

Polymer–metal complexes: 1. Synthesis and characterization of poly(2-hydroxy-4-methacryloxyacetophenone)–metal complexes

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2-Hydroxy-4-methacryloxyacetophenone (2H4MAP) was prepared and polymerized in methyl ethyl ketone using benzoyl peroxide as initiator. Poly(2H4MAP) was characterized by infra-red and ^1H nuclear magnetic resonance spectroscopic techniques. The molecular weight of the polymer was determined by gel permeation chromatography. Cu(II) and Ni(II) chelates of poly(2H4MAP) were synthesized. Elemental analysis of the polychelates suggests a metal-to-ligand ratio of 1:2. The polychelates were further characterized by infra-red and electronic spectral studies, and electrical conductivity measurements. Thermogravimetric analysis of the polychelates has been carried out in air.

(Keywords: poly(2-hydroxy-4-methacryloxyacetophenone); metal chelates; characterization; thermogravimetric analysis)

INTRODUCTION

Recently, anchoring chelating ligands to polymer supports for the preparation of immobilized transition-metal complexes has been an active field of research¹. A number of polymer-bound chelating ligands, including polydentate amines, crown ethers and porphyrins, have been reported^{2–4}. Melby demonstrated selective chelation of specific metal ions from a metal ion mixture by using a number of tetradentate ligands attached to polystyrene-divinylbenzene⁵. Polymer-bound hydroxamic acid has been reported as a polymeric chelating agent for iron⁶. Polymeric Schiff's base chelates based on 2-hydroxy-5-vinylbenzaldehyde have been investigated⁷.

In the present paper the synthesis, characterization and thermal properties of poly(2-hydroxy-4-methacryloxyacetophenone) and its Cu(II) and Ni(II) complexes are reported.

EXPERIMENTAL

Materials

2,4-Dihydroxyacetophenone was recrystallized from ethanol. Benzoyl peroxide was recrystallized from chloroform–methanol mixture. Methacrylyl chloride was prepared according to Stempel *et al.*⁸.

Synthesis of 2-hydroxy-4-methacryloxyacetophenone (2H4MAP)

2,4-Dihydroxyacetophenone (30.4 g), triethylamine (20.2 g), hydroquinone (0.5 g) and 2-butanone (100 ml) were placed in a 500 ml three-necked flask and cooled from 0 to -5°C . Methacrylyl chloride (20.3 g in 25 ml

2-butanone) was added dropwise with constant stirring and cooling. Then the reaction mixture was stirred at 30°C for 2 h, filtered, washed with distilled water, dried over anhydrous sodium sulphate and solvent was evaporated. The crude 2H4MAP was recrystallized from ethanol; m.p. $65–67^\circ\text{C}$. I.r. and ^1H n.m.r. spectra of the compound were consistent with the structure.

Polymerization

2-Hydroxy-4-methacryloxyacetophenone was polymerized as 4 M solution of methyl ethyl ketone (MEK) using benzoyl peroxide (BPO) (0.5 wt% of monomer) as initiator. Monomer, BPO and MEK were placed in a polymerization tube, flushed with nitrogen, sealed and kept in a thermostat at 60°C . After 10 h, the polymer was precipitated in methanol, redissolved in chloroform, reprecipitated by methanol, filtered and dried in vacuum.

Synthesis of polychelates

Polymer (3.5 g) was dissolved in tetrahydrofuran (THF) (50 ml) and the pH of the solution was adjusted to 7 with dilute NH_4OH . An aqueous Cu(II) (5.78 g)/Ni(II) (5.62 g) acetate solution was added dropwise with constant stirring. The resulting mixture was digested on a hot water bath for 4 h and kept overnight at room temperature. The isolated polymeric metal chelate was filtered, washed with hot distilled water, followed by ethanol, and dried at 60°C in vacuum.

Measurements

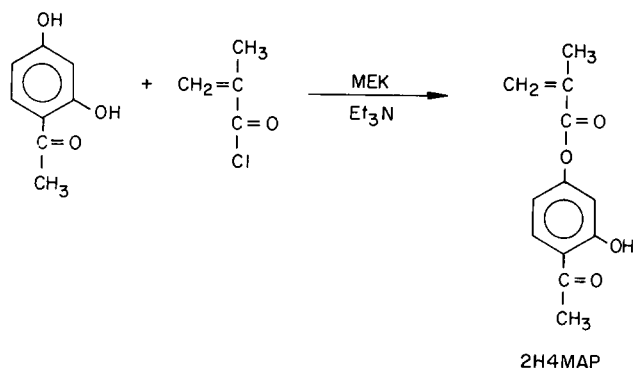
I.r. spectra were recorded on a Hitachi 270-50 i.r. spectrophotometer as potassium bromide pellets. ^1H n.m.r. spectra were recorded on a Hitachi 60 MHz spectrometer as 15% solution of CDCl_3 with tetramethylsilane (TMS) as internal standard. Molecular weights (\bar{M}_w and \bar{M}_n) of poly(2H4MAP) were deter-

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mined by gel permeation chromatography (Waters model 410) using THF as eluent. T.g.a. and d.t.g. were performed on a Mettler TA 3000 system at a heating rate of $15^{\circ}\text{C min}^{-1}$ in air. The diffuse reflectance spectra ($8000\text{--}25\,000\text{ cm}^{-1}$) were measured on a Karl-Zeiss VSU-28 spectrophotometer. The electrical conductivity of the polychelates was measured on pellets of 10 mm diameter and 2–3 mm thickness, using a Keithley electrometer.

RESULTS AND DISCUSSION

2-Hydroxy-4-methacryloxyacetophenone (2H4MAP) was prepared according to the following scheme:



2H4MAP was polymerized in MEK using BPO as the initiator. The polymer was soluble in chloroform, dimethylformamide (DMF), dimethylsulphoxide (DMSO) and THF. It was insoluble in non-polar and hydroxy solvents like benzene, toluene, methanol, water, etc.

I.r. spectra

The i.r. spectrum of the polymer shows a broad band in the region $3200\text{--}3000\text{ cm}^{-1}$, which may be assigned to inter- and intramolecular hydrogen-bonded phenolic --OH stretching⁹. The strong bands at 1650 and 1760 cm^{-1} were due to the C=O vibrations of ketone and ester groups respectively. The strong absorptions at 1603 and 1500 cm^{-1} were due to the C=C stretchings of the aromatic nucleus. The medium-intensity band at 1320 cm^{-1} may be assigned to the phenolic C--O vibration. The weak bands at $980\text{--}990\text{ cm}^{-1}$ correspond to CH_3 deformations.

¹H n.m.r. spectra

The ¹H n.m.r. spectrum of the poly(2H4MAP) shows resonance signals at 8.15 ppm due to Ar-OH. The signals at 6.75–7.6 ppm were due to aromatic protons. The $\text{--CH}_2\text{--}$, $\text{CH}_3\text{C=O}$ and --CH_3 proton signals were observed at 1.75, 1.35 and 0.90 ppm respectively.

Molecular weights

The number- and weight-average molecular weights of the polymer determined by gel permeation chromatography are $\bar{M}_w = 2.15 \times 10^4$, $\bar{M}_n = 1.67 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 1.29$.

POLYMER-METAL CHELATES

Polymer-metal chelates were obtained when the THF solution of the polymer containing a few drops of ammonia was treated with the aqueous solution of Cu(II) / Ni(II) . All the polychelates were moderately soluble in THF and DMF. The elemental analysis has shown that the metal-to-ligand ratio in all the polychelates is 1:2.

I.r. spectra

Although i.r. spectral studies are employed in investigations of the complexes, such studies have been strictly empirical and have proved of little use in solving stereochemical problems. In the present study, an attempt has been made to understand the mode of coordination of the metal ion with the ligand system. The presence or absence and the shift of certain bands in the polychelate spectrum have been utilized to arrive at the nature of coordination.

In the i.r. spectra of polychelates (Table 1) the absence of a broad band at $3200\text{--}3000\text{ cm}^{-1}$ indicates the cleavage of the hydrogen bond, deprotonation of the phenolic oxygen and its coordination to metal ion^{10,11}.

The lowering of ketonic C=O stretch in polychelates indicates the participation of ketonic oxygen in complex formation¹². The marked shifts towards high frequency of phenolic C--O vibration in polychelates indicate the involvement of oxygen of phenolic C--O in bonding with metal ion¹³.

From the i.r. spectral studies, the elemental analysis of the polychelates and the structure of the poly-ligand, it appears that the chelation of metal ions may be occurring between two groups from different polymeric chains as shown in structures A and B:

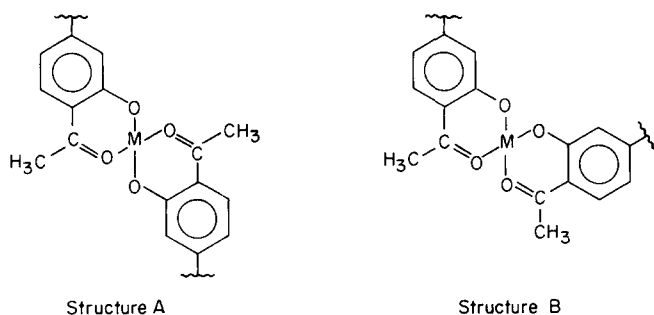
Table 1 I.r. spectral data of poly(2H4MAP) and its metal chelates

Sample no.	Polymer sample	OH str.	Wavenumber (cm^{-1})				
			C=O str.		Ar ring vibr.	CH_3 def.	C-O str.
			Ester	Ketone			
1	Poly(2H4MAP)	3200–3000(b)	1760(s)	1650(s)	1500(s)	1435(w)	1320(m)
2	Poly(2H4MAP)–Cu(II)		1760(s)	1630(s)	1500(s)	1440(w)	1350(m)
3	Poly(2H4MAP)–Ni(II)		1760(s)	1630(s)	1510(s)	1440(w)	1350(m)

s, strong; m, medium; w, weak; b, broad

Table 2 Thermogravimetric data of poly(2H4MAP) and its metal chelates

Sample no.	Polymer sample	Weight loss (%) at temperatures shown					
		200°C	300°C	400°C	500°C	600°C	700°C
1	Poly(2H4MAP)	2.40	15.85	41.22	81.71	97.56	98.23
2	Poly(2H4MAP)-Cu(II)	3.49	28.57	40.48	76.19	90.48	95.24
3	Poly(2H4MAP)-Ni(II)	4.61	63.33	86.67	96.00	96.67	97.32



Electronic spectra

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.

The electronic spectrum of Cu(II)-poly(2H4MAP) contains a broad band at $15\,100\text{ cm}^{-1}$ and a weak band at $23\,700\text{ cm}^{-1}$. The position of the band at $15\,100\text{ cm}^{-1}$ is in quite good agreement with those generally observed for planar Cu(II) complexes and may be assigned to the transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$. The weak band at $23\,700\text{ cm}^{-1}$ may be assigned to the symmetry-forbidden ligand \rightarrow charge transfer transition. Similar observations were reported by several workers¹⁴⁻¹⁷, who have assigned a planar configuration for Cu(II) complexes. A planar configuration may be tentatively assigned for Cu(II)-polychelate in the present case also.

The electronic spectrum of Ni(II)-poly(2H4MAP) shows two broad bands at $16\,800$ and $14\,000\text{ cm}^{-1}$ and a weak band at $12\,300\text{ cm}^{-1}$. 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. Several workers¹⁸⁻²¹ have made similar observations and assigned a tetrahedral geometry for Ni(II) complexes. Based on comparison of the present data with that of the literature, a tetrahedral configuration may be assigned for Ni(II)-polychelate, but not without reservation.

Electrical conductivity

The electrical conductivity of the Cu(II) and Ni(II) polychelates is 2.27×10^{-9} and $0.31 \times 10^{-9}\text{ ohm}^{-1}\text{ cm}^{-1}$ respectively. The data indicate that the polychelates are poor electrical conductors.

Thermogravimetric analysis

T.g.a. traces of poly(2H4MAP) and its Cu(II) and Ni(II) chelates are presented in Figure 1. The differential thermal analytical data are presented in Table 2. All the polychelates start to decompose at 250°C . At about

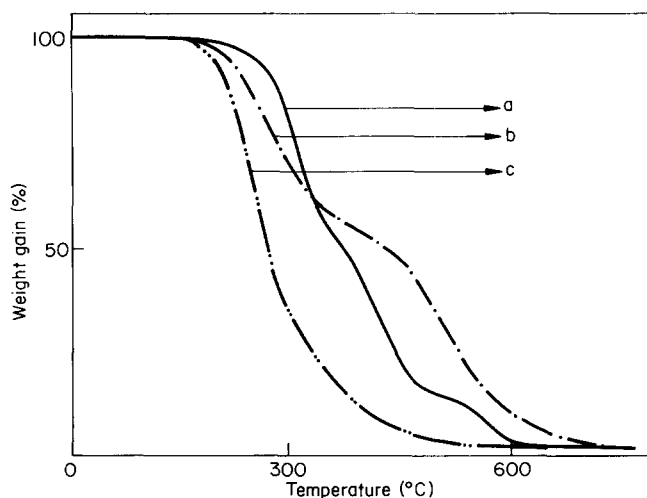


Figure 1 T.g.a. curves of (a) poly(2H4MAP), (b) poly(2H4MAP)-Cu(II), and (c) poly(2H4MAP)-Ni(II)

700°C all the polychelates lose about 90% weight. The Cu(II) chelates are somewhat more stable than Ni(II) chelates.

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