

# Studies on Poly(8-hydroxy-4-azoquinolinephenylmethacrylate) and its Metal Complexes

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

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

Received 19 July 2003; accepted 4 February 2005

DOI 10.1002/app.22231

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** 8-Hydroxy-4-azoquinolinephenylmethacrylate (8H4AQPMA) was prepared and polymerized in ethyl methyl ketone (EMK) at 65°C using benzoyl peroxide as free radical initiator. Poly(8-hydroxy-4-azoquinolinephenylmethacrylate) poly(8H4AQPMA) was characterized by infrared and nuclear magnetic resonance techniques. The molecular weight of the polymer was determined by gel permeation chromatography. Cu(II) and Ni(II) complexes of poly(8H4AQPMA) were prepared. Elemental analysis of

polychelates suggests that the metal-ligand ratio is about 1 : 2. The polychelates were further characterized by infrared spectra, X-ray diffraction, spectral studies, and magnetic moments. Thermal analyses of the polymer and polychelates were carried out in air. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1516–1522, 2006

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

## INTRODUCTION

In recent years, polymer metal complexes gained considerable interest owing to their attractive applications in diversified fields, such as catalysis, extraction of metals including radioactive elements, and bio-inorganic chemistry water and waste water treatments<sup>1–6</sup>. The complexation of metal ions with polymer matrices containing functional ligands results in superior properties compared with the simple compound counterparts. Organic polymers when complexed with inorganic metals impart flexibility due to the organic moiety and stability due to inorganic functions. The chelate forming polymeric ligands, characterized by reactive functional groups containing O, N, and S donor atoms and capable of coordinating to different metal ions, have been extensively studied.<sup>7–11</sup> Acrylates, methacrylates, and their corresponding acid chlorides are vinyl monomers that are readily converted to functional monomers, and radical polymerization in suitable solvents was found to be effective for a metal-ion scavenger. Oxine is extensively used in analytical chemistry as a photometric agent and/or extraction agent. Oxine is a selective and has consequently attracted great interest as a potential chelator for these metallic ions. Separation of transition metal ions on various oxine chelating resins, including commercial oxine, was reported by Parrish and col-

leagues.<sup>12,13</sup> Oxine groups bound to polymers via carbon-carbon bonds prepared by Friedel-Crafts alkylation of Amberlite XE-305 with 5-chloromethyl-8-hydroxyquinoline have led to hydrophobic resins of low capacity. These materials also exhibit amazing structural variations. A hydrophilic oxine resin with enhanced copper ion exchange capacity has been synthesized from alkylated poly(benzylamine) and 5-chloromethyl-8-hydroxyquinoline.<sup>14</sup> The electronic and EPR studies on Spheron-1000 shows a 2 : 1 mol ratio for Ni(II) and Co(II) complexes. In continuation of our research in polymer-metal complexes,<sup>15,16</sup> the present investigation deals with the synthesis, characterization and thermal property of new poly(8-hydroxy-4-azoquinolinephenylmethacrylate) and its Cu(II) and Ni(II) complexes.

## EXPERIMENTAL

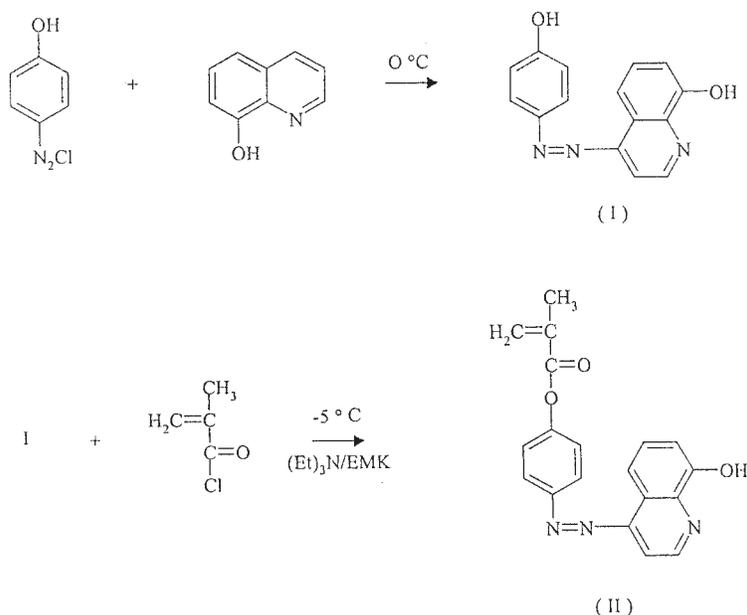
### Materials

8-hydroxy-4-azoquinolinehydroxybenzene was prepared according to Mang and coworkers.<sup>17</sup> Benzoyl peroxide was recrystallized from a chloroform-methanol mixture. Methacryloyl chloride was prepared by a reported procedure.<sup>18</sup>

### Monomer synthesis

8-hydroxy-4-azoquinolinehydroxybenzene (5.3g, 0.02M), triethylamine (2.78 mL, 0.02M), hydroquinone (0.5g), and 2-butanone 25 mL were placed in a three necked flask fitted with a stirrer, thermometer, and separating funnel. The contents in the flask were cooled to -5°C.

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



Scheme 1

Methacryloylchloride (1.8 mL, 0.02M) in 20 mL of 2-butanone was added dropwise with constant stirring and cooling. The reaction mixture was gradually allowed to reach room temperature, and stirring was continued for 2h. The quaternary ammonium salt formed was then filtered off. The filtrate was washed with distilled water and dried over anhydrous sodium sulfate, and the solvent was evaporated *in vacuo* (yield 97%). The IR and  $^1\text{H}$  NMR spectra were consistent with the assigned structure (Scheme 1).

### Polymerization

8-hydroxy-4-azoquinolinephenylmethacrylate (3.5M) in DMF (10 mL) and benzoyl peroxide (0.5g) were placed in a standard reaction tube and deaerated by passing oxygen free nitrogen gas for 30 min. The reaction tube was closed and kept in a thermostat at 65°C for 8h. The contents were then cooled and poured over methanol (100 mL). The precipitated poly

8-hydroxy-4-azoquinolinephenylmethacrylate [poly-(8H4AQPMA)] was filtered, washed with methanol, and dried. (Yield 85%.)

### Preparation of polychelates

The polymer (6.0mmol of repeat unit) was dissolved in 30 mL of DMF. An aqueous solution of Cu(II)/Ni(II) 0.62g acetate 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 in a water bath for 2h and kept overnight at room temperature. The precipitated poly(8H4AQPMA)Cu(II)/Ni(II) complex was filtered, washed with hot distilled water, and dried.

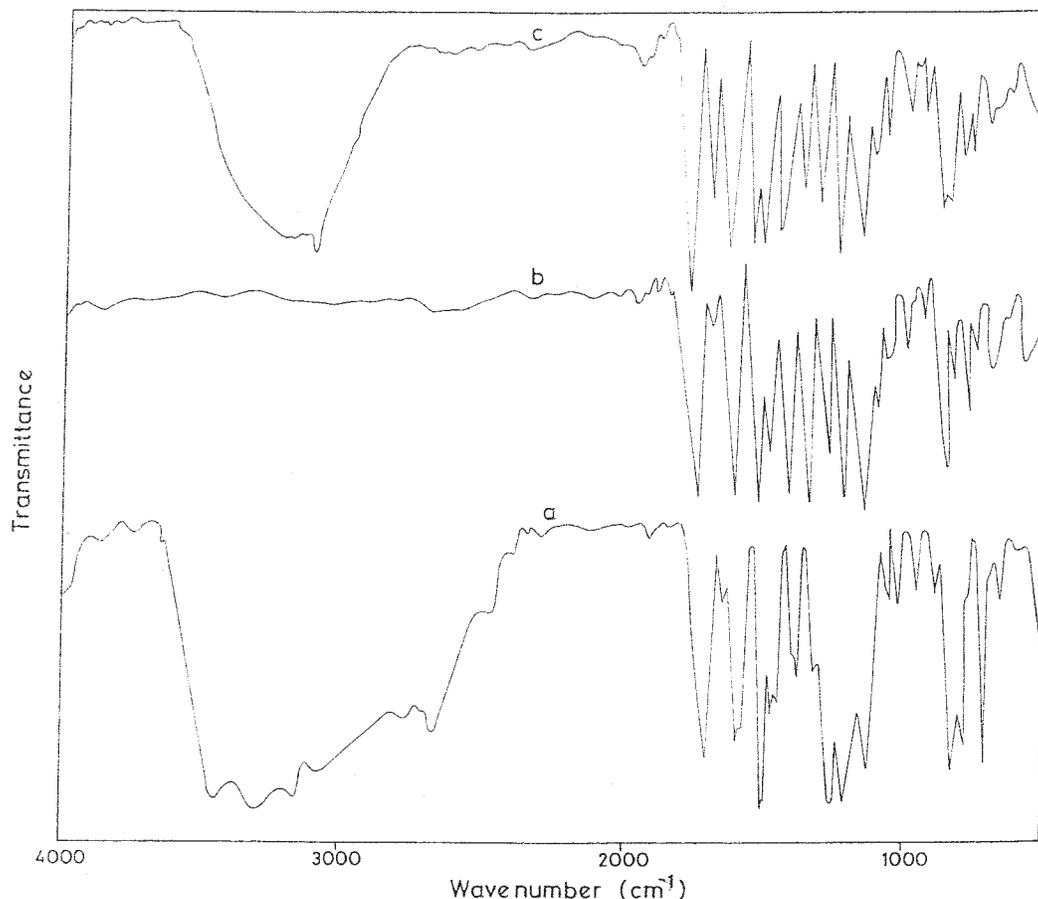
### Measurements

The IR spectra of the polymer and polymer metal complexes were recorded using KBr pellets. The  $^1\text{H}$

TABLE I  
Elemental Analysis for Poly (8H4AQPMA) 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(8H4AQPMA)	$\text{C}_{19}\text{H}_{15}\text{O}_3\text{N}_3$	68.47	68.45	4.53	4.55	14.40	14.39	12.60	12.61	—	—
Poly(8H4AQPMA)-Cu(II)	$(\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_3)_x\text{-Cu(II)}$	57.55	57.56	3.60	3.62	12.12	12.10	10.60	10.58	16.13	16.14
Poly(8H4AQPMA)-Ni(II)	$(\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_3)_x\text{-Ni(II)}$ $(\text{H}_2\text{O})_y$	58.44	58.45	3.65	3.66	12.29	12.28	10.76	10.74	14.86	14.87

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



**Figure 1** IR spectra of poly(8H4AQPMA) (a), poly(8H4AQPMA)-Cu (II) (b), and poly(8H4AQPMA)- Ni(II) (c).

NMR spectra of the polymers were recorded on a JEOL GSX 400 MHz spectrometer in DMSO  $d_6$  using tetramethylsilane as the internal standard. Molecular weights ( $M_w$  and  $M_n$ ) of the polymers were determined by GPC (Water's model 410) using THF as eluent. Elemental analyses were performed on a Coleman CHN analyzer. The metal content of polymer metal complexes was determined using the titrimetric procedure after decomposing the polychelates with concentrated HCl, perchloric,  $HNO_3$ , and  $H_2SO_4$ . The viscosity measurements were made in THF at  $30^\circ C$  with an Ubbelohde suspended level viscometer.

The magnetic moments were measured using the Guoy method. The diffuse reflectance spectra (500–2000nm) were measured on a Varian Cary 5E UV-vis

NIR spectrophotometer. X-ray diffraction experiments were performed with a Philips PW1820 diffractometer. Thermogravimetric analysis (TGA) was carried out in a Seiko thermal analyser. A 5mg sample was used at a heating rate of  $15^\circ C \text{ min}^{-1}$  in air.

## RESULTS AND DISCUSSION

The monomer (I) was prepared and polymerized in DMF using benzoyl peroxide as initiator with a good yield. Polymer metal complexes were obtained in a DMF containing polymer in an aqueous solution of 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

**TABLE II**  
IR Spectral Data of Poly(8H4AQPMA) and Its Metal Complexes

Sample	$OH_{str}$	$C=O_{ester_{str}}$	$N=N_{str}$	Phenolic C—O	Esteric C—O <sub>str</sub>	M—N <sub>str</sub>
Poly (8H4AQPMA)	2900–3300 <sub>b</sub>	1750 <sub>m</sub>	1565 <sub>s</sub>	1350	1185	—
Poly(8H4AQPMA)-Cu(II)	—	1700 <sub>m</sub>	1550 <sub>s</sub>	1325	1190	720
Poly (8H4AQPMA)-Ni(II)	3100 <sub>b</sub>	1700	1570 <sub>s</sub>	1335	1170	735

b = broad, m = medium, s = strong.

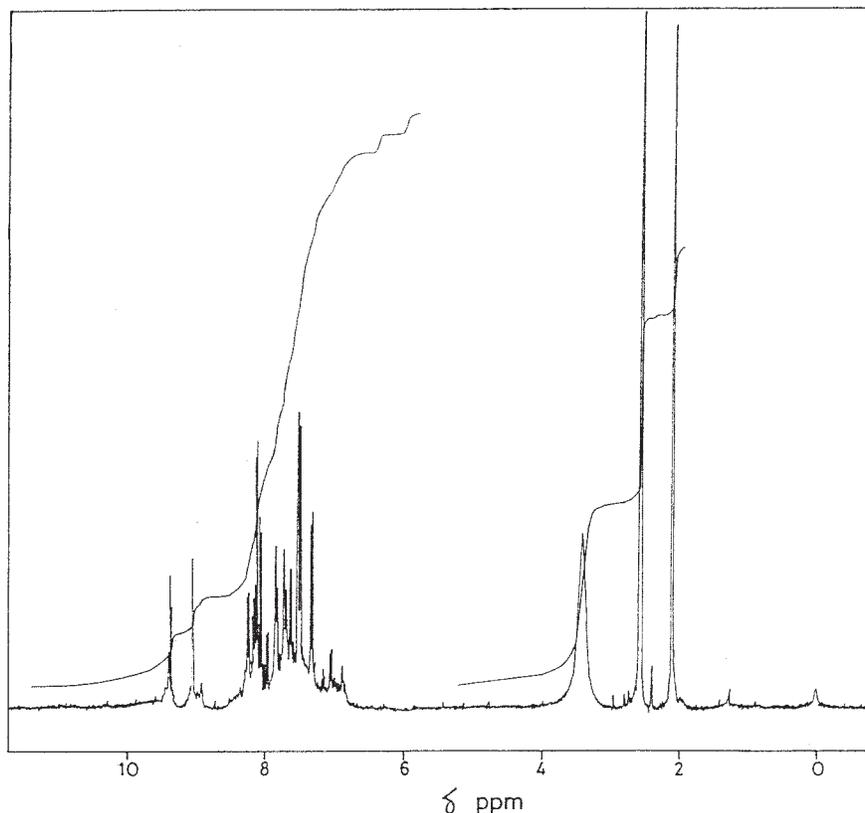


Figure 2  $^1\text{H}$  NMR spectrum of poly(8H4AQPMA).

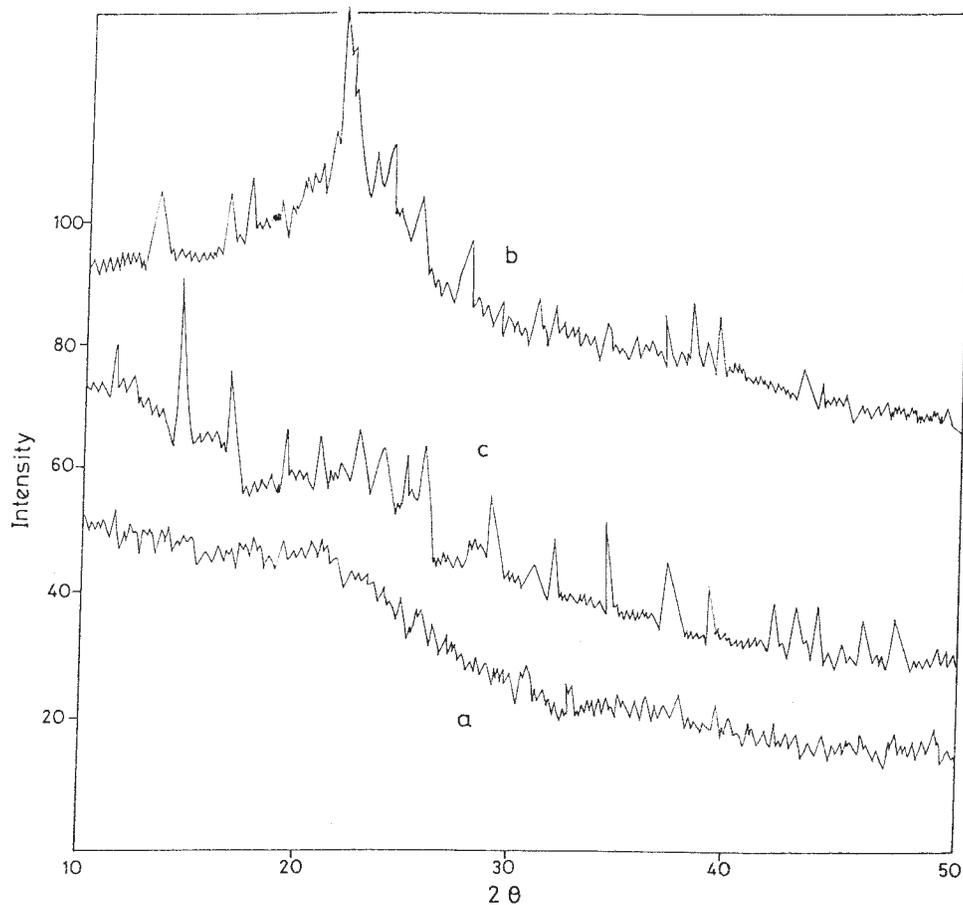
organic solvents like benzene, toluene, methanol, and water. All the polychelates are sparingly soluble in THF and DMF. The elemental analysis data for polymers and polymer-metal complexes are presented in Table I. The elemental analysis data suggest that the metal to polymer ratio is 1 : 2. The intrinsic viscosity  $[\eta]$  was obtained by extrapolating  $\eta_{sp}/C$  to zero concentration. The intrinsic viscosity of poly(8H4AQPMA) was determined to be 0.51dL/g.

The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) of the poly(8H4AQPMA) were determined by gel permeation chromatography using tetrahydrofuran ( $M_n$   $1.76 \times 10^4$   $M_w = 3.94 \times 10^4$ ). The polydispersity index ( $M_w/M_n$ ) for poly(8H4AQPMA) is 2.16. The theoretical value of  $M_w/M_n$  for poly(8H4AQPMA) suggests a strong tendency for chain termination by radical recombination.

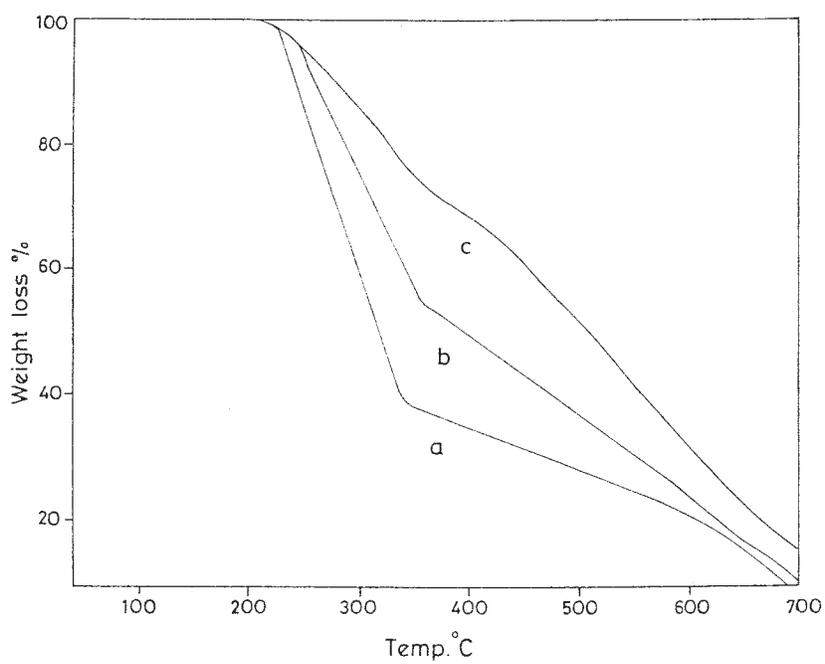
The IR spectra of poly(8H4AQPMA) and its polychelates are shown in Figure 1. The absorption band near  $3300\text{ cm}^{-1}$  corresponds to phenolic -OH stretching. This band disappears in the spectra of the metal complex, establishing the involvement of phenolic -OH in the coordination polymer. Ni(II) polychelates show a strong band at a higher frequency region ( $3400\text{ cm}^{-1}$ ) than that assigned for the phenolic -OH group. The fact that this band remains even when the poly-

mer metal complex was heated up to  $150^\circ\text{C}$  suggests the coordination of  $\text{H}_2\text{O}$  molecules to Ni(II) polychelates. The strong bands at  $1750\text{ cm}^{-1}$  and  $1570\text{ cm}^{-1}$  may be ascribed to C-O ester and ketonic groups, respectively. The medium intensity band at  $1190\text{ cm}^{-1}$  in the spectrum of the polymer is due to the hydrogen bonded ring system of the ligand. The band around  $725\text{ cm}^{-1}$  corresponds to metal-oxygen vibration. The other absorptions observed are presented in Table II. The  $^1\text{H}$  NMR spectrum of poly(8H4AQPMA) is shown in Figure 2. Signals due to aromatic protons appear as broad multiples in the region  $8.11\text{--}6.23\delta$ . The signals at  $9.12\delta$  are due to aromatic -OH. The signals around  $3.9\text{--}2.01\delta$  are due to methylene and methyl 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>19-22</sup> The electronic spectrum of Cu(II) polychelates contains a broad band at  $15,250\text{ cm}^{-1}$  and a weak band at  $23,750\text{ cm}^{-1}$ . The position of the band at  $15,250\text{ cm}^{-1}$  is in good agreement with those generally observed for square planar Cu(II) complexes and may be assigned to the transition  $B_{1g} \rightarrow {}^2A_{1g}$ . The weak band at  $23,750\text{ cm}^{-1}$  may be assigned to the symmetry forbidden ligand  $\rightarrow$  metal charge transfer



**Figure 3** X-ray diffraction of poly(8H4QPMA) (a) poly(8H4QPMA)-Cu (II) (b), and poly(8H4QPMA)- Ni(II) (c).



**Figure 4** TGA traces of poly(8H4QPMA) (a), poly(8H4QPMA)-Cu (II)(b), and poly(8H4QPMA)- Ni(II) (c).

TABLE III  
Thermogravimetric Data of Poly(8H4AQPMA) and Its Metal Chelates

Sample	$T_g$ (°C)	Temperature (°C) corresponds to					Char % at 700°C
		10	30	50	70	90	
Poly(8H4AQPMA)	150	275	300	345	475	625	0
Poly(8H4AQPMA)-Cu(II)	325	365	450	540	620	685	8
Poly(8H4AQPMA)-Ni(II)	265	385	425	585	625	635	6

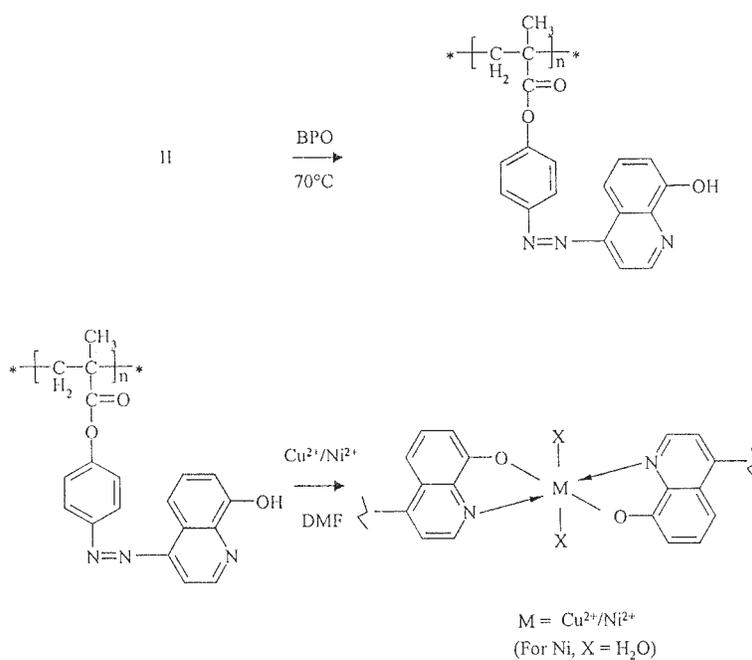
transition.<sup>23-25</sup> A square planar configuration may be tentatively assigned for the Cu(II) polychelates.

The electronic spectrum of Ni(II) polychelates shows two broad bands at  $16,500\text{ cm}^{-1}$  and  $14,150\text{ cm}^{-1}$  and a weak band at  $12,250\text{ cm}^{-1}$ . The first two bands may 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  ${}^1D$  state of the free ion. Manch and Fernolias have made similar observations and assigned an octahedral geometry for Ni(II) complexes.<sup>26,27</sup> Based on the comparison of the present data with that of the literature, an octahedral configuration may be assigned for the Ni(II) complex.

The e.p.r spectrum of the cupric complex shows a strong signal characteristic to that of bivalent copper, which is attributed to the square planar cupric ion in the center with the oxygen of the phenolic -OH and heterocyclic nitrogen groups on the x and y axis. Low spin Ni(II) in an octahedral field with tetragonal distortion is expected to have a spin orbit coupling parameter of  $g > 0$  and, as a consequence,  $g^{\parallel} > g^{\perp}$ . The e.p.r parameters calculated for the Ni(II) complex

are  $g^{\parallel} = 2.44$  and  $g^{\perp} = 2.14$ . The  $g$  values are very consistent with Ni(II) in an octahedral environment.

Cu(II) polychelates have a magnetic moment of 1.48BM, indicating the square planar configuration. The magnetic moment of 3.35BM and the paramagnetic behavior of Ni(II) complexes suggest distorted octahedral geometry for Ni(II) polychelates. The X-ray diffractogram of poly(8H4AQPMA) and its Cu(II) and Ni(II) complexes are shown in Figure 3. The X-ray diffraction studies indicate that poly(8H4AQPMA) is amorphous, whereas its polychelates possess good crystallinity. The crystallinity in polychelates may not be due to any ordering in poly(8H4AQPMA) induced during metal chelates anchoring, more so since the anchoring of metals to the polymer would imply inter chain crosslinking between poly(8H4AQPMA) inter chains, which should further reduce rather than enhance any such ordering. The appearance of crystallinity in poly(8H4AQPMA)-metal complexes may be because of the inherent crystalline nature of the metallic compounds.



Scheme 2

The glass transition temperature for poly(8H4AQPMA), poly(8H4AQPMA)-Cu(II), and poly(8H4AQPMA)-Ni(II) chelates is found to be 150, 325, and 265°C, respectively. The difference in transition may be ascribed to the crystallinity of the polymer-metal complexes and is in accordance with X-ray diffraction study. The TGA traces of poly(8H4AQPMA), poly(8H4AQPMA)-Cu(II), and poly(8H4AQPMA)-Ni(II) chelates are shown in Figure 4. The differential thermal analytical data are presented in Table III. All the polychelates lose about 90% weight. The Cu(II) polychelates are found to be more stable than Ni(II) poly chelates. The IR, <sup>1</sup>H NMR, e.p.r, electronic spectra, and magnetic moments studies confirmed that the chelation of metal ions may possibly be occurring between two groups from different polymeric chains, as shown in Scheme 2.

The authors are grateful to RSIC IIT (Madras) Chennai for providing instrumental facilities. One of the authors, TK, is grateful to DST, Government of India for the award of Young Scientist.

## References

- Kaliyappan, T.; Kannan, P. *Prog Polym Sci* 2000, 25, 343.
- Huang, W.-S.; Hu, Q.-S.; Pu, L. *J Org Chem* 1999, 64, 7940.
- Lee, C. H.; Kim, J. S.; Suh, M. Y.; Lee, W. *Anal Chim Acta* 1997, 339, 303.
- Vernon, L. P.; Seely, G. R. *The Chlorophylls*; Academic Press: New York, 1966.
- Bolto, B. A. *J Macromol Sci Chem* 1980, A14, 107.
- Bolto, B. A. *Ion Exch Pollut Control* 1979, 2, 213.
- Pederson, C. J.; Frensdroff, H. K. *Angew Chem Int Ed Engl* 1962, 11, 6.
- Rollman, L. D. *J Am Chem Soc* 1975, 97, 2132.
- Drago, R. S.; Gaul, J.; Zombeck, A.; Stamb, D. K. *J Am Chem Soc* 1980, 102, 1033.
- Rivas, B. L.; Sequel, G. V.; Geckeler, K. E. *J Appl Polym Sci* 2001, 81, 1310.
- Kurimara, Y.; Tsuchida, E.; Kaneko, M. *J Polym Sci* 1971, A19, 3511.
- Parrish, J. R. *Ann Chem* 1982, 54, 1890.
- Parrish, J. R. *Lab Pract* 1975, 24, 399.
- Warsawsky, A.; Deshe, A.; Rossey, G.; Patchornix, A. *React Polym* 1984, 2, 301.
- Kaliyappan, T.; Rajagopan, S.; Kannan, P. *J Appl Polym Sci* 2083 2003, 90.
- Kaliyappan T.; Rajagopan, S.; Kannan P. *J Appl Polym Sci* 2004, 91, 494.
- Mang, X.; Natansolin, A.; Rochon, P. *Supramol Sci* 1996, 3, 207.
- Stempel, G. H.; Gross, R. P.; Mariella, R. P. *J Am Chem Soc* 1950, 72, 2299.
- Luston, J.; Managek, Z.; Palovcick, R. *J Macromol Sci Chem* 1975, A9, 1413.
- Malaviya, J.; Shukla, P. R.; Srivastava, L. N. *J Inorg Nucl Chem* 1973, 35, 1706.
- Martini, R. L.; Mitra, S. *POC Chem Soc, London, Se* 1970, A32, 473.
- Syamal, A.; Kale, K. S. *Ind J Chem* 1978, A16, 46.
- Dubicki, L.; Martini, R. L. *Inorg Chem* 1966, 7, 2203.
- Jorgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon Press: Oxford, 1962; 15.
- Figgis, B. N. *Introduction to Ligand Fields*; Wiley Interscience: New York, 1962; 25.
- Manch, W.; Fernolias, W. J. *J Chem Soc* 1961, 38, 192.
- Bostop, O.; Jorgenson, C. K. *Acta Chem Scand* 1957, 11, 1223.