

## Polystyrene Supported Coordination Compounds of Dibasic Tridentate Schiff Base Derived from Glycine

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The reaction of appropriate metal ions and the polystyrene-supported dibasic tridentate Schiff base (PS-LH<sub>2</sub>) derived from the condensation of chloromethylated polystyrene, 3-formylsalicylic acid and glycine in DMF produces polystyrene supported coordination compounds of the types: PS-LM·DMF (where M = Cu, Zn, Cd, MoO<sub>2</sub>, UO<sub>2</sub>); PS-LFeCl·2DMF; PS-LZr(OH)<sub>2</sub>·2DMF and PS-LM'·3DMF (where M' = Co, Mn, Ni). These compounds have been characterized by elemental analyses, IR, reflectance, ESR spectral and magnetic susceptibility measurements. PS-LCu·DMF is square planar, PS-LM·DMF (M = Zn, Cd) is tetrahedral; PS-LMO<sub>2</sub>·DMF (M = Mo, U); PS-LFeCl·2DMF and PS-LM'·3DMF (M' = Co, Mn, Ni) are octahedral; while PS-LZr(OH)<sub>2</sub>·2DMF is pentagonal bipyramidal. The coordination compounds of Cu(II), Fe(III), Co(II), Mn(II) and Ni(II) are paramagnetic, while others are diamagnetic.

**Key Words:** Polystyrene, Polystyrene-anchored Schiff base, Polystyrene-anchored coordination compounds, Resins, Diamagnetic and magnetic susceptibility.

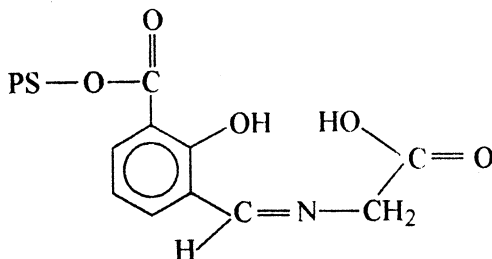
### INTRODUCTION

The coordination compounds of Schiff bases derived from salicylaldehyde and amino acids have been used to model *N*-pyridoxylidene amino acids which are considered to be an important intermediate in biological amination process<sup>1</sup>. The interest in functionalized polymers with chelating properties is due to the enforcement of ideal magnetically dilute environment around the polymer bound metal ions<sup>2</sup>. These insoluble reagents have the advantages over their soluble counterparts of easy separation from reaction mixture leading to operational flexibility, of higher selectivity, of their facile regenerability, of continuous reaction product removal leading to automation; of entrusting higher stability, of more efficient utilization of expensive metals and of increased potential for catalyst *via* systematic variation of the ligand attached to the metal centre. In this paper, we describe the synthesis and characterization of polystyrene-anchored dibasic tridentate Schiff base (PS-LH<sub>2</sub>) (I) and its coordination compounds with

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Cu(II), Zn(II), Cd(II), MoO<sub>2</sub>(II), UO<sub>2</sub>(II), Fe(III), Zr(IV), Co(II), Mn(II) and Ni(II) ions.



(PS-LH<sub>2</sub>)(I)

Fig. 1.

## EXPERIMENTAL

Chloromethylated polystyrene (containing 1.17 mmol of Cl per g of resin and 2% crosslinked with divinylbenzene) and glycine were the products of Fluka AG (Switzerland) and Ranbaxy respectively. 3-Formylsalicylic acid, zirconium(IV) acetate and bis(acetylacetonato)dioxomolybdenum(VI) were prepared according to published procedures<sup>3</sup>. The other chemicals/solvents were obtained from the sources mentioned in our recent publications<sup>4</sup>.

### Synthesis of polystyrene 3-formylsalicylate(PS-FSal)

Chloromethylated polystyrene (PS-Cl) (1.0 g) was allowed to swell in DMF (20 mL) for 45 min. To this, a DMF solution (20 mL) of 3-formylsalicylic acid (0.78 g, 4.68 mmol) was added. Ethyl acetate(100 mL) and triethylamine (1.5 g, 15 mmol) were added to above mixture. The mixture was heated under reflux for 8 h, while stirring magnetically. This was allowed to cool to room temperature. The pale-yellow coloured product obtained was suction filtered, washed several times with DMF, ethyl acetate, ethanol and acetone and was dried under vacuum at room temperature. IR (KBr) (cm<sup>-1</sup>): 3250 [ν(O—H)], 1730 [ν(C=O) (ester)], 1690 [ν(C=O) (aldehyde)] and 1520 [ν(C—O)(phenolic)].

### Synthesis of polystyrene-anchored Schiff base (PS-LH<sub>2</sub>)(I)

Polystyrene 3-formylsalicylate (PS-FSal) (1.0 g) was allowed to swell in methanol (50 mL) for 45 min. To this, an aqueous methanolic solution (50 mL) of glycine (0.35 g, 4.68 mmol) was added. The mixture was refluxed for 2 h, while stirring magnetically and then cooled to room temperature. The yellow coloured polystyrene-anchored ligand obtained was suction filtered, washed several times with methanol, ethanol and acetone and dried as mentioned above. IR (KBr) (cm<sup>-1</sup>): 3250 [ν(O—H)], 1725 [ν(C=O) (ester)], 1710 [ν(C=O) (acid)], 1640 [ν(C=N) (azomethine)] and 1525 [ν(C—O) (phenolic)].

**General method for the syntheses of polystyrene-anchored coordination compounds, PS-LM·DMF [where M = Cu(II), Zn(II), Cd(II), UO<sub>2</sub>(II)] and PS-LM'·3DMF (where M' = Mn(II), Ni(II)]**

PS-LH<sub>2</sub> (I) (0.5 g) was allowed to swell in DMF (20 mL) for 45 min. A DMF solution (30–50 mL) of the appropriate metal acetate (1.17 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically and then allowed to cool to room temperature. The products obtained were suction filtered, washed thoroughly with DMF, ethanol, methanol and acetone. The compounds were dried as mentioned above.

**Synthesis of PS-LMoO<sub>2</sub>·DMF**

PS-LH<sub>2</sub> (I) (0.5 g) was allowed to swell in DMF (20 mL) for 45 min. A DMF solution (70 mL) of bis(acetylacetonato)dioxomolybdenum(VI) (0.38 g, 1.17 mmol) was added to the above suspension. The mixture was refluxed for 7 h, while stirring magnetically. The brown coloured product obtained was allowed to cool to room temperature. The product was suction filtered, washed with DMF, ethanol and acetone and was dried as mentioned above.

**Synthesis of PS-LFeCl·2DMF**

PS-LH<sub>2</sub> (I) (0.5 g) was allowed to swell in DMF (20 mL) for 45 min. A DMF solution (50 mL) of iron(III) chloride anhydrous (0.19 g, 1.17 mmol) was added to the above suspension. The mixture was refluxed for 7 h, while stirring magnetically under anhydrous conditions. The brownish-red coloured product obtained was cooled to room temperature. It was suction filtered, washed thoroughly with DMF, absolute ethanol and petroleum ether and was dried as mentioned above.

**Synthesis of PS-LZr(OH)<sub>2</sub>·2DMF**

PS-LH<sub>2</sub> (I) (0.5 g) was allowed to swell in DMF (20 mL) for 45 min. To this, a freshly prepared DMF solution (40 mL) of zirconium(IV) acetate (1.17 mmol) was added. The mixture was heated under reflux for 7 h, while stirring magnetically. The cream coloured product obtained was cooled to room temperature. It was suction filtered, washed with DMF, ethanol and petroleum ether and was dried as mentioned above.

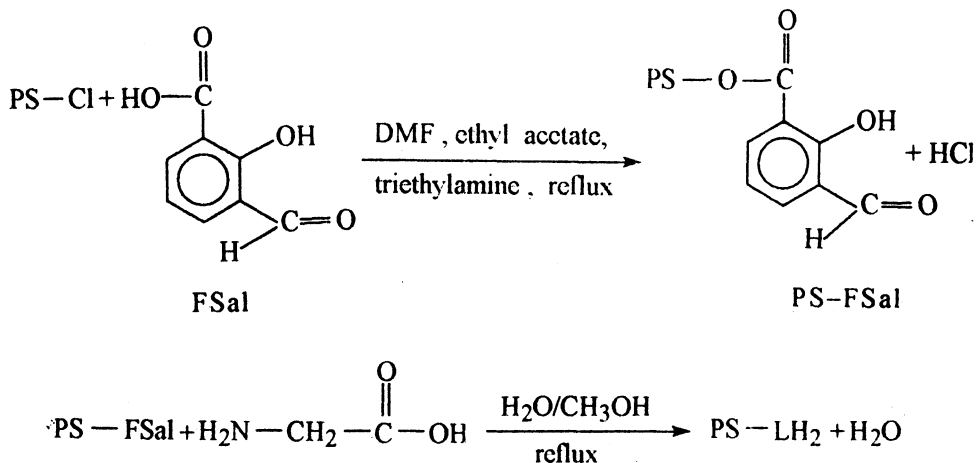
**Synthesis of PS-LCo·3DMF**

PS-LH<sub>2</sub> (I) (0.5 g) was allowed to swell in DMF (20 mL) for 45 min. To this, a hot DMF solution (40 mL) of cobalt(II) acetate tetrahydrate (0.29 g, 1.17 mmol, flushed with N<sub>2</sub>) was added. The mixture was heated under reflux for 8 h in the nitrogen atmosphere, while stirring magnetically. The brown coloured product obtained was cooled to room temperature. It was suction filtered, washed thoroughly with de-aerated (by passing nitrogen) DMF, ethanol and acetone and was dried as mentioned above.

The metal contents, coordinated DMF, IR, reflectance, ESR spectral studies and magnetic susceptibility measurements on the polystyrene-anchored coordination compounds were determined/carried out as per our earlier publications<sup>5</sup>.

## RESULTS AND DISCUSSION

The synthesis of PS-LH<sub>2</sub> was carried out in two steps. In the first step, a DMF suspension of PS-Cl and 3-formylsalicylic acid (FSal) in 1 : 4 molar ratio was refluxed in presence of ethyl acetate and triethylamine to produce polystyrene 3-formylsalicylate (PS-FSal). In the second step, PS-FSal (suspended in methanol) and glycine (dissolved in aqueous methanol) in 1 : 4 molar ratio were condensed to give PS-LH<sub>2</sub> (**1**) (Scheme-1).



**Scheme-1.** Preparative method of polystyrene supported Schiff base

Since the starting materials, *i.e.*, 3-formylsalicylic acid and glycine both have carboxylic acid group, therefore, the conventional method for the condensation of PS-Cl with Schiff base was not adopted. In such case, the ester formation might have taken place either on 3-formylsalicylic acid side or glycine side or on both sides. Therefore, the two steps synthesis of PS-LH<sub>2</sub> was carried out in order to avoid the ester formation on both sides.

PS-Cl is white, while PS-LH<sub>2</sub> is yellow. The yellow colour of PS-LH<sub>2</sub> remains unchanged even after repeated washings with DMF, ethyl acetate, ethanol and acetone. In the syntheses of polystyrene-anchored coordination compounds, PS-LH<sub>2</sub> was reacted with metal salt/metal coordination compounds in 1 : 2 molar ratio in DMF. PS-LH<sub>2</sub> and its coordination compounds are insoluble in water and in common organic solvents. The reaction of metal salt/metal coordination compounds with PS-LH<sub>2</sub> leads to the colour change of PS-LH<sub>2</sub> from yellow to dark-brown, cream, brown, orange, brownish-red and green. The colours of polystyrene-anchored coordination compounds remain unchanged, even after exhaustive washings with solvents. The per cent reaction conversion of PS-LH<sub>2</sub> to polystyrene-anchored coordination compounds lies in the range: 38.91–98.65 and the metal binding capacity of PS-LH<sub>2</sub> is 0.281–0.749 mmol of metal per g of resin (Table-1).

TABLE 1  
COLOUR AND ANALYTICAL DATA OF POLYSTYRENE-ANCHORED  
COORDINATION COMPOUNDS

Compound	Colour	Found (Calculated) (%)			Metal binding capacity <sup>b</sup> ( $\times 10^{-2}$ ) (mmol/g of resin)	Conversion <sup>c</sup> (%)
		M	Cl	DMF		
PS-LCu-DMF	Dark-brown	4.10 (5.40)	—	4.60 (6.21)	64.6	75.92
PS-LZn-DMF	Cream	3.40 (5.55)	—	3.80 (6.20)	52.0	61.26
PS-LCd-DMF	Cream	8.30 (9.18)	—	5.50 (5.96)	73.8	90.41
PS-LMoO <sub>2</sub> -DMF	Brown	4.60 (7.74)	—	3.60 (5.89)	47.9	59.43
PS-LUO <sub>2</sub> -DMF	Orange	6.70 (17.22)	—	2.00 (5.28)	28.1	38.91
PS-LFeCl <sub>2</sub> -2DMF	Brownish-red	2.00 (4.37)	1.40 (2.78)	5.60 (11.43)	35.8	45.77
PS-LZr(OH) <sub>2</sub> -2DMF	Cream	5.70 (6.96)	—	9.10 (11.14)	62.5	81.89
PS-LCo-3DMF	Brown	2.30 (4.47)	—	8.60 (16.63)	39.0	51.45
PS-LMn-3DMF	Dark-Brown	3.10 (4.18)	—	12.60 (16.68)	56.4	74.16
PS-LNi-3DMF	Green	4.40 (4.46)	—	16.30 (16.63)	74.9	98.65

<sup>a</sup>Abbreviations: PS-LH<sub>2</sub> = I, DMF = dimethylformamide.

<sup>b</sup>Calculated from the observed value of metal ion percentage in the resin using the formula  $[M\% \text{ (observed)} \times 10] / (\text{atomic weight of metal})$ .

<sup>c</sup>Percentage reaction conversion (p) = (observed metal ion percentage  $\times$  100)/(calculated metal ion percentage on the basis of 100% reaction conversion of polymer-anchored ligand to polymer-anchored compound).

The IR spectral data of PS-LH<sub>2</sub> and its coordination compounds were recorded in KBr (Table-2). The  $\nu(\text{C}=\text{O})$ (carboxylic) stretch<sup>3</sup> in 3-formylsalicylic acid occurs at  $1660 \text{ cm}^{-1}$ . PS-LH<sub>2</sub> exhibits a band at  $1725 \text{ cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$  (ester). The positive shift of the  $\nu(\text{C}=\text{O})$  (carboxylic) by  $65 \text{ cm}^{-1}$  indicates that the covalent bond formation has occurred between 3-formylsalicylic acid and PS-Cl *via* ester linkage<sup>6</sup>. PS-Cl shows a band at  $1250 \text{ cm}^{-1}$  due to  $\nu(\text{CH}_2-\text{Cl})$  stretch. This band disappears both in PS-FSal and PS-LH<sub>2</sub> which further support the covalent bond formation between these groups *via* ester linkage<sup>7</sup>. PS-LH<sub>2</sub> exhibits  $\nu(\text{C}=\text{N})$ (azomethine) and  $\nu(\text{C}-\text{O})$ (phenolic) stretches at  $1640$  and  $1525 \text{ cm}^{-1}$  respectively. In the polystyrene-anchored coordination compounds, the  $\nu(\text{C}=\text{N})$  (azomethine) undergoes a negative shift by  $5-25 \text{ cm}^{-1}$  indicating nitrogen coordination with metal ions<sup>3</sup>. The  $\nu(\text{C}-\text{O})$  (phenolic) stretch shifts to higher energy by  $\leq 10 \text{ cm}^{-1}$  in the coordination compounds indicating phenolic oxygen coordination with metal ions<sup>8</sup>. The  $\nu_{\text{sym}}(\text{COO})$  and  $\nu_{\text{asym}}(\text{COO})$  stretches of the free carboxylate group occur at  $1420$  and  $1570 \text{ cm}^{-1}$  respectively<sup>9</sup>. In the

present coordination compounds, these bands appear in the ranges: 1390–1365 and 1610–1595  $\text{cm}^{-1}$  respectively. The energy difference ( $\Delta\nu = 205\text{--}245 \text{ cm}^{-1}$ ) between  $\nu_{\text{sym}}(\text{COO})$  and  $\nu_{\text{asym}}(\text{COO})$  is  $>144 \text{ cm}^{-1}$  indicating unidenticity of carboxylate group, since in case of bidentate coordination of carboxylate group<sup>9</sup>,  $\Delta\nu$  is  $< 144 \text{ cm}^{-1}$ . Thus, the IR data are indicative of the ONO donor behaviour of PS-LH<sub>2</sub>. PS-LMoO<sub>2</sub>·DMF shows two bands, one at 945  $\text{cm}^{-1}$  and the other at 910  $\text{cm}^{-1}$  due to  $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$  stretches respectively. The IR data indicate the presence of the *cis*-MoO<sub>2</sub> structure, since a compound with a *trans*-MoO<sub>2</sub> moiety is expected to show only the  $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$  band as the  $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$  stretch is IR inactive<sup>10</sup>. PS-LUO<sub>2</sub>·DMF exhibits  $\nu_{\text{asym}}(\text{O}=\text{U}=\text{O})$  at 910  $\text{cm}^{-1}$ . The observation of only one  $\nu_{\text{asym}}(\text{O}=\text{U}=\text{O})$  band indicates the presence of the *trans*-UO<sub>2</sub> structure, since the  $\nu_{\text{sym}}(\text{O}=\text{U}=\text{O})$  stretch is IR inactive. The force constant ( $f_{\text{U-O}}$ ) and U—O bond length ( $R_{\text{U-O}}$ ) are 6.88  $\text{mdyn}/\text{\AA}$  and 1.74  $\text{\AA}$  respectively. The absence of a new band at 860–820  $\text{cm}^{-1}$  due to  $\nu_{\text{asym}}(\text{Fe—O—Fe})$  stretch in PS-LFeCl<sub>2</sub>·2DMF is indicative of the absence of an oxo-bridged structure<sup>3–5</sup>. Such oxo-bridge formation is not possible here due to long distance between the adjacent iron centres in this compound. The absence of a new band at 950–850  $\text{cm}^{-1}$  due to the  $\nu(\text{Zr}=\text{O})$  stretch in PS-LZr(OH)<sub>2</sub>·2DMF favours the formulation of the compound as PS-LZr(OH)<sub>2</sub>·2DMF and not as PS-LZrO(H<sub>2</sub>O)·2DMF. The appearance of a new band at 1115  $\text{cm}^{-1}$  due to the  $\delta(\text{Zr—OH})$  bending mode also supports the proposed structure<sup>11</sup>. DMF exhibits a band at 1680  $\text{cm}^{-1}$  due to the  $\nu(\text{C}=\text{O})$  stretch, which shifts to lower energy by 10–35  $\text{cm}^{-1}$  in the coordination compounds indicating oxygen coordination of DMF<sup>3–5</sup>.

TABLE 2  
IR SPECTRAL DATA( $\text{cm}^{-1}$ ) OF PS-LH<sub>2</sub>(I) AND ITS COORDINATION COMPOUNDS

Compound	$\nu(\text{C}=\text{N})$ (azomethine)	$\nu(\text{C}=\text{O})$ (phenolic)	$\nu(\text{C}=\text{O})$ (DMF)	$\nu_{\text{sym}}(\text{COO})$	$\nu_{\text{asym}}(\text{COO})$	$\Delta\nu$
PS-LH <sub>2</sub> (I)	1640	1525	—	—	—	—
PS-LCu·DMF	1630	1530	1660	1365	1610	245
PS-LZn·DMF	1630	1535	1665	1380	1605	225
PS-LCd·DMF	1615	1530	1660	1385	1595	210
PS-LMoO <sub>2</sub> ·DMF	1625	1530	1650	1375	1610	235
PS-LUO <sub>2</sub> ·DMF	1620	1530	1670	1390	1600	210
PS-LFeCl <sub>2</sub> ·2DMF	1625	1530	1650	1370	1595	225
PS-LZr(OH) <sub>2</sub> ·2DMF	1615	1535	1645	1370	1605	235
PS-LCo·3DMF	1620	1535	1645	1390	1595	205
PS-LMn·3DMF	1635	1530	1670	1390	1610	220
PS-LNi·3DMF	1635	1535	1665	1380	1600	220

The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored compounds are presented in Table-3. The polystyrene-anchored Cu(II), Fe(III), Co(II), Mn(II) and Ni(II) compounds exhibit magnetic

moments 1.89, 5.93, 4.66, 5.97 and 3.06 B.M. respectively. These values are indicative of magnetically dilute nature of the compounds<sup>12, 13</sup>. The magnetic interaction in the present polystyrene-anchored compounds is precluded due to the long distance caused by the presence of polystyrene backbone between the metal centres. The compounds of Zn(II), Cd(II), MoO<sub>2</sub>(II), UO<sub>2</sub>(II) and Zr(IV) are diamagnetic.

TABLE 3  
MAGNETIC MOMENTS AND THE REFLECTANCE SPECTRAL DATA OF  
POLYSTYRENE-ANCHORED COORDINATION COMPOUNDS

Compound	$\chi_{dia}$ (10 <sup>-6</sup> cgs units)	$\chi_M^{corr}$ (10 <sup>-6</sup> cgs units)	Magnetic moment <sup>a</sup> (B.M.)	Temp. (K)	$\nu_{max}$ (cm <sup>-1</sup> )	D <sub>q</sub> (cm <sup>-1</sup> )	B' (cm <sup>-1</sup> )	$\beta$	$\beta^0$ (%)
PS-LCu-DMF	-928	1501	1.89	296.0	15400				
PS-LFeCl <sub>2</sub> -2DMF	-1448	14625	5.93	300.0	12900 14800 19300				
PS-LCo-3DMF	-1441	9116	4.66	297.0	9000 18000	1006	670	0.69	31
PS-LMn-3DMF	-1031	15068	5.97	295.0	16000 21800 25000				
PS-LNi-3DMF	-827	3931	3.06	297.5	10800 17200 26300	1080	708	0.67	33

$$^a \mu_{eff.} = 2.83 (\chi_M^{corr} \times T)^{1/2} \text{ B.M.}$$

The electronic spectra of the present polystyrene-anchored compounds could not be recorded in nujol mull, as these compounds do not form a good mull. Therefore, their reflectance spectra were recorded (Table-3). PS-LCu-DMF exhibits a broad band at 15400 cm<sup>-1</sup> due to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub>, <sup>2</sup>B<sub>2g</sub> and <sup>2</sup>E<sub>g</sub> transitions, characteristic of square-planar CuNO<sub>3</sub> coordination sphere<sup>14</sup>. The absence of a band at 8000–10000 cm<sup>-1</sup> precludes the presence of a tetrahedral structure<sup>15</sup>. PS-LFeCl<sub>2</sub>-DMF exhibits three bands at 12900, 14800 and 19300 cm<sup>-1</sup> due to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(G), <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub>(G) and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>A<sub>1g</sub>(G) transitions, respectively in an octahedral symmetry<sup>16</sup>. PS-LCo-3DMF exhibits two bands at 9000 and 18000 cm<sup>-1</sup> due to the <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(v<sub>1</sub>), and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(v<sub>3</sub>) transitions, respectively in an octahedral symmetry<sup>16</sup>. The v<sub>3</sub>/v<sub>1</sub> value is 2.0 which occurs in the usual range (2.0–2.80) reported for the majority of the octahedral cobalt(II) coordination compounds<sup>16</sup>. The spectral parameters<sup>3-5</sup> are: D<sub>q</sub> = 1006 cm<sup>-1</sup>, B' = 670 cm<sup>-1</sup>, β = 0.69 and β<sup>0</sup> = 31%. The reduction of Racah parameter from the free ion value (971 cm<sup>-1</sup>) to 670 cm<sup>-1</sup> and β<sup>0</sup> value (31%) are indicative of the presence of strong M—L covalent bonding in the compound. PS-LMn-3DMF exhibits three bands at 16000, 21800 and 25000 cm<sup>-1</sup> due to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(G),

${}^6A_{1g} \rightarrow 4T_{2g}(G)$  and  ${}^6A_{1g} \rightarrow 4A_{1g}(G)$  transitions respectively, in an octahedral coordination around the metal ion<sup>17</sup>. PS-LNi-3DMF exhibits three bands at 10800, 17200 and 26300  $\text{cm}^{-1}$  due to the spin-allowed transitions:  ${}^3A_{2g} \rightarrow {}^3T_{2g}(v_1)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(v_2)$  and  ${}^3A_{2g} \rightarrow {}^3t_{1g}(P)(v_3)$ , respectively, in an octahedral symmetry<sup>16</sup>. The  $v_2 : v_1$  value is 1.6 which occurs in the usual range (1.60–1.82) reported for the majority of octahedral nickel(II) coordination compounds<sup>16</sup>. The spectral parameters<sup>3–5</sup> are:  $D_q = 1080 \text{ cm}^{-1}$ ,  $B' = 708 \text{ cm}^{-1}$ ,  $\beta = 0.67$  and  $\beta^0 = 33\%$ . The reduction of Racah parameter from the free ion value ( $1056 \text{ cm}^{-1}$ ) to  $708 \text{ cm}^{-1}$  and  $\beta^0$  value (33%) are indicative of the presence of strong covalence in the compound.

The ESR spectrum of PS-LCu-DMF exhibits two  $g$  values ( $g_{\parallel} = 2.28$ ,  $g_{\perp} = 2.08$ ) and this indicates the presence of tetragonal type symmetry about the Cu(II) ion<sup>3</sup>. The ESR parameters<sup>18</sup> of the present Cu(II) compound are:  $A_{\parallel}^{\text{Cu}} = 1.50 \times 10^{-2} \text{ cm}^{-1}$ ,  $A_{\perp}^{\text{Cu}} = 3.0 \times 10^{-2} \text{ cm}^{-1}$ ,  $G = 3.56$ ,  $\alpha_{\text{Cu}}^2 = 0.77$ ,  $(\alpha')^2 = 0.31$ ,  $\kappa = 0.49$  and  $P_d = 1.54 \times 10^{-2} \text{ cm}^{-1}$ . The values  $g_{\parallel} > g_{\perp}$  and  $A_{\parallel}^{\text{Cu}} > A_{\perp}^{\text{Cu}}$  indicate the presence of the unpaired electron in the  $d_{x^2-y^2}$  orbital<sup>19</sup>. The higher  $g_{\parallel}$  value (2.28) is due to higher elongation in the  $z$ -axis of the compound with  ${}^2B_{1g}$  ground state<sup>20</sup>. The  $g_{\parallel}$  value indicates that the metal-ligand bonding in the compound is covalent<sup>20</sup>. In the present copper(II) compound, the  $G$  value (3.56) indicates the strong field nature of the polystyrene-anchored ligand. The  $\alpha_{\text{Cu}}^2$  value (0.77) and  $(\alpha')^2$  (0.31) indicate the covalent nature of the present Cu(II) compound<sup>20</sup>. The positive value of  $\kappa$  (0.49) suggests that  $A_{\parallel}^{\text{Cu}}$  should be greater than  $A_{\perp}^{\text{Cu}}$  and this trend in  $A_{\parallel}^{\text{Cu}}$  and  $A_{\perp}^{\text{Cu}}$  values was also observed by us<sup>18</sup>. The lower value of  $P_d$  ( $1.54 \times 10^{-2} \text{ cm}^{-1}$ ) in the copper(II) compound in comparison to that of the free ion value ( $3.5 \times 10^{-2} \text{ cm}^{-1}$ ) indicates the presence of covalent character between the metal-ligand bonding. The ESR spectrum of PS-LCu-DMF does not show any band at *ca.* 1500 G due to the  $\Delta M_s = 2$  transition and this precludes the presence of M—M interaction. From the chlorine content of the starting chloromethylated polystyrene, it is clear that the metal atoms are placed on phenyl rings (of polystyrene) which are 6 to 7 styrene units apart when the per cent conversion is 100% and the styrene units are more than seven when the per cent conversion is <100%. This results in a magnetically dilute environment around the metal atom as the pathway for the dimer formation with M—M interaction is blocked. However, since the polymer is cross-linked, the polymer chains get overlapped and twisted and some of the reactive groups may come close to one another resulting in some M—M interaction which was not detectable by ESR studies.

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