

Effect of the Nature and Degree of Crosslinking on the Catalase-Like Activity of Polystyrene-Supported Schiff Base-Metal Complexes

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ABSTRACT: Catalase-like activity of the metal complexes of various crosslinked polystyrene-supported Schiff bases were carried out and correlated with the nature and degree of crosslinking in the polymer support. Polystyrenes with 2–20 mol % ethyleneglycol dimethacrylate (EGDMA), 1,4-butanediol dimethacrylate (BDDMA) and 1,6-hexanediol diacrylate (HDODA) were used as polymer supports. Functions of diethylenetriamine and salicylaldehyde were incorporated to the chloromethylpolystyrene by polymer analogous reactions and complexed with Fe(II), Fe(III), Co(II), Ni(II), and Cu(II) ions. The metal uptake decreased in the order: Cu(II) > Co(II) > Ni(II) > Fe(III) > Fe(II), and extent of metal uptake by the various crosslinked system varied with the nature and degree of the crosslinking agent. The polymeric ligands and the metal complexes were character-

ized by various analytical techniques. The catalytic activities of these metal complexes were investigated towards the decomposition reaction of hydrogen peroxide. Generally among the various metal complexes, the catalytic activities decreased in the order: Co(II) > Cu(II) > Ni(II) > Fe(III) \cong Fe(II). With increasing rigidity of the crosslinking agent their catalytic activity also decreased. Of the various crosslinked systems, the catalytic activity decreased in the order: HDODA- > BDDMA- > EGDMA-crosslinked system. Also, the catalytic activity is higher for low crosslinked systems and decreased further with increasing degree of crosslinking. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1271–1278, 2004

Key words: catalysts; supports; metal-polymer complexes

INTRODUCTION

The chemistry and applications of functional polymers have received immense attention during the last few decades.^{1–3} The architectural characteristics and interdependence of the polymer microstructure and reactivity of functional groups in functional polymers dictates the applications of such systems in a number of areas of functional and technological interest.^{4–6} Polymer–metal complexes are widely used as immobilized catalysts, in which a specific catalytic behavior is induced by the polymer matrix.⁷ In addition to this catalytic activity, polymeric ligands have immense applications in various areas like conductivity, modifications of material surface by study of metal complexes, separation of metal ions, hydrogenation, and in the mimicking of a bioinorganic system.^{8–10} The nature of the polymer backbone, the conformation of the mac-

romolecular chain, the microenvironment of the reactive functional groups, the relative occurrence of functional groups in the chain, the stereochemistry around the functional group, the overall topology of the macromolecular matrix, and the solvation and swelling characteristics decide the reactivity of a functional group attached to a macromolecular backbone. The enzyme *catalase* catalyses the disproportionation of hydrogen peroxide.^{11–15} This enzyme protect against the buildup of dangerous concentration of hydrogen peroxide in living systems as a consequence of the partial reduction of dioxygen. The metal ion decomposition of hydrogen peroxide has received the attention of research workers as well as industry. The decomposition of hydrogen peroxide in homogeneous medium has been studied using metal ions and their complexes as catalysts. The applications of polymer metal complex has received much more interest in recent years.^{16,17}

The present article describes the synthesis, characterization, and catalase-like activities of the metal complexes of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrene-supported Schiff bases. The metal complexations of the various ligands were carried out towards Fe(II), Fe(III), Co(II), Ni(II), and Cu(II) ions. The decomposition reaction of hydrogen peroxide was selected as a model reaction to investigate the catalase-like activities of the synthe-

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sized polymer–metal complexes. The interdependence of the metal ion complexation and catalase-like activity with the nature and degree of EGDMA, BDDMA, and HDODA crosslinking are discussed in the following sections.

EXPERIMENTAL

All the reagents were of certified ACS reagent grade. Styrene, ethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, and 1,6-hexanediol diacrylate were purchased from Aldrich Company, Milwaukee, WI. Diethylenetriamine and salicylaldehyde were purchased from SRL, Mumbai, India. The purest available metal salts were used to prepare metal ion solutions. The IR spectra were recorded on Shimadzu IR 470 spectrophotometer. UV measurements were made on Shimadzu 160 A spectrophotometer. EPR spectra were recorded on Varian E-112 at 303 K under nitrogen atmosphere and SEM in Hitachi S-2400 instrument.

Preparation of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrenes

Two- to 20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrenes were prepared by suspension polymerization using benzoyl peroxide as the initiator and toluene as diluent. The monomer mixture was added to 1% PVA solution at 80°C kept under stirring. Stirring and heating continued for 6 h. The polymer beads were collected and washed with water, acetone, chloroform, and methanol and dried at 50°C. Polymers with varying degree of EGDMA, BDDMA, and HDODA crosslinking were prepared by varying the composition of the monomers in the monomer mixture as given in Table I.

Chloromethylation of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrenes

The polystyrene beads (10 g) were allowed to swell in dichloromethane (10 mL), SnCl₄ (99.9%) was added to the swollen crosslinked polymer containing chloromethyl methyl ether (60 mL) at 0°C with stirring. The temperature was allowed to rise slowly to room temperature and stirring continued for 55 h. The resin was collected by filtration, washed with THF–water (1 : 1), water, THF–water–HCl (1 : 1 : 1), water, methanol, and soxhletted in dichloromethane, and finally washed with methanol, and dried under vacuum. The extent of chloromethylation was followed by the modified Volhard's method. For this, the dry chloromethylpolystyrene (200 mg) was fused with pyridine (3 mL) for 4 h at 100°C. It was quantitatively transferred using 50% acetic acid (30 mL). Concentrated nitric acid (5 mL) was added followed by the slow addition of silver

TABLE I
Preparation of 2–20 mol % EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrenes

EGDMA	Styrene (mL)	EGDMA (mL)	Yield (g)
2	22.46	0.7544	13.26
4	21.99	1.5088	13.9
8	21.08	3.0176	14.31
12	20.17	4.5264	14.82
20	18.33	7.5440	15.2
BDDMA	Styrene (mL)	BDDMA (mL)	Yield (g)
2	22.46	0.8847	14.26
4	21.99	1.7695	14.89
8	21.08	3.5390	15.30
12	20.17	5.3086	16.24
20	18.33	8.8477	16.4
HDODA	Styrene (mL)	HDODA (mL)	Yield (g)
2	22.46	0.8962	14.2
4	21.99	1.7924	14.9
8	21.08	3.5846	15.6
12	20.17	5.3770	15.82
20	18.33	8.9616	16.90

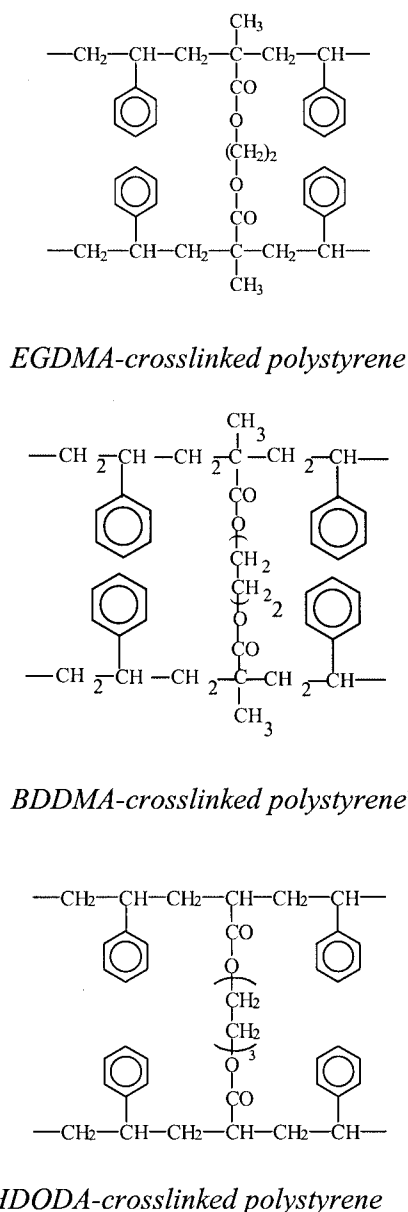
nitrate (0.1 N, 10 mL) with stirring. Water (50 mL) was added followed by sufficient amount of toluene to form a layer over the water surface. The suspension was mixed well and the excess silver nitrate was back titrated with standard ammonium thiocyanate solution using ferric alum as indicator.

Preparation of *N,N*-bis(salicylidene-2-aminoethyl)aminomethyl polystyrenes

Chloromethyl polystyrene (10 g) was allowed to swell in dioxane and stirred with the Schiff base of salicylaldehyde and diethylenetriamine (3 molar excess of the chlorine capacity) for about 48 h at 90°C. The resin was thoroughly washed with water and then soxhletted with dioxane and dried in vacuum.

Preparation of polystyrene-supported schiff base-metal complexes

Crosslinked polystyrene-supported Schiff base (200 mg) was stirred with 100 mL (0.05 N) metal salt solution for 24 h at their natural pH. The polymer–metal complexes were washed with distilled water to remove the uncomplexed metal ions. The metal uptake by the polymeric ligand was obtained from the determination of concentration of metal salt solution before and after complexation. The concentrations of Fe(III), Co(II), Ni(II), and Cu(II) were determined by spectrophotometry and Fe(II) by permanganate titration.



Scheme 1 EGDMA-, BDDMA-, and HDODA-crosslinked polystyrenes.

Catalase-like activities of crosslinked polystyrene-supported schiff base-metal complexes

A weighed quantity of the catalyst (10 mg) was stirred with 5 mL (0.2 N H₂O₂) in a thermostated reaction vessel at 30°C. After a definite time, the insoluble polymer was collected by filtration and the concentration of hydrogen peroxide (filtrate) was estimated by titrating against standard potassium permanganate solution.

RESULTS AND DISCUSSION

Preparation of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrenes

Polystyrenes with 2–20 mol % EGDMA, BDDMA, and HDODA crosslinks were prepared by suspension po-

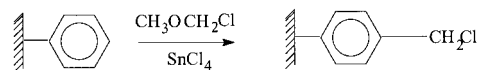
lymerization at 80°C using benzoyl peroxide as initiator and toluene as diluent. The structures of the various crosslinked systems are depicted in Scheme 1. The compositions of monomers for the preparation of different crosslinked systems and the yield of the polymers are detailed in Table I. The polymer obtained was in bead shape and of range 200–400 mesh size were used for further study.

Preparation of *N,N*-bis(salicylidene-2-aminoethyl)aminomethyl polystyrenes

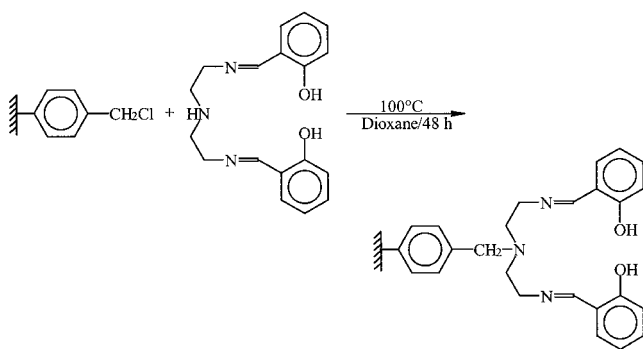
The first of the polymer-analogous reaction series employed for the introduction of the function into the polystyrene matrix is the chloromethylation of the aromatic ring. The reaction was carried out using chloromethyl methylether with anhydrous stannic chloride as the Lewis acid catalyst¹⁸ (Scheme 2). The modified Volhard's method¹⁹ was used for determining the chlorine capacity to find out the degree of chloromethylation. The chloromethyl polystyrene resins were treated with Schiff base derived from salicylaldehyde and diethylenetriamine. For the preparation of Schiff base of diethylenetriamine and salicylaldehyde, the amine and aldehyde was mixed in a 1 : 2 ratio, and this was further treated with the chloromethyl polystyrene to get the pentadentate ligand as indicated in Scheme 3. The extent of incorporation of the ligand function was followed by estimating the residual chlorine content by the modified Volhard's method and the results are given in Table II. The nature of crosslinking agent in the polymer support exerts a definite influence on the extent of functionalization. The variation observed in ligand capacity of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked systems are shown in Table II. In all crosslinked systems 2 mol % crosslinked system has maximum ligand capacity. But as the degree of crosslinking increases the ligand capacity decreases. This decrease in capacity with increasing crosslinking is less in polymers with flexible crosslinking agents. Comparing the three crosslinked systems, HDODA-crosslinked system exhibit maximum ligand capacity due to its high flexible nature.

Complexation of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrene-supported Schiff bases

On comparing the EGDMA-, BDDMA-, and HDODA-crosslinked systems, as the spacing between the two



Scheme 2 Chloromethylation of crosslinked polystyrenes.



Scheme 3 Preparation of polystyrene-supported salicylaldehyde-diethylenetriamine Schiff bases.

vinyl groups increases the extent of functionalization increased as: HDODA- > BDDMA- > EGDMA-crosslinked system. As the crosslinking agent became more flexible the low molecular weight species and metal ions can penetrate into the interior of the three-dimensional crosslinked networks facilitating more functionalization. Also, the decrease in capacity with increasing degree of crosslinking is due to the decreased availability of the reactive sites by the presence of consecutive crosslinking points. This prevents the diffusion of the low molecular reagents to enter into the interior of the networks. Complexation is significantly slow in aqueous medium presumably due to its three-dimensional network and hydrophobic character of the polystyrene matrix. This hinders the effective interaction between metal ions in the aqueous phase and the ligand sites in the dense hydrophobic polystyrene matrix. The complexation of

polystyrene-supported Schiff base of 2–20 mol % EGDMA-, BDDMA-, and HDODA-crosslinked resins were investigated towards Fe(II), Fe(III), Co(II), Ni(II), and Cu(II) ions at their natural pH. The influence of the nature and degree of crosslinking agent on metal ion complexation of different systems are given in Table II. The observed general trend in complexation in these crosslinked systems are: Cu(II) > Co(II) > Ni(II) > Fe(III) > Fe(II).

In the case of EGDMA-, BDDMA-, and HDODA-crosslinked systems the extent of Cu(II) ion complexation decreased as the degree of crosslinking increased. With increasing degree of crosslinking, ligand groups are getting buried into the polymer matrix. But this variation with degree of crosslinking is less in the more flexible HDODA-crosslinked system. In this case also lightly crosslinked systems have high ligand capacity and maximum metal uptake. Also, with increasing flexibility of the crosslinking agent, the metal uptake increased. Thus, the HDODA-crosslinked system has the highest complexation.

Characterization

The IR spectrum of the crosslinked polystyrene-supported ligand showed characteristic absorption band of benzene ring, ester, and oxime groups. The band at 3200 cm^{-1} attribute to phenolic OH-vibrations. Another band found at 2900 cm^{-1} indicated intramolecular hydrogen bonding resulting from the lowering of OH-vibration.²⁰ The bands appearing between $1020\text{--}1250\text{ cm}^{-1}$ are attributed to aliphatic N and the band at 1615 cm^{-1} can be assigned to C=N vibration. The

TABLE II
Metal Ion Uptake by EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrene-Supported Schiff Bases

Crosslink density (mol %)	Ligand capacity (mmol/g)	Metal uptake (mEq/g)				
		Fe(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)
EGDMA						
2	2.02	2.08 ± 0.06	2.10 ± 0.05	2.36 ± 0.05	2.19 ± 0.07	2.62 ± 0.04
4	1.97	1.95 ± 0.05	1.98 ± 0.04	2.25 ± 0.03	2.10 ± 0.05	2.53 ± 0.04
8	1.65	1.90 ± 0.05	1.86 ± 0.01	2.20 ± 0.02	2.02 ± 0.03	2.50 ± 0.07
12	1.50	1.81 ± 0.04	1.75 ± 0.02	2.12 ± 0.06	1.90 ± 0.05	2.42 ± 0.05
20	1.42	1.62 ± 0.03	1.62 ± 0.07	2.06 ± 0.01	1.85 ± 0.02	2.38 ± 0.04
BDDMA						
2	2.20	1.92 ± 0.06	2.02 ± 0.01	2.52 ± 0.02	2.38 ± 0.03	2.72 ± 0.03
4	1.96	1.85 ± 0.05	1.90 ± 0.06	2.48 ± 0.05	2.30 ± 0.08	2.60 ± 0.08
8	1.75	1.80 ± 0.09	1.85 ± 0.01	2.35 ± 0.07	2.28 ± 0.04	2.52 ± 0.06
12	1.62	1.60 ± 0.01	1.72 ± 0.01	2.20 ± 0.03	2.21 ± 0.04	2.48 ± 0.08
20	1.50	1.52 ± 0.08	1.68 ± 0.06	2.12 ± 0.07	2.13 ± 0.01	2.38 ± 0.02
HDODA						
2	2.12	2.30 ± 0.02	2.39 ± 0.08	2.82 ± 0.05	2.62 ± 0.04	2.90 ± 0.02
4	2.02	2.10 ± 0.04	2.30 ± 0.06	2.60 ± 0.01	2.50 ± 0.07	2.82 ± 0.06
8	1.85	1.90 ± 0.09	2.15 ± 0.08	2.52 ± 0.01	2.40 ± 0.01	2.80 ± 0.04
12	1.80	1.75 ± 0.04	2.00 ± 0.07	2.42 ± 0.04	2.32 ± 0.01	2.75 ± 0.02
20	1.75	1.72 ± 0.03	1.90 ± 0.02	2.25 ± 0.06	2.25 ± 0.07	2.68 ± 0.08

sharp decrease in intensity of the band near 3400 cm^{-1} and at 2900 cm^{-1} supports the involvement of the phenolic oxygen in metal ion coordination. The distortion of $\text{C}=\text{N}$ shifts towards lower frequency in the spectra of the polymer-metal complexes is due to the involvement of azomethine group in metal ion complexation.

The actual position of the band maximum observed in the electronic spectra is a function of the geometry and strength of the corresponding ligand.²¹ The absorption maximum around 40000 cm^{-1} is due to the azomethine chromophore ($\pi-\pi^*$) transition. In the complexes the band due to this transition is shifted to $40,160-40,223\text{ cm}^{-1}$, indicating the coordination of azomethyl group to metal ion. The polymer-anchored Co(II) complexes exhibit band in the region of $15,432-19,380\text{ cm}^{-1}$ due to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition, indicating a near-tetrahedral geometry. Polymer anchored Ni(II) complexes exhibit band in the region of $15,160-16,367\text{ cm}^{-1}$ due to the ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ transition indicating a near tetrahedral geometry. The polymer anchored Cu(II) complexes obtained in the range $17,036-18,832\text{ cm}^{-1}$ supported the square planar geometry. Fe(II) complexes exhibit bands in the region of $18,382-19,379\text{ cm}^{-1}$, ${}^1\text{T}_{1g} \rightarrow {}^1\text{T}_{2g}$ transition showing a near octahedral geometry. The polymer anchored Fe(III) complexes exhibit bands at $23,753-24,938\text{ cm}^{-1}$ due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ in a near-octahedral field.

The molecular orbital approach has proved most successful in the explanation of EPR spectra. The bonding parameter $\alpha^2\text{Cu}$ was calculated by the expression given by Kivelson and Neiman.²²

$$\alpha^2\text{Cu} = -(A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

The EPR data of Cu(II) complexes with differently crosslinked polystyrene-supported Schiff bases are in agreement with the square planar geometry of Cu(II) complex (Table III). The g_{\parallel} values almost coincide with the values of 2.3, indicating the covalent character of metal-ligand bond, i.e., $g_{\parallel} < 2.3$ for covalent character and $g_{\parallel} \geq 2.3$ for ionic character. The value of $g_{\parallel} > g_{\perp}$ shows the unpaired electron localized in the dx^2-y^2 orbital of Cu(II) ions and spectral characteristics of axial symmetry. The values of $\alpha^2\text{Cu}$ observed in the range of 0.47–0.56 support the covalent character.

The SEM technique was extensively used for studying the morphological features and the mechanism of formation of beaded polymers.^{23,24} SEM has been used as a tool for the determination of functional group distribution in the polymer matrix. The SEM of 2 mol % HDODA-crosslinked resin and complexed resin is given in Figure 1. In all cases the surface of the uncomplexed bead is smoother than that of complexed

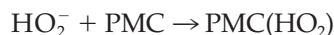
TABLE III
EPR Parameters of Various Crosslinked Polystyrene-Supported Diethylenetriamine-Salicylaldehyde Schiff Base-Cu (II) Complexes

Crosslinking agents (mol %)	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	α^2	g_{av}
EGDMA						
2	2.2006	2.1044	190	126.7	0.5275	2.130
4	2.1890	2.1079	200	123.3	0.5556	2.140
8	2.1931	2.1044	195	128.3	0.5416	2.130
12	2.2080	2.1110	175	120.0	0.4861	2.140
20	2.2006	2.1010	190	130.0	0.5277	2.134
BDDMA						
2	2.1860	2.1110	200	126.7	0.5555	2.136
4	2.2010	2.1044	185	128.3	0.5319	2.137
8	2.2040	2.1010	180	130.0	0.4999	2.135
12	2.2156	2.1045	175	128.3	0.4861	2.141
20	2.2006	2.1044	190	126.7	0.5277	2.136
HDODA						
2	2.1890	2.1110	200	121.7	0.5555	2.137
4	2.2120	2.1040	180	126.7	0.4999	2.140
8	2.2120	2.1010	175	123.3	0.4862	2.067
12	2.2160	2.1078	170	130.0	0.4722	2.108
20	2.2010	2.1010	190	123.3	0.5277	2.101

resin. The rough surface of the beads appeared because of the rearrangement of the polymer chains on complexation with metal ions.

Catalase-like activities of various crosslinked polystyrene-supported Schiff base-metal complexes in the decomposition of hydrogen peroxide

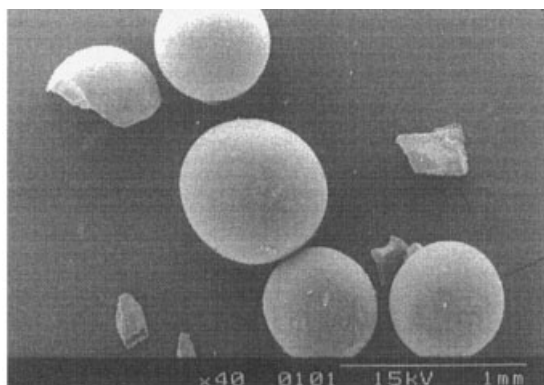
To investigate the catalase-like activity of polystyrene-supported Schiff base-metal complexes with different crosslinking, the decomposition reaction of hydrogen peroxide was chosen as a model reaction. The catalytic decomposition of hydrogen peroxide can be schematically represented as:



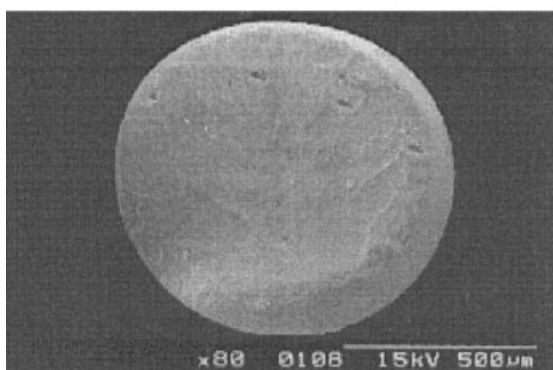
(PMC = Polymer Metal Complex)

The reactivity of a ligand function on a crosslinked polymer support is highly dependent on the variables of the polymeric network structure. The catalytic activities of the different crosslinked systems of polystyrene-Schiff base-metal complexes showed variation in reactivity with the nature and degree of crosslinking agent.

In all polystyrene systems the catalytic activity decreased in the order: Co(II) > Cu(II) > Ni(II) > Fe(III) \cong Fe(II). The variation in reactivity with metal com-



(a)



(b)

Figure 1 Scanning electron micrographs of HDODA-crosslinked (a) polystyrene-supported Schiff base, and (b) polystyrene Schiff base complex.

plexes can be explained in terms of the coordination geometry and nature of crosslinking agents. In the case of Fe(II) and Fe(III) complexes, no considerable changes were observed in reactivity with time. Representation of the variations in reactivities of the metal complexes of various crosslinked systems is given in Figure 2(a)–(c). The Ni(II), Fe(II), and Fe(III) complexes have metal–ligand ratio below 1 : 1. But compared with other metal ions, high reactivity of the Co(II) complexes are due to its vacant coordination site and its near tetrahedral geometry. The Cu(II) complexes also have similar unsaturation making them reactive by the easy accessibility of the peroxide ion for complexation.

In the case of EGDMA- and BDDMA-crosslinked systems the ligand capacity and catalytic activity are observed to be lower than that of HDODA-crosslinked system due to its lower flexible nature. In all crosslinked systems the catalytic activity of the 2 mol % crosslinked system is found to be higher and decreased with increasing crosslinking. Comparing the three crosslinked sys-

tems the catalytic activity decreased in the order: HDODA- > BDDMA- > EGDMA-crosslinked system.

Kinetics of hydrogen peroxide decomposition by polystyrene-supported Schiff base-metal complexes

The kinetics of the decomposition of hydrogen peroxide by the various metal complexes of different crosslinking agents were followed and found to be first order. The activation energy required for the decomposition decreased in the order: Fe(III) > Fe(II) > Ni(II) > Cu(II) > Co(II). This trend is irrespective of the nature of the crosslinking agent. The less activation energy of Co(II) complex compared with Cu(II) complex could arise from the unsaturation in the Co(II) coordination sphere making the easy accessibility of hydrogen peroxide molecule to get involved in the catalytic decomposition. The rather high activation energy for the Cu(II) complex results from its stability in the coordination sphere preventing easy coordination of hydrogen peroxide for catalyzing the decomposition.

In the case of HDODA-crosslinked system, the kinetics of all the complexes with varying degrees of HDODA crosslinks were studied in the decomposition of hydrogen peroxide. In 2 mol % HDODA-crosslinked polystyrene–Schiff base systems Co(II) is also a more efficient catalyst, having activation energy $15.72 \text{ kJ mol}^{-1}$ compared with other crosslinked systems. The high activation energy and the low reactivity associated with Fe(II), Fe(III), and Ni(II) complexes are due to the variation in their coordination geometry. The kinetic parameters of 2–20 mol % HDODA-crosslinked polystyrene–Schiff base-metal complexes are shown in (Table IV). As the degree of HDODA crosslinking increased the activation energy also increased. This arises from the reduced availability of the catalytic site for the catalytic decomposition of hydrogen peroxide.

In the case of BDDMA-crosslinked polystyrene–Schiff base systems the kinetics of all complexes were studied with various crosslink extents. In 2 mol % BDDMA-crosslinked systems, all the metal complexes showed less activation energy indicating higher catalytic activity. The catalytic activity of BDDMA-crosslinked system is higher than the EGDMA-crosslinked system. In the case of EGDMA-crosslinked polystyrene–Schiff base systems also Co(II) complexes required less activation energy, while Fe(III) had higher activation energy. For varying degrees of EGDMA crosslinking, the activation energy of all metal complexes decreased with increasing the degree of EGDMA crosslinking. The 2 mol % EGDMA-crosslinked polystyrene Co(II) complex showed high activity with an activation energy of 19.59 and Cu(II) with $22.14 \text{ kJ mol}^{-1}$. Comparing the three crosslinked systems, the HDODA-crosslinked system is more ef-

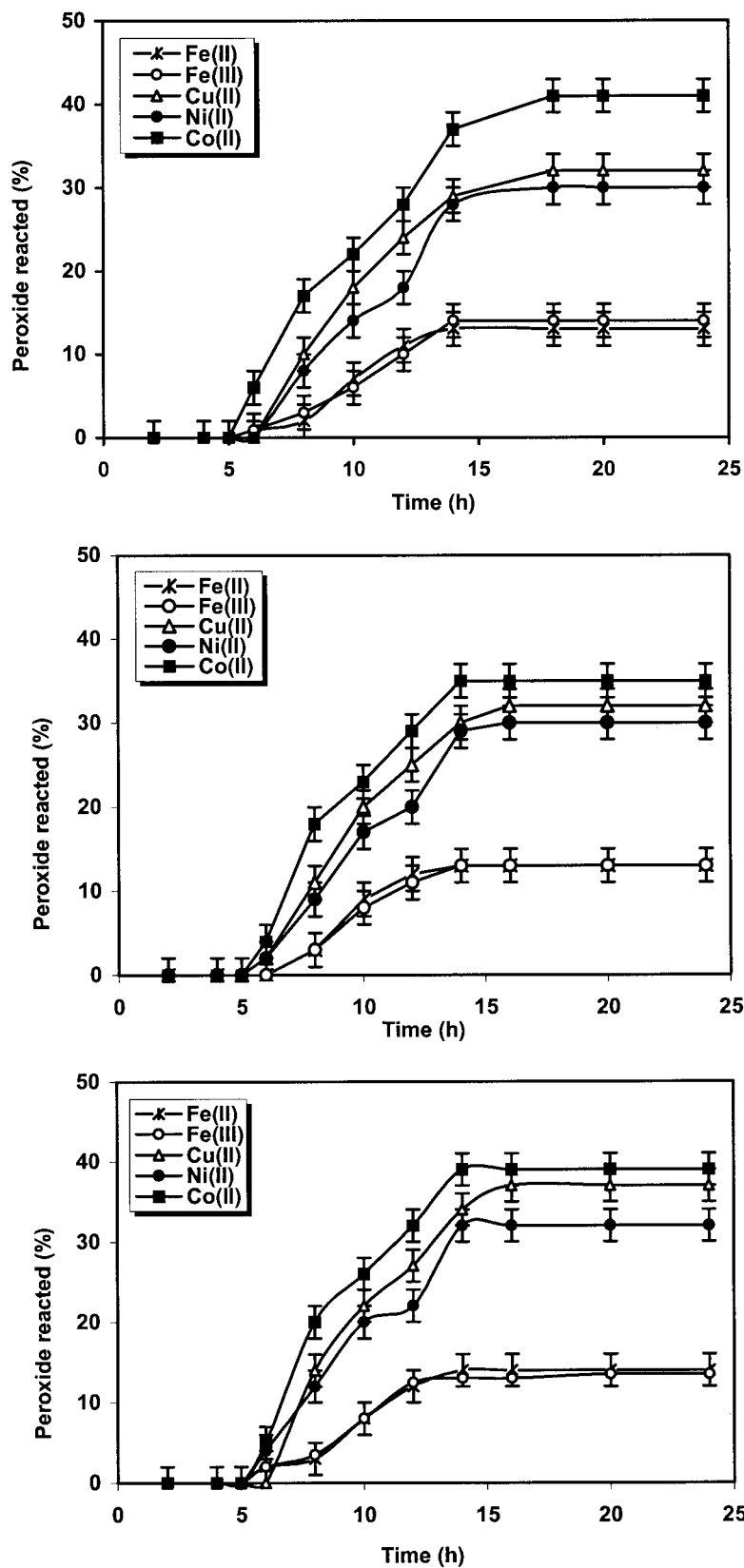


Figure 2 Catalytic activity of the various metal complexes of 2 mol % EGDMA-, BDDMA-, and HDODA-crosslinked polystyrene-Schiff base systems.

TABLE IV
Kinetic Parameters of the Decomposition of Hydrogen Peroxide Catalysed by the Various Metal Complexes of 2 mol % EGDMA-, BDDMA-, and HDODA-Crosslinked Polystyrene-Schiff Base Systems

Metal ions	ΔE (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)
EGDMA			
Fe(II)	29.690	0.1388	-261.509
Fe(III)	37.820	4.5975	-232.406
Cu(II)	22.137	2.4896×10^{-2}	-275.800
Ni(II)	22.830	2.3903×10^{-2}	-276.139
Co(II)	19.594	9.4489×10^{-3}	-283.857
BDDMA			
Fe(II)	34.224	0.5295	-250.379
Fe(III)	38.239	0.7247	-239.276
Cu(II)	21.918	2.0825×10^{-2}	-277.286
Ni(II)	22.497	2.6243×10^{-2}	-275.363
Co(II)	19.043	5.5763×10^{-3}	-288.242
HDODA			
Fe(II)	26.279	4.9103×10^{-2}	-270.153
Fe(III)	31.391	0.1679	-259.926
Cu(II)	19.826	1.0809×10^{-2}	-282.739
Ni(II)	24.901	6.4326×10^{-2}	-267.907
Co(II)	15.722	1.5380×10^{-3}	-298.950

ficient than the BDDMA- and EGDMA-crosslinked systems. This trend is in connection with the nature of the crosslinking agent in which increased separation of the polymer chains through the methylene groups of the crosslinking agents favor more reactivity.

CONCLUSION

The present investigation of different types of polymer-metal complexes and their catalase-like activity revealed the role of the characteristics of the polymer support in controlling its catalytic activity. The nature and extent of crosslinking agent has a considerable role in the present study. In all crosslinked systems metal uptake varied in the order: Cu(II) > Co(II) > Ni(II) > Fe(III) > Fe(II). The extent of metal ion uptake is controlled by the nature and degree of crosslinking in the polymer matrix. Generally, the metal uptake of crosslinked systems decreased in the order: HDODA > BDDMA > EGDMA. This is due to the increased ligand concentration in the flexible crosslinked systems. The IR absorption of the ligand functions were shifted to lower frequencies on compl-

exation. The nature of attachment of the ligand with Cu(II) ion and the coordination geometry were followed by UV-vis. and EPR spectra. The change in the surface morphology on metal ion complexation was followed by SEM. Kinetics of the decomposition was found to be first order. The factors like nature of support, extent, and nature of the crosslinking agent had a considerable role in the present study. The derived metal complexes are found to be effective models to explain catalase-like activity.

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