Journal of Organometallic Chemistry 751 (2014) 711–716

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of polymer-immobilized TsDPEN ligand and its application in asymmetric transfer hydrogenation of cyclic sulfonimine

Haruki Sugie, Yosuke Hashimoto, Naoki Haraguchi, Shinichi Itsuno*

Department of Environmental & Life Sciences, Toyohashi University of Technology, Tempaku-cho, 441-8580 Toyohashi, Japan

ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form
1 September 2013
Accepted 5 September 2013

Keywords:
Polymer-immobilized chiral catalyst
Cyclic sulfonimine
Amphiphilic polymer ligand
Hydrophobic–hydrophilic balance
Catalyst recycle

ABSTRACT

Crosslinked polymers containing chiral *N*-sulfonylated diamine (TsDPEN) structure were synthesized by radical polymerization of chiral N^1-(4-vinylbenzenesulfonyl)-1,2-diphenylethylene-1,2-diamine, divinylbenzene and achiral vinyl monomer. The polymer-immobilized chiral complex was prepared from the polymeric TsDPEN with ruthenium dichloride *p*-cymene. Asymmetric transfer hydrogenation of cyclic sulfonimine was performed using the polymer-immobilized TsDPEN–Ru (II) complex. The hydrophobic–hydrophilic balance of the polymers was tuned by means of the incorporation of the achiral vinyl monomers, which strongly influenced on the catalytic activity of the polymeric catalyst. In most cases the amphiphilic polymer-immobilized chiral catalysts are highly active in the asymmetric transfer hydrogenation. Enantioenriched sultam with up to 98% ee was obtained by using polymer-immobilized chiral catalysts containing quaternary ammonium salt in CH_2Cl_2. Some of the polymer-immobilized chiral catalysts containing quaternary ammonium salt were successfully used in water. Up to 95% ee was obtained by using the polymeric catalyst in water. Most of the quaternized polymeric catalysts showed sufficient reactivity and higher enantioselectivities compared with that of low-molecular-weight catalyst in water.

1. Introduction

Optically active amines are definitely important intermediates or building blocks for the synthesis of biologically active molecules. For their applications in medicinal, pharmaceutical, and agricultural field, the discovery of new and efficient methods of chiral amine synthesis is a matter of continued interest. Although numerous different methods have emerged for the preparation of enantiomerically pure amines in the past decades [1], the catalytic asymmetric transfer hydrogenation of imines offers simple procedure and mild reaction condition for the chiral amine synthesis [2]. Various chiral catalysts based on complexes of Ti, Ru, Rh and Ir have been developed for the transfer hydrogenation [3]. Among them, the most significant to date is the ruthenium (II) complex with optically active N^1-toluenesulfonyl-1,2-diphenylethylene-1,2-diamine (TsDPEN) developed by Ikariya and Noyori's group [3a]. The complex was mostly applied to asymmetric transfer hydrogenation of prochiral ketones [3d,4]. The asymmetric transfer hydrogenation of prochiral imines have been much less investigated [5–7].

Polymer-immobilized chiral catalysts are useful mainly due to their easy separation and recyclability [8]. We have developed crosslinked polymer-immobilized TsDPEN, which was allowed to complex with $RuCl_2$ to generate the polymeric chiral catalyst. Increasing demand for environmentally friendly method requires the practical asymmetric catalysis under green chemical process [9]. The use of water as a reaction media is always important to design a reaction. Since the Ru–TsDPEN complexes are tolerant of water, water soluble chiral ligands have been developed and used in aqueous system [10]. Most of the polymer-immobilized chiral catalysts developed are suitable for the use of organic solvent. We would like to develop polymer-immobilized chiral catalysts which are active both in organic solvent and in aqueous phase. The first example of the polymer-immobilized 1,2-diamine monosulfona mide as a chiral ligand of an asymmetric transfer hydrogenation catalyst was developed by Lemaire and co-workers in 1997 [11]. They synthesized the polystyrene-supported chiral monosulfona mide by radical polymerization of (*S*,*S*)-N^1-(4-vinylbenzenesul fonyl)- 1,2-diphenylethylene-1,2-diamine with styrene and divinyl benzene in CH_2Cl_2. A similar polystyrene-immobilized chiral TsDPEN was applied to synthesis of (*S*)-fluoxtine by Li et al. [12] The polystyrene-based polymers for asymmetric transfer hydrogenation was swollen in CH_2Cl_2 and shown high catalytic activity but the same polymer was totally inactive in water because of their

* Corresponding author. Tel.: +81 532 44 6813.
E-mail address: itsuno@ens.tut.ac.jp (S. Itsuno).

0022-328X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jorganchem.2013.09.008

hydrophobicity. Poly(ethylene glycol)-supported chiral TsDPEN developed by Xiao was effective in asymmetric transfer hydrogenation of simple ketones by sodium formate in water [4h]. Silica supported chiral catalysts have been utilized in water and showed activity in ketone reduction when SDS surfactant was used [13]. We have also successfully prepared crosslinked polymer-immobilized chiral TsDPENs containing hydrophilic functional groups such as carboxylate and sulfonate. These polymeric catalysts were applied to asymmetric transfer hydrogenation of ketones in water [14].

In this study we have introduced a novel type of amphiphilic polymer support that consists of a polystyrene main chain and a quaternary ammonium salt and quaternary phosphonium salt as its side chain functionality and applied to asymmetric transfer hydrogenation of cyclic sulfonimine. We would like to show the catalytic activity of amphiphilic polymer-immobilized chiral catalysts both in organic solvent and in water. We also describe the detailed results of asymmetric transfer hydrogenation of cyclic sulfonimine in various conditions.

2. Experimental

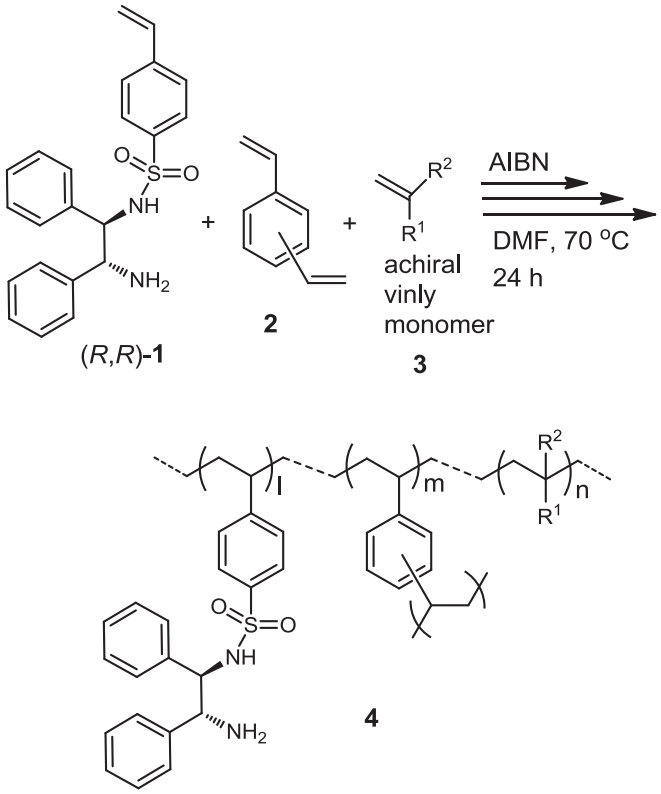
2.1. General

(*R*,*R*)-1,2-Diphenylethylenediamine ((*R*,*R*)-DPEN) was purchased from Fuji Molecular Planning Co., Ltd. *p*-Styrenesulfonyl chloride was prepared according to the method reported in the literature [15]. All other commercial reagents were purchased from Aldrich, Wako or TCI. Styrene and divinylbenzene were washed with aqueous sodium thiosulfate and aqueous sodium hydroxide and distilled over calcium hydride under a reduced pressure just before use. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization three times from anhydrous methanol. Water was purified by a Millipore Milli-Q purification system. DMF was purified by distillation over calcium hydride under a reduced pressure. All other chemicals were used without purification.

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). Melting points were taken on a Yanaco micro melting apparatus and are uncorrected. Optical rotations were measured on a JASCO DIP-140 digital polarimeter with a 10-cm thermostated microcell. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury 300 (300 MHz ^{1}H, 75 MHz ^{13}C) spectrometer, and the *J* values were recorded in Hertz. IR spectra were recorded with a JASCO FT/IR-230 Fourier transform infrared spectrometer and were reported in reciprocal centimeters (cm^{-1}). Elemental analyses (carbon, hydrogen and nitrogen) were performed by a Yanaco-CHN coder MT-6 analyzer. High-performance liquid chromatography (HPLC) analyses were performed with a Jasco HPLC system composed of a DG-980-50 three-line degasser, a PU 980 HPLC pump, and a CO-965 column oven equipped with a chiral column (Chiralcell OD-H, AS-H or AD-H, Daicel) with hexane/2-propanol as an eluent. A Jasco UV-975 UV detector was used for the peak detection.

2.2. General procedure for the preparation of polymer-immobilized chiral 1,2-diamine monosulfonamide ligands **4**

A glass ampoule equipped with a magnetic stirring bar was charged with DMF (0.78 g), (1*R*,2*R*)-**1** (71.9 mg, 0.19 mmol), divinylbenzene (25.0 mg, 0.19 mmol), vinyl monomer (1.52 mmol) and AIBN (6.5 mg, 40 μmol). The ampoule was sealed after three freeze-thaw cycles under liquid nitrogen. Copolymerization was carried out at 60 °C for 24 h. The ampoule was opened and the resulting mixture was poured into ether. The obtained polymer was collected on a glass filter and washed with THF, methanol and water and dried under vacuum.



Scheme 1. Preparation of polymer-immobilized chiral 1,2-diamine monosulfonamide **4**.

2.3. General procedure for asymmetric transfer hydrogenation in CH_2Cl_2

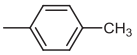
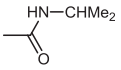
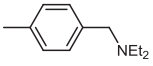
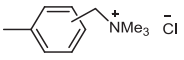
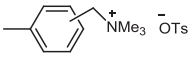
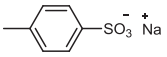
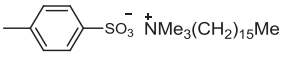
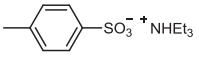
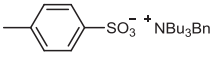
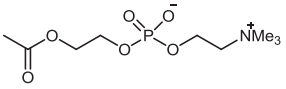
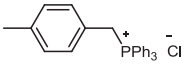
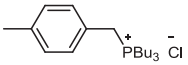
A 10 mL round-bottomed flask equipped with a magnetic stirring bar was charged [$RuCl_2$(*p*-cymene)]$_2$ (1.5 mg, 0.0025 mmol) and the polymer-immobilized chiral 1,2-diamine monosulfonamide **4** (0.006 mmol) in CH_2Cl_2 (1 mL) under argon atmosphere. After three cycles of freeze-thaw under liquid nitrogen, the mixture was heated to 40 °C. After 1 h, the mixture was cooled to room temperature to give polymer–ruthenium (II) complex. Cyclic sulfonimine **5a** (0.50 mmol) and 5:2 HCO_2H–Et_3N azeotropic mixture (HCO_2H 2.5 mmol) were then added and stirred at room temperature for 24 h. After the removal of the polymeric catalyst by filtration, the organic compounds were extracted twice with ether. The conversion and enantioselectivity were determined by GC and HPLC analysis, respectively.

In case of the reuse of the polymeric catalyst, the recovered polymeric catalyst by filtration was transferred with CH_2Cl_2 (1 mL) into a 10 mL round-bottomed flask equipped with a magnetic stirring bar. Cyclic sulfonimine **5a** (0.50 mmol) and 5:2 HCO_2H–Et_3N azeotropic mixture (HCO_2H 2.5 mmol) were then added and stirred at room temperature for 24 h.

2.4. General procedure for asymmetric transfer hydrogenation in water

A 10 mL round-bottomed flask equipped with a magnetic stirring bar was charged [$RuCl_2$(*p*-cymene)]$_2$ (1.5 mg, 0.0025 mmol) and the polymer-immobilized chiral 1,2-diamine sulfonamide **4**

Table 1
Synthesis of polymer-immobilized TsDPEN **4** crosslinked with divinylbenzene.[a]

Chiral polymer	R^2	R^3	Yield%
4a	H		99
4b	H		99
4c	Me	$-CO_2H$	99
4d	Me	$-CO_2Me$	99
4e	H		99
4f	H		86
4g[b]	H		99
4h	H		95
4i[c]	H		48
4j[d]	H		74
4k[b]	H		85
4l	H		72
4m	Me		99
4n[c]	H		97
4o[c]	H		99

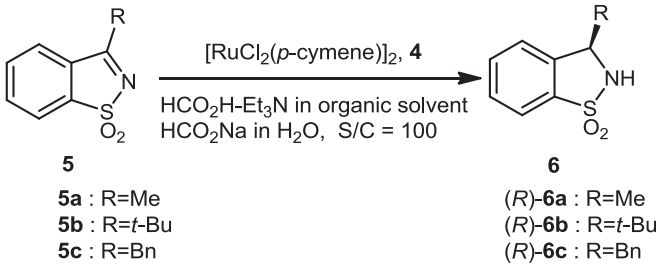
[a] DMF was used as polymerization solvent unless otherwise noted.
[b] DMF–H_2O was used as polymerization solvent.
[c] DMSO was used as polymerization solvent.
[d] **4j** was prepared from **4i** and cetyltrimethylammonium chloride in H_2O at 60 °C.

(0.006 mmol) in water (1 mL) under argon atmosphere. After the mixture had been degassed by three cycles of freeze-thaw under liquid nitrogen, the mixture was stirred at 40 °C for 1 h under an argon atmosphere. Cyclic sulfonimine **5a** (0.50 mmol) and HCO_2Na (2.5 mmol) were added and stirred at room temperature for 24 h. After removal of the polymeric catalyst by filtration, ether was added and extracted the organic compounds. The conversion and enantioselectivity were determined by GC and HPLC analysis, respectively.

3. Results and discussion

3.1. Preparation of polymer-immobilized chiral 1,2-diamine monosulfonamide ligands

Chiral monosulfonamide monomer (*R*,*R*)-**1** [11] was copolymerized with achiral vinyl monomer **3** and divinylbenzene **2** as a crosslinking agent under radical polymerization condition to give the corresponding polymer-immobilized chiral ligand **4** (Scheme 1).



Scheme 2. Asymmetric transfer hydrogenation of cyclic sulfonimine **5** to chiral sultam **6**.

Synthesis of these polymers is summarized in Table 1. The polymeric chiral ligands **4a**–**f** were well suspended in organic solvent such as CH_2Cl_2, DMF, THF and toluene. In water, however, these polymers showed no swellability due to their hydrophobic nature. Achiral vinyl monomers **3** having quaternary ammonium and phosphonium salt structure have amphiphilic property. The hydrophobic–hydrophilic balance of polymers can be precisely controlled by incorporation of such amphiphilic vinyl monomers in polymerization. We have thus prepared the polymers **4g**–**o** containing quaternary ammonium or phosphonium salt pendant groups. These crosslinked polymers were well suspended both in organic solvent and in water.

These polymeric chiral ligands **4** were then allowed to react with $[RuCl_2(p\text{-cymene})]_2$ to form polymer-immobilized chiral monosulfonated diamine–Ru complex [16]. When the polymeric chiral ligand **4a** was treated with $[RuCl_2(p\text{-cymene})]_2$ in CH_2Cl_2 at 40 °C for 1 h, the orange colored polymeric complex was formed.

The catalytic activity of the polymer-immobilized complex prepared from **4a** in the asymmetric transfer hydrogenation of cyclic sulfonimine **5a** [7a] was investigated (Scheme 2). Since the polystyrene based polymer **4a** is swollen in good solvents for polystyrene such as THF, DMF, DMSO, we used these solvents for the reaction (Table 2). Although the polymeric complex was insoluble in these solvents, the asymmetric transfer hydrogenation of **5a** smoothly occurred in the presence of the polymeric complex to give the corresponding chiral sultam **6a** in quantitative conversion. Of the solvents used, $CHCl_3$ and CH_2Cl_2 gave the highest enantioselectivity (95% ee) in the reaction (entries 5, 6). Instead of Ru complex prepared from **4a**, we used Rh and Ir complexes under the same reaction condition to give somewhat lower enantioselectivities (entries 7, 8).

Table 2
Enantioselective transfer hydrogenation of **5a** using polymeric catalyst derived from **4a**.[a]

Entry	Solvent	Conversion%[b]	ee%[c]	Config.
1	THF	100	89	*R*
2	DMF	100	87	*R*
3	DMSO	100	84	*R*
4	CH_3CN	100	16	*R*
5	$CHCl_3$	100	95	*R*
6	CH_2Cl_2	100	95	*R*
7[d]	CH_2Cl_2	100	64	*R*
8[e]	CH_2Cl_2	100	86	*R*

[a] All the reactions were carried out at room temperature for 24 h with HCO_2H–Et_3N, $S/C = 100$. $l:m:n = 0.1:0.1:0.8$.
[b] Conversion was determined by ^1H NMR.
[c] ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.
[d] $[RhCl_2Cp^*]_2$ was used for the polymeric complex formation.
[e] $[IrCl_2Cp^*]_2$ was used for the polymeric complex formation.

Table 3
Asymmetric transfer hydrogenation of **5a** catalyzed by polymer-immobilized ruthenium (II) complex in CH_2Cl_2.[a]

Entry	Ligand[b]	Conversion%[c]	ee%[d]	Config.
1	None	4	0	–
2	**4a**	100	95	*R*
3	**4ax**[g]	100	94	*R*
4	**4b**	100	94	*R*
5	**4c**	71	80	*R*
6	**4d**	100	94	*R*
7	**4e**	100	95	*R*
8	**4f**	100	92	*R*
9	**4g**	100	81	*R*
10	**4h**	100	85	*R*
11	**4hx**[g]	100	92	*R*
12	**4i**	1	ND	ND
13	**4j**	100	90	*R*
14	**4k**	12	76	*R*
15	**4kx**[g]	100	91	*R*
16	**4l**	100	94	*R*
17[e]	**4l**	100	94	*R*
18[f]	**4l**	92	94	*R*
19	**4lx**[g]	100	95	*R*
20	**4m**	14	81	*R*
21	**4n**	100	92	*R*
22	**4o**	100	92	*R*

[a] All the reactions were carried out at room temperature for 24 h with HCO_2H–Et_3N, $S/C = 100$.
[b] l:m:n = 0.1:0.1:0.8.
[c] Conversion was determined by ^1H NMR.
[d] ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.
[e] Polymeric catalyst used in entry 16 was recovered and reused.
[f] Polymeric catalyst used in entry 17 was recovered and reused.
[g] Ethyleneglycol dimethacrylate was used as crosslinker.

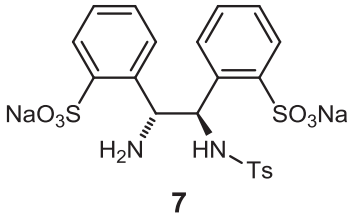
In order to evaluate the catalytic activity of the polymeric complexes derived from polymers **4**, we chose CH_2Cl_2 as solvent for the asymmetric transfer hydrogenation of **5a**. The results obtained by using these polymeric catalysts were summarized in Table 3. In CH_2Cl_2, most of the hydrophobic polymeric catalysts showed high catalytic activity in the asymmetric reaction. Polymers containing highly hydrophilic functionalities such as sodium sulfonate (entry 12), ammonium sulfonate (entry 14) and phosphorylcholine [17] (entry 20) were shrunk in CH_2Cl_2. No effective interaction between the substrate molecules and the catalytic moieties in the polymer was available in this solvent. On the other hand, polymers containing quaternary ammonium salts and phosphonium salt of amphiphilic character were suspended adequately in CH_2Cl_2 and performed properly as catalyst for the asymmetric reaction.

The crosslinker structure also influences the catalytic activity of the polymeric catalyst. Divinylbenzene **2** gives relatively tight crosslinked structure. Flexible crosslinker such as ethyleneglycol dimethacrylate may give higher mobility of the immobilized catalyst in the polymer chains, which will result in higher catalytic activity of the polymeric catalyst. The reaction in CH_2Cl_2, the flexible crosslinker gave somewhat higher enantioselectivities in most cases (entries 11, 15, 19).

Table 4
Effect of the cross-linking degree on the enantioselective transfer hydrogenation of **5a** using polymeric catalyst derived from **4a** in CH_2Cl_2.[a]

Entry	Polymeric chiral ligand l:m:n	Conversion%[b]	ee%[c]	Config.
1	0.10:0.30:0.60	72	85	*R*
2	0.10:0.20:0.70	100	88	*R*
3	0.10:0.15:0.75	100	90	*R*
4	0.10:0.10:0.80	100	95	*R*
5	0.10:0.05:0.85	100	95	*R*
6	0.10:0.02:0.88	100	96	*R*
7	0.10:0:0.90	100	95	*R*

[a] All the reactions were carried out at room temperature for 24 h with HCO_2H–Et_3N, $S/C = 100$.
[b] l:m:n = 0.1:0.1:0.8. Conversion was determined by ^1H NMR.
[c] ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.



7

Fig. 1. Bis *o*-sodiumsulfonyl TsDPEN **7**.

Polymeric catalysts used for the asymmetric transfer hydrogenation were easily separated from the reaction mixture by simple filtration. They can be reused for the same reaction. The catalyst derived from **4l** was recovered and reused several times without any loss of enantioselectivity (entries 16–18).

Degree of crosslinking always influences on the catalytic activity of polymeric catalyst. We synthesized chiral polymers having different crosslinking degrees. Not only the reactivity, but also the enantioselectivity differs depend on the crosslinking degree. Lightly crosslinked polymers gave higher enantioselectivity (Table 4).

3.2. Asymmetric transfer hydrogenation of cyclic sulfonimine *5a* in water

Next we have examined the same asymmetric reaction in water. Since the catalyst is tolerant in water, the reaction can be conducted in water. Wu et al. reported the water soluble chiral ligand **7** having highly hydrophilic SO_3Na functionality [10] (Fig. 1).

They used the Ru complex derived from **7** for the asymmetric transfer hydrogenation of **5a** to give the corresponding chiral sultam **6a** in high conversion with 65% ee (Table 5, entry 1).

When polystyrene based polymeric ligand **4a** was used in water, the polymeric chiral Ru complex showed no catalytic activity mainly due to its highly hydrophobic property as expected (Table 5, entry 2). Almost no reaction occurred with the polymeric catalysts of hydrophobic property (entries 2–7). Interestingly, quaternary ammonium structure in the polymer significantly improved the catalytic activity in water. Polymers **4g**, **4h**, and **4m** having ionic pendant groups gave high conversions over 95% (entries 8, 10, 16). Although the substrate **5a** is not soluble in water, the amphiphilic polymer chains should have efficient interaction with the substrate molecule, which may facilitate the catalytic reaction in the polymer chain. By using these polymeric chiral ligands, the enantioselectivities obtained were all higher than that of the low-molecular-weight catalyst prepared from **7**. The highest ee value of 86% was attained with the polymeric chiral ligand **4g** in water (entry 8). Other polymers containing sulfonate (entry 11), ammonium salt (entries 10, 12, 13, 16) or phosphonium salt (entries 17, 18) structure in their side chain also efficiently accelerated the reaction in water. Flexible crosslinker gave negative effect on the reaction in water (entries 9, 15). Some polymeric catalysts prepared from polyethylene glycol modified TsDPEN have been developed for the asymmetric transfer hydrogenation of ketones in water [12,18]. Most cases slightly decreased enantioselectivities were obtained by using PEG immobilized catalysts. Polymeric catalysts developed in this work is the first example of the high performance catalyst that shows higher enantioselectivities compared with the water soluble TsDPEN in aqueous solution.

In order to see the effect of some other reaction media on the catalytic activity of the polymeric catalysts, different mixed solvent

Table 5
Asymmetric transfer hydrogenation of **5a** catalyzed by polymer-immobilized ruthenium (II) complex in H_2O.[a]

Entry	Ligand[b]	Conversion%[c]	ee%[d]	Config.
1	**7**[e]	97	65	*R*
2	**4a**	2	ND	ND
3	**4b**	0	ND	ND
4	**4c**	7	ND	ND
5	**4d**	0	ND	ND
6	**4e**	0	ND	ND
7	**4f**	13	70	*R*
8	**4g**	99	86	*R*
9	**4gx**[f]	67	81	*R*
10	**4h**	95	80	*R*
11	**4i**	52	76	*R*
12	**4j**	56	83	*R*
13	**4k**	64	78	*R*
14	**4l**	15	65	*R*
15	**4lx**[f]	9	ND	ND
16	**4m**	99	78	*R*
17	**4n**	45	77	*R*
18	**4o**	78	82	*R*

[a] Unless otherwise noted, reactions were carried out at room temperature for 24 h with HCO_2Na. $S/C = 100$.
[b] $l{:}m{:}n = 0.1{:}0.1{:}0.8$.
[c] Conversion was determined by ^1H NMR.
[d] ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.
[e] Cetyltrimethylammonium was used as an additive [6].
[f] Ethyleneglycol dimethacrylate was used as crosslinker.

systems were examined and the results obtained are gathered in Table 6. With the polymeric catalyst prepared from **4o** containing the phosphonium salt pendant groups, the reaction smoothly occurred in water to give the product with 82% ee (entry 1). Somewhat higher enantioselectivities were obtained in THF–water (entry 2) and CH_2Cl_2–water (entries 5–7). In aqueous DMF and aqueous DMSO the reaction occurred with lowering the enantioselectivity (entries 3, 4). In CH_2Cl_2 the polymeric catalyst would provide suitable microenvironment for the reaction.

3.3. Asymmetric transfer hydrogenation of various cyclic sulfonimines

Encouraged by the results mentioned above, asymmetric transfer hydrogenation of some other cyclic sulfonimines **5b**, **5c** were investigated. The results are summarized in Table 7. Since both substrates contain relatively bulky substituent, somewhat lower reactivity was observed with most of the polymeric catalysts. For example, polymeric catalyst derived from **4g** in CH_2Cl_2 gave 35, 32% yield with 93, 96% ee, respectively (entries 2, 8). The same catalyst was also active in water to give the product with 95% ee (entry 3). Interestingly, polymeric catalyst prepared from **4l** having quaternary ammonium sulfonate pendant groups showed excellent

Table 6
Asymmetric transfer hydrogenation of **5a** catalyzed by polymeric catalyst derived from **4o** in mixed solvent system.[a]

Entry	Solvent	Conversion%[b]	ee%[c]	Config.
1	H_2O	78	82	*R*
2	THF:H_2O = 1:1	98	85	*R*
3	DMF:H_2O = 1:1	94	79	*R*
4	DMSO:H_2O = 1:1	68	80	*R*
5	CH_2Cl_2:H_2O = 1:9	84	87	*R*
6	CH_2Cl_2:H_2O = 1:3	100	88	*R*
7	CH_2Cl_2:H_2O = 1:1	100	92	*R*
8	CH_2Cl_2	100	92	*R*

[a] All the reactions were carried out at room temperature for 24 h with HCO_2Na, $S/C = 100$. $l{:}m{:}n = 0.1{:}0.1{:}0.8$.
[b] Conversion was determined by ^1H NMR.
[c] ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.

Table 7
Asymmetric transfer hydrogenation of cyclic sulfonimines **5b**, **5c** catalyzed by polymer-immobilized ruthenium (II) complex.[a]

Entry	Imine	Ligand[b]	Solvent	Conversion%[c]	ee%[d]	Config.
1	**5b**	**4f**	CH_2Cl_2	31	93	*R*
2	**5b**	**4g**	CH_2Cl_2	35	93	*R*
3	**5b**	**4g**	H_2O	40	95	*R*
4	**5b**	**4i**	H_2O	5	ND	ND
5	**5b**	**4l**	CH_2Cl_2	100	98	*R*
6	**5b**	**4l**	H_2O	7	ND	ND
7	**5c**	**4f**	CH_2Cl_2	7	ND	ND
8	**5c**	**4g**	CH_2Cl_2	32	96	*R*
9	**5c**	**4g**	H_2O	8	ND	ND
10	**5c**	**4l**	CH_2Cl_2	100	93	*R*

[a] All the reactions were carried out at room temperature for 24 h with HCO_2H–Et_3N in CH_2Cl_2 or HCO_2Na in water, $S/C = 100$.
[b] $l{:}m{:}n = 0.1{:}0.1{:}0.8$.
[c] Conversion was determined by ^1H NMR.
[d] ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.

performance in the same reaction to give the corresponding chiral sultam products **6b**, **6c** in quantitative conversion with high level of enantioselectivities in CH_2Cl_2 (entries 5, 13).

4. Conclusions

In conclusion, we have successfully synthesized novel crosslinked polymers **4** containing chiral 1,2-diamine monosulfonamide and achiral amphiphilic repeating unit. The polymeric complexes with ruthenium dichloride *p*-cymene were used as catalyst for asymmetric transfer hydrogenation of cyclic sufonimine **5**. The achiral amphiphilic repeating units in the polymeric chiral Ru complex strongly influenced on the catalytic activity. In CH_2Cl_2, hydrophobic and amphiphilic polymers (**4a**, **4e**, **4lx**) showed high performance in the asymmetric catalysis. Hydrophilic polymers prohibited the catalytic activity in CH_2Cl_2. On the other hand, in water, hydrophobic polymers showed no catalytic activity in the reaction. However, amphiphilic polymer chain efficiently accelerated the catalytic reaction in water. Crosslinked polymers **4g**, **4m** containing quaternary ammonium chloride or zwitterionic phosphorylcholine attained quantitative conversion in water. Polymeric catalyst prepared from **4g** showed the highest enantioselectivity in water. Enantioselectivities obtained by using these polymeric catalysts showed higher than that obtained from the corresponding low-molecular-weight catalyst in aqueous solution system.

Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 23350053) and by a Grant-in-Aid for Scientific Research on Innovative Areas “New Polymeric Materials Based on Element-Blocks” from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.09.008.

References

[1] (a) S. Kobayashi, H. Ishitani, Chem. Rev. 99 (1999) 1069–1094;
(b) J.M. Brunel, Recent Res. Dev. Org. Chem. 7 (2003) 155–190;
(c) C.J. Cobley, J.P. Henschke, Adv. Synth. Catal. 345 (2003) 95–201.
[2] (a) S. Hoffmann, A.M. Seayad, B. List, Angew. Chem. Int. Ed. 44 (2005) 7424–7427;
(b) M. Rueping, E. Sugiono, C. Azap, T. Theissmann, M. Bolt, Org. Lett. 7 (2005) 3781–3783;

(c) M. Rueping, A.P. Antonchick, T. Theissmann, Angew. Chem. Int. Ed. 45 (2006) 3683–3686.
[3] (a) S. Hashiguchi, A. Fujita, J. Takehara, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 117 (1995) 7562–7563;
(b) R. Noyori, S. Hashiguchi, Acc. Chem. Res. 30 (1997) 97–102;
(c) X. Verdaguer, E. Udo, W. Lange, S.L. Buchwald, Angew. Chem. Int. Ed. 37 (1998) 1103–1107;
(d) T. Ikariya, A.J. Blacker, Acc. Chem. Res. 40 (2007) 1300–1308;
(e) N.A. Cortez, G. Aguirre, M.P. Hake, R. Somanathan, Tetrahedron Asym. 19 (2008) 1304–1309.
[4] (a) K. Matsumura, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 119 (1997) 8738–8739;
(b) Y. Jiang, Q. Jiang, G. Zhu, X. Zhang, Tetrahedron Lett. 38 (1997) 215–218;
(c) D.A. Alonso, D. Guijarro, P. Pinho, O. Temme, P.G. Andersson, J. Org. Chem. 63 (1998) 2749–2751;
(d) Y. Jiang, Q. Jiang, X. Zhang, J. Am. Chem. Soc. 120 (1998) 3817–3818;
(e) K. Murata, T. Ikariya, J. Org. Chem. 64 (1999) 2186–2187;
(f) D.G.I. Petra, J.N.H. Reek, J.W. Handgraaf, E.J. Meijer, P. Dierkes, P.C.J. Kamer, J. Brussee, H.E. Schoemaker, P.W.N.M. van Leeuwen, Chem. Eur. J. 6 (2000) 2818–2829;
(g) Y. Ma, H. Li, L. Chen, X. Cui, J. Zhu, J. Deng, Org. Lett. 5 (2003) 2103–2106;
(h) X. Wu, X. Li, W. Hems, F. King, J. Xiao, Org. Biomol. Chem. 2 (2004) 1818–1821;
(i) P.N. Liu, P.M. Gu, F. Wang, Y.Q. Tu, Org. Lett. 6 (2004) 169–172;
(j) M.T. Reetz, X. Li, J. Am. Chem. Soc. 128 (2006) 1044–1045;
(k) X. Wu, X. Li, A.Z. Gerosa, A. Pettman, J. Liu, A.J. Mills, J. Xiao, Chem. Eur. J. 14 (2008) 2209–2222;
(l) A. Mikhailine, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 131 (2009) 1394–1395.
[5] N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 4916–4917.
[6] N. Haraguchi, K. Tsuru, Y. Arakawa, S. Itsuno, Org. Biomol. Chem. 7 (2009) 69–75.
[7] (a) K.H. Ahn, C. Ham, S.K. Kim, C.W. Cho, J. Org. Chem. 62 (1997) 7047–7048;
(b) Y.C. Chen, T.W. Fei, J.G. Deng, H. Liu, X. Cui, J. Zhu, Y.Z. Jiang, M.C.K. Choi, A.S.C. Chan, J. Org. Chem. 67 (2002) 5301–5306;
(c) Y.C. Chen, T.W. Wu, L. Jiang, J.G. Deng, H. Liu, J. Zhu, Y.Z. Jiang, J. Org. Chem. 70 (2005) 1006–1010.
[8] (a) S. Itsuno, N. Haraguchi, Y. Arakawa, Recent Res. Dev. Org. Chem. 9 (2005) 27–47;
(b) S. Itsuno, in: S. Itsuno (Ed.), Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis, Wiley, 2011, p. 2 (Chapter 1).
[9] (a) S. Itsuno, Y. Arakawa, N. Haraguchi, J. Soc. Rubber Ind. 79 (2006) 448–454;
(b) K. Manabe, S. Kobayashi, Chem. Eur. J. 8 (2002) 4095–4101;
(c) D. Sinou, Adv. Synth. Catal. 344 (2002) 221–237;
(d) U.M. Lindström, Chem. Rev. 102 (2002) 2751–2772;
(e) Y. Hayashi, W. Tsuboi, M. Shoji, N. Suzuki, J. Am. Chem. Soc. 125 (2003) 11208–11209;
(f) T. Hamada, K. Manabe, S. Kobayashi, J. Am. Chem. Soc. 126 (2004) 7768–7769;
(g) C.J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68–82;
(h) N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka, C.F. Barbas III, J. Am. Chem. Soc. 128 (2006) 734–735;
(i) S.S.V. Ramasastry, K. Albertshofer, N. Utsumi, C.F. Barbas III, Org. Lett. 10 (2008) 1621–1624;
(j) G. Bianchini, A. Cavarzan, A. Scarso, G. Strukul, Green Chem. 11 (2009) 1517–1520.
[10] J. Wu, F. Wang, Y. Ma, X. Cui, L. Cun, J. Zhu, J. Deng, B. Yu, Chem. Commun. (2006) 1766–1768.
[11] R. ter Halle, E. Schulz, M. Lemaire, Synlett (1997) 1257–1258.
[12] Y. Li, Z. Li, Q. Wang, F. Tao, Org. Biomol. Chem. 3 (2005) 2513–2518.
[13] (a) P.N. Liu, J.G. Deng, Y.Q. Tu, S.H. Wang, Chem. Commun. (2004) 2070–2071;
(b) P.N. Liu, J.G. Deng, Y.Q. Tu, Y.P. Ma, Eur. J. Org. Chem. 70 (2005) 3221–3227.
[14] (a) Y. Arakawa, N. Haraguchi, S. Itsuno, Tetrahedron Lett. 47 (2006) 3239–3243;
(b) Y. Arakawa, A. Chiba, N. Haraguchi, S. Itsuno, Adv. Synth. Catal. 350 (2008) 2295–2304.
[15] T. Ishizone, J. Tsuchiya, A. Hirao, S. Nakahama, Macromolecules 25 (1992) 4840–4847.
[16] A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 2521–2522.
[17] B. Yu, A.B. Lowe, K. Ishihara, Biomacromolecules 10 (2009) 950–958.
[18] (a) W. Shan, F. Meng, Y. Wu, F. Mao, X. Li, J. Organomet. Chem. 696 (2011) 1687–1690;
(b) X. Wu, C. Wang, J. Xiao, Platinum Metals Rev. 54 (2010) 3–19.