

## Synthesis, characterization and antimicrobial activity of co-ordination polymers

H. M. Shukla, A. I. Shah, P. J. Shah and D. S.Raj\*

Chemistry Department, M. B. Patel Science College, C.E. Society, Anand

### ABSTRACT

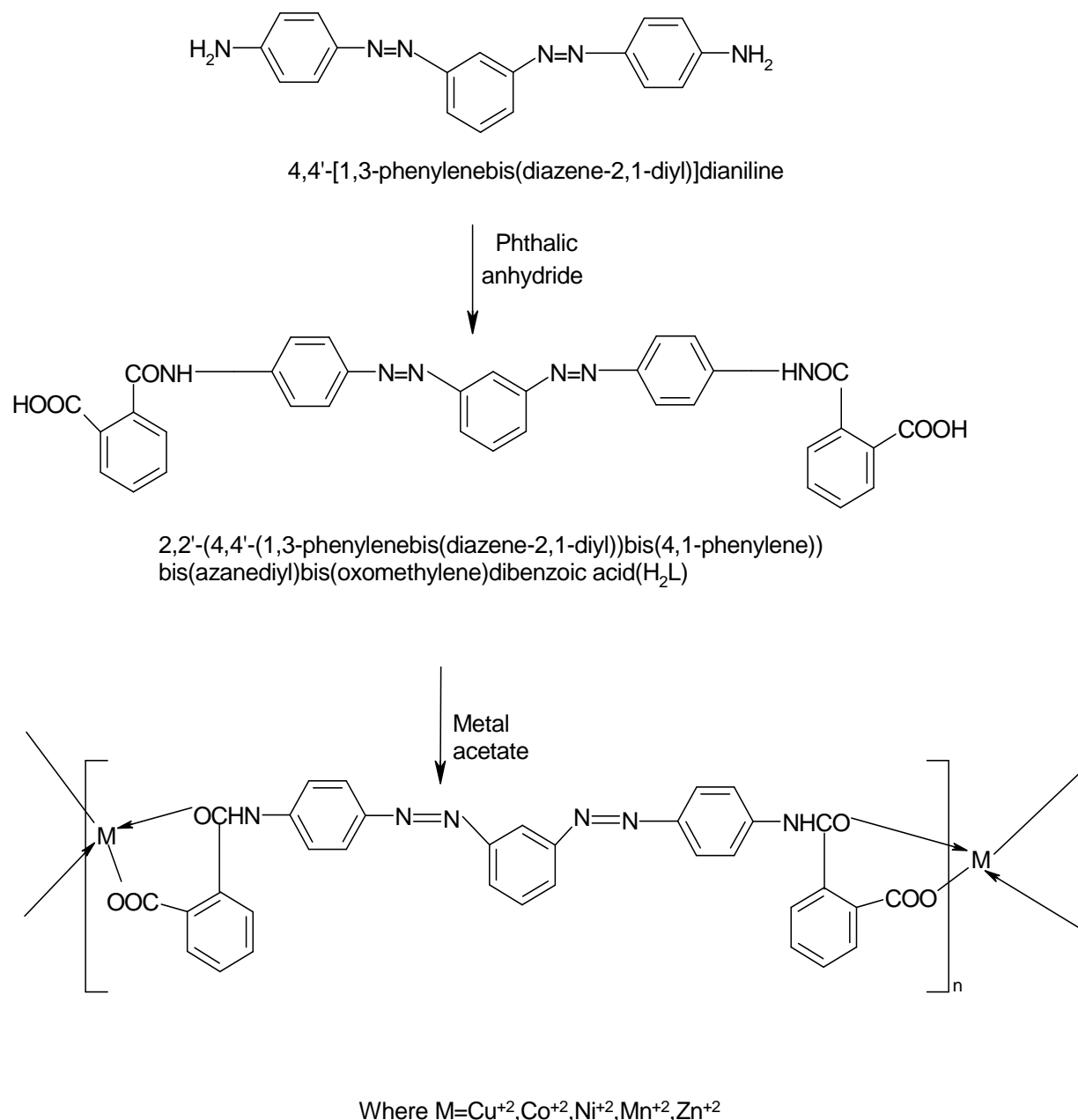
Novel bis ligand namely 2,2'-(4,4'-(1,3-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))-bis(azanediyl)-bis(oxomethylene)-dibenzoic acid has been prepared and characterized. The co-ordination polymers based on this bis ligand with transition metal ions viz,  $\text{Cu}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Co}^{+2}$  and  $\text{Zn}^{+2}$  were prepared and studied for their metal:ligand (M/L), stoichiometry, magnetic moment, spectral features, number-average molecular weight ( $\overline{M}_n$ ) and by thermogravimetry. The microbicidal activity of all the samples had also been monitored against plant pathogens.

**Keywords:** co-ordination polymer, bis azo dye, magnetic moment, spectral features, thermogravimetry and microbicidal activity.

### INTRODUCTION

In recent years, the study of co-ordination polymers has been made much progress [1,2]. co-ordination polymers mostly derived from bichelating ligands in which metal ions and chelating agents arrayed alternatively. Most of bichelating ligands are derived from well known chelating agents like salicylaldehyde, 8-hydroxy quinoline, hydroxyl acetophenone, salicylic acid etc [3-5]. The joining segment of these similar ligands are mainly  $-\text{N}=\text{N}-$ ,  $-\text{SO}_2-$ ,  $-\text{CH}_2-\text{O}-$  or  $-\text{CH}_2-\text{S}-\text{CH}_2-$  etc [3-6]. The area in which the co-ordination polymers having azo dye moiety has been reported by one of author [DSR][7].

In extension of this work, the present paper comprises the study of co-ordination polymers based on bis azo dye with phthalamic acid segment. Though phthalamic acid also act as good metal chelating agent. Thus paper connecting with the studies of co-ordination polymers based on amic acid functionalized bis azo dye. The research is shown in scheme-1.



Scheme - 1

## MATERIALS AND METHODS

### Materials

1,3-benzenediamine was obtained from local dealer. All other chemicals used were of analytical grade.

### Synthesis of 4, 4'-[1, 3-phenylenebis-(diazene-2,1-diyl)]-dianiline

1,3-benzenediamine(10.8gm,0.1mole) was dissolved in dilute HCl (30ml,1:3v/v). The solution was cooled to 0-2°C in ice bath and HCl (12ml) was added with stirring. To the ice-cold solution was added dropwise a solution of NaNO<sub>2</sub> (15.8gm, 0.2mole). To the resulting solution of the tetrazonium salt was rapidly added a solution of aniline (19.6gm, 0.2mole) in dil. HCl. The mixture was stirred for 10-15 minutes.

In another beaker, sodium acetate (22g, 0.2mole) was dissolved in water (30ml). The sodium acetate solution was added to the reaction mixture and allowed to stand in ice bath for 1hr. with occasional stirring. The reaction mixture was allowed to stand at room temperature and aq.NaOH solution (10ml, 20%) was added with stirring till a color of aniline was observed. The mixture was left for 1hr. The separated product was filtered, then wash with cold water and dry it over night. Yield 76%, m.p.189<sup>0</sup>c (uncorrected). Analysis C<sub>18</sub>H<sub>16</sub>N<sub>6</sub> ( Cal : %C 68.35 ,% H 5.06 ,% N 26.58 ; Found: % C 68.26 , % H 5.02, % N 26.50).

**Synthesis of 2,2'-(4,4'-(1,3-phenylenebis(diazene-2,1-diyl))-bis(4,1-phenylene)) bis (azanediy)-bis(oxomethylene)-dibenzoic acid (H<sub>2</sub>L)**

The solution of 4, 4'-[1, 3-phenylenebis (diazene-2,1-diyl)] dianiline (0.1mole) in acetone was cooled to 10<sup>0</sup>C.To this solution the phthalic anhydride (0.2mole) was added with stirring. The resulting product was then filtered and air-dried. Yield 85% and M.P.256<sup>0</sup>C(uncorrected). Analysis: C<sub>34</sub>H<sub>24</sub>N<sub>6</sub>O<sub>6</sub> (Cal : %C 66.67,% H 3.92,% N 13.73; Found: % C 66.36, % H 3.71, % N 13.42). The predicted structure and formation of polymeric ligand is shown in Scheme-1.

**TABLE 1 Analytical and spectral data of the co-ordination polymers of H<sub>2</sub>L**

Compound	Empirical Formula	Formula Weight	Analyses % Found(Calculated)				Absorption band (cm <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)	$\overline{(Mn)} \pm 60$	$\overline{Dp}$
			%M	%C	%H	%N				
H <sub>2</sub> L	C <sub>34</sub> H <sub>24</sub> N <sub>6</sub> O <sub>6</sub>	612	- -	66.4 (66.67)	3.7 (3.92)	13.5 (13.73)	-	-	-	-
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Cu.C <sub>34</sub> H <sub>22</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	709.54	8.7 (8.95)	57.4 (57.50)	3.5 (3.66)	11.7 (11.84)	22852 15672	2.00	4312	6
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Co.C <sub>34</sub> H <sub>22</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	704.94	8.0 (8.36)	57.6 (57.87)	3.5 (3.68)	11.8 (11.91)	15740 22196	2.86	4280	6
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Ni.C <sub>34</sub> H <sub>22</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	704.71	8.1 (8.33)	57.7 (57.89)	3.6 (3.68)	11.8 (11.92)	14974 22888	4.02	4276	6
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Mn.C <sub>34</sub> H <sub>22</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	700.94	7.7 (7.83)	58.1 (58.20)	3.8 (3.70)	11.8 (11.98)	15742 17566 22708	4.79	3552	5
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	Zn.C <sub>34</sub> H <sub>22</sub> N <sub>6</sub> O <sub>6</sub> .2H <sub>2</sub> O	711.38	9.0 (9.19)	57.1 (57.35)	3.5 (3.65)	11.7 (11.80)	-	Diamagnetic	3604	5

**Acid Value**                      Theoretical: 183 mg KOH/1g. Sample.

Found: 184.8 mg KOH/1g. Sample.

**IR Features**                      3040, 1530, 1650 cm<sup>-1</sup>                      Aromatic  
1690 cm<sup>-1</sup>    CO  
3400 cm<sup>-1</sup>    Sec.NH  
1625 cm<sup>-1</sup>    N=N

NMR (DMSO)	1660, 3400 cm <sup>-1</sup> 3200-3600 cm <sup>-1</sup>	CONH OH of COOH	
	$\delta$ ppm		
	7.1 – 7.7 (20H)	Multiplet	Aromatic
	12.5 (2H)	Singlet	COOH
	9.2 (2H)	Singlet	NH

### Preparation of co-ordination polymers

All co-ordination polymers were synthesized by using metal acetate in general method described.

A warm and clear solution (pH~8) of H<sub>2</sub>L (6.12gm,0.01mole) in aq.NaOH (200ml) was added to a solution of copper acetate (1.99gm,0.01mole) in 50% aq.formic acid (50ml) with constant stirring. After complete addition of metal salt solution, the pH of reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelates were separated out in the form of suspension, digested on a water bath for one hour and eventually filtered, washed with hot water followed by acetone, dimethyl formamide (DMF) and then dried in air at room temp. The yields of all co-ordination polymers were almost quantitative.

### Measurements

#### Elemental Analysis

The metal analysis of co-ordination polymers comprised decomposition of a weighted amount of the polymer followed by EDTA titration following standard procedures [8]. C,H,N analysis of H<sub>2</sub>L and its coordination polymers were carried out by C,H,N elemental analyzer (Italy).

IR spectra of the ligand and of each of the polymer samples were scanned in KBr on a Nicolet 760 D spectrophotometer.

The solid diffusion reflectance spectra of all co-ordination polymer samples were recorded on a Backman DU spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

The number average molecular weight ( $\overline{M}_n$ ) of all the coordination polymers were determined by method reported in earlier communications [9].

TABLE 2 Thermo gravimetric analysis co-ordination polymers of H<sub>2</sub>L

Compounds	% weight loss at temperature T(°C)					
	100	200	400	500	600	700
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	2.4	4.7	12.7	42.3	47.3	53.0
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.5	8.6	16.5	21.7	43.2	59.2
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.5	8.4	14.7	26.8	45.2	59.2
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	4.6	6.5	9.6	15.5	24.9	36
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	2.0	3.2	4.6	15.3	23.2	35.2

Magnetic Susceptibility measurements of all co-ordinated polymers were carried out at room temperature by the Gouy method, Hg[Co(NCS)] used for calibration. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant.

Thermogravimetry of polymer samples was carried out on a Universal DTA-TGA analyzer in air at a heating rate of 10°C min.

The diffuse reflectance spectra of the solid polymeric chelates were recorded on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

### Antibacterial Activities

Antibacterial activity of H<sub>2</sub>L ligand and its coordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *Staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *Salmonella typhi*) at a concentration of 50µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.

TABLE 3 Antibacterial activities of co-ordination polymers

Compounds	Zone of Inhibition			
	Gram +Ve		Gram -Ve	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>E.coli</i>
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	64	71	72	72
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	65	75	65	70
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	67	72	75	84
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	65	73	86	85
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	68	66	77	69

### Antifungal Activities

The fungicidal activities of all the compounds were studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *Penicillium expansum*, *Nigrospora Sp.*, *Trichothesium Sp.* and *Rhizopus nigricum*. The antifungal activity of ligand and its coordination polymers were measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200gm, dextrose 20gm, agar 20gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000ppm) in a PDA medium and autoclaved at 120° C for 15 min. at 15atm. pressure. These medium were poured into sterile petri plates and the organisms were inoculated after cooling the petri plates. The percentage inhibition for fungi was calculated after five days using the formula given below:

$$\text{Percentage of inhibition} = 100(X-Y) / X$$

Where, X = Area of colony in control plate

Y = Area of colony in test plate

TABLE 4 Antifungal activities of co-ordination polymers

Compounds	<i>Penicillium expansum</i>	<i>Nigrospora Sp.</i>	<i>Trichothesium Sp.</i>	<i>Rhizopus nigricum</i>
[CuL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	77	75	60	58
[CoL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	68	69	64	75
[NiL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	76	80	69	72
[MnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	75	69	86	75
[ZnL(H <sub>2</sub> O) <sub>2</sub> ] <sub>n</sub>	58	75	70	74

## RESULTS AND DISCUSSION

The synthesis of the bisazo ligand, 2,2'-(4,4'-(1,3-phenylenebis(diazene-2,1-diyl))bis(4,1-phenylene))bis(azanediyl)bis(oxomethylene)dibenzoic acid (H<sub>2</sub>L) has not been reported

previously. The ligand H<sub>2</sub>L was isolated in the form of a red crystalline powder. It was soluble in DMF, dioxane, acetone, acetic acid and dilute hydrochloric acid.

The important IR spectral features are a broad band extending from 3200-3600 cm<sup>-1</sup> OH of COOH. The band around 1690 cm<sup>-1</sup> may be due to ν<sub>CO</sub>. The bands around 1660, 3400 cm<sup>-1</sup> may be due to amide group. The strong band at 1625 cm<sup>-1</sup> may be due to N=N group. The others bands are at their respective positions.

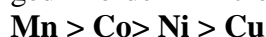
The NMR data of H<sub>2</sub>L shown in experimental part are also confirming the structure of H<sub>2</sub>L. The co-ordination polymers derived from H<sub>2</sub>L were insoluble in common organic solvents. Hence, it is not possible to characterize the co-ordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. These co-ordination polymers did not melt up to 360°C. Examination of the metal content in the polymers (Table-1) revealed that the 1:1 metal: ligand (M:L) stoichiometry for all the polymers.

Comparison of the IR spectrum of the ligand H<sub>2</sub>L and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm<sup>-1</sup> for H<sub>2</sub>L has virtually disappeared for the spectra of polymers. However the weak bands around 3200 cm<sup>-1</sup> in the spectra of H<sub>2</sub>L.Co<sup>2+</sup>, H<sub>2</sub>L.Ni<sup>2+</sup>, H<sub>2</sub>L.Mn<sup>2+</sup> indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. An indication of this aspect is made later. The weak band around 1110 cm<sup>-1</sup> is attributed to the C-O-M stretching frequency [10]. The band at 1430 cm<sup>-1</sup> in the IR spectrum of H<sub>2</sub>L is attributed to the in-plane OH deformation [10]. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These features suggest that the structure of the co-ordination polymer.

Magnetic moments (μ<sub>eff</sub>) of polymeric chelates are given in Table-1. The diffuse electronic spectrum of H<sub>2</sub>L.Cu<sup>2+</sup> co-ordination polymers shows two broad bands around 15,380 cm<sup>-1</sup> and 22,730 cm<sup>-1</sup>. The first band may be due to <sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>g</sub> transition. While the second may be due to charge transfer. The first band shows a distorted octahedral structure for the H<sub>2</sub>L.Co<sup>2+</sup> polymers. The higher value of μ<sub>eff</sub> of the H<sub>2</sub>L.Cu<sup>2+</sup> polymer supports this view. The H<sub>2</sub>L.Ni<sup>2+</sup> and H<sub>2</sub>L.Co<sup>2+</sup> polymers give two absorption bands respectively at 17,250 and 24,000 cm<sup>-1</sup> and at 17,240 and 23,730 cm<sup>-1</sup> which can be assigned respectively to <sup>4</sup>T<sub>1g</sub> → <sup>2</sup>T<sub>2g</sub>, <sup>4</sup>T<sub>1g</sub> → <sup>4</sup>T<sub>1g(P)</sub> transitions. These absorption bands and the values of μ<sub>eff</sub> indicate an octahedral configuration for the H<sub>2</sub>L.Ni<sup>2+</sup> and H<sub>2</sub>L.Co<sup>2+</sup> polymers.

The TGA data for the polymers are presented in Table-2. The weight loss of the polymer samples at different temperatures indicates that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature lying between 400°C and 500°C depending upon the nature of the polymers. Each polymer lost about 55% of its weight when heated up to 700°C. Inspection of the thermograms of H<sub>2</sub>L.Co<sup>2+</sup>, H<sub>2</sub>L.Mn<sup>2+</sup> and H<sub>2</sub>L.Ni<sup>2+</sup> samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may be due to the presence of water strongly absorbed by the polymers. It has also been indicated earlier that the IR spectra of these three polymer samples have OH bands at around 3200 cm<sup>-1</sup> due to associated water.

On the basis of the relative decomposition (% wt. loss) and the nature of thermograms, the co-ordination polymers may be arranged in order of increasing stability as:



This trend also coincides with the stability order already reported for the metal oxinates [11] and for co-ordination polymers of H<sub>2</sub>L [12].

The antimicrobial activity of H<sub>2</sub>L and its coordination polymers are presented in Table-3 and 4. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the percentage of bacteria or fungus is inhibited in the range of 63 to 86% depending upon the biospecies and coordination polymers. All the polymers have good microbicidal activity.

### REFERENCES

- [1] T. Kaliyappan and P. Kannan, *Prog.Polym.Sci.*, (2000), 25(3),343-370.
- [2] T. B. Shah, H. S. Patel, R. B. Dixit and B. C. Dixit, *Int. J. of Polym. Anal. and Charact.*,(2003) 8, 369.
- [3] H, Horowitz and J.P. Perrors, *J.Inorg Nucle.Chem.*, (1964),26, 139-159.
- [4] R.D.Patel, H.S. Patel and S.R. Patel, *Eur. Polym.J.*, (1987), 23, 229-231.
- [5] A.K. Rana, N.R.Shah, A.M. Karampurwala and J.R.Shah, *Makromol.Chem*, (1981), 182(12), 3387.
- [6] H.S. Patel, R.B. Dixit and T.B. Shah, *Int. J. Polym. Material.*, (2001),49, 271.
- [7] D.S. Raj,,*Research Journal Of Chemistry And Environment*, (2001),5(1),35.
- [8] A.I.Vogel, *Textbook of Quantitative Chemical Analysis* ELBS,5<sup>th</sup>Edn. London, (1996), 588.
- [9] T. B. Shah, H. S. Patel, R. B. Dixit and B. C. Dixit, *Int. J. of Polym. Anal. and Charact.*,(2003) 8, 369.
- [10] R.G.Charles, H.Freiser, R. Priedel, L.E. Hilliand and R.D. Johnston, *Spectrochim Acta*,(1958) 8,1.
- [11] R.G. Charles and A.Langer, Heat Stabilities and Volatilities of Some Metal Chelates Derived from 8-Hydroxyquinoline, (1959),63,603.
- [12] H, Horowitz and J.P. Perrors, *J.Inorg Nucle.Chem.*, (1964),26, 139-159.