CHAPTER III

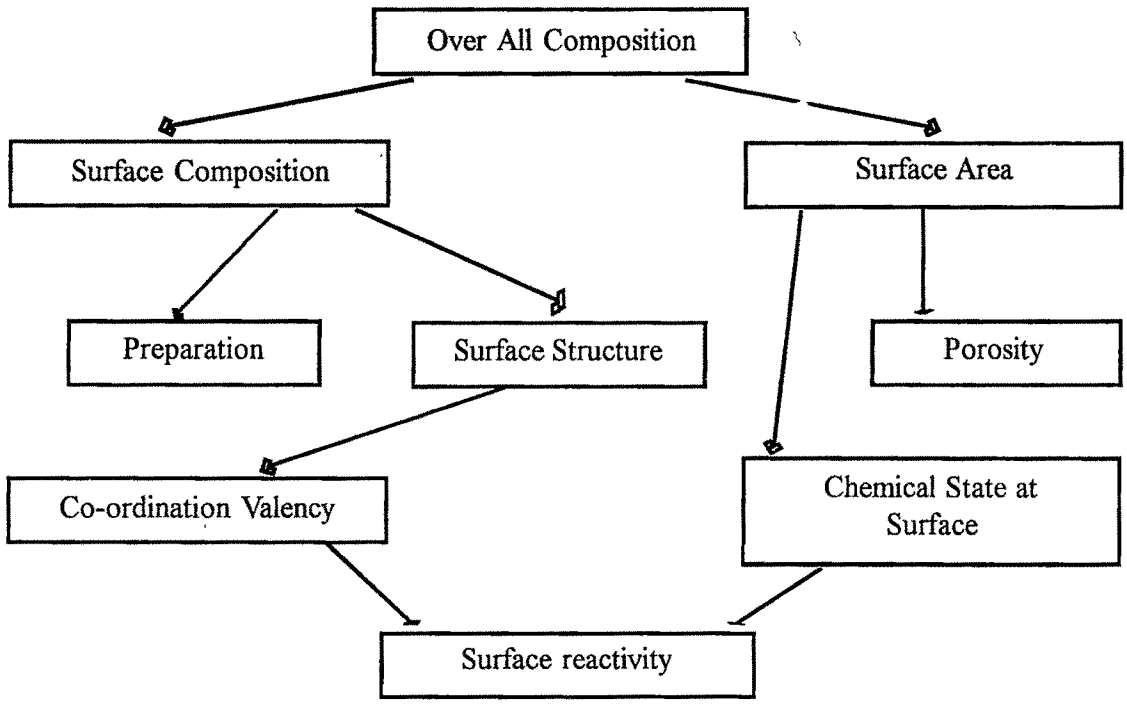
CHARACTERIZATION

CHAPTER 3 : CATALYST CHARACTERIZATION

3.1	INTRODUCTION	33
3.2	CHEMICAL COMPOSITION	34
3.3	APPARENT BULK DENSITY & MOISTURE CONTENT	35
3.4	SURFACE AREA MEASUREMENT	36
3.5	SWELLING STUDIES	37
3.6	SPECTRAL CHARACTERIZATION	39
3.7	INFRARED SPECTROSCOPY	39
3.8	ELECTRON PARAMAGNETIC RESONANCE (EPR)	40
3.9	MORPHOLOGY OF POLYMER BOUND CATALYSTS (SEM)	41
3.10	THERMAL STUDIES	42
3.11	REFERENCES	41

CATALYST CHARACTERIZATION

3.1 INTRODUCTION : Catalyst Characterization is very important, as most practical catalyst are highly complex materials.To characterize a polymer bound catalysts precisely the constitution of the catalysts has to be understood in its bulk as well as on the surface, mainly surface composition and nature and proporation of surface fuctional group.It is also required to know the modification of the polymer during different stages of its preparation, the thermal stability as well as the swelling behaviour of the support and the catalysts. In addition, it is also necessary to understand the structure of the catalyst i.e. geometric structure and morphology, particularly change in the morphology by supporting on polymer, Finally, characterization should be carried out in terms of catalysts activity which is quantitative measurement of the ability of the catalyst to carry out a particular chemical transformation under specified condition.[1]



A general scheme of characterization is mentioned above

Present chapter deals with characterization of polymer-bound catalysts as also that of unbound transition metal complexes. An attempt has been made to arrive at surface composition and catalyst structure using various methods to be introduced for characterization. viz elemental analysis, swelling studies, investigation of moisture content and apparent bulk density as well as the measurement of surface area by such as

infra-red and reflectance UV-visible spectra, electron spin resonance (ESR) were carried out in order to investigate co-ordination structure of anchored complexes and oxidation state of metal atom.Morphology of the supports and catalysts was studied using scanning electron Microscope (SEM),while the thermal stability was investigated using thermogravimetric (TG) analysis. Based on the spectroscope and physico-chemical characteristics, the probable structures of metal complexes on the polymer matrix have been proposed. The catalytic activity of the catalysts have been investigated for the oxidation of toluene.

3.2 Chemical Composition

Elemental analysis of C,H,N,Cl and metal content for polymer-bound Mn and Ni complexes at various stages of preparation of the catalysts are given in table 3.1. The number of ligand molecules attached with the polymer were calculated from difference of two chloride ion content (estimated gravimetrically) before and after introduction of ligand. The calculated and experimental values were found to be in close agreement.The loading of the metal ions and hence the chelation on the polymer matrix was achieved by carrying out the reaction with the ligand and metal ions under mild conditions in presence of a good swellimg agent. It may be taken into account that each fuctional group or ligand comes in contact with metal ions and co-ordinates with this to form inner co-ordination complex.Then the spatial arrangement of the complexing groups over the polymer ligand takes various concentrations with respect to the main chain. As a result the total polymer complex as a whole is formed. The polymer complex formation also represents relaxation process which relates to the probability of transition of the system from one state of equilibriom to another.[2]

Table 1

Elemental anlysis at different stages of preparation of polymer bound manganese and nickel complexes (wt %)

A			B			X Unit of Metal ions
6% (C.L)	C,	H, N,	C,	H,	N,	Mn
76 70	6 6	3 094	76.37	6 619	2 596	1.373 x 10^{-3}
74.87	6.636	0.976	73.45	6.560	Nil	1.649 x 10^{-3}
A			B			X Unit of Metal ions
8 % (C L)	C,	H, N,	C,	H,	N,	Mn
73 75	6 68	4 573	70 65	6 6	3 998	5 49 x 10^{-4}
67.51	5 995	1 932	67 54	5 9	1.716	2 474 x 10^{-3}

A 14 % (C.L) C, H, N,	B C, H, N,	X Unit of Metal ions Mn
71.76 6.7 6.039	81.68 7 19 2 463	1.922 x 10^{-3}
69.82 6.09 4.626	80.52 6.913 1.963	1.37 x 10^{-4}
A 6% (C L.) C, H, N,	B C, H, N,	X Unit of Metal ions Ni
76.70 6.6 3.094	76.37 6.624 2 463	3.81 x 10^{-4}
74.87 6 636 0.976	74 66 6.627 Nil	2.494 x 10^{-3}
A 8 % (C.L) C, H, N,	B C, H, N,	X Unit of Metal ions Ni
73 75 6 8 4.573	67.19 6 20 2.970	2.488 x 10^{-3}
67 51 5.995 1.932	67.54 5.849 1 716	1 907 x 10^{-3}
A 14 % (C.L) C, H, N,	B C, H, N,	X Unit of Metal ions Ni
71 70 6.6 6.039	82.22 7.117 2.514	2 001 x 10^{-3}
69.82 6.09 4.626	80.39 7.058 1.999	1.907 x 10^{-3}

3.3 Apparent Bulk Density & Moisture Content :

Apparent bulk density and percentage of moisture content of all polymer supports and catalysts are given in Table-II. A decrease in moisture content was observed on increasing the percentage (%) cross link from 6 to 8 percent, though no significant change was observed for higher cross linking of the polymer.Thus for 6% OPDA Mn(II), the moisture content was found to be 0.50% for 8% of the same catalyst it was observed to be 0.491 % while for 14% of the catalyst the moisture content was found to be 0.495%. This might be due to hygroscope nature of the polymer at lower percentage of the degree of cross-linking ; hydrogen bonding of water with amino group or co-ordination with metal atom may not also be ruled out.

The importance of apparent bulk density lies in indication of mass of catalyst that can be packed into specified volume of reactor. However, volume occupied by swollen polymer is different than than occupied by dry polymer. Therefore, this parameter is not significant when catalyst is used in liquid phase slurry reactor. However, volume occupied by the swollen polymer is different than that occupied by dry polymer. Therefore, this parameter is not significant when catalyst is used in liquid phase slurry reactor but useful for vapour phase reactor.

The results for apparent bulk densities are as follows :

On increasing the percent of the cross-linking from 6% to 8% the bulk density was observed to increase while at a higher percent it was found to decrease.Thus, for catalyst 6 OPDA Ni(II) to 8 OPDA Ni(II) , the bulk density was found to be enhanced from 0.354 g/cc to 0.455 g/cc, while for 4 OPDA Ni(II) it was observed to be 0.422 g/cc respectively.

Table II

Moisture Content and bulk density of Polymer Supports and Catalyst

Support (%)	Moisture Content wt (%)	Apparent Bulk density (g ml^{-1})
6	0.308	0.310
8	0.280	0.390
14	0.310	0.385
Catalyst		
6 OPDA Mn (II)	0.501	0.371
8 OPDA Mn (II)	0.491	0.434
14 OPDA Mn (II)	0.465	0.435
Catalyst	Moisture Content wt (%)	Apparent Bulk density (g ml^{-1})
6 OPDA (Ni II)	0.521	0.354
8 OPDA Ni (II)	0.504	0.455
14 OPDA Ni (III)	0.521	0.422
6 PPDASB Mn (II)	0.529	0.350
8 PPDASB Mn (II)	0.485	0.485
14 PPDASB Mn (II)	0.482	0.416
6 PPDASB Ni (II)	0.459	0.391
8 PPDASB Ni (II)	0.481	0.464
14 PPDASB Ni (II)	0.462	0.424

3.4 Surface area Measurement :

Most practical catalysts are highly complex materials and a basic problem is how to correlate catalyst behaviour with physical and chemical structure. Some methods of characterization are standardized.These include determination of total surface area measurement and comparison of surface area of the supports and the catalysts which give an idea about a change in surface area upon immobilization or anchoring of support as also relation between change in activity as well as in surface area. Adsorption method was used for the measurement of the total surface area of polymer supports and polymer

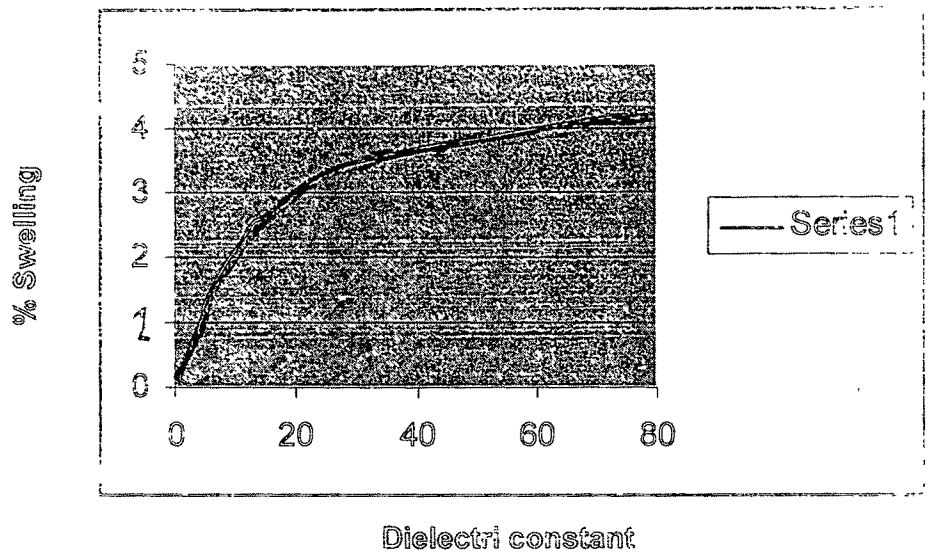
bound catalyst[3]. Adsorption - desorption isotherms of nitrogen were recorded on a Carlo-Erba sorptiomatic series - 1900 at liquid N_2 temperature (i.e - 196°C) after degassing the sample at 80°c for 4 hrs. From the isotherms specific surface area and pore volume were calculated using BET equation. The results are given in table 3.3. In some cases a decrease in surface area was observed while in some other cases an increase was found after the complex formation. A decrease was observed in the surface area of some of the catalysts which may be due to blocking of pores of the support by successive introduction of chloromethyl group, Schiff base ligand and metal ions on the polymer matrix. This is in accordance with the results obtained earlier by Ram et al[4-6] while an increase may be attributed to complexing of highly fuctionalized polymer with bulky ligand [7].

Table 3.3

Support (%)	Surface area (m^3g^{-1})	Pore Volume ($cm^{-3}g^{-1}$)
6	35.21	0.034
8	32.37	0.043
14	62.03	0.098
6OPDAMn(II)	34.6	0.131
6OPDANi(II)	30.79	0.169
6PPDAMn(II)	32.574	0.141
6PPDANi(II)	29.32	0.337
8OPDAMn(II)	40.95	0.183
8OPDANi(II)	35.21	0.159
8PPDAMn(II)	34.64	0.206
8PPDANi(II)	37.42	0.119
14OPDAMn(II)	59.30	0.229
14OPDANi(II)	64.50	0.231
14PPDAMn(II)	55.54	0.444
14PPDANi(II)	53.69	0.361

3.5 Swelling studies :

The interaction of polymers with low molecular mass solvents, resulting in limited or unlimited swelling, has long been the subject of investigation from theoretical and practical points of view[8-9]. The swelling theory was formulated many years ago and has been developed more recently[10]. There has been notable efforts to find a relation between swelling behaviour and structural parameters, such as extent of crosslink of polymer network.



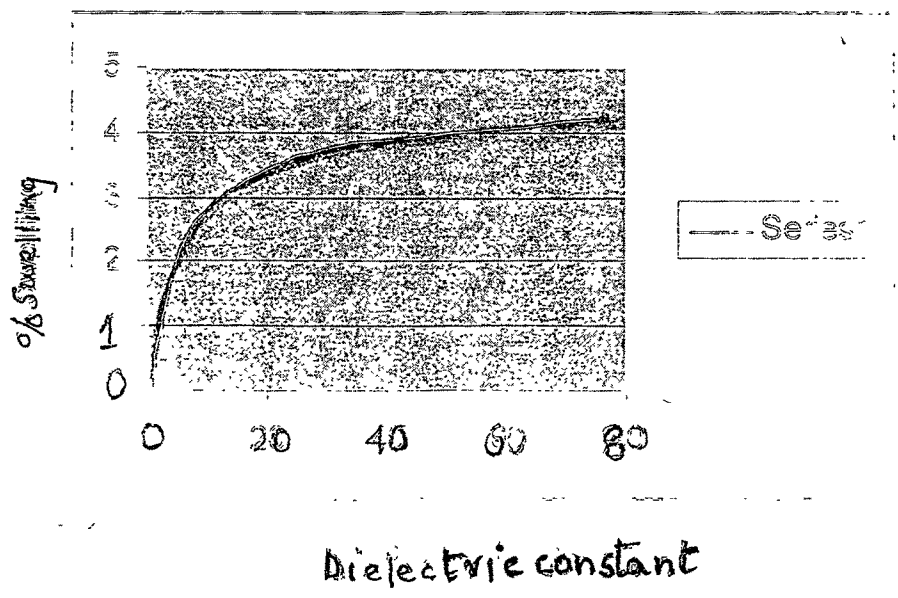
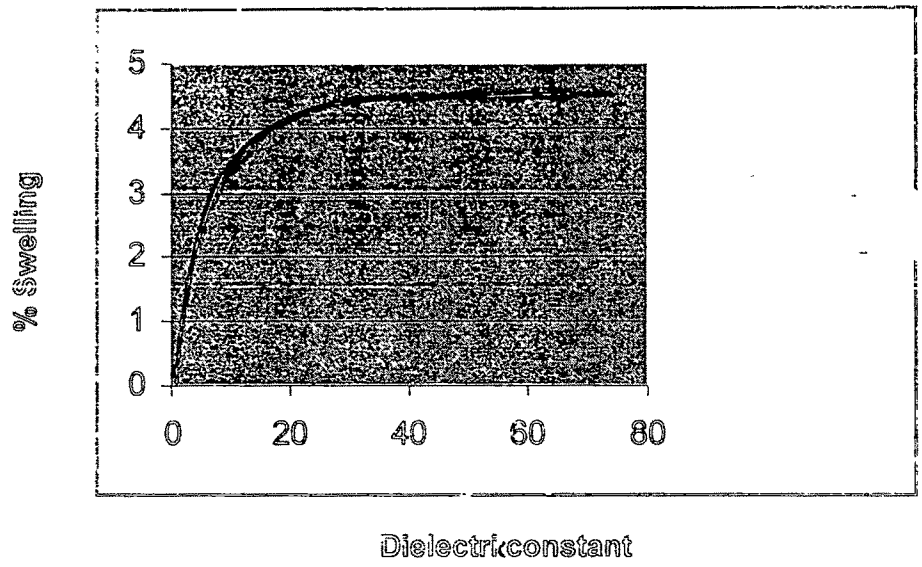


Fig 3(a) Plot of Swelling (mole %) v/s. dielectric constant of
(a) 6OPDAMn(II) (b) 6PPDANi(II)



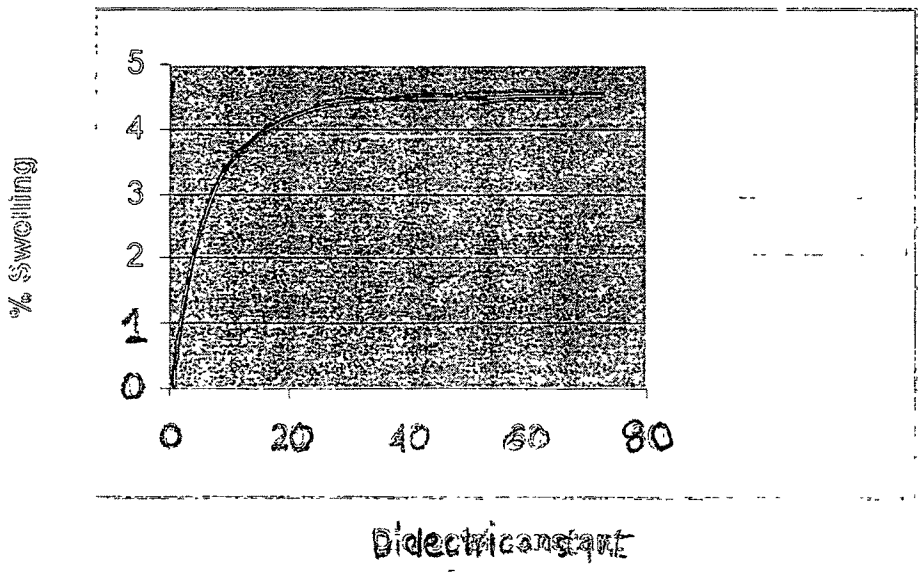
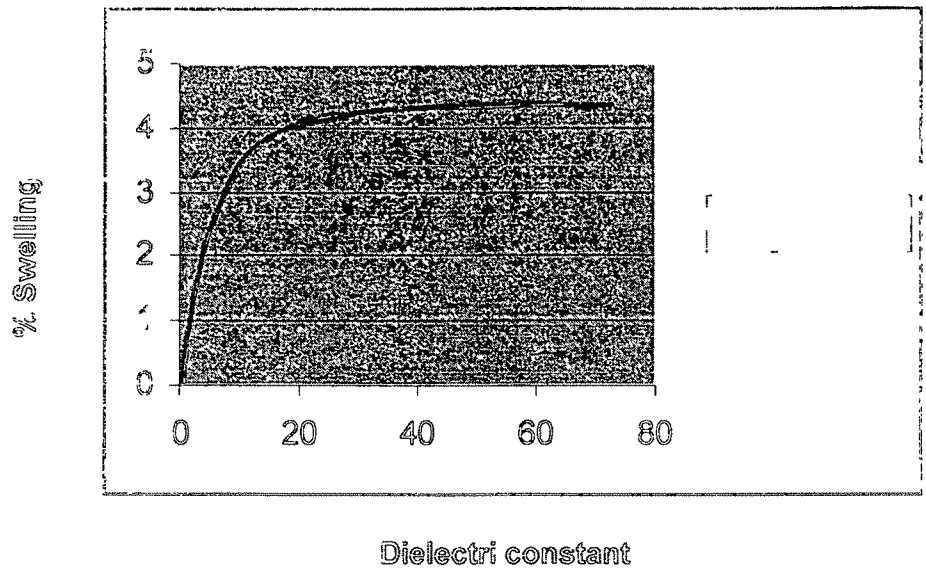


Fig. 3(b) Plot of Swelling (mole %) v/s. dielectric constant of
(c) 8OPDAMn(II) (d) 8PPDANi(II)



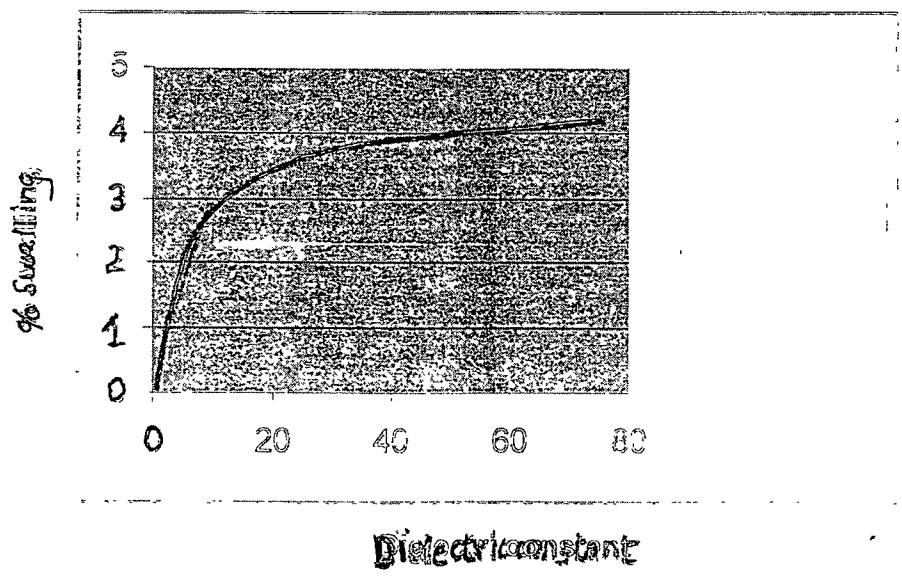
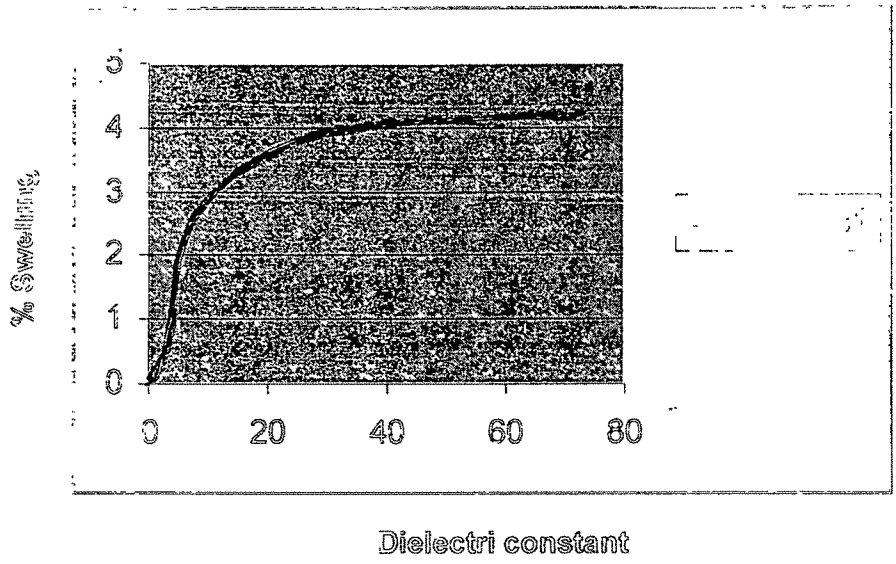


Fig 3(c) Plot of Swelling (mole %) v/s. dielectric constant of

(e) 14OPDAMn(II) (f) 14PPDANi(II)



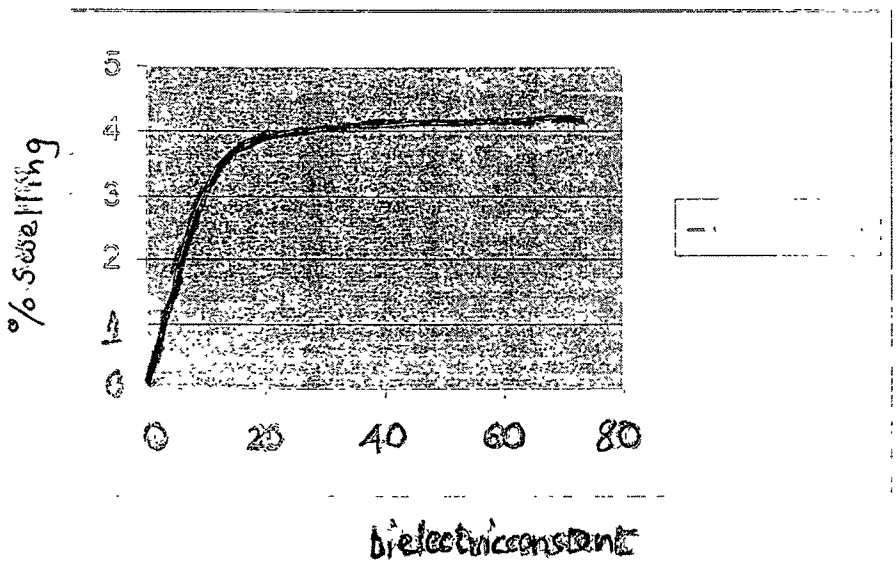


Fig 3(d) Plot of Swelling (mole %) v/s. dielectric constant of

(g) 14PPDAMn (II) (h) 14OPDANiNi(II)

Swelling is a very important parameter especially using polymer bound complexes as catalysts where the reaction is carried out using appropriate solvent.

Higher activity and selectivity can be achieved with polymer - bound catalysts if the reactant molecules are accessible to all catalytic sites both on the surface and interior of beads.This could be achieved by using a solvent in which the polymer has maximum swelling, so that the matrix expand sufficiently to allow the reactant molecules to diffuse within solvent channel and encounter the catalytic centers.

The extent of swelling depends on the polymer solvent interaction which is determined by (i) the nature of the solvent and the polymer matrix and (ii) reactive groups attached to the polymer matrix.

Thus, the nature of the solvent plays an important role in the rate of reaction. Polymer swelling is a useful parameter to control both specificity and selectivity in a batch reactor. However, it becomes undesirable in a fix bed reactor as it leads to blocking of the inter-bead channels and so prevents flow through the bed reactor.

In the present investigation, an attempt is made to ensure that the metal complexes are anchored uniformly during the synthesis and all catalytic centres are accessible during the reaction by carrying out an exhaustive study of swelling of the polymer support and the catalysts using eleven various solvents of different nature.(i.e. aliphatic, aromatic, polar and non-polar).The results are given in table 3.4 to 3.6 from polar to a non-polar characteristics.

The plot Fig. (3a to 3d) of swelling (mol.%) vs dielectric constant shows that on increasing the dielectric constant of the solvent, an increase in swelling was observed. This indicates that the swelling is enhanced as the solvent varies from a non polar to a polar characteristic.

Thus, the maximum swelling of the catalysts was found to be with water while with n-hexane it was observed to be minimum. The maximum swelling in water may be due to

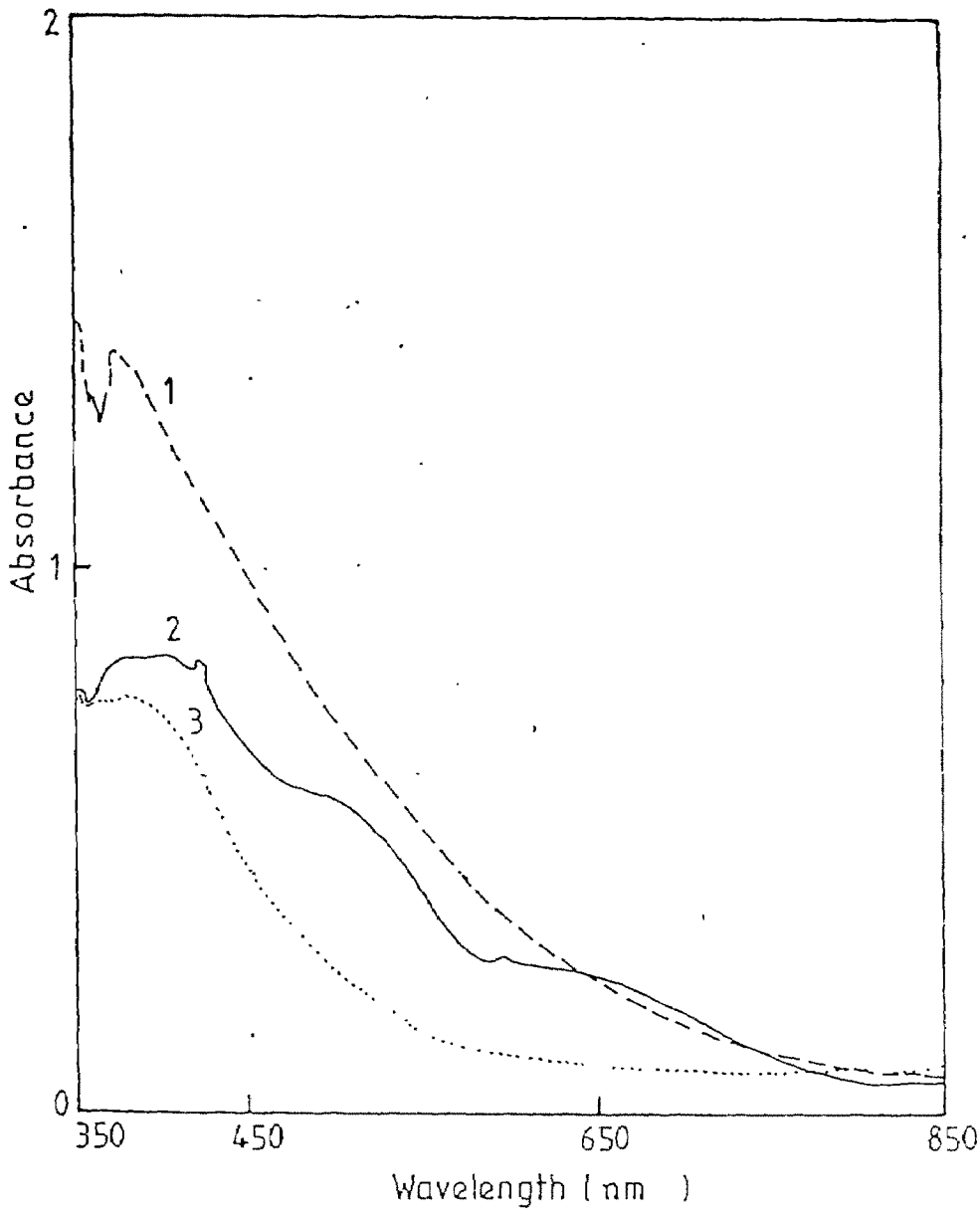


Fig 3(e) UV-Vis reflectance spectra of (1) 6 OPDA Mn (II) (2) 6 PPDA Mn (II) (3) 6 PPDA Ni (II).

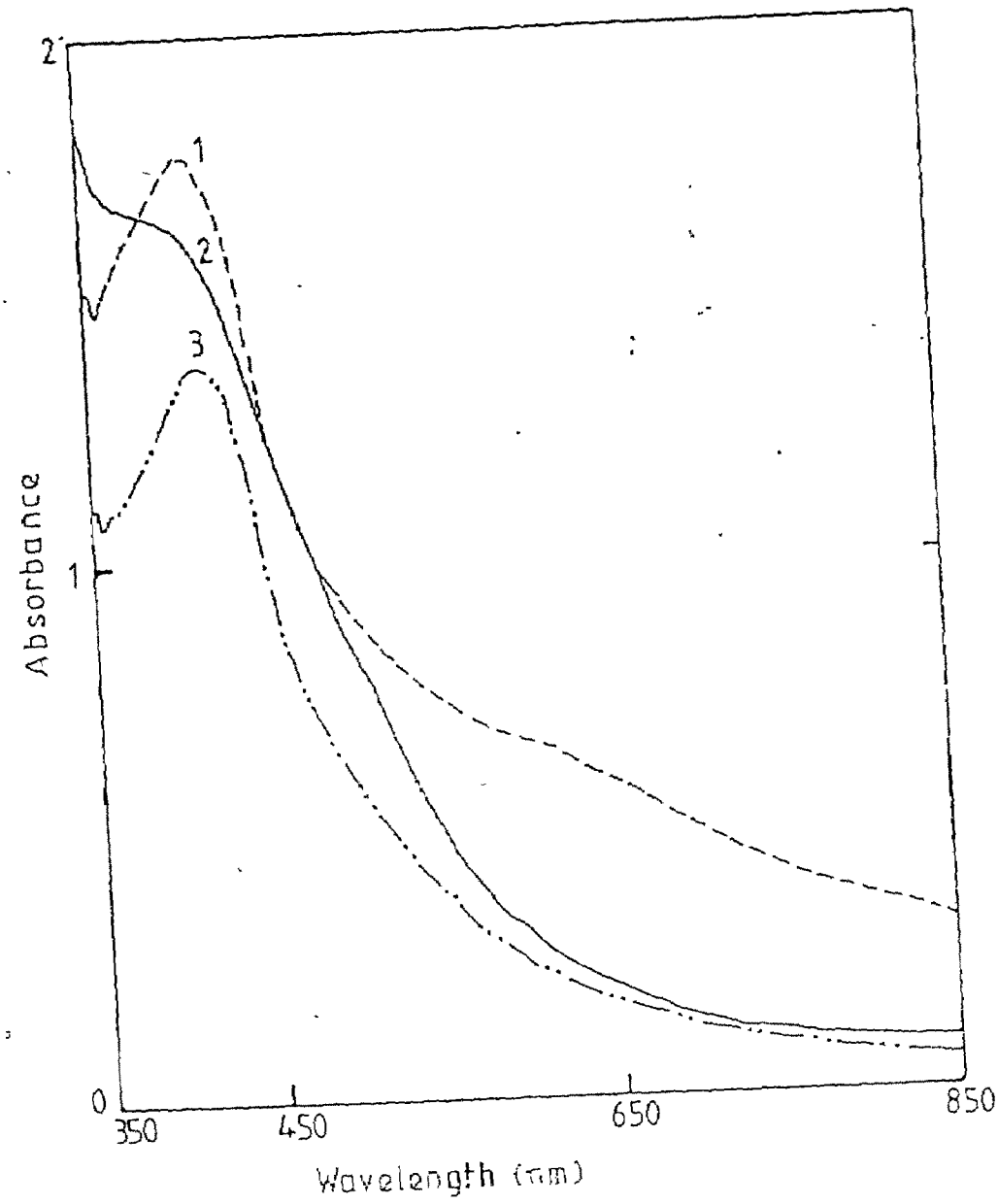


Fig 3(f) UV –Vis reflectance spectra of (1) 8 OPDA Mn (II) (2) 14 OPDA Mn (II) (3) 8 PPDA Mn (II) (4) 14 PPDA Mn (II).

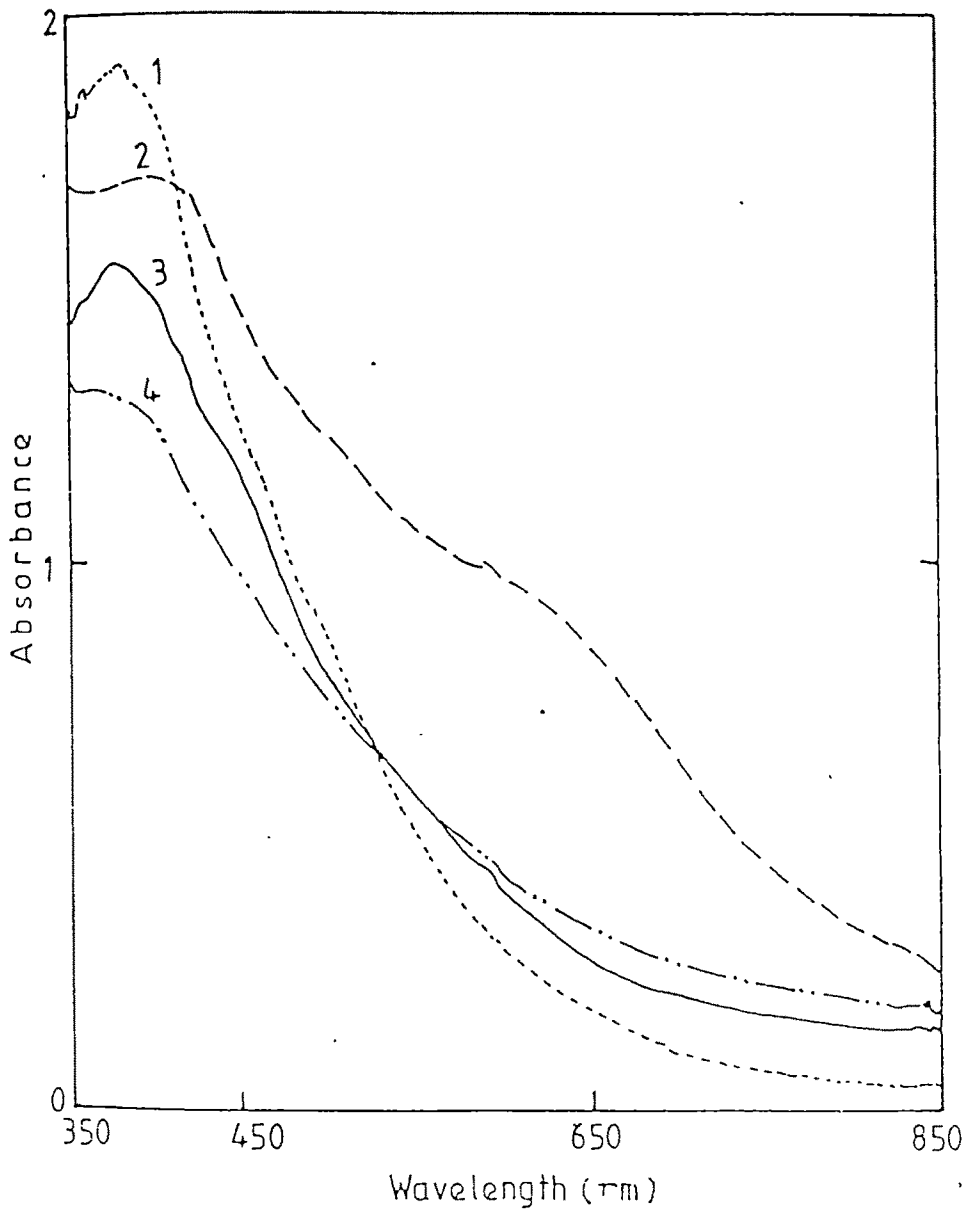


Fig3(g) UV-Vis reflectance spectra of (1) 8 OPDA Ni (II) (2) 14 OPDA Ni (II) (3) 8 PPDA Ni (II) (4) 14 PPDA Ni (II)

hydrogen bonding of water molecules with 1-amino groups. It was also observed from the results that on increasing the cross-linking of the polymer matrix, a decrease in swelling is observed. This is indicative of the fact that due to the hardness of the polymer, the interaction with the solvent was found to be less.

3.6 Spectral Characterization :

UV Visible Spectroscopy :

The interaction of light with catalyst particles is regarded as a major tool in the characterization of catalysts.The transitions involved in UV-Visible region are electronic. The d-d transitions are observed when degenerate d-orbitals are split by placing a transition metal ion in a crystal field.The splitting of the energy levels is affected by number of d-electrons, the effective change on the ion, the distribution and the change of the surroundings. These transitions usually occur in the visible region of the spectrum. Charge transfer transitions involve more than one atom and include transitions from metal to ligand or vice versa. or between two neighbouring metal atoms of different oxidation states.

Usually such transitions occur in the UV-Visible Spectroscopy for powdered samples involve in the measurement of diffusely reflected light[11]. In supported catalysts UV-Visible spectra are normally interpreted by comparison with the spectra of corresponding homogeneous complex. Fig. 3e to 3g show the UV-Visible diffuse reflectance spectra of polymer bound Mn(II) and Ni(II) catalyst using $BaSO_4$ as standard. Polymer bound manganese catalysts show peak at 370 nm which may be due to d-d transition of Mn(II). The homogeneous manganese and nickel Schiffbase complex also shows a peak at 400 nm confirming that manganese is present in +2 oxidation state both in homogeneous and heterogenized systems. The broad peak observed between 350 & 410 nm in the case of polymer - bound nickel catalysts might be due to d-d transition of Ni(II).

3.7 Infrared Spectroscopy :

Infrared spectroscopy is most widely used technique for the study of supported metal complex catalyst.It is used to study adsorbed molecules and their binding with catalyst surface. It provides reliable information about the organic compounds in the IR (600-4000cm^{-1}) region and that of metal - ligand vibration in Far-IR (50-600cm^{-1}) region.

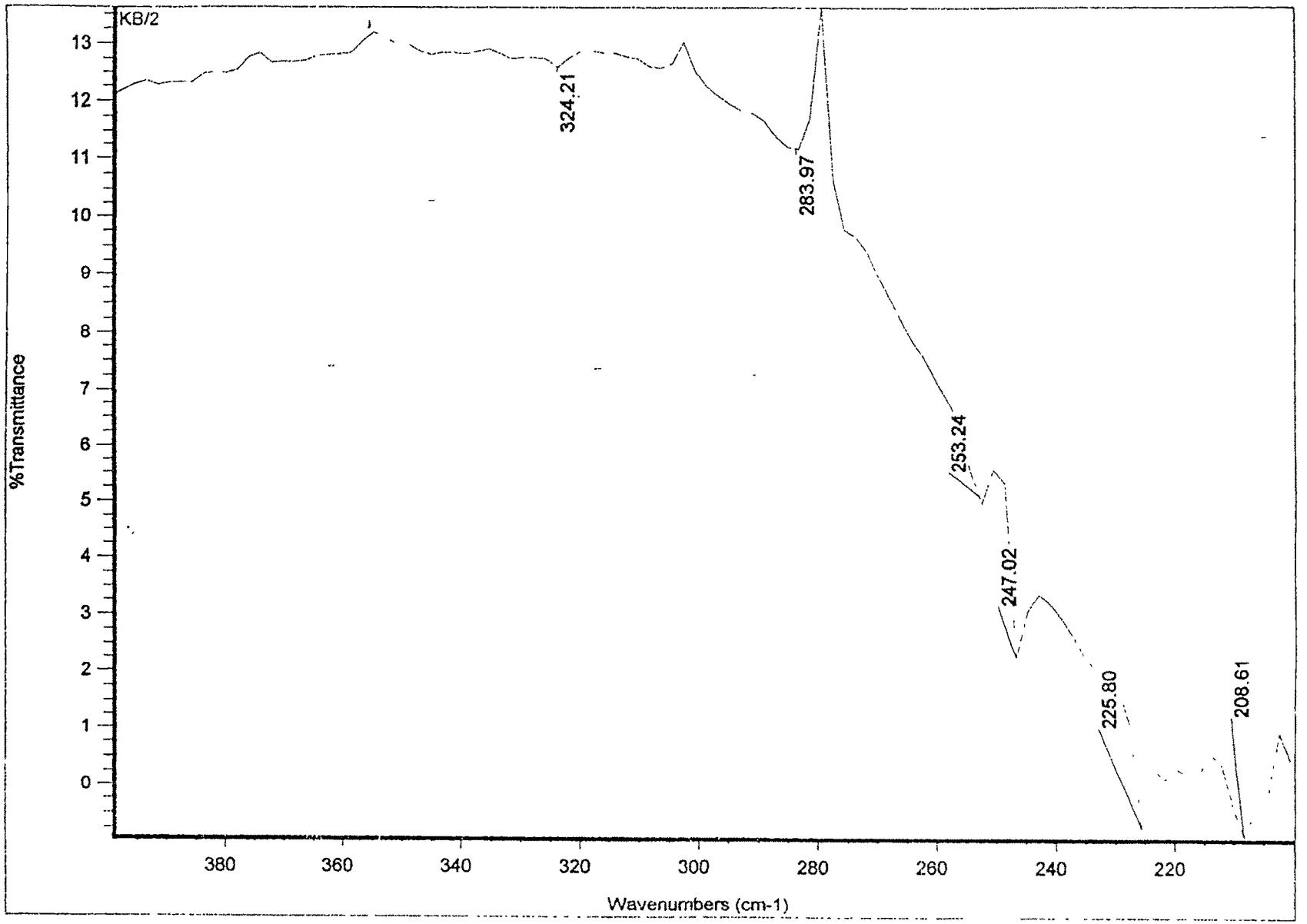


Fig.3(h) FTIR Spectrum of 8PPDANi(II)

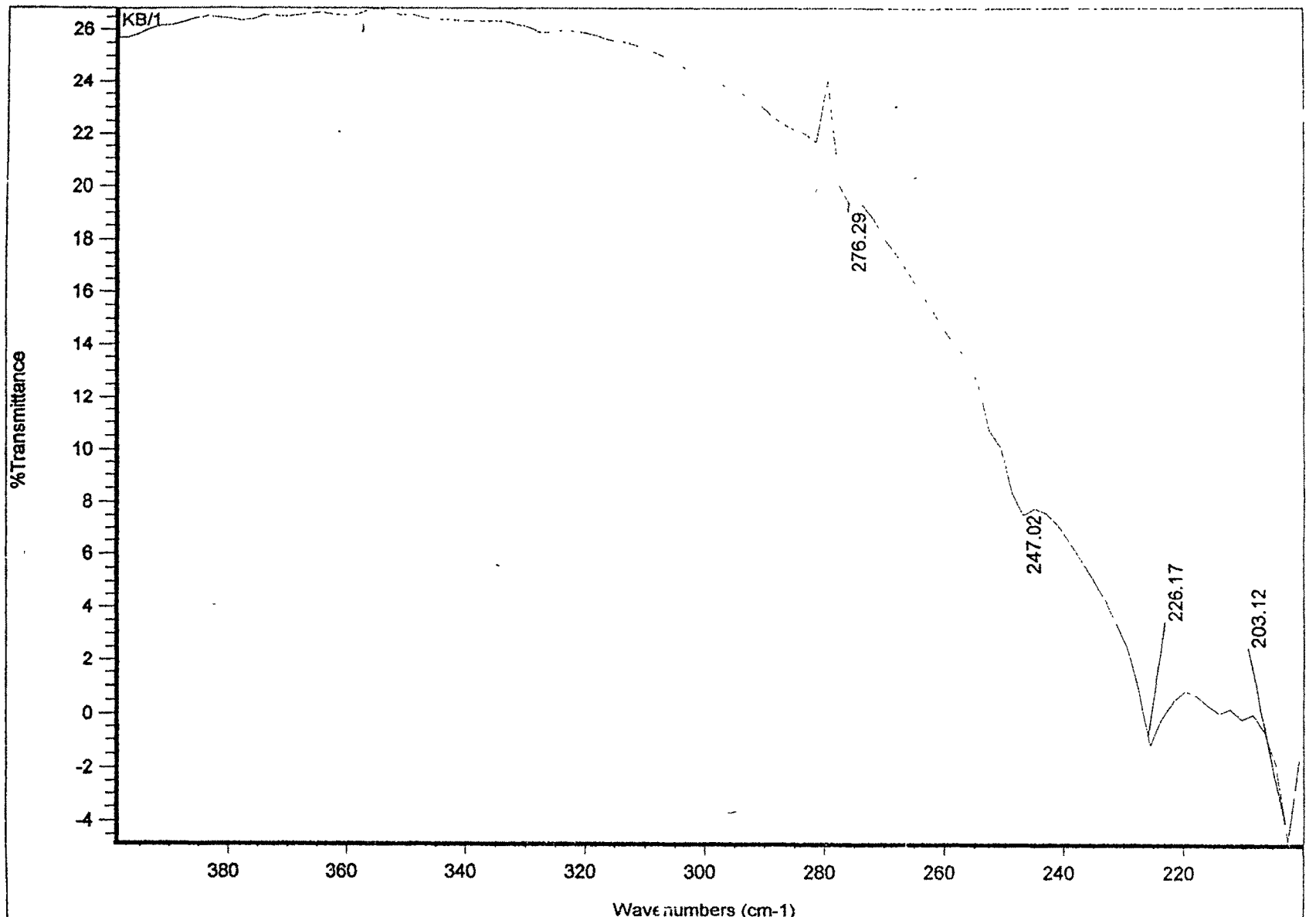


Fig. (3(i)) FTIR Spectrum of 8PPDAMn(II)

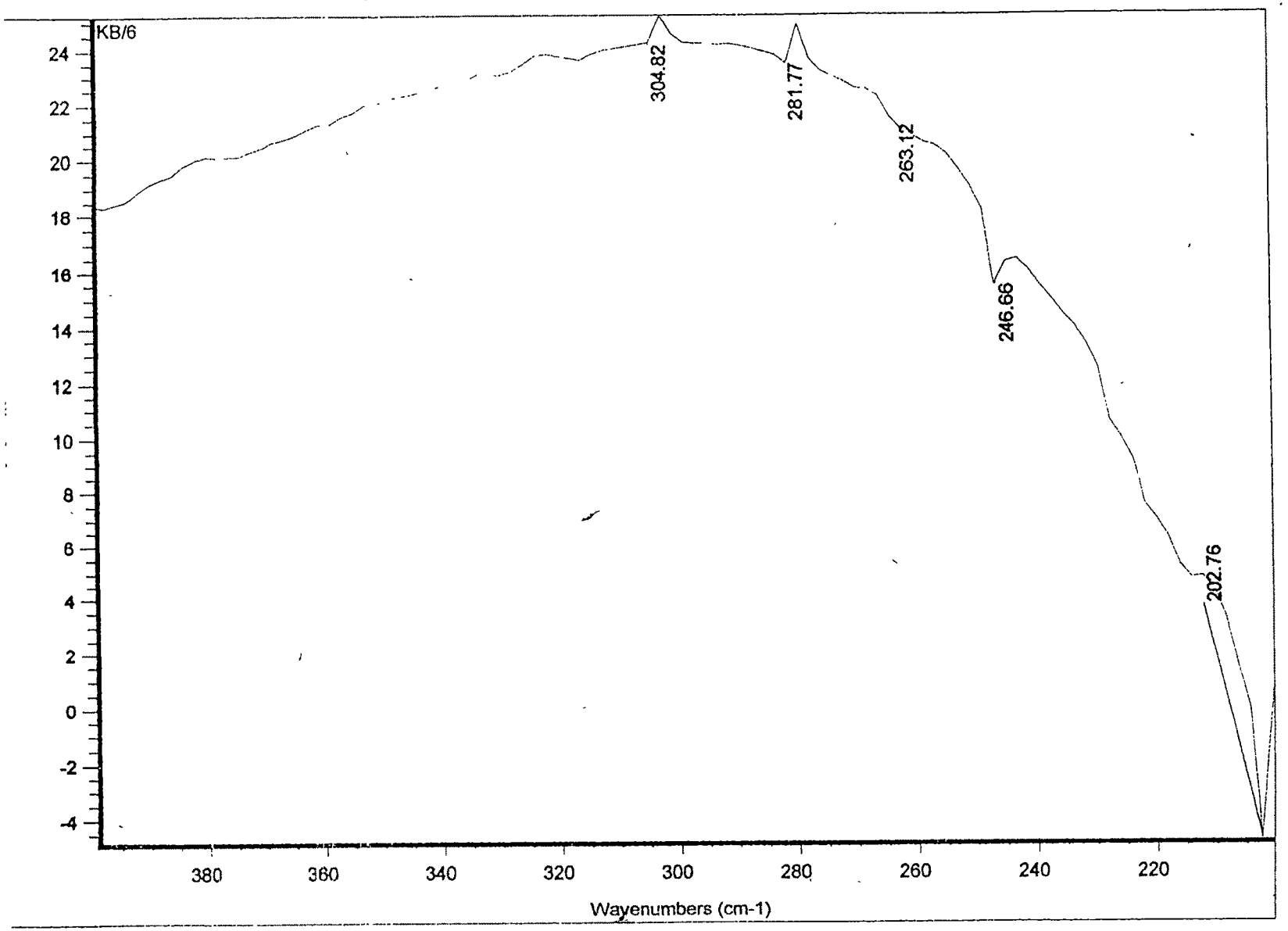


Fig. 3(j) FTIR Spectrum of 14PPDANi(II)

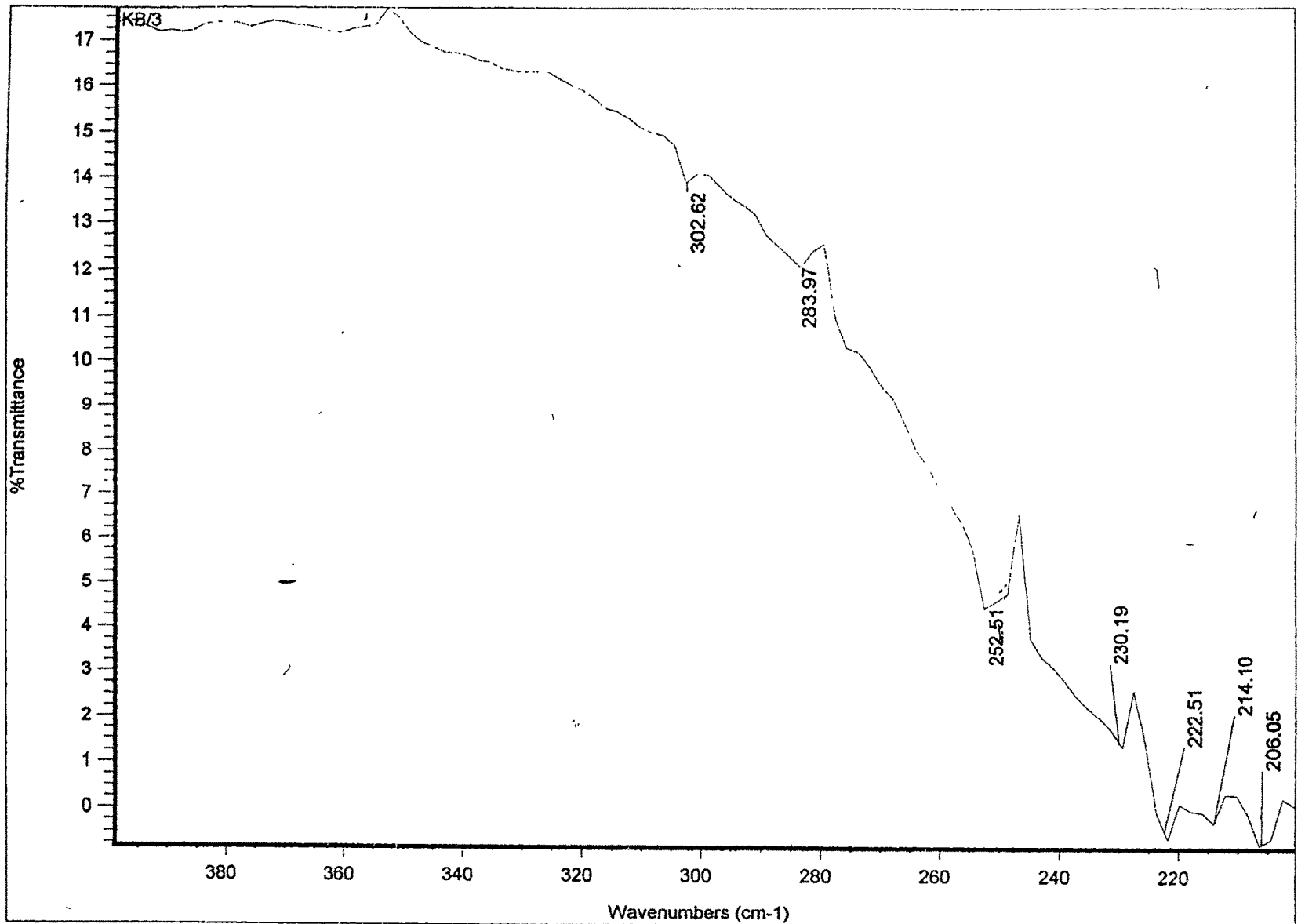


Fig. 3(K) FTIR Spectrum of 14OPDAMn(II)

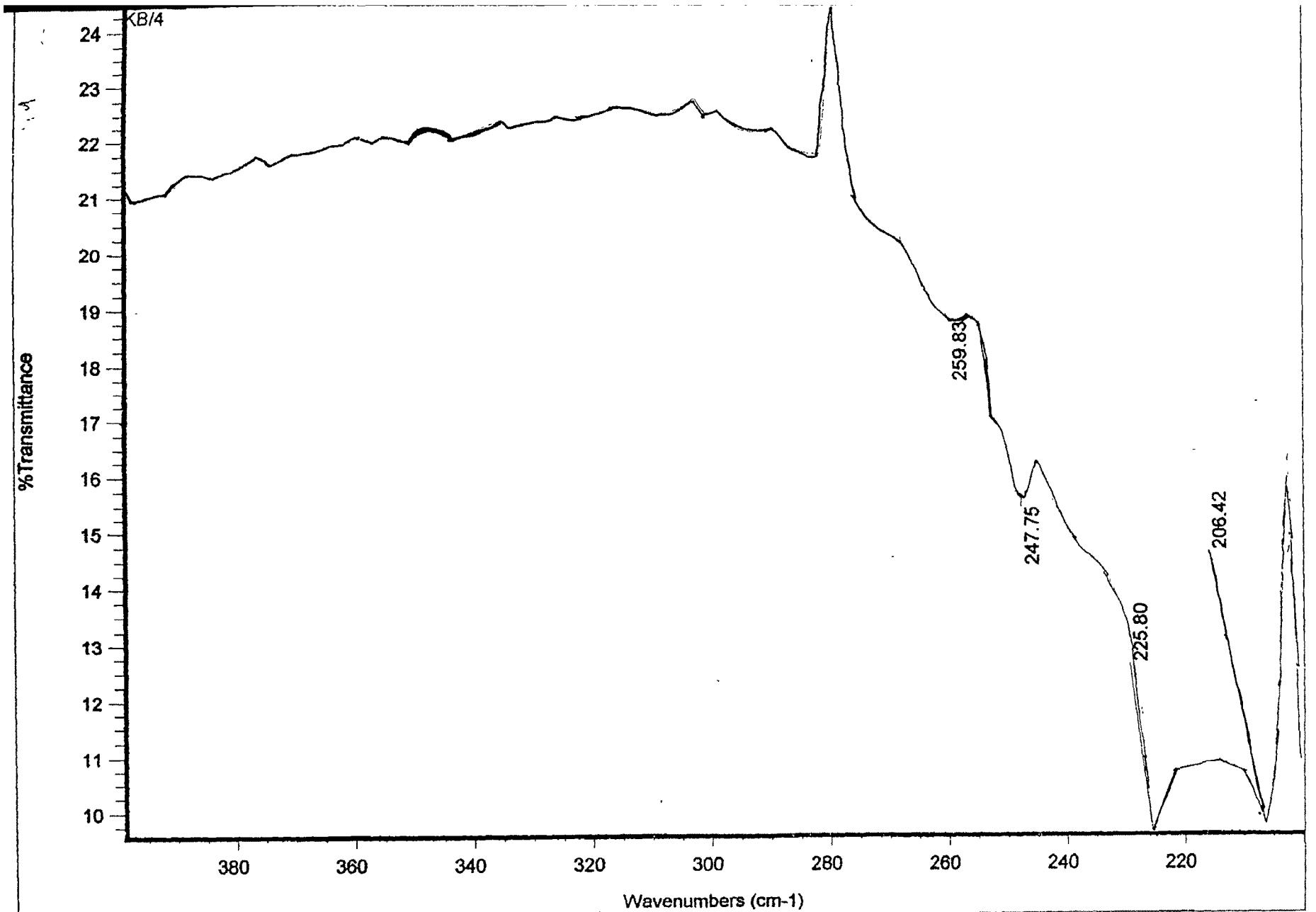


Fig. 3(I) FTIR Spectrum of 14OPDANi(II)

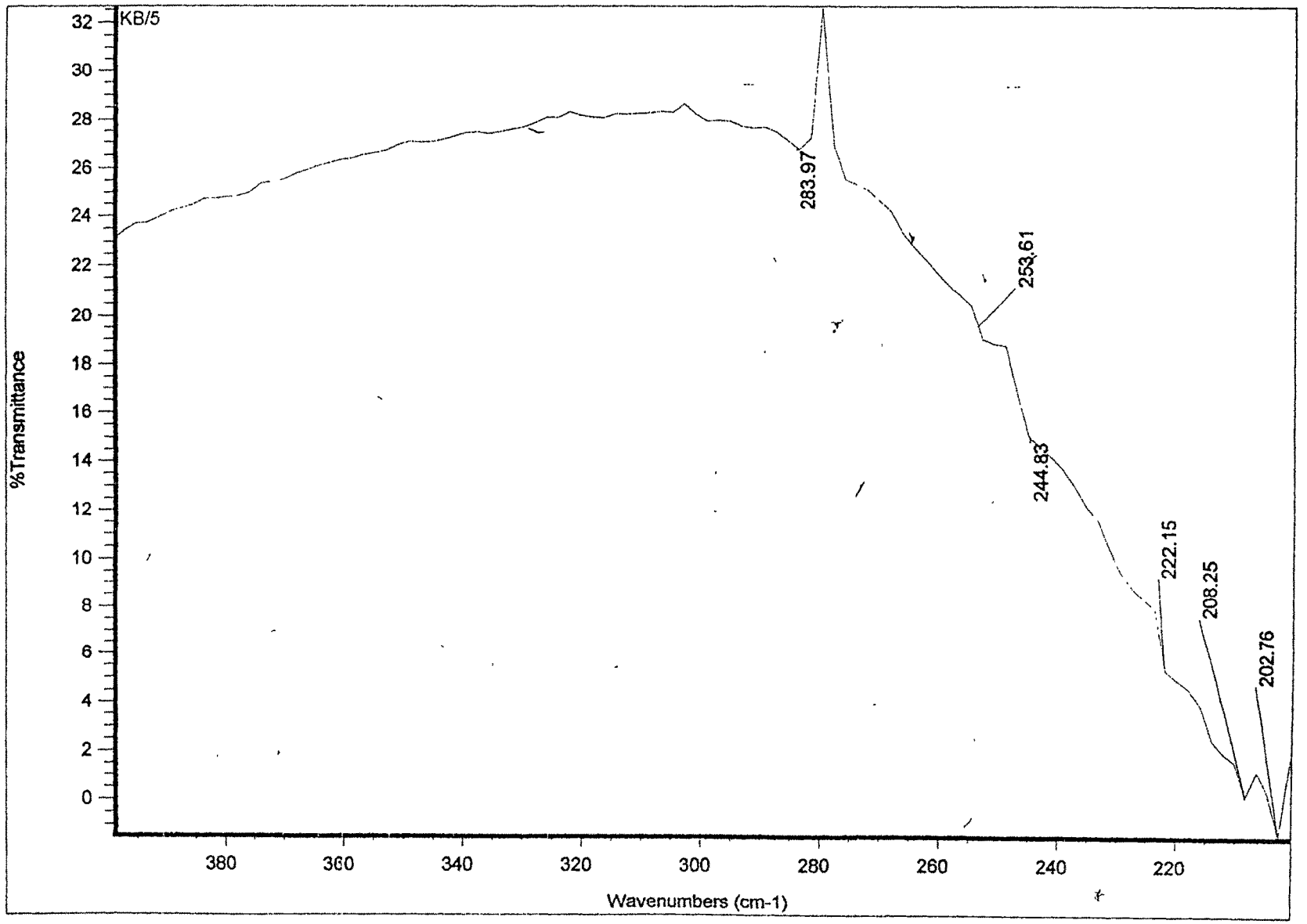


Fig 3(m)FTIR Spectrum of 14PPDAMn(II)

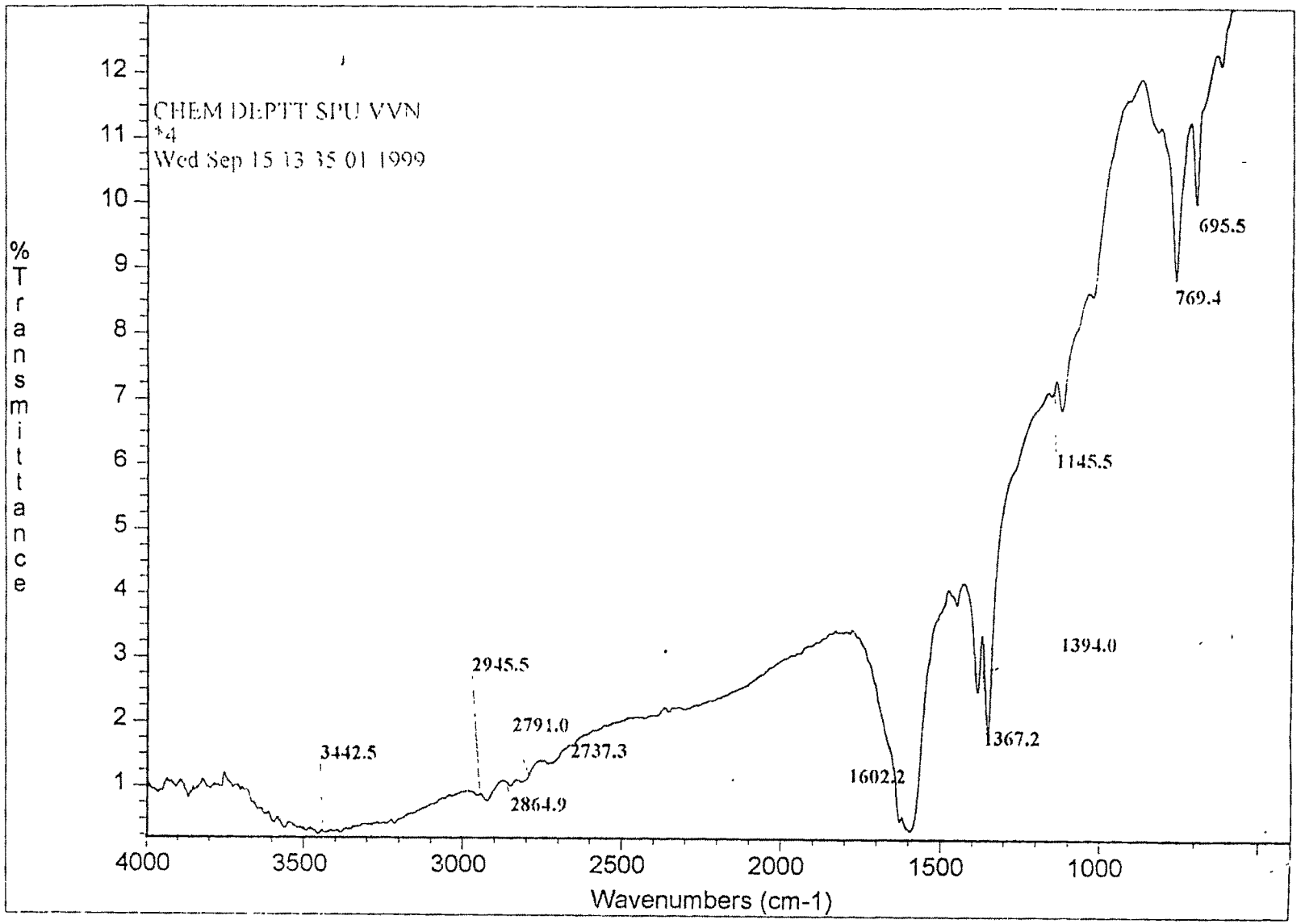


Fig. 3(n) IR Spectrum of 6OPDAMn(II)

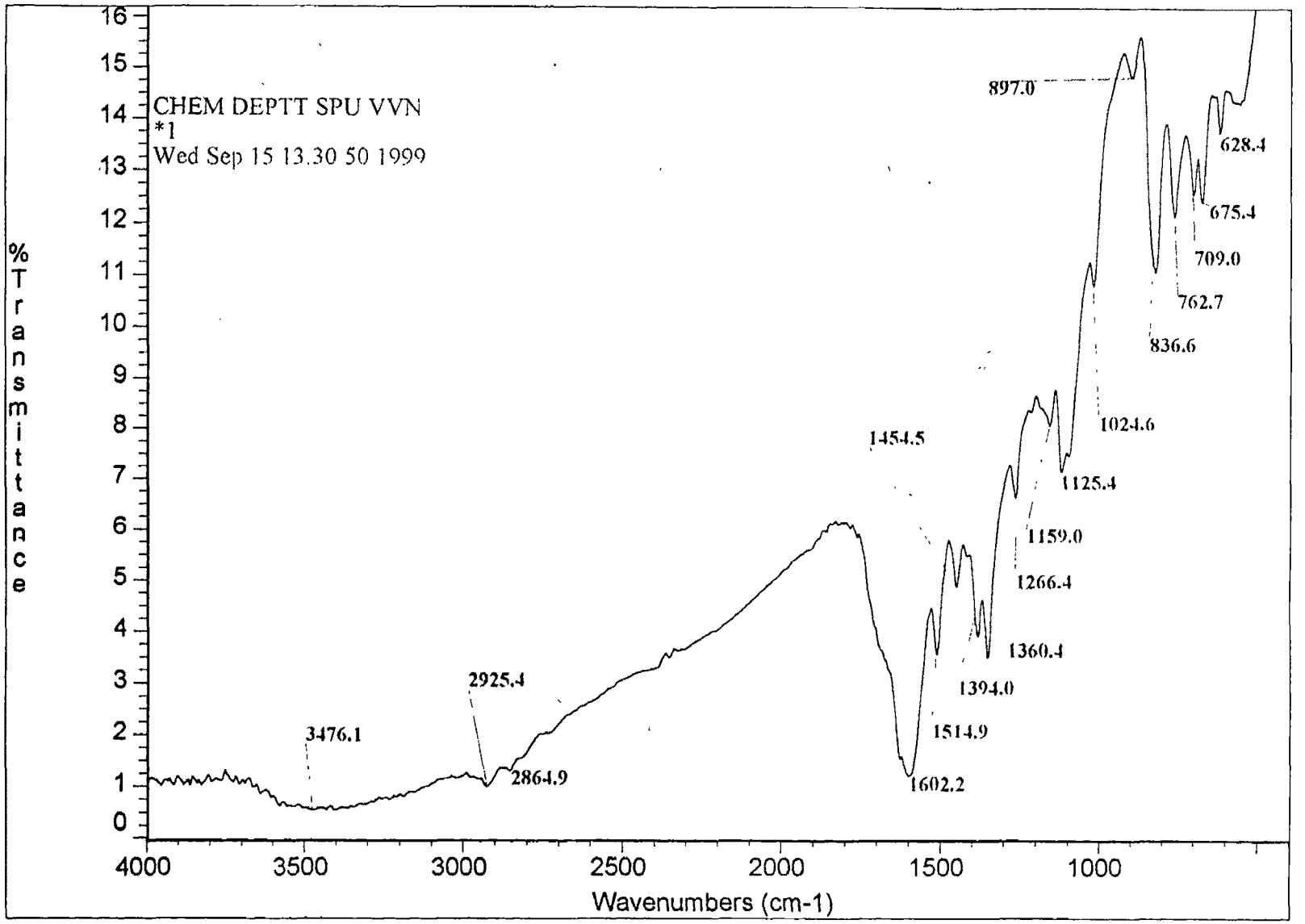


Fig. 3(o) IR Spectrum of 8OPDAMn(II)

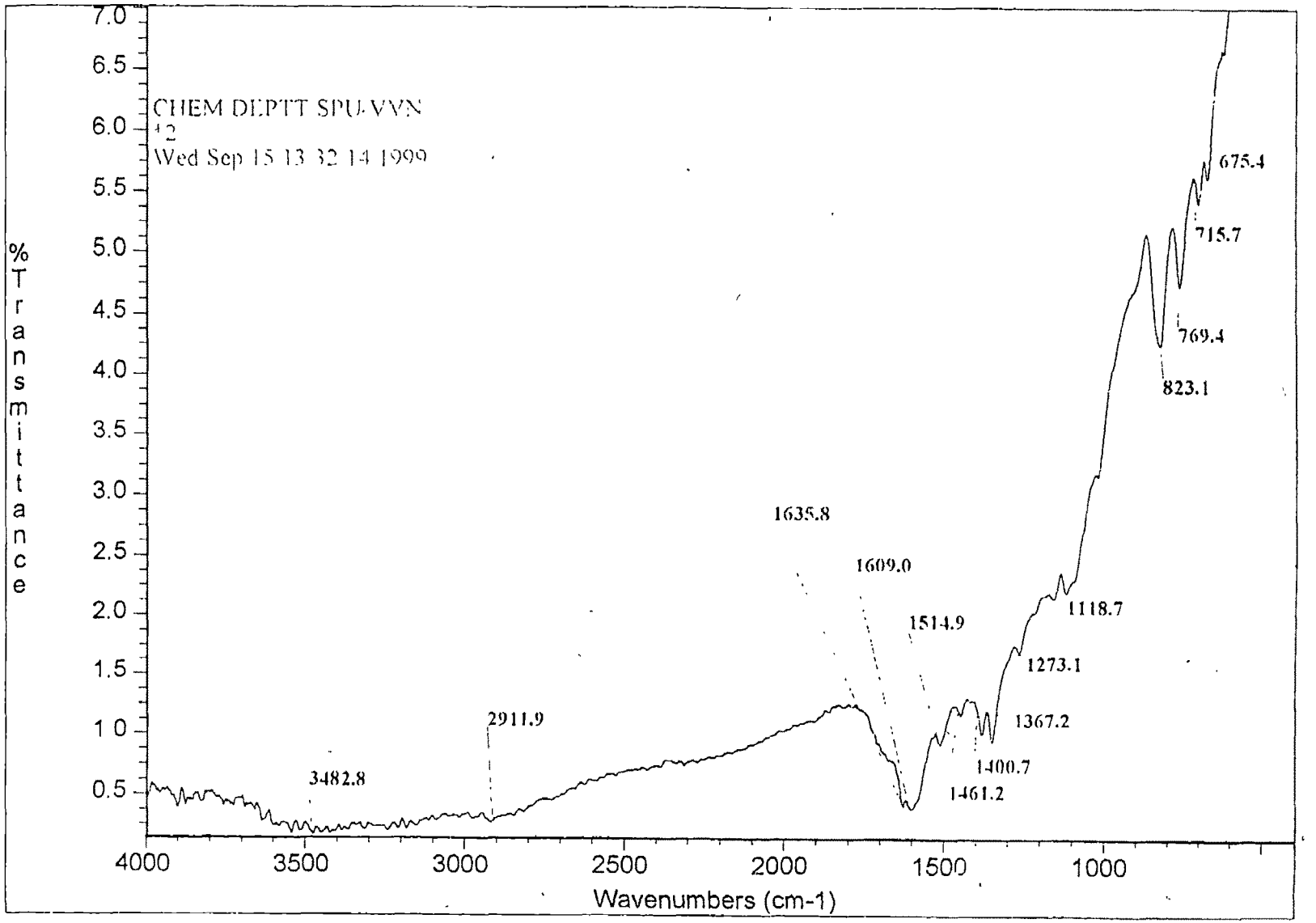


Fig. 3(p) IR Spectrum of 8OPDANi(II)

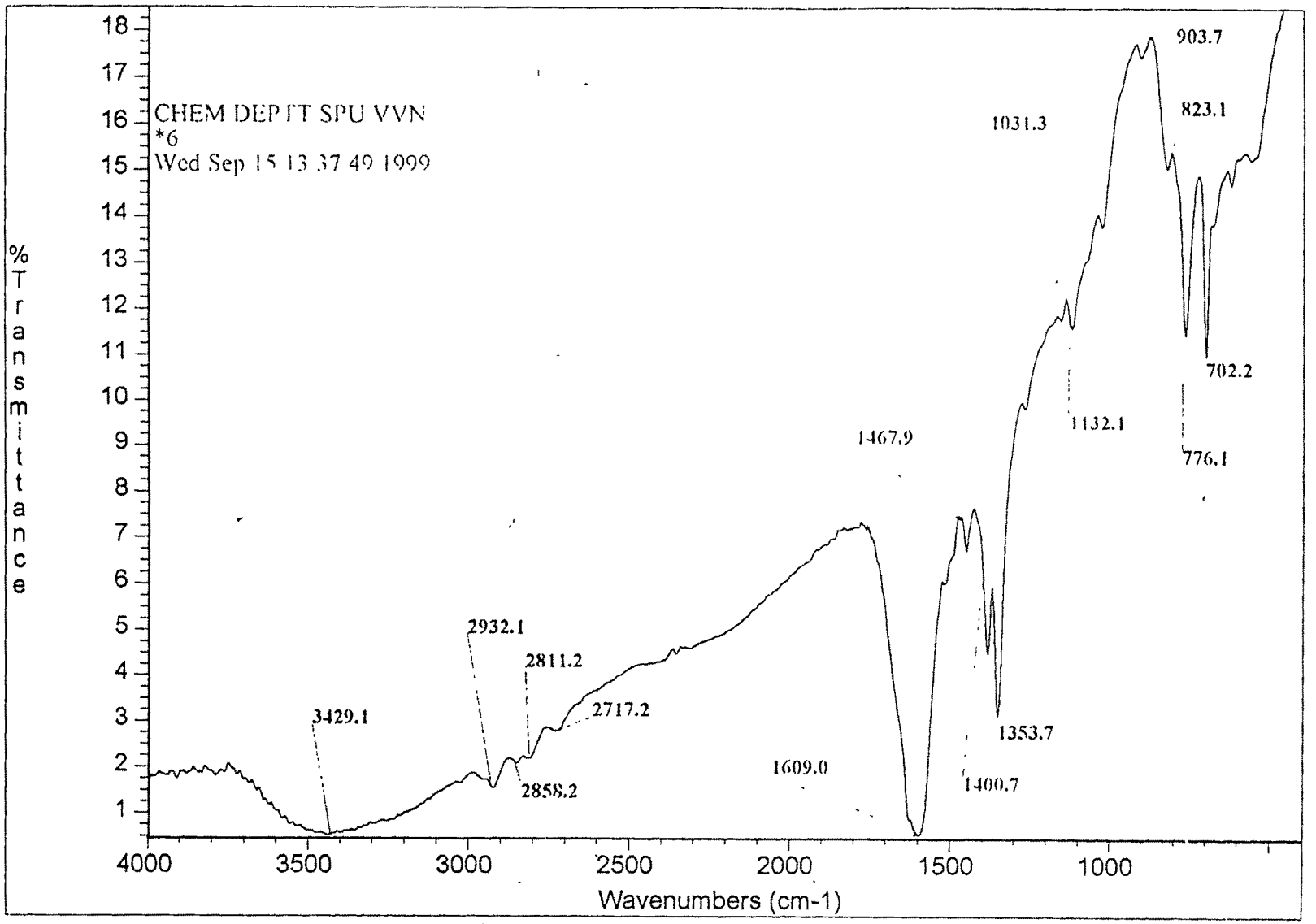


Fig. 3(q) IR Spectrum of 8PPDANi(II)

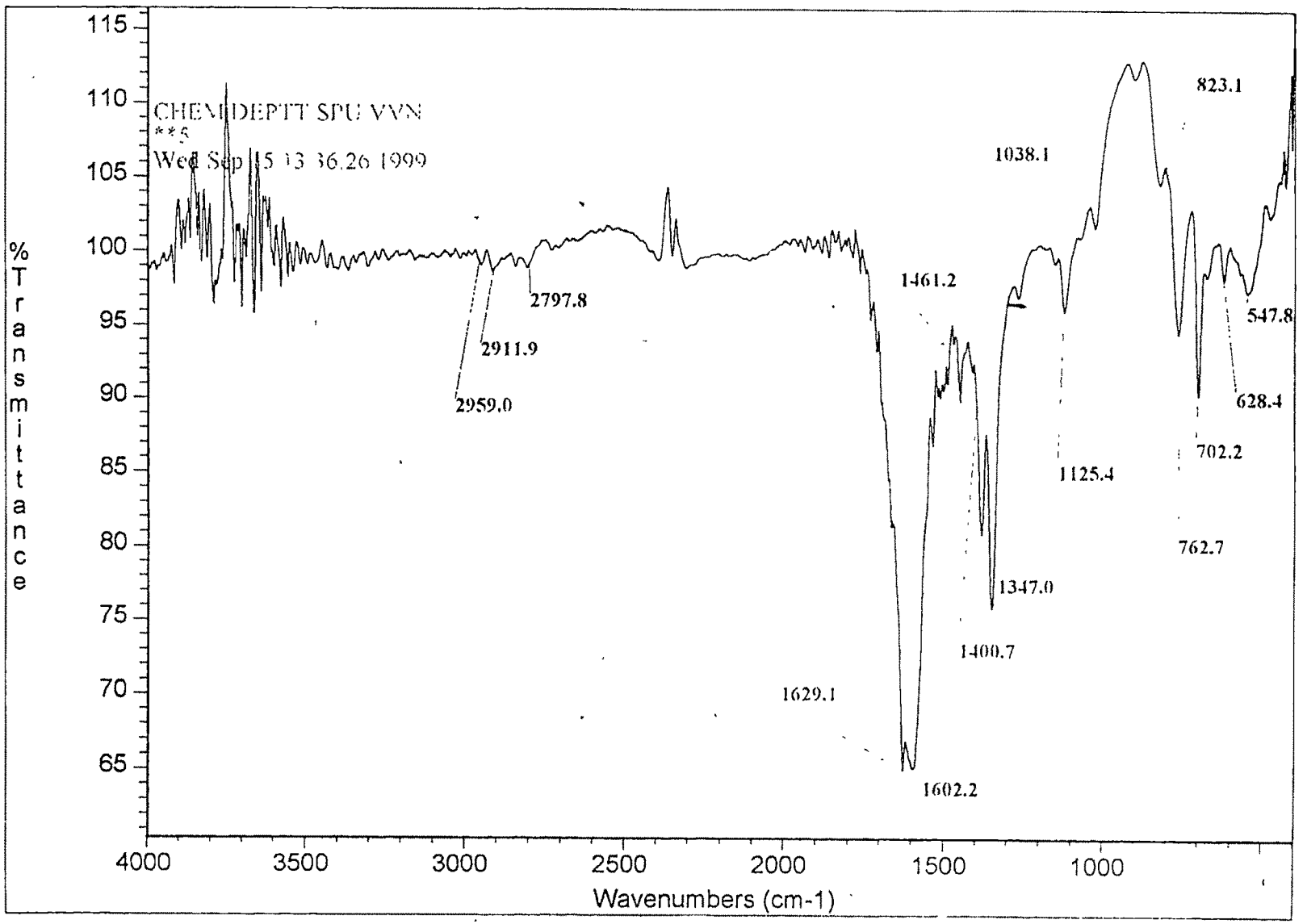


Fig. 3(r) IR Spectrum of 14PPDAMn(II)

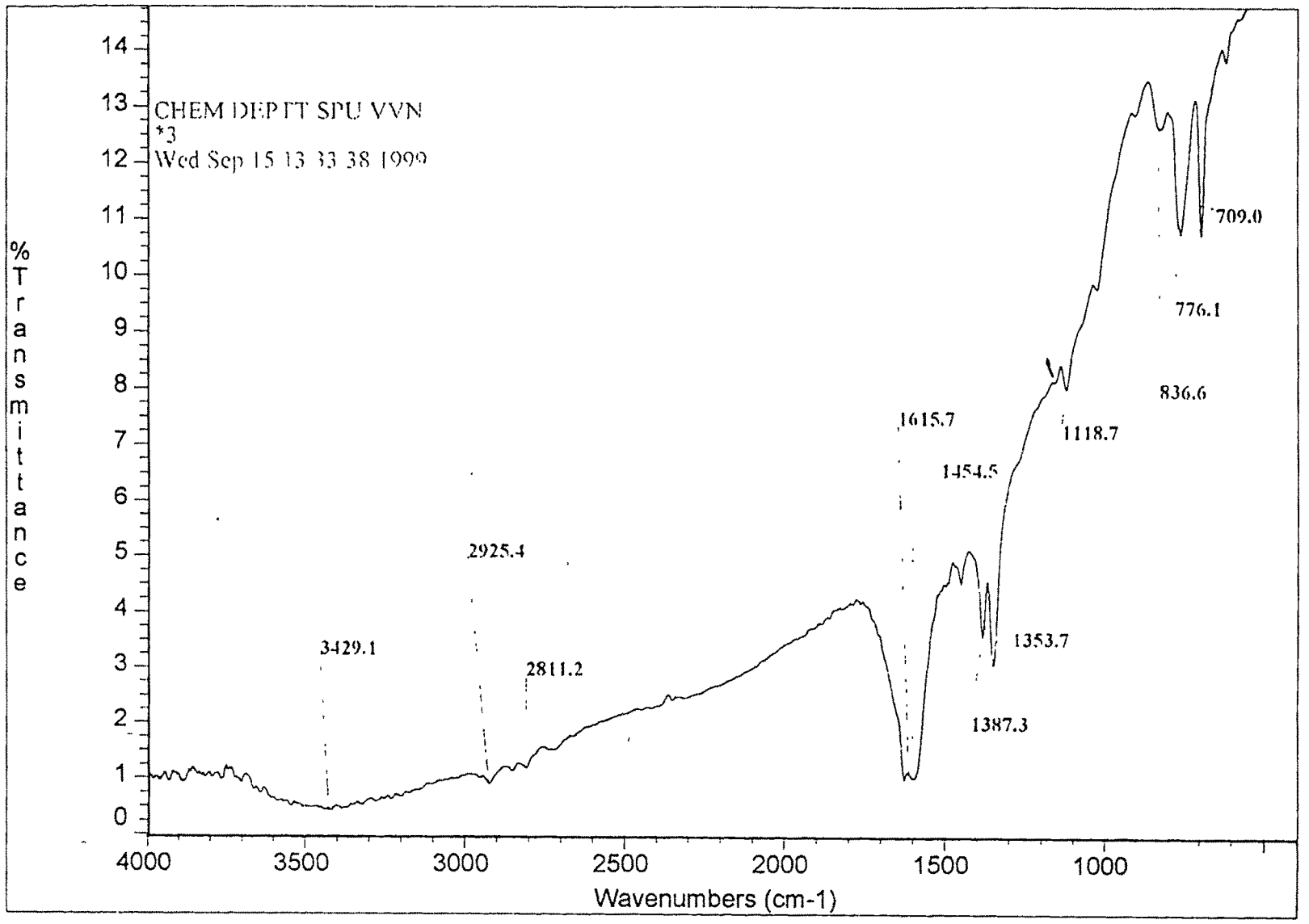


Fig. 3(s) IR Spectrum of 14OPDAMn(II)

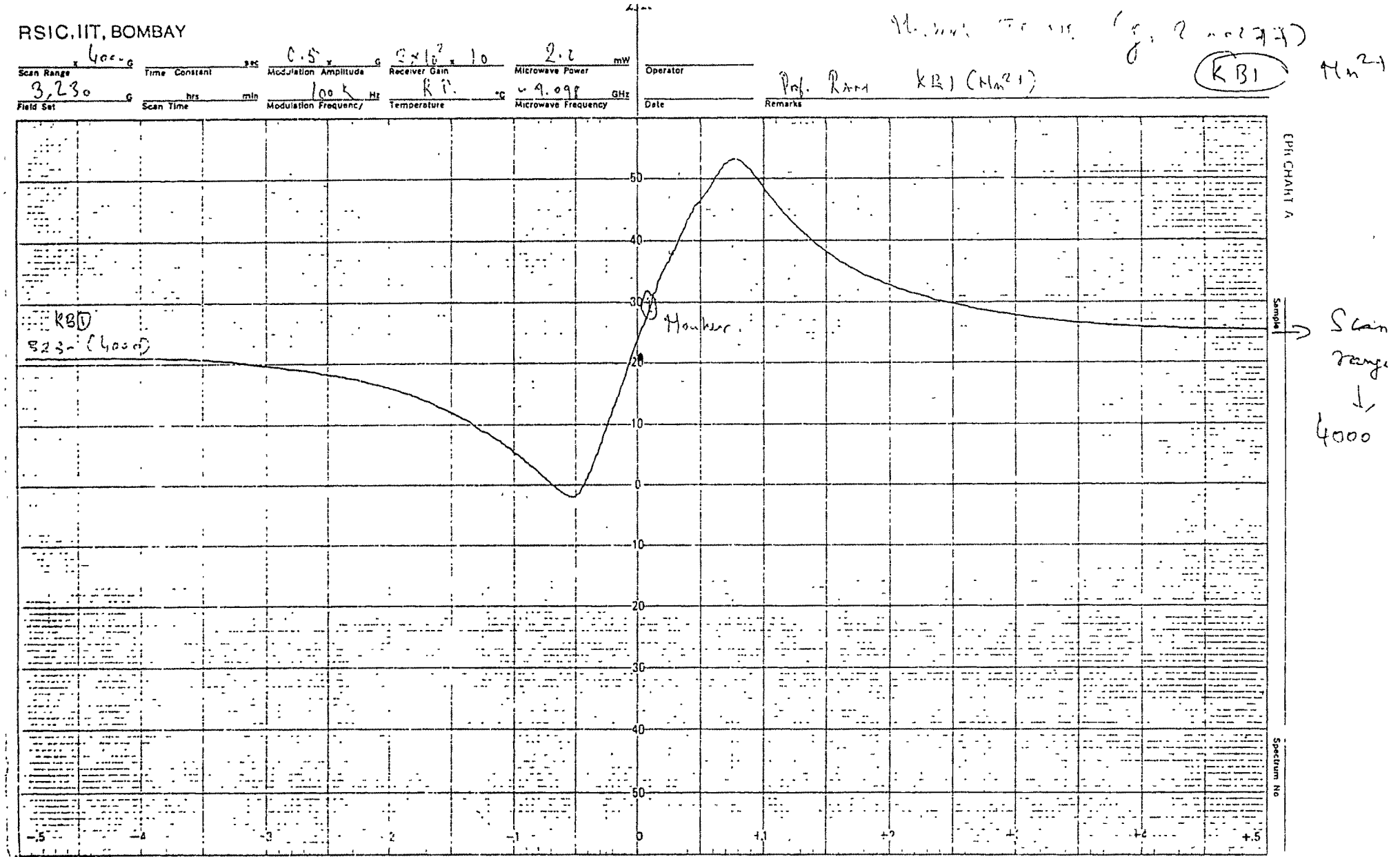


Fig. 3(c) EPR Spectra of 8OPDAMn(II)

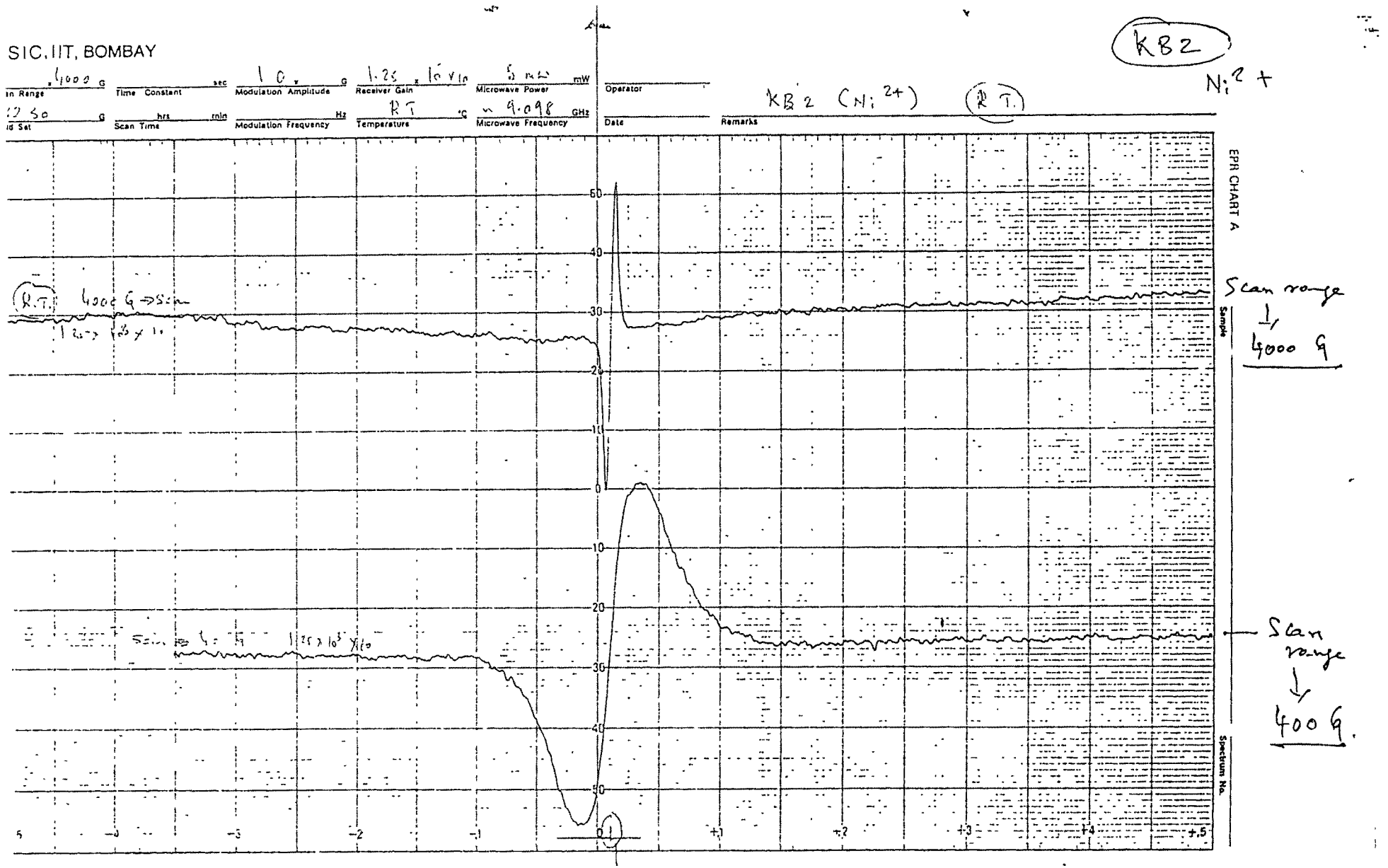


Fig. (3U) EPR Spectra of 8PPDANi(II)

The bond formed between the metal atom and the co-ordinating atom of the ligand molecules & consequently metal - complex formation can be understood by the nature and position of absorption bands.

Absorption spectra of polymeric ligands may change drastically by complex formation. The polymer chain adjacent to co-ordinating group influences the absorption band in the spectra.

FTIR has emerged as fast and sensitive technique which is well suited for catalyst studies. FTIR offers number of advantages over disperse IR. The principal advantage of FTIR over IR lies in the much higher signal to noise ratio obtained by FT techniques[12].

Infra-red and FTIR spectra of polymer bound Manganese and Nickel catalyst are given in fig. (3h to 3s). Infra-red frequencies assignment for the catalyst are summarised in tables 3.7 & 3.8. Metal - oxygen, metal-chlorine, metal-nitrogen bonds are observed.

3.8 Electron-Para Magnetic resonance (EPR) :

The electron paramagnetic resonance (EPR), since its discovery by Zaviosky in 1945, has evolved into a very powerful spectroscopic tool for investigating a variety of physico-chemical problems for systems constitubg paramagnetic species. For conducting EPR investigations, a suitable paramagnetic probe, either intrinsic or extrinsic, would form a part of system and this probe should not preferably perturb the environment. This technique finds wide application in the study of surface species[13-15].

EPR is essential due to transitions between two energy levels of an unpaired electron, corresponding to two spin states in the presence of an external magnetic field. For a free electron, which is not interacting with the surroundings the transition energy is given by

$vh = \Delta E = geHb$

Where h = planck's constant

v = microwave frequency

b = Bohr magneton

H = Strength of external magnetic field

ge = free electron with g valve equal to 2.0023.

Thus, EPR proves to be an ideal method to probe (i) g factor (ii) identification of paramagnetic species and (iii) for the characterization of environmental symmetry of the ion.

EPR has been used extensively to study Cu(II). on poly-4-vinyl pyridine, polymer supported[16] chelating amines and schiff bases[17]. Ti(IV) on Vinyl pyridine divinyl benzene co- polymer.[18] EPR spectra of catalysts and are given in fig. 3t to 3u values of catalysts was found to be + 2.

3.9 Morphology of Polymer bound catalysts (SEM)

Scanning electron microscopy (SEM) used for imaging topography of a solid surface, is based on the analysis of the yield of secondary electrons (coming mostly from the sample surface) or back-scattered electrons (which arise from within the sample, where scattering by heavier atoms is more important) as a fuction of the location of the primary beam with respect to the sample . The contrast arises from the orientation of the surface with respect to the detector.

The catalytic behaviour depends upon the structure and composition of active components as well as morphology of its supporting medium. Morphology of polymer bound catalysts can be observed at a range of magnification (few hundred to few million times) which provides information about the nature of porosity, the nature and the distribution of the active components etc. Comparison of porosity of different supports is also possible.

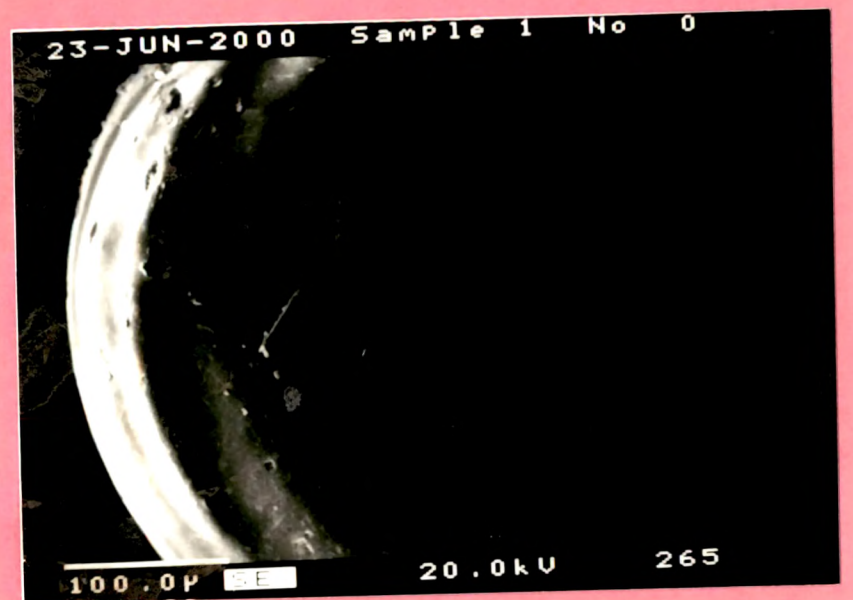
The morphology of polymer supports and catalysts was studied using SEM -

Plate 3.1 : Scanning Electron Micrographs of

(1) 6 % Cross-linked P(S-DVB)

(2) 8% Cross-linked P(S-DVB)

Plate 3.1


23-JUN-2000 Sample 1 No 0
100.0µ
20.0kV
265

23-JUN-2000 Sample 1 No 0
500.0µ
20.0kV
77

23-JUN-2000 Sample 2 No 0
100.0µ
20.0kV
243

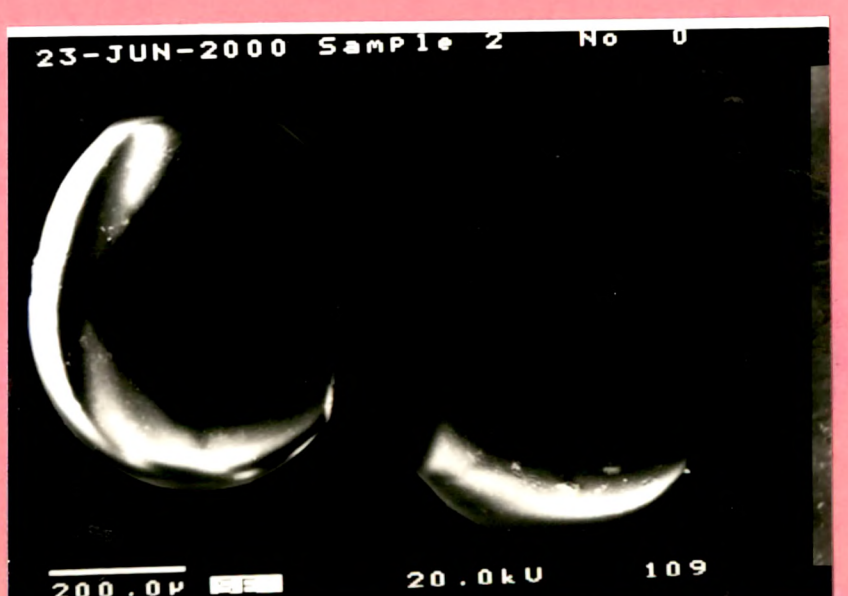

23-JUN-2000 Sample 2 No 0
200.0µ
20.0kV
109

Plate 3.2 : **Scanning Electron Micrographs of**

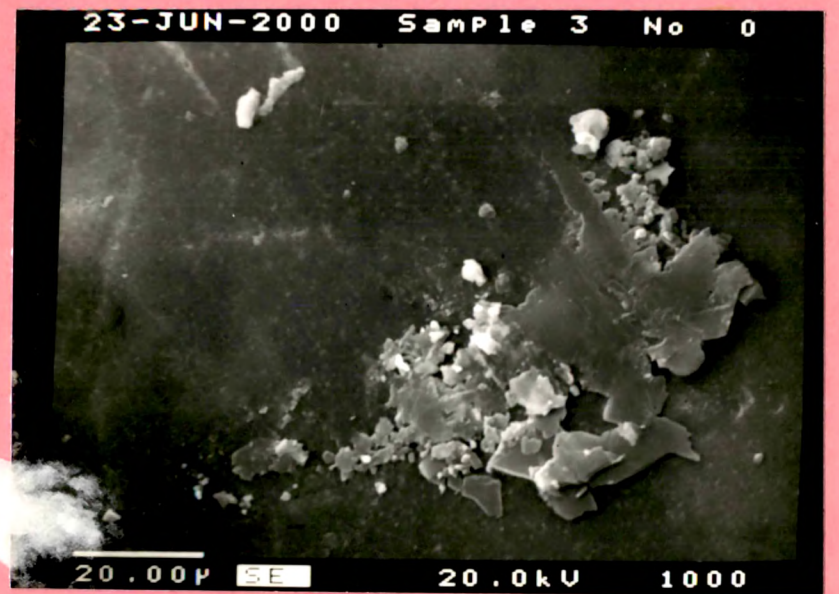
(1) 6OPDAMn(II)

(2) 8PPDANi(II)

(3) 14PPDAMn(II)

(4) 14OPDANi(II)

Plate 3.2


23-JUN-2000 Sample 3 No 0
20.00µ SE 20.0kV 1000

23-JUN-2000 Sample 5 No 0
100.0µ SE 20.0kV 300

23-JUN-2000 Sample 6 No 0
20.00µ SE 20.0kV

Micrographs are given in plates. It was observed that the beads are porous and the texture changes with the change in degree of cross-linking. A change in the shape of polymer beads has been observed after anchoring the metal complexes.

Plate 1 indicates the photograph of 6% cross linked chloromethylated polymer. While plate 2 shows the anchoring of Mn(II) or phenylene diamine. There is a formation of cluster on plate 2. Similar results have also been observed in other cases.

3.10 Thermal Studies

Thermal stability of a catalyst has a direct consequence / impact on its applicability. The change in weight and thermal property of a catalyst Fig. 3u & 3v shows thermogravimetric analysis (TGA) of styrene divinyl benezene co polymer of different cross linking used as polymer supports 6% and 8% cross linked polymer supports are less stable than 14 % cross linked support. The catalysts are thermally stable upto 150°C and then the degradation starts. Initial weight loss found is due to moisture content. After that a decrease was observed due to breaking of the polymers. Since the study was made in the solution phase, the catalysts was used only upto 50°C where it was found to be highly stable with changing experimental conditions and can be used in a variety of studies. In case of polymer - bound metal complex catalysts weight loss or heat change may reveal the stability and phase change as a function of environment.

Thermal stability of homogeneous metal complexes is reported to be enhanced when supported on organic polymer or inorganic oxides. [21] Thermal property of the polymer support vary with the cross linking of the polymer. Thus, determination of thermal behaviour of polymer supports and polymer bound catalysts need investigation in order to know about the limit of catalysts reaction temperature.

Table - 3.4
Swelling of polymer supported metal complexes in different solvents (C.L. 6 %)

Catalyst Solvent	OPDA Mn (II)	OPDA Ni (II)	OPDASB Mn (II)	OPDASB Ni (II)
Water	5.70	5.10	4.95	5.54
Methanol	4.42	4.29	4.25	5.00
Exhanol	3.21	3.35	3.29	4.75
Di-Chloromethane (DCM)	2.10	2.55	2.75	4.38
N-N Dimethyl Formamide (DMF)	1.59	1.72	2.50	4.10
Tetrahydrofuran	1.55	1.58	2.25	3.75
Dioxane	1.29	1.22	2.05	3.10
Acetone	1.10	1.12	1.79	1.85
Benzene	0.90	1.03	1.31	1.15
Cyclonexane	0.72	0.81	1.15	0.75
N Hexane	0.61	0.55	0.75	0.62

Table 3.5
Swelling of polymer supported metal complexes in different solvents (8% Cross-linked)

Catalyst Solvent	OPDA Mn (II)	OPDA Ni (II)	OPDASB Mn (II)	OPDASB Ni (II)
Water	5.52	4.92	4.50	5.30
Methanol	3.92	3.98	3.52	4.75
Exhanol	3.20	3.0	3.10	4.50
Di-Chloromethane (DCM)	2.02	2.10	2.50	4.21
N-N Dimethyl Formamide (DMF)	1.89	1.52	2.25	3.80
Metrahydrofuran	1.42	1.24	2.00	3.30
Dioxane	1.190	1.10	1.75	2.90
Acetone	1.00	1.00	1.50	1 40
Benzene	0.75	0.75	1.00	0.85
Cyclonexane	0.64	0.70	0.75	0.65
N Hexane	0.59	0.45	0.50	0 48

Table - 3.6
Swelling of polymer supported metal complexes in different solvents
(C.L. 14 %)

Catalyst Solvent	OPDA Mn (II)	OPDA Ni (II)	OPDASB Mn (II)	OPDASB Ni (II)
Water	4.50	4.20	4.25	4.75
Methanol	3.49	3.19	3.29	4.50
Exhanol	2.29	2.52	2.75	4.75
Di-Chloromethane (DCM)	1.59	1.70	2.40	4.00
N-N Dimethyl Formamide (DMF)	1 21	1.20	1.97	3.59
Metrahydrofuran	1.12	1.02	1.91	3.15
Dioxane	0.90	0.92	1.55	2.55
Acetone	0.82	0.62	1.25	1.25
Benzene	0.62	0.50	0.85	0.69
Cyclonexane	0.51	0.40	0.51	0.49
N Hexane	0.40	0.25	0.35	0.38

Table - 3.7
Summary of the IR Frequency assignment for the polymer hound O-Phenylene diamine complex

Catalyst	M - CL	M - N	C - H
8 OPDA Mn (II)	222.51	206.05	2911
8 OPDA Ni (II)	247.75	206.42	2903
14 OPDA Mn (II)	252.51	206.05	2925.4
14 OPDA Ni (II)	247.75	206.42	2922

Table - 3.8
Summary of the IR Frequency assignment for the polymer hound p-Phenylene Schiff Base complexes

Catalyst	M - CL	M - N	C - H	M - O	C - N
8 PPDA Mn (II)	247.07	203.12	2925.4	276.29	1602.2
8 PPDA Ni (II)	247.08	208.16	2920	283.97	1610.0
14 PPDA Mn (II)	253.61	202.76	2911.9	283.97	1602.2
14 PPDA Ni (II)	263.12	202.76	2932.	281.77	1609.0

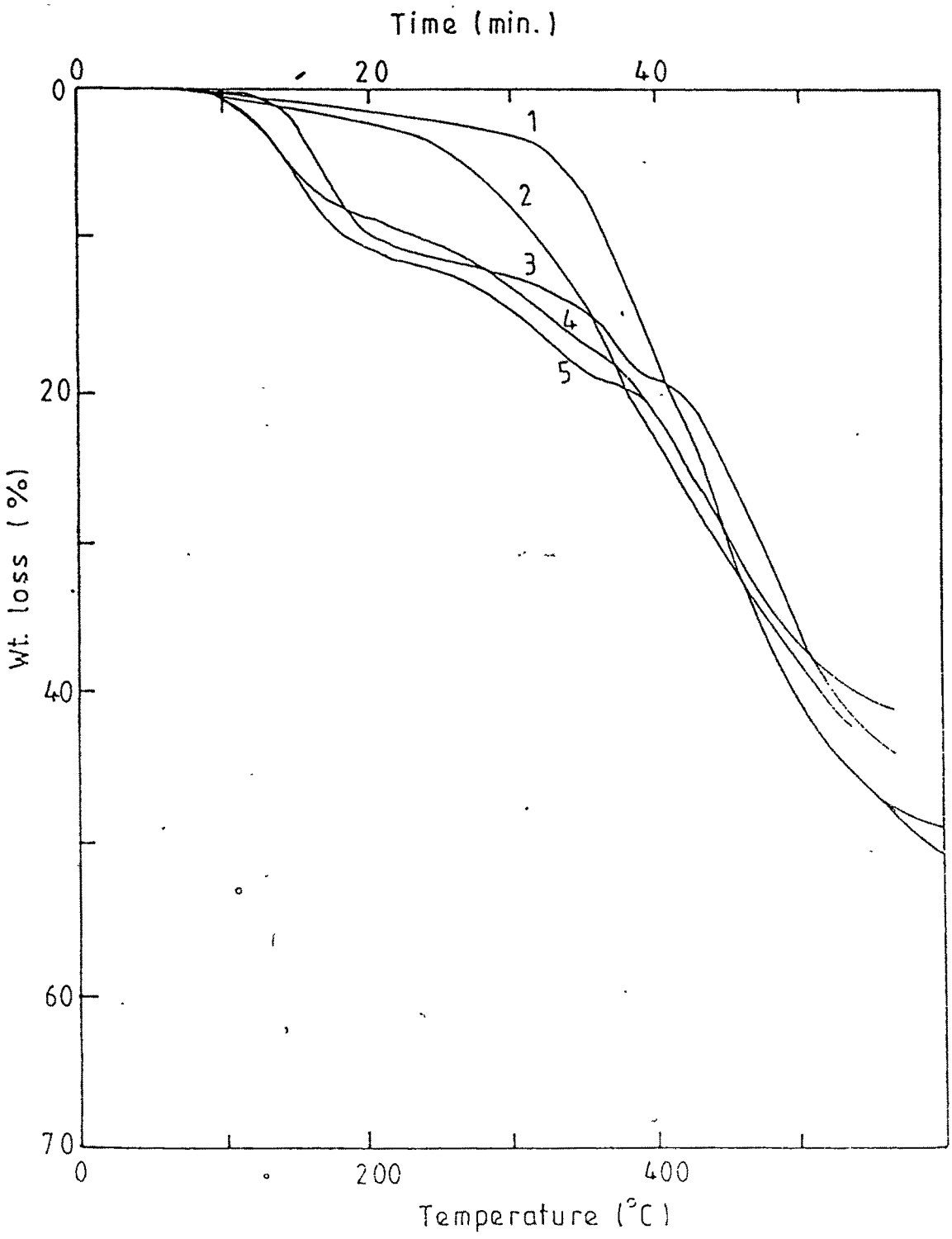


Fig 3(v) Thermogravimetric curves of (1) 8 OPDA Mn (II) (2) 8 PPDA Mn (II) (3) PCS-DVB) 8 % cross-linked (4) 8 OPDA Ni (II) (5) 8 PPDA Ni (II).

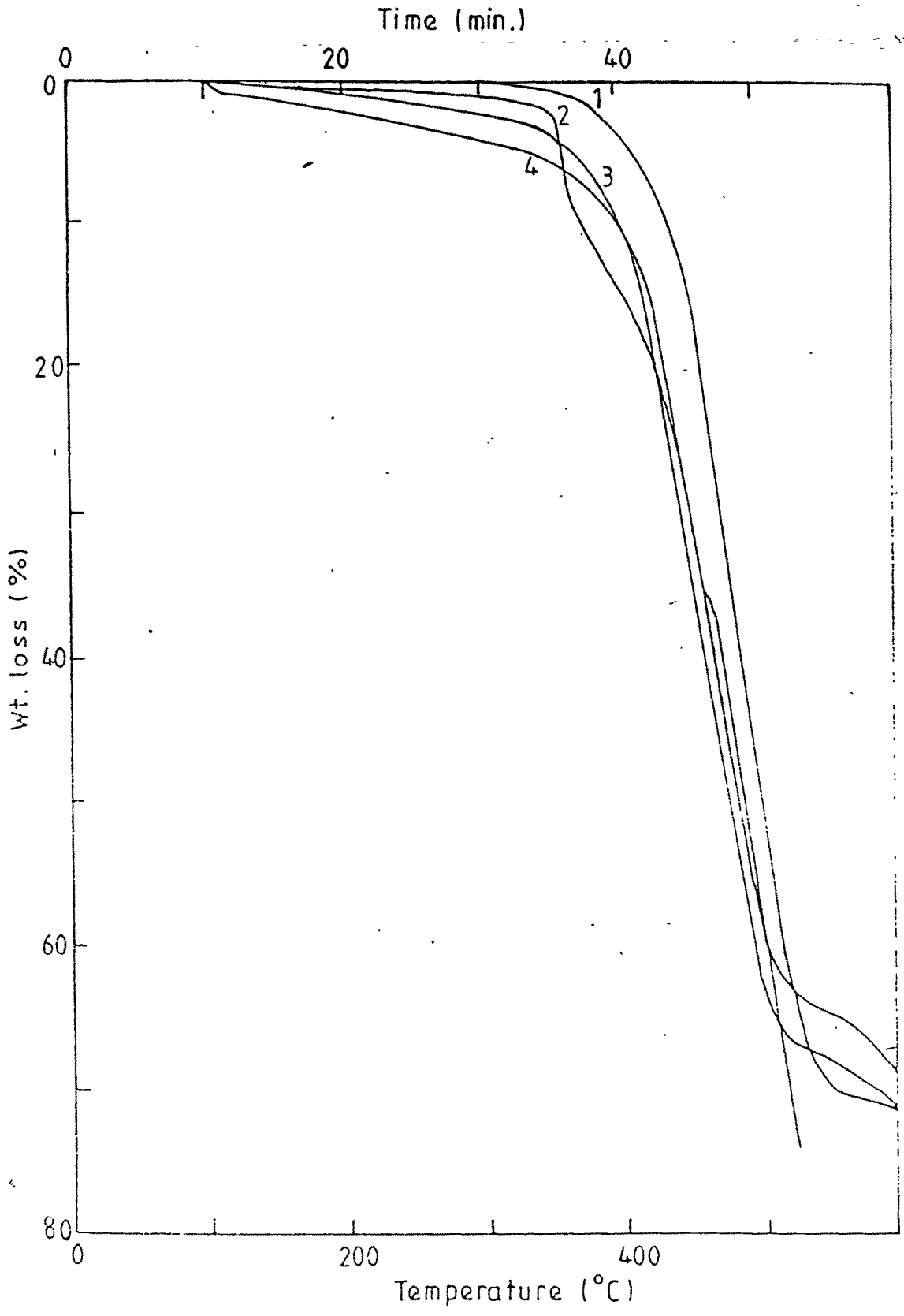
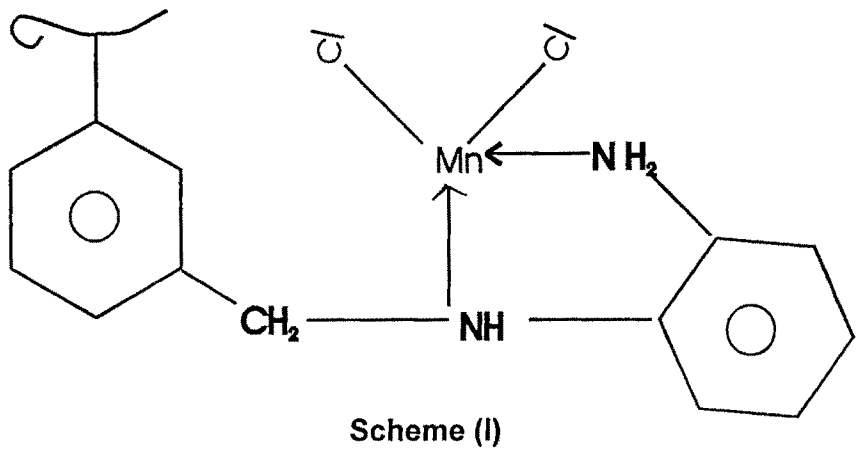
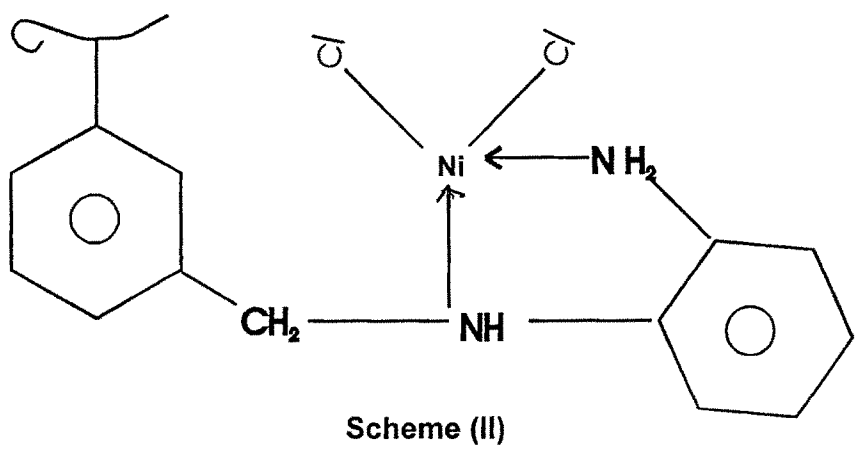


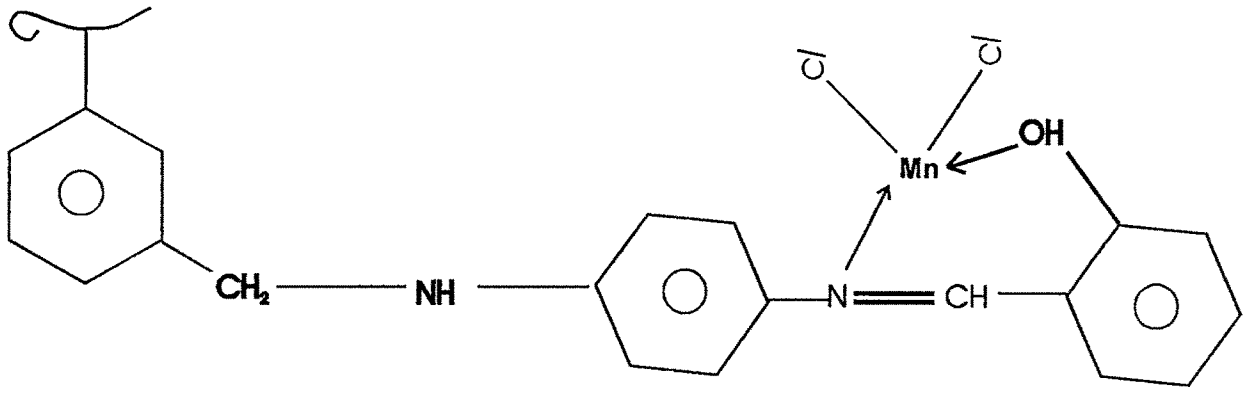
Fig 3(w) Thermogravimetric Curve of (1) 14 OPDA Mn (II) (2) PCS –DVB, 14% cross linked (3) 14 PPDA Mn (II) (4) 14 OPDA Ni (II).



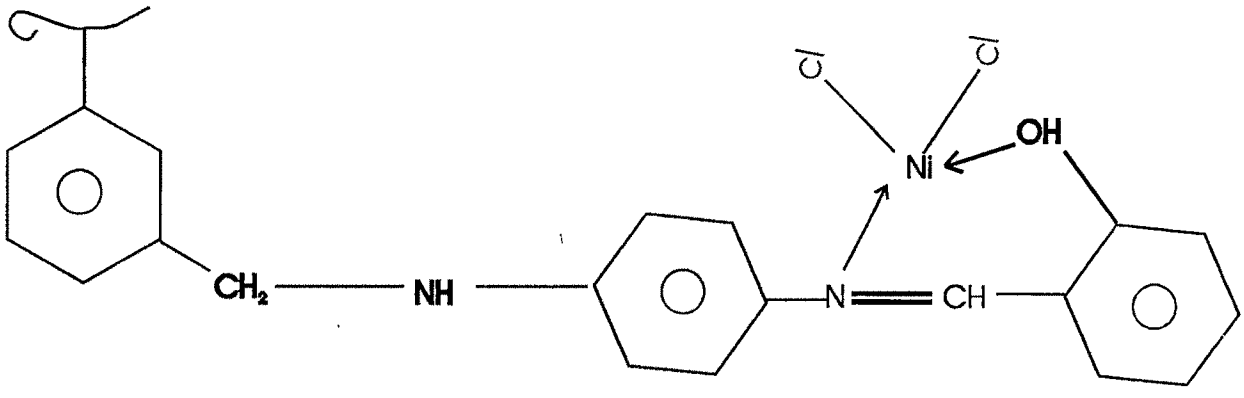
Scheme (I)



Scheme (II)



Scheme (III)



Scheme (IV)

REFERENCES

1. F. Dalanny (Ed) Characterisation of heterogeneous catalysts. Marcel Dekker New-York, 1984.
2. R. Kunin, Ion Exchange Resin John Wiley & Sons Ltd., New York, 1958
3. C. N. Shatterfield, Heterogeneous Catalysis in industrial practice, Mc Graw Hill Inc. New York, 1983
4. D. Gokak, B. V. Kamath and R. N. Ram, J. Appl. Polymer Sci. 35, 1523, 1988.
5. D. I. Gokak, B. V. Kamath and R. N. Ram Ractive polymers, 10, 37, 1989
6. J. N Shah and R. N. Ram J. Mol. Catal, 77, 235, 1992.
7. T. Teranishi and N. Toshimg, J. Chem, Soc, Dalton Tans, 2967, 1994
8. F. R. Hartley, Supported Metal complexes, D. Reidel Dordrecht, 1985.
9. H. J. Mencer and Z Gomzi, European polymer J. 30, 33, 1994.
10. B. Erman and P.J. Flory macromolecules 129, 2342, 1986.
11. G. Kortom, Reflectance spectroscopy, principles, Methods and applications squanger verlag bertin 1965.
12. R.P. Graffiths and J.R. Delta seth, fourier transformer infrared spectrometry, wilegs interscience, New York 1986.
13. J. Reed, P.E.L. Senberger, B. K. Teo and B.M. Kinchaid, J. Am-Chem. Soci., 100, 2375, 1978.
14. A. I. Kokonn and K.I. Zamaraev, Proc 17th Int. Co-ord, Chem. Conf. Hemburg, 238, 1976.
15. R. S. Drago J. Gaul. A. Zaombeck and D. K. Straug, J. Amer. Chem. Soc., 102(3), 1033, 1980.
16. Y. Chimura, M. Beppu's, Yoshida and K. Tarama Bull Chem. Soc. Japan, 50, 691, 1977.
17. S. Sasaki, Y. Yanase, N Hagiwala T. Takeshila, H. Naganuma, A Ohyosh and Kohkubo. J. Phys. Chem. Soc. 86, 1038, 1982.
18. M. M. Taqir Khan, D. Srinivas R. I. Kureshy and N. H. Khan, inorg Chem. 29, 2326, 1990.
19. N. L. Holy J. org. Chem., 44, 239, 1979.