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Synthesis, characterization and thermal studies of polymer–metal complexes derived from poly(2-methacryloxy-5-methyl benzophenone)-divinylbenzene isonicotinoyl hydrazone resins

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Abstract 2-Methacryloxy-5-methyl benzophenone was prepared and subjected to suspension polymerization with divinylbenzene as a cross-linking agent. The resulting network polymer was ligated with isonicotinoyl hydrazone. The functionalized polymer was treated with transition metal ions, copper(II) and nickel(II). The polymer metal complexes 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.

Introduction

The interaction between metal ions and polymerized ligands may lead to the formation of coordination polymers in which the chelated metal ions are binded 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 photosensitizers and immobilized transition metal complexes are also frequently reported [4]. Synthesis of polymer anchored transition metal chelates is a field of active research. In recent years, 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 trace 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 meth(acrylates) 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 copper(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]. Besides 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 of benzophenone incorporated into the polymer, the 2-methacryloxy-5-methyl benzophenone (MMBP) cross-linked with divinylbenzene (DVB) was selected. The hydrazone derivative of the cross-linked copolymer acts as insoluble polymeric ligand towards Cu(II) and Ni(II) ions. We report herein the preparation, characterization and thermal studies of hydrazone derivatives of poly(MMBP)-DVB copolymer towards Cu(II) and Ni(II) ions. The metal

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uptake efficiency and reusability of the resin are studied and compared with other structurally related polymers reported [19] in the literature.

Experimental

2-Hydroxy-5-methyl benzophenone is prepared by a known method [20]. A three-dimensional polymer matrix has been prepared from MMBP, DVB and benzoyl peroxide (BPO) by suspension polymerization. The keto group is subjected to chemical modification using isonicotinoyl hydrazine (INH) to enhance chelating ability of the parent keto group of the resin. The functionalized resins are characterized by elemental analysis and IR spectral studies. The chelating efficiency of the polymer to work as metal specific and to use as reusable source of chelation is established.

The standard salt solutions were prepared by taking requisite amounts in 50 mL distilled water and standardized by the known methods [21].

Buffer solutions of pH range 3–6 were prepared from 1 M acetic acid and 1 M sodium acetate solution. Buffer solutions of pH range 8–10 were prepared from 1 M ammonium hydroxide and 1 M ammonium chloride.

The pH measurements were made with ELICO digital pH meter having a glass electrode model LI 127. Elemental analysis of the cross-linked copolymers and their metal complexes were carried out on Thermo Finningan FLASH EA 1112 CHNS analyzer at IISc, Bangalore. ^{1}H-NMR and Proton decoupled ^{13}C-NMR spectra were run on a Bruker-DPX, 200 MHz spectrometer $CDCl_3$ solution with TMS as internal standard at CDRI, Lucknow. Solid State (CP/MAS) NMR spectra were recorded on a Bruker-DSX, 300 MHz CP/MAS at IISc, Bangalore. The IR spectra were recorded on Perkin-Elmer IR spectrophotometer model 983 G using KBr pellets at IICT, Hyderabad. Thermogravimetric analysis was carried out on Mettler TA 3000 with 10 mg samples at a heating rate of 10°C min^{-1} in air at IICT, Hyderabad. EPR spectra of the copolymer metal complexes were recorded on varion E-4X band spectrophotometer at 303 K at University of Hyderabad, Hyderabad. SEM of the copolymers were taken on JMS-840 JEOL Japan model at IISc, Bangalore. The polymer was coated with gold. An ELICO UV-VIS SL 164 double beam spectrophotometer is used for absorbance measurements.

Preparation of monomer

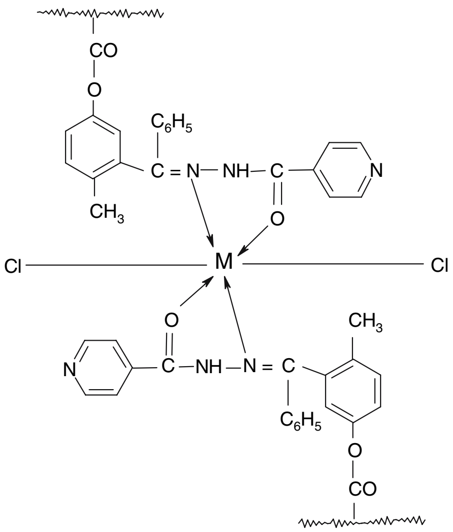
To a solution of 2-hydroxy-5-methyl benzophenone (0.2 M) in 2-butanone was added triethylamine (0.2 M) and stirred at 0–5 °C. Thermometer and mechanical stirrer and dropping funnel is arranged. To this mixture, methacryloyl chloride (0.2 M) in ether was added in a period of 60 min. The condensation of methacryloyl chloride with 2-hydroxy-5-methyl benzophenone liberates hydrochloride, which is adsorbed by triethylamine (TEA), which ultimately results into the quaternary salt (triethylamine hydrochloride). This quaternary salt is filtered, washed with ether and the filtrate collected. The filtrate which contains the monomer is washed with aqueous 5% NaOH followed by water. Then the filtrate is extracted with ether and the solvent evaporated to get the monomer. The formation of MMBP is confirmed by IR and ^{1}H-NMR spectral data. The data is consistent with the Structure 1 (cf. Scheme 1). m.p. 58–60 °C.

IR (cm^{-1}, KBr): 3040 (Ar C–H stretching), 2980 (C–H stretching in methyl), 2950 (methylene C–H stretching), 1750 (ester carbonyl), 1600 (C=C skeletal vibration), 1660 (keto carbonyl).

^{1}H-NMR (δ ppm): 1.6 (3H, s, CH_3–C=C), 2.0 (3H, s, CH_3–Ar), 5.8 & 6.3 (2H, s, CH_2=C<), 7.2–8.1 (8H, m, Ar–H).

Preparation of homopolymer

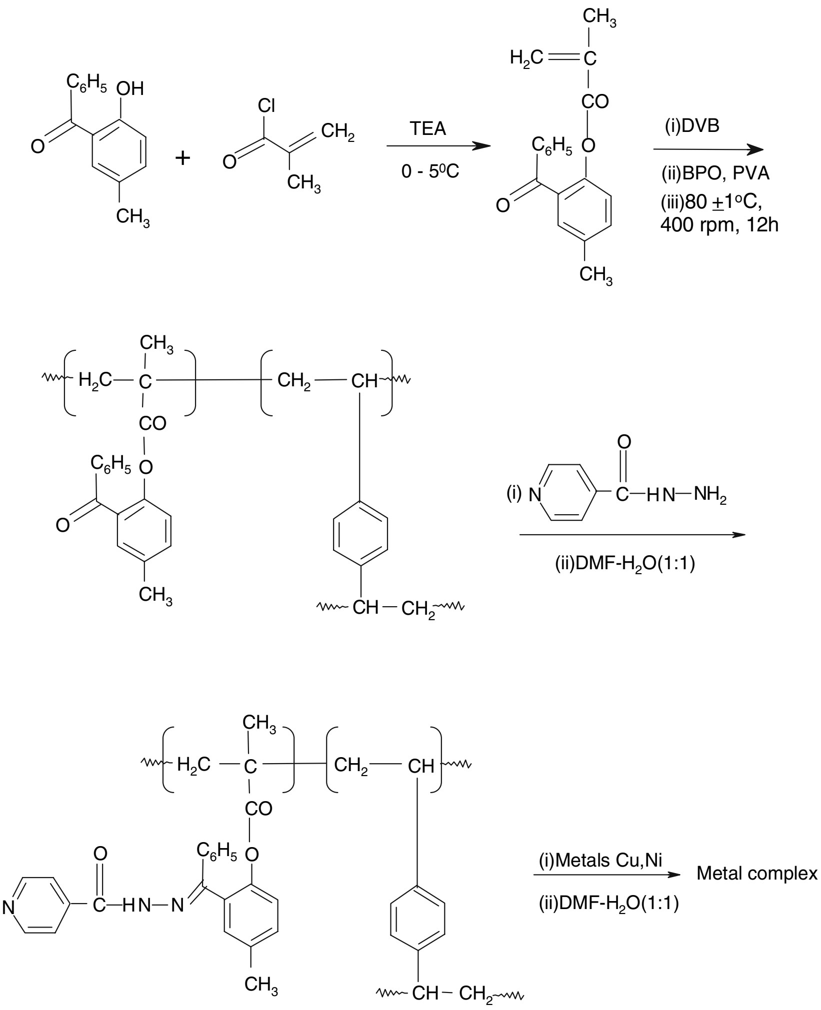
Poly(2-methacryloxy-5-methyl benzophenone) was prepared as 4 M solution in butan-2-one using benzoyl peroxide as initiator at 70 °C in a thermostatic water bath. The entire system was kept in an inert atmosphere by continuous passage of nitrogen. The polymer was precipitated by the addition of non-solvent like methanol and purified by dissolving the polymer in chloroform and precipitating it in methanol. The purification procedure was repeated twice



M = Metals like Ni(II) & Cu(II)

Structure 1

Scheme 1



and the product was finally dried in vacuum oven at 30 °C. Yield 70%. It is characterized by proton decoupled ^{13}C-NMR spectrum (Fig. 3).

^{13}C-NMR (*δ* ppm): 37.36 (backbone –CH carbons), 45.89 (backbone –CH_2 carbons), 121.81–154.68 (aromatic carbon atoms), 165.21 (ester carbonyl), 196.82 (keto carbonyl).

Preparation of copolymer

Bead polymerization of the monomer (30 g) was carried out at 80 ± 1 °C in a thermostatic water bath, 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 (5.2 g) was added as the cross-linking agent. The beads formed were filtered and washed with petroleum ether, butan-2-one, acetone and dichloromethane to remove the unreacted monomer. The product was dried in a vacuum oven at 30 °C. Yield 75%. It is characterized by elemental analysis, IR spectral data and ^{13}C-CP/MAS NMR.

IR (cm^{-1}, KBr): 3050 (Aromatic –CH stretching), 2900 (backbone –CH stretching), 1720 (ester carbonyl), 1690 (keto carbonyl), 1590 (C=C skeletal vibration of phenyl group), 1170 (C–O–C stretching).

^{13}C-CP/MAS NMR (*δ* ppm): 41.34 (backbone methylene and methine carbons), 155.47 (aromatic carbons), 173.37(ester carbonyl), 191.24 (keto carbonyl).

Functionalization of polymer

Functionalization of poly(MMBP)-DVB was achieved by incorporating an isonicotinoyl hydrazone moiety through a post-polymerization reaction. Cross-linked polymer (5 g) and INH (10 g) in dimethylformamide–water (DMF–H_2O) mixture (1:1) were placed in a 500 mL round-bottomed flask and refluxed for 12 h. The contents were filtered; the functionalized beads were collected, washed with DMF, ethyl acetate and water. The functionalized resin was identified by elemental analysis and IR spectrum.

Preparation of metal complexes

Five grams of metal salts ($NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$), respectively, in a DMF–H_2O (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 greenish yellow (nickel) and green (copper) metallated polymers were washed in hot water, ethyl acetate, acetone and dried in a vacuum oven at 60 °C. The metal complexes are characterized by elemental analysis, IR spectral data and EPR studies.

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 [Cu(II) titrimetrically and Ni(II) gravimetrically], after acid treatment of the complexes [21]. The anion content in the polymer–metal complexes was estimated by a titrimetric method [21] by precipitating the anion as its silver salt by adding excess of dilute solution of silver nitrate.

Results and discussion

Elemental analysis

Elemental analysis data is presented in Table 1. The data show that the conversion of keto groups to hydrazone function was 29% by weight (only the surface aldehyde groups were converted to isonicotinoyl hydrazones. The remaining aldehyde groups, deeply buried in the polymer chains were unaffected. Metallation was 24% and 26%, respectively, for Cu(II) and Ni(II) complexes.

Table 1 Elemental analysis data of MMBP-DVB copolymer, functionalized copolymers

S.No.	System	Found (%)		
		C	H	N
1.	MMBP-DVB	76.28	5.79	–
		(79.49)	(6.06)	–
2	Functionalized MMBP-DVB-INH	72.31	5.39	2.68
		(74.48)	(5.58)	(9.30)
3.	Functionalized MMBP-DVB-INH-Cu(II) chelates	63.74	4.72	1.97
		(64.81)	(4.85)	(8.09)
4.	Functionalized MMBP-DVB-INH-Ni(II) chelates	64.38	4.68	2.09
		(65.12)	(4.87)	(8.13)

Calculated values are given in parenthesis

IR spectral studies

The IR spectrum of MMBP monomer is shown in Fig. 1a. It shows bands at 3040 cm^{-1} and 2980 cm^{-1} because of aromatic –CH and back bone methylene stretching vibrations. The ester carbonyl of MMBP appeared at 1750 cm^{-1} as a sharp intense band whereas the ketonic carbonyl of benzophenone appeared as sharp band at 1660 cm^{-1}. The presence of strong absorption band at 1600 cm^{-1} is attributed to the C=C stretching vibrations of phenyl ring.

The IR spectrum of MMBP-DVB copolymer Fig. 1b shows absorption around 2900 cm^{-1}, which has been identified as aromatic –CH backbone methylene stretching vibrations. The ester carbonyl is identified through the appearance of a strong absorption band at 1720 cm^{-1}.

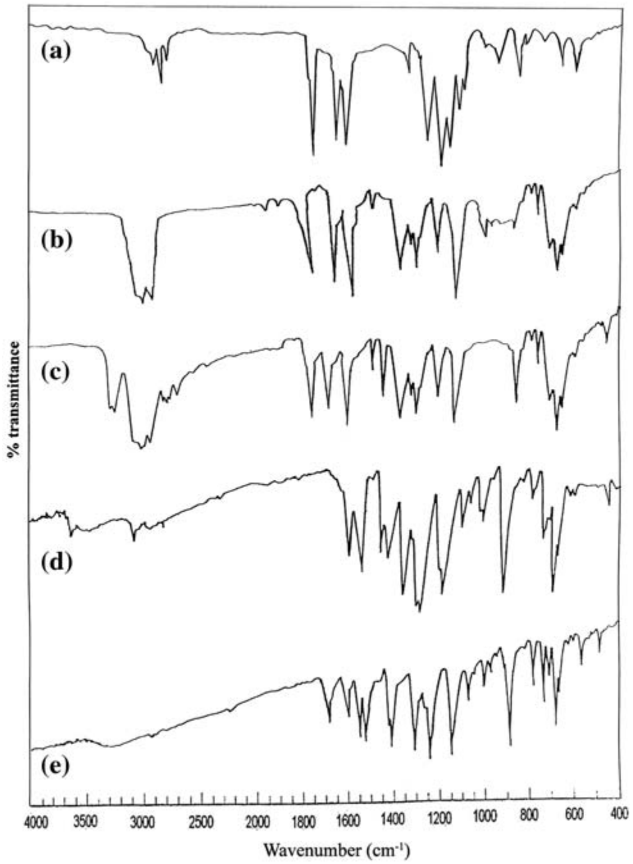


Fig. 1 IR spectrum of (**a**) MMBP monomer; (**b**) Copoly(MMBP-DVB); (**c**) Isonicotinoyl hydrazone derivative of MMBP-DVB copolymer; (**d**) MMBP-DVB functionalized resin Ni(II) complex; and (**e**) MMBP-DVB functionalized resin Cu(II) complex

A strong absorption around 1590 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 peak at 1170 cm^{-1}. The keto carbonyl functionality is identified by a sharp peak around 1690 cm^{-1} [22–24]. The formation of isonicotinoyl hydrazone is confirmed (Fig. 1c) by a set of distinct vibrations at 3280, 1610 and 1150 cm^{-1} which are due to –NH, C=N and N–N stretching respectively. The disappearance of the band at 1690 cm^{-1} indicates the removal of keto carbonyls of substituted benzophenone units. The IR spectrum of the Ni(II) complex (Fig. 1d) shows peak at 1600 cm^{-1}, which are lowered from 1610 cm^{-1} (C=N str.), in functionalized resin. Amide group vibrations increase in frequency from 1530 cm^{-1} to 1545 cm^{-1}. These changes in >C=O group vibrations suggest oxygen coordination in keto form. The bands observed at 400 cm^{-1} to 420 cm^{-1} are assigned to Ni–N bond vibrations [25, 26]. It is therefore inferred that the ligands coordinate in bidentate fashion. The IR spectrum of functionalized copolymer, Fig. 1c, shows intense band at 1680 cm^{-1} due to C=O stretching in hydrazone and its downward shift in Cu(II) complex (Fig. 1e) suggest coordination of metal ion through oxygen atoms. There is a downward shift of C=N vibration of azomethine from 1610 cm^{-1} to 1595 cm^{-1} which indicates the coordination of azomethine nitrogen atom.

Thus, in each complex the metal atom binds to the ligand through azomethine nitrogen and hydrazone carbonyl oxygen atoms.

^{1}H-NMR studies

The ^{1}H spectrum of MMBP is taken $CDCl_3$ solution and shown in Fig. 2. Two singlets observed at δ value 1.6 ppm and 2.0 ppm corresponds to CH_3–C=C and CH_3–Ar protons respectively. The signals at δ value 5.8 ppm and 6.3 ppm corresponds to olefinic (CH_2=C<) protons. They are characteristic of vinyl CH_2 group. The signals at δ value 7.2–8.1 ppm range are due to aromatic protons.

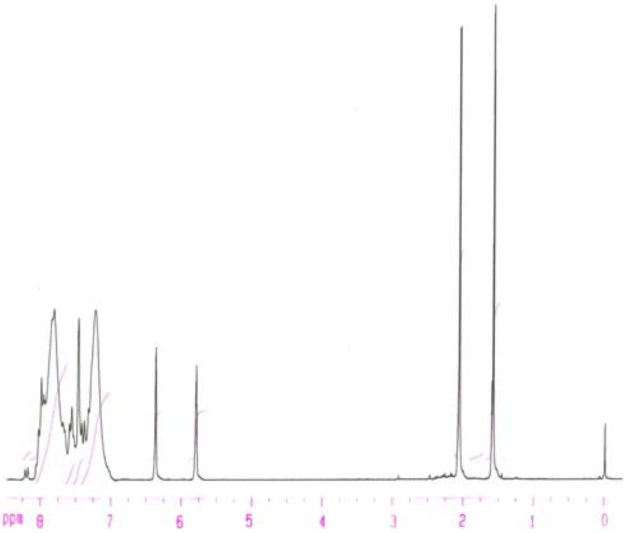


Fig. 2 ^{1}H-NMR spectrum of MMBP

Solid state ^{13}C-CP/MAS NMR spectroscopy

In the present investigation ^{13}C-CP/MAS NMR [27–29] 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-NMR spectra of MMBP homopolymer and ^{13}C-CP-MAS of cross-linked copolymers are shown in Figs. 3 and 4

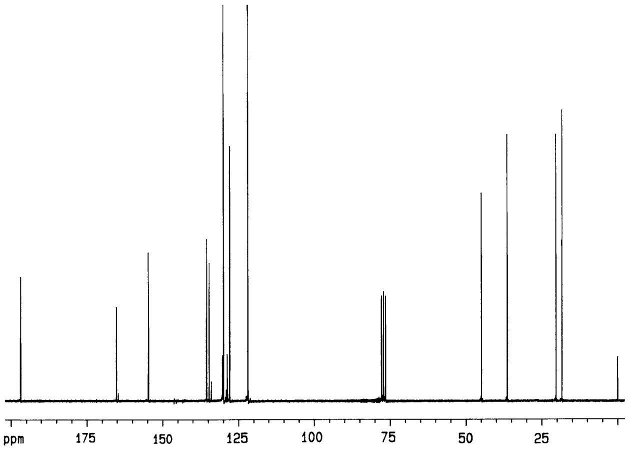


Fig. 3 ^{13}C-NMR spectrum of MMBP homopolymer in $CDCl_3$ solution

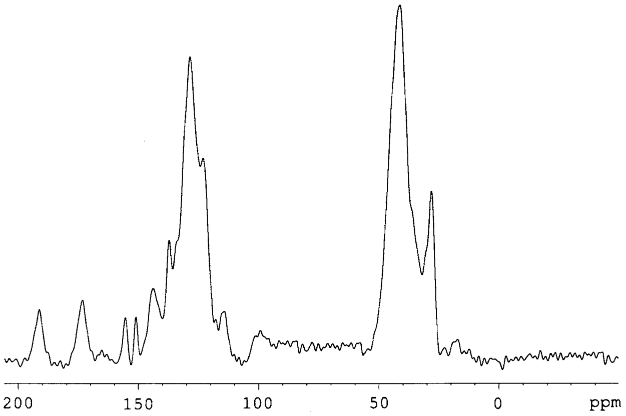


Fig. 4 Solid state ^{13}C-CP-MAS NMR spectrum of MMBP-DVB copolymer

respectively. The backbone –CH_2 and –CH groups 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 keto carbonyl of MMBP appeared at 196.82 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 [30] gave sharp line at 165.21 ppm in homopolymer and as a sharp peak in cross-linked system at 173.37 ppm. The aromatic carbons of homopolymer gave sharp lines at 121.81–154.68 ppm. 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 155.47 ppm with a shoulder at 128.58 ppm. The polymer chain termination occurs by disproportionation which is the case with methyl methacrylates. Similar observations have been made in the literature [31] for structurally related resins such as poly(2-hydroxy-4-methacryloxy acetophenone semicarbazone).

EPR spectroscopy

The EPR spectrum of MMBP-DVB-INH Cu(II) complex is shown in Fig. 5. 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 spectra show good resolution that three of four hyperfine lines are visible. The fourth hyperfine line is expected to be overlapping with high field component ($g_\perp$). The $g_\parallel$ and $g_\perp$ 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 [32]. The values $g_\parallel$ and $g_\perp$ for Cu(II) complex was 2.24 and 2.03, indicate covalent character for the metal–ligand bond in the complex. The EPR signal corresponding to Ni(II) complexes are not observed at room temperature.

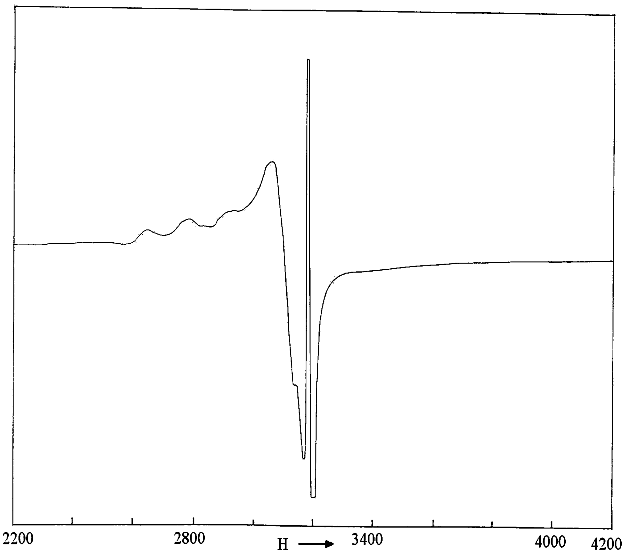


Fig. 5 EPR spectrum of MMBP-DVB isonicotinoyl hydrazone Cu(II) complex

A survey of the literature reveals that polymer metal chelates of related structure, such as Cu(II) and Ni(II) metal complexes poly(salicylaldehyde acrylate)-divinylbenzene semicarbazone resin [19] exhibit paramagnetic property. The nature of metal–ligand bond was reported to be covalent in these complexes. Similarly Ni(II) complex poly(2-hydroxy-4-methacryloyloxy acetophenone-formaldehyde) was also reported [33] to exhibit paramagnetic behavior with a distorted octahedral geometry [34]. Hence, based on the covalent nature of the metal–ligand bond observed in the present studies and also based on the reports made in the literature [19, 33, 34], octahedral geometry is suggested for the metal complexes presently investigated (Structure 1).

Thermogravimetric analysis

To study the thermal stability and decomposition patterns of cross-linked copolymers, dynamic thermogravimetric analysis is undertaken [35] and the data is presented in Table 2. The thermograms of the copolymer and its functionalized resins were run in air. The thermograms of MMBP-DVB copolymer and its isonicotinoyl derivatives are shown in Fig. 6. The degradation of MMBP-DVB copolymer occurred in two stages. The first stage, in the temperature range 150–400 °C, had a weight loss of 73%. The second stage of decomposition from 400 to 600 °C, had a weight loss of 22%.

The isonicotinoyl hydrazone derivative also decomposed in a two-stage process. The first stage of decomposition commenced at 230 °C and was completed at 400 °C with a weight loss of 85.5%. The second stage of decomposition was between 400 °C and 550 °C and the weight loss was 10.5%.

The thermograms of the functionalized copoly(MMBP-DVB)-Cu(II) and Ni(II) chelates are show in Fig. 6. The IDTs of copoly(MMBP-DVB)-Cu(II) and Ni(II) chelates are 166 °C and 216 °C respectively. The degradation occurred mainly in two stages and decomposition is fast up to 400 °C with a weight loss 78% and 73% respectively. The second stage of decomposition was between 400 °C and 600 °C with a weight loss of 19%. The first decomposition may be due to the rupture of weak linkages and volatilization of low molecular weight fragments. The

Table 2 TG data of MMBP-DVB copolymer, functionalized copolymer and functionalized metal chelates

S. No.	System	Weight loss (%) at temperature (°C)									
		IDTs	250	300	350	400	450	500	550	600	650
1.	MMBP-DVB copolymer	150	12.5	39.8	55.9	73.0	90.5	91.5	93.0	95.0	–
2.	Functionalized MMBP-DVB copolymer	230	3.0	25.7	52.3	85.5	92.8	94.0	96.0	–	–
3.	Functionalized MMBP-DVB-Cu(II) chelate	166.0	6.0	19.0	56.5	73.0	80.0	84.0	90.5	94.0	–
4.	Functionalized MMBP-DVB-Ni(II) chelate	216.0	5.0	11.0	27.5	78.0	84.0	85.0	89.5	91.5	92.0

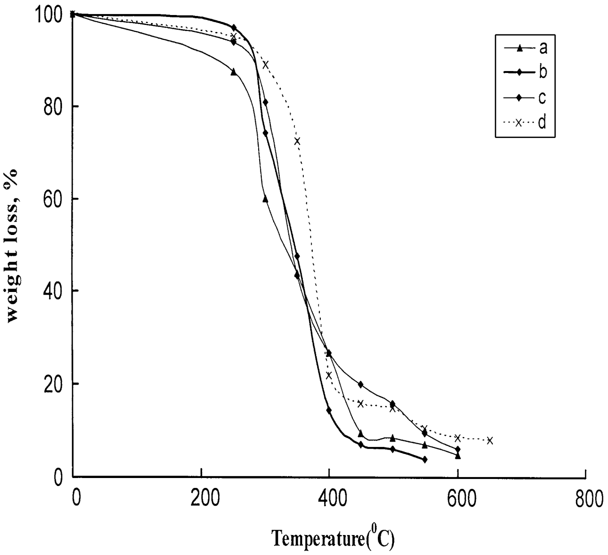


Fig. 6 TG curves of (a) MMBP-DVB copolymer; (b) Functionalized MMBP-DVB copolymer; (c) Functionalized MMBP-DVB Cu(II) chelate; and (d) Functionalized MMBP-DVB Ni(II) chelate

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.

The decomposition pattern of the metal chelates and the macromolecular chelate exhibits some interesting trends. The initial weight loss at 250 °C is maximum in the case of the free copolymer chelate (12.5%) which is followed by Cu(II)-macromolecular chelate (6.0%). This is followed by the Ni(II)-macromolecular chelate (5.0%), and then functionalized polymer chelate (3.0%). After 250 °C there is a change in the pattern of the percentage weight loss. The metal macromolecular chelates are much stable than the functionalized and free copolymer up to 300 °C. At 450 °C, the percentage weight loss for the above four systems are 90.5, 80.0, 84.0 and 92.8 respectively.

The thermal property of poly(salicylaldehyde acrylate)-divinylbenzene semicarbazone resins has been investigated [19] and these systems were reported to have thermal stability up to 247 °C. However, the poly(2-methacryloxy-5-methyl benzophenone)-divinylbenzene isonicotinylhydrazone as well as its metal chelates synthesized in the present study do not exhibit such a high thermal stability. The cleavage of isonicotinyl hydrazone from the backbone occurs at much lower temperature when compared to semicarbazone resins.

Scanning electron microscopy

The SEM is the technique employed for studying the shape, size and morphological features of the polymers in beaded form [36–38]. The SEM photographs are presented in Fig. 7. The SEM photographs of INH functionalized MMBP-DVB Cu(II) and Ni(II) metal complexes are shown in Fig. 7c and d. Functionalized resin appears smoother (Fig. 7b) than that of the metal anchored resins. The rough appearance of the resin surface is as a result of the doping of the metal ions. The copolymer beads (Fig. 7a) are spherical and of various sizes. The beaded nature of the polymer confirms the success of suspension polymerization.

Applications

Effect of time on adsorption

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 [39, 40] 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 Cu(II) and Ni(II) ions, batch studies were carried out [41]. The time dependence of the complexation of Cu(II) and Ni(II) by the functionalized MMBP-DVB resin

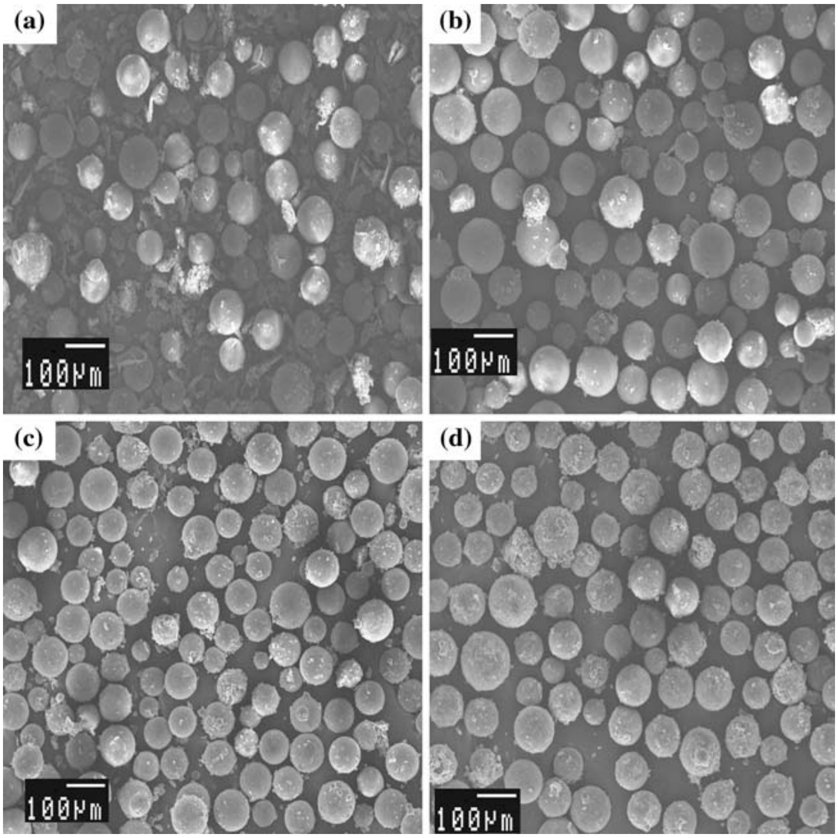


Fig. 7 SEM photographs of (**a**) Copoly(MMBP-DVB) copolymer surface; (**b**) Isonicotinoyl hydrazone derivative of MMBP-DVB copolymer; (**c**) MMBP-DVB functionalized resin Ni(II) complex; and (**d**) MMBP-DVB functionalized resin Cu(II) complex

was followed by the change in the concentrations of the metal-salt solutions at regular intervals. The data is presented in the form of Fig. 8.

The complexation of Cu(II) and Ni(II) was completed in 60 and 50 min for functionalized resin.

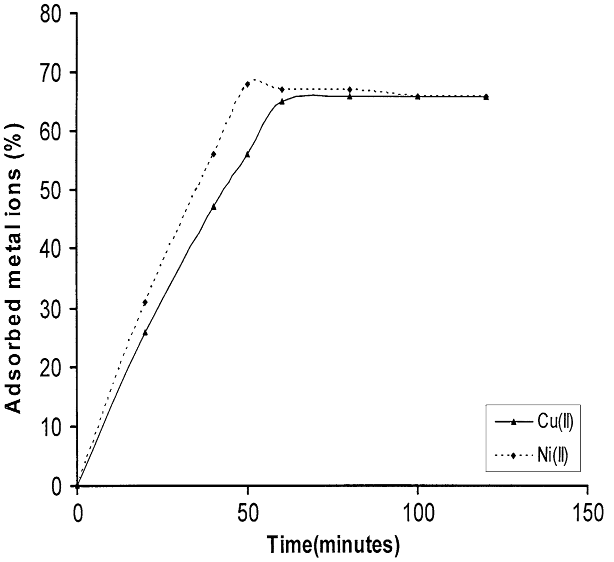


Fig. 8 Cu(II) and Ni(II) uptake by the functionalized MMBP-DVB copolymer

Effect of pH on uptake of metal ion

To various buffer solutions (pH 3–10), metal ion [Cu(II), Ni(II) (0.1) bulk concentration], functionalized MMBP-DVB resin (5 g) was added and maintained under shaking for 90 min. The metallated beads were filtered and

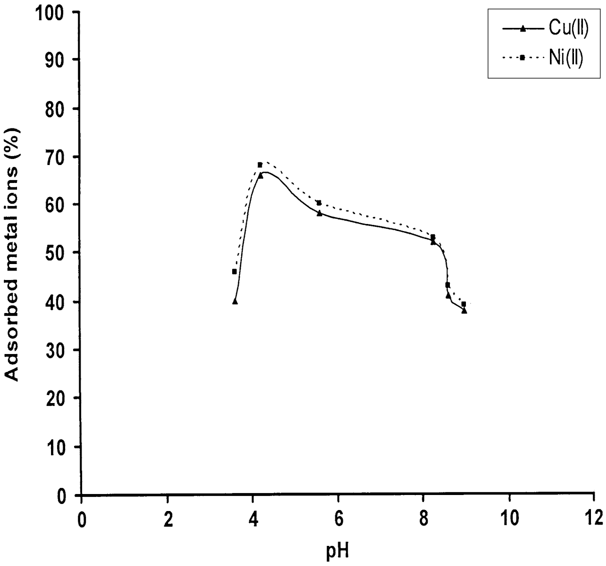


Fig. 9 Effect of pH on adsorption of metal ions Cu(II) and Ni(II)

Table 3 Comparison of retention properties of the resin system

System	Metal ion	Time taken for maximum uptake of metal ion (min)	Optimum pH	Amount of metallation (%)	Reusability
MMBP-DVB- isonicotinoyl hydrazone system	Cu(II)	60	4–5	24	4
	Ni(II)	50	4–5	26	4
SAA-DVB-semicarbazone system	Cu(II)	30	3–10	75	5
	Ni(II)	20	3–10	25	5

thoroughly washed. The bound metal ion was released by acid treatment and the metal content determined spectrophotometrically and is presented in Fig. 9. From the studies it can be concluded that the polymer uptake both the metal ions to a greater extent in the pH range 4–5.

Reusability of complexed MMBP-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 Cu(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.

Comparison of the retention properties of the resins

The time taken for the maximum uptake of metal ions by the isonicotinoyl functionalized resin has been found to be much higher compared to poly(salicylaldehyde acrylate)-divinylbenzene semicarbazone resins [19]. The optimum pH for maximum uptake metal ion is found to be about 4–5 for the present resins where as not much effect of pH was observed in the case semicarbazone resins. In the case of Ni(II) ion, the amount of metallation has been found to be almost the same in the present system and semicarbazone resin. Whereas the amount of Cu(II) ion up taken by the semicarbazone resins has been found to be much higher (75%) as compared to that of present resins which is 24%. The reusability of the present system is comparatively the same as that of the semicarbazone system and both can be reused even after four cycles of repeated operations. The results are presented in Table 3.

Conclusions

Suspension polymerization of 2-methacryloxy-5-methyl benzophenone using benzoyl peroxide as catalyst and divinylbenzene as a cross-linking agent was carried out. The isonicotinoyl hydrazone ligand was attached to the keto functional group and the resulting ligand polymer used to prepare polymer–metal complexes. IR spectral studies showed that the azomethine nitrogen and isonicotinoyl carbonyl group and chloride anions were involved in coordination to the metal ions such as Cu(II) and Ni(II). Elemental analysis confirmed that the percentage of functionalization was 29, while the metallation was 24 and 26 for Cu(II) and Ni(II) complexes, respectively. The EPR spectra of the Cu(II) complex showed that the metal–ligand bond is covalent in nature. Thermal studies were carried out and the thermal dissociation patterns discussed. SEM photographs indicate the success of suspension polymerization. A bead structure was observed for the polymers. The maximum uptake efficiency for the metal ions was determined. The reusability of the polymer ligand was tested and it was shown that even after four cycles, the efficiency of the uptake was not altered. The thermal stability, metal uptake efficiency and reusability of the ligand polymer was compared with the polymers of related structure.

References

1. Block BT (1970) Inorg Macromol Rev 1:115
2. Bailar JC Jr (1978) In: Carraher CE Jr, Sheats JE, Pittman CV Jr (eds) Organometallic polymers. Academic, New York, pp 313–321
3. Merrifield RB (1965) Science 150:178
4. Neckers DC (1975) J Chem Educ 52:695
5. Li W, Coughlin M, Albright RL, Fish RH (1995) React Funct Polym 28:89
6. Jovanovic SM, Nastasovic A, Jovanovic NN, Jeremic K, Savic Z (1994) Angew Makromol Chem 219:161
7. Jovanovic SM, Nastasovic A, Jovanovic NN, Jeremic K (1996) Mater Sci Forum 214:155
8. San Roman J, Madruga EL, Pargada L (1987) J Polym Sci Polym Chem Ed 25:203

9. He B, Su J, Li M, Wang L (1998) Shiyou Huayong 17:668 (CA:110:156404k)
10. Jiang W, Huang W, Zong H (1988) Fenzi Cuihua 2:202
11. Menger FM, Tsuno T (1989) J Am Chem Soc 111:4903
12. Wiley RH, Clevenger RL (1962) J Med Pharm Chem 5:1876
13. Montegazza P, Panchiane F, Cavalind G (1961) Antibiot Chemother 11:405
14. Katyal M, Dutt J (1975) Talanta 22:156
15. Babaiah O, Rao CK, Reddy TS, Reddy VK (1996) Talanta 43:551
16. Babaiah O, Reddy PR, Reddy VK, Reddy TS (1999) Indian J Chem Sect A 38:1035; (2004) J Indian Chem Soc 81:670
17. Gangadharappa M, Reddy PR, Reddy VK, Reddy TS (2004) J Indian Chem Soc 81:525
18. Reddy VK, Thippaiah J, Rao CK, Reddy PR, Reddy TS (1999) J Indian Chem Soc 76:275
19. Prabhakar LD, Marysaral A (1997) Polym Int 42:149
20. Dey BB, Sitaraman MV (1992) Laboratory manual of organic chemistry (Revised by Govindachari TR), 4th edn. Allied Publishers Ltd., New Delhi
21. Vogel AI (1978) A text book of quantitative inorganic analysis. Longman, London
22. Weiliao I, Eichinger BE (1990) J Polym Sci Part A Polym Chem 28:559
23. Bender ML, Figueras J (1953) J Am Chem Soc 75:6304
24. Torikai A, Takeuchi A, Nagaya S, Fueki K (1986) Polym Photochem 7:279
25. Gosavi RK, Rao CNR (1969) J Inorg Nucl Chem 29:1937
26. Mikami M, Nakagawa I, Shimanouchi T (1967) Spectrochim Acta 23A:1037
27. Cunliffe AV (1978) In: Dawkins JV (ed) Developments in polymer characterization-1, Chapter 1. Applied Science, London
28. Schaefer J, Stejskal EO (1979) In: Levy GC (ed) Topics in carbon-13 NMR spectroscopy, Chapter 4, Vol. 3. Wiley Interscience, New York
29. Bovey FA (1976) In: Ivin KJ (ed) Structural studies of macromolecules by spectroscopic methods. John Wiley & Sons, New York
30. Rao BS, Modec PJ, Marechal BC (1987) Macromol Soc Chem A24:719
31. Thamizharasi S, Venkata Rami Reddy A, Balasubramanian S (1998) Eur Polym J 34:605
32. Okawa H, Tokii T, Noraka N, Muto Y, Kida S (1973) Bull Chem Soc Jpn 46:1462
33. Kaliyappan T, Kannan P (1994) J Polym Mater 11:121
34. Bostop O, Jorgensen CK (1957) Acta Chem Scand 11:1223
35. Wendlandt WW (1964) Thermal methods of analysis. Interscience, New York
36. Arshady R (1989) J Microencapsul 6:1
37. Kun KA, Kunin P (1968) J Polym Sci Polym Chem 7:2689
38. Sederal WL, Dejong GJ (1973) J Appl Polym Sci 17:2835
39. Torse R, Rieman V (1961) J Phys Chem 65:1821
40. Mart Suzura M, Wadachi Y (1975) Bull Chem Soc J Pr 48:3456
41. Nishide H, Deguchi J, Suchida ET (1977) Polym Sci Poly Chem Ed 15:3028