Removal of Heavy Metal Ions using the Chelating Polymers Derived by the Condensation of Poly(3-Hydroxy-4-acetylphenyl methacrylate) with Different Diamines

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ABSTRACT: A series of methacrylate-based chelating polymers was synthesized by the reaction of 3-hydroxy-4-acetylphenyl methacrylate with amines (e.g., ethylenediamine, propylenediamine, and phenylenediamine) in tetrahydrofuran. The chelating polymers were characterized by infrared (IR) and carbon-13 nuclear magnetic resonance (^{13}C–NMR) spectroscopic techniques. The thermal stabilities of these polymers were investigated by thermogravimetric (TG) and differential thermal analyses (DTA). Heavy metal ions [viz., Pb(II), Hg(II), Cd(II), and Cr(VI)] were removed with these chelating polymers, and metal ion uptake efficiency, reusability of the resins, and effects of pH and time on the metal removal were also studied. The chelating polymers possess appreciable selectivity for Pb(II) and Hg(II) compared with Cd(II) and Cr(VI). The chelating ability of the polymers towards the heavy metal ions is a sensitive function of the nature of the substituent on the nitrogen atom. The amount of metal uptake by the chelating polymer was determined by atomic absorption spectrophotometry (AAS). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 414–421, 2003

Key words: heavy metal ions; removal; chelating polymers; selectivity

INTRODUCTION

A growing demand for more selective chelating agents is evident in many applications, such as wastewater treatment, toxic metal removal, and enrichment of precious metals from hydrometallurgical liquids. The chelating polymers with mixed donor atoms are receiving a great deal of attention because they display high selectivity towards metal cations.

In the past, many types of metal-chelating adsorbents have been synthesized.[1] Syntheses have been accomplished with either polymerization or simple functionalization principles. The former involves the polymerization of monomers containing the desired ligands. The modification of a preshaped polymer by functionalization reactions is a favorite process of enhancing metal selectivity.

Functionalized polymers are used for a variety of applications; these include organic syntheses,[2, 3] metal ion separation,[4, 5] pollution control,[6] polymer drug grafts,[7] waste water treatment,[8] and uptake of trace metal ions.[9, 10] Although, derivatives of 2,4-dihydroxyacetophenone have been used as analytical reagents[11–14] and ligands[15, 16] for the preparation of metal complexes, chelating polymers derived from this precursor have not yet been reported. Hence, the present investigation deals with the preparation of new chelating polymers formed by the reaction between poly(3-hydroxy-4-acetylphenyl methacrylate) and various diamines.

EXPERIMENTAL

Materials

Methacrylic acid (Merck) was used without further purification. Benzoyl chloride (S.d. fine) was used as received for the preparation of methacryloyl chloride. 2,4-Dihydroxyacetophenone was prepared according to the literature procedure[17] and recrystallized from distilled water. Ethylenediamine, propylenediamine, and phenylenediamine were purified before use. The polymerizations were initiated with benzoyl peroxide (BPO; 97% active compound; BDH Chemicals Limited). Stock solutions of metal ions were prepared using AR grade lead nitrate, mercuric chloride, cadmium nitrate, and potassium dichromate salts.

Physicochemical measurements

Elemental analyses of the chelating polymers were carried out with a Hereaus Carlo Erba DP-200 instrument (CDRI, Lucknow). Fourier transform infrared (FTIR) spectra were recorded with a Bruker IFS 66 V

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spectrophotometer as potassium bromide pellets. Solid-state cross-polarization/magic-angle spinning (CP/MAS) ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectra were recorded with a Brucker DSX 300 MHz spectrometer. A NETZSCH-Geratebau-GmbH thermal analysis system (TAS) was used to evaluate the thermal stability, decomposition temperature, and kinetic parameters of the polymers at a heating rate of 10°C min^{-1}. The metal removal was determined with a UNICAM UK Model 839 atomic absorption spectrophotometer.

Preparation of 3-hydroxy-4-acetylphenyl methacrylate (HAPM)

Methacryloyl chloride was prepared according to the method of Stempel et al.[18] A solution of 2,4-dihydroxyacetophenone (30.4 g), triethylamine (38 mL), methyl ethyl ketone (200 mL), and hydroquinone (0.5 g) in a three-necked flask equipped with a stirrer, thermometer, and dropping funnel was cooled to 0–5°C. Methacryloyl chloride (12.4 mL in 25 mL of methyl ethyl ketone) was added in a dropwise manner with stirring. The reaction mixture was stirred for another 2 h at room temperature, and the quaternary ammonium salt was filtered. The filtrate was washed with distilled water and dried over anhydrous sodium sulfate, and the methyl ethyl ketone was evaporated. The crude HAPM was recrystallized from petroleum ether.

Polymerization of HAPM

A solution of HAPM (5 g, 0.024 mol), methyl ethyl ketone (30 mL), and BPO (0.5 g) were placed in a 100-mL polymerization tube that was deaerated by passing oxygen-free nitrogen gas through it for 0.5 h. The tube was sealed and placed in a thermostat at 70 ± 1°C for 17 h. The contents were poured into a large excess of methanol. The precipitated poly(3-hydroxy-4-acetylphenyl methacrylate) (PHAPM) was filtered, washed with methanol, and purified by dissolution in
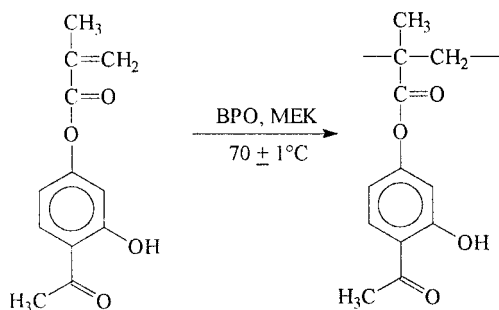
Figure 1 Polymerization of 3-hydroxy-4-acetylphenyl methacrylate (HAPM).
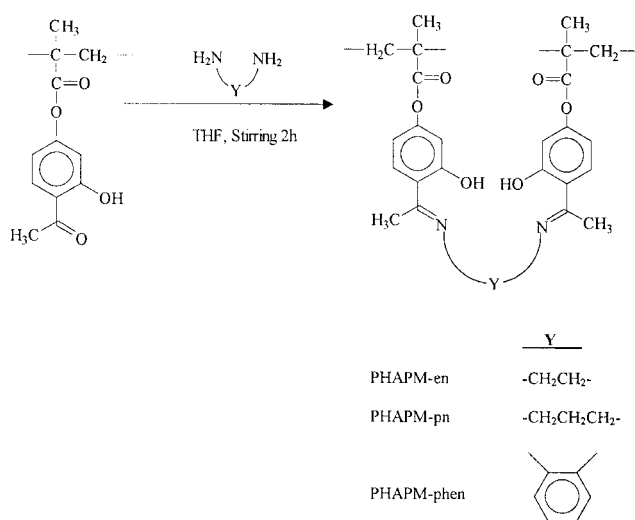
Figure 2 Syntheses of chelating polymers.

dimethylformamide and reprecipitating by addition of methanol. The purified polymer was dried under reduced pressure at 60°C to constant weight.

Preparation of chelating polymers by the condensation of poly(3-hydroxy-4-acetylphenyl methacrylate) with different diamines

A solution of PHAPM (0.02 mol, 4.4g) and diamine [ethylenediamine (0.6 g), 1,3-propylenediamine (0.74 g), or 1,2-phenylenediamine (1.08 g)] (0.01 mol) in tetrahydrofuran in a 500-mL flask was stirred magnetically for 2 h. The mixture was filtered, and the filtered material was washed with tetrahydrofuran, diethylether, and water and dried under reduced pressure at 60°C to constant weight.

Procedure for the sorption of metal ion at different pHs

A mixture of 2.5 mL of 1×10^{-2} M metal [Pb(II), Hg(II), Cd(II) or Cr(VI)] solution, 7.5 mL of buffer (pH 2–10) solution, and resin (0.2 g) in a 100-mL beaker was stirred magnetically for 1 h. The metallated resin was filtered and washed thoroughly with distilled water. The filtrate and washings were transferred to a 25-mL volumetric flask and diluted to the mark with distilled water. The amounts of Pb(II), Cd(II), or Cr(VI) present in the filtrate were determined by atomic absorption spectroscopy [Pb, 283.3; Cd, 228.8; and Cr, 357.9 nm] and Hg(II) was determined spectrophotometrically (at 470 nm) using 1,10-phenanthroline.[19]

Procedure for sorption of Hg(II) at different time intervals

A mixture of 2.5 mL of 1×10^{-2} M Hg(II) solution, 7.5 mL of buffer (pH 10) solution, and resin (0.2 g) was

Resin	Yield (%)	C % Found (calcd)	H % Found (calcd)	N % Found (calcd)
PHAPM	64	65.40 (65.40)	5.67 (5.45)	—
PHAPM-en	78	64.83 (67.24)	5.98 (6.03)	5.95 (6.03)
PHAPM-pn	69	66.76 (67.77)	6.47 (6.27)	5.79 (5.85)
PHAPM-phen	64	69.73 (70.31)	5.56 (5.46)	5.07 (5.46)

placed in a 100-mL beaker and stirred magnetically for different periods of time (15, 30, 45, 60, and 120 mines). The metallated resin was filtered and washed thoroughly with distilled water. The filtrate and washings were transferred into a 25-mL volumetric flask and diluted to the mark with distilled water. The amount of Hg(II) present in the filtrate was estimated spectrophotometrically with 1,10-phenanthroline.

Procedure for competitive metal ion sorption by the chelating polymers

A mixture of metal solution [containing 0.1 M Pb(II) (0.5 mL), 0.1 M Hg(II) (0.5 mL), 0.1 M Cd(II) (1 mL), and 0.1 M Cr(VI) (2 mL)], 7.5 mL of buffer (pH 10) solution, and resin (1 g) was in a 100-mL beaker and stirred magnetically for 1 h. The metallated resin was filtered and washed with distilled water. The filtrate

and washings were transferred to a 100-mL volumetric flask and diluted to the mark with distilled water. The amounts of Pb(II), Cd(II), and Cr(VI) present in the filtrate were determined by atomic absorption spectroscopy and Hg(II) was determined spectrophotometrically with 1,10-phenanthroline.

RESULTS AND DISCUSSION

By reaction of methacryloylchloride and 2,4-dihydroxyacetophenone, the monomer HAPM was prepared. The polymerization of HAPM produced PHAPM (Figure 1). Condensation of PHAPM with ethylenediamine, propylenediamine, and 1,2-phenylenediamine in THF gave PHAPM-en, PHAPM-pn and PHAPM-phen, respectively (Figure 2). PHAPM is colorless, and the chelating polymers have a pale yellow or yellow color. Combustion analysis data and yields
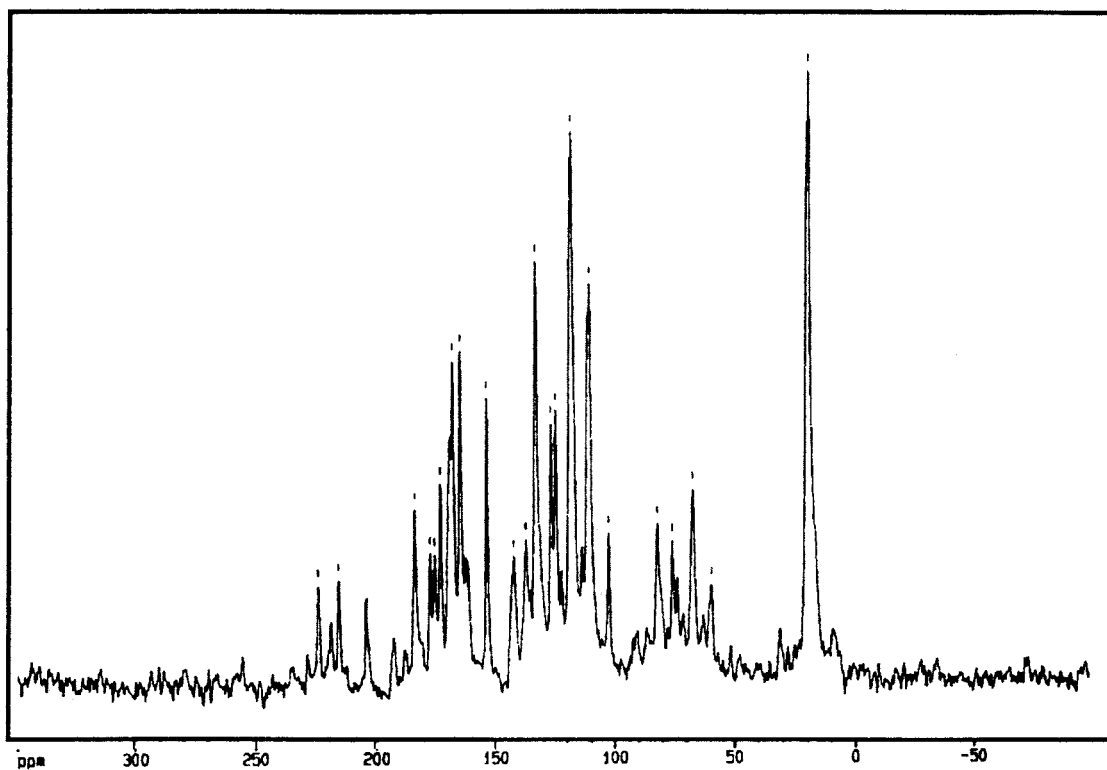

Figure 3 Solid-state CP/MAS ¹³C-NMR spectra of poly(3-hydroxy-4-acetylphenyl methacrylate-phenylenediamine) (PHAPM-phen).

TABLE II
Solid-State CP/MAS ^{13}C-NMR Spectral Data of the Polymers

δ ppm of				Assignment
PHAPM	PHAPM-en	PHAPM-pn	PHAPM-phen	
27.61	16.61	17.54	19.25	CH$_3$ group of (H$_3$C—C=N—) 27.61 ppm in PHAPM was due to CH$_3$ group in (O=C—CH$_3$)
47.66	47.65	48.76	48.35	Methylene (—CH$_2$—) backbone
65.54	72.05	73.40	67.50	(—C—) of (C—CH$_3$)
111.96	111.10	115.61	118.33	Aromatic carbon (Due to residual brodening, a clear separation was not observed)
119.04	130.91	133.96	124.80	
134.08			126.78	
			133.14	
			137.18	
			142.18	
158.20	157.48	158.57	164.99	Phenylester carbonyl
—	176.71	177.33	177.65	(>C=N) group
205.21	—	—	—	(C=O) of CH$_3$—C=O group

for the resins are given in Table I. The former are in agreement with the calculated values.

Because the chelating polymers are insoluble in organic solvents, NMR spectral data for these polymers were obtained in the solid state. A typical CP/MAS solid-state ^{13}C-NMR spectrum is shown in Figure 3. The backbone methylene carbons appear as sharp peaks at 47.66, 47.65, 48.76, and 48.35 ppm, respectively, for PHAPM, PHAPM-en, PHAPM-pn, and PHAPM-phen. The C=O group in PHAPM appears at 205.2 ppm. For PHAPM-en, PHAPM-pn, and PHAPM-phen, the peak due to the C=O group was replaced by peaks at 176.71, 177.33, and 177.65 ppm, respectively. The NMR peak assignments are given in Table II.

Infrared (IR) spectra of the chelating polymers were recorded in the range 4000–400 cm^{-1} using KBr discs. A comparison of IR spectra of PHAPM with the chelating polymers shows the absence of νC=O (1603 cm^{-1}) and the presence of νC=N (azomethine) at 1620, 1601, and 1612 cm^{-1} for PHAPM-en, PHAPM-pn, and PHAPM-phen, respectively. The IR spectral data for these resins are given in Table III. The lowering of the OH stretching frequencies of all the chelating polymers (3602 to 3340 cm^{-1}) is due to hydrogen bonding in polymeric association.

Thermal analyses of chelating polymers

Thermogravimetric analyses

Thermograms of the chelating polymers are shown in Figure 4. A mathematical interpretation of thermogravimetric curves enables one to determine kinetic parameters for the pyrolysis reactions. Horowitz and Metger[20] demonstrated the method of calculation of energy of activation (E) of polymeric substances:

$$\ln \ln\left(\frac{W_o}{W_t}\right) = \frac{E\theta}{RTs^2} \quad (1)$$

where $\theta = T - Ts$, W_o is the initial weight, W_t is the weight at any time t, T_s is the peak temperature, and T is the temperature at a particular weight loss. A plot of $\ln \ln W_o/W_t$ versus θ gives a straight line. The slope is related to the activation energy by,

$$\text{Slope} = \frac{E}{RTs^2} \quad (2)$$

Representative plots are shown in Figure 5, with calculated values for the activation energy of decomposition given in Table IV. The activation associ-

TABLE III
IR Spectral Data (cm^{-1}) of the Polymers

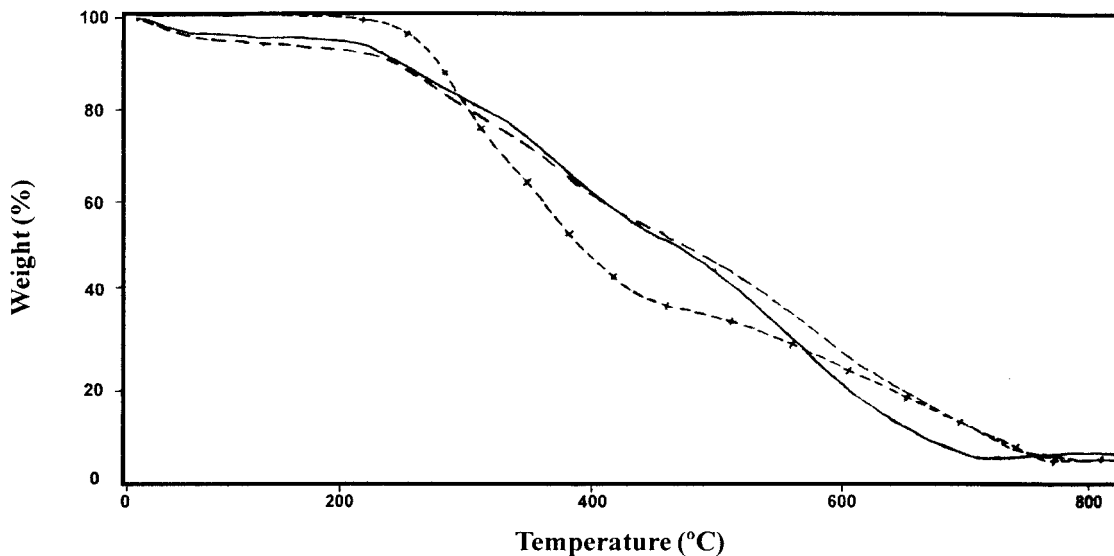| Polymer	ν_{OH}	ν_{CH}	$\nu_{C=N}$	$\nu_{C=O}$ (ketonic)	$\nu_{C=O}$ (ester)
PHAPM	3602(m)	2857(m)	—	1603(m)	1720(s)
PHAPM-en	3350(w)	2995(m)	1620(s)	—	1750(s)
PHAPM-pn	3340(w)	2937(w)	1601(m)	—	1743(s)
PHAPM-phen	3350(m)	3021(m)	1612(m)	—	1730(s)

Figure 4 Thermograms of polymers. Key: (¯) PHAPM-en; (——) PHAPM-pn; and (–+–) PHAPM-phen.

ated with each stage of decomposition was also evaluated by the well-known Broido method.[21] The equation used for the calculation of activation energy (E) was:

$$\ln \ln\left(\frac{1}{Y''}\right) = \left(\frac{-E}{R}\right)\frac{1}{T} + \text{Constant} \qquad (3)$$

where $Y'' = (W_t - W_\infty)/(W_o - W_\infty)$; that is, Y'' is the fraction of the number of initial molecules not yet decomposed, W_t is the weight at any time t, W_∞ is the weight at infinite time ($=$ zero), and W_o is the initial weight. A plot of $\ln \ln (1/Y'')$ versus $1/T$ gives a straight line over a range $0.999 > Y'' > 0.001$. The slope is related to the activation energy. Representative plots are shown in Figure 6, and the calculated values for the activation energy of decomposition are listed in Table IV.

Differential thermal analysis

The DTA plots of the polymers are given in Figure 7. The Kissinger[22, 23] method was used to determine the
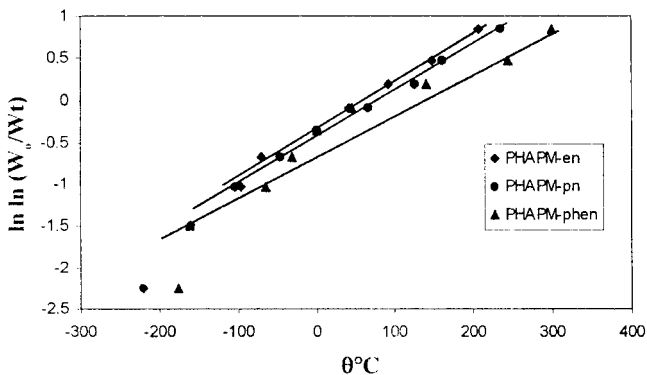
activation energy (E). The equation used for the calculation of E was:

$$\frac{d\left(\ln \dfrac{\phi}{T_m^2}\right)}{d\left(\dfrac{1}{T}\right)} = -\frac{E}{R} \qquad (4)$$

where φ is a constant rate of temperature rise, T_m is the temperature at which the peak differential thermal analyses deflation occurs, and T is the temperature. A plot of $(\ln \varphi/T_m^2)$ versus the reciprocal of the absolute temperature ($1/T$) gives the E of decomposition using the following equation:

$$\text{Slope} = -\frac{E}{R} \qquad (5)$$

Representative plots are shown in Figure 8. The calculated values for the activation energy of decom-
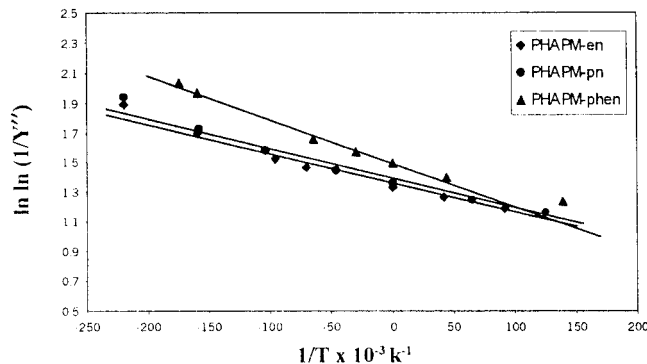

Figure 5 Representative Horowitz and Metger plot for methacrylate-supported chelating polymers.

Figure 6 Representative Broido plot for methacrylate-supported chelating polymers.

TABLE IV
Activation Energy of Decomposition for the Chelating Polymer Resins Determined by Thermogravimetric Analysis

Polymer	Peak temperature, T_3,(°C)	Decomposition temperature range (°C)	Weight loss (%)	Method[a]	Activation energy (kJ mol^{-1})
PHAPM-en	212	52–253	8	HM	43.03
				BR	100.13
	381	253–555	23	HM	42.70
				BR	48.55
	651	555–720	32	HM	131.12
				BR	291.30
PHAPM-pn	210	55–290	16	HM	56.83
				BR	31.86
	464	290–593	54	HM	27.10
				BR	57.32
	678	593–760	16	HM	66.80
				BR	145.64
PHAPM-phen	297	190–360	36	HM	29.71
				BR	72.83
	440	360–530	30	HM	169.06
				BR	45.52
	639	530–780	33	HM	207.46
				BR	50.97

[a] HM, Horowitz and Metger method; BR, Broido method.

position are 7.28, 9.50, and 10.40 kJ mol^{-1} for PHAPM-en, PHAPM-pn, and PHAPM-phen, respectively. All the chelating polymers were stable and showed maximum peak differential thermal analyses deflection in the temperature range 280–600°C.

Removal of heavy metal ions

Effect of pH on removal of metal ions

The effect of pH on the removal of heavy metal ions by the chelating polymers is shown in Figure 9 for pH 2,

6, and 10. It is evident that metal ion uptake by the resins depended strongly on the pH. In general, as the pH increases, uptake of metal ion by resin also increases.

Effect of time on metal ion uptake

The effect of time on metal ion uptake was studied at pH 10 and the results are shown in Figure 10. The chelating resins required 1 h for maximum and constant metal ion uptake.
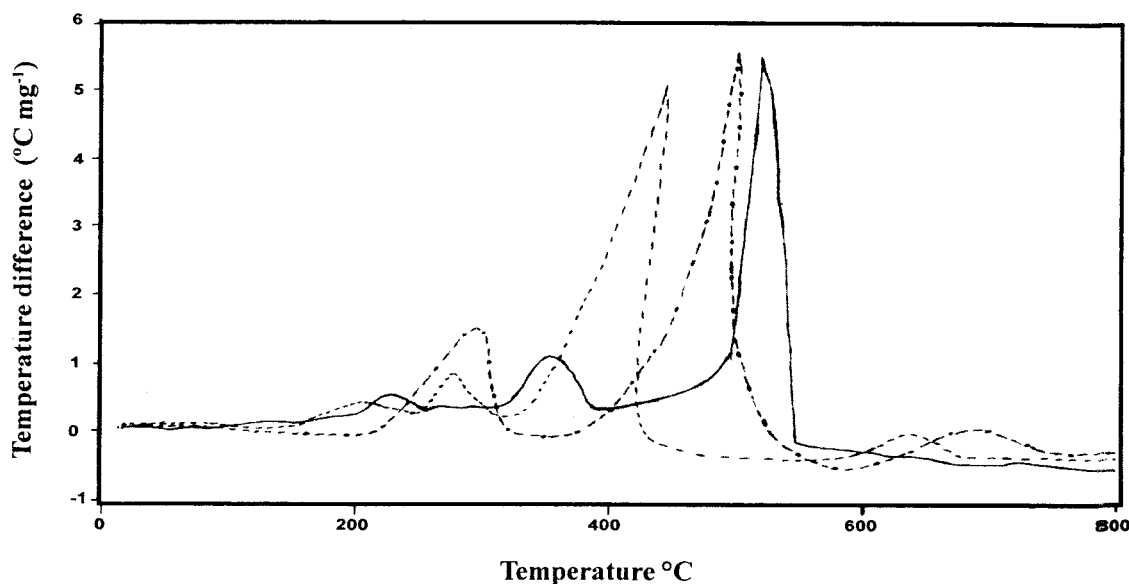

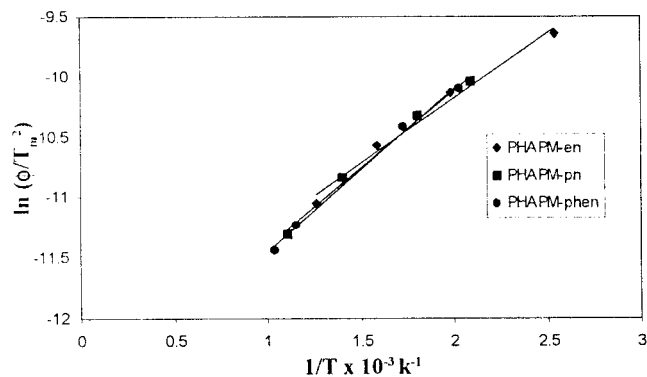**Figure 7** DTA curves of the polymers. Key: (··) PHAPM-en; (——) PHAPM-pn; and (—·—) PHAPM-phen.

Figure 8 Representative Kissinger plot for methacrylate-supported chelating polymers.

Figure 10 Effect of time on the removal of Hg(II) using methacrylate-supported chelating polymers.

Sorption selectivity

Competitive sorption studies were conducted by stirring solutions comprised of 100 ppm of Cd(II), Cr(VI), Hg(II), and Pb(II), at pH 10, with the chelating polymer for 1 h. The overall metal uptake capacities of the resins at pH 10 under competitive conditions are in good agreement with the results obtained in the noncompetitive experiments. The sorption selectivity order is Pb(II) $\geq$ Hg(II) > Cd(II) > Cr(VI), and data are presented in Figure 11. The chelating efficiencies of the polymers increased in going from PHAPM-en to PHAPM-pn and then decreased for PHAPM-phen. This result is probably due to the increase in the stability of the complex in the aforementioned order. The decrease in the efficiency of PHAPM-phen is attributed to steric and electronic effects.

Recyclability of the chelating resins

A most important property of a chelating polymer resins is its capacity for reuse. The chelating resins could be brought into their original state by desorbing
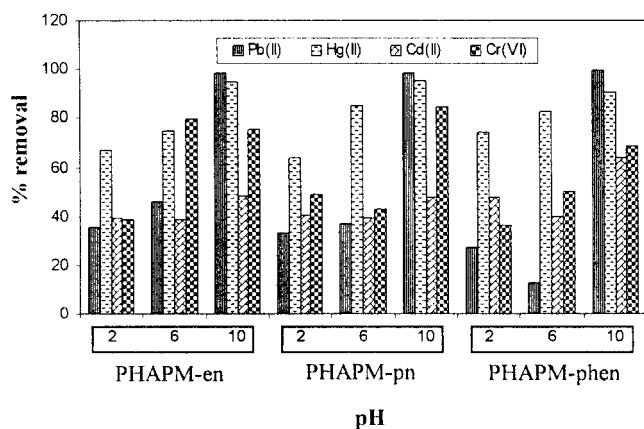
the metals from the metallated resins with 6M HCl in tetrahydrofuran. The metal free resins could be reused after nuetralization. In acidic medium, the metallated chelating resins are protonated, which releases the metal into the solution. Metal ion uptake was almost same, even after 4 cycles. For every cycle, the percent metal ion desorption and uptake were estimated. The data are given in Table V.

CONCLUSIONS

Heavy metal ions of Pb(II), Hg(II), Cd(II), and Cr(VI) are known inorganic pollutants, and their presence in aquatic systems pose heavy risk to human health. Therefore, removal of such metal ion from water bodies is an important research activity.

Novel functionalized chelating polymers were synthesized and characterized based on combustion analysis and IR and solid-state ^{13}C-NMR spectral data. The chelating polymers studied are highly stable as evidenced by kinetic data and may be used for the removal of metal ions at room temperature. The metal uptake efficiency of the chelating polymers increases

Figure 9 Effect of pH on the removal of heavy metal ions using methacrylate-supported chelating polymers.

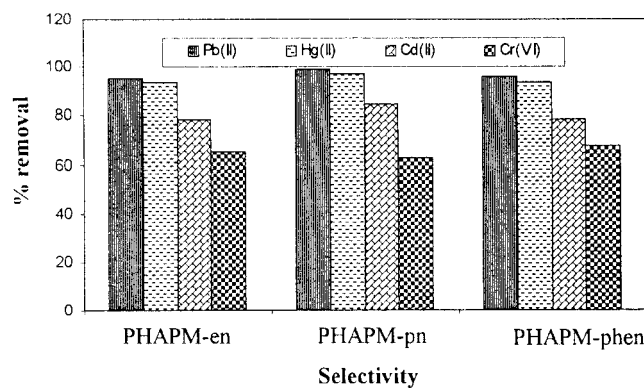**Figure 11** Sorption selectivity of the polymers in removal of heavy metal ions.

TABLE V
Recyclability of the Resins on the Uptake of Metal Ions at pH 10 from Solutions of 207.2 ppm of Pb(II), 200.6 ppm of Hg(II), 112.4 ppm of Cd(II), and 52.0 ppm of Cr(VI)

Cycle no.	Resin	Pb(II)		Hg(II)		Cd(II)		Cr(VI)	
		Uptake (ppm)	Desorption (%)	Uptake (ppm)	Desorption (%)	Uptake (ppm)	Desorption (%)	Uptake (ppm)	Desorption (%)
1		203.8	96.4	190.4	96.4	54.5	98.2	39.3	97.4
2		202.2	97.7	188.3	97.3	53.2	97.3	38.5	99.6
3	PHAPM-en	200.4	98.2	186.2	96.3	22.6	98.4	37.9	97.4
4		198.7	97.5	185.3	97.1	50.5	97.4	37.5	96.4
1		204.0	95.5	171.2	95.5	53.3	96.9	43.9	98.5
2		202.5	97.9	169.3	96.4	52.1	99.7	42.9	98.3
3	PHAPM-pn	198.3	97.6	166.6	97.8	50.1	98.2	41.8	96.9
4		195.6	98.4	162.4	96.4	48.4	97.7	41.1	97.2
1		205.9	99.7	193.4	97.2	72.1	96.5	35.8	98.2
2		204.3	98.6	191.5	97.2	71.3	98.6	34.6	98.4
3	PHAPM-phen	202.8	97.3	188.7	98.5	69.5	98.4	33.5	97.8
4		200.3	96.5	185.4	98.5	68.3	96.5	32.5	96.9

with pH and reaches a plateau value around pH 10. A favorable characteristic of chelating polymers is the time required for maximum and constant uptake of metal ion from aqueous medium. Just 1 h is sufficient for the maximum and constant uptake of metal ion, whereas recently reported methods[24–26] require longer periods of time. Sorption selectivity of the polymers is of the order Pb(II) ≥ Hg(II) > Cd(II) > Cr(VI). The metal ion uptake efficiency of the resin is not altered much, even after five cycles.

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