Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 17 (2006) 952–960

Catalytic asymmetric oxidation of sulfide and styrene derivatives using macroporous resins containing chiral metalloporphyrins (Fe, Ru)

Yann Ferrand, Romain Daviaud, Paul Le Maux and Gérard Simonneaux*

Ingénierie Chimique et Molécules pour le Vivant, UMR 6226, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

Received 28 January 2006; accepted 7 March 2006
Available online 4 April 2006

Abstract—Chiral metalloporphyrin (Fe, Ru) complexes, functionalized with four vinyl groups, have been polymerized with styrene and divinylbenzene (or ethylene glycol) to obtain supported iron and ruthenium complexes. The heterogeneous asymmetric oxidation of sulfides and styrene derivatives was carried out by using these polymers as catalysts. The reaction proceeded under mild conditions and gave sulfoxides and epoxides with good enantiomeric excesses (up to 75–76%). The catalysts keep constant ee values for the recycle tests of up to six times for asymmetric oxidation of styrene derivatives and of up to 14 times for asymmetric oxidation of sulfides with only traces of sulfones.

1. Introduction

Catalytic asymmetric oxidation of sulfides and olefins is an important and rapidly growing area in organic synthesis. Recently, attention has been focused on the immobilization of homogeneous chiral catalysts.[1–3] This is particularly important for oxidation reactions both from a practical and mechanistic point of view, since chiral sulfoxides and epoxides are versatile building block for the synthesis of numerous natural products and biological active substances. Immobilization can avoid the necessity of chiral ligand recovery and hence improve asymmetric catalyst application. One of the simplest ways to prepare a polymer-immobilized catalyst is a direct reaction of a simple functionalized polymer, such as Merrifield's resin with a derivative of the desired ligand and then insertion of the metal. This route has been used many times and is still the preparative method of choice.[4] There are however, disadvantages to grafting metal complexes onto previously prepared polymers. Treatment of cross-linked polymers can lead to unwanted side reactions, such as an attack on the carbon–carbon double bonds of the divinyl cross-linking. Also metal insertion in the active site may be far from complete.

Another alternative approach is to use functionalized complexes, which can be co-polymerized or self-polymerized to form cross-linked insoluble polymers.[1] It was expected that these polymers contain large pores, which are well-suited for use in asymmetric reactions catalyzed by rigid and large chiral metalloporphyrin species.

We have previously shown that chiral ruthenium porphyrins immobilized in spirobifluorene polymers[5] or in macroporous polymers[6] are effective catalysts in the asymmetric carbene transfer to olefins. We herein report the preparation of optically active Frechet type polymers bearing chiral metalloporphyrins and asymmetric heterogeneous oxidation catalyzed by these polymers. It is expected that these polymers containing large pores are well-suited for use in asymmetric oxidation reactions, catalyzed by rigid and large chiral metalloporphyrin species. To the best our knowledge, this system is the first example showing such asymmetric oxidation with chiral metalloporphyrins co-polymerized to form cross-linked insoluble polymers as catalysts and also the first asymmetric sulfoxidation under heterogeneous conditions with chiral metalloporphyrins.

2. Results

2.1. Preparation of metallopolymers

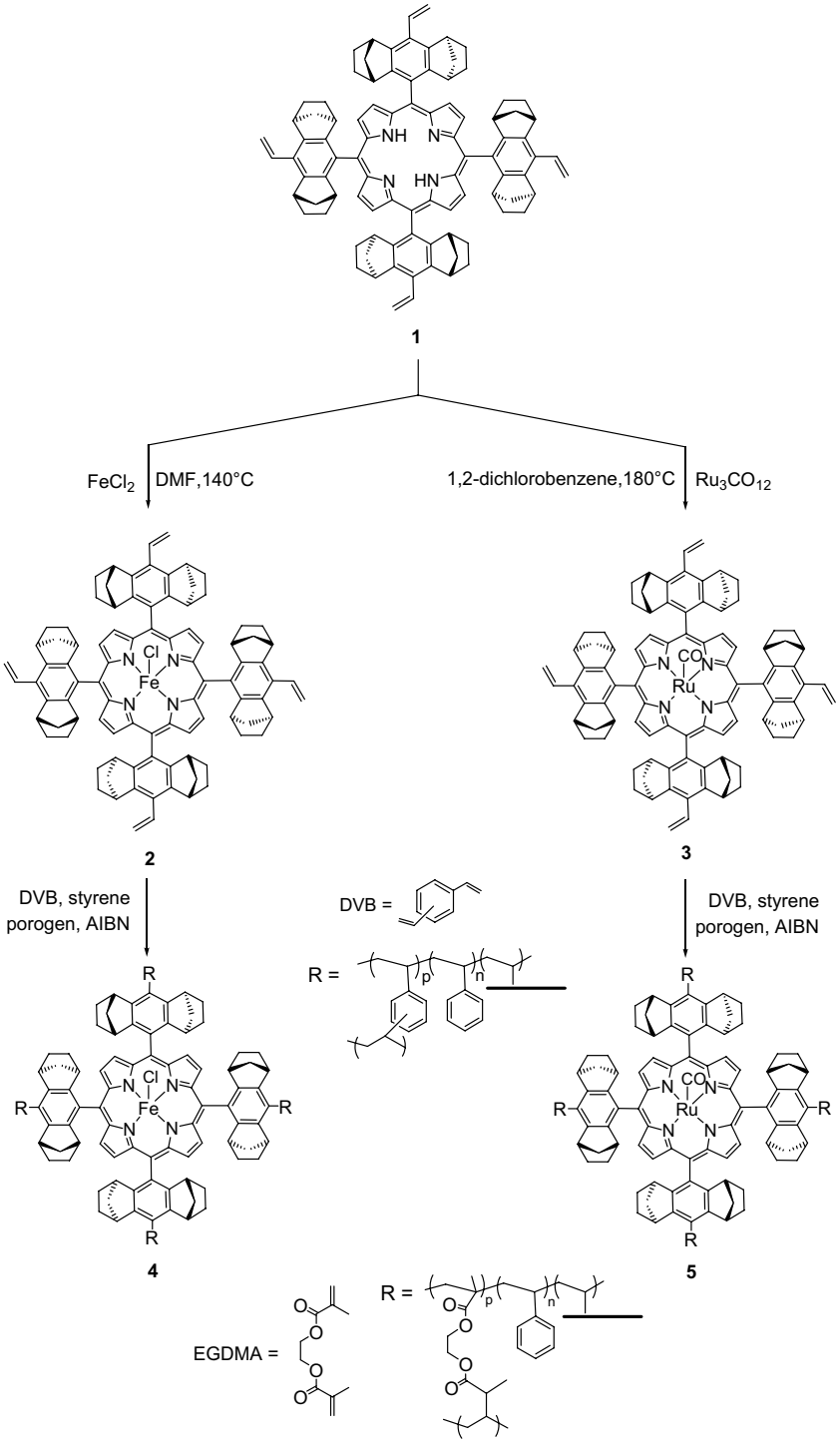
The starting point of the work described herein was the introduction of a vinyl group into an optically active

* Corresponding author. Tel.: +33 22 323 6285; fax: +33 22 323 5637; e-mail: gerard.simonneaux@univ-rennes1.fr

0957-4166/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2006.03.003

porphyrin, with the aim of preparing polymers using the chiral porphyrin as a co-monomer. We have previously reported such a synthesis with ruthenium leading to carbonyl-[5,10,15,20-tetrakis-[(1*S*,4*R*,5*R*,8*S*)-10-vinyl-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]-porphyrinato]ruthenium(II) as monomer **3** (Scheme 1).[6] The corresponding iron complex was prepared by the addition of iron dichloride to the free-base porphyrin **1** in dimethyl formamide to give **2** with a 47% yield (Scheme 1).

Next, chiral iron vinylporphyrin **2** was used in different random co-polymerizations with divinyl benzene (DVB) using a protocol previously described[7] for the preparation of monolithic resins (Scheme 1). Three different chiral iron polymers **P1-FeCl**, **P2-FeCl**, and **P3-FeCl** were prepared from **2** by changing the degree of cross-linking and the porogen (toluene or chloroform/dodecane), using AIBN as a radical initiator. The different ratios are summarized in Table 1. The brown polymers were ground and the near



Scheme 1.

Table 1. Polymerization conditions used for the preparation of Fe and Ru catalysts

Polymer	Monomer (w/w)	DVB/styrene	Porogen	AIBN (%)
P1-FeCl 4a **P1-RuCO 5a**	**2** (10%) **3** (10%)	1.2	Toluene	3
P2-FeCl 4b **P2-RuCO 5b**	**2** (10%) **3** (10%)	5.0	Toluene	3
P3-FeCl 4c **P3-RuCO 5c**	**2** (10%) **3** (10%)	1.2	$CHCl_3$/ dodecane (1/1)	3
P4-FeCl 4d **P4-RuCO 5d**	**2** (10%) **3** (10%)	1.2[a]	Toluene	3

[a] Ethylene glycol dimethacrylate (EGDMA)/styrene.

quantitative incorporation of the iron porphyrin in the polymer was evidenced by the fact that the chloroform washing solutions were colorless. These polymers were characterized by UV–vis (large absorption band at 424 nm corresponding to the Soret band of the porphyrin) and scanning electronic microscopy (Fig. 1). All of the porous polymers showed small holes of about 0.5 μm diameter. The iron contents were determined by electronic microanalysis. The more polar monomer ethyleneglycol dimethacrylate (EGDMA) was also chosen because it forms highly cross-linked polymers, which can be used as supports for metal catalysts.[8,9] Thus, co-polymerization of iron monomer **2** with ethylene glycol dimethacrylate in the presence of toluene as the porogen, which is necessary for creating the pore structure, resulted in the orange, insoluble polymer **P4-FeCl**. All the ruthenium polymers showed in the IR spectrum, a C=O absorption at $\sim$1945 cm^{-1} which is similar to the value observed for the monomer **2**. Their characterization has previously been reported.[6]

2.2. Catalytic asymmetric sulfoxidation

Following, the successful synthesis of the iron porphyrin polymers, their catalytic activity was tested in the oxidation of sulfides. Sulfoxidation was initially catalyzed by the chiral iron porphyrin **6a**[10] to obtain a reference. Although the asymmetric induction in the iron-catalyzed sulfoxidation with **6a** is reasonable (68% ee), the viability of the process is limited, owing to low conversion of the sulfide. Thus, under homogeneous conditions, large amounts of unconverted sulfides remained and the best yield of sulfoxide was only 43% (Table 2, entry 1). Moreover, we noted a significant amount of sulfone through over oxidation ($\sim$5%).

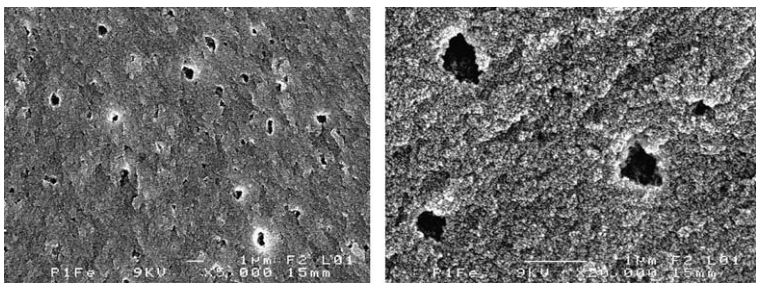
Table 2. Asymmetric oxidation of sulfides by [Fe][a]

Run	Substrates	Catalysts	Yield[b] (%) sulfoxide (sulfone)	ee[c] (%) (configuration)
1	Ph–S–Me	**6a**	43 (5)	68 (*S*)
2		**P1-FeCl**	75 (1)	66 (*S*)
3		**P2-FeCl**	73 (1)	68 (*S*)
4		**P3-FeCl**	89 (1)	65 (*S*)
5		**P4-FeCl**	85 (1)	60 (*S*)
6	*p*-MePh–S–Me	**6a**	31 (2)	68 (*S*)
7		**P1-FeCl**	82 (1)	65 (*S*)
8	*p*-OMePh–S–Me	**6a**	75 (6)	54 (*S*)
9		**P1-FeCl**	84 (1)	56 (*S*)
10	$PhCH_2$–S–Ph	**6a**	15 (15)	52 (*S*)
11		**P1-FeCl**	45 (3)	49 (*S*)
12	*p*-NO_2Ph–S–Me	**6a**	58 (11)	75 (*S*)
13		**P1-FeCl**	83 (3)	75 (*S*)
14	*p*-BrPh–S–Me	**6a**	67 (10)	49 (*S*)
15		**P1-FeCl**	83 (1)	69 (*S*)

[a] Reaction conditions: a mixture containing alkene (400 μmol), PhIO (200 μmol) and catalyst (1 μmol) in degassed CH_2Cl_2 (1 ml) was stirred at room temperature for 5 h.
[b] Yields are based on the limiting reactant: PhIO.
[c] The ee values were determined by HPLC on a chiral phase.
[d] The absolute configuration was obtained from optical rotations.

In contrast, the observed sulfoxide yields increased to 75–84% with ees of about 65% with the chiral iron polymers **P1-FeCl** for all the substrates, if we exclude the more-challenging substrate phenyl benzyl sulfide, which gave the corresponding sulfide with 49% ee. However, even in this case, the yield was much better than under homogeneous conditions: 45% versus 15%. The improved ee, 75%, was obtained with *p*-nitrophenyl methyl sulfoxide. The ees of sulfoxides with a substituent electroacceptor on the phenyl (*p*-NO_2, *p*-Br), 75% and 69%, respectively, were better than the sulfoxides with a substituent electron donor (*p*-Me, *p*-OMe), 65% and 56%, respectively.

We also investigated the efficiency of three other chiral iron polymers **P2-FeCl**, **P3-FeCl**, and **P4-FeCl**, which were prepared from **2** by changing the degree of cross-linking and

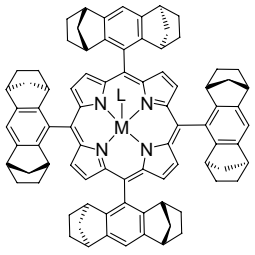


x 5000 x 20000

Figure 1. Scanning electronic microscopy of **P1-FeCl**.

the porogen (toluene or chloroform/dodecane), using AIBN as a radical initiator (see Table 1). Thus it can be seen from Table 2 that the use of $CHCl_3$/dodecane as a porogenic mixture: **P3-FeCl** does not seem to be detrimental to the enantiomeric excess and yield (entry 4). To shed some light on this area, we also carried out a comparative study with a different polymer **P4-FeCl**, using a different cross-linker, ethylene glycol. As can be seen in Table 2 (entries 3, 4, and 5), the ees are only slightly lower than those obtained with **P1-FeCl**.

Sulfoxidation with chiral ruthenium monomer **6b**,[11,12] polymers **P1-RuCO** and **P1-Ru(O)$_2$** was also examined. First, the homogeneous oxidation of thioanisole was investigated using **6b** (Scheme 2) as catalyst (Table 3, entries 1 and 2). At both 22 and 60 °C, the oxidation yields were very low (<5%). Since it was previously reported that dioxoruthenium analogues are more efficient, the dioxo complex **6c** was used as a catalyst under similar reaction conditions. Accordingly, the yield increased from 13% (22 °C) to 97% (60 °C) with 55% ee for the sulfoxide in the latter case. Thus, high temperature and preoxidation of the catalyst seem necessary. For polymeric catalysts, the latter conditions were also examined. The best results were obtained with **P1-Ru(O)$_2$**, leading to an oxidation of the substrate with 92% yield after 24 h, but with a quite moderate enantiomeric excess (48%).



ML= **6a** FeCl, **6b** RuCO, **6c** Ru(O)$_2$

Scheme 2.

Table 3. Asymmetric oxidation of thioanisole by [Ru][a]

Run	Catalysts	Time (h)	Temperature (°C)	Yield[b] (%) sulfoxide	ee[c] (%)
1	**6b**	24	22	2	14
2	**6b**	24	60	4	24
3	**6c**[d]	24	22	13	13
4	**6c**	24	60	97	55
5	**P1-RuCO**	24	60	27	50
6	**P1-Ru(O)$_2$**[d]	5	60	48	—
7	**P1-Ru(O)$_2$**	24	60	92	48

[a] Reaction conditions: a mixture containing thioanisole (400 μmol), 2,6-dichloropyridine *N*-oxide (200 μmol) and catalyst (1 μmol) in degassed toluene (1 ml) was stirred at 60 °C.
[b] Yields are based on the limiting reactant: 2,6-dichloropyridine *N*-oxide.
[c] The ee values were determined by HPLC on a chiral phase.
[d] Prepared by addition of *m*-CPBA.

The most important advantages of heterogeneous catalysis over its homogeneous counterpart are a high increase of the complex stability in the reaction media and the possibility of reusing the catalyst after reaction by simple filtration. We have selected the catalyst **P1-FeCl** using thioanisole as a model substrate for the recycling study. The results are summarized in Figure 2. If we except the decrease of ee in the second run, from 68% to 58%, the enantioselectivity together with the reactivity is maintained after 14 runs, confirming the high stability of the system. For comparison to the previous system, the recovery–reuse outcome from the oxidation of the same substrate with 2,6-dichloropyridine *N*-oxide catalyzed with **P1-Ru(O)$_2$** is reported in Figure 3. In contrast, we should note a progressive decrease of the reactivity with the Ru/thioanisole system, whereas the enantioselectivity was maintained at a moderate level (~48%).

2.3. Catalytic asymmetric epoxidation

We first employed the system previously reported by Hirobe et al.,[13] which is 2,6-dichloro-pyridine *N*-oxide as the oxygen donor in toluene at room temperature, with chiral ruthenium porphyrin polymers. This system was preferred to the iodosylbenzene with iron catalyst, since it has previously been found to give lower yields and lower enantiomeric excesses than the ruthenium system under similar conditions.[10] It must be emphasized that a different system, supporting nonchiral ruthenium porphyrins, has recently been reported by Nestler and Severin for the epoxidation of olefins.[8] Our results obtained in epoxidation catalysis with ruthenium polymers are summarized in Table 4.

The epoxide was formed in 70% yield and 71% enantioselectivity from unsubstituted styrene with **P1-RuCO** (entry 2). We also investigated the oxidation of *ortho*-, *meta*-, and *para*-trifluoromethyl substituted styrenes with the same polymer (Table 4). As shown in Table 4, *para*- or *meta*-substitution does not have a significant effect upon the enantioselectivity of styrene epoxidation; the ee (73% and 74%) for the epoxide were maintained with the *para*- and *meta*-CF_3 derivatives. In contrast, with the *ortho*-CF_3 styrene, we noted a decrease of the yield (~39%) probably due to steric reasons, and a decrease in the enantioselectivity (~44%). It can also be seen from Table 4 that the use of **P2-RuCO**, a polymer prepared with a high DVD/styrene ratio (entry 3) seems to be detrimental to the yield (entry 3). This may be due to the high cross-linking and consequently, reduced accessibility of the sites. In contrast, changing **P1-RuCO** to **P3-RuCO** (entry 4) has only a weak influence, as evidenced by the results obtained with $CHCl_3$/dodecane as a porogenic mixture, since the amount of cross-linking is maintained in this case.

The recovery and recyclability of the **P1-RuCO** polymer have been also examined for the epoxidation reaction. The polymer was tested for enantioselectivity and reactivity in the epoxidation of styrene with 2,6-dichloropyridine *N*-oxide leading to three recycling steps with a weak progressive decrease of enantioselectivity (from 71% to 64%) and a decrease of yield (from 70% to 19%) (Fig. 4). Thus, the yield markly decreased to 13% after the third run whereas the enantioselectivity was maintained at ~64%. A progressive

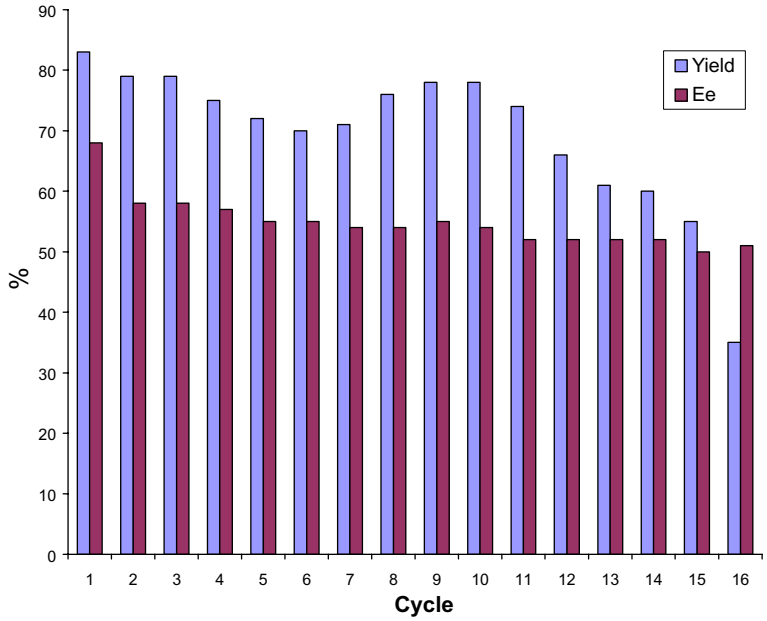


Figure 2. Recovery–reuse from the oxidation of thioanisole with PhIO using **P1-FeCl** as catalyst. Reaction time: 24 h.

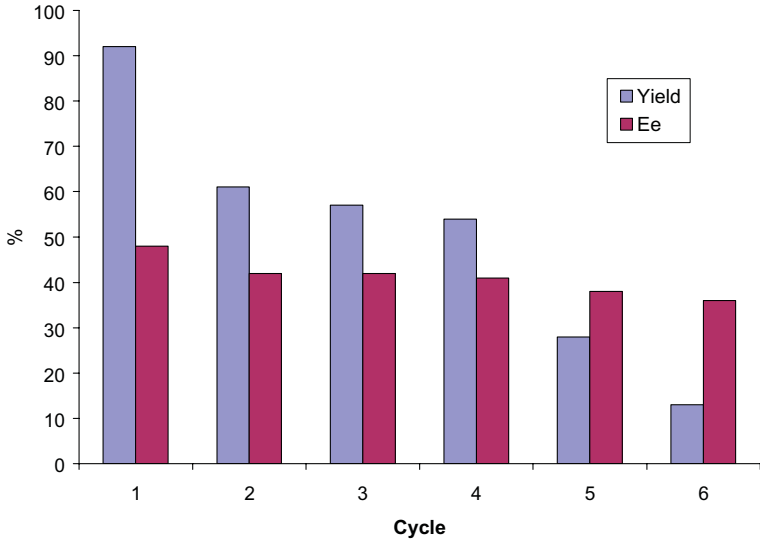


Figure 3. Recovery–reuse from the oxidation of thioanisole with 2,6-dichloropyridine *N*-oxide using **P1-Ru(O)$_2$** as catalyst for 24 h.

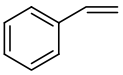
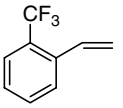
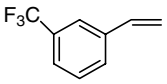
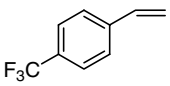
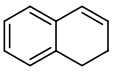
decrease of the number of active sites may explain this result, since the enantioselectivity was only slightly decreased.

The heterogeneous asymmetric epoxidation of styrene catalyzed by Fe polymers **P1-FeCl** together with its homogeneous counterpart, **6a**, is summarized in Table 5. In both cases, the enantiomeric excess was quite moderate. Furthermore, we observed a large decrease of the chemical yield under heterogeneous conditions, especially in a toluene solvent (from 60% to 14%). Accordingly, the recovery and recyclability of polymer **P1-FeCl** have not been examined for epoxidation reaction.

3. Discussion

Although some progress has been made in heterogeneous organic oxidations catalyzed by soluble and insoluble polymer-supported metalloporphyrins, a similar strategy was not suitable for the development of polymer-supported chiral metalloporphyrins because of the difficulty involved in attaching a chiral porphyrin ligand, particularly D_4-symmetric porphyrin, onto a polymer chain.[14] An alternative method has previously been reported by Che et al.,[15] which attaches a ruthenium chiral porphyrin to meso-porous silica material by coordinative grafting. We herein report a different system that circumvents the problem encountered

Table 4. Asymmetric oxidation of alkenes by [Ru][a]

Run	Substrates	Catalysts	Yield (%)	ee (%)	Turn over
1		**6b**	78	76	257
2		**P1-RuCO**	70	71	231
3		**P2-RuCO**	13	74	43
4		**P3-RuCO**	72	72	238
5		**6b**	57	44	188
6		**P1-RuCO**	39	44	129
7		**P2-RuCO**	5	43	16
8		**P3-RuCO**	35	43	115
9		**6b**	77	76	254
10		**P1-RuCO**	59	74	195
11		**P2-RuCO**	6	42	20
12		**P3-RuCO**	52	71	171
13		**6b**	71	76	234
14		**P1-RuCO**	89	73	293
15		**P2-RuCO**	9	72	30
16		**P3-RuCO**	40	73	132
17		**6b**	41	71	135
18		**P1-RuCO**	30	70	99
19		**P2-RuCO**	7	62	23
20		**P3-RuCO**	33	68	109

[a] Reaction conditions: a mixture containing alkene (330 μmol), Cl_2pyNO (330 μmol) and catalyst (1 μmol) in degassed toluene (1 ml) was stirred at room temperature for 24 h.

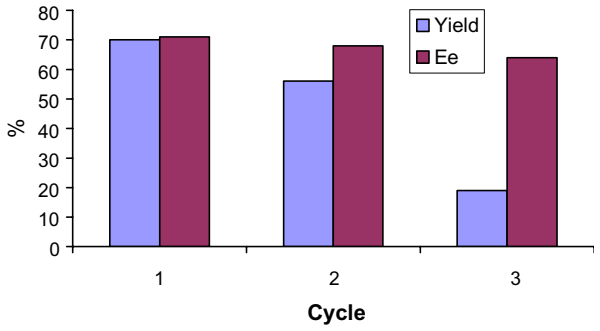


Figure 4. Recovery–reuse from the oxidation of styrene with 2,6-dichloropyridine *N*-oxide using **P1-RuCO** as catalyst for 24 h.

in the structural modification of the chiral porphyrin ligand, which involved the introduction of a vinyl group into an optically active porphyrin with the aim of preparing polymers using the chiral metalloporphyrin as a co-monomer.

Catalytic asymmetric sulfide oxidations for the synthesis of biologically active sulfoxides are currently applied on an industrial scale.[16] However, new technological advances are still necessary to overcome the limitations of the current systems.[17] Despite careful control of the reaction temperature, reaction time and the relative amounts of oxidants, it is difficult to completely avoid over-oxidation. Moreover, catalysts based on nontoxic and inexpensive metal, such as iron, are relatively rare, if we make the comparison to titanium, manganese, and vanadium counterparts.[18,19] This work presents a possible example of the use of heterogeneous catalysis to solve this problem. For all the sulfide substrates assessed, the heterogeneous system greatly improved results with enantioselectivities of up to 75% and yields up to 82%. Whereas 43% was the best yield under homogeneous conditions with thioanisole, almost all sulfoxides were now obtained in more than 70%, using the different polymers, and only traces of sulfones were observed. In contrast, a significant amount of sulfone was detected under the homogeneous conditions. Thus, the results herein suggest that the oxidation promoted by the catalyst in our case is a fully enantioselective process, without a significant contribution from kinetic resolution since there were only traces of sulfones.

Table 5. Asymmetric oxidation of styrene by [Fe][a]

Run	Catalysts	Time	Solvent	Yield[b] (%)	ee[c] (%)
1	**6a**	5	CH_2Cl_2	45	50
2	**6a**	5	Toluene	60	59
3	**P1-FeCl**	24	CH_2Cl_2	30	41
4	**P1-FeCl**	24	Toluene	14	47

[a] Reaction conditions: a mixture containing styrene (1000 μmol), PhIO (200 μmol) and catalyst (1 μmol) in degassed toluene or CH_2Cl_2 (1 ml) was stirred at room temperature.
[b] Yields are based on the limiting reactant: PhIO.
[c] The ee values were determined by GC on a chiral phase.

There are previously reported homogeneous metalloporphyrin-catalyzed sulfide oxidations in the literature.[10,20–23] Complexation of sulfoxides to iron(III) porphyrins, which have previously been reported[24] in solution, is weak and needs a high concentration of the ligand. However, this situation can be detrimental to the turn-over of the catalytic reaction and may explain why the yield herein of the sulfoxidation is low under homogeneous conditions and much higher in heterogeneous conditions. The small cavity inside the polymer will decrease the local amount of the newly prepared sulfoxide near the metal and will facilitate a second catalytic cycle. This also may explain why the ruthenium polymers are very poor catalysts, since it is well known that the strength of the ruthenium–sulfoxide bond is much higher than that of the corresponding iron–sulfoxide bond.[25]

Recently, there has also been a renewed interest in reactions catalyzed by porphyrin ruthenium(II) complexes, simultaneously with the development of new chiral ruthenium porphyrins.[26] These reactions focus mainly on asymmetric epoxidation of olefins, although in some cases, a gradual inactivation of the catalytic system is observed due to the possible formation of inactive carbonyl complexes when *trans*-dioxo(tetramesitylporphyrinato)ruthenium(VI) is used as the catalyst.[27] However, very few metalloporphyrin polymers bearing chiral groups have been tested in the heterogeneous catalytic epoxidation reactions.[15,28] Our polymers are monolithic resins bearing ruthenium porphyrins, previously used by us in asymmetric cyclopropanation.[6] This system was quite efficient for the first run (253 turnovers), since there is a stoichiometric ratio of alkene/oxidant, and the enantiomeric excess was

close to that obtained in solution (70–74%). Unfortunately, we observed a gradual decrease of activity over three successive reactions. The diminishing activity of this heterogeneous catalyst was ascribed to catalyst deactivation through a blocking of the reactant (possibly 2,6-dichloropyridine *N*-oxide or 2,6-dichloro-pyridine) to the active sites of the resins. These results are in contrast to those observed with the sulfoxidation reaction, since both the enantiomeric excess and the yield are maintained in this case, due to high accessibility of the reactant to active sites through large pores in such resins.

4. Conclusion

In conclusion, we have developed an asymmetric iron polymer-catalyzed sulfide oxidation with iodosyl benzene as oxidant, which provides sulfoxides with up to 89% yield in good ee (up to 75%). The simplicity of the process (room temperature, catalyst easily recovered), the high yields and good enantioselectivity render this heterogeneous process an attractive alternative to the few existing heterogeneous methods available for metal-catalyzed asymmetric sulfide oxidation. The analogous ruthenium polymers are much less efficient for this reaction. In contrast, the reverse is true for the epoxidation reaction; the better system is related to the use of the ruthenium polymers, although the recycling outcome needs to be increased. Ongoing work includes investigations of an extended range of substrates, particularly those of pharmaceutical importance and further optimization of the reaction medium and oxidants.

5. Experimental

5.1. General experimental

All reactions were performed under argon. Solvents were distilled from an appropriate drying agent prior to use: Et_2O and THF from sodium and benzophenone, toluene from sodium, CH_2Cl_2 from CaH_2, $CHCl_3$ from P_2O_5, and all other solvents were HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck pre-coated aluminum foil sheets (Silica gel 60 with fluorescent indicator UV_{254}). Compounds were visualized with UV light at 254 and 365 nm. Column chromatographies were carried out using silica gel from Merck (0.063–0.200 mm). ^1H NMR and ^{13}C NMR in $CDCl_3$ were recorded using Bruker (Advance 500dpx and 300dpx spectrometers) at 500 and 75 MHz, respectively. High-resolution mass spectra were recorded on a ZabSpec TOF Micromass spectrometer in ESI positive mode at the CRMPO. Liquid UV–visible spectra were recorded on a UVIKON XL from Biotech. Solid UV–visible spectra were recorded on a Cary 5000 NIR spectrophotometer. Scanning electronic microscopy and microanalyses were realized on a Jeol JSM 6301F and Jeol JSM 6400 spectrometers, respectively, at the CMEBA. All catalytic reactions were controlled on a Varian CP-3380 Gas Chromatograph equipped with a CP-Chirasil-Dex Column. The enantiomeric excesses of the sulfoxides were determined on a HPLC Varian Prostar 218 system equipped with Chiralcel OD-H and OJ-H columns. For the *p*-bromophenyl methyl sulfoxide and the *p*-methoxyphenyl methyl sulfoxide, the enantiomeric excesses were determined on a Merck Hitachi D-7000 system equipped with a Chiralcel OB-H column at the Laboratoire de Stéréochimie Dynamique et Chiralité of P^r Roussel, Université Aix-Marseille III.

5.2. Preparation of iron porphyrin monomer 2

A mixture of the free base porphyrin, 50 mg (40 μmol) and $FeCl_2{\cdot}4H_2O$, 80 mg (0.4 mmol), in refluxing dimethyl formamide under argon was left to react for 24 h. Then, the solution was evaporated to dryness. The purple-brown residue was dissolved in $CHCl_3$ (20 ml) and washed with water (20 ml) containing concentrated HCl (0.5 ml). The organic portion was removed and dried. After evaporation, the crude product was chromatographed on silica gel to first yield any recovered free base porphyrin (24 mg) (eluant: pentane/CH_2Cl_2, 1/1), then metalloporphyrin (25 mg, yield: 47%) (eluant: CH_2Cl_2/CH_3OH, 4/1). ^1H NMR ($CDCl_3$, ppm): δ: 80 ppm (8H, br s); UV–vis (CH_2Cl_2): λ_{max}/nm ($\log\varepsilon$): 381 (4.42), 426 (4.71), 511 (3.86), 577 (3.25), 697 (3.23); MS (ESI, CH_2Cl_2/CH_3OH 9/1) (*m*/*z*): calculated for $C_{93}H_{88}N_4O$ ^{56}F (M−Cl+CH_3OH)+: 1332.6307, found: 1332.6321.

5.3. Preparation of polymers

In an oven dried test tube, iron porphyrin complex (9.6 mg, 7.2 μmol) was dissolved in the porogen 160 μl (toluene 1.5 mmol). Then, styrene (32 μl, 277 μmol) and divinylbenzene (49 μl, 340 μmol) were added to the solution. The polymerization reaction was initiated by AIBN (10 mg, 60 μmol). The mixture was heated at 65 °C for 16 h without stirring. The resulting polymer was extracted from the polymerization tube, crushed in a mortar, washed with dichloromethane, and filtered on Büchner funnel. Recovered: 80 mg. UV–vis (powder): λ_{max}/nm: 424 (Soret band).

5.4. General procedure for homogeneous asymmetric oxidation of sulfides with iron porphyrin complexes 6a

Iron porphyrin complex **6a** (1.2 mg, 1 μmol) and PhIO (44 mg, 200 μmol) were placed in a test tube under argon. Then, 1 ml of degassed dichloromethane was added via syringe, followed by sulfide (400 μmol). After 5 h, the mixture was analyzed by GC for yield. The ee of the sulfoxide was determined by chiral HPLC after purification by flash chromatography on silica gel (pentane/dichloromethane 1:1, then ethyl acetate).

5.5. General procedure for heterogeneous asymmetric oxidation of sulfides with iron polymers 4

Iron polymer **P1-FeCl 4** (12 mg) and PhIO (44 mg, 200 μmol) were placed in a test tube under argon. Then, 1 ml of degassed dichloromethane was added via syringe, followed by sulfide (400 μmol). After 5 h, the mixture was filtered and analyzed by GC for yield. The ee of the sulf-

oxide was determined by chiral HPLC after purification by flash chromatography on silica gel (pentane/dichloromethane 1:1, then ethyl acetate).

5.6. General procedure for homogeneous and heterogeneous asymmetric oxidation of thioanisole with ruthenium porphyrin 6b and polymer P1-RuCO

Ruthenium porphyrin complex **6b** (1.3 mg, 1 μmol) (or 12 mg of polymer **P1-RuCO**) and 2,6-dichloropyridine *N*-oxide (33 mg, 200 μmol) were placed in a test tube under argon. Then, 1 ml of degassed toluene was added via syringe, followed by thioanisole (40 μmol). After 24 h at 60 °C the mixture was analyzed by chiral GC for yield. The ee of the phenyl methyl sulfoxide was determined by chiral HPLC after purification by flash chromatography on silica gel (pentane/dichloromethane 1:1, then ethyl acetate).

5.7. General procedure for homogeneous and heterogeneous asymmetric oxidation of thioanisole with ruthenium dioxo porphyrin 6c and polymer P1-Ru(O)$_2$

The ruthenium dioxo porphyrin complex was prepared as follows: to (1.5 mg, 1.2 μmol) ruthenium carbonyl porphyrin **6b** in a test tube under argon were added 0.5 mg (2.5 μmol) of *m*-CPBA and 0.5 ml of degassed dichloromethane. After 5 min, the solution was purified by flash chromatography on basic alumina eluted with dichloromethane and the solvent was removed. Then, the procedure for catalysis was the same as described for ruthenium carbonyl porphyrin **6b**.

The polymer **P1-Ru(O)$_2$** was prepared as following: to 12 mg of polymer **P1-RuCO 5** in a test tube under argon were added (0.5 mg, 2.5 μmol) of *m*-CPBA and 1 ml of degassed dichloromethane. After 30 min, the solvent was removed and the polymer was washed two times with 0.5 ml dichloromethane. The IR spectrum show the disappearance of CO band at 1945 cm^{-1}. Then, the procedure for catalysis was the same as described for ruthenium carbonyl porphyrin **6b**.

5.7.1. (*S*)-(−)-Phenyl methyl sulfoxide. HPLC: t_R (*R*) = 27.5 min, t_R (*S*) = 29.9 min (Chiralcel OD-H; flow rate: 0.5 ml min^{-1}; hexane/*i*-PrOH (9/1), 25 °C, detection at 225 nm.

5.7.2. (*S*)-(−)-Tolyl methyl sulfoxide. HPLC: t_R (*R*) = 38.6 min, t_R (*S*) = 41.2 min (Chiralcel OD-H; flow rate: 0.5 ml min^{-1}; hexane/*i*-PrOH (9.5/0.5), 25 °C, detection at 225 nm.

5.7.3. (*S*)-(−)-*p*-Methoxyphenyl methyl sulfoxide. HPLC: t_R (*S*) = 6.1 min, t_R (*R*) = 10.3 min (Chiralcel OB-H; flow rate: 1 ml min^{-1}; hexane/*i*-PrOH (1/1), 25 °C, detection at 254 nm.

5.7.4. (*S*)-(−)-*p*-Bromophenyl methyl sulfoxide. HPLC: t_R (*S*) = 5.4 min, t_R (*R*) = 6.6 min (Chiralcel OB-H; flow rate: 1 ml min^{-1}; hexane/*i*-PrOH (1/1), 25 °C, detection at 254 nm.

5.7.5. (*S*)-(−)-*p*-Nitrophenyl methyl sulfoxide. HPLC: t_R (*R*) = 62.6 min, t_R (*S*) = 70.1 min (Chiralcel OJ-H; flow rate: 0.5 ml min^{-1}; hexane/*i*-PrOH (8/2), 25 °C, detection at 225 nm.

5.7.6. (*S*)-(−)-Phenyl benzyl sulfoxide. HPLC: t_R (*R*) = 31.3 min, t_R (*S*) = 36.3 min (Chiralcel OD-H; flow rate: 0.5 ml min^{-1}; hexane/*i*-PrOH (9/1), 25 °C, detection at 225 nm.

5.8. General procedure for homogeneous asymmetric oxidation of styrene derivatives with ruthenium porphyrin 6

Ruthenium porphyrin complex **6b** (1.3 mg, 1 μmol) and 2,6-dichloropyridine *N*-oxide (54 mg, 330 μmol) were placed in a test tube under argon. Then, 1 ml of degassed toluene was added via syringe, followed by styrene derivative (330 μmol). After 24 h, the mixture was analyzed by chiral GC for yield and ee.

5.9. General procedure for heterogeneous asymmetric oxidation of styrene derivatives with ruthenium polymers

Ruthenium polymer **P1-RuCO** (1 mg) and 2,6-dichloropyridine *N*-oxide (54 mg, 330 μmol) were placed in a test tube under argon. Then, 1 ml of degassed toluene was added via syringe, followed by styrene derivative (330 μmol). After 24 h, the mixture was filtered and analyzed by chiral GC for yield and ee.

5.10. General procedure for homogeneous and heterogeneous asymmetric oxidation of styrene with iron porphyrin 6a and polymer P1-FeCl

Iron porphyrin complex **6a** (1.3 mg, 1 μmol) (or 12 mg of polymer **P1-FeCl** and PhIO (44 mg, 200 μmol) were placed in a test tube under argon. Then, 1 ml of degassed toluene (or CH_2Cl_2) was added via syringe, followed by styrene derivative (1 mmol). After 24 h, the mixture was analyzed by chiral GC for yield and ee.

5.11. Gas chromatography conditions for oxidation of sulfides and styrene derivatives

CP-Chirasil-Dex column, temperature: 120 °C (hold 1 min) to 200 °C at 2.5 °C min^{-1}, pressure 15 psi, injector (pulsed split mode) at 200 °C, detector (FID) at 220 °C.

Acknowledgements

We thank GIREX S.A., for financial support (Y.F.) and C. Roussel (Université Aix-Marseille III), for his technical assistance.

References

1. Fan, Q. H.; Li, Y. M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385–3466.
2. Rechavi, D.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 3467–3494.

3. Song, C. E.; Lee, S. G. *Chem. Rev.* **2002**, *102*, 3495–3524.
4. Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217–3274.
5. Ferrand, Y.; Poriel, C.; Le Maux, P.; Rault-Berthelot, J.; Simonneaux, G. *Tetrahedron: Asymmetry* **2005**, *16*, 1463–1472.
6. Ferrand, Y.; Le Maux, P.; Simonneaux, G. *Tetrahedron: Asymmetry* **2005**, 3829–3836.
7. Fréchet, J. M. *Tetrahedron* **1981**, *37*, 663–683.
8. Nestler, O.; Severin, K. *Org. Lett.* **2001**, *3*, 3907–3909.
9. Burri, E.; Öhm, M.; Daguenet, C.; Severin, K. *Chem. Eur. J.* **2005**, *11*, 5055–5061.
10. Halterman, R. L.; Jan, S. T.; Nimmons, H. L.; Standlee, D. J.; Khan, M. A. *Tetrahedron* **1997**, *53*, 11257–11276.
11. Lo, W. C.; Che, C. M.; Cheng, K. F.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1997**, 1205–1206.
12. Berkessel, A.; Frauenkron, M. *J. Chem. Soc., Perkin Trans.* **1997**, 2265–2266.
13. Higushi, T.; Ohtake, H.; Hirobe, M. *Tetrahedron Lett.* **1989**, *30*, 6545–6548.
14. Xia, Q. H.; Ge, H. Q.; Ye, C. P.; Liu, Z. M.; Su, K. X. *Chem. Rev.* **2005**, *105*, 1603–1662.
15. Zhang, J. L.; Liu, Y. L.; Che, C. M. *Chem. Commun.* **2002**, 2906–2907.
16. Legros, J.; Dehli, J. R.; Bolm, C. *Adv. Synth. Catal.* **2005**, *347*, 19–31.
17. Kowalski, P.; Mitka, K.; Ossowska, K.; Kolarska, Z. *Tetrahedron* **2005**, *61*, 1933–1953.
18. Legros, J.; Bolm, C. *Chem. Eur. J.* **2005**, *11*, 1086–1092.
19. Kaczorowska, K.; Kolarska, Z.; Mitka, K.; Kowalski, P. *Tetrahedron* **2005**, *61*, 8315–8327.
20. Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628–3634.
21. Naruta, Y.; Tani, F.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1378–1380.
22. Naruta, Y.; Tani, F.; Maruyama, K. *Tetrahedron: Asymmetry* **1991**, *2*, 533–542.
23. Chiang, L. C.; Konishi, K.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1992**, 254–256.
24. Mashiko, T.; Kastner, M. E.; Spartalian, K.; Scheidt, R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6354–6362.
25. Pacheco, A.; James, B. R.; Rettig, S. J. *Inorg. Chem.* **1999**, *38*, 5579–5587.
26. Berkessel, A.; Kaiser, P.; Lex, J. *Chem. Eur. J.* **2003**, *9*, 4746–4756.
27. Scharbert, B.; Zeisberger, E.; Paulus, E. *J. Organomet. Chem.* **1995**, *493*, 143–147.
28. Zhang, R.; Yu, W. Y.; Wong, K. Y.; Che, C. M. *J. Org. Chem.* **2001**, *66*, 8145–8153.