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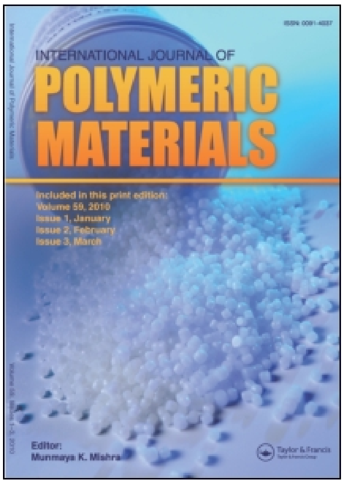

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# Synthesis, Characterization and Chelating Properties of Poly[4-(8-Hydroxy-5-Quinolinyl)-3-Methyl Butan-2-One]

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Poly [4-(8-hydroxy-5-quinolinyl)3-methylbutan-2-one]s (PQMBs) were prepared by Michael condensation of 8-hydroxyquinolinyl-5-aldehyde (8-FHQ) and 2-butanone (i.e. Methyl ethyl keton; MEK). The polymers thus obtained are denoted as 8-FHQ-MEK. Several proportions of alkali concentrations were used as catalyst. The resulting polymers were characterized by elemental analysis, IR spectral-studies, number average molecular weight (*Mn*) and thermogravimetry. Metal chelates of a selected PQMB sample with metal ions viz; $Cu^{+2}$, $Co^{+2}$, $Zn^{+2}$, $Cd^{+2}$, $Mn^{+2}$ and $Mg^{+2}$ have also been prepared and characterized by elemental analysis, IR spectral studies, magnetic moment and thermogravimetry. The electrical conductivity of undoped and iodine-doped polymers and their polychelates has been studied.

KEY WORDS Poly[4-(8-hydroxy-5-quinolinyl)3-methyl butan-2-one], synthesis, chelating properties, structure.

## INTRODUCTION

In our earlier communication[1] we reported the polycondensation reaction between 8-hydroxyquinolinyl-5-aldehyde and acetone which afforded the polymeric product through Michael addition reaction. The polymeric metal chelates and their electrical properties of these polymeric products have also been described. In continuation of this work,[1] the present communication deals with the synthesis, characterization and chelation with metal ions of PQMB. The electrical properties of undoped and iodin-doped PQMB polymers and chelates of PQMB with metal ions have also been studied with a view to investigate the increase in conductivity due to doping.

## RESULTS AND DISCUSSION

All the PQMB polymers prepared using various alkali concentration are green powder. They are insoluble in common organic solvents and soluble only in formic acid. They

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TABLE I

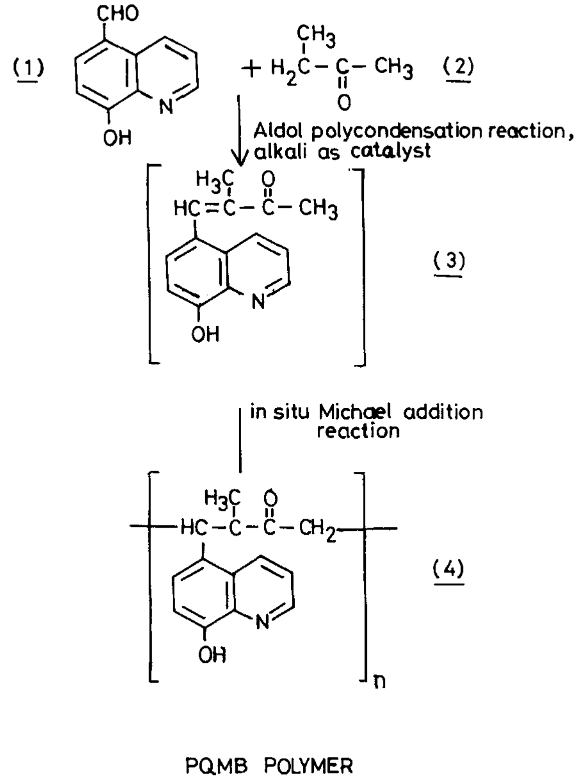
Characterization of 8-hydroxyquinoline-5-aldehyde-methyl ethyl ketone (PQMBs) polymers

| Polymer Sample | Percentage of Alkali[a] | Elemental Analysis[b] | | | $\overline{\text{Mn}}$ Estimated by conductometric titration[c] | Weight loss (%) at various temperature (°c) by TGA | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | %C | %H | %N | | 100 | 200 | 300 | 350 | 400 | 450 | 500 | 600 |
| PQMB-A | 5 | 73.20 | 5.25 | 6.00 | 2270 | 3.00 | 3.50 | 7.00 | 10.50 | 17.50 | 38.50 | 58.00 | 85.00 |
| PQMB-B | 10 | 74.50 | 6.00 | 6.30 | 1930 | 4.50 | 7.00 | 10.50 | 16.00 | 37.00 | 60.50 | 77.50 | 94.50 |
| PQMB-C | 15 | 73.80 | 5.50 | 6.07 | 1792 | 4.50 | 7.50 | 10.50 | 13.50 | 18.00 | 37.00 | 60.00 | 82.50 |
| PQMB-D | 20 | 74.10 | 5.60 | 6.10 | 1703 | 5.50 | 8.00 | 10.50 | 13.50 | 18.50 | 37.00 | 57.00 | 85.00 |
| PQMB-E | 30 | 74.25 | 5.80 | 6.25 | 1589 | 4.50 | 6.50 | 10.00 | 15.00 | 22.50 | 36.50 | 54.50 | 87.00 |
| PQMB-F | 40 | 74.15 | 5.95 | 5.95 | 1702 | 4.50 | 7.00 | 19.50 | 23.50 | 27.50 | 35.00 | 48.00 | 80.00 |

[a] Percentage of alkali based on weight of 8-FHQ.

[b] Calculated $(C_{14}H_{13}NO_2)_n$ $(227)_n$; (C 74%, H 5.72%, O 14% and N 6.16%).

[c] In pyridine against standard sodium methoxide as a titrant.



SCHEME I

did not melt up to 360°C. The carbon, hydrogen and nitrogen content of PQMB polymer samples (shown in Table I) is consistent with predicted structure of PQMB polymer (Scheme I). The IR spectra of all the PQMB polymers prepared by using different alkali concentration were found to be similar in all aspects. The main characteristics frequencies of these IR spectra are described in following discussion.

A broad band in the region of 3300–3420 $cm^{-1}$ is assigned to O—H stretching vibration of 8-hydroxyquinoline nucleus. The fact that the sharp band does not appear in the spectral region around 3030 $cm^{-1}$ is explicable on the basis of presence of variety of aromatic C—H stretching.[8–11] The broad band at 2940 $cm^{-1}$ and 2970 $cm^{-1}$ are due to aliphatic C—H stretching of ethylene ($—CH_2—CH_2—$) and/or methylene bridges between 8-FHQ units. The sharp band for normal carbonyl group (—C═O) is observed at 1680 $cm^{-1}$. The another sharp band at 1640 $cm^{-1}$ is correspond to hetero aromatic ring.[8] Finally the medium and sharp peak is observed for O—H bending vibration in the spectral region at 1280 $cm^{-1}$. The IR spectra of a selected polymer, its chelate and monomer (8-FHQ) are shown in Figure 1.

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

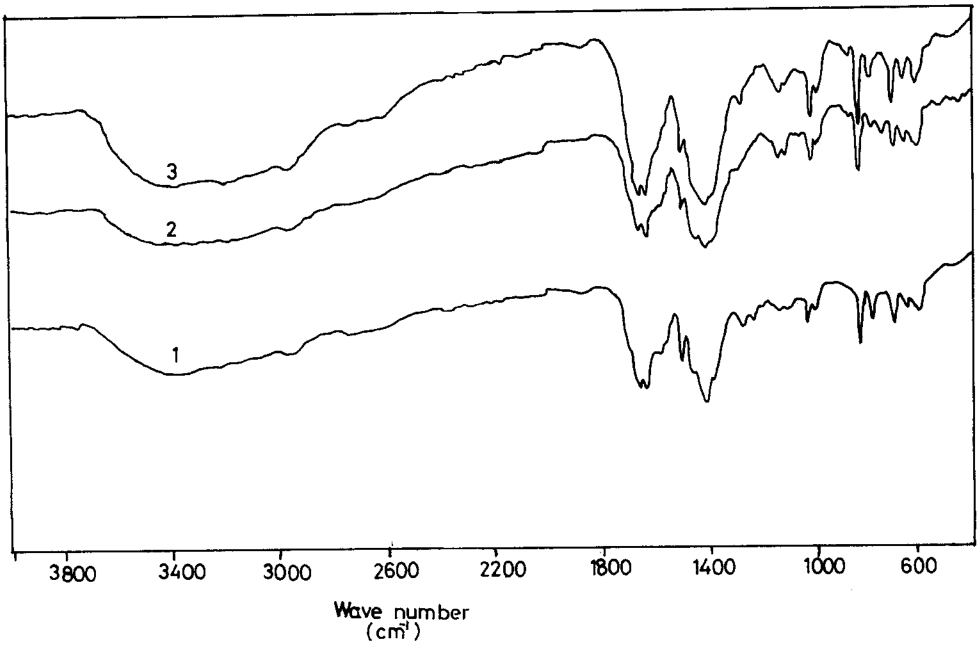


FIGURE 1 IR spectra of: (1) 8-FHQ, (2) PQMB-Cu$^{+2}$ polychelate, (3) PQMB-D polymer.

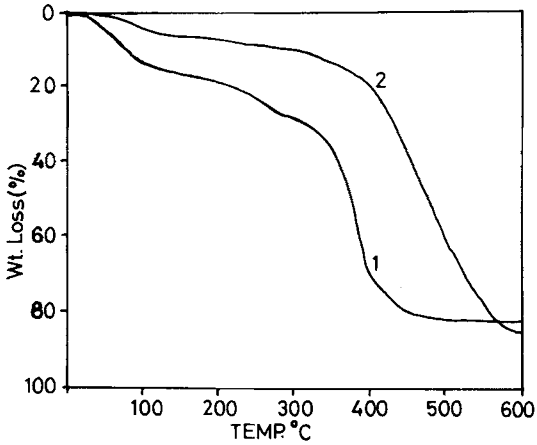


FIGURE 2 TG thermograms of: (1) PQMB-Cu$^{+2}$ polychelate, (2) PQMB-D polymer.

The thermal stability of the PQMB polymers was assessed by thermogravimetric analysis in air (Table I). TG curves of two of these samples are shown in Figure 2. Examination of these TG data reveals that the PQMB sample degrade in a single step. In all samples the decomposition begins at about 50°C, occurs more rapidly in the region of 400°C to 600°C and 85% loss in weight occurs in the range of 550–600°C depending upon the nature of the polymer. As expected the polymer prepared of low concentration of alkali has been thermal stability than that of others.

## EXPERIMENTAL

### Materials

8-hydroxyquinoline-5-aldehyde was prepared according to the method reported earlier.[2] Methyl ethyl ketone (i.e. 2-butanone) (MEK) was purified by method discussed in literature.[3] All other chemicals were of LR grade and used without purification.

### Preparation of Polymers

The polycondensation of 8-hydroxyquinoline-5-aldehyde (1) with MEK (2) was performed according to the polymerization reaction of benzaldehyde/furfural and Methyl ethyl ketone.[4] The reaction actually form the intermediate 4-(8-hydroxy-5-quinolinyl)3-methyl but-3-en-2-one (3) by aldol condensation reaction, which followed and yield the polymeric product Poly[4-(8-hydroxy-5-quinolinyl)3-methylbutan-2-one] (PQMB) (4) through insitu Michael addition reaction[1] in concentrated alkali. As the objective of the present work is to synthesize polymeric product from 8-FHQ-MEK the preparation of the intermediate product is not attempted.

All the Poly[4-(8-hydroxy-5-quinolinyl)3-methyl butan-2-one]s (PQMB) polymers shown in Table I were prepared using different concentrations of alkali as catalyst. A general procedure is given here.

### Polycondensation of 8-hydroxyquinoline-5-aldehyde with Methyl Ethyl Ketone (8-FHQ-MEK)

A mixture of 8-FHQ (0.025 mole), MEK (0.025 mole) and 10% alkali solution of sodium hydroxide (8.64 ml, 20% based on weight of 8-FHQ) was refluxed at 110–115°C for 12 h. The resulting reaction mixture was allowed to cool and poured into ice-water. It was then acidified with dil. 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 4.22 g. The polymer was dark green powder and did not melt up to 360°C. Results of thermogravimetric analysis are presented in Table I.

### Preparation of Polymeric Chelates

As a typical procedure, the synthesis of PQMB-$Cu^{+2}$ polychelate has been described here.

A dried PQMB polymer (0.01 mole) was dissolved in 40 ml of formic acid, diluted with distilled water (200 ml) and warmed on a waterbath for 20 min. To this warm and clear solution, a warm solution of cupric nitrate (0.01 mole) in 50% aqueous formic acid solution (25 ml) was added dropwise with constant stirring. The polymeric chelate which formed was green in color. After the addition of metal ion solution, the pH of reaction mixture was adjusted to pH 5 by adding dilute liq. ammonia. The colloidal suspension so obtained was digested on 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 h.

Following the same procedure, the polychelates of PQMB-$Zn^{+2}$, PQMB-$Cd^{+2}$, PQMB-$Mn^{+2}$, PQMB-$Mg^{+2}$ and PQMB-$Co^{+2}$ were prepared. The details and results of analyses of these polychelates are presented in Table II.

## MEASUREMENTS

### Characterization of Polymers

Elemental analyses (Table I) of polymeric samples were carried out on an C, H, N Elemental Analyser, (Heraeus Rapid Analyser; Germany). The analyses of metal ion of poly-chelates was carried out by decomposition of a known amount of polychelate by mineral acids. The metal content (Mt) was estimated by a method reported elsewhere.[5]

The IR spectra of all polymer samples was taken in KBr on a Perkin-Elmer 983 Spectrophotometer. The non-aqueous conductometric titrations of polymer samples were carried out against sodium methoxide in pyridine. The number average molecular weight ($\overline{Mn}$) values (Table I) of the polymer samples were calculated following the method reported for conductometric titration.[2]

Thermogravimetry of polymers and polychelates was carried out on a Metler unit (T6-10ATA-3000) in air at a heating rate of 10°C $min^{-1}$ (Table I and Figure 2 in results section).

### 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 II) of metal analysis 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 relative intensity of bands. Comparison of IR spectrum of polymeric chelates with that of its parent polymer reveals some similarities as expected. The noticeable difference is observed in the nature of O—H stretching and O—H bending spectra region of parent polymer and its metal chelate. The O—H stretching band is less broad in parent polymer compared to that in the IR spectrum of polymeric chelate due to presence of water molecules in the polymeric chelate. While the band at 1280 $cm^{-1}$ due to O—H bending is vanished indicating the participation —OH group in chelate formation. Further the depiction of new band at 1100 $cm^{-1}$ in polymeric chelate indicates the fact that H atom of —OH group of 8-FHQ unit of polymeric chelate is replaced by the metal ion and represents C—O stretching at C—O—M site.[12–14]

Magnetic moment of the polymeric chelates are given in Table II $Mt = Cu^{+2}$, $Cd^{+2}$, $Co^{+2}$, $Mn^{+2}$, $Zn^{+2}$ and $Mg^{+2}$. The diffuse electronic spectrum of the $Cu^{+2}$ polychelate shows two broad band around 13010 and 23005 $cm^{-1}$. The first band shows structure suggesting a distorted octahedral structure for the $Cu^{+2}$ polychelate. The higher value of the magnetic moment of $Cu^{+2}$ polychelate supports the

TABLE II

Analysis of polymeric chelates of 8-hydroxyquinoline-5-aldehyde-methyl ethyl ketone (PQMBs) polymers

| Polymer chelates of PQMB(M) | Color | Molecular weight of repeating unit (g/mol) | Metal (%) | | N (%) | | $\mu_{eff}$[a] | Weight loss (%) of various temperature | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd. | Found | Calcd. | Found | BM | 100 | 200 | 300 | 350 | 400 | 450 | 500 |
| PQMB-$Mn^{+2}$ | Brown | 506.94 | 10.83 | 10.79 | 5.52 | 5.55 | 5.61 | 5.00 | 7.00 | 11.50 | 50.00 | 63.00 | 82.00 | 84.50 |
| PQMB-$Co^{+2}$ | Pink | 510.94 | 11.53 | 11.19 | 5.48 | 5.50 | 4.14 | 14.00 | 16.50 | 18.50 | 53.00 | 65.50 | 83.50 | 86.00 |
| PQMB-$Cd^{+2}$ | Green | 564.41 | 19.91 | 19.69 | 4.96 | 4.95 | diamagnetic | 7.00 | 9.00 | 11.00 | 60.50 | 84.50 | 84.00 | 85.00 |
| PQMB-$Zn^{+2}$ | Green | 517.38 | 12.63 | 12.70 | 5.41 | 5.38 | diamagnetic | 10.50 | 13.00 | 14.00 | 50.00 | 56.50 | 83.00 | 88.50 |
| PQMB-$Mg^{+2}$ | Brown | 476.32 | 5.03 | 5.00 | 5.87 | 5.80 | diamagnetic | 9.50 | 12.00 | 12.00 | 48.50 | 53.00 | 82.00 | 84.50 |
| PQMB-$Cu^{+2}$ | Green | 515.54 | 12.32 | 12.25 | 5.49 | 5.49 | 1.72 | 16.00 | 19.00 | 28.00 | 37.00 | 71.00 | 80.00 | 81.50 |

[a] Measured by Geuy method

same. The $Co^{+2}$ polychelate gives rise to two absorption bands at 23810 and 19045 $cm^{-1}$ which can be assigned to $4T_{1g} \rightarrow 2T_{2g}$, $4T_{1g} \rightarrow 4T_{1g}$ $(P)$ transitions. These absorption bands and $\mu_{eff}$ values indicates an octahedral configuration of the $Co^{+2}$ polychelate also.

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 found to be diamagnetic and $Mn^{+2}$, $Co^{+2}$ and $Cu^{+2}$ shows a magnetic moment lower than required for only one spin.

The examination of the TG thermograms and TG data (Table II, Figure 2) 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. It is observed that the polychelate is comparatively thermally less stable than the parent ligand. It seems that metal ions accelerate decomposition of the polychelate.

### Electrical Conductivity Measurements

For the electrical conductivity measurements of PQMB polymer and its polymeric chelates, all the 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 has been employed to stabilize the structure of sample and to remove impurities such as water, organic solvent etc. The electrical conductivities were measured on pellets (1.00 cm diameter, 0.182 cm thickness) between 35°C to 200°C using a Millan Magohmmeter RM 160 (India). The preparation of pellets of all the polymer samples and other details was as given in an earlier report.[6] Plots of log $\sigma$ ($\sigma$:electrical conductivity) versus $1/T$($T$:Temperature) were made according to the exponential relation.

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

Values of $\sigma_0$ at room temperature (35°C) included in Table III.

### Doping of Iodine in Chelate Polymers

This was carried out by a method reported in the literature.[7] The polymer samples were finely powered and spread in a petridish and the dish was kept in an iodine-saturated chamber for 24 h. Thus exposure of the polymer samples to iodine vapor resulted into iodine doped samples which are stable in air, the iodine cloud only be driven off by prolonged heating above 100°C. The iodinated polymer samples were pelletized according to the method reported.[6] A thin layer of colloidal graphite in methyl ethyl ketone (Silver paste could not be applied it forms silver iodide with iodine-doped polymers) was applied and the pellets were dried in vacuum (35°C). The electrical conductivity of all the iodine doped samples was measured (35°C to 200°C) as already described and are also included in Table III.

TABLE III

Electrical conductivities of PQMB-metal-chelate polymers

| Polymer or Polychelate | Temperature range ($^{o}K$) | Electrical Conductivity $\sigma\ \Omega^{-1}cm^{-1}$ at $35^{o}c$ |
|---|---|---|
| PQMB(D) | 308 to 473 | $2.18 \times 10^{-11}$ |
| Iodinated PQMB(D) | | $17 \times 10^{-9}$ |
| PQMB-$Zn^{+2}$ | 308 to 473 | $6.52 \times 10^{-11}$ |
| Iodinated PQMB-$Zn^{+2}$ | | $5.1 \times 10^{-8}$ |
| PQMB-$Co^{+2}$ | 308 to 473 | $4.67 \times 10^{-11}$ |
| Iodinated PQMB-$Co^{+2}$ | | $3.8 \times 10^{-8}$ |
| PQMB-$Cd^{+2}$ | 308 to 473 | $1.43 \times 10^{-9}$ |
| Iodinated PQMB-$Cd^{+2}$ | | $3.77 \times 10^{-7}$ |
| PQMB-$Mg^{+2}$ | 308 to 473 | $3.92 \times 10^{-11}$ |
| Iodinated PQMB-$Mg^{+2}$ | | $4.83 \times 10^{-8}$ |
| PQMB-$Cu^{+2}$ | 308 to 473 | $1.37 \times 10^{-11}$ |
| Iodinated PQMB-$Cu^{+2}$ | | $3.66 \times 10^{-9}$ |
| PQMB-$Mn^{+2}$ | 308 to 473 | $5.55 \times 10^{-8}$ |
| Iodinated PQMB-$Mn^{+2}$ | | $8.3 \times 10^{-6}$ |

## Electrical Conductivity Data

The electrical conductivity data of all the PQMB-metal chelates and iodine-doped PQMB-metal chelates are furnished in Table III. The examination of the results presented in Table III and plots of log $\sigma$ Vs $1/T$ (not shown) reveals that the conductivity of iodine-doped polychelates is higher than that of undoped polychelate at room temperature and that the conductivity increases with an increase in the temperature irregularly. Due to non linearity of the plots the calculation of *Ea* and $\sigma_0$ were not attempted. The undoped polychelates at room temperature have an electrical conductivity in the range $1.43 \times 10^{-11}$ to $5.55 \times 10^{-8}\ \Omega^{-1}\cdot cm^{-1}$. Similarly, the electrical conductivity of iodine-doped polychelate falls in the range $3.66 \times 10^{-9}$ to $8.3 \times 10^{-6}\ \Omega^{-1}\cdot cm^{-1}$ at room temperature.

The electrical conductivities of polymeric chelates at room temperature (35°C) are in the following order

$$Mn > Cd > Zn > Co > Mg > Cu$$

and this is in good agreement with the literature data.[15] Similarly 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 conductivity. In conclusion, the electrical conductivity rises appropriately due to iodine doping. This may be due to the 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.[5,16]

$$I_3^-, I_5^-, I_7^- \text{ etc.}$$

## CONCLUSION

Polycondensation of 8-FHQ and methyl ethyl ketone using different concentration of aq. alkali resulted into formation of polymers of low molecular weight ranging from 1600–2400. The formation polymer was confirmed by elemental analyses and IR studies. The applicability of these polymers was explored by preparing polymeric chelates using different metal ions indicating that the polymers have good chelating properties. Lastly the PQMB and its chelates were studied further for examining their thermal stability and electrical conductivity. It was observed that both have good thermal stability however chelates are thermally less stable than that of the parent polymer. While the electrical conductivity of both—polymers and their chelates—observed to a range of semiconducting material. The electrical conductivity is further enhanced to almost hundred fold or more due to iodine doping.

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