Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Thamizharasi, S. , Reddy, A. Venkata Rami and Balasubramanian, S.(1998) 'Polymer-Metal Complexes: Synthesis and Characterization of Poly-(2-Hydroxy-4-acryloxyacetophenone-semicarbazone) Metal Complexes', Journal of Macromolecular Science, Part A, 35: 9, 1573 — 1586

To link to this Article: DOI: 10.1080/10601329808007317

URL: http://dx.doi.org/10.1080/10601329808007317

J.M.S.—PURE APPL. CHEM., A35(9), pp. 1573–1586 (1998)

POLYMER-METAL COMPLEXES: SYNTHESIS AND CHARACTERIZATION OF POLY-(2-HYDROXY-4-ACRYLOXYACETOPHENONE-SEMICARBAZONE) METAL COMPLEXES

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Key Words: Poly(2-Hydroxy-4-acryloxyacetophenone-semicarbazone), Polymer Metal Complexes, Magnetic Moments and Electronic Spectra

ABSTRACT

2-Hydroxy-4-acryloxyacetophenone (HAAP) was synthesized and polymerized in 2-butanone using benzoyl peroxide as initiator at 65°C. Poly(2-hydroxy-4-acryloxyacetophenone-semicarbazone) (HAAPS) was prepared from poly(HAAP) and semicarbazide hydrochloride and was characterized by IR and NMR spectral studies. The molecular weights of the polymer was determined by gel permeation chromatography. Cu(II) and Ni(II) chelates of poly(HAAPS) were synthesized. Thermogravimetric analysis of the polychelates have been carried out. Elemental analysis of the polychelates suggest a metal to ligand ratio as 1:2. The polychelates were also characterized by infrared, electronic spectral studies, magnetic, and conductivity measurements.

INTRODUCTION

The synthesis of metal containing polymers has received the attention of various groups as the coordinated metal ion drastically altering the strength as well as the functional properties of the polymer backbone. The applications of these polymers are numerous and their utility as catalyst for a wide variety of organic reactions like hydroformylation, oxidation [1], hydrogenation, polymerization [2] etc. have been well documented [3, 4]. The polymer metal chelates were also found to act as electrochromic materials, since the color of the polymer varies with the oxidation state of the metal ion present in the chelate [5, 6]. Horrocks *et al.* [7] have investigated the binding properties of trivalent ions to polyelectrolytes through Tb(III) luminescence studies. The transport of oxygen through a poly(butyl methacrylate) membrane containing Cobalt(II) α-α″,α‴-meso-(tetrakis-co-pivalamidophenyl)porphyrin-1-methylimidazole complex has also been reported in which the cobalt ion undergoes reversible oxygenation at a faster rate [8]. Macromolecular chelates capable of forming complexes with transition metal ions have been reported [9, 10].

The polymeric Schiff base complexes display unique structural features, and are capable of binding small molecules. These complexes also exhibit catalytic activity and are employed in several organic reactions. This communication deals with the synthesis and characterization of poly(2-hydroxy-4-acryloxyacetophenone-semicarbazone) and its metal complexes with Cu(II) and Ni(II) ions. The conductivity, magnetic properties and the type of chelation with metal ions are discussed. The present study, not only aims at the synthesis and characterization of a new series of macromolecular metal chelates, but also demonstrates the enhanced thermal stability over the free polymers.

EXPERIMENTAL

Materials

Acryloyl chloride was prepared according to the method described by Stempel *et al.* [11]. 2,4-Dihydroxyacetophenone was recrystallized from ethanol. Benzoyl peroxide was recrystallized from chloroform-ethanol mixture. All the solvents were fractionally distilled before use.

Synthesis of 2-Hydroxy-4-acryloxyacetophenone (HAAP)

2,4-Dihydroxyacetophenone (23 g, 0.15 mol), triethylamine (15.3 ml, 0.15 mol) and hydroquinone (0.5 g) dissolved in 2-butanone (100 ml) were taken in a

500 ml three-necked flask and the temperature of the reactants was maintained in the range -5°C -0°C. Acryloyl chloride (14.9 ml in 25 ml 2-butanone) was added dropwise to this solution with constant stirring and cooling. The temperature of the reaction mixture was allowed to raise to 30°C and the contents were stirred for 2 hours. Then the reaction mixture was filtered, washed with distilled water, dried over anhydrous sodium sulphate, and the solvent was evaporated in a rotary evaporator. The crude HAAP obtained as a white solid was recrystallized from ethanol. Yield: 64%, m.p. 65-67°C.

Synthesis of Poly(2-hydroxy-4-acryloxyacetophenone) [Poly(HAAP)]

2-Hydroxy-4-acryloxyacetophenone (8.2 g, 2M) was polymerized in 2-butanone (20 ml) using benzoyl peroxide (BPO) (0.5 wt% of monomer) as initiator. The monomer, BPO and solvent were mixed, degassed with nitrogen, and kept at 65°C in a polymerization tube. The polymer was precipitated by the addition of methanol. The product was redissolved in chloroform and reprecipitated by the addition of methanol, filtered, and finally dried *in vacuo*. Yield: 72%.

Synthesis of Poly(2-hydroxy-4-acryloxyacetophenone-semicarbazone) [Poly-(HAPPS)]

Poly(2-hydroxy-4-acryloxyacetophenone-semicarbazone) was synthesized by dissolving, poly(HAPPS) (5 g) in 150 ml of tetrahydrofuran. Then, a mixture of semicarbazide-hydrochloride (5.6 g) and sodium acetate (6.8 g) dissolved in 10 ml water was added and the contents were refluxed on a water bath for 8 hours and the product was precipitated in excess methanol, filtered, washed with methanol and dried at 40°C under reduced pressure. Yield of poly(HAAPS): 68%.

Polymer-Metal Chelates

The polymer-metal chelates were prepared by dissolving the polymer (1 g) in tetrahydrofuran (THF) (75 ml) and Cu(II)/Ni(II) acetate (1 g) solution was added with constant stirring at pH 7. The reaction mixture was digested on a water bath, and the resulting solid polymer-metal chelate was washed with chloroform and finally dried in vacuum at 40°C. Yield of poly(HAAPS)-Cu(II) is 58% and poly(HAAPS)-Ni(II) is 54%.

Elemental analysis data for polymer-metal complexes: % Calculated: (% Found).

Poly(HAAPS)-Cu(II): C% = 49.02 (47.86); H% = 4.08 (3.86); N% = 14.30 (14.62) and Cu%= 10.82 (9.63).

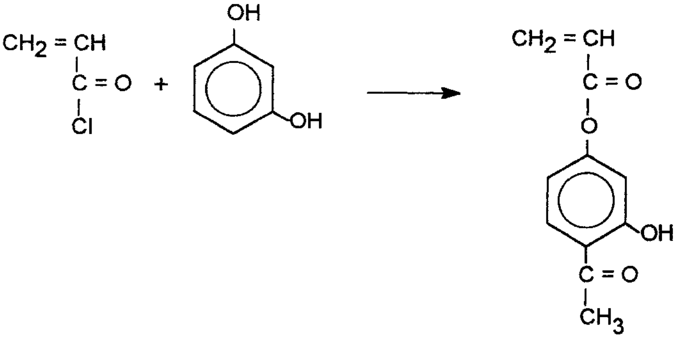
Poly(HAAPS)-Ni(II): C% = 49.43 (47.34); H% = 4.12 (3.93); N% = 14.42 (14.56) and Ni%= 10.07 (8.67).

Measurements

IR spectra of the samples were recorded on a Hitachi 270-50 Infrared spectrophotometer as KBr pellets. The ^{1}H NMR spectra were recorded on a Hitachi-90 MHz spectrometer and ^{13}C NMR spectra were recorded on a Bruker - 270 MHz spectrometer as 15% solution in $CDCl_3$ with TMS as internal standard. Elemental analysis was done on a Coleman C-H-N analyzer. The amount of metal content in the polymer-metal chelates was determined by titrimetric procedure after decomposing the polymer by heating in $H_2SO_4/HClO_4$ acid mixture. The molecular weights of the polymers were determined by gel permeation chromatograph (Waters model 410) equipped with a RI detector and calibrated with polystyrene standard. Tetrahydrofuran was used as an eluent. The magnetic moments ($\mu_{eff} = 2.83\sqrt{\chi_m \times T}$ were measured by the Gouy method and corrected for diamagnetism of the components using Pascal's constants. The diffuse reflectance spectra (8000-25000 cm^{-1}) were measured on a Carl-Zeiss VSU-2P spectrophotometer. The electrical conductivity of the polychelates were measured as pellets of 10 mm diameter and 2-3 mm thickness using a Keithley electrometer. The thermogravimetric analysis of the polymers were performed on a Mettler 2000-TA thermal analyzer.

RESULTS AND DISCUSSION

2-Hydroxy-4-acryloxyacetophenone (HAAP) was prepared according to the following scheme:



Scheme I

Characterization of Poly(HAAP)

The monomer HAAP was then polymerized in 2-butanone using BPO as the initiator. The polymer was characterized by IR and NMR spectroscopic techniques. The IR spectrum of poly(HAAP) shows a broad band in the region 3000-3250 cm^{-1}, which may be due to inter and intra molecular hydrogen bonded phenolic -OH stretching vibration [12]. The intense bands at 1655cm^{-1} and 1765cm^{-1} are due to the stretching vibrations of the keto and ester carbonyl groups respectively. The strong bands at 1600cm^{-1} and 1500 cm^{-1} are due to the >C=C< stretching of the aromatic ring. The medium intense band at 1325 cm^{-1} may be due to C-O vibration of the hydrogen- bonded ring system.

The structure of the polymer is further confirmed by NMR spectral studies. The aromatic protons exhibit multiplets in the region 6.85-7.85 ppm. The assignments for other signals in the proton NMR spectrum of the polymer are as follows. The resonance signals at 8.01-8.2 ppm are due to the phenolic -OH, while the multiplets seen in the region 6.8-7.6 ppm are due to aromatic protons. The backbone carbons $-CH_2-$ and -CH- appear at 1.76 and 2.48 ppm, respectively which are downfield from TMS.

Characterization of Poly(HAAPS)

IR Spectra

The IR spectrum of the polymer shows a broad band in the region 3150-3350 cm^{-1} which may be attributed to the NH, NH_2 stretchings and intermolecular hydrogen-bonded phenolic -OH stretching frequency [12]. The intense peak at 1755cm^{-1} is due to the >C=O vibration of ester group. The strong bands at 1640 and 1660 cm^{-1} are due to the >C=O vibration of the ketone and primary amide groups respectively[13]. The strong absorption at 1600 cm^{-1} is attributed to >C=N stretching vibration and the band at 1510cm^{-1} is due to the >C=C< stretching vibration of the aromatic nucleus. The sharp band at 1535 cm^{-1} may be attributed to the N-H stretching vibration of C-N-H group (Table 1).

Molecular Weights

The molecular weight of the macromolecular system has been determined by gel permeation chromatography. The molecular weight of the free functionalized polymer is found to lie in the range of 10^4. The reactivity ratios of copolymers derived from 2-hydroxy ethyl methacrylate have been reported [14]. The number and weight average molecular weights of the polymer determined by gel permeation chromatography are $\overline{M}_w = 2.3x10^4$ and $\overline{M}_n = 1.2x10^4$, respectively and their ratio (polydispersity index) is found to be $(\overline{M}_w/\overline{M}_n) = 1.90$.

TABLE 1. IR Spectral Data of Poly(HAAPS) and its Metal Chelates

Sl.	**Polymer samples**	**Wavenumber (cm^{-1})**						
		-OH str.	**NH_2**	**C=O str. ester**	**C=0 amide**	**C=N**	**Ar. ring**	**C-O Str.**
1.	Poly(HAAPS)	$3200\text{-}3000_{(b)}$	$3400_{(b)}$	$1760_{(s)}$	$1650_{(s)}$	$1620_{(s)}$	$1520_{(s)}$	$1200_{(m)}$
2.	Poly(HAAPS)-Ni(II)	-	$3400_{(b)}$	$1760_{(s)}$	$1630_{(s)}$	$1600_{(s)}$	$1520_{(s)}$	$1140_{(m)}$
3.	Poly(HAAPS)-Cu(II)	-	$3400_{(b)}$	$1760_{(s)}$	$1630_{(s)}$	$1600_{(s)}$	$1520_{(s)}$	$1140_{(m)}$

b = broad; s = strong; m = medium

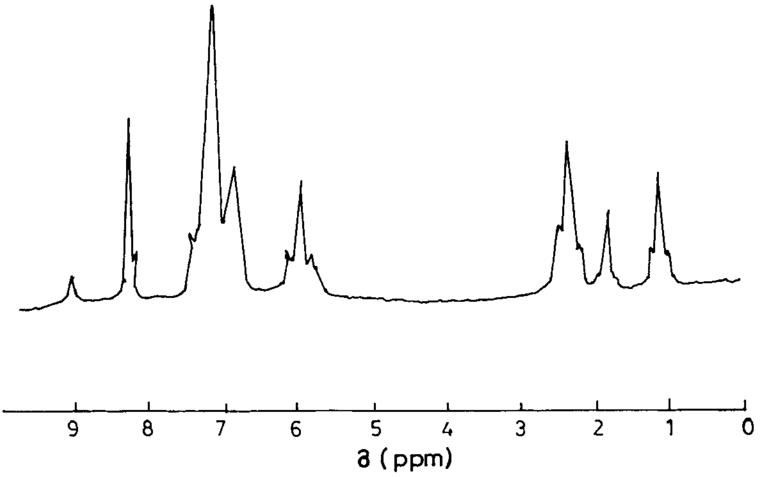


Figure 1. ^{1}H NMR spectrum of Poly(HAAPS).

NMR Spectra

The ^{1}H and ^{13}C NMR spectra of the polymer provide valuable information regarding the structure of the molecule. The extensive application of these techniques in the structural elucidation of poly[(meth)acrylate] systems have been reported [15, 16]. ^{1}H NMR spectrum of poly(HAAPS) (Figure 1) shows resonance signals at 8.6, 8.2 ppm and 6.0 ppm which are due to the NH, phenolic -OH and NH_2 protons, respectively, whereas the multiplets appearing at 6.9-7.5 ppm are attributed to the aromatic protons. The -CH-, CH_3-C=O and -CH_2- protons of the backbone appear at 1.78, 1.21 and 2.61 ppm, respectively.

The proton-decoupled ^{13}C NMR spectrum of poly(HAAPS) is shown in Figure 2. The resonances of the backbone carbons, viz. methylene and methine carbons appear at 35.7 ppm and 56.4 ppm, respectively. The aromatic carbons ^{2}C/^{6}C, ^{3}C/^{5}C and ^{4}C appear at 129.6, 120.4 and 135.4 ppm, respectively. The azomethine (C=N), amide ($CONH_2$) and methyl (CH_3) resonances are found to lie at 159.2, 178.4 and 21.3 ppm, respectively (Table 2). The elemental analysis data of the product confirms the proposed molecular formula for poly(HAAPS).

Polymer-Metal Chelates

The Schiff base-metal chelates are dark colored solids, particularly soluble in dimethyl formamide and tetrahydrofuran. The elemental analysis shows that the metal to ligand ratio is approximately 1:2. The polymer chelate essentially takes up

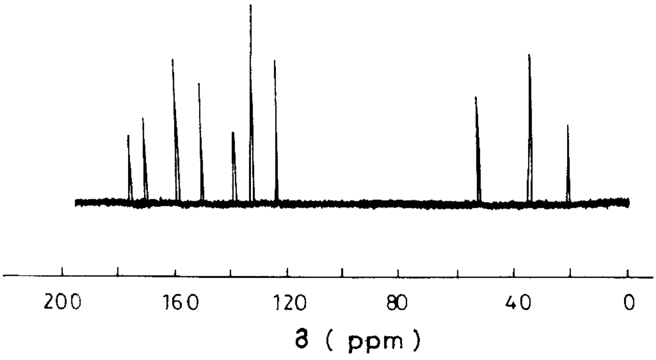


Figure 2. Proton decoupled ^{13}C NMR spectrum of Poly(HAAPS).

TABLE 2. NMR Spectral Data of the Macromolecular Chelate Poly(HAAPS)

Sample	**^{1}H NMR data (ppm)**	**^{13}C NMR data (ppm)**
Poly (HAAPS)	1.42 (3H, N=C-CH_3) 1.78 (H, -CH-) 2.81 (2H, -CH_2-) 6.9-7.5(3H, Aromatic) 8.0-8.2(4H, OH, NH_2, NH)	35.7 (-CH_2-) 56.4 (-C-) 120.4 (^{2}C/^{6}C) 129.6 (^{3}C/^{5}C) 135.4 (^{4}C)

a coiled form in solution. Besides, the steric constraints imposed by the geometry around the metal ion do not facilitate the occupation of the metal ion in all available sites for coordination.

IR Spectra

The IR spectral studies of the polymer-metal chelates provide important clues regarding the complexation of the metal ion with the polymer. The ligand stretching frequency of the functional groups which are involved in coordination undergo shift which can be taken as an evidence of coordination. The IR spectrum of the polymer-metal chelate indicates the absence of a broad band in the region 3000-3300 cm^{-1} which is due to the cleavage of hydrogen bond, deprotonation of

TABLE 3. Electronic Spectral Data, Magnetic and Conductance Data

Sl. No.	**Sample**	**Electronic spectral data (cm^{-1})**	**Magnetic moment (BM)**	**Electrical conductance (10^{-9} ohm^{-1} cm^{-1})**
1	Poly (HAAPS)-Ni(II)	12418, 13160, 16928	2.99	1.34
2	Poly(HAAPS)-Cu(II)	10194, 13079, 15268	2.07	2.46

the phenolic oxygen and its subsequent coordination with metal ion [18]. The lowering of >C=N stretching frequency in polychelates indicates the coordination of metal ion through azomethine nitrogen [19]. The shift of band at 1600 cm^{-1} towards the low frequency region may probably be due to the bonding between >C=N group and metal ion on coordination. The characteristic medium intensity band at 1300-1340 cm^{-1} observed in the polymers, due to phenolic C-O vibration shows marked shift towards high frequency in the spectrum of polychelates, thus indicating the involvement of oxygen of phenolic C-O in bonding with metal ion [20].

Electronic Spectra

The Ni(II) polychelate exhibits three bands in the region 12000 cm^{-1} -17000 cm^{-1}. The positions of these bands clearly rule out the possibility of tetrahedral or octahedral geometry for the system. The energy separation between the d_{x2-y2} orbital and the next lowest orbital is invariably greater than 10,000 cm^{-1} in the case of square planar complexes. The frequencies observed in the present case (Table 2) viz. 12,418 cm^{-1}, 13,610 cm^{-1} and 16,928 cm^{-1} clearly point to a slightly distorted planar geometry[21]. The ν_1 and ν_2 bands are close to each other with a separation of 800 cm^{-1}. However, the ν_3 band which is normally oberved as an intense band between 23,000 cm^{-1} - 30,000 cm^{-1} is not seen, while an extra band is observed at 16,928 cm^{-1}. The absence of ε values make it difficult to assign the transitions to these bands.

The copper chelate also exhibits three bands in between 10,000 cm^{-1} and 15,500 cm^{-1}. The formation of regular tetrahedral geometry in Cu(II) systems is very rare as there is flattening of tetrahedron leading to D_{2d} symmetry due to the Jahn-Teller effect that lifts the degeneracy of $2\pi_2$ ground state. A classical example of square planar system is $CuCl_4^{2-}$ ion which exhibits bands in the visible region around 10,000 cm^{-1}. The three bands lying at 10,194 cm^{-1},13,079 cm^{-1} and 15,268

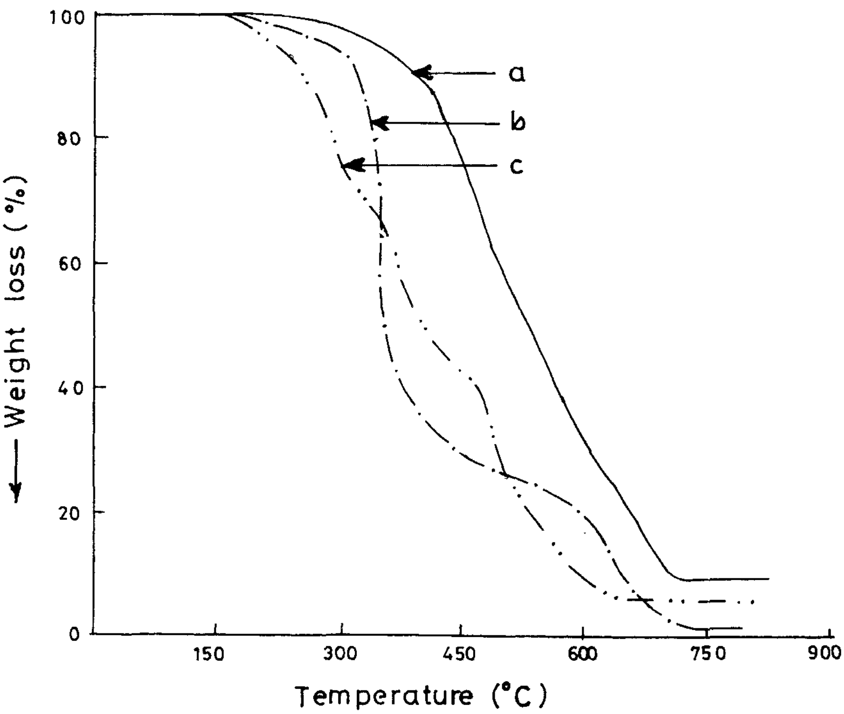


Figure 3. TGA curves of (a) Poly(HAAPS-Ni(II), (b) Poly(HAAPS), and (c) Poly(HAAPS)- Cu(II.

cm^{-1} indicate that copper-polymer chelate has essentially a planar geometry (Table 3).

Magnetic Moments

The room temperature magnetic moments of the nickel(II) and copper(II) polymer-metal chelates, obtained by the Guoy method, are found to be 2.99 BM and 2.07 BM respectively. The values obtained for these systems indicate a slightly distorted planar geometry for the metal chelates [22, 23]. The electronic spectral data in conjunction with magnetic moment values clearly rule out the possibility of both tetrahedral and octahedral geometries for these complexes (Table 3).

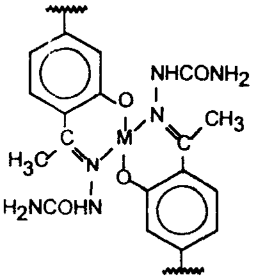
Electrical Conductivity

The electrical conductivity of Cu(II) and Ni(II) polychelates are 2.46x10^{-9} and 1.34 x10^{-9} ohm^{-1} cm^{-1}, respectively. The data indicate that the polychelates are poor electrical conductors.

Thermogravimetric Analysis

The TGA curves of poly(HAAPS) and its metal chelates are shown in Figure 3. The decomposition of the polymer ligand and its copper(II) and nickel (II) complexes occur in two stages. However, in the case of nickel(II) polymer complexes the separation is not distinct. The incorporation of the metal ion usually enhances the thermal stability of the polymer and metal chelates used as hardeners of epoxy oligomers result in polymer possessing increased strength and heat resistance [24]. The initial decomposition temperature of the polymer and its copper(II) complex is very close to each other and the latter has a slightly lower temperature, which is rather unusual and this may be attributed to the unfavorable geometry around the central metal ion. The entire process of decomposition is complete in between 160°C-710°C for all three systems. However, the nickel(II)-polymer system has a higher initial decomposition temperature (IDT) when compared to the other two systems and the final temperature is also higher. This trend is also consistently reflected in the temperature vs weight loss of polymer (Table 4). The metal containing polyimides were reported [25] to have less thermal oxidative stability when compared with those of parent polyimides. From the TGA curves, it is evident that the decomposition of polychelates commence at 200°C and almost complete decomposition occur at about 700°C. The decomposition at lower temperatures may be due to the volatilization of low molecular weight species and at higher temperatures due to the cleavage of the polymeric chain followed by the volatilization of the cleaved products. The temperature at which the decomposition occurs clearly indicates that the Ni(II) chelates are more stable than Cu(II) chelates.

The following general structure has been proposed for the polymer-metal complex based on the spectral and magnetic studies and also from elemental analysis data (Scheme 1).



Structure I

TABLE 4. Thermogravimetric Data of Poly(HAAPS) and its Metal-Complexes

Sl. No.	**Polymer**	**Decomposition temperature (°C)**		**Temperature (°C) Vs weight loss (%) of polymer**				
		Stage I	**Stage II**	**10**	**25**	**50**	**75**	**90**
1.	Poly(HAAPS)	172-458	458-704	315	343	359	523	647
2.	Poly(HAAPS)-Cu(II)	161-419	419-696	254	302	398	508	605
3.	Poly(HAAPS)- Ni(II)	217-709	--	401	450	532	642	700

CONCLUSION

The functionalized polymer poly(HAAPS) was synthesized from the poly(HAAP) and semicarbazide hydrochloride. The monomer 2-hydroxy-4-acryloxyacetophenone was obtained by the reaction of 2,4-dihydoxyacetophenone with acryloyl chloride in presence of triethylamine, which was subsequently polymerized by using BPO as an initiator. Metal chelates of poly(HAAPS) were obtained by the reaction of poly(HAAPS) with Ni(II) and Cu(II) acetates. The polychelate, as well as the polymer-metal chelates, were characterized by spectral studies and elemental analysis. The electrical conductivity of the polymer-metal chelates indicate the non-conducting nature of the complexes. The metal ions do not occupy all the available sites in the polymer chelate due to steric constraints. The thermal stability of the Ni(II) chelate is more than that of the Cu(II) chelate. Spectral data of the complexes coupled with magnetic moments suggest a distorted planar geometry for both the system.

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Received February 28, 1998
Revision received March 10, 1998