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Enantioselective Epoxidation of Olefins Catalyzed by Polymer-Bound Optically Active Mn(III)-Salen Complex†

Binod B. De, Braj B.Lohray, Swaminathan Sivaram* and Pradeep K. Dhal*, §

Division of Polymer Chemistry, National Chemical Laboratory, Pune 411 008, INDIA

Abstract: The synthesis of the first polymeric chiral Mn(III)-salen complex is reported along with its application as a recyclable asymmetric catalyst for enantioselective epoxidation of unfunctionalized olefins.

Catalytic enantioselective epoxidation of unfunctionalized olefins is an appealing strategy for the syntheses of important optically active organic compounds.[1] Amongst various catalysts developed so far for this purpose, chiral metalloporphyrins[2] and chiral Mn(III)- Schiff base (salen) complexes[3] are noteworthy. Chiral Mn(III)-salen complexes are particularly interesting, because unlike porphyrin systems, they can be synthesized more expeditiously and are amenable to structural tuning.[4]

Although, impressive progress has been made towards development of a variety of catalytically active Chiral Mn(III)-salen complexes, no effort has been reported to date towards developing polymeric analogs of this versatile asymmetric catalyst system. Polymer supported catalysts offer the combined advantages and/or minimize the disadvantages associated with individual homogeneous and heterogeneous catalysts.[5] In recent years, use of polymeric chiral auxiliaries and catalysts for asymmetric organic transformations has brought about impressive results.[6] As a part of our ongoing research efforts towards developing polymeric transition metal catalysts[7] and to explore the potential of chiral Mn(III)-salen complex as more practical asymmetric catalyst, we set out to synthesize this interesting chiral catalyst immobilized on a polymer matrix. Here we report the first example of the synthesis of a polymeric chiral Mn(III)-salen complex and its utilization as a recyclable catalyst for the enantioselective epoxidation of unfunctionalized olefins.

Construction of the desired structural framework for the polymeric chiral metal complex requires the synthesis of the requisite vinyl monomer bearing optically active Mn(III)-salen moiety and its subsequent polymerization. As an appropriate polymerizable analog of the well-known chiral salen derivative bearing a rigid *tert*-butyl group ortho to the hydroxyl group[8], we designed the vinyl salen derivative *N,N'*-bis[8*R*, 8*R'*-5-(4-vinylbenzyloxy)-3-*tert*-butyl-salicylidene]-1,2-diphenylethylene diamine. This Schiff base monomer was obtained by reacting 5-(4-vinylbenzyloxy)-3-*tert*.-butyl salicyladehyde[9] with (1*R*, 2*R*) (+)-diphenyl ethylenediamine.[10] Subsequent reaction of this bis-Schiff base monomer with $Mn(OAc)_2.H_2O$ in the presence of excess LiCl offered the desired chiral metal complex monomer **1**.[11] Overall yields during different steps of reactions were satisfactory. Chiral metal-complex polymer was obtained by copolymerization of **1** with ethylene glycol dimethacrylate (EGDMA) as the cross linking monomer. This

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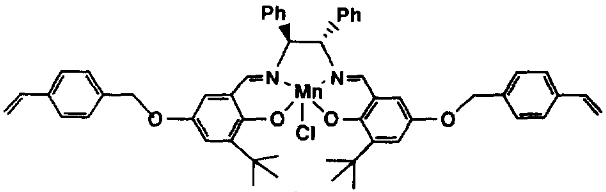
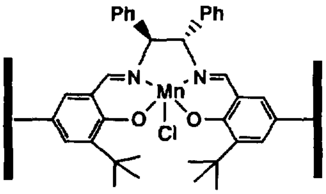
§ Present Address: Materials Research Laboratory, Polaroid Corporation. 750 Main Street - 5C, Cambridge, MA 02139, USA.

would offer insoluble polymeric matrix bearing the chiral catalytic species. The monomer mixture consisted of 10 mol% of **1** and 90 mol% of EGDMA. Polymerization of this monomer mixture using AIBN as the free radical initiator and toluene as the porogenic agent[12] offered the desired macroporous functional copolymer **2**. The polymer thus obtained was ground, soxhlet extracted with ethanol for 24 h to remove soluble fractions and was subsequently dried to constant weight. Mercury porosimetry and scanning electron microscopy of this non-swellable insoluble polymer revealed the presence of macroporous morphology with high surface area. This implies easy accessibility of the catalytic functionalities to the substrates during chemical transformation. Ability of this chiral Mn(III)-salen containing polymer as an asymmetric catalyst for the enantioselective epoxidation of unfunctionalized olefins was evaluated with a number of olefins using iodosyl benzene (PhIO) as the terminal oxidant (monooxygen source), in a manner analogous to the corresponding homogeneous system. A typical reaction procedure involves addition of PhIO (2.0 equiv. with respect to olefin) to a stirred suspension of olefin and the polymeric catalyst at a molar ratio of 25:1(the active catalyst fraction in the polymer) in acetonitrile at 25°C. The suspension was stirred for 24 h and formation of the epoxide was monitored by TLC. The product epoxide was purified by column chromatography after removal of the polymeric catalyst and solvent.



1



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Conversion of olefins to epoxides was quite satisfactory and was comparable to the homogeneous system. The extent of enantioselectivity (enantiomeric excess, ee) of this transformation for different olefins was estimated by ^{1}H NMR spectroscopy using chiral lanthanide shift reagent as well as polarimetry. The results on the chemical conversion and ee of different epoxides thus formed are summarized in Table 1. A number of structural variations of the olefins were attempted which include monosubstituted olefin (styrene), *trans*- disubstituted olefin (*trans*- stilbene) and *cis* disubstituted olefin (dihydronaphthalene and indene). Enantioselectivity of epoxide formation for styrene and *trans*-stilbene was quite low (Table 1, entries 1 and 2). On the other hand, *cis* disubstituted olefins showed higher enantioslectivity. This trend is similar to that observed with the corresponding homogeneous system, where poor enantioselectivity was observed with monosubstituted and *trans*- disubstituted olefins as the substrates.[3] However, with regard to enantioselectivity of epoxide formation in absolute terms with *cis* olefins as substrates, the homogeneous system gave superior ee (> 90%) compared to the heterogeneous polymeric system employed in the present study (30%). In the homogeneous system, use of an additional donor ligand such as N-methyl imidazole or pyridine-N-oxide in the catalyst system was found to enhance the enantio-facial discrimination of the epoxidation reaction.[13] Unfortunately, with the polymeric catalyst, use of pyridine-N-oxide brought about only marginal improvement. (Table 1, entries 5-7).

Although, chiral framework of this polymeric metal complex is quite similar to its low molecular weight counterpart, poor enantioselectivity using the former catalyst system is rather surprising. However, in terms of chemoselectivity, the homogeneous and heterogeneous catalysts gave comparable results. We speculate that this difference in enantioselectivity between the polymeric and low molecular weight chiral Mn(III)-salen catalysts may be attributable to the steric reasons and/or certain microenvironmental effects associated with the macromolecular systems. Efforts are currently underway to unravel this effect and improve the ee to an extent comparable to the homogeneous system.

Table 1 Asymmetric epoxidation of unfunctionalzed Olefins catalyzed by polymeric chiral Mn(III)-salen complex **3**.[a]

Entry	Olefin substrate	external donor	Yield, %[b]	ee, %[c]	Confign[d]
1	Styrene		72	< 2	*R*(+)
2	*trans*-Stilbene		55	9	1*R*, 2*R*(+)
3	DHNP[c]		70	28	1*R*, 2*S*(+)
4	Indene		60	25	1*R*, 2*S*(-)
5	Styrene	PNO[f]	68	<1	*R*(+)
6	DHNP	-do-	68	30	1*R*, 2*S*(+)
7	Indene	-do-	65	26	1*R*, 2*S*(-)

[a] Reactions were run at 25°C in 10 mL of acetonitrile containing 0.058 mmol catalyst, 1.92 mmol olefin and 3.84 mmol iodosylbenzene; [b] Isolated yield based on olefin; [c] Determined by polarimetry reading and/or by ^1H NMR spectroscopy in the presence of chiral shift reagent; [d] Assigned by comparison of polarimetry measurements with literature; [e] Dihydronaphthalene; [f] pyridine-N-oxide.

A major limitation of low molecular weight metal-salen complex as homogeneous catalyst is their propensity to oxidative degradation and dimerization to μ-oxo-manganese(IV) species which leads to deactivation of the catalytic species. Anchoring to a solid polymeric carrier results in site isolation of the catalytic sites which results in minimization of this deactivating side reaction, thus producing robust catalyst systems.[14] Robustness of the polymeric Mn(III)-salen catalyst in the present study is evident from the fact that this catalyst could be recycled up to 5 times without any significant loss of its chemoselective and enantioselective activity. Finally, although modest at the present time, this is the first report of the design of a polymeric asymmetric metal-complex catalyst for the enantioselective epoxidation of unfunctionalized olefins.

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