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Polymer Supported Transition Metal Complexes for Catalytic Epoxidation of Olefins* *

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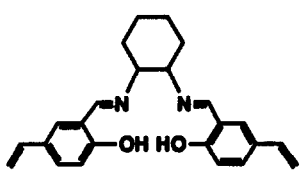
Abstract. Catalytic epoxidation of different alkenes has been reported using polymer supported Mn(III)-Salen complex in the presence of iodosylbenzene as terminal oxidant.

Development of transition metal catalysts for selective epoxidation of alkenes is of great significance.[1] Besides being biomimetic models for Cytochrome P-450, these catalysts can be used for efficient synthesis of a variety of important organic molecules.[2] Transition metal complexes for alkene epoxidation studied so far largely include porphyrin type ligands.[3] Among the non-porphyrin systems[4], the cationic manganese complexes of bis Schiff base (Mn(III)-Salen complex) developed by Kochi et. al.[5] are some of the most ineteresting examples.

Reagents and catalysts immobilized on polymer supports offer several practical advantages.[6,7] Retention of the catalytic activity along with ease of operation and recycling render polymer bound transition metal catalysts attractive with dual advantage of homogeneous and heterogeneous catalysts.[8] Recently, polymer bound metal porphyrins have been found to be efficient catalysts for epoxidation of alkenes.[9] Thus, design of well defined polymeric Mn(III) -Salen complex as recyclable and efficient catalyst for alkene epoxidation appears to be an interesting approach to develop a new generation of synthetically important catalysts. We disclose here the first example of a well defined polymer bound Mn(III)-Salen complex as a highly efficient and selective catalyst for the epoxidation of several cis and trans olefins.



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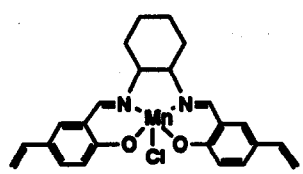

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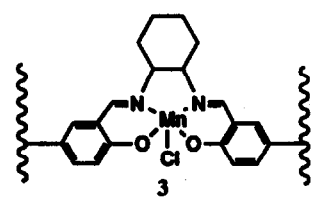

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Design of the desired metal-complexing polymeric catalyst involves the synthesis of the appropriate vinyl monomer bearing Salen (1) and Mn(III)-Salen functionality (2) and its subsequent polymerization with appropriate cross-linking agent. Vinyl monomer bearing Schiff base [N,N'- bis(2-hydroxy, 5-vinyphenyl) methylene]1,2-diaminocyclohexane (vinyl Salen) (1) was obtained by reacting 5-vinyl salicylaldehyde[10]

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with 1,2-diaminocyclohexane. Reaction of 1 with Mn $(OAc)_2.H_2O$ in the presence of excess LiCl offered the metal complexing monomer 2 in good yield.[11] Free radical polymerization of 2 with ethylene glycol dimethacrylate (EGDMA) (at a molar ratio of 5:95 for 2: EGDMA) in toluene gave the desired macroporous polymer 3a. This polymer 3a was ground and extracted with refluxing ethanol in order to remove any soluble contaminants and was subsequently dried to constant weight. The purified polymer was tested for its catalytic efficiency. The epoxidation reactions of olefins were carried out at 25^0C in acetonitrile using polymer 3a as the catalyst in the presence of excess of iodosyl benzene (PhIO) as the terminal oxidant. The rate of epoxidation using this polymeric catalyst is relatively slow, but proceeds steadily . It takes around 32 hrs to reach the degree conversion comparble with the homogeneous system (see Table 1). In homogeneous epoxidation reaction of olefins using soluble Mn(III)-Salen complex, epoxidation was completed within 1 h.[5] Slow reaction rate is commonly observed in hetereogeneous reactions mediated by insoluble polymers, where reagent diffusion to the catalytic site is the rate determining process.[12] In the present case, poor solubility of PhIO in acetonitrile and use of insoluble macroporous polymeric catalyst renders the system triphasic(solid/solid/liquid). Pronounced retardation of the rate of epoxidation was observed even during homogeneous catalysis using less polar solvents[5] and encapsulation of the Mn(III)-Salen inside zeolite cavity.[13] With this polymeric metal-complex which barely swells (<3%) in acetonitrile, high conversion of the olefins to epoxides testifies to the ready accessibility of the catalytic sites to the reagents. A variety of alkenes were successfully transformed to their corresponding epoxides and the results thus obtained are summarized in Table 1.

Table 1 Epoxidation of Different Alkenes by Iodosylbenzene Catalyzed by Polymer Supported Mn(III)-Salen Complex (3a)[a].

Entry	Alkene (conc in mmol)	% yield of epoxide	% yield of side products[b]	Catalyst turnover[c]
1	styrene (1.92)	82	10 (PhCHO)	27
2	(E)-β-methyl styrene(1.0)	90	trace	22
3	*trans*-stilbene (1.46)	57	-----	14
4	indene (2.15)	51	-----	18
5	2,3-cyclohexene ketal (1.75)	62	-----	11

[a] 250 mg of polymer 3a (containing 0.058meqv/g of the Mn(III)-Salen Complex) was used as the catalyst. Molar ratio of olefin to PhIO was 1:2. The reactions were allowed to proceed for 32 hrs; [b] Formation of cleavage or rearranged products were monitored by GLC; c Turnover number is expressed as the molar ratio of epoxide formed to the Mn(III)-Salen species present in the polymer.

Examination of the data in Table 1 reveals that selectivity and product yields with this polymeric Mn(III)-Salen complex is comparable and sometimes better than the corresponding soluble complex[5] and heterogeneous systems based on Zeolite encapsulated Mn(III)-Salen complex.[13] Thus, epoxidation of styrene gave 10% benzaldehyde as byproduct along with 82% yield of the epoxide. In contrast no significant side products were detected with(E)-β-methyl styrene and *trans* stilbene, unlike the homogeneous system where 8% of the corresponding carbonyl compounds were formed as side products.[5] This reflects the superior

specificity of the catalyst after its immobilization on the polymer support. Moreover, polymer microenvironment appears to provide further synergism for the catalytic selectivity and predominant formation of the desired oxidation product.

In order to optimize reaction conditions for epoxidation, a systematic kinetic study was carried out using styrene as the substrate. Figure 1a shows the formation of epoxides at different time intervals using polymer **3a**. From the figure it appears that the reaction is a diffusion controlled process, where steady and sustained diffusion of the terminal oxidant to the metal site to form oxomanganese(V) species followed by oxygen transfer to the alkene double bond takes place to afford the desired epoxide.

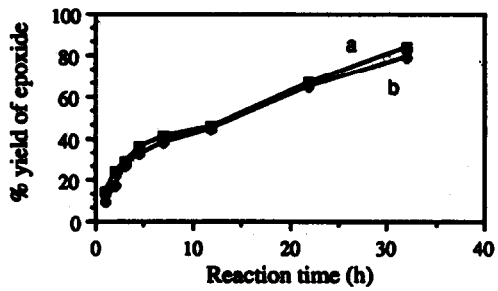

Figure 1. Time course of styrene epoxidation using: a) polymer **3a** and b) polymer **3b** as the catalyst.

Alternatively the metal-complexing polymer was obtained by preparation of macroporous vinyl-Salen containing copolymer from monomer **1** and EGDMA and its subsequent metalation . This process also enabled quantitative loading of Mn(III) to this poly-**1** producing polymer **3b**. After careful purification of this metalated polymer **3b** (by exhaustive extraction of all the non-complexing manganese ions), it was utilized for epoxidation of styrene. Figure1b shows the formation of styrene oxide at various time intervals. With minor variations, the catalytic efficiency of this modified polymer **3b** for styrene epoxidation is comparable to that of the polymer **3a**. This reveals easy accessibility and the reactivity of the Schiff base moieties in the polymer matrix. Close resemblance of the results obtained with both the polymers for catalysis rules out the presence of any unspecifically bound metal ions. These results suggest that it would be possible to introduce a variety of metal ions to a given polymer bound Schiff base without affecting the catalytic efficiency and selectivity .

We have also examined the reuse of these polymer bound catalysts and found that atleast for five cycles of operation for epoxidation of styrene, the catalytic efficiency remained virtually unaffected and styrene oxide was isolated in comparable yield.

High turnover number, selective oxidation to a desired product and multiple recycling are a few salient features of this new generation of heterogenized homogeneous catalysts. Chiral polymeric metal-complexing catalysts for asymmetric epoxidation of alkenes[14] are obvious extension of our research programme. Currently efforts are directed towards realizing these goals.

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