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Synthesis of Polymer-Supported Chiral *N*-Sulfonylamino Acids and Their Use in Asymmetric Diels–Alder Reaction of Cyclopentadiene with Methacrolein

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Abstract: Crosslinked polymer-supported chiral *N*-sulfonylamino acids have been synthesized by two methods; namely the chemical modification method and the copolymerization method. In the chemical modification method, the chlorosulfonyl group was introduced into styrene-divinylbenzene copolymers **1** by sulfonation with chlorosulfonic acid followed by chlorination with thionyl chloride. The degree of functionalization could be well controlled by the feed ratio of chlorosulfonic acid to aromatic rings of the polymer. Treatment of L-valine with the polymer having the chlorosulfonyl group **4** gave polymer-supported *N*-sulfonylated L-valine **5**. An alternative approach to the synthesis of chiral polymers involves the copolymerization of monomers containing the desired chiral groups with styrene and divinylbenzene (DVB). Suspension copolymerization of chiral monomers **6**, styrene, and DVB afforded the chiral polymers **7** in good yield. The *N*-sulfonylamino acid group in the polymer reacted with borane or monobromoborane to form chiral oxazaborolidinone **8**, which catalyzed the Diels–Alder reaction of cyclopentadiene with methacrolein, leading to optically active cycloadduct having enantiomeric purity of 65% ee.

INTRODUCTION

Since the early reports on the enantioselective Diels–Alder reactions catalyzed by chiral Lewis acids,[1] considerable work has been undertaken to establish the mechanism and the stereochemical outcome of the reaction.[2] In order to enable easy recovery and reuse of the chiral ligands and catalysts, the use of catalysts grafted on insoluble polymeric supports is attractive.[3] It is also important to understand polymer effects in the immobilized catalyst on the asymmetric reactions. In previous papers, we have described that treatment of polymers having bifunctional chiral moieties with boranes or dialkylzincs provided the polymeric Lewis acids, presumed to be metallacycles, which were used for several asymmetric transformations including alkylation of aldehydes[4] and reduction of ketones[5] and oximes.[6] Recently, we also reported that the polymeric chiral Lewis acids catalyzed Diels–Alder reaction of methacrolein with cyclopentadiene to give chiral cycloadduct.[7] Of the various polymeric catalysts tested, catalysts derived from *N*-sulfonylamino acid polymers are the most effective for the Diels–Alder reaction.[8] Asymmetric Diels–Alder reactions in solution reported by Yamamoto[9] and Helmchen[10] also suggested that chiral oxazaborolidinones derived from *N*-sulfonylamino acids were useful for the reaction. Thus we have prepared various chiral polymers possessing *N*-sulfonylamino acid moieties. These polymers were prepared by two methods involving either attachment of a chiral moiety as a

Dedicated to the memory of Professor Hidemasa Takaya, deceased on 5 October 1995

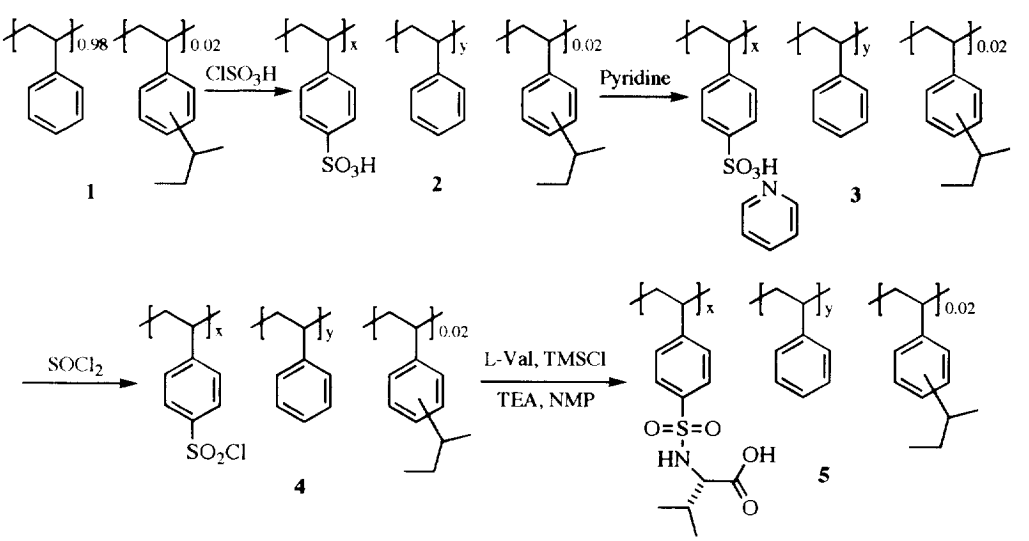
side chain onto a reactive crosslinked polystyrene, or the terpolymerization of a chiral monomer with styrene and DVB as crosslinking agent. Although the catalytic asymmetric Diels–Alder reactions have been studied extensively, there are fewer reports that involve polymeric chiral catalysts. Here we report the preparation of crosslinked chiral polymers and their use in asymmetric Diels–Alder reactions.

RESULTS AND DISCUSSION

Synthesis of chiral polymers: Chemical modification method.

The preparation of chiral polymers by chemical modification of polymers has been used extensively due to the relative simplicity of the method.[11] Various chiral polymers have been prepared by this method.[3] Therefore, an attachment of amino acid to partly chlorosulfonylated polystyrene crosslinked with 2% of DVB was performed to prepare polymer-supported *N*-sulfonylated amino acid **5** as shown in Scheme 1. However, although a number of reactive polymers have been prepared satisfactorily by modification of crosslinked polystyrene resins,[3] there are few reports on the preparation of polymers containing chlorosulfonyl groups. Sulfonation of polystyrene beads is a well known reaction and the sulfonylated polymers have been widely used as ion exchange resins, however, the reaction conditions for introduction of chlorosulfonyl group into the crosslinked polystyrene has not been established.[12] Of various reaction conditions tested, we found that the use of chlorosulfonic acid in chloroform at 40 °C is the method of choice for the partial introduction of the sulfonyl group into the crosslinked polystyrene beads. The degree of sulfonation was easily controlled by the molar ratio of chlorosulfonic acid with aromatic ring of the polystyrene. The pyridine salt of the obtained partly sulfonylated polymer **3** was then chlorinated with thionyl chloride to give the desired polymer beads **4** having chlorosulfonyl groups as reactive site. Chlorosulfonyl polymers of DF = 0.10 to 0.64 were prepared by this method. Other reagents such as phosphorous pentachloride and phosphorous oxychloride, which are usually used in the transformation of sulfonic acids to chlorosulfonyl compounds, did not give sufficient results in chlorination of the polymer. Table 1 shows the results of chlorosulfonation.

Scheme 1



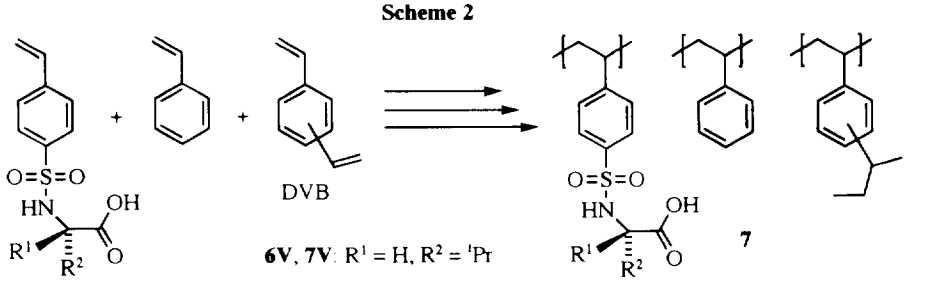
Chemical modification reactions on the insoluble polymer sometimes suffer from sluggish conversion due to their heterogeneous reactions. Even though chlorosulfonyl group is highly reactive to amines, insoluble amino acid in organic solvent showed no reaction with the solid polymer. The use of trimethylsilyl ester of amino acid, which is soluble in *N*-methyl-2-pyrrolidone as solvent, facilitated the reaction to provide the chiral polymer with complete conversion of the chlorosulfonyl groups. This method made it possible to prepare the desired polymer **5** in quantitative yield by chemical modification method (Scheme 1).

Table 1. Chlorosulfonation of 2% crosslinked polystyrene[a]

Run	$[ClSO_3H]$ / [Ar][b]	DF[c] calcd from S[d] analysis in **4**	DF[c] calcd from Cl[d] analysis in **4**
1	0.3	0.11	0.10
2	0.5	0.30	0.31
3[e]	0.6	0.16	0.16
4	0.8	0.31	0.31
5	1.0	0.41	0.41
6	2.0	0.64	0.64

[a]Sulfonation was carried out at 40 °C for 2 h. Yield of the functionalized polymer was almost 100% in each case. [b]Aromatic ring in polystyrene. [c]Degree of functionalization. [d]Determined by titration. [e]Sulfonation was carried out at room temperature.

Scheme 2



6V, **7V**: R^1 = H, R^2 = ^{i}Pr

6I, **7I**: R^1 = H, R^2 = ^{s}Bu

6P, **7P**: R^1 = Ph, R^2 = H

6T, **7T**: R^1 = H, R^2 = CH(OH)Me

Polymerization of chiral monomers.

A general problem in the preparation of polymer-supported chiral ligands by the chemical modification method is that complete removal of byproducts from the polymer is not possible, which leads to contaminate the polymer. If chiral monomer can be easily prepared, the chiral polymers can be synthesized by polymerization. Indeed, chiral monomers **6** were readily prepared by a single step synthesis from 4-vinylbenzenesulfonyl chloride[13] and amino acid in the presence of triethylamine. Amino acids used in this study are L-valine (**V**), L-isoleucine (**I**), D-2-phenylglycine (**P**), and L-threonine (**T**). A mixture of chiral

monomer **6**, styrene, DVB, and benzoyl peroxide as radical initiator in benzene/THF was suspended in water including a small amount of poly(vinyl alcohol) as suspension stabilizer at 0 °C. Polymerization in each oil droplet was initiated when the temperature was raised to 80 °C to give chiral polymer **7** having a spherical beads form (Scheme 2). The particle diameter is in the range of 50 to 100 micrometer. Small amount of fine powdered polymers formed that cause difficulties in filtration were removed through a sieve (400 mesh). In the polymerization method for the chiral polymers, degree of functionalization and degree of crosslinking are controlled simply by changing a monomers feed ratio. Suspension polymerization with various molar ratio of **6V**, styrene, and DVB were conducted in preparation of the chiral polymers **7Va–c** as shown in Table 2. Monomers derived from other amino acids were polymerized in the same way. These insoluble polymer beads can be readily purified by washings with various organic solvents and water on a glass filter. Loading of amino acid residues in the polymer, which was determined by both elemental analysis and sulfur titration, is closely paralleling the value calculated from the starting monomers feed ratio (Table 2). These polymers swelled well in organic solvents such as benzene, toluene or tetrahydrofuran.

Table 2. Suspension polymerization of *N*-sulfonylamino acid monomer 6 and styrene with DVB

Run	Chiral monomer **6**	[**6**]	[Styrene]	[DVB]	Chiral polymer **7**	Loading of amino acid residues in polymer **7** (mmol/g)[a]	Yield of **7** (%)
1	**6V**	10	88	2	**7Va**	0.85	69
2	**6V**	10	80	10	**7Vb**	0.88	85
3	**6V**	50	40	10	**7Vc**	2.55	73
4	**6I**	10	80	10	**7I**	0.79	93
5	**6P**	10	80	10	**7P**	0.78	84
6	**6T**	10	80	10	**7T**	0.80	96

[a]Determined by N and S analysis.

Asymmetric Diels-Alder reactions.

The various chiral polymers (**5**, **7V**, **7I**, **7P**, and **7T**) synthesized were examined as chiral ligands for catalysts in the Diels–Alder reaction of cyclopentadiene with methacrolein (Scheme 3); results are summarized in Table 3. It is assumed that polymer-bound chiral oxazaborolidinone **8** is formed upon mixing of the chiral polymer and borane as shown in Scheme 3. After hydrogen evolution ceased to complete the formation of **8**, resulting polymeric catalyst was employed for asymmetric Diels–Alder reaction of cyclopentadiene with methacrolein. Without catalyst essentially no reaction occured between these substrates. On the contrary, Diels–Alder cycloadduct was smoothly formed even at -78 °C with the polymeric catalyst. In the presence of polymeric catalyst derived from borane and **7Va** the corresponding Diels–Alder adduct was obtained in high yield and high *exo* selectivity with 57% enantioselectivity (run 1). In spite of chiral polymer **5** having the same structure as **7V**, the reaction with **5** resulted in very low selectivity (run 2). Both *exo*- and

Scheme 3

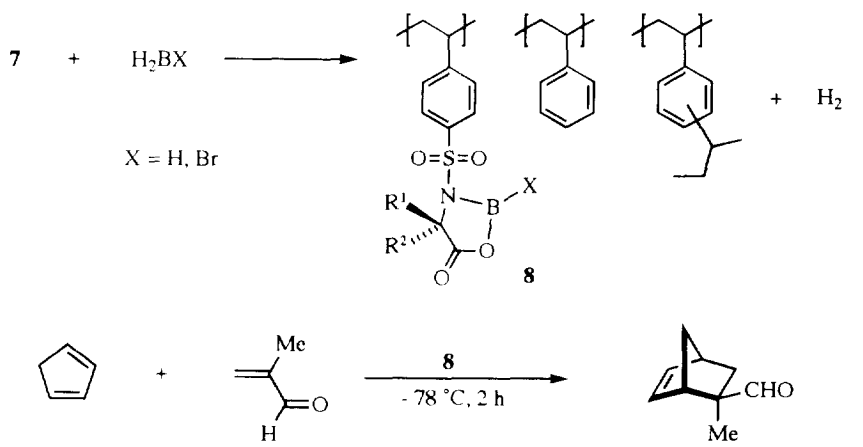


Table 3. Asymmetric Diels–Alder reaction of cyclopentadiene with methacrolein using polymeric catalyst[a]

Run	Chiral polymer	Borane	Solvent	Yield,[b] %	*endo*/*exo*[c]	% ee[d]	$[\alpha]_D$ (EtOH)	*Config.*
1	**7Va**	BH_3	CH_2Cl_2	95	<1 : 99	57	- 13.29	*R*
2	**5**	BH_3	CH_2Cl_2/THF	85	13 : 87	1	- 0.24	*R*
3	**7Vb**	BH_3	CH_2Cl_2/THF	87	<1 : 99	65	- 15.08	*R*
4[e]	**7Vb**	BH_3	CH_2Cl_2/THF	79	<1 : 99	64	- 14.90	*R*
5[f]	**7Vb**	BH_3	CH_2Cl_2/THF	93	<1 : 99	65	- 15.14	*R*
6	**7I**	BH_3	CH_2Cl_2/THF	99	3 : 97	49	- 11.42	*R*
7	**7P**	BH_3	CH_2Cl_2/THF	99	4 : 96	49	+ 11.50	*S*
8	**7T**	BH_3	CH_2Cl_2/THF	65	8 : 92	10	- 2.35	*R*
9	**7Va**	BH_2Br	CH_2Cl_2	95	<1 : 99	43	- 9.93	*R*
10	**7Vb**	BH_2Br	CH_2Cl_2	99	<1 : 99	44	- 10.34	*R*
11	**7Vb**	BH_2Br	CH_2Cl_2/THF	90	<1 : 99	52	- 12.06	*R*
12	**7Vc**	BH_2Br	CH_2Cl_2	76	10 : 90	10	- 2.25	*R*

[a]All reactions were carried out in the presence of 15 mol % polymeric boron catalyst. [b]Isolated yields. [c]Determined by ^1H NMR. [d]The optical purity of the *exo* isomer was calculated by the observed optical rotation on the basis of the rotation reported by Koga.[1] [e]100 mol % of polymeric catalyst was used. [f]Recycled polymer was used.

enantioselectivity in the asymmetric Diels–Alder reaction is critically dependent on their preparation method. We then used **7** prepared by copolymerization method for other asymmetric reactions.

Helmchen reported that the Diels–Alder reaction performed in dichloromethane at -78°C yielded the cycloadduct in 20% ee, in the presence of a soluble catalyst prepared from *N*-sulfonylated L-valine and borane.[9] He also claimed that solvent used in the reaction is very important for the enantioselectivity. In addition of THF to the reaction mixture, the enantioselectivity of the same reaction was dramatically increased to 86% ee. The association structure of the catalysts *via* the carbonyl group and boron atom would exist in dichloromethane, which may result in decrease of enantioselectivity. Donor solvents may destroy such association to increase enantioselectivity. On the other hand, polymeric catalyst derived from **7V** gave 57% ee in dichloromethane as solvent, which is much better selectivity than that of the monomeric reaction. A number of catalytic species in the polymer would be hindered to be associated each other since each catalyst site is immobilized to the crosslinked rigid polymer support. Addition of THF to the reaction using polymeric catalyst **7V** increased enantioselectivity to 65% ee (Table 3, run 3), but not 86% ee. Thus, the effect of donor solvent is not significant on the enantioselectivity in the case of polymeric catalyst. This is also due to the rigid structure of polymeric catalyst.

After the Diels–Alder reaction was complete the polymeric catalyst was easily removed by simple filtration. The use of recycled polymer showed no loss in reactivity or selectivity (run 5). Of the polymeric catalysts **8** derived from various amino acids, L-valine derived catalyst **8V** gave the highest enantioselectivity in the Diels–Alder reaction. Polymeric catalysts derived from L-amino acids gave the cycloadduct of *R* configuration, while polymer from D-amino acid gave *S* adduct (run 7). Polymeric catalysts were also prepared by treatment of monobromoborane with chiral polymers **7**. These catalysts were effective for the reaction to give chiral cycloadducts. Enantioselectivities obtained with these catalysts, however, were somewhat lower than those obtained from borane. Higher loading of chiral catalyst site in the polymer resulted in lowering both *exo* selectivity and enantioselectivity (run 12). In this case catalyst sites exsist very closely to each other in the polymer to form highly associated structure.

EXPERIMENTAL SECTION

General. All reactions were carried out under an atmosphere of nitrogen. Cyclopentadiene was obtained by thermal decomposition of dicyclopentadiene. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried over sodium benzophenone ketyl, and were freshly distilled just before use. *N,N'*-dimethylformamide (DMF) and dichloromethane were distilled from calcium hydride. All other commercial chemicals were used without further purification. Both ^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were recorded on a JEOL JNM-GX270 spectrometer. IR spectra were recorded on a JEOL JIR-7000 FT-IR spectrometer. Microanalyses were obtained using YANACO MT-3 CHN CORDER. Melting points were taken on a Yanaco micro melting apparatus and were uncorrected. Optical purity was determined by Shimadz Capillary Gas Chromatograph 14A with a chiral capillary column (Astec Chiraldex G-TA, 20 m or 30 m). Precoated silica gel plates (Merck 5554, $60F_{254}$) were used for thin layer chromatography. Silica gel (Wakogel C-200) was used for column chromatography. Optical rotations were taken on a JASCO DIP-140 digital polarimeter using a 10 cm thermostatted microcell. Capacities of the polymers determined by gravimetry, microanalysis, and titrimetry 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.

Preparation of polymeric sulfonylchloride 4.

To a chloroform (50 ml) suspension of polystyrene beads crosslinked with 2% DVB (1g, 9.6 mequiv of phenyl ring) was added a chloroform (20 ml) solution of chlorosulfonic acid (1.12 g, 9.6 mmol) and the mixture was stirred at 40 °C for 2 h. The polymer was then filtered and washed repeatedly with chloroform. The partially sulfonylated polymer was then treated with pyridine for 1 h at 40 °C to give the pyridinium salt which was filtered and washed with chloroform, THF, THF-water (1 : 1), and THF. After drying in vacuo at 40 °C, the polymer was then treated with thionyl chloride for 6 h at reflux temperature to give the partly chlorosulfonylated polystyrene beads. The polymer was filtered and washed with pyridine and THF. After drying in vacuo at 40 °C, 1.39 g of polymer was obtained. Both sulfur and chlorine analyses indicated the same value of a loading of chlorosulfonyl group (DF = 0.41) while no nitrgen remains on the polymer. IR (KBr): 1600, 1415, 1367, 1174, 935, 582 cm^{-1}.

Polymer-supported N-sulfonyl-L-valine 5 : Chemical modification procedure.

To a suspension of L-valine (0.66g, 5.66mmol) in 150ml of *N*-methyl-2-pyrrolidone (NMP) was added chlorotrimethylsilane (0.72ml, 5.66mmol) at room temperature. After stirring for 30 min triethylamine (0.98ml, 7.08mmol) and chlorosulfonylated polymer **2** (3.18 g, 0.89 mequiv of Cl/g, DF = 0.1). The resulting mixture was stirred at room temperature for 20 h under nitrogen. The polymer was then filtered and washed repeatedly with methanol, water, THF-water (1 : 1), THF, and methanol. After drying in vacuo at 40 °C, 3.45 g of polymer (**5**) was obtained. Nitrogen and sulfur analyses indicated a loading of chiral amino acid corresponding to 0.82 mmol/g (DF = 0.1) while no chlorine remained on the polymer. IR (KBr): 3280, 2913, 1724, 1600, 1487, 1158, 1092 cm^{-1}.

4-Vinylbenzenesulfonamide of L-valine 6V. 4-Vinylbenzenesulfonyl chloride was prepared by the reported procedure.[13] To a solution of L-valine (6.8g, 73mmol) in triethylamine (13.5 ml) and water (100 ml) was added a THF solution of 4-vinylbenzenesulfonyl chloride. The resulting mixture was stirred for 18 h at room temperature. Aqueous solution of 2N HCl (50 ml) was then added slowly at 0 °C, organic layer was removed, and the aqueous layer was extracted with ether. Organic layer was washed with water, dried ($MgSO_4$) and concentrated to give pale yellow solid. The crude product was recrystallized from benzene to give 12.2g (88%) of chiral monomer **6V** as colorless needles : m.p. 137-139 °C, $[\alpha]_D^{23}$ +36.6 (*c* 1.33, $CHCl_3$) .^{1}H NMR (270 MHz, $CDCl_3$) δ 9.50 (br, 1H) 7.78 (d, 2H, *J* = 8.3 Hz), 7.48 (d, 2H, *J* = 8.3 Hz), 6.72 (dd, 1H, *J* = 10.8, 17.6 Hz), 5.87 (d, 1H, *J* = 17.6 Hz), 5.43 (d, 1H, *J* = 10.8 Hz), 5.37 (d, 1H, *J* = 9.8 Hz), 3.79 (dd, 1H, *J* = 4.5, 9.8 Hz), 2.00-2.20 (m, 1H), 0.95 (d, 3H, *J* = 6.8 Hz), 0.85 (d, 1H, *J* = 6.8 Hz). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 175.9, 142.0, 138.4, 135.3, 127.6, 126.6, 117.5, 60.6, 31.4, 19.0, 17.1. IR (KBr): 3180, 1728, 1691, 1468, 1375, 1346, 1190, 1141, 1049 cm^{-1}. Anal. Calcd. for $C_{13}H_{17}NO_4S$: C, 55.11; H, 6.05; N, 4.94. Found: C, 55.10; H, 6.05; N, 4.95.

4-Vinylbenzenesulfonamide of L-isoleucine 6I. Chiral monomer **6I** was obtained from 4-vinylbenzenesulfonyl chloride and L-isoleucine by the conditions described for **6V** in 96% yield. Crystals, m.p. 126.0-127.0 °C (from methanol-water); $[\alpha]_D$ +43.3 (*c* 5.12, ethanol); IR (KBr) 3330, 1732, 1692, 1373, 1342, 1134 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$-DMSO-d_6) δ 7.80 (d, 2H, 8.3 Hz), 7.50 (d, 2H, 8.3 Hz), 6.83 (d, 1H, *J* = 9.5 Hz), 6.74 (dd, 1H, *J* = 10.7, 17.6 Hz), 5.89 (d, 1H, *J* = 17.6 Hz), 5.42 (d, 1H, *J* = 10.7 Hz), 3.69 (dd, 1H, *J* = 5.4, 9.5 Hz), 2.59 (m, 1H), 1.45 (m, 1H), 1.18 (m, 1H), 0.91 (d, 3H, *J* = 6.8

Hz), 0.85 (t, 3H, J = 7.3 Hz) ; ^{13}C-NMR (67.8 MHz, $CDCl_3$-DMSO-d_6) δ 175.8, 142.1, 138.4, 135.3, 127.6, 126.6, 117.5, 59.9, 38.2, 24.5, 15.4, 11.3. Anal. Calcd. for $C_{14}H_{19}NO_4S$: C, 56.55; H, 6.44; N, 4.71. Found: C, 56.50; H, 6.40; N, 4.70.

4-Vinylbenzenesulfonamide of D-2-phenylglycine 6P. Chiral monomer **6P** was obtained from 4-vinylbenzenesulfonyl chloride and D-2-phenylglycine by the conditions described for **6V** in 65% yield. Crystals, m.p. 149-151 °C (from ethanol-water); $[\alpha]_D$ -113.8 (c 4.23, ethanol); IR (KBr) 3302, 1736, 1599, 1327, 1169, 1135 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$-DMSO-d_6) δ 7.68 (d, 2H, 8.3 Hz), 7.38 (d, 2H, 8.3 Hz), 7.15-7.35 (m, 5H), 6.70 (d, 1H, J = 7.7 Hz), 6.70 (dd, 1H, J = 10.7, 17.6 Hz), 5.83 (d, 1H, J = 17.6 Hz), 5.40 (d, 1H, J = 10.7 Hz), 4.98 (d, 1H, J = 7.7 Hz) ; ^{13}C-NMR (67.8 MHz, $CDCl_3$-DMSO-d_6) δ 170.8, 140.7, 139.0, 134.9, 127.9, 127.5, 126.8, 126.7, 125.7, 116.5, 59.1. Anal. Calcd. for $C_{16}H_{15}NO_4S$: C, 60.55; H, 4.76; N, 4.41. Found: C, 59.92; H, 4.77; N, 4.39.

4-Vinylbenzenesulfonamide of L-threonine 6T. Chiral monomer **6T** was obtained from 4-vinylbenzenesulfonyl chloride and L-threonine by the conditions described for **6V** in 71% yield. Crystals, m.p. 154.0-155.5 °C (from ethanol-water); $[\alpha]_D$ +25.0 (c 5.55, ethanol); IR (KBr) 3465, 3303, 1724, 1600, 1403, 1344, 1282, 1197, 1167, 1089 cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6) δ 7.79 (d, 2H, 8.3 Hz), 7.53 (d, 2H, 8.3 Hz), 7.17 (d, 1H, J = 9.3 Hz), 6.75 (dd, 1H, J = 10.7, 17.6 Hz), 5.91 (d, 1H, J = 17.6 Hz), 5.42 (d, 1H, J = 10.7 Hz), 4.52 (br, 1H), 4.02-4.18 (m, 1H), 3.70 (dd, 1H, J = 2.9, 9.3 Hz), 1.13 (d, 3H, J = 6.3 Hz). ^{13}C-NMR (67.8 MHz, DMSO-d_6) δ 171.1, 140.7, 140.2, 135.4, 127.0, 126.4, 117.3, 66.9, 61.4, 20.0. Anal. Calcd. for $C_{12}H_{15}NO_5S$: C, 50.52; H, 5.30; N, 4.91. Found: C, 50.60; H, 5.30; N, 4.90.

Polymer-supported N-sulfonylamino acid: Copolymerization procedure.
To a well stirred solution of poly(vinyl alcohol) (0.2g, degree of polymerization : 2000, 78-82% hydrolyzed) in 100ml of water cooled to 0 °C was added a solution of **6V** (0.6g, 2mmol), styrene (1.83g, 18mmol), divinylbenzene (0.052g, 0.4mmol) and benzoyl peroxide (0.32g, 1mmol) in a mixed solvent of benzene-THF (4:1). 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, 1.93 g of polymer **7V** was obtained. Sulfur analysis indicated a loading of chiral amino acid corresponding 0.84 mmol/g (DF = 0.1). IR (KBr): 3280, 2913, 1724, 1601, 1487, 1156, 1091 cm^{-1}. Other polymers **7** were prepared by suspension polymerizations using the procedure described for **7V**. The molar ratios of the monomers used were as given in Table 2. The loadings of amino acid residues, as estimated by nitrogen and sulfur analysis, are also given in Table 2.

Asymmetric Diels–Alder reactions using polymer-supported chiral catalyst. A typical experimental procedure is as follows: the chiral catalyst was generated in situ by stirring borane-methyl sulfide complex (1 M solution in dichloromethane, 1.5 mmol) and **7Va** (1.5 mmol) suspended in 10 ml of dichloromethane for 4 h at room temperature. To the catalyst was added a dichloromethane solution of methacrolein (0.83 ml, 10 mmol) and cyclopentadiene (1.2ml, 12mmol) at - 78 °C. The mixture was stirred

for 2 h at -78 °C, and then quenched with aqueous sodium hydrogen carbonate. After removal of the chiral polymer by filtration, the usual work-up gave the Diels–Alder adduct (yield, 95 %). Silica gel chromatography (hexane-ethyl acetate 24 : 1) gave pure *exo* adduct; it was characterized by ^{1}H NMR spectroscopy. The specific rotation for the ethanol solution was $[\alpha]_D$ -13.29 (*c* 5.0, ethanol). The optical yield (57% ee) was calculated by the observed specific rotation and the known maximum rotation of the adduct, $[\alpha]_{Dmax}$ 23.3 (ethanol).[1] The optical yield was also determined to be 57 % ee by GLC analysis after conversion to chiral acetal with (2*R*, 4*R*)-(-)-2,4-pentanediol.[14]

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REFERENCES

1. Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.*, **1979**, 437. Bednarski, M.; Maring, C.; Danishefsky, S. *Tetrahedron Lett.*, **1983**, *24*, 3451.
2. Narasaka, K. *Synthesis*, **1991**, 1. Kagan, H. B.; Riant, O. *Chem. Rev.*, **1992**, *92*, 1007. Bao, J.; Wulff, W. D. *J. Am. Chem. Soc.*, **1993**, *115*, 3814. Maruoka, K.; Murase, N.; Yamamoto, H. *J. Org. Chem.*, **1993**, *58*, 2983.
3. Itsuno, S. *The Polymeric Materials Encyclopedia Synthesis, Properties and Applications*, Salamone, J. C., Ed., CRC Press, in press. Tomoi, M.; Ford, W. T. *Synthesis and Separations using Functional Polymers*, Sherrington, D. C; Hodge, P. Eds.; Wiley, Chichester, 1988, Chapter 5, p. 181. Blossey, E. C.; Ford, W. T. *Comprehensive Polymer Science*, Allen, G. Ed., Pergamon, Oxford, 1989, Vol. 6, Chapter 3, p. 81.
4. Itsuno, S.; Sakurai, Y.; Ito, K.; Maruyama, T.; Nakahama, S.; Fréchet, J. M. J. *J. Org. Chem.*, **1990**, *55*, 304.
5. Itsuno, S.; Ito, K.; Maruyama, T.; Kanda, N.; Hirao, A.; Nakahama, S. *Bull. Chem. Soc. Jpn.*, **1986**, *59*, 3329.
6. Itsuno, S.; Sakurai, Y.; Ito, K.; Hirao, A.; Nakahama, S. *Polymer*, **1987**, *28*, 1005.
7. Itsuno, S.; Watanabe, K.; Koizumi, T.; Ito, K. *Reactive Polymers*, **1995**, *24*, 219.
8. Itsuno, S.; Kamahori, K.; Watanabe, K.; Koizumi, T.; Ito, K. *Tetrahedron: Asymmetry*, **1994**, *5*, 523.
9. Takasu, M.; Yamamoto, H. *Synlett*, **1990**, 194.
10. Sartor, D.; Saffrich, J.; Helmchen, G.; Richards, C. J.; Lambert, H. *Tetrahedron: Asymmetry*, **1991**, *2*, 639. Sartor, D.; Saffrich, J.; Helmchen, G. *Synlett*, **1990**, 197.
11. Fréchet, J. M. J. *Tetrahedron*, **1981**, *37*, 663.
12. Kamogawa, H.; Kanazawa, A.; Kadoya, M. *Bull. Chem. Soc. Jpn.*, **1983**, *56*, 762.
13. Ishizone, T.; Tsuchiya, J.; Hirao, A.; Nakahama, S. *Macromolecules*, **1992**, *25*, 4840.
14. Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.*, **1989**, *54*, 1483. Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. *Angew. Chem. Int. Engl.*, **1995**, *34*, 798.

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