

## Polymer supported catalysts for epoxidation reactions

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**DVB crosslinked polystyrene supported  $\beta$ -diketone linked complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) have been prepared and characterized. The catalytic activity of these metal complexes has been studied in epoxidation reactions. A possible mechanism for the reaction is also suggested.**

THE field of polymer metal complexes as catalysts in organic synthesis has remained active ever since the first example of catalysis by a polymer metal complex was reported by Lautsch *et al.*<sup>1</sup>. Crosslinked organic macromolecular species have found wide applications in recent years because of the ease with which the work up of the reaction mixture could be carried out as also their reusability<sup>2,3</sup>. Epoxidation of olefins in presence of metal catalysts has been widely investigated<sup>4-18</sup>. This paper discusses the catalytic activity of polystyrene supported  $\beta$ -diketone-linked metal complexes in epoxidation reactions.

Differently crosslinked polymers of styrene with divinyl benzene as the crosslinking agent were prepared by suspension polymerization using benzoyl peroxide as the initiator. The synthesis of polystyrene supported  $\beta$ -diketone linked metal complexes involved a series of polymer analogous reactions (Scheme 1). A carboxy function was anchored onto polystyrene support and was converted into  $\beta$ -diketone function by Claisen condensation using 4'-substituted acetophenones in the presence of sodium ethoxide. Five different metals of the first transition series, viz. Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were complexed with polystyrene supported  $\beta$ -diketones and the metal intake capacity in each case was determined.

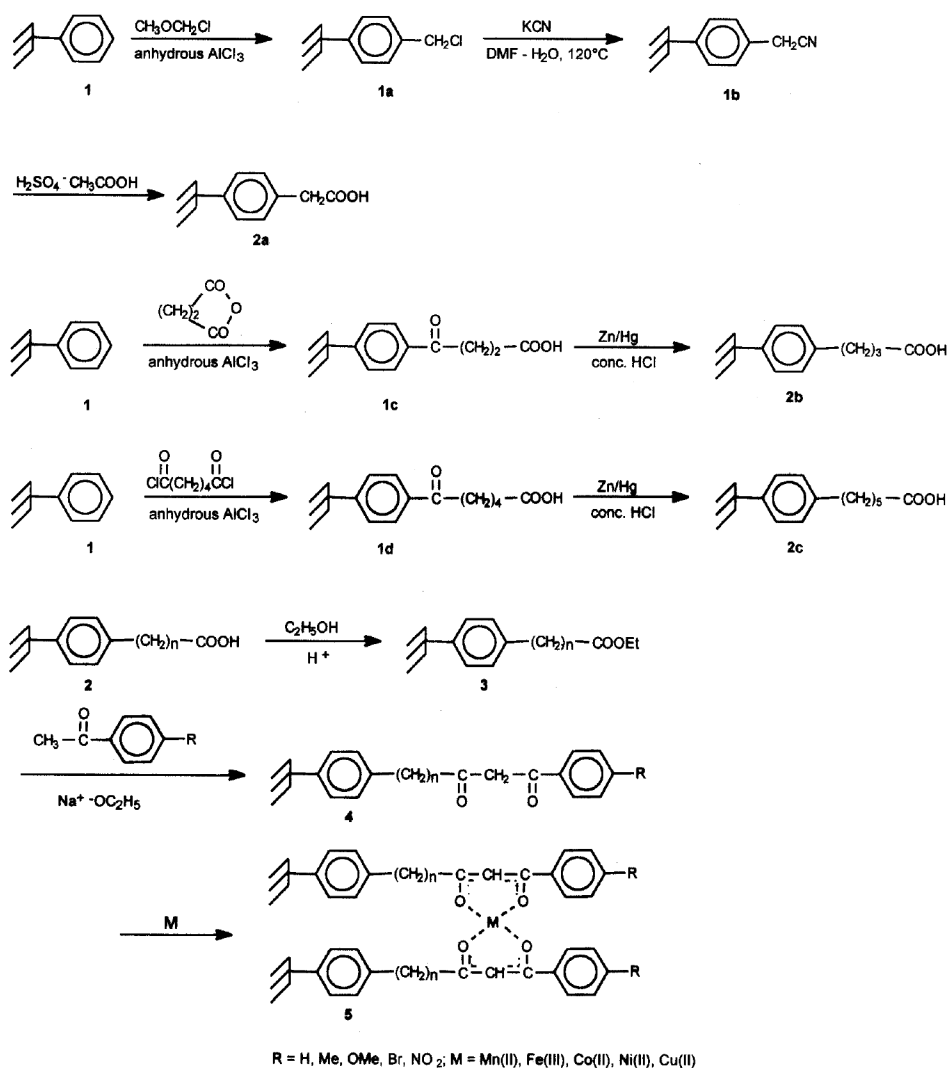
The polystyrene supported  $\beta$ -diketones exhibited strong absorption bands at 1720 and 1630  $\text{cm}^{-1}$  corresponding to C=O and C=O...H stretching. But on complexing it with copper a negative shift of 40  $\text{cm}^{-1}$  was observed. The electronic spectrum of Cu(II) complex contains characteristic bands at 23440 and 18230  $\text{cm}^{-1}$ . The former may be due to a charge transfer transition while the latter is due to the overlapping of the three allowed transitions in the  $D_{4h}$  symmetry. Copper(II) is susceptible to Jahn-Teller distortion and the formation

of regular octahedral complexes does not occur. Instead weakly or strongly distorted octahedral complexes with the latter approaching a square planar configuration are formed. Thus the symmetry is lowered from  $O_h$  to  $D_{4h}$ . Magnetic moment calculations exhibited a value of 1.85 BM. Thus the electronic spectrum suggests a  $D_{4h}$  symmetry and a square planar configuration for the Cu(II) complex. The ESR spectrum corresponds to an axial symmetry with  $g_{\parallel}$ ,  $g_{\perp r}$ ,  $A_{\parallel}$ ,  $A_{\perp r}$  values of 2.2, 2.0,  $80 \times 10^{-4}$  and  $15 \times 10^{-4} \text{ cm}^{-1}$  respectively. Evaluation of  $\alpha^2$ , the covalency parameter using the relation,  $\alpha^2 = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.002) + 3/7(g_{\perp r} - 2.002) + 0.04$ , gave a value of 0.02 which confirmed the covalent nature of the metal-ligand bond. Thermogravimetric studies revealed a first stage decomposition of 6.1% and a second stage decomposition of 90.4% at temperature intervals of 105–270°C and 280–440°C respectively. A residue of 3.5% which may be the oxide of the metal remained at the end.

IR spectral studies of the Co(II) complex showed a shift in the C=O frequency from 1720 to 1680  $\text{cm}^{-1}$  due to complexing. Absorption bands at 18450 and 16200  $\text{cm}^{-1}$  correspond to  ${}^4A_2(F) \rightarrow {}^4T_1(P)$  and  ${}^4A_2(F) \rightarrow {}^4T_1(F)$ . On the basis of these transitions a tetrahedral geometry can be assigned for the complex which is further supplemented by an observed magnetic moment of 4.3 BM.  $g_{\parallel}$  and  $g_{\perp r}$  values of 2.1 and 1.9 obtained from the ESR measurements together with the hyperfine coupling constants of  $80 \times 10^{-4}$  and  $60 \times 10^{-4} \text{ cm}^{-1}$  for the parallel and perpendicular components confirm the geometry of the complex. A first stage decomposition of 7.4% and a second stage decomposition of 90.0% were observed at temperature intervals of 110–280°C and 290–440°C respectively. The TG data also recorded a 3.5% residue of the corresponding metal oxide.

The TG curve of the Fe(III) complex showed a decomposition of 6.1% in the temperature range of 100–280°C followed by 90.4% in the range of 290–440°C. A residue of 3.5% was left behind. In iron(III) octahedral complexes, the ground state is  ${}^6A_{1g}$  derived from the  ${}^6S$  ground term for the free ion. For the high spin complexes of iron(III) having sextet ground state, all the  $d-d$  transitions are forbidden. In many cases the charge transfer bands are found to obscure the very weak spin forbidden  $d-d$  bands. The electronic spectrum contains absorption bands at 24590 and 19000  $\text{cm}^{-1}$ . The former could be attributed to the charge transfer transition whereas the latter could be assigned to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transition. A magnetic moment value of 5.8 BM was observed for the Fe(III) linked  $\beta$ -diketone as against a theoretical value of 5.92 BM. Considering all the aforesaid spectral details together with the ESR parameters,  $g_{\parallel} = 2.1$ ,  $g_{\perp r} = 2.0$ ,  $A_{\parallel} = 130 \times 10^{-4}$  and  $A_{\perp r} = 180 \times 10^{-4} \text{ cm}^{-1}$ , an octahedral geometry can be assigned for the complex.

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**Scheme 1.** Preparation of polystyrene supported  $\beta$ -diketone linked metal complexes.

**Table 1.** Polystyrene-supported  $\beta$ -diketone linked metal complexes as catalyst for epoxidation reactions

Substrate	Product	Time (h)	Yield (%)
Styrene	Phenyl oxirane	22	85.8
$\alpha$ -Methyl styrene	$\alpha$ -Methyl phenyl oxirane	18	88.3
Cholesterol	Cholestan-5,6-oxo-3-ol	35	68.2
Cyclopentene	Cyclopentene oxide	27	82.4
Cyclohexene	Cyclohexene oxide	30	87.1

Substrate, 0.01 mol;  $\text{H}_2\text{O}_2$ , 0.3570 N, 25 ml; catalyst, 200 mg; methanol, 20 ml.

Electronic spectrum reveals a charge transfer band at  $25000\text{ cm}^{-1}$  and a ground state to the first excited state transition of  $13900\text{ cm}^{-1}$  for the Mn(II) complex. The ground term of  ${}^6\text{S}$  for the free Mn(II) transforms into  ${}^6\text{A}_{1g}$  in  $\text{O}_h$  field. Even though the transition to higher states are spin and parity forbidden in octahedral field, they do occur due to spin-orbit coupling but with weak

intensity. Magnetic moment measurements gave a value of 5.92 BM. The IR spectrum revealed a negative shift of  $40\text{ cm}^{-1}$  for the C=O frequency due to complexing. The  $g_{\parallel}$  and  $g_{\perp}$  values of 2.17 and 2.1 together with the hyperfine coupling constants of  $75 \times 10^{-4}$  and  $130 \times 10^{-4}\text{ cm}^{-1}$  for the parallel and perpendicular components form the supporting evidence for the above facts. The TG graph exhibited weight losses of 6.5% and 89.0% at temperature intervals of  $110\text{--}260^\circ\text{C}$  and  $270\text{--}440^\circ\text{C}$  respectively. No change was observed on further heating as the metal oxide residue of 4.5% was left behind.

From an overview of the spectral details, an octahedral geometry can be assigned for the Ni(II) complex. The suggestion is supported by infrared absorption bands at  $1680$  and  $1590\text{ cm}^{-1}$ , electronic absorption bands at  $11110$ ,  $16660$  and  $24750\text{ cm}^{-1}$  for respective transitions of  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  supplemented by an observed magnetic moment of 2.83 BM. The salient ESR parameters

**Table 2.** Epoxidation of  $\alpha$ -methyl styrene to  $\alpha$ -methyl phenyl oxirane

Crosslink density	Yield (%)	No. of methylene spacer groups	Yield (%)	Ligand environment	Yield (%)	Metal	Yield (%)	No. of times recycled	Yield (%)
2	88.3	1	81.5	R=OMe	91.6	Mn(II)	88.3	1	88.3
5	85.7	3	88.3	R=Me	88.3	Fe(III)	85.5	2	88.0
10	82.3	5	91.1	R=H	83.6	Co(II)	78.8	3	87.8
15	74.6			R=Br	77.9	Ni(II)	75.2	4	87.6
				R=NO <sub>2</sub>	77.2	Cu(II)	83.7	5	87.4

$\alpha$ -methyl styrene, 0.01 mol; H<sub>2</sub>O<sub>2</sub>, 0.3570 N, 25 ml; catalyst, 200 mg; methanol, 20 ml.

with  $g_{||} = 2.2$ ,  $g_{\perp} = 2.1$ ,  $A_{||} = 135 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp} = 60 \times 10^{-4} \text{ cm}^{-1}$  give a proper perspective and conclusive evidence for assigning an octahedral geometry. The thermogravimetric plot witnesses first and second stage decompositions of 6.5% and 90.0% in the temperature ranges of 105–290°C and 300–450°C respectively. Residue of the metal oxide amounting to 3.5% was left behind.

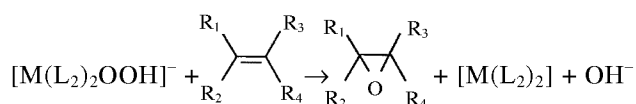
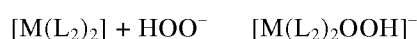
Two units of  $\beta$ -diketone moiety are co-ordinated with the metal ion such that four vacant sites are satisfied. In the case of Mn(II), Fe(III) and Ni(II), two molecules of H<sub>2</sub>O are also utilized to fill the fifth and sixth coordination sites.

The epoxidation reactions involved refluxing of a few olefin substrates, viz. styrene,  $\alpha$ -methyl styrene, cholesterol, cyclopentene and cyclohexene with aqueous hydrogen peroxide solution in the presence of polystyrene supported metal complexes using methanol as the solvent (Table 1). The epoxidation reactions were found to be influenced by the degree of crosslinking of the polymer support, spacer group between the polymer matrix and metal complex, structural environment of the ligand and nature of the metals (Table 2). Metal complexes were anchored onto polystyrene support having different crosslink densities of 2, 5, 10 and 15. Epoxidation reactions using a definite quantity of these catalysts exemplified the fact that as the crosslink density was increased, catalytic efficiency decreased which could possibly be due to the lesser metal intake capacity. Polystyrene supports with one, three and five methylene spacer groups between the polymer matrix and metal complex were prepared and epoxidation reactions were carried out to establish its influence on the course of the reactions. Considering the relative positions of the metal complexes attached to the polymer matrix, it is found that those nearer to the polymer backbone are less reactive because of steric hindrance or due to the interference of the polymer chain with it. Studies were further extended to understand the role of varying structural environment of the polystyrene supported  $\beta$ -diketones and accordingly  $\beta$ -diketones having different substituent groups such as 4'-methoxyphenyl, 4'-methylphenyl, phenyl, 4'-bromophenyl and 4'-nitrophenyl were prepared and complexed with different

metals. Epoxidation reactions employing these catalysts led to the conclusion that as the electron donating nature of the ligand increased, catalytic efficiency also increased. Polystyrene supported  $\beta$ -diketo ligands complexed with different metals, viz. Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) were employed in epoxidation reactions. On comparison of their relative efficiencies, Mn(II) was found to be the most effective.

An important advantage of polymer-supported metal catalysts is their reusability. They can be removed by simple filtration upon completion of the reaction and can be reused several times without any loss of catalytic activity. From experimental results it could be seen that there was no appreciable difference in reactivity after recycling. The catalysts can also be stored indefinitely without any loss of capacity and activity.

The epoxidation reactions could be explained by the following mechanism.



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## Presence of stable active oxygen scavenging enzymes superoxide dismutase, ascorbate peroxidase and catalase in a desiccation-tolerant cyanobacterium *Lyngbya arboricola* under dry state

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**Freshly collected and one- and two-year-old dry mats of a desiccation-tolerant cyanobacterium *Lyngbya arboricola*, inhabiting the bark-surface of *Mangifera indica* exhibited enhancement in the activity of active oxygen scavenging enzymes superoxide dismutase (SOD), ascorbate peroxidase (APX) and catalase in their cell-free extracts on increasing the incubation period. Comparatively, the dry mats showed considerable activity of all these enzymes in the cell-free extracts, but lower than that of freshly collected mats. Five, two and three isoforms of SOD, APX and catalase enzymes respectively, were observed in the crude extracts of the freshly collected mats on native PAGE. SOD comprised of one Mn, one Fe-Mn and three Fe-containing isoforms. Excepting the disappearance of Mn and Fe-Mn SODs and a minor loss in the intensity of the isoforms of APX and catalase on native gels, the AOS enzymes were found stable on storage of the mats for one and two years respectively, under dry state.**

CYANOBACTERIA inhabiting the surfaces of barks of trees, besides frequent drying and wetting during rainy season (growing season), are found invariably exposed to extremes of desiccation from the months of October to June with variable temperatures of cold winter and hot summer seasons<sup>1</sup>. Recovery of photochemical reactions, <sup>14</sup>C-fixation and C<sub>2</sub>H<sub>2</sub> reduction on rehydration have reflected their capacity to survive such extremes of conditions—desiccation, in particular<sup>2-4</sup>. Certain metabolic activities of these cyanobacteria recovered even after their treatment in dry heat at

100°C for 1 h (ref. 4). Generation of highly reactive active oxygen species (AOS), which need to be scavenged in order to maintain normal plant growth, is almost inevitable on imposition of almost all types of stresses, particularly, in photosynthetic organisms<sup>5,6</sup>. Scavenging of AOS is reported to follow the Halliwell–Asada cycle<sup>6,7</sup>. Activity of some of the enzymes of the cycle has been found absent in cyanobacteria<sup>8</sup>. Also, there is no information about purification and characterization of ascorbate peroxidase (APX) in cyanobacteria<sup>8</sup>. Effect of salinity on superoxide dismutase (SOD) and APX activity from *Microcoleus chthonoplastes* Strain SC7B9002-1 obtained from tidal channel have been studied<sup>9</sup>. Nevertheless, there is no information about behaviour of AOS systems in the desiccation-tolerant cyanobacteria subjected to variations in the levels of their hydration and especially under dry state. The main purpose of the present study was to find out any roles of AOS enzymes such as catalase, SOD and APX in survival of subaerial cyanobacterium *Lyngbya arboricola* under the extreme oxidative conditions and drought in its natural habitats.

Mats of the cyanobacterium, freshly collected as well as stored for one and two years respectively, over silica gel at 25 ± 1°C in dark just after the rainy season under dry state from their natural habitats, were used during the study. The freshly collected mats were placed over filter papers soaked with double distilled water (0 MPa, osmotic water potential) and were incubated under light intensity of 35 μE m<sup>-2</sup> s<sup>-1</sup> at 25 ± 1°C for 72 h and thereafter dried over conc H<sub>2</sub>SO<sub>4</sub> overnight. The freshly collected mats and those stored for one and two years respectively, after treatment with dry and wet heat at 100°C for 1 h as described by Talpasayi and Tripathi<sup>4</sup>, were incubated under growing condition at 0 MPa at different time periods. Thereafter, at each time period of incubation, <sup>14</sup>C-fixation and activity of AOS enzymes in cell-free extract as well as on native polyacrylamide gels were recorded. <sup>14</sup>C-fixation was measured by employing the Conway dish method<sup>10</sup>.

For preparing cell-free extract, nearly 1 g algal mats were homogenized at 4°C with 100 mM phosphate buffer (pH 7.8) containing 2 mM EDTA, 1% polyvinylpyrrolidone and 1 mM phenyl-methane sulphonyl fluoride by using mortar and pestle, and thereafter, sonicating them for

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