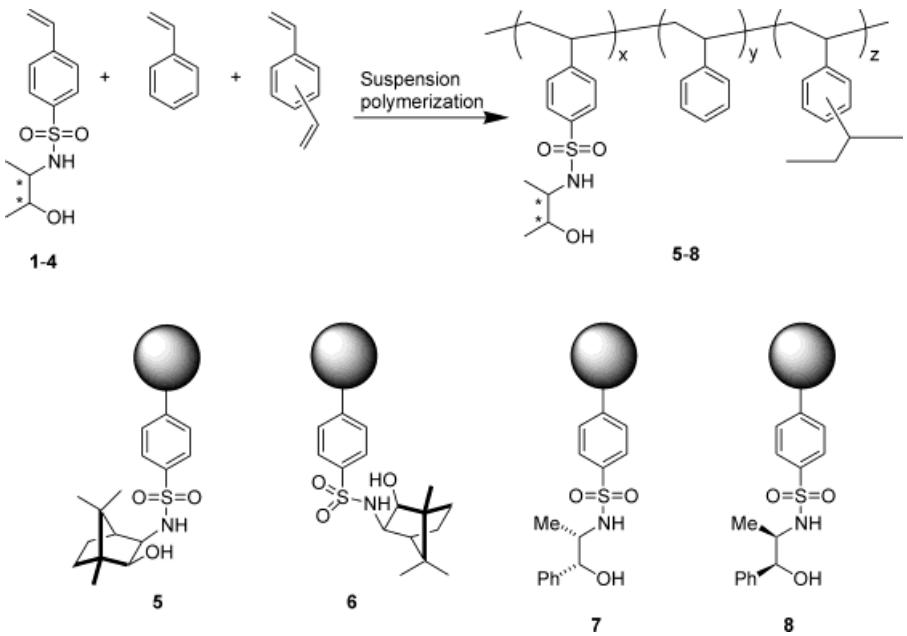
Table 1. Synthesis of polymer-supported chiral *N*-sulfonylamino alcohols

Polymer	Chiral monomer	Degree of crosslinking [%]	Yield [%]	Loading of *N*-sulfonylamino alcohol residues [mmol/g][a] (DF)[b]
5	**1**	10	88	0.77 (0.10)
6	**2**	10	89	0.77 (0.10)
7 a	**3**	2	78	0.79 (0.10)
7 b	**3**	10	91	0.78 (0.10)
7 c	**3**	30	92	0.75 (0.10)
7 d	**3**	10	93	1.80 (0.30)
7 e	**3**	10	95	2.34 (0.50)
8	**4**	10	90	0.78 (0.10)

[a] Determined by elemental analysis.
[b] Degree of functionalization.



Scheme 2. Preparation of polymer-supported allylboron reagents



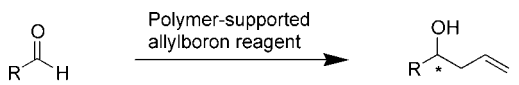
Scheme 1. Preparation of polymer-supported chiral *N*-sulfonylamino alcohol ligands

Table 2. Enantioselective allylation of aldehyde using polymer-supported chiral allylboron reagent[a]

Entry	Polymer	Aldehyde	Solvent	Temp. °C	Homoallylic alcohols		
					Yield [%]	ee [%]	*Config.*
1	**7b**	PhCHO	Ether	–78	93 (91)[c]	75 (73)[c]	*S*
2	**8**	PhCHO	Ether	–78	93	75	*R*
3	**5**	PhCHO	THF	–40	91	65	*R*
4	**5**	PhCHO	THF	–78	94 (88)[c]	78 (74)[c]	*R*
5	**5**	PhCHO	THF	–100	96	88	*R*
6	**6**	PhCHO	Ether	–78	92 (89)[c]	74 (71)[c]	*S*
7	**5**	PhCHO	Toluene	–78	91	72	*R*
8	**5**	PhCHO	Ether	–78	93 (90)[c]	85 (81)[c]	*R*
9	**5**[b]	PhCHO	Ether	–78	93	85	*R*
10	**5**	MeCHO	Ether	–78	51	92[d]	*S*
11	**5**	Me_3CCHO	Ether	–78	84	84[d]	*R*

[a] Reaction time: 7 h.
[b] Recycled polymer was used.
[c] Yields and % ees in parenthesis were obtained from the corresponding low-molecular-weight reagents in homogeneous system. See Ref. [7].
[d] Determined by comparison of the specific rotation with the literature values, Ref. [17].

In the first series of experiments, the asymmetric allylboration of aldehydes with the polymer-supported chiral allylboron reagents was investigated (Scheme 3). Although several excellent reagents have been reported for the asymmetric allylboration of aldehydes,[11] no example of a heterogeneous system using cross-linked polymer-supported chiral allylboron reagents has been published. We found that the heterogeneous reactions of polymer-supported allylboron reagents with aldehyde took place smoothly to afford the corresponding homoallylic alcohols in high yields as shown in Table 2. The enantioselectivity of the allylboration was found to be temperature dependent as expected. Lowering the temperature resulted in increasing enantioselectivity (entries 3–5, Table 2). The reaction occurred even at –100 °C using the polymeric reagent prepared from **5** to give a higher enantioselectivity (entry 5). Somewhat better yields of homoallyl alcohols were always obtained when the polymeric reagent was used, since the heterogeneous system facilitated the work-up process. No decrease in the enantioselectivities was observed in the heterogeneous system compared to those in the homogeneous system (Table 2). Polymers were easily separated from the reaction mixture by simple filtration and could be reused. The recycled polymer showed the same reactivity and enantioselectivity in the same reaction (entry 9, Table 2).



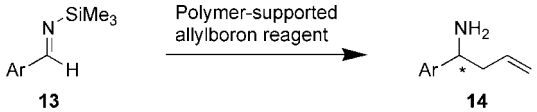
11

11a: R = Ph
11b: R = Me
11c: R = *t*Bu

12

Scheme 3. Enantioselective allylboration of aldehydes

Next, we applied the polymer-supported chiral allylboron reagents to the allylboration of *N*-silylimines **13** (Scheme 4). Of various imines tested for the asymmetric allylboration in homogeneous system, *N*-silylimines gave good results both in terms of the yield and the enantioselectivity.[5] Thus, we chose *N*-silylimines as substrates in the asymmetric allylboration using our polymeric reagent. As in the case of the asymmetric allylboration of aldehydes mentioned above, the polymeric allylboron reagent was prepared in the special flask and used for the enantioselective allylboration of the *N*-silylimine. In spite of the heterogeneous reaction, the polymeric allylboron reagent smoothly reacted with *N*-silylimine even at low temperature to afford the desired homoallylic amine. The structure of the polymeric chiral ligands influenced the enantioselectivity of the obtained homoallylamine. Loading and degree of crosslinking also affected the enantioselectivity. At –78 °C in THF, **7b** (DF = 0.10, 10% crosslinking) gave the best enantioselectivity in the allylboration of the *N*-silylimine. The temperature effect on enantioselectivity was the same as that in the case of aldehyde allylboration, with better enantioselectivities being obtained at lower temperature (entries 2–4, Table 3). The solvent of choice is diethyl ether in all cases, which gave higher enantioselectivity. The asymmetric allylboration of **13a** occurred even at –100 °C in ether to give 94% ee (entry 9).



13

13a: Ar = Ph
13b: Ar = *p*-ClPh
13c: Ar = *p*-MeOPh
13d: Ar = *p*-MePh

14

Scheme 4. Enantioselective allylboration of *N*-silylamines

In asymmetric synthesis it would be important that both enantiomers can be prepared. Both (1*R*,2*S*)- and (1*S*,2*R*)-norephedrine being commercially available, we have prepared the polymer-supported chiral ligand **8** from (1*S*,2*R*)-norephedrine. The polymeric allylboron reagent derived from **8** worked as well as those derived from **7** and led to the homoallylamine having the opposite configuration (entry 14). In the case of camphor-derived chiral ligands, the *exo*-derivative **5** led to the *S*-amine, while the *R*-amine was obtained from the *endo*-derivative **6**. The polymers used for the allylboration of *N*-silylimine were recovered quantitatively. The recovered polymer **7b** was used several times for the allylboration of **13a**. As can be seen from Figure 1, the yield and the enantioselectivity hardly changed after five runs.

Not only allylboron reagents, but also methallyl- and prenylboron reagents were prepared from the re-

Table 3. Enantioselective allylation of *N*-trimethylsilylimine using polymer-supported chiral allylboron reagent **10a**[a]

Entry	*N*-Silylimine	Polymer	Solvent	Temp. °C	Homoallylamine		
					Yield[%]	ee[%]	*Config.*
1	**13a**	**7a**	THF	–78	87	85	*S*
2	**13a**	**7b**	THF	–78	92 (91)[b]	87 (87)[b]	*S*
3	**13a**	**7b**	THF	0	94	39	*S*
4	**13a**	**7b**	THF	–40	93	67	*S*
5	**13a**	**7b**	Ether	–78	93 (89)[b]	91 (92)[b]	*S*
6	**13b**	**7b**	Ether	–78	87	82	*S*
7	**13c**	**7b**	Ether	–78	85	77	*S*
8	**13d**	**7b**	Ether	–78	90	80	*S*
9	**13a**	**7b**	Ether	–100	92 (80)[b]	94 (96)[b]	*S*
10	**13a**	**7b**	Toluene	–78	82 (76)[b]	73 (77)[b]	*S*
11	**13a**	**7c**	THF	–78	79	80	*S*
12	**13a**	**7d**	THF	–78	88	80	*S*
13	**13a**	**7e**	THF	–78	86	70	*S*
14	**13a**	**8**	THF	–78	93 (90)[b]	91 (92)[b]	*R*
15	**13a**	**5**	THF	–78	89	73	*S*
16	**13a**	**5**	Ether	–78	99 (90)[b]	89 (89)[b]	*S*
17	**13a**	**6**	Ether	–78	94 (93)[b]	81 (72)[b]	*R*
18	**13a**	**6**	THF	–78	89 (92)[b]	73 (64)[b]	*R*
19	**13a**	**6**	THF	–100	92	78	*R*

[a] Reaction time: 6 h.
[b] Yields and % ees in parenthesis were obtained from the corresponding low molecular weight reagents in homogeneous system. See Ref. [5].

Table 4. Enantioselective allylation of *N*-trimethylsilylbenzaldehyde imine using polymer-supported chiral allylboron reagent[a]

Polymer	Borane (**9**)	Solvent	Temperature	Homoallylamine		
				Yield [%]	ee [%]	*Config.*
7b	**9b**	THF	–78	93	90	*S*
7b	**9b**	Toluene	–78	81	78	*S*
7b	**9b**	Ether	–78	93 (92)[b]	94 (94)[b]	*S*
7b	**9b**	Ether	–100	90 (94)[b]	95 (96)[b]	*S*
7b	**9c**	THF	–78	92	80	*S*
7b	**9c**	Ether	–78	91 (89)[b]	85 (87)[b]	*S*
5	**9b**	Ether	–78	93	90	*S*
5	**9c**	Ether	–78	91	84	*S*
6	**9b**	THF	–78	94 (89)[b]	79 (72)[b]	*R*
6	**9b**	THF	–100	92	83	*R*
6	**9c**	THF	–78	83	69	*R*
6	**9c**	THF	–100	95	75	*R*

[a] Reaction time: 6 h.
[b] Yields and % ees in parenthesis were obtained from the corresponding low molecular weight reagents in homogeneous system. See Ref. [5].

action of the polymeric chiral ligands **7b**, **5**, **6** with **9b** or **9c**. As shown in Table 4, asymmetric addition of polymer-supported methallyl- and prenylboron reagents smoothly occurred at low temperature to give the corresponding enantio-enriched homoallylamines in excellent yield. The enantioselectivities obtained were almost the same as those from the low-molecular-weight counterparts in a homogeneous system. By using polymer **7b**, 95% ee was attained in the addition of the methallylboron reagent, which is the highest enantioselectivity obtained using a polymer-supported chiral allylborating agent. The polymeric prenylboron reagent also reacted with *N*-silylimine to give the corresponding homoallylamine with a somewhat lower enantioselectivity.

In conclusion, we have investigated the enantioselectivity in the reaction of polymer-supported chiral allylboron reagents with aldehydes and *N*-silylimines. The crosslinked polymer-supported chiral ligands were prepared easily by suspension polymerization of the chiral monomers with styrene and divinylbenzene. Heterogeneous reactions of the polymeric allylboron reagents with aldehydes and *N*-silylimines took place smoothly even at a low temperature such as –100 °C. Polymer-supported chiral allylboron reagents exhibited high level of enantioselectivities which were almost the same as those obtained from the solution system. They can be reused several times without any loss of activity.

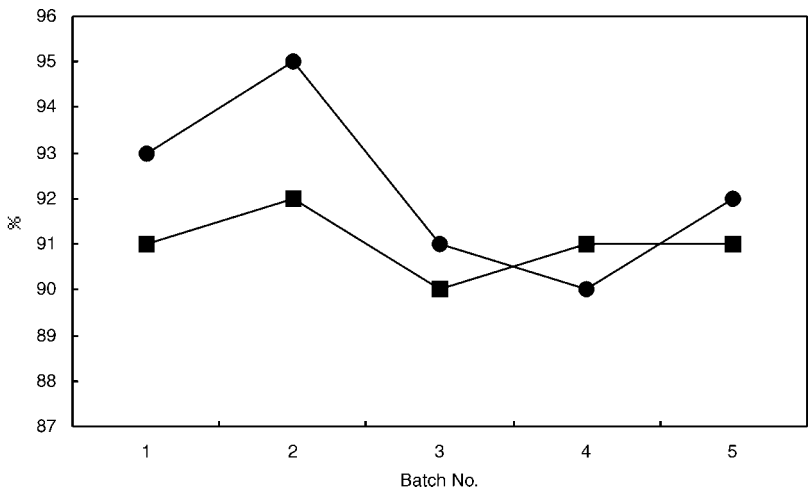


Fig. 1. Yield and enantioselectivities of the allylboration of *N*-silylimine **13a** with multiple use of the polymer-supported chiral allylboron reagent prepared from **7b**. ● % yield of **14a**; ■ %ee of **14a.**

Experimental Section

General Methods

All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium benzophenone ketyl under nitrogen immediately before use. Divinylbenzene (96% divinylbenzene, 4% ethylbenzene) was a gift from Nippon Steel Chemical Co., Ltd. *N*-(Trimethylsilyl)imines were obtained by reaction of the corresponding aldehydes with lithium hexamethyldisilazide according to the literature procedure.[13] Reactions were monitored by thin layer chromatography (TLC) using Merck precoated silica gel plates (Merck 5554, $60F_{254}$). Flash column chromatography was performed over Wako silica gel (Wakogel C-200, 100–200 mesh). Microanalyses were obtained using a YANACO MT-3 CHN CORDER. ^{1}H NMR spectra were measured on a JEOL JNM-GX270 spectrometer using Me_4Si as an internal standard. Infrared spectra (IR) were recorded with a JEOL JI*R*-7000 FT-IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). Optical purity was determined with a JASCO HPLC system composed of 3-line degasser DG-980-50, HPLC pump PV-980, and column oven CO-965, equipped with a chiral column (Chiralcel OD-H, Daicel) using hexane : 2-propanol : diethylamine (90 : 10 : 0.1). A UV detector (JASCO UV-975) was used for the peak detection. Optical rotations were taken on a JASCO DIP-140 digital polarimeter using a 10 cm thermostated microcell. Loadings of the polymers are expressed in millimoles of functional groups per gram of dry resin (mmol/g) or as degree of functionalization (DF). For example, DF = 0.10 if 10% of the styrene units are functionalized.

Synthesis of Chiral Monomers

Chiral monomer 1: ((1R,2S,3R,4S)-3-(4-vinylbenzenesulfonyl)amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol)

(–)-*exo*-2-Hydroxy-*exo*-3-aminobornane was prepared from (1*R*)-(+)-camphor according to the literature method.[14] A THF solution of 4-vinylbenzenesulfonyl chloride[15] (10 mmol) prepared from sodium 4-vinylbenzene sulfonate was added to a solution of the *exo*-amino alcohol (1.69 g, 10 mmol) and triethylamine (1.4 mL, 10 mmol) in 50 mL of dry THF. After being stirred for 3 h at room temperature, the reaction mixture was poured into 1 M aqueous HCl at 0 °C, and the THF was evaporated under vacuum. The resulting aqueous solution was extracted with ether (3×25 ml). The combined extracts were dried over $MgSO_4$ and evaporated at reduced pressure to give the crude product. Recrystallization from ethanol-water gave **1** in 86% yield; mp 149 °C; ^{1}H NMR (270 MHz; $CDCl_3$): δ = 7.84 (d, *J* = 8.3 Hz, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 6.76 (dd, *J* = 10.7, 17.6 Hz, 1 H), 5.88 (d, *J* = 17.6 Hz, 1 H), 5.44 (d, *J* = 10.7 Hz, 1 H), 5.33 (d, *J* = 6.8 Hz, 1 H), 3.60–3.55 (m, 1 H), 3.28-3.22 (m, 1 H), 2.19 (d, *J* = 4.4 Hz, 1 H), 1.70–1.17 (m, 5 H), 1.05 (s, 3 H), 0.89 (s, 3 H), 0.76 (s, 3 H); $[\alpha]_D^{25}$ –25.9 (*c* 1.50, ethanol); anal. calcd for $C_{18}H_{25}NO_3S$ (335.46): C 64.45, H 7.51, N 4.18%; found: C 64.38, H 7.45, N 4.18%.

Chiral monomer 2: ((1R,2R,3S,4S)-3-(4-vinylbenzenesulfonyl)amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol):

(–)-*endo*-2-Hydroxy-*endo*-3-aminobornane was prepared from (1*R*)-(+)-camphor according to the literature method.[16] Compound **2** was obtained in 73% yield; mp 147 °C; ^{1}H NMR (270 MHz; $CDCl_3$): δ = 0.84 (d, *J* = 8.3 Hz, 2 H), 7.52 (d, *J* = 8.3 Hz, 2 H), 6.75 (dd, *J* = 10.7, 17.6 Hz, 1 H), 5.89 (d, *J* = 17.6 Hz, 1 H) , 5.43 (d, *J* = 10.7 Hz, 1 H), 5.26 (d, *J* = 6.4 Hz, 1 H), 3.82–3.70 (m, 2 H), 1.96 (d, *J* = 3.9 Hz, 1 H), 1.78–1.05 (m, 5 H), 0.85 (s, 3 H), 0.83 (s, 3 H), 0.80 (s, 3 H); $[\alpha]_D^{25}$ 32.9 (*c* 3.0, CH_2Cl_2); anal. calcd for $C_{18}H_{25}NO_3S$ (335.46): C 64.45, H 7.51, N 4.18%; found: C 64.40, H 7.52, N 4.17%.

Chiral monomer 3: ((1R,2S)-2-(4-vinylbenzenesulfonyl)-amino-1-phenylpropan-1-ol):

Yield: 96%; mp 93–95 °C; ^{1}H NMR (270 MHz; $CDCl_3$): δ = 7.84 (d, *J* = 8.3 Hz, 2 H), 7.51, (d, *J* = 8.3 Hz, 2 H), 7.34–7.22 (m, 5 H), 6.74 (dd, *J* = 10.7, 17.6 Hz, 1 H), 5.87 (d, *J* = 17.6 Hz, 1 H), 5.43 (d, *J* = 10.7 Hz, 1 H), 5.16 (d, *J* = 8.8 Hz, 1 H), 4.80 (d, *J* = 2.9 Hz, 1 H), 3.62–3.55 (m, 1 H), 2.75 (br, s, 1 H), 0.85 (d, *J* = 6.8 Hz, 3 H); $[\alpha]_D^{25}$ –12.07 (*c* 2.78, $CHCl_3$); anal. calcd for $C_{17}H_{19}NO_3S$ (317.40): C 64.33, H 6.03, N 4.41%; found: C 64.40, H 6.00, N 4.42%.

Chiral monomer 4: ((1S,2R)-2-(4-vinylbenzenesulfonyl)amino-1-phenylpropan-1-ol):

Yield: 96%; mp 93–95 °C; ^{1}H NMR (270 MHz; $CDCl_3$): δ = 7.84 (d, *J* = 8.3 Hz, 2 H), 7.51, (d, *J* = 8.3 Hz, 2 H), 7.34–7.22 (m, 5 H), 6.74 (dd, *J* = 10.7, 17.6 Hz, 1 H), 5.87 (d, *J* = 17.6 Hz, 1 H), 5.43 (d, *J* = 10.7 Hz, 1 H), 5.16 (d, *J* = 8.8 Hz, 1 H), 4.80 (d, *J* = 2.9 Hz, 1 H), 3.62–3.55 (m, 1 H), 2.75 (br, s, 1 H), 0.85 (d, *J* = 6.8 Hz, 3 H); $[\alpha]_D^{25}$ 12.07 (*c* 2.78, $CHCl_3$); anal. calcd for $C_{17}H_{19}NO_3S$ (317.40): C 64.33, H 6.03, N 4.41%; found: C 64.27, H 5.97, N 4.40%.

Preparation of Polymer-Supported Chiral *N*-Sulfonylamino Alcohols

Chiral polymer 5

A solution of **1** (3.35 g, 10 mmol), styrene (8.32 g, 80 mmol), divinylbenzene (1.36 g, 10 mmol), and 2,2′-azobis(2,4-dimethylvaleronitrile) (0.25 g, 1 mmol) in a mixed solvent of benzene-THF (4 : 1) was added to a well stirred solution of poly(vinyl alcohol) (0.4 g, degree of polymerization: 2000, 78–82% hydrolyzed) in 200 mL of water at 0 °C. After 1 h of stirring at 0 °C to homogenize the particle size, the temperature was raised to 80 °C and the reaction mixture was stirred vigorously for 24 h at the same temperature. The resulting polymer beads were filtered and washed with water, methanol, THF-methanol, THF, and methanol, respectively. After drying in vacuo at 40 °C, 11.5 g of polymer **5** were obtained. Elemental analysis indicated a loading of *N*-sulfonylamino alcohol corresponding to 0.77 mmol/g (DF = 0.10). IR: ν = 3500, 3300, 1320, 1150, 1090 cm^{-1}; anal. calcd for $(C_8H_8)_{0.8}(C_{10}H_{10})_{0.1}(C_{19}H_{25}NO_3S)_{0.1}$: C 85.21, H 7.61, N 1.07, S 2.44%; found C 85.11, H 7.60, N 1.07, S 2.45%.

Chiral polymer 6

Suspension polymerization of **2** (3.35 g, 10 mmol), styrene (8.32 g, 80 mmol), divinylbenzene (1.36 g, 10 mmol) gave 11.6 g of polymer **6**. Both sulfur and nitrogen analyses indicated a loading of chiral amino alcohol corresponding to 0.77 mmol/g (DF = 0.10).

Chiral polymer 7b

Suspension polymerization of **3** (3.17 g, 10 mmol), styrene (8.32 g, 80 mmol), divinylbenzene (1.36 g, 10 mmol) gave 11.7 g of polymer **7 b**. Both sulfur and nitrogen analyses indicated a loading of chiral amino alcohol corresponding to 0.78 mmol/g (DF = 0.10).

Chiral polymer 8
Suspension polymerization of **4** (3.17 g, 10 mmol), styrene (8.32 g, 80 mmol), divinylbenzene (1.36 g, 10 mmol) gave 11.6 g of polymer **8**. Both sulfur and nitrogen analyses indicated a loading of chiral amino alcohol corresponding to 0.78 mmol/g (DF = 0.10).

General Procedure for the Enantioselective Allylation of Aldehyde with Polymer-Supported Chiral Allylboron Reagent
The transformation of **12a** to **13a** is typical. A THF solution (15 mL) of triallylborane (5 mmol) prepared from $BF_3 \cdot OEt_2$ (0.61 mL, 5 mmol) and allylmagnesium chloride (15 mmol, 1.2 M) at 0 °C was added to a suspension of **7b** (5.13 g, 4 mmol). The mixture was stirred at room temperature for 2 h and then heated at reflux for 12 h to complete the formation of the polymer-supported chiral allylboron reagent. After cooling, excess of triallylborane was removed by filtration through a sintered glass pad attached to the flask. The polymeric reagent was washed carefully with 25 mL of dry THF and dry ether. Then an ether solution of benzaldehyde (0.36 mL, 3.5 mmol) was added dropwise to the ether suspension of the polymeric reagent. The reaction mixture was stirred at −78 °C for 7 h and quenched with 2 N HCl aqueous solution. After removal of the chiral polymer by filtration, the filtrate was extracted with CH_2Cl_2 (2×50 mL) and the extract was washed with water (2×50 mL). The organic solution was dried ($MgSO_4$) and concentrated on a rotary evaporator to give the crude product, which was purified by column chromatography (hexane/ethyl acetate 10:1). The enantioselectivity of 75% ee was determined by HPLC analysis using a chiral stationary-phase column (Daicel, Chiralcel OD–H; hexane:propan-2-ol:diethylamine, 90:10:0.1, flow rate 0.5 ml/min); t_R = 16.7 min (*R*), t_R = 17.6 min (*S*). The absolute configuration of the product was correlated to that described in the literature.[17]

General Procedure for the Enantioselective Allylation of *N*-Silylimine with Polymer-Supported Chiral Allylboron Reagent
The transformation of **14a** to **15a** is typical. A THF solution of *N*-(trimethylsilyl)benzaldehyde imine (0.62 g, 3.5 mmol) was added dropwise to the THF suspension of the polymer-supported allylboron reagent prepared from **7b** (5.13 g, 4 mmol). The reaction mixture was then stirred for 6 h at –78 °C and quenched with 2 N HCl aqueous solution. After removal of the chiral polymer by filtration, the filtrate was neutralized with NH_4OH and extracted with CH_2Cl_2 (2 50 mL) and the extract was washed with water (2×50 mL). The organic solution was dried ($MgSO_4$) and concentrated on a rotary evaporator to give the crude product, which was purified by column chromatography (Et_2O:hexane, 4:1). The enantioselectivity of 87% ee was determined by HPLC analysis using a chiral stationary-phase column (Daicel, Chiralcel OD–H; hexane:propan-2-ol:diethylamine, 90:10:0.1, flow rate 0.5 ml/min); t_R = 16.3 min (*R*), t_R = 20.7 min (*S*). The absolute configuration of the product was correlated to that described in the literature.[18]

Acknowledgments

This work was supported in part by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. Financial support from the Ogasawara Foundation for the Promotion of Science & Technology is also greatly acknowledged.

References

[1] (a) E. C. Blossey, W. T. Ford in *Comprehensive Polymer Science, Vol. 6* (Ed.: G. Allen), Pergamon, Oxford, **1989**, pp. 81–114; (b) S. Itsuno, in: *Polymeric Materials Encyclopedia: Synthesis, Properties and Applications, Vol. 10* (Ed.: J. C. Salamone), CRC Press, Boca Raton, **1996**, pp. 8078–8087; (c) S. J. Shuttleworth, S. M. Allin, P. K. Sharma, *Synthesis*, **1997**, 1217–1239; (d) L. Pu, *Chem. Eur. J.* **1999**, *5*, 2227–2232.
[2] S. Itsuno, in: *Lewis Acids in Organic Synthesis*, (Ed.: H. Yamamoto), Ch. 21, Wiley-VCH, Weinheim, **2000**.
[3] (a) P. Hodge, in: *Synthesis and Separations Using Functional Polymers,* (Eds.: D. C. Sherrington, P. Hodge), Wiley, Chichester, **1988**, pp. 43–122; (b) S. Itsuno in *Macromolecules 1992*, (Ed.: J. Kahovec) VSP, Utrecht, **1993**, pp. 413–422.
[4] D. Obrecht, J. M. Villalgord, *Solid-Supported Combinatorial and Parallel Synthesis of Small-Molecular-Weight Compound Libraries, Tetrahedron Organic Chemistry Series, Vol. 17*, Pergamon, Oxford, **1998**.
[5] S. Itsuno, K. Watanabe, T. Matsumoto, S. Kuroda, A. Yokoi, A. El-Shehawy, *J. Chem. Soc., Perkin Trans. 1* **1999**, 2011–2016.
[6] S. Itsuno, K. Watanabe, K. Ito, A. A. El-Shehawy, A. A. Sarhan, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 109–110.
[7] S. Itsuno, A. A. El-Shehawy, *React. Funct. Polym.*, **1998**, *38*, 283–287.
[8] S. Itsuno, A. Yokoi, S. Kuroda, *Synlett* **1999**, 1987–1989.
[9] K. Watanabe, S. Kuroda, A. Yokoi, K. Ito, S. Itsuno, *J. Organomet. Chem.* **1999**, *581*, 103–107.
[10] A. A. El-Shehawy, M. Y. Abdelaal, K. Watanabe, K. Ito, S. Itsuno, *Tetrahedron: Asymmetry* **1997**, *8*, 1731–1734.
[11] (a) P. R. Short, S. Masamune, *J. Am. Chem. Soc.* **1989**, *111*, 1892–1894; (b) W. R. Roush, L. K. Hoong, M. A. J. Palmer, J. C. Park, *J. Org. Chem.* **1990**, *55*, 4109–4117; (c) E. J. Corey, C.-M. Yo, S. S. Kim, *J. Am. Chem. Soc.* **1989**, *111*, 5495–5495; (d) U. S. Racherla, H. C. Brown, *J. Org. Chem.* **1991**, *56*, 401–404; (e) H. C. Brown, U. S. Racherla, Y. Liao, V. V. Khanna, *J. Org. Chem.* **1992**, *57*, 6608–6614; (f) U. S. Racherla, Y. Liao, H. C. Brown, *J. Org. Chem.* **1992**, *57*, 6614–6617; (g) H. C. Brown, S. V. Kulkarni, U. S. Racherla, *J. Org. Chem.* **1994**, *59*, 365–369; (h) M. T. Reetz, T. Zierke, *Chem. Ind.* (London) **1988**, 663–664; (i) R. W. Hoffmann, T. Herold, *Chem. Ber.* **1981**, *114*, 375–383.
[12] K. Kamahori, S. Tada, K. Ito, S. Itsuno, *Tetrahedron: Asymmetry* **1995**, *6*, 2547–2555.
[13] D. J. Hart, K. Kanai, D. G. Thomas, T. K. Yang, *J. Org. Chem.* **1983**, *48*, 289–294.
[14] R. A. Chittenden, G. H. Cooper, *J. Chem. Soc. (C)* **1970**, 49–54.
[15] T. Ishizone, J. Tsuchiya, A. Hirao, S. Nakahama, *Macromolecules* **1992**, *25*, 4840–4847.
[16] A. M'Boungou-M'Passi, F. Henin, J. Muzart, J. P. Pete, *Bull. Soc. Chim. Fr.* **1993**, *130*, 214–217.
[17] R. W. Hoffmann, T. Herold, *Chem. Ber.* **1981**, *114*, 375–383.
[18] T. Basile, A. Bocoum, D. Savoia, A. Umani-Ronchi, *J. Org. Chem.* **1994**, *59*, 7766–7773.