Synthesis and characterization of nickel(II), cobalt(II) and copper(II) complexes of poly(salicylaldehyde-acrylate)divinylbenzene resins

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The polymeric chelates of Ni(II), Co(II) and Cu(II) have been prepared from poly(salicylaldehyde-acrylate) crosslinked with divinylbenzene derivatized with oxime, semicarbazone, thiosemicarbazone ethylenediamine and Schiff’s base. The spectra (IR, ¹H, ¹³C and solid state ¹³C-CP/MAS NMR) and applications of the coordination polymers have been studied.

Attachment of multidentate ligands to insoluble polymeric supports is a technique commonly utilized for the preparation of selective ion exchange resins, which are capable of separation and purification of metal ions¹². Anchoring reagents to insoluble supports has become to be known as solid phase synthesis based on the pioneering effects of Merrifield³ in polypeptide synthesis. Rapid developments not only make polypeptide synthesis on polymer supports, but immobilized photосensitizers and immobilized transitional metal complexes are also frequently reported⁴. Thus an insoluble metal complex anchoring to polymer supports have many advantages over those in solution, when used as catalysts in many chemical processes⁵-⁶. The synthesis of polymer anchored transition metal chelates is a field of active research⁷-¹¹. In continuation of our earlier work¹²-¹³ we report herein the preparation and chelating properties of oxime, semicarbazone, thiosemicarbazone and ethylenediamine derivatives of poly(salicylaldehyde-acrylate)-divinylbenzene copolymer towards Cu(II), Ni(II) and Co(II) ions.

Materials and Methods
A three dimensional polymer matrix (support) has been prepared from salicylaldehyde-acrylate, divinylbenzene and benzoyl peroxide using suspension polymerization technique. The aldehydic functional group is subjected for chemical modification using oxime, semicarbazone, thiosemicarbazone, and ethylenediamine reagents to enhance chelating ability of the parent aldehydic resin. These functionalized resins are characterized by IR, ¹H, ¹³C – NMR and solid state ¹³C-CP/MAS NMR spectra. The surface characteristics of prepared resins are examined by optical and Scanning Electron Micro photographs. The chelating efficiency of the polymer to work as metal specific and to use as reusable source of chelation are established for all resins and compared with one another.

The standard salt solutions were prepared by taking appropriate quantities in 50 ml water and were standardized by known procedure¹⁴. Buffer solutions of pH range 3-6 were prepared from 1M acetic acid and 1 M sodium acetate solution, whereas the buffer of range pH 8-10 were prepared from 1 M ammonium hydroxide and 1 M ammonium chloride.

The pH measurements were made with an ITL digital (pH/MV) meter having a glass electrode, model DPH-14. A spectrophotometer Model UV-DEC 340 was used for absorbance measurements. The FT-IR spectra of the crosslinked copolymer and their metal complex samples were recorded on Nicolet 20 DXB using KBr pellets. The ¹H NMR and ¹³C NMR spectra of the samples were run on a Bruker CXP operating at 90 and 22.6 MHz respectively in CDCl₃ with TMS as internal standard. High resolution ¹³C NMR spectra of the crosslinked copolymer samples were recorded on Bruker 300 MSL CP-MAS at IISc, Bangalore.

Preparation of monomer (ref. 15)
To a solution of salicylaldehyde (0.2 mol) in 2-butanol was added triethylamine (0.2 mol) and stirred at 0.5°C. To this mixture, acryloylchloride (0.2 mol) in ether (50 ml) was added dropwise in a period of 45 min. The condensation of acryloylchloride with salicylaldehyde liberates hydrochloride which is absorbed by triethylamine which ultimately results
into the quaternary salt (triethylamine hydrochloride). This quaternary salt is filtered and washed with ether and the filtrate collected. The filtrate which contains salicylaldehydeacrylate monomer is successively washed with aqueous 5% NaOH solution to remove any traces of unreacted salicylaldehyde. Then the filtrate is extracted with ether and the solvent evaporated to get the salicylaldehyde-acrylate monomer. The formation of 2-hydroxybenzaldehyde acrylate is confirmed by $^1$H and $^{13}$C NMR spectra.

$^1$H NMR (δ ppm): 9.8 (H), 6.11-7.01 (3H), 7.3-7.9 (4H); $^{13}$C NMR (δ ppm): 133.2 (CH$_2$), 126.8 (CH), 163.7 (C), 151.5 (4C), 134.8 (4C), 129.9 (6C), 127.9 (C), 136.5 (9C), 196.0 (1C).

Polymerization of monomer

Bead polymerization was carried out at 80 ± 0.2°C, using polyvinyl alcohol as stabilizer and benzoyl peroxide as catalyst in a four necked reaction kettle, fitted with a water condenser, a synchronized mechanical stirrer, a dropping funnel and a nitrogen inlet. The stirring rate was controlled at 400 RPM and maintained for 12 h. Divinylbenzene (4%) was used as a crosslinking agent. The spherical beads which resulted were filtered and washed with pet. ether, 2-butane, ethyl acetate and dichloromethane to remove the unreacted monomer. The polymer was dried in vacuo oven at 30°C, yield 80%.

The prepared crosslinked copolymer was identified by IR and solid state $^{13}$C-CP/MAS NMR spectra.

IR: (cm$^{-1}$) 2936 (backbone −CH stretching), 1755 (ester carbonyl), 1602 (C=C), 1125 (C−O−C), 1201 (aldehydic ketone).

Solid state $^{13}$C-CP/MAS NMR (ppm): 40.16 (backbone −CH stretching), 160.6 (ester carbonyl), 186.3 (aldehydic carbonyl).

Functionalization of polymer

Functionalization of poly(salicylaldehyde-acrylate)-divinylbenzene was achieved by incorporating an oxime moiety through a post polymerization reaction.

The crosslinked (SAA-DVB) copolymer (5 g) and hydroxylamine hydrochloride (10 g) in DMF (1:1) were placed in a 500 ml round bottomed flask and refluxed for 12 h. The functionalization was maximized and attained constancy after 12 h. The contents were filtered, the functionalized beads were collected, washed with DMF, ethyl acetate and water. The oximated resin was identified by elemental analysis and IR spectra.

By adopting the same procedure, semicarbazone, thiosemicarbazone and ethylenediamine derivatives of SAA-DVB copolymer were prepared.

Preparation of metal complexes

The metal salts (5 g each) in a DMF : water (1:1) mixture were treated with a functionalized polymer (5 g) and refluxed for 10 h in triply distilled water at a pH 6.9 ± 0.1. The reaction mixture was filtered, and the resulting light green (nickel), pink (cobalt) and green (copper) metallated polymers were washed with hot water, solvents and dried in vacuo over at 60°C.

Preparation of samples for electrical conductivity measurements

The polymeric metal complexes were powdered and pressed into the form of pellets using 15 ton hydraulic press for conductivity measurements. The thickness 't' and diameter 'D' of the pellets were measured using a screw gauge. The amount of the sample was taken such that the thickness of the pellet suited in between the ratio of its length to area as 3:5. Silver paint was applied on both sides of the pellets to act as supporting electrodes as well as for a high gain of conducting contact between sample and electrode. A 2-probe method was used for the conductivity measurements.

Results and Discussion

Effect of time on metal uptake

A batch type equilibrium procedure was used to determine the amount of metal ion uptake from bulk solution by the polymer. The two phases were shaken on a mechanical shaker at room temperature and separated by filtration. The metallated beads were digested with mineral acids and the metal ion leached out was determined spectrophotometrically. This gave the contents of the metal ion present in the polymer. The same procedure was adopted after taking fresh quantity of polymer for different time
Table I—Current-voltage curves of SAA-DVB-ethylenediamine and its metal complexes

<table>
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<th>Volts</th>
<th>SAA-DVB</th>
<th>SAA-DVB-Ethylenediamine</th>
<th>Copper Complex</th>
<th>Cobalt Complex</th>
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</tbody>
</table>

l = thickness of the pellet or length between electrodes
a = area of cross section, l = microampheres, V = volts

Effect of pH on uptake of metal ion
To the buffers of which pH (3-10), metal ions [Cu(II), Ni(II), Co(II), 0.1 N bulk concentration] and different polymeric resins (5 g) were added and shaked for 75 min. The metallated beads were filtered and thoroughly washed. The bound metal ion was released by acid treatment and the metal content determined spectrophotometrically. From the plots, it can be concluded that the best polymer which uptake the Ni(II) ion to a greater extent is oxime in the pH range 4 to 5. Similarly, for copper, the optimum pH is 4 with the semicarbazone derivative.

To test the selectivity of functionalized polymers towards Co(II), Ni(II) and Cu(II), a column chromatography technique was adopted by taking a different functionalized polymers as absorbing gels. Different functionalized polymers were grinded to a fine powder and a slurry prepared in solvent ether. The slurry was carefully poured into a micro pipette to a level of 10 cm length. Precaution was taken to avoid air gaps. The swelled beads inside the column were brought to the normal level by flushing hot air through the column which promotes the evaporation of the solvent which was present in the column along with the beads. A mixture of metal ions [Co(II), Ni(II) and Cu(II)] of 0.1 N bulk concentration was injected into the column and held for 45 min. The metal solution was then allowed to drain through the column. The percolated column was washed with water a number of times to remove the absorbed metal ions from the column which was confirmed through the absence of metal ions in the leached water.

The loaded column was treated with different pH buffers and the leached metal ion solutions were collected. The process was repeated till the column was free from any metal ion. The leached metal ion solution was concentrated and neutralized and the different metal contents [Ni(II), Co(II), Cu(II)] were estimated through titrimetric and or gravimetric procedures. The results obtained on different functionalized polymers were as follows from the above data that preferential loading of Ni(II) occurs with the oxime derivative. Similarly, the thiosemicarbazone derivative shows preference for Ni(II) ions to Co(II) and Cu(II) ions. Semicarbazone ligand did not show any preferential absorption for one metal to the other.

The most important advantage of chelating resins is their reuse. The resin once used can be brought into its original form by desorbing the complexed Ni(II), Cu(II) and Co(II) by treatment with hydrochloric acid and the metal free resin can be reused after
purification (washing with water several times). The recycling of the purified resin by the addition of fresh Ni(II), Cu(II) and Co(II) solution results in the uptake of almost the same amount of Ni(II), Cu(II) and Co(II) ions initially present. The process was repeated four times. The retention of the initial capacity even after four cycles of repeated operations suggests that the resin can be used several times without any reduction in capacity. If the resin decomposes on acid treatment it can be again functionalized.

The transition metals when loaded on to a crosslinked polymer acquires heterogenity. This facilitates encroached metal ions to improve the catalytic activity. To study the effect of metallated resins on the rates of some simple reactions such as ester hydrolysis, the resins were incorporated into the system and kinetics of ester hydrolysis was followed. No catalytic effects by the metallated resins were detected or the rates of ester hydrolysis by mineral acids.

The electrical conductance of the polymer salicylaldehyde - acrylate - divinylbenzene - ethylenediamine and its metal complexes (Ni, Cu and Co) at room temperatures were measured by studying the current-voltage curves of these specimen at room temperature. The potential was applied through a variable DC source and recorded on a philips PK 5230 voltmeter. The current was measured using a nanoammeter (model NM-122, scientific equipment). The graphs are shown in Fig. 1.

The data presented in Table I show that both the polymer and its metal complexes have a linear relationship between current and voltage. It has been calculated on salicylaldehyde-acrylate-divinyl-