Synthesis and Metal Uptake Studies on Poly(8-hydroxy-5-azoquinolinephenylacrylate-formaldehyde) Resin and its Metal Complexes

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ABSTRACT: 8-hydroxy-5-azoquinolinephenylacrylate-formaldehyde (8H5AQPA-F) macromonomer was prepared from acryloylchloride, with condensation products of 8-hydroxy-5-azoquinolinephenol-formaldehyde, and polymerized in DMF at 70°C using benzoyl peroxide as free radical initiator. Poly(8H5AQPA-F) was characterized by infrared and nuclear magnetic resonance spectroscopic techniques. Polychelates were obtained in alkaline solution of polymeric ligand, with the aqueous solution of Cu(II) and Ni(II). Elemental analysis of polychelates suggests that the metal to ligand ratio is about 1:2. The polymer metal complexes were also characterized by IR, XRD, magnetic moments, and thermal analysis. The effects of pH and electrolyte on the metal uptake behavior of the resin were also studied. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 797–802, 2007

Key words: 8-hydroxy-5-azoquinoline; diffuse reflectance spectrum; thermal analysis; metal uptake; spectroscopic studies

INTRODUCTION

Chelating polymers can play an important role in solving environmental problems. Chelating resin is basically an organic polymer containing donor atoms that can successfully interact with the metal ions through coordinate bond and polymer backbone makes them more efficient by offering large surface area.

Polymer metal complexes have been of interest to many researchers during the past three decades in the light of their potential applications in diversified fields like organic synthesis,[1] waste water treatment,[2] hydrometallurgy,[3] polymer drug grafts,[4] recovery of trace metal ions,[5] and nuclear chemistry.[6] In addition, they are also used as models for enzymes.[7,8]

The determination of trace toxic metal ions and their removal with chelating polymers have gained great importance in environmental applications because of their high degree of selectivity, high loading capacity, versatility, durability, and enhanced hydrophilicity.[9] Chelating ion-exchange resins with specific chelating groups attached to polymers have found extensive use in the separation and preconcentration of metal ions.[10–12]

In recent years, the development of suitable functionalized chelating resin for trace metal preconcentration and separation provides a new impetus to extraction approach. El-Sonbati and coworkers have studied the new solid polymer metal complexes of several sterically hindered heterocyclic ligands.[13–15] Most of the workers characterized N=N-linkage by the presence of a band in the region 1570–1579 cm^{-1} in IR spectrum. As the chelating resin contains a weak basic functional group like phenolic —OH, it is expected that the sorption of the metal depend on the pH of the medium. In continuation of our research work in polychelates,[16,17] in this article, we report synthesis, characterization, and application study on poly(8-hydroxy-5-azoquinolinephenylacrylate-formaldehyde) [poly(8H5AQPA-F)] resin and its metal complexes.

EXPERIMENTAL

Benzoyl peroxide (BDH, India) was recrystallized from chloroform/methanol mixture. 8-hydroxy quinoline (BDH, India) was recrystallized from methanol. Acryloyl chloride and 8-hydroxy-5-azoquinoline hydroxy benzene were prepared by the procedure reported.[18,19]

Synthesis of 8-hydroxy-5-azoquinoline phenol-formaldehyde

A mixture of 1:1.1, 8-hydroxy-5-azoquinoline hydroxybenzene and 37% formalin solution, and 3%(W/W) of oxalic acid were placed in a round-bottom flask, sealed and put in an oil bath at 100°C for 24 h. The
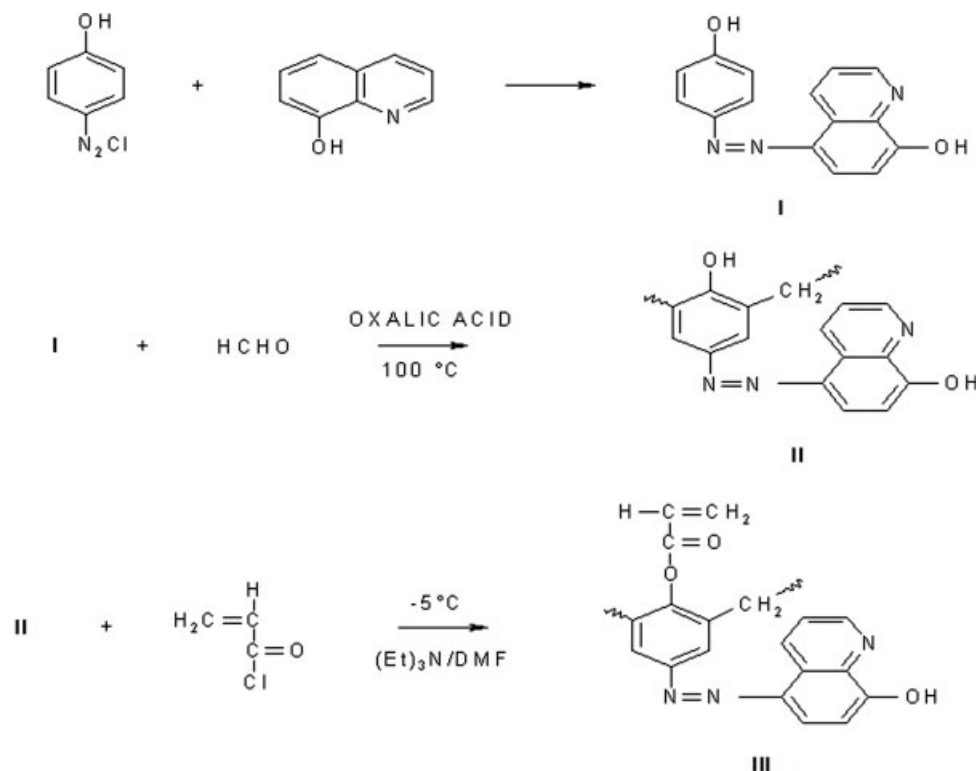
Scheme 1 Synthesis of macromonomer 8-hydroxy-5-azoquinolinephenylacrylate-formaldehyde.

flask was then cooled to room temperature and desealed and water was decanted. The solid remaining in the flask is dissolved in N,N-dimethyl formamide, and the resulting solution was added dropwise to large excess of 10% aqueous sodium chloride solution with constant stirring. Then, the red compound was filtered and washed several times with distilled water until free of chloride ion and dried at 60°C.

Synthesis of 8H5AQPA-F

8H5AQPA-F (2.6 g, 0.02M), triethylamine (2.78 mL, 0.02M), hydroquinone (0.5 g), and DMF (25 mL) were taken in a three-neck flask equipped with a stirrer, thermometer, and separating funnel, and the contents were cooled to 0 to −5°C. Acryloyl chloride (1.8 mL, 0.02M) was added dropwise with constant stirring at that temperature. The reaction mixture was then stirred for another 2 h at room temperature and the quaternary ammonium salt was filtered off. The filtrate was thoroughly washed with distilled water and dried over anhydrous sodium sulfate, and the solvent is removed to get a solid. The IR and ^{1}H-NMR spectra were consistent with the assigned structure (Scheme 1).

POLYMERIZATION

8H5AQPA-F (3.5M) in DMF and benzoyl peroxide (0.5 g) were taken in a standard reaction tube and

deaerated by passing oxygen free Nitrogen for 30 min. The reaction tube was closed and kept in a thermostat at 70°C for 8 h. A large excess of methanol was added to the contents and the precipitated poly(8H5AQPA-F) was filtered, washed with methanol, and purified by N,N-dimethyl formamide/methanol mixture. Polymer was dried under reduced pressure at 60°C for constant weight.

Synthesis of poly(8H5AQPA-F) metal chelates

Polymer metal chelates were prepared at room temperature by solution technique. A typical procedure for the preparation of polymer-Cu(II) chelate is as follows. Poly(8H5AQPA-F) (5 mmol of repeat unit) in DMF (75 mL) and the pH of the solution was adjusted to 7 with dilute ammonium hydroxide. An aqueous solution of Cu(II) acetate (2 mmol) was added dropwise to the polymer solution with constant stirring. The mixture was then digested on a water bath for 2 h and kept over night at room temperature. The precipitated Poly(8H5AQPA-F)-metal complex was filtered, washed with hot distilled water, followed by methanol, and dried at 60°C *in vacuo*. A similar procedure was adopted for the preparation of Ni(II) chelate. Yield: 83% for Cu(II) and 85% for N(II).

Measurements

IR spectra were recorded on a Bomem MB 104 FTIR spectrophotometer using KBr pellets. The ^{1}H-NMR

TABLE I
Elemental Analysis for Poly(8H5AQPA-F) and Its Metal Complexes

		Elemental analysis (weight percent)									
		Carbon		Hydrogen		Oxygen		Nitrogen		Metal	
Abbreviation	Empirical formula	Cal.[a]	Fd.	Cal.[a]	Fd.	Cal.[a]	Fd.	Cal.[a]	Fd.	Cal[a]	Fd.
Poly(8H5AQPA-F)	$C_{19}H_{13}O_3N_3$	68.87	68.86	3.95	3.96	14.5	14.52	12.68	12.66	–	–
Poly(8H5AQPA-F)-Cu(II)	$(C_{19}H_{12}O_3N_3)_x$-Cu(II)	57.94	57.93	3.07	3.08	12.19	12.17	10.67	10.68	16.13	16.14
Poly(8H5AQPA-F)-Ni(II)	$(C_{19}H_{12}O_3N_3)_x$-Ni(II) $(H_2O)_y$	58.76	58.73	3.11	3.12	12.37	12.39	10.82	10.84	14.94	14.92

[a] Calculated percentage of C, H, N, O and metal ions for polymer–metal complexes based on the value of $x = y = 2.00$, Found: $x = 2.02$, $y = 2.01$.

spectra were recorded on a JEOL-GSX 400 MH$_z$ spectrometer in deuterated DMSO as solvent using TMS as internal standard. The molecular weights (M_w and M_n) were determined by gel permeation chromatograph (Waters model 401). The diffuse reflectance spectra of the polychelates were recorded on a Carl-Zeiss VSU-2P spectrophotometer. The magnetic moments were determined by Guoy method and corrected for the diamagnetism of the components using Pascal's constant. The thermogravimetric analysis of the polymer was performed on a Mettler 2000 TA thermal analyzer. The C, H, and N contents were determined with an Elemental analyzer (Elementar, vario EL, Hanau, Germany).

Metal uptake studies of polymer in the presence of electrolytes

The polymer sample (25 mg in 25 mL of DMF) was added in an electrolytic solution (25 mL) of a known concentration. The pH of the solution was adjusted by using 0.1M HCl or 0.1M NH$_3$. The solution was stirred for 24 h at room temperature. To this solution, 10 mL of 0.1M solution of metal ion Cu(II)/Ni(II) was added and the pH was adjusted to the required value. The mixture was again stirred at 25°C for 24 h and filtered. The solid was washed and the Cu(II) ion content was determined iodimetricallly and Ni by gravimetrically. The amount of the metal ion uptake of the polymer was calculated from the difference between a blank experiment without the polymer and the reading in the actual experiments. The experiments were performed in the presence of several electrolytes with Cu(II) and Ni(II) ions.

Effect of pH on metal ion uptake

The optimum pH of the metal ion uptake was determined with a batch equilibration technique. Excess of metal ions Cu(II)/Ni(II) (10 mL, 0.1M) were shaken with 25 mg of the resin for 24 h. The pH of the solution was adjusted before equilibration over a range of 1–10, with weak acid/base. The complex was filtered off, and the concentration of the Cu(II) ion remaining in the filtrate was determined by iodometrically and Ni(II) by gravimetrically.

RESULTS AND DISCUSSION

The polychelates were insoluble in common organic solvents but moderately soluble in DMF. The elemental analysis data for poly(8H5AQPA-F) and metal complexes are presented in Table I. The elemental analysis data suggested a metal to polymer ratio of 1 : 2, and it is in good agreement with the calculated values.

Viscosity measurements were done by using Ubbelohde suspended level viscometer. The intrinsic viscosity [η] was obtained by extrapolating η$_{sp}$/C to zero concentration and it was found to be 0.61 dL/g. The results reveal that the molecular weight of the polymer is moderately high. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the macromonomer (8H5AQPA-F) were determined by gel permeation chromatography using tetrahydrofuran as solvent, and found $M_n = 1.43 \times 10^3$, $M_w = 2.79 \times 10^3$ and for the polymer[poly(8H5AQPA-F)]. $(M_n) = 1.83 \times 10^4$, $(M_w) = 3.96 \times 10^4$ and the polydispersity

TABLE II
IR Spectral Data of Poly(8H5AQPA-F) and Its Metal Complexes

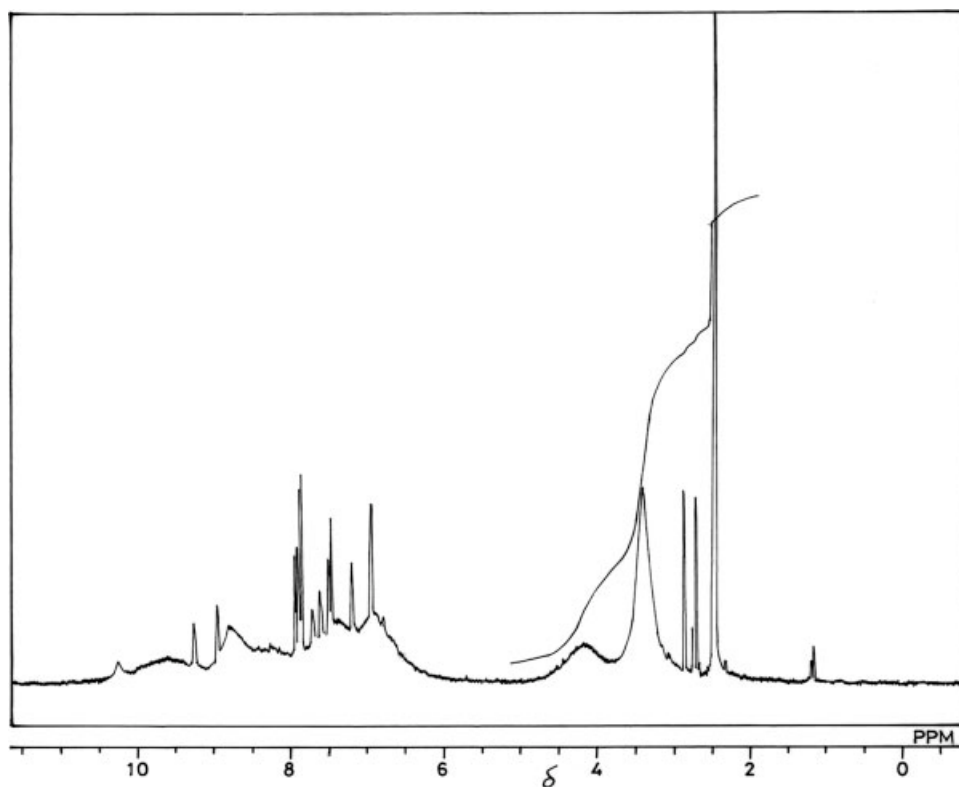| Sample	OH$_{str}$	C=Oester$_{str}$	N=N$_{str}$	Phenolic C—O	M—N$_{str}$	M—O$_{str}$
Poly (8H5AQPA-F)	3000–3300[a]	1730[b]	1565[c]	1375	–	–
Poly(8H5AQPA-F)-Cu(II)	–	1735[b]	1555[c]	1380	720	530
Poly (8H5AQPA-F) –Ni(II)	3100[a]	1735[b]	1555[c]	1385	735	525

[a] Broad.
[b] Medium.
[c] Strong.

Figure 1 ^{1}H-NMR spectrum of poly(8H5AQPA-F).

index $(M_w)/(M_n) = 2.16$ for poly(8H5AQPA-F) suggests for chain termination by radical combination.

Characterization

The IR spectrum of poly (8H5AQPA-F) shows a medium broad band in the region 3600–3200 cm^{-1}which may be assigned to phenolic —OH stretching. The phenolic —OH band is not present in the spectra of Cu(II) polychelates. This indicates the loss of phenolic —OH and participation of oxygen of the —OH group in metal coordination.[20] The absorption band around 1600–1700 cm^{-1} due to C=N of quinoline also undergo a shift, which is due to N of quinoline coordinating with the metal.

Ni(I) polychelates show a strong band around 3400 cm^{-1}, and this band remains even when the polymer metal complexes were heated up to 150°C. This suggests coordination of water molecules to Ni(II). poly(8H5AQPA-F) shows strong bands at 1730 cm^{-1}, which may be assigned to C=O of ester.[21–23] The other absorptions are presented in Table II.

The ^{1}H-NMR spectrum of poly(8H5AQPA-F) (Fig. 1) characterized by a multiplet around 6.75–7.6 ppm was due to aromatic protons, and the signal at 7.95 ppm may be assigned to protons of Ar-OH. The resonance signals at 1.85 and 2.2 ppm may be assigned to methylene and methine protons, respectively. As the polychelates were not soluble in common organic solvents, the ^{1}H-NMR spectra of the polychelates were not reported.

The diffuse reflectance spectrum of Cu(II) poly chelates contains two bands, one at 14,800 cm^{-1} and another at 22,500 cm^{-1}, which may be assigned to d-d transition corresponding to $E_{g \to} T_{2g}$ transition.

In the electronic spectra, the Ni(II) chelate polymers are characterized by three bands at 9550 cm^{-1}, 15,730 cm^{-1}, and 24,625 cm^{-1}, which may be assigned to $^3A_{2g(F)}$

TABLE III
Thermogravimetric Data of Poly(8H5AQPA-F) and Its Metal Chelates

| Sample	T_g (°C)	Temperature (°C) corresponds to					Char % at 700°C
		10	30	50	70	90	
Poly(8H5AQPA-F)	165	98	280	420	490	600	0
Poly(8H5AQPA-F)-Cu(II)	350	180	350	480	600	–	10
Poly(8H5AQPA-F)-Ni(II)	385	240	425	570	–	–	37
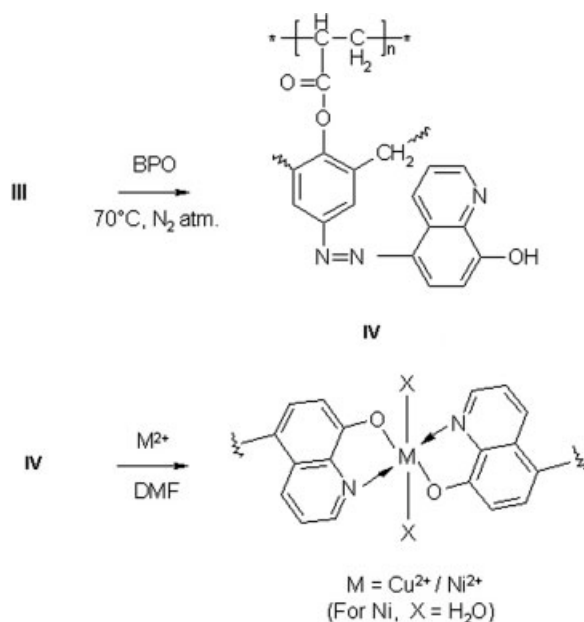
Scheme 2 Synthesis of poly(8-hydroxy-5-azoquinoline-phenylacrylate-formaldehyde) resin and its Cu/Ni complexes.

$\rightarrow$ $^3T_{2g(F)}$ and $^3T_{2g(F)} \rightarrow$ $^3T_{1g(P)}$ transitions, respectively. Generally, octahedral spin free Ni(II) complexes exhibit three bands in their electronic spectra.[24–26]

Cu(II) polychelates have a magnetic moment of 1.75 BM, indicating square planar configuration. The magnetic moment of 3.81 BM and the paramagnetic behavior of Ni(II) complexes suggest distorted octahedral geometry for Ni(II) polychelates.[27–30]

The X-ray diffraction studies indicate that poly(8-H5AQPA-F) is amorphous whereas its polychelates possess good crystalline nature. The crystallinity in polychelates may not be due to any ordering in poly (8H5AQPA-F) induced during metal chelates anchoring, more so since anchoring of metals to polymer
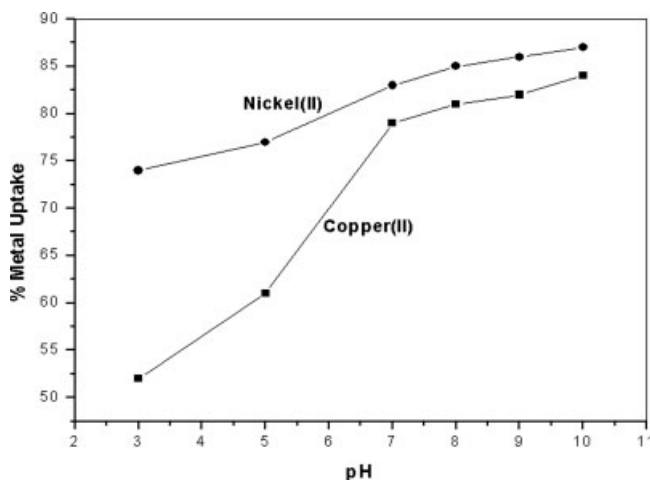
Figure 2 Metal ion uptake behavior of poly(8H5AQPA-F) resin at different pH.

would imply interchain crosslinking between poly (8H5AQPA-F) interchains, which should further reduce rather than enhance any such ordering. The appearance of crystallinity in poly(8H5AQPA-F) metal complexes may be because of inherent crystalline nature of the metallic compounds.

The TGA data for poly (8H5AQPA-F) and polychelates are presented in Table III. The thermal analytical data indicate that in poly(8H5AQPA-F) loss of weight begins at 120°C and degradation of the polymer occurs at 600°C whereas the polychelates were very stable up to 700°C, and this indicate higher thermal stability of the polychelates compared with the parent polymer (Scheme 2).

The results of the batch equilibrium study, carried out with the polymer sample of poly(8H5AQPA-F), are shown in the Figure 2. From this study certain generalizations may be made about the behavior of the polymer sample. By keeping the concentration of Cu(II) and Ni(II) fixed, when the pH of the solution was varied, the resin showed higher uptake percentage of Cu(II) and Ni(II) at pH 7. The amount of metal ions taken up by the poly(8H5AQPA-F) increases with the increasing pH of the medium. The magnitude of the increase, however, is different for different metal cations.

Influence of electrolytes on metal uptake

Table IV reveals that the amount of metal ions taken up from a given amount of a polymer depends on the nature and concentration of the electrolyte pres-

TABLE IV
Percentage Metal Uptake of Poly(8H5AQPA-F) with Different Electrolytes at Different pH

Metal ion	pH	Electrolyte (mol L^{-1})	Percentage of the metal ion taken up in the presence of	
			NaCl	Na_2SO_4
Cu^{2+}	3	0.01	73	36
		0.05	75	52
		0.1	90	56
	5	0.01	77.9	71.8
		0.05	85.2	80
		0.1	90	79
	7	0.01	95	96
		0.05	96	96.5
		0.1	97	96
Ni^{2+}	3	0.01	80	40
		0.05	81	42
		0.1	82	46
	5	0.01	83	71
		0.05	86	79
		0.1	88	82
	7	0.01	85.3	90
		0.05	86	92
		0.1	90	95

ent in the solution. In the presence of chloride and sulfate ions the uptake of Cu(II) and Ni(II) ions increases with an increasing concentration of the electrolytes. Earlier research workers also observed this type of trend.[31,32]

The results of such a type of study are helpful in selecting the optimum pH for a selective metal ion from a mixture of different metal ions.[33,34] It can be concluded that poly(8H5AQPA-F) may be found useful in recycle plant for removing the metal ions in continuous column operation.

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