Studies on Polyacrylates Containing Pendant Ligand with Carbonyl and Hydroxyl Functions and Their Divalent Metal Complexes

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ABSTRACT: A series of monomers were prepared by reacting (meth)acryloyl chloride with 2,4-dihydroxybenzophenone, 2,4-dihydroxybenzaldehyde, and 2,4-dihydroxyacetophenone, respectively. The monomers were polymerized in dimethylformamide (DMF) at 70°C using benzoyl peroxide as an initiator. Polymer–metal complexes were obtained from DMF solutions of polymers with an aqueous solution of metal ions. The polymers and polymer–metal complexes were characterized by elemental analysis and spectral studies. The IR spectra of these complexes suggest that the metals are coordinated through the oxygen of the carbonyl group and the oxygen of the phenolic–OH group. The electronic spectra, electron paramagnetic resonance (EPR) spectra, and magnetic moments of polychelates showed an octahedral and square planar structure for Ni(II) and Cu(II) complexes, respectively. X-ray diffraction studies revealed that polychelates are highly crystalline. The thermal and electrical properties, catalytic activity, and structure–property relationships are discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 2083–2090, 2003

Key words: differential scanning calorimetry (DSC); metal-polymer complexes; radical polymerization; gel permeation chromatography (GPC)

INTRODUCTION

Research on metal-containing polymers began three decades ago with the discovery of polymers incorporating a potential reactive metal ion. These polymers have a wide range of applications, such as for semiconductors,[1] catalysts,[2] or controlled-release agents for drugs, biocides,[3] recovery of trace metals ions,[4] and nuclear chemistry. In addition, they are also used as models for enzymes.[5] A number of polymer-bound chelating ligands including polydentate amines, crown ethers, and porphyrins were reported.[6–8] The free-radical polymerization of a Cu complex with a Schiff base ligand containing a vinyl group was also reported.[9] Osada[10] reported the radical polymerization of methacrylate monomers coordinated to the Co(III) metal ion. Melby[11] prepared a uniform structure of pendant-type polymer–metal complexes by a substitution reaction between a polymer ligand and Co(III) or Cr(III) ions. Bajpai et al.[12] prepared poly(ethylene asparate) (PEA), containing amino and carbonyl groups in its repeating chain, which was used as a polymeric ligand for complexation with metal ions, namely, Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Cd(II), Ca(II), Mg(II), Pb(II), and Hg(II). A series of new cation exchangers was prepared based on the monomer N-(3-hydroxy-4-acetylphenylmaleimide) by addition polymerization.[13] A porous polymer containing hydroxamic acid was studied as a polymeric chelating agent for iron.[14] Polymeric Schiff's base chelates based on bis(salicylaldehyde) and o-phenylenediamine were investigated.[15] In continuation of our research work on polymer–metal complexes,[16–23] we herein report studies on polyacrylate pendant ligands containing carbonyl and hydroxyl functions and their divalent metal complexes and their structure–property relationships.

EXPERIMENTAL

Materials

Benzoyl peroxide (BDH, India) was recrystallized from a chloroform/methanol mixture, and 2,4-dihydroxybenzaldehyde (Aldrich, US), 2,4-dihydroxyacetophenone (Aldrich), and 2,4-dihydroxybenzophenone (Aldrich) were recrystallized from ethanol. Acryloyl chloride and methacryloyl chloride were prepared by a procedure reported elsewhere.[24] Copper(II) acetate (Fluka, Switzerland) and nickel(II) acetate were used as received.

Monomer synthesis

2,4-Dihydroxybenzophenone (5 mmol), triethylamine (5 mmol), methyl ethyl ketone (MEK) (200 mL), and

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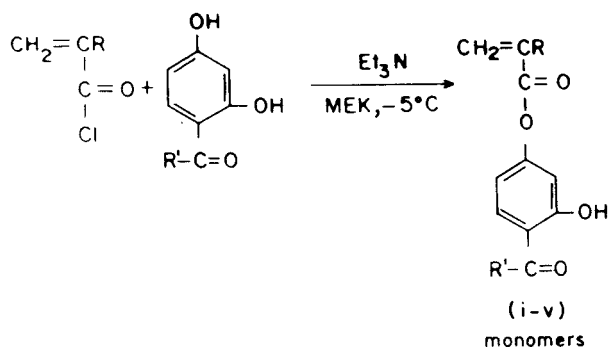
	R = H	R' = C$_6$H$_5$	2H4ABP
i	R = H	R' = C$_6$H$_5$	2H4ABP
ii	R = CH$_3$	R' = C$_6$H$_5$	2H4MBP
iii	R = H	R' = H	2H4ABA
iv	R = CH$_3$	R' = H	2H4MBA
v	R = H	R' = CH$_3$	2H4AAP

Scheme 1

hydroquinone (0.5 g) were taken in a three-necked flask equipped with a stirrer, a thermometer, and a stoppered funnel. The contents were cooled to −5°C. Acryloyl chloride (5 mmol) in MEK (25 mL) was added dropwise with constant stirring at that temperature. The reaction mixture was gradually allowed to attain ambient temperature and stirring was continued for another 2 h. The quaternary ammonium salt formed was filtered. The filtrate was thoroughly washed with distilled water and dried over anhydrous sodium sulfate and the solvent was evaporated *in vacuo*. The crude 2-hydroxy-4-acrloyloxybenzophenone (2H4ABP) (**i**) was recrystallized from ethanol. By adopting a similar procedure, the other monomers, namely, 2-hydroxy-4-methacryloyloxybenzophenone (2H4MBP) (*ii*), 2-hydroxy-4-acryloyloxybenzaldehyde (2H4ABA) (**iii**), 2-hydroxy-4-methacryloyloxybenzaldehyde (2H4MBA) (**iv**), and 2-hydroxy-4-acryloyloxyacetophenone (2H4AAP) (**v**) were prepared. The IR and ^{1}H-NMR spectra were consistent with the assigned structure.

Polymerization

The monomers (**i**)–(**v**) were polymerized by free-radical polymerization using BPO as the initiator. A typical procedure for the polymerization of 2H4ABP is described: 2H4ABP (3.5 mmol) was dissolved in MEK (50 mL) and taken in a reaction tube. BPO (0.5 g) was added to that and purged with nitrogen for 30 min. Then, the reaction tube was closed and kept in a thermostat at 70°C for 8 h and cooled. A large excess

of methanol was added to the content and the precipitated poly(2H4ABP) was filtered, washed with methanol, and purified by dissolving in *N,N*-dimethylformamide (DMF) and reprecipitating with methanol. The purified polymer was dried *in vacuo* at 50°C to a constant weight.

Synthesis of polymer–metal complexes

Polymer–metal complexes were prepared at room temperature by a solution technique. A typical procedure for the preparation of a poly(2H4ABP)–Cu(II) complex (**Ia**) is as follows: Poly(2H4ABP) (6 mmol of repeat units) was dissolved in 100 mL DMF. An aqueous solution of copper(II) acetate (3 mmol dissolved in 20 mL distilled water) was added dropwise to the polymer solution with constant stirring and the pH of the solution was adjusted to 7 with a dilute ammonium hydroxide solution. The mixture was then kept overnight at ambient temperature. The precipitated poly(2H4ABP)–Cu(II) complex was filtered, washed with hot distilled water followed by ethanol, and dried at 60°C *in vacuo*.

Measurements

The elemental analyses of the monomer, polymer, and polymer–metal complexes were carried out using a Heareus carbon–hydrogen analyzer. The amount of copper and nickel present in the polymer–metal complexes was estimated using a titrimetric procedure after decomposing the polymers. The viscosity measurements of the polymers were made using an Ubbelohde suspended level viscometer at ambient temperature. The weight-average and the number-average molecular weights ($\overline{M}_w$ and $\overline{M}_n$) of polymers were determined by gel permeation chromatography (GPC; Waters 501) using THF and calibrated with polystyrene standards. The IR spectra of the polymer and metal complexes were recorded on a Perkin–Elmer 782 spectrophotometer using KBr pellets. The ^{1}H-

R = C$_6$H$_5$, CH$_3$, H } For polymer I, II, III, IV, V
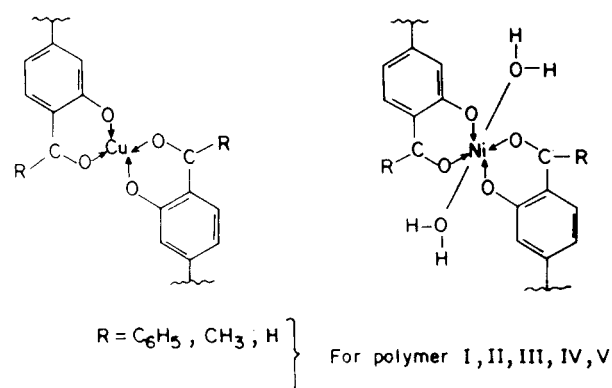
Scheme 2

TABLE I
Elemental Analysis Data of Polymers I–V

No.	Polymer	Elemental formula	$\lvert\eta\rvert$	$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	$\bar{M}_w/\bar{M}_n$	Carbon Found	Carbon Calcd.	Hydrogen Found	Hydrogen Calcd.	Oxygen Found	Oxygen Calcd.
I	Poly(2H4ABP)	$(C_{16}H_{12}O_4)_n$	0.40	3.01	1.85	1.62	71.62	71.64	4.49	4.47	23.89	23.88
II	Poly(2H4MBP)	$(C_{17}H_{14}O_4)_n$	0.41	3.10	1.88	1.64	72.31	72.35	4.97	4.96	22.72	22.70
III	Poly(2H4ABA)	$(C_{10}H_8O_4)_n$	0.26	2.03	1.15	1.76	62.48	62.50	4.20	4.17	33.31	33.33
IV	Poly(2H4MBA)	$(C_{11}H_{10}O_4)_n$	0.30	2.75	1.95	1.41	64.30	64.10	4.60	4.90	31.10	31.00
V	Poly(2H4AAP)	$(C_{11}H_{10}O_4)_n$	0.28	2.83	1.86	1.52	63.98	64.07	4.93	4.89	31.09	31.04

NMR spectra of the polymers were recorded on a Hitachi 90-MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. ^{13}C-NMR spectra of the polymers were recorded on a Bruker 300 MSL nuclear magnetic resonance spectrometer at room temperature in DMSO-d_6 using TMS as the internal standard.

The magnetic moments were measured using the Gouy method and corrected for the diamagnetism of the component using Pascal's constant. The diffuse reflectance spectra (8000–2600 cm^{-1}) were measured on a Karl–Zeiss VSU-28 spectrophotometer.

Electron paramagnetic resonance (EPR) analyses were carried out at room temperature using a Varian spectrophotometer. X-ray diffraction experiments were performed with a Philips PW 1820 diffractometer and a Statton camera using CuKα radiation of wavelength 1.542. Thermogravimetric analyses (TGA) were carried out in a Mettler TA 3000 thermobalance. A 5-mg sample was used at a heating rate of 15°C min^{-1} in air. The glass transition temperatures of the polymers and metal complexes were determined by differential scanning colorimetry (DSC) with a DuPont 900 thermal analyzer at a heating rate of 15°C min^{-1} in air.

The electrical conductivity of the polychelates were measured on pellets of 10-mm diameter and 2-mm thickness using a Keithley electrometer. Three different preliminary studies were performed to determine the catalytic activity of the polymer–metal complexes in the hydrolysis of ethyl acetate and the polymerization initiation of N-vinylpyrrolidone by poly(2H4ABP) Cu(II)/Ni(II) chelates at 65 and 70°C, respectively, in the reported manner.[25,26] The catalytic oxidation of cyclohexanol to cyclohexanone was carried out in a Schlenk tube under an oxygen atmosphere. Cyclohexanol (2.5 mmol), MEK (4 mL), the poly(2H4ABP)–Cu(II) complex (0.5 mmol based on metal), and H_2O_2 (0.5 mmol) were inserted and stirred magnetically at 80°C for 7 h. Aliquots (1 μL) were withdrawn at 15-min intervals and analyzed by GC.

RESULTS AND DISCUSSION

The monomers (i)–(v) were prepared and polymerized in MEK using BPO as the initiator with a good yield (Scheme 1). Polymer–metal complexes were obtained in a DMF-containing polymer with an aqueous solution of metal ions [Cu(II) and Ni(II)] in the presence of a few drops of ammonia. Ni(II) complexes were

TABLE II
Elemental Analysis Data of Polymer–Metal Complexes Ia–Vb

No.	Polymer–metal complex	Elemental formula	Carbon Found	Carbon Calcd.	Hydrogen Found	Hydrogen Calcd.	Oxygen Found	Oxygen Calcd.	Cu/Ni[a] Found	Cu/Ni[a] Calcd.
Ia	Poly(2H4ABP)–Cu(II)	$(C_{16}H_{11}O_4)_x$ Cu(II)	64.71	64.86	3.78	3.71	21.64	21.62	9.87	9.72
Ib	Poly(2H4ABP)–Ni(II)	$(C_{16}H_{11}O_4)_y$ Ni(II)(H$_2$O)$_y$	61.20	61.34	4.27	4.15	25.89	25.55	8.64	8.94
IIa	Poly(2H4MBP)–Cu(II)	$(C_{17}H_{13}O_4)_x$ Cu(II)	65.78	65.80	4.21	4.19	28.61	28.66	10.40	9.35
IIb	Poly(2H4MBP)–Ni(II)	$(C_{17}H_{13}O_4)_y$ Ni(II)(H$_2$O)$_y$	62.40	62.38	4.51	4.58	32.45	32.46	8.64	8.56
IIIa	Poly(2H4ABA)–Cu(II)	$(C_{10}H_7O_4)_x$ Cu(II)	55.56	54.54	3.15	3.18	29.15	29.10	13.21	13.18
IIIb	Poly(2H4ABA)–Ni(II)	$(C_{10}H_7O_4)_y$ Ni(II)(H$_2$O)$_y$	50.63	50.61	3.80	3.83	28.84	28.82	11.80	11.82
IVa	Poly(2H4MBA)–Cu(II)	$(C_{11}H_9O_4)_x$ Cu(II)	56.50	56.40	3.40	3.90	27.60	27.40	12.50	12.30
IVb	Poly(2H4MBA)–Ni(II)	$(C_{11}H_9O_4)_y$ Ni(II)(H$_2$O)$_y$	52.46	52.50	4.20	4.18	31.80	31.87	11.54	11.55
Va	Poly(2H4AAP)–Cu(II)	$(C_{11}H_9O_4)_x$ Cu(II)	55.83	55.75	3.88	3.83	27.02	27.00	13.27	13.41
Vb	Poly(2H4AAP)–Ni(II)	$(C_{11}H_9O_4)_x$ Ni(II)(H$_2$O)$_y$	52.24	52.31	4.40	4.39	31.76	31.68	11.57	11.62

Calculated percentage of C, H, O, Cu, and Ni for polymer–metal complexes based on the value $x = y = 2$; found: $x = 2.02$; $y = 2.01$.
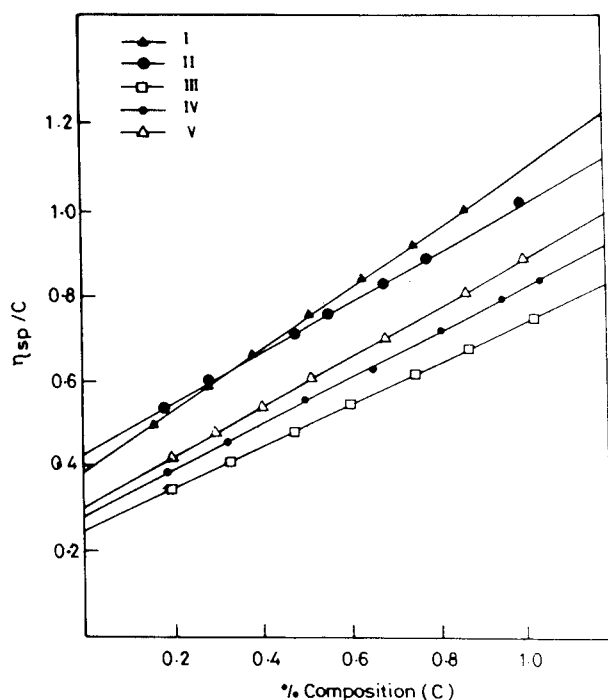
[a] Estimated error $\pm 1\%$.

Figure 1 Viscometric results of polymers.

formed in a lower yield than that of the Cu(II) complexes. This is in accordance with the report by Gustafson[40] that the formation constant of a poly-(methacrylic acid)–metal complex decreased in the order Cu(II) > Ni(II) > Zn(II). The polymers were soluble in chloroform, THF, DMSO, and DMF and insoluble in common organic solvents like benzene, toluene, methanol, and water. The polychelates were insoluble in all these solvents. The elemental analysis data for polymers and polymer–metal complexes are

presented in Tables I and II. The elemental analyses data reveal that the metal-to-ligand ratio in all the polychelates is 1:2 and it is in good agreement with the calculated values.

The viscometric results are shown in Figure 1. The intrinsic viscosity was obtained by extrapolating $\eta_{sp/c}$ to zero concentration. The results reveal that the molecular weights of these polymers are moderately high. The weight-($\overline{M}_w$) and number ($\overline{M}_n$)-average molecular weight and polydispersity index ($\overline{M}_w/\overline{M}_n$) of the polymers were determined by GPC and the data are presented in Table I. The polydispersity index of the polymers are around 1.43–1.76. This is suggestive of chain termination by radical recombination.

The IR spectral data of polymers and their polychelates are presented in Table III. (See also Fig. 2.) The absorption band near 3000–3260 cm^{-1} corresponds to phenolic–OH stretching rather than to that expected at 3600 cm^{-1} due to intramolecular and intermolecular hydrogen bonding[27,28] formed between phenolic–OH and carbonyl oxygen. This band completely disappears in the spectra of the copper–metal complex, establishing the involvement of phenolic–OH in the coordination.[29] However, in the case of the Ni(II) complex, there is a strong absorption around 3500 cm^{-1}, which does not disappear even when the sample is being heated to 150°C. This band, therefore, has to be due to water molecules taken along with Ni(II) ions during coordination. Polymers display strong bands at 1730 and 1625 cm^{-1}, which may be ascribed to the C—O of ester and ketonic groups, respectively. In the spectra of polychelates, the band at 1620 cm^{-1} shifts to a lower frequency, indicating the coordination thorough the oxygen of the keto group. The medium-intensity band at 1120 cm^{-1} in the spectrum of the

TABLE III
IR Spectral Data of Polymer and Polymer–Metal Complexes I–Vb

| No.	OH$_{str}$	C=O$_{str}$ Ester	C=O$_{str}$ Carbonyl	Phenolic C—O$_{str}$	Esteric C—O$_{str}$	M—O$_{str}$
I	3300–3000 (b)	1755 (s)	1670 (s)	1355 (s)	1150 (m)	—
Ia	—	1755 (s)	1640 (s)	1365 (s)	1150 (m)	530 (s)
Ib	3400 (b)	1755 (s)	1660 (s)	1370 (s)	1150 (m)	540 (s)
II	3200–3000 (b)	1750 (s)	1650 (s)	1350 (m)	1150 (m)	—
IIa	—	1750 (s)	1625 (s)	1350 (m)	1150 (m)	500 (s)
IIb	3500 (b)	1750 (s)	1640 (s)	1360 (m)	1150 (m)	520 (s)
III	3550–3200 (b)	1760 (s)	1640 (s)	1330 (m)	1150 (m)	—
IIIa	—	1760 (s)	1625 (s)	1345 (m)	1150 (m)	550 (s)
IIIb	3600 (b)	1760 (s)	1625 (s)	1350 (m)	1150 (m)	540 (s)
IV	3400–3000 (b)	1750 (s)	1630 (s)	1350 (m)	1150 (m)	—
IVa	—	1750 (s)	1615 (s)	1365 (m)	1150 (m)	530 (s)
IVb	3500 (b)	1750 (s)	1615 (s)	1360 (m)	1150 (m)	500 (s)
V	3250 (b)	1740 (s)	1620 (s)	1365 (m)	1150 (m)	—
Va	—	1740 (s)	1610 (s)	1370 (m)	1150 (m)	500 (s)
Vb	3400 (b)	1740 (s)	1605 (s)	1370 (m)	1150 (m)	525 (s)

b, broad; m, medium; s, strong.
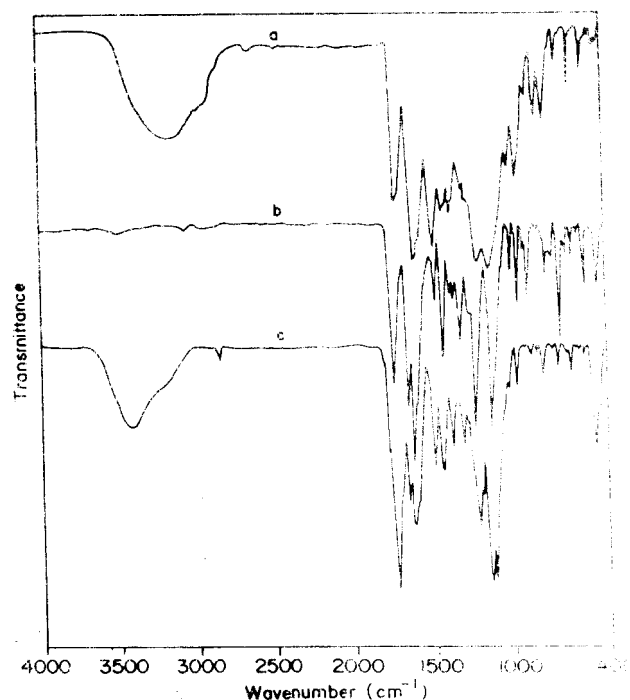
Figure 2 Representative IR spectra of (a) poly(2H4ABP), (b) poly(2H4ABP)–Cu(II), and (c) poly(2H4ABP)–Ni(II).

Figure 3 ¹H-NMR spectrum of poly(2H4MBA).

polymers is due to the hydrogen-bonded ring system of the ligand. On coordination, this band shows a small positive shift indicating the involvement of phenolic–OH in the bonding with the metal ion.[30,31] The band around 550 cm⁻¹ corresponds to the metal–oxygen vibration.[32]

¹H-NMR chemical-shift values of the polymers are presented in Table IV. (See also Fig. 3.) All the spectra show a broad singlet around 11δ due to intermolecular hydrogen-bonded aromatic–OH proton. In polymers III and IV, the multiplet around 9.51–9.36δ is due to aldehydic proton. In all the polymers, signals due to the aromatic protons appear as a broad multiplet in the region 7.01–6.13δ. The resonance signals around 2.9–2.28, 1.9–1.28, and 1.4–1.28δ are due to backbone methine, methylene, and α-methyl protons, respectively.

The ¹³C-NMR chemical-shift assignments were carried out using the normal additivity parameters of the substituent in the benzene ring and off-resonance

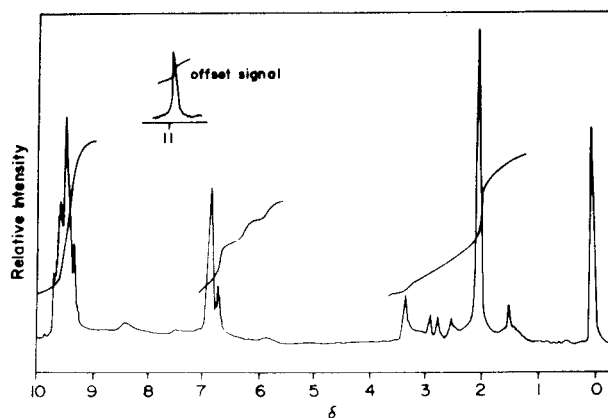spectra in conjunction with the difference in intensities. The data are presented in Table V. The aldehyde/ketone carbonyl (C=O) carbon resonances are observed at 197.7–193.1δ. The resonance signal around 178δ corresponds to ester carbonyl (C=O). The aromatic and olefinic carbon resonance signals appear at 159.7–120.9δ. The signals at 58.78 and 46.48δ are assignable to the backbone carbons (CH₂ and —C—). The α-methyl carbon of the methacrylate polymers appears at 18.6δ.

The diffuse reflectance spectra of all the Cu(II) polymer–metal complexes contain two bands, one at 14,950 cm⁻¹ and another at 22,655 cm⁻¹, which may be assigned to the d–d transition corresponding to a symmetry-forbidden configuration. Similar observations for Cu(II) complex reflectance spectra of all Ni(II) polymer–metal complexes show three bands at 9500, 15,725, and 24,665, which may be due to $^3A_{2g} \rightarrow T_{2g}(F)$, $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ transition octahedral spin-free nickel complexes exhibiting three bands in their electronic spectra.[33,34]

The EPR parameters give a measure of the nature of the complexation with the metal ion which is decided by g values. The EPR parameters are calculated following the Kneubuhl method and are presented in Table VI. The EPR spectra of the Cu(II) complex show a strong signal characteristic of bivalent copper, which is attributed to the oxygen of the phenolic–OH and carbonyl oxygen groups on the x and y axis. Low-spin

TABLE IV
¹H-NMR Spectral Data of Polymers I–V

Polymer	Chemical-shift values (δ)						
	Ar—OH	—CHO	Ar—H	—CH	—CH₂	—CH₃	—COCH₃
I	8.25	—	7.63–6.73	2.82	1.85	—	—
II	8.57	—	7.59–6.90	—	1.85	1.25	—
III	10.75	9.57	7.36–6.50	2.25	1.85	—	—
IV	10.55	9.29	7.02–6.51	—	1.92	1.35	—
V	8.25	—	6.98–6.13	2.29	1.85	—	1.25

TABLE V
^{13}C-NMR Spectral Data of Polymers I–V

	Chemical-shift values (δ)					
	C=O		Aromatic/olefinic			
Polymer	Ketone/aldehyde	Ester	carbon	—CH$_2$	—C—	α-CH$_3$
I	195.7	178.8	157.1–123.2	58.7	46.4	—
II	193.1	178.3	158.7–123.9	58.9	45.6	18.6
III	197.9	178.8	155.7–120.9	53.0	46.3	—
IV	195.1	178.6	153.1–121.8	52.0	45.4	18.9
V	197.7	178.9	161.4–115.9	55.7	46.7	—

Ni(II) in an octahedral field with tetrahedral distortion is expected to have a spin–orbit coupling parameter of $g > 0$, and, as a consequence, $g^{\parallel} > g^{\perp}$ and, similarly, $A^{\parallel}(G) > A^{\perp}(G)$. The observed values are consistent with Ni(II) in an octahedral environment.[35,36]

The magnetic moments of all the complexes were measured and the data are furnished in Table VI. The magnetic moment values of all the Cu(II) polymer–metal complexes are in the range 1.58–1.78 BM, which is in close agreement for a square planar structure. The values of the Ni(II) polymer–metal complexes show a range around 3.13–3.75 BM, which is in accordance with octahedral configuration. X-ray diffraction studies show that all the polymers are amorphous, whereas their polymer–metal complexes are crystalline. The crystallinity in polymer–metal complexes may not be due to any ordering in polymers induced during metal chelate anchoring, more so since the anchoring of metals to polymers would imply interchain crosslinking between polymeric chains, which should further reduce rather than enhance any such ordering. The appearance of crystallinity in polymer–metal complexes may be due to the inherent crystalline nature of the metallic compounds.[37]

The glass transition temperatures are presented in Table VII. (See also Fig. 4) The data reveal a minimum T_g value of 115°C for polymer **V**. The comparatively higher T_g values for benzophenone polymers and their metal complexes may be ascribed to the bulky nature of the substituent group.[37] The T_g values of the methacrylate polymers and their metal complexes are 20–50°C higher than those of the corresponding acrylate polymer–metal complexes and are controlled by the free-volume contribution of the metal ions. A similar observation of a higher T_g for polymer–metal complexes over a polymer was reported,[38,39] ascribing the same observation to strong ion–dipole interaction and decreased average segmental mobility.

The thermoanalytical data are presented in Table VII. All the polymers and polymer–metal complexes start to decompose around 240–375°C and around 310–400°C, respectively. Around 700°C, the polymers lose 99%, while the polymer–metal complexes lose 88–96% weight. The residue left behind in the complexes may be due to the formation of the respective metal oxides. The Cu(II) complexes are comparatively more stable than are Ni(II) complexes. From the TGA traces of the polymers, it is inferred that the thermal stability follows the order **III < IV < V < I < II**. (See Fig. 5.) A similar trend was observed in the both cases

TABLE VI
EPR Parameters, Magnetic Moments, and Conductivity of Polymer–Metal Complexes Ia–Vb

No.	$g^{\parallel}$	$g^{\perp}$	$A^{\parallel}G$	$A^{\perp}G$	Magnetic moment (BM)	Conductivity (ohm^{-1} cm^{-1}) $\times 10^{-9}$
Ia	2.23	2.14	35.6	32.8	1.76	2.97
Ib	2.20	2.18	38.0	31.9	3.17	0.78
IIa	2.25	2.16	35.6	33.1	1.78	3.00
IIb	2.23	2.15	38.3	31.5	3.19	0.37
IIIa	2.27	2.16	36.01	32.7	1.58	2.05
IIIb	2.52	2.16	37.8	32.0	3.21	0.38
IVa	2.33	2.17	35.7	31.9	1.63	2.75
IVb	2.25	2.13	37.9	32.2	3.75	0.83
Va	2.50	2.19	35.6	31.2	1.70	3.13
Vb	2.24	2.15	38.3	31.3	3.15	0.63

TABLE VII
T_g and TGA of Polymers and Polymer–Metal Complexes I–Vb

		Temperature (°C) corresponding to % wt loss					
		10	30	50	70	90	Char % at
No.	T_g (°C)			% Wt loss			700 °C
I	146	360	405	490	635	665	0
Ia	225	395	465	580	640	635	9
Ib	197	380	445	565	630	650	4
II	150	375	410	470	620	660	0
IIa	270	400	450	575	655	690	10
IIb	227	385	425	560	625	670	4
III	132	240	275	395	400	510	0
IIIa	182	280	325	425	590	660	9
IIIb	175	275	350	410	575	625	4
IV	148	270	320	390	495	645	0
IVa	230	330	385	480	605	685	10
IVb	175	290	340	425	585	655	5
V	115	280	350	375	530	595	0
Va	181	345	370	465	590	630	11
Vb	165	320	360	415	615	615	6

of the Ni(II) and Cu(II) complexes. In all the cases, the polymer and the respective Cu(II) complex showed two-step degradation, whereas Ni(II) complexes showed three-step degradation. This may be ascribed to the elimination of water molecules followed by chain scission and carbonization, in the case of the Ni(II) complexes. The IR, ^{1}H-NMR, EPR, electronic spectra, and magnetic moment studies confirmed that the chelation of metal ions may possibly be occurring between two groups from different polymeric chains (Scheme 2).

The electrical conductivity values are listed in Table VI. The electrical conductivity data reveals that all the polymer–metal complexes are poor electrical conductors. On reduction of the carbonyl group by NaBH$_4$, the polymers failed to coordinate through the oxygen of the carbonyl group. Cu(II)/Ni(II) polymer–metal complexes initiated the polymerization of N-vinylpyrrolidone, giving a yield of 20 and 18% respectively. Cu(II) polymer–metal complexes were found to catalyze the oxidation of cyclohexanol to cyclohexanone (11%) in the presence of H$_2$O$_2$, whereas the Ni(II) complexes showed negative results. The hydrolysis of ethyl acetate with distilled water and methanol was catalyzed by both Ni(II) and Cu(II) polymer–metal complexes, the later resulting in comparatively more yield (20%) than that of the former (16%). The catalytic activity of the polychelates may be due to the formation of a substrate–polychelate complex intermediate leading to products. Treatment of both Cu(II) and Ni(II) complexes with dilute HCl (7M) resulted in quantitative regeneration of the polymer. The dechelated polymers showed complexation of the original efficiency. The reproducibility of the above result was established by repeating the sequence several times, revealing, thereby, the good recyclability as well as the stability of the polymers under acidic conditions.
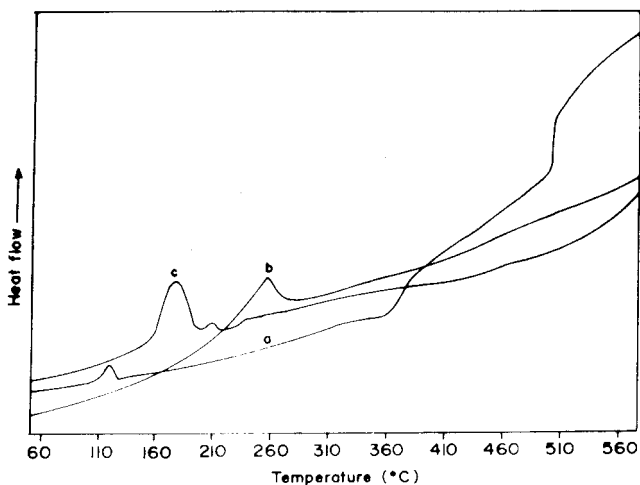

Figure 5 TGA curves of (a) poly(2H4ABA), (b) poly(2H4ABA)–Cu(II), and (c) poly(2H4ABA)–Ni(II).
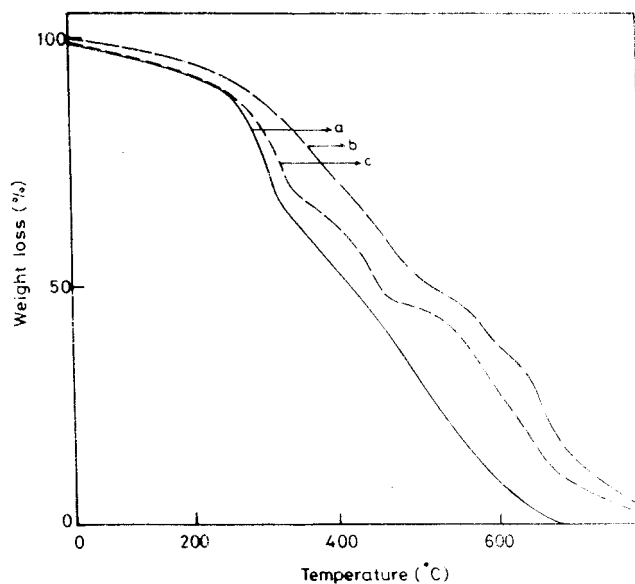
References

1. Kato, J. E. Organic Semiconducting Polymers; Edward Arnold: London, 1968.
2. Sheats, J. E.; Carraher, Z. E., Jr.; Pittman, C. U., Jr. Metal Containing Polymeric Systems; Plenum: New York, 1985.
3. Seiyama, T. Chemical Sensor Technology; Kodansha, Elsevier: Tokyo, 1989; Vols. 1 and 2.
4. Tsuchida, E. Makromol Sci Pure Appl Chem A 1994, 31, 1.
5. Bamaszal, L.; Weston, J. C.; Kendrew, J. C. J Mol Biol 1965, 2, 130.
6. Pedersen, C. J.; Frensdroff, H. K. Angew Chem Int End Engl 1972, 11, 16.
7. Rollman, L. D. J Am Chem Soc 1975, 97, 2132.
8. Drago, R. S.; Gaul, J.; Zombeck, A.; Stamb D. K. J Am Chem Soc 1980, 102, 1033.
9. Kurimara, Y.; Tsuchida, E.; Kaneko, M. J Polym Sci 1971, 9, 3511.
10. Osada, Y. Makromol Chem 1974, 176, 1983.
11. Melby, L. J Am Chem Soc 1975, 97, 4044.
12. Bajpai, U. D. N.; Raj, S.; Bajpai, A. Polym Int 1993, 32, 215.
13. Patel, D. K.; Patel, C. G.; Parmer, J. S. Macromol Rep 1994, 31, 297.
14. Lee, T. S.; Hong S. I. J Polym Sci Polym Chem Ed 1995, 33, 203.
15. Wohrle, D.; Bohlen, H.; Meyer, G. Polym Bull 1984, 11, 143.
16. Kaliyappan, T.; Nanjundan, S.; Reddy, A. V. R. J Polym Mater 1993, 10, 69.
17. Kaliyappan, T.; Kannan, P.; Reddy, A. V. R. J Polym Mater 1994, 11, 121.
18. Kaliyappan, T.; Kannan, P.; Reddy, A. V. R. Iran J Polym Sci Tech 1995, 4, 18.
19. Kaliyappan, T.; Kannan, P. J Appl Polym Sci 1996, 60, 947.
20. Kaliyappan, T.; Swaminathan, C. S.; Kannan, P. Polymer 1996, 37, 2865.
21. Kaliyappan, T.; Kannan, P. J Polym Sci Part A Polym Chem A 1996, 31, 3551.
22. Kaliyappan, T.; Swaminathan, C. S.; Kannan, P. Eur Polym J 1997, 33, 59.
23. Kaliyappan, T.; Murugavel, S. C.; Kannan, P. Polym Int 1998, 45, 278.

Figure 4 DSC curves of (a) poly(2H4AAP), (b) poly(2H4AAP)–Cu(II), and (c) poly(2H4AAP)–Ni(II).

24. Stempel, G. H.; Gross, R. P.; Mariella, R. P. J Am Chem Soc 1950, 72, 2299.

25. Nozawa, T.; Akimotom, Y.; Hatano, M. Makromol Chem 1972, 158, 21.

26. Tsuchida, E.; Nishide, H. Adv Polym Sci 1977, 24, 59.

27. Garg, C. L.; Narasimhan, K. V.; Tripathi, B. N. Inorg Nucl Chem 1971, 33, 387.

28. McMurray, H. L.; Thornton, V. Anal Chem 1952, 24, 318.

29. Nakamoto, K.; McCarthy, P. J. Spectroscopy and Structure of Metal Chelate Compounds; Wiley: New York, 1968; p 269.

30. Patil, M. S.; Shah, N. R.; Rana, A. K.; Karumpurawala, A. M.; Shah, J. R. J Macromol Sci Chem A 1981, 16, 737.

31. Bailey, D.; Tirrol, D.; Pinazzi, C.; Vogl, O. Macromolecules 1978, 11, 312.

32. Patel, M. N.; Patil, S. H. J Macromol Sci Chem A 1982, 19, 675.

33. Veno, K.; Martell, A. E. J Phys Chem 1955, 59, 998.

34. Birodar, N. S.; Kulkarni, V. H. J Inorg Nucl Chem 1974, 33, 2451.

35. Dubicki, L.; Martini, R. L. Inorg Chem 1966, 7, 2203.

36. Jorrgensen, C. K. Absorption Spectra and Chemical Bonding in Complexes; Pergamon: Oxford, 1972; p 15.

37. Figgis, B. N. Introduction to Ligand Fields; Wiley-Interscience: New York, 1972; p 25.

38. Eigenberg, A.; King, M. Ion-containing Polymers: Physical Properties and Structure; Academic: New York, 1977; Vol. 2, p 45.

39. Tamizharasi, S.; Reddy, A. V. R. Polymer 1992, 33, 2421.

40. Gustafson, R. L. J Phys Chem 1965, 69, 2849.