

# Studies of Poly(8-hydroxy-4-azoquinolinephenol-formaldehyde) and Its Metal Complexes

S. Vijayalakshmi, S. Subramanian, S. Rajagopan, T. Kaliyappan

Department of Chemistry, Pondicherry Engineering College, Pondicherry 605014, India

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**ABSTRACT:** Poly(8-hydroxy-4-azoquinolinephenol-formaldehyde) resin (8H4AQPF) was prepared by condensing 8-hydroxy 4-azoquinoline phenol with formaldehyde (1 : 1 mol ratio) in the presence of oxalic acid. Polychelates were obtained when the DMF solution of poly(8H4AQPF) containing a few drops of ammonia was treated with the aqueous solution of Cu(II) and Ni(II) ions. The polymeric resin and polymer-metal complexes were characterized with elemental analysis and spectral studies. The elemental analysis of the polymer-metal complexes suggested that the metal-to-ligand ratio was 1 : 2. The IR spectral data of the polychelates indicated that the metals were coordinated through

the nitrogen and oxygen of the phenolic —OH group. Diffuse reflectance spectra, electron paramagnetic resonance, and magnetic moment studies revealed that the polymer-metal complexes of the Cu(II) complexes were square planar and those of the Ni(II) complexes were octahedral. X-ray diffraction studies revealed that the polymer metal complexes were crystalline. The thermal properties of the polymer and polymer-metal complexes were also examined. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1506–1510, 2006

**Key words:** metal-polymer complexes; radical polymerization; ion exchangers; macromonomers; viscosity

## INTRODUCTION

Polymer-metal complexes have been of interest to many researchers during the past three decades in light of their potential applications in diversified fields such as organic synthesis, wastewater treatment, hydrometallurgy, polymer drug grafts, recovery of trace metal ions including radioactive elements, catalytic reactions, and models for enzymes.<sup>1</sup> A number of polymer-containing chelating ligands, including polydentate amines, crown ethers, and porphyrin, have been reported.<sup>2</sup> Selective chelation of specific metal ions from a metal ion mixture by using a number of tetradentate ligands attached to polystyrene divinylbenzene was demonstrated by Melby et al.<sup>3</sup> Chelating resins prepared by copolycondensation of 8-hydroxyquinoline or phenol derivatives like 2-amino phenol,  $\beta$ -resorcylic acid, or resorcinol with formaldehyde were reported by Pennington and Williams<sup>4</sup> and Aristov et al.<sup>5</sup> Sykora et al.<sup>6</sup> prepared a selective ion-exchange resin by reacting a condensation product of 2,4-dihydroxyacetophenone and anthranilic acid with formaldehyde. Parmer et al.<sup>7</sup> synthesized 2,4-dihydroxy acetophenone formaldehyde resin in an acidic medium and studied its chelation properties. Preparation of a copper-selective polymeric ligand by the

reaction of phenol formaldehyde and piperazine was reported by Hodgkin et al.<sup>8</sup> In continuation of our research<sup>9,10</sup> in this area, the present article deals with the synthesis and characterization of poly(8-hydroxy-4-azoquinolinephenol-formaldehyde) and its Cu(II) and Ni(II) metal complexes.

## EXPERIMENTAL

8-Hydroxyquinoline and 4-aminophenol (Fluka, France) were purified according to standard procedures, the solvents were purified using standard procedures and then used, and 8-hydroxy-4-azoquinolinehydroxybenzene was prepared according to Mang et al.<sup>11</sup>

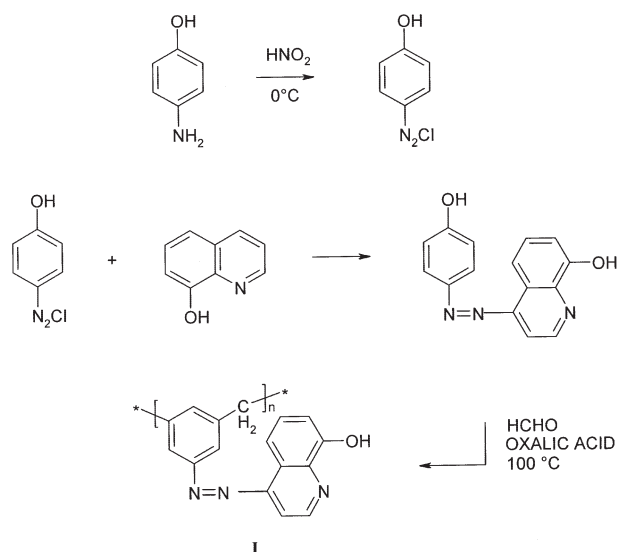
### Synthesis of macromonomer

8-Hydroxy-4-azoquinolinehydroxybenzene (5.3 g, 0.02M), formaldehyde (Loba, India) (1.2 g, 0.04M), and oxalic acid [(Merck, India) 0.18 g, 3 % (w/w)] were added to a round-bottomed flask, sealed, and kept at 100°C for 24 h in an oil bath. The formaldehyde resin formed in the flask was washed with distilled water and then dissolved in DMF, and NaCl (10%) solution was added to precipitate the resin. Then the resin was filtered and dried. The IR and <sup>1</sup>H-NMR spectra were consistent with the assigned structure (Scheme 1).

### Synthesis of polymer metal complexes

Polymer metal complexes of Cu(II)/Ni(II) were prepared in an alkaline medium at room temperature.

Correspondence to: T. Kaliyappan (tkaliyappan2001@yahoo.com).



Scheme 1

The polymer (1.37 g, 0.005M) was dissolved in 30 mL of DMF. An aqueous solution of Cu(II)/Ni(II) acetate (0.62 g) was added dropwise with constant stirring, and the pH of the solution was adjusted to 7 with dilute ammonium hydroxide solution. The resulting mixture was digested on a water bath for 2 h and kept overnight at room temperature. The precipitated poly(8H4AQPF)Cu(II)/Ni(II) complex was filtered, washed with hot distilled water, and dried.

### Measurements

The IR spectra of the polymer and polymer metal complexes were recorded on a Bomem MB 104 FTIR spectrometer from 500 to 4000  $\text{cm}^{-1}$  using KBr pellets. The  $^1\text{H-NMR}$  spectra of the polymer were recorded on a JEOL GSX 400 MHz spectrometer using DMSO- $d_6$  as the solvent and tetramethylsilane as the internal standard. The molecular weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) of the polymers were determined by GPC (Water's model 410) using THF as the eluent. Elemental analyses were performed on a Coleman CHN analyzer. The metal

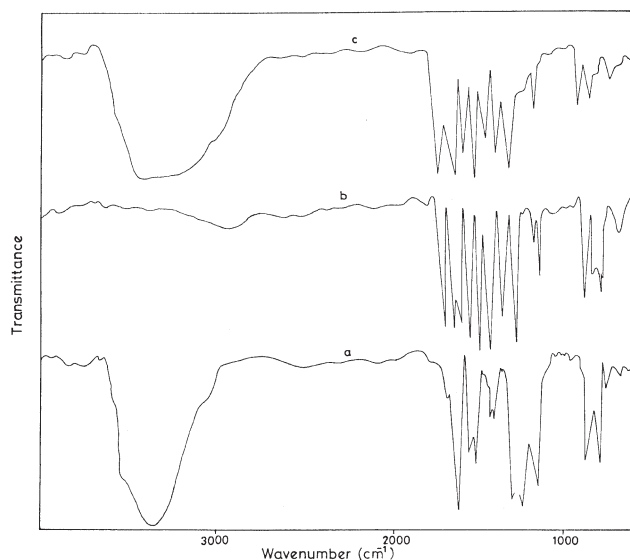


Figure 1 IR spectra of (a) poly(8H4AQPF), (b) poly(8H4AQPF)-Cu(II), and (c) poly(8H4AQPF)-Ni(II).

content of the polymer metal complexes was determined using a titrimetric procedure after decomposing the polychelates with concentrated HCl, perchloric,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ . The viscosity measurements were made in THF at 30°C with an Ubbelohde suspended level viscometer. The glass-transition temperatures of the polymers and metal complexes were determined by differential scanning calorimetry (DSC) with a Dupont 900 thermal analyzer at a heating rate of 15°C/min in air.

The magnetic moments were measured using the Guoy method. The diffuse reflectance spectra (500–2000 nm) were measured on a Varian Cary 5E UV-vis-NIR spectrophotometer. X-ray diffraction experiments were performed in a Philips PW1820 diffractometer. Thermogravimetric analysis (TGA) was carried out in a Seiko Instruments Inc. A 5-mg sample was used at a heating rate of 15°C/min in air.

### RESULTS AND DISCUSSION

The novel poly(8H4AQPF) was synthesized from 8-hydroxy-4-azoquinolinehydroxybenzene and form-

TABLE I  
Elemental Analysis of Poly(8H4AQPF) and Its Metal Complexes

Abbreviation	Empirical formula	Elemental analysis (weight percent)									
		Carbon		Hydrogen		Oxygen		Nitrogen		Metal	
		Cal. <sup>a</sup>	Fd.	Cal. <sup>a</sup>	Fd.	Cal. <sup>a</sup>	Fd.	Cal. <sup>a</sup>	Fd.	Cal. <sup>a</sup>	Fd.
(Poly(8H4AQPF))	$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$	69.31	69.33	4.00	4.01	11.54	11.52	15.15	15.14	—	—
Poly(8H4AQPF)-Cu(II)	$(\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_3)_x\text{-Cu(II)}$	56.54	56.52	2.96	2.97	9.42	9.43	12.37	12.35	18.71	18.73
Poly(8H4AQPF)-Ni(II)	$(\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_3)_x\text{-Ni(II)}$ $(\text{H}_2\text{O})_y$	57.36	57.37	3.01	3.02	9.55	9.53	12.55	12.56	17.53	17.52

<sup>a</sup> Calculated percentage of C, H, N, O, and metal ions for polymer-metal-complexes based on the value  $x = y = 2.00$ . Found:  $x = 2.02$   $y = 2.01$ .

TABLE II  
IR Spectral Data of Poly(8H4AQPF) and Its  
Metal Complexes

Sample	OH <sub>str</sub>	C—N <sub>str</sub>	N—N <sub>str</sub>	M—N <sub>str</sub>
Poly(8H4AQPF)	3100 <sub>(b)</sub>	1600 <sub>(s)</sub>	1560 <sub>(s)</sub>	—
Poly(8H4AQPF)-Cu(II)	—	1605 <sub>(s)</sub>	1545 <sub>(s)</sub>	725
Poly(8H4AQPF)-Ni(II)	3300 <sub>(b)</sub>	1605 <sub>(s)</sub>	1540 <sub>(s)</sub>	735

b—broad, s—strong.

aldehyde in the presence of oxalic acid. Polymer metal complexes were obtained from a DMF solution of polymer and an aqueous solution of the metal ions Cu(II) and Ni(II) in the presence of a few drops of ammonia. The polymers were soluble in DMF, THF, and DMSO and insoluble in common organic solvents like benzene, toluene, methanol, and water. The elemental analysis data for the polymer and polymer-metal complexes are presented in Table I. The elemental analysis data suggested that the metal to polymer ratio was 1 : 2. The intrinsic viscosity  $[\eta]$  was obtained by extrapolating  $\eta_{sp}/C$  to a zero concentration. The intrinsic viscosity of poly(8H4AQPF) was determined to be 0.59 dL/g.

The number-average molecular weight ( $\bar{M}_n$ ) and the weight-average molecular weight ( $\bar{M}_w$ ) of the poly(8H4AQPF) were determined by gel permeation chromatography using tetrahydrofuran ( $\bar{M}_n = 1.81$  and  $\bar{M}_w = 3.99 \times 10^4$ ). The polydispersity index ( $\bar{M}_w/\bar{M}_n$ ) for poly(8H4AQPF) was 2.204. The theoretical value of  $\bar{M}_w/\bar{M}_n$  for poly(8H4AQPF) suggested a strong tendency for chain termination by radical recombination.

The IR spectra of poly(8H4AQPF) and its polychelates are shown in Figure 1. The IR spectra show a

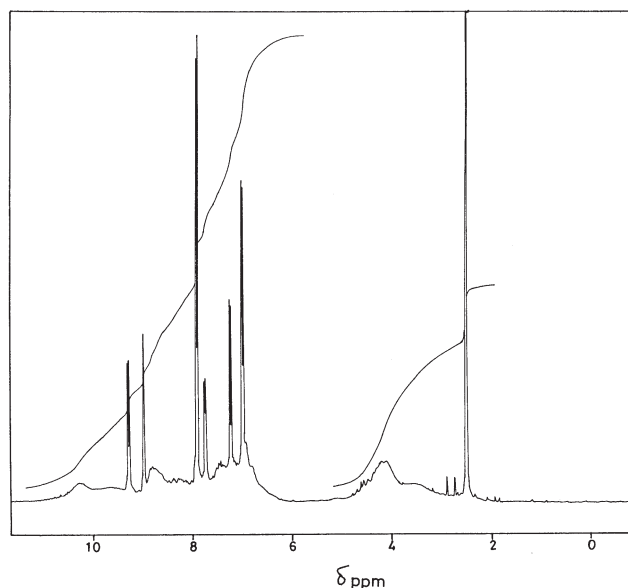


Figure 2 <sup>1</sup>H-NMR spectrum of poly(8H4AQPF).

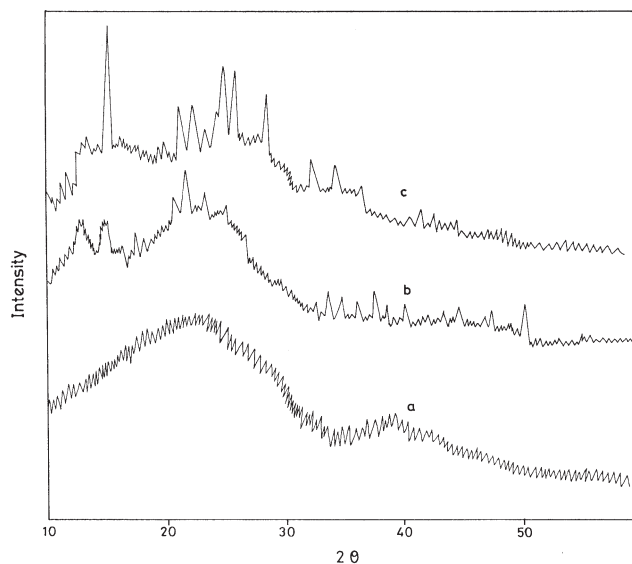


Figure 3 X-ray diffraction of (a) poly(8H4AQPF)-Cu(II), (b) poly(8H4AQPF)-Ni(II).

medium broad band extending from 2800 to 3600  $\text{cm}^{-1}$  that is assigned to the overlapping peaks because of aliphatic C—H stretch ( $< 3000 \text{ cm}^{-1}$ ), aromatic C—H stretch ( $> 3010 \text{ cm}^{-1}$ ), and intramolecular and intermolecular hydrogen-bonded phenolic O—H stretch (3100–3600  $\text{cm}^{-1}$ ). In the spectra of the polychelates this band disappeared, leaving behind sharp peaks for aliphatic and aromatic C—H stretching vibrations. So there was a loss of phenolic —OH hydrogen in coordination with the metal ions. The Ni(II) polychelates showed a strong band in a higher-frequency region (3300  $\text{cm}^{-1}$ ), suggesting the coordination of H<sub>2</sub>O molecules with Ni(II). The frequency at 1600–1605  $\text{cm}^{-1}$  suggests C—N absorption and a frequency of 900  $\text{cm}^{-1}$  represents a 1,2,4,6-tetrasubsti-

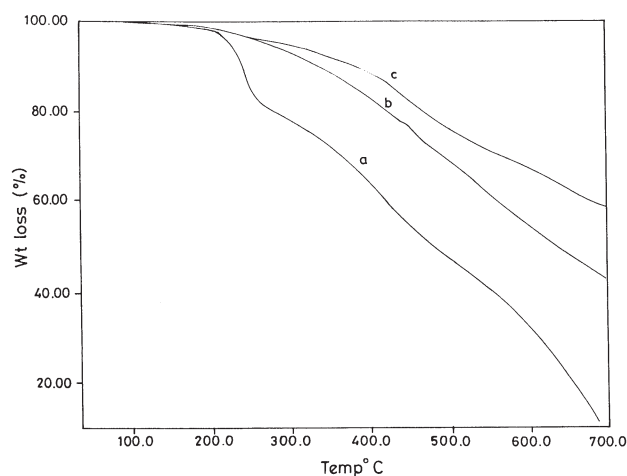


Figure 4 TGA traces of (a) poly(8H4AQPF), (b) poly(8H4AQPF)-Cu(II), and (c) poly(8H4AQPF)-Ni(II).

TABLE III  
Thermal Analysis Data of Poly(8H4AQPF) and Its Metal Complexes

Sample	$T_g$ (°C)	Temperature (°C) corresponds to				Above 700
		10	30	50	70	
Poly(8H4AQPF)	135	240	330	450	605	0
Poly(8H4AQPF)-Cu(II)	305	320	445	610	—	40
Poly(8H4AQPF)-Ni(II)	245	325	510	—	—	60

tuted phenyl ring.<sup>12</sup> The other absorptions observed are presented in Table II. The <sup>1</sup>H-NMR spectrum of poly(8H4AQPF) is shown in Figure 2. Signals from aromatic protons appear as broad multiplets in the region 8.11–6.23  $\delta$ . The signals at 9.53–8.6  $\delta$  are a result of aromatic —OH. The signal around 2.55  $\delta$  resulted from methylene protons.

The relationship between the electronic properties of the metal ion in the complex and the stereochemistry of the ligand in the environment present was arrived at tentatively on the basis of the data available in the literature.<sup>13–16</sup> The electronic spectrum of Cu(II) polychelates contained a broad band at 15,430  $\text{cm}^{-1}$  and a weak band at 23,900  $\text{cm}^{-1}$ . The position of the band at 15,430  $\text{cm}^{-1}$  was in good agreement with those generally observed for square planar Cu(II) complexes and could be assigned to the transition  $B_{1g} \rightarrow {}^2A_{1g}$ . The weak band at 23,900  $\text{cm}^{-1}$  could be assigned to the symmetry forbidden ligand  $\rightarrow$  metal charge transfer transition.<sup>17–19</sup> The Cu(II) polychelates could be assigned a square planar configuration.

The electronic spectrum of Ni(II) polychelates showed two broad bands, at 16,300  $\text{cm}^{-1}$  and 14,350  $\text{cm}^{-1}$ , and a weak band at 12,525  $\text{cm}^{-1}$ . The first two bands could be assigned to the transition  ${}^3T_1(F) \rightarrow {}^3T_1(P)$  and the latter to a spin-forbidden transition to an upper state arising from the <sup>1</sup>D state of the free ion. Manch and Fernolias have made similar observations and assigned an octahedral geometry for Ni(II) complexes.<sup>20,21</sup> Based on a comparison of the present data with that in the literature, the Ni(II) complex could be assigned an octahedral configuration.

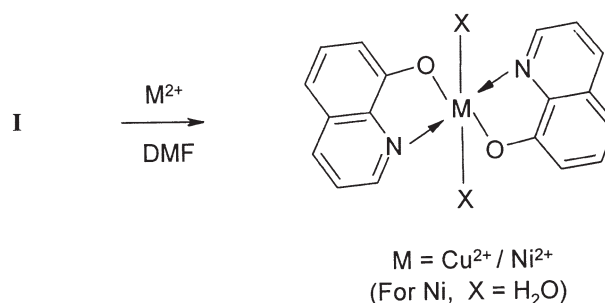
The EPR spectrum of the cupric complex showed a strong signal characteristic of that of bivalent copper, which was attributed to the square planar cupric ion in the center with the oxygen of phenolic —OH and the heterocyclic nitrogen groups on the  $x$  and  $y$  axes. Low-spin Ni(II) in an octahedral field with tetragonal distortion was expected to have a spin orbit coupling parameter of  $g > 0$  and as a consequence,  $g'' > g^\perp$ . The EPR parameters calculated for the Ni(II) complex were  $g'' = 2.601$  and  $g^\perp = 2.10$ . The  $g$  values were very consistent with Ni(II) in an octahedral environment.

The Cu(II) polychelates had a magnetic moment of 1.48 BM, indicating a square planar configuration. The magnetic moment of 3.35 BM and the paramagnetic behavior of Ni(II) complexes suggest a distorted octa-

hedral geometry of the Ni(II) polychelates. The X-ray diffractogram of poly(8H4AQPF) and its Cu(II)/Ni(II) complexes are shown in Figure 3. The X-ray diffraction studies indicated that poly(8H4AQPF) was amorphous, whereas its polychelates possessed good crystallinity. The crystallinity of the polychelates may not have been a result of any ordering in poly(8H4AQPF) induced during metal chelate anchoring, more so because anchoring of metals to polymer would imply interchain crosslinking of poly(8H4AQPF) interchains, which should have further reduced rather than enhanced any such ordering. The appearance of crystallinity in the poly(8H4AQPF)-metal complexes may have occurred because of the inherently crystalline nature of the metallic compounds.

The glass-transition temperatures of poly(8H4AQPF), poly(8H4AQPF)-Cu(II), and poly(8H4AQPF)-Ni(II) chelates were found to be 135°C, 305°C, and 245°C, respectively. The difference in transition may be ascribed to the crystallinity of the polymer-metal complexes and was in accordance with the results of the X-ray diffraction study. The TGA traces of the poly(8H4AQPF), poly(8H4AQPF)-Cu(II), and poly(8H4AQPF)-Ni(II) chelates are shown in Figure 4 and Table III. All the polychelates lost about 90% of their weight. The Cu(II) polychelates were found to be more stable than the Ni(II) polychelates. The IR, <sup>1</sup>H-NMR, EPR, electronic spectra, and magnetic moments studies confirmed that chelation of the metal ions may possibly have been occurring between two groups from different polymeric chains, shown in Scheme 2.

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Scheme 2

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