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A novel polymeric chiral salen Mn(III) complex as solvent-regulated phase transfer catalyst in the asymmetric epoxidation of styrene

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Abstract

A novel solvent-regulated phase transfer catalyst of polymeric chiral salen Mn(III) complex with chiral diamine bridging was synthesized and its performance in the asymmetric epoxidation of styrene was investigated. In comparison with its low molecular weight counterpart of the homogeneous monomeric chiral salen Mn(III) complex, the polymeric chiral salen Mn(III) complex showed similar yield and enantioselectivity of the epoxide under the same reaction conditions. The effects of axial base, reaction temperature, and solvent on the catalytic performance of the polymeric chiral salen Mn(III) complex were investigated systematically. It was found that, under optimal reaction conditions, the yield of the epoxide and the enantioselectivity were as high as 98 and 47%, respectively. Furthermore, the polymeric chiral salen Mn(III) complex could be conveniently recovered for recycled use. Indeed the complex could be reused at least three times without significant losses of both activity and enantioselectivity.

Keywords: Salen Mn(III) complex; Styrene; Asymmetric epoxidation; Enantioselectivity

1. Introduction

Asymmetric epoxidation of unfunctional olefins catalyzed by chiral salen Mn(III) complexes has proved to be one of the most useful reaction in organic synthesis, as the epoxides obtained can be easily transformed into a large variety of compounds via highly region- and stereo-selective ring opening reactions [1] and direct oxygen transfer to the alkenes is the most common route to the preparation of epoxides [2]. Great success has been achieved for the asymmetric epoxidation using monomeric Jacobsen chiral salen Mn(III) complex as catalysts [3,4]. Such catalysts have chiral centers in the diamine bridge, eventually also with bulky chiral groups near the metal center, and therefore high catalytic activity and enantioselectivity could be obtained for a wide variety of olefins [5–8]. However, a major problem associated with the monomeric catalyst system is the separation and recycling of the expensive chiral catalyst. To address the issue, significant effort has been made to "heterogenize" the Jacobsen chiral salen Mn(III) complex, such as grafting monomeric catalyst systems onto mesoporous materials [9–11], non-covalent immobilization on zeolites [12,13], supporting on poly-system [14,15], dissolving in ionic liquids [16]. Unfortunately, although such modified catalysts show the advantages of easy separation and reuse, significant gaps exist in the scope of these methodologies. First, the leaching of salen Mn(III) complexes during reaction is often troublesome. Second, most of modified catalysts are less efficient than their corresponding unmodified catalysts, partly, because of the inaccessibility of the reagents to the active centers in the heterogeneous reaction [14]. Thus, the development of a novel class of catalyst with high activity, enantioselectivity and easily separation from the reaction mixture is highly desirable.

Recently, a number of reports have appeared describing efforts to polymerized monomeric salen Mn(III) as polymeric one [17,18]. These polymeric complexes with the increased number of active reaction sites showed higher activity and turnover frequency compared to their corresponding monomeric counterpart, more importantly, appropriately increased the

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molecular weight of the catalysts resulted from the polymerization lower their solubility in certain solvents, thus opening an opportunity for product isolation and catalyst recovery. Based on the concept of "one-phase catalysis and two-phase separation" [19], we herein reported on a novel polymeric chiral salen Mn(III) complex that can be used as highly effective solvent-regulated phase transfer catalyst in the asymmetric epoxidation of styrene. This polymeric salen Mn(III) complex derived from 1*R*,2*R*-(+)-1,2-diaminocyclohexane and 3-*t*-butyl-5-(chloro-methyl)-2-hydroxy benzaldehyde (3TBSCMB) and showed high catalytic activity (up to 99%) and enantioselectivity (up to 47%). Furthermore, the polymeric chiral salen Mn(III) complex could be conveniently recovered from the products by the control of solvent.

2. Experimental

2.1. Materials and methods

L(+)-Tartaric acid, 1,2-diaminocyclohexane, 3-chloroperoxybenzoic acid (*m*-CPBA), 4-methylmorpholine-*N*-oxide (NMO), and 4-phenylpyridine-*N*-oxide (4-PhPyNO) were purchased from Acros. Pyridine-*N*-oxide (PyNO), 2-*tert*-butylphenol, and 4-(3-phenylpropyl) pyridine-*N*-oxide (4-PPPyNO) were bought from Fluka, Alfa Aesar, and Aldrich, respectively. Other commercially available chemicals were laboratory grade reagents from local suppliers. All the chemicals were used as received.

FT-IR and diffuse reflectance UV–vis spectra of samples were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer and a HITACHI U-3310 spectrophotometer equipped with a diffuse reflectance attachment, respectively. ^{1}H NMR spectra of samples were recorded on a Varian-400 spectrometer. The molecular weight was measured by Ubbelohde viscosimeter. The optical rotation of catalysts was measured in dichloromethane on a WZZ-2A Automatic Polarimeter. Mn ion content was measured by complexiметry with ethylenediamine tetraacetic acid (EDTA) according to Ref. [20]. The enantiomeric excess (ee) for styrene oxide and analysis of the product epoxide were determined by a Agilent Technologies 6890 gas chromatograph equipped with a 19091G-B213 chiral capillary column (30 m × 0.32 mm × 0.25 um), and a flame ionization detector (FID). Nitrogen was used as carrier gas with a flow rate of 14 mL/min and the injection port temperature and column temperature were kept at 250 and 100 °C, respectively. Synthetic standard of the product was used to determine yields by comparison of peak height and area.

2.2. Preparation of the monomeric salen Mn(III) complex

For comparison purpose, the monomeric Jacobsen chiral complex **1** and monomeric non-chiral complex **2** (see Scheme 1) were synthesized according to the method outlined in the previous report [21].

2.3. Synthesis of polymeric chiral salen Mn(III) complex (*3*)

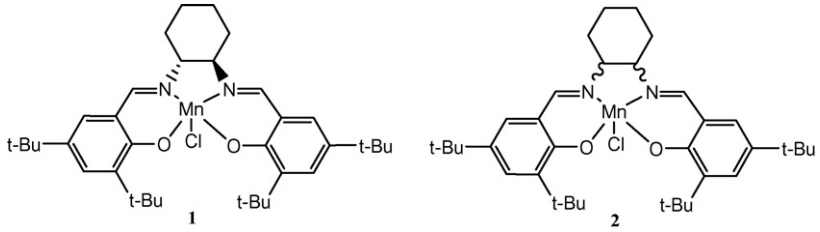
The synthesis of polymeric chiral Mn(III) complex **3** and the corresponding intermediates were shown in Scheme 2.

2.3.1. Synthesis of 3-tert-butyl-2-hydroxybenzaldehyde (*4*)

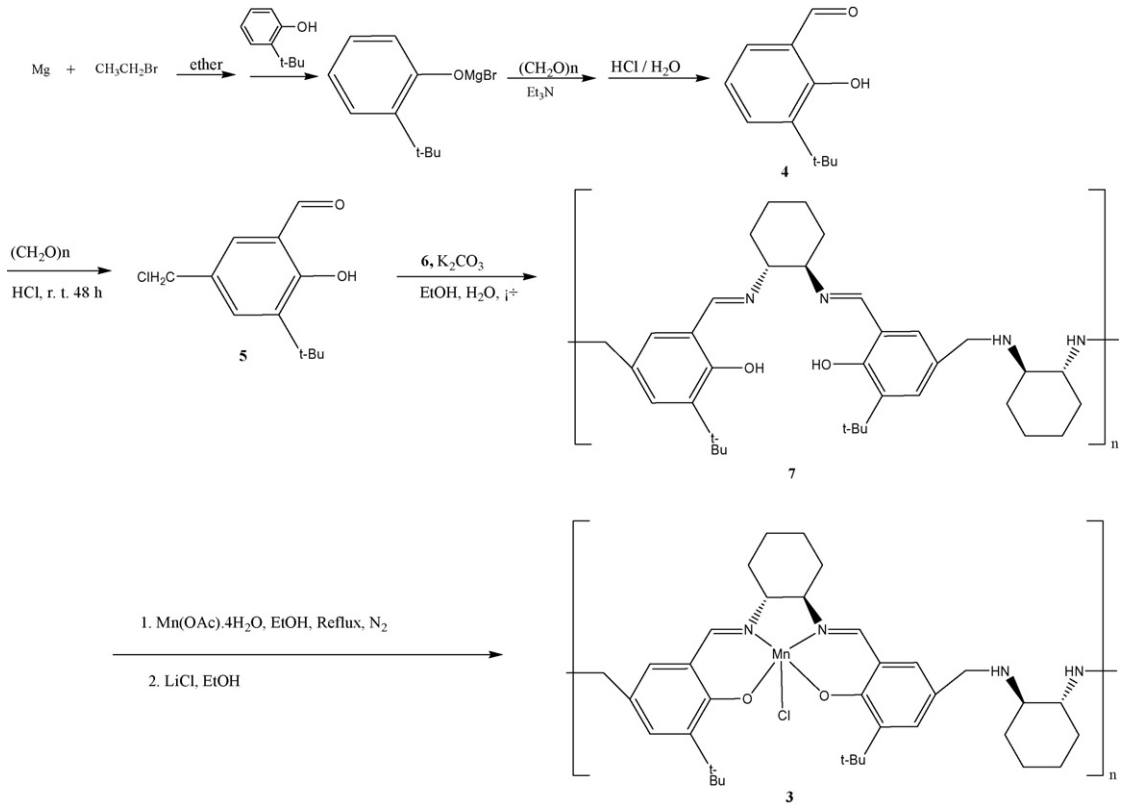
The compound of **4** was prepared using a modified procedure reported in the literature [22]. About 6 mL of ethylbromide was drop-wise added to 20 mL of ether (dried by zeolite A) containing 1.6 g of magnesium within 1 h. The mixture obtained was heated to reflux until the complete conversion of magnesium achieved, and then cooled to ambient temperature. The 10 g of 2-*tert*-butylphenol dissolved in 27 mL of tetrahydrofuran was slowly added into the above mixture with stirring at ambient temperature and a white precipitate was formed, followed by the addition of 134 mL of benzene. After removal of ether and a majority of tetrahydrofuran by distillation, another 34 mL of benzene was added. Then 10 g of triethylamine and 15 g of paraformaldehyde were added into the above mixture with stirring at 100 °C for 3 h. After cooling, the mixture obtained was acidified with 334 mL of 10 wt.% HCl and separated by a separatory funnel. The aqueous phase was extracted with petroleum ether for several times and the combined extract was washed with 50 mL of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. After the evaporation of volatile solvents, the residue was purified by silica gel column chromatography using a mixed solvent of petroleum ether and ethyl acetate (15:1, v/v) as eluent to give 3-*tert*-butyl-2-hydroxybenzaldehyde (10.1 g, 85%). ^{1}H NMR ($CDC1_3$, 400 MHz): δ (ppm) 1.43 (s, 9 H), 6.89–7.91 (m, 3 H), 9.91 (s, 1 H), 11.88 (s, 1 H); FT-IR (KBr): 3530, 3060, 2998, 2958, 2912, 2871, 1650, 1609, 1584, 1502, 1483, 1442, 1391, 1362, 1331, 1294, 1266, 1248, 1224, 1197, 1088, 1028, 931, 853, 796, 750, 679, 543, 495 cm^{-1}.

2.3.2. Synthesis of 3-tert-butyl-5-(chloro-methyl)-2-hydroxybenzaldehyde (3TBSCMB) (*5*)

3TBSCMB was synthesized from 3-*tert*-butyl-2-hydroxybenzaldehyde by chloromethylation, which was reported in Ref. [23]. The 7.24 g of 3-*tert*-butyl-2-hydroxybenzaldehyde was



Scheme 1. The monomeric Jacobsen chiral salen Mn(III) complex **1** and non-chiral salen Mn(III) complex **2**.



Scheme 2. Synthesis of the polymeric chiral salen Mn(III) complex **3** ($n = \sim 14$).

treated with 2.7 g of paraformaldehyde in 27 mL of 36 wt.% HCl at ambient temperature. After stirring for 48 h, the product was repeatedly extracted with ether. The combined organic phase was washed with saturated aqueous sodium bicarbonate and brine until it became neutral, and then dried over anhydrous magnesium sulfate. Rotation evaporation of the solvent led to 3TBSCMB as the viscous oil (8.4 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.43 (s, 9 H), 4.58 (s, 2H), 7.43 (d, 1H), 7.52 (d, 1H), 9.86 (s, 1H), 11.85 (s, 1H); FT-IR (KBr): 3528, 2958, 2909, 2870, 1650, 1613, 1476, 1433, 1391, 1362, 1260, 1230, 1209, 1182, 974, 771, 691 cm^{-1}.

2.3.3. Synthesis of polymeric chiral Schiff-base ligand (7)

The 1.7 g of (*R*, *R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt **6**, prepared from a technical-grade *cis–trans* mixture according to the reported method [21], 1.78 g of potassium carbonate, and 100 mL of ethanol–water (5:1, v/v) were added to a 250 mL three-necked flash equipped with an additional funnel and a reflux condenser. The obtained clouding mixture was vigorously stirred under nitrogen protection and heated to reflux (80 °C) until dissolution was achieved. Then 30 mL of ethanol–dichloromethane (10:1, v/v) containing 1.4 g of 3TBSCMB was drop-wise added into the above mixture with the funnel within 45 min. Additional 5 mL of ethanol was employed to rinse the funnel in order to confirm all 3TBSCMB presented here participated in the reaction. After stirring for another 6 h, the resulted slurry was cooled in ice-water bath over 3 h. After collected by vacuum filtration and washed with hexane to remove some small molecule substance, the crude product was recrystallized with ethanol to obtain the pure polymeric chiral Schiff-base ligand (1.65 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.43 (s, 18H), 1.89 (m, 16H), 2.67 (m, 2H), 3.56 (bs, 4H), 3.74 (s, 2H), 4.63 (m, 2H), 6.95 (d, 2H), 7.18 (d, 2H), 8.31 (s, 2H), 13.83 (bs, 2H); FT-IR (KBr): 3396, 2952, 2906, 2865, 1633, 1506, 1472, 1435, 1391, 1360, 1255, 1226, 1095, 930, 880, 790, 756 cm^{-1}.

2.3.4. Synthesis of polymeric chiral salen Mn(III) complex (3)

Under nitrogen protection and stirring, 1.42 g of manganese acetate dissolved in 15 mL of ethanol was drop-wise added into a solution containing 1.61 g of compound **7** and 25 mL of ethanol at 50 °C. After vigorously stirring for 1 h and then heated to reflux (80 °C) for additional 5 h, the reaction mixture was cooled to ambient temperature, followed by the addition of a solution containing 0.74 g of lithium chloride and 15 mL ethanol under stirring for 3 h. After bubbled with a gentle stream of air for 2 h, the above mixture was exposed to air overnight. The resulting slurry was cooled to 5 °C for 2 h, and then washed with 50 mL of brine. Under reduced pressure, the product was collected and dried in vacuum, yielding brown powder of polymeric chiral salen Mn(III) complex **3** (1.78 g, 92%). FT-IR (KBr): 3392, 2949, 2898, 2865, 1614, 1591, 1543, 1437, 1389, 1341, 1308, 1265, 1236, 1202, 1145, 1091, 871, 831, 754, 659, 572, 478, 414 cm^{-1}; UV–vis ($BaSO_4$): 505, 433, 327, 244 nm; $[\alpha]_D^{15} = +363$ (C = 0.04, CH_2Cl_2). The

polymeric chiral salen Mn(III) complex **3** is miscible with dichloromethane, slightly soluble in acetonitrile and immiscible in hexane.

2.4. Enantioselective epoxidation of styrene

Enatioselective epoxidation reactions were typically performed according to the established procedure [24]. A solution of 0.02 mmol of the selected catalyst in 1 mL of dichloromethane was treated with 0.5 mmol of styrene and a varied axial base including pyridine-*N*-oxide (PyNO), *N*-methylmorpholine-*N*-oxide (NMO), 4-phenylpyridine-*N*-oxide (4-PPNO), or 4-(3-phenyl-propyl)pyridine-*N*-oxide (4-PPPyNO). The mixture was pre-cooled to the indicated temperature, and the desirable amount of *m*-CPBA was added in five equal portions over 5 min periods. GC was employed to monitor the progress of the epoxidation reaction. After the completion of the reaction, the catalyst was precipitated out from the reaction system by the addition of hexane and subsequently used without further purification.

3. Results and discussion

3.1. Characterizations of the catalysts

The synthesized the polymeric chiral salen Mn(III) complex **3**, as well as the monomeric Jacobsen chiral complex **1** for comparison, was characterized by IR and UV–vis. As shown in Fig. 1, the main characteristic bands in the IR spectra of the polymeric chiral complex **3** were similar to the monomeric Jacobsen chiral complex **1**. Both the samples **1** and **3** showed the same band at 1614 cm^{-1} attributed to the vibration of imine group, suggesting that the two complexes have the similar structure of salen Mn(III) complex for catalytic epoxidation of alkene. In addition, an additional band around 3390 cm^{-1} was observed for the sample **3**, which is assigned to the stretching vibration of N–H groups [25]. The formation of N–H group comes from the reaction between chloromethane group (–CH_2Cl) and diamine group (–NH_2) in the 5- and 5′-positions (see Scheme 2). The presence of intact catalytic active centers of the monomeric and polymeric chiral salen Mn(III) complex of **1** and **3** were further confirmed by UV–vis observation (see Fig. 2), which presented ligand-to-metal charge transfer band and metal-to-metal charge transfer band. These spectroscopic features agree with the data reported in the literature [26]. Mn ion content of the polymeric chiral complex **3** measured by compleximetry was 1.49 mmol/g, which was close to the theoretical value (1.54 mmol/g). Based on the above results, together with measured molecular weight of 9100, it can be concluded that the polymeric catalyst presented here consists of ca. 14 monomeric chiral Mn(III)-Schiff-base units.

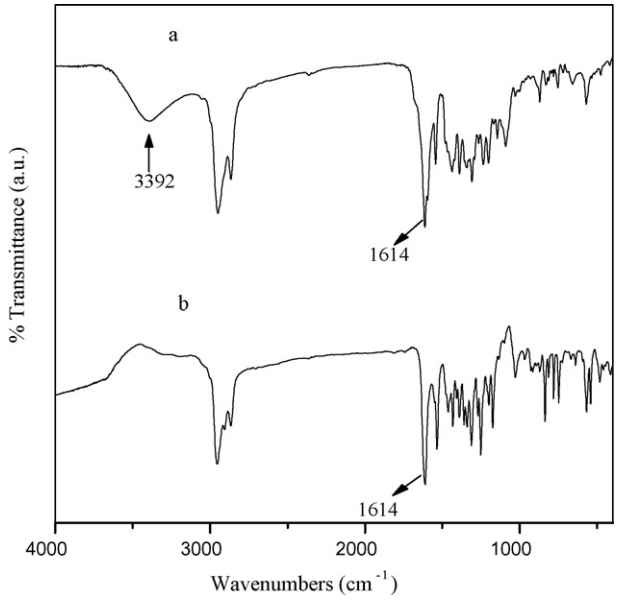


Fig. 1. FT-IR spectra of the polymeric chiral complex **3** (a) and the monomeric Jacobsen chiral complex **1** (b).

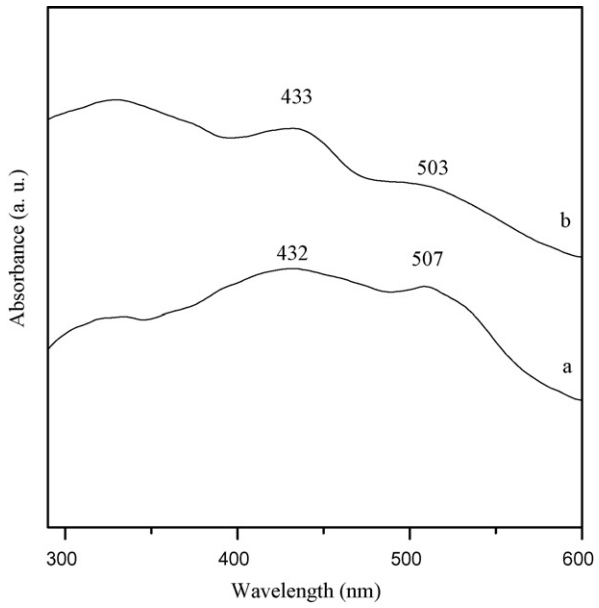


Fig. 2. UV–vis spectra of the monomeric Jacobsen chiral complex **1** (a) and the polymeric chiral complex **3** (b).

3.2. Comparison of the enantioselective epoxidation of styrene over different complexes

Under identical reaction conditions, the catalytic performances of the complexes **1**, **2** and **3** in the enantioselective epoxidation of styrene are listed in Table 1. When the complexes **1** and **3** with chiral active sites were used as catalysts, the epoxide with *R*-configuration was obtained (entries 1 and 3), whereas the employment of non-chiral complex of **2** led to the racemic epoxide (entry 2). Apparently, the absolute configuration of the epoxide obtained was controlled by the chirality in the diamine bridge of the complexes **1** and **3**. It is notable that the polymeric chiral catalyst **3** performed as a homogenous catalyst in the reaction system presented here, and showed the similar yield and enantioselectivity of the epoxide compared to the monomeric chiral complex **1** (entry 1 versus entry 3).

Table 1
The comparative results of the asymmetric epoxidation of styrene over the different salen Mn(III) complexes

Entry	Catalyst	Yield (%)[a]	ee (%)[b]	TOF ($\times 10^{-3}$ s^{-1})[c]	References
1	Monomeric complex **1**[d]	92	35[e]	3.19	This work
2	No chiral monomeric complex **2**[d]	94	0	3.26	This work
3	Polymeric chiral complex **3**[d]	>99	35[e]	3.44	This work
4	Polymeric chiral complex **3**[f]	98	43[e]	3.40	This work
5	MCM-48 supported chiral salen Mn(III) complex[g]	35	32[h]	1.62	[27]
6	MCM-41 supported chiral salen Mn(III) complex[i]	91	37[h]	0.70	[28]

[a] Yield of the isolated epoxide.
[b] Determined by GC.
[c] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).
[d] Reaction conditions: catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), pyridine-*N*-oxide (1 mmol), *m*-CPBA (1 mmol). Reaction time and temperature are 2 h and 0 °C, respectively.
[e] Epoxide is *R*-configuration.
[f] Reaction conditions: catalyst (4% of styrene) with *m*-CPBA/NMO in CH_2Cl_2 at 0 °C for 2 h.
[g] Reaction conditions: catalyst (3% of styrene) with *m*-CPBA/NMO in CH_2Cl_2 at 0 °C for 2 h.
[h] Epoxide is *S*-configuration.
[i] Reaction conditions: catalyst (6% of styrene) with *m*-CPBA/NMO in CH_2Cl_2 at 0 °C for 6 h.

Furthermore, the catalytic performances at analogous reaction conditions over the polymeric chiral salen Mn(III) complex in this work were compared with that over the supported chiral salen Mn(III) complexes in the literatures [27,28], which were shown in Table 1 (entries 4–6). It is found that the catalytic activity (TOF) over mesoporous silica supported chiral salen Mn(III) complexes is lower than that over the polymeric chiral salen Mn(III) complexes in this work, which is due to the slow diffusion of the reactants to the active catalytic centers in the heterogeneous catalysts [14]. Also, MCM-48 supported the chiral salen Mn(III) catalyst showed only 32% of enantioselectivity (entry 5), which is lower than 43% of enantioselectivity in this work. Therefore, it can be easily understood that the polymeric chiral complex should be dissolve in dichloromethane with the reactants to become homogeneous and gives higher catalytic efficiency.

3.3. Influence of axial base on the enantioselective epoxidation of styrene

It is well known that the axial base acts as additional donor ligand by forming a strong bond with the transition meter center, which endows it with a dual role in activating the catalyst and stabilizing the oxo intermediate [29–31]. The effects of various axial bases, such as PyNO, NMO, 4-PhPyNO and 4-PPPyNO, as well as their different amounts on the asymmetric epoxidation of styrene in the presence of the polymeric chiral complex **3** were investigated and the results are listed in Table 2. As expected,

Table 2
The results of the asymmetric epoxidation of styrene catalyzed by the complex **3** using different axial base[a]

Entry	Axial base	Content of axial base (mmol)	Yield (%)[b]	ee (%)[c]	TOF ($\times 10^{-3}$ s^{-1})[d]
1	–	0	54	0	1.87
2	NMO	0.5	58	18	2.01
3	NMO	1.0	74	31	2.56
4	NMO	1.5	83	40	2.87
5	NMO	2.0	98	43	3.40
6	NMO	2.5	89	43	3.08
7	PyNO	0.5	96	30	3.32
8	PyNO	1.0	>99	35	3.44
9	PyNO	1.5	97	35	3.36
10	PyNO	2.0	95	35	3.30
11	PyNO	2.5	92	35	3.19
12	4-PhPyNO	1.0[e]	95	36	3.29
13	4-PPPyNO	1.0[e]	95	35	3.29

[a] Same as in Table 1 exception of the axial base of pyridine-*N*-oxide (1 mmol).
[b] Yield of the isolated epoxide.
[c] Determined by GC.
[d] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).
[e] The optimum amount.

Table 3
The results of the asymmetric epoxidation of styrene catalyzed by the complex **3** at different temperature for 2 h[a]

Entry	Axial base (mmol)	Temperature (°C)	Yield (%)[b]	ee (%)[c]	TOF ($\times 10^{-3}$ s^{-1})[d]
1	PyNO (1)	40	46	24	1.60
2		17	94	33	3.27
3		0	>99	35	3.44
4		−16	>99	39	3.44
5	NMO (2)	0	98	43	3.40
6		−16	98	47	3.40
7	4-PhPyNO (1)	0	95	36	3.29
8		−16	95	40	3.29
9	4-PPPyNO (1)	0	95	35	3.29
10		−16	95	38	3.29

[a] Reaction conditions: catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), *m*-CPBA (1 mmol).
[b] Yield of the isolated epoxide.
[c] Determined by GC.
[d] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).

a rather low yield of the epoxide without any enantioselectivity was obtained in the absence of the additive axial base (entry 1), whereas the addition of axial base led to the increase of the yield and enantioselectivity of the epoxide (entries 2–13), suggesting that the presence of axial base is essential to the asymmetric epoxidation of styrene. Moreover, the enantioselectivity to the epoxide with *R*-configuration was influenced by the kinds of the axial bases added. The axial base of NMO gave the highest enantioselectivity when the added amount reached 2 mmol (entry 5) due to the big steric hindrance on the N atom. Also, the amount of various axial bases had a crucial influence on the yield and enantioselectivity of the epoxide. In general, with an increase amount of the axial base, the yield of the epoxide passed through a maximum and then decreases and the enantioselectivity increased to a constant (entries 2–6 and 7–11). The maximum yield and enantioselectivity of target product was obtained when the amount of PyNO, 4-PhPyNO or 4-PPPyNO was 1 mmol in the reaction system presented here (entries 8, 12 and 13). However, in the case of NMO possessing the biggish steric hindrance on the N atom, the optimum amount was 2 mmol (entry 5). An excess of axial base would lower the activity of the catalyst, thus resulting in a decrease of the yield of target product, but it did not affect the enantioselectivity.

3.4. Influence of reaction temperature on the enantioselective epoxidation of styrene

The effect of reaction temperature on the epoxidation reaction over the polymeric chiral complex **3** and PyNO, NMO, 4-PhPyNO or 4-PPPyNO as axial base is shown in Table 3. A decrease of reaction temperature from 40 to 0 °C led to the increase of the epoxide yield from 46 to >99%. However, an increase of enantioselectivity without the change of the yield of epoxide was observed with further decreasing reaction temperature from 0 to −16 °C, which was similar to the results reported previously [18,32]. The reason should be due to both an increase in enantiofacial selectivity in the initial C–O bond forming step, as well as suppression of the trans pathway in the second step at low temperature [33]. It should be noted that an enantioselectivity as high as 47% could be obtained when the reaction performed at −16 °C using the complex **3** as a catalyst and NMO as an axial base (entry 6).

Table 4
The results of the asymmetric epoxidation of styrene catalyzed by the complex **3** in different solvent[a]

Entry	Solvent	Yield (%)[b]	ee (%)[c]	TOF ($\times 10^{-3}$ s^{-1})[d]
1	Dichloromethane	>99	35	3.44
2	Acetone	91	30	3.16
3	Acetonitrile	83	21	2.88

[a] Reaction conditions: catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), pyridine-*N*-oxide (1 mmol), *m*-CPBA (1 mmol). Reaction time and temperature are 2 h and 0 °C, respectively.
[b] Yield of the isolated epoxide.
[c] Determined by GC.
[d] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).

3.5. Influence of solvent on the enantioselective epoxidation of styrene

Table 4 summarizes the results of a comparative study of the enantioselective epoxidation of styrene over the polymeric chiral salen Mn(III) complex **3** and axial base of PyNO in the solvent of dichloromethane, acetone, and acetonitrile, respectively. It was found that dichloromethane was the optimal solvent for the reaction (entry 1), whereas acetonitrile appeared to be unsuitable for the enantioselective epoxidation of styrene presented here (entry 4). The difference among these solvents should be that the polymeric chiral salen Mn(III) complex **3** is more readily dissolvable in dichloromethane than in acetonitrile. Also, *m*-CPBA used as an oxidant is active to give the products of the racemate with no enantioselectivity. Indeed, as reported in the reference of [34], *m*-CPBA was capable of inducing the epoxidation of styrene in the absence of catalyst, giving poor yield of racemic epoxide in the reaction presented here. In the case of acetonitrile in which complex **3** could not well dissolve, the oxidant of *m*-CPBA plays an important role in the epoxidation of styrene, i.e., a part of the obtained epoxide exclusively originated from the oxidation process of *m*-CPBA, leading to low

Table 5
The results of reuse of the complex **3** in the asymmetric epoxidation of styrene[a]

Run	Time (h)	Yield (%)[b]	ee (%)[c]	TOF ($\times 10^{-3}$ s^{-1})[d]
1	2	>99	35	3.44
2	2	97	35	3.37
3	2	94	33	3.26
4	2	64	29	2.22
5	2	52	24	1.80

[a] Reaction conditions: catalyst (4% in 1 mL CH_2Cl_2), styrene (0.5 mmol), pyridine-*N*-oxide (1 mmol), *m*-CPBA (1 mmol). Reaction time and temperature are 2 h and 0 °C, respectively.
[b] Yield of the isolated epoxide.
[c] Determined by GC.
[d] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).

yield of the epoxide and enantioselectivity. In contrast, the complex **3** could dissolve in dichloromethane completely, therefore, resulting in high yield and enantioselectivity.

*3.6. Recycling of the polymeric chiral catalyst **3** in the enantioselective epoxidation of styrene*

Based on the solubility of the polymeric chiral complex **3** mentioned in the experimental section, the solvent-regulated phase transfer catalyst of the complex **3** should be easily recovered by using hexanes from the concentrated reaction mixture and then dissolved in dichloromethane again for successive reaction. The results of the recovered polymeric chiral complex **3** after five recycling are listed in Table 5. Obviously, reuse of the complex **3** for three times decreased slightly in both the yield and the enantioselectivity. However, after recycled for three times, any further attempt to recover the complex **3** always gave poor yield and enantioselectivity. As can be seen from Table 5, the significant decrease in both the yield and the enantioselectivity was observed in fourth and fifth runs. We also suspected that the polymeric chiral salen Mn(III) complex could be decomposed in presence of the oxidant [17,35], which was characterized by UV–vis spectra. Fig. 3 displays the UV–vis spectra of the fresh and the used polymeric chiral salen Mn(III) complex **3** after three times. It is clearly observed that the characteristic bands of catalytic active sites of salen Mn(III) complex at 433 and 503 nm^{-1} disappeared after the complex used three times, and therefore resulted in decrease of the activity and the enantioselectivity for the fourth and fifth runs.

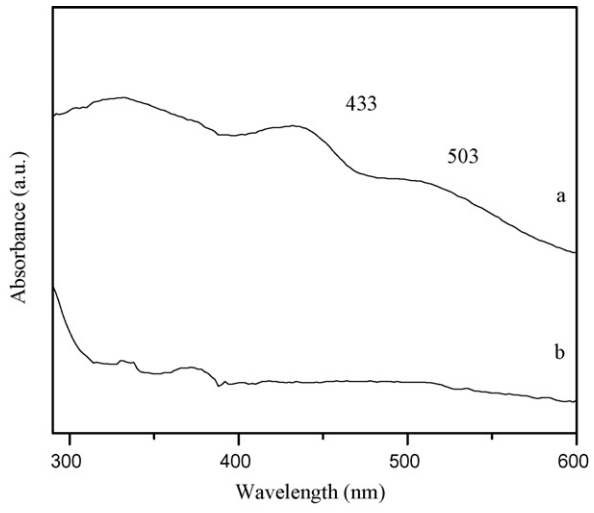


Fig. 3. UV–vis spectra of the fresh complex **3** (a) and the used complex **3** for three times (b).

4. Conclusion

The work herein presented the application of a novel polymeric chiral salen Mn(III) complex in the asymmetric epoxidation of styrene. The polymeric complex acted as a solvent-regulated phase transfer catalyst under the given reaction conditions. Compared with the homogeneous monomeric chiral salen Mn(III) complex, it showed the similar yield and enantioselectivity of the epoxide. Moreover, the polymeric chiral salen Mn(III) complex could be conveniently recovered and be repeatedly used at least three times without losses of both activity and enantioselectivity. These observations suggested that the polymeric complex presented here is a promising chiral catalyst for the enantioselective epoxidation of unfunctional olefins. The use of this solvent-regulated phase transfer catalyst of polymeric chiral salen Mn(III) complex in enantioselective epoxidation of other unfunctional olefins was in progress.

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