Pergamon

Eur. Polym. J. Vol. 34, No. 8, pp. 1185–1190, 1998

Printed in Great Britain
0014-3057/98 $—see front matter

PII: S0014-3057(97)00244-9

POLYMER–METAL COMPLEXES OF GLYCINE FUNCTIONS SUPPORTED ON *N,N′*-METHYLENE-BIS-ACRYLAMIDE (NNMBA)-CROSSLINKED POLYACRYLAMIDES: SYNTHESIS, CHARACTERISATION AND CATALYTIC ACTIVITY

G. S. VINODKUMAR and BEENA MATHEW*
School of Chemical Sciences, Mahatma Gandhi University, Kottayam Kerala 686 560, India

(Received 14 February 1997; accepted in final form 17 June 1997)

Abstract—Polyacrylamides with 2–20 mol% NNMBA crosslinks were prepared by the solution polymerisation of the monomers in water. Glycine functions were incorporated by transamidation with excess sodium salt of glycine. Metal ion complexations of these glycine functions in varying structural environments were investigated towards Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. The metal uptake varied in the order: Cu(II) > Ni(II) ≈ Co(II) > Fe(III) > Fe(II). With increasing degree of crosslinking, the metal uptake increased till 8% crosslinking and decreased further. The metal complexes were characterised by IR and UV spectra. The catalase-like activities of these insoluble metal complexes were investigated by the decomposition of hydrogen peroxide. Co(II) and Cu(II) complexes were found to be effective in the catalytic decomposition of hydrogen peroxide. The catalytic decomposition was found to be first order. The effect of the variables of catalysis like time, temperature, pH, amount of catalyst and the concentration of hydrogen peroxide on the decomposition of hydrogen peroxide were followed. The extent of catalysis varies with the degree of NNMBA crosslinking. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The study of polymer-supported ligands and derived metal complexes is relevant in the areas of metal ion separation, catalysis and in bioinorganic chemistry [1–3]. In a polymeric ligand or polymer–metal complex, the ligand function is often only a small part of the three-dimensional polymer support. Hence it is subjected to a number of structural variables compared to a low molecular weight ligand. This indicates a definite dependence on the complexing abilities of the insoluble polymeric ligands and physicochemical properties of the derived polymer–metal complexes [4–6]. Polymer–metal complexes are widely used as immobilised catalysts with high specificity [7]. The three-dimensional macromolecular matrix imparts selectivity and increased catalytic activity to the polymer–metal complexes when compared to the corresponding low molecular weight species. The insolubility of the polymer–metal complexes makes easy separation of the catalyst from the reaction mixture. The macromolecular characteristics of the polymer support, like the nature of the polymer backbone, chemical nature and degree of crosslinking and the microenvironment around the coordination sphere, determine the catalytic activities of the polymer–metal complexes [8, 9]. Several attempts have been made to use fully synthetic polymeric catalysts that incorporate all the functional features like specificity and activity of the natural enzymes [10]. Various polymer–metal complexes are found to be effective in mimicking catalase-like activity in the decomposition of hydrogen peroxide [11].

This paper describes in detail the synthesis, characterisation and catalytic activities of the metal complexes of glycine functions supported on 2–20 mol% NNMBA-crosslinked polyacrylamides. The decomposition of hydrogen peroxide is selected as a model reaction to investigate the catalytic activities of the synthesised polymer–metal complexes. The interdependence of the metal ion complexation and catalytic activity on the degree of NNMBA crosslinking are followed. Kinetics of catalysis and the dependence of various factors of the catalytic reactions on the decompositions of hydrogen peroxide are also described.

EXPERIMENTAL

General

All the reagents were of certified ACS reagent grade. The purest available metal salts were used to prepare metal ion solutions. The IR spectra were recorded on a Shimadzu IR 470 spectrophotometer. UV measurements were made on a Shimadzu 160 A spectrophotometer.

Synthesis of NNMBA-crosslinked polyacrylamides

For the preparation of 2 mol% NNMBA-crosslinked polyacrylamide, acrylamide (14 g) and NNMBA (0.6 g) were dissolved in water (100 ml). Potassium persulphate

---

*To whom all correspondence should be addressed.

Table 1. Composition of monomers and yield for the synthesis of 2–20 mol% NNMBA-crosslinked polyacrylamides

NNMBA	Weight of monomers (g)		Yield
(mol%)	Acrylamide	NNMBA	(g)
2	13.98	0.64	13.04
4	13.77	1.28	14.40
8	13.06	2.46	14.78
12	12.51	3.70	15.00
20	11.36	6.16	16.00

(100 mg) was added and the mixture was heated at 80°C for 30 min. The lumps were powdered, washed with water, ethanol, methanol and dried at 70°C. Polyacrylamides with 4–20 mol% crosslinking were prepared by varying the composition of the monomers in the feed (Table 1).

Functionalisation of acrylamide using glycine

Ten grams of NNMBA-crosslinked polyacrylamide was treated with the sodium salt of glycine and refluxed at 90–100°C for 20 h. The unreacted glycine and NaOH were removed by washing with distilled water, ethanol, methanol and soxhletted using acetone and dried at 50°C.

Estimation of carboxyl capacity

For the determination of carboxyl content of different resins, 100 mg each of the resins was equilibrated with HCl (0.2 N, 10 ml) for 24 h with magnetic stirring. The resin samples were filtered, washed with distilled water to remove unreacted HCl and the filtrate was titrated with NaOH (0.2 N) to a phenolphthalein end point.

Complexation of metal ions with carboxyl resins

The complexation of carboxyl resins with varying extents of NNMBA crosslinks were carried out towards Fe(II), Fe(III), Co(II), Ni(II), Cu(II) ions by batch equilibration technique. A quantity (100 mg) of the resin was stirred in an aqueous metal salt solution (0.05 N, 50 ml) for 24 h. The complexed resins were collected by filtration and washed with distilled water to remove uncomplexed metal ions. The concentration of metal salt solutions were estimated by UV spectrophotometric methods.

Kinetic study of hydrogen peroxide decomposition by polymer–metal complexes

A weighed quantity of the catalyst (10 mg) stirred with 5 ml (0.2 N H_2O_2) in the 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 standardised potassium permanganate solution. The experiment was repeated until a steady state was attained.

Effect of reaction conditions on the decomposition of hydrogen peroxide

The dependence of time, temperature, amount of catalyst and concentration of hydrogen peroxide on the catalytic decomposition of hydrogen peroxide was followed using a Cu(II) complex prepared with 2 mol% crosslinking. The influence of pH in the kinetic study of polyacrylamide supported glycine Co(II) complexes (8 mol%) was studied at 303 K.

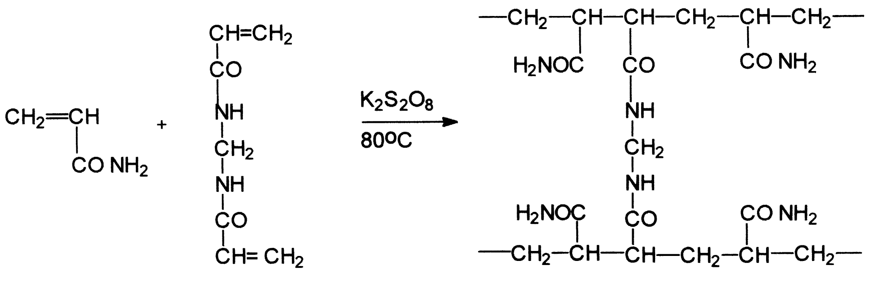
RESULTS AND DISCUSSION

Preparation of NNMBA-crosslinked polyacrylamides

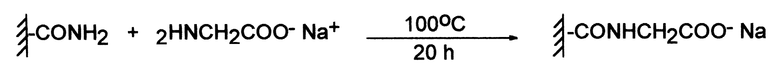
Polyacrylamides with 2–20 mol% NNMBA crosslinks were prepared by copolymerisation of the monomers in water at 80°C using potassium persulphate as the initiator (Scheme 1). The crosslink density was adjusted by varying the composition of the monomers in the feed (Table 1). With increasing crosslinking, the polymer matrix become more rigid and the swelling in water also decreased.

Functionalisation of crosslinked polyacrylamides using sodium salt of glycine

Glycine functions were incorporated into NNMBA-crosslinked polyacrylamides by transamidation with excess sodium salt of glycine at 90–100°C for 20 h (Scheme 2). The carboxyl capacity was estimated by equilibrating a definite amount of the resin with known concentration of excess HCl and back titrating the excess acid with alkali. With increasing crosslinking, the carboxyl capacity increases till 8% crosslinking and decreased further (Fig. 1). Generally, the extent of functionalisation decreases with increasing crosslinking [12]. The anomalous observation in this case arises from the heterogeneous distribution of the NNMBA crosslinks during polymerisation [13]. Similar variation in reactivity with degree of NNMBA-crosslinking is reported in polyacrylamide-supported reagents [14]. The network structure of the crosslinked polyacryl-



Scheme 1. Preparation of NNMBA-crosslinked polyacrylamides.



Scheme 2. Transamidation of NNMBA-crosslinked polyacrylamide with sodium salt of glycine.

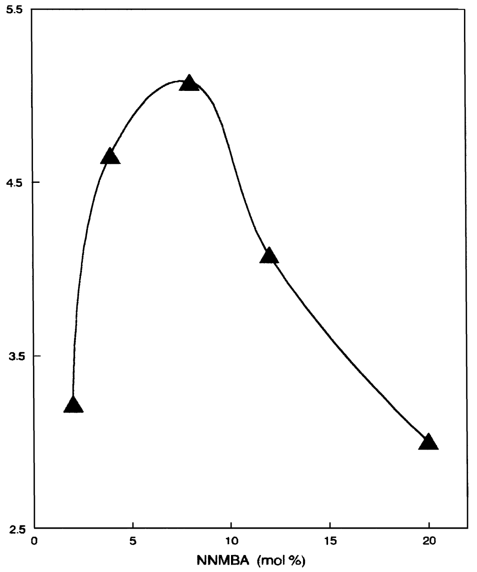


Fig. 1. Dependence of NNMBA crosslinking on the extent of transamidation.

amides is highly dependent on the concentrations of acrylamide and the tetrafunctional crosslinking agent [15]. Since this polymerisation involve three stages viz. pre-gel reaction, gelation and post-gel reaction, the composition of the polymer formed in each stage is different and therefore microdomains of different structures will be formed.

Metal ion complexation of NNMBA-crosslinked polyacrylamide-supported carboxyl resins

The complexing ability of glycine incorporated NNMBA-crosslinked polyacrylamides was investigated for Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. The metal ion uptake of the resins are given in Table 2. For all the metal ions, the complexation increases till 8 mol% and then decreases. Complexation is maximum for the 8% crosslinked system. The observed trend in complexation is: Cu(II) > Ni(II) > Co(II) > Fe(III) > Fe(II).

Characterisation: infrared spectra and UV spectra

The IR spectrum of the NNMBA-crosslinked polyacrylamides showed the characteristic absorptions of amide (N–H) and amide carbonyl (C–O) at 3500 and 1658 cm^{-1} respectively. The absorption of the secondary amide group in the NNMBA crosslinking is observed at 1570–1500 cm^{-1}. In the functionalised polymers the carboxylate groups absorb strongly near 1673 cm^{-1} and weakly at 1400 cm^{-1}. The structure and geometry of the resulting polymer metal complex are largely determined by the microenvironments around the polymer domain [16]. Polymer anchored Co(II) complexes exhibit bands at 9500–11000 and 18000–20500 cm^{-1} due to $4T_1g$ (F)–$4T_2g$ (ν_1) and $4T_1g$ (F)–$4T_1g$ (P) (ν_3) transitions in an octahedral geometry. For the Cu(II) d^9 configuration due to Jahn–Teller distortion we get a distorted octahedral structure. xy–(x^2y^2) and xz, yz–(x^2y^2) transitions occur. As the axial bond lengthens the xy–(x^2y^2) transition shifts to the blue region. The polymer anchored Ni(II) complexes with three transitions, $3A_2g$–$3T_2g$, 10048–15543 cm^{-1}, $3A_2g$–$3T_2g$ (F), 15543–15699 cm^{-1} and $3A_2g$–$3T_1g$ (P), 23624–24570 cm^{-1} give a near octahedral geometry. For Fe(III) complexes three spin transitions are observed i.e., 28571 cm^{-1} ($\pi \rightarrow \pi^*$ transition), 12620 cm^{-1} ($6A_1g$–$4T_1g$ (G) transition) and at 20360 cm^{-1} ($6A_1g$–$4T_2g$ (G) transition) suggestive of the octahedral coordination geometry.

Catalysis of hydrogen peroxide decomposition by NNMBA-crosslinked polyacrylamide-supported glycine–metal complexes

In order to investigate the catalase-like activity of the polyacrylamide-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:

$$H_2O_2 \longrightarrow HO_2^- + H^+$$

$$HO_2^- + PMC \longrightarrow PMC(HO_2)^-$$

$$PMC(HO_2)^- + H_2O_2 \longrightarrow PMC + H_2O + O_2 + OH^-$$

(PMC = polymer metal complex).

Of the various polymer–metal complexes, the catalytic activity decreased in the order: Co(II) > Cu(II) > Ni(II) > Fe(III) > Fe(II) (Fig. 2). This variation in reactivity with metal ion can be explained in terms of their coordination geometry. In the case of Fe(II), Fe(III) there is no considerable change in reactivity with time. The increased reactivity of the Co(II) complex may be due to the unsaturation of its coordination geometry by a nearly 1:2 metal:ligand ratio. For the Co(II) complex, a 1:3 geometry is preferred for its octahedral geometry. The Cu(II) complexes also show a similar unsaturation making them reactive by the easy accessibility of the peroxide ion for complexation. For Ni(II), Fe (II) and Fe(III), the complexes are saturated with ligands. Thus the accessibility of hydrogen peroxide to the coordination site is less, making their catalytic activity much less.

Table 2. Metal ion uptakes of 2–20 mol% NNMBA-crosslinked polyacrylamide-supported glycine

	Metal ion uptake (meq/g)				
NNMBA (mol%)	Fe(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)
2	0.429	1.206	1.790	1.481	2.600
4	1.143	1.316	2.182	2.353	2.946
8	1.857	1.960	2.498	2.561	3.580
12	1.143	1.190	1.812	2.396	3.010
20	0.429	1.012	1.262	0.850	2.019

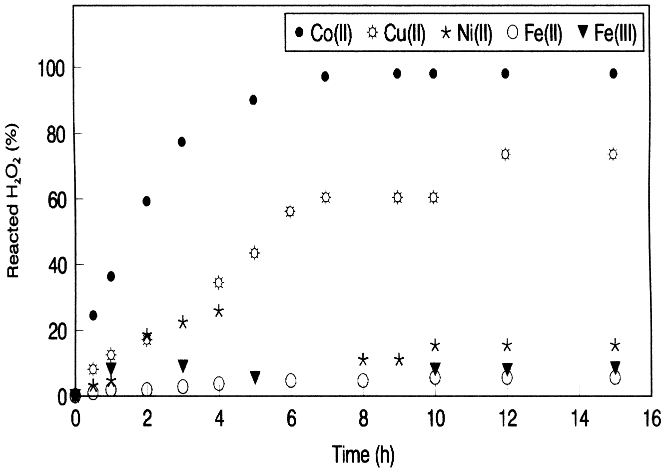


Fig. 2. Catalytic activities of Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of 8 mol% NNMBA-crosslinked polyacrylamide-supported glycine in the decomposition of H_2O_2.

Kinetics of hydrogen peroxide decomposition by polyacrylamide-supported glycine–metal complexes

Since the catalytic activities of the Co(II) and Cu(II) complexes are higher than the other metal complexes, the kinetics of catalytic decomposition was followed by using Co(II) and Cu(II) complexes of the 4% crosslinked system. The kinetics of hydrogen peroxide decomposition catalyzed by these complexes was found to be first order (Fig. 3.) The activation energy required for the decomposition of hydrogen peroxide by the Co(II) complex is less than the Cu(II) complexed system. This could arise from the unsaturation in the Co(II) coordination sphere making the easy accessibility of the hydrogen peroxide molecule and its subsequent catalytic decomposition (Table 3). The rather higher activation energy for the Cu(II) complex results from its stability in the coordination sphere preventing the coordination of hydrogen peroxide and thus inhibiting its catalytic decomposition.

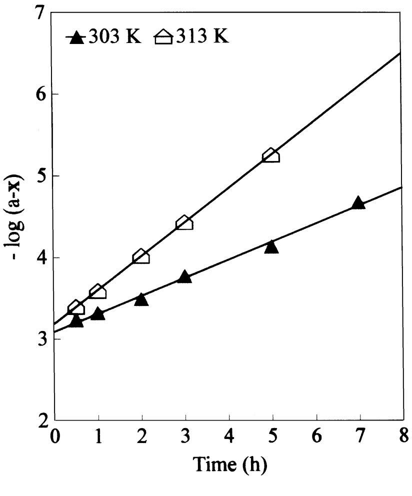


Fig. 3. Kinetic curves for the decomposition of H_2O_2 catalyzed by Co(II) complexes of 4 mol% NNMBA-crosslinked polyacrylamide-supported glycine.

Effect of the variables of catalysis on the decomposition of hydrogen peroxide

The effect of variables like time, temperature, amount of catalyst, concentration of hydrogen peroxide and pH were found to have vital roles in the decomposition of hydrogen peroxide. Cu(II) complex of 2% NNMBA-crosslinked polyacrylamide-supported glycine was used for these investigations. In the catalytic decomposition of hydrogen peroxide, the extent of decomposition increased with time, temperature, and amount of the catalyst. When the concentration of hydrogen peroxide was increased, decomposition increased till 3×10^{-2} M and decreased further for a definite amount of the catalyst (Fig. 4(a)–(d)). The influence of pH in the kinetic study of polymer-supported Co(II) complexes (2 mol%) was studied by using phosphate buffer with pH values of 5.8, 6.1, 7.1, 7.9, and 8.5. It was observed that at room temperature (303 K) the catalytic activity is decreased in the order $6.1 \approx 8.5 > 5.8 > 7.1 > 7.9$.

Effect of degree of NNMBA crosslinking on catalysis

In order to investigate the effect of the degree of NNMBA crosslinking on the decomposition of hydrogen peroxide, linear and 2–20 mol% NNMBA-crosslinked Cu(II) complexes with definite amount of Cu (II) centers were used. The catalytic activity varied with degree of crosslinking in the order: 2 > 20 > 4 > 8 > 12 > linear (Fig. 5). The increased reactivity of the 2 and 20 mol% crosslinked systems can be explained by the increased accessibility and higher surface concentration of metal centers on the surface of the polymer. The low degree of crosslinking in the 2% crosslinking

Table 3. Kinetic parameters for the decomposition of H_2O_2 catalyzed by Co(II) and Cu(II) complexes of 4 mol% NNMBA-crosslinked polyacrylamide-supported glycines

Metal complex	ΔE (kJ mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})
Co(II)	77.46	9.79×10^{8}	−72.94
Cu(II)	97.34	2.01×10^{12}	−9.53

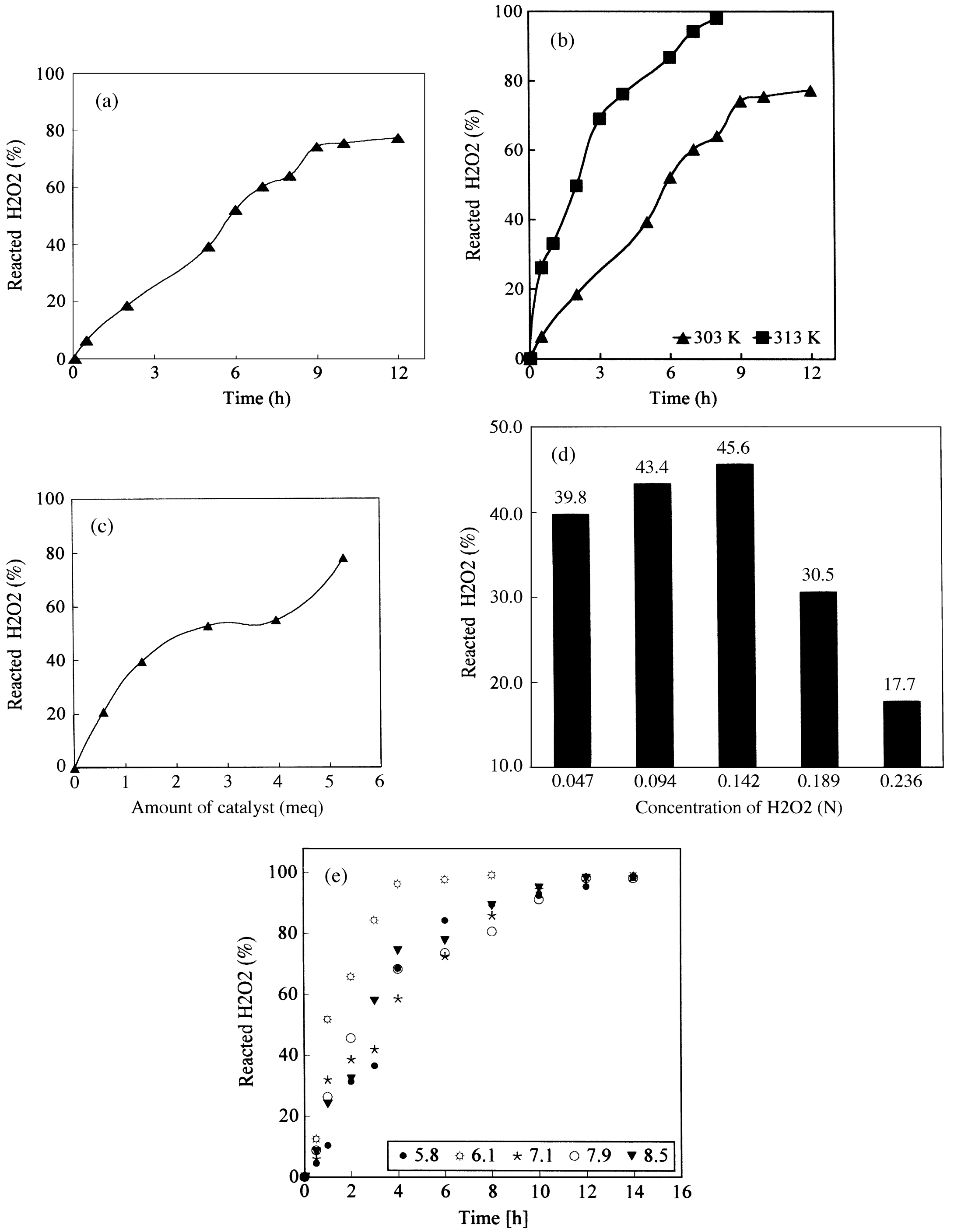


Fig. 4. (a) Effect of time on the decomposition of H_2O_2 catalyzed by Cu(II) complex of 2 mol% NNMBA-crosslinked polyacrylamide-supported glycine. (b) Effect of temperature on the decomposition of H_2O_2 catalyzed by Cu(II) complex of 2 mol% NNMBA-crosslinked polyacrylamide-supported glycine. (c) Effect of amount of catalyst on the decomposition of H_2O_2 catalyzed by Cu(II) complex of 2 mol% NNMBA-crosslinked polyacrylamide-supported glycine. (d) Effect of concentration of H_2O_2 on the decomposition of H_2O_2 catalyzed by Cu(II) complex of 2 mol% NNMBA-crosslinked polyacrylamide- supported glycine. (e) Effect of pH on the decomposition of H_2O_2 catalyzed by Cu(II) complex of 2 mol% NNMBA-crosslinked polyacrylamide-supported glycine.

system increases the accessibility of the metal centers for catalysis. In 20% crosslinked system, the metal centers are mainly on the surface of the crosslinked polymer support making them more accessible for substrate and thereby increasing catalytic activity. The reactivities of the 4 and 8% crosslinked systems is almost similar but the extent of reactivity is higher for the 8% crosslinked system.

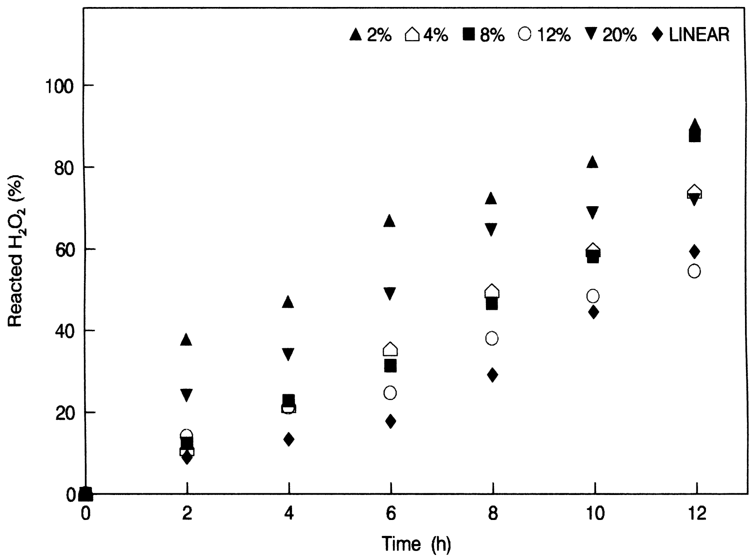


Fig. 5. Dependence of degree of NNMBA crosslinking on the H_2O_2 decomposition catalyzed by Cu(II) complexes of polyacrylamide-supported glycine.

The decreased availability of the metal centers in the interior of the crosslinks makes the catalysis by Cu(II) centers slow with a delayed action. But the decreased reactivity of the 12% crosslinked system is believed to be due to a steric effect by the crosslinks and the low metal content. Reactivity of the linear system is lower than expected. This is thought to originate from the decreased availability of copper centers resulting from the aggregation of the polymer chains and interchain complexation.

CONCLUSION

These investigations suggest that the interaction of crosslinked polyacrylamide-supported glycine ligands with metal ions depends on the degree of NNMBA crosslinking in the polymer support. The polymeric ligands and the metal complexes were characterised by IR and UV analysis. The derived metal complexes are found to be effective models for its catalase-like activity. The catalytic activity depends on the microenvironments around the metal centers. The catalytic activity decreased in the order: Co(II) > Cu(II) > Ni(II) > Fe(III). The extent of catalytic decomposition is subject to the variables of the reaction conditions and the kinetics of catalysis were found to be first order. The degree of NNMBA crosslinking has a significant effect on the catalytic activities of the crosslinked polymer–metal complexes.

REFERENCES

1. Warshawsky, A., Polymeric ligands in hydrometallurgy. In *Syntheses and Separations Using Functional Polymers*, ed. D. C. Sherrington and P. Hodge. Wiley, New York, 1988, p. 327.
2. Akelah, A. and Moet, A., *Functionalised Polymers and Their Applications*. Chapman and Hall, London, 1990, p. 93.
3. Van Den Berg, H. J. and Challa, G., Polymeric models of reactive biological systems. In *Syntheses and Separations Using Functional Polymers*, ed. D. C. Sherrington and P. Hodge. Wiley, New York, 1988, p. 227.
4. Mathew, B. and Pillai, V. N. R., *Angew. Makromol. Chem.*, 1993, **208**, 1.
5. Mathew, B. and Pillai, V. N. R., *Eur. Polym. J.*, 1994, **30**, 61.
6. Mathew, B., Madhusudanan, P. M. and Pillai, V. N. R., *Thermochim. Acta*, 1992, **207**, 265.
7. Ciardelli, F., Attomare, A., Conti, G., Arribas, G., Mendez, B. and Ismayel, A., *Macromol. Symp.*, 1994, **80**, 29.
8. Ciardelli, F., Carlini, C., Pertici, P. and Valentini, G., *J. Macromol. Sci. Chem.*, 1989, **A26**(2/3), 327–347.
9. Garrou, P. E. and Gates, B. C., Polymer-bound transition metal complexes as catalysts. In *Syntheses and Separations Using Functional Polymers*, ed. D. C. Sherrington and P. Hodge. Wiley, New York, 1988, p. 123.
10. Walsh, C., *Enzymatic Reaction Mechanisms*. Freeman, San Francisco, 1979.
11. Baselga, J., Liorenta, M. A., Hernandez-Fuentes, I. and Pierola, I. F., *Eur. Polym. J.*, 1989, **25**, 477.
12. Sreekumar, K. and Pillai, V. N. R., *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1989, **101**, 335.
13. Tobita, H. and Hamielec, A. E., *Polymer*, 1990, **31**, 1546.
14. Chandy, M. C. and Pillai, V. N. R., *Polymer*, 1995, **36**, 1083.
15. Baselga, J., Liorenta, M. A., Hernandez-Fuentes, I. and Pierola, I. F., *Eur. Polym. J.*, 1989, **25**, 477.
16. Kurimura, Y., *Adv. Polym. Sci.*, 1990, **90**, 105.