Materials and Methods

3.1 Reagents

4-Vinyl pyridine, styrene and divinyl benzene (DVB) used were commercial products obtained from Sigma Chemical Company, USA. 2,4-Dihydroxy benzaldehyde used for hooking Schiff-base on polymer support is obtained from Aldrich Chemical Company, USA. Solvents used were commercially available sample and were purified by known procedures. Metal salts used were BDH grade and used as such. All the low molecular weight compounds used were commercially available and were purified by literature procedures. All other reagents used were prepared by standard methods.

3.2 Spectral methods

The following instruments were used for investigation.

1. Shimadzu IR-470 infrared spectrophotometer operating in the range 4000-400 cm^{-1}. Well dried very pure potassium bromide is used for making KBr pellets with samples.
2. The solid state electronic spectra were recorded on a carry-2390 UV-VIS near IR spectrophotometer.
3. ESR spectra of all the paramagnetic compounds were recorded in IIT, Bombay and from Physics Department of Aligarh Muslim University. The measurements were carried out for solid samples at room temperature.

4. The TG analysis of the polymer metal complexes were carried out using TGA-7 thermal analyser. The analysis were carried out in nitrogen atmosphere at a heating rate of 10°C per minute.
5. C, H, N analysis obtained from RSIC of IIT, Madras.

3.3 Experimental

3.3.1 Polymer supports

(a) 2% DVB-crosslinked polystyrene

The monomer styrene and DVB were washed with 1% sodium hydroxide solution (30 ml, 3 times) and with water to remove the inhibitor. Polyvinyl alcohol (PVA) (0.3 g, mol. wt. 72000) was added to water (300 ml) at 80°C and stirred until dissolution. A mixture of styrene (10.2 g) and DVB (0.52 g) was dissolved in toluene (10 ml) and added to PVA solution. Benzoyl peroxide (6.2 g) was added and the mixture was heated at 80°C with mechanical stirring for 8 h. The polymer was kept overnight, filtered, washed with hot water, methanol, chloroform, benzene and finally with acetone. The resin was dried in air oven at 70°C. IR (KBr) spectrum gives 1600 cm^{-1} (C=C) and 2900 cm^{-1} C-H.

(b) 2% DVB-crosslinked chloromethyl polystyrene (A-Cl)

Polystyrene (3g) was allowed to swell in dichloromethane (50 ml). Stannic chloride (7 g) was added to a well-stirred mixture of polymer beads in dichloromethane and chloromethyl methyl ether at 0°C. The temperature was allowed to rise up to room temperature during a period of one hour. The mixture was stirred for 50 h. The resin was collected by filtration and washed with dioxane, water, 0.4N HCl, water, methanol and finally with dichloromethane. Then it was dried in an air oven at 60°C. IR (KBr) gives an absorption at 780 cm^{-1} (C-Cl).

(c) Anchoring ethylene diamine on chloromethyl polystyrene

2% DVB-crosslinked chloromethyl polystyrene (10 g) was suspended in dioxane (100 ml) for 3 h. Five fold molar excess of ethylene diamine (14 ml) and pyridine (34 ml) was added. The mixture was heated with stirring under reflux at 100°C for 9 h. The reaction mixture was filtered, washed with water, dioxane and ethanol and then dried in vacuum. Test with ninhydrin reagent showed deep blue colour indicating the presence of amino group on the polymer.

(d) Preparation of aminomethyl polystyrene from 2% DVB-crosslinked chloromethyl polystyrene

Chlorine function on the polystyrene support was substituted by amino functions by Gabriel's phthalimide synthesis. The method adopted is described in chapter 4.

(e) Anchoring 2,4-dihydroxy benzaldehyde on DVB-crosslinked chloromethyl polystyrene

An orthohydroxy benzaldehyde function was attached on chloromethyl polystyrene by anchoring 2,4-dihydroxy benzaldehyde on the support. This is used for synthesising polymer supported Schiff-bases. Polymer is attached through carbon atom of azomethine group. 5 g of DVB-crosslinked chloromethyl polystyrene was taken in 150 ml of DMF and it was kept for three hours. A solution of 2.76 g (20 mmol) of 2,4-dihydroxy benzaldehyde in 25 ml DMF was then poured into the above solution and the mixture was heated at 110°C with 2 ml of pyridine with constant stirring for six hours. The resin was then repeatedly washed with hot DMF, methyl alcohol, ehtyl alcohol and finally with acetone and dried in an oven at 100°C. This polymer supported aldehyde **A(3)**H was employed for preparing a variety of Schiff-bases by reacting the polymer support with appropriate primary amine.

(f) Synthesis of Schiff-base anchored polymer support

Aminomethyl polystyrene was condensed with three different orthohydroxy benzaldehydes to synthesise SB anchored polymer supports. These aldehydes were salicylaldehyde, 2-hydroxy naphthalene 1-carbaldehyde, and 2,4-dihydroxy benzaldehyde. Details of the synthesis is presented in chapter 4.

(g) Synthesis of tetradentate Schiff-base supported on polymer matrix

Two different tetradentate Schiff-bases were prepared in a view to generate it on chloromethyl polystyrene. One tetradentate Schiff-base is that formed by the condensation of 2,4-dihydroxy benzaldehyde with ethylene diamine and the second is by the condensation of 2,4-dihydroxy benzaldehyde with O-phenylene diamine. Details of the method adopted for the synthesis are given in chapter 4.

(h) Preparation of DVB-crosslinked poly(4-vinyl pyridine)

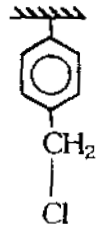
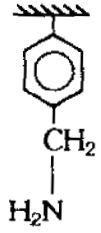
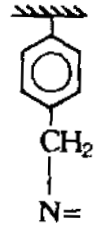
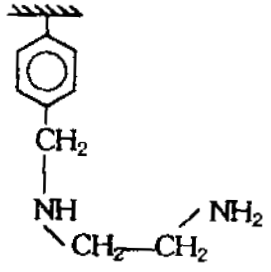
Monomers were purified by distillation under reduced pressure immediately before use. The distilled monomers were washed with 1% solution of NaOH to remove stabilisers. The monomers were redistilled and dried over anhydrous Na_2SO_4 or $MgSO_4$.

2.4 g of polyvinyl alcohol was dissolved in 550 ml of boiling distilled water and the solution was taken in a 2L round-bottom flask fitted with a reflux condenser, nitrogen at 80°C and a solution of 4-vinyl pyridine (25 g) and DVB in toluene (50 ml) were added. After the addition of 1 g of AIBN the polymerisation was allowed to take place under constant vigorous stirring. The polymer beads start to appear rapidly. The mixture was kept at 80°C overnight. After cooling, the resin beads were collected by filtration through a sintered glass funnel and washed extensively with water, acetone, ether, dichloromethane, and

finally with methanol. After drying under vacuum 25 g of white resin beads were obtained.

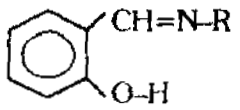
3.4 Polymer supports and metallated species—Abbreviations used

(a) Polymer supports

Polymer supports	Name	Abbreviation
	DVB-crosslinked chloromethyl polystyrene	**A**-Cl
	DVB-crosslinked aminomethyl polystyrene	**B**-H_2 or **C**
		**B**
	DVB-crosslinked poly(4-vinyl pyridine)	**D**
	Ethylene diamine supported chloromethyl polystyrene	**E**

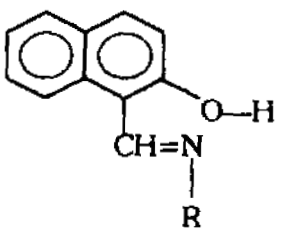
(b) Metal complexes and their abbreviations

Complexes using salicylaldehyde Schiff-base



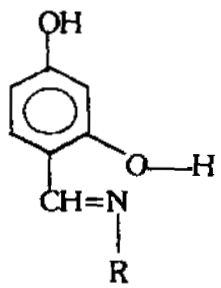
R	Representation of the ligand	Representation of metal complexes (M^{2+})
CH_3–	**11**H	M(**11**)$_2$
C_2H_5–	**12**H	M(**12**)$_2$
C_4H_9–	**13**H	M(**13**)$_2$
C_6H_5–	**14**H	M(**14**)$_2$
pCH_3–C_6H_4–	**15**H	M(**15**)$_2$
pCl–C_6H_4–	**16**H	M(**16**)$_2$
pBr–C_6H_4–	**17**H	M(**17**)$_2$
H	**18**H	M(**18**)$_2$
OH	**19**H	M(**19**)$_2$
$C_6H_5CH_2$–	**28**H	M(**28**)$_2$

(c) Complexes using SBs from 2-hydroxy naphthalene-1-carbaldehyde



R	Representation of the ligand	Representation of metal complexes (M^{2+})
CH_3–	**21**H	M(**21**)$_2$
C_2H_5–	**22**H	M(**22**)$_2$
C_4H_9–	**23**H	M(**23**)$_2$
C_6H_5–	**24**H	M(**24**)$_2$
pCH_3–C_6H_4–	**25**H	M(**25**)$_2$
pCl–C_6H_4–	**26**H	M(**26**)$_2$
pBr–C_6H_4–	**27**H	M(**27**)$_2$

(d) Complexes using SBs from 2,4-dihydroxy benzaldehyde



R	Representation of the ligand	Representation of metal complexes (M^{2+})
CH_3–	**31**H	M(**31**)$_2$
C_2H_5–	**32**H	M(**32**)$_2$
C_4H_9–	**33**H	M(**33**)$_2$
C_6H_5–CH_2	**34**H	M(**34**)$_2$

(e) Abbreviation of some other complexes

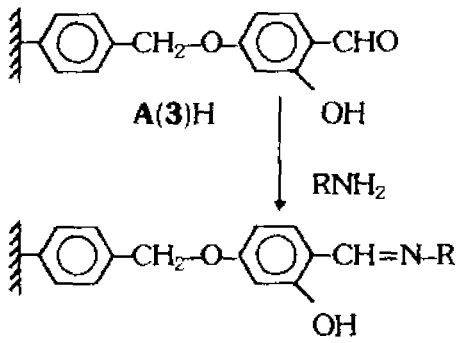
Complex	Abbreviation of complex (M^{2+})	Ligand devoid of active hydrogen (s)
Metal dimethyl glyoximate	M(**35**)$_2$	**35**
Metal acetyl acetonate	M(**45**)$_2$	**45**
Metal 8-hydroxy quinolinate	M(**55**)$_2$	**55**
Metal benzoyl acetonate	M(**65**)$_2$	**65**
Metal salen	M(**50**)	**50**
Metal salphen	M(**60**)	**60**
Metal napen	M(**70**)	**70**
Metal naphen	M(**80**)	**80**
Metal ethylene diamine acetylacetonate	M(**88**)	**88**
Metal ethylene diamine benzoylacetonate	M(**98**)	**98**
Metal 2-mercaptobenzothaizolate	M(**75**)$_2$	**75**
Metal 2-mercaptobenzimidazolate	M(**85**)$_2$	**85**
Metal 2-mercaptobenzoxazolate	M(**95**)$_2$	**95**

(f) Short name of SBs used

Aldehyde	Diamine	Name of SB used
Salicylaldehyde	Ethylene diamine	Salen
Salicylaldehyde	O-phenylene diamine	Salphen
2-Hydroxy naphthalene 1-carbaldehyde	Ethylene diamine	Napen
2-Hydroxy naphthalene 1-carbaldehyde	O-phenylene diamine	Naphen

(g) Polymer-supported Schiff-bases—polymer attached through C-atom

Bidentate ligand generated on polymer-support by anchoring 2,4-dihydroxy benzaldehyde on **A**-Cl.

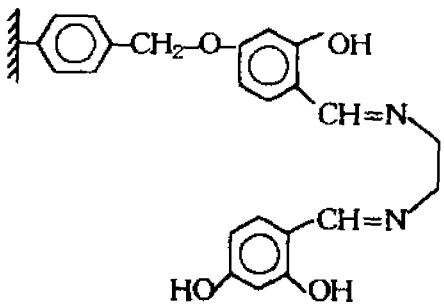


SB anchored PS formed

R	Abbreviation of SB anchored support	Abbreviation of metallated polymer support. MX_2 is used for metallation
CH_3–	**A(4)**H	**A(4)**MX
C_2H_5–	**A(5)**H	**A(5)**MX
C_4H_9–	**A(6)**H	**A(6)**MX
C_6H_5–	**A(7)**H	**A(7)**MX
pCH_3–C_6H_4–	**A(8)**H	**A(8)**MX
pCl–C_6H_4–	**A(9)**H	**A(9)**MX

X is uninegative anion.

Tetradentate ligand generated on polymer-support by anchoring SB (ethylene diamine and 2,4-dihydroxy benzaldehyde) on **A**Cl.



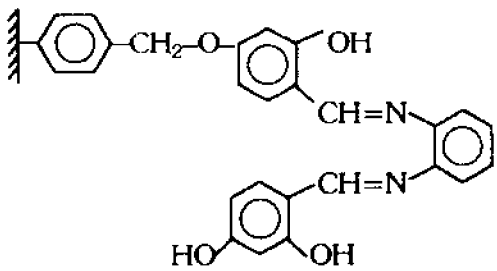
A(1)H_2

Representation of metallated support

A(1)M_2X_2 or **A(1)**M

X is uninegative ion.

Tetradentate ligand generated on polymer support by anchoring SB (O-phenylene diamine and 2,4-dihydroxy benzaldehyde) on **A**Cl.

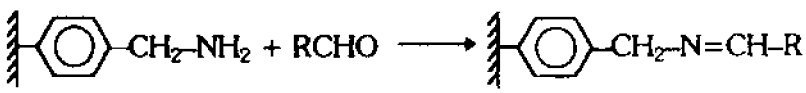


A(2)H_2

Representation of metallated support

A(2)M_2X_2 or **A(2)**M.

(h) Polymer supported Schiff-bases—Polymer attached through N atom



BH_2 Aldehyde Polymer supported SB

Name of aldehyde used	Abbreviation of SB anchored PS	Abbreviation of metallated PS. MX_2 salt is used
Salicylaldehyde	**B(10)**H	**B(10)**MX
2-Hydroxy naphthalene 1-carbaldehyde	**B(20)**H	**B(20)**MX
2,4-Dihydroxy benzaldehyde	**B(30)**H	**B(30)**MX

X is uninegative anion.

(i) Abbreviation of mixed ligand complexes generated on polymer supports

SB anchored polymer support	Complex used	Mixed ligand complex on polymer support
B(10)H	M(**11**)$_2$	**B(10)** M(**11**)
B(10)H	M(**12**)$_2$	**B(10)** M(**12**)
B(20)H	M(**11**)$_2$	**B(20)** M(**11**)
B(10)H	M(**35**)$_2$	**B(10)** M(**35**)
B(10)H	M(**55**)$_2$	**B(10)** M(**55**)
B(10)H	M(**75**)$_2$	**B(10)** M(**75**)
B(10)H	M(**85**)$_2$	**B(10)** M(**85**)
B(10)H	M(**95**)$_2$	**B(10)** M(**95**)

(j) Representation of Co(III) Schiff-base complex generated on polymer support.

Representation of PS used	Co(III) SB complex used	Representation of metallated PS
B(10)H	Co(**11**)$_3$	**B(10)** Co(**11**)$_2$
B(10)H	Co(**12**)$_3$	**B(10)** Co(**12**)$_2$
B(20)H	Co(**11**)$_3$	**B(20)** Co(**11**)$_2$

*(k) Representation of metal complexes supported on polymer supports like **C**, **D** and **E***

Polymer supports	Metal complex used	Symbol of polymer supported complex
C	M(**11**)$_2$	C.M(**11**)$_2$
C	M(**12**)$_2$	C.M(**12**)$_2$
C	M(**21**)$_2$	C.M(**21**)$_2$
C	M(**75**)$_2$	C.M(**75**)$_2$
C	M(**85**)$_2$	C.M(**85**)$_2$
C	M(**95**)$_2$	C.M(**95**)$_2$
C	M(**50**)	C.M(**50**)
C	M(**60**)	C.M(**60**)
C	M(**70**)	C.M(**70**)
C	M(**80**)	C.M(**80**)
C	M(**88**)	C.M(**88**)
C	M(**98**)	C.M(**98**)
D	M(**11**)$_2$	D.M(**11**)$_2$
D	M(**12**)$_2$	D.M(**12**)$_2$
D	M(**13**)$_2$	D.M(**13**)$_2$
D	M(**14**)$_2$	D.M(**14**)$_2$
D	M(**75**)$_2$	D.M(**75**)$_2$
D	M(**85**)$_2$	D.M(**85**)$_2$
D	M(**95**)$_2$	D.M(**95**)$_2$
D	M(**50**)	D.M(**50**)
D	M(**60**)	D.M(**60**)
D	M(**88**)	D.M(**88**)
D	M(**98**)	D.M(**98**)
D	M(**35**)$_2$	D.M(**35**)$_2$
D	M(**45**)$_2$	D.M(**45**)$_2$
D	M(**55**)$_2$	D.M(**55**)$_2$
E	M(**11**)$_2$	E.M(**11**)$_2$
E	M(**12**)$_2$	E.M(**12**)$_2$