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Asymmetric hydrogenation of aromatic ketones using polymeric catalyst prepared from polymer-supported 1,2-diamine

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Abstract

tert-Butyloxycarbonyl (Boc) protected chiral 1,2-diamine monomers **3** were copolymerized with achiral vinyl monomers such as styrene, methacrylates, acrylates, methacrylamide, and acrylamide to give crosslinked polymers **P2** containing chiral 1,2-diamine moieties. Deprotection of the Boc groups in the polymer afforded the crosslinked chiral 1,2-diamine polymer **P3**. The diamine polymer was allowed to react with $RuCl_2$/BINAP in DMF to form polymeric complex. Asymmetric hydrogenation of aromatic ketones smoothly proceeded using the polymeric complex to give the corresponding secondary alcohol in quantitative yield with high level of enantioselectivity up to 98% ee in a mixed solvent of DMF and 2-propanol. The polymeric catalyst can be recycled several times without loss of the activity.
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1. Introduction

Chiral, enantiomerically pure 1,2-diamines and their derivatives are currently used increasingly in asymmetric synthesis [1]. Of chiral 1,2-diamines the most frequently used enantiopure ones are 1,2-diphenylethylenediamine (DPEN) and 1,2-diaminocyclohexane. These chiral 1,2-diamines having C_2-symmetry offer especially great promise as stereoselective reagents and catalysts for asymmetric synthesis. Many examples of chiral catalyst systems containing these 1,2-diamines involve those used for hydrogenation [2], epoxidation [3], Diels–Alder reactions [4], aldol reactions [5], dihydroxylations of olefins [6], nucleophilic additions of carbonyls [7], conjugate additions [8], protonation of enolates [9], cyclopropanations [10], and aziridinations [11]. The chiral catalysts derived from the 1,2-diamines showed excellent activity with high level of asymmetric induction in various kinds of asymmetric transformations including above mentioned reactions.

On the other hands, from a viewpoint of efficiency in organic synthesis polymer-supported catalysts are extremely useful for enantioselective reaction mainly due to their easy separation from the reaction mixture. A considerable number of papers on the immobilization of chiral compound to polymer have been reported [12]. Polymer-supported chiral compounds can be used as chiral auxiliary, reagent, or ligands for asymmetric catalyst. However study on the immobilization of enantiopure 1,2-diphenylethylenediamine is quite limited. Some unique method should be required in order that the immobilization may maintain primary amino groups in the 1,2-diamine structure. We have designed and synthesized enantiomerically pure 1,2-diamine monomer **3** having 1,2-diphenylethylenediamine structure. Vinylphenyl group in the chiral monomer can be easily polymerized under radical polymerization condition to give the polymer-supported chiral 1,2-diamine **P3** after deprotection of Boc group in **P2**, which can be utilized as chiral ligand for asymmetric catalyst in the above reactions. We have chosen enantioselective hydrogenation of unfunctionalized ketones as one of the most important application of chiral 1,2-diamine as a

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ligand of the catalyst. Chiral free diamine is necessary to prepare efficient catalyst for this reaction. Thus, the chiral catalyst prepared from a combination of enantiopure 1,2-diamine, RuCl$_2$, and BINAP [13] shows powerful catalytic activity in the asymmetric hydrogenation of ketones [2]. Previously we have reported that styrene based polymer-supported 1,2-diamine **P1** performed as a polymeric chiral ligand of the catalyst for asymmetric hydrogenation of ketones [14,15]. In order to investigate the polymer effect on the enantioselective reaction we have prepared various kinds of polymers containing the chiral 1,2-diamine structure. In this paper we have copolymerized the chiral monomer **3** with various achiral vinyl monomers to give crosslinked chiral 1,2-diamine polymers **P3**, which have been applied to the preparation of the catalyst for the asymmetric hydrogenation of aromatic ketones.

2. Experimental

2.1. Materials

All reactions were carried out under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was freshly distilled from calcium hydride under reduced pressure. All ketones used were distilled from calcium hydride under argon. Reactions were monitored by TLC using Merck Precoated silica-gel plates (Merck 5554, 60F254). Column chromatography was performed with a silica gel column (Wakogel C-200, 100–200 mesh).

2.2. Measurements

^{1}H NMR (300 MHz) spectra were recorded on Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard, and *J* values are recorded in hertz. ^{13}C NMR (100 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a Varian Inova 400 spectrometer. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). Elemental analyses were performed at 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 (CHIRALCEL OD, Daicel) using hexane/2-propanol as an eluent. A UV detector (JASCO UV-975) was used for the peak detection. GC analyses of reaction conversion were performed with a Shimadzu Capillary Gas Chromatograph 14A equipped with a capillary column (Astec Chiraldex G-TA, 30 m × 0.25 mm).

2.3. General procedure for copolymerization of chiral 1,2-diamine monomer 3 with achiral monomer

A 20 mL glass ampoule equipped with magnetic stirring bar was charged with DMF (2.0 mL), **3** (0.295 mmol) [14], achiral monomer (5.60 mmol), and AIBN (13 mg,

80 μmol). The ampoule was sealed after three cycles of freeze–thaw under liquid nitrogen. Copolymerization was carried out at 70 °C. After 5 min stirring, viscosity of the solution increased and gel was formed within 15 min. The whole mixture was continued to be heated at the same temperature for 24 h. The ampoule was opened and the resulting mixture was poured into methanol. The obtained polymer **P2a** was washed with THF and methanol and dried in vacuo.

The above polymer having Boc-NH groups was then transferred to a flask containing 15 mL of 4 N HCl/THF solution at room temperature and stirred for 5 h. The insoluble polymer was filtered and washed with THF, water and THF again. The chiral 1,2-diamine hydrochloride polymer was then treated with THF (20 mL)/triethylamine (20 mL) mixture at room temperature for 12 h. The polymer **P3a** was collected on a glass filter and washed with THF, water, methanol and dried in vacuo at 40 °C for 20 h. Free primary amino groups on the polymer were detected by a bromophenol blue test of the polymer [16].

2.3.1. Copolymerization of 3a with methyl methacrylate (MMA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aMMA** was isolated in 91% yield. IR (KBr): 3530, 2994, 2950, 1727, 1516, 1146 cm^{-1}. Anal. Calc. for $(C_5H_8O_2)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 64.12, H 7.80, N 1.18. Found: C 64.37, H 7.89, N 1.16%.

2.3.2. Copolymerization of 3a with 2-hydroxyethyl methacrylate (HEMA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aHEMA** was isolated in 95% yield. IR (KBr): 3500, 2950, 1728, 1518, 1458, 1276, 1157 cm^{-1}. Anal. Calc. for $(C_6H_{10}O_3)_{0.95}(C_{32}H_{32}N_2O_2)_{0.05}$: C 59.46, H 7.59, N 0.95. Found: C 60.01, H 7.55, N 0.98%.

2.3.3. Copolymerization of 3a with isopropyl methacrylate (PMA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aPMA** was isolated in 99% yield. IR (KBr): 3535, 2992, 2950, 1727, 1515, 1146 cm^{-1}. Anal. Calc. for $(C_7H_{12}O_2)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 68.06, H 9.00, N 0.96. Found: C 68.12, H 8.98, N 1.01%.

2.3.4. Copolymerization of 3a with butyl methacrylate (BMA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aBMA** was isolated in 93% yield. IR (KBr): 3530, 2994, 2950, 1727, 1516, 1146 cm^{-1}. Anal. Calc. for $(C_8H_{14}O_2)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 69.53, H 9.45, N 0.88. Found: C 69.66, H 9.50, N 0.85%.

2.3.5. Copolymerization of 3a with methyl acrylate (MA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aMA** was isolated in 76% yield. IR (KBr): 3448, 2952, 1736,

1612, 1517, 1438, 1161 cm^{-1}. Anal. Calc. for $(C_4H_6O_2)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 61.41, H 6.97, N 1.33. Found: C 61.55, H 7.03, N 1.29%.

2.3.6. Copolymerization of 3a with butylacrylate (BA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aBA** was isolated in 75% yield. IR (KBr): 3450, 2955, 1735, 1612, 1517, 1438, 1160 cm^{-1}. Anal. Calc. for $(C_7H_{12}O_2)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 68.06, H 9.00, N 0.96. Found: C 68.10, H 9.08, N 0.95%.

2.3.7. Copolymerization of 3a with N,N-dimethylacrylamide (DMA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aDMA** was isolated in 81% yield. IR (KBr): 3565, 2930, 1637, 1509, 1254, 1145 cm^{-1}. Anal. Calc. for $(C_5H_9NO)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 64.63, H 8.67, N 12.47. Found: C 64.50, H 8.59, N 12.36%.

2.3.8. Copolymerization of 3a with isopropylacrylamide (PAA) followed by deprotection

The desired polymer-supported 1,2-diamine **P3aPAA** was isolated in 99% yield. IR (KBr): 3520, 2930, 1635, 1510, 1254, 1145 cm^{-1}. Anal. Calc. for $(C_6H_{11}NO)_{0.95}$-$(C_{32}H_{32}N_2O_2)_{0.05}$: C 66.76, H 9.25, N 11.20. Found: C 66.84, H 9.18, N 11.32%.

2.4. Asymmetric hydrogenation of acetophenone with polymeric catalyst prepared from (S,S)-P3aMMA

A 20 mL Schlenk vessel equipped with a Teflon-coated magnetic stirring bar was charged with polymer-supported chiral 1,2-diamine **P3aMMA** (0.02 mmol), RuCl$_2$/(S)-BINAP(dmf)$_n$ (0.01 mmol) and 2 ml of dry DMF. The above mixture was degassed and heated at 80 °C for 2.5 h. After removal of DMF under reduced pressure to dryness, the solid obtained was transferred to a 100 mL glass autoclave equipped with a pressure gauge and a gas inlet tube attached to a hydrogen source. Air present in the autoclave was replaced by argon. A solution of acetophenone (0.58 mL, 5 mmol) in a 1:1 mixture of 2-propanol (2 mL) and DMF (2 mL), and a 1.0 M tert-BuOK solution in tert-BuOH (0.1 mL), which had been degassed, were added to the autoclave. Hydrogen was then introduced into the autoclave and pressurized to 1 MPa. The reaction mixture was stirred for 5 h at 30 °C. After carefully venting the hydrogen gas, the reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a glass filter equipped with silica gel. The solvent was removed under reduced pressure and the yield determined by GC was 100%. Enantioselectivity of 1-phenylethanol [17] was determined by HPLC analysis using chiral stationary phase (CHIRALCEL OD, Daicel): hexane/2-propanol = 20:1, flow rate, 0.4 mL/min, temperature 30 °C, $t_R(R) = 22.8$ min, $t_R(S) = 25.9$ min.

The polymeric complex formation of **P3aMMA** and RuCl$_2$/(S)-BINAP was confirmed by gel-phase ^{31}P NMR. Short-time (20 min) polymerization of **3a** with MMA yielded a lightly crosslinked polymer **P2aMMA**, which made it possible to take a gel-phase NMR. The obtained soft gel polymer was treated with HCl/THF followed by neutralization to give **P3aMMA**. Gel-phase ^{31}P NMR of the polymeric complex of **P3aMMA** and RuCl$_2$/(S)-BINAP was measured. ^{31}P NMR (CDCl$_3$): $\delta = 46.3$.

In the case of recycle use, after the product was removed by filtration the polymeric catalyst used was quickly washed with 2-propanol–DMF (1:1) on a glass filter. The whole polymeric catalyst washed was returned to the original autoclave and used for the next reaction.

2.5. Asymmetric hydrogenation of other aromatic ketones

The polymeric catalyst was prepared from polymer-supported chiral 1,2-diamine (0.01 mmol), RuCl$_2$/(S)-BINAP(dmf)$_n$ (0.01 mmol) and 2 mL of dry DMF. Asymmetric hydrogenation of aromatic ketone (5.0 mmol) was performed in 2-propanol (2 mL) and DMF (2 mL) in the presence of a 1.0 M tert-BuOK solution in tert-BuOH (0.1 mL) under hydrogen pressurized to 1 MPa. After the reaction was completed, carefully venting the hydrogen gas, then the reaction mixture was diluted with ethyl acetate (10 mL). The obtained mixture was filtered through a glass filter equipped with silica gel. The solvent of the filtrate was removed under reduced pressure and the yield was determined by GC analysis.

2.5.1. Asymmetric hydrogenation of propiophenone

The enantiomeric excess of (R)-1-phenyl-1-propanol [17] was determined by chiral HPLC: column, CHIRALCEL OD; eluent, 1:20 2-propanol–hexane; temperature 30 °C; flow rate, 0.2 mL/min; $t_R(R) = 43.6$ min, $t_R(S) = 46.9$ min.

2.5.2. Asymmetric hydrogenation of butyrophenone

The enantiomeric excess of (R)-1-phenyl-1-butanol [18] was determined by chiral HPLC: column, CHIRALCEL OD; eluent, 1:99 2-propanol–hexane; temperature 30 °C; flow rate, 0.5 mL/min; $t_R(R) = 47.2$ min, $t_R(S) = 52.0$ min.

2.5.3. Asymmetric hydrogenation of valerophenone

The enantiomeric excess of (R)-1-phenyl-1-pentanol [19] was determined by chiral HPLC: column, CHIRALCEL OD; eluent, 1:99 2-propanol–hexane; temperature 30 °C; flow rate, 0.5 mL/min; $t_R(R) = 41.0$ min, $t_R(S) = 45.7$ min.
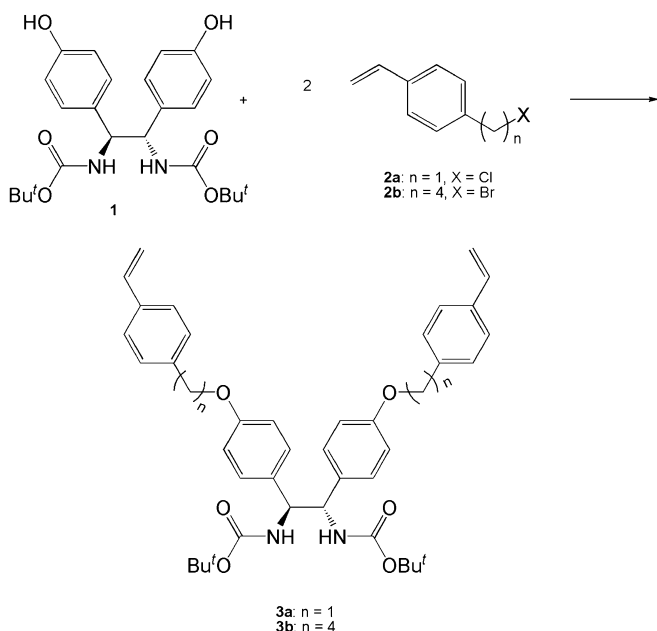
2.5.4. Asymmetric hydrogenation of 4′-methoxyacetophenone

The enantiomeric excess of (R)-1-(4′-methoxyphenyl)ethanol [17] was determined by chiral HPLC: column, CHIRALCEL OD; eluent, 1:20 2-propanol–hexane; temperature 30 °C; flow rate, 0.4 mL/min; $t_R(R) = 39.8$ min, $t_R(S) = 43.1$ min.
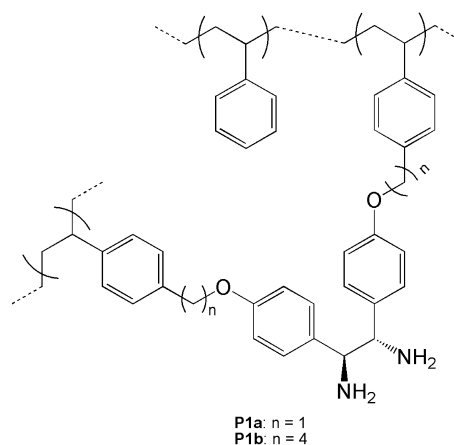
2.5.5. Asymmetric hydrogenation of 4′-bromoacetophenone

The enantiomeric excess of (*R*)-1-(4′-bromophenyl)ethanol [17] was determined by chiral HPLC: column, CHIRALCEL OD; eluent, 1:20 2-propanol–hexane; temperature 30 °C; flow rate, 0.2 mL/min; $t_R(R) = 50.3$ min, $t_R(S) = 47.2$ min.

2.5.6. Asymmetric hydrogenation of 2′-methylacetophenone

The enantiomeric excess of (*R*)-1-(2′-methylphenyl)ethanol [20] was determined by chiral HPLC: column, CHIRALCEL AD; eluent, 1:20 2-propanol–hexane; temperature 30 °C; flow rate, 0.3 mL/min; $t_R(R) = 30.8$ min, $t_R(S) = 33.9$ min.

2.5.7. Asymmetric hydrogenation of 1-acetonaphthone

The enantiomeric excess of 1-(1-naphthyl)ethanol [21] was determined by chiral HPLC: column, CHIRALCEL OD; eluent, 1:20 2-propanol–hexane; temperature 30 °C; flow rate, 0.5 mL/min; $t_R(R) = 47.4$ min, $t_R(S) = 31.3$ min.

3. Results and discussion

3.1. Synthesis of chiral monomer and its polymerization with achiral vinyl monomer

We have prepared chiral monomer **3** [14,22] having two 4-vinylphenyl groups as polymerizable group (Scheme 1). We have reported the copolymerization of the monomer **3** with styrene to give the chiral polymers **P1** in high yield (Scheme 2) [14]. Since the chiral monomer possesses vinylphenyl group which can be copolymerized with other vinyl monomers under radical condition. First, we studied the copolymerization of **3a** with methyl methacrylate (MMA). DMF solution of the chiral monomer **3a** and
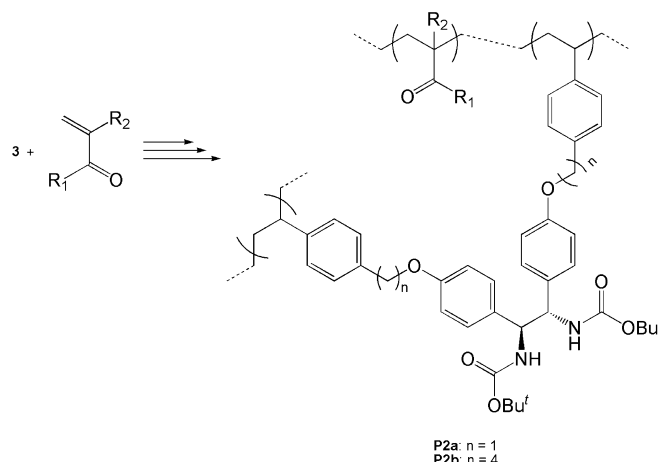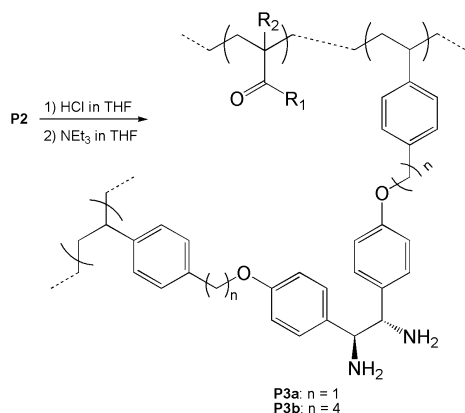
P1a: n = 1
P1b: n = 4

Scheme 2. Polystyrene based polymer-support.

MMA in the presence of AIBN polymerization smoothly occurred to become gel within 15 min since the chiral monomer possesses two vinylphenyl groups as polymerizable group and acted as crosslinking agent (Scheme 3). The obtained gel (**P2aMMA**) was readily broken to granular solid which is insoluble in organic solvent. The polymer however is swelled well in DMF and THF. The crosslinked polymer **P2aMMA** was then treated with HCl/THF to remove amino protecting group (Scheme 4). The Boc protecting groups in the polymer were readily removed to afford the corresponding crosslinked polymer **P3aMMA** after neutralization with a base. The polymer **P3aMMA** contains free primary amino groups, which were detected by bromophenol blue test [16]. As well as methyl methacrylate other several methacrylates, acrylates, methacrylamides could be easily copolymerized with the same chiral monomer **3** to give the crosslinked chiral polymers. In all cases polymerization smoothly occurred and the gel formed within 15 min to give the insoluble polymers in high yield. Yield of the obtained crosslinked chiral polymers are listed in Table 1.

3a: n = 1
3b: n = 4

Scheme 1. Synthesis of the chiral monomers **3**.

P2a: n = 1
P2b: n = 4

Scheme 3. Copolymerization of **3** and achiral vinyl monomer.

Scheme 4. Deprotection of Boc groups to give the chiral 1,2-diamine polymers **P3**.

3.2. Asymmetric hydrogenation using polymeric catalyst derived from P3

2-Propanol is known to be the best solvent for the hydrogenation using RuCl$_2$/(S)-BINAP/(S,S)-DPEN system to give high enantioselectivity with quantitative conversion for various kinds of ketones [23]. However, unfortunately no reaction occurred in 2-propanol with the catalyst prepared from **P3aMMA**, which was thoroughly shrank in the solvent (Table 2, entry 1). In order to increase the affinity of the polymer with alcoholic solvent we have prepared **P3aHEMA** bearing hydroxyl pendant groups by copolymerization of **3a** and 2-hydroxyethyl methacrylate (HEMA). Although very low conversion was observed in 5 h even in the case of the hydroxylated polymer, after 24 h at 30 °C the reaction proceeded to give the product chiral alcohol in quantitative yield with the enantioselectivity of 65% (entry 2). We have found that a mixed solvent system worked very well in the case of polymeric catalyst derived from **P1** [14,24]. By using **P1a** acetophenone was completely hydrogenated within 5 h to give (R)-1-phenylethanol with 76% ee (entry 15) [14]. We have tested the enantioselective hydrogenation of acetophenone by using the catalyst prepared from polymer-supported chiral 1,2-diamine **P3a** in the same solvent system. As shown in Table 2 the polymeric chiral catalyst prepared from **P3aMMA** performed well in the mixed solvent to give (R)-1-phenylethanol in 78% ee with quantitative conversion at 30 °C (entry 4). Lowering the reaction temperature to 10 °C slightly higher enantioselectivity (80% ee) was obtained after 24 h (entry 5). Temperature effect (entries 7–10) was also observed in the reaction using the catalysts prepared from **P3aPMA**, **P3aBMA**. When XylBINAP [25] was used instead of BINAP higher enantioselectivity (97% ee) was obtained as expected from the low-molecular-

Table 1
Preparation of crosslinked polymer-supported chiral 1,2-diamine

Chiral 1,2-diamine polymer				Yield (%)
	R$_1$	R$_2$	n	
P3aMMA	OMe	Me	1	91
P3bMMA	OMe	Me	4	100
P3aHEMA	OCH$_2$CH$_2$OH	Me	1	95
P3aPMA	O^{i}Pr	Me	1	99
P3aBMA	OBu	Me	1	93
P3bBMA	OBu	Me	4	90
P3bTBMA	O^{t}Bu	Me	4	88
P3aMA	OMe	H	1	76
P3bMA	OMe	H	4	85
P3aBA	OBu	H	1	75
P3bBA	OBu	H	4	82
P3aDMA	NMe$_2$	H	1	81
P3bDMA	NMe$_2$	H	4	90
P3aPAA	NH^{i}Pr	H	1	99
P3bPAA	NH^{i}Pr	H	4	94

Table 2
Asymmetric hydrogenation of acetophenone with polymer-supported chiral catalyst prepared from **P3a**[a]

| Entry	Chiral 1,2-diamine polymer	Temperature (°C)	Time (h)	Conversion (%)	Ee (%)	Configuration
1[b]	**P3aMMA**	30	24	0	–	–
2[b]	**P3aHEMA**	30	24	>99	65	R
3	**P3aHEMA**	30	5	81	74	R
4	**P3aMMA**	30	5	>99	78	R
5	**P3aMMA**	10	24	96	80	R
6[c]	**P3aMMA**	30	5	>99	97	R
7	**P3aPMA**	15	24	>99	80	R
8	**P3aPMA**	30	5	71	76	R
9	**P3aBMA**	15	36	>99	79	R
10	**P3aBMA**	30	5	>99	76	R
11	**P3aMA**	30	5	81	73	R
12	**P3aBA**	30	5	>99	77	R
13	**P3aDMA**	30	5	>99	76	R
14	**P3aPAA**	30	5	80	72	R
15	**P1a**	30	5	>99	76	R

[a] Reactions were conducted at 1 MPa of H$_2$ using ketone (5 mmol), tert-BuOK(1 M, 100 μL), (S,S)-1,2-diamine polymer (0.02 mmol) and (S)-BINAP/RuCl$_2$ (0.01 mmol) in 2-propanol (2 mL) and DMF (2 mL).
[b] Reaction was performed in 2-propanol.
[c] XylBINAP was used instead of BINAP.

Table 3
Asymmetric hydrogenation of acetophenone with polymer-supported chiral catalyst prepared from p3b[a]

Entry	Chiral 1,2-diamine polymer	Temperature (°C)	Time (h)	Conversion[b] (%)	Ee[c] (%)	Configuration
1	**P3bMMA**	30	5	>99	77	R
2	**P3bBMA**	30	5	>99	79	R
3	**P3bTBMA**	30	5	>99	79	R
4	**P3bBA**	30	5	>99	78	R
5	**P3bDMA**	30	5	95	78	R
6	**P3bPAA**	30	5	85	77	R
7	**P1b**	30	5	>99	77	R

[a] Reaction conditions: see footnote in Table 2.
[b] Determined by GC analysis.
[c] Determined by HPLC using Chiralcel OD.

Table 4
Asymmetric hydrogenation of aromatic ketones with polymer-supported chiral catalyst prepared from **P3aMMA**[a]

| Ketone	Time (h)	Conversion[b] (%)	Ee[c] (%)
Ph acetophenone	5	>99	78
Ph propiophenone	12	>99	84
Ph butyrophenone	12	>99	86
Ph valerophenone	12	>99	87
MeO 4′-methoxyacetophenone	12	>99	79
Br 4′-bromoacetophenone	12	>99	49
2′-methylacetophenone	12	>99	94[d]
1′-acetonaphthone	12	>99	96

[a] Reaction conditions: see footnote in Table 2.
[b] Determined by GO analysis.
[c] Determined by HPLC using Chiralcel OD.
[d] Determined by HPLC using Chiralcel AD.

Table 5
Asymmetric hydrogenation of aromatic ketones with RuCl$_2$/(S)-BINAP/(S,S)-DPEN in 2-propanol–DMF[a]

Ketone	Time (h)	Conversion[b] (%)	Ee[c] (%)
Ph acetophenone	1	>99	80
Ph propiophenone	1	>99	84
Ph butyrophenone	1	>99	83
Ph valerophenone	1	>99	91
MeO 4′-methoxyacetophenone	1	>99	76
Br 4′-bromoacetophenone	1	>99	50
2′-methylacetophenone	4	>99	94[d]
1′-acetonaphthone	1	>99	97

[a] Reactions were conducted at 1 MPa of H$_2$ using ketone (5 mmol), tert-BuOK (1 M, 100 μL), (S,S)-1,2-diphenylethylenediamine (0.05 mmol) and (S)-BINAP/RuCl$_2$ (0.025 mmol).
[b] Determined by GO analysis.
[c] Determined by HPLC using Chiralcel OD.
[d] Determined by HPLC using Chiralcel AD.

weight catalyst developed by Noyori et al. [3,26] (entry 6). Polyacrylates (**P3aMA**, **P3aBA**) and polyacrylamides (**P3aDMA**, **P3aPAA**) can be also used as polymer-support for the same reaction (entries 11–14) to give the results similar to that from **P3aMMA**.
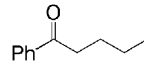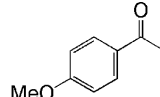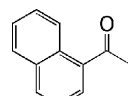
3.3. Asymmetric hydrogenation using polymeric catalyst derived from P3b

We have prepared another chiral monomer **3b** having longer methylene chain between chiral diamine and polymerizable group [22]. Copolymerization of **3b** with methyl methacrylate followed by deprotection gave an insoluble polymer **P3bMMA** containing chiral 1,2-diamine moieties. In this polymer 1,2-diamine moiety has conformationally more flexible structure, which might cause a suitable complex formation in the polymer network. Table 3 shows the results obtained from the polymer-supported catalysts derived from the methylene spacer type ligand **P3b**. In most cases slightly increased enantioselectivities were obtained compared to those from **P3a** in the asymmetric hydrogenation of acetophenone.

3.4. Asymmetric hydrogenation of various aromatic ketones

Various aromatic ketones other than acetophenone were also subjected to the same reaction using **P3aMMA** derived

Table 6
Asymmetric hydrogenation of aromatic ketones with polymer-supported chiral catalyst prepared from **P3bBMA**[a]

Ketone	Time (h)	Conversion[b] (%)	Ee[c] (%)	
Ph—C(=O)CH₃	5	>99	79	(80)[e]
	5	>99	77[d]	
Ph—C(=O)CH₂CH₃	12	>99	83	(84)[e]
Ph—C(=O)CH₂CH₂CH₃	12	>99	88	(91)[e]
MeO—C₆H₄—C(=O)CH₃	12	>99	84	(76)[e]
naphthyl—C(=O)CH₃	12	>99	96	(97)[e]

[a] Reaction conditions: see footnote in Table 2.
[b] Determined by GC analysis.
[c] Determined by HPLC using Chiralcel OD.
[d] P3bMMA was used as polymeric 1,2-diamine.
[e] $RuCl_2$/(S)-BINAP/(S,S)-DPEN was used as a catalyst in DMF–2-propanol.

Table 7
Recycle use of polymeric catalyst in asymmetric hydrogenation of acetophenone at 30 °C[a]

Polymer	BINAP	Run	Time (h)	Conversion[b] (%)	Ee[c] (%)
P1b	BINAP	1	12	>99	76
		2	12	>99	76
		3	12	>99	75
		4	12	>99	76
P1b	XylBINAP	1	18	>99	97
		2	18	>99	98
		3	18	>99	97
		4	18	>99	98
		5	18	>99	97
		6	18	>99	97
P3aMMA	BINAP	1	12	>99	78
		2	12	>99	78
		3	12	>99	78
		4	12	>99	78

[a] Reaction conditions: see footnote in Table 2.
[b] Determined by GC analysis.
[c] Determined by HPLC using Chiralcel OD.

catalyst. High level of asymmetric induction was observed in all cases (Table 4). In order to compare these results and those obtained from the corresponding low-molecular-weight counterpart in solution system the same ketones were hydrogenated by using $RuCl_2$/(S)-BINAP/(S,S)-DPEN in a mixed solvent of 2-propanol and DMF (Table 5). As shown in Table 5 the enantioselectivity values are nearly equal to those from polymeric catalyst. Chiral catalyst prepared from **P3bBMA** having longer methylene chain spacer was also used for the reaction and the similar results were attained as shown in Table 6.

3.5. Recyclability of the polymer-supported catalyst

Since the catalysts used in this article are all made of crosslinked insoluble polymer, the separation of the catalyst and solvent containing resulting product is easy to do by simple filtration. After the removal of the solvent including the product, the remaining polymeric catalyst was ready to use for the following reaction. Table 7 shows the results of repeated use of the polymeric catalyst in the asymmetric hydrogenation of acetophenone. In the case of **P1b**/$RuCl_2$/XylBINAP combination high level of enantioselectivity with quantitative conversion was maintained until six recycling.

4. Conclusion

We have prepared enantiomerically pure 1,2-diamine monomers **3**, which were copolymerized with various kinds of achiral vinyl monomers including styrene, methacrylates, acrylates, methacrylamide, and acrylamide to give polymer-supported chiral 1,2-diamine **P3** after the removal of Boc protecting groups. The diamine polymer was allowed to react with $RuCl_2$–BINAP to form polymeric chiral complex in DMF. Enantioselective hydrogenation

of aromatic ketones successfully occurred by using the polymeric catalyst in 2-propanol/DMF (1:1). The enantioselectivities obtained with the polymeric catalyst exhibited almost the same level as those obtained from the low-molecular-weight counterpart in solution system. Since the polymers have crosslinked structure the insoluble polymeric catalyst could be easily separated from the reaction mixture and recycled several times without loss of its activity.

Acknowledgements

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