Synthesis, Characterization and Applications of Polymer-metal chelates derived from Poly(4-acryloxybenzaldehyde)-divinylbenzene salicyloyl hydrazone resins

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ABSTRACT

4-acryloxybenzaldehyde was prepared and subjected to suspension polymerization with divinylbenzene as a cross-linking agent. The resulting network polymer was ligated with salicyloyl hydrazine. The functional polymer was treated with transition metal ions, Co(II) and Ni(II). The copolymer and its metal chelates were characterized by elemental analysis, IR, ^{1}H-NMR, solid state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR, electron paramagnetic resonance (EPR), thermogravimetric and scanning electron microscopy (SEM) studies. The maximum uptake of the metal ions was determined. Metal uptake efficiency and reusability of the ligated polymer resin were also studied.

Keywords: 4-Acryloxy benzaldehyde, Divinyl benzene, Functionalized polymers, Polymer-metal chelates.

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INTRODUCTION

The interaction between metal ions and polymerized ligands may lead to the formation of coordination polymers in which the chelated metal ions are bounded by ligand molecules [1-2]. Anchoring reagents to insoluble supports has come to be known as solid phase synthesis based on the pioneering efforts of Merrifield [3] in polypeptide synthesis. Rapid developments now not only make polypeptide synthesis on polymer supports, but immobilized photo sensitizers and immobilized transition metal complexes are also frequently reported [4]. Polymer-metal complexes have been of interest to many chemists, because not only they are excellent models for metalloenzymes, but they have also led to developments in metal ion separation and recovery of metal ions. Increasing environmental concerns in waste-water treatment has led to the use of organic ligands anchored to solid supports in order to remove and recover important metal ions from aqueous solutions [5-7]. Copolymers of activated methacrylates have been utilized to synthesize macromolecular drug carriers [8]. Wang et al. [9] have indicated that the polymeric support and the polymeric end groups affect the catalytic activity and selectivity of these complexes in hydrogenation reaction. The complexes obtained from maleic acid-styrene, acrylic acid-vinyl pyrrolidone copolymers and nickel(II), platinum(II) and palladium(II) metal ions were found to be useful catalysts for the hydrogenation of 2-chloro-4-nitrotoluene [10], while cobalt(II) chelates synthesized from chloromethylated polystyrene were reported [11] to catalyze Diels-Alder cyclization reactions. A survey of the literature reveals that hydrazones derived from low molecular weight aromatic ketones like

acetophenone and benzophenone draw the attention of synthetic chemists due to their varied biological activities [12-14]. Hydrazones also find their application in analytical chemistry. They act as multidentate ligands with metals forming colored chelates. These chelates are then used in selective and sensitive determination of metal ions [15-18]. With a view to the complexing abilities of hydrazone derivatives and in continuation of our earlier work [19], the acryloxybenzaldehyde(ABA) cross-linked with divinylbenzene(DVB) was selected. The salicyloyl hydrazone(SAH) derivative of the cross-linked copolymer acts as insoluble polymeric ligand towards Co(II) and Ni(II) ions. We report herein the preparation, characterization and applications of salicyloyl hydrazone derivative of poly ABA-DVB copolymer towards Co(II) and Ni(II) ions.

MATERIALS AND METHODS

Physico-chemical measurements: Elemental analysis of the cross-linked copolymers and their metal complexes were carried out on Thermo Finningan FLASH EA 1112 CHNS analyzer. The IR spectra were recorded on Perkin-Elmer IR spectrophotometer model 983 G using KBr pellets. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of the samples were run on a dpx 200 MHz in CDCl$_3$ with tetramethylsilane (TMS) as internal standard. ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were recorded on a Bruker-dsx-300 MHz CP/MAS at IISc, Bangalore. A Perkin Elmer model 3700 with TGA-7 computer and a Mettler TA 3000 system were used to evaluate the thermal stability and decomposition temperature of the copolymers and their metal complexes. EPR spectra of the copolymer metal complexes were recorded on Varion E-4X band spectrophotometer at 303 K. Particle size distribution is taken using a Malvern particle analyzer and scanning electron microscopy (SEM) was carried out using a JEOL-JSM 840 model. The copolymer was coated with gold. The pH measurements were made with ELICO digital pH meter having a glass electrode model LI 127.

Standard solutions were prepared by taking requisite amounts in 50 ml distilled water and standardized by the known methods [20].

Preparation of monomer: To a solution of 4-hydroxybenzaldehyde (0.2 mol) in 2–butanone, triethylamine(TEA) (0.2 mol) was added and stirred at 0-5°C. Thermometer, mechanical stirrer and dropping funnel were arranged. To this mixture, acryloyl chloride (0.2 mol) in ether was added in a period of 60 min. The condensation of acryloyl chloride with 4-hydroxybenzaldehyde liberates hydrochloride, which was adsorbed by TEA, which ultimately results into the quaternary salt (TEA hydrochloride). This quaternary salt was filtered and washed with ether and the filtrate collected. The filtrate which contains the monomer was washed with aqueous 5% NaOH followed by water. Then the filtrate was extracted with ether and the solvent evaporated to get the monomer. m. p. 46-48°C. The formation of ABA is confirmed by IR and ^{1}H NMR. The spectral data is consistent with the structure of monomer.

IR (cm^{-1}, KBr): 3050 (Ar C-H stretching), 1750 (ester carbonyl), 1600 (C=C skeletal vibration), 1660 (carbonyl group), 1156 (C-O stretching in esters).

^{1}H NMR (δ ppm): 5.96, 6.68 (2H, <u>CH$_2$</u>=CH-), 6.36 (1H, CH$_2$=<u>CH</u>-), 7.30-8.00 (4H, Ar-H), 10.0 (aldehydic proton).

Polymerization of monomer: Bead polymerization of the monomer (30g) was carried out at 80 ± 1ºC using polyvinyl alcohol (PVA) as the stabilizer and BPO as catalyst in a four necked reaction kettle fitted with a water condenser, a synchronized mechanical stirrer, a dropping funnel and a nitrogen inlet. A controlled stirring rate of 400 rpm was maintained for 12 h. DVB (5.2g) was added as the cross-linking agent. The beads formed were filtered, washed with petroleum ether, butan-2-one, acetone and dichloromethane to remove the unreacted monomer. It was finally washed with water to remove PVA. The product was dried in a vacuum oven at 30ºC. Yield 75%. It is characterized by elemental analysis and IR spectral data.

Functionalization of polymer: Functionalization of poly(ABA)-DVB was achieved by incorporating SAH moiety through a post-polymerization reaction. Cross-linked polymer (5 g.) and SAH (10 g.) in

dimethylformamide-water (DMF-H$_2$O) mixture (1:1) were placed in a 500 ml round-bottomed flask and refluxed for 8 h. The contents were filtered; the functionalized beads were collected, washed with DMF and water. The functionalized resin is identified by elemental analysis and IR spectrum.

Preparation of metal chelates: 5g. of metal salts (NiCl$_2$. 6H$_2$O or CoCl$_2$. 6H$_2$O), respectively, in a DMF-H$_2$O (1:1) were treated with 5 g. of a functionalized polymer and refluxed for 10 h. in double-distilled water at a pH of 6.9 ± 0.1. The reaction mixture was filtered and the resulting light brown (nickel) and dark brown (cobalt) metallated polymers were washed in hot water, ethyl acetate, acetone and dried in a vacuum oven at 60°C. The steps involved in the synthesis are presented in Scheme 1.
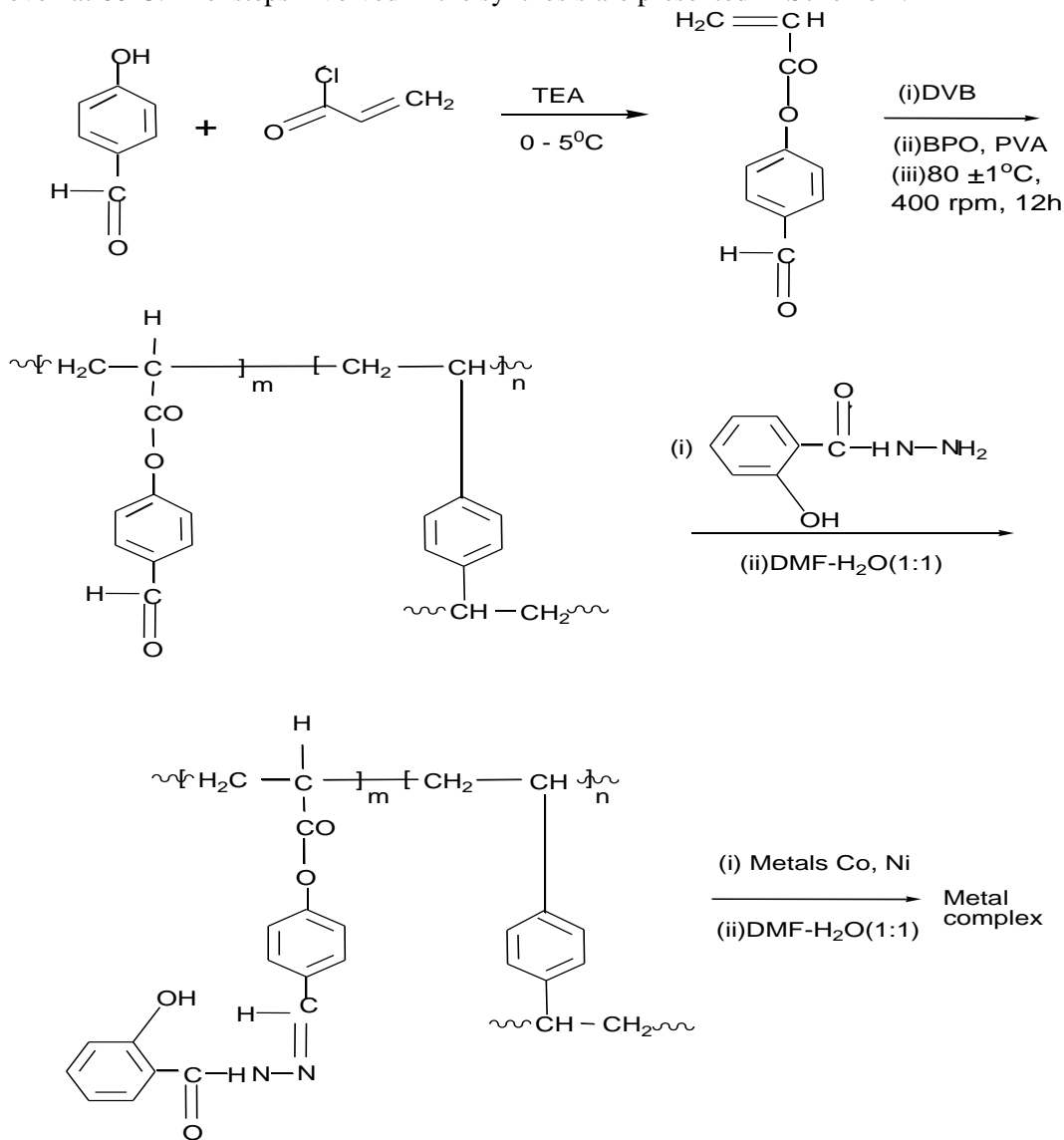
Scheme 1

Physical properties: Both the polymer metal complexes are insoluble in common organic solvents and non-hygroscopic in nature.

Chemical analysis: The metal contents in the polymer-metal complexes were estimated titrimetrically [Co(II)] and gravimetrically [Ni(II)], after acid treatment of the complexes [20].

RESULTS AND DISCUSSION

Elemental analysis: Elemental analysis data is presented in table 1. The data show that the conversion of aldehydic carbonyl groups to hydrazone function was 51% by weight (only the surface aldehyde groups were converted to salicyloyl hydrazone). The remaining aldehyde groups, deeply buried in the polymer chains were unaffected. Metallation was 28% and 26% respectively for Co(II) and Ni(II) complexes.

Table 1 Elemental analysis of ABA–DVB copolymer, salicyloyl hydrazone functionalized polymer and metal chelates

Element	Found %			
	ABA-DVB	ABA-DVD-SAH	ABA-DVD-SAH-Co(II)	ABA-DVB-SAH-Ni(II)
C	69.71	71.26	65.51	65.72
H	6.43	6.29	6.02	6.10
N	-	4.39	1.78	1.57
Metal	-	-	2.12	1.95
		51*		

* indicates the percentage of conversion

IR spectral studies: The IR spectrum of ABA-DVB copolymer shows absorption band at 2929 cm^{-1}, which has been identified as -CH backbone methylene stretching vibrations. The ester carbonyl is identified through the appearance of a strong absorption band at 1732 cm^{-1}. A strong absorption around 1605 cm^{-1} is due to C=C stretching vibration of the phenyl rings. The (C-O-C) stretching vibrations in compound are confirmed by a sharp absorption at 1143 cm^{-1}. The aldehydic carbonyl functionality is identified by a sharp absorption around 1680 cm^{-1} [21-23]. The formation of hydrazone is confirmed by a set of distinct vibrations at 3425 and 1610 cm^{-1} which are due to –OH and C=N stretching respectively. The disappearance of the band at 1680 cm^{-1} indicates the removal of carbonyl function of aldehydic units. The IR spectrum of functionalized copolymer shows intense band at 1640 cm^{-1} due to C=O stretching in hydrazone and its downward shift in Co(II) complex suggest coordination of metal ion through oxygen atoms. There is a downward shift of C=N vibration of azomethine from 1610 cm^{-1} to 1594 cm^{-1} which indicates the coordination of azomethine nitrogen atom. The Ni(II) complex shows absorption at 1590 cm^{-1}, which are lowered from 1610 cm^{-1} (C=N str.), in functionalized resin. It is therefore inferred that the ligands coordinate in bidentate fashion. Thus, in each complex the metal atom binds to the ligand though azomethine nitrogen and hydrazone carbonyl oxygen atoms. The IR spectra ABA-DVB copolymer and its salicyloyl hydrazone functionalized resin are shown in fig. 1.
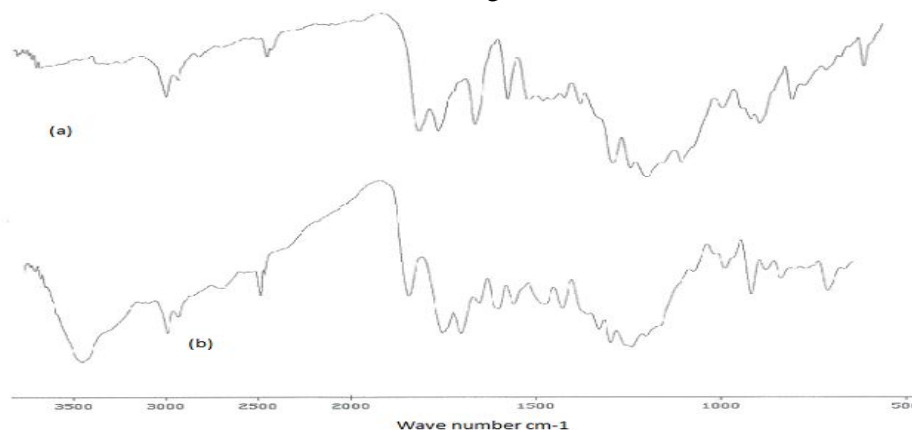

Fig. 1 IR spectra of (a) ABA-DVB and (b) ABA-DVB-SAH

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Solid State ^{13}C CP–MAS NMR spectroscopy: In the present investigation in addition to elemental analysis and FT IR spectroscopy, ^{13}C CP–MAS NMR [24-26] is used for identifying the polymer units. The sample is spun at two different spins and by comparing the two spectra, the spinning side bands are eliminated. The ^{13}C CP–MAS of cross-linked copolymer is compared with its soluble homopolymer analogue. Proton decoupled spectra of homopolymer is taken in CDCl$_3$ solution. The ^{13}C CP–MAS of ABA-DVB copolymer and its salicyloyl hydrazone functionalized resin are shown in fig. 2. The backbone ^{1}C and ^{2}C carbons of homopolymer appeared as clear distinct lines at 45.89 and 37.36 ppm respectively. In the case of cross linked copolymer, the intense peak at 41.34 is attributed to the backbone carbons. Because of the residual broadening, the peaks due to methylene and methine carbons are not clearly resolved. The aldehydic carbonyl of ABA appeared at 197.51 ppm as sharp intense line in homopolymer, whereas in cross-linked polymer it appeared at 191.24 ppm as a medium intense peak. The phenyl ester carbonyl [27] gave sharp line at 173.51 ppm in homopolymer and as a sharp peak in cross-linked system at 173.18 ppm. The ^{4}C of phenyl ring appeared at 152.49 ppm. The ^{5}C and ^{9}C, ^{6}C and ^{8}C aromatic carbons of homopolymer gave sharp lines at 135.51 and 130.06 ppm. The line observed at 126.42 ppm is attributed to ^{7}C of aromatic ring. In the case of ^{13}C CP–MAS NMR, because of residual broadening the clear splitting of aromatic signals are not observed. The aromatic carbons of solid sample gave only a sharp intense line at 128.59 ppm with a shoulder at 122.62 ppm. The ^{13}C CP-MAS NMR spectrum of salicyloyl hydrazone derivative of ABA–DVB copolymer shows an intense peak at 41.42 which is attributed to the backbone carbons. The aromatic carbons of solid sample gave only a sharp intense line at 128.89 ppm. The phenyl ester carbonyl gave medium intense peak at 173.05 ppm. The disappearance of peak at 191.24 ppm indicates the absence of aldehydic carbon atom of benzaldehyde unit. This clearly explains the formation of salicyloyl hydrazone derivative. Due to residual broadening, a clear separation of the signals is not observed in the spectrum.
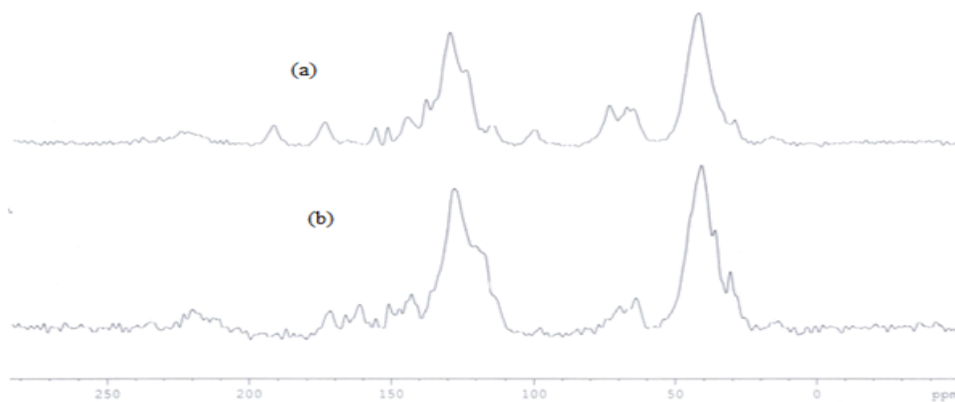

Fig. 2 Solid state C-13 CP-MAS NMR spectra of (a) ABA-DVB, (b) ABA-DVB-SAH

EPR spectroscopy: The EPR parameters gave a measure of the nature of the complexation with the metal ion. Anisotropic spectra are obtained for polychelates in crystalline state at 303 K. The $g_∥$ and $g_⊥$ are computed from the spectra using DPPH free radical as g marker. For the covalent complexes, g is less than 2.3 and for ionic environment it is normally 2.3 or larger [28]. The values $g_∥$ and $g_⊥$ for Co(II) complex was 2.14 and 2.09, thereby indicating covalent character for the metal-ligand bond in the complex. The EPR signal corresponding to Ni(II) complexes are not observed at room temperature.

A survey of the literature reveals that Co(II) and Ni(II) metal complexes of poly(salicylaldehyde acrylate)-divinylbenzene semicarbazone resin [29] exhibit paramagnetic property. The nature of metal-ligand bond was reported to be covalent in these complexes. Similarly Ni(II) complex of poly(2-hydroxy-4-methacryloyloxy acetophenone-formaldehyde) was also reported [30] to exhibit paramagnetic behaviour with a distorted octahedral geometry [31]. Hence, based on the covalent nature of the metal-ligand bond

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observed in the present studies and also based on the reports made in the literature [29-31], octahedral geometry is suggested for the metal complexes presently investigated.

Thermogravimetric analysis: In order to study the thermal stability and decomposition pattern of cross-linked copolymers, dynamic thermogravimetric analysis is under taken [32] and the data presented in the table 2**.** The thermograms of the copolymer and its functionalized resins are run in air atmosphere. The degradation of ABA–DVB copolymer occurred in two stages. The first stage decomposition is observed from 218-415°C and the weight loss found is 66%. The second stage degradation of the copolymer resin is in the temperature range of 415-635°C. The weight loss involved in this stage is 33.6%.

Table 2 TG data of ABA-DVB copolymer, salicyloyl hydrazone functionalized copolymer and its metal chelates

S. No.	System	Weight loss (%) at temperature (^{o}C)						
		IDT's	200	300	400	500	600	700
1	ABA-DVB copolymer	155	5	28	58	95	95	95
2	ABA-DVB-SAH copolymer	138	3	16.1	32.6	71.2	85.8	89.4
3	ABA-DVB-SAH-Co(II) chelate	157	5.3	11	50	89.5	91.9	92.4
4	ABA-DVB-SAH-Ni(II) chelate	143	4.6	18.4	71.8	90.2	95.1	95.1

The SAH derivative also decomposed in a two-stage process. The first stage of decomposition commenced at 145°C and was completed at 305°C. The initial weight loss of 23%. The second stage of decomposition is in the temperature range 305-570°C, with a weight loss of 67%.

The initial decomposition temperatures of Co(II) and Ni(II) metal chelates 157 and 143°C respectively. The complexes decomposed mainly in two stages. The first stage decomposition is an elimination of benzaldehyde and bezaldehyde salicyloyl hydrazone units. The second slow decomposition of chelates at higher temperatures may be due to the breakage of main chain accompanied by the volatilization of the cleaved products.

Particle size analysis: The success and reproducibility of the suspension polymerization is determined by measuring the average particle size of the beads formed [33-34]. The particle size distribution of the ABA–DVB copolymer is determined by Malvern particle size analyzer. . The average particle size of the system is 77.6 μm and the distribution curve is relatively broad.

Scanning electron microscopy: SEM is the technique employed for studying the shape, size and morphological features of the polymers in beaded form [35-37]. Functionalized resin appears smoother [cf. fig. 3] than that of the metal anchored resins [cf. fig. 3]. The rough appearance of the resin surface is as a result of the doping of the metal ions. The copolymer beads were spherical and of various sizes. The beaded nature of the polymer confirms the success of suspension polymerization.
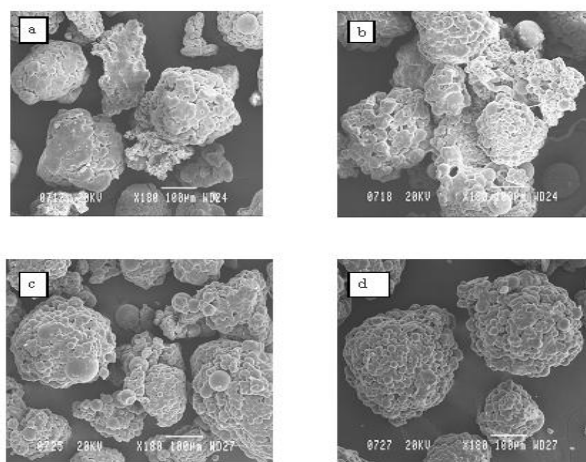
Fig. 3 SEM photographs of (a) ABA-DVB (b) ABA-DVB-SAH (c) ABA-DVB-SAH-Co(II) (d) ABA-DVB-SAH-Ni(II)

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APPLICATIONS

The time course of resin-metal interaction is of considerable importance if the resin is to be used in a dynamic system such as a packed column or a flowing system. If complexation is not sufficiently rapid for certain metal ions, then their retention on a column will be low owing to the short contact time between the resin and solution. Thus absorption of resin should be examined over an extensive period. Slow exchange rates of many chelating resins have been reported [38] to prevent their commercial use. The rate of complexation depends on the chemical nature of the metal ion and the ligand, as well as the structure of the polymer matrix. The steric constraints in a dense macromolecular matrix lower the reactivity of ligand function.

In order to optimize the time required for complexation towards Co(II) and Ni(II) ions, batch studies were carried out [39]. The time dependence of the complexation of Co(II) and Ni(II) by the functionalized ABA-DVB resin was followed by measuring the change in the concentration of the metal-salt solutions at regular intervals. The results are presented in the form of fig. 4. The complexation of Co(II) and Ni(II) was completed in 45 and 40 min respectively for functionalized resin.
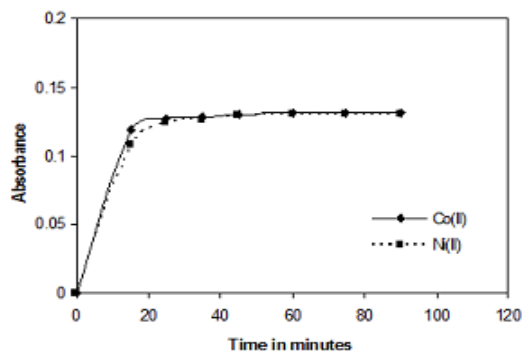

Fig. 4 Effect of time on the uptake of Co(II) and Ni(II) by ABA-DVB-SAH resin

Effect of pH on uptake of metal ion: To various buffer solutions (pH 3-10), metal ion [Co(II), Ni(II) (0.1) bulk concentration], functionalized ABA-DVB resin (5 g) was added and maintained under shaking for 90 min. The metallated beads were filtered and thoroughly washed. The bound metal ion was released by acid treatment and the metal content determined titrimetrically. The results are presented in fig. 5. From the plot, it can be concluded that the change in pH has relatively little effect on the uptake of metal ions by the functionalized resin.
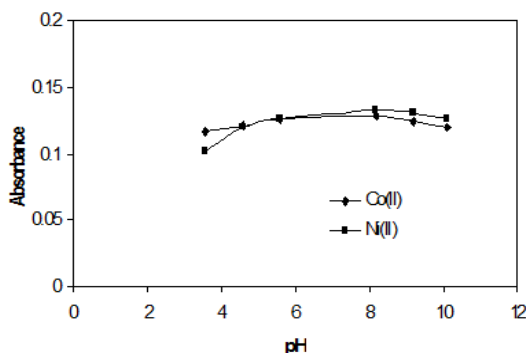

Fig. 5 Effect of pH on the uptake of metal ions by ABA-DVB-SAH resin

Reusability of complexed ABA-DVB functionalized resin: The most important advantage of chelating resin is their possible reuse after a particular process. The resin, once used, can be returned to its original form by desorbing the complexed metal ions with hydrochloric acid. The metal free resin can be reused after washing with water several times. The recycling of the purified resin with the addition of Co(II) and Ni(II) solution results in the intake of almost the same amount of respective metal ions as initially adsorbed. 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. Here, it is noteworthy that if the resin defunctionalize on acid treatment, it could be subjected to functionalization again.

CONCLUSIONS

IR spectral studies showed that the azomethine nitrogen and salicyloyl carbonyl group and chloride anions were involved in coordination to the metal ions such as Co(II) and Ni(II). Elemental analysis confirmed that the percentage of functionalization was 51%, while the metallation was 28% and 26% for Co(II) and Ni(II) complexes, respectively. The EPR spectra of the Co(II) complex showed that this is covalent in nature. The thermal dissociation patterns show that the copolymer, functionalized resin and metal chelates decompose in two stages and are consistent with the structural features of the copolymer resins. SEM photographs indicate the success of suspension polymerization. A bead structure was observed for the polymers. The time taken for complexation of Co(II) and Ni(II) was 45 and 40 min respectively for the functionalized resin. 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.

ACKNOWLEDGEMENTS

REFERENCES

[1]   B. T. Block, *Inorg. Macromol. Rev.,* **1970**, 1, 115.
[2]   J. C. Bailar Jr., In: C. E. Carraher Jr., J. E. Sheats, C.V. Pittman Jr. (ed), "Organometallic Polymers", Academic, New York, **1978,** p 313.
[3]   R. B. Merrifield, *Science*, **1965**, 150, 178.
[4]   D. C. Neckers, *J. Chem. Educ.*, **1975**, 52, 695.
[5]   W. Li, M. Coughlin, R. L. Albright and R. H. Fish, *React. Funct. Polym*, **1995**, 28, 89.
[6]   S. M. Jovanovic, A. Nastasovic, N. N. Jovanovic, K. Jeremic and Z. Savic, *Angew. Makromol. Chem.*, **1994**, 219, 161.
[7]   S. M. Jovanovic, A. Nastasovic, N. N. Jovanovic and K. Jeremic, *Mater. Sci. Forum.*, **1996**, 214, 155.
[8]   J. Sam Roman, E. L. Madruga and L. Pargada, *J. Polym. Sci. Polym. Chem. Ed.*, **1987**, 25, 203.
[9]   B. He, J. Su, M. Li and L. Wang, *Shiyou Huayong.*, **1998**, 17, 668. (CA: 110:156404k).
[10]   W. Jiang, W. Huang and H. Zong, *Fenzi Cuihua.,* **1988**, 2, 202.
[11]   F. M. Menger and T. Tsuno, *J. Am. Chem. Soc.*, **1989**, 111, 4903.
[12]   R. H. Wiley and R. L. Clevenger, *J. Med. Pharm. Chem.*, **1962**, 5, 1876.
[13]   P. Montegazza, F. Panchiane and G. Cavalind, *Antibiot. Chemotherapy*, **1961**, 11, 405.
[14]   M. Katyal and J. Dutt, *Talanta*, **1975**, 22, 156.

[15]   O. Babaiah, C. K. Rao, T. S. Reddy and V. K. Reddy, *Talanta*, **1996**, 43, 551.
[16]   O. Babaiah, P. R. Reddy, V. K. Reddy and T. S. Reddy, *Indian J. Chem. Sect. A.* **1999**, 38, 1035; *J. Indian chem. Soc.*, **2004**, 81, 670.
[17]   M. Gangadharappa, P. R. Reddy, V. K. Reddy and T. S. Reddy, *J. Indian Chem. Soc.*, **2004**, 81, 525.
[18]   V. K. Reddy, J. Thippaiah, C. K. Rao, P. R. Reddy and T. S. Reddy, *J. Indian Chem. Soc.*, **1999**, 76, 275.
[19]   T. Ravi Sankar, K. Kesavulu and P. Venkata Ramana, *J. Mater. Sci.*, **2007**, 42, 8571.
[20]   A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longman, London **1978**.
[21]   I. Weiliao and B. E. Eichinger, *J. Polym. Sci. Part A, Polym. Chem.*, **1990**, 28, 559.
[22]   M. L. Bender and J. Figueras, *J. Am. Chem. Soc.*, **1953**, 75, 6304.
[23]   A. Torikai, A. Takeuchi, S. Nagaya and K. Fueki, *Polym. Photochem.*, **1986**, 7, 279.
[24]   A. V. Cunliffe, "^{13}C NMR Spectroscopy of polymers" Chapter 1 In: J. V. Dawkins (ed), Developments in polymer characterization-1, Applied science, London, **1978**.
[25]   Jacob Schaefer and E. O. Stejskal, "High Resolution ^{13}C NMR of solid polymers" Chapter 4 In: C. George Levy (ed), Topics in Carbon-13 NMR Spectroscopy, Wiley Interscience, New York, **1979**, Vol. 3.
[26]   F. A. Bovey, "High-resolution Carbon-13 studies of polymer structure", Chapter 10 In: K. J. Ivin (ed), Structural studies of Macromolecules by spectroscopic methods, John Wiley & sons, New York, **1976**.
[27]   B. S. Rao, P. J. Modec and B. C. Marechal, *Macromol. Soc. Chem.*, **1987**, A24, 719.
[28]   H. Okawa, T. Tokii, N. Noraka, Y. Muto and S. Kida, *Bull. Chem. Soc. Jpn.*, **1973**, 46, 1462.
[29]   L. D. Prabhakar and A. Marysaral, *Polymer International*, **1997**, 42, 149.
[30]   T. Kaliyappam and P. Kannan, *J. Polym. Mater*, **1994**, 11, 121.
[31]   O. Bostop and C. K. Jorgensen, *Acta Chem. Scand.*, **1957**, 11, 1223.
[32]   W. W. Wendlandt, "Thermal Methods of Analysis", Interscience, New York, **1964**.
[33]   T. Allen, "Particle Size Measurement", 3rd ed., Chapman and Hall, New York, **1981**.
[34]   H. Barth, "Modren Methods of Particle Size Analysis", Wiley, New York, **1984**.
[35]   R. Arshady, *J. Microencapsulation*, **1989**, 6, 1.
[36]   K. A. Kun and P. Kunin, *J. Polym. Sci. Polym. Chem.*, **1968**, 7, 2689.
[37]   W. L. Sederal and G. J. Dejong, *J. Appl. Polym. Sci.*, **1973**, 17, 2835.
[38]   (a) R. Torse and V. Rieman, *J. Phys. Chem.*, **1961**, 65, 1821; (b) M. Mart Suzura and Y. Wadachi, *Bull. Chem. Soc. J. Pr.*, **1975**, 48, 3456.
[39]   H. Nishide, J. Deguchi and E. T. Suchida, *Polym. Sci. Poly. Chem. Ed.*, **1977**, 15, 3028.