

# Studies on Poly(2-hydroxy-4-acryloyloxybenzophenone)-Metal Complexes

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## SYNOPSIS

2-Hydroxy-4-acryloyloxybenzophenone (HABP), prepared from acryloyl chloride with 2,4-dihydroxybenzophenone, was polymerized in methyl ethyl ketone at 70°C using benzoyl peroxide as initiator. Polychelates were obtained in the dimethylformamide solution of poly(HABP) containing a few drops of ammonia with the aqueous solution of Cu(II)/Ni(II) ions. The polymer and polychelates were characterized by elemental analyses and spectral studies. Elemental analyses of the polychelates suggest a metal to ligand ratio of 1 : 2. The IR spectral data of polychelates indicate that the metals were coordinated through the oxygen of the keto group and the oxygen of the phenolic-OH group. The diffuse reflectance spectra, electron paramagnetic resonance, and magnetic moments of the polychelates show an octahedral and square planar structure for poly(HABP)-Ni(II) and poly(HABP)-Cu(II) complexes, respectively. X-ray diffraction studies revealed a high crystalline nature of the polychelates. The thermal properties of polymer and metal complexes and their catalytic activity are discussed. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Considerable attention has been paid in the past two decades to the synthesis of polymer-metal complexes because of their interesting features. The polymer-metal complexes, prepared by complexation of metal ions with functional groups in the polymer matrices, have superior properties that are difficult to achieve from corresponding monomeric metal complexes. The chelate resin, functionalized by the multidentate ligand, is often used for these purposes. The free radical polymerization of a Cu complex with Schiff's base ligand containing the vinyl group and radical polymerization of methacrylate monomers coordinated to Co(III) were reported.<sup>1-4</sup> A series of pendant type polymer-metal complexes having a uniform structure by the substitution reaction between a polymer ligand and a metal ion such as Co(III) or Cr(III) was also reported.<sup>5</sup> Dingman et al. studied the adsorption of metal ion on poly(ethylenimine) crosslinked with

toluene diisocyanate and showed the amount of metal ions adsorbed decreases with an increase in the degree of crosslinking.<sup>6</sup> In continuation of our earlier research in this domain,<sup>7-9</sup> herein the authors report the synthesis, characterization, and thermal properties of a new poly(2-hydroxy-4-acryloyloxybenzophenone) [poly(HABP)] and its Cu(II) and Ni(II) complexes.

## EXPERIMENTAL

### Materials

Benzoyl peroxide (BPO; from BDH) was recrystallized from a chloroform-methanol mixture. 2,4-Dihydroxybenzophenone (Fluka) was recrystallized from ethanol. Acryloyl chloride was prepared by the procedure reported elsewhere.<sup>10</sup> Copper acetate and nickel acetate (Fluka) were used as received.

### Synthesis of HABP

2,4-Dihydroxybenzophenone (2 mmol), triethylamine (2 mmol), methyl ethyl ketone (MEK, 200

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mL), and hydroquinone (0.5 g) were placed in a three-necked flask equipped with a stirrer, thermometer, and stoppered funnel, and the contents were cooled to approximately  $-5^{\circ}\text{C}$ . Acryloyl chloride (2 mmol in 25 mL of MEK) was added dropwise with constant stirring and cooling. The reaction mixture was gradually allowed to attain room temperature and was maintained for 2 h. Thus the by-product, quaternary ammonium salt, formed was filtered off. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulfate, and the solvent was evaporated *in vacuo*. The crude HABP was recrystallized from ethanol (mp  $72-74^{\circ}\text{C}$ ). The IR and  $^1\text{H-NMR}$  spectra were consistent with the assigned structure. IR (KBr):  $3600\text{ cm}^{-1}$

( $-\text{OH}$ );  $1760\text{ cm}^{-1}$  ( $\text{C}-\text{O}$  ester);  $1650\text{ cm}^{-1}$   
 $\text{C}-\text{O}$  ketone);  $1600\text{ cm}^{-1}$  (Ar,  $\text{C}-\text{C}$ ).  $^1\text{H-NMR}$ :  
 Ar-OH(s)  $9\delta$ , Ar-H(m)  $6.90-7.8\delta$ ;  $\text{CH}_2$ (s)  $1.85\delta$ .

### Polymerization

HABP (3 mmol), MEK (50 mL), and BPO (0.5 g) were placed in a standard reaction tube (100 mL) and purged with nitrogen gas for half an hour. Then the tube was closed and kept at  $70^{\circ}\text{C}$  for 10 h. Then a large excess of methanol was added to the contents, and the precipitated poly(HABP) was filtered, washed with methanol, and purified by *N,N*-dimethylformamide (DMF)-methanol solution. The purified polymer was dried under vacuum at  $50^{\circ}\text{C}$  for constant weight.

### Synthesis of Poly(HABP)-Metal Chelates

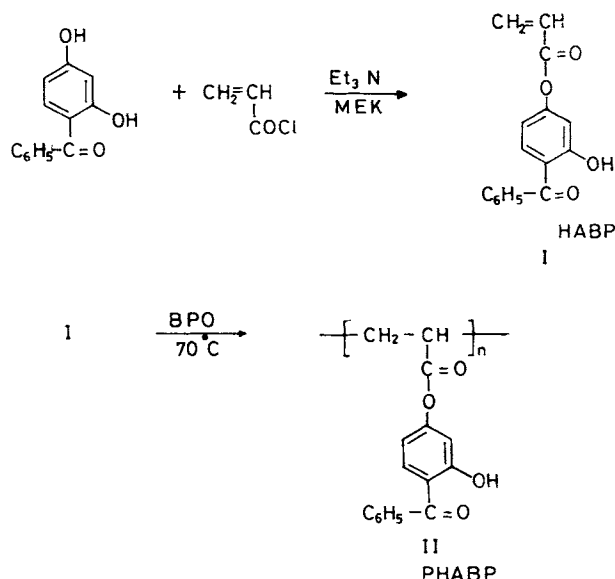
Polymer-metal complexes were prepared at room temperature by the solution technique. A typical procedure for the preparation of polymer-Cu(II) chelate is as follows: poly(HABP) (4.12 g) was dissolved in 100 mL of DMF and the pH of the solution was adjusted to 7 with dilute  $\text{NH}_4\text{OH}$ . An aqueous solution of Cu(II) (5 mmol) acetate solution was added dropwise to the polymer solution with constant stirring. The mixture was then digested in a water bath for 2 h and kept overnight at room temperature. The precipitated poly(HABP)-metal complex was filtered, washed with hot distilled water followed by ethanol, and dried at  $60^{\circ}\text{C}$  *in vacuo*. A similar procedure was adopted for the preparation of Ni(II) chelates.

### Measurements

The elemental analyses of HABP, poly(HABP), and the polychelates were carried out using a Heareus carbon-hydrogen analyzer. The amount of copper and nickel present in the polymer-metal complexes was estimated using titrimetric procedures after decomposing the polymers. The viscosity measurement of poly(HABP) was made in an Ubbelohde suspended-level viscometer using DMF at  $30^{\circ}\text{C}$ . The molecular weights ( $M_w$  and  $M_n$ ) of poly(HABP) were determined by a Waters 501 gel permeation chromatograph, using THF as solvent, equipped with a RI detector and calibrated with polystyrene standards. IR spectra of poly(HABP) and poly(HABP)-metal complexes were recorded on a Perkin-Elmer 782 spectrophotometer using a KBr pellet. The  $^1\text{H-NMR}$  spectrum of poly(HABP) was recorded on a Hitachi 90 MHz spectrometer in  $\text{CDCl}_3$  using tetramethylsilane (TMS) as the internal standard. The  $^{13}\text{C-CP/MAS}$  (cross polarization/magic angle spinning) NMR spectrum of the polymer was recorded on a Bruker MSL CP-MAS spectrometer.

The magnetic moments ( $\mu_M = 2.83\sqrt{\chi_M \times T}$ ) were measured using the Gouy method and corrected for the diamagnetism of the component using Pascal's constant. The diffuse reflectance spectra ( $8,000-26,000\text{ cm}^{-1}$ ) were measured on a Karl Zeiss VSU-28 spectrophotometer. Electron paramagnetic resonance (EPR) analyses were carried out at room temperature using a Varian spectrophotometer. X-ray diffraction experiments were performed with a Philips PW 1820 diffractometer and a Statton camera using  $\text{CuK}_\alpha$  radiation of wavelength  $1.542\text{ \AA}$ . Thermogravimetric analyses (TGA) were carried out in a Mettler TA3000 thermobalance. Five milligrams of sample was used at a heating rate of  $15^{\circ}\text{C min}^{-1}$  in air. The glass transition temperatures of poly(HABP) and the metal complexes were determined by differential scanning calorimetry with Du Pont 900 thermal analyzer at a heating rate of  $15^{\circ}\text{C min}^{-1}$  in air.

The electrical conductivity of the polychelates was measured on pellets of 10 mm diameter and 2-3 mm thickness using a Keithley electrometer. Hydrolysis of ethylacetate and polymerization of *N*-vinylpyrrolidone by Cu(II)/Ni(II) chelates at  $65$  and  $70^{\circ}\text{C}$ , respectively, were carried out in the usual manner. The catalytic oxidation of cyclohexanol to cyclohexanone was carried out in Schlenk tube under oxygen atmosphere. Cyclohexanol (2.5 mmol), 2-butanone (4 mL), polymer Cu(II)/Ni(II) complex (0.5 mmol based on metal), and  $\text{H}_2\text{O}_2$  (0.5 mmol)



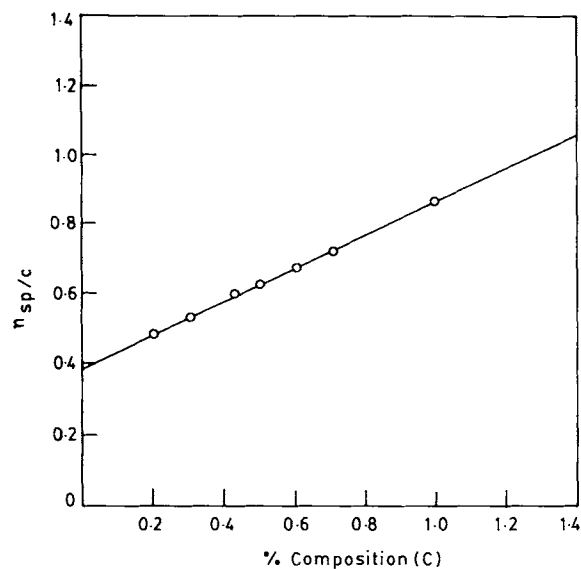
**Scheme 1** Synthesis of monomer and polymer.

were inserted and stirred magnetically at 80°C for 6 h. Aliquots (1  $\mu$ L) were withdrawn and analyzed by GC.

## RESULTS AND DISCUSSION

HABP was prepared and polymerized in MEK using BPO as initiator according to Scheme 1.

The polymer is soluble in chloroform, DMF, THF, and DMSO and insoluble in common organic solvents like benzene, toluene, methanol, and water. Polymer-metal complexes were obtained in DMF containing poly(HABP) with the aqueous solution of metal ions [Cu(II) and Ni(II)] in the presence



**Figure 1**  $\eta_{sp}/c$ -C plot for the determination of intrinsic viscosity of poly(HABP).

of a few drops of ammonia. The polychelates were insoluble in common organic solvents but sparingly soluble in DMF. The elemental analyses data for poly(HABP) and metal complexes are listed in Table I. The elemental analyses data reveals that metal to polymer ratio is 1:2.

Viscometric results are shown in Figure 1. The intrinsic viscosity  $[\eta]$  was obtained by extrapolating  $\eta_{sp}/c$  to zero concentration. The intrinsic viscosity of poly(HABP) was determined to be 0.39 dL g<sup>-1</sup>. The result revealed that the polymer was of moderately high molecular weight. The number average molecular weight ( $\bar{M}_n$ ) and weight average molecular weight ( $\bar{M}_w$ ) of poly(HABP) were obtained by gel

**Table I** Elemental Analyses of HABP, Poly (HABP), and Polychelates

Compound	Elemental Formula	Calculated (wt %)				% Found (wt %)			
		C	H	O	Cu/Ni	C	H	O	Cu/Ni
HABP	C <sub>16</sub> H <sub>12</sub> O <sub>4</sub>	71.64	4.47	23.88		71.62	4.49	23.89	
Poly (HABP)	C <sub>16</sub> H <sub>12</sub> O <sub>4</sub>	71.64	4.47	23.88		71.63	4.46	23.91	
Poly (HABP)-Cu (II) complex	(C <sub>16</sub> H <sub>11</sub> O <sub>4</sub> ) <sub>x</sub> Cu	64.86	3.71	21.62	9.72	64.71	3.78	21.64	9.87
Poly (HABP)-Ni (II) complex	(C <sub>16</sub> H <sub>11</sub> O <sub>4</sub> ) <sub>y</sub> Ni (H <sub>2</sub> O) <sub>y</sub>	61.34	4.15	25.55	8.94	61.20	4.27	25.89	8.64

Calculated percentage of C, H, O, Cu, and Ni for polymer-metal complexes are based on the value of  $x = y = 2$ , found  $x = 2.02$ ,  $y = 2.01$ .

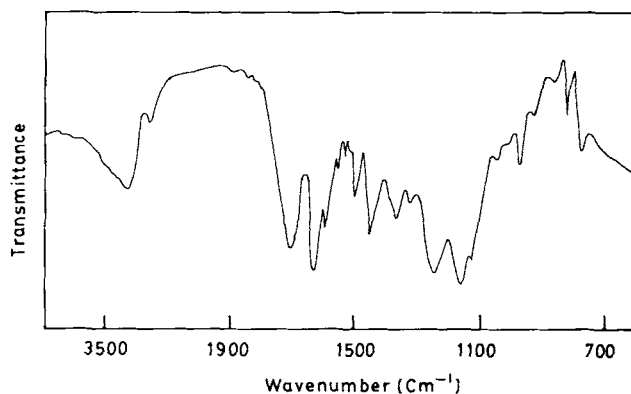


Figure 2 IR Spectrum of poly(HABP).

permeation chromatography using THF:  $\bar{M}_n$   $1.85 \times 10^4$ ;  $\bar{M}_w$   $3.01 \times 10^7$ . The polydispersing index ( $\bar{M}_w/\bar{M}_n$ ) for poly(HABP) is 1.62. The theoretical value of  $\bar{M}_w/\bar{M}_n$  for poly(HABP) suggests a strong tendency for chain termination by radical recombination.

The IR spectrum of poly(HABP) is shown in Figure 2. The absorption band near  $3000\text{--}3260\text{ cm}^{-1}$  corresponds more to phenolic-OH stretching than that desired at  $3600\text{ cm}^{-1}$  due to intramolecular and intermolecular hydrogen bonding,<sup>11</sup> presumably formed between phenolic-OH and ketonic oxygen. The phenolic-OH stretching disappears in the spectra of polychelates indicating the coordination and participation with metal ions.<sup>12</sup> Ni(II) polychelates show a strong absorption band in the region ( $3500\text{ cm}^{-1}$ ) owing to coordination of  $\text{H}_2\text{O}$  molecules to Ni(II). This band remains even when polymer-metal complexes were heated up to  $150^\circ\text{C}$ . Poly(HABP) displays strong bands at  $1730$  and  $1625\text{ cm}^{-1}$ , ascribed to C—O of ester and ketonic groups, respectively. In the spectra of polychelates, the band at  $1620\text{ cm}^{-1}$  shifts to a lower frequency indicating the coordination through the oxygen of the keto group.<sup>13–15</sup> The medium intensity band at  $1120\text{ cm}^{-1}$  in the spectrum of poly(HABP) may be assigned to C—O vibration of the hydrogen-bonded ring system of the ligand.<sup>16</sup> On coordination, this band shows a small positive shift indicating involvement of phenolic-OH in bonding with the metal ion.<sup>17,18</sup>

The typical  $^1\text{H-NMR}$  spectrum of poly(HABP) is shown in Figure 3. A broad multiplet resonance signal appearing at  $7.90\delta$  may be attributed to the phenolic-OH proton. A singlet at  $6.90\delta$  corresponds to the substituted phenyl ring. The resonance signals around  $6.73\text{--}7.6\delta$  are due to the aromatic protons.

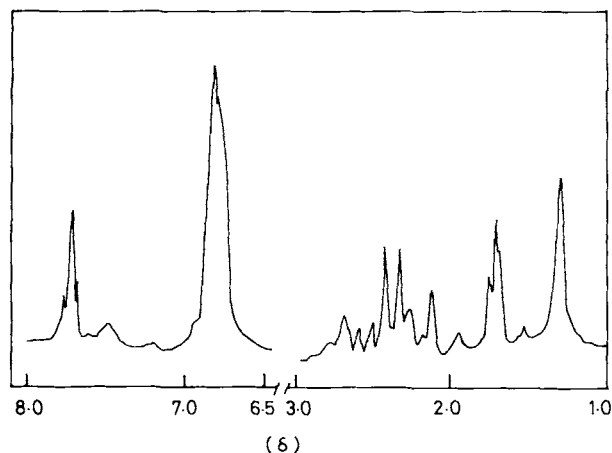


Figure 3  $^1\text{H-NMR}$  spectrum of poly(HABP).

The resonance signals at  $1.85\delta$  and  $2.82\delta$  are due to methylene and methine protons. The  $^{13}\text{C-CP/MAS}$  NMR spectrum of poly(HABP) is shown in Figure 4. The broad singlet between  $20$  and  $50\delta$  is due to methylene and methine carbons. The esteric carbonyl carbon signal appears at  $171\delta$ . The intramolecular hydrogen-bonded keto carbonyl carbon appeared at  $199\delta$ . The aromatic ring carbons produced very broad signals from  $100$  to  $140\delta$ .

The diffuse reflectance spectrum of Cu(II) polymeric chelate contains two bands, one at  $15,075\text{ cm}^{-1}$

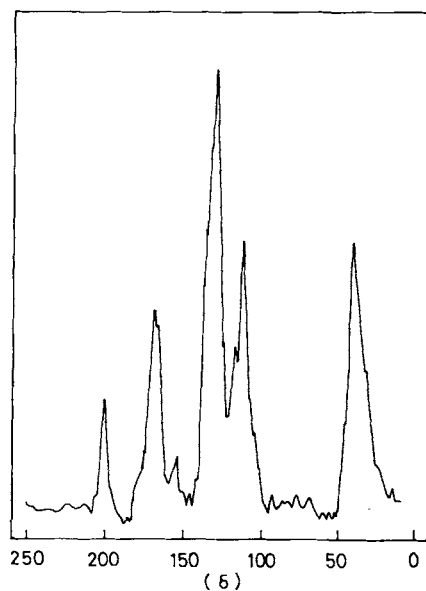
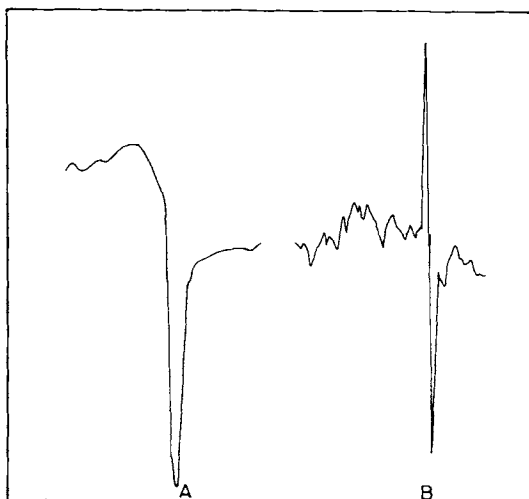


Figure 4 Solid-state  $^{13}\text{C-C/MAS}$  NMR spectrum of poly(HABP).



**Figure 5** EPR spectra of poly(HABP) (A) Cu(II) (B) Ni(II) complexes.

and the other at  $23,785\text{ cm}^{-1}$ , that may be assigned to  $d-d$  transition corresponding to the  ${}^2E_g \rightarrow T_{2g}$  transition and to a symmetry-forbidden ligand-metal charge-transfer band.<sup>19-21</sup> The electronic spectra of the Ni(II) chelate polymer shows three bands at  $12,345$ ,  $13,954$ , and  $16,932\text{ cm}^{-1}$ . These may be due to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ , and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions, respectively. Based on comparison of the present data with that of the literature, an octahedral configuration may be assigned for Ni(II) polychelates.<sup>22-27</sup>

The EPR spectra of Cu(II) and Ni(II) are shown in Figure 5. The EPR spectrum of the cupric complex shows a strong signal characteristic of that of bivalent copper. This is attributed to the square planar cupric ion in the center with the oxygen of the phenolic-OH and carbonyl oxygen groups on the  $x$  and  $y$  axis. Low spin Ni(II) in an octahedral field with tetragonal distortion is expected to have spin orbit coupling parameter of  $g > 0$ , and as a consequence,  $g_{\parallel} > g_{\perp}$ . The EPR parameters calculated for the Ni(II) complex are shown in Table II; the  $g$  values are very consistent with Ni(II) in an octahedral environment.

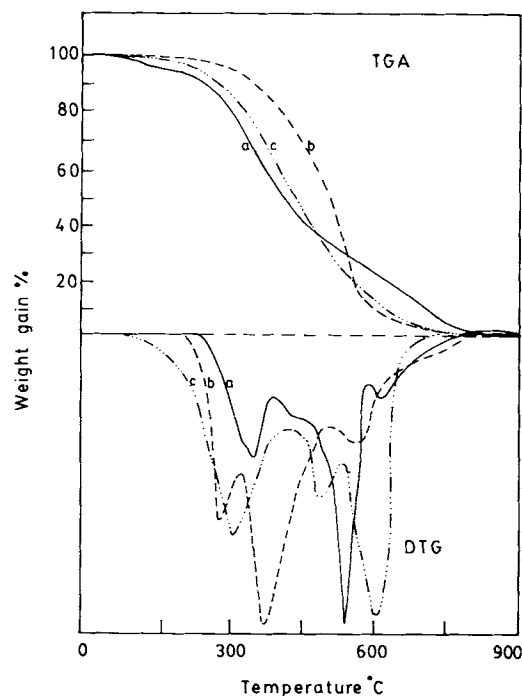
Cu(II) polychelate has a magnetic moment of  $1.76\text{ BM}$ , indicating a square planar configuration. The magnetic moment of  $3.17\text{ }\mu_B$  and the paramagnetic behavior of Ni(II) complexes suggest that distorted octahedral geometry for Ni(II) polychelates.<sup>28</sup> The X-ray diffraction studies showed that poly(HABP) is amorphous whereas its polychelates possess good crystallinity. The crystallinity in polychelates may not be due to any ordering in poly(HABP) induced

**Table II** EPR Parameter of Cu(II)/Ni(II) Complexes

Complexes	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel G}$	$A_{\perp G}$
Cu(II)	2.23	2.14	35.6	32.8
Ni(II)	2.20	2.18	38.0	31.9

during metal-chelates anchoring. It is more because anchoring of metals to poly(HABP) would imply interchain crosslinking between poly(HABP) chains, which should further reduce rather than enhance any such ordering. The appearance of crystallinity in poly(HABP)-metal complexes may be because of the inherent crystalline nature of the metallic compounds.

The TGA and DTG traces of poly(HABP) and polychelates are shown in Figure 6. The differential thermal analytical data are listed in Table III. The poly(HABP) was found to be stable up to  $200^{\circ}\text{C}$  and degraded in air thereafter; the corresponding polychelates started to decompose above  $300^{\circ}\text{C}$ . Around  $750^{\circ}\text{C}$  all the polychelates lost  $\approx 98\%$  of their weight. The Cu(II) polychelates were found to be more stable than Ni(II) polychelates. The glass-transition temperature for poly(HABP), poly(HABP)-Cu(II), and poly(HABP)-Ni(II) chelates was found to be  $145$ ,



**Figure 6** TGA and DTG curves of (a) poly(HABP), (b) poly(HABP)-Cu(II), and (c) poly(HABP)-Ni(II) chelates.

**Table III Thermogravimetric Data of Poly (HABP)**

Sample No.	Sample	Weight Loss (%)					
		200°C	300°C	400°C	500°C	600°C	700°C
1	Poly (HABP)	2.45	15.72	45.22	81.70	97.50	98.17
2	Poly (HABP)-Cu (II)	3.50	29.01	41.48	77.16	92.48	95.14
3	Poly (HABP)-Ni (II)	4.69	65.32	85.98	96.20	96.69	97.73

225, and 197°C, respectively. The IR, <sup>1</sup>H-NMR, <sup>13</sup>C-CP/MAS, EPR, electronic spectra, and magnetic moments studies confirmed that the chelation of metal ions may possibly occur between two groups from different polymeric chains as shown in the Scheme 2.

On reduction of the keto groups by NaBH<sub>4</sub>, the polymer failed to form complexes confirming the coordination through the oxygen of the keto groups and the oxygen of the phenolic-OH groups. The Cu(II) complex catalyzed the oxidation of cyclohexanol to cyclohexanone (13% yield) in the presence of H<sub>2</sub>O<sub>2</sub>, whereas the Ni(II) complex showed negative results. The esterhydrolysis of ethylacetate to ethanol and acetic acid with 15% yield as well as polymerization of *N*-vinylpyrrolidone with 20% conversion were achieved using the Cu(II)/Ni(II) polychelates. The electrical conductivity of the Cu(II) and Ni(II) polychelates is  $2.97 \times 10^{-9}$  and  $0.78 \times 10^{-9}$  ohm cm<sup>-1</sup>, respectively, in other words, the polychelates are poor electrical conductors.

## CONCLUSION

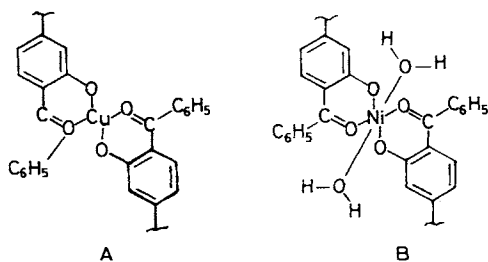
Poly(HABP) was synthesized from 2-hydroxy-4-acryloyloxybenzophenone, and its polychelates were characterized spectroscopically. Transition metal ions (Cu<sup>2+</sup> and Ni<sup>2+</sup>) were attached through coordinate bonds to a functionalized backbone. Magnetic studies reveal that all the complexes are paramag-

netic. The conductivity study suggests that the metal complexes behave as an insulator. The copper complex is square planar whereas the Ni<sup>2+</sup> is octahedral. Their possible structures are assigned for the two complexes. The catalytic studies confirmed that these polychelates possess catalytic activity.

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**Scheme 2** Structure of polychelates.

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