Polystyrene Anchored Vanillin Schiff Base—Complexation and Ion Removal Studies

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ABSTRACT: A set of six new polystyrene anchored metal complexes have been synthesized by the reaction of the metal salt with the polystyrene anchored Schiff base of vanillin. These complexes were characterized by elemental analyses, Fourier transform infrared spectroscopy, diffuse reflectance studies, thermal studies, and magnetic susceptibility measurements. The elemental analyses suggest a metal : ligand ratio of 1 : 2. The ligand is unidentate and coordinates through the azomethine nitrogen. The Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) complexes are all paramagnetic while Zn(II) is diamagnetic. The Cu(II) complex is assigned a square planar structure, while Zn(II) is assigned a tetrahedral structure and Mn(II), Fe(III), Co(II), and Ni(II) are all assigned octahedral geometry. The thermal analyses were done on the ligand and its complexes to reveal their stability. Further, the application of the Schiff base as a chelating resin in ion removal studies was investigated. The polystyrene anchored Schiff base gave 96% efficiency in the removal of Ni(II) from a 20-ppm solution in 15 min, without any interference from ions such as Mn(II), Co(II), Fe(III), Cu(II), Zn(II), U(VI), Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, NO_3^-, NO_2^-, and $CH_3CO_2^-$. The major advantage is that the removal is achieved without altering the pH. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1536–1539, 2005

Key words: polystyrene; polymer bound Schiff base; metal-polymer complexes; vanillin; ion exchanges

INTRODUCTION

Polymer metal complexes have been of great interest as they may result in materials that possess some desirable properties of both their inorganic and organic components and also because of their practical convenience and operational flexibility. Functionalized polymers have been used as carriers in various organic and inorganic synthetic transformations.

Synthesis of polystyrene anchored Schiff base metal complexes is a field of active research,[1–3] especially as they have wide applications in a variety of fields such as nonlinear optical materials,[4] biologically active materials,[5] flame retardants,[6] catalysts,[7,8] and ion exchange resins.[9,10]

Of the many technologies that exist for the removal of metal ions from water, the most common are solvent extraction and ion exchange techniques and, of these, the ion exchange technique is far superior. The advantages of the use of functionalized polymers as ion exchange resins over conventional ion exchangers include high metal-to-polymer bond energies and selective separation.

This paper describes the syntheses and characterization of coordination complexes of the polystyrene bound Schiff base with Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). The application of the currently synthesized polymeric ligand in the removal of Ni(II) from solutions has also been investigated. The currently developed technique for the removal of Ni(II) has some clear advantages when compared with the literature methods.[11–15]

EXPERIMENTAL

Methods

Analytical grade solvents and chemicals were used throughout. Aminomethylated polystyrene (2% crosslinked with divinylbenzene) was obtained from Thermax India, Mumbai, as a gift sample. Vanillin, metal salts (sulfates of Co(II), Ni(II), Cu(II), and Zn(II); acetate of Fe(III) and U(VI), and chloride of Mn(II)), and the organic solvents like DMF and ethyl alcohol were all products of Merck.

The elemental analyses were performed on an Elementar Vario EL III CHN analyzer and the metal content was analyzed using the ICP technique on a Thermo Elemental, Iris Intrepid II XSP DUO. The electronic spectra were recorded on an Ocean Optics UV–vis spectrophotometer attached with a CCD detector.
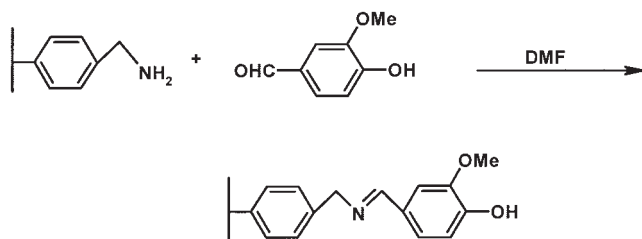
Scheme 1 Vanillin Schiff base of amino methylated polystyrene.

The IR spectra were recorded on a Thermo Nicolete (Avatar 370) FTIR spectrometer. Magnetic susceptibility measurements were done on a P.A.R. 155 vibrating sample magnetometer. The thermal analyses were done on a Perkin-Elmer (Diamond) DTA analyzer.

Synthesis of the polystyrene anchored schiff base resin (PS-LH)

Aminomethylated polystyrene (10 g), preswollen in DMF (20 mL) for 1 h, was refluxed with a DMF solution of vanillin (10 g in 30 mL) for 4 h. The brown resin was then cooled to room temperature, washed with DMF, water, alcohol, and finally acetone, and then dried in a vacuum desiccator at room temperature.

Syntheses of the polystyrene anchored metal complexes $(M(PS-LH)_2Y.x$DMF$)$ [M = Cu, Zn; x = 1; Y = SO$_4^{2-}$]; $(M(PS-LH)_2Y.x$DMF$)$ [M = Mn, Fe, Co, Ni; x = 3; Y = SO$_4^{2-}$/Cl$^-$/CH$_3$CO$_2^-$]

The polymeric Schiff base ligand (2 g), preswollen in DMF (20 mL) for 1 h, was refluxed with the metal ion solution (1 g in 20 mL) for 12 h under stirring. The polymer anchored complex formed was then suction filtered and washed thoroughly with DMF, water, alcohol, and acetone. The complexes were then dried in a vacuum desiccator at room temperature.

Ion removal studies

A known amount of the polymer ligand (vanillin Schiff base of aminomethylated polystyrene as shown in Scheme 1) was soaked in DMF for 1 h. Solution of Ni(II) of known concentration was added to this suspension and the mixture was refluxed for 15 min. It was then filtered through a Whatman 41 filter paper. The solution was diluted quantitatively to known volume (50 mL). From this, a definite quantity (5 mL) was taken and the amount of metal ion present was determined by the standard spectrophotometric procedure.[16] The above experiment was repeated to study the effect of time, pH, metal ion concentration, ligand concentration, and finally interference due to other ions like Mn(II), Co(II), Zn(II), U(VI), Na$^+$, K$^+$, NH$_4^+$, Ca^{2+}, Cl$^-$, Br$^-$, NO$_3^-$, NO$_2^-$, and CH$_3$CO$_2^-$ to establish the optimum conditions.

RESULTS AND DISCUSSION

The polystyrene anchored Schiff base metal complexes were characterized using CHN analysis, metal analysis, IR and UV–vis spectral analysis, thermal, and magnetic moment studies.

The analytical data show that the polymer anchored complexes have a composition of 1 : 2 with respect to metal and ligand. The complexes may be represented as given in Table I.

The ligand and its complexes are all insoluble in water and alcohols. The thermal studies show the elimination of the coordinated DMF molecules and the volatile ligand. The Mn(II), Fe(III), Co(II), and Ni(II) complexes lose their weight (35 to 40%) in the temperature range 110 to 140 °C, which can be attributed to the loss of three molecules of the coordinated DMF, respectively, from the metal complexes. Cu(II) and Zn(II) complexes lose their weight (12 to 15%) in the temperature range 100 to 120 °C, which may be attributed to the elimination of one molecule of coordinated

TABLE I
Analytical Data of the Complexes

Complex and color	Cl found (calc.) (%)	M found (calc.) (%)	μ_{eff} (BM)	Assigned geometry
Mn(PS-LH)$_2$Cl(DMF)$_3$	4.10	6.28	5.81	
Brown	(4.20)	(6.51)	(5.92)	Octahedral
Fe(PS-LH)$_2$CH$_3$CO$_2$(DMF)$_3$		6.35	5.90	
Reddish–brown		(6.43)	(5.92)	Octahedral
Co(PS-LH)$_2$SO$_4$(DMF)$_3$		6.19	4.10	
Ash		(6.48)	(3.88)	Octahedral
Ni(PS-LH)$_2$SO$_4$(DMF)$_3$		6.33	3.12	
Chocolate		(6.46)	(2.83)	Octahedral
Cu(PS-LH)$_2$SO$_4$DMF		8.52	1.75	Square planar
Greenish–brown		(8.28)	(1.73)	
Zn(PS-LH)$_2$SO$_4$DMF		8.07		
Brown		(8.50)	Dia.	Tetrahedral

TABLE II
FTIR Spectral Data (in cm^{-1}) of the Ligand and Its Metal Complexes

Ligand/complex	C=N stretching	M-N stretching
PS-LH	1640	
Mn(PS-LH)$_2$Cl(DMF)$_3$	1608	552
Fe(PS-LH)$_2$CH$_3$CO$_2$(DMF)$_3$	1602	558
Co(PS-LH)$_2$SO$_4$(DMF)$_3$	1619	563
Ni(PS-LH)$_2$SO$_4$(DMF)$_3$	1618	570
Cu(PS-LH)$_2$SO$_4$DMF	1613	564
Zn(PS-LH)$_2$SO$_4$DMF	1620	557

TABLE III
Optimum Conditions for the Removal of Ni(II)

Amount of ligand	0.01 g
Time of reflux	15 min
pH range	4.2–4.9
Percentage removal	96
Metal ion concentration	20 ppm

DMF from the complexes. The second step is in the range of 390–480 °C, which is due to the decomposition of the ligand with subsequent formation of the metal oxide.

The infrared spectral data of the ligand and the complexes are given in Table II and the spectra are represented in Figure 1. The spectra of the ligand gave a band at 1640 cm^{-1} due to the presence of the azomethine (C = N) group, and this confirms the formation of the Schiff base. This band shifts to a lower frequency by 20–30 cm^{-1} in the metal complexes, indicating coordination through the nitrogen of the azomethine group. All the complexes gave a band around 550–570 cm^{-1}, confirming the M–N bond.[17]
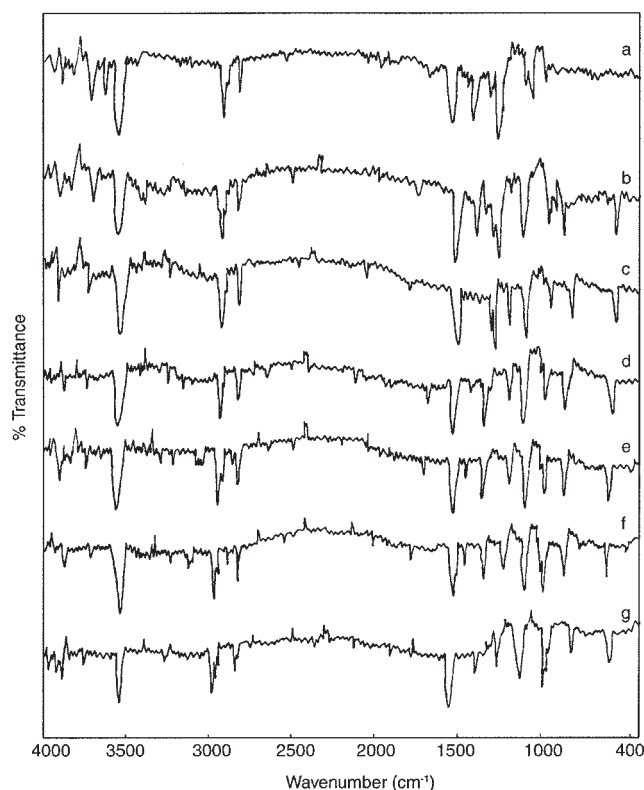

Figure 1 Infrared spectra of ligand (a) and its complexes: (b) Mn(II), (c) Fe(III), (d) Co(II), (e) Ni(II), (f) Cu(II), (g) Zn(II).

The free O-H group in the ligand, which gives a sharp band at 3521 cm^{-1}, does not seem to be coordinating. The bands seen in the region 2800–2950 cm^{-1} can be due to the methyl C-H stretch of the methoxy group.

The magnetic moment values of the polymer anchored Mn(II) and Co(II) complexes were 5.81 and 4.10 BM, respectively. The electronic spectra of Mn(II) shows three bands at 18,240, 23,010, and 25,200 cm^{-1} (assigned $^6A_{1g\rightarrow}{}^4T_{1g}$ (G), $^6A_{1g\rightarrow}{}^4T_{2g}$ (G), $^6A_{1g\rightarrow}{}^4A_{1g}$ (G)) and that of Co(II) shows two bands at 11,900 and 18,020 cm^{-1} (assigned $^4T_{1g}$ (F) $\rightarrow{}^4T_{2g}$ (F), $^4T_{1g}$ (F) $\rightarrow{}^4T_{1g}$ (P)).[18] These facts support an octahedral geometry for these complexes. The polymer anchored Fe(III) complex exhibits a magnetic moment of 5.90 BM, which falls well within the range expected. The electronic spectrum of Fe(III) complex has three bands at 12,740, 19,610, and 25,100 cm^{-1} (assigned $^6A_{1g\rightarrow}{}^4T_{1g}$ (G), $^6A_{1g\rightarrow}{}^4T_{2g}$ (G), $^6A_{1g\rightarrow}{}^4T_{1g}$ (G)), suggesting an octahedral shape.[19]

The magnetic moment of the polymer anchored Ni(II) complex is 3.12 BM and its electronic spectrum shows three bands at 8256, 14,500, and 25,000 cm^{-1} (assigned $^3A_{2g\rightarrow}{}^3T_{2g}$, $^3A_{2g\rightarrow}{}^3T_{1g}$(F), $^3A_{2g\rightarrow}{}^3T_{1g}$ (P)), which are characteristic of an octahedral symmetry.

The magnetic moment of the polymer anchored Cu(II) complex is 1.75 BM, which lies close to the range of magnetic moments expected for magnetically dilute complexes (1.8–2.2 BM). The electronic spectrum of polymer anchored Cu(II) complex exhibits a band at 16,580 cm^{-1}, which is characteristic of a square planar structure.[20]

The polymer anchored Zn(II) complex is diamagnetic and its electronic spectrum shows no bands, as expected, and the complex may be assigned a tetrahedral geometry.[21]

Ion removal studies

The currently synthesized ligand is developed as an excellent reagent for the removal of Ni(II) from solutions. Optimum conditions have been developed for the removal of Ni(II) and the results are presented in Table III.

Effect of time of reflux

As the time of reflux increases, the percentage removal also increases. Within a period of 15 min about 96%

removal was achieved. Hence, the optimum time of reflux was fixed at 15 min.

Effect of pH

The metal removal studies have been carried out at different pH. The maximum removal was obtained in the pH range 4.2–4.9, which was the mixing pH. Hence, there is no need for any control of pH for effective removal.

Effect of metal ion concentration

The effect of metal ion concentration on the removal was studied with solutions of Ni(II) in the range 10 to 70 ppm using 0.01 g of the ligand. At lower concentrations (10 to 20 ppm) almost complete removal of the metal ion was achieved and as the concentration increased metal ion uptake capacity decreased due to an insufficient amount of the ligand. The most efficient removal occurred in the 10- to 30-ppm range for the studied amount of the ligand.

Effect of ligand concentration

Studies have been conducted with different amounts of the ligand for a fixed amount of the metal ion (20 ppm). A minimum of 0.01 g of the ligand is required for achieving 96% removal of the metal ion from a 20-ppm solution.

Interference due to other ions

The experiment is repeated in the presence of different ions and the ions such as Mn(II), Co(II), Fe(III), Cu(II), Zn(II), U(VI), Na^+, K^+, NH_4^+, Ca^{2+}, Cl^-, Br^-, NO_3^-, NO_2^-, and $CH_3CO_2^-$ did not interfere with the removal of Ni(II) using vanillin Schiff base of aminomethylated polystyrene.

The currently developed technique for the removal of Ni(II) is very simple and the time taken for the effective removal of the metal is only 15 min, unlike the reported methods,[11–14] which require 1 h or more. Similarly, some of the existing methods need strict control of pH,[15] whereas for the developed method there is no need for any pH control. Further, the complexed metal can be easily leached out to regenerate the reagent. The fact that the method is capable of removing Ni(II) up to 96% of the metal concentration is the most important advantage.

CONCLUSIONS

Vanillin Schiff base of the aminomethylated polystyrene has been synthesized and characterized. The ligand on refluxing with metal ions forms complexes. The metal complexes have been characterized and suitable geometries have been proposed. Further, the analytical applicability of the polymer anchored ligand is exploited in the removal of Ni(II) ion from solutions and optimum conditions have been developed for the removal of Ni(II). This method is superior, as the percentage of removal is very high and the removal is achieved without any control of pH.

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