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Easily recyclable polymeric ionic liquid-functionalized chiral salen Mn(III) complex for enantioselective epoxidation of styrene

Rong Tan [a], Donghong Yin [a,b,*], Ningya Yu [a,*], Haihong Zhao [a], Dulin Yin [a]

[a] Institute of Fine Catalysis and Synthesis, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, Hunan, China

[b] Technology Center, China Tobacco Hunan Industrial Corporation, No. 426 Laodong Road, Changsha, Hunan, 410014, China

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ABSTRACT

A polymeric ionic liquid (IL)-functionalized chiral salen ligand (PICL) was synthesized by covalent polymerization between amino ($-NH_2$) group of 1,3-dipropylamineimidazolium bromide with chloromethyl ($-CH_2Cl$) group at two sides of 5,5′ positions in the typical chiral salen ligand. Treatment of the synthesized PICL with $Mn(OAc)_2{\cdot}4H_2O$ and LiCl under aerobic oxidation yielded the corresponding polymeric IL-functionalized chiral salen Mn(III) complex (PICC). The typical IR bands at 1613, 1540, 570, and 412 cm^{-1}, as well as the maximum UV–vis absorbed peaks around 433 nm of the PICC were proposed as characteristics of the monomeric salen Mn(III) complex. The PICC was used as a catalyst in the enantioselective epoxidation of styrene. Comparable catalytic activity and enantioselectivity relative to the monomeric chiral salen Mn(III) complex were observed. Furthermore, recovery of the polymeric catalyst was readily accomplished by simple precipitation in *n*-hexane, and subsequently reused (10 times) without significant loss of reactivity and enantioselectivity.

1. Introduction

Asymmetric epoxidation of prochiral alkenes presents a powerful strategy for the synthesis of enantiomerically enriched epoxides. Chiral salen Mn(III) complexes are recognized as one of the most effective and selective catalysts for enantioselective epoxidation of unfunctionalized olefins since the first chiral C_2-asymmetric salen-type complex synthesized by Zhang et al. in the 1990s [1]. With bulky chiral groups near the metal center, such catalysts give high catalytic activity and enantioselectivity (ee) for a wide variety of unfunctionalized alkenes [2,3]. However, the homogeneous chiral salen Mn(III) catalysts are difficult to recover and recycle. An approach for overcoming this difficulty is to immobilize the chiral complex on some supports; thereby creating heterogeneous chiral catalysts that can be readily recovered from reaction mixtures. Many attempts were made to develop supported Mn(III) salen complexes using organic polymer [4], polymeric membrane [5] encapsulation in zeolite [6,7] and inorganic supports [8–14] so as to minimize the degradation of the catalysts, allowing easy recovery and reusability of the catalyst for a number of cycles. Unfortunately, comparing with the homogeneous counterparts, some of the immobilized complexes often suffer from various disadvantages even easy recovery, such as poor activity, leaching of the active species into the reaction medium, and low accessibility of substrates. Therefore, for industrial practical merit and academic interest of homogeneously catalyzed reactions, the development of an efficient strategy for catalyst recovery is still challenging. Cavazzini et al. [15] reported that sterically hindered chiral salen Mn(III) complexes bearing long perfluoroalkyl substituents showed similar ee and yield of epoxides compared with standard homogeneous salen Mn(III) complexes. The advantage was that the catalysts could be readily recovered from the fluorous layer by simple phase separation techniques at room temperature. However, the toxic compounds which derived from the decomposition of fluorous solvents and fluorous derivatives at high temperature are often unfriendly to environment. Recently, we had reported a polymeric chiral salen Mn(III) complex acting as solvent-regulated phase transfer catalyst in the asymmetric epoxidation of styrene, which can be performed in “one-phase catalysis and two-phase separation” by changing solvent [16]. The complex showed dual advantages of facile separation and high catalytic efficiencies relative to the corresponding homogeneous chiral salen Mn(III) complex.

Room temperature ionic liquids (RTILs) have recently attracted considerable interests as important solvent in the synthesis and catalysis owing to their unique solvent power for many organic and

* Corresponding authors at: Institute of Fine Catalysis and Synthesis, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education), Hunan Normal University, Changsha 410081, Hunan, China. Fax: +86 731 8872531.

E-mail addresses: yindh@hunnu.edu.cn (D. Yin), yuningya@yahoo.com.cn (N. Yu).

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inorganic substances [17,18]. With the attractive feature of tunable miscibility, many efforts have been made to use RTILs as phase tags to facilitate recycling and reuse of the catalysts [19], especially, using biphasic reaction systems containing RTILs [20]. Song and Roh reported that the chiral salen Mn(III) epoxidation catalyst immobilized in 1-butyl-3-methylimidazolium hexafluorophosphate offered comparable enantioselectivity as well as increased activity in the asymmetric epoxidation of olefins than that obtained without employment of RTILs [21], probably due to the positive influence of the polarity of the RTILs on the stabilization of the transition state [13]. However, the high viscosity of RTILs often limits mass transfer in the fast chemical reaction. Moreover, some catalysts even in trace quantities are often extracted during the recovery from the reaction system, causing contamination of the reaction products and resulting in decrease of catalytic activity. Some attempts were dedicated to minimize the disadvantages by supporting RTILs phases to immobilize homogeneous catalysts [22–25]. The supported RTILs catalyst combines the advantages of RTILs and heterogeneous supports. Active species in the RTILs phase acted as a homogeneous catalyst. For example, Lou et al. [23] developed an effective method based on supported RTILs system to immobilize chiral Mn(III) salen complexes, which exhibited excellent activity and enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins. The immobilized catalysts were stable and could be recycled three times without loss of activities. Lately, we have found that anchoring RTILs moiety onto chiral salen Mn(III) complex could make the catalysts recoverable by change of solvent [26]. This method can also provide an ideal way for combining the advantages of homogeneous catalysts and reusability.

Herein, we described a successful synthesis of a PICL by covalent polymerization between amino ($-NH_2$) group of 1,3-dipropylamineimidazolium bromide with chloromethyl ($-CH_2Cl$) group at two sides of 5,5′ positions in the salen ligand of (*R*,*R*)-{*N*-(3-*tert*-butyl-5-chloromethyl-salicylidine)-*N*′-(3′-*tert*-butyl-5′-chloromethyl-salicylidine)}-1,2-cyclohexanediamine. One of the most appealing features of the obtained polymeric complex was that the ordered distribution of chiral catalytic sites for the single dimension polymer matrix offered unique microenvironments for the reactions, thus, might lead to an enhanced activity. It is expected that high activity and comparable enantioselectivity can be obtained over the PICC for the asymmetric epoxidation of styrene because of its special 'ionophilicity' and the positive effect of the polarity of the IL moiety on the stabilization of the transition state. Also, the PICC with larger molecular weight is miscible with dichloromethane and insoluble in *n*-hexane. It therefore will work under homogeneous conditions during the reaction stage but will be precipitated at the end of the reaction by simple addition of *n*-hexane extraction resulting in facile separation and reuse.

2. Experimental

2.1. Materials

L-(+)-Tartaric acid, 1,2-diaminocyclohexane, meta-chloroperoxybenzoic acid (*m*-CPBA), 3-bromopropylamine, 4-methylmorpholine N-oxide (NMO), and 4-phenylpyridine N-oxide (4-PhPyNO) were purchased from Acros. Pyridine N-oxide (PyNO) was bought from Fluka. 2-*tert*-Butyl phenol and 4-(3-phenylpropyl) pyridine N-oxide (4-PPPyNO) were obtained from Alfa Aesar and Aldrich, respectively. Other commercially available chemicals were laboratory grade reagents from local suppliers. All solvents were purified by standard procedures before being used. (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt, 3-*tert*-butyl-2-hydroxybenzaldehyde, and 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde were prepared according to the procedures described in [27–29], respectively.

2.2. Characterization methods

FT-IR spectra were obtained as potassium bromide pellets with a resolution of 4 cm^{-1} and 32 scans in the range 400–4000 cm^{-1} using an AVATAR 370 Thermo Nicolet spectrophotometer. The ultraviolet–visible light (UV–vis) spectra were recorded on a UV–vis Agilent 8453 spectrophotometer. The solution of samples in dichloromethane (ca. 1.0 mM) was poured into a 1 cm quartz cell for UV–vis adsorption with dichloromethane as the reference. ^1H NMR spectra of samples were recorded with a Varian-400 spectrometer using tetramethylsilane (TMS) as internal reference. Thermogravimetric and differential thermogravimetric (TG-DTG) curves were obtained on a NETZSCH STA 449C thermal analyzer. Samples were heated from room temperature up to 800 °C under flowing air using alumina sample holders. The sample weight was ca. 10 mg and the heating rate was 10 K/min. A reference sample holder contained alumina. Elemental analyses of C, H and N were carried out on Vario EL III Elemental analyses made in Germany. The optical rotation of catalysts was measured in dichloromethane on a WZZ-2A Automatic Polarimeter. Mn ion content was measured by the method of complexiметry with ethylenediamine tetraacetic acid (EDTA) according to [30]. The molecular weight was measured by Ubbelohde viscosimeter. The ee value for styrene epoxide and analysis of the product were determined by an Agilent Technologies 6890N gas chromatography equipped with 19091G-B213 chiral capillary column (30 m × 0.32 mm × 0.25 um) and flame ionization detector (FID).

2.3. Preparation of the polymeric IL-functionalized chiral salen Mn(III) complex (**PICC**)

The preparation of the **PICC** was outlined in Scheme 1.

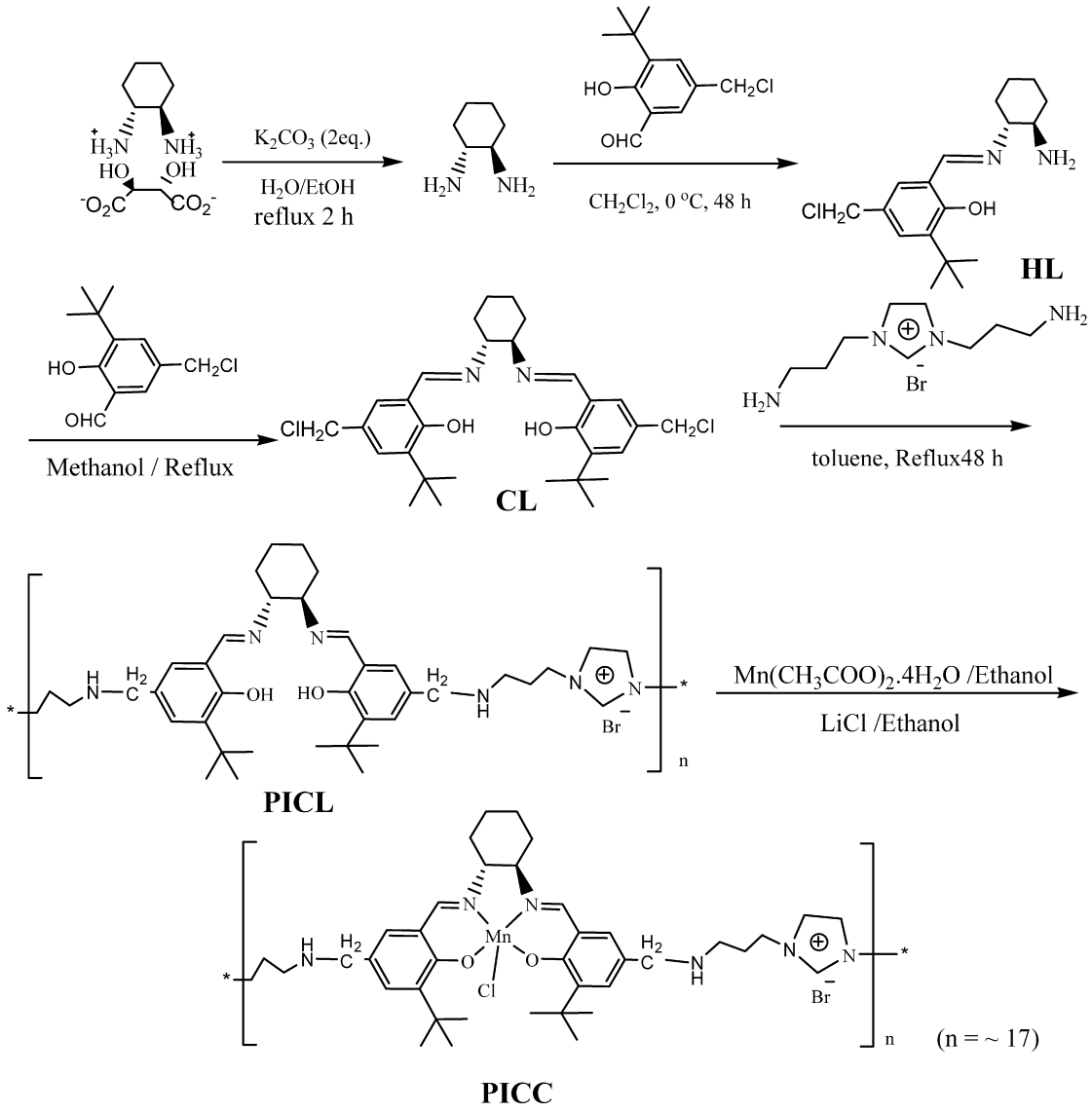
2.3.1. Synthesis of 1,3-dipropylamineimidazolium bromide (**IL**)

1,3-Dipropylamineimidazolium bromide was synthesized according to the modified procedure described in [31], which was outlined in Scheme 2.

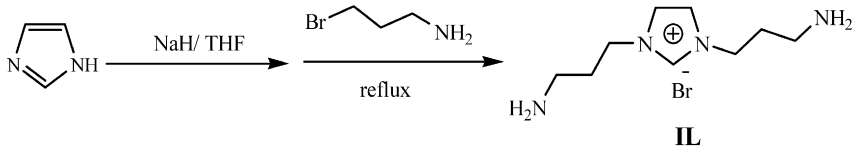
95% Sodium hydride powder (10.0 mmol) dissolved in tetrahydrofuran (8 ml) was cooled in an ice bath, followed by dropwise addition of a solution of imidazole (10.0 mmol) in tetrahydrofuran (8 ml). The ice bath was removed and the resulting mixture was stirred for 2 h at room temperature. Then 3-bromopropylamine (20.0 mmol) dissolved in tetrahydrofuran (25 ml) was slowly added at room temperature. The mixture was stirred under reflux for another 7 h. The lower IL layer was thoroughly rinsed with tetrahydrofuran and dried in vacuum to give a pale yellow viscous liquid of 1,3-dipropylamineimidazolium bromide (**IL**) (2.1 g, yield of 78%). **IL**: ^1H NMR ($CDC1_3$, 400 MHz): δ ppm 8.70 (s, 1 H, ring NCHN), 7.48 (m, 2 H, ring NCH), 4.30 (t, 4 H, CH_2–N_{ring}, J = 6.6 Hz), 4.18 (m, 4 H, CH_2), 2.72 (t, 4 H, CH_2–N_{amine}, J = 6.6 Hz), 2.51 (m, 4 H, NH_2). FT-IR (KBr): 3426, 2977, 2643, 2013, 1600, 1580, 1491, 1462, 1285, 1168, 1085, 1047, 996, 957, 900, 862, 762, 621 cm^{-1}.

2.3.2. Synthesis of chiral half-unit of ligand (**HL**)

(*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (11.2 mmol) was treated with potassium carbonate (22.5 mmol) in ethanol-distilled water (20 mL, ethanol:H_2O = 4:1 (v/v)) under vigorously stirring. The resulted cloudy mixture was stirred for another 2 h under reflux. The liberated diamine was extracted with chloroform (4 × 5 mL), and then 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde (11.2 mmol) in chloroform (20 mL) was



Scheme 1. Synthesis of the PICC.

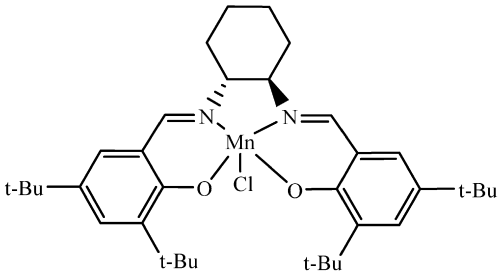


Scheme 2. Synthesis of 1,3-dipropylamineimidazolium bromide (IL).

added dropwise to the solution of diamine at 0 °C. The resulted mixture was stirred under reflux for 48 h. Upon filtration, a precipitate was collected and recrystallized from ethanol to get a pale-yellow powder of *N*-(3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde)-1-amino-2-cyclohexeneimine (**HL**) (3.23 g, yield of 89%). **HL**: Calc. for $C_{18}H_{27}ClN_2O$: C, 66.96; H, 8.43; N, 8.68%. Found: C, 66.89; H, 8.52; N, 8.57%. ^{1}H NMR ($CDC1_3$, 400 MHz): δ ppm 13.78 (s, 1 H, OH), 8.29 (s, 1 H, CH=N), 7.28 (d, 1 H, ArH, $J = 2.0$ Hz), 7.11 (d, 1 H, ArH, $J = 2.0$ Hz), 4.58 (s, 2 H, CH_2Cl), 3.32 (m, 1 H, C=NCH), 2.60 (m, 1 H, C=NCH), 2.21 (m, 2 H, NH_2), 2.05–1.44 (m, 8 H, cyclohexyl-H), 1.42 (s, 9 H, *t*-butyl-H). FT-IR (KBr): 3449, 2956, 2858, 1630, 1582, 1547, 1480, 1468, 1442, 1386, 1351, 1340, 1325, 1291, 1270, 1240, 1224, 1200, 1173, 1153, 1081, 1054, 1043, 942, 859, 823, 798, 717, 646 cm^{-1}.

*2.3.3. Synthesis of chiral salen ligand (**CL**)*

The above-obtained **HL** (8 mmol) dissolved in anhydrous ethanol (20 ml) was added dropwise to 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde (8 mmol) in anhydrous ethanol (20 ml) at room temperature. The mixture was heated to 60 °C for 8 h under stirring, and then cooled in ice-water bath over 3 h. The resulted solid was filtered and recrystallized from ethanol to give a pale-yellow powder of (*R*,*R*)-{*N*-(3-*tert*-butyl-5-chloromethyl-salicylidine)-*N*′-(3′-*tert*-butyl-5′-chloromethyl-salicylidine)}-1,2-cyclohexanediamine (**CL**) (3.38 g, yield of 82%). **CL**: Calc. for $C_{30}H_{40}Cl_2N_2O_2$: C, 67.79; H, 7.58; N, 5.27%. Found: C, 67.71; H, 7.69; N, 5.32%. ^{1}H NMR ($CDC1_3$, 400 MHz): δ ppm 13.68 (s, 2 H, OH), 8.42 (s, 2 H, CH=N), 7.31 (d, 2 H, ArH, $J = 2.0$ Hz), 7.26 (d, 2 H, ArH, $J = 2.0$ Hz), 4.58 (s, 4 H, CH_2Cl), 3.55–3.30 (m, 2 H, C=NCH), 1.89–



Scheme 3. Structure of monomeric chiral salen Mn(III) complex.

1.44 (m, 8 H, cyclohexyl-H), 1.42 (s, 18 H, *t*-butyl). FT-IR (KBr): 3449, 2952, 2866, 1630, 1594, 1545, 1466, 1439, 1390, 1361, 1308, 1266, 1229, 1200, 1167, 1142, 1091, 1030, 974, 930, 871, 778, 753, 669 cm^{-1}.

*2.3.4. Synthesis of **PICL***

The obtained IL (5 mmol) was added to the synthesized CL (5 mmol) in dry toluene (15 mL), and then the mixture was refluxed for 48 h under nitrogen protection. After cooled to 5 °C overnight, the obtained **PICL** was collected by removal of toluene, and then washed completely with hexane several times, dried in vacuum to obtain a deep yellow solid of **PICL** (2.26 g, yield of 91%). **PICL**: Calc. for $(C_{39}H_{57}BrN_6O_2)_{17}$: C, 64.89; H, 7.96; N, 11.64%. Found: C, 64.54; H, 8.39; N, 11.63%. ^{1}H NMR ($CDC1_3$, 400 MHz): δ ppm 13.71 (s, 2 H, OH), 8.67 (s, 1 H, ring NCHN), 8.26 (s, 2 H, CH=N), 7.49 (m, 2 H, ring NCH), 7.39 (d, 2 H, ArH, $J = 2.2$ Hz), 7.23 (d, 2 H, ArH, $J = 2.2$ Hz), 4.31 (t, 4 H, CH_2–N_{ring}, $J = 7.1$ Hz), 4.15 (m, 4 H, CH_2), 3.97 (m, 4H, $ArCH_2N$), 3.55–3.30 (m, 2 H, C=NCH), 2.70 (t, 4 H, CH_2–N_{amine}, $J = 7.1$ Hz), 2.4 (s, 2 H, CNHC), 1.89–1.44 (m, 8 H, cyclohexyl-H), 1.32 (s, 18 H, *t*-butyl). FT-IR (KBr): 3434, 2962, 2864, 1630, 1592, 1468, 1439, 1391, 1361, 1307, 1270, 1252, 1240, 1202, 1173, 1135, 1085, 1037, 982, 939, 879, 862, 828, 804, 772, 715, 644, 621 cm^{-1}.

*2.3.5. Preparation of **PICC***

Under nitrogen protection and stirring at 50 °C, a solution of $Mn(OAc)_2{\cdot}4H_2O$ (8 mmol) in ethanol (15 ml) was added dropwise to the above-obtained **PICL** (4 mmol) in ethanol (15 ml). After refluxing for 5 h, the mixture was cooled to room temperature. Lithium chloride (24 mmol) in ethanol (10 ml) was added to the above mixture under stirring for 3 h. After bubbled with a gentle stream of air for another 2 h, the mixture was exposed to air overnight. The resulting slurry was cooled to 5 °C for 2 h, filtered and washed with 50 ml of water. The obtained solid was dried under vacuum at 40 °C to give a brown powder of **PICC** (2.85 g, yield of 85%). **PICC**: Calc. for $(C_{39}H_{55}BrClMnN_6O_2)_{17}$: C, 57.82; H, 6.84; N, 10.37%. Found: C, 57.53; H, 7.06; N, 10.39%. FT-IR (KBr): 3384, 2954, 2924, 2856, 1613, 1596, 1542, 1457, 1436, 1390, 1359, 1304, 1265, 1231, 1201, 1145, 1089, 1028, 1000, 926, 869, 797, 752, 699, 661, 621, 570, 412 cm^{-1}; UV–vis (CH_2Cl_2): 433, 326 nm; Mn ion content: 1.13 mmol/g (theoretical value: 1.19 mmol/g); $[\alpha]_D^{28} = +610$ (C = 0.04, CH_2Cl_2).

2.4. Preparation of the monomeric chiral salen Mn(III) complex

For comparison with the PICC, we also synthesized the monomeric chiral salen Mn(III) complex according to the previous report [27], which was outlined in Scheme 3.

2.5. Enantioselective epoxidation of styrene

Enantioselective epoxidation of styrene was typically performed according to the following procedure. Styrene (0.5 mmol) and a desirable amount of donor ligand were added into dichloromethane (1 mL) containing 4% of the catalyst (based on monomeric unit of the PICC) under stirring. The mixture was pre-cooled to the indicated temperature, and then *m*-CPBA (1 mmol) was added in 4 equal portions at interval of 15 min in a reaction period. Gas chromatograph was employed to monitor the progress of the epoxidation reaction. After completion of the reaction, hexane was added to extract the reaction product. The catalyst was separated from the reaction system as precipitate and subsequently used without further purification. The supernatants separated from the reaction system were concentrated, and further purification of the extractive by flash column chromatography afforded the pure styrene epoxides. The reaction products were analyzed by Agilent Technologies 6890N gas chromatography (FID, 19091G-B213 chiral capillary column (30 m × 0.32 mm × 0.25 um)) using nitrogen as a carrier gas with flow rate 30 ml/min. The injector temperature, detector temperature, and oven temperature were 250, 250, and 100 °C, respectively. The retention times of styrene, R-configuration styrene epoxide, and S-configuration styrene epoxide were 3.37, 10.1, and 10.5 min, respectively. The authentic samples of R- and S-configuration styrene epoxide were used as the standard product to determine the yields by comparison of peak height and area.

3. Results and discussion

3.1. Preparation of the PICC

Chiral salen Mn(III) complexes bearing electrondonating groups has been reported to exhibit higher asymmetric induction than those bearing electron-withdrawing groups [32]. Ionic liquids derived from *N*,*N*-dialkylimidazolium with special polarity can increase the "ionophilicity" of the salen catalyst [13]. In additional, *N*,*N*-dialkylimidazolium cations had positive influence on the stabilization of the transition state during reaction [23]. With these points in mind, we chose ionic liquid containing imidazolium moiety to functionalize the chiral salen Mn(III) complex bearing electrondonating groups. As outlined in Scheme 1, a strategy that we have designed here is to link covalently an IL moiety with CL by covalent polymerization to make the polymeric ABAB type ligand resemble RTILs. The covalent linkage between the end amino ($-NH_2$) groups of 1,3-dipropylamineimidazolium bromide and chloromethyl ($-CH_2Cl$) groups at two sides of 5,5′ positions of (*R*,*R*)-{*N*-(3-*tert*-butyl-5-chloromethyl-salicylidine)-*N*′-(3′-*tert*-butyl-5′-chloromethyl-salicylidine)}-1,2-cyclohexanediamine was used to form the PICC. At first, the reaction between 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde and (*R*,*R*)-diaminocyclohexane yielded a compound of HL, and then the obtained HL was directly reacted with another 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde to produce a CL. Subsequently, the polymerization of 1,3-dipropylamineimidazolium bromide reacted with the obtained CL to afford the PICL. Treatment of the PICL with manganese(II) acetate tetrahydrate under nitrogen gave the dianionic complex. The acetic ion was replaced by chloride ion with lithium chloride at room temperature. The dianionic complex was readily oxidized by oxygen, affording the PICC. The average viscosimetric molecular weight of the PICC measured by Ubbelohde viscosimeter was ca. 13727, and the number of repeating units of the polymer was determined on the basis of the average viscosimetric molecular weight of the PICC and the molecular weight of one building block ($M_v = \sim 13727$, $n = \sim 17$). In addition, Mn ion content of the PICC measured by complexiметry was 1.13 mmol/g, which was close to the theoretical value (1.19 mmol/g). Moreover, it is found that the PICC with the characteristic of 'ionophilicity' is miscible with polar and weak polar solvent such as dichloromethane, but insoluble in non-polar solvent such as *n*-hexane. It is suggested that the ionophilical PICC should be an easily recoverable catalyst

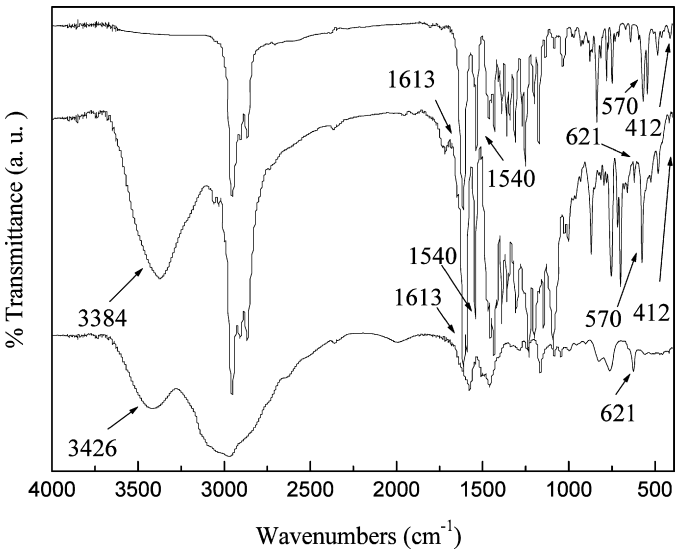


Fig. 1. FT-IR spectra of the monomeric chiral salen Mn(III) complex (a), PICC (b) and IL (c).

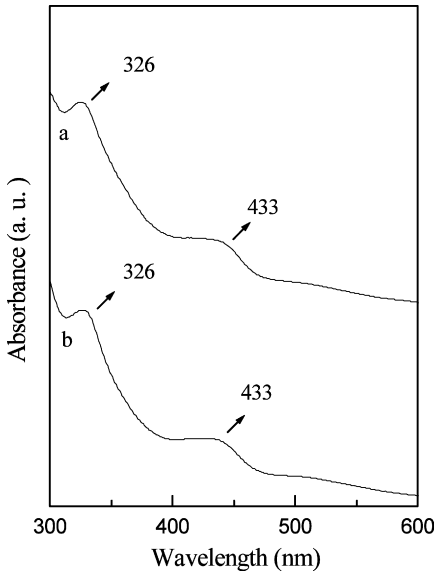


Fig. 2. UV–vis spectra of the monomeric chiral salen Mn(III) complex (a) and the PICC (b).

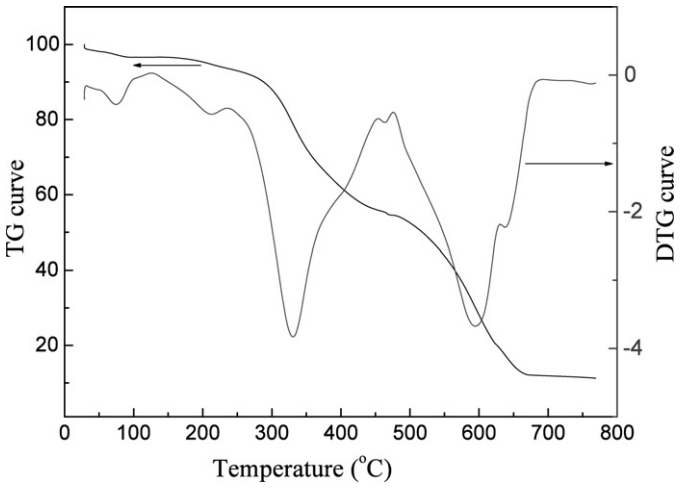


Fig. 3. TG-DTG curves of the PICC.

for asymmetric epoxidation of alkenes by simple phase separation techniques via change of solvents.

3.2. Sample characterizations

3.2.1. FT-IR and UV–vis spectroscopy

The synthesized PICC, as well as monomeric chiral salen Mn(III) complex and IL for comparison, was characterized by FT-IR and UV–vis spectra. As shown in Fig. 1b, the FT-IR spectra of the PICC exhibited characteristic IR bands at 1613, 1540, 570, and 412 cm^{-1}, which were associated with the stretching vibration modes of CH=N, C–O, Mn–O, and Mn–N [10], respectively. The typical IR bands were resemble to that in the spectra of monomeric chiral salen Mn(III) complex (Fig. 1a). Furthermore, Fig. 1b presented new characteristic band at 3384 cm^{-1} assigned to N–H stretching vibrations of the second amine group [33], which confirmed the formation of second amine resulting from the reaction between the end amino ($-NH_2$) groups of IL and chloromethyl ($-CH_2Cl$) groups of the salen ligand. Comparing with the spectrum of IL (Fig. 1c), the PICC showed another band at 621 cm^{-1} (Fig. 1b) that is ascribed to imidazolium fragments [34]. All of the IR spectra results proposed that the PICC contained characteristics of salen Mn(III) complex and imidazolium moiety of IL.

Fig. 2 showed UV–vis spectra of the PICC and monomeric chiral salen Mn(III) complex. The UV–vis spectra of the PICC and the monomeric one were almost identical, which indicated that no change in the local environment of the Mn(III) coordination center in the complex took place. The main broad absorbed peak appeared near 433 nm of the two complexes ascribed to the characteristic charge transfer band of the ligand-to-metal charge transfer transitions (MLCT) [35]. The UV–vis spectra further confirmed the presence of intact catalytic active sites in the PICC, which should be similar as the monomeric chiral salen Mn(III) complex in the catalytic epoxidation of alkenes.

3.2.2. Thermoanalysis

Thermal analysis (TG-DTG) had been used to monitor the decomposition profiles of the PICC, which was presented in Fig. 3. The polymeric complex showed four distinct steps of weight loss in the combined TG-DTG curves, when heated under airflow. The first loss in weight (ca. 4.4%) centers at 130 °C. As mentioned, this weight loss was due to a release of chloride anions as hydrogen chloride (theoretical loss: 4.36%) [36]. It was indicated that the positive charge of the complex was balanced by chloride ion but not by the amine group of the IL. A second weight loss appeared at 230 °C and was followed by an additional large weight loss at 320 °C which extended up to ca. 440 °C. The two steps (ca. 56%) were well distinguished in the corresponding DTG curve, which were assigned to the successive cleavage of the salen ligand moieties (theoretical loss: 56.2%) [37]. The final large weight loss (ca. 32%) centers at 600 °C. From the loss in weight, we tentatively assigned these steps to the complete decomposition of the IL (theoretical loss: 32.4%). Above this temperature, the remaining organics were oxidized up to 800 °C. The non-removable residue of ca. 11% belonged to the formation of manganese oxide in air atmosphere at high temperature. The thermal analysis further demonstrated that the imidazolium cation moiety was successfully polymerized with chiral salen Mn(III) complex by covalent polymerization to form the PICC, and also the synthesized PICC was quite stable at room temperature.

3.3. Catalytic performances

As expected according to its structure, the PICC was miscible with dichloromethane and completely insoluble in *n*-hexane.

Table 1
The results of the enantioselective epoxidation of styrene over different chiral salen Mn(III) complexes.[a]

Catalyst	Donor ligand (mmol)	Run times	Yield (%)[b]	ee (%)[c]	TOF[d] $\times 10^{-3}$ (s^{-1})
No	PyNO (1)	/	32	0	/
No	NMO (2)	/	36	0	/
Monomeric chiral salen Mn(III) complex[e]	PyNO (1)	Fresh	92	35 (*R*)	3.19
PICC[e]	PyNO (1)	Fresh	99	39 (*R*)	3.44
	PyNO (1)	2nd	98	38 (*R*)	3.41
	PyNO (1)	4th	98	38 (*R*)	3.41
	PyNO (1)	7th	98	38 (*R*)	3.41
	PyNO (1)	10th	98	38 (*R*)	3.41

[a] The epoxidation of styrene was performed with 0.5 mmol styrene and 1 mmol *m*-CPBA in 1 mL CH_2Cl_2 at 0 °C for 2 h.
[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 amount of catalyst is 4% of styrene.

Therefore, we chose dichloromethane as reaction medium in the asymmetric epoxidation of styrene. The catalytic activity and enantioselectivity, as well as conditions employed, were contained in Table 1. For the sake of comparison, the results of a control experiment in dichloromethane in which monomeric chiral salen Mn(III) complex was used as a catalyst was also included in Table 1. It is found that low styrene epoxide yield was obtained with racemic epoxide (0% ee) when catalyst was absent even in the presence of donor ligand of PyNO or NMO. Therefore, the use of catalyst becomes very important for improving the yield and enantioselectivity of styrene epoxides. In comparison with monomeric chiral salen Mn(III) complex, the PICC showed comparable catalytic activity (TOF) and ee value. This is due to the fact that the PICC can dissolve in dichloromethane acting as homogeneous catalyst in the reaction system, leading to excellent catalytic activity (>99% yield) and comparable enantioselectivity (39% ee value) when *m*-CPBA was used as an oxidant.

After completion of the reaction, the PICC was recovered from the reaction mixture by simply adding solvent of *n*-hexane and, used for the subsequent catalytic runs. Table 1 described the use of the PICC in ten catalytic cycles. As can be seen in Table 1, the PICC could be recycled up to 10 times with no appreciable loss in yield and enantioselectivity of styrene epoxides. The maintenance of catalytic activity observed for the PICC should origin from the unique solubility and the stable structure of the complex. More importantly, the possibility of formation of undesired inactive dimeric μ-oxo-manganese(IV) dimmers, a main reason for deactivation of homogeneous salen Mn(III) complex, can be avoided because of the severe restriction of active site (site isolation) in the rigid one-dimension polymer framework [37]. The retention of catalytic efficiency suggested that the PICC is perfectly stable during the epoxidation reaction presented here, and is readily recyclable from the reaction system.

After recovery of the PICC by extraction with *n*-hexane, the PICC could be precipitated and separated easily by decantation. The molecular weight of the recovered catalyst ($M_v = 13709$) was measured which was very similar to the fresh complex ($M_v = 13727$). The chemical analysis of manganese of the recovered PICC gave manganese content identical to that of the fresh one. And also, the Mn content in the supernatants was further detected and no Mn leaching was found for the catalytic system. FT-IR spectra and UV–vis spectra of the PICC with fresh and reused 10 times (see Fig. 4, a vs a′ and Fig. 5, a vs a′) indicated that no significant changes took place even after reuse for 10 times. The supernatants extracted from the catalyst separation after ten recycles were also characterized by FT-IR spectrum (see Fig. 4b) and UV–vis spectrum (see Fig. 5b). The characteristic IR bands of the supernatants at 1613, 1540, 570, and 412 cm^{-1} of the PICC were not observed in Fig. 4b. The characteristic UV–vis absorbed peak of the supernatants near 433 nm was also not presented in Fig. 5b. These observations suggested that there is no extraction metal complex in the supernatants, which clearly indicated that the polymeric complex was insoluble completely in *n*-hexane and could be reused in consecutive runs without loss of manganese complex during the enantioselective epoxidation reaction.

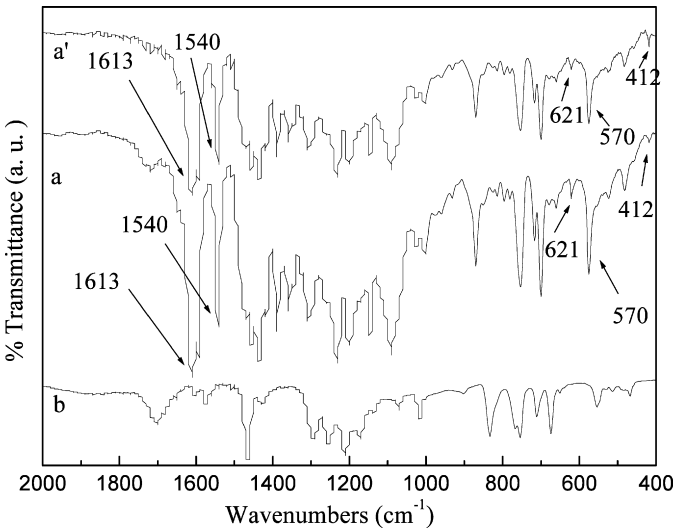


Fig. 4. FT-IR spectra of the fresh PICC (a), the PICC after the 10th reuse (a′); and the supernatants by the addition of *n*-hexane (b).

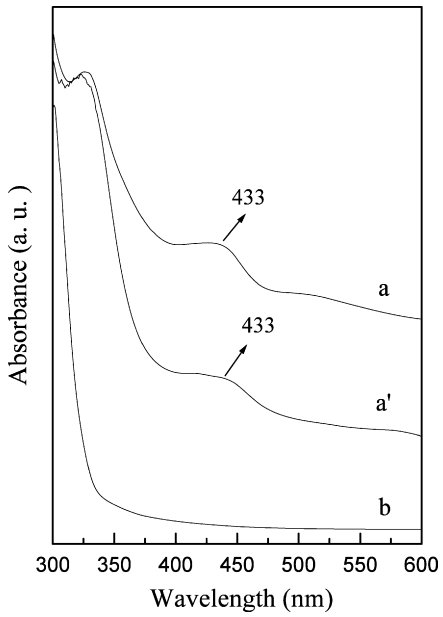


Fig. 5. UV–vis spectra of the fresh PICC (a), the PICC after the 10th reaction (a′), and the supernatants by addition of *n*-hexane (b).

It is well known that the mechanism of olefins epoxidation catalyzed by salen Mn(III) complexes is oxygen transfer from the oxo-manganese complex to the olefin [38–40], where the $O{=}Mn^{V}(salen)^{+}$ formation by oxidation is regarded as the catalytic active site. We used UV–vis spectroscopy technique to monitor online the formation of $O{=}Mn^{V}(salen)^{+}$ in the PICC catalytic process with addition of *m*-CPBA. Herein, 1 mmol of *m*-CPBA was added to the reaction mixture in 4 equal portions at interval of 15 min in a reaction period. The stepwise overlay of UV–vis spectra with

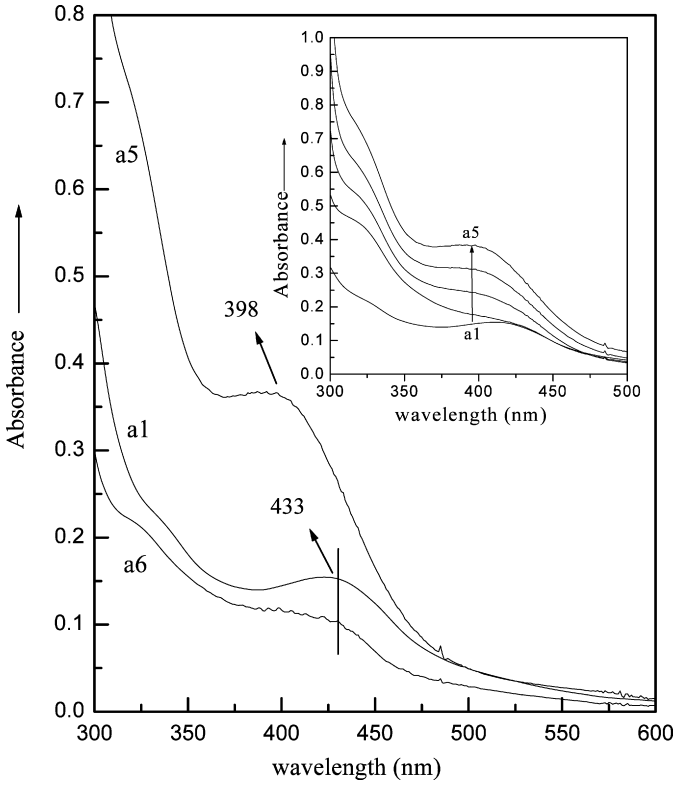


Fig. 6. UV–vis spectra of the solution of PICC in dichloromethane (5×10^{-7} M) containing styrene (1.25×10^{-5} M) and PyNO (2.5×10^{-5} M) by addition of *m*-CPBA at different time, (a1) before addition of *m*-CPBA, (a5) the last interval addition of *m*-CPBA, (a6) after the last interval addition of *m*-CPBA for another 1 h. Inset shows the successive changes of UV–vis spectra observed upon adding the dichloromethane solution of *m*-CPBA (2.5×10^{-5} M, 4 mL) in four equal portions at average 15 min intervals, (a1) 0 min, (a2) 15 min, (a3) 30 min, (a4) 45 min, (a5) 60 min.

each addition of the oxidant of *m*-CPBA were recorded in Fig. 6 inset. Curve of a1 was the UV–vis spectrum of the PICC dissolved in dichloromethane containing styrene and donor ligand of PyNO before addition of *m*-CPBA. The typical adsorbed peak around 433 nm assigned to the MLCT of salen Mn(III) complex could be observed. After the first addition of *m*-CPBA, the typical peak (MLCT) shifted from 433 nm to 414 nm (see Fig. 6 inset curve a2), which indicated the beginning formation of $O{=}Mn^{V}(salen)^{+}$ species in the process by addition of oxidant [2]. The curves a3–a5 recorded the UV–vis spectrum of the PICC after 2nd, 3rd and 4th addition of *m*-CPBA, respectively. The gradual shift from 433 nm (Fig. 6a1) to 398 nm (Fig. 6a5) was attributed to the formation of $O{=}Mn^{V}(salen)^{+}$ during the epoxidation process with addition of oxidant. The absorption attributable to $O{=}Mn^{V}(salen)^{+}$ present throughout the reaction until all the *m*-CPBA has been consumed, which implies that O-transfer from the complex to styrene is a rate-limiting step under the reaction conditions. After complete reaction for 2 h, the recorded UV–vis spectrum was very similar to the original one (Fig. 6, a6 vs a1). These characteristic changes recorded by UV–vis spectra strongly suggested that the PICC is perfectly stable and not easy degradation during the epoxidation reaction, and can be readily reused for the subsequent catalytic runs.

3.4. Effect of donor ligands and reaction temperature

Donor ligand plays a crucial role in the asymmetric epoxidation of alkenes catalyzed by salen Mn(III) complex using *m*-CPBA as oxidants [41]. The influence of various donor ligands viz NMO, PyNO, 4-PPPyNO, and 4-PhPyNO on the enantioselective epoxidation of styrene were summarized in Table 2. In the absence of donor ligands, low yield (52%) and racemic epoxides (0% ee) of styrene were obtained even in the case of PICC. Dramatic increases of the yield and enantioselectivity of the epoxide were achieved by addition of donor ligands, which suggested that the donor ligands were essential to the attainment of high activity and enantioselectivity. It is well known that adding donor ligands to chiral salen Mn(III) complex lead to a well-defined molecular geometry about the Mn center which is otherwise absent, thus optimizing the reactivity and conformation of the complex [38]. Moreover, the additives were coordinated to the metal atom at the axial position through the oxygen atom, which weakens the O=Mn bond in $O{=}Mn^{V}(salen)^{+}$ ion and prevented the formation of unreactive Mn(IV)-oxo dimmers, hence activated and stabilized the catalyst [42]. Comparing with the various donor ligands of NMO, PyNO, 4-PhPyNO and 4-PPPyNO, the most excellent enantioselectivities (48%) could be obtained with NMO, but the kinds of donor ligands had little effects on the yield of styrene epoxide. It was reported that NMO had some additional roles for the Jacobsen's epoxidation system. Palucki et al. observed that a 1:1 salt was generated between NMO and *m*-CPBA in CH_2Cl_2 which was unreactive towards alkenes but oxidizes the chiral salen Mn(III) catalyst even at low temperature to form the catalytic active species Mn(V)-oxo complexes. Also, excess NMO was critical in preventing the uncatalyzed epoxidation pathways that take place in the absence of the additive [43].

Table 2
The catalytic results of the asymmetric epoxidation of styrene with various donor ligands and performed at different temperature.[a]

Donor ligand (mmol)	Temperature (°C)	Yield (%)[b]	ee (%)[c]	TOF[d] $\times 10^{-3}$ (s^{-1})
No	0	52	0	1.80
NMO (2)	−40	96	39 (*R*)	3.34
	−20	99	48 (*R*)	3.44
	0	99	44 (*R*)	3.44
	20	93	37 (*R*)	3.23
	35	88	34 (*R*)	3.06
PyNO (1)	−20	99	41 (*R*)	3.44
	0	99	39 (*R*)	3.44
4-PPPyNO (1)	−20	99	40 (*R*)	3.44
	0	99	37 (*R*)	3.44
4-PhPyNO (1)	−20	98	39 (*R*)	3.41
	0	98	35 (*R*)	3.41

[a] PICC (4% of styrene), styrene (0.5 mmol), *m*-CPBA (1 mmol), CH_2Cl_2 (1 mL), 2 h.
[b] Same as in Table 1.
[c] Same as in Table 1.
[d] Same as in Table 1.

Low temperature was well known to be conducive to high efficiency of the salen Mn(III) complexes for the epoxidation of nonfunctionalized alkenes [44]. The effect of reaction temperature on the epoxidation in the presence of the PICC catalyst was listed in Table 2. Obviously, the catalytic activity and enantioselectivity of the PICC in the epoxidation of styrene were improved at low temperature. With a decrease of reaction temperature from 35 to −20 °C, a significant increase of styrene epoxide yield (from 88% to 99%) and enantioselectivity (from 34% to 48%) to the styrene epoxide with *R*-configuration were obtained over the donor ligand of NMO. The increase in styrene epoxide yield with a decrease of temperature could be due to that low temperature restrained the decomposition of *m*-CPBA, enhancing the availability of the oxidant. Furthermore, asymmetric epoxidation of terminal olefins was subject to a special type of enantiomeric "leakage" pathway, which has been demonstrated to proceed via stepwise, nonstereospecific oxo-transfer mechanism [43]. At low temperature, the enantiofacial selectivity in the first C–O bond-forming step of epoxidation was enhanced and the *trans*-pathway in the second C–O bond-forming step was suppressed, thereby, increasing the ee value in the asymmetric epoxidation of alkenes. Although low temperature was found to induce catalytic activity and enantioselectivity

under the conditions presented here, both the epoxide yield and enantioselectivity decreased with further decreasing reaction temperature from −20 to −40 °C. The reason is that the extremely low reaction temperature limits the solubility of the PICC. After completion of the reaction, some solid catalyst granules could be observed, which indicated that the PICC could not be dissolved in dichloromethane completely at −40 °C. It should be noted that under optimal reaction conditions, 99% of the epoxide yield with 48% ee value could be obtained using the PICC as a catalyst and NMO as a donor ligand.

4. Conclusions

In conclusion, by covalent polymerization between the end amino (–NH_2) groups in a imidazolium cation and chloromethyl (–CH_2Cl) groups in a salen ligand, we have obtained a polymeric IL-functionalized chiral salen ligand and the corresponding polymeric chiral salen Mn(III) complex. The obtained polymeric complex was insoluble in non-polar organic solvents but totally miscible with dichloromethane. With the intriguing peculiarity of solubility, the polymeric chiral complex showed comparable activity and enantioselectivity as a catalyst in asymmetric epoxidation of styrene relative to the monomeric chiral salen Mn(III) complex and readily recovered from reaction system by simple precipitation. Moreover, with the catalytic site isolation of the rigid polymer framework, the polymeric chiral complex could be used at least 10 times without significant loss of catalytic activity and enantioselectivity. On the basis of styrene enantioselective epoxidation results, the present study provides a novel and promising chiral salen catalyst for the enantioselective epoxidation of unfunctional olefins.

Acknowledgments

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