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Effect of the Degree of NNMBA Crosslinking on the Physicochemical Characteristics and Catalytic Activity of 4–20 mol% NNMBA-Crosslinked Polyacrylic Acid–Metal Complexes

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ABSTRACT

Metal complexation behavior and catalytic activity of 4–20 mol% *N*, *N*′-methylene-*bis*-acrylamide (NNMBA)-crosslinked polyacrylic acids were investigated. The polymeric ligands were prepared by solution polymerization. The metal ion complexations were investigated towards Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal uptake followed the order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II). The polymeric ligands and the metal complexes were characterized by various spectral methods. The catalytic activity of the metal complexes were investigated towards the hydrolysis of *p*-nitrophenyl acetate and Co(II) complexes exhibited high catalytic activity. The kinetics of catalysis was found to be first order. The hydrolysis was controlled by pH, time, amount of the catalyst, and temperature. The metal complexation and catalytic activity were influenced by the degree of NNMBA crosslinking. Thus, 4 mol% NNMBA-crosslinked polyacrylic acid system has the highest metal ion complexation and catalytic activity among the four NNMBA-crosslinked polyacrylic acid systems.

Key Words: Polymer–metal complexes; Catalytic activity; Ester hydrolysis; Degree of crosslinking.

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INTRODUCTION

Polymer–metal complexes have been of interest to many researchers during the past three decades. Interest focuses on their potential applications in diversified fields i.e., organic synthesis,[1] waste water treatment, hydrometallurgy, recovery of trace metal ions, [2] and environmental protection.[3] In addition, they are also used as enzyme models[4] and catalysts.[5,6] A polymer–metal complex is composed of synthetic polymer and metal ions, wherein the metal ions are bound to the polymer ligand by a coordinate bond. A polymer ligand containing anchoring sites such as nitrogen, oxygen, or sulfur are obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability. The synthesis results in an organic polymer with inorganic functions. The metal atoms attached to polymer backbone are found to exhibit characteristic catalytic behavior, which are distinctly different from their low molecular weight analogue. Indeed, many synthetic polymer–metal complexes have been found to possess high catalytic efficiency, in addition to semi conductivity, heat resistance, and biomedical potentials.

This study describes the detailed investigations of the synthesis of 4–20 mol% NNMBA-crosslinked polyacrylic acids and their complexation towards Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. Swelling studies and physicochemical characterization of the polymeric ligands and their metal complexes, using FT-IR, ^{13}C CP-MAS NMR, UV-VIS, EPR spectra, thermogravimetric analysis (TG), and scanning electron microscopy (SEM) and the catalytic activity of the metal complexes in the hydrolysis of *p*-nitrophenyl acetate are evaluated. The results of these studies are correlated with the degree of NNMBA crosslinking in the polymer support.

EXPERIMENTAL

Materials and Methods

N,*N*′-methylene-*bis*-acrylamide (NNMBA) was purchased from SRL, Mumbai, India. Acrylic acid (AA) was obtained from Fluka, Switzerland. All metal salts were commercially available. All other solvents and reagents were commercially available and were purified by literature procedures.

The FT-IR spectra were recorded on a Bruker IFS-55 spectrometer using KBr pellets. UV-VIS spectra were recorded on a Shimadzu UV-160A spectrophotometer. ^{13}C CP-MAS NMR spectra were recorded using DSX 300 MHz instrument. Thermogravimetric curves were recorded on a Shimadzu D-740 thermal analyser at a heating rate of 10°C min^{-1} in air. Scanning electron microscopy photographs were taken using Jeol JSM 35CF model and Varian E-4X band spectrophotometer was used to record EPR spectra.

Synthesis of 4–20 mol% NNMBA-Crosslinked Polyacrylic Acids

Following the same procedure, four types of NNMBA-crosslinked polymers with varying amount of NNMBA crosslinking were prepared. In order to prepare 4 mol% NNMBA-crosslinked polyacrylic acid, 60 mL water and 0.5 g AIBN initiator were heated in an oil bath with stirring under nitrogen atmosphere. When the temperature attained 85–90°C, 6.59 mL AA and 0.62 g NNMBA were added to water. Stirring was continued until a glassy solid mass separated out. It was Soxhlet extracted using acetone and dried under vacuum. Polyacrylic acids with 8, 12, and 20 mol% of NNMBA crosslinking were prepared by varying the amounts of NNMBA and AA.

Derivatization of NNMBA-Crosslinked Polyacrylic Acids

The polymers were treated with excess sodium hydroxide solution (0.2 M) with stirring for 24 hr. The polymer samples were filtered, washed with distilled water to remove excess NaOH till the filtrate was free from excess NaOH, confirmed with a litmus test.

Estimation of Carboxyl Capacity of Polyacrylic Acids

The carboxylate polymers (100 mg) were equilibrated with HCl (0.2 N, 10 mL) with stirring for 24 hr. The polymer samples were filtered, washed with distilled water to remove unreacted HCl and the filtrate was titrated against sodium hydroxide (0.2 N) to a phenolphthaline end point.

Preparation of Polymer–Metal Complexes: General Procedure

Polymeric ligand (50 mg) was stirred with 20 mL (0.05 M) metal salt solution for 7 hr at its natural pH. From the decrease in concentration of metal ion solution, the amount of metal ion complexed by 50 mg resin was calculated. The polymer–metal complexes were washed with distilled water to remove the uncomplexed metal ions. The metal complexes were dried in vacuum. The concentration of Cr(III), Fe(III), Co(II), Ni(II), and Cu(II) were determined spectrophotometrically, whereas Zn(II) and Mn(II) were determined by standard titrimetric methods.

Influence of pH on Metal Ion Binding

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 1 M HCl or 1 M NaOH as shown by a pH meter. The carboxylate resin (50 mg) was reacted with 20 mL of the metal salt solution of definite pH and kept for complexation for 7 hr. The concentrations of metal salt solution before and after complexation were estimated. The metal ion binding studies were carried out in a thermostated shaker.

Swelling Studies: General Procedure

The different polymers (100 mg each) were equilibrated with distilled water for 24 hr. The swollen resins were collected by filtration, adhering traces or water were removed carefully by wiping with a blotting paper and the swollen weights were determined. The samples were then dried in vacuum for 24 hr and finally the weights of dry resins were also recorded. From the weights of wet and dry resins, equilibrium water content (EWC) was calculated using the equation:

$$\mathrm{EWC}\ (\%) = \frac{\text{weight of wet resin} - \text{weight of dry resin}}{\text{weight of wet resin}} \times 100$$

Catalytic Activity of Metal Complexes of 4–20 mol% NNMBA-Crosslinked Polyacrylic Acid: General Procedure

p-Nitrophenyl acetate (1.1×10^{-4} M) was dissolved in dioxane (2 mL), and phosphate buffer (0.05 M, 48 mL) of definite pH was added. A weighed quantity (4×10^{-4} M) of the polymer–metal complex was added to the above solution at room temperature and stirred. Concentrations of *p*-nitrophenol liberated at different time intervals were measured at 400 nm. A blank was run using the ester in dioxane/buffer without the metal complex. The effect of various parameters like time, temperature, amount of catalyst, pH, and concentration of buffer were also studied.

RESULTS AND DISCUSSION

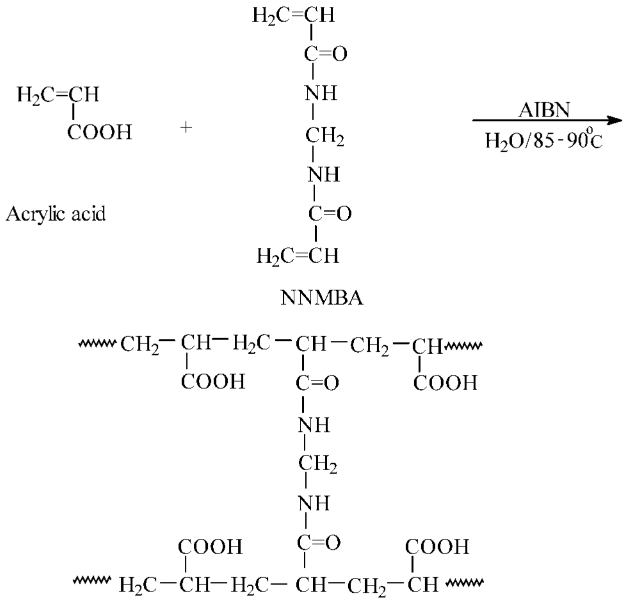
Synthesis of 4–20 mol% NNMBA-Crosslinked Polyacrylic Acids

The NNMBA-crosslinked polyacrylic acids (4–20 mol%) were prepared in water at 85–90°C, using AIBN as the initiator. The polymerization reaction is shown in Sch. 1. Four types of polymers were prepared by varying the amount of the monomer and crosslinking agent. The details are given in Table 1. Rigidity of the polymers increased as the percentage of the crosslinking agent increased.

Preparation of Sodium Salt of NNMBA-Crosslinked Polyacrylic Acids

The NNMBA-crosslinked (4–20 mol%) polyacrylic acids were converted to their corresponding sodium salts due to the complexing difficulty of the carboxyl groups. For this a definite amount of the polymer was treated with excess sodium hydroxide solution (0.2 M) with shaking for 24 hr. The alkali treated polymer was washed with distilled water until free from alkali. Carboxyl capacity was estimated by equilibrating a definite amount of the carboxylate polymer with known concentration of excess hydrochloric acid, and the unreacted hydrochloric acid was back titrated with standard alkali. The variation of carboxyl capacity with crosslink density is shown in Fig. 1.

The 4 mol% crosslinked system has the highest carboxyl capacity (8.94 mmol/g) and 20 mol% has the lowest (5.60 mmol/g). Normally, a high carboxyl capacity would be expected for low crosslinked system because of the increased availability of



Scheme 1. Synthesis of NNMBA-crosslinked polyacrylic acid.

the reactive sites. The carboxyl capacity decreases from 4 to 8 mol%. For 12 mol% crosslinked system a slight increase occurs. After 12 mol% crosslinking, the carboxyl capacity decreases with increasing crosslinking due to the reduced availability of functional groups buried within the dense polymer network. The anomalous observation in reactivity with increasing crosslink density arises from the heterogeneous distribution of the NNMBA crosslinking which is inevitable in NNMBA-crosslinked systems.[7] Similar variation of reactivity with crosslink density in different NNMBA-crosslinked polymers are reported.[8,9]

Metal Ion Complexation of NNMBA-Crosslinked Polyacrylic Acids

The complexation of polymer-supported ligands is influenced by the characteristics of the macromolecular matrix, i.e., the nature and extent of the crosslinking agent, nature

Table 1. Preparation of 4–20 mol% NNMBA-crosslinked polyacrylic acid.

NNMBA (mol%)	Acrylic acid (mL)	NNMBA (g)	Yield (g)
4	6.59	0.62	6.5
8	6.32	1.23	6.7
12	6.04	1.85	6.9
20	5.49	3.08	7.3

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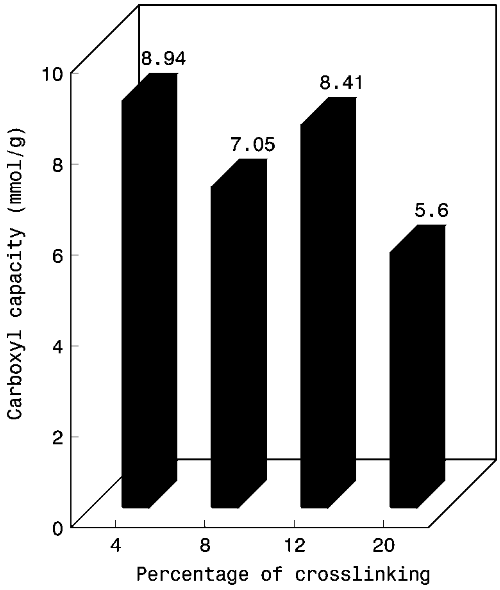


Figure 1. Variation of carboxyl capacity with NNMBA crosslinking.

of the polymer backbone and separation of the ligand functions from the polymer matrix.[10,11] In order to investigate the effect of the degree of crosslinking on the metal ion complexation of carboxylate functions supported on NNMBA-crosslinked polyacrylic acid, a batch equilibration method was carried out towards Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions. For all complexation studies, a definite weight of the polymeric ligand was equilibrated with excess metal salt solution of known concentration at natural pH for 7 hr. The concentration of Cr(III), Fe(III), Co(II), Ni(II), and Cu(II) ions was followed using spectrophotometry and Mn(II) and Zn(II) ions by complexometric titration using EDTA. The metal uptake by the various crosslinked systems are given in Table 2.

In all cases the metal uptake decreased in the order: Cu(II) > Cr(III) > Mn(II) > Co(II) > Fe(III) > Zn(II) > Ni(II). The hydrophilicity of the polymer support is important in the collection of metal ions from aqueous solution. Generally, with a higher extent of crosslinking, the polymer matrix becomes more rigid and the permeation of the solvent and metal ions to the ligand site is difficult. Thus, metal ion intake decreases with an increasing degree of crosslinking in the support. But, in the present study, the metal ion uptake follows the same trend as a variation of ligand capacity with the extent of NNMBA crosslinking. Generally, a higher metal ion uptake would be expected for a low crosslinked system because of the increased accessibility of the ligand functions for complexation. The highly crosslinked polymer support is only slightly swollen and the effective solvent medium is less favorable for the reaction if the swelling of the gel is less. The exceptional behavior of 12 mol% NNMBA-crosslinked polyacrylic acid is due to its high carboxyl capacity which in turn is due to the heterogeneous distribution of the NNMBA crosslinks. This results in regions with non-uniform distribution of crosslinking agent in the polymer matrix.

Table 2. Metal uptake by 4–20 mol% NNMBA-crosslinked polyacrylic acids.

NNMBA (mol%)	Carboxyl capacity (mmol/g)	Metal ion uptake (meq/g)						
		Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)
4	8.94	3.35	3.20	2.98	3.01	2.72	3.87	2.97
8	7.05	2.87	2.75	2.60	2.69	2.37	3.20	2.57
12	8.41	3.15	2.95	2.78	2.88	2.63	3.70	2.72
20	5.60	2.25	1.99	1.85	1.93	1.65	2.60	1.80

Influence of pH on Metal Ion Binding

The interaction of the ligand functions of various crosslinked polyacrylic acids were investigated towards Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions in different pH conditions by the batch equilibration method. The optimum pH of the medium for maximum uptake of metal ion depends only on the nature of the metal ion and is independent of the extent of crosslinking. A general representation of the variation of metal uptake with pH is given in Fig. 2. In all cases, the upper limit of pH was just below the precipitation. The optimum pH for the complexation of various metal ions are Cr(III) 2.6, Mn(II) 4.4, Fe(III) 2.2, Co(II) 5.6, Ni(II) 5.1, Cu(II) 4.5, and Zn(II) 5.3.

Swelling Studies

The effectiveness with which a functional polymer can act as an alternative to its low molecular counterpart is governed by the accessibility of the reactive functional groups anchored on it. The solvent has a significant effect on the physical nature and the chemical reactivity of anchored species. With linear polymers, this is not a problem because they are soluble in good solvents. In the case of crosslinked polymers, they are macroscopically insoluble. By absorbing a considerable amount of a suitable solvent, the crosslinked polymeric network can expand greatly and becomes extremely porous forming a pseudo-gel. Swelling of resin beads is very important as it brings the polymer to a state of complete solvation allowing easy permeation of the metal ions through the network. The crosslink ratio controls the behavior of a resin in contact with a solvent and is inversely proportional to the degree of swelling. With an increase in crosslink density, the tendency of the polymer backbone to expand in a good solvent is reduced and penetration of the solvents and metal ions into the interior become impaired. The presence of hydrophobic/hydrophilic crosslinking agents would lead to the formation of crosslinked system with varying solvation and swelling characteristics. Crosslinked polymers exhibit considerable difference in properties depending on the degree of crosslinking and the method of preparation. They can be conveniently characterized in terms of their total surface area (internal and external), total pore volume and average pore diameter. In general, the degree of crosslinking determines the solubility, extent of swelling, pore size, total surface area, and mechanical stability of the polymer. In the present study, the extent of swelling of 4–20 mol% NNMBA-crosslinked polyacrylic acids, their derivatives and Cu(II) complexes in distilled water were represented as EWC and the results are given in Fig. 3.

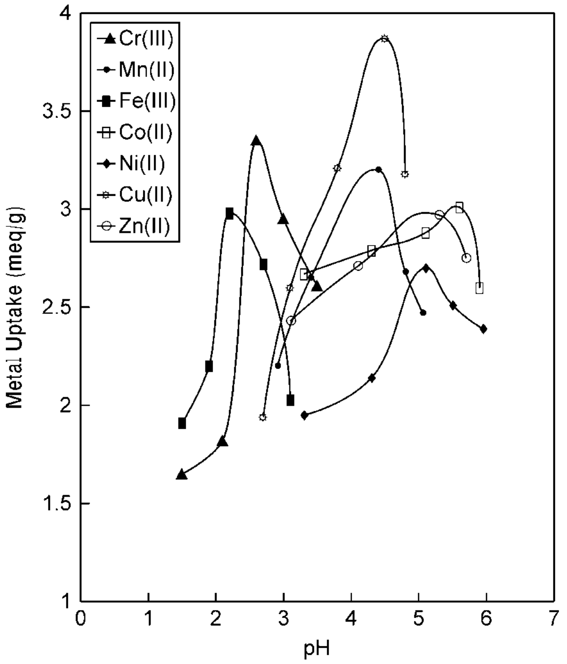


Figure 2. Effect of pH on the metal ion complexation of 4 mol% NNMBA-crosslinked polyacrylic acids.

The 4-mol% NNMBA-crosslinked polyacrylic acid was found to be more fragile especially when in contact with good solvents such as water, whereas 20 mol% NNMBA-crosslinked polyacrylic acid was more stable due to the increased crosslinking. At higher concentrations of the crosslinking agent, in addition to crosslinking considerable chain entanglement also occurs. This reduces the extent of the swelling in the presence of water. This is the reason why 20 mol% NNMBA-crosslinked polyacrylic acid, its sodium salt and Cu(II) complex exhibited less swelling compared to other crosslinked resins. The swellings of the sodium salt of the crosslinked polyacrylic acids were higher than the corresponding polyacrylic acids whereas it decreased on Cu(II) ion complexation. This is due to the increased solvation of the carboxylate groups. Metal ion complexation acts as interchain crosslinking. This results in considerable reduction in water uptake. This reduction is much higher in the 4 mol% crosslinked system. The cooperative contribution of the ligand sites in the loosely connected polymer chains on metal ion complexation resulted in remarkable reduction in water uptake. Similarly, this reduction decreases with increasing degree of crosslink density.

Characterization of 4–20 mol% NNMBA-Crosslinked Polyacrylic Acids and Their Metal Complexes

The FT-IR spectra of the polymeric ligands and metal complexes are of considerable value for determining the chemical nature and also in the location of binding sites in the metal complexes.[12] The FT-IR spectra of 4 mol% NNMBA-crosslinked polyacrylic acid

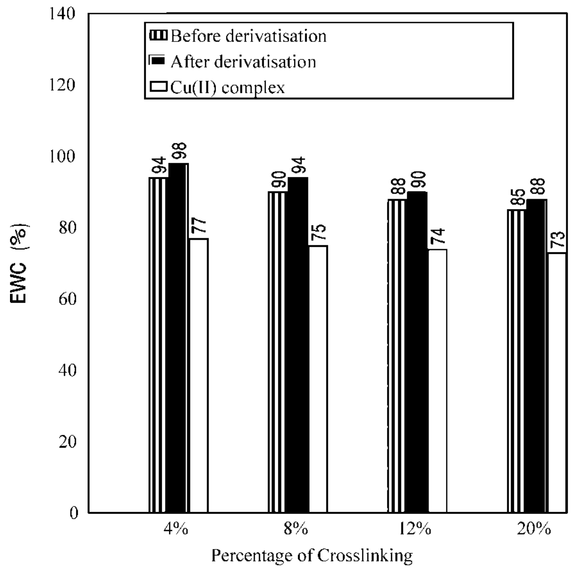


Figure 3. Swelling characteristics of various NNMBA-crosslinked polyacrylic acids, their sodium salts and Cu(II) complexes.

and its Cu(II) complex have a very broad intense band at 3300–3500 cm^{-1} region due to the –O–H stretching vibration (Fig. 4). The weak –C–H stretching bands were seen superimposed upon the broad –OH band. Fine structure observed on the long wavelength side of the broad –OH band represented overtones and combination tones of fundamental bands occurring at long wavelengths. The –C═O group in 4 mol% NNMBA-crosslinked polyacrylic acid showed absorbance at 1728 cm^{-1} with a small shoulder at 1703 cm^{-1}. Complexation with Cu(II) ion resulted in the shift of absorption from 1728 to 1694 and 1703 to 1663 cm^{-1}. In the case of the Cu(II) complex the –OH bonding appeared at 1460 cm^{-1} is shifted to 1406 cm^{-1}. This is due to complexation through carboxylate group. A stretching at 1660 cm^{-1} in the FTIR of 4 mol% NNMBA-crosslinked polyacrylic acid is due to the –NH stretching of NNMBA crosslinking agent.

The ^{13}C CP-MAS NMR spectra of 4–20 mol% NNMBA-crosslinked polyacrylic acid were found to be identical. The backbone methylene carbon appeared as a very sharp peak at 43.902 ppm. The carbonyl carbon of the carboxylate group, was observed as an intense peak at 180.556 ppm. Due to the low concentration of the NNMBA crosslinking in the polymer support, the peak due to NNMBA is not observed in the NMR spectrum. The ^{13}C CP-MAS NMR spectrum of 4 mol% NNMBA-crosslinked polyacrylic acid is given in Fig. 5.

The actual position of the band maxima observed in the electronic (UV-VIS) spectra is a function of the geometry and the strength of the coordinating ligand.[13] The UV-VIS spectra of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes of 4 mol% NNMBA-crosslinked sodium salt of polyacrylic acid are given in Fig. 6.

Two bands corresponding to $^4A_{2g}$–$^4T_{2g}$ (17,391–17,761 cm^{-1}) and $^4A_{2g}$–$^4T_{1g}$ (F) (23,640–23,809 cm^{-1}) transitions were observed in the UV-VIS spectra of Cr(III) complexes. These transitions lead to an octahedral geometry for Cr(III) complexes.[14]

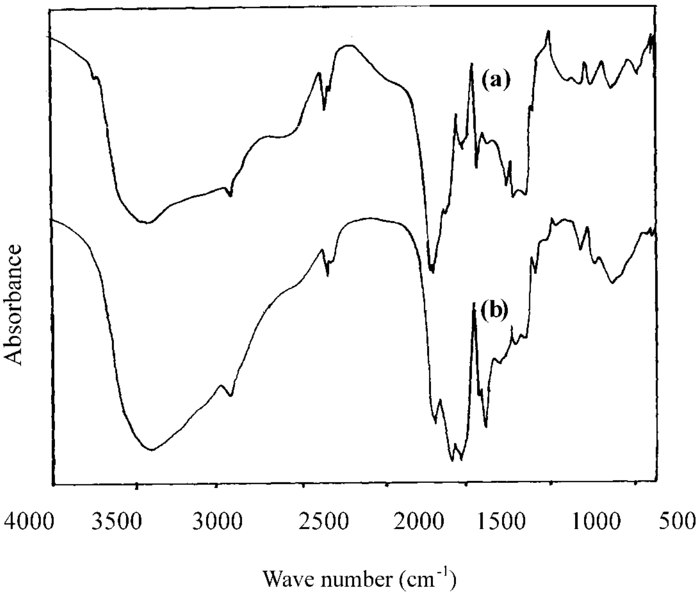


Figure 4. FTIR spectra of 4 mol% NNMBA-crosslinked: (a) polyacrylic acid and (b) Cu(II) complex.

In Mn(II), there are five unpaired electrons with parallel spins. Any electronic transition within the d level must involve a reversal of spins, hence adsorption bands will be extremely weak. This accounts for the pale pink color of the Mn(II) complexes. Mn(II) complexes gave a broad band corresponding to the combined transitions, $^6A_{1g}$–^4E_g and $^6A_{1g}$–$^4A_{1g}$ with an octahedral geometry.

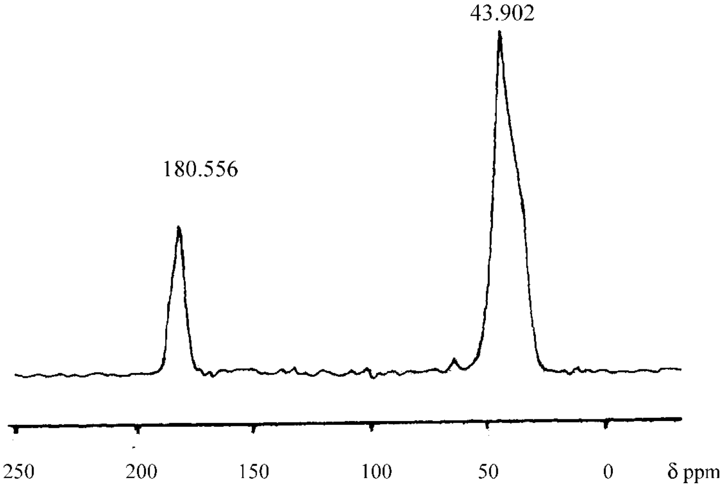


Figure 5. ^{13}C CP-MAS NMR spectrum of 4 mol% NNMBA-crosslinked polyacrylic acid.

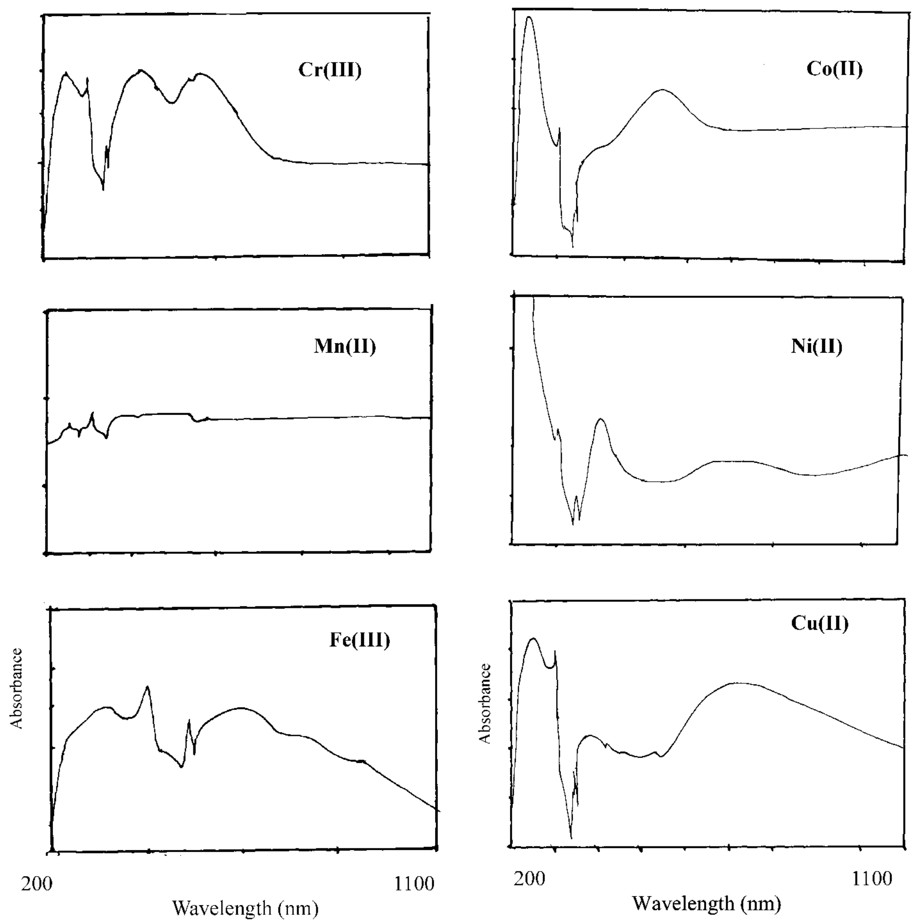


Figure 6. UV-VIS spectra of the various metal complexes of 4 mol% NNMBA-crosslinked polyacrylic acid.

Fe(III) also has a d^5 electronic configuration with five unpaired electrons in a high spin octahedral field. In the present study, Fe(III) complexes exhibited two bands corresponding to $^6A_{1g}$–$^4T_{1g}$ and $^6A_{1g}$–$^4T_{2g}$ transitions. Fe(III) has an extra charge compared to Mn(II) and hence, it is more able to polarize the ligands and hence there is the chance for charge transfer spectra. Hence, Fe(III) complexes are more colored than Mn(II) complexes. Co(II) complexes may be tetrahedral or octahedral. Tetrahedral complexes of Co(II) are intensely blue compared with the pale pink color of octahedral complexes. The deep blue color of the Co(II) complexes of the present study changes to pink when they are exposed to moisture due to change in the geometry.

The UV-VIS spectra of Ni(II) complexes of NNMBA-crosslinked polyacrylic acid gave two spin allowed transitions $^3A_{2g}$–$^3T_{1g}$ (F) (18,518–18,867 cm^{-1}) and $^3A_{2g}$–$^3T_{1g}$ (P) (24,390–24,875 cm^{-1}) in an octahedral field. The broad absorption band in the region 13,947–14,084 cm^{-1} is due to ^2E_g–$^2T_{2g}$ transition in a distorted octahedral field (Jahn–Teller effect).[15] So there is more than one transition. This overlap results in a asymmetrical broad band. In a polymer anchored Zn(II) complex, the spectrum obtained is ligand related and no d–d transition occurs. Therefore, it would have a tetrahedral geometry.

The EPR spectra of Cu(II) complexes of 4–20 mol% NNMBA-crosslinked polyacrylic acids are shown in Fig. 7. This provides direct information on the structure, property and concentration of free radicals. The spectral pattern of paramagnetic Cu(II) complex is influenced by the number of coordinating ligands as well as geometry of the complex. The EPR parameters of various Cu(II) complexes are summarised in Table 3.

The value of $g_{\parallel} > g_{\perp}$ showed that the unpaired electron is in the $dx^2{-}y^2$ orbital of Cu(II) ion and spectral characteristics of axial symmetry.[16] The bonding parameter (α^2 Cu) is calculated by the expression given as:[17]

$$\alpha^2\text{Cu} = -\left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - 2.002) + \frac{3}{7}(g_{\perp} - 2.002) + 0.04$$

For covalent bonding α^2Cu is between 0.75 and 0.80 and for ionic it approaches one. The α^2Cu values for the present Cu(II) complexes of 4–20 mol% NNMBA-crosslinked polyacrylic acids support the covalent character. The smaller the value of α^2Cu, the greater will be the covalent character. Of the four NNMBA-crosslinked systems 4 mol% shows maximum covalent character, while 20 mol% crosslinked system exhibits least covalent character, due to the heavy strain in the polymer matrix.

To study the thermal stability and decomposition patterns of the crosslinked polymers, dynamic thermogravimetric analysis was undertaken.[18] The TG curve of the

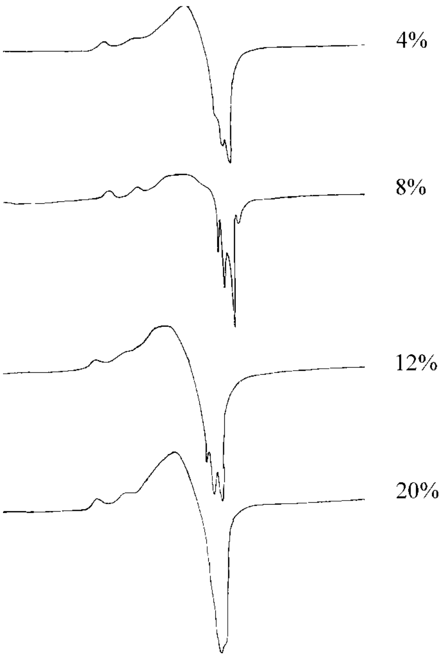


Figure 7. EPR spectra of Cu(II) complexes of 4–20 mol% NNMBA-crosslinked polyacrylic acids.

Table 3. EPR parameters of Cu(II) complexes of 4–20 mol% NNMBA-crosslinked polyacrylic acids.

NNMBA (mol%)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	α^2Cu
4	2.32	2.05	140.00	96.66	0.76
8	2.33	2.07	146.66	76.66	0.79
12	2.34	2.09	130.00	93.33	0.77
20	2.34	2.08	136.66	86.66	0.79

4 mol% NNMBA-crosslinked polyacrylic acid, its sodium salt and Cu(II) complex were run in air. The corresponding TG curves are shown in Fig. 8.

The first stage decomposition of NNMBA-crosslinked polyacrylic acid occurred (32–305°C) with a weight loss of 29%. This is due to the evolution of adsorbed and co-ordinated water molecules. The second stage decomposition occurred (305–440°C) with a weight loss of 42%. This may be due to rupture of the crosslinking agent and breakup of the polymeric networks From 440°C onwards, the whole substance was converted to gaseous products with a weight loss of 29%.

In the case of derivatized resin the first stage decomposition occurred (46–349°C) with a weight loss of 34% due to the evolution of adsorbed and co-ordinated water molecules. The second stage decomposition (349–362°C) occurred with a weight loss of about 42% due to the rupture of polymeric linkages and crosslinkings. The third stage

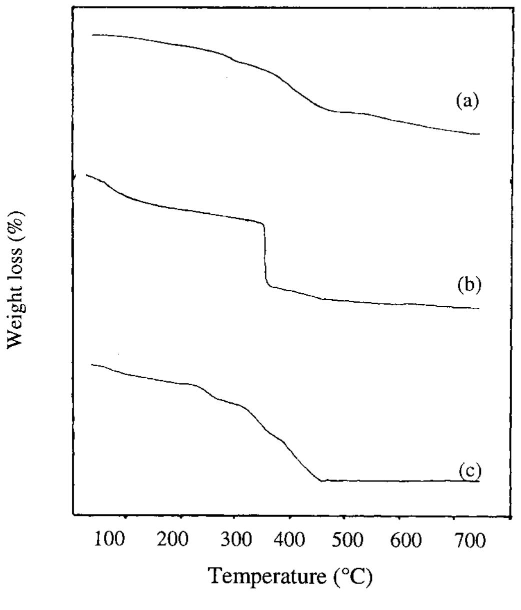


Figure 8. Thermogravimetric curves of 4 mol% NNMBA-crosslinked: (a) polyacrylic acid, (b) sodium salt, and (c) Cu(II) complex.

decomposition (362–456°C) with a weight loss of 8% occurred due to the evolution of gaseous products like carbon dioxide. About 11% Na_2O remained at 676°C.

Since the swelling and water uptake capacity of Cu(II) complex is less compared to the derivatized resin and polyacrylic acid, the first stage decomposition occurred (34–240°C) with a weight loss of about 14%. This is due to the evolution of adsorbed and co-ordinated water. The second stage decomposition occurred (240–378°C) with a weight loss of about 13%. This may be due to the rupture of polymer–copper coordinate bond. As a continuation of this, the rupture of crosslinking and polymeric linkages occurred with a weight loss of 16% (318–361°C). From 361 to 453°C, the whole polymeric moiety might have transformed to gases like carbon dioxide and water with a weight loss of 20%. About 26% CuO remained at 727°C.

Scanning electron microscopy is the most widely used technique to study the shape, size, morphology and porosity of polymers.[19] The change in the surface morphology of the polymeric ligand with complexation has been investigated using this technique.

In the present study SEM was used to probe the change in morphological features of the NNMBA-crosslinked polymeric ligand on complexation. Polyacrylic acid with 4 mol% NNMBA crosslinking and its Cu(II) complex were investigated by the SEM technique. The SEMs of 4 mol% NNMBA-crosslinked polyacrylic acid and its Cu(II) complex are given in Fig. 9. The SEM of uncomplexed resin has a smooth surface. The voids/channels present in the crosslinked polymer matrix are responsible for the swelling of the polymer and the reactivity of the active sites buried within the three dimensional crosslinked polymer matrix. The voids disappeared on complexation due to the contraction of the polymer matrix. The surface became rough resulting from the rearrangement of the macromolecular chains for complexation.

Catalytic Activity of 4–20 mol% NNMBA-Crosslinked Polyacrylic Acid–Metal Complexes

Metal complexes of 4–20 mol% NNMBA-crosslinked polyacrylic acids showed variation in catalytic activity with crosslink density. The reactivity of a ligand function on a crosslinked polymer support is highly dependent on the variables of the polymeric network structure. The catalytic activity of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II),

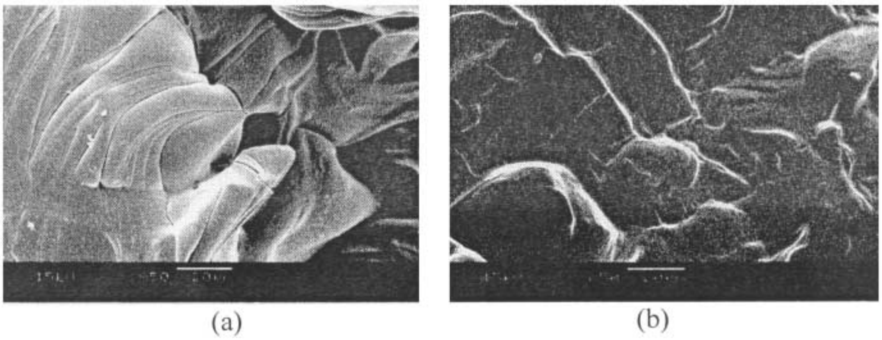

(a) (b)

Figure 9. Scanning electron micrographs of 4 mol% NNMBA-crosslinked: (a) polyacrylic acid and (b) Cu(II) complex.

and Zn(II) complexes of NNMBA-crosslinked polyacrylic acid of different crosslink densities were investigated in the hydrolysis of *p*-nitrophenyl acetate, as shown in Fig. 10. The catalytic activity decreased in the order: Co(II) > Ni(II) > Cu(II) ≈ Zn(II) > Cr(III) > Mn(II) > Fe(III).

Transition metals with their variable valency and unpaired electrons in the d-orbital may form unstable intermediate compounds and hence enhance the reaction. Co(II) complexes of 4–20 mol% polyacrylic acids exhibit maximum catalytic activity. This can be explained by its tetrahedral/octahedral geometry where coordination sites are vacant, thereby form the intermediate compound. Mn(II) and Fe(III) showed less activity compared to Co(II) due to the presence of half filled d-orbital. Complexes where the metal is in the (III) oxidation state are generally more stable than those where metal is in the (II) state. Hence Fe(III) and Cr(III) have less tendency to form intermediate complex compared to Ni(II) and Co(II) and therefore shows lower catalytic activity.

Catalytic activity was followed by comparing the absorbance at 400 nm for definite time interval of two samples of *p*-nitrophenyl acetate of known concentration (1) with catalyst, and (2) without catalyst for about 3 hr. Absorbance at 400 nm is directly proportioned to the amount of *p*-nitrophenol liberated as a result of hydrolysis (Sch. 2).

The amount of *p*-nitrophenol was calculated from the working curve of *p*-nitrophenol at pH 7.8 prepared by plotting concentration against absorbance at 400 nm of known concentrations of *p*-nitrophenol.

Effect of Degree of NNMBA Crosslinking on the Catalytic Activity of Metal Complexes 4–20 mol% Polyacrylic Acids

In order to investigate the effect of NNMBA crosslinking degree on the catalytic activity, the hydrolysis of *p*-nitrophenyl acetate was followed using Co(II) complexes of 4–20 mol% NNMBA-crosslinked polyacrylic acids. The variation in reactivity with different crosslink densitiy is given in Fig. 11. The reactivity of 4 mol% was higher than all other systems. As the crosslink density of the resin increases the accessibility of the reactive site to the reaction medium decreases. In low crosslinked systems, the catalytic site is randomly arranged and it is more easily accessible to the reaction medium. As the

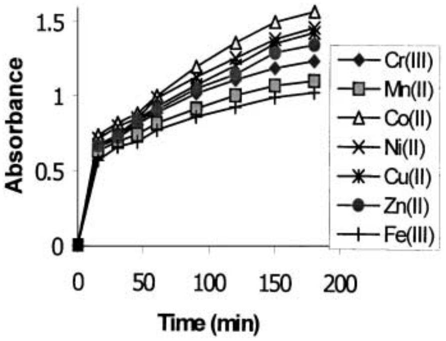
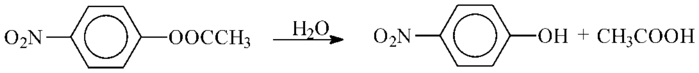


Figure 10. Catalytic activity of the various metal complexes of 4 mol% NNMBA-crosslinked polyacrylic acids.



Scheme 2. Hydrolysis of *p*-nitrophenyl acetate.

crosslink density increases, steric effect by the crosslinks of the entire system increases and the mobility of active center becomes difficult. Hence, the 8–20 mol% NNMBA-crosslinked polyacrylic acid–metal complexes showed less catalytic activity than metal complexes of 4 mol% NNMBA-crosslinked polyacrylic acid. Due to the unequal distribution of NNMBA crosslinks, Co(II) complex of 12 mol% polyacrylic acid exhibited more catalytic activity than Co(II) complex of 8 mol% polyacrylic acid.

Kinetics of Hydrolysis of *p*-Nitrophenyl Acetate Catalyzed by Co(II) Complex of 4 mol% NNMBA-Crosslinked Polyacrylic Acid

In the present study, kinetic study of hydrolysis of *p*-nitrophenyl acetate was followed by Co(II) complex of 4 mol% NNMBA-crosslinked polyacrylic acid at three different temperatures (20°C, 29°C, and 38°C). The hydrolysis was found to be first order. The variation of rate constants with temperature is given in Fig. 12. Compared to other metal complexes Co(II) complex is very active since it requires less activation energy. The kinetic parameters for the Co(II) complex catalyzed hydrolysis were calculated using the Arrhenius equation $k = Ae^{-E/RT}$. The kinetic parameters are:

$$E = 29.7\,\mathrm{kJ}; \quad A = 1.08 \times 10^5\,\mathrm{sec}^{-1}; \quad \Delta S = -148.69\,\mathrm{J}$$

The less activation energy of Co(II) complex is due to the unsaturation in the coordination sphere making the easy accessibility of *p*-nitrophenyl acetate molecule to get involved in catalytic hydrolysis.

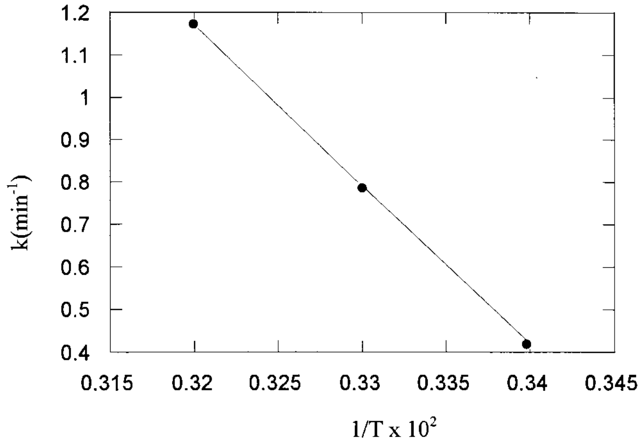


Figure 11. Variation of catalytic activity with NNMBA crosslinking.

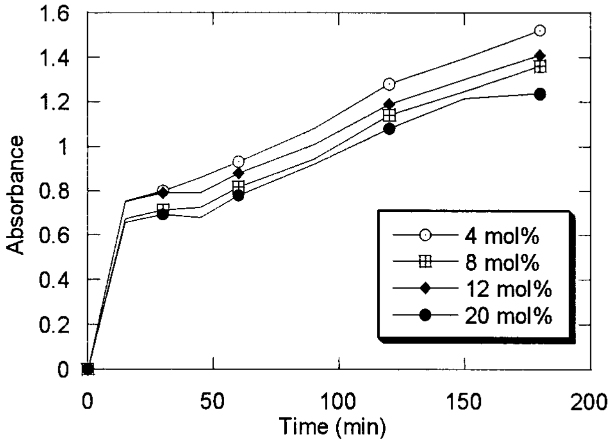


Figure 12. Variation of rate constant with temperature in the hydrolysis of NPA catalyzed by Co(II) complex of 4 mol% NNMBA-crosslinked polyacrylic acid.

Effect of Various Parameters on the Catalytic Activity of Acrylic Acid Based Polymer–Metal Complexes in the Hydrolysis of *p*-Nitrophenyl Acetate

The effect of various parameters like time, temperature, amount of catalyst, pH, and concentration of buffer were found to play a vital role in the hydrolysis of *p*-nitrophenyl acetate. Co(II) complex of 4 mol% NNMBA-crosslinked polyacrylic acid was used for these investigations and the results are depicted in Fig. 13. Heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction. Often this modification takes the form of a fragmentation of the reactant molecules. The activity of a catalyst depends on the strength of chemisorption. To be active, the catalyst should be extensively covered by adsorbate, which is the case if chemisorption is strong. If the strength of the substrate–adsorbate bond becomes too great, the activity declines either because the other reactant molecules cannot react with the adsorbate or because the adsorbate molecules are immobilised on the surface. This pattern of behavior suggests that the reactivity of a catalyst should initially increase and then decrease. This is the reason why the rate of catalysis is not uniform with time. This suggests an acetylation–deacetylation mechanism for the catalytic activity of the polymer–metal complexes in ester hydrolysis. The catalysis starts with the adsorption of the acetyl group which takes place at a higher rate initially. As adsorption increased, the rate of catalysis also increases to some extent and then decreases.

The influence of pH was studied using phosphate buffer with pH values 6.8, 7.6, 7.8, and 8.4 and was in the order $6.8 < 7.6 < 7.8 > 8.4$. The absorbance at 400 nm was observed only after 45 min at pH 6.8, since the rate of hydrolysis of *p*-nitrophenyl acetate at pH 6.8 is very low. Though the rate of hydrolysis increased with increase in pH, maximum catalytic activity was observed at pH 7.8 and then decreased. From this it is concluded that acid hydrolysis of *p*-nitrophenyl acetate is not catalysed by Co(II) complex of polyacrylic acid and the optimum pH is 7.8. Buffer at different concentrations were used and maximum catalytic activity was noticed for 0.05 M buffer. Catalytic activities of

Co(II) complex of 4 mol% NNMBA-crosslinked polyacrylic acid at room temperature and 38°C were compared and found that as temperature increased, catalytic activity also increased. This complex could be used several times without loss of efficiency.

CONCLUSION

The present study revealed that the metal ion complexation of the 4–20 mol% polyacrylic acid, and catalytic activity of their metal complexes decreased as the degree of

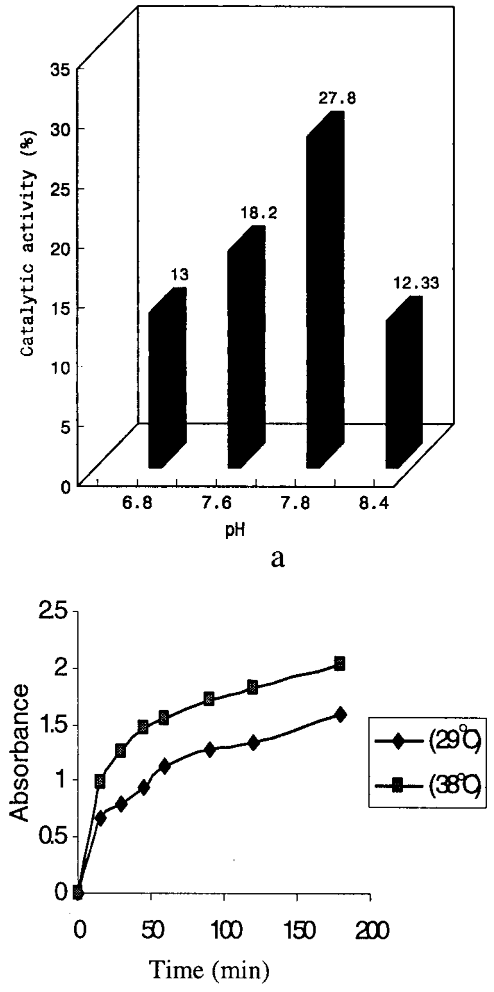
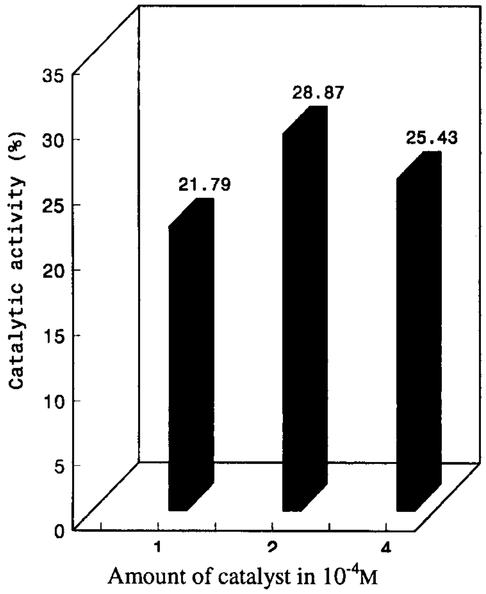
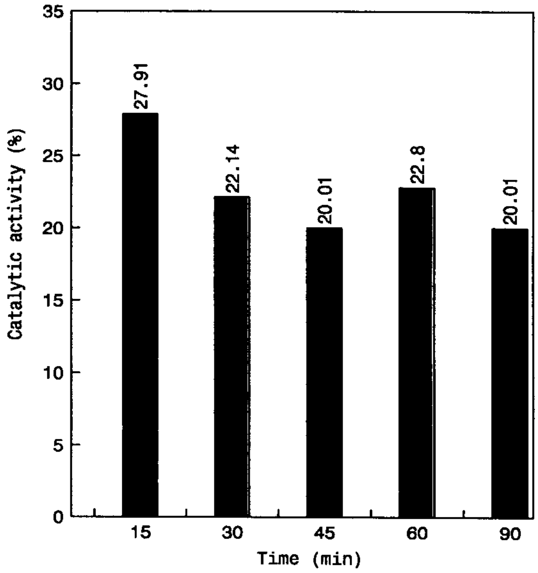


Figure 13. Effect of various parameters on the hydrolysis of *p*-nitrophenyl acetate catalyzed by Co(II) complex of 4 mol% NNMBA-crosslinked polyacrylic acid (a) pH, (b) temperature, (c) amount of the catalyst, and (d) time.



c



d

Figure 13. Continued.

crosslinking increased. The swelling characteristics was measured as equilibrium water content to follow the swelling ability of the studied system in water. The FT-IR and ^{13}C CP-MAS NMR spectral studies were used for the identification of polymeric ligands and their complexation behavior towards various metal ions. The complexation of metal ion lowered the stretching frequencies of the ligand. The UV-VS absorption studies indicated the geometry and structure of different metal complexes. EPR parameters of the polymer anchored Cu(II) complexes provided a definite clue about the nature of ligand to metal bond. Thermal studies were also carried out and thermal dissociation patterns discussed. SEM revealed the change in surface morphology of the polymer on metal ion complexation. The 4 mol% NNMBA-crosslinked polyacrylic acid system exhibited the highest metal ion complexation and catalytic activity among the four NNMBA-crosslinked polyacrylic acid systems studied.

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