

Synthesis, Characterization, and Ligating Behavior of Poly[*N,N*-*p*-phenylene bisacryl (methacryl)amide]

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ABSTRACT: Monomers of diacylated amine were synthesized by the reaction of acryloyl chloride or methacryloyl chloride with *p*-phenylenediamine. Heating DMF solution of these monomers at 75°C in the presence of AIBN as an initiator gave the corresponding polymer. The solid metallopolymer complexes with different metal salts were isolated either by the *in situ* addition of the monomer, metal salt, and initiator at 75°C or by the reaction of the isolated polymer with the metal salt at 150°C. The monomers, polymers, and their metallopolymer compounds were characterized using elemental analysis, IR, NMR (¹H and ¹³C), and MS spectral measurements in addition to thermal analysis. The IR data showed that the coordinating atoms of the

polymer are dependent on the reaction temperature. The ion selectivity of the isolated polymers toward different metal ions either for a single metal ion or in a mixture as aqueous solutions are studied by the batch techniques. Energy dispersive spectroscopy (EDS) measurements showed that both polymers are more selective to Hg²⁺ and Pb²⁺. The morphology of the polymers and their metallopolymer complexes at different temperature was also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2412–2422, 2006

Key words: synthesis; polyamides; metal–polymer complexes; morphology

INTRODUCTION

The preparation of functional polymers by chemical modification is an important technique, which has been used extensively both in the industries to modify the properties of the polymers for various technological applications and in the area of polymer-supported chemistry to prepare chemically reactive polymers.^{1–14} In principle, the functional groups may be a part of the polymer backbone or linked to a side chain as a pendant group. The required active functional groups can be incorporated onto a polymeric chain by (a) incorporation during the preparation of the polymer itself through polymerization of monomers containing the desired functional groups and (b) chemical modification of a suitably nonfunctionalized polymer.^{11,15} The reaction of metal ions with polymeric ligands containing pendant functional groups, which act as chelating groups, in bonding polyvalent metal ions procedures coordinated systems with enhanced thermal stability and biological activity.^{8–16} The aim of this study was to synthesize the polymers resulted from the polymerization of diacylated amines, from the reaction of ac-

ryloyl- or methacryloyl chloride with *p*-phenylenediamine, as well as their metallopolymer complexes. The metal uptake and metal ion selectivity of the prepared polymers are also discussed.

EXPERIMENTAL

Materials

p-Phenylenediamine, acryloyl chloride, and methacryloyl chloride (Aldrich, Milwaukee, WI) were used as received. All metal salts and other chemicals were of reagent grade and used without further purification.

Elemental analyses and physical measurements

Elemental analysis was performed at the ANALAB, on LECO CHNS-932 elemental analyzer. IR spectra were recorded as KBr discs of monomers, polymers, and the metallopolymer complexes on PerkinElmer System 2000 FTIR spectrophotometer (Kyoto, Japan). ¹H- and ¹³C-NMR spectra were recorded on a Bruker DPX 400, 400 MHz superconducting NMR spectrometer, with DMSO-*d*₆ as solvent and TMS as an internal standard; chemical shifts are reported as δ ppm. Scanning electron microscopic (SEM) analyses for the polymers and their metallopolymer complexes were examined at room temperature using JSM 6300 JEOL scanning electron microscope (Akishima, Japan) at 20 kV. TGA was carried out in air using a Shimadzu DSC 50

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TABLE I
Monomer Structures, Names, and Abbreviations

Compound No.	Symbol	Name	Abbreviation	Corresponding polymer abbreviation
1	$(\text{CH}_2=\text{CHCONH})_2\text{C}_6\text{H}_4$	<i>N,N</i> - <i>p</i> -Phenylene bisacylamide	PBA	PPBA
2	$(\text{CH}_2=\text{C}(\text{Me})\text{CONH})_2\text{C}_6\text{H}_4$	<i>N,N</i> - <i>p</i> -Phenylene bismethacrylamide	PBM	PPBM

analyzer (Japan) set at a heating rate of 10°C/min and at the temperature range of 25–800°C. Energy dispersive spectroscopy (EDS) chemical area mapping the metallopolymer complexes was performed with LINK'S exl II energy dispersive spectrometer (Oxford instruments, Analytical, Hywycombe, Bucks, UK) attached to the SEM to measure the absorbed ions from solution. Mass spectra were recorded on GS/MS IN-COS XL Finnegan MAT.

Synthesis of the monomers, polymers and complexes

Synthesis of monomers (1) and (2)

A solution of acryloyl or methacryloyl chloride (0.02 mol) in acetone or dichloromethane (30 cm³) was added drop wise to a solution of *p*-phenylenediamine (0.01 mol), in the same solvent (50 cm³), in an ice bath. The reaction mixture was then neutralized with saturated solution of (NH₄)HCO₃. The solid product was collected by filtration, washed with iced water (200 cm³), crystallized from MeOH or EtOH. Melting point (m.p.) of compound 1 (242°C) (Lit.¹⁶ m.p. = 243°C) and compound 2 equals to 248°C (Lit.^{17,18} m.p. = 249–251°C¹⁷, 242–244°C¹⁸), yield 85%.

Polymerization

Polymerization of the prepared monomers (0.01 mol) was carried out in DMF (50 cm³) and 0.02 mol of AIBN at 75°C (water-bath). The polymer was obtained after cooling and treating the reaction mixture with ethanol

or ethanol:water (1:1 v/v) mixture in case of methacryloyl derivative. The polymer formed was obtained as a swelled product while hot in case of acryloyl derivative. The solid product in each case was filtered off and washed with cold ethanol. The isolated polymer was refluxed in ethanol for 3 h for purification, filtered off while hot, and dried at 50°C under a reduced pressure for 48 h.

Synthesis of the metallopolymer complexes

Method A. To a suspension of dry polymer PPBA or PPBM (0.01 mol, 2.16 or 2.44 g, respectively) in DMF (20 cm³), a preprepared filtered DMF (copper (II) acetate, cobalt (II) chloride or cobalt (II) nitrate, nickel (II) chloride, mercury (II) sulfate, lead (II) acetate, and vanadyl acetylacetonate) solution (0.01 mol, 20 cm³) was added. The reaction mixture was heated under reflux at 75 or 150°C for 3 h, left overnight, filtered, and washed several times with the deionized water, ethanol, and diethyl ether, followed by drying in vacuum at 60°C for 24 h.

Method B. To a DMF solution (50 cm³) of the monomers 1 or 2 (0.01 mol), the corresponding metal salt (0.01 mol) and AIBN (0.02 mol) were added. The reaction mixture was heated at 75°C for 3 h, left overnight, filtered, and washed several times with the deionized water, ethanol, and diethyl ether, followed by drying in vacuum at 60°C for 24 h.

Ion selectivity measurements

To an aqueous solution containing (0.01 mol) of M(OAc)₂·*n*H₂O or 0.01 mol of a mixture of

TABLE II
Elemental Analysis and Mass Spectra of the Prepared Compounds

Compound No.	MS (<i>m/z</i>)	Elemental analysis Found/Calcd.		
		C	H	N
1	C ₁₂ H ₁₂ N ₂ O ₂ (216)	66.60	5.67	12.91
	(84%); 161 (55%); 107(90%);	66.64	5.60	12.95
	80 (15%); 69 (18%); 55 (100%)			
2	C ₁₄ H ₁₆ N ₂ O ₂ (244)	68.65	6.99	11.73
	244 (84%); 176 (8%); 166 (8%);	68.85	6.55	11.47
	144 (4%); 107(9%); 69 (100%).			

TABLE III
The ¹H-NMR and ¹³C-NMR Data of the Prepared Monomers

Monomer	¹ H-NMR/ ¹³ C-NMR (ppm)
1	10.16 (s, 1H, NH); 7.62 (s, 4H, C ₆ H ₄); 6.44 (s, 1H, CH=); 6.22, 5.75 (d, 2H, CH ₂ =); 165.98 (C=O), 137.23 (ethylenic carbon, CH=), 135.46, 121.26 (aromatic carbons), 122.40 (ethylenic carbon, =CH ₂).
2	9.76 (s, 1H, NH); 7.56 (s, 4H, C ₆ H ₄); 5.78, 5.49 (d, 2H, CH ₂ =); 1.94 (s, 3H, CH ₃); 167.55 (C=O), 141.43 (ethylenic carbon), 135.66, 120.76 (aromatic carbons), 121.40 (ethylenic carbon, =CH ₂) 19.80 (methyl carbon).

TABLE IV
IR of Monomer, Polymer, and Complexes at 75 and 150°C

Compound	IR (cm ⁻¹)
PBA	3270 (NH), 3159, 3081 (CH—aromatic and ethylenic), 2928, 2847 (CH—aliphatic), 1884, 1580 (—CH=CH ₂), 1663 (CO), 1635 (C=C), 833, 764 (<i>p</i> -substituted)
PPBA	3444 (H ₂ O), 3264 (NH), 3148, 3059 (CH—aromatic), 2926, 2861 (CH—aliphatic), 1663 (CO), 1610 (C=C), 834, 796, (<i>p</i> -substituted)
PPBA-Cu (II) ^a	3437 (br., H ₂ O and NH), 3162, 3084 (CH—aromatic), 2931, 2847 (CH—aliphatic), 1663 (CO), 1610 (C=C), 1412, 1293 (acetate anion)
PPBA-Cu(II) ^b	3273 (NH), 1657 (CO), 1602, 1328 (monodentate acetate group)
PPBA-Co(II) ^a	3273 (NH), 2930 (CH—aliphatic), 1656 (CO), 1436, 1384 (monodentate nitrate)
PPBA-Co(II) ^b	3411 (br., H ₂ O and NH), 2930 (CH—aliphatic), 1659 (CO), 1438, 1385 (monodentate nitrate)
PPBA-Ni (II) ^a	3313 (br., H ₂ O and NH), 2929, 2809 (CH—aliphatic), 1654 (CO), 901, 688 (coordinated water), 837, 662 (<i>p</i> -substituted).
PPBA-Ni(II) ^b	3268 (br., H ₂ O and NH), 2930 (CH—aliphatic), 1656 (CO), 901, 687 (coordinated water), 834, 662 (<i>p</i> -substituted).
PPBA-Pb(II) ^a	3432 (H ₂ O), 3270 (NH), 3081 (CH—aromatic), 2932 (CH—aliphatic), 1663 (CO), 834, 661 (<i>p</i> -substituted).
PPBA-Pb(II) ^b	3264 (br., H ₂ O and NH), 3043 (CH—aromatic), 2928, 2362 (CH—aliphatic), 1663 (CO), 1609 (C=C), 832, 660 (<i>p</i> -substituted).
PPBA-VO(II) ^a	3408 (H ₂ O), 3264 (NH), 2930 (CH—aliphatic), 1658(CO), 977 (V=O), 834, 704 (<i>p</i> -substituted)
PPBA-VO(II) ^b	3433 (br., H ₂ O and NH), 2995 (CH—aliphatic), 1648 (CO), 967 (V=O), 836, 617(<i>p</i> -substituted)
PPBA-Hg(II) ^a	3525 (H ₂ O), 3265 (NH), 2920 (CH—aliphatic), 1661 (CO), 830, 662 (<i>p</i> -substituted).
PPBA-Hg(II) ^b	3444 (H ₂ O), 3282 (NH), 2928 (CH—aliphatic), 1660 (CO), 831, 660 (<i>p</i> -substituted).
PBM	3255(NH), 3142, 3043 (CH—aromatic and ethylenic), 2928 (CH—aliphatic), 1867, 1547 (—C(Me)=CH ₂), 1659 (amide carbonyl), 1623 (C=C), 829, 782 (<i>p</i> -substituted).
PPBM	3435 (H ₂ O), 3319 (NH), 2980, 2928 (CH—aliphatic), 1663 (CO), 1610 (C=C), 930, 827 (<i>p</i> -substituted).
PPBM-Cu (II) ^a	3447 (H ₂ O), 3330 (NH), 1661 (CO), 917, 832 (<i>p</i> -substituted).
PPBM-Cu(II) ^b	3345 (br., H ₂ O and NH), 2976, 2927 (CH—aliphatic), 1662 (CO), 931, 827 (<i>p</i> -substituted).
PPBM-Co (II) ^a	3342 (br., H ₂ O and NH), 2978, 2932 (CH—aliphatic), 1660 (CO), 930, 828 (<i>p</i> -substituted).
PPBM-Co(II) ^b	3322 (br., H ₂ O and NH), 2976, 2930 (CH—aliphatic), 1662 (CO), 938, 829 (<i>p</i> -substituted).
PPBM-Ni(II) ^a	3299 (NH), 2976, 2930 (CH—aliphatic), 1661 (CO), 933, 831(<i>p</i> -substituted).
PPBM-Ni(II) ^b	3369 (NH), 2985, 2928 (CH—aliphatic), 1658 (CO), 940, 830 (<i>p</i> -substituted).
PPBM-Pb (II) ^a	3312 (NH), 2924, 2823 (CH—aliphatic), 1664 (CO), 1631 (C=C), 931, 830 (<i>p</i> -substituted).
PPBM-Pb(II) ^b	3346 (NH), 2976, 2926 (CH—aliphatic), 1662 (CO), 934, 828 (<i>p</i> -substituted).
PPBM-Hg (II) ^a	3255 (br., H ₂ O), 3138 (NH), 1660 (CO), 930, 828 (<i>p</i> -substituted).
PPBM-Hg(II) ^b	3398 (br., H ₂ O and NH), 2976, 2927 (CH—aliphatic), 1659 (CO), 932, 827(<i>p</i> -substituted).
PPBM-VO(II) ^b	3322 (br., H ₂ O and NH), 2976, 2930 (CH—aliphatic), 1662 (CO), 938, 829 (<i>p</i> -substituted).

^aComplex at 75°C.

^bComplex at 150°C.

M(OAc)₂·*n*H₂O (M = Pb²⁺, Hg²⁺, Cu²⁺, and Ni²⁺), 2.16 g of PPBA was added. The mixture was left for 24 h with moderate stirring. The reaction product was filtered, and atomic absorption measurements of the metal contents in the obtained filtrate are measured.

RESULTS AND DISCUSSION

Monomer synthesis

Synthesis of *N*-arylacrylamide and *N*-arylmethacrylamide was described earlier.^{16–18} *N*-Arylmethacrylamide was synthesized using two different methods, with 50% yield (addition of the aromatic amine to the methacryloyl in benzene in the course of 5–10 min)¹⁷ and very low yield (reaction of the aromatic amine with methacryloyl in the presence of P₂O₅ and H₃PO₄).¹⁸ We have developed the method of synthesis of these compounds by the reaction of *p*-phenylenediamine with acryloyl or methacryloyl chloride in a 1:2

mol ratio in acetone or dichloromethane to get the monomers **1** or **2**, respectively, (Table I). The synthesized monomers were confirmed from their elemental analysis and spectral data (cf. Table II–IV and Figs. 1–3).

Mass spectra of the prepared monomers

The mass spectra of PBA and PBM show *m/z* at 216 (84%) and 244 (84%), respectively. Fragments pattern of PBA is shown in Scheme 1.

¹H- and ¹³C-NMR spectra

The ¹H-NMR spectra of the monomers were recorded for *d*₆-DMSO solutions in the absence and in the presence of D₂O. Representative spectra are shown in Figure 1, and the spectral data are given in Table III. The spectra of the monomers **1** and **2** exhibit a weak and

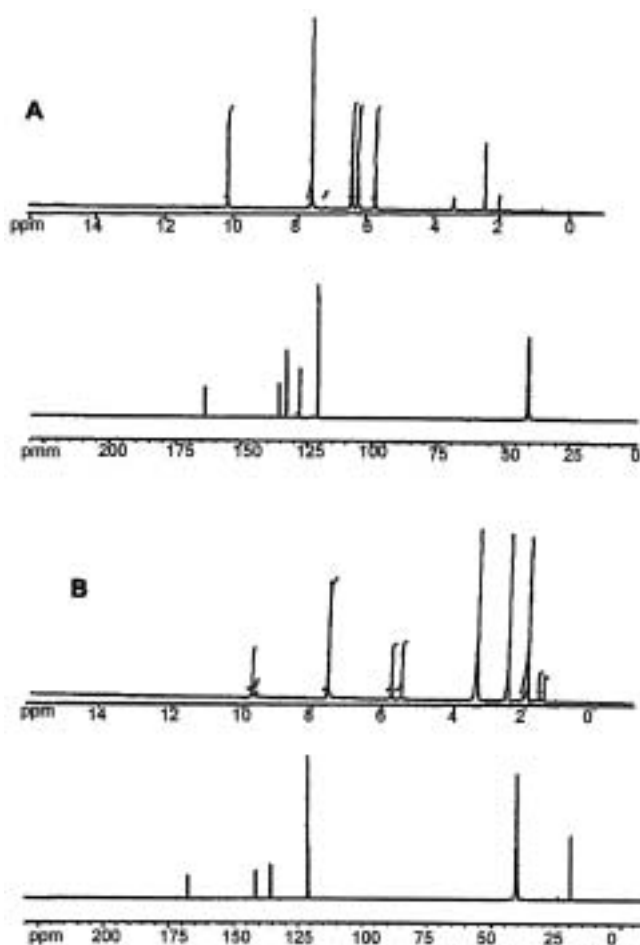


Figure 1 ^1H - and ^{13}C -NMR spectra of (A) PBA and (B) PBM in d_6 -DMF.

broad signal at $\delta = 10.16$ and 9.76 ppm, respectively, which disappeared in the presence of D_2O . Therefore, this signal is assigned to N—H protons. Its low field position and shape could be referred to the participation of the N—H protons in hydrogen bonding. The up field position of the N—H signal for **2** relative to **1** could be referred to the shielding effect of the neighbor $-\text{CH}_3$ of the methacryloyl moiety. The signals due to the ethylenic protons, $=\text{CH}_2$, appeared as a doublet at $\delta = 5.75$ and 6.22 ppm for **1** and 5.49 and 5.78 ppm for **2**. The signal at $\delta = 1.94$ ppm in case of **2** is assigned to the methyl protons. The phenyl protons are traced as a signal at 7.56 – 7.62 ppm. The ^{13}C -NMR spectral data for the monomers are in agreement with those of the ^1H -NMR data, confirming the assumed structures of the monomers.

Characterization of polymers and their metallopolymer complexes

General

Radical solution polymerization of the prepared monomer was carried out in DMF solvent in the pres-

ence of AIBN at 75°C . A precipitate of polymer was obtained during heating process in case of acryloyl chloride. In case of methacryloyl chloride, a large amount of ethanol or ethanol/water mixture (1:1 v/v), respectively, was needed for precipitation. The polymer was collected by filtration, purified by refluxing in ethanol for 3 h, and dried under a reduced pressure for 48 h. The rate of polymerization was found to be dependent on the amount of AIBN and the concentration of the monomer. This is in agreement with the previously reported results.¹⁹ The insolubility of the synthesized polymers at room temperature in most of the common solvents made difficulties to determine the molecular weight, ^1H -NMR, or ^{13}C -NMR.

Infrared spectra of the monomers and their polymers

The IR spectra of the synthesized monomers, polymers, and the metallopolymer complexes were recorded as KBr discs. Representative spectra are shown in Figures 2 and 3, and the main bands with their tentative assignments are given in Table IV. The spectral data showed the following points:

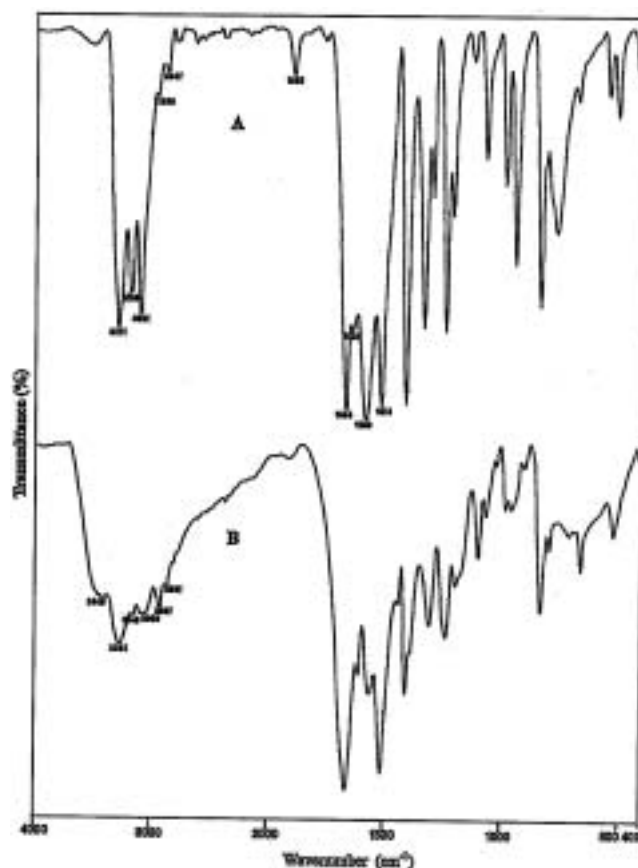


Figure 2 IR spectra of (A) monomer PBA and (B) polymer PPBA.

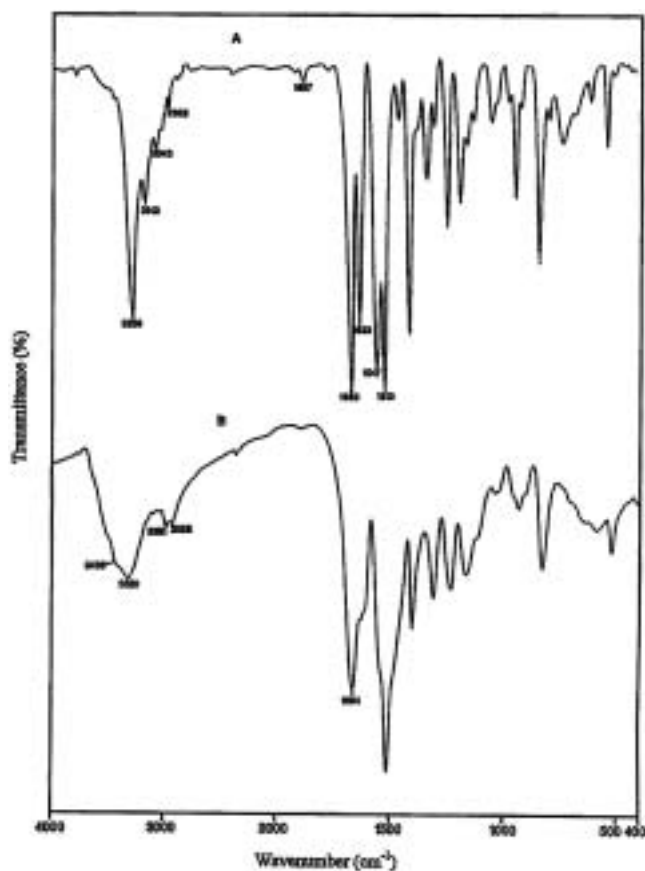
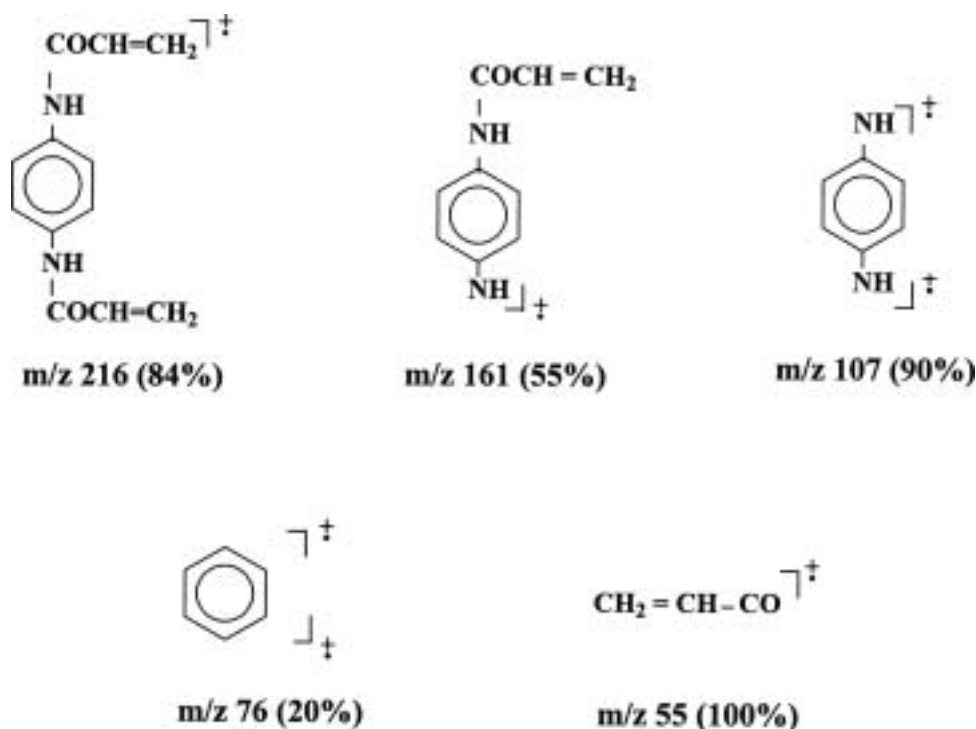
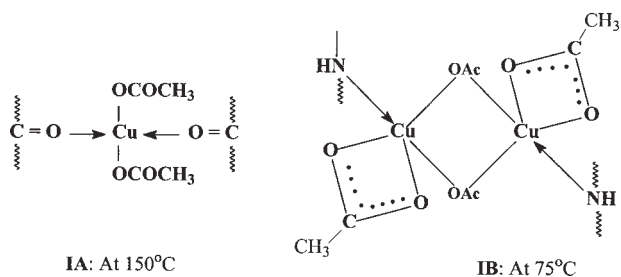


Figure 3 IR spectra of (A) monomer PBM and (B) polymer PBM.

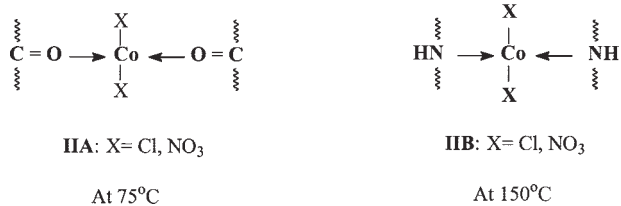
1. The spectrum of the acryloyl monomer [Fig. 2(A)] displays bands at 1884 and 1580 cm^{-1} , while that of the methacryloyl monomer at 1867 and 1547 cm^{-1} [Fig. 3(A)], due to overtone $-\text{CH}=\text{CH}_2$ and $\text{C}=\text{CH}_2$ respectively. These bands are not observed in the spectra of their corresponding polymers [Fig. 3(B)], indicating the polymerization via $\text{CH}=\text{CH}_2$. The spectra of all polymers did not exhibit bands at 3081 and 3142 cm^{-1} due to $=\text{CH}_2$ confirming the polymerization via this group.
2. The ν_{CO} of the amide band was traced at 1663 and 1659 cm^{-1} for the monomers **1** and **2**, respectively, while for their polymers at 1663 cm^{-1} . The appearance of this band at lower wave number in cases of monomers and their polymers compared with that at 1685 cm^{-1} for free ν_{CO} amide could be attributed to the involvement of this group in H-bonding.
3. The medium band at 1635 and 1623 cm^{-1} in case of monomers **1** and **2**, respectively, due to the aromatic $\text{C}=\text{C}$, is shifted to a lower wave number appearing at 1610 cm^{-1} in their polymers.
4. The ν_{NH} was appeared as a strong band at spectra at 3270 and 3255 cm^{-1} , for monomers **1** and **2**, respectively, while at 3264 and 3319 cm^{-1} as a broad bands in their corresponding polymers. Furthermore, *p*-disubstituted characteristic bands at 833 and 764 cm^{-1} with $\Delta\nu = 69\text{ cm}^{-1}$ was ob-



Scheme 1

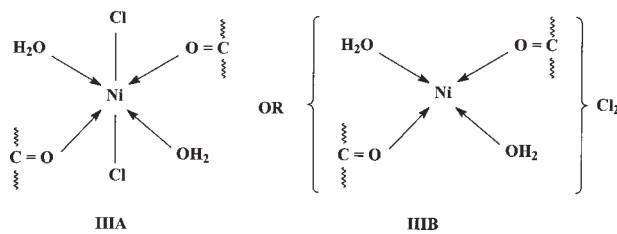


Scheme 2



Scheme 3

served in case of PBA, while in the corresponding polymer appears at 834 and 796 cm⁻¹ with Δν = 38 cm⁻¹. This may be due to the presence of poly-*p*-substituted phenylene group in the polymeric chain.



Scheme 4

TABLE V
Content of Metal (0.01M) Complexed with the Polymer Expressed in (ppm)

	Before	After
Copper (II)	577	378
Nikel (II)	568	540
Mercury (II)	2025	1150
Lead (II)	2281	2013

TABLE VI
Content of Metal (0.01M) Complexed with the Polymer After Mixing Metal Salt in (ppm)

	Before	After
Copper (II)	593	381
Nikel (II)	613	583
Mercury (II)	1775	925
Lead (II)	2447	2124

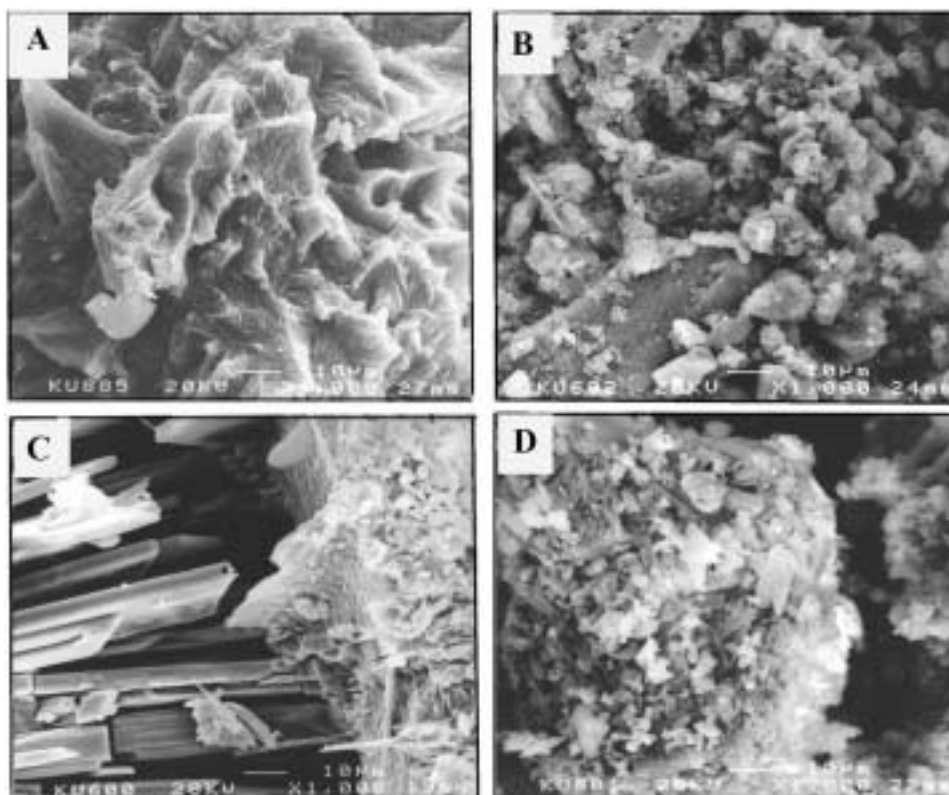


Figure 4 SEM micrograph of (A) PPBA, (B) PPBA-Co(II), (C) PPBA-Pb(II), and (D) PPBA-Cu(II).

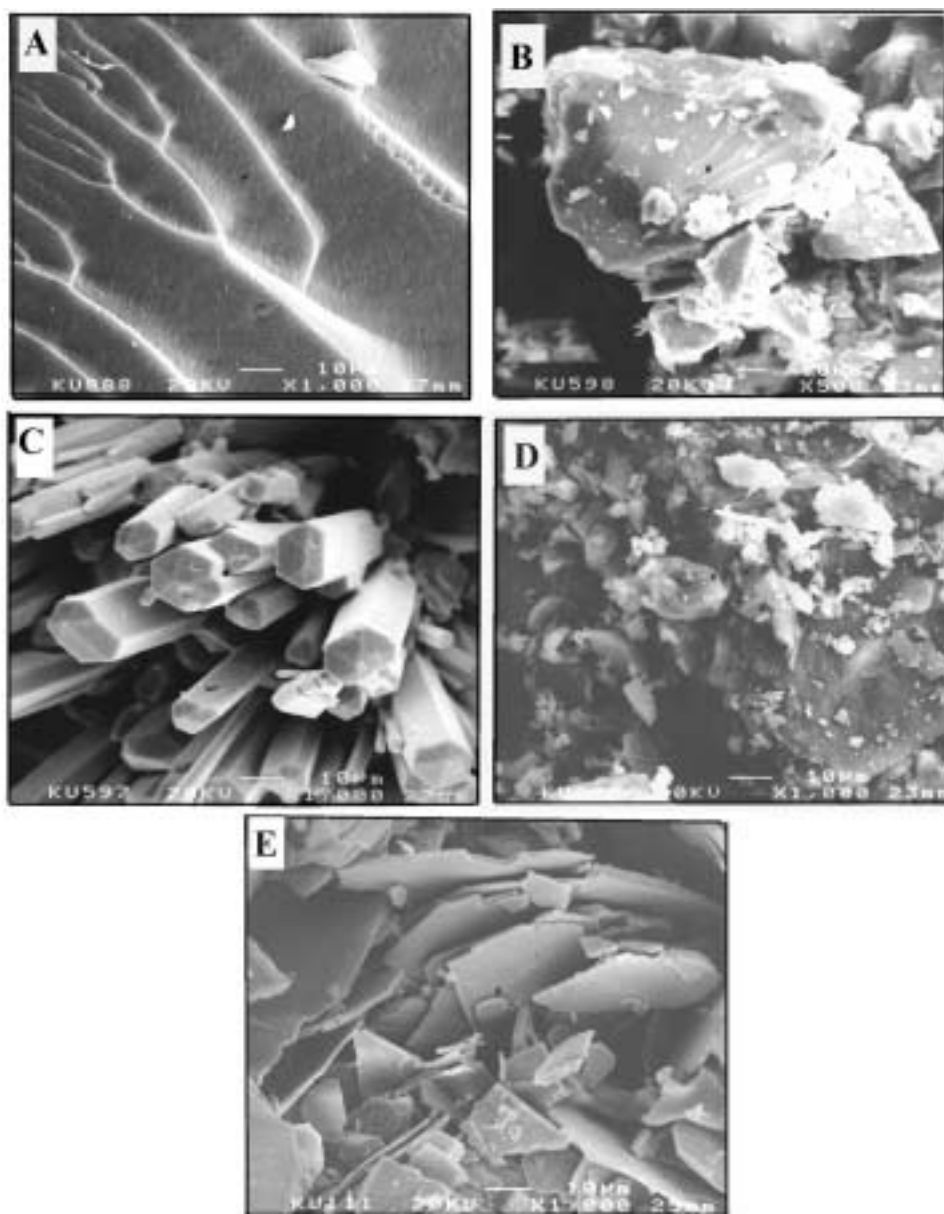


Figure 5 SEM micrograph of (A) PPBM, (B) PPBM-Co(II), (C) PPBM-Pb(II), (D) PPBM-Ni(II), and (E) PPBM-Hg(II).

Infrared spectra of the metallopolymer complexes

The IR of the metallopolymer complexes showed the following:

1. In the IR spectrum of copper containing polymer, the band due to $\nu_{\text{C=O}}$ remained unchanged upon complexation while that due to ν_{NH} is upward shifted, relative to that of the free polymer, and overlapped with that of H_2O in case of the complexes prepared at 75°C . In case of the complexes prepared at 150°C , there is a downward shift for the $\nu_{\text{C=O}}$, while that due to ν_{NH} is not greatly affected. Therefore,

the polymers act as monodentate bonding to the copper (II) via the ketoamide oxygen or nitrogen atom. Accordingly, the temperature is considered as an important factor that determined the mode of bonding of the polymer and therefore its metal selectivity. Furthermore, the acetate anion exhibits two bands at 1412 and 1293 cm^{-1} , with $\Delta\nu = 119\text{ cm}^{-1}$ in case of the complexes prepared at 75°C suggesting its bidentate nature. In case of the complexes prepared at 150°C , the two bands appeared at 1602 and 1328 cm^{-1} with $\Delta\nu = 274\text{ cm}^{-1}$ characteristic of the monodentate acetato group. Accord-

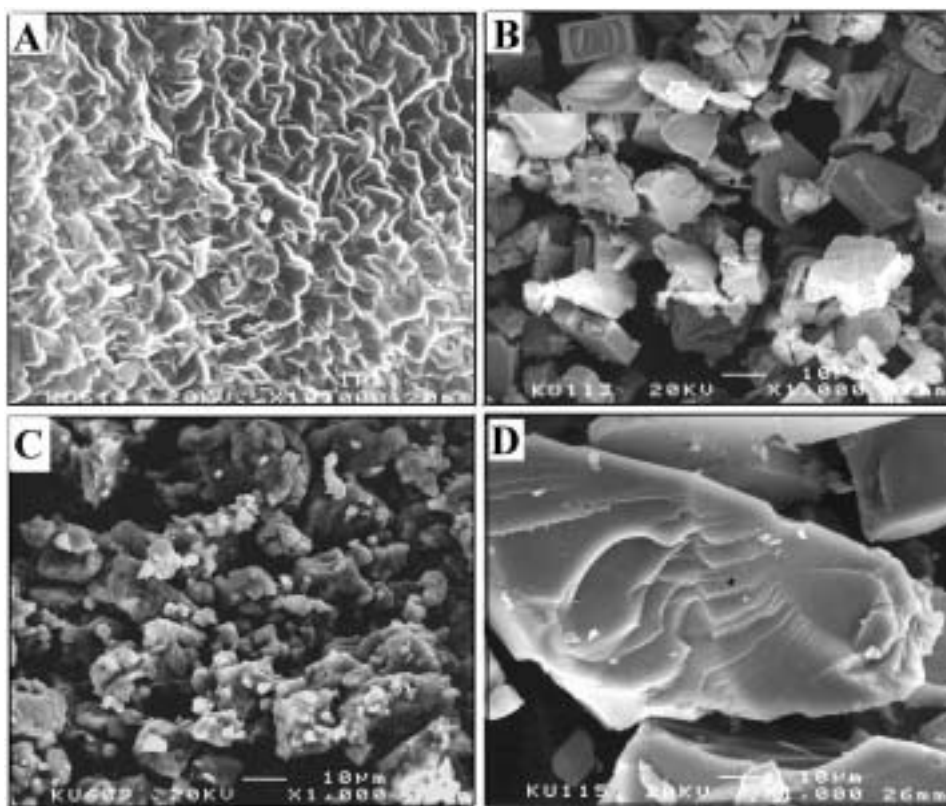


Figure 6 SEM micrographs of (A) PPBA-Co(II) at 75°C, (B) PPBA-Hg(II) at 75°C, (C) PPBA-Co(II) at 150°C, and (D) PPBA-Hg(II) at 150°C.

ingly, the structures IA and IB could be assumed (Scheme 2).

- The IR spectrum of cobalt(II) complex prepared at 75°C showed a downward shift for $\nu_{\text{C=O}}$ compared with the free polymer while that of ν_{NH} remains mainly unchanged. This indicates the coordination of the polymer to the cobalt(II) ion via the carbonyl oxygen. On the other hand, the complex prepared at 150°C exhibits a great change in the shape and position of NH while the $\nu_{\text{C=O}}$ remains unchanged indicating the bonding of —NH— to the cobalt ion. This indicates that the bonding of the donor is temperature dependent. Furthermore, the spectra of both complexes display new two bands at 1436, 1385 and 1438, 1384 cm^{-1} characteristic of monodentate nitrate anion. Therefore, structures (IIA and IIB) could be proposed (Scheme 3).
- The IR spectra of the nickel (II) complexes obtained at 75°C and 150°C exhibit a downfield shift for the $\nu_{\text{C=O}}$ relative to that of the parent polymer while that due to ν_{NH} is not greatly affected. This suggests that the polymer bonded only to the nickel (II) ion through the carbonyl oxygen independent on the temperature. The spectra in both cases show new bands at 687, 688,

and 901 cm^{-1} (w) characteristic of coordinated water. Accordingly, structure IIIA or IIIB could be assumed (Scheme 4).

- The IR spectrum of the lead containing polymer are not changed from that of the polymer itself, especially in the positions of ν_{NH} and $\nu_{\text{C=O}}$. The Pb^{2+} may probably be absorbed by the polymer within the pores or adsorbed on the surface of the polymer.
- The spectrum for the vanadium–polymer complexes exhibits a downward shift of the carbonyl toward a lower wave number by ca. 7–15 cm^{-1} in both cases of the reactions, while the band due to ν_{NH} is not greatly changed compared to the free ligand. This indicates the bonding of the VO^{2+} to the ligand through the carbonyl oxygen atom. The $\nu_{\text{V=O}}$ appeared at 977 and 967 cm^{-1} for the in situ refluxed reactions. The appearance of the bands at a lower wave number relative to the monomeric vanadyl complexes could be attributed to participate in hydrogen bonding or acting as a bridge between the two chromospheres.
- The IR spectra of the Hg–polymer complexes exhibit red shifts in the positions of ν_{NH} and $\nu_{\text{C=O}}$ reflecting their bonding to the Hg either *in situ* or under reflux. In general, the small shift in these two

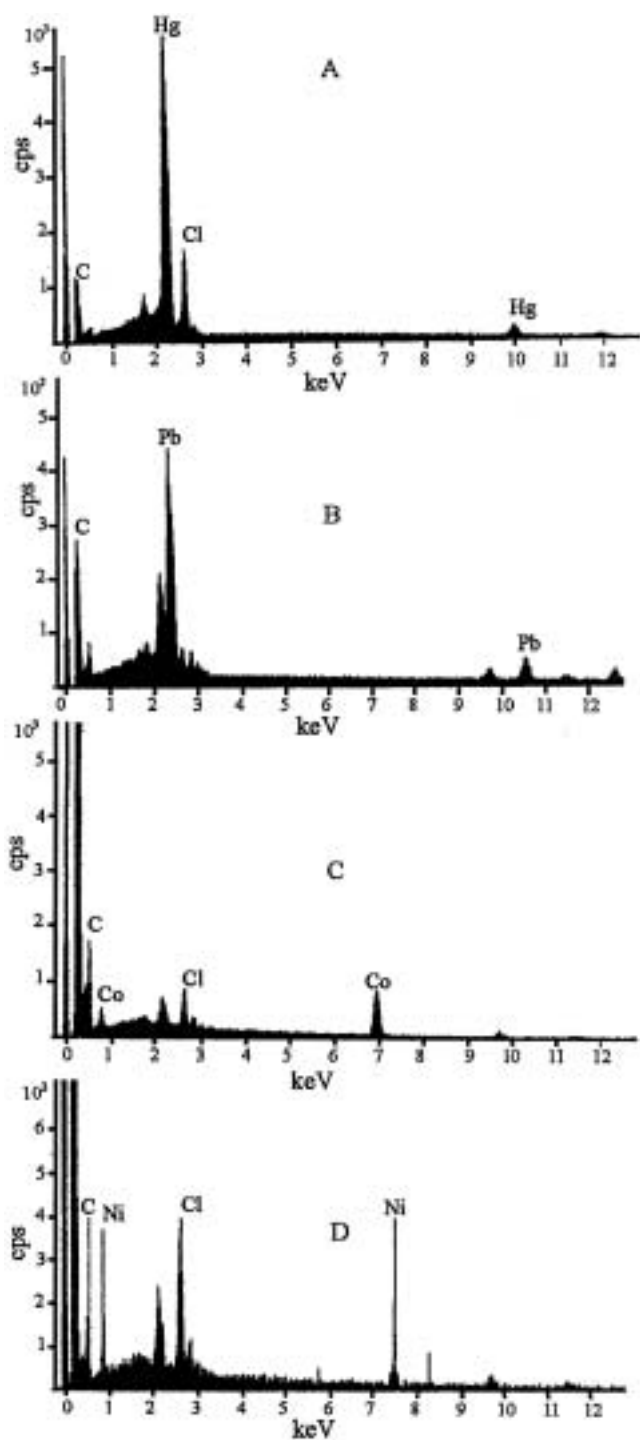


Figure 7 EDS of (A) PPBA-Hg(II), (B) PPBA-Pb(II), (C) PPBA-Co(II), and (D) PPBA-Ni(II).

bands may be due to the weak bonding to the metal ion due to the bulkiness effects of the ligand.

Ion selectivity

Atomic absorption spectroscopy determination of PPBA with a separate or a mixture of 0.01M solution

of $M(OAc)_2 \cdot nH_2O$, $M = Cu^{2+}$, Ni^{2+} , Hg^{2+} , or Pb^{2+} before and after treating with the polymer are given in Tables V and VI. The data showed that the order of concentration of metal ion introduced into the polymer chain is $Hg^{2+} > Pb^{2+} > Cu^{2+} > Ni^{2+}$. Both Hg^{2+} and Pb^{2+} are of higher ionic size than Cu^{2+} and Ni^{2+} ; they appeared to be quite fit within the cavities of polymer in case of mixture or may probably be adsorbed on the surface of the polymer.

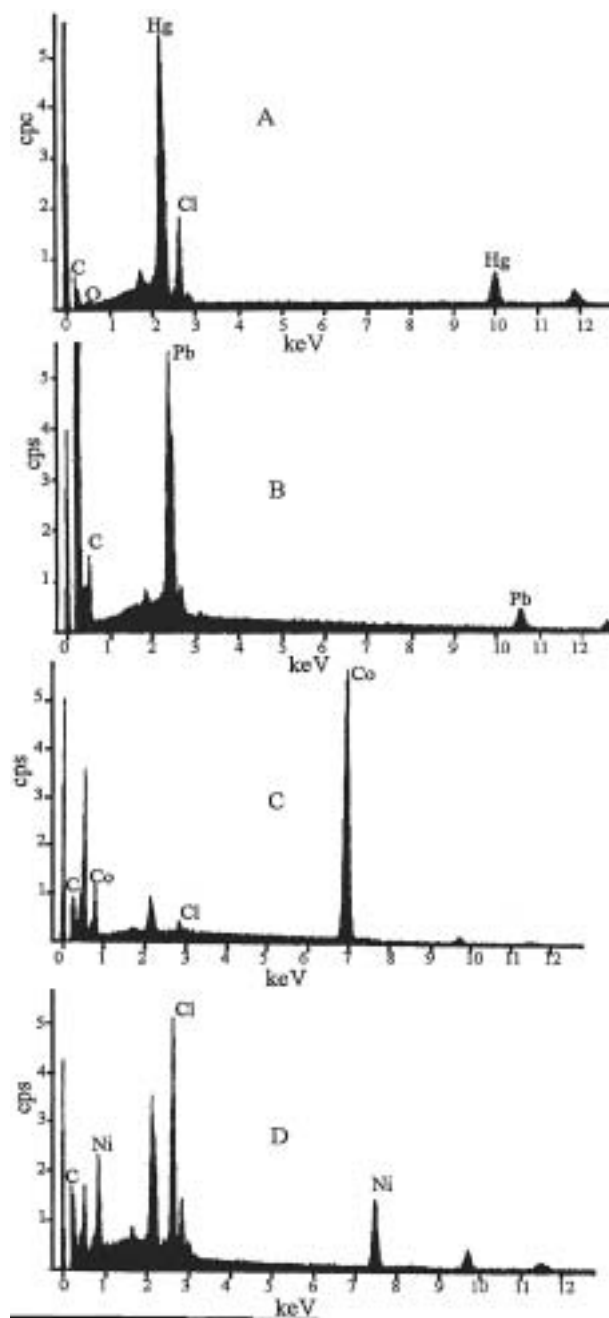


Figure 8 EDS of (A) PPBM-Hg(II), (B) PPBM-Pb(II), (C) PPBM-Co(II), and (D) PPBM-Ni(II).

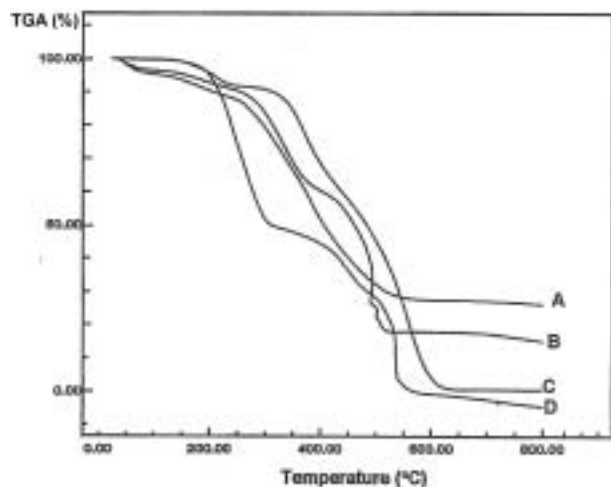


Figure 9 TG curves for (A) PPBM-Cu(II), (B) PPBM-Pb(II), (C) PPBM, and (D) PPBM-Ni(II). All of these metallopolymer complexes prepared at 150°C.

Structure and morphological investigation

The morphologies of PPBA and its metallopolymer complexes of Co^{2+} , Pb^{2+} , and Cu^{2+} synthesized at 75°C are shown in Figure 4(A–D). In addition, the morphologies of PPBM and its complexes with Co^{2+} , Pb^{2+} , Ni^{2+} , and Hg^{2+} are shown in Figure 5(A–E). The SEM micrographs of PPBA-Pb, PPBM-Pb, and PPBM-Hg showed a rod, a hexagonal, and palettes shapes, respectively. This could be attributed to the stronger embedding of Pb^{2+} and Hg^{2+} in the matrix of the polymer, than other tested metals. The difference in the morphologies of the PPBA-Hg and PPBA-Co polymer complexes synthesized at 75 and 150°C (Fig. 6) indicate that the morphology of the complexes are dependent on the synthetic temperature.

Energy dispersive spectroscopy

Figures 7 and 8 showed the EDS of the metallopolymer complexes of PPBA and PPBM, respectively. The

data obtained from Figure 7 show that PPBA highly absorbs Hg^{2+} , Pb^{2+} , and Ni^{2+} from the solution. On the other hand, PPBM is shown to highly absorb Hg^{2+} , Pb^{2+} , and Co^{2+} (Fig. 8). In addition, the data reflects that PPBA and PPBM are selective to Hg^{2+} and Pb^{2+} . This could be attributed to the stronger embedding of Hg^{2+} and Pb^{2+} in the matrix of the polymer, than the others.

Thermogravimetry

TGA of PPMA, PPBA, and their metallopolymer complexes are shown in Figure 9, and the data are given in Table VII. The weight loss (wt %) for the polymer and its complexes in the temperature range 25–200°C is due to the loss of water absorbed or adsorbed within the compound, in addition to H-bonded in polymeric material. The total weight loss of PPMA and Co-PPMA (Fig. 9) illustrates the TGA curves of the polymer (PPMA) and polymer metal complexes (prepared at 150°C). These data are obtained in air with heating rate of $10^\circ\text{C min}^{-1}$. Table VII shows the TGA data of PPBA and its metal complexes. It can be observed that the polymer is more stable than that of polymer–metal complexes. Moreover, the PPMA-Co (II) is less stable than that of PPMA-Pb (II) and PPMA-Cu (II), respectively. This result indicates that as TGA of the polymeric compounds increases, the stability is decreased. Furthermore, the thermal data given in Table VII showed that the residual metal oxides in the complexes synthesized at 150°C are greater than those synthesized at 75°C. This result indicates that the metal uptake is greater at 150°C than at 75°C.

CONCLUSIONS

1. Monomers and corresponding polymers of diacetylated amine were prepared.

TABLE VII
Thermogravimetric Analysis of PPBA and Its Complex with Different Metal Ions at 75 and 150°C

Compound No.	25–100	100–200	200–300	300–400	400–500	500–600	600–700	Total weight loss (%)	Residual (%)
PPBA	2	2	4	4	29	29	30	100	0.0
PPBA-Co(II) ^a	4	16	15	17	13	29	–	94	6
PPBA-Ni(II) ^a	3	22	14	6	13	10	24	92	8
PPBA-Pb(II) ^a	5	4	3	8	10	64	–	94	6
PPBA-Cu(II) ^a	1	7	4	33	25	17	–	89	11
PPBA-Co(II) ^b	1	9	11	19	14	34	–	88	12
PPBA-Ni(II) ^b	3	12	10	6	14	8	32	85	15
PPBA-Pb(II) ^b	3	13	8	9	24	19	–	74	26
PPBA-Cu(II) ^b	3	1	3	28	–	–	–	35	65

^aComplex at 75°C.

^bComplex at 150°C.

- The ability to prepared solid metallopolymer complexes with different metal salts at different temperatures was verified.
- The IR data showed that the coordinating atoms of the polymer are dependent on the reaction temperature.
- The prepared polymers showed a highly ion selective for both Hg^{2+} and Pb^{2+} .
- EDS measurements supported that both polymers are more selective to Hg^{2+} and Pb^{2+} .

Analytical facilities provided by SAF are highly appreciated.

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