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STUDIES ON POLY(8-ACRYLOYLOXY-QUINOLINE) AND ITS METAL COMPLEXING ABILITY IN AQUEOUS MEDIUM

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Key Words: Poly(8-acryloyloxyquinoline), Polymer-Metal Complexes, Electronic Spectra, Crystallinity, Magnetic Moments

ABSTRACT

8-Acryloyloxyquinoline(8-AOQ), prepared from acryloyl chloride and 8-hydroxyquinoline, was polymerized in methyl ethyl ketone at 70°C using benzoyl peroxide as a free radical initiator. Polychelates were obtained when aqueous solution of Th(II)/Cd(II)/Zn(II)/Ni(II) and Mg(II) ions were added to the polymer dissolved in sodium hydroxide solution. The IR spectra of these polychelates suggest that metals are coordinated through oxygen of the esteric carbonyl with nitrogen atom. Elemental analysis of polychelates suggests that the metal-ligand ratio is about 1:2. The electronic spectra, EPR, and magnetic moments of polychelates showed an octachedral and square planar structure for poly(8-AOQ)- Ni(II)/Th(II) and poly(8-AOQ)-Zn(II)/Cd(II)/Mg(II) complexes respectively. X-ray diffraction studies reveal that the polychelates are highly crystalline. The thermal properties of polymer metal complexes are discussed.

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INTRODUCTION

Polychelates have found widespread applications [1-4] in nuclear chemistry, preconcentration and recovery of trace metal ions, pollution control, hydrometallurgy, polymer drug grafts and waste water treatments. In addition they are also used as mechano-chemical systems [5] and models for bio-inorganic systems [6]. A number of polymer bound chelating ligand including polydentate amines, crown ethers and porphyrins have been reported [7-9]. Kurimara *et al* [10] prepared the uniform pendant type polymer-metal complexes by the substitution reaction between a polymer ligand and Co(III) or Cr(III) ions. The radical polymerization of Cu-complexes with Schiff base ligand containing the vinyl group and radical polymerization of methacrylate monomers coordinated to Co(III) have been studied [11]. Selective chelations of specific metal ions from a metal ion mixture by using a number of tetradentates ligands attached to poly(styrene) and poly(divinylbenzene) mixture have been reported [12]. A polymer containing hydroxamic acid has been studied as polymeric chelating agent for iron [13]. A macroreticular polystyrene-based chelating resin with nitroso resorcinol as functional group for selective chelation of Cu(II), Fe(II) and Co(II) were reported by Sugii *et al.* [14]. Polymeric Schiff base chelates based on naphthalaldehyde and Mannich base have been investigated [15]. El-Sonbati and coworkers [16] found that the poly-Schiff base ligands play a key role in understanding the coordination chemistry of transition metal ions. Polyene polymers containing palladium or nickel in the main chain were synthesized for the first time by polycondensation and/or oxidative coupling methods [17]. Preliminary results on the preconcentration of cadmium ion on a polymeric matrix, poly(methyl methacrylate), poly(methacrylonitrile) and the effect of pH on the holding ability of the resins were reported [18]. Percec *et al.* [19] prepared streoregular/irregular poly-(p-phenylenes) by Ni-catalyzed homo or copolymerization of arylene bimesylates. Coordination polymers of poly(vinyl ketone) were prepared with the metal ions Cu(II), Ni(II), Co(II), Cd(II) and Hg(II). The metal contents in all polymers were consistent with 1:2 (metal:ligand) stoichiometry [20]. The use of Cu(II) complexes in the therapy of rheumotoid arthritis and other degenerative diseases in humans and lab animals was studied by Sorenson *et al.* [21]. Kaliyappan *et al.* [22-26] synthesized the series of polymer-metal complexes both in aqueous and non-aqueous medium for multifacet applications. In continuation of our research in this domain, the present work deals with the synthesis, spectral, and thermal properties of poly(8-acryloyloxyquinoline), and its metal complexes in aqueous medium for the effective removal of metal ions from the wastewater streams.

EXPERIMENTAL

Materials

Benzoyl peroxide(BDH) was recrystallized from a chloroform/methanol mixture, 8-hydroxyquinoline(Fluka) was used as received. Acryloyl chloride was prepared by the procedure reported elsewhere [27]. Metal acetates were used as received.

Synthesis of 8-Acryloyloxyquinoline

8-Hydroxyquinoline (0.206 mol), MEK (10 ml) triethylamine (30 ml) were taken in a three-necked flask equipped with stirrer, stoppered funnel, and gas inlet tube. The nitrogen gas was passed and the contents cooled to -5˚C. Acryloyl chloride (9.15 ml) in MEK was added dropwise with constant stirring at that temperature. The reaction mixture was gradually allowed to attain room temperature and stirring was continued for 2 hours. The byproduct, quaternary ammonium salt, was filtered off. The filtrate was thoroughly washed with distilled water, dried over anhydrous sodium sulfate, and the solvent evaporated in vacuum. The crude 8-acryloyloxyquinoline was recrystallized from ethanol, m.p:83˚C. The IR and ^{1}H-NMR spectra are consistent with the assigned structure.

Polymerization

8-Acryloyloxyquinoline(8-AOQ) (2.5 mmol), DMF (50 ml), and benzoyl peroxide (0.5 g) were placed in a standard reaction tube (100 ml) and purged with nitrogen gas for 0.30 hours. The tube was closed and kept in a thermostat at 70˚C for 6 hours and cooled. A large excess of methanol was added and the precipitated poly(8-AOQ) was filtered, washed with methanol and purified by an N,N-dimethylformamide/methanol mixture. The purified polymer was dried *in vacuo* at 50˚C to constant weight: Yield 72%.

Synthesis of Poly(8-Acryloyloxyquinoline)(8-AOQ)-Metal Complexes

A series of polymer-metal complexes viz., Th(II), Cd(II), Zn(II), Ni(II) and Mg(II) were prepared at room temperature in aqueous medium with poly(8-

AOQ). A typical procedure for the preparation of poly(8-AOQ) - Ni(II) complex is as follows. Poly(8-AOQ) (6 mmol of repeat unit) was dissolved in dilute sodium hydroxide (100 ml, 3 N) solution. An aqueous solution of Ni(II) - acetate (3 mmol) dissolved in distilled water (20 ml) was added dropwise to the polymer solution with constant stirring and pH of the solution was adjusted to 7 with sodium hydroxide (1 N). The precipitated poly(8-AOQ)-Ni(II) complex was filtered, washed with hot distilled water, followed by ethanol and dried at 60˚C *in vacuo*. A similar procedure was adopted for the preparation of the other polychelates.

Measurements

The elemental analysis of 8-AOQ, poly(8-AOQ) and the polychelates were carried out on a Heareus carbon-hydrogen analyzer. The amount of metal ions present in the polymer-metal complexes were estimated using a titrimetric/gravimetric procedure after decomposing the polymers: 1 gm of polymer-metal complex was decomposed in muffle furnace at 250˚C for 2 hours. The decomposed product was washed with distilled water, the residue was dissolved in concentrated sulphuric acid (10 ml) and made up to 100 ml in a standard measuring flask. 20 ml of the made up solution was complexed with standard DMG/tetrathio cyanatomercurate (II) quinoldic acid gravimetrically for Ni(II)/Cd(II) and Th(II) respectively, whereas Mg(II), Ca(II) were determined by EDTA method. The viscosity measurements of poly(8-AOQ) was made in an Ubbelohde suspended level viscometer using DMF at 30˚C. The molecular weights ($\overline{M}$w and $\overline{M}$n) of poly(8-AOQ) were determined by gel permeation chromatography (Water 501) using THF and calibrated with polystyrene standards. The IR spectra of poly(8-AOQ) and its metal complexes were recorded on a Perkin-Elmer 782 spectrophotometer using KBr pellet.

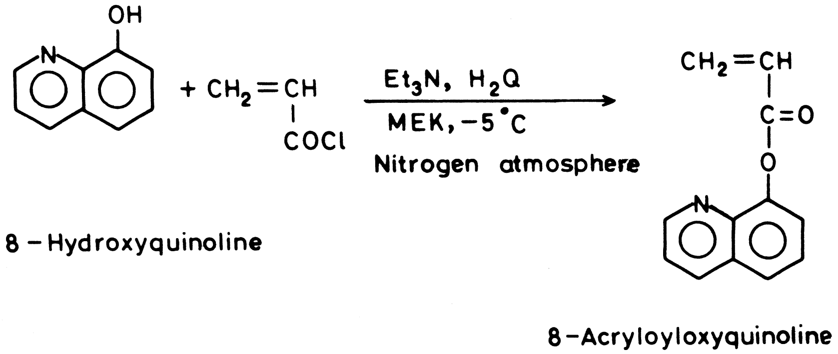
The magnetic moments were measured by the Gouy method and corrected for diamagnetism of the component, using Pascal's constant. The diffuse reflectance spectra (8000-2500 cm^{-1}) were measured on a Karl-Zeiss VSU-28 spectrophotometer. The EPR analysis were carried out at room temperature on a Varian spectrophotometer. X-ray diffraction experiments were performed on a Phillips, PW 1820 diffractometer with Staton camera, using CuKα radiation of wavelength 1.542Å. Thermogravimetric analysis was carried out on a Mettler TA 3000 thermobalance, (0.5mg of sample) at a heating rate of 15˚C min^{-1} in air.

RESULTS AND DISCUSSION

The new 8-acryloyloxyquinoline(8-AOQ) monomer was prepared and polymerized in DMF using benzoyl peroxide as initiator according to Scheme 1. Polymer-metal complexes were obtained when the alkaline solution of poly(8-AOQ) was treated with the aqueous solution of metal ions with sodium hydroxide solution. The polymer is soluble in chloroform, THF, DMF, and DMSO and insoluble in common organic solvents like benzene, toluene, methanol, and water. On the other hand, the polychelates were insoluble in these solvents. The elemental analysis data for polymer and polymer metal complexes were presented in Table 1. The elemental analysis data reveal that the metal to ligand ratio in all the polychelates is 1:2 and it is in good agreement with the calculated values.

The intrinsic viscosity [η] was obtained by extrapolating $\eta_{sp/c}$ to zero concentration. The intrinsic viscosity of poly(8-AOQ) was found to be 0.491 dl/g. The result reveals that the polymer is of moderately high molecular weight. The number average molecular weight (Mn) and weight average molecular weight (Mw) of poly(8-AOQ) were obtained by gel permeation chromatography using tetrahydrofuran are n = 1.93×10^4; w = 3.52×10^4. The polydispersing index w/n for poly(8-AOQ) is 1.82.

Representative IR spectra of poly(8-AOQ) and Th(II) complexes are shown in Figure 1. The IR spectrum of polymer exhibits strong absorption bands around 1750cm^{-1} due to carbonyl group of ester. In the polymer-metal complexes there was a shift of C=O stretching towards lower frequency indicating the involvement of oxygen of carbonyl group in co-ordinating with metal ion. The absorption band around 1600-1700cm^{-1} due to C=N of quinoline also undergoes a shift which is due to N of quinoline coordinating with the metal. In the case of



Scheme 1

TABLE 1. Elemental Analysis Data of 8-AOQ, Poly(8-AOQ) and its Metal Complexes

Compound	Empirical Formula	% Calculated					% Found				
		C	H	O	N	M^{2+}	C	H	O	N	M^{2+}
8-AOQ	$C_{12}H_9O_2N$	72.36	4.52	16.08	7.04	-	72.33	4.56	16.06	7.05	-
Poly(8-AOQ)	$(C_{12}H_9O_2N)_n$	72.36	4.52	16.08	7.04	-	72.35	4.53	16.09	7.03	-
Poly(8-AOQ) - Th(II)	$(C_{12}H_9O_2N)_x$ $Th(H_2O)_v$	44.82	3.11	11.07	4.84	31.16	49.80	3.15	11.05	4.81	31.19
Poly(8-AOQ) - Cd(II)	$(C_{12}H_9O_2N)_x$ Cd	58.29	3.64	12.95	5.69	19.43	58.33	3.63	12.92	5.65	19.47
Poly(8-AOQ) - Zn(II)	$(C_{12}H_9O_2N)_x$ Zn	62.88	3.93	13.97	6.11	13.11	62.91	3.90	13.94	6.13	13.12
Poly(8-AOQ) - Ni(II)	$(C_{12}H_9O_2N)_x$ $Ni(H_2O)_v$	63.43	3.96	14.12	6.16	12.33	63.47	3.93	14.13	6.15	12.30
Poly(8-AOQ) - Mg(II)	$(C_{12}H_9O_2N)_x$ $Mg(H_2O)_y$	68.24	4.26	15.16	6.66	5.68	68.19	4.31	15.19	6.67	5.64

Calculated percentage of C, H, N, O and metal ions for polymer-metal complexes based on the value x = y = 2, found x = 2.02; y = 2.01.

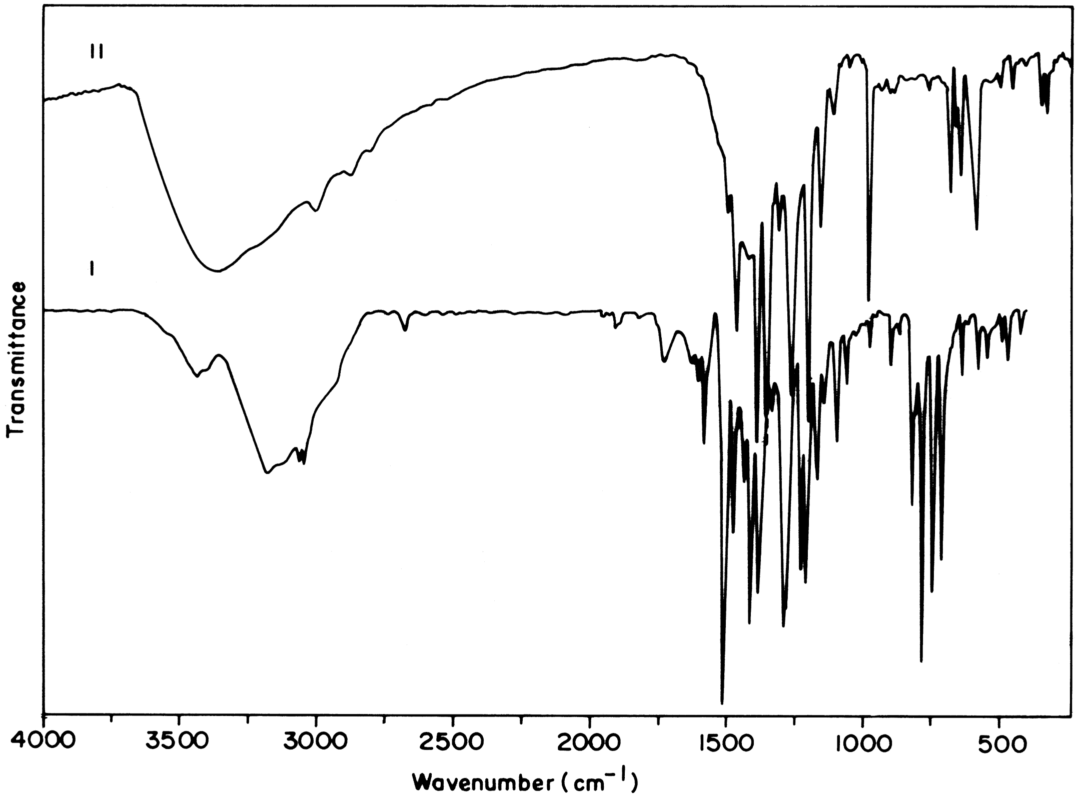


Figure 1. Representative IR spectra of poly(8-AOQ) (I) and poly(8-AOQ) -Th(II) (II).

Th(II), Ni(II) and Mg(II) complexes, there is strong absorption around 3500cm^{-1}, which does not disappear even on the sample being heated up to 150°C. This may be attributed to water molecules taking part along with these ions during coordination [28]. The absorption band around 550 cm^{-1} corresponds to M-O vibration [29, 30]. The other absorptions observed are presented in Table 2.

The magnetic moment, diffuse reflectance and EPR (Figure 2) data are given in Table 3. The results reveal that the structure of Th(II) and Ni(II) complexes are octahedral. Zn(II), Mg(II) and Cd(II) polymer-metal complexes are diamagnetic. The diamagnetic nature coupled with elemental analysis data suggest a tetrahedral environment of chelating ligands around the metal ions [21-36].

The TGA traces of poly(8-AOQ) and polychelates are shown in Figure 3. The polymer and polymer-metal complexes start to decompose around 240-375°C and 310-400°C. Around 700°C, the polymer loses 99%, while the poly-

TABLE 2. IR Spectral Data of Polymer and Polymer-Metal Complexes

Sample	Wave Number (cm^{-1})			
	OH_{str}	C = O Ester	$C = N_{str}$	$M\text{-}O_{str}$
Poly(8-AOQ)	3500 (b)	1750 (m)	1600-1700 (b)	-
Poly(8-AOQ)-Th (II)	3450 (b)	1710 (m)	1580-1650 (b)	450 (s)
Poly(8-AOQ)-Zn (II)	-	1750 (m)	1590-1675 (b)	390 (s)
Poly(8-AOQ)-Cd (II)	-	1715 (m)	1570-1680 (b)	425 (s)
Poly(8-AOQ)-Ni (II)	3400 (b)	1725 (m)	1580-1690 (b)	400 (s)
Poly(8-AOQ)-Mg (II)	3425 (b)	1730 (m)	1575-1680 (b)	430 (s)

b = broad, m = medium, s = strong

mer-metal complexes 88-96% weight. The char residue corresponds to the formation of respective metal oxides. The thermal stability follows the order Mg(II) < Ni(II) < Zn(II) < Cd(II) < Th(II). The polymer, Zn(II) and Cd(II) complex show two step degradation, whereas Th(II), Ni(II) and Mg(II) complexes show three step degradation. This may be attributed to the elimination of water mole-

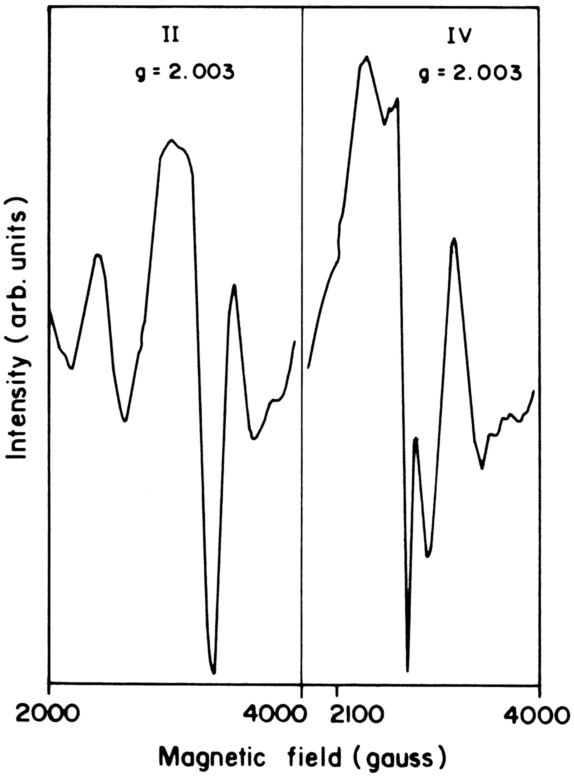


Figure 2. EPR spectra of poly(8-AOQ) - Th (II) (II), poly(8-AOQ)-Ni(II) (IV).

TABLE 3. Magnetic Moment, Diffuse Reflectance and EPR Spectral Data of Polymer-Metal Complexes

Polymer - metal complex	Magenetic moment (BM)	Electronic transitions (cm^{-1})	Assignment	ESR		Geometry
				g"	g	
Poly(8-AOQ)-Ni (II)	3.23	9,859, 15,725, 25,450	$^3A_{2g}$ (F) $^3T_{2g}$ (F) $^3A_{2g}$ (F) $^3T_{1g}$ (F) $^3A_{2g}$ (F) $^3T_{1g}$ (P)	2.29	2.13	Octahedral
Poly(8-AOQ)-Th (II)	3.39	8,850, 15,925, 24,900	$^4A_2$ (F) $^4T_1$ (F) $^4A_2$ (F) $^4T_1$ (P) Charge Transfer	2.45	2.27	Octahedral
Poly(8-AOQ)-Zn (II)	Diamagnetic	-	-	-	-	Tetrahedral
Poly(8-AOQ)-Cd (II)	Diamagnetic	-	-	-	-	Tetrahedral
Poly(8-AOQ)-Mg (II)	Diamagnetic	-	-	-	-	Tetrahedral

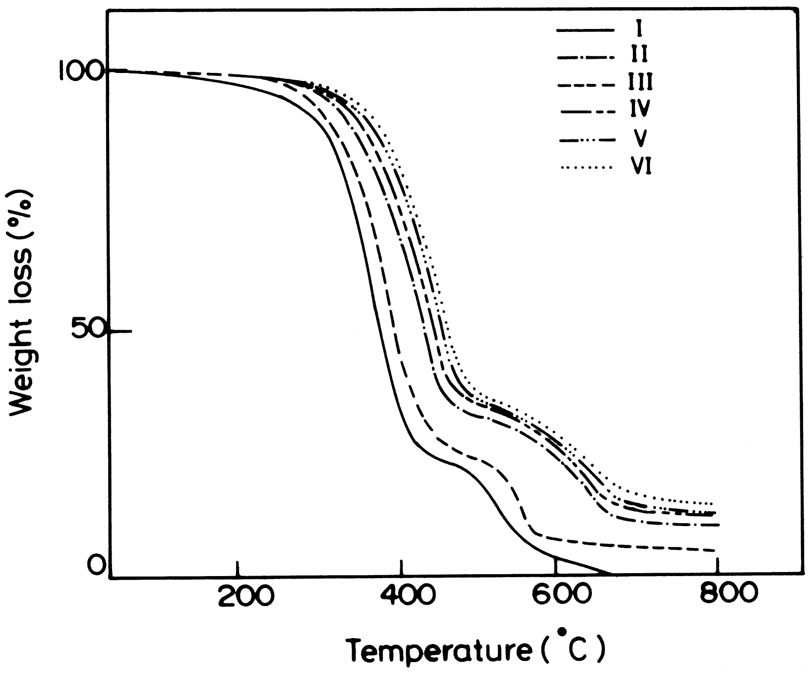


Figure 3. TGA curves of poly(8-AOQ) (I), poly(8-AOQ)-Th(II) (II), poly(8-AOQ)-Cd(II) (III), poly(8-AOQ)-Zn(II) (IV), poly(8-AOQ)-Ni(II) (V) and poly(8-AOQ)-Mg(II) (VI).

cule followed by chain scission and carbonization in case of Th(II), Ni(II) and Mg(II).

The representative X-ray diffractograms of poly(8-AOQ) and poly(8-AOQ)-Th(II) complexes are shown in Figure 4. The X-ray diffraction studies show that the polymer is amorphous, whereas the polymer-metal complexes are crystalline. The crystallinity in polymer-metal complexes may not be due to any ordering in polymers induced during metal chelates anchoring. The anchoring of metals to the polymer would imply inter chain cross-linking between polymeric chains. This may be further reduce rather than enhance any such ordering. The appearance of crysallinity in polymer-metal complexes may be due to the inherent crystalline nature of the metallic compounds. The IR, EPR, electronic spectra, magnetic moments studies confirmed that the chelation of metal ions may be possibly be occurring between two groups from different polymeric chains as shown in the Scheme 2.

Treatment of metal complex with dil/HCl (1M) results in quantitative regeneration of the polymer. The dechelated polymer undergoes complexation

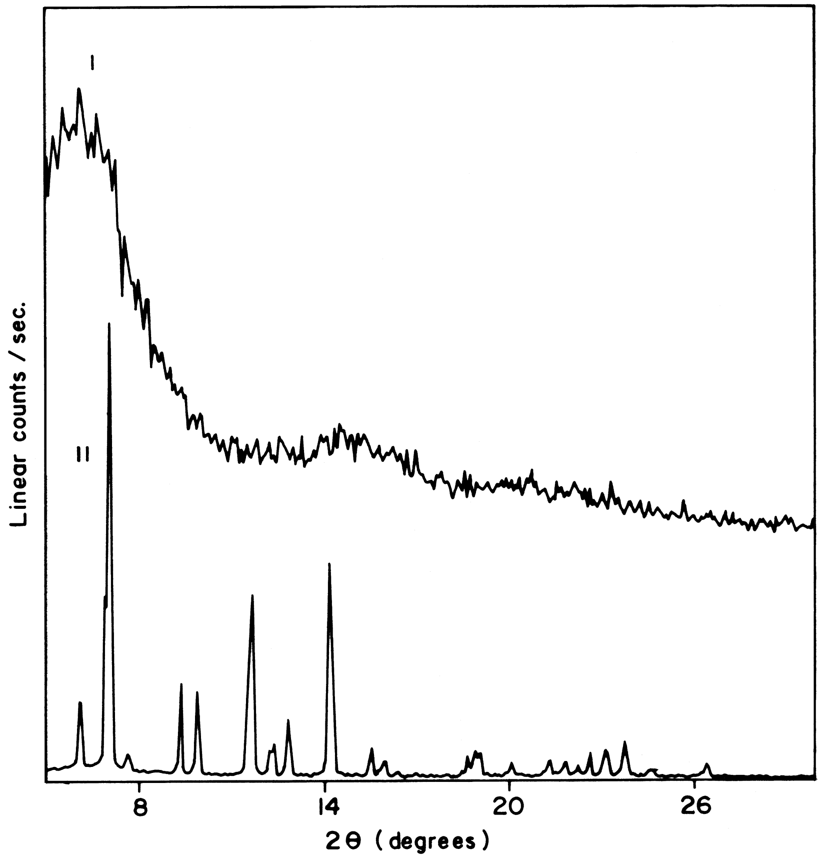
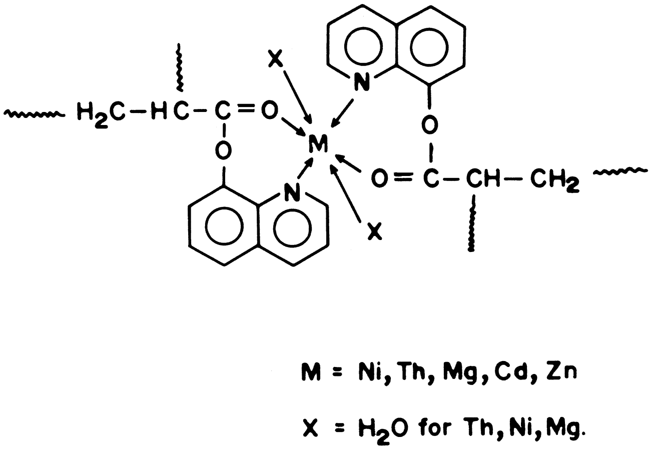


Figure 4. Representative X-ray diffractograms of poly(8-AOQ) (I) and poly(8-AOQ)-Th(II) (II).



Scheme 2

with original efficiency. The reproducibility of the above results was established by repeating the sequence several times, thereby revealing the good recyclability, as well as stability of the polymer under acidic conditions. Finally, it may be concluded that the complex forming ability of this polymer with various divalent metal ions in aqueous medium at pH 7 could be effectively utilized for the removal of heavy metals from water and waste waters.

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