

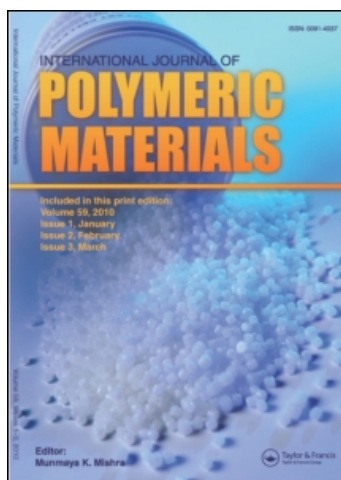
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### Synthesis, Characterization and Material Application of Novel Polyimide

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## Synthesis, Characterization and Material Application of Novel Polyimide

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*Novel polyimide-II containing 8-hydroxyquinoline as pendent groups was prepared by reacting N,N'-(1,1'-biphenyl)-4,4'-diyl bismaleimide-diamine polyimide-I (BPBMDDM) with 5-chloromethyl-8-hydroxyquinoline hydrochloride (CMHQ) in the presence of base catalyst. N,N'-(1,1'-biphenyl)-4,4'-diyl bismaleimide-diamine polyimide-I (BPBMDDM) was prepared by Michael addition reaction of N,N'-(1,1'-biphenyl)-4,4'-diyl bismaleimide (BPBM) with 4,4'-diaminodiphenyl methane (DDM). The resulting polyimide-II (BPBMDDMCMHQ) was characterized by spectral techniques. Polymeric metal chelates of polyimide-II were prepared using the transition metal ions Zn(II), Cu(II), Ni(II), Co(II), and Mn(II), and were characterized. Ion-exchange properties of polyimide-II (BPBMDDMCMHQ) for Fe(III), Zn(II), Ni(II) and Cu(II) metal ions were also studied by batch-equilibration method. The polyimide-II (BPBMDDMCMHQ) has good metal uptake capacity at varying pH range and can be recycled. It has thermal stability up to 240°C.*

**Keywords:** batch-equilibration method, ion-exchange properties, Michael addition reaction, polyimide, polymeric chelates, thermogravimetric analysis

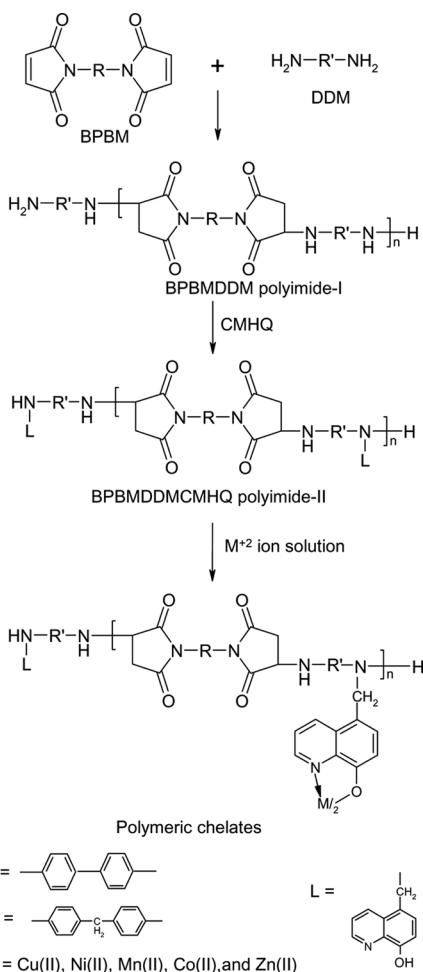
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## INTRODUCTION

Metal-ion toxicity has increased tremendously in water resources, due to pollution of water resources by industrial effluents. Therefore, the determination of metal content and their removal using chelating polymers has gained much attention. A literature survey reveals that ion-exchange resins have been widely used for water purification, effluent treatment and chromatographic separation [1–4]. Mostly, these ion-exchange resins are based on crosslinked styrene-divinylbenzene



**Scheme 1** Synthesis steps.

copolymers. The drawback of such ion-exchange resins is having limited hydrophilic and thermal stability. Infusible and insoluble polymers like heterocyclic polymers are reported, but are nonprocessable due to these properties. However, polyimides have excellent high performance properties in terms of their high hydrolytic stability, chemical resistance and thermal stability [5–7]. To such polyimide, if we introduce metal gripping moiety, as a pendant group then the resulting polyimide (BPBMDDMCMHQ) may be used as “ion-exchange resin” without any further processing. Because 8-hydroxyquinoline and its derivatives are well-known as metal capturing reagents and having applications in wastewater treatment for metal recovery [8–10]. It was chosen as the pendant group of choice in this work.

Hence, the present communication comprises synthesis, characterization and use of the above polyimide-II as novel ion-exchange resin (BPBMDDMCMHQ). Polymeric metal chelates of polyimide-II have also been prepared with several transition metal ions like Zn(II), Cu(II), Ni(II), Co(II), and Mn(II). Ion-exchange properties of polyimide-II were also studied to evaluate the effects of electrolytes, rate of metal uptake and distribution of metal-ion between polyimide and electrolyte over a wide pH range by batch equilibration method. The whole synthetic route is shown in Scheme 1.

## EXPERIMENTAL

### Materials

All the chemicals used were of analytical reagent grade and were acquired from the local market.

### Procedures

#### **Synthesis of *N,N'*-(1,1'-biphenyl)-4,4'-diyl Bismaleimide (BPBM)**

It was synthesized by condensation of maleic anhydride with benzidine by following the reported method [11].

#### **Synthesis of *N,N'*-(1,1'-biphenyl)-4,4'-diyl Bismaleimide—diamine Polyimide-I (BPBMDDM)**

It was synthesized by reported method [11]. Accordingly a suspension of 4,4'-diaminodiphenyl methane (DDM) (1.98 g, 0.01 mole) and *N,N'*-(1,1'-biphenyl)-4,4'-diyl bismaleimide (BPBM) (3.44 g, 0.01 mole) in acetone (50 ml) was refluxed for 8 h in the presence of  $K_2CO_3$ . The resultant suspension was then poured into ice-cooled excess solvent

ether. The solvent ether was decanted and the product was washed with more ether to remove unreacted DDM. The dried dark brown powder was then washed with dimethyl formamide (DMF) (50 ml) to remove unreacted bismaleimide. The resultant polyimide-I (BPBMDDM) was then dried in a vacuum oven its characteristics are summarized in Table 1.

### **Synthesis of 5-chloromethyl-8-hydroxyquinoline Hydrochloride**

It was prepared by chloromethylation of 8-hydroxyquinoline according to the method reported in the literature [12]. The yield was 81%. It was yellow in color and melted at 280–283°C (decomposition).

### **Synthesis of *N,N'*-(1,1'-biphenyl)-4,4'-diyl Bismaleimide—diamine Polyimide-II Containing 5-methyl-8-hydroxyquinoline Hydrochloride as a Pendent Group (BPBMDDMCMHQ)**

It was prepared by condensation of polyimide-I (BPBMDDM) with 5-chloromethyl-8-hydroxyquinoline hydrochloride (CMHQ) by adopting the following process:

A suspension of polyimide-I (5.42 g, 0.01 mole) and 5-chloromethyl-8-hydroxyquinoline hydrochloride (1.93 g, 0.01 mole) in tetrahydrofuran (THF) (50 ml) solvent was refluxed for 12 h in the presence of KOH. The resultant suspension was then poured into ice-cold excess ether. The solvent ether was decanted and the product was washed twice with hot acetone to remove unreacted reactants. The resultant novel polyimide-II (BPBMDDMCMHQ) was then dried in a vacuum oven. The details are given in Table 1.

### **Preparation of Polymeric Chelates**

Polymeric metal chelates were prepared using metal acetates by the general method described here.

A dried polyimide-II (6.99 g, 0.01 mole) was dissolved in 200 ml aqueous solution of 50% formic acid and warmed on a water bath for 10–5 min. To this solution, a warm solution of metal acetate (0.005 mole) in 50% aqueous formic acid was added dropwise with constant stirring. The reaction mixture was made alkaline with dilute ammonia solution to precipitate out polymeric chelates. The resultant mixture was further digested on water bath for 1 h. Finally, the solids thus obtained were filtered off, washed with hot water followed by DMF and acetone, and were then dried in air at room temperature. The yield of all polymeric chelates were almost quantitative. The details of the polymeric metal chelates is given in Table 1.

**TABLE 1** Physicochemical Parameters of Polyimide-I, Polyimide-II, and Polymeric Chelates

Compounds	Molecular formula of repeating unit	Molecular weight of repeating unit	Yield (%)	% Elemental analysis					$\bar{M}_n$
				% Found/(Calcd.)					
				C	H	N	M	$\mu_{\text{eff}}$ (B.M.)	
Polyimide-I	$C_{33}H_{26}N_4O_4$	542.6	85	72.86 (73.05)	4.62 (4.72)	11.86 (12.01)	—	—	2270
Polyimide-II	$C_{43}H_{33}N_5O_5$	699.77	80	73.66 (73.81)	3.90 (4.08)	11.89 (12.17)	—	—	2899
$[CuL(H_2O)]_n$	$Cu.C_{86}H_{66}N_{10}O_{10}.H_2O$	1479.11	77	69.71 (69.84)	3.92 (4.00)	9.70 (10.09)	4.05 (4.30)	1.78	6016
$[CoL(H_2O)_2]_n$	$Co.C_{86}H_{66}N_{10}O_{10}.2H_2O$	1488.51	73	69.01 (69.39)	3.87 (4.01)	9.74 (10.29)	3.52 (3.69)	3.89	5954
$[NiL(H_2O)_2]_n$	$Ni.C_{86}H_{66}N_{10}O_{10}.2H_2O$	1492.51	75	69.05 (69.21)	3.89 (4.11)	9.84 (10.29)	3.69 (3.95)	3.5	6570
$[MnL(H_2O)_2]_n$	$Mn.C_{86}H_{66}N_{10}O_{10}.2H_2O$	1492.29	73	69.16 (69.22)	3.84 (4.09)	9.87 (10.23)	3.73 (3.93)	5.82	5869
$[ZnL(H_2O)_2]_n$	$Zn.C_{86}H_{66}N_{10}O_{10}.2H_2O$	1496.95	79	68.76 (68.91)	3.91 (4.15)	9.89 (10.33)	4.19 (4.36)	D	6487

L = Polyimide-II (BPBMDDMCMHQ),  $\bar{M}_n = DP \times (\text{Molecular weight of repeating unit})$ .

D = diamagnetic in nature.

## Measurements

Carbon, hydrogen and nitrogen measurements of all the samples were carried out on Perkin Elmer CHNS/O Analyzer 2400 Series II. The metal content of the polymeric chelates were determined by decomposing a weighed amount of each polymeric chelates followed by EDTA titration [13]. Number average molecular mass ( $\overline{M}_n$ ) of polyimide-I, polyimide-II and polymeric chelates were measured by non-aqueous conductometric titration method using perchloric acid as a titrant base and formic acid as a solvent. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocyanatocobaltate(II),  $\text{Hg}[\text{Co}(\text{NCS})_4]$ , was used as a calibrant. The diffuse reflectance spectra of the polymeric chelates were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment using  $\text{MgO}$  as the reference compound. IR spectra of all the samples were scanned on a Spectrum GX FTIR spectrophotometer, Perkin Elmer, USA, in KBr. Thermal stability studies of the polymeric metal chelates were carried out by thermogravimetric analyzer (TGA) on a Perkin Elmer Pyris 1 TGA, USA, in presence of air, at a heating rate of  $10^\circ\text{C min}^{-1}$ .

The batch equilibration method was employed to evaluate the influence of different electrolytes and different ionic strengths on the metal-ion absorptions under equilibration condition. The rate of metal uptake under specified conditions, and the distribution of metal-ion at different pH values, have been measured by reported method [14].

## RESULTS AND DISCUSSION

The physicochemical data of polyimide-I (BPBMDDM), polyimide-II (BPBMDDMCMHQ) and polymeric chelates are furnished in Table 1. The polyimide prepared was brown-colored amorphous powder and did not melt up to  $240^\circ\text{C}$ , but above  $240^\circ\text{C}$  it softened with some decomposition and turned into either a viscous liquid or a black mass. The yield was 85% as a solid powder which was insoluble in almost all of the common organic solvents, but was soluble in formic acid. Polyimide showed the azo dye test, confirming the presence of terminal primary amine ( $-\text{NH}_2$ ) group in the structure of polyimide. The C, H, N content and number average molecular mass data of polyimide are quite consistent with the reported data [6].

The prepared polyimide-II (BPBMDDMCMHQ) was dark brownish-colored amorphous powder and did not melt up to  $240^\circ\text{C}$ , but above  $240^\circ\text{C}$  it softened with some decomposition. The yield was 80% and

was insoluble in almost all of the common organic solvent. The polymeric chelates of polyimide-II with the metal ions Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) varied in color from greenish-brown to dark brown. The yields were nearly 73–79% and the products were completely insoluble in all common organic solvents.

Results of the elemental analyses for the polyimide-I, polyimide-II and polymeric chelates (data are given in Table 1) are consistent with the predicted structures as shown in Scheme 1, and their molecular formulae. Examination of the metal content in each polymeric chelate (Table 1) indicated metal to ligand (M/L) stoichiometry ratio of 1:2 with a variation of  $\pm 1.5\%$  from this theoretical values, suggesting that in the formation of polymeric metal chelates, pendent groups 8-hydroxyquinoline of two polyimide-II chains, coordinates with the central metal atom at four coordination sites along with two water molecules at two coordination sites. Hence, the general molecular formula of the resulting polymeric chelates is  $M.C_{86}H_{66}N_{10}O_{10} \cdot x H_2O$  ( $x = 1$  or  $2$ ). The data of elemental analyses reported in Table 1 are in close agreement with the calculated values of C, H and N based on the above mentioned molecular formulae of the polyimide-I (BPBMDDM), polyimide-II (BPBMDDMCMHQ) and polymeric metal chelates.

Number average molecular mass ( $\bar{M}_n$ ) of all the sample was calculated according to the method reported in the literature [15,16]. The data of  $\bar{M}_n$  of each sample is reported in Table 1.

The IR spectra of polyimide-I, polyimide-II and all of its polymeric metal chelates show that they resemble each other in their general shape. However, comparison of their IR spectra has shown some important characteristic differences.

The IR spectra of polyimide-I shows band at  $3334\text{ cm}^{-1}$ , attributed to the secondary  $-\text{NH}-$  group, and bands around  $3500$  and  $3440\text{ cm}^{-1}$  may arise from terminal  $-\text{NH}_2$  group. The spectra show strong bands around  $1712$ ,  $1670$ ,  $1055$  and  $752\text{ cm}^{-1}$  due to the presence of imide groups [17].  $N,N'$ -(1,1'-biphenyl)-4,4'-diyl bismaleimide (BPBM) shows band at  $3110\text{--}3042\text{ cm}^{-1}$ , but its absence in the spectra of polyimide indicating that the Michael addition polymerization reaction occurred between bismaleimide (BPBM) and diamine (DDM). The band observed around  $1729\text{ cm}^{-1}$ , is assigned to the stretching vibration of  $\text{C}=\text{O}$ , which is in conjugation with the other  $\text{C}=\text{O}$  group. The pair of bands at  $1730$  and  $1792\text{ cm}^{-1}$  is assigned to the stretching vibration of the five member cyclic carbonyl group [18]. The IR spectra of polyimide-II shows strong broad band in the region of  $3300\text{--}3480\text{ cm}^{-1}$  due to phenolic  $-\text{OH}$  group of 8-hydroxyquinoline pendent group. The absorption bands at  $1620$ ,  $1580$ ,  $1518$  and  $1470\text{ cm}^{-1}$  are



assigned to the aromatic skeletal vibrations of heterocyclic ring system of 8-hydroxyquinoline [19].

One of the significant differences to be expected between IR spectrum of polyimide-II and its polymeric metal chelates is that the band of  $\text{-OH}$  has become much more broad in the region of  $3300\text{--}3600\text{ cm}^{-1}$  of polymeric chelates due to the formation of the metal-oxygen bond between O-H group of the 8-hydroxyquinoline and the metal ions. Another, noticeable difference is that the band due to the C=N stretching vibration of 8-hydroxyquinoline at  $1582\text{ cm}^{-1}$  in the IR spectrum of polyimide-II is shifted to lower frequency, whereas the band at  $1420\text{ cm}^{-1}$  in the IR spectrum of polyimide-II, assigned to in-plane  $\text{-OH}$  deformation [20], is shifted towards lower frequency in the spectra of the polymeric chelates due to the formation of metal-oxygen bonds. Further, the appearance of two sharp new bands at  $1110$  and  $500\text{ cm}^{-1}$  corresponding to the stretching vibration of C-O-M bond and M-O bond [20] formed in chelation, and the coordination of ligand with the metal ion through nitrogen atom of the 8-hydroxyquinoline ring, can be evident from the negative shift ( $5\text{--}20\text{ cm}^{-1}$ ) in the characteristic stretching frequency of C=C/C=N at  $1620$  and  $1582\text{ cm}^{-1}$ , respectively, in the IR spectra of chelates. Thus, all these characteristic features of the IR studies are in close agreement with the predicted structure of the polyimide-I, polyimide-II and their polymeric metal chelates as shown in Scheme 1.

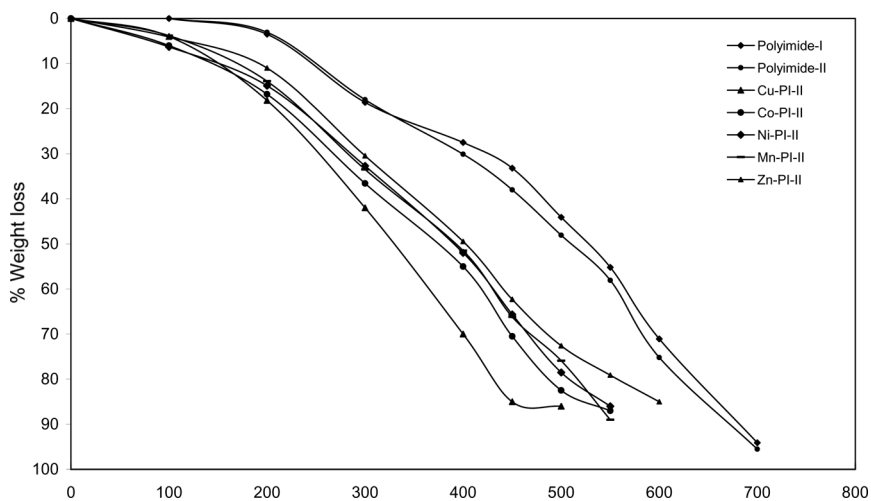
The diffuse electronic spectrum of the  $[\text{CuL}(\text{H}_2\text{O})_n]$  polymeric chelate shows two broad band at  $15,962$  and  $26,205\text{ cm}^{-1}$  due to the  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$  transition and charge transfer, respectively, suggesting a distorted octahedral structure of the  $[\text{CuL}(\text{H}_2\text{O})_n]$ , polymeric chelate. The  $[\text{NiL}(\text{H}_2\text{O})_2]_n$  and  $[\text{CoL}(\text{H}_2\text{O})_2]_n$  polymeric chelates gave three absorption bands, respectively, at  $9,310$ ,  $16,558$ ,  $26,300$  and  $8,918$ ,  $15,525$ ,  $23,205\text{ cm}^{-1}$  corresponding to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{P})$ ,  ${}^3\text{A}_{2g}(\text{P}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  transitions [21]. Thus, the absorption bands of the diffuse reflectance spectra and the values of their magnetic moments ( $\mu_{\text{eff}}$ ) (as shown in Table 1) indicate an octahedral configuration for the  $[\text{NiL}(\text{H}_2\text{O})_2]_n$  and  $[\text{CoL}(\text{H}_2\text{O})_2]_n$  polymeric chelates [22]. The spectra of  $[\text{MnL}(\text{H}_2\text{O})_2]_n$  shows weak bands at  $15,630$ ,  $18,668$  and  $22,540\text{ cm}^{-1}$  assigned to the transitions  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(4\text{G})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(4\text{G})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ ,  ${}^4\text{E}_g$ , respectively, suggesting an octahedral structure for the  $[\text{MnL}(\text{H}_2\text{O})_2]_n$  polymeric chelate [23]. As the spectrum of the  $[\text{ZnL}(\text{H}_2\text{O})_2]$  polymeric chelate is not well-resolved, it is not interpreted but its magnetic moment value shows that it is diamagnetic in nature as expected.

**TABLE 2** Tga Data of Polyimide-I, Polyimide-II, and Polymeric Chelates

Compounds	Percentage weight loss at different temperature (°C)									Activation energy ( $E_a$ ) Kcal/mol
	100	200	300	400	450	500	550	600	700	
Polyimide-I	—	3.50	15.00	27.50	33.20	44.10	55.80	71.08	94.10	15.50
Polyimide-II	—	3.06	16.02	30.09	38.00	48.07	58.08	75.20	95.50	13.15
[CuL(H <sub>2</sub> O)] <sub>n</sub>	4.00	18.20	32.00	70.00	85.00	86.00	—	—	—	10.8
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	6.00	16.80	30.04	55.00	70.50	82.50	87.00	—	—	9.9
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	6.30	14.90	32.70	52.00	65.65	78.50	86.00	—	—	9.6
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	3.80	13.90	33.50	51.50	66.20	75.90	89.00	—	—	10.6
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.10	11.00	30.45	49.47	62.30	72.60	79.10	85.00	—	11.5

L = Polyimide-II (BPBMDDMCMHQ).

The thermal behavior of polyimide-I, polyimide-II and polymeric chelates was investigated by thermogravimetric analysis (TGA). The TGA data of all the compounds are summarized in Table 2 and are shown in Figure 1. Scrutinization of this data envisages that polyimide-I and polyimide-II follow single-step thermal degradation. The initial thermal degradation up to 200°C might be due to loosely held moisture present or solvent trapped in the polymer sample. The weight loss commences in the range of 200–300°C. The rate of degradation increases between 300–550°C and complete weight loss up to 95% was observed at about 700°C. It is interesting to note that around

**FIGURE 1** Thermograms of polyimide-I, polyimide-II and polymeric chelates.

10% weight loss was observed around 240°C. This indicates that polyimide-I and polyimide-II are stable up to 240°C.

Further, the initial thermal degradations in all of the polymeric chelates commencing below 150°C may be due to removal of hydrated water, whereas weight loss obtained in the temperature range 150–200°C might be due to the presence of two coordinated water molecules [24]. The rate of decomposition for the entire polymeric chelates is initially low up to 200°C. Eventually, the maximum rate of decomposition with 55–87% weight loss was observed in the temperature range of 400–550°C for polymeric chelates of  $\text{Cu}^{+2}$  and  $\text{Co}^{+2}$  metal ions, while 51–89% weight loss was observed in the temperature range of 400–550°C for polymeric chelates of  $\text{Ni}^{+2}$  and  $\text{Mn}^{+2}$  metal ions, and 49–89% weight loss was observed in the temperature range of 400–600°C for polymeric chelate of  $\text{Zn}^{+2}$  metal ion. There is a remarkable difference in the mode of thermal degradation for polyimide-II and its polymeric metal chelates. Thus, the TGA studies show that the decomposition of polymeric metal chelates propagated fast as compared to its polyimide-II. Consequently, one may conclude that polyimide-I and polyimide-II are thermally more stable than polymeric metal chelates of polyimide-II. These results of thermal behavior can be explained by the fact that the decomposition in polymeric chelates was catalytically induced by the metal ions [25].

The energy of activation ( $E_a$ ) was estimated by a reported [26] method for the thermal decomposition of polyimide-I, polyimide-II and its polymeric chelates. The equation followed is:

$$\ln[\ln(1/y)] = (E_a/RT_m + 1) \ln T + \text{constant.}$$

The energy of activation ' $E_a$ ' was computed from the slope of the plot of  $\ln(\ln 1/y)$  versus  $(1/T)$  and reported in Table 2.

$$\text{Slope} = -E_a/R$$

where,  $R = 1.987$  kcal/mol.

The energies of activation for polyimide-I, polyimide-II and polymeric metal chelates are around 13–15.50 Kcal/mol and 9.6–11.5 kcal/mol, respectively.

## Ion-Exchange Capacity of Polyimide-II

### **Effect of Electrolyte**

Results of the ion-exchange data are shown in Table 3. They reveal that the amount of  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Ni(II)}$ , and  $\text{Fe(III)}$  ions taken up

**TABLE 3** Evaluation of the Influence of Different Electrolytes in the 0.1 Mol/lit Metal Nitrate<sup>a</sup> Solution

Sr. No.	Metal ion	pH	Conc. of electrolyte	Adsorption of mmol $\times 10^1$ of the metal ion on polyimide-II <sup>b</sup>			
				NaClO <sub>4</sub>	NaNO <sub>3</sub>	NaCl	Na <sub>2</sub> SO <sub>4</sub>
1	Cu(II)	5	0.01	0.14	0.21	0.18	0.55
			0.1	0.38	0.48	0.49	0.36
			1.0	0.72	0.74	0.69	0.12
2	Ni(II)	5.5	0.01	0.21	0.18	0.15	0.59
			0.1	0.38	0.35	0.42	0.29
			1.0	0.71	0.69	0.72	0.18
3	Fe(III)	3	0.1	0.19	0.19	0.15	0.49
			1.0	0.30	0.42	0.47	0.22
			0.01	0.78	0.71	0.69	0.12
4	Zn(II)	4.5	0.1	0.19	0.20	0.18	0.58
			0.1	0.37	0.48	0.48	0.36
			1.0	0.81	0.75	0.84	0.18

Time: 24 h at room temperature.

<sup>a</sup>Volume of electrolyte solution taken = 25 ml, Volume of metal-ion solution taken is 1 ml.

<sup>b</sup>Weight of Polyimide-II (BPBMDDMCMHQ) taken is  $25 \pm 0.010$  mg.

by the polyimide-II increases with an increase in the concentration of perchlorate, nitrate and chloride ions. However, in the presence of sulfate ions the reverse trend was observed [14].

**TABLE 4** Comparison of the Rates of Metal Ion Uptake<sup>a</sup> by Polyimide-II

Time (h)	% Attainment of equilibrium state <sup>b</sup>			
	Fe(III)	Zn(II)	Ni(II)	Cu(II)
1\2	58	70	74	70
1	78	75	77	82
2	83	85	89	90
3	91	94	95	94
4	96	98	96	97
5	98	98	98	98

<sup>a</sup>Metal nitrate (0.1 mol/ltr), Volume = 1 ml NaNO<sub>3</sub> mol/ltr, Volume 25 ml at room temperature, Weight of Polyimide-II = 24.91 mg.

<sup>b</sup>Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h at 100%.

**TABLE 5** Distribution Ratio ( $k_d^a$ ) for Polyimide-II (BPBMDDMCMHQ)

PH	Values for metal-ion <sup>b</sup> (ml/gm)			
	Cu(II)	Zn(II)	Ni(II)	Fe(III)
1.0	—	—	—	—
1.5	—	—	—	126
2.0	—	—	—	279
2.5	—	—	—	692
3.0	128	123	134	—
4.0	481	286	305	—
5.0	2005	482	489	—
6.0	—	2128	2288	—

$$^aK_D = \frac{\text{meq. of ions taken up by 1 g of polyimide-II}}{\text{meq. of metal ions present in 1 ml of the solution phase}}$$

0.1 mole/ltr Metal nitrate, Volume = 1 ml.

Weight of Polyimide-II = 25 mg.

1 mole/ltr  $\text{NaNO}_3$ , Volume = 25 ml, at room temperature, Time 24 h (equilibrium state).

<sup>b</sup>Possibility of error  $\pm 5\%$ .

### Rate of Metal Uptake

Examination of the metal uptake data summarized in Table 4, reveals that the time required for attaining the state of equilibration under given set of experimental conditions depends upon the nature of the metalion. The time required to attain the state of equilibration and the amount of the metalion taken up at the stage of equilibration increases in the order of  $\text{Fe(III)} < \text{Zn(II)} < \text{Ni(II)} < \text{Cu(II)}$ .

### Distribution Ratio of Metal Ions

Examination of the data of the effect of pH on the amount of metal ions distributed between two phases, in Table 5, shows that the relative amount of metalions taken up by the polyimide-II increases with an increase in the pH of the medium. The distribution ratios of Cu(II) at pH 5 and of Ni(II) and Zn(II) at pH 6 are comparable. The distribution ratios of Fe(III) are about 692 at pH 2.5. The lower value of the distribution ratios for Fe(III) may be due to steric hindrances in the accommodation of ligand around a single metalion.

## CONCLUSIONS

1. Novel polyimide-II (BPBMDDMCMHQ) was prepared in a good yield having ion-exchange properties.
2. It has thermal stability up to  $240^\circ\text{C}$  and can be used over a wide pH range.

3. It has good metal-ion uptake capacity at varying pH range and can be recycled over a longer period. It is effective up to 50% to uptake Cu(II) and Fe(III) metals successfully from the polluted water of industry.
4. Polymeric chelates of polyimide-II (BPBMDDMCMHQ) are thermally less stable than parent polyimide-II but overall stability is comparable to other polymeric chelates. However,  $[\text{ZnL}(\text{H}_2\text{O})_2]_n$  polymeric chelate was found to be more stable than other polymeric chelates.

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