

Polymer–Metal Complexes: Synthesis and Characterization of Poly(4-acetyl-3-hydroxyphenylacrylate) and Its Metal Chelates

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ABSTRACT: 4-Acetyl-3-hydroxyphenylacrylate (AHAH) was synthesized and polymerized in 2-butanone using benzoyl peroxide as initiator. Poly(4-acetyl-3-hydroxyphenylacrylate) (PAHAH) 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) chelates of PAHAH were synthesized. The diffuse reflectance spectra and magnetic moments of the polychelates show distorted planar and octahedral structures for poly[Ni(AHA)₂] and poly[Cu(AHA)₂(OH₂)₂] complexes, respectively. The thermal properties of the polychelates are also discussed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 177–182, 1998

Key words: poly(4-acetyl-3-hydroxyphenylacrylate); polymer complexes; magnetic moments; electronic spectra

INTRODUCTION

The synthesis and study of metal-containing polymers are important, as these systems offer several advantages over unbound metal complexes and metal salts in a variety of chemical reactions.¹ Many of them behave with enhanced efficiency when they are anchored to the polymer backbone. The catalytic activity of such systems has been well documented.^{2–5} The macromolecular chelates with Rh(III) were found to be good hydrogenation catalysts for olefins and some acid derivatives.^{4,5} The platinum group metal complexes have been extensively employed as catalysts. Similarly, the Ru(II) complex attached to a polymer behaves as a photosensitizer in the photochemical reduction of water.⁶ The ferric salen complex anchored to a chloromethylated divinylbenzene–styrene copol-

mer has been reported to be a good catalyst for the decomposition of hydrogen peroxide.⁷

The polymer chelates provide a unique structural environment for complexation.^{8,9} The polymeric chelates functionalized by the multidentate ligand are often used for this purpose. In this article the synthesis, characterization, and thermal properties of poly(4-acetyl-3-hydroxyphenylacrylate) (PAHAH) and its metal complexes with Cu(II) and Ni(II) are reported.

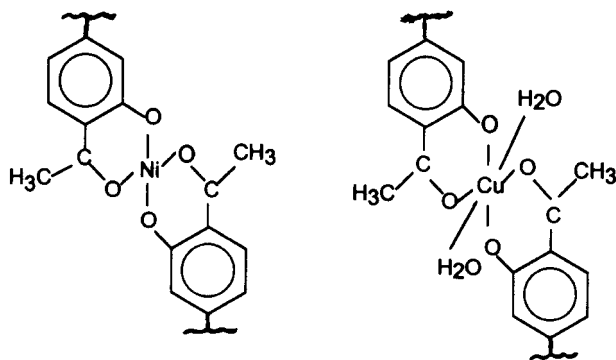
EXPERIMENTAL

Materials

2-Butanone, *N,N'*-dimethyl formamide, tetrahydrofuran, and chloroform were distilled before use. Benzoyl peroxide was recrystallized from chloroform–methanol mixture. 2,4-Dihydroxyacetophenone was recrystallized from ethanol. Acryloyl chloride was prepared according to Stempel, Cross, and Mariella.¹⁰

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Structure 1

Preparation of Ligand 4-Acetyl-3-hydroxyphenyl acrylate (AHAH)

The 4-hydroxy group of dihydroxy acetophenone (DHAPO) was esterified with the acryloyl group, as in the case of the unhindered 4-hydroxy group of dihydroxy benzophenone.¹¹ The product (AHAH) monomer was recrystallized from ethanol.

The IR and ¹H-NMR spectra of the compound were consistent with the assigned structure.

Polymer Synthesis

The monomer was polymerized in polymerization tubes as solution of 2-butanone using benzoyl peroxide (BPO) (1 wt % of monomer) as initiator. The reaction mixture was degassed by passing nitrogen gas, sealed, and kept in a thermostat at 65°C. After 12 h, the polymer was precipitated by the addition of methanol, further purified by reprecipitation by methanol from chloroform solution, and dried in vacuum at 40°C for several days (structure 1). The yield was 62%.

Preparation of the Polymer Complexes

Polychelates were prepared by dissolving the polymer in tetrahydrofuran (THF) (0.02M) and the pH of the solution was adjusted to 7 with ammonia. An aqueous solution of Cu(II), Ni(II) acetates (0.12M) was added dropwise with constant stirring. The reaction mixture was heated for 2 h on a water bath. The resulting solid was filtered, washed with hot water, followed by ethanol, and dried in vacuum at 50°C.

Measurements

Microanalysis of all the samples was carried out on a Coleman C, H, and N analyzer and the metal

contents of all the polymer complexes were calculated by a standard technique¹² (Table I). IR spectra were recorded on a Hitachi 270-50 spectrophotometer, as potassium bromide pellets. ¹H-NMR spectra were obtained with a Bruker 270-MHz spectrometer, with CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard. The molecular weights of PAHAH were determined by gel permeation chromatograph (Waters model 410) using THF as eluent and polystyrene as standard. The magnetic measurements were carried out at room temperature using Gouy's method, employing Hg[Co(SCN₄)] for calibration purposes, corrected for diamagnetism by Pascal's constants. Electrical conductivity of the polychelates was measured as pellets of 10 mm diameter and 2–3 mm thickness coated with silver paint using a Keithley electrometer. The thermogravimetric analysis of the polymers was performed on a Mettler-2000 TA thermal analyzer. The diffuse reflectance spectra of the polychelates were recorded on a Carl Zeiss VSU-2P spectrophotometer.

RESULTS AND DISCUSSION

Characterization of the Homopolymer

The monomer (AHAH) was prepared by the esterified reaction of acryloyl chloride with the 4-hydroxy group of dihydroxy acetophenone.¹¹ The monomer was then polymerized by radical polymerization initiated by benzoyl peroxide (BPO).

PAHAH is soluble in MEK, THF, DMSO, DMF, and chloroform. It is insoluble in nonpolar and hydroxy solvents like benzene, toluene, methanol, and water.

The IR spectrum of the new ligand (Table II) exhibits absorption due to OH, CO, and the phenyl ring. The IR frequency of the polymer shows a broad band in the region 3000–3250 cm⁻¹, which may be due to inter and intramolecular hydrogen-bonded phenolic —OH stretching vibration.¹³ The intense bands at 1655 and 1765 cm⁻¹ are due to the stretching vibration of the keto and ester carbonyl groups. The strong bands at 1600

and 1500 cm⁻¹ are due to the $\begin{matrix} \diagdown & & \diagup \\ & \text{C}=\text{C} & \\ \diagup & & \diagdown \end{matrix}$ 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 ¹H-NMR spectrum of PAHAH shows resonance signals at 8.01–8.2 (H, OH),¹⁴ 6.85–7.84

Table I Analytical Data of the Isolated Polymer Complexes

Complex	Composition	Yield (%)	Exp (Calcd) (%)				μ_{eff} (BM)
			C	H	Metal	H ₂ O	
1	PAHAH	62.8	64.39	4.39	—	—	—
			(64.32)	(4.32)	—	—	
2	PolyCu(AHA) ₂ (OH ₂) ₂	58.4	51.81	3.53	12.46	7.06	1.72
			(51.68)	(3.46)	(12.57)	(7.13)	
3	Poly(Ni(AHA) ₂)	56.7	56.37	3.84	12.44	—	3.06
			(56.29)	(3/89)	(12.49)	—	

(3H, C₆H₃), 1.76 (2H, CH₂), 1.54 (3H, CH₂), and 2.48 ppm (H, CH) which are downfield from TMS.

The number- and weight-average molecular weights of the polymer determined by gel permeation chromatography are $M_w = 2.84 \times 10^4$, $M_n = 1.96 \times 10^4$, and $M_w/M_n = 5.67$.

Characterization of the Polymer Complexes

The most significant change in the PAHAH bands upon complexing (Table II) is the decrease in $\nu_{\text{C=O}}$ ketone. This shift to lower frequencies in the spectra of the complexes is likely to be due to involvement of the oxygen atom of the keto group in bond formation,^{15,16} whereas the ν_{OH} band almost disappears due to ionization of the OH group.¹⁷ This is further confirmed by a shift to lower frequencies in $\nu_{\text{C-O}}$ by 10 cm⁻¹. The appearance of some new bands in the regions near 300–650 cm⁻¹ and 250–500 cm⁻¹ are probably due to the formation of (M—O) keto and (M—O) phenolic bands, respectively.¹⁸

Electronic Spectra

The diffuse reflectance spectrum of poly[Cu(AHA)₂(OH₂)₂] shows a broad band at 14,640 cm⁻¹ and a weak band at 26,210 cm⁻¹. The structural

determination of bis(3-methylpentane-2,4-dienato)Cu(II) and bis(1-phenyl-1,3-butanediato)Cu(II) clearly show that the “O₄” coordination around the central metal ion results in square planar arrangement in both the cases.^{19,20} However, in the present case steric constraints do not permit a perfectly planar geometry around the metal ion. The investigation on Cu(sal)₂·4H₂O reveals^{21,22} that this system exists in three (α , β , and γ) different forms, and the γ form exhibits bands at 14,600 cm⁻¹ and 26,000 cm⁻¹. The geometry of this system has been reported to be octahedral, with two water molecules occupying the apical position. The low energy transition observed in the present case is attributed to a $d-d$ transition involving the transition from 2E_g level to $^2T_{2g}$ level to [$^2E_g \leftarrow ^2T_{2g}$]. The weak band observed at 26,210 cm⁻¹ may be assigned to the charge transfer (CT) band. The close similarity of the spectral characteristics and donor sites of the salicylaldehyde complex with that of the present system indicates an octahedral geometry for the copper polychelate complex. The apical position of the complex is likely to be occupied by water molecules.

The electronic spectrum of poly[Ni(AHA)₂] exhibits two broad bands at 14,215 cm⁻¹ and 17,158 cm⁻¹. In the case of square planar Ni(II) complexes three spin-allowed transitions are possible.

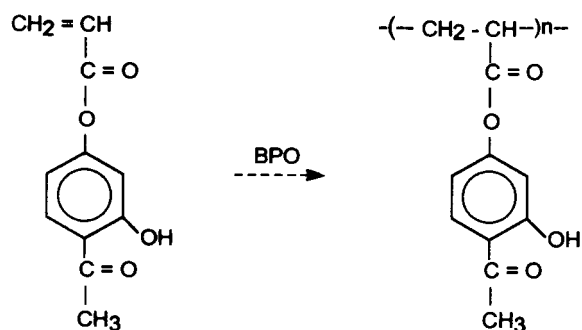
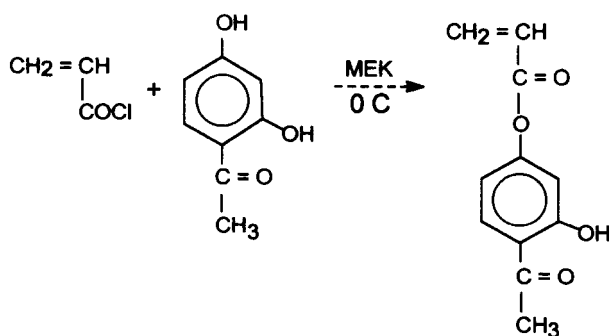
Table II IR Data of PAHAH and Its Metal Chelates

(Complexes)	Frequency (cm ⁻¹)				
	OH	C=O			C—O
		Ester	Ketone	Aromatic	
PAHAH	3250 _(b)	1760 _(s)	1650 _(s)	1510 _(s)	1360–1125
Poly[Cu(AHA) ₂ (OH ₂) ₂]	—	1760 _(s)	1635 _(s)	1520 _(s)	1355–1125
Poly[Ni(AHA) ₂]	—	1755 _(s)	1635 _(s)	1520 _(s)	1355–1130

However, the band at $22,000\text{ cm}^{-1}$ is an intense one and the nature of solvent strongly influences the ϵ value.^{23,24} The band at this region is characteristic for low-spin square planar Ni(II) complexes. However, in the present case two strong bands are observed at $17,158(\nu)\text{ cm}^{-1}$ and $14,215(\nu)\text{ cm}^{-1}$ and a weak band at $12,390\text{ cm}^{-1}$. The absence of any bands in the region $8000\text{--}10,000\text{ cm}^{-1}$ and $> 20,000\text{ cm}^{-1}$ clearly rules out the possibility of octahedral geometry for this complex. The precise assignment of transition in this case could not be made due to lack of ϵ values. However, comparison of the band positions with analogous systems suggest a distorted planar geometry for the Ni(II) polychelate complex.

Magnetic Measurements

The magnetic susceptibility of the polymer metal chelates was measured by the Gouy method. The magnetic moments of the metal complexes with either monomeric or polymeric ligands give a fairly good idea about the geometry of these systems around the metal ion. However, the intermediate magnetic moments observed in polynuclear systems as well as in some of the mononuclear



Scheme 1

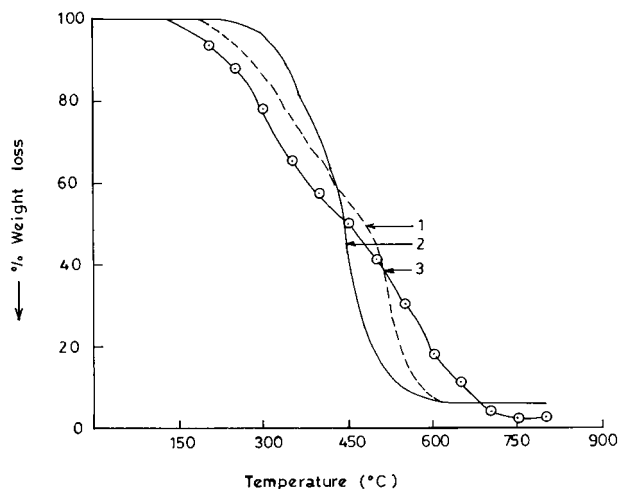


Figure 1 TGA curves of (1) PAHAH, (2) poly[Cu(AHA)₂(OH₂)₂], and (3) poly[Ni(AHA)₂].

complexes do not reflect the type of geometry around the metal ions. The magnetic moments of the metal complexes derived from poly(vinylsali-cylideneaminopyridine) have been reported²⁵ to have 1.5 BM in the case of Cu(II) complexes while the Ni(II) complex is diamagnetic. The polymer metal chelates investigated in the present study exhibit a magnetic moment of 1.72 BM in the case of the poly[Cu(AHA)₂(OH₂)₂] complex, while the moment for poly[Ni(AHA)₂] system is 3.06 BM. The values suggest a distorted planar geometry for the nickel complex, while an octahedral geometry is likely in the case of the copper complex.^{26,27}

Electrical Conductivity

The electrical conductivity of poly[Cu(AHA)₂(OH₂)₂] is 2.29×10^{-9} , and that for poly[Ni(AHA)₂] is $0.64 \times 10^{-9}\text{ Ohm}^{-1}\text{ cm}^{-1}$. The above data prove that these complexes are poor conductors.

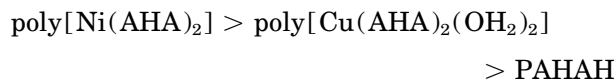
Thermogravimetric Analysis

The thermal analysis of macromolecular chelate PAHAH and its metal chelates poly[Ni(AHA)₂] and poly[Cu(AHA)₂(OH₂)₂] was carried out in air and the relevant data are presented in Table III and Figure 1. The decomposition of these systems essentially occurs in two stages. The initial decomposition temperature of the free polymer is the lowest (127°C) while the Ni(II) and Cu(II) polymer chelates have appreciably higher temperature. The temperature observed in the first case was 188°C , while in the case of the latter system

Table III TGA Data for PAHAH and Its Metal Chelates

Sample	IDT (°C)	Weight Loss (%) at Temperature (°C)								
		250	300	350	400	450	500	550	600	650
PAHAH	127	11.73	22.22	34.57	43.21	50.62	58.03	69.75	80.25	88.89
Poly[Cu(AHA) ₂ (OH ₂) ₂]	204	02.74	04.10	14.50	32.00	56.31	82.01	91.00	94.00	94.82
Poly[Ni(AHA) ₂]	188	10.22	21.59	27.27	34.07	45.48	55.68	81.82	93.32	94.39

it was observed at 204°C. The percentage weight loss of all three systems has also been tabulated and the values were recorded in the temperature range between 250°C and 700°C. The Cu(II) complex shows almost negligible weight loss till 300°C, while the remaining two systems have appreciable weight loss even at 250°C. However, this trend changes after 350°C and the Cu(II) chelate decomposes at a faster rate. When the temperature reaches 450°C, the extent of decomposition is 56.62%, whereas it is 45.48% in the case of Ni(II) chelate and 50.62% in the case of free polymer. Similar behavior is observed till 700°C and the maximum decomposition is noted in the case of free polymer. The relative thermal stabilities of the system under investigation are as follows.



The enhanced thermal stability of the macromolecular metal complexes is comparable to what has been observed in the case of polyacrylates containing hexafluoro groups.²⁸

CONCLUSIONS

The monomer 4-acetyl-3-hydroxyphenylacrylate (AHAH) was synthesized and polymerized using BPO as initiator. The polymer was characterized by IR and ¹H-NMR spectral studies. The polymers were complexed with Cu(II) and Ni(II) ions, resulting in metal containing macromolecular chelates, which were subsequently characterized by spectral, magnetic, and conductivity studies. Thermal studies indicate that metal chelates exhibit higher stability when compared to free macromolecular chelate. The order of thermal stability is poly[Ni(AHA)₂] > poly[Cu(AHA)₂(OH₂)₂] > PAHAH. The spectral and magnetic studies suggest an octahedral geometry for the Cu(II)

system and a distorted planar geometry for the Ni(II) system.

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