

# Synthesis, Characterization, and Catalytic Activity of Crosslinked Poly(*N*-vinyl-2-pyrrolidone acrylic acid) Copolymer–Metal Complexes

Jincy Jose, Magi John, M. G. Gigimol, Beena Mathew

School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, Kerala, India 686 560

Received 10 June 2002; accepted 18 November 2002

**ABSTRACT:** This article describes the development of a new crosslinked poly(*N*-vinyl-2-pyrrolidone acrylic acid) copolymer for potential applications in catalase-like activity for the decomposition of hydrogen peroxide. The copolymer, crosslinked with hexanediol diacrylate (4 mol %), was prepared by the suspension polymerization of the monomers in water. The metal-ion complexation of copolymer-derived sodium salts was investigated for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal uptake varied in the following order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Ni(II) > Zn(II). The polymer and metal complexes were characterized by  $^{13}\text{C}$  cross-polarity/magic-angle spinning NMR, Fourier transform infrared, ultraviolet–visible, electron paramagnetic resonance, thermogravim-

etry, and scanning electron microscopy analyses. The catalase-like activities of these insoluble metal complexes were investigated for the decomposition of hydrogen peroxide. Co(II) and Cu(II) complexes were effective for the catalytic decomposition of hydrogen peroxide. The catalytic decomposition was first-order. The effects of various parameters, such as the time, temperature, pH, amount of the catalyst, concentration of hydrogen peroxide, and recyclability of the catalyst, were examined. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 895–904, 2003

**Key words:** catalysts; hydrophilic polymers; supports; metal-polymer complexes

## INTRODUCTION

The study of metal-containing polymers is important, as these systems offer several advantages over low-molecular-weight metal complexes and metal salts in a variety of chemical reactions.<sup>1</sup> The complexes of synthetic macromolecular ligands with transition-metal ions have widely been investigated.<sup>2–5</sup> Polymer–metal complexes are widely used as immobilized catalysts with high specificity.<sup>6</sup> Many behave with enhanced efficiency when they are anchored to polymer systems.<sup>7–10</sup> The intrinsic advantages of these polymer–metal complexes in synthetic chemistry are that they may be used in excess to drive the reaction to completion without the product being contaminated and that they can be removed by simple filtration upon the completion of a reaction. The macromolecular characteristics of the polymer support, such as the nature of the polymer backbone, the chemical nature of the crosslinking agent, and the microenvironment around the coordination sphere, control the catalytic activity of polymer–metal complexes.<sup>11,12</sup> Polymer–metal complexes have attracted the interest of many

researchers as models for enzymes.<sup>13,14</sup> Various polymer–metal complexes are effective in mimicking catalase-like activity in the decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).<sup>15–17</sup>

This article describes in detail the synthesis, characterization, and catalytic activities of metal complexes supported by the *N*-vinyl-2-pyrrolidone (NVP)/acrylic acid (AA) copolymer crosslinked with 4 mol % hexanediol diacrylate. The decomposition of  $\text{H}_2\text{O}_2$  was selected for a model study investigating the catalytic activities of the synthesized polymer–metal complexes. The kinetics of the catalysis and the dependence of the various parameters of the catalytic reactions on the decomposition of  $\text{H}_2\text{O}_2$  were also examined.

## EXPERIMENTAL

### Materials and methods

NVP and AA were purchased from Fluka (St. Gallen, Switzerland), and HDODA was supplied by Aldrich Chemical Co. (USA). The purest available metal salts were used to prepare the metal salt solutions.  $\text{H}_2\text{O}_2$  was purchased from Merck (Mumbai, India). Fourier transform infrared (FTIR) spectra were recorded on a Bruker IFS-55 spectrophotometer. Ultraviolet (UV) measurements were taken on a Shimadzu 160A spec-

Correspondence to: B. Mathew (mgu@md2.vsnl.net.in).

trophotometer. The  $^{13}\text{C}$  cross-polarity/magic-angle spinning (CP-MAS) NMR spectra were recorded on a DSX 300-MHz instrument. The nitrogen analysis was carried out on a Hereaus Carlo Erba DP-200 instrument. Electron paramagnetic resonance (EPR) spectra were recorded at 303 K with a Varian E-4X band spectrophotometer at 303 K under a nitrogen atmosphere. Thermogravimetry (TG) curves were recorded on a Shimadzu D-740 thermal analyzer at a heating rate of  $10^\circ\text{C min}^{-1}$ . Scanning electron microscopy (SEM) photographs were taken on a JEOL JSM 35 CF.

#### Preparation of the HDODA (4 mol %)-crosslinked NVP-AA copolymer

A mixture of AA (3.3 mL, 48 mmol), NVP (5.1 mL, 48 mmol), HDODA (0.896 mL, 4 mmol), and 500 mg of azobisisobutyronitrile (AIBN) was added to a 10% aqueous solution of sodium sulfate containing 0.46 g of sodium dibasic phosphate, and the suspension was stirred mechanically at  $80\text{--}85^\circ\text{C}$  for 6 h. White, hygroscopic solids that formed were filtered, washed with water for the removal of excess sodium sulfate, and purified by Soxhlet extraction with acetone followed by methanol. The polymers were stirred with 0.2N NaOH for 24 h. The polymer was filtered and washed with distilled water for the removal of excess NaOH, which was confirmed by a negative blue litmus test.

#### Estimation of the carboxyl capacity

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

#### Metal-ion complexation of the carboxyl polymers

The complexation of the carboxyl polymers was carried out with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions by a batch equilibration technique. A quantity (100 mg) of the polymer was stirred in an aqueous metal salt solution (0.05N, 50 mL) for 24 h. The complexed polymers were collected by filtration and washed with distilled water for the removal of uncomplexed metal ions. The concentrations of metal salt solutions of Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) were estimated by UV spectrophotometry methods, and the concentrations of metal salt solutions of Mn(II) and Zn(II) were estimated by titrimetric methods.

#### pH dependence of the metal-ion complexation

The carboxyl polymer (50 mg) was added to a metal salt solution (50 mL) of a definite pH and kept for complexation with stirring for 8 h. The metal-ion concentrations before and after complexation were estimated.

#### Swelling studies

The copolymer (200 mg), its sodium salt, and the Cu(II) complex were equilibrated with 50 mL of distilled water for 48 h. The excess water in the polymers was removed by centrifugation, and the swollen weight was determined. The samples were dried *in vacuo* and weighed.

#### $\text{H}_2\text{O}_2$ decomposition by the polymer-metal complexes

A weighed quantity of the catalyst containing 1 mmol of metal was stirred with 5 mL (0.2N) of  $\text{H}_2\text{O}_2$  in a reaction vessel at 303 K. After a definite time, the insoluble polymer was collected by filtration, and the concentration of  $\text{H}_2\text{O}_2$  was estimated by titration against a standard potassium permanganate solution.

#### Effects of the various parameters on the decomposition of $\text{H}_2\text{O}_2$

The dependence of the time, temperature, amount of the catalyst, and concentration of  $\text{H}_2\text{O}_2$  on the catalytic decomposition of  $\text{H}_2\text{O}_2$  was followed with the Co(II) complex. The influence of the pH, kinetics of decomposition, and recyclability was studied at 303 K.

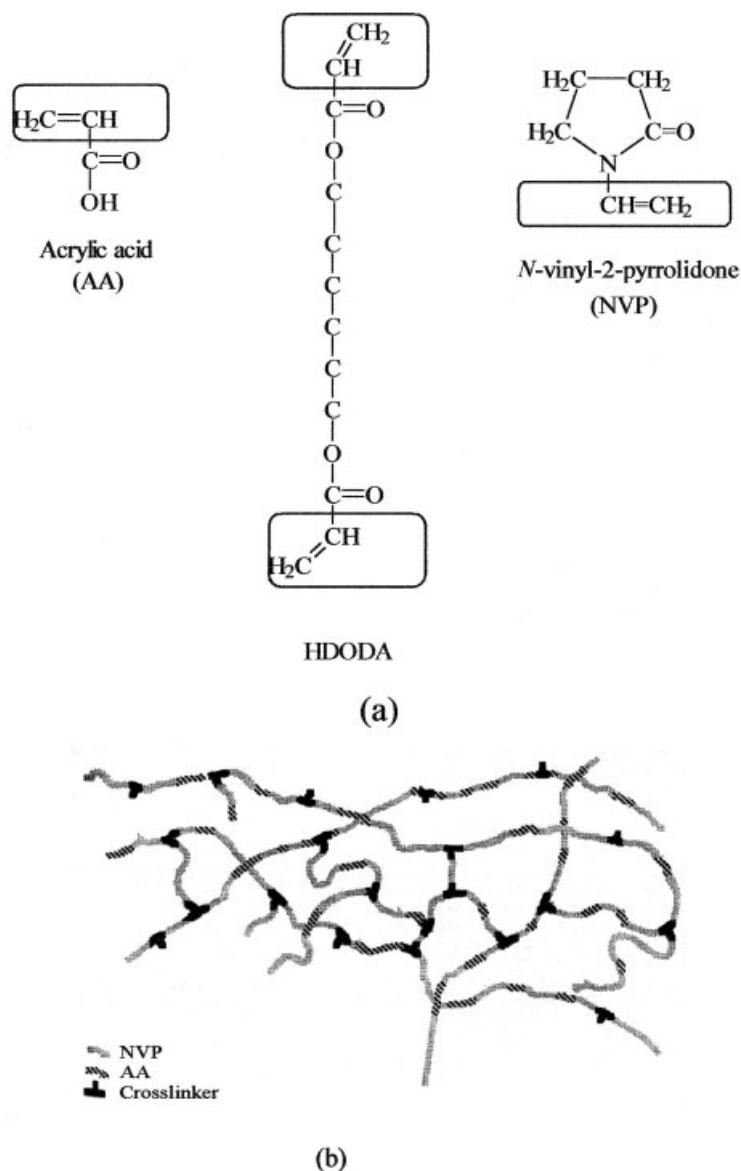
## RESULTS AND DISCUSSION

#### Preparation of the HDODA (4 mol %)-crosslinked NVP-AA copolymer

The NVP-AA copolymer with 4 mol % HDODA crosslinking was prepared by suspension polymerization at  $80^\circ\text{C}$  with AIBN as an initiator (Scheme 1). The polymer was obtained as beads with a nearly 100% yield. The polymer was then treated with a dilute sodium hydroxide solution for the preparation of the corresponding sodium salt. The carboxyl capacity of the copolymer was followed by acid-alkali titration and was found to be 5.94 mmol/g.

#### Complexation of the HDODA-crosslinked NVP-AA copolymer

The complexation of the NVP-AA copolymer was investigated for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions at their natural pH by a batch



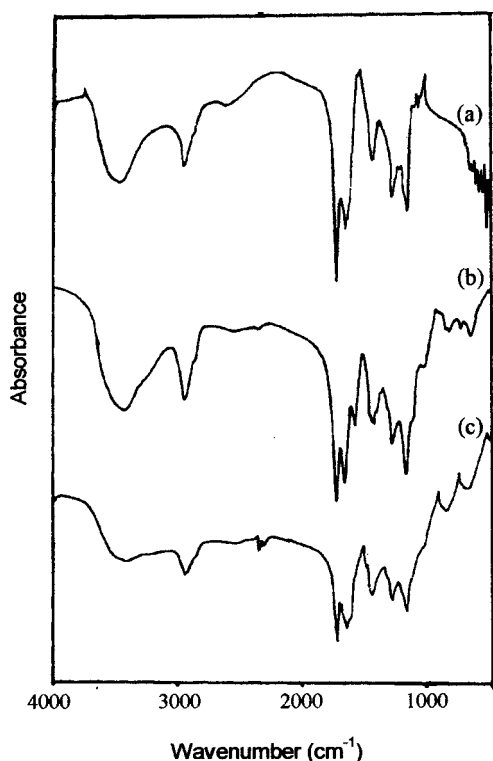
**Scheme 1** (a) Chemical structures of the monomers showing the reactive groups involved in the polymerization process and (b) a simplified model of the structure of the synthesized crosslinked copolymer.

equilibration method. The natural pHs of 0.05N solutions of various metal salts were found for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). The general trend for complexation was as follows: Cu(II) > Cr(III) > Mn(II) > Co(II) > Ni(II) > Fe(III) > Zn(II). The complexation of Cu(II) ions was higher than that of the other metal ions (Table I). This was due to the

optimum distribution of the ligand function for satisfying the stereochemical requirement for Cu(II) ion complexation. The complex formation made the macromolecular chain coil more tightly by the contraction of polymeric ligand because of inter/intra polymer chelation.<sup>18,19</sup> This was evidenced by the reduction in swelling of the ligands with metal-ion complexation.

**TABLE I**  
Metal Uptake by HDODA (4 mol %)-cross linked NVP-AA Copolymers

Crosslinking agent	Metal uptake (mequi/g)						
	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
HDODA	3.01	2.88	2.22	2.54	1.99	3.24	1.63

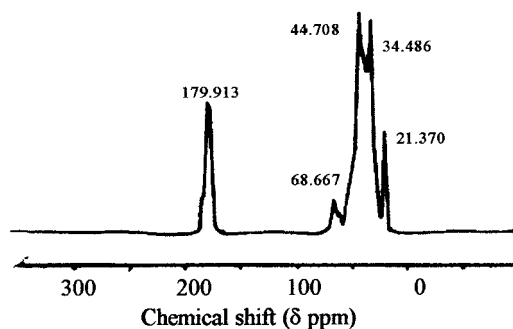


**Figure 1** FTIR spectra of (a,b) the HDODA-crosslinked NVP-AA copolymer before and after functionalization, respectively, and (c) the Cu(II) complex.

### Characterization

#### FTIR spectroscopy

The FTIR spectra of linear and crosslinked NVP-AA copolymers showed the characteristic absorption of an amide carbonyl (C=O) of NVP at  $1725\text{ cm}^{-1}$  (Fig. 1). A band at  $2971\text{ cm}^{-1}$  was attributed to a C—H stretching vibration. A broad band at  $3491\text{ cm}^{-1}$  indicated intramolecular hydrogen bonding resulting from the lowering of the —O—H vibration. The carboxylate ion gave rise to a strong, asymmetrical stretching band at  $1657\text{ cm}^{-1}$  and a weak, symmetrical stretching band at  $1450\text{ cm}^{-1}$ . The conversion of the carboxylic acid into



**Figure 2**  $^{13}\text{C}$  CP-MAS NMR spectrum of the HDODA-crosslinked NVP-AA copolymer.

the sodium salt of the carboxylate ion was evidenced by the shift to  $1663\text{ cm}^{-1}$ , and with metal-ion complexation, this shifted further to  $1638\text{ cm}^{-1}$ . The FTIR absorptions of the copolymer, the sodium salt of the copolymer, and the metal-copolymer complexes are given in Table II. Metal-ion complexation weakened the double-bonding character of the carboxylate group because of the coordinate bond between the oxygen atoms of the carboxylate group with metal ions.<sup>20</sup>

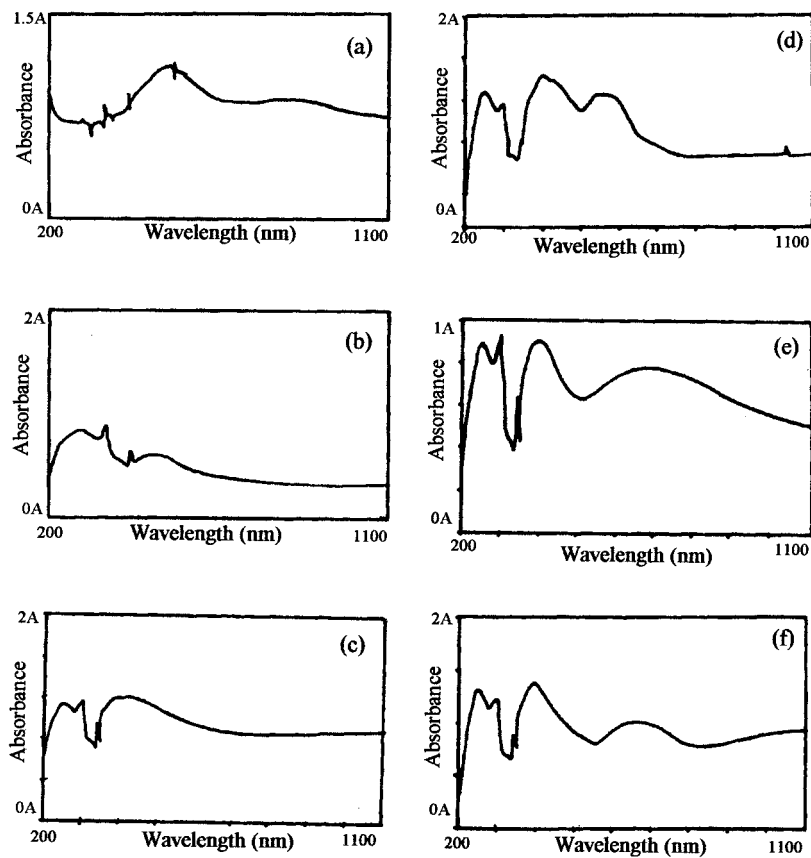
#### $^{13}\text{C}$ CP-MAS NMR spectroscopy

The  $^{13}\text{C}$  CP-MAS NMR spectrum of HDODA (4 mol %)-crosslinked NVP-AA copolymer showed intense peaks at 44.708 and 34.486 ppm corresponding to the polymer backbone and at 21.370 ppm due to aromatic ring carbons. The methylene carbon of the crosslinking agent appeared at 68.667 ppm. The carboxyl group of the polymer backbone showed a peak at 179.913 ppm (Fig. 2).

It was assumed that the three monomer units (NVP, AA, and the crosslinker) reacted in a random fashion depending on their molar ratios to form the main copolymer chains. Because all the polymerizations were carried out essentially to 100% conversions, the final composition of the copolymer was assumed to be the same as the comonomer ratio used. From the

**TABLE II**  
Typical FTIR Absorptions of the Copolymer, Sodium Salt of the Copolymer, and Metal-copolymer Complexes

Sample	FTIR absorption ( $\text{cm}^{-1}$ )		
	>C=O (amide)	C—H (str.)	>C=O (carboxyl)
Polymer	1725	2971	1657, 1450
Sodium salt of the copolymer	1725	2970	1663
Cr(III) complex	1725	2969	1639
Mn(II) complex	1723	2970	1641
Fe(III) complex	1724	2971	1644
Co(II) complex	1727	2968	1642
Ni(II) complex	1724	2969	1646
Cu(II) complex	1723	2971	1638
Zn(II) complex	1725	2969	1649



**Figure 3** UV-vis spectra of the various metal complexes of the HDODA-crosslinked NVP-AA copolymer: (a) Fe(III), (b) Co(II), (c) Mn(II), (d) Cr(II), (e) Cu(II), and (f) Cr(III).

elemental analysis, the percentage of nitrogen was found to be 5.2, additional evidence that the copolymer was being formed.

#### Ultraviolet-visible (UV-vis) spectra

The structure and geometry of the resulting polymer-metal complex were largely determined by the micro-environments around the polymer domain.<sup>21</sup> The Cu(II) complex showed  $\lambda_{\text{max}}$  at 13,037 and 25,641  $\text{cm}^{-1}$  corresponding to  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$  transitions in distorted octahedral/square planar geometry due to Jahn Teller distortion. Cr(III), Fe(III), and Mn(II) showed transitions of octahedral geometry, with absorption maxima at 17,361 and 23,752  $\text{cm}^{-1}$  due to  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  (F) and  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  (F) for Cr(III) and at 11,737 and 18,903  $\text{cm}^{-1}$  due to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  (G) and  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  for Fe(III), and a broad band in the region of 20,000–25,000  $\text{cm}^{-1}$  due to the combination of two transitions,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (G) and  ${}^6A_{1g} \rightarrow {}^4E_g$  (G), in high-spin octahedral geometry. Co(II) and Ni(II) exhibited bands at 18,656 and 34,322  $\text{cm}^{-1}$  due to  ${}^4T_{1g} \rightarrow {}^4T_{2g}$  ( $\nu_1$ ) and  ${}^4T_{1g}$  (F)  $\rightarrow$   ${}^4T_{1g}$  (P) ( $\nu_3$ ) and at 13,280 and 24,401  $\text{cm}^{-1}$  for  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (P) and  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (F) for the Ni(II) complex, which suggested nearly octahedral geometry. The UV-vis spectra of the various metal com-

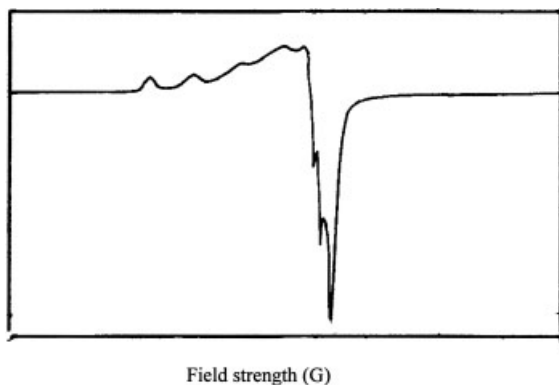
plexes of the HDODA (4 mol %)-crosslinked copolymer are given in Figure 3.

#### EPR spectroscopy

The EPR spectrum of the Cu(II) complex of the NVP-AA copolymer is given in Figure 4. The EPR parameters suggested a distorted octahedral geometry for the Cu(II) complex<sup>22</sup> ( $g^{\parallel} = 2.31$ ,  $g^{\perp} = 2.056$ ,  $A^{\parallel} = 151.66$ ,  $A^{\perp} = 30$ ).  $\alpha^2\text{Cu}$ , a measure of the in-plane  $\sigma$  bonding of the Cu—OOC bond, was calculated with the expression given by Kivelson and Neiman.<sup>23</sup> The value of  $\alpha^2\text{Cu}$ , 0.746, supported the covalent character of the Cu—O bond.

#### TG analysis

The TG curves of the NVP-AA copolymer, its sodium salt, and the Cu(II) complex are shown in Figure 5. The degradation of the NVP-AA copolymer occurred in three stages. The first stage was due to the loss of adsorbed water. Both NVP and AA were highly hygroscopic. About 16% of the water was lost from the polymer at 30–100°C, and the second stage of the decomposition of the polymer matrix started at 239°C.



**Figure 4** EPR spectrum of the Cu(II) complex of the 4 mol % HDODA-crosslinked NVP-AA copolymer.

The third stage of decomposition stopped at 473°C, and the TG curves remained constant thereafter. In the functionalized copolymer, the final product was NaO, which was unstable, whereas in the Cu(II) complex, a stable metallic oxide (CuO) was formed above 663°C.

#### SEM

The change in the morphology of the polymer surface with complexation was investigated by SEM. The SEM micrographs of the 4 mol % crosslinked (NVP-AA) copolymer and the corresponding Cu(II) complex are given in Figure 6. The SEM images of the uncomplexed polymers show smooth surfaces with few voids and channels responsible for the swelling and reactivity of the active sites buried within the polymer matrix. In the Cu(II)-complexed polymer, the morphology was entirely different from that in the corresponding uncomplexed polymer. The surface became rough because of the rearrangement of orderly arranged macromolecular chains for Cu(II) ion complexation.<sup>24</sup>

#### pH dependence on the metal-ion complexation

The metal-ion intake of the polymer 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 the addition of dilute HCl or NaOH. The use of buffer solutions for the control of pH could cause undesirable results because of the coordination of the ionic species with the metal ions. The variation of pH with different metal ions is given in Figure 7. The optimum pHs for the various metal ions were as follows: Cr(III), 2.68; Mn(II), 4.5; Fe(III), 2.2; Co(II), 5.5; Ni(II), 5.2; Cu(II), 4.31; and Zn(II), 5.39.

#### Swelling studies

The complexation of a metal ion with a polymer-supported ligand in an aqueous environment is gov-

erned by the extent of swelling of the crosslinked polymer in water.<sup>25</sup> The polymer cannot dissolve because of its three-dimensional network structure, but the chains do expand. In this study, the extent of swelling of the polymer in water was represented as follows:

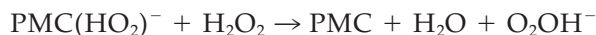
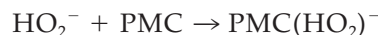
Equilibrium water content

$$= \frac{\text{Weight of wet resin} - \text{Weight of dry resin}}{\text{Weight of wet resin}} \times 100$$

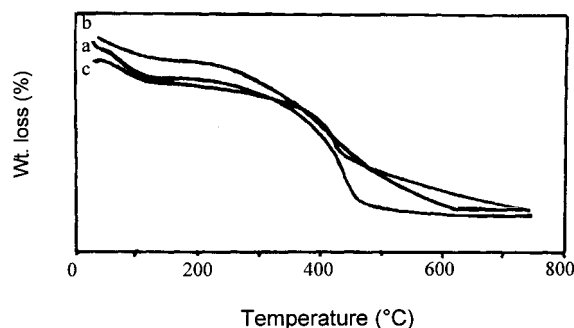
The equilibrium water contents of the unfunctionalized copolymer, functionalized copolymer, and Cu(II) complexes are given in Figure 8. The swelling of the functionalized polymer was higher than those of the respective crosslinked copolymers. In the metal-ion-complexed state, the ligand groups were less amenable to binding with water, and this resulted in the reduction in the equilibrium water content. The complexation with metal ions acted as additional crosslinking.

#### Catalysis of H<sub>2</sub>O<sub>2</sub> decomposition by the NVP-AA copolymer/metal complexes

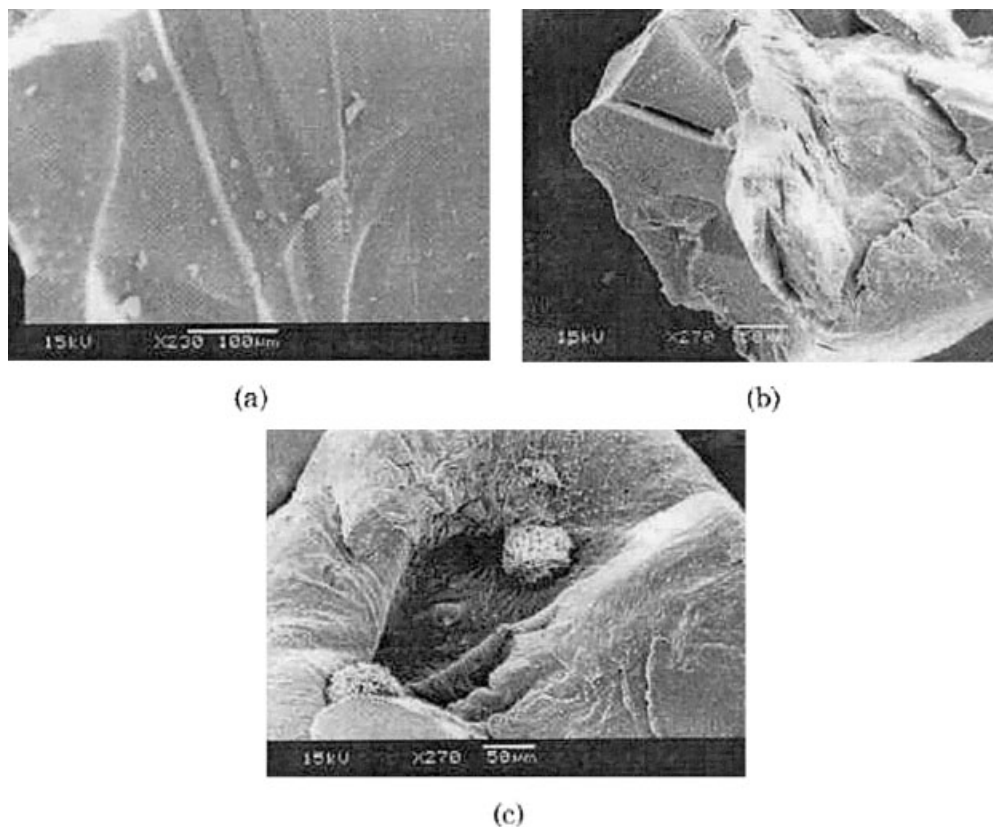
To investigate the catalase-like activity of the NVP-AA copolymer/metal complexes, we chose the decomposition of H<sub>2</sub>O<sub>2</sub> as a model study. The catalytic decomposition of H<sub>2</sub>O<sub>2</sub> can be schematically represented as follows:



where PMC is the polymer-metal complex. For the various polymer-metal complexes, the catalytic activ-



**Figure 5** TG curves of (a,b) the HDODA-crosslinked NVP-AA copolymer before and after functionalization, respectively, and (c) the Cu(II) complex.

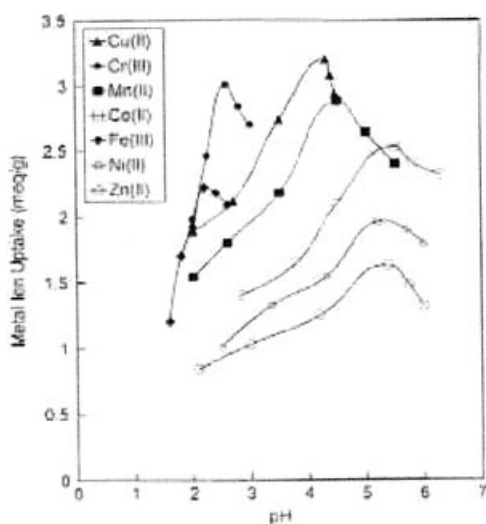


**Figure 6** SEM micrographs of (a,b) the HDODA-crosslinked NVP-AA copolymer before and after functionalization, respectively, and (c) the Cu(II) complex.

ity decreased in the following order: Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II) (Fig. 9).

This variation in the reactivity with metal complexes could be explained in terms of their coordination geometry. For Zn(II), there was no considerable change in the reactiv-

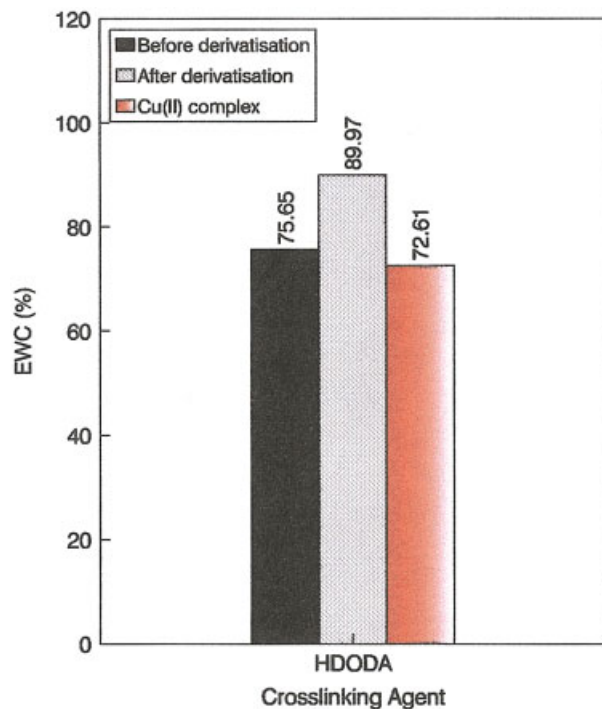
ity with time. The increased reactivity of the Co(II) complex might be due to the unsaturation of its coordination geometry by a nearly 1:2 metal/ligand ratio. The Cu(II) complexes also showed a similar unsaturation making them reactive by the easy accessibility of the peroxide ion for complexation. For other metal complexes, the accessibility of  $H_2O_2$  to the coordination site was less, and this made their catalytic activity low.



**Figure 7** Effect of pH on the metal-ion complexation of the 4 mol % HDODA-crosslinked NVP-AA copolymer.

#### Kinetics of $H_2O_2$ decomposition by the NVP-AA copolymer/metal complexes

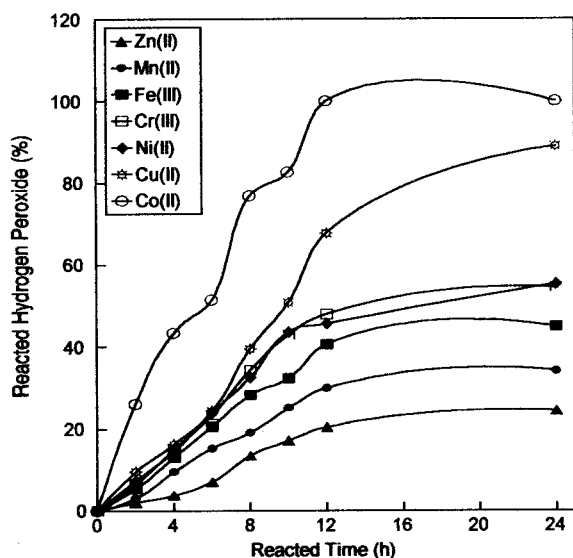
Because the catalytic activities of the Co(II) complexes were higher than those of the other metal complexes, the kinetics of the catalytic decomposition were followed with the Co(II) complex. The kinetics of  $H_2O_2$  decomposition catalyzed by the metal-polymer complex were first-order (Figs. 10 and 11). The kinetic parameters were  $\Delta E = 7.48 \text{ kJ mol}^{-1}$ ,  $A = 2.47 \times 10^{-3} \text{ s}^{-1}$ , and  $\Delta S = -310.7 \text{ J}$ . This arose from the unsaturation in the Co(II) coordination sphere, which provided easy accessibility to the  $H_2O_2$  molecule and its subsequent catalytic decomposition.



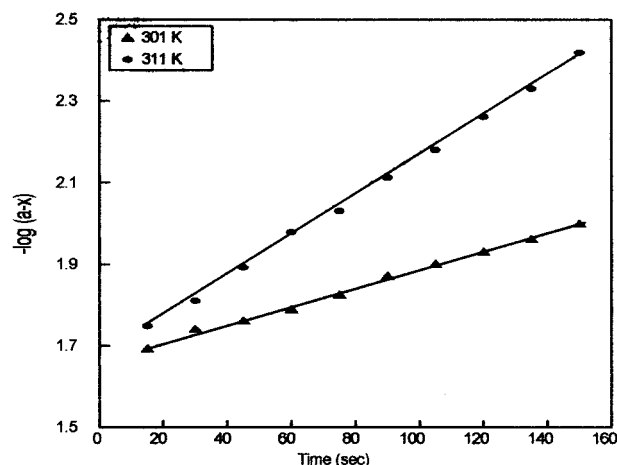
**Figure 8** Equilibrium water contents (EWCs) of the 4 mol % HDODA-crosslinked copolymer sodium salt and Cu(II) complex. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Effect of the various parameters on the catalytic decomposition of  $H_2O_2$

Variables such as the time, temperature, amount of the catalyst, concentration of  $H_2O_2$ , and pH were found to have vital roles in the decomposition of  $H_2O_2$ . The Co(II) complex was used for these investigations



**Figure 9** Catalytic activities of the various metal complexes of the HDODA-crosslinked NVP-AA copolymer system.

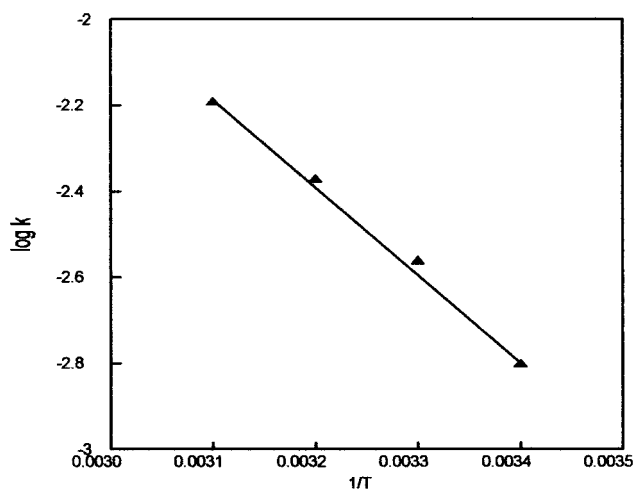


**Figure 10** Kinetic curves for the decomposition of  $H_2O_2$  catalyzed by the HDODA-crosslinked NVP-AA copolymer Co(II) complex.

into the catalytic decomposition of  $H_2O_2$ . The extent of decomposition increased with the time, temperature, and amount of the catalyst. When the concentration of  $H_2O_2$  was increased, the decomposition increased until 0.15N and decreased with a greater amount of the catalyst [Fig. 12(a-d)]. The influence of the pH on the catalytic decomposition was studied with phosphate buffers with various pH values. At room temperature (303 K), the catalytic activity decreased with the pH in the following order: 7.2 > 7.9  $\approx$  8.5 > 6.5 > 5.6.

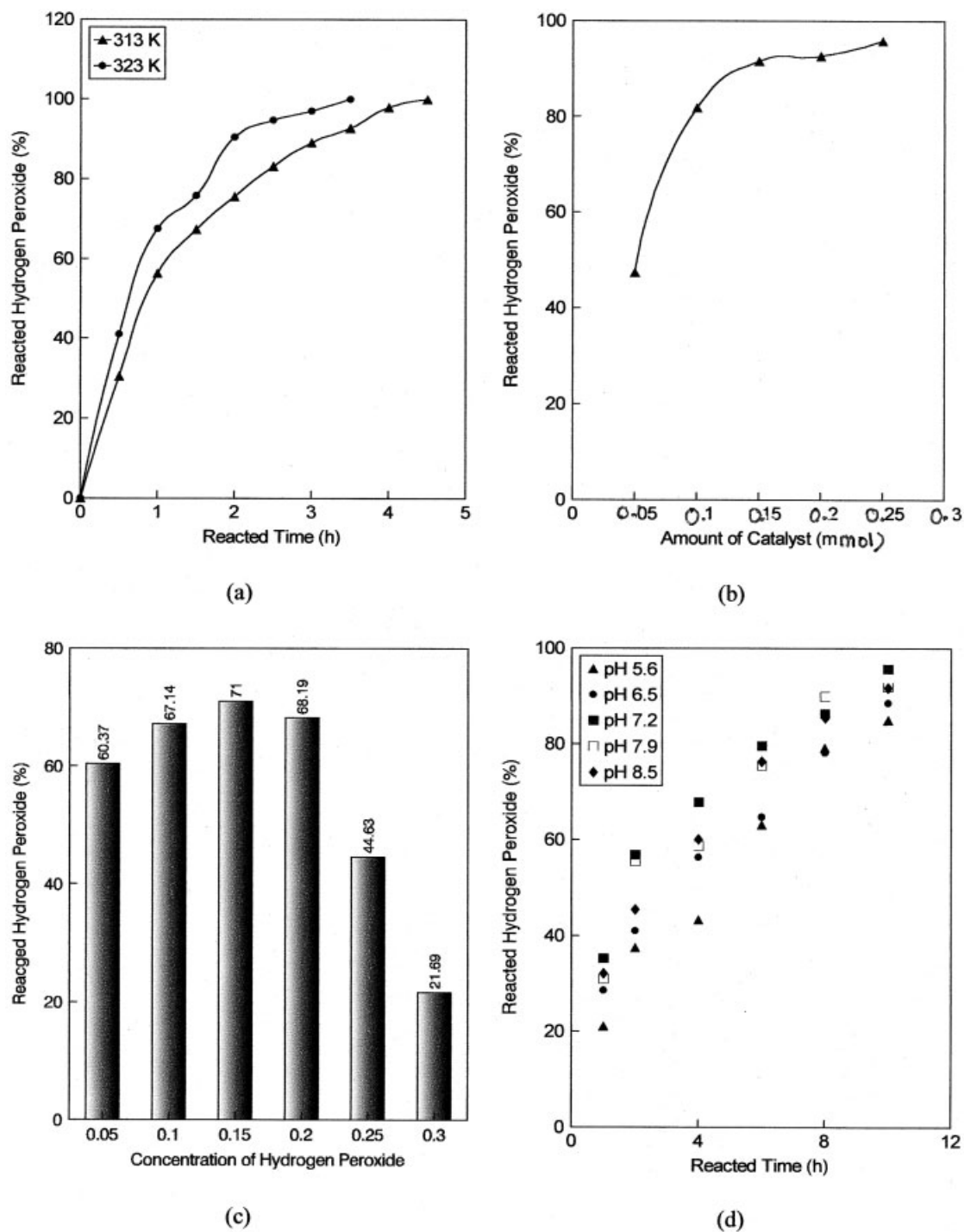
Recyclability

The Co(II) complex of HDODA-crosslinked NVP-AA was used several times without a loss of efficiency, as shown in Figure 13.



**Figure 11** Variation of the rate constant with the temperature in the decomposition of  $H_2O_2$  catalyzed by the Co(II) complex of the HDODA-crosslinked NVP-AA copolymer.





**Figure 12** Effects of the various parameters on the catalytic decomposition of  $H_2O_2$ : (a) the temperature, (b) the amount of the catalyst, (c) the concentration of  $H_2O_2$ , and (d) the pH of the medium.

**CONCLUSIONS**

The NVP-AA copolymer was found to be an efficient ligand for the complexation of transition-metal ions. The polymeric ligand and the various metal complexes were characterized by various spectral methods. The derived metal complexes were effective models for their catalase-

like activity. The catalytic activity varied with the metal complexes in the following order:  $Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II)$ . The effect of the catalytic decomposition was subject to the variables of the reaction conditions, and the kinetics of catalysis were first-order.

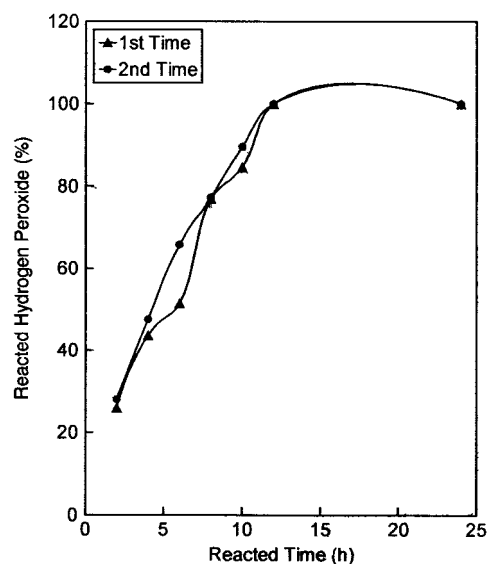


Figure 13 Recyclability of the NVP-AA Co(II) complex.

## References

- Lohray, B. B.; Sivaram, S.; Dhal, P. K. *Macromolecules* 1994, 27, 1291.
- Abet, G.; Meusier, B. *J Chem Soc Chem Commun* 1990, 1414.
- Gokak, D. T.; Kamath, B. V.; Ram, R. N. *J Appl Polym Sci* 1988, 35, 1523.
- Berbrrieter, D. E.; Morvat, M.; Chen, B. *Tetrahedron Lett* 1991, 32, 2731.
- Stoessel, S. J.; Stille, J. K. *Macromolecules* 1992, 25, 1832.
- Ciardelli, F.; Attomare, A.; Conti, G.; Arribas, G.; Mendez, B.; Ismayel, A. *Macromol Symp* 1994, 80, 29.
- Davylova, S. L.; Plate, N. A. *Coord Chem Rev* 1976, 16, 196.
- Tsuchida, E.; Nishide, H. *Adv Polym Sci* 1977, 24, 1.
- Kaneko, M.; Tsuchida, E. *Macromol Rev* 1981, 16, 397.
- Geckeler, K.; Weingartner, K.; Bayer, E. *Pure Appl Chem* 1980, 52, 1883.
- Ciardelli, F.; Carlini, C.; Pertici, P.; Valentini, G. *J Macromol Sci Chem* 1989, 26, 327.
- Garron, P. E.; Gater, B. C. In *Synthesis and Separations using Functional Polymers*; Sherrington, D. C.; Hodge, P., Eds.; Wiley: New York, 1988; p 123.
- Banazak, J. L.; Watson, H. O.; Kendrew, J. C. *J Mol Biol* 1965, 2, 130.
- Palumbo, M.; Cosani, A.; Terbojevich, M.; Peggion, T. M. *Macromolecules* 1978, 10, 813.
- Vinod Kumar, G. S.; Mathew, B. *Eur Polym J* 1998, 34, 1185.
- Bekturov, E. A.; Kudibergenov, S. E.; Sigitov, V. B. *Polymer* 1986, 27, 127.
- Elsonbati, A. Z.; Hassameir, A. M.; Mohamed, M. T.; Elmoiz, A. B. A. *Polym Degrad Stab* 1994, 46, 31.
- Kaliyappan, T.; Kannan, P. *Prog Polym Sci* 2000, 25, 343.
- Mathew, B.; Pillai, V. N. R. *Indian J Technol* 1993, 31, 304.
- Mackawa, E.; Koshijima, T. *J Appl Polym Sci* 1990, 6, 1601.
- Kurimura, Y. *Adv Polym Sci* 1990, 90, 105.
- Peisach, J.; Blumberg, W. C. *Arch Biochem Biophys* 1970, 165, 691.
- Kivelson, D.; Neiman, R. *J Chem Phys* 1961, 35, 149.
- Jose, L.; Pillai, V. N. R. *J Appl Polym Sci* 1996, 60, 1864.
- Mathew, B.; Pillai, V. N. R. *Angew Makromol Chem* 1993, 1, 208.