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SYNTHESIS, CHARACTERIZATION, AND CHELATING PROPERTIES OF POLY[4-(8-HYDROXY-5-QUINOLINYL)BUTAN-2-ONE]

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ABSTRACT

Poly[4-(8-hydroxy-5-quinoliny)butan-2-one]s (PHQBs) were prepared by Michael condensation of 8-hydroxyquinoline-5-aldehyde and acetone. Several alkali concentrations were used as catalyst. The resulting polymers were characterized by elemental analyses, IR spectral studies, number-average molecular weight, and thermogravimetry. Metal chelates of one PHQB sample with metal ions (Cu^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} , and Mg^{2+}) were also prepared and characterized by elemental analyses, IR spectral studies, magnetic moment, and thermogravimetry. The electrical conductivities of undoped and iodine-doped polymers and polychelates have been studied.

INTRODUCTION

The polycondensation reaction between benzaldehyde and acetone affords a polymeric product through the Michael addition reaction [1]. However, such polymers have not found any practical use [1]. Perusal of the literature reveals that no polymers have been prepared from 8-hydroxyquinoline-5-aldehyde and acetone in spite of the well-defined chelating application of 8-hydroxyquinoline-based polymers [2-7]. Such a polycondensation may yield chelating polymers with good electrical properties. These electrical properties can be enhanced by doping the polymer with reagents such as iodine, alkali metals, perchlorates, and transition metal ha-

lides [8]. Hence, it was thought it would be interesting to study a 8-hydroxyquinoline-5-aldehyde with acetone (8-FHQ-Ac) based polymer, namely poly[4-(8-hydroxy-5-quinolinyl)butan-2-one] (PHQB). The work described in the present communication is connected with the synthesis, characterization, and chelation with metal ions of PHQB. The electrical properties of undoped and iodine-doped PHQB polymers and chelates of PHQB with metal ions have also been studied with a view to investigating the increase in conductivity due to doping.

EXPERIMENTAL

Materials

8-Hydroxyquinoline-5-aldehyde was prepared according to a method reported earlier [2]. Acetone was purified by a method discussed in the literature [9]. All other chemicals were of LR grade and used without purification.

Preparation of Polymers

The polycondensation of 8-hydroxyquinoline-5-aldehyde (**1**) with acetone (**2**) was performed according to the polymerization reaction of benzaldehyde/furfural and acetone [1]. The reaction actually forms the intermediate 4-(8-hydroxy-5-quinolinyl)but-3-en-2-one (**3**) by the aldol condensation reaction, which yielded the polymeric product PHQB (**4**) through the in-situ Michael addition reaction [1] in concentrated alkali. Because the objective of the present work was to synthesize the polymeric product from 8-FHQ-Ac, the preparation of the intermediate product was not attempted.

All the PHQB polymers shown in Table 1 were prepared using different concentrations of alkali as catalyst. A general procedure is given here.

Polycondensation of 8-FHQ-Ac

A mixture of 8-FHQ (4.325 g, 0.025 mol), acetone (1.83 mL, 0.025 mol), and a 10% alkali solution of sodium hydroxide (8.64 mL, 20% based on weight of 8-FHQ) was refluxed at 110–115°C for 12 hours. The resulting reaction mixture was allowed to cool and poured into ice water. It was then acidified with dilute HCl (pH 6 to 7). The polymer so obtained was filtered off, and washed with water and then twice with 50 mL DMF (50%) to remove unreacted 8-FHQ, and air dried. The yield was 3.88 g. The polymers was a dark green powder and did not melt up to 360°C. Results of thermogravimetric analyses are presented in Table 1.

Preparation of Polymeric Chelates

As a typical procedure, the preparation of PHQB-Cu²⁺ polychelate is described here.

A dried PHQB polymer (2.13 g, 0.01 mol) was dissolved in 40 mL formic acid, diluted with distilled water (200 mL), and warmed on a water bath for 20 minutes. To this warm and clear solution a warm solution of cupric nitrate (2.41 g, 0.01 mol) in 50% aqueous formic acid solution (25 mL) was added dropwise with

TABLE 1. Characterization of 8-Hydroxyquinoline-5-aldehyde-Acetone (PHQB) Polymers

Polymer sample	Percentage of alkali ^a	Elemental analysis ^b			\bar{M}_n estimated by conductometric titration ^c	Weight loss (%) at various temperatures (°C) by TGA							
		% C	% H	% N		100	200	300	350	400	450	500	600
PHQB-A	5	72.82	5.373	6.37	2341.00	3.50	9.50	14.00	18.50	40.00	63.00	83.00	92.00
PHQB-B	10	73.43	4.986	6.82	1917.00	4.50	8.50	13.00	18.50	47.50	61.50	80.00	89.00
PHQB-C	15	72.92	5.326	6.18	1704.00	8.00	11.50	15.50	19.50	27.00	47.00	66.00	91.50
PHQB-D	20	73.04	4.955	6.42	1491.00	4.00	7.50	12.00	16.50	21.00	31.50	48.50	90.00
PHQB-E	30	71.98	5.169	6.90	1597.00	5.00	7.00	11.50	16.50	21.50	35.00	53.50	86.50
PHQB-F	40	73.42	5.244	6.13	1618.00	4.00	6.50	18.00	24.50	28.00	35.50	48.50	78.00

^aPercentage of alkali based on weight of 8-FHQ.^bCalculated (C₁₃H₁₁NO₂)_n (213)_n; C, 73.23%; H, 5.16%; N, 6.57%; and O, 15.02%.^cIn pyridine against standard sodium methoxide as the titrant.

constant stirring. The polymeric chelates which formed were green in color. After the addition of metal ion solution, the pH of the reaction mixture was adjusted to pH 5 by adding dilute liquid ammonia. The colloidal suspension so obtained was digested on a water bath at 60–70°C for about an hour and filtered. The solid was washed with distilled water followed by alcohol and dried at 100°C for 24 hours.

The polychelates PHQB-Zn²⁺, PHQB-Cd²⁺, PHQB-Mn²⁺, PHQB-Mg²⁺ and PHQB-Co²⁺ were prepared by following the same procedure. The details and results of analyses of these polychelates are presented in Table 2.

Characterization of Polymers

Elemental analyses (Table 1) of polymeric samples were carried out on an C, H, O, N Elemental Analyser (Heraeus Rapid Analyzer, Germany). The analyses of metal ions polychelates were carried out by decomposition of a known amount of polychelate by mineral acids. The metal content (Mt) was estimated by a method reported elsewhere [10].

The IR spectra of all polymer samples were taken in KBr on a Perkin-Elmer 983 spectrophotometer. Conductometric titrations of polymer samples were carried out against sodium methoxide in pyridine. The number-average molecular weight (\bar{M}_n) values (Table 1) of the polymer samples were calculated following the method of conductometric titration [2].

Thermogravimetry of polymers and polychelates was carried out on a Mettler unit (Tc-10ATA-3000) in air at a heating rate of 10°C·min⁻¹ (Table 1 and Fig. 1).

Electrical Conductivity Measurements

For electrical conductivity measurements of PHQB polymer and its polymeric chelates, all samples were heated twice to 100°C and subsequently cooled to room temperature. Then the electrical conductivity measurements were conducted on these thermally pretreated samples at different temperatures. This treatment was employed to stabilize the structure of the samples and to remove such impurities as water, organic solvent, etc. The electrical conductivities were measured on pellets (1.02 cm diameter, 0.180 cm thickness) between 35 and 200°C by using a Millan Megohmmeter RM 160 (India). Pellet preparation of the polymer samples and other details are given in an earlier report [11]. Plots of log σ (σ = electrical conductivity) versus $1/T$ (T = temperature) were made according to the exponential relation

$$\sigma = \sigma_0 e^{-E/RT}$$

Values of σ at room temperature (35°C) are included in Table 3.

Doping of Iodine in Chelate Polymers

This was carried out by a method reported in the literature [12]. The polymer samples were finely powdered and spread in a petri dish, and the dish was kept in an iodine-saturated chamber for 24 hours. Exposure of the polymer samples to iodine vapor resulted in the formation of iodine-doped polymers. The doped samples were stable in air; the iodine cloud could only be driven off by prolonged heating above 100°C. The iodinated polymer samples were pelletized according to a reported

TABLE 2. Analysis of Polymeric Chelates of 8-Hydroxyquinoline-5-aldehyde-Acetone (PHQBs) Polymers

Polymer chelates of PHQB(Mt)	Color	Molecular weight of repeating unit, g/mol	Metal, %		N, %		Weight loss (%) at various temperatures								
			Calcd.	Found	Calcd.	Found	100	200	300	350	400	450	500	600	
PHQB-Zn ²⁺	Green	489.38	13.35	13.05	5.72	5.60	Dimagnetic	5.00	8.00	10.00	14.00	35.00	65.00	80.00	82.00
PHQB-Cu ²⁺	Green	487.54	13.03	12.90	5.74	5.80	1.77	10.50	14.00	20.50	26.00	53.00	76.00	79.00	80.00
PHQB-Mn ²⁺	Brown	478.94	11.47	11.20	5.84	5.75	5.49	4.00	6.00	9.00	12.50	20.50	64.00	89.00	92.00
PHQB-Mg ²⁺	Brown	448.32	5.42	5.39	6.24	6.15	Dimagnetic	2.50	2.0	4.00	6.50	12.00	41.50	60.50	75.00
PHQB-Cd ²⁺	Green	536.41	20.95	20.23	5.21	5.29	Dimagnetic	4.00	6.00	8.00	12.50	20.50	60.00	78.00	82.00
PHQB-Co ²⁺	Pink	482.94	12.20	11.78	5.79	5.75	4.05	7.50	11.00	12.50	35.00	60.00	71.50	77.00	80.00

^aMeasured by the Geuy method.

TABLE 3. Electrical Conductivities of PHQB-Metal-Chelate Polymers

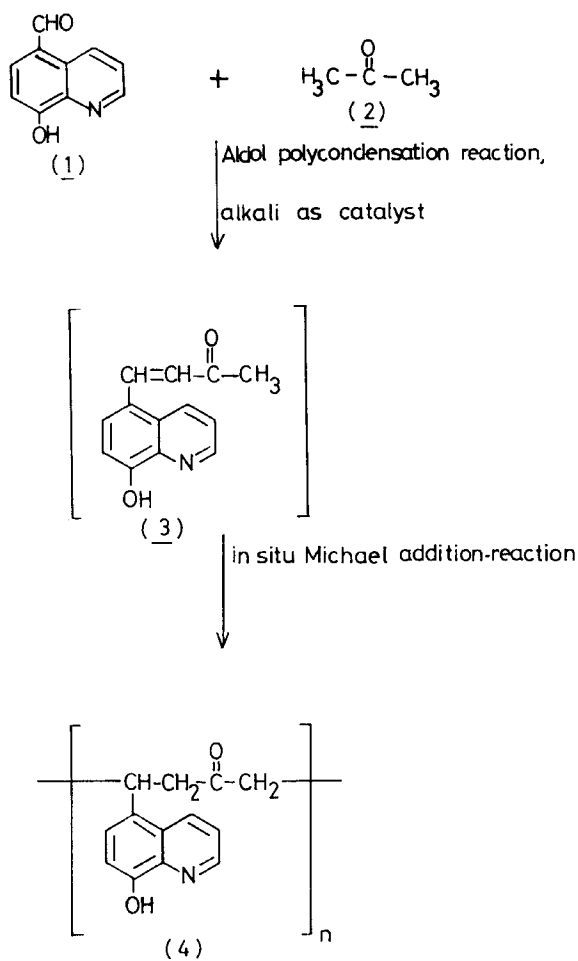
Polymer or polychelate	Temperature range, °K	Electrical conductivity σ , $\Omega^{-1} \cdot \text{cm}^{-1}$ at 35°C
PHQB(D)	308 to 473	2.30×10^{-11}
Iodinated PHQB(D)		19×10^{-9}
PHQB-Cu ²⁺	308 to 473	1.50×10^{-11}
Iodinated PHQB-Cu ²⁺		3.2×10^{-9}
PHQB-Cd ²⁺	308 to 473	1.30×10^{-9}
Iodinated PHQB-Cd ²⁺		4.2×10^{-7}
PHQB-Mn ²⁺	308 to 473	5.75×10^{-8}
Iodinated PHQB-Mn ²⁺		6.12×10^{-6}
PHQB-Zn ²⁺	308 to 473	5.84×10^{-11}
Iodinated PHQB-Zn ²⁺		5.5×10^{-8}
PHQB-Mg ²⁺	308 to 473	4.00×10^{-11}
Iodinated PHQB-Mg ²⁺		6.00×10^{-8}
PHQB-Co ²⁺	308 to 473	5.15×10^{-11}
Iodinated PHQB-Co ²⁺		4.82×10^{-8}

method [11]. A thin layer of colloidal graphite in acetone (silver paste could not be applied because it forms silver iodide with iodine-doped polymers) was applied, and the pellets were dried in vacuum (35°C). The electrical conductivity of the iodine-doped samples was measured (35 to 200°C) as already described, and the values are included in Table 3.

RESULTS AND DISCUSSION

PHQB polymers prepared using various alkali concentrations are green powders. They are insoluble in common organic solvents and soluble only in formic acid. They did not melt up to 360°C. The carbon, hydrogen, and nitrogen content of PHQB polymer samples (shown in Table 1) is consistent with the predicted structure of PHQB polymer (Scheme 1).

The IR spectra of all PHQB polymer samples prepared in various alkali concentrations were found to be similar in all aspects. A broad band in the 3430–3450 cm^{-1} region is assigned to stretching vibration of O—H bonded with a ring containing nitrogen [13]. This band is broader than the corresponding band in the spectrum of 8-FHQ. This may be due to intermolecular H-bonding from the —OH group of 8-FHQ. The broad bands in the form of inflections at 2990 and 3120 cm^{-1} are



PHQB POLYMER

SCHEME 1.

attributed to aromatic stretching vibrations. A small and broad band observed at 2920 cm^{-1} in the IR spectra of all polymeric samples reveals the presence of the $-\text{CH}_2$ group in the polymeric chain since such a band is not observed in the IR spectra of monomer 8-FHQ. The sharp band at 1710 cm^{-1} is due to the normal $-\text{C}=\text{O}$ group while all the other spectral characteristics of the polymer samples are similar to those of 8-FHQ.

Examination of the molecular weight of polymer samples estimated by non-aqueous conductometric titration reveals that the polymer sample obtained with a low concentration of alkali has the highest molecular weight in the series, as expected.

The thermal behavior of these PHQB polymers was studied by thermogravimetric analyses in air (Table 1). TG curves of two of these samples are shown in

Fig. 1. Examination of these TG data reveals that all the PHQB samples degrade in a single step. In all samples the decomposition begins at about 50°C and occurs more rapidly in the 400 to 600°C region. A 90% loss in weight occurs in the 550 to 600°C range, the exact temperature depending upon the nature of the polymer. As expected, polymers prepared with a smaller concentration of alkali have better stabilities.

Characterization of Polymeric Chelates

All the polymeric chelates are insoluble in common organic solvents. Each of them is decomposed by mineral acids, affording the parent polymeric ligand. All the polymeric chelates are apparently unaffected when heated up to 300°C. Examination of the results (Table 2) of metal analyses of the polymeric chelates reveals that the metal-ligand ratio is 1:2 for polychelates of all the bivalent metals.

The IR spectra of all the polymeric chelates resemble each other in shape and the relative intensity of the bands. Comparison of the IR spectrum of a polymeric chelate with that of its parent polymer reveals some similarities, as expected. There is a noticeable difference in the nature of the O—H stretching region in the IR spectra of a parent polymer than in the IR spectrum of the polymeric chelate due to presence of water molecules in the polymeric chelates. The band due to the —OH group vanishes due to chelate formation. A new band at 1160 cm^{-1} in the polymeric chelate is attributed to the H atom of the —OH group of the 8-FHQ unit of the polymeric chelate being replaced by the metal ion [14–16]. Thus, this band represents C—O stretching at the C—O—M site.

Magnetic moments of the polymeric chelates are given in Table 2 (Mt = Cu^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} , and Mg^{2+}). The diffuse electronic spectrum of the Cu^{2+} polychelate shows two broad bands around 13,000 and 23,000 cm^{-1} . The first band may be due to a $2_{T_{2g}} \rightarrow 2_{E_g}$ transition, while the second band may be due

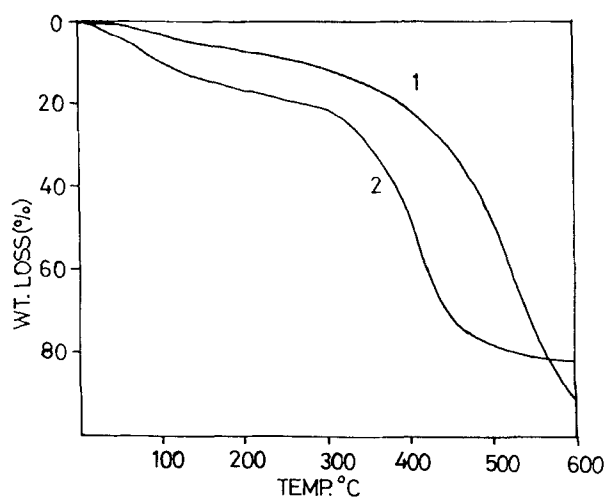


FIG. 1. TG thermograms of (1) PHQB-D polymer and (2) PHQB- Cu^{2+} polychelate.

to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} polychelate. The higher value of the magnetic moment of Cu^{2+} polychelate supports this view. The Co^{2+} polychelate gives rise to absorption bands at 23,800 and 19,040 cm^{-1} , which can be assigned to $4_{\text{T}_{1\text{g}}} \rightarrow 2_{\text{T}_{2\text{g}}}$, $4_{\text{T}_{1\text{g}}} \rightarrow 4_{\text{T}_{1\text{g}}}(\text{P})$ transitions. These absorption bands and M_{eff} indicate an octahedral configuration of the Co^{2+} polychelate.

As the spectra of the polychelates of Mn^{2+} , Zn^{2+} , Co^{2+} , and Cd^{2+} are not well resolved, no attempt was made to analyze them. As expected, Zn^{2+} , Cd^{2+} , and Mg^{2+} are diamagnetic and Mn^{2+} , Co^{2+} , and Cu^{2+} show a magnetic moment lower than required for only one spin.

Examination of the TG thermograms and TG data (Table 2, Fig. 1) of all the polymeric chelates reveals that like the parent polymer, each polychelate degrades in one step. The rate of decomposition of the polychelate is higher than that of the parent polymer. The polychelate is comparatively less stable thermally than the parent ligand. It seems that metal ions accelerate decomposition of the polychelate.

Electrical Conductivity Data

The electrical conductivity data of all the PHQB-metal chelates and iodine-doped PHQB-metal chelates are furnished in Table 3. Examination of the results presented in Table 3 and plots of $\log \sigma$ vs $1/T$ (not shown) reveal that the conductivity of iodine-doped polychelates is higher than that of undoped polychelates at room temperature and that the conductivity increases irregularly with an increase in the temperature. Due to the nonlinearity of the plots, calculations of E_a and σ_0 were not attempted. The undoped polychelates at room temperature have electrical conductivity in the 1.5×10^{-11} to $5.75 \times 10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$ range. The electrical conductivity of iodine-doped polychelates falls in the 1.9×10^{-9} to $6.12 \times 10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$ range at room temperature.

The electrical conductivities of polymeric chelates at room temperature (35°C) are in the following order: $\text{Mn} > \text{Cd} > \text{Zn} > \text{Co} > \text{Mg} > \text{Cu}$. This is in good agreement with the literature data [17]. The electrical conductivity of iodine-doped chelate polymers at room temperature decreases in the same order. Longer exposure of these polymers to iodine does not show any significant effect on their electrical conductivities. In conclusion, the electrical conductivity rises appropriately due to iodine doping. This may be due to a redox reaction of the chelate polymers with iodine, in which formation of some holes in the polymer moiety takes place, and this produces polyiodide ions, viz. I_3^- , I_5^- , I_7^- , etc. [10, 18].

CONCLUSION

Polycondensation of 8-FHQ and acetone using different concentrations of aqueous alkali resulted in the formation of polymers of low molecular weight (1500–2300). The formation of polymer was confirmed by elemental analyses and IR studies. The applicability of these polymers was explored by preparing polymeric chelates using different metal ions, and this indicates the polymers have good chelating properties. PHQB and its chelates were studied by examining their thermal stabilities and electrical conductivities. It was observed that they all have good

thermal stabilities but that the chelates are thermally less stable than the parent polymers. The electrical conductivity of both polymers and their chelates is in the range of semiconducting materials. The electrical conductivity is further enhanced a hundredfold or more by iodine doping.

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