Effect of the Nature of Crosslinking Agent on the Catalase-Like Activity of Polystyrene-Bound Glycine-Metal Complexes

Jincy Jose[a]; Magi John[a]; Beena Mathew[a]

[a] School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India

PLEASE SCROLL DOWN FOR ARTICLE

Effect of the Nature of Crosslinking Agent on the Catalase-Like Activity of Polystyrene-Bound Glycine–Metal Complexes

Jincy Jose, Magi John, and Beena Mathew[*]

School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills, Kottayam, Kerala, India

ABSTRACT

Catalase-like activity of metal complexes of various crosslinked polystyrene-supported glycines were carried out and correlated with the nature of crosslinking agent in the polymer support. Polystyrenes with 2 mol% divinyl benzene (DVB), ethylene glycol dimethacrylate (EGDMA), and 1,6-hexanediol diacrylate (HDODA) crosslinking were used as polymer supports. Glycine functions were incorporated to the chloromethylpolystyrenes by polymer analogues reactions and complexed with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal uptake varied in the order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Ni(II) > Zn(II), and extent of metal uptake by various crosslinked systems varied with the nature of crosslinking agent. The polymeric ligands and the metal complexes were characterized by various analytical techniques. The catalytic activities of these metal complexes were investigated towards the decomposition of hydrogen peroxide and was found to decrease in the order: Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II). With increasing rigidity of the crosslinking agent the catalytic activity also decreased.

Key Words: Polymer–metal complex; Polymer-supported; Catalase-like activity; Nature of crosslinking.

[*]Correspondence: Beena Mathew, School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, Kerala, India-686 560; E-mail: mgu@md2.vsnl.net.in.

863

INTRODUCTION

Polymer-supported catalysts are particularly attractive because of its high reactivity, selectivity, and reusability.[1] The metal centers anchored on the polymeric backbone are found to exhibit characteristic catalytic behavior, which are distinctly different from their low molecular weight analogue.[2] The ease of reaction work up, nontoxicity and recyclability are the intrinsic advantages of polymer bound catalysts over the low molecular weight analogue.[3] Polymer–metal complexes have been of interest to many researchers during the last few decades in the light of their potential applications in diversified fields like organic synthesis, recovery of trace metal ions, enzyme immobilization, nuclear chemistry, and catalysis.[4–6] The reactivity of a functional group attached to a macromolecular backbone is affected by nature of the polymer backbone, conformation of the macromolecular chain, microenvironment of the reactive functional groups, overall topology of the macromolecular matrix and the solvation and swelling characteristics. The enzyme "catalase" catalyzes the disproportionation of hydrogen peroxide.[7,8] This enzyme protects against the build up of dangerous concentrations 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.[9,10]

The present paper describes the synthesis, characterization and catalase-like activities of 2 mol% divinyl benzene (DVB)-, ethylene glycol dimethacrylate (EGDMA)-, and 1,6-hexanediol diacrylate (HDODA)-crosslinked polystyrene–bound glycine–metal complexes. The metal complexations of the various glycine ligands were carried out towards Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. The decomposition reaction of hydrogen peroxide was selected as a model reaction to investigate the catalase-like activities of the synthesized polymer–metal complexes. The interdependence of metal ion complexation and catalase-like activity with the nature of crosslinking agents is discussed in the following sections.

EXPERIMENTAL

All the reagents were of certified ACS reagent grade. Styrene, DVB, EGDMA, and HDODA were purchased from Aldrich Chemical Company, USA. Glycine was purchased from SRL, Mumbai, India. The purest available metal salts were used to prepare metal ion solutions. ^{13}C CP-MAS NMR spectra were recorded on a DSX 300 MHz instrument. The IR spectra were recorded on a Bruker IFS-55 spectrometer and UV–VIS spectra on a Shimadzu UV-160A spectrophotometer. EPR spectra were recorded on Varian E-4X band spectrophotometer at 303K under nitrogen atmosphere. A scanning electron micrograph (SEM) was carried out using a Jeol JSM 35 CF model.

Preparation of Divinyl Benzene-, Ethylene Glycol Dimethacrylate-, and 1,6-Hexanediol Diacrylate-Crosslinked Polystyrene-Supported Glycines: General Procedure

Preparation of 2 mol% Divinyl Benzene-, Ethylene Glycol Dimethacrylate-, and 1,6-Hexanediol Diacrylate-Crosslinked Polystyrenes[11]

Styrene (destabilized with 1% NaOH followed by washing with distilled water) was dried over anhydrous Na$_2$SO$_4$. Styrene and the respective crosslinking agents in

the required amount along with the initiator, benzoyl peroxide (500 mg) and toluene as the diluent were added to a 1% PVA solution in water kept under stirring at 80°C. The polymerization was allowed to proceed for 6 h. The white shining beads obtained were collected and washed thoroughly with water, acetone, benzene, and methanol to remove all low molecular weight impurities. The polymer beads were washed with dichloromethane followed by acetone, dried at 50°C.

Chloromethylation of Crosslinked Polystyrenes[12]

The various crosslinked polystyrene beads (10 g) were allowed to swell in dichloromethane (100 mL), $SnCl_4$ (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.

Estimation of Chlorine Capacity: Volhard's Method[13]

Chloromethyl resin (50 mg) was digested with pyridine (4 mL) at 110°C for 6 h. The mixture was quantitatively transferred with a acetic acid–water mixture (1 : 1 v/v, 30 mL) to a conical flask. To this, water (25 mL), conc.HNO_3 (5 mL), and $AgNO_3$ (0.05 M, 5 mL) were added and titrated against standard ammonium thiocyanate (0.1 M) using a ferric alum indicator. A blank was also performed.

Preparation of Polystyrene-Bound Glycines

Chloromethylpolystyrene (10 g) was allowed to swell in dioxane (50 mL). Triethylamine (0.5 mL) was added as an acid acceptor and refluxed at 90°C with excess sodium salt of glycine for 48 h. The reaction mixture was poured in to water containing crushed ice. The resin was collected by filtration, washed with water, dioxane, methanol, and acetone until the filtrate was free from sodium hydroxide confirmed from the litmus test, and from glycine by a negative ninhydrin test, soxhletted using methanol and acetone, and dried under vacuum.

Estimation of Carboxyl Capacity of Glycine Incorporated Polystyrenes

Each of the various crosslinked polystyrene-supported glycine (100 mg) was equilibrated with HCl (0.2 N, 10 mL) for 24 h with stirring. The resin samples were filtered, washed with distilled water to remove unreacted HCl and the filtrate was titrated aganist NaOH (0.2 N) to a phenolphthalein end point.

Preparation of Polystyrene Bound Glycine–Metal Complexes

Crosslinked polystyrene-bound glycines (100 mg) was stirred with 50 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 concentration of Cr(III), Fe(III), Co(II), Ni(II), and Cu(II) were determined specrophotometrically, and Mn(II) and Zn(II) by complexo-metric titrations.

pH Dependence of Metal Ion Complexation

The metal ion intake of the resin was studied as a function of pH to determine the optimum pH for maximum complexation. The pH of the metal ion solution was adjusted by adding diluted HCl or NaOH. The use of buffer solutions for the control of pH will cause undesirable results due to the coordination of the ionic species with metal ions. The glycine resin (50 mg) was added to the metal salt solution (50 mL) of definite pH and kept for complexation by stirring for 8 h. The metal ion concentrations before and after complexation were estimated.

Swelling Studies

Two hundred milligram each of the different polymers were equilibrated with 50 mL distilled water for 48 h. The swollen resin was collected by filteration, adhering traces of water were removed by wiping with blotting paper, and the swollen weight was determined. The samples were dried in vacuum and weighed.

Catalase-Like Activities of Crosslinked Polystyrene Bound Glycine–Metal Complexes

A weighed quantity of the catalyst (10 mg) was stirred with 5 mL (0.2 N H_2O_2) in a thermostated reaction vessel at 30°C. After a definite time, the insoluble polymer was collected by filtration and the concentration of unreated hydrogen peroxide was estimated by titrating against standard potassium permanganate solution.

RESULTS AND DISCUSSION

Preparation of Various Crosslinked Polystyrenes

Polystyrenes with different crosslinking agents were prepared by suspension polymerization (Sch. 1). The polymers were obtained as beads with >95% yield.

Preparation of Polystyrene Bound Glycines

The first of the polymer-analogous reaction series employed for the introduction of glycine function into the polystyrene matrix is the chloromethylation of the aromatic ring. The reaction was carried out using chloromethyl methyl ether with anhydrous stannic chloride as the Lewis acid catalyst (Sch. 2). The extent of chloromethylation was followed by Volhard's method. The chloromethylated polystyrene was further treated with excess sodium salt of glycine as shown in Sch. 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 1.
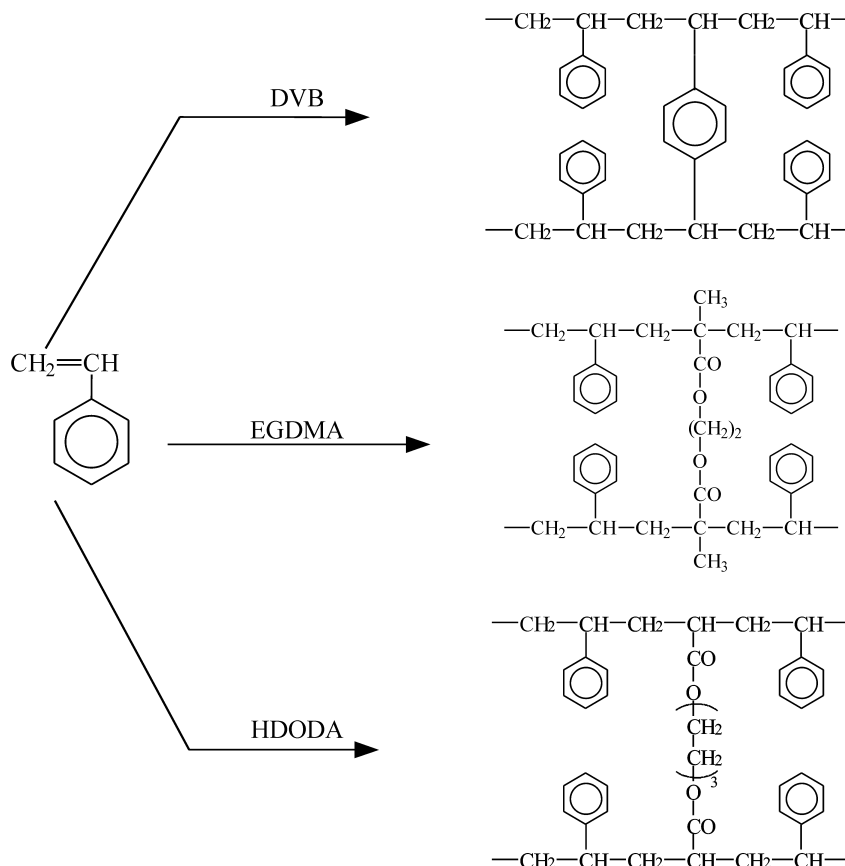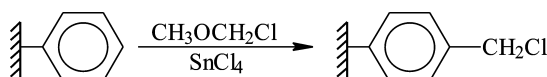
Scheme 1. Preparation of 2 mol% DVB-, EGDMA-, and HDODA-crosslinked polystyrenes.

The nature of crosslinking agent in the polymer support exerts a definite influence on the extent of functionalization. Comparing the three crosslinked systems, HDODA-crosslinked system exhibits maximum ligand capacity due to its high flexible nature.

Complexation of Divinyl Benzene-, Ethylene Glycol Dimethacrylate-, and 1,6-Hexanediol Diacrylate-Crosslinked Polystyrene-Bound Glycines

The complexation of polystyrene-supported glycines were investigated towards Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions at their natural pH by batch equilibration method. The observed general trend in complexation in these

Scheme 2. Chloromethylation of 2 mol% DVB-, EGDMA-, and HDODA-crosslinked polystyrenes.
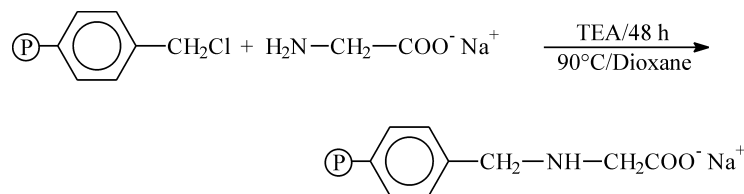
Scheme 3. Preparation of various polystyrene bound glycines.

crosslinked systems are: Cu(II) > Cr(III) > Mn(II) > Co(II) > Ni(II) > Fe(III) > Zn(II). General coordination pattern of the derived metal complexes is given in Sch. 4.

On comparing the DVB-, EGDMA-, and HDODA-crosslinked systems, the extent of functionalization decreased as HDODA- > EGDMA- > DVB-crosslinked system. The complexation of HDODA-crosslinked polystyrene-supported glycines is high when compared with DVB and EGDMA systems (Table 2). This is due to the increased flexibility of the HDODA-crosslinked system, which imparts greater flexibility and spacing between the polymer chains. With an increase in flexibility, metal ions can penetrate into the interior of the crosslinks, thereby giving effective interaction between the ligand sites buried within the three dimensional network, and metal ions in an aqueous medium resulting in higher complexation values.

In the case of EGDMA, the metal ion complexation is found to be less compared with HDODA due to the less flexible nature. With rigid and hydrophobic DVB crosslinks, the polystyrene system becomes totally rigid and hydrophobic. This increased hydrophobicity and low ligand capacity were the reason for less complexation of this system.

Characterization

In order to characterize various crosslinked polystyrenes ^{13}C CP-MAS NMR spectra of DVB-, EGDMA-, and HDODA-crosslinked polystyrenes were recorded. The ^{13}C-NMR spectrum of 2 mol% DVB-crosslinked polystyrene gave an intense peak at 130.931 ppm corresponding to the aromatic carbon and a small peak at 148.541 ppm corresponding to the C-3 carbon of the polystyrene ring. The backbone carbon of the polymer appears as a single peak at 43.243 ppm. In the case of the EGDMA-crosslinked system these characteristic peaks are at 130.773, 148.723, and 42.959 ppm, respectively. While the

Table 1. Extent of incorporation of chloromethyl and carboxyl groups in crosslinked glycine incorporated polystyrenes.

Crosslinking agent	Chlorine capacity (mmol g^{-1})	Carboxyl capacity (mmol g^{-1})
DVB	4.74	3.72
EGDMA	4.99	4.28
HDODA	5.45	4.94
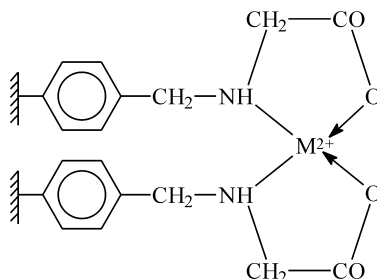
Scheme 4. General coordination pattern of polystyrene bound glycine–metal complexes.

HDODA-crosslinked system gave peaks at 130.629 and 42.991 ppm for the aromatic ring and C-3 carbon of the polystyrene ring (Fig. 1). Because of the very low concentration of the crosslinking agents, the peaks corresponding to the crosslinking agents are absent in the respective NMR spectrum.

The FTIR spectra of chloromethylated polystyrene showed a characteristic absorption band for the aromatic ring at $1597 \, cm^{-1}$. The absorption at $1720 \, cm^{-1}$ indicates the presence of ester linkage of the EGDMA and HDODA crosslinking agents. The peak at $850 \, cm^{-1}$ is characteristic of a benzene ring of DVB crosslinking. Also, chloromethyl-polystyrene shows a strong absorption band at $690 \, cm^{-1}$ due to C—Cl stretching modes. Another band at $2900 \, cm^{-1}$ indicated the presence of —CH_2 group. In the glycine incorporated polymer, the carboxylate group absorbs strongly at $1660 \, cm^{-1}$ and weakly at $1410 \, cm^{-1}$. These bands originate from the asymmetric $(C\text{-}O)_2$ stretching of the carboxylate group. Complexation with metal ion resulted in the shift of absorption from 1660 to $1639 \, cm^{-1}$. Metal ion complexation weakens the double bonding character of the carboxylate group due to the coordinate bond between the oxygen atom of carboxyl group with the metal ion.[14] Similar observation of shifts in the carboxyl group frequencies on complexation were reported.[15]

The actual position of the band maximum observed in the electronic spectra is a function of the geometry and the strength of the coordinating ligand.[16] The Cu(II) complexes exhibit a broad band corresponding to the d–d transitions $^2B_{1g} \rightarrow \, ^2B_2g$ with λ_{max} between $14,285$–$14,534 \, cm^{-1}$ and $^2B_{1g} \rightarrow \, ^2Eg$ in the range $25,316$–$29,069 \, cm^{-1}$. These suggest a distorted octahedral/square planar geometry for the polystyrene-supported glycine–Cu(II) complexes.[17] Cr(III), Fe(III), and Mn(II) complexes showed

Table 2. Metal ion uptake by DVB-, EGDMA-, and HDODA-crosslinked polystyrene-supported glycines.

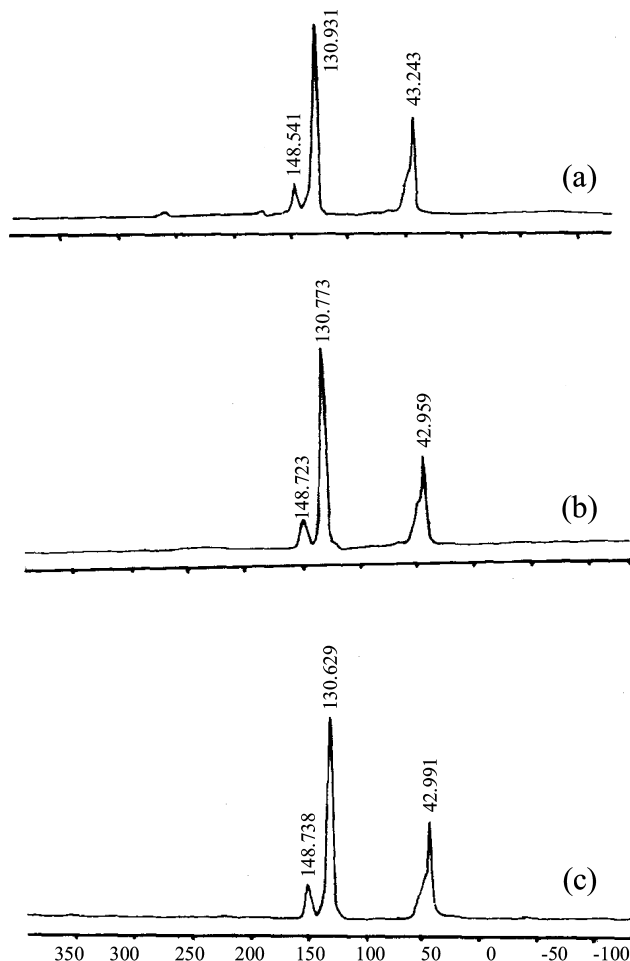| Cross-linking agent	Ligand capacity (mmol g^{-1})	Metal uptake (meq g^{-1})						
		Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
DVB	3.72	1.90	1.82	1.09	1.64	1.35	2.1	0.94
EGDMA	4.28	2.42	2.25	1.34	2.08	1.67	2.60	1.01
HDODA	4.94	2.64	2.41	1.58	2.25	1.89	2.88	1.30

Figure 1. ^{13}C CP-MAS NMR spectra of (a) DVB-, (b) EGDMA-, and (c) HDODA-crosslinked polystyrenes.

transitions of octahedral geometry, with absorption maxima in the region 18,301–18,927 cm^{-1} (^4A_2g–^4T_2g) (F) and 24,213–24,509 cm^{-1} (^4A_2g–^4T_1g) (F) for Cr(III) complex, 12,121–13,227 cm^{-1} (^6A_1g–^4T_1g) (G), 18,331–19,762 cm^{-1} (^6A_1g–^4T_2g) (G) for Fe(III) complex, a broad band between 24,000–24,510 cm^{-1} which is supposed to be the combination of ^6A_1g–^4T_2g (G), and ^6A_1g–^4Eg (G) for the Mn(II) complex. The Ni(II) complex shows as near octahedral geometry with λ_{max} in the region 15,337–16,666 cm^{-1} (^3A_2g–^3T_1g) (P) and 24,271–25,445 (^3A_2g–^3T_2g) (F). The polymer anchored Co(II) complexes exhibits bands in the region 26,041–27,472 cm^{-1} and 38,610–41,152 cm^{-1} due to (^4T_1g–^4T_2g) (F) and ^4T_1g (F)–^4T_1g (P) transitions of near octahedral geometry. In the polymer anchored Zn(II) complex, the spectrum obtained is ligand related and no d–d transition occurs, therefore, it has a tetrahedral geometry.

The molecular orbital approach has proved most successful in the explanation of EPR spectra. The bonding parameter $\alpha^2 Cu$ was calculated by the expression given by Kivelson and Neiman.[18]

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

The EPR spectra of the DVB-, EGDMA-, and HDODA-crosslinked polystyrene-supported glycine–Cu(II) complexes are given in Fig. 2. The EPR data of Cu(II) complexes with differently crosslinked polystyrene-supported glycines are in agreement with distorted octahedral/square planar geometry for Cu(II) complex[19] (Table 3). The $g_\parallel$ values 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 the ionic character. The value of $g_\parallel > g_\perp$ shows the unpaired electron localized in $dx^2 - y^2$ orbital of Cu(II) ions and spectral characteristics of axial symmetry. The value of $\alpha^2 Cu$ together with the value of $g_\parallel < 2.3$, suggests the covalent nature of the complex formed.

The SEM technique was extensively used for studying the morphological features and the mechanism of the formation of beaded polymers.[20] The SEM of 2 mol% HDODA-crosslinked polystyrene-supported glycine and the corresponding Cu(II) complex are given in Fig. 3. In all cases, the surface of the uncomplexed bead is smoother than that of the complexed resin. Metal ion complexation acts as additional crosslinking between the neighboring ligands through metal ions, resulting in the rearrangement of the polymer chains from their normal position for complexation with metal ions.
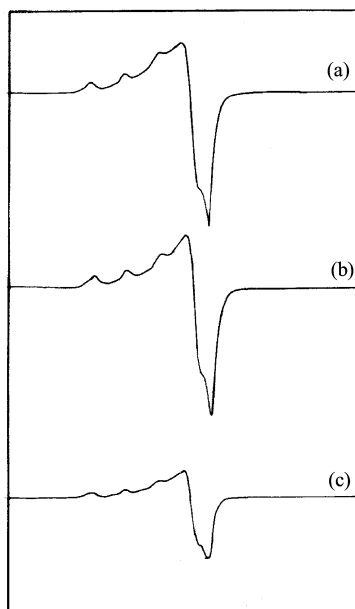

Figure 2. EPR spectra of 2 mol%, (a) DVB-, (b) EGDMA-, and (c) HDODA-crosslinked polystyrene-supported glycine–Cu(II) complexes.

Table 3. EPR parameters of the Cu(II) complexes of DVB-, EGDMA-, HDODA-crosslinked polystyrene-supported glycines.

Crosslinking agents (mol%)	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$\alpha^2 Cu$
DVB	2.25	2.04	156.67	38.33	0.7489
EGDMA	2.26	2.05	160.00	43.33	0.7581
HDODA	2.27	2.045	155.00	43.00	0.7456

pH Dependence of Complexation

The metal ion complexation of polymeric ligands is highly dependent on the equilibrium pH of the medium.[21] In order to investigate the optimum pH for maximum complexation, batch studies were carried out at varying pH. The pH dependence of complexation was studied for the regions above and below the natural pH of the metal salts solution in aqueous medium. In all cases, the upper limit was just below the precipitation. The results of the pH studies reveal that at low pH values, the non-ionic bonding mechanism (e.g., hydrogen bonding) as well as protonation of carboxylate group occur and this lowers the metal ion binding. Since the proton dissociation of carboxyl group is favored in the alkaline pH region, high metal ion binding should take place at higher pH values (Fig. 4). The results indicate that the optimum pH for different metal ions are Mn(II)—5.5, Cr(III)—3, Fe(III)—2.6, Co(II)—6.0, Ni(II)—6.0, Cu(II)—4.47, and Zn(II)—6.0. In all the above cases pH dependence of metal ion binding is independent of the nature of the crosslinking agent. It is also found that the metal ion intake reaches a maximum at the optimum pH and decreases thereafter.

Swelling Studies of Various Crosslinked Polystyrenes, Polystyrene-Supported Glycines, and Cu(II) Complexes

For a crosslinked polymer, the extent of swelling depends on the solvent–polymer interaction which is determined not only by the nature of the solvent and polymer matrix
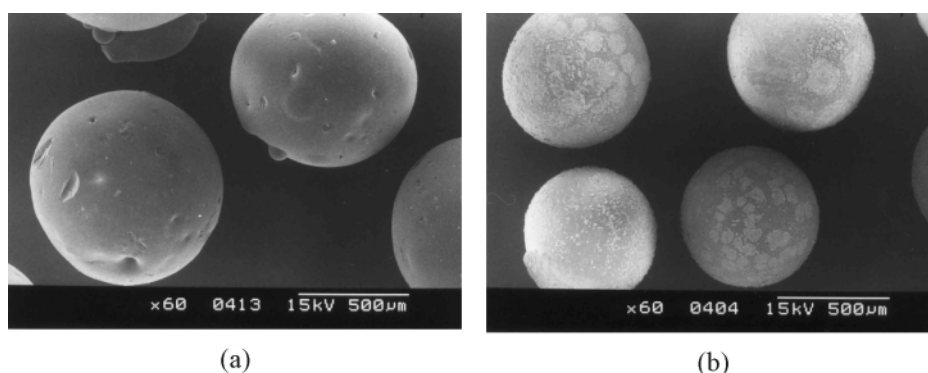

Figure 3. Scanning electron micrograph of (a) HDODA-crosslinked polystyrene supported glycine, and (b) Cu(II) complex.
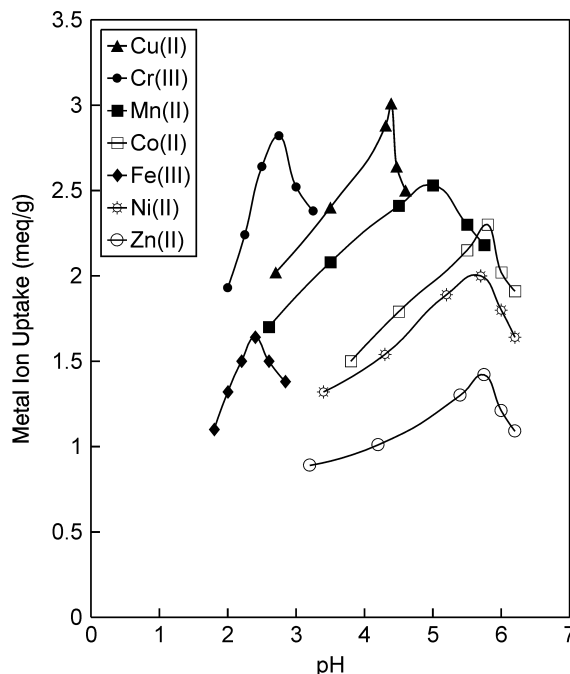
Figure 4. pH dependence on metal ion complexation of HDODA-crosslinked polystyrene-supported glycines.

but also by the active groups introduced in the polymer matrix. The extent of swelling of the polymer in water is represented as the equilibrium water content (EWC), which is expressed as,

$$EWC = \frac{Wt.\ of\ wet\ resin - Wt.\ of\ dry\ resin}{Wt.\ of\ wet\ resin} \times 100$$

In the present investigation, swelling properties of DVB-, EGDMA-, and HDODA-crosslinked polystyrenes before and after functionalization and their Cu(II) complexes were followed. The swelling behavior of various crosslinked polystyrenes is less than those with the polar glycine moieties. This is because of the change in polarity of the support on functionalization with the sodium salt of glycine. But on metal ion complexation the swelling decreased drastically. The metal-ligand bond acts as an additional crosslinking, leading to strong chain contraction, eventually resulting in decreased swelling of the polymer.[22] This results in the overall decrease in the swelling behavior of the polystyrene-supported glycine–Cu(II) complexes (Fig. 5). This decrease is much higher in the case of the more flexible HDODA-crosslinked system. These polystyrene supports differ in rigidity and hydrophilic/hydrophobic nature arising from the nature of crosslinking.
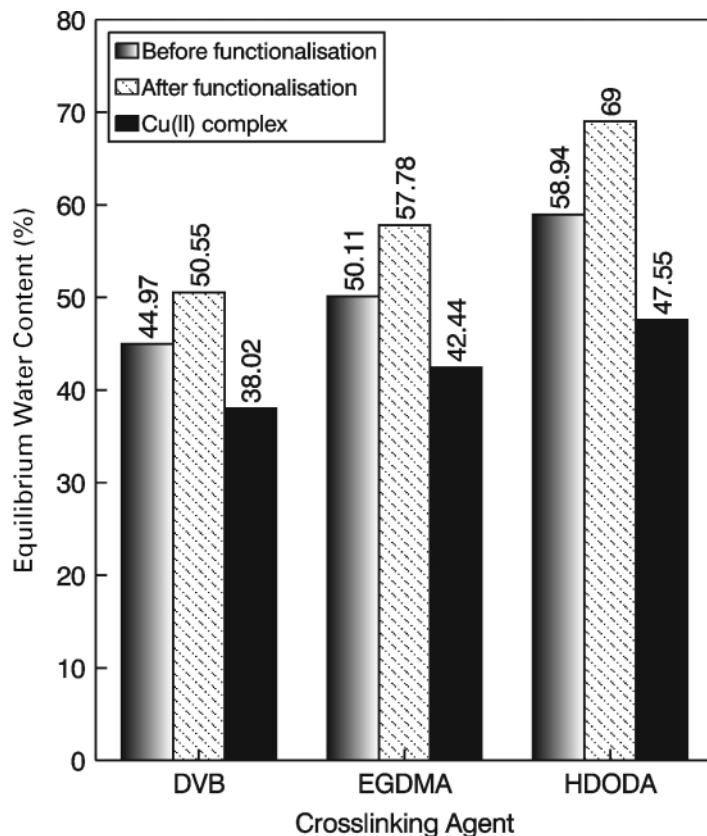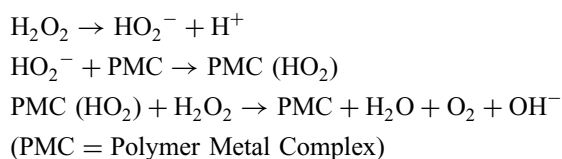
Figure 5. Swelling studies of polystyrene-supported glycines.

Catalysis of H_2O_2 Decomposition by 2 mol% Divinyl Benzene, Ethylene Glycol Dimethacrylate, and 1,6-Hexanediol Diacrylate-Crosslinked Polystyrene-Supported Glycine–Metal Complexes

In order to investigate the catalase-like activity of the polystyrene-supported glycine metal complexes, the decomposition of hydrogen peroxide was chosen as a model reaction. The catalytic decomposition of hydrogen peroxide can be schematically represented as:

$$H_2O_2 \rightarrow HO_2^- + H^+$$
$$HO_2^- + PMC \rightarrow PMC\,(HO_2)$$
$$PMC\,(HO_2) + H_2O_2 \rightarrow PMC + H_2O + O_2 + OH^-$$
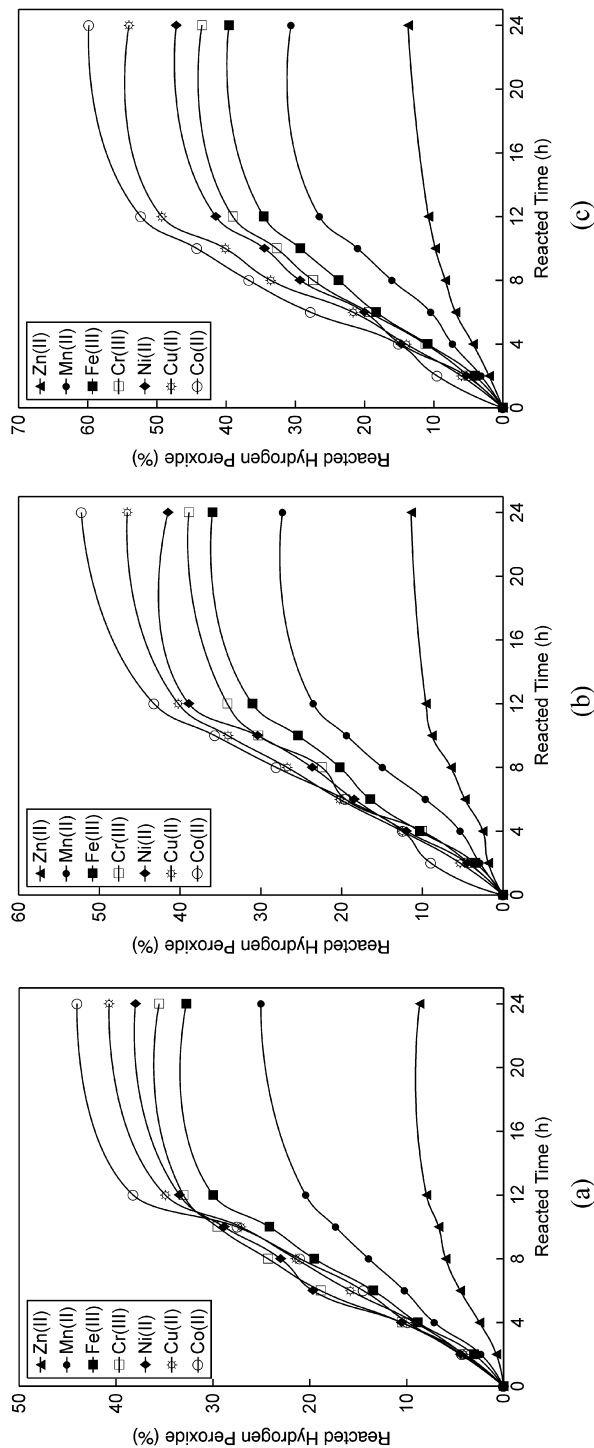$$(PMC = Polymer\ Metal\ Complex)$$

Figure 6. Catalytic activity of the various metal complexes of 2 mol% (a) DVB-, (b) EGDMA-, and (c) HDODA-crosslinked polystyrene-glycine metal complexes.

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 different crosslinked systems of polystyrene-supported glycine systems showed variation in reactivity with nature of the crosslinking agent.

In all polystyrene systems, irrespective of the nature of crosslinking agent, the catalytic activity decreased in the order: $Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II)$. The variation in reactivity with metal ions can be explained in terms of their coordination geometry. In the case of $Zn(II)$ complexes, no considerable change was observed in reactivity with time. Representation of variations in reactivities of the metal complexes of various crosslinked systems are given in Fig. 6. Compared with other metal complexes, the high reactivity of the $Co(II)$ complexe is due to its vacant coordination site and its near octahedral geometry. The $Cu(II)$ complexes also have similar unsaturation making them reactive by the easy accessibility of the peroxide ion for complexation. Comparing the three crosslinked systems, the catalytic activity decreased in the order HDODA- > EGDMA- > DVB-crosslinked system (Fig. 7). Of the various crosslinked systems, the HDODA-crosslinked system shows higher catalytic activity due to the flexible and hydrophilic nature of the crosslinking agent.

Kinetic studies of hydrogen peroxide decomposition by $Co(II)$ complexes of different crosslinked systems were followed. The decomposition of H_2O_2 was found to be first order (Figs. 8 and 9). The kinetic parameters calculated by following the reaction at two different
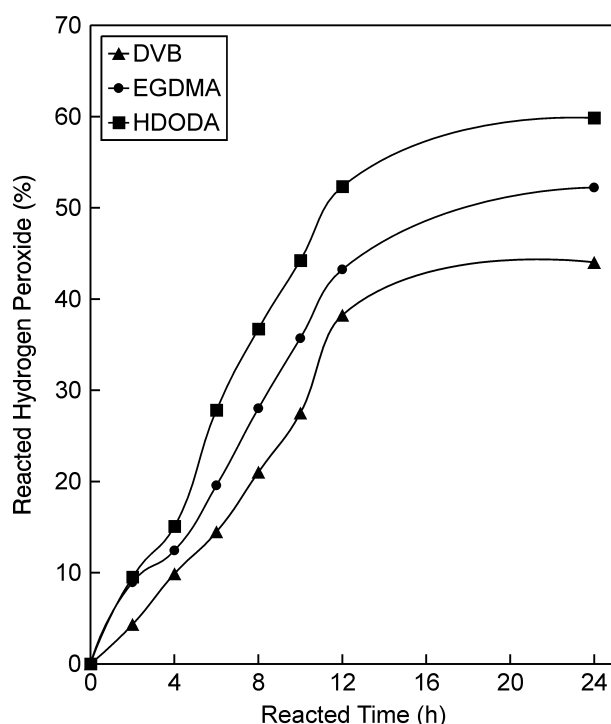
Figure 7. Effect of nature of crosslinking agent on the catalytic decomposition of H_2O_2 by DVB-, EGDMA-, and HDODA-crosslinked polystyrene-supported glycine–Co(II) complexes.
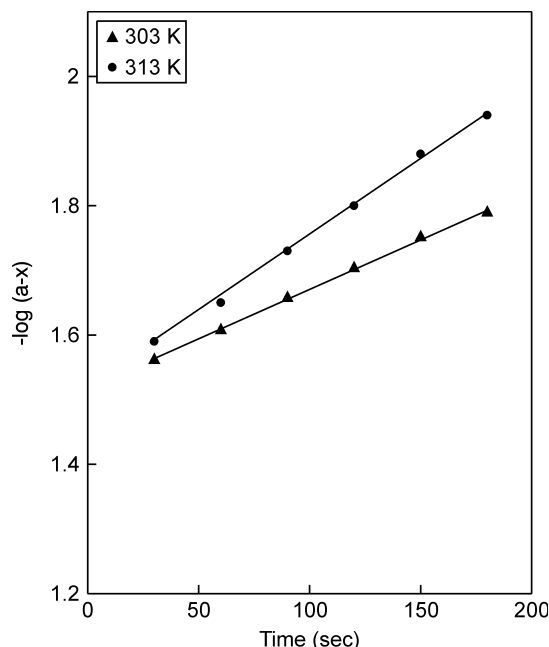
Figure 8. Kinetic curves for the decomposition of H_2O_2 catalyzed by 2 mol% HDODA-crosslinked polystyrene-supported glycine–Co(II) complex (*a*—initial concentration of H_2O_2; *x*—fraction decomposed at time *t*).

temperatures and from the rate constants of the reaction at a series of temperatures are found to be consistent (Table 4).

The less activation energy of Co(II) complex compared with other metal complexes arise from the unsaturation in the coordination sphere resulting in easy accessibility of hydrogen peroxide molecules to get involved in the catalytic decomposition. HDODA-crosslinked system has low activation energy due to easy accessibility of the catalytic sites compared with other crosslinked systems. The activation energy of EGDMA-crosslinked system is less when compared to DVB-crosslinked system and high compared to HDODA-crosslinked system. DVB-crosslinked system requires high activation energy due to the hydrophobic and rigid nature of the crosslinking agent.

CONCLUSION

The foregoing investigations on the metal ion complexation behavior of polystyrene-supported glycines in different structural environments suggest that the metal ion complexation depends on the nature of crosslinking agent in the polymer support. The metal ion complexation followed the order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Ni(II) > Fe(III) > Zn(II) and was found to be increased as the crosslinking agent changes from DVB to EGDMA to HDODA. ^{13}C CP-MAS NMR spectra were used to characterize all the
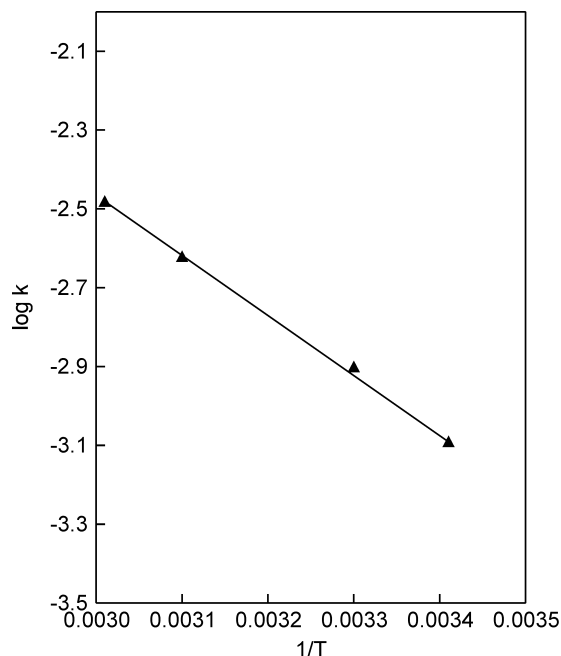
Figure 9. Variation of rate constant with temperature in the decomposition of hydrogen peroxide catalyzed by Co(II) complexes of HDODA-crosslinked polystyrene-supported glycine.

prepared crosslinked polymers. The FTIR band characteristics of the ligand group absorptions were used to follow the complexation with metal ion. UV–VIS absorption studies indicated that the Cu(II) has distorted octahedral/square planar geometry. Cr(III), Fe(III), Mn(II) were assigned to have octahedral geometry, Ni(II) and Co(II) have near octahedral geometry and Zn(II) has tetrahedral geometry. The EPR spectra also indicated a distorted octahedral geometry for Cu(II) complexes. The changes in the surface morphology of the crosslinked polystyrene supported glycine on metal complexation were followed by SEM. The swelling and solvation characteristics of the crosslinked polymer, functionalized resin, and their Cu(II) complexes were followed. In general, the metal ion complexation behavior of a crosslinked polymer-supported ligand depends on the nature as well as the relative rigidity and flexibility of the crosslinking agent used in the polymer

Table 4. Kinetic parameters of the decomposition of H_2O_2 catalyzed by Co(II) complexes of various polystyrene-supported glycines.

Crosslinking agent	E (kJmol^{-1})	A (s^{-1})	ΔS (J)
DVB	24.09	9.45×10^{-2}	−270.54
EGDMA	19.42	4.26×10^{-2}	−281.85
HDODA	15.772	1.55×10^{-2}	−291.95

support The investigation based on the catalase-like activity of polystyrene-supported glycine–metal complexes reveals that they are effective models to portrait the enzyme-like activity.

REFERENCES

1. Hodge, P. Chem. Soc. Rev. **1997**, *26*, 417.
2. Kaliyappan, T.; Kannan, P. Prog. Polym. Sci. **2000**, *25*, 343.
3. Shuttleworth, S.J.; Allin, S.M.; Wilson, R.D.; Nastunica, D. Synthesis **2000**, *8*, 1035.
4. Pillai, V.N.R.; Mathew, B. Ind. J. Tech. **1993**, *31*, 302.
5. Rivas, B.L.; Seguel, G.V.; Ancatripal, C. Polym. Bull. **2000**, *44*, 445.
6. Thamizharasi, S.; Venkata Rami Reddy, A.; Balasubramanian, S. J. Appl. Poly. Sci. **1998**, *67*, 177.
7. Sigel, H.; Wyass, K; Fischer, B.E.; Prijs, B.E. Inorg. Chem. **1979**, *18*, 1354.
8. Gokak, D.T.; Kamath, B.V.; Ram, R.N. J. Appl. Polym. Sci. **1988**, *35*, 1523.
9. Vinodkumar, G.S.; Mathew, B. Eur. Polym. J. **1998**, *34* (8), 1185.
10. Elsonbati, A.Z.; Hussaeir, A.M.; Mohamed, M.T.; Elmoiz, A.B.A. Polym. Degr. Stab. **1994**, *46*, 31.
11. Sherrington, D.C.; Hodge, P. Eds. *Polymer Supported Reactions in Organic Synthesis*; J. Wiley & Sons: New York, 1980.
12. Pepper, W.; Paisely, H.M.; Young, M.A. J. Chem. Soc. **1953**, 4097.
13. Stewart, J.M.; Young, J.D. *Solid Phase Peptide Synthesis*, 2nd Ed.; Pierce Chemical Co.: Illinois, 1984; 54 pp.
14. Mackawa, E.; Koshijima, T. J. Appl. Polym. Sci. **1990**, *6*, 1601.
15. Nakamoto, K.; McCarthy, P.J. *Spectroscopy and Structure of Metal Chelate Compounds*; Wiley: New York, 1968; 269 pp.
16. Kurimura, Y. Adv. Polym. Sci. **1990**, *90*, 105.
17. Deepa, K.P.; Aravindakshan, K.K.; Suhara, F. Asian J. Chem. **2001**, *13*, 1549.
18. Kivelson, D.; Neiman, R. J. Chem. Phys. **1961**, *35*, 149.
19. Peisach, J.; Blumberg, W.C. Arch. Biochem. Biophys. **1970**, *165*, 691.
20. Mathiowitz, E.; Klive, D.; Langer, K. Scanning Microscopy **1990**, *4*, 329.
21. Janes, J.; Morcellet, M.M.; Delporte, M.; Morcellet, H. Eur. Polym. J. **1992**, *28*, 185.
22. Quin, F.X.; Kampt, E.; Symyth, G.; McBriety, V.J. Macromolecules **1988**, *21*, 3191.