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Synthesis of Catalytically Active Polymer-Bound Transition Metal Complexes for Selective Epoxidation of Olefins[†]

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ABSTRACT: Catalytically active metal-complexing polymers containing Mn(III) moieties were synthesized for use in the selective epoxidation of olefins. For this purpose two different monomers, **1b** and **2b**, bearing the Mn^{III}-Salen moiety (known to be a good candidate for catalyzing olefin epoxidation) were synthesized and subsequently copolymerized with ethylene glycol dimethacrylate, producing insoluble cross-linked polymer networks possessing a macroporous morphology. Metal-containing polymers were also obtained by chemical modification of cross-linked polymers bearing the Salen units (obtained by polymerizing **1a** and **2a**). The catalytic activities of all these polymers were evaluated during epoxidation of olefins. The polymers were able to catalyze the epoxidation of a variety of olefins at room temperature in the presence of iodosylbenzene (PhIO) as the terminal oxidant. The rates of epoxidations using these polymeric catalysts were relatively slow compared to that of the corresponding homogeneous system. However, the epoxidation reactions were selective with predominant formation of the desired epoxides over other side oxidation products. No significant influence of the spacer length between the polymer backbone and metal-complexing sites on the rate of epoxidation was observed.

Introduction

Development of transition metal complexes as catalysts for selective epoxidation of olefins has attracted a great deal of attention in recent years.[1,2] Apart from their biochemical significance (as models to mimic the function of cytochrome P-450), these catalysts offer a variety of synthetic advantages. A number of metal complexes have been developed for this purpose with the objective of elucidating the mechanism of the oxygenation process as well as for maximizing the catalytic efficiencies. Of the variety of ligands employed so far, the noteworthy examples include porphyrin derivatives, macrocyclic polyamines, and Schiff bases.[3-5] A number of transition metal ions, viz., Mn(III), Fe(III), Ni(II), Cr(III), etc., have been utilized. Almost all of these catalysts require a monooxygen source such as hydrogen peroxide, *tert*-butyl peroxide, sodium hypochlorite, iodosylbenzene, etc., to carry out oxygen transfer to the olefins. [These monooxygen sources are strong oxidizing agents. Therefore, appropriate precautions should be taken for their handling.] One of the interesting examples among these transition metal complexes for epoxidation is the cationic manganese complex of the bis Schiff base Salen (Mn^{III}-Salen complex) developed by Kochi *et al.*[6] To make this useful catalyst system recyclable and economical while preserving its catalytic efficiency, we intended to synthesize well-defined polymeric versions of this Mn^{III}-Salen complex.

The design and synthesis of cross-linked polymers carrying catalytically active species offer several practical advantages over soluble homogeneous catalysts.[7,8] In addition to retaining the activity and selectivity of well-defined homogeneous catalysts, the polymeric approach to catalyst design offers an efficient means for recovery and recycling of expensive catalysts and is amenable for scaling up for continuous industrial processes.[9,10] Thus, the present study would provide a rational approach toward developing a new generation of such synthetically important catalyst systems. Metal-complexed porphyrin and phthalocyanines anchored to polymeric supports have recently been reported to be suitable oxidation catalysts.[11,12]

In this paper we present the synthesis of two different polymerizable Mn^{III}-Salen complexes and their cross-linking polymerization to obtain insoluble metal-complexing polymer matrices. In addition, polymerization of the metal-free Salen monomers and their subsequent

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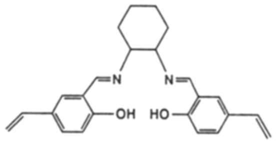
metalation during a postpolymerization step were carried out. The catalytic activity of these newly synthesized metal-complexing polymers was evaluated from their ability to epoxidize a variety of olefins.

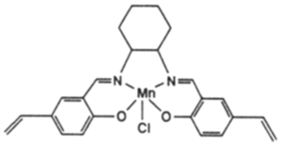
Results and Discussion

Synthesis and Polymerization of Metal-Complexing Monomers. A number of methods are available for attaching catalytically active metal complexes to polymer supports. One of the most widely used approaches involves attachment of such moieties to a polymeric carrier through postpolymerization chemical modification procedures.[13,14] We have adopted the approach of synthesis of the appropriate functional monomers carrying the desired ligands (with and without the coordinating metal ions). Copolymerization of these monomers and cross-linking monomers would offer the insoluble functional polymer matrices. Specific advantages offered by this approach for the synthesis of polymer-bound transition metal catalysts include the following: (i) the purity of the catalytic species can be assured; (ii) by adjusting the amount of the monomers, the concentration of the catalytically active species in the polymer matrix can be controlled; (iii) careful consideration of polymerization parameters would enable one to engineer the physico-mechanical properties of the polymer matrices, leading to efficient utilization of their catalytic activities.

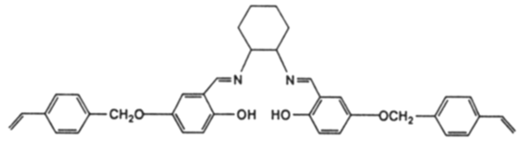
As functional monomers for complexing transition metal ions, we synthesized two different polymerizable bis Schiff bases (Salen), **1a** and **2a**. These Salen derivatives (**1a** and **2a**) were obtained by reacting the respective salicylaldehyde derivatives (synthesized according to literature[15,16]) with racemic *trans*-1,2-diaminocyclohexane. The Salen compounds were obtained as light yellow crystalline solids and showed satisfactory spectral properties. Structurally, the two monomers differ in the distance between the polymerizable double bonds and Schiff base components (to be used for metal complexation). The corresponding metal-complexing monomers containing Mn(III) ions (**1b** and **2b**) were obtained by reacting **1a** and **2a** with $Mn(OAc)_2{\cdot}H_2O$ in the presence of LiCl. Refluxing in ethanol followed by recrystallization offered the metal-containing monomers in pure form.



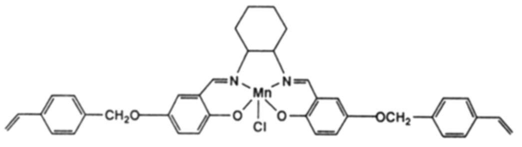
1a



1b



2a



2b

Copolymerization of the functional monomers with ethylene glycol dimethacrylate (EGDMA) as the cross-linker produced the insoluble functional polymer matrices. Polymers obtained with **1b** and **2b** contain metal-complexed Mn^{III}-Salen moieties imbedded in the matrix. To elucidate the ability of the Salen units in the solid phase to interact with metal ions during a postpolymerization process, copolymer matrices containing **1a** and **2a** were also synthesized. These polymers can be subsequently metalated to obtain the metal-complexed polymers carrying Mn^{III}-Salen units. Polymer supports having superior dimensional properties yet exhibiting easy accessibility of the functional groups (e.g., catalytic sites) to chemical reagents and substrates require tailoring of the polymer structures that possess macroporous morphologies. After considerable experimentation, we were able to prepare polymer particles possessing the desired pore size and surface areas. A typical polymerization recipe consisted of 5 mol % of functional monomer and 95 mol % of EGDMA using toluene:ethanol (70:30 v/v) as the porogenic agent. The light brown (with **1b** and **2b**) and light yellow (with **1a** and **2a**) polymers thus obtained were ground to appropriate particle sizes (37–68 μm) and Soxhlet extracted overnight with ethanol to remove any soluble contaminants. Specific surface areas and pore volumes of these polymers were determined by mercury porosimetry, which reveals high surface area and pore volumes for the materials. The macroporous morphology of these polymers is also evident from their scanning electron micrographs (see Figure 1). The results on the surface properties and chemical compositions of these polymers are summarized in Table 1.

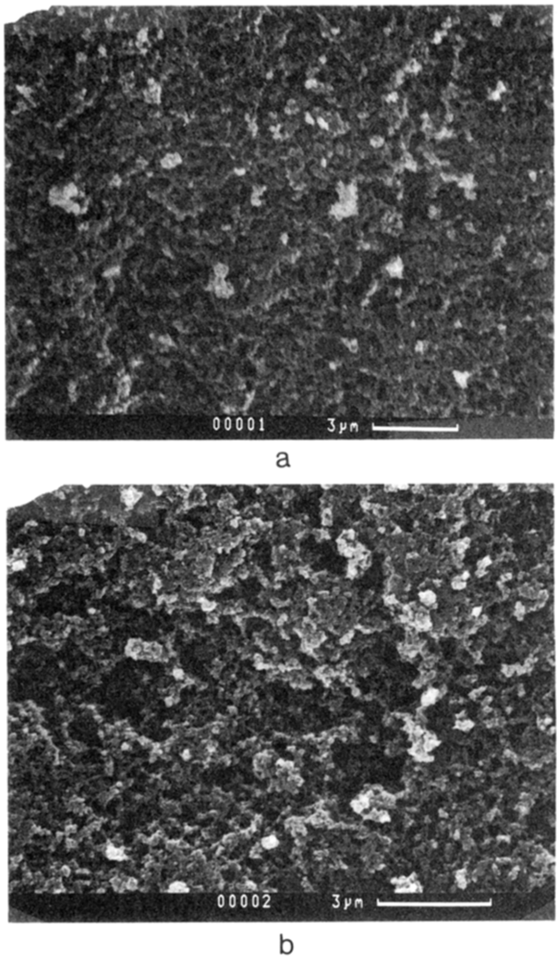


Figure 1. Scanning electron micrographs of the macroporous copolymers obtained using Mn^{III}-Salen comonomers: (a) with **1b** as the functional comonomer; (b) with **2b** as the functional comonomer.

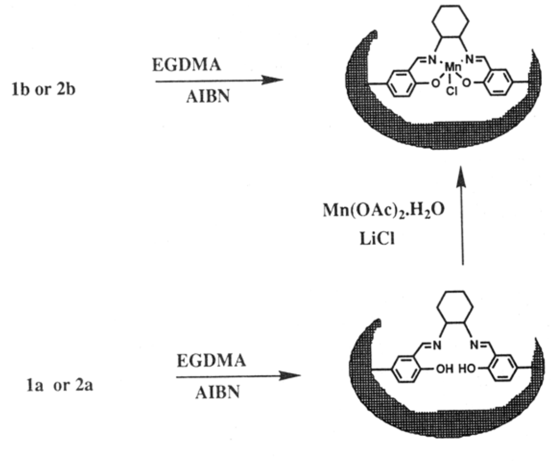
To evaluate the accessibility and reactivity of the functional groups in these macroporous polymeric ma-

Table 1. Polymerization and Characterization of the Metal-Complexing Schiff Base Polymers[a]

polymer code	functional monomer used	surface area (m^2/g)	mean pore vol (cm^3/g)	mean pore diameter (Å)
P-1a	**1a**	234	1.76	123
P-2a	**2a**	215	1.63	114
P-1b	**1b**	248	2.78	172
P-2b	**2b**	218	1.88	112

[a] Polymerization mixture consisted of the respective functional monomer and EGDMA at a molar ratio of 5:95. Polymerizations were carried at 80 °C in toluene: ethanol (70:30 v/v) and were initiated by AIBN.

Scheme 1



trices, we attempted to metalate polymers **P-1a** and **P-2a**. This reaction offered the $\mathrm{Mn^{III}}$-Salen-containing polymeric matrices similar to polymers **P-1b** and **P-2b** obtained by direct copolymerization of the corresponding metal-containing monomers. Comparison of the catalytic activities of these two sets of polymers would reveal the coordinative environments of the metal centers in the polymers obtained by the different methods. Refluxing of polymers **P-1a** and **P-2a** with $Mn(OAc)_2{\cdot}H_2O$ in ethanol followed by addition of LiCl furnished the desired metal-containing polymers (**P-1b′** and **P-2b′**) as brown solids. In addition to the change in color, completion of metalation was evident from their infrared spectra. A schematic representation of the polymerization and metal-complexing polymer by the two different routes is illustrated in Scheme 1.

Catalytic Activities of Polymeric $\mathrm{Mn^{III}}$-Salen Complexes. The ability of these polymer-bound transition metal complexes to catalyze chemical transformations has been demonstrated for epoxidation of olefins. Using iodosylbenzene (PhIO) as the monooxygen source, the low molecular weight $\mathrm{Mn^{III}}$-Salen complex is known to catalyze the epoxidation of olefins.[6] In a typical experiment, epoxidation of an olefin catalyzed by such a polymeric metal complex was carried out by stirring a suspension of the polymer, the respective olefin, and PhIO in a suitable solvent such as acetonitrile. The reaction was allowed to proceed for 24 h at 25 °C. After appropriate workup, the reaction products were analyzed by either gas chromatography or HPLC. The efficacy of these polymeric metal complexes to catalyze the epoxidation of different olefins was investigated. Using polymer **P-1b** as the catalyst, five different olefins were subjected to epoxidation. All the olefins underwent selective epoxidations with high yield under these experimental conditions.

Using the soluble $\mathrm{Mn^{III}}$-Salen complex as the catalyst under homogeneous conditions, epoxidation of olefins proceeded rapidly and was completed within an hour.[6] In the present system involving polymeric metal complexes, an induction period of ca. 30 min was observed. Furthermore, it took ca. 24 h to achieve a comparable degree of conversion of olefins to epoxides as with the homogeneous systems. Slower rates of catalysis have been encountered by other workers using polymer-bound catalysts.[17] Diffusion of substrates and reagents from the solution phase to the metal centers in the polymer matrix is the slow and rate-limiting process. Furthermore, poor solubility of PhIO in acetonitrile along with the insoluble polymer-bound metal complex renders this system triphasic (solid/solid/liquid). In fact, with the homogeneous $\mathrm{Mn^{III}}$-Salen system use of less polar solvents (leading to poor solubility of PhIO) resulted in retardation of the rate of epoxidation.[6] Encapsulation of this $\mathrm{Mn^{III}}$-Salen complex inside a zeolite cavity has also been found to catalyze epoxidation of olefins at a slower rate.[18] Thus, in the present case, where the macroporous polymeric metal complex barely swells (<5%) in common solvents, the high conversion of olefins to epoxides attributes to the predominant localization of the catalytic sites in the accessible regions of the matrices.

Table 2. Epoxidation of Representative Olefins with Iodosylbenzene Catalyzed by Polymer-Supported $\mathrm{Mn^{III}}$-Salen Complex (1b)[a]

entry	olefin used (amt in mmol)	% yield of epoxide	% yield of side products[b]	catalyst turnover[c]
1	styrene (1.92)	90	8 (PhCHO)	30
2	(*E*)-β-methylstyrene (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
6	1,2-dihydronaphthalene (1.53)	60		20

[a] Epoxidation reactions were conducted by suspending 250 mg of the polymer (**1b**) in 10 mL of acetonitrile along with olefin and PhIO in a molar ratio of 1:2. The suspension was allowed to stir at 25 °C for 24 h. [b] Formation of the side products was monitored by GLC. [c] Turnover number is expressed as the molar ratio of epoxide formed to the $\mathrm{Mn^{III}}$-Salen units present in the polymer.

In all cases (except sytrene) pure epoxides were obtained without formation of any side products. Epoxidation of styrene resulted in the formation of 90% styrene epoxide along with ~8% benzaldehyde as the byproduct. This type of product composition is comparable with that observed with the corresponding homogeneous catalyst system. On the other hand, no significant side products were detected with (*E*)-β-methylstyrene, *trans*-stilbene, or indene. Under homogeneous catalysis conditions using soluble $\mathrm{Mn^{III}}$-Salen, ca. 8% of the corresponding carbonyl compounds was reported to be formed as the side product.[6] The results on the epoxide formation with polymer **P-1b** as the catalyst are summarized in Table 2. Comparable (or better) selectivity of this polymer catalyst manifests specificity and defined structures of the catalytic sites in the polymer matrix. Furthermore, microenvironmental effects of the immobilized catalyst such as site isolation in the polymer matrix are likely to contribute to this improved selectivity during epoxidation.

A systematic study toward the elucidation of the nature of these polymer-bound metal complexes, *viz.*, the flexibility/steric effect etc., and the role of the coordination geometry of the metal ions in the ligands (through different modes of their incorporation) on the kinetics and extent of epoxidation was carried out using styrene as the model substrate. Data on the epoxidation of styrene at different time intervals using polymers **P-1b** and **P-2b** as the

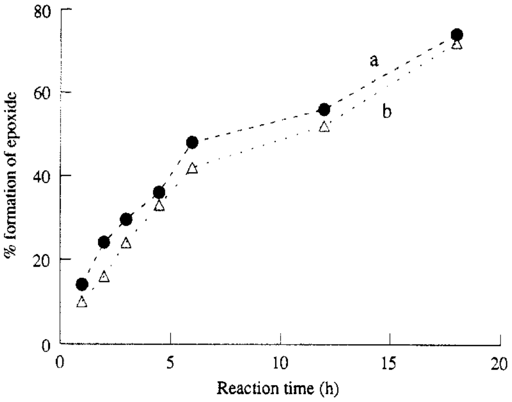


Figure 2. Formation of styrene epoxide as a function of time using (a) polymer **P-1b** as the catalyst and (b) polymer **P-2b** as the catalyst.

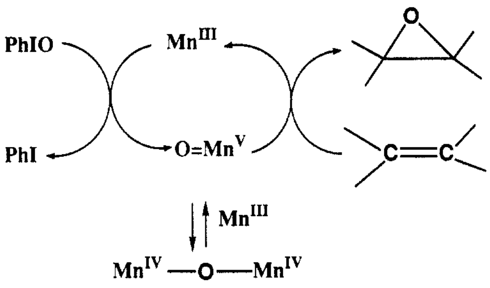
Table 3. Progress of the Epoxidation Reaction of Styrene Using Iodosylbenzene Catalyzed by the Polymers P-1b′ and P-2b′ Obtained by Chemical Modification Metalation of the Corresponding Salen Polymers

		polymer **P-1b′**		polymer **P-2b′**	
entry	time of reaction (h)	% styrene epoxide formed	% PhCHO formed	% styrene epoxide formed	% PhCHO formed
1	1	14.0		13.2	
2	2	24.0		22.0	
3	3	29.5		28.5	
4	5	36.1	3.0	34.7	2.5
5	6	48.2	4.0	46.0	3.8
6	12	56.2	4.8	53.8	4.2
7	18	74.2	9.4	71.0	9.2

catalysts are illustrated in Figure 2. In the case of polymer **P-2b**, the Mn^{III}-Salen moieties are located at a longer distance from the polymer backbone compared to that in the case of polymer **P-1b**. However, both polymers exhibited almost identical catalytic and kinetic behavior toward the epoxidation of styrene. This suggests that probably given a favorable morphology of the polymer matrix, the molecular structure of the metal complex does not appear to influence the diffusion rate of the substrates to the catalytic sites. However, use of longer and flexible spacers as polymethylene chains might enable verification of this fact conclusively. This study merits further investigation. The metal complexing polymers **P-1b′** and **P-2b′** obtained by post polymerization metalation of the corresponding Salen polymers **P-1a** and **P-2a** also catalyzed the epoxidation of styrene at comparable efficiency with polymers **P-1b** and **P-2b** obtained by direct polymerization of the metal-containing monomers. The rate of the epoxidation of styrene with these postmetalated polymers is comparable to that of their structural analogs, **P-1b** and **P-2b** (see Table 3). This implies that incorporation of the Mn(III) ions into the polymer matrices by postpolymerization modification is quantitative and that the metal ions are selectively coordinated to the bis Schiff base units without any nonspecific adsorption. The catalytic sites generated in the polymer matrix by this modification procedure are significant, since it will be possible to introduce a variety of metal ions to a given polymer. This approach would enable the generation of an array of polymer-bound catalysts for modulating metal ion dependent catalytic functional group transformation of organic compounds.

One of the most important characteristics of polymer-bound catalysts is their stability and their regeneration with retained activity. This enables multiple uses of such catalyst systems in continuous processes. We attempted to recycle these polymer-bound Mn^{III}-Salen complexes and tested the ability of these recycled polymers for olefin epoxidation. Up to five cycles of operation (attempted so far), these polymers showed catalytic activities of comparable efficiency. Thus by using polymer **P-1b** as the catalyst, epoxidation of styrene was attempted with the recycled polymer. In each step the yield of epoxide was in the range 85–90%. In contrast, its soluble homogeneous counterpart is known to lose its activity after a few cycles. The different behavior of this catalyst upon anchoring to a polymer support is a notable observation. The retained catalytic activity of the regenerated polymer-bound metal complexes can be explained by considering the mechanism of oxygen transfer involving this metal complex.[6] The role of Mn^{III}-Salen complex during epoxidation is to pick up an oxygen atom from the monooxygen source (PhIO). This results in conversion of Mn(III) to an oxomanganese(V) species. This oxomanganese(V) species is the catalytically active species that transfers oxygen to the olefinic double bond. This process is reversible with manganese shuttling between the Mn(III) and O═Mn(V) state. In addition to this redox pathway, dimerization of O═Mn(V) with Mn(III) can also take place, leading to a μ-oxomanganese(IV) species. The latter is an inactive species whose formation leads to depletion of the catalytically active species. The pathway for this catalytic cycle is presented in Scheme 2. Contrary to this situation with homogeneous catalysts, in the case of the polymer-bound system the lower local concentration of the metal complex anchored to the rigid network would result in site separation of the Mn^{III}-Salen units. This site isolation would preclude the possibility of dimerization of Mn ions, thus suppressing the formation of undesired μ-oxomanganese(IV) species during catalysis.

Scheme 2



Conclusions

Macroporous polymer matrices carrying the Mn^{III}-Salen complex have been synthesized following two different approaches: (i) polymerization of the metal-complexing monomers and (ii) metalation of Salen-bearing functional polymer. Both types of polymers show similar behavior as catalysts for the epoxidation of olefins. Although the rate of epoxidation is slower with these polymeric systems, the reactions do proceed to completion. These polymeric systems show comparable (or superior) selectivity in terms of product formation compared to the homogeneous system. The ability of the polymer-bound Salen to coordinate with different metal ions makes this system attractive as catalyst carriers to tune the catalytic activity of transition metal complexes for different organic transformations by appropriate choice of metal ions. The rigid and macroporous structures of these polymers combined with retained catalytic activity over several cycles make these functional polymers suitable candidates for continuous chemical processes.

Experimental Section

Materials. All the solvents used were reagent grade obtained from S. D. Fine Chemicals, Bombay, and were purified by following standard purification procedures prior to use. Unless specified all chemicals and reagents were obtained from Aldrich Chemical Co., Milwaukee, WI. Whenever required, reagents were purified by either recrystallization or distillation prior to use. 2,3-Cyclohexene ketal[19] and iodosylbenzene[20] were synthesized according to literature procedures.

Instrumentation and Analyses. Elemental analyses were carried out at the National Chemical Laboratory Microanalysis Facility. Melting points were determined using a Büchi melting point apparatus. Infrared spectra were recorded using a Perkin-Elmer 16PC FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker MX-200 spectrometer operating at 200 MHz. Chemical shift values reported are relative to tetramethylsilane (TMS) as the internal reference. Gas chromatography was performed on a Blue Star 421 gas chromatograph using a $6 \times {}^1/_8$ in. Chromato-Pak packed column using an fid detector. Mass spectra were obtained with a Finnigan MAT 1020B mass spectrometer. Specific surface areas and pore volumes were determined using a Quanta chrome mercury porosimeter. Electron micrographs were taken with a Cam Scan Series 2 scanning electron microscope after vacuum coating the samples with gold.

Monomer Synthesis. *N,N′*-Bis[(2-hydroxy-5-vinylphenyl)methylene]-1,2-diaminocyclohexane (1a). To a solution of 0.77 g (6.76 mmol) of racemic *trans*-1,2-diaminocyclohexane in 17 mL of dry ethanol was slowly added 2.0 g of 2-hydroxy-5-vinylbenzaldehyde[15] dissolved in 20 mL of dry ethanol. With continuous stirring, the reaction mixture was heated to reflux for 3 h followed by removal of the solvent under reduced pressure. The residue was recrystallized from aqueous ethanol, yielding 2.28 g (90%) of the product **1a** as a light yellow solid. Mp 142 °C; IR (Nujol) 3480 (OH), 1640 (CH═N), 1605 (aromatic) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.3–1.5 (m, 8 H, cyclohexyl CH$_2$), 3.3 (t, 2 H, cyclohexyl CHN), 5.1 (d, 2 H, vinyl CH$_2$), 5.5 (d, 2 H, vinyl CH$_2$), 6.5–6.7 (q, 2 H, vinyl CH), 6.9–7.4 (m, 6 H, aromatic H), 8.3 (s, 2 H, CH═N), 13.3 (broad, 2 H, OH); MS *m/e* 374 (M$^+$). Anal. Calcd for $C_{24}H_{26}N_2O_2$: C, 76.96; H, 7.00; N, 7.48. Found: C, 76.86; H, 6.90; N, 7.51.

***N,N′*-Bis[(2-hydroxy-5-(4-vinylbenzyloxy)phenyl)methylene]-1,2-diaminocyclohexane (2a).** Compound **2a** was synthesized following the procedure adopted for **1a** by reacting *trans*-1,2-diaminocyclohexane and 5-(*p*-vinylbenzyloxy)salicyladehyde.[16] Yield 85%; mp 92 °C; IR (Nujol) 3482 (OH), 1640 (CH═N), 1604 (aromatic), 1140 (CHO) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 1.3–1.6 (m, 8 H, cyclohexyl CH$_2$), 3.3 (t, 2 H, cyclohexyl CHN), 4.8 (s, 4 H, OCH$_2$Ar), 5.1 (d, 2 H, vinyl CH$_2$), 5.6 (d, 2 H, vinyl CH$_2$), 6.5–6.7 (q, 2 H, vinyl CH), 7.0–7.6 (m, 14 H, aromatic H), 8.2 (s, 2 H, CH═N), 13.3 (broad, 2 H, OH). Anal. Calcd for $C_{38}H_{38}N_2O_4$: C, 77.70; H, 6.53; N, 4.78. Found: C, 77.62; H, 6.40; N, 4.78.

[*N,N′*-Bis[(2-hydroxy-5-vinylphenyl)methylene]-1,2-diaminocyclohexane]manganese(III) Chloride (1b). To 1.0 g (2.67 mmol) of Salen monomer **1a** dissolved in 25 mL of absolute ethanol was added 2.2 g of solid Mn(OAc)$_2$·H$_2$O (2 equiv) in one portion. The reaction mixture was refluxed for 2 h. After addition of 0.4 g (9.42 mmol) of LiCl to the mixture, it was refluxed for an additional 1 h. Cooling the reaction mixture to 0 °C afforded the desired Mn(III) complex (**1b**) as dark brown crystals. The crystals were filtered, washed thoroughly with water, and dried under vacuum. Yield 80%, IR (KBr) 1650, 1544, 1490, 1450, 1420, 1160, 1005, 700, 660 cm^{-1}. Anal. Calcd for $C_{24}H_{24}N_2O_2$-MnCl: C, 62.25; H, 5.23; N, 6.05. Found: C, 62.30; H, 5.15; N, 6.35.

[*N,N′*-Bis[(2-hydroxy-5-(4-vinylbenzyloxy)phenyl)methylene]-1,2-diaminocyclohexane]manganese(III) Chloride (2b). Using **2a** as the ligand, this compound was synthesized in a manner similar to the synthesis of **1b** with 85% yield. IR (KBr) 1650, 1542, 1490, 1453, 1420, 1315, 1160, 1005, 705, 660 cm^{-1}. Anal. Calcd for $C_{38}H_{36}N_2O_4MnCl$: C, 67.60; H, 5.37; N, 4.15. Found: C, 67.48; H, 5.45; N, 4.06.

Polymerization and Workup. The recipe for the polymerization mixtures consists of 5 mol % of the functional monomers and 95 mol % of the EGDMA cross-linker. In a typical polymerization process, 0.5 g of **1a** and 4.1 g of EGDMA were dissolved in 10 mL of toluene:ethanol (7:3 v/v). After addition of 2,2′-azobis(isobutyronitrile) (1 wt % with respect to total monomer) the polymerization mixture was bubbled with nitrogen for 3 h. Polymerization was carried out at 80 °C for 24 h. After cooling to room temperature, the solid mass thus obtained was ground and was extracted with refluxing ethanol overnight to remove any soluble contaminants. The polymer was filtered off, washed three times with hot ethanol, and dried under vacuum at 60 °C for 12 h. These polymer particles were sieved to appropriate particle sizes before subsequent use.

Metal Loading of the Polymer Based on 1a and 2a. Typically, to a suspension of 3 g of the purified polymer particles in 50 mL of absolute ethanol was added 3.0 equiv (with regard to the calculated Salen component in the polymers) of Mn(OAc)$_2$·H$_2$O. The mixture was heated to reflux for 8 h, during which time the polymer changed color from yellow to brown. At this time 4.0 equiv of LiCl was added and the mixture was refluxed for an additional 4 h. The residue was filtered while hot and washed four times with hot ethanol and twice with water. Finally, it was extracted with refluxing ethanol overnight. After filtration, the polymer was dried under vacuum at 60 °C for 12 h.

Epoxidation of Olefins Using Polymeric Catalysts. To a suspension of the metal-complexing polymer in acetonitrile (typically 0.5 g of polymer in 15 mL of acetonitrile) in a 50-mL round-bottom flask were added iodosylbenzene and the respective olefins (2:1 mol/mol). Typically, the molar ratio of olefin to Mn^{III}-Salen units was 25:1. The suspension was allowed to stir at room temperature for 24 h, and the progress of the reaction was monitored by TLC. At the end of the reaction, the suspension was filtered off and the polymer particles were washed with acetonitrile. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (silica gel 60–120 mesh size, hexane/ether 1:0 to 19:1). For kinetic analysis, small amounts of the samples were removed at appropriate time intervals and were analyzed by gas chromatography.

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References and Notes

(1) McMurray, T. J.; Groves, J. T. In *Cytochrome P-450, Structure, Mechanism, Biochemistry*; Oritz de Montellano, P. R., Ed.; Plenum Press: New York, 1986; Chapter 1, p 1. Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.

(2) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. Tabushi, I. *Coord. Chem. Rev.* **1988**, *86*, 1.

(3) Mansuy, D. *Pure Appl. Chem.* **1990**, *62*, 741. Groves, J. T.; Viski, P. *J. Org. Chem.* **1990**, *55*, 3628. Colman, J. P.; Zhang, X.; Hambre, R. T.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 5356.

(4) Yoon, H.; Wagler, T. R.; O'Connor, K. J.; Burrows, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 4568. Nam, W.; Ho, R.; Valentine, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7052.

(5) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606. Upadhyay, M. J.; Bhattacharya, P. K.; Ganeshpure, P. A.; Satish, S. *J. Mol. Catal.* **1992**, *73*, 277.

(6) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.

(7) Hodge, P. *Encyl. Polym. Sci. Eng.* **1988**, *12*, 618. Blossey, E. C.; Ford, W. T. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon Press: Oxford, 1989; Vol. 6, p 81.

(8) Pittman, C. U. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: London, 1982; Vol. 8, p 553. Hartley, H. R. *Supported Metal Catalysts*; Reidel: Dordrecht, 1985. Sherrington, D. C. *Pure Appl. Chem.* **1988**, *60*, 401.

(9) Moberg, C.; Rakos, L. *J. Organomet. Chem.* **1987**, *335*, 125. Chen, W.; Boven, G.; Challa, G. *Macromolecules* **1991**, *24*, 3982.

(10) Parrinello, G.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7122. Lohray, B. B.; Thomas, A.; Chittari, P.; Ahuja, J.; Dhal, P. K. *Tetrahedron Lett.* **1992**, *33*, 5453.

(11) Turk, H.; Ford, W. T. *J. Org. Chem.* **1991**, *56*, 1253. Cooke, P. R.; Smith, J. R. L. *Tetrahedron Lett.* **1992**, *33*, 2737.

(12) Razenberg, J. A. S. J.; van der Made, A. W.; Smeets, J. W. H.; Nolte, R. J. M. *J. Mol. Catal.* **1985**, *31*, 271.

(13) Campestrini, S.; Muenier, B. *Inorg. Chem.* **1992**, *31*, 1999. Bhaduri, S.; Darshane, V. S.; Sharma, K.; Mukesh, D. *J. Chem. Soc., Chem. Commun.* **1992**, 1738.
(14) Knolker, H. J.; Gonser, P. *Synlett* **1992**, *6*, 517. Park, K. S.; Ihm, S. K. *Polym. Bull.* **1992**, *27*, 399.
(15) Wulff, G.; Akelah, A. *Makromol. Chem.* **1978**, *179*, 2647.
(16) Fujii, Y.; Matsutami, K.; Kikuchi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 415.
(17) Kurusu, Y.; Masuyama, Y.; Saito, M.; Saito, S. *J. Mol. Catal.* **1986**, *37*, 235.
(18) Bowers, C.; Dutta, P. K. *J. Catal.* **1990**, *122*, 271.
(19) Garbisch, E. W. *J. Org. Chem.* **1965**, *30*, 2109.
(20) Vogel, A. I. *Textbook of Practical Organic Chemistry*, 3rd ed.; Longman: London, 1973; p 541.