

Synthesis and Characterization of Polymer-Metal Chelates Derived from Poly(4-methacryloxy acetophenone)-Methyl Methacrylate Isonicotinoyl Hydrazone Resins

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Abstract: Copolymers of 4-methacryloxyacetophenone with methyl methacrylate were prepared in ethyl methyl ketone using benzoyl peroxide as the initiator at 70 °C. They were characterized by elemental analysis, Fourier transform infrared, ¹H NMR, ¹³C NMR and scanning electron microscopy. Cu(II) and Ni(II) chelates of the functionalized copolymer were prepared and characterized by elemental analysis, Fourier transform infrared, scanning electron microscopy and EPR spectra. Thermogravimetric analysis of polymers and metal chelates were performed.

Keywords: Polymer-metal chelates, Copper(II) and Nickel(II) complexes, Cross-linking agent, chemical modification, EPR, Scanning electron microscope

Introduction

The synthesis of polymers containing reactive functional groups has been an active field of research in polymer science. It provides an approach to a subsequent modification of the polymer for the required application. The synthesis and properties of polymers having chelating ligands¹⁻³ have been reported. Polymer-bound chelating ligands including polydentate amines, crown ethers, schiff bases and porphyrins have been described^{4,6}. A survey of the literature also reveals that hydrazones derived from low molecular weight aromatic carbonyl compounds draw the attention of synthetic chemists due to their varied biological activities^{7,8}. 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 ions⁹⁻¹². With a view to the complexing abilities of hydrazone derivatives of acetophenone incorporated into the polymer, the 4-methacryloxy acetophenone (MAP) cross-linked with methyl methacrylate (MMA) was selected. The isonicotinoyl hydrazone (INH) derivative of the cross-linked copolymer acts as polymeric ligand towards metal ions. We report herein the synthesis and characterization of hydrazone derivatives of poly MAP-MMA copolymer towards Cu(II) and Ni(II) ions.

Experimental

To 0.2 mol 4-hydroxy acetophenone in ethyl methyl ketone, 0.2 mol triethylamine (TEA) was added with stirring at 0-5 °C. To this mixture 0.2 mol methacryloyl chloride in ether was added drop wise over 45 min. Stirring was continued for 1 h. The precipitate that resulted was filtered and washed thrice with ether. The ethereal layer was evaporated to obtain 4-methacryloxy acetophenone (MAP) monomer.

Methyl methacrylate (MMA) was freed from the inhibitor and distilled under vacuum. Benzoyl peroxide (BPO) was recrystallized from chloroform-methanol (1:1) mixture and the solvents were purified by distillation.

Polymerization

Poly(MAP-MMA) was prepared in ethyl methyl ketone using BPO as the free radical initiator at 70 °C. The monomer concentration was 5 M and that of the initiator was 0.25 wt% based on the monomers, MAP and MMA. Appropriate amounts of monomers, initiator and solvent were mixed in a polymerization tube, degassed, sealed and kept at 70 °C in a thermostatic water bath for 18 h. The copolymer was precipitated in methanol, purified by at least two reprecipitations by methanol from chloroform solution and dried in vacuum at 60 °C.

Functionalization of polymer

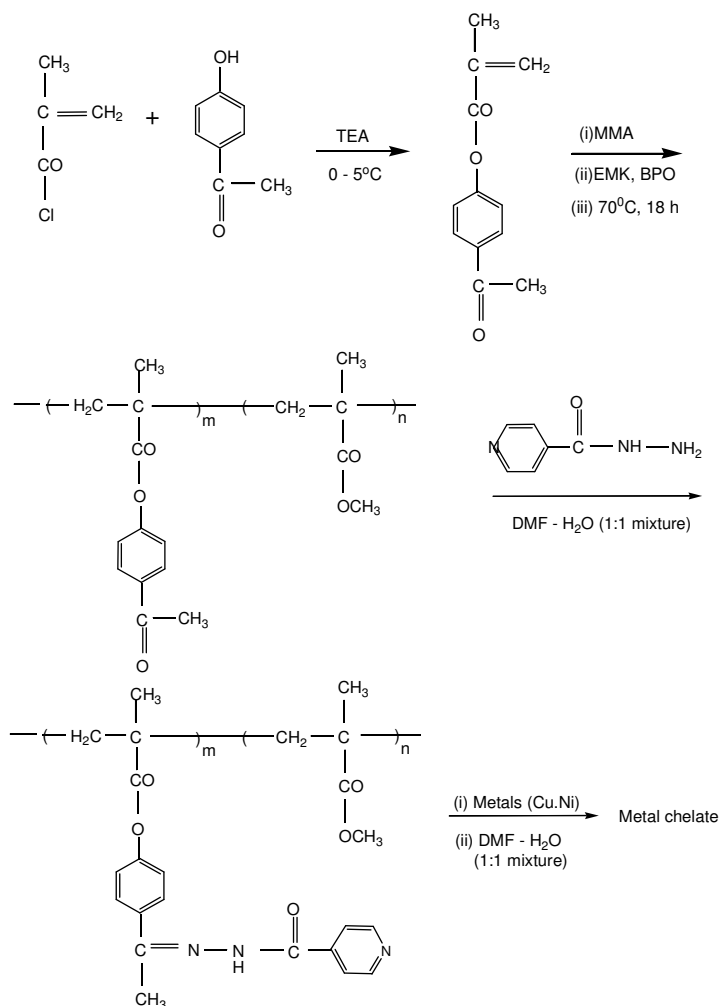
Functionalization of copoly(MAP-MMA) was achieved by incorporating an isonicotinoyl hydrazone moiety through a post polymerization reaction. Cross-linked polymer (5 g), Isonicotinic acid hydrazine (INH) (10 g) and sodium acetate (6.8 g) in dimethylformamide-water (DMF-H₂O) mixture (1:1) were placed in a 500 mL round-bottomed flask and refluxed for 12 h. The addition of excess of methanol to the reaction mixture results in the precipitation of the polymer. The contents were filtered, the functionalized polymer (MAP-MMA-INH) was collected, washed with water and dried.

Polymer-metal chelates

The polychelates were prepared by reacting a DMF solution of functionalized polymer (5 g) and an aqueous solution of CuCl₂·2H₂O, NiCl₂·6H₂O (5 g) after adjusting the pH to 7 with ammonia. The reaction mixture was refluxed for 10 h. and the resulting solid polychelate was washed with hot water followed by ethanol and dried under vacuum. The reaction of 2-hydroxy acetophenone with methacryl chloride, its copolymerization with MMA and the final conversion to the hydrazone functionality are presented in Scheme 1.

Measurements

Infrared spectra were recorded with a Perkin-Elmer spectrophotometer 983-G using KBr pellets and FT-IR spectra of the cross-linked copolymers and their metal chelates were recorded on Digilab FT IR-Win-IR Pro using KBr pellets. ¹H-NMR spectra were run on a Bruker CXP 90 MHz spectrometer CDCl₃ solution with TMS as internal standard. Proton decoupled ¹³C NMR spectra were recorded on a Bruker CXP 90 operating at 22.6 MHz spectrometer in CDCl₃. Tetramethylsilane (TMS) was the internal standard. Thermogravimetric analysis was carried out on a Perkin Elmer model 3700 with TGA 7 computer and Mettler TA 3000 thermal analyzer in air. Thermograms were recorded with 10 mg samples at a heating rate of 10 °C min⁻¹. EPR spectra of the polymer metal chelates were recorded on a JEOL-FA 200 spectrometer at 303 K. Elemental analysis was carried out with Thermo Finnigan FLASH EA 1112 CHNS analyzer. Scanning electron micrographs were taken on JSM-840A Jeol-Japan. The copolymer was coated with gold.



Scheme 1

Results and Discussion

Characterization of the monomer

IR spectra

The IR spectrum of MAP monomer shows an absorption band at 2977 cm^{-1} due to CH stretching vibrations in alkane. The ester carbonyl of MAP appeared at 1718 cm^{-1} . The presence of absorption band at 1414 cm^{-1} is attributed to the C=C skeletal vibration of phenyl ring. The C-O-C stretching vibrations are noticed at 1131 cm^{-1} .

¹H NMR

The ¹H-NMR of MAP shows two singlets at δ 2.1 and 2.5 ppm corresponding to methacryloyl and keto methyl protons respectively. Two signals at δ value 5.9 and 6.5 ppm correspond to vinyl protons. The signals at δ 7.0 and 8.2 ppm arise from the protons of disubstituted phenyl ring.

Characterization of the copolymer

Elemental analysis

Elemental analysis data are presented in Table 1. The data show that the conversion of carbonyl groups to hydrazone function was 41% by weight.

Table 1. Elemental analysis of MAP-MMA copolymer, isonicotinoyl hydrazone functionalized polymer and metal chelates

Element	Found, %			
	MAP-MMA	MAP-MMA-INH	MAP-MMA-INH-Cu(II)	MAP-MMA-INH-Ni(II)
C	68.94	62.74	52.29	52.58
H	5.98	5.71	4.86	4.67
N	-	4.72	2.53	2.47
Cu(II)	-	-	1.47	-
Ni(II)	-	-	-	1.58
		41*		

* Indicates the percentage of conversion

IR spectra

The IR spectrum of copoly(MAP-MMA) is shown in Figure 1. The IR spectrum shows bands at 3010 and 2929 cm^{-1} because of aromatic CH and back bone methylene stretching vibrations respectively. The absorption band at 1737 cm^{-1} corresponds to the ester carbonyl group. The ketonic functionality is identified by a sharp absorption¹³⁻¹⁵ band around 1690 cm^{-1} .

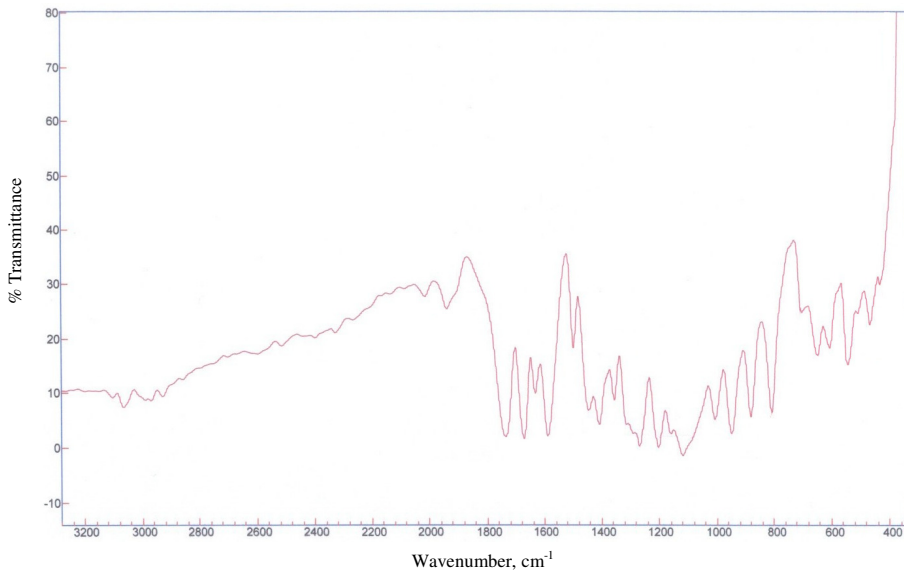


Figure 1. FT-IR spectrum of MAP-MMA copolymer

¹H NMR spectra

The NMR study helps in the confirmation of copolymer formation. ¹H NMR spectrum of copoly(MAP-MMA) shows a signal at δ value 1.3 is due to backbone methyl (CH_3) protons. The signals at δ 2.1 and 2.2 ppm arise from the backbone methylene ($-\text{CH}_2$) protons. The signal

at δ value 2.5 ppm corresponds to methyl protons of $-\text{CO}-\text{CH}_3$. The resonance signal at δ 3.6 ppm is due to the $-\text{OCH}_3$ protons of MMA unit. The multiplet between δ value 7.2-8.2 ppm correspond to the protons of disubstituted phenyl ring.

¹³C NMR spectra

The ¹³C NMR spectrum of MAP-MMA cross-linked copolymer is shown in Figure 2. The resonance signal at 48.3 ppm is due to the $-\text{OCH}_3$ (C_{17}) carbon of MMA. The signal for backbone methyl groups (C_2 , C_{14}) appear at 17.2 ppm. The resonance signals at 39.6 and 38.3 ppm are due to backbone methylene groups, C_1 and C_{13} respectively. The resonance signal at 18.39 ppm is attributed to C_3 & C_{15} carbons. The resonance signal at 27.46 ppm is attributed to methyl carbon (C_{12}). The ketonic carbonyl (C_{11}) of MAP-MMA appeared at 196.82 ppm as sharp intense signal. The ester carbonyl groups appear at 165.21 (C_{16}) and 164.52 (C_4) ppm. The C_5 of phenyl ring appeared at 135.54 ppm. The C_6 & C_9 , C_7 & C_8 aromatic carbons gave sharp signals at 130.64 and 122.32 ppm. The signal observed at 154.68 ppm is attributed to C_{10} of the phenyl ring.

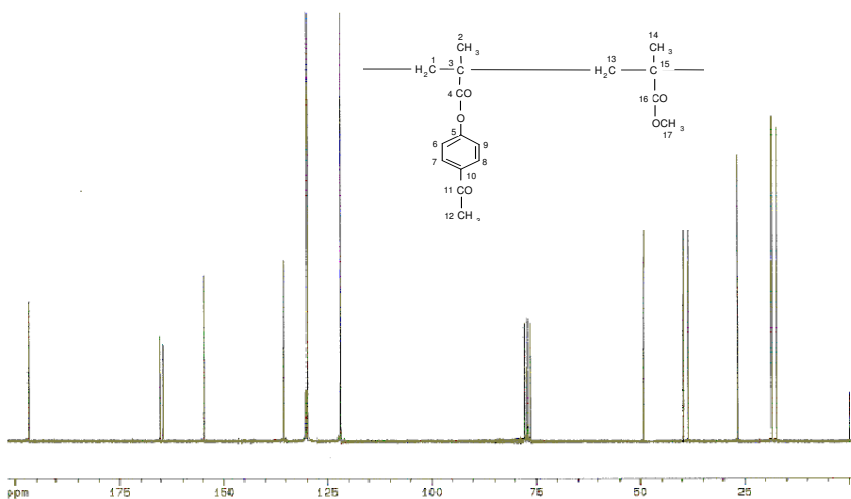


Figure 2. ¹³C NMR spectrum of MAP-MMA copolymer

Characterization of the functionalized copolymer

IR spectra

The formation of hydrazone is confirmed by a set of distinct vibrations at 3426 and 1630 cm^{-1} which are due to $-\text{NH}$ and $\text{C}=\text{N}$ stretching, respectively. The disappearance of the band at 1690 cm^{-1} indicates the removal of the surface ketonic carbonyls of the MAP units. The presence of another absorption band around 1700 cm^{-1} clearly indicates the intactness of ester carbonyl of acrylate units. This clearly indicates formation of hydrazone derivative.

Thermogravimetric analysis

To study the thermal stability and decomposition patterns of the cross-linked copolymers dynamic thermogravimetric analysis was undertaken. The thermograms of MAP-MMA copolymer and its isonicotinoyl hydrazone derivative were run in air. The thermograms are shown in Figure 3. The initial decomposition of MAP-MMA begins at 138 °C. The degradation of MAP-MMA copolymer occurred in two stages. The first stage decomposition

is observed from 176-372 °C and the weight loss is about 50%. The second stage degradation of the copolymer resin is in the temperature range 372-530 °C. The weight loss involved in this stage is 46.7%. The decomposition of MAP-MMA-INH begins at 146 °C. The isonicotinoyl hydrazone derivative also decomposed in a two-stage process. The first stage of decomposition commenced at 220 °C and completed at 413 °C with a weight loss of 72%. The second stage decomposition is between 413 and 558 °C and the weight loss is about 25.6%.

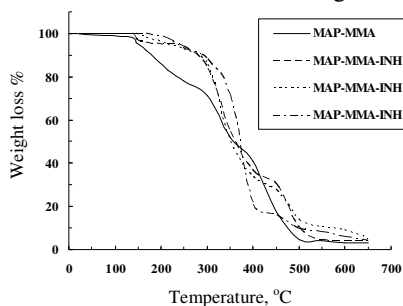


Figure 3. Thermograms

Characterization of the metal complexes

Elemental analysis

The metal chelates are coloured solids and insoluble in common organic solvents. The C, H and N elemental values of the resin complex decreased when compared to the functionalized resin. The amount of the metal incorporated in the copolymer is determined by estimation the metal ions. Metallation was 20% and 23% for the Cu(II) and Ni(II) complexes respectively. Elemental analyses have shown that ligand (MAP-MMA-INH) to metal ratio is 2:1 in both the polychelates.

IR spectra

Comparison of the IR spectra of functionalized polymer and polychelates gives information regarding the nature of chelation. The presence or absence and shift of some bonds may be utilized to establish the nature of chelation. The IR spectra of functionalized copolymer shows intense band due to C=O stretching at 1658 cm^{-1} and its downward shift to 1640 cm^{-1} in Cu(II) complex suggest coordination of metal ion through oxygen atoms. There is a downward shift of C=N stretching band of azomethine group from 1630 cm^{-1} to 1595 cm^{-1} which indicates the coordination of azomethine nitrogen atom. This indicates the participation of the carbonyl groups (present in the hydrazone units) and C=N groups in coordination with the metal ions^{16,17}. Similarly in the case of the Ni(II) complex azomethine nitrogen and hydrazone carbonyl groups were involved in coordination. The C=O and C=N stretching frequency of Ni(II) complex are lower than those of the hydrazone and noticed at 1595 and 1520 cm^{-1} respectively. Thus, in each complex the metal atom binds to the ligand through azomethine nitrogen and hydrazone carbonyl oxygen atom.

EPR spectroscopy

The EPR spectrum of the MAP-MMA-INH Cu(II) complex is shown in Figure 4. The EPR parameters (g values) give a measure of the nature of the complexation with the metal ion. The EPR parameters calculated by Kneubuhl¹⁸ method for the copper complex is found to be g_{\parallel} , 2.18; g_{\perp} , 2.06. For the covalent complexes, g_{\parallel} is less than 2.3 and for ionic environments it is normally 2.3 or larger¹⁹. The g_{\parallel} values of the Cu(II) complex is 2.18, indicating the covalent nature of the complex.

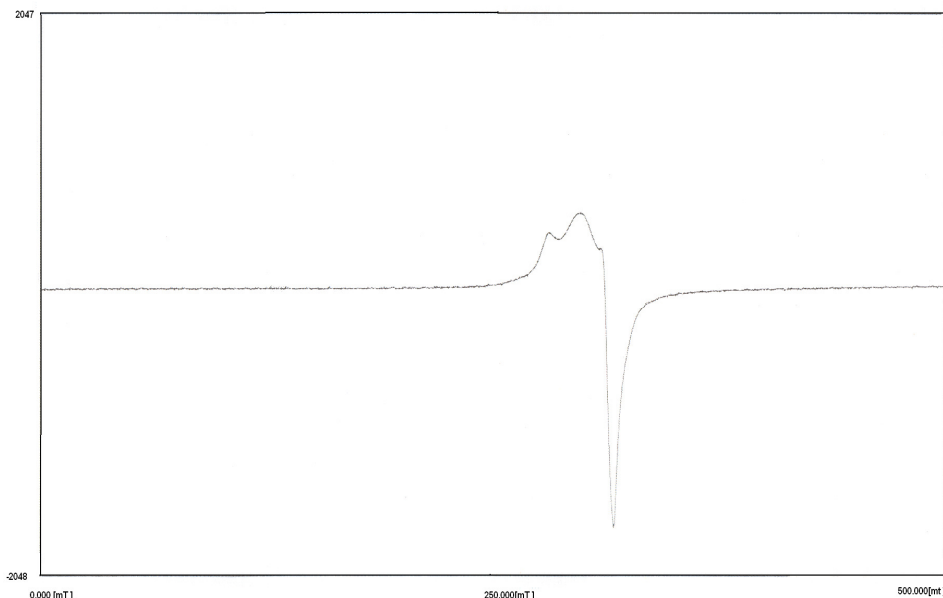


Figure 4. EPR spectrum of MAP-MMA-INH-Cu(II) chelate

Thermogravimetric analysis

The TGA curves of the polychelates are shown in Figure 3. The initial decomposition temperature (IDT) of the polychelates is higher than that of the copolymers and above 166 °C. The degradation Copper chelate begins at 167 °C and that of Nickel chelate at 214 °C. The degradation occurred mainly in two stages and decomposition is fast up to 400 °C. The first stage decomposition may be due to the rupture of weak linkages and volatilization of low molecular weight fragments. The second slow decomposition of chelates at higher temperature may be due to the breakage of main chain accompanied by the volatilization of the cleaved products.

Scanning electron microscopy

Scanning electron microscopy has been employed for studying the shape, size and morphological features of the polymer. The micrograph of MAP-MMA is presented in Figure 5. It can be seen from the microphotograph that the copolymer particles are of varied shape and size. The functionalized polymer shows some amorphous nature when compared to copolymer indicating the success of functionalization. The surface of the polychelate has a rough appearance, indicating doping of the metal ions.

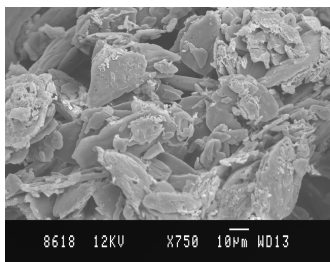


Figure 5. SEM microphotograph of MAP-MMA copolymer

Conclusion

Poly 4-methacryloxyacetophenone-methyl methacrylate was prepared in ethyl methyl ketone using benzoyl peroxide as the initiator. The isonicotinoyl hydrazone ligand was attached to the keto functional group and the resulting ligand polymer used to prepare polymer-metal chelates. IR spectral studies showed the azomethine nitrogen and isonicotinoyl carbonyl group and chloride anions were involved in coordination to the metal ions, Cu(II) and Ni(II). Elemental analysis confirmed that the percentage of functionalization was 41, while the metallation was 20 and 23 for Cu(II) and Ni(II) chelates, 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 polymerization.

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