SYNTHESIS, CHARACTERIZATION AND CHELATING PROPERTIES OF POLY[AZO-(1-NAPTHOL)]

Subhash B. Thakor*[1], P. S. Patel[2] and V. G. Patel[3]

[1]Shri PHG Muni. Arts and Science College, Guj. University, Kalol – 382721.

[2]Department of Chemistry, Sheth L.H. Science College, Mansa, Gujarat.

[3]Municipal Arts and Urban Bank Science College, Mehsana.

*Corresponding Author
Subhash B. Thakor
Shri PHG Muni. Arts and
Science College, Guj.
University, Kalol - 382721.

ABSTRACT

Poly [azo (1—Napthol)] was prepared by alcoholic alkaline reduction of 4, 6 dinitro resorcinol. The polymers prepared at time intervals were characterized by elemental analysis, IR spectra and thermogravimetric analysis. The number Average molecular weight ($\overline{M_n}$) was determined by non-aqueous titration. Polymetric metal chelates of Cu^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2}, Ni^{+2} with Poly [azo (1-Napthol)] polymer were prepared and characterized.

KEYWORDS: 4, 6 dinitro Resorcinol, Poly Chelates of Poly [azo (1-napthol)].

1. INTRODUCTION

The number of new conducting polymer structures that are reported in open literature continues to grow at nearly 500 articles per month. The incredible amount of research devoted to the study of electrical active polymers attests to their Unique scientific properties and their potential widespread use in commercial applications.

The most stable electrical active polymers are oxidized, cationic salts of highly conjugated polymers, although stability varies widely with chemical composition. Some cationic salts are quite stable in air[1], while others are highly reactive. The cationic salts (or P-doped polymers) are obtained by oxidation of neutral polymers or of monomers. Chemical oxidation i.e. removal of electrons performed using a oxidant ferric chloride.[2]

Whereas electrochemical oxidation occurs and or an applied potential in the presence of an electrolyte[3], Anionic salts (n-doped polymers) can also be prepared from conjugated

polymers by reduction with regards such as sodium naptholide, However anionic salts typically less stable them their cationic counter parts because they can reach with air and water[4] stability of both salts of electrical active polymers varies with chemical composition. It has been reported that the molecular weight of an essentially linear polymer which contain –OH, -NH$_2$ or –COOH group per each repeating unit could be estimated using a proper titrating agent and a suitable medium. It has been shown that the manner in which the conductance changes in the course of the titration suggests a method for the estimation of average degree of polymerization[5-12]

Mircea and stelian[13] has prepared yellow coloured polymeric ethers by polycondensation of disodium 4, 4'-azo diphenolate with bis (chloromethyl) benzenes.

Korshak, vinogradova et al[14] have reported coloured aromatic polyesters from coloured bisphenols and dicarboxylic acids. These authors have also prepared coloured polyacrylates by polycondensation of 4; 4'-azo diphenol with acid chlorides of iso and terephthalic acids.[15]

Meek, feazel and co-workers[16] have prepared coloured polymers by reacting dye molecules having several functional groups like –NH$_2$, -OH, -SO$_3$H or–COOH with monomeric or polymeric materials containing acidic and basic functional groups. In these azo polymers the colouring matter is an integral part of the polymer and fibre can be produced from which the color can not be removed.

Desousa and deoliveria[17] have prepared aromatic azo polymers by reductive polymerization of aromatic dinitro compounds in tri ethylene glycol and potassium hydroxide.

The azo polymers i.e. poly (azo arylene)s and azo poly chelates, because of their infusible and insoluble nature make them difficult to apply for dyeing, pigmentation or to fabricate. The introduction of OH groups into these polymer chains may alter the properties up to great extent. In recent years the study of the electrical properties of organic polymers has made much progress. Most of the conducting polymers are of conjugated chain systems. Some dopents enhance the conductivity of the polymers, one such area in which poly (azoarylene)s having conjugated system are reported but their conducting properties has not been studied. Hence, so called azo polymers and poly azo chelates have been thought to prepare for its electrical conducting properties.

2. *Experimental*

All the chemicals used were of either analytical grade or laboratory grade.

Preparation of Poly [azo (1Napthol)] polymers by self – polymerization of (4, 6, dinitro resorcinol) self-polymerization was carried out by the method – reported for polymerization of dinitro arylenes (Desouza and Deoliveria 1978). The Polymerization was carried out for different intervals. A typical method of polymerization is given here.

To a solution of 4, 6 – dinitro resorcinol (17.0 gms, 0.1 mole) in tri ethylene glycol (Trigol) (150 ml), KOH (44.8 gm, 0.8 mole) was added gradually and stirred well at room temperature up to complete dissolution of KOH. Then the reaction mixture, under mechanical stirring was warmed to 80 – 85^{0}C for 15 min. The temperature was then increased to 135 – 140^{0}C and the reaction was continued for 5h. The reaction was stopped by lowering to temperature to 100^{0}C and neutralized by adding a mixture of ethanol – HCL (50 : 50 V/v) the resulting neutralized mixture was then poured into ice water (500 ml) and the solid product was collected by filteration, washed with water and dried in an oven. Finally, it was purified by dissolving in DMF and reprecipitating by addition of water. The yield of black powder was 90%.
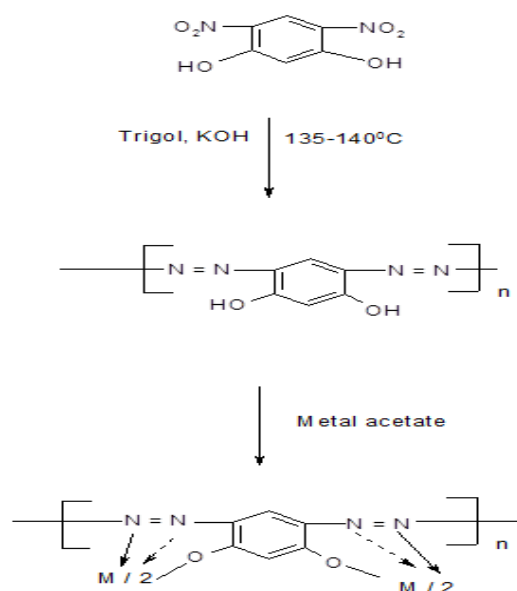
ELEMENTAL ANALYSIS					
% C		**%H**		**%N**	
Calculated	**Found**	**Calculated**	**Found**	**Calculated**	**Found**
43.90	43.8	2.43	2.4	34.14	34.1

Preparation of Polychelates of Poly[Azo(1-napthol)]polymers

As a typical Procedure, Polychelate of Poly[Azo(1-napthol)] is described below (PAC – 1 to PAC – 5).

- *Formation of Cu^{2+} chelates i.e. PAC-1*

The Sodium salt solution (0.01M ligand) of AP i.e. ligand was added drop wise to a solution of cupric nitrate hexahydrate (0.005 mole) in 100 ml of water with rapid stirring. The so called pH of the resultant solution was 4.5. A greenish blue solid precipitated out. It was allowed to settle. Then it was digested on water bath at 70ºC for about 2 hours. The solid mass was filtered, washed with 1:1 mixture of water: ethanol and finally with acetone, and air-dried, yield was 74%. The resulting complex was powdered well and further dried at 70ºC over a period of 24 hrs.

- *Formation of Co^{2+} chelates i.e. PAC-2*

It was obtained as black precipitate by mixing a solution of Sodium-salt of AP i.e. ligand (0.01 mole) with that of cobalt nitrate hexahydrate (0.005 mole) in 100 ml of water. The final pH was 6.0. Complex was purified in the same manner described earlier. The purified chelate yielded 70%.

- *Formation of Mn^{2+} chelates i.e. PAC-3*

The Sodium salt solution (25ml) of each AP i.e. ligand (0.01 mole) was stirred in a solution of manganese chloride hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The yield of chelate was 76%.

- *Formation of Zn^{2+} chelates i.e. PAC-4*

The Sodium solution of each AP i.e. ligand (0.01 mole) was added to that of zinc nitrate hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The product was purified in the same manner described earlier. The dried chelate in black powder, yield 68%.

- *Formation of Ni^{2+} chelates i.e. PAC-5*

The Sodium solution of each AP i.e. ligand (0.01 mole) was added to that of nickel chloride hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The product was purified in the same manner described earlier. The dried chelate in balck powder, yield 72%.
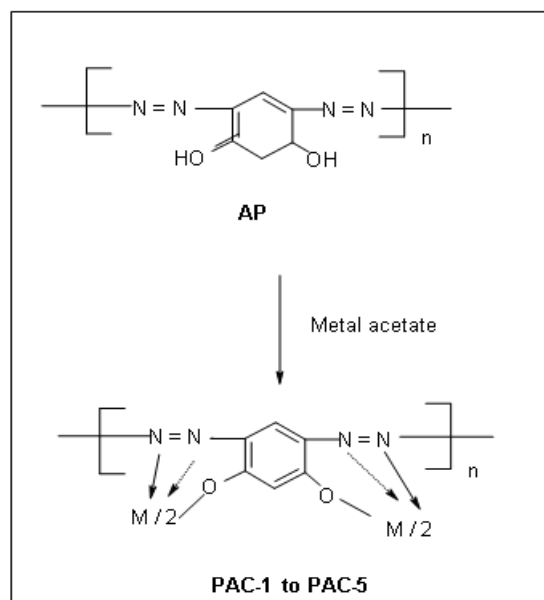
Where, M= Cu, CO, Mn, Zn, Ni etc.

3. *(a) Analysis of POLY [AZO (1-NAPTHOL)] polymers and polymeric chelates.*

The details and the results of analyses of these polychelates are presented in table below.

Characterization of Poly Azo Chelates i.e. PAC-1 to PAC-5

Poly azo Chelates	Molecular Formula	M.Wt Gm/mole	Yield %
PAC-1	$C_{20}H_{10}N_8O_2 \, Cu^{+2}.2H_2O$	493.5	74
PAC-2	$C_{20}H_{10}N_8O_2 \, Co^{+2}.2H_2O$	489	70
PAC-3	$C_{20}H_{10}N_8O_2 \, Mn^{+2}.2H_2O$	485	76
PAC-4	$C_{20}H_{10}N_8O_2 \, Zn^{+2}.2H_2O$	495	68
PAC-5	$C_{20}H_{10}N_8O_2 \, Ni^{+2}.2H_2O$	489	72

The elemental analysis of polymers and their polychelates were carried out on a C, H. N, O, S elemental analyzer, carlo Erba, Italy. The analyses of metal ions in the polymetric chelates were carried out by the decomposition of unknown amount of chelate by mineral acids. The metal content was estimated by a method reported in literature (Vogel 1979).

Poly azo Chelates	% Metal Analysis		Elemental analysis					
			%C		%H		%N	
	Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
PAC-1	12.86	12.80	48.63	48.60	2.43	2.40	22.69	22.65
PAC-2	12.09	12.00	49.07	49.00	2.45	2.45	22.90	22.90
PAC-3	11.34	11.30	49.48	49.45	2.47	2.45	23.09	23.00
PAC-4	13.13	13.10	48.48	48.45	2.42	2.40	22.62	22.60
PAC-5	12.06	12.00	49.07	49.00	2.45	2.45	22.90	22.90

IR Spectral Data

IR Spectra were performed by using KBr pelletes on Nicolet FTIR – 760 spectro photometer. Poly [azo-(1-napthol)] polymer and polychelates were characterized by infra-red spectra.

Anticipated IR spectrum for Azo Polymers i.e. Poly [azo (1-Napthol)] & Poly Chelates 1 to 5.

| Sr. No.	GROUPS	IR frequencies(Cm^{-1})
1.	-N=N-	1406 ± 14
2.	Aromatic.	3050, 1600, 1010
3.	-OH of Quinoline moieties	3400-3360 1420 1090, 1280
4.	$-CH_2-$	2780-2820
5.	$-CH_3-$	3200-3650

Thermo gravimetric analysis of polymers and poly chelates were carried out on a PERKIN ELEMER PYRIS in air at a heating rate of 10^0C/min.

Experimental (TGA)

The thermogravimetric analyses (TGA) of sample have been carried out by using "PERKIN ELMER PYRIS 1 TGA" in a slow stream of air. The boat prepared from platinum foil would hold the sample for analysis. It is properly washed and dried. It was suspended on the quartz rod in the TG balance. The powdered sample (about 5 mg) was placed in the boat. The sample in the boat is covered by a quartz tube in which the flow of air was maintained. The weight of sample was noted on TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was started by the heating the system at a constant rate of 10°C/min. Simultaneously change in the weight was recorded automatically with time (temperature). This will reveal percentage weight loss of material s a function of the time and also of temperature. The experiment was stopped at about 650 °C, when there was no further decrease in weight.

Thermogravimetric analysis of metal chelates of Poly [azo (1-Napthol)].

Chelate	% wt loss at temperature			
	250	300	350	400
PAC-1 (Cu^{+2})	6.2	7.8	16	70
PAC-2 (Co^{+2})	2.8	5.3	24	67
PAC-3 (Mn^{+2})	6.6	14.8	24	68
PAC-4 (Zn^{+2})	7.0	2O.0	60	75
PAC-5 (Ni^{+2})	7.5	24.8	66	70

Thermogram of Polyazochelate PAC-1
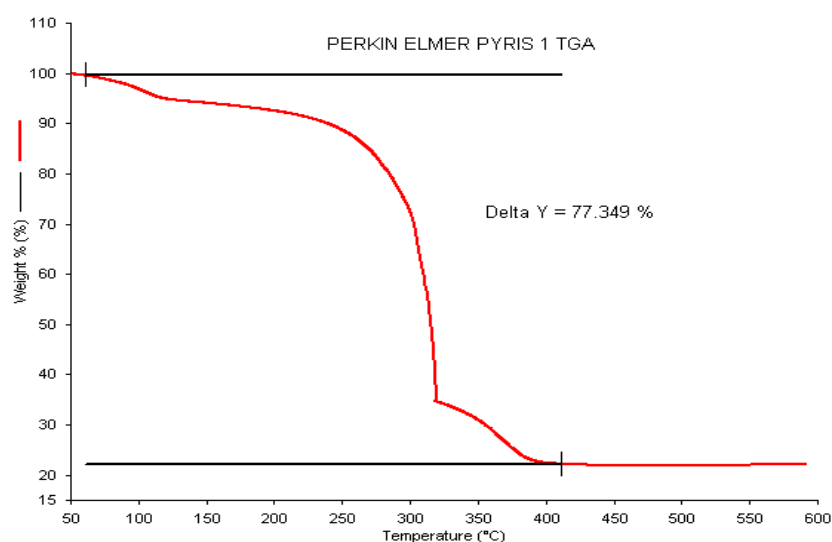
The reflectance spectra of the poly chelates were recorded on a Beckman-DK-2A spectrophotometer with reflectance attachment using MgO as the reference.

Reflectance spectrum data of Cu^{2+} chelates

Metal Chelates	Observed transition energies (cm-1)	
	CT	$^2B_{1g} \rightarrow {}^2A_{1g}$
PAC-1	23370	15650

Reflectance spectrum data of Co^{2+} chelates.

Metal Chelates	Observed transition energies (cm^{-1})		
	$^4T_{1g}(F) \rightarrow$		
	$^6T_{2g}(\upsilon^1)$	$^4A_{2g}(\upsilon^2)$	$^4T_{1g}(P)$
PAC-2	24660	19990	8792

Reflectance spectrum data of Mn^{2+} chelates

Metal Chelates	Observed transition energies (cm^{-1})		
	$^6A_{1g} \rightarrow$		
	$^6A_{1g}(^4E_g)$	$^4T_{2g}(^4G)$	$^4T_{1g}(_4G)$
PAC-3	24040	18650	16225

Reflectance spectrum of PAC-1 chelate
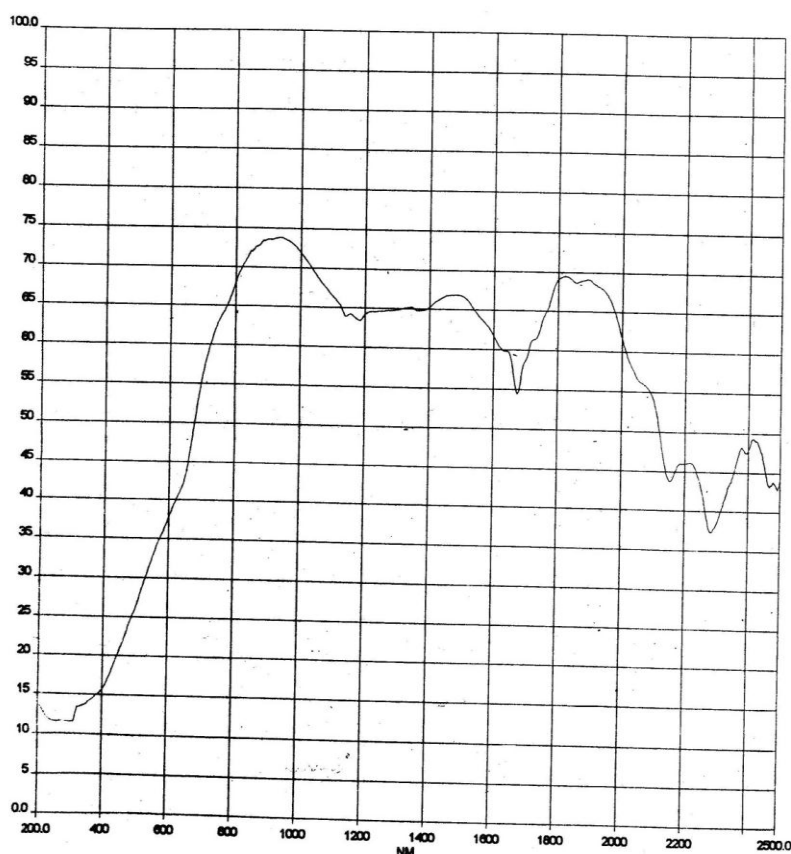
Conductometric Titration of poly [azo (1-napthol)] were carried out in pyridine against sodium methoxide (MgOme) in pyridine as standard. The valur of the number average molecular weight (M_n^-) was calculated following a method of conductometric titration reported by chatterjee 1970.

Conductance measurements was METROHM KONDUCTO SKOP E 365.

Experimental and Calculations

The azo polymer (50 mg) was dissolved in pyridine (50 ml). the solution was introduce into the conductivity cell. The solution was stirred well throughout the titration with the help of a magnetic stirrer. Standard sodium methoxide solution (0.1 N prepared in pyridine) was taken in a microburette and was added to the solution in the conductivity cell in amounts as shown below.

(a) 0.05 ml upto 1.0 ml

(b) 0.1 ml upto 3.0 ml

 (c) 0.20 ml upto the end

About 1 to 2 min time lapse was allowed after each addition of sodium methoxide solution and before addition of new lot of the titrant. 1.0 equivalent of the dye would require 1.0 equivalent (1000 milliequivalents) of the base for compete neutralization since out of the hydroxyl group present on repeat unit only hydroxyl group will be neutralized. Hence total moleequivalents (X) of the base required to neutralize 100 gm of the polymer would be,

$$= \frac{1000 \times 100}{\text{Mol. wt. of the repeating unit}} = X$$

Let "Y" be the milliequivalents of the base used up in the shortest break (first break) in the titration curve. Then by principle the degree of polymerization would be,

$$\overline{P} = \frac{X}{Y}$$

And the number average molecular weight of polymer would be,

The assumption in which the degree of polymerization is calculated would be invalid firstly. If some of the chains do not contribute any hydroxyl group during the shortest interval and secondly. If some of the chains contribute more than one group during the first interval.

The results of the conductormetric study are presented in tabl. the selected curves for conductormetric titrations are shown in figure.

Results of conductometric study of azo polymers Poly [azo (1-Napthol)].

Polymer	Milliequivalents of base required for neutralization of one OH Group (First Break) (Y)	Milliequivalents of base required for Complete neutralization (X)	Degree of polymerization Dp = X/Y	Number average molecular weight Mn
Poly [azo (1-Napthol)]	80	835	10.5	1250

Conductometric titration curve of Poly [azo (1-Napthol)]
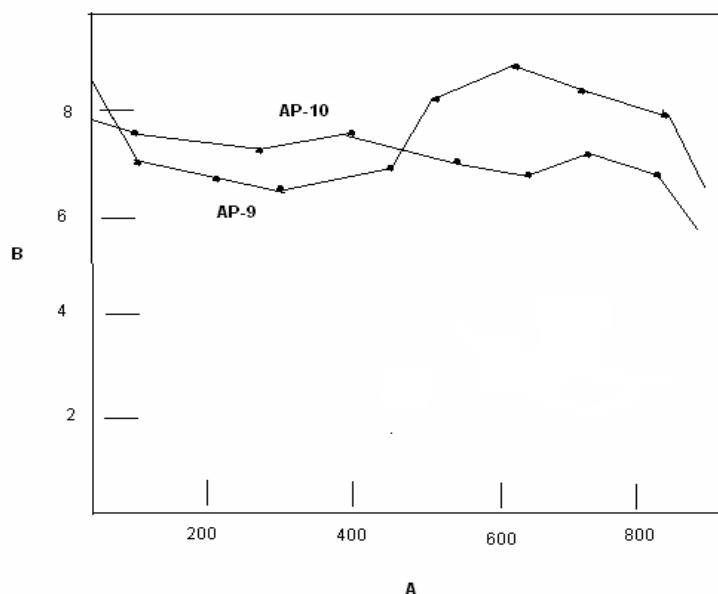
3(b) RESULTS AND DISCUSSIONS

The brief account of the thermal behavior of samples in air is given below:

(I) Each chelate degradation in two steps.

(II) The degradation of all the chelates start in the temperature Range of 200^0 to 350^0C depending upon the natures of chelate.

(iii) The wt. loss amount in this first stage is in between 4.5 to 7% this may be due to water molecules associated in to the chelates. This is supported by Nikolaev et al.[18]

(IV) The second stage of decomposition of all chelates is rapid with the loss of mass about 50%. This is due to "in situ" formation of metal oxide during degradation. Which accelerate the rapid degradation of chelate.

(V) The last stage of digression cause a mass loss of about 80%. This is due to loss molecular fragments of polymers.

Reflectance spectroscopy is specially useful technique in the study of geometric & electronics structure of metal chelates of transition metal complexes.[19] The diffuse electronic spectrum of Cu^{+2} complex shows two broad bands 15650 cm^{-1} and 23370 cm^{-1}, $^2B_{1g} \rightarrow A_{1g}$ translation and charge transfer respectively. This indicates the octahedral structure. These findings are in agreement with data reported by several research works.[20-24]

Electronic spectral data of Co^{+2} indicates that transition observed in the 8792 cm^{-1} are assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(v_1)$ and another bands 19990 cm^{-1} and 24660cm^{-1} may be

attributed to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(v_2)$ and $^4T_{1g}(F) \rightarrow {}^4T_{19}(P)(v_3)$ transitions. This indicates the octahedral structure. Similar observations are also reported in the literature.[25,26]

The Mn^{+2} complex also the bands at 16225 cm^{-1}, 18650 cm^{-1}, 24040 cm^{-1} suggest the $^6A_{1g} \rightarrow$ $^4T_{1g}(^4G)$, $^6A_{1g} \rightarrow {}^4E_g(^4G)$ and $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ Transition. This indicates the octahedral structure. Similar observations are also reported in the literature.[27]

The values of Mn of the azo polymers estimated by the above said methods agree well. Within limits of experimental errors. The degree of polymerization of polymers varies from 10 to 14 depending upon the nature of monomer used. The result shows that the degree of polymerization increase with increases in reaction time.

4. *CONCLUSION*

Structures of Poly [azo- (1 –napthol)] is confirmed by elemental analysis, IR spectra, TGA and reflectance spectra. Poly [azo- (1 –napthol)] complexes exhibit octahedral structure by reflectance spectra, conductometric study of azo polymers Poly [azo- (1 –napthol)] shows that the degree of polymerization increases with increase in reaction time. This study may afford good electrical conducting properties of complexes and good electrical conducting material.

5. *ACKNOWLEDGEMENT*

6. REFERENCES

1. Pron, A.; Prog. Poly. Sci., 2002; 27: 135.
2. Searson, P. C.; Crit. Rev. Surf. Chem., 1994; 3(3/4): 171.
3. Evans, G. P.; advances in electrochemical science and engineering, New york, 1990; "1".
4. Chen, D.; Phys. Rev. B: Condens Metter, 1992; 45: 2035.
5. K. Nakamoto, Infrared spectra of Inorganic and co-ordination compounds, Wiley, New York, 1970.
6. Chatterjee, S. K. and Mitra, J. Sc. Ind. Res., 1961; 20B: 310.

7. Chatterjee, S. K. Indian J. Chem., 1969; 7: 605.

8. Mitra, R. P. and Chatterjee, S. K. Indian J. Chem., 1963; 1: 62.

9. Sprengling, J. Am. Chem. Soc., 1954; 76: 1190.

10. Mitra, R. P. and Chatterjee, S. K. Indian J. Chem., 1964; 2: 85.

11. Chatterjee, S. K. and Mitra, P. R. J. Polymer Sci., Part. A-1, 1970; 1299.

12. Chattterjee, S. K. and Mitra, P. R. J. Polymer Sci., Part. A-1, 1971; 3325.

13. Micrea, I.; Makromol, Chem., 1975; 174: 883.

14. Korshak, V. V.; Izu. Akad. Nauk SSSR, 1969; 5: 1078.

15. Korshak, V. V.; Vysokomolekul Soedin, 1965; 7(12): 2052.

16. Meek, L. R.; USP, 1966; 3(278): 486.

17. Desousa, G. A.; J. Poly. Sci. Polym. Chem., 1978; 16: 2671.

18. Nikolav, A. V.; Logvineko, V. A. and Mychina, L. T.; Thermal Analysis, Academic Press, New York, 1969; 2: 779.

19. Kuvelka, P and Munk, F.; Z. Tech. Phys., 1931; 12: 593.

20. Hathway, B J and Tomilson, A.A.G.; Co-ord. Chem. Rev., 1970; 5: 1.

21. Patel, A. K.; Patel, V. M.; Patel, R. M.,; Singh, s and Joshi, J. D.; Synth. React. Inorg. Met. Org. Chem., 1999; 29(2): 193.

22. Raddy, S.N and Agraval, B.V.; Syn. React. Inrg. Chem., 1987; 17: 6.

23. Furlani, C. and Morpurgo, G.; Theor. Chim. Acta, 1965; 1: 1181.

24. Jorgenson, C.K.; Acta. Chem. Scand., 1955; 9: 1362.

25. Satpathi, S.; Rai, H.C and Sahoo, B.S.; J. Ind. Chem. Soc., 1975; 52: 701.

26. Holm, R.H.; Everett, G.W and Chakravorty, A.; Prog. Inorg. Chem., 1966; 7: 83.

27. Sing, B and Sing, R.; J. Inorg. Nucl. Chem., 1972; 34: 3449.