Asymmetric transfer hydrogenation of imines catalyzed by a polymer-immobilized chiral catalyst†

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Received 3rd September 2008, Accepted 6th October 2008
First published as an Advance Article on the web 6th November 2008
DOI: 10.1039/b815407b

The asymmetric transfer hydrogenation of imines was performed with the use of a polymer-immobilized chiral catalyst. The chiral catalyst, prepared from crosslinked polystyrene-immobilized chiral 1,2-diamine monosulfonamide, was effective in the asymmetric transfer hydrogenation of *N*-benzyl imines in CH_2Cl_2 to give a chiral amine in high yield and good enantioselectivity. Furthermore, an amphiphilic polymeric catalyst prepared from crosslinked polystyrene containing sulfonated groups successfully catalyzed the asymmetric transfer hydrogenation of cyclic imines in water. Enantioenriched secondary amines with up to 94% ee were obtained by using a polymeric catalyst.

Introduction

Enantiomerically pure amines are highly important intermediates or building blocks for biologically active molecules in medical, pharmaceutical, and agricultural science. Numerous completely different methods have emerged for the preparation of enantiomerically pure amines in the past few years.[1] One of the popular methods for preparation of chiral amines is asymmetric transfer hydrogenation of imines. Among the various chiral catalysts reported for asymmetric transfer hydrogenation, the most significant to date is the ruthenium(II) complex with optically active *N*-toluenesulfonyl-1,2-diphenylethylenediamine (TsDPEN) developed by Ikariya and Noyori's group.[2] As the catalytic system, chiral TsDPEN/$RuCl_2$(*p*-cymene) complex is well known as a highly effective and enantioselective catalyst for asymmetric transfer hydrogenation of various kinds of ketones and imines.

On the other hand, the use of a polymer-support technique is now going to be recognized as one of the standard techniques in modern organic synthesis.[3] The advantage of immobilization of a chiral catalyst to a polymer is not only easy separation of the chiral catalyst from the reaction mixture and its reuse but the easy modification of the characters (*e.g.* contents of chiral catalyst, degree of crosslinking, hydrophilic–hydrophobic balance, and so on). The first study on polymer-immobilization of Ikariya and Noyori's catalyst was reported by Lemaire.[4] A similar polystyrene-immobilized chiral TsDPEN was utilized for the synthesis of (*S*)-fluoxtine.[5] Since this catalyst is known to be tolerant in asymmetric transfer hydrogenation in aqueous media,[6] a polymeric chiral catalyst suitable for aqueous conditions was developed. Poly(ethylene glycol)-supported chiral TsDPEN developed by Xiao[7] was highly effective in asymmetric transfer hydrogenation of simple ketones by sodium formate in neat water.

Recently, we have successfully synthesized novel crosslinked polymer-immobilized chiral TsDPENs containing hydrophilic functional groups such as carboxylate and sulfonate. The polymeric ruthenium(II) complex prepared from polymer-immobilized chiral TsDPEN and [$RuCl_2$(*p*-cymene)] was applied to asymmetric transfer hydrogenation of ketones in water.[7] Interestingly, both reactivity and enantioselectivity in the reaction by using the polymeric chiral catalyst was somewhat higher than those obtained by using Ikariya's original catalyst in homogeneous solution. We found that a chiral polymeric ligand having a quaternary ammonium salt structure at the polymer side chains was highly suitable for use in water.

Although prochiral imines are subject to hydrogenation by Ikariya catalyst, asymmetric transfer hydrogenation of prochiral imines with the use of a supported version of the catalyst has been much less investigated than that of the ketones. Very recently, Ying *et al.* reported the successful preparation of siliceous mesocellular foam-immobilized chiral TsDPEN.[8] The ruthenium complex showed high catalytic activity and recyclability in organic solvent, but the reaction in water is not investigated. In this article, we demonstrate asymmetric transfer hydrogenation of imines catalyzed by a polymer-immobilized chiral catalyst. The influence of polymer structure on the reaction was mainly investigated.

Results and discussion

Preparation of polymer-immobilized ruthenium(II) complex

Three types of polymer-immobilized chiral TsDPENs were prepared by radical polymerization of enantiopure 1,2-diamine monosulfonamide monomer,[9] styrene derivative, and divinylbenzene in DMF (Fig. 1). (*R*,*R*)-**1**, (*R*,*R*)-**2**, and (*R*,*R*)-**3** were obtained in 92, 94, and 86% yields, respectively. The styrene-based polymer (*R*,*R*)-**1** was well swollen in a good solvent for crosslinked polystyrene such as DMF, THF and toluene, but completely shrunk in water due to the hydrophobic character. In contrast, polymers bearing sulfonate groups (*R*,*R*)-**2**, and (*R*,*R*)-**3** were found to be swollen in dimethylsulfoxide and water.

Polymer-immobilized ruthenium(II) complex was prepared according to Ikariya's procedure. The polymer-supported chiral TsDPEN was treated with [$RuCl_2$(*p*-cymene)]$_2$ in an organic solvent such as CH_2Cl_2 and CH_3CN at 80 °C for 1 h. The obtained polymer-immobilized complex showed an orange color,

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of compounds. See DOI: 10.1039/b815407b

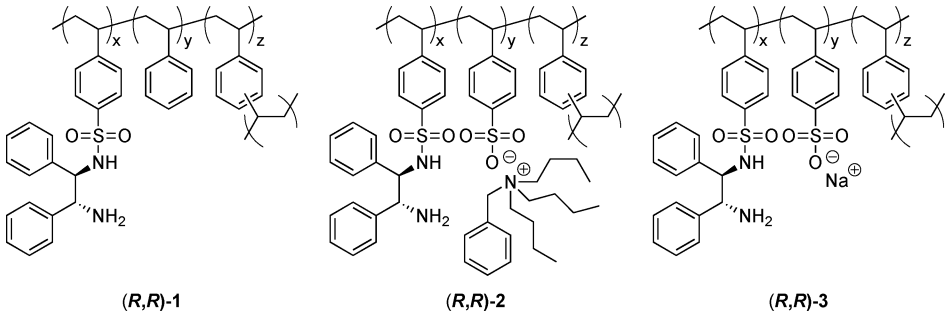


Fig. 1 Polymer-immobilized chiral ligands.

which is typical of the ruthenium(II) complex. Although the polymer complex is insoluble due to its crosslinked structure, we measured the gel-phase ^{1}H NMR of the polymers. The ^{1}H NMR spectrum of the crosslinked polymeric complex showed that methyl and aromatic proton signals assigned to *p*-cymene were clearly observed after the complexation (Fig. 2). The result indicated that the ruthenium(II) complex was formed on the polymer.

Asymmetric transfer hydrogenation of *N*-benzylimine 4 using polymer-immobilized chiral catalyst in organic solvent

At first, asymmetric transfer hydrogenation of *N*-benzyl imine **4** with the use of polymer-immobilized ruthenium(II) complex was carried out to investigate the catalytic activity in CH_2Cl_2. The results are summarized in Table 1. The asymmetric transfer hydrogenation of *N*-benzyl imine **4** was performed by using Et_3N–HCO_2H (5 : 2, v/v, 5 equiv. to **4**) as a hydrogen source in CH_2Cl_2. The ruthenium(II) complex derived from chiral TsDPEN catalyzed the asymmetric transfer hydrogenation of **4** and the enantioenriched secondary amine (*R*)-**5** was obtained in quantitative conversion with 78% ee (Table 1, entry 12).[10] We have examined three types of polymer-immobilized ruthenium(II) complex for the same reaction in CH_2Cl_2. Hydrophobic polymeric ruthenium(II) complex prepared from (*R*,*R*)-**1** (x–y–z = 0.1 : 0.8 : 0.1) successfully catalyzed the reaction at room temperature to afford (*R*)-**5** in 95% conversion with 84% ee after 48 h (entry 1). In contrast to the results, the reactions with the use of polymeric ruthenium(II) complexes prepared from amphiphilic polymer (*R*,*R*)-**2** and hydrophilic polymer (*R*,*R*)-**3** resulted in very low conversions (3%) (entries 2 and 3). The catalyst moiety in the hydrophilic polymer chain would not have sufficient interaction with the substrate and hydrogen source. These results indicate that the effect of the hydrophobic and/or hydrophilic segment is significant in the reaction.

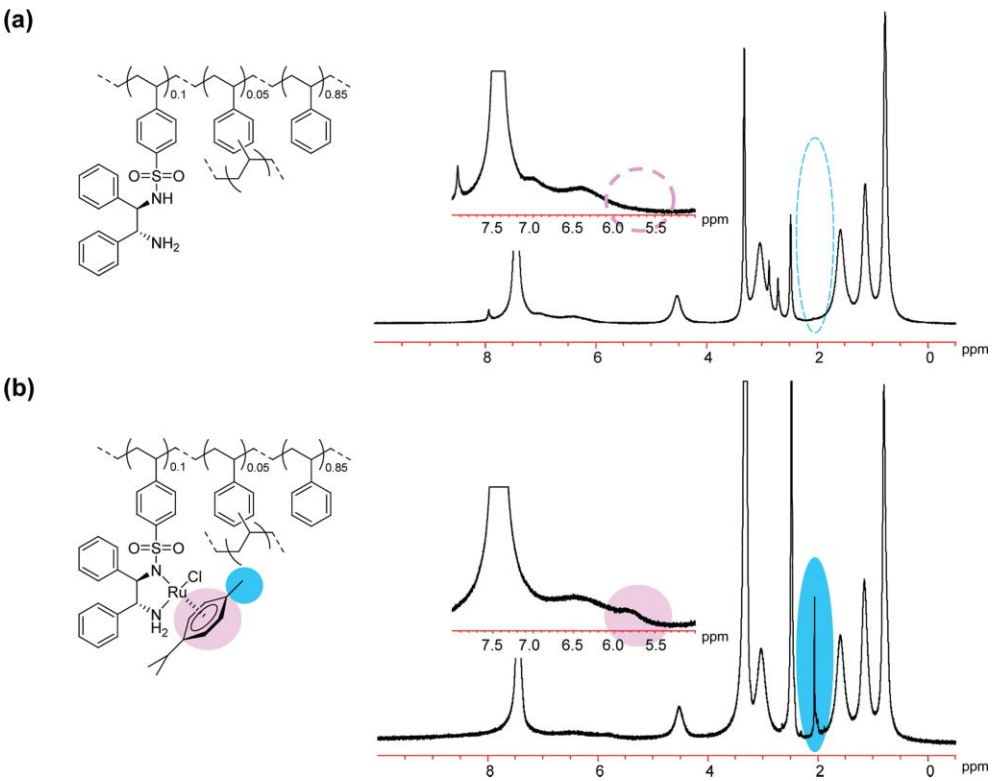
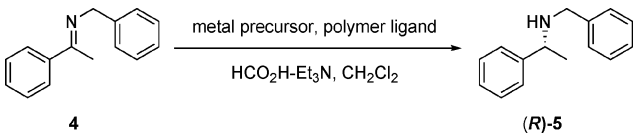


Fig. 2 Gel-phase ^{1}H NMR spectra of polymer-immobilized chiral TsDPEN (**a**) and ruthenium(II) complex (**b**).

Table 1 Asymmetric transfer hydrogenation of **4** catalyzed by polymer-immobilized ruthenium(II) complex in CH_2Cl_2[a,b,c]

					(*R*)-**5**	
Entry	Ligand[c]	Metal precursor	Temp/°C	Time/h	Conv (%)[d]	Ee (%)[e]
1	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	rt	48	95	84
2	(*R*,*R*)-**2**	$[RuCl_2(p\text{-cymene})]_2$	rt	120	3	ND
3	(*R*,*R*)-**3**	$[RuCl_2(p\text{-cymene})]_2$	rt	24	3	ND
4	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	rt	3	92	88
5[f]	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	rt	36	96	86
6[g]	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	rt	24	99	63
7	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	40	48	87	69
8	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	0	48	80	93
9[h]	(*R*,*R*)-**1**	$[RuCl_2(p\text{-cymene})]_2$	rt	48	0	ND
10	(*R*,*R*)-**1**	$[RhCl_2Cp^*]$	rt	48	> 99	29
11	(*R*,*R*)-**1**	$[IrCl_2Cp^*]$	rt	24	> 99	77
12	TsDPEN	$[RuCl_2(p\text{-cymene})]_2$	rt	3	> 99	78

[a] Unless otherwise stated, the reaction was carried out with Et_3N–HCO_2H (5 : 2, v/v, 5 equiv. to **4**). [b] S/C = 100. [c] The ratio of x–y–z was 0.1 : 0.8 : 0.1. [d] The conversion was determined by ^1H NMR. [e] The ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column. [f] In CH_3CN. [g] In DMF. [h] HCO_2Na was used instead of Et_3N–HCO_2H.



Scheme 1 Asymmetric transfer hydrogenation of **4** using polymer-immobilized chiral catalyst in CH_2Cl_2.

Since the hydrophobic polymeric ruthenium(II) complex derived from (*R*,*R*)-**1** was found to be suitable for asymmetric transfer hydrogenation of imine **4**, a further investigation into the reaction conditions was performed. The conversion of (*R*)-**5** was 92% even after 3 h, which indicated that **4** was smoothly hydrogenated by the polymer-immobilized chiral catalyst (entry 4). Enantioselectivity obtained in CH_3CN (86%) was similar to the value obtained in CH_2Cl_2 (entries 1, 4, and 5). These enantioselectivities obtained from the polymeric chiral catalysts was apparently higher than that obtained from TsDPEN and $[RuCl_2(p\text{-cymene})]_2$. The use of DMF gave the higher conversion of 99% but lowered the enantioselectivity (entry 6). The temperature effect on the enantioselectivity was examined in CH_2Cl_2. A significant enhancement in ee value was observed when the reaction temperature was decreased to 0 °C (entry 8). No conversion was observed when sodium formate was used instead of a 5 : 2 triethylamine–formic acid azeotropic mixture[11] as a hydrogen source (entry 9). Although both rhodium and iridium complex could be used as a metal precursor in the reaction, these ee values were inferior to that of ruthenium (entries 10 and 11). The effect of polymer segment on the reactivity and enantioselectivity is still obscure, but one possible explanation is that the steric hindrance of the polymer chain and network might affect the enantioselectivity if the polymer chain leads to the suitable conformation of chiral catalyst and substrate. The other possibility is due to the structural difference of the chiral ligand. The structure we employed is *N*-isopropylbenzenesulfonyl-1,2-diphenylethylenediamine rather than *N*-toluenesulfonyl-1,2-diphenylethylenediamine.

The polymeric chiral catalyst could be easily separated from the reaction mixture due to its insolubility and reused for the following reaction. The reuse examination was carried out under conditions similar to those of entry 1 in Table 1. From the catalyst derived from (*R*,*R*)-**1**, we obtained **5** in >90% yield with 84, 77, 78% ees for three recycling experiments. Reuse of the polymeric catalyst was possible with keeping the catalytic activity.

Asymmetric transfer hydrogenation of various imines in CH_2Cl_2

Encouraged by the results mentioned above, asymmetric transfer hydrogenation of various imines by using the polymer-immobilized chiral catalyst prepared from (*R*,*R*)-**1** was investigated in CH_2Cl_2 (Table 2). Acyclic *N*-benzyl imine prepared from 4′-bromoacetophenone **6a** was converted into the corresponding optically active secondary amine with 64% ee (entry 2). The transfer hydrogenation of **6b** resulted in the decomposition of the substrate (entry 3). Cyclic imines such as **10** and **12** could be subjected to asymmetric transfer hydrogenation, which yielded (*S*)-**11** and (*S*)-**13** with higher enantioselectivities (92% ee and 95% ee, respectively) (entries 5 and 6). Unfortunately, no or trace reaction was observed when *N*-aryl imine **14**, **15**, and **16** were employed as substrates.

Table 2 Asymmetric transfer hydrogenation of various imines catalyzed by polymer-immobilized chiral catalyst in CH_2Cl_2[a,b,c]

Entry	Imine	Temp/°C	Time/h	Amine	Conv (%)[d]	Ee (%)[e]	*Config.*
1	**4**	rt	48	**5**	95	84	*R*
2	**6a**	rt	24	**7a**	>99	64	*R*
3	**6b**	rt	24	**7b**	Degrad.	—	—
4	**8**	rt	144	**9**	86	49	*R*
5	**10**	rt	24	**11**	>99	92	*S*
6	**12**	rt	24	**13**	91	95	*S*
7	**14**	rt	168	—	0	—	—
8	**15**	rt	24	—	0	—	—
9	**16**	rt	24	—	<5	ND	—

[a] Unless otherwise stated, the reaction was carried out with Et_3N–HCO_2H (5 : 2, v/v, 5 equiv. to substrate). [b] S/C = 100. [c] The ratio of x–y–z was 0.1 : 0.8 : 0.1. [d] The conversion was determined by ^1H NMR. [e] The ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column.

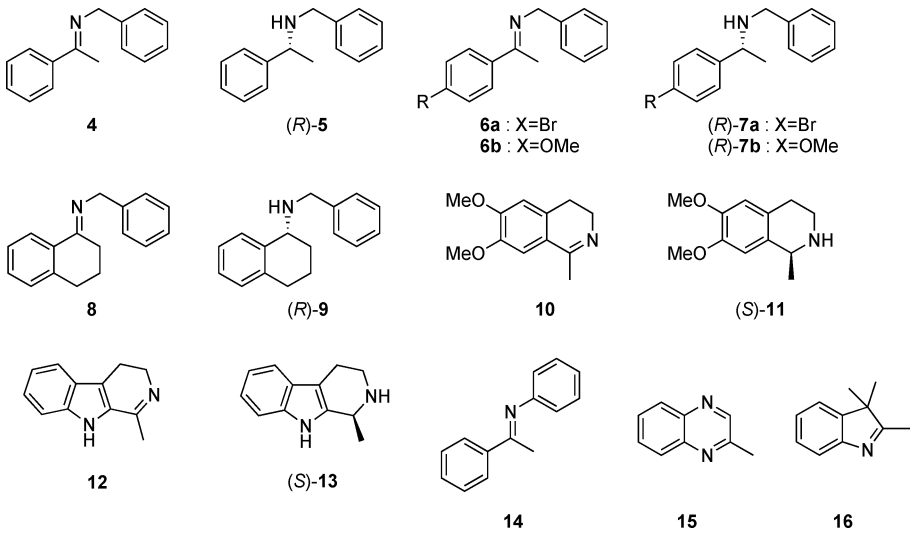
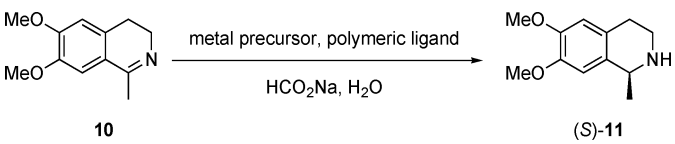


Fig. 3 Imines and corresponding chiral amines.

Asymmetric transfer hydrogenation of cyclic imine 10 using polymer-immobilized chiral catalyst in H_2O

Since this type of catalyst is known to be tolerant in water, we used the polymer-immobilized catalyst in water (Scheme 2). Despite the progress made in the asymmetric transfer hydrogenation of ketones in water,[12] little work on asymmetric transfer hydrogenation of imines[13] in water has been reported. Zhu and Deng have recently reported the first asymmetric transfer hydrogenation of imines and iminiums in aqueous media.[14] They utilized a water soluble ruthenium(II) complex of a designed Ts-DPEN bearing two sulfonated groups as a chiral catalyst and cetyltrimethylammonium chloride as an additive. They concluded that the formation of micelles and the electrical charge on a micelle are important to achieve high enantioselectivity. They also reported a water-soluble rhodium(III) catalyst bearing two amino groups to enhance the hydrophilicity.[15] These catalysts were found to be suitable in asymmetric transfer hydrogenation of imines in neat water. New water-soluble arene ruthenium catalysts were also designed by Süss-Fink *et al.*[16] They examined the catalytic potential for asymmetric transfer hydrogenation of imines in aqueous solution.



Scheme 2 Asymmetric transfer hydrogenation of **10** using polymer-immobilized chiral catalyst in H_2O.

In our system, the use of a polymer-immobilized chiral catalyst enabled us to change the hydrophilic–hydrophobic balance as well as the electrical effect easily because the various functional groups could be introduced at the pendant position of the polymer main chain. We expected that the polymeric effect would lead to successful asymmetric transfer hydrogenation of imines in water.

We attempted transfer hydrogenation of **4** in water with the use of a polymeric chiral catalyst in the beginning. However, no reaction occurred in water and longer reaction time and higher temperature caused the hydrolysis of the substrate. Cyclic imine **10**, which was stable in water for an even longer reaction time and at a higher temperature, was then employed as a substrate of transfer hydrogenation in water. The reaction was carried out in water with 5 equivalents of HCO_2Na to substrate **10**. The results are summarized in Table 3.

Polystyrene-immobilized chiral catalyst derived from (*R*,*R*)-**1**, which consists of a hydrophobic polymer chain, was not suitable for the reaction due to the shrinkage in water (Table 3, entry 1). Even though the reaction in water is slower than in organic solvent, the polymer-immobilized chiral catalysts prepared from (*R*,*R*)-**2** and (*R*,*R*)-**3** showed good catalytic activities in neat water (entries 2, 3 and 4). The reaction could be accelerated when polymeric catalyst with 2 mol% crosslinking was used (entry 5). The enantioselectivities of (*S*)-**11** obtained at 40 °C were slightly higher than those obtained at room temperature (entries 6 and 7). Addition of benzyltributylammonium chloride resulted in lowering the enantioselectivity (entry 8). However, interestingly, cetyltrimethylammonium chloride and bromide, possessing longer alkyl chains, as additives were effective in obtaining the enantioenriched amine (entries 9 and 10). Only a trace amount of product was obtained by employing Et_3N–HCO_2H as the hydrogen donor (entry 11). Rhodium and iridium complexes were also found to be effective metal precursors in the asymmetric transfer hydrogenation of **10** in water. Both the conversions and enantioselectivities were similar to the values obtained with ruthenium(II) complex (entries 12 and 13). These results clearly indicate that the polymeric chiral catalysts prepared from (*R*,*R*)-**2** and (*R*,*R*)-**3** are one of the most effective chiral catalysts of asymmetric transfer hydrogenation of imines in water.

Conclusions

In conclusion, we have developed the catalytic asymmetric transfer hydrogenation of imines with the use of a polymer-immobilized chiral catalyst both in organic solvent and in water. Polystyrene-immobilized ruthenium(II) complex prepared from (*R*,*R*)-**1** was effective for the asymmetric transfer hydrogenation

Table 3 Asymmetric transfer hydrogenation of **10** catalyzed by polymer-immobilized ruthenium(II) complex in H_2O[a,b]

					(*S*)-**11**	
Entry	Ligand	Monomer ratio x–y–z	Temp/°C	Time/h	Conv (%)[c]	Ee (%)[d]
1	(*R*,*R*)-**1**	0.1 : 0.8 : 0.1	rt	24	<1	ND
2	(*R*,*R*)-**2**	0.1 : 0.8 : 0.1	rt	24	50	89
3	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	6	24	ND
4	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	75	89
5	(*R*,*R*)-**3**	0.1 : 0.88 : 0.02	rt	24	88	88
6	(*R*,*R*)-**2**	0.1 : 0.8 : 0.1	40	48	82	91
7	(*R*,*R*)-**3**	0.1 : 0.88 : 0.02	40	48	95	90
8[e]	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	66	86
9[f]	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	69	94
10[g]	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	61	93
11[h]	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	6	ND
12[i]	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	72	89
13[j]	(*R*,*R*)-**3**	0.1 : 0.8 : 0.1	rt	24	79	86

[a] Unless otherwise stated, the reaction was carried out with $[RuCl_2(p\text{-cymene})]_2$ and HCO_2Na (5 equiv. to **10**). [b] S/C = 100. [c] The conversion was determined by ^1H NMR. [d] The ee was determined by HPLC analysis with a Daicel Chiralcel OD-H column. [e] Benzyltributylammonium chloride was added. [f] Cetyltributylammonium chloride was added. [g] Cetyltributylammonium chloride was added. [h] Et_3N–HCO_2H was used instead of HCO_2Na. [i] $[RhCl_2Cp^*]$ was used instead of $[RuCl_2(p\text{-cymene})]_2$. [j] $[IrCl_2Cp^*]$ was used instead of $[RuCl_2(p\text{-cymene})]_2$.

of *N*-benzyl imines in organic solvent such as CH_2Cl_2 and CH_3CN. The corresponding amines were obtained in good yields with good enantioselectivities. In contrast, polymer-immobilized ruthenium(II) complexes prepared from amphiphilic (*R*,*R*)-**2** and hydrophilic (*R*,*R*)-**3** were found to be effective for the asymmetric transfer hydrogenation of cyclic imines in water. We concluded that the hydrophilic–hydrophobic balance in a polymer-immobilized chiral catalyst on the asymmetric reaction was an important factor in controlling the catalytic activity. To our knowledge, this is the first successful report on the asymmetric transfer hydrogenation of imines by utilizing a polymer-supported chiral catalyst in water.

Experimental

General

Materials. Unless otherwise stated, all solvents and styrene, ketone, and amine derivatives were distilled from calcium hydride (CaH_2) under reduced pressure or ambient pressure. Sodium 4-vinylbenzenesulfonate, benzyltributylammonium chloride, cetyltrimethylammonium chloride, cetyltrimethylammonium bromide, and sodium formate were used as received. (*R*,*R*)-1,2-Diphenylethylenediamine ((*R*,*R*)-DPEN) was purchased from Fujimoto Molecular Planning. Co. and used without purification.

Measurements. 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. ^1H (300 MHz) and ^{13}C (75 MHz) spectra were measured on a Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard, and *J* values are reported in Hertz. ^{31}P (162 MHz) spectra were measured on a Varian Inova 400 spectrometer. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and are reported in reciprocal centimetres (cm^{-1}). Elemental analyses were performed at the Microanalytical Center of Kyoto University. GC analyses were performed with a Shimadzu Capillary Gas Chromatograph 14B equipped with a capillary column (SPERCO β-DEX 325, 30 m x 0.25 mm). HPLC analyses were performed with a JASCO HPLC system composed of a 3-line degasser DG-980–50, HPLC pump PV-980, column oven CO-965, equipped with a chiral column (CHIRALCEL OD or AD, Daicel) using hexane/2-propanol as eluent. A UV detector (JASCO UV-975 for JASCO HPLC system) was used for the peak detection. Optical rotations were taken on a JASCO DIP-149 digital polarimeter using a 10 cm thermostatted microcell. Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution of linear polymers was conducted at 40 °C with a JASCO PU-980 as a pump, JASCO UVIDEC- 100-III as a UV detector, and Shodex column A-802 (pore size: 20 Å) × 2 as columns. The eluent was THF, and the flow rate was 1.0 mL min^{-1}. A molecular weight calibration curve was obtained by using a series of polystyrene standards (Tosoh Co., Japan).

Preparation of polymer-immobilized chiral catalyst

Synthesis of (1*R*,2*R*)-*N*^{1}-(4-vinylbenzenesulfonyl)-1,2-diphenylethane-1,2-diamine[9]. A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with (1*R*,2*R*)-1,2-diphenylethane-1,2-diamine (0.997 g, 4.70 mmol), triethylamine (0.950 g, 9.39 mmol) and 7 mL of dry CH_2Cl_2 under dry nitrogen. 4-Vinylbenzene-1-sulfonyl chloride[1] (0.865 g, 4.27 mmol) and 3 mL of dry CH_2Cl_2 were then added to the mixture at 0 °C and the mixture was stirred under an atmosphere of dry nitrogen. After the mixture was stirred for 24 h, the solvent was removed with a pump and the residual solid was purified by silica gel column chromatography (with 1 : 1 ethyl acetate–hexane as an eluent). Removal of the solvents under reduced pressure gave (1*R*,2*R*)-*N*^{1}-(4-vinylbenzenesulfonyl)-1,2-diphenylethane-1,2-diamine (1.37 g, 3.62 mmol) as a white powder. Yield 85%; $[\alpha]_D = -36.7$ (c = 1.00 g/dL in $CHCl_3$); ^1H NMR (300 MHz, DMSO-d_6, δ = 0 ($(CH_3)_4Si$)): δ = 3.96 (d, J = 7.3 Hz, 1H, CH), 4.34 (d, J = 7.4 Hz, 1H, CH), 5.36 (d, J = 10.9 Hz, 1H, vinyl), 5.88 (d, J = 17.6 Hz, 1H, vinyl), 6.69 (dd, J = 10.9, 11.2 Hz, 1H, vinyl), 6.91–7.42 ppm (m, 14H, Ar-H); ^{13}C NMR (75 MHz, DMSO-d_6, δ = 0 ($(CH_3)_4Si$)): δ = 60.64, 64.86, 117.05, 126.06, 126.38, 126.51,

126.57, 127.27, 127.34, 127.40, 127.59, 135.44, 139.77, 140.10, 140.28, 142.50 ppm; FT-IR (KBr): ν = 3350, 3294 (NH_2), 3160 (NH), 3086, 3026 (CH=CH_2), 2861 (CH), 1323, 1152 cm^{-1} (SO_2); Elem. Anal. for $C_{22}H_{22}N_2O_2S$: calcd. C 69.8, H 5.86, N 7.40, S 8.47%, found: C 69.6, H 5.83, N 7.36, S 8.57%.

Synthesis of 4-vinylbenzenesulfonic acid benzyltributylammonium salt. A 50 mL round-bottomed flask equipped with a magnetic stirring bar was charged with sodium 4-vinylbenzenesulfonate (0.680 g, 3.30 mmol) and 10 mL of H_2O. Benzyltributylammonium chloride (0.686 g, 2.20 mmol) and 10 mL of CH_2Cl_2 were then added to the mixture at room temperature and the mixture was stirred vigorously for 30 min. The aqueous layer was extracted with 10 mL of Et_2O three times and the combined organic layer was dried with anhydrous $MgSO_4$. Removal of $MgSO_4$ by filtration and removal of solvent under high vacuum gave 4-vinylbenzenesulfonic acid benzyltributylammonium salt (1.01 g, 2.20 mmol) as a colorless viscous liquid. Yield >99%; ^{1}H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 0.99 (t, J = 7.3 Hz, 9H, CH_3), 1.37–1.45 (q, J = 7.4 Hz, 6H, CH_2), 1.76 (m, 6H, CH_2), 3.24 (t, J = 10.9 Hz, 2H, CH_2), 4.74 (s, 2H, Ph-CH_2), 5.21–5.25 (d, J = 17.6 Hz, 1H, vinyl), 5.71–5.77 (d, J = 11.2 Hz, 1H, vinyl), 6.65–6.74 (dd, J = 10.9, 11.2 Hz, 1H, CH), 7.34–7.52, 7.86–7.89 ppm (m, 14H, Ar-H); ^{13}C NMR (75 MHz, DMSO-d_6, δ = 0 ($(CH_3)_4Si$)): δ = 13.38, 19.13, 23.26, 57.40, 61.27, 114.52, 125.34, 125.77, 127.99, 128.90, 130.19, 132.54, 136.14, 137.06, 147.87 ppm; FT-IR (KBr): ν = 3089, 3040 (CH=CH_2), 1380, 1199 cm^{-1} (SO_3); Elem. Anal. for $C_{27}H_{41}NO_3S$: calcd. C 70.6; H 8.99; N 3.05; S, 6.98%, found: C 70.5, H 8.96, N 2.99, S 6.94%.

General procedure for the preparation of polymer-immobilized chiral ligand. A 10 mL glass ampoule equipped with a magnetic stirring bar was charged with (1*R*,2*R*)-N^1-(4-vinylbenzenesulfonyl)-1,2-diphenylethane-1,2-diamine, divinylbenzene, styrene derivative, AIBN, and solvent under nitrogen. After three cycles of freeze–thaw under liquid nitrogen, the ampoule was sealed and then heated to 60 °C. After 24 h, the ampoule was opened and the mixture was filtrated by glass filter. The resulting polymer was washed with THF, methanol, and water and dried at 40 °C under high vacuum.

Polystyrene-based chiral ligand ((*R*,*R*)-1). ((1*R*,2*R*)-N^1-(4-Vinylbenzenesulfonyl)-1,2-diphenylethane-1,2-diamine (75.7 mg, 0.20 mmol), divinylbenzene (26.0 mg, 0.20 mmol), styrene (0.167 g, 1.60 mmol), AIBN (6.6 mg, 0.04 mmol), and 1 mL of DMF gave 0.247 g of (*R*,*R*)-**1** as a white solid. Yield = 92%; Gel phase ^{1}H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 0.6–2.5 (br, CH and CH_2 of styrene), 4.0–4.5 (br, CH of DPEN), 6.0–6.7, 6.7–7.0, and 8.0–8,1 ppm (br, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 20–56, 57–75, 120–135 ppm; FT-IR (KBr): ν = 3383, 3299 (NH_2), 1333 cm^{-1} (SO_2 of sulfonamide); Elem. Anal.: calcd C 85.9; H 7.21; N 2.09; S 2.39%, found C 85.9; H 7.18; N 2.03, S 2.33%.

Poly(4-vinylbenzenesulfonate benzyltributylammonium salt)-based chiral ligand ((*R*,*R*)-2). (1*R*,2*R*)-N^1-(4-Vinylbenzenesulfonyl)-1,2-diphenylethane-1,2-diamine (75.7 mg, 0.20 mmol), divinylbenzene (26.0 mg, 0.20 mmol), 4-vinylbenzenesulfonic acid benzyltributylammonium salt (0.735 g, 1.60 mmol), AIBN (6.6 mg, 0.04 mmol), and 1 mL of DMF gave 0.793 g of (*R*,*R*)-**3** as a white solid. Yield = 94%; Gel phase ^{1}H NMR (300 MHz, $CDCl_3$, δ = 0 ($(CH_3)_4Si$)): δ = 7.9–7.1 and 7.1–6.4 (m, Ar-H), 4.5 (br, CH_2Ph), 3.1 (br, CH_2N), 1.6 (br, CH_2), 1.1 (br, CH_2), 0.8 ppm (br, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, δ = 0 ($(CH_3)_4Si$)): δ = 134–125, 62–56, 24–22, 20–18, 13.4 ppm; FT-IR (KBr): ν = 1333 cm^{-1} (SO_2 of sulfonamide); Elem. Anal.: calcd C 71.2; H 8.67; N 3.35; S 6.89%, found C 71.1; H 8.61; N 3.29; S 6.86%.

Poly(sodium 4-vinylbenzenesulfonate)-based chiral ligand ((*R*,*R*)-3). (1*R*,2*R*)-N^1-(4-Vinylbenzenesulfonyl)-1,2-diphenylethane-1,2-diamine (75.7 mg, 0.20 mmol), divinylbenzene (26.0 mg, 0.20 mmol), sodium 4-vinylbenzenesulfonic acid (0.323 g, 1.60 mmol), AIBN (6.6 mg, 0.04 mmol), and 1.2 mL of DMSO gave 0.371 g of (*R*,*R*)-**2** as a white solid. Yield = 86%; The measurements of Gel phase ^{1}H NMR and ^{13}C NMR in DMSO-d_6 and D_2O were found to be difficult. FT-IR (KBr): ν = 1341 cm^{-1} (SO_2 of sulfonamide); Elem. Anal.: calcd C 52.3; H 4.02; N 1.27%, found C 52.0; H 3.98; N 1.23%.

General procedure for the preparation of polymer-immobilized chiral catalyst

General procedure for the preparation of polymer-immobilized chiral catalyst in organic solvent. A 10 mL round-bottom flask equipped with a magnetic stirring bar was charged with polymer-immobilized chiral ligand (diamine: 0.015 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (0.0050 mmol), and 1 mL of organic solvent under argon. After three cycles of freeze–thaw under liquid nitrogen, the mixture was heated to 80 °C. After 1 h, removal of the solvent under high vacuum gave polymer-immobilized chiral catalyst as a reddish solid. The resulting chiral catalyst was directly used for the next asymmetric transfer hydrogenation of imines.

General procedure for the preparation of polymer-immobilized chiral catalyst in water. A 10 mL round-bottom flask equipped with a magnetic stirring bar was charged with polymer-immobilized chiral ligand (diamine: 0.015 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (0.0050 mmol), and 1 mL of degassed water under argon. After three cycles of freeze–thaw under liquid nitrogen, the mixture was heated to 40 °C. After 1 h, removal of the solvent under high vacuum gave polymer-immobilized chiral catalyst as a reddish solid. The resulting chiral catalyst was used for asymmetric transfer hydrogenation without further purification.

Asymmetric transfer hydrogenation of imines

Representative asymmetric transfer hydrogenation of imine 4 in CH_2Cl_2 (Table 1, entry 8). A 10 mL round-bottom flask equipped with a magnetic stirring bar was charged with **4** (0.209 g, 1.00 mmol), polymer-immobilized chiral catalyst (Ru: 0.010 mmol), a 5 : 2 HCO_2H–Et_3N azeotropic mixture (HCO_2H: 5.0 mmol), and 2.0 mL of CH_2Cl_2 under argon. After three cycles of freeze–thaw under liquid nitrogen, the mixture was stirred at 0 °C for 24 h. After adding saturated Na_2CO_3, the mixture was filtrated by glass filter. The solvent of the filtrate was removed with a vacuum pump and the residual solid was purified by silica gel column chromatography (with 1 : 4 ethyl acetate–hexanes as an eluent). *N*-Benzyl-1-phenylethanamine **5** was obtained as a colorless liquid. Yield: 80% by ^{1}H NMR in $CDCl_3$; 93% ee by HPLC analysis (Chiralcel OD-H, hexanes–2-propanol = 99 : 1 (v/v), 0.4 mL min^{-1}, rt, 254 nm, $t_{(S)}$ isomer (minor) = 39.2 min, $t_{(R)}$ isomer (major) = 41.2 min).

Representative asymmetric transfer hydrogenation of imine 10 in H_2O (Table 3, entry 7). A 10 mL round-bottom flask equipped with a magnetic stirring bar was charged with **10** (0.205 g, 1.00 mmol), polymer-immobilized chiral catalyst (Ru: 0.010 mmol), HCO_2Na (74 mg, 5.0 mmol), cetyltrimethylammonium chloride (0.16 g, 0.50 mmol) and 2.0 mL of degassed water under argon. After three cycles of freeze–thaw under liquid nitrogen, the mixture was stirred at room temperature for 24 h. After adding saturated Na_2CO_3, the mixture was filtrated by glass filter. The solvent of the filtrate was removed with a vacuum pump and the residual solid was purified by silica gel column chromatography (with 92 : 5 : 3 ethyl acetate–methanol–triethylamine as an eluent). 1,2,3,4-Tetrahydro-6,7-dimethoxy-1-methylisoquinoline **11** was obtained as a colorless liquid. Yield: 69% by ^{1}H NMR in $CDCl_3$; 94% ee by HPLC analysis (Chiralcel OD-H, hexanes–2-propanol–Et_2NH = 90 : 10 : 0.1 (v/v), 0.4 mL min^{-1}, rt, 254 nm, $t_{(S)}$ isomer (major) = 36.4 min, $t_{(R)}$ isomer (minor) = 52.6 min).

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