

Synthesis, Characterization, and Heavy Metal Ion Adsorption Studies of Polyamides, Polythioamides Having Pendent Chlorobenzylidene Rings

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ABSTRACT: Aromatic polyamides and polythioamides with pendent chlorobenzylidene rings were synthesized through direct polycondensation of 2-(*p*-chlorobenzalimino) terephthalic acid with the diamines 4,4'-oxidianiline (1a), 4,4'-methylenediamide (1b), 4,4'-diaminodiphenyl sulfone (1c), and thioamines 4,4'-(bisthiourea) diphenyl ether (3a), 4,4'-(bisthiourea) diphenyl methane (3b), 4,4'-(bisthiourea) diphenyl sulfone (3c), respectively, in DMF using P(OPh)₃/pyridine. The polymers were precipitated using water as nonsolvent. FTIR and ¹H-NMR spectroscopic analysis was used to characterize the monomers and polymers. Representative polyamides and polythioamides were used

for the removal of heavy metal ions such as Pb(II), Cd(II), Cu(II), and Cr(III) from aqueous solutions. The effects of pH, contact time, and initial concentration on the uptake of metal ions have been investigated. The adsorption capacities under competitive conditions were in the order Pb (II) > Cu (II) > Cr (III) > Cd (II). The adsorbed ions were eluted by treatment with 2N HCl, and the activities of the polymers are retained after fourth regeneration. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1634–1642, 2011

Key words: polyamides; polythioamides; chlorobenzylidene rings; phenylthiourea; metal ion adsorption

INTRODUCTION

Polymeric Schiff bases are of great interest because of their semiconducting properties,^{1,2} formation of metal chelates,^{3,4} thermal stability,⁵ opto-electronic properties,⁶ and also due to their ability in the removal of metal ions.⁷ Phenyl thiourea and its derivatives have also gained importance due to their good properties such as high corrosion resistance,⁸ in opto-electronics,⁹ and in the removal of heavy metal ions,¹⁰ and toxic elements such as mercury.¹¹ On the basis of the aforementioned advantages of azomethine and phenyl thiourea groups, it is of interest to synthesize new generation of polymers containing these groups in the polymer backbone. Earlier works from this laboratory were aimed at synthesis of poly (azomethine ester)s¹² and poly (azomethine amide)s.¹³ Such polymers show good corrosion control on Al in alkaline medium,¹⁴ and good conductivity when blended with different poly anilines.¹⁵

Environmental pollution by toxic metals occurring through waste disposal from various sources has

become an ecotoxicological hazard of prime interest due to their ill effects. As a consequence, separation and removal of metal ions have become an attractive area of research and have led to the development of new polymeric materials for the removal of metal ions from water bodies and other wastes. Various polymeric resins were reported for the adsorption of metal ions from aqueous solutions.^{16,17} Hollow fibers composed of modified polyamide were reported for the removal of Cu(II), Zn(II), and Ni(II) in aqueous media.¹⁸ When azomethine and thiourea groups are incorporated into the polyamide backbone, such polymers possess increased adsorbing sites per repeat unit for the removal of metal ions. For these reasons, we have focused our attention on the development of new poly (azomethine thiourea amide)s and to examine their removal of heavy metal ions. This article describes the preparation, characterization, and adsorption of metal ions such as Pb (II), Cd (II), Cu (II), and Cr (III) by poly (azomethine amide)s and poly (azomethine thiourea amide)s.

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EXPERIMENTAL

Materials

4-aminoterephthalic acid (Aldrich), triphenyl phosphite (Fluka), chlorobenzaldehyde (Fluka), and diaminodiphenyl sulfone (Merk) were used as received.

Diaminodiphenylether (Merk) and diaminodiphenylmethane (Aldrich) were recrystallized from ethanol before use. *N,N*-dimethylformamide was stored over calcium sulfate, filtered, and distilled under reduced pressure. All other chemicals or solvents were either of analytical grades or purified using standard procedures.

Monomer synthesis

2-(*p*-chlorobenzalimino)terephthalic acid (2)

This modified terephthalic acid was prepared according to our earlier report.¹³ A solution of 4-aminoterephthalic acid (0.01 mol) and chlorobenzaldehyde (0.01 mol) in DMF (50 mL) was mixed in a 250-mL round-bottomed flask with catalytic amount of *p*-toluenesulfonic acid, and the contents were heated to 110°C. Initially 10–15 mL of azeotrope/DMF was removed under reduced pressure and then refluxed for 1 h. The reaction mixture was then poured in to distilled water to precipitate the monomer. The pale yellow product was filtered, dried, and recrystallized from DMF/water mixture. Yield: 69%. The characteristic IR (KBr) assignments are as follows: 1678 cm⁻¹ (carbonyl of acid), 2917 cm⁻¹ (imine —CH), 1617 cm⁻¹ (—CH=N—), and 1088 (C—Cl). The ¹H-NMR (DMSO-*d*₆) signals are: δ 9.9 (s, 2H, COOH), 8.2 (s, H, —CH=N—), 7.7–6.9 (m, Ar—H).

4, 4'-(bisthiourea) diphenyl methane

4,4'-diaminodiphenyl methane (0.02 mol), 80 mL of deaerated water, 20 mL of concentrated HCl, and a pinch of activated charcoal were charged in to a 250-mL round-bottomed flask equipped with a magnetic stirrer and warmed to 50°C with constant stirring for 30 min. The resulting reaction mixture was filtered and transferred into another 250 mL round-bottomed flask equipped with a magnetic stirrer and condenser and heated to 90°C with stirring for 6–7 h. The yellow product obtained was filtered, washed with hot water and recrystallized from DMF/water, and dried in vacuum (Yield = 78%). The assignment of IR (KBr) peaks is as follows: 3265 cm⁻¹ (—NH₂), 3163 cm⁻¹ (—NH), 1065 cm⁻¹ (C=S). The ¹H-NMR (DMSO-*d*₆) assignments of signals is as follows: δ 9.57 (2H, s, NH), δ 6.80 (2H, d, ArCH), δ 6.78 (2H, d, ArCH), δ 6.46 (2H, d, ArCH), δ 6.44 (2H, d, ArCH), δ 4.76 (4H, s, NH₂), δ 3.5 (2H, —CH₂—). 4, 4'-(bisthiourea) diphenyl ether and 4, 4'-(bisthiourea) diphenyl sulfone were prepared using the aforementioned procedure with diaminodiphenylether and diaminodiphenyl sulfone respectively, as starting materials.

Polymer synthesis

The synthesis of P4 is given as a typical example for the preparation of polythioamides and polyamides. A mixture of equimolar amounts (2.5 mmol) of diacid 2, (2.5 mmol) monomer 3a, triphenyl phosphite (5.2 mmol) in DMF (12–18 mL) which contained dissolved LiCl (1.5 g), pyridine (6–10 mmol), and HCl (2–4 drops) was heated with stirring at 140°C for 3–4 h. The viscous reaction mixture was poured into water and precipitated with stirring. The solid polymers formed were filtered; washed with dilute Na₂CO₃, dilute HCl to remove the unreacted monomers. It was then washed with water, ethanol, and dried under vacuum.

Adsorption experiments

Batch adsorption experiments were conducted in 50 mL flasks. Polymer (0.02 g) was added into 10 mL solution of known metal ion concentration with desired pH value. The mixture was shaken in a shaker for the predetermined time interval at room temperature. After filtration the concentrations of the metal ions Pb (II), Cd (II), Cu (II), and Cr (III) were analyzed with an atomic absorption spectrophotometer. Initial concentrations of all the metal ions were kept at 300 ppm for the pH, time variation, and competitive adsorption experiments. In the competitive and recycling experiments, the total volume of solution was kept at 50 mL, and the amount of adsorbent used was 40 mg. The adsorption capacity was calculated using the following mass balance equation:

$$q_{eq} = (C_0 - C_{eq})V/W$$

Where q_{eq} is the equilibrium adsorption capacity (mg/g), C_0 and C_{eq} are the initial and equilibrium liquid-phase solute concentrations (mg/L), respectively, V is the liquid phase volume (L), and W is the amount of polymer (g). The desorption study was carried out in 50 mL portions of 2N HCl for the reuse of the adsorbent.

Measurements

IR measurements were carried out on a Spectromone, Perkin-Elmer ATR, without KBr. ¹H-NMR spectra were recorded in DMSO-*d*₆ using a Bruker instrument. Inherent viscosities were determined by using an Ubbelohde suspended-type viscometer with polymer concentration of 0.5 g/dL in DMF at 25°C. Thermo gravimetric analysis (TGA) was recorded using a Perkin-Elmer analyzer at a heating rate of 10°C/min in static air. The metal ion

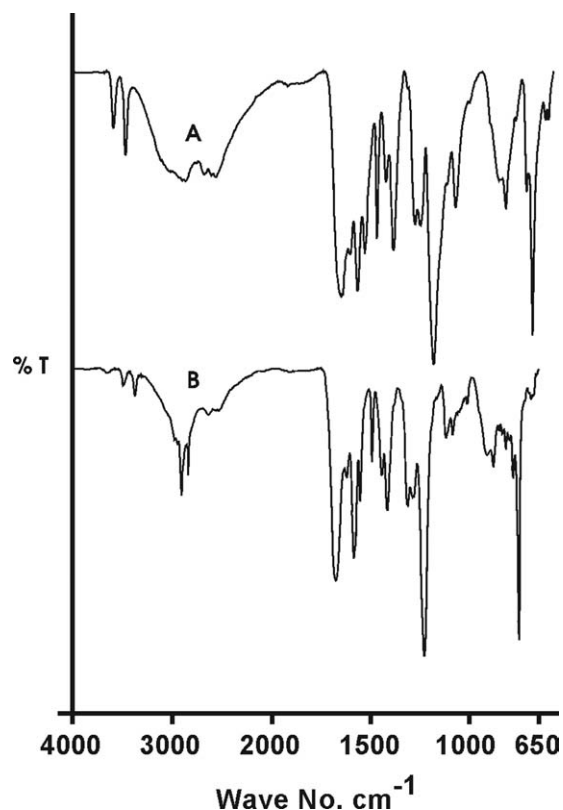


Figure 1 IR spectra of A: 4-aminoterephthalic acid. B: 2-(*p*-chlorobenzalimino) terephthalic acid (2).

concentrations were analyzed using AA-6300 (SHIMADZU) atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of monomers

2-(*p*-chlorobenzalimino)terephthalic acid

The synthesis of this modified terephthalic acid monomer (2) was carried out according to the earlier reports.¹³ The IR spectra of 4-aminoterephthalic acid and that of the monomer 2-(*p*-chlorobenzalimino) terephthalic acid (2) are shown in Figure 1. The disappearance of the -NH_2 stretching frequency of 4-aminoterephthalic acid (3505cm^{-1} and 3388cm^{-1}) and the appearance of imine -CH stretching frequency at 2917cm^{-1} along with the -N=CH- stretching frequency at 1617cm^{-1} supports the formation of the monomer 2-(*p*-chlorobenzalimino)terephthalic acid. The chloroaromatic stretching frequency of monomer appears at 1088cm^{-1} . The $^1\text{H-NMR}$ spectrum of 2-(*p*-chlorobenzalimino)terephthalic acid is shown in Figure 2. The signals at $\delta = 8.2\text{ppm}$ confirms the formation -N=CH- group. No signals attributed to amino group can be observed, indicating the formation of monomer 2-(*p*-chlorobenzalimino)terephthalic acid. The other peaks of the monomer are explained in Figure 1.

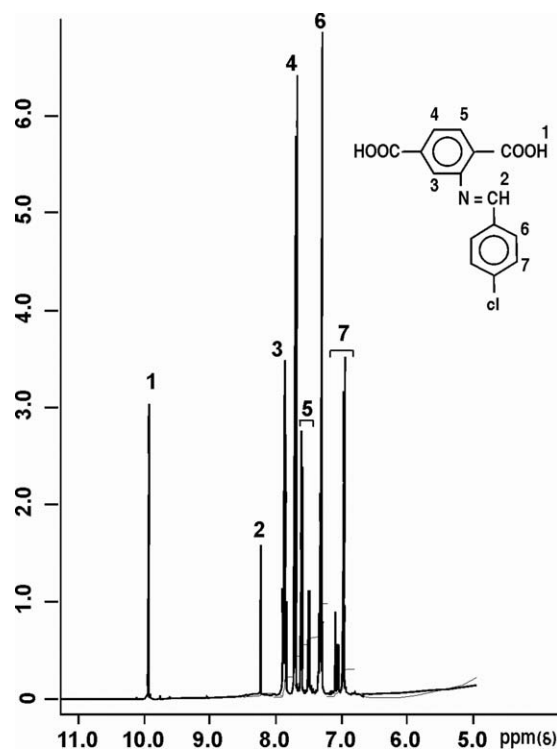


Figure 2 $^1\text{H-NMR}$ spectrum of 2-(*p*-chlorobenzalimino) terephthalic acid (2).

4, 4'-bis (thiourea) diphenyl methane

IR spectra of 4, 4'-diamino diphenyl methane (1b) and that of the monomer 4,4'-bis (thiourea) diphenyl methane (3b) are shown in Figure 3. The shifting of

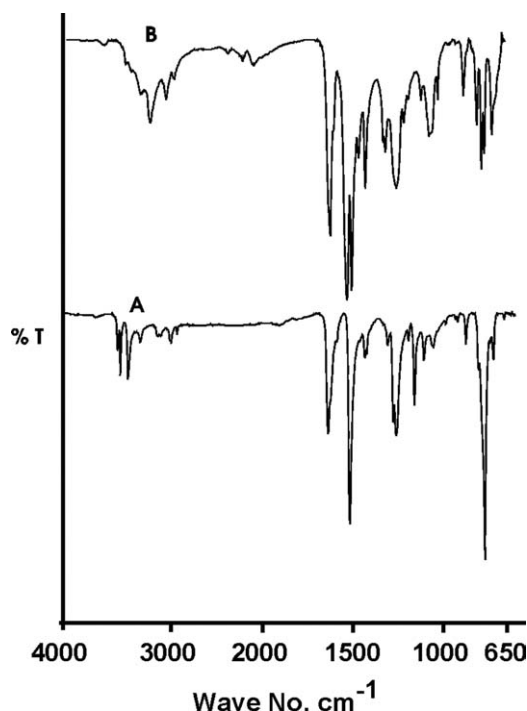


Figure 3 IR spectra of A: 4, 4'-diaminodiphenyl methane (1b) and B: monomer (3b).

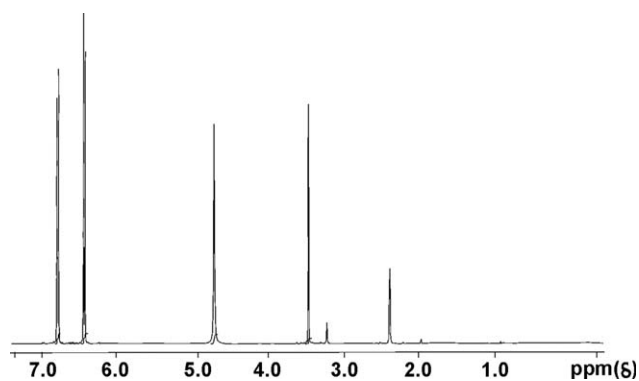


Figure 4 $^1\text{H-NMR}$ spectrum of 4,4'-diamino diphenyl methane (1b).

free $-\text{NH}_2$ stretching frequency of the diamine (two short bands at 3413 and 3334 cm^{-1}) and the appearance of $-\text{NH}$ stretching frequency of the thioamide at 3163 cm^{-1} in the monomer 4,4'-bis (thiourea) diphenyl methane along with the appearance of $-\text{C}=\text{S}$ stretching frequency of thioamide at 1065 cm^{-1} supports the formation of thioamide monomer. The $-\text{NH}_2$ stretching frequency of thioamide appears as a doublet at 3265 cm^{-1} . $^1\text{H-NMR}$ spectrum of 4,4'-diaminodiphenyl methane (1b) and 4,4'-bis(thiourea)diphenyl methane (3b) are shown in Figures 4 and 5, respectively. For better and clear evidence the $^1\text{H-NMR}$ spectra of both 4,4'-diaminodiphenyl methane and 4,4'-bis (thiourea)diphenyl methane were recorded in $\text{DMSO-}d_6$ solvent and are compared. Formation of the thioamide is confirmed by the appearance of the characteristic peak at $\delta = 9.57$. The assignment of peaks for 4,4'-diaminodiphenyl methane (Fig. 4) are: δ : 6.80(2H,d, ArCH), δ 6.78 (2H,d,ArCH), δ 6.46 (2H, d, ArCH), δ 6.44 (2H,d,ArCH), δ 4.76 (4H,s, NH_2), δ 3.5 (2H, $-\text{CH}_2$). The peaks absorbed at 2.5 and 3.3 are due to the solvent and water, respectively. The assignment of peaks of 4,4'-bis (thiourea)diphenyl methane (Fig. 5) are as follows: δ 9.57 (2H, $-\text{NH}_2$), δ 7.28 (2H,d,ArCH), δ 7.26 (2H,d,ArCH), δ 7.18 (2H,d,ArCH), δ 7.15 (2H,d,ArCH), δ 3.85 (4H, s, $-\text{NH}_2$) δ 3.80

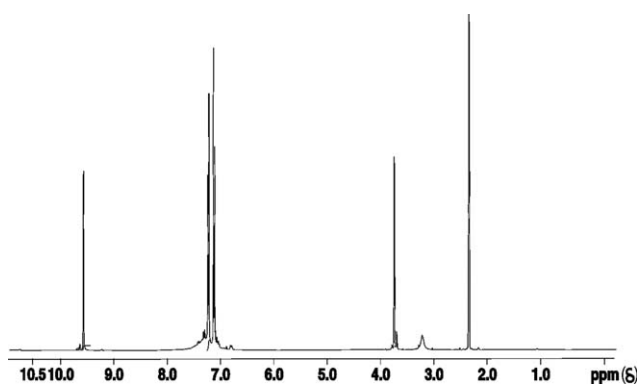


Figure 5 $^1\text{H-NMR}$ spectrum of (3b).

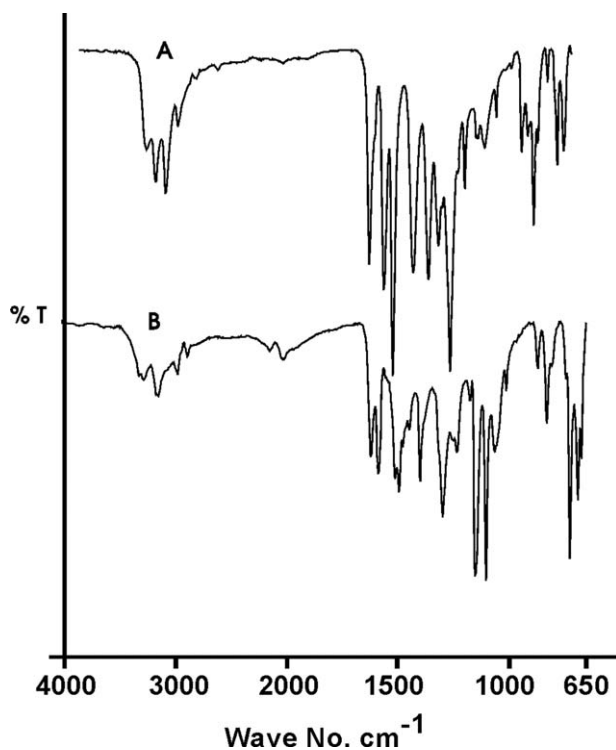


Figure 6 IR spectra of (3a) and (3c).

(2H,s, $-\text{CH}_2$) peaks at δ 2.48 and 3.3 are due to solvent and water, respectively. The shifting of ArCH proton to a higher δ value and the absorption of $-\text{NH}$ proton at δ value of 9.57 conforms the formation of thioamide monomer (3b) from its precursor 4,4'-diaminodiphenyl methane (1b).

IR spectra of the thioamide monomers 4,4'-bis (thiourea) diphenyl ether (3a) and 4,4'-bis (thiourea) diphenyl sulfone (3c) are shown in Figure 6. The thioamide $-\text{NH}$ stretching frequency of 3a appeared at 3175 and that of 3c appeared at 3164 cm^{-1} . The $-\text{C}=\text{S}-$ stretching frequency of 3a and 3c appeared at 1067 and 1066 cm^{-1} , respectively. The SO_2 stretching frequency of monomer (3c) is observed as a sharp peak at 1105 cm^{-1} and the $-\text{NH}_2$ group attached to the thioamide appeared as a doublet at $3268, 3262\text{ cm}^{-1}$.

Synthesis of polymers

Formation of poly (azomethine amide)'s and poly (azomethine thioamide)'s through direct poly

TABLE I
Properties of Polymers

Polymer	Yield (%)	Color	η_{inh} (g/dL)
1	76	Dark yellow	0.63
2	72	Yellow	0.54
3	69	Orange	0.51
4	79	Brownish yellow	0.71
5	65	Brownish yellow	0.66
6	61	Dark orange	0.59

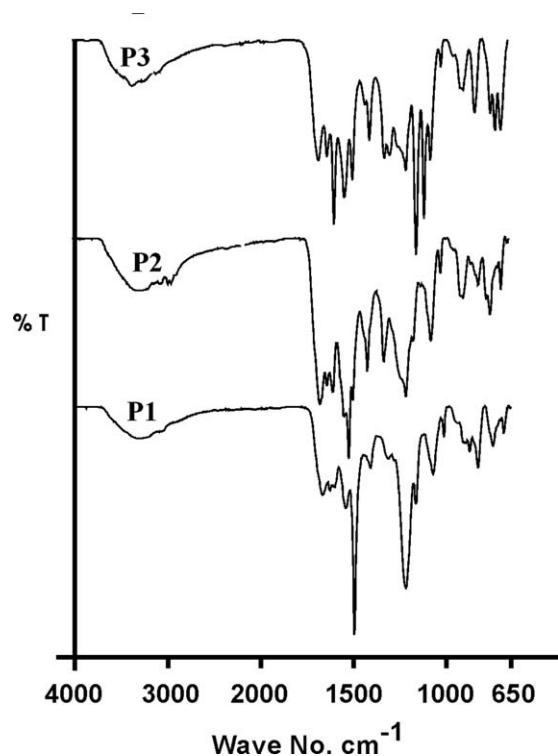


Figure 7 IR spectra of P1, P2, and P3.

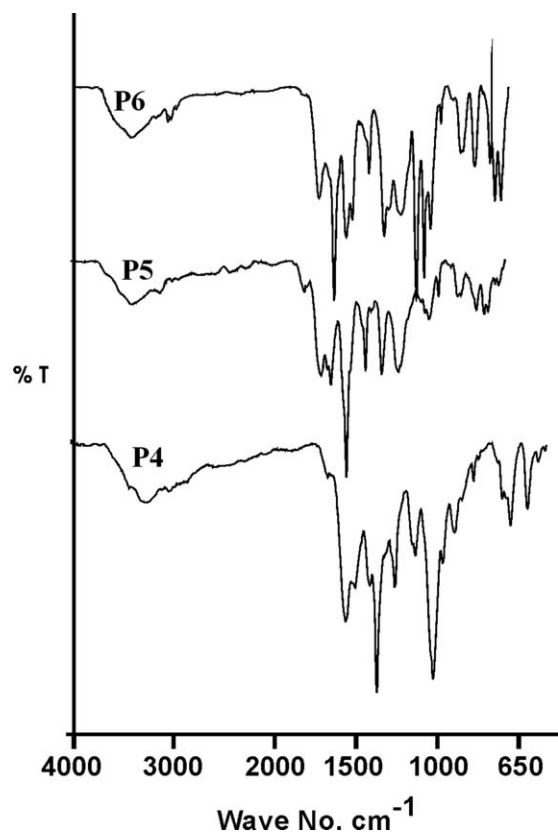


Figure 8 IR spectra of P4, P5, and P6.

TABLE II
IR Frequencies of Polymers

Polymer	Amide —NH (cm ⁻¹)	Amide (I) —C=O (cm ⁻¹)	Amide(II) —N—C=O (cm ⁻¹)	—C=S (cm ⁻¹)
1	3279	1647	1595	—
2	3336	1658	1594	—
3	3360	1672	1590	—
4	3314	1666	1595	1072
5	3303	1665	1597	1069
6	3365	1673	1590	1071

condensation using $P(\text{O}Ph)_3$, pyridine in DMF is outlined in Scheme 1 and 2, respectively. Yield, color, and inherent viscosities (η_{inh}) of the polymers are given in Table I.

The color of the polymers are due to the presence of azomethine chromophores and thioamide groups. With triphenylphosphate and pyridine as condensing agents, the polyamide formation occurs via an acyloxy *N*-phosphonium salt followed by aminolysis.¹⁹ The molecular weight of polyamides obtained through phosphorylation depends on various factors and are still matter of speculation.²⁰ However, the

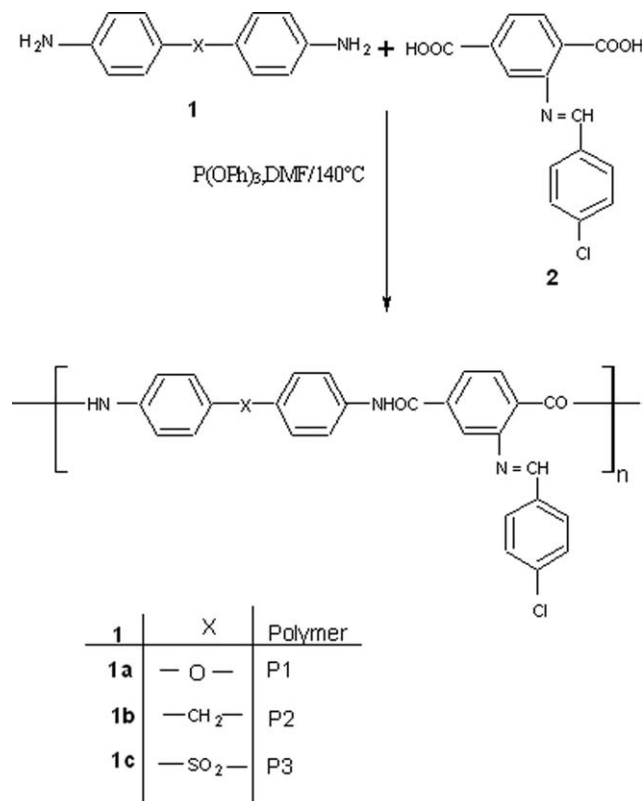


Figure 9 Scheme 1.

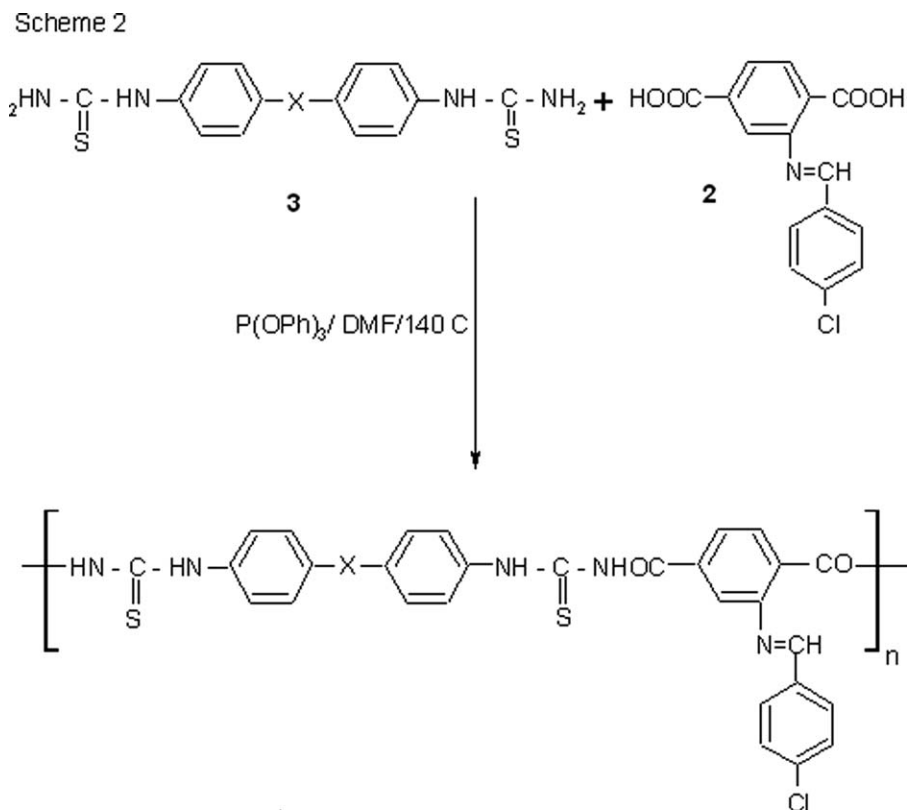


Figure 10 Scheme 2.

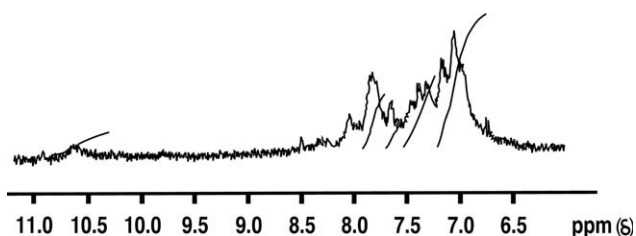
inherent viscosity values obtained in the present work are fairly good and are comparable to those values of polyamides obtained from modified isophthalamides,²¹ terephthalamides,¹³ and aromatic dicarboxylic acids containing phthalazinone moiety.²²

Aromatic polyamides generally have low solubility in most of the organic solvent due to the strong hydrogen bonding and rigid backbone chain structure. Introduction of benzothiazole and oxybenzoyl pendent groups into the polyamide backbone increases the solubility of the polymers.^{23,24} In this study, the polyamides synthesized show enhanced solubility in aprotic polar solvents like NMP, DMF, DMSO, and DMAc due to the presence of pendent chlorobenzylidene groups and thioamide groups.

IR spectra of poly (azomethine amide)s (P1-P3) and poly (azomethine thioamide)s (P4-P6) are shown

in the Figures 7 and 8, respectively. Important IR absorption of the polymers is shown in Table II.

The disappearance of —NH₂ stretching frequencies of the diamines and thioamide monomers and the appearance of the amide bands suggests the formation of amide linkages. Appearance of stretching frequencies of amide-I and amide-II bands in the

Figure 11 ¹H-NMR spectrum of polymer P4.

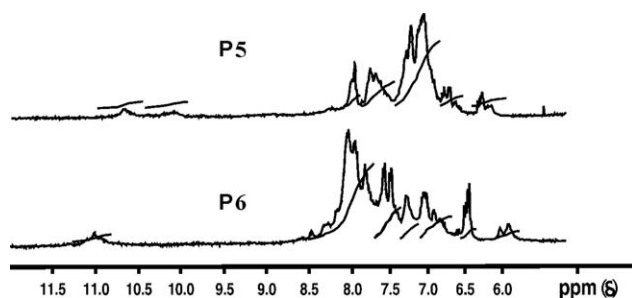


Figure 12 $^1\text{H-NMR}$ spectra of polymer P5 and P6.

polymers at the expense of the free $-\text{NH}_2$ frequencies of the respective precursors are in support of the polymers structures shown in the Figures 9 and 10. The $-\text{CH}=\text{N}-$ stretching frequency also falls in the same region of that of carbonyl stretching frequency of amide link, it appeared as a shoulder in some polymers and in some cases the azomethine absorption appeared around 1620 cm^{-1} . To further examine the formation of the polymers the $^1\text{H-NMR}$ of the polymer P4 is shown in Figure 11. $\delta = 10.7$ ppm is due to the amide proton and that of $-\text{CH}=\text{N}-$ proton appeared at $\delta = 8.0$ ppm. The complex aromatic region of the polyamide appeared as broad signals in the region $\delta = 7.9\text{--}6.9$ ppm. $^1\text{H-NMR}$ spectra of polymers P5 and P6 are shown in the Figure 12. The peaks at 10.6 and 10.8 ppm confirmed the formation of amide linkages. The $-\text{CH}=\text{N}-$ proton appeared at $\delta 8.2$ ppm. The aromatic protons appeared as broad peaks in the region $\delta = 8.0\text{--}6.3$ ppm and $7.9\text{--}6.1$ ppm for the polymers P4 and P4, respectively.

Thermal stability

Thermal stability of the polyamides and polythioamides based on 10, 20, and 50% weight loss temperature are summarized in Table III.

Polymers undergo three stages of degradation. TG curves of polythioamides P4–P6 are shown in Figure 13. First stage involves weight loss of 2.5–5.9% in the temperature range $30\text{--}130^\circ\text{C}$ and this is due to the evaporation of occluded solvent and moisture. Even though the polymers were dried before the thermal analysis, the initial weight loss in the temperature

TABLE III
Thermal Properties of Polymers

Polymer	$T_{d,10}$ ($^\circ\text{C}$)	$T_{d,20}$ ($^\circ\text{C}$)	$T_{d,50}$ ($^\circ\text{C}$)
P1	254	334	625
P2	239	334	658
P3	230	344	614
P4	238	318	638
P5	230	344	624
P6	212	342	646

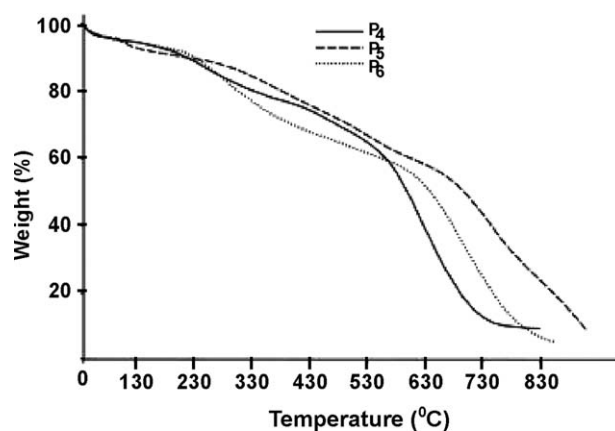


Figure 13 TG curves of polythioamides P4–P6.

range $30\text{--}130^\circ\text{C}$ indicates the moisture regaining capacity of the polyamides. Second stage of degradation occurs in the temperature range $100\text{--}430^\circ\text{C}$ with a weight loss of 17–20%. About 50–64% weight loss occurs in the third stage in the temperature range $400\text{--}840^\circ\text{C}$. When compared to the polyamides with benzylidene rings obtained from isophthalamides,²¹ polymers obtained in this study with terephthalamides shows better thermal stability. Thermal stability of the polymers based on 10% weight loss temperature having different linking groups between phenyl rings was found to be of the order $-\text{O}- > -\text{CH}_2- > -\text{SO}_2-$.

Extraction of heavy metal ions

The heavy-metal-ion uptake abilities of representative polyamide and polythioamide polymers were examined by shaking the polymers (20 mg of each) in 20 mL of a solution containing Pb (II) and Cr (III), respectively. The heavy metal ion loading capacities were assayed by analysis of residual metal concentrations. The effect of pH on loading capacities of the polymers is given in Figure 14. The pH values were varied between 2.0 and 10.0 ± 0.1 . In adsorption studies, pH is a critical parameter because it

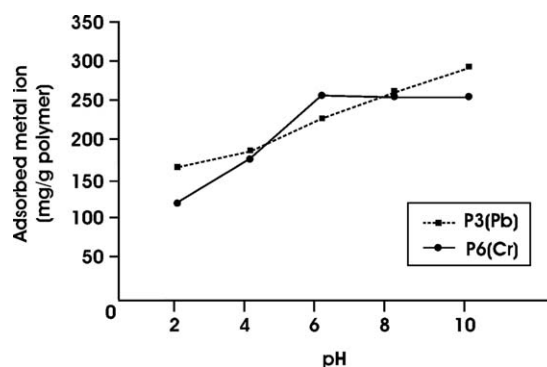


Figure 14 Effect of pH on loading capacities of the polymers.

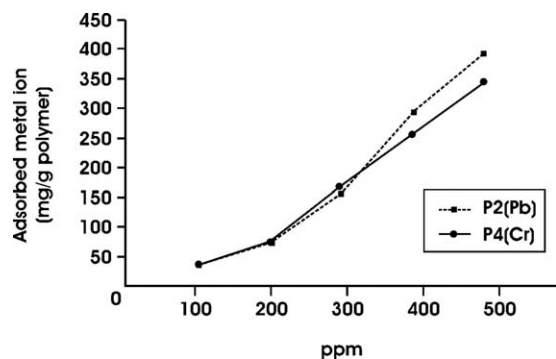


Figure 15 Cr^{3+} and Pb^{2+} adsorption isotherms of the polymers.

influences the chemistry of active binding sites on the adsorbent. With the initial metal ion concentration of 300 ppm solutions, the maximum adsorption capacity of Pb^{2+} and Cr^{3+} are found to be 274.6 and 255.2 mg/g, respectively. The loading capacity of the polyamide and polythioamide polymers in this study is either higher or comparable to the previously reported amidoximated and other polymers.^{16,25-27} With Pb^{2+} maximum adsorption was achieved at pH value of 10 and for Cr^{3+} adsorption maximum was found to occur at a $\text{pH} \geq 6$. Hence for the determination of effect of adsorption time and initial concentrations on loading capacities, the pH values were fixed at 6.0 and 10.0 for the metal ions Cr^{3+} and Pb^{2+} , respectively. Figure 15 shows the Cr^{3+} and Pb^{2+} adsorption isotherms of the polymers. With an increase in the initial Cr^{3+} and Pb^{2+} concentration, the adsorption capacity of the polymers increases significantly. The effect of contact time on the adsorption capacity of the polymers is shown in Figure 16. At 20 min contact time itself a rapid adsorption of the metal ions was noticed. More than 90% of Cr^{3+} and 80% of Pb^{2+} were adsorbed during the first 20 min and the adsorption equilibrium was established after 60 min. The effect of selectivity and recyclability under competitive conditions with the solutions of metal ions Pb (II),

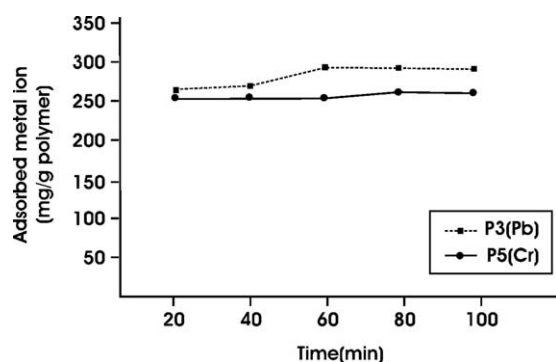


Figure 16 Effect of contact time on the adsorption capacity of the polymers.

TABLE IV
Heavy Metal Ion Adsorption Capacity of Poly (azomethine amide)s and Poly (azomethine thiourea amide)s After Repeated Adsorption–Elution Cycles

Cycle no.	Adsorption (mg/g)		Polymer: P3	
	Pb(II)	Cu(II)	Cr(II)	Cd(III)
1	108.7	102.5	91.8	60.1
2	106.4	102.4	71.1	58.2
3	104.9	100.9	65.7	53.8
4	99.7	98.1	64.7	49.6
	Adsorption (mg/g)		Polymer: P5	
	Pb(II)	Cu(II)	Cr(II)	Cd(III)
1	109.4	108.5	82.6	60.1
2	107.5	100.9	71.8	56.5
3	105.9	99.5	71.1	44.6
4	103.8	96.7	65.7	37.8

Initial concentration of metal ions = 300 ppm, $\text{pH} = 8$, and time = 60 min.

Cd (II), Cu (II), and Cr (III) by poly (azomethine amide)s and poly (azomethine thiourea amide)s are shown in Table IV. The results suggest that the metal ion uptake decreases in the order $\text{Pb (II)} > \text{Cu (II)} > \text{Cr (III)} > \text{Cd (II)}$ for both poly (azomethine amide) and poly (azomethine thiourea amide) type polymers. An aqueous solution of hydrochloric acid (2N) is capable of eluting the heavy metal ions from the new polyamides, and the polymers are acid resistant and thus can be used for multiple cycles of adsorption/elution experiments. Table IV suggests that the loading capacities of both poly (azomethine amide) and poly (azomethine thiourea amide) type polymers did not change after four cycles of adsorption–desorption even under competitive conditions

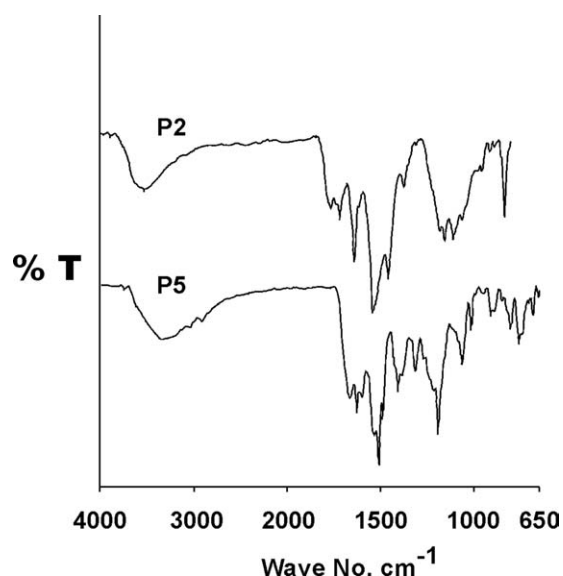


Figure 17 IR spectra of: Pb^{2+} ion adsorbed polymer P2, Cr^{3+} ion adsorbed polymer P5.

because of the functional groups are inherently bound in the polymer backbone.

To understand the possible interaction between metal ions and the reactive groups of the adsorbents used in this study, FTIR spectra of samples P2 and P5 after Pb^{2+} and Cr^{3+} metal ion adsorption were taken and is shown in Figure 17. When compared to the untreated polymers, amide $-NH$ stretching frequency of P2 and P5 (3336 and 3303 cm^{-1}) shifted to 3333 and 3366 cm^{-1} , respectively, in the metal adsorbed polymers. The amide I and II bands along with $-N=CH-$ absorptions have also undergone significant changes, thus indicating the possible sites of metal ion absorptions.

CONCLUSIONS

Polyamides and polythioamides with pendent chlorobenzylidene rings reported in this work are good adsorbents of Pb^{2+} and Cr^{3+} ions from aqueous solutions. The maximum adsorption capacity for Pb^{2+} and Cr^{3+} were found to be 274.6 and 255.2 mg/g , respectively. The amide carbonyl, amide, thioamide, and azomethine groups present in the polymer backbone are responsible for the higher efficiency and recyclability towards the adsorption of Pb (II), Cd (II), Cu (II), and Cr (III) metal ions from aqueous solutions.

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