Novel Aromatic and Aromatic–Aliphatic Poly(thiourea-amide)s for the Extraction of Toxic Heavy Metal Ions

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ABSTRACT: A series of novel aromatic and aromatic–aliphatic diamines [isophthaloyl bis(3-(3-aminophenyl)thiourea), terephthaloyl bis(3-(3-aminophenyl)thiourea), adipoyl bis(3-(3-aminophenyl)thiourea), sebacoyl bis(3-(3-aminophenyl)thiourea)] were synthesized starting from the dinitro compounds. Spectroscopic and elemental analyses were carried out for the structure elucidation of the monomers. Three series of poly(thiourea-amide)s (PTAMs) bearing C=S groups were prepared through the condensation of new diamines with the diacid chlorides such as isophthaloyl, terephthaloyl and adipoyl chloride. The ensuing PTAMs were characterized using FTIR, ^{1}H-NMR and ^{13}C-NMR techniques. Physical properties of the polymers such as solution miscibility, crystallinity, solution viscosity, molecular weight, and thermal properties were measured. Consequently, good organosolubility of these polymers was experiential in amide solvents as DMAc, DMF, DMSO and NMP. Moreover, PTAMs exhibited η_{inh} in the range of 0.92–1.56 dL/g and GPC measurements revealed M_w around 607×10^2-851×10^2. DSC served to envisage the glass transition temperatures (T_g) of poly(thiourea-amide)s located between 232 and 258°C and the initial decomposition temperatures (T_0) probed by thermogravimetry were in the range of 305–419°C. Structure-property relationship of these polymers was also studied. Eventually, solid–liquid extraction tests of the selected poly(thiourea-amide)s systems revealed excellent results because these polymers show nearly 100% elimination of lead and mercury cations from water media. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 373–385, 2012

Key words: polymer synthesis and characterization; FTIR; thermogravimetric analysis (TGA); high performance polymers; glass transition

INTRODUCTION

Polyamides are among the most important synthetic polymers. They present excellent physical and chemical properties in addition to thermal and oxidative stability that render them valuable high-performance materials for advanced technologies.[1] Most of the polyamides are infusible before decomposition since rigid backbone structure restricts their fabrication, processing as well as application. To overwhelm these shortcomings, considerable efforts have been directed en route for enhanced solubility or melt processability via molecular design.[2,3] Hence, novel soluble aromatic polyamides have been fabricated by carefully changing their molecular structure while upholding high-performance characteristics.[4,5] Useful approaches to fortify the processability without altering their outstanding properties are specific incorporation of flexible groups (—O—, —SO₂—, —S—, —C (CH₃)₂—), bulky side groups or heterocyclic moieties along the polymer backbone, so as to augment overall chain mobility.[6–10] Generally, it is endorsed that flexible linkages lessen the internal rotation energy of polymer chains leading to lower glass-transition temperature (T_g). Nonetheless, introduction of bulky side groups or noncoplanar moieties supplements the solubility without sacrificing thermal stability of polyamides. Since the presence of massive groups disarrays the intermolecular packing of polymer chains. Eventually, depending on specific properties of substituted groups and characteristic properties of polymeric molecules, reactive functionalized polymers have recently secured much

attention for broad span of relevance in various technological fields.[11–13]

This work described the synthesis and characterization of twelve novel soluble aromatic and semiaromatic poly(thiourea-amide)s (PTAMs) bearing C=S moieties. In this study, deliberate incorporation of phenylthiourea groups into the polymer backbones enhanced the solubility and processability of polyamides without any significant reduction in thermal stability. In view of the fact that, thiocarbonyl is capable of developing feeble hydrogen-bonding interactions (C=S·······....H) as compared with amide carbonyl (C=O·····H). This prompted us to synthesize new series of polyamides bearing both carbonyl and thiocarbonyl moieties, with the object of obtaining new multifunctional polymers. It was carefully investigated that thiourea moieties undermined the packing efficiency of polyamides by forming flexible intermolecular hydrogen-bonding networks.[14] Although, inclusion of thiourea group as flexibilising agent into polyamide backbone is rather an unexplored area. Besides the introduction of thiourea groups in the monomer structures, two more approaches have been employed in this work. First, the high structural regularity and rigidity of poly(thiourea-amide)s backbone was disrupted by the introduction of m-oriented phenyl rings to decrease the interchain interactions and improve the solvent miscibility. Since the processability of polyamides is often complicated because of their high crystallinity, structural regularity, and rigidity attributable to the presence of p-phenylene structure in the backbones. Hence, one of the aspects of improvement in poly(thiourea-amide)s processability is the introduction of m-phenylene structure into the monomers that is successfully applied here. Another approach to improve the solubility of polymers was the introduction of flexible alkyl spacers, $(CH_2)_4$ or $(CH_2)_8$, into the backbone. A decrease in thermal properties and T_g with the increase in carbon chain length was also observed in this case.

Presently synthesis of new thiourea-based diamines, isophthaloyl bis(3-(3-aminophenyl)thiourea) (BAPTa), terephthaloyl bis(3-(3-aminophenyl)thiourea) (BAPTb), adipoyl bis(3-(3-aminophenyl)thiourea) (BAPTc), and sebacoyl bis(3-(3-aminophenyl)thiourea) (BAPTd), is explained. The condensation of novel BAPTa-d with several diacid chlorides yielded PTAMs via low-temperature solution method. Consequently, PTAMs were characterized for investigating the effect of thiourea group on their solubility, crystallinity, thermal behavior, solution viscosity as well as molecular weights. In brief, it was found that introduction of thiourea moieties along the main chain rendered these high molecular weight poly(thiourea-amide)s organically soluble and thermally stable. Furthermore, the introduction of thiourea moieties along the polymers backbone broadens the scope of their technological

applications. Thioureas serve as a useful scaffold in material chemistry pertaining to electroluminescent organic dyes.[15,16] Besides, thiourea along with its related molecules is significant as structural components in agricultural and pharmaceutical chemistry.[17,18] One of the most essential applications of thiourea-based polymers is that they can act as coordinating resins for selective binding of heavy metal cations such as Pb^{2+} and Hg^{2+} from aqueous solution. Mercury and lead along with their salts, are extensively exploited in pharmaceutical, petro-chemical and electrical industries, are well-known poisons. In the past decades, the recognition of Hg and Pb toxicity and the cycling of their compounds in nature have resulted in a successive decrease of the maximum disposable level (ppb). In this regard, polymers bearing sulfur functionality especially resins containing thiol[19] and thiourea[20] groups exhibited highly selective adsorption of mercury cations from acidic or neutral solution. Consequently, new thiourea based polymers found to have high affinity for soft acids such as Pb^{2+} and Hg^{2+} from aqueous solution. Hence, poly(thiourea-amide)s were found to be efficient materials to eliminate environmentally toxic heavy metal cations (Pb^{2+} and Hg^{2+}).

EXPERIMENTAL

Materials

Isophthaloyl chloride (IPC) (98%), terephthaloyl chloride (TPC) (99%), potassium thiocyanate (98%), dimethylformamide (DMF) (99%) tetrahydrofuran (THF) (99.5%), hydrazine hydrate (80%), sodium chloride (99.8%) formic acid (85%) and celite were supplied by Fluka. N-methylpyrrolidone (NMP) (99%), dimethyl sulfoxide (DMSO) (99%), chloroform (99%) and benzene (99%) were procured from Merck. Adipoyl chloride (AC) (98%), sebacoyl chloride (SC) (92%) and N,N-dimethylacetamide (DMAc) (99%) provided by Aldrich were used as received. Zinc dust (fine powder) was purchased from BDH.

Measurements

FTIR Spectrometer, Model No. FTSW 300 MX, manufactured by BIO-RAD (4 cm^{-1} resolution) was used for recording IR spectra of the monomers and polymers at room temperature. NMR spectra were recorded at room temperature using BRUKER Spectrometer operating at 300.13 MHz for ^{1}H-NMR and at 75.47 MHz for ^{13}C-NMR. Solvent used for analysis was deutrated dimethyl sulfoxide (DMSO-d_6). Perkin–Elmer 2400 CHN elemental analyzer was utilized for elemental analysis. Inherent viscosity (η_{inh}) was measured in DMSO at 30°C with an Ubbelohde viscometer on 0.5 g/dL polymer solutions. Gel

permeation chromatography (GPC) was carried out using DMF as an eluent. The weight-average molecular weight (M_w) was calculated through GPC with a refractive index (RI) detector. Thermal stability of the poly(thiourea-amide)s was determined by MET-TLER TOLEDO TGA/SDTA 851^e thermo gravimetric analyzer using 1–5 mg of the sample in Al_2O_3 crucible at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed by MET-TLER TOLEDO DSC 822^e differential scanning calorimeter taking 5–10 mg of the samples encapsulated in aluminum pans and heated at a rate of 10°C/min. X-ray diffractometer (3040/60 X'pert PRO) with Ni-filtered Cu Kα radiation (40 kV, 30 mA) was used to obtain X-ray diffractograms of polymers at room temperature. The solid−liquid extraction tests of nitrates or chloride salts of Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} were carried out with PTAM 1a and 2a. About 10 mg of the polymer sample was stirred with 1 mL of an aqueous solution of the metal salt for five days at 25°C. The molar ratio of each cation to thiourea subunits (two per polymer structural units) was kept at 1 : 1. After filtration, the concentration of each cation in the liquid phase was determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500). Consecutive dilutions of sample aliquots with ultra-pure water/nitric acid (5% v/v) were performed to reach concentrations in the range of the calibration curve (0–40 ppb), thus direct information regarding the extraction percentages of metal ions by polyamides was acquired.

Monomer Synthesis

Preparation of diisothiocyanates (DITCs)

A saturated solution of potassium thiocyanate (40 g) in boiling ethanol (300 mL) was poured into 1.5 L ethyl ether, forming a fine white powder. The solid was collected by filtration and washed with 300 mL ethyl ether. Finely isolated potassium isothiocyanate was dried in vacuum at 110°C for 10 h. In a 250-mL two-necked round bottom flask, 0.25 mol diacid chloride (IPC, TPC, AC, or SC) and 48 g potassium isothiocyanate were refluxed in 100 mL dry benzene at 110–120°C for 6 h. After the completion of reaction, diisothiocyanate was removed by filtration and dried in vacuum oven at 80°C.[21]

Synthesis of terephthaloyl bis (3-(3-nitrophenyl) thiourea (BNPTb)

Terephthaloyl diisothiocyanate (100 mmol) was charged into a three-necked round bottom flask (300 mL) equipped with gas inlet tube, magnetic stirrer and thermometer, followed by addition of 100 mL dichloromethane with vigorous stirring. The reaction
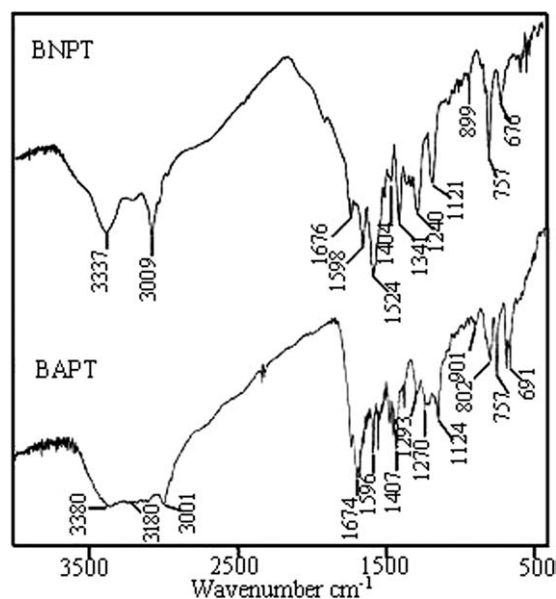

Figure 1 FTIR spectra of monomer.

flask was cooled to 0°C; afterward 3-nitroaniline (10 mmol) was added with continuous stirring of 1 h under N_2 atmosphere.[22] Subsequently, precipitates obtained were washed with 1% HCl, distilled water, and brine. Ultimately, solvent was removed by filtration and dried under vacuum at 70°C yielding the solid product. Similarly, other dinitro compounds were prepared by the above-mentioned procedure using the appropriate diisothiocyanate.

Terephthaloyl bis (3-(3-nitrophenyl) thiourea (BNPTb)

Yellow solid; Yield 95%; Elemental analysis of $C_{22}H_{16}N_6O_6S_2$: Calculated = % C 50.38, % H 3.07, % N 16.02, Found = % C 50.37, % H 3.06, % N 16.01; FTIR (KBr)(Fig. 1): 1524 and 1341 cm^{-1} (asymmetric and symmetric nitro N=O stretch), 3337, 1598 cm^{-1} (sec. amine N−H stretch and bend), 3009 cm^{-1} (aromatic C−H stretch), 1676 cm^{-1} (amide C=O stretch), 1404 cm^{-1} (C−N stretch), 1121 cm^{-1} (C=S stretch). ^{1}H-NMR (300.13 MHz, DMSO-d$_6$, δ ppm) presented in Figure 2: 7.35 (s, 2H, H$_a$), 7.53 (d, 2H, H$_b$), 7.24 (t, 4H, H$_c$), 6.85 (d, 2H, H$_d$), 9.21 (s, 2H, H$_e$), 10.43 (s, 2H, amide H$_f$), 8.13 (4H, p-aromatic H$_g$). ^{13}C-NMR (75.47 MHz, DMSO-d$_6$, δ ppm) specified in Figure 3: m-aromatic carbons 148.7 (C$_1$), 117.0 (C$_2$), 130.0 (C$_3$), 133.6 (C$_4$), 138.1 (C$_5$), 120.5 (C$_6$), thiocarbonyl C = S 180.0 (C$_7$), amide carbonyl C=O 169.2 (C$_8$), p-aromatic carbons 137.6 (C$_9$), 127.6 (C$_{10}$).

Isophthaloyl bis(3-(3-nitroyphenyl) thiourea) (BNPTa)

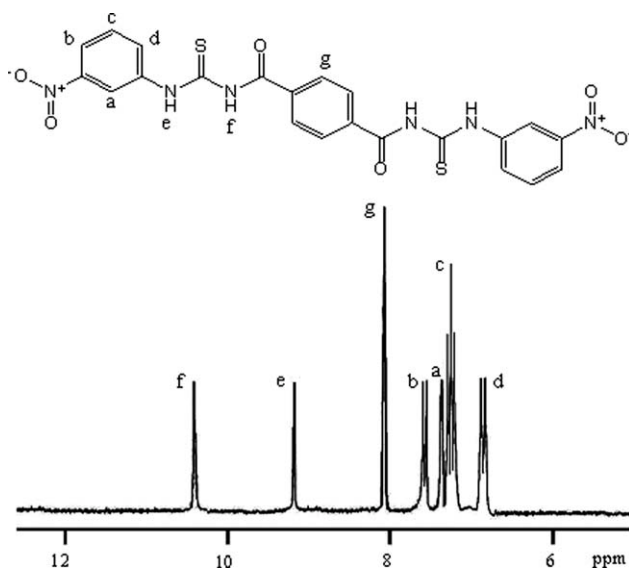Yellow solid; Yield 95%; Elemental analysis of $C_{22}H_{16}N_6O_6S_2$: Calculated = % C 50.38, % H 3.07, %

Figure 2 ^{1}H-NMR spectrum of BNPTb.

N 16.02, Found = % C 50.37, % H 3.07, % N 16.01; FTIR (KBr, cm^{-1}): 1521,1342 (N=O), 3335, 1598 (N—H), 1678 (amide C=O), 1404 (C—N), 1129 (C=S) cm^{-1}; ^{1}H-NMR (DMSO-d$_6$,δ ppm): 7.55 (d, 2H, ArH), 7.27 (t, 2H, ArH), 6.85 (d, 2H, ArH), 8.64 (s, 1H, ArH), 8.20 (d, 2H, ArH), 7.62 (s, 1H, ArH), 9.20 (s, 2H, ArNH), 10.43 (s, 2H, amide NH); ^{13}C-NMR (DMSO-d$_6$, δ ppm): 117.06, 120.31, 129.9, 132.5, 138.03, 148.71, 125.12, 134.31, 130.99, 129.11, 180.90 (C=S), 168.91 (amide C=O).

Adipoyl bis(3-(3-nitrophenyl) thiourea) (BNPTc)

Orange solid; Yield 96%; Elemental analysis of C$_{20}$H$_{20}$N$_6$O$_6$S$_2$: Calculated = % C 47.61, % H 4.00, % N 16.66, Found = % C 47.60, % H 3.99, % N 16.64; FTIR (KBr, cm^{-1}): 1524,1341 (N=O), 3341, 1599 (N—H), 1676 (amide C=O), 1407 (C—N), 1121 (C=S) cm^{-1}; ^{1}H-NMR (DMSO-d$_6$, δ ppm):7.54 (d, 2H, ArH), 7.25 (t, 2H, ArH), 6.83 (d, 2H, ArH), 9.19 (s, 2H, ArNH), 10.41 (s, 2H, amide NH), 2.17 (t, CH$_2$), 1.55 (m, CH$_2$); ^{13}C-NMR (DMSO-d$_6$,δ ppm): 117.01, 120.23, 130.11, 132.43, 138.12, 148.55, 180.88 (C=S), 168.86 (amide C=O), 24.57, 36.45.

Sebacoyl bis(3-(3-nitrophenyl) thiourea) (BNPTd)

Orange solid; Yield 95%; Elemental analysis of C$_{24}$H$_{28}$N$_6$O$_6$S$_2$: Calculated = %C 51.42, % H 5.03, % N 14.99, Found = %C 51.41, % H 5.01, % N 14.98; FTIR (KBr, cm^{-1}): 1520,1343 (N=O), 3343, 1599 (N-H), 1676 (amide C=O), 1407 (C-N), 1121 (C=S) cm^{-1}; ^{1}H-NMR (DMSO-d$_6$,δ ppm): 7.53 (d, 2H, ArH), 7.20 (t, 2H, ArH), 6.82 (d, 2H, ArH), 9.18 (s, 2H, ArNH), 10.39 (s, 2H, amide NH), 2.16 (t, CH$_2$),

1.55 (m, CH$_2$), 1.29 (m, CH$_2$); ^{13}C-NMR (DMSO-d$_6$,δ ppm): 116.91, 120.21, 130.02, 132.40, 138.10, 148.53, 180.84 (C=S), 168.85 (amide C=O), 26.34, 28.10, 29.17, 36.43.

Synthesis of terephthaloyl bis (3-(3-aminophenyl) thiourea) (BAPTb)

Hydrazinium monoformate was initially prepared in a 500-mL round bottom flask placed in an ice water bath using equal moles of hydrazine hydrate and 85% formic acid through neutralization with constant stirring under N$_2$ atmosphere. Thus obtained hydrazinium monoformate solution was used for reduction. A suspension of BNPTb (5 mmol) and zinc dust (20 mmol) in THF (50 mL) was agitated with hydrazinium monoformate (4 mL) at room temperature. Here the reaction was exothermic and effervescent. After the completion of reaction, mixture was filtered through celite. Consequently, organic layer was evaporated and residue was dissolved in chloroform. To remove excess of hydrazinium monoformate, solution was washed with saturated sodium chloride. Later on, drying and evaporation of organic layer yielded BAPTb. Similarly, other diamines were obtained using the same procedure.

Terephthaloyl bis (3-(3-aminophenyl) thiourea) (BAPTb)

Orange solid; Yield 95%; Elemental analysis of C$_{22}$H$_{20}$N$_6$O$_2$S$_2$: Calculated = % C 56.88, % H 4.34, % N 18.09; Found = % C 56.86, % H 4.33, % N 18.01; FTIR (KBr) (Fig. 1): 3380, 3180 cm^{-1} (N—H stretch), 1596 cm^{-1} (N—H bend), 3001 cm^{-1} (aromatic C—H stretch), 1674 cm^{-1} (amide C=O stretch), 1407 cm^{-1} (C—N stretch), 1124 cm^{-1} (C=S stretch). ^{1}H-NMR
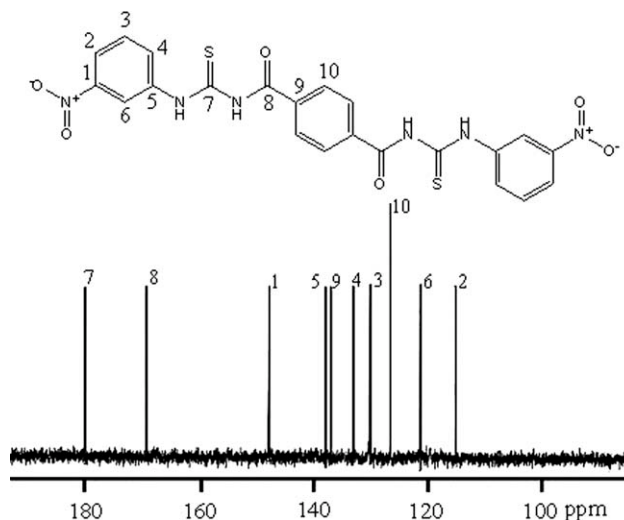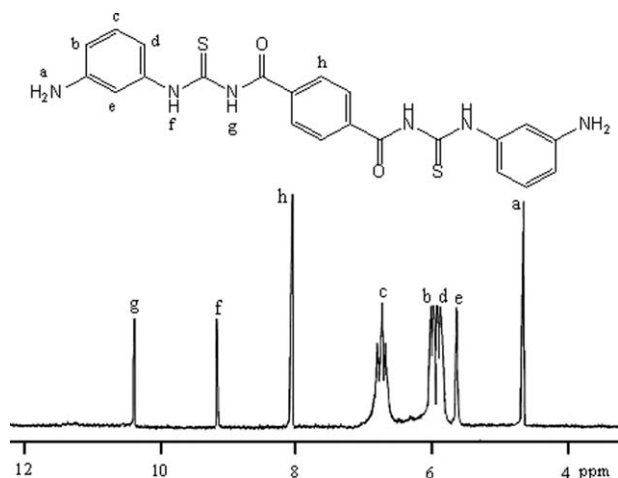

Figure 3 ^{13}C-NMR spectrum of BNPTb.

Figure 4 ^{1}H-NMR spectrum of BAPTb.

(300.13 MHz, DMSO-d$_6$, δ ppm) in Figure 4: 4.64 (s, 4H, H$_a$, primary amine), 5.82 (d, 4H, H$_b$), 6.78 (t, 2H, H$_c$), 5.89 (d, 4H, H$_d$), 5.64 (s, 2H, H$_e$), 9.17 (s, 2H, H$_f$), 10.39 (s, 2H, amide H$_g$), 8.12 (4H, p-aromatic H$_h$). ^{13}C-NMR (75.47 MHz, DMSO-d$_6$, δ ppm) (Fig. 5): m-aromatic carbons at 148.9 (C$_1$), 112.4 (C$_2$), 130.0 (C$_3$), 116.5 (C$_4$), 138.6 (C$_5$), 113.9 (C$_6$), thiocarbonyl C=S 181.3 (C$_7$), amide carbonyl C=O 169.1 (C$_8$), p-aromatic carbons 137.6 (C$_9$), 127.3 (C$_{10}$).

Isophthaloyl bis(3-(3-aminophenyl) thiourea) (BAPTa)

Orange solid; Yield 95%; Elemental analysis of C$_{22}$H$_{20}$N$_6$O$_2$S$_2$: Calculated = % C 56.88, % H 4.34, % N 18.09; Found = % C 56.87, % H 4.32, % N 18.02; FTIR (KBr, cm^{-1}): 3244, 1596 (N-H), 3000 (C-H), 1674 (amide C=O), 1406 (C-N), 1124 (C=S) cm^{-1}; ^{1}H-NMR (DMSO-d$_6$, δ ppm): 5.82 (d, 2H, ArH), 6.78 (t, 2H, ArH), 5.83 (d, 2H, ArH), 5.67 (s, 2H, ArH), 8.56 (s, 1H, ArH), 8.18 (d, 2H, ArH), 7.56 (s, 1H, ArH), 9.18 (s, 2H, ArNH), 10.12 (s, 2H, amide NH); ^{13}C-NMR (DMSO-d$_6$, δ ppm): 112.36, 112.90, 116.51, 129.9, 137.9, 148.62, 125.10, 134.22, 130.94, 129.11, 180.81 (C=S), 168.69 (amide C=O).

Adipoyl bis(3-(3-aminophenyl) thiourea) (BAPTc)

Brown solid; Yield 94%; Elemental analysis of C$_{20}$H$_{24}$N$_6$O$_2$S$_2$: Calculated = % C 54.03, % H 5.44, % N 18.90; Found = % C 54.01, % H 5.42, % N 18.88; FTIR (KBr, cm^{-1}): 3324, 1597 (N-H), 3006, 2911 (C-H), 1676 (amide C=O), 1406 (C-N), 1124 (C=S); ^{1}H-NMR (DMSO-d$_6$, δ ppm): 5.80 (d, 2H, ArH), 6.73 (t, 2H, ArH), 5.82 (d, 2H, ArH), 5.65 (s, 2H, ArH), 9.10 (s, 2H, ArNH), 10.03 (s, 2H, amide NH), 1.52 (m, CH$_2$), 2.15 (t, CH$_2$); ^{13}C-NMR (DMSO-

d$_6$, δ ppm): 112.33, 112.88, 116.43, 129.67, 137.78, 148.60, 180.72 (C=S), 168.64 (amide C=O), 25.01, 35.43.

Sebacoyl bis(3-(3-aminophenyl) thiourea) (BAPTd)

Brown solid; Yield 95%; Elemental analysis of C$_{24}$H$_{32}$N$_6$O$_2$S$_2$: Calculated = % C 57.57, % H 6.44, % N 16.79; Found = % C 57.55, % H 6.42, % N 16.77; FTIR (KBr, cm^{-1}): 3259, 1598 (N-H), 3001, 2895 (C-H), 1677 (amide C=O), 1407 (C-N), 1124 (C=S). ^{1}H-NMR (DMSO-d$_6$, δ ppm): 5.76 (d, 2H, ArH), 6.67 (t, 2H, ArH), 5.79 (d, 2H, ArH), 5.54 (s, 2H, ArH), 9.09 (s, 2H, ArNH), 10.01 (s, 2H, amide NH), 2.11 (t, CH$_2$), 1.52 (m, CH$_2$), 1.24 (m, CH$_2$); ^{13}C-NMR (DMSO-d$_6$, δ ppm): 112.31, 112.84, 116.39, 129.53, 137.73, 148.54, 180.51 (C=S), 168.29 (amide C=O), 25.33, 28.53, 29.21, 36.21.

Synthesis of PTAMS

Poly(thiourea-amide)s were prepared from the condensation of monomers at low temperature. For this purpose, a 250-mL three-necked round bottom flask was charged with 10 mmol BAPTb, followed by the addition of 50-mL DMAc along with constant stirring. The reaction flask was then placed in an ice-salt bath and cooled at 0°C for 15 min. TPC (10 mmol) was added into the flask with continuous stirring. Soon after, the mixture was agitated at room temperature for 8 h under N$_2$ atmosphere. As the condensation proceeded, the solution gradually became viscous. The polymer solution was poured into 300-mL methanol with constant stirring to precipitate out poly(thiourea-amide). PTAM 2b was isolated by filtration and
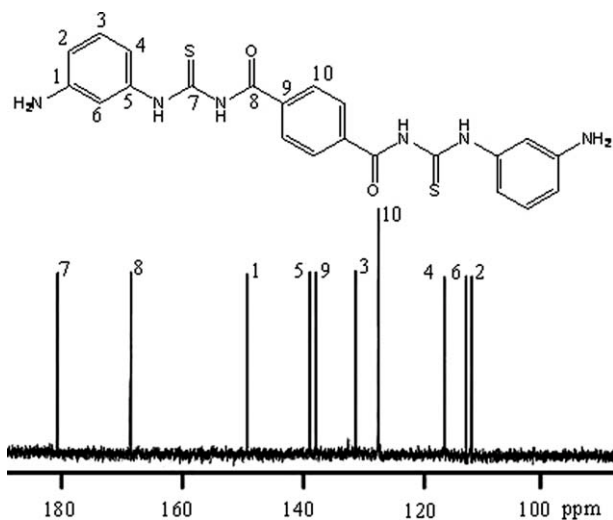

Figure 5 ^{13}C-NMR spectrum of BAPTb.

TABLE I
FTIR Data of Different PTAMs

Polymer	N—H stretch (cm^{-1})	Ar C—H Stretch (cm^{-1})	C=O amide stretch (cm^{-1})	N—H bend (cm^{-1})	C—N (cm^{-1})	C=S (cm^{-1})
PTAM 1a	3385	3015	1676	1598	1403	1126
PTAM 1b	3330	3010	1676	1597	1409	1128
PTAM 1c	3328	3001	1675	1593	1406	1129
PTAM 1d	3336	3099	1676	1594	1409	1124
PTAM 2a	3349	3102	1674	1596	1404	1124
PTAM 2b	3341	3100	1673	1596	1403	1123
PTAM 2c	3363	3045	1671	1595	1405	1124
PTAM 2d	3338	3037	1672	1597	1407	1123
PTAM 3a	3353	3010	1674	1596	1409	1124
PTAM 3b	3361	3025	1668	1593	1407	1123
PTAM 3c	3381	3024	1672	1593	1405	1125
PTAM 3d	3370	3021	1670	1598	1409	1126

washed with methanol. The polymer was redissolved in minimum amount of DMAc and again precipitated out in methanol. The polymer obtained was dried under vacuum at 80°C for 24 h. FTIR (KBr) data of PTAM 1a-d, PTAM 2a-d, and PTAM 3a-d are given in Table I: 3328–3385 cm^{-1} (N—H stretch), 1593–1598 cm^{-1} (N—H bend), 3001–3102 cm^{-1} (aromatic C—H stretch), 1668–1676 cm^{-1} (amide C—O stretch), 1403–1409 cm^{-1} (C—N stretch), 1123–1129 cm^{-1} (C=S stretch). ^{1}H-NMR (300.13 MHz, DMSO-d$_6$, δ ppm) of PTAM 1a-d and PTAM 2a-d: revealed multiplets between 5.63–8.36 ppm corresponding to aromatic protons of all benzene rings in polymer backbone. These poly(-thiourea-amide)s also indicated chemical shifts between 10.30–10.52 ppm which are assignable to amide N—H. They displayed signals for N—H attached to aromatic rings in the range of 9.20–9.45 ppm. Besides PTAM 1c and d and PTAM 2c and d showed chemical shifts at about 1.50–2.62 ppm due to aliphatic protons. Likewise, ^{1}H-NMR spectra of PTAM 3a-d exhibited multiplets nearly 5.66–8.13 ppm due to aromatic protons. The peaks in the region of 10.29–10.54 ppm for amide N—H and 9.15–9.48 ppm for N—H attached to aromatic rings were also observed. In addition, PTAM 3a-d showed aliphatic proton signals around 1.40–2.65 ppm.
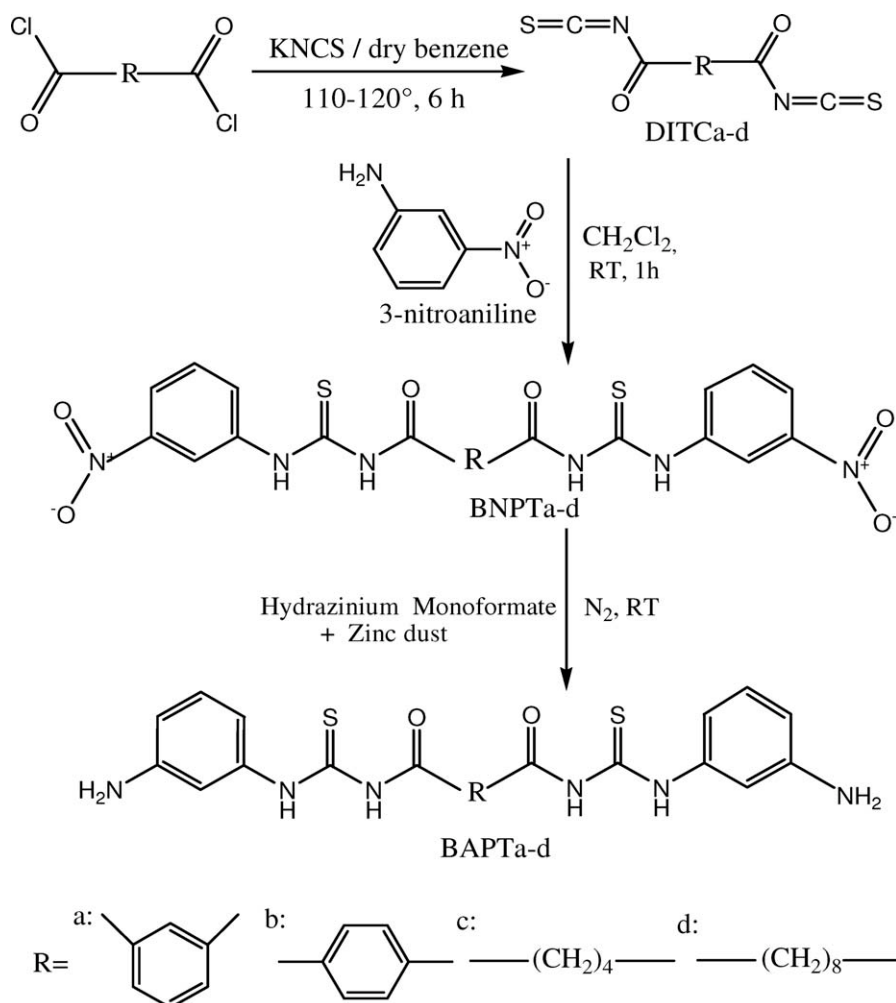
**Scheme 1** Scheme for the synthesis of monomers.
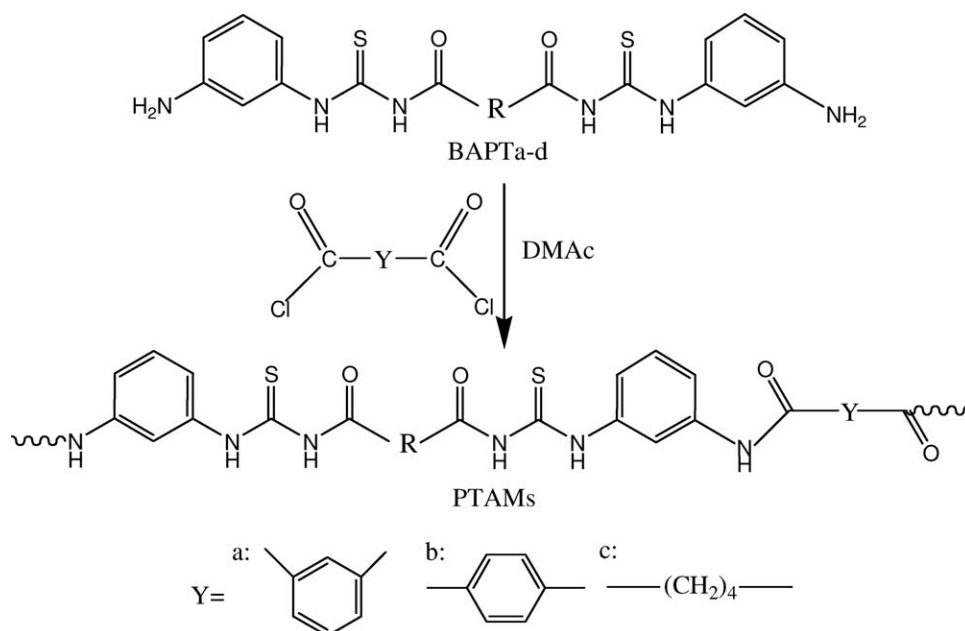
Scheme 2 Scheme for the synthesis of PTAMs.

RESULTS AND DISCUSSION

Monomer and polymer synthesis

Convenient and inexpensive synthetic routes were optimized to prepare new monomers containing thiourea groups, in high yield. Four diamines containing thiourea group (BAPTa-d) were synthesized via three-step procedure outlined in Scheme 1. First step encompassed the condensation of diacid chlorides (IPC, TPC, AC, SC) with potassium thiocyanate producing diisothiocyanates (DITCa-d). In second step, intermediate compounds, DITCa-d, were reacted with 3-nitroanniline to make dinitro compounds (BNPTa-d). During third stage, BNPTa-d were catalytically hydrogenated to corresponding diamines. Since, metal mediated reductions of nitro compounds found to have wide scope in organic synthesis owing to their simple work-up and selectivity.[23] As a consequence, nitro group can be selectively and rapidly reduced to corresponding amines employing hydrazinium monoformate together with commercial zinc dust.[24] Structures of intermediates and monomers were identified through elemental analyses, FTIR, and NMR spectroscopy. Novel diamines, BAPTa-d, were exploited as condensation monomers in combination with three diacid chlorides to yield PTAMs (Scheme 2). Solution condensation[25] of BAPTs with diacid chlorides proved to be an easy method for the fabrication of PTAMs in fairly high yield, good η_{inh}, and high molecular weights. Structure explication of polyamides was carried out by FTIR, ¹H-NMR and ¹³C-NMR techniques. Moreover, organosolubility, crystallinity, thermal stability, T_g,

η_{inh} and molecular weights of PTAMs were scrutinized. This investigation revealed that introduction of C=S groups along the backbone to enhance solubility and processability of poly(thiourea-amide)s, is one of the successful approaches. Hence, multiple hydrogen bonding interactions (C=S·····H and C=O·····H) were experiential in poly(thiourea-amide)s as depicted in Scheme 3. Additionally, thiourea is an efficient host entity for metal cations, thus these poly(thiourea-amide)s can be employed as solid extracting phases for the elimination/removal of different metal/counter ion, particularly environmentally toxic cations, from water bodies.
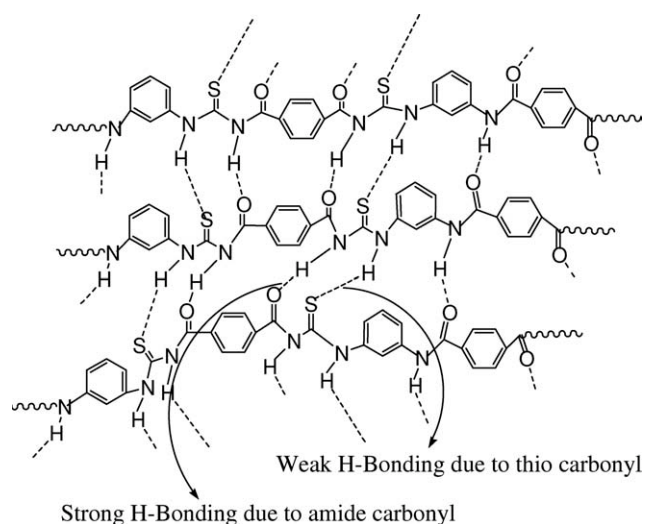
Scheme 3 Pattern of hydrogen-bonding in poly (thiourea-amide)s.

Polymer	Solvent					
	NMP	DMAc	DMF	DMSO	THF	m-cresol
PTAM 1a	++	++	++	++	−	+−
PTAM 1b	++	++	++	++	−	+−
PTAM 1c	++	++	++	++	−	+−
PTAM 1d	++	++	++	++	−	+−
PTAM 2a	++	++	++	++	−	+−
PTAM 2b	++	++	++	++	−	+−
PTAM 2c	++	++	++	++	−	+−
PTAM 2d	++	++	++	++	−	+−
PTAM 3a	++	++	++	++	+−	+−
PTAM 3b	++	++	++	++	+−	+−
PTAM 3c	++	++	++	++	+−	+−
PTAM 3d	++	++	++	++	+−	+−

Organosolubility

The qualitative solubility tests of PTAMs in various solvents (DMF, DMAc, NMP, DMSO, THF, and m-cresol) are summarized in Table II. It was interesting to note that PTAM 2a-d despite bearing symmetrical and rigid p-phenylene rings had excellent solubility in these solvents. Excellent solubility of PTAMs was apparently due in part to the presence of packing disruptive C=S units in polymer backbone, which resulted in enhanced chain-packing distances and diminished intermolecular interactions. Nevertheless, PTAM 1a-d having m-phenylene linkage were rapidly soluble at room temperature relative to PTAM 2a-d. On the contrary, somewhat gradual dissolution of PTAM 2a-d in amide solvents at room temperature was attributable to p-aromatic structure. Moreover, swift solubility was observed for PTAM 3a-d, containing CH_2 repeating units together with thiourea moieties in backbone. For that reason, PTAM 3a-d demonstrated partial solubility in THF as well. Thermal analysis also substantiated these observations, where aromatic–aliphatic PTAMs revealed reduced thermal stability in addition to lower T_g. Consequently, one of the major factors contributing here to enhanced solubility of poly(thiourea-amide)s was the introduction of C=S functionality that produced a chain separation effect, so, increased overall solvent accessibility. Furthermore the superior solubility of newly synthesized poly(thiourea-amide)s was observed relative to the comparable aromatic and aromatic–aliphatic,[25] sulfur containing[26] polyamides and poly(amide ureas)s[27] attributable to the presence of thiourea structural units that alleviated macromolecule interactions between the chains.

Viscometry and molecular weight

η_{inh} of PTAMs, as a good criterion for assessment of molecular weight, was in the range of 0.92–1.56 dL/

g that revealed reasonable molecular weights (Table III). According to the results wholly aromatic polyamides possessed higher η_{inh} compared with aliphatic–aromatic poly(thiourea-amide)s. In addition, it was observed that η_{inh} increased with the increase of p-phenylene content similar to PTAM 2a-d. Among PTAMs, comparatively high η_{inh} (1.47-1.56 dL/g) values were presented by PTAM 2a-d. Accordingly, PTAM 2b exhibited highest η_{inh} of 1.56 dL/g owing to better chain symmetry and packing efficiency of p-aromatic units. Whereas, introduction of less symmetrical m-aromatic rings into poly(thiourea-amide)s (PTAM 1a-d) led to intermediate η_{inh} of 1.45–1.54 dL/g. Unsurprisingly PTAM 3a-d demonstrated lower η_{inh} provided that flexible aliphatic units brought about a decrease of crystallinity, thus, reduced polymer chain rigidity. Correspondingly, PTAM 3a-d derived from AC displayed lowest η_{inh} (0.92 dL/g), having loser molecular packing in consequence of long supple CH_2 sequence. In addition, GPC measurements of PTAMs well supported the above discussion for η_{inh}. The weight-average molecular weight (M_w) and polydispersity index determined by GPC are specified in Table III. Eventually, M_w about 607×10^2-851×10^2 indicated fairly high molecular weights of PTAMs bearing C=S moieties. PTAM 2a-d with p-oriented rigid units in the backbone exhibited highest M_w of 698×10^2 – 851×10^2. Eventually, rationally high η_{inh} and M_w were disclosed by PTAMs bearing C=S moieties.

Thermal analysis

Thermal behavior of PTAMs was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC); the results are given in Table IV. TGA data indicated that thiourea based poly(thiourea-amide)s possessed fairly high thermal stability. TGA curves for PTAM 1a-d, PTAM 2a-d, and PTAM 3a-d are represented in Figures 6–8 respectively. The results undoubtedly demonstrated that PTAM 2a-d derived from the condensation of BAPTa-d with TPC, disclosed higher values in thermal property (T_0 and T_{10}) compared with analogous polymers. Subsequently, initial decomposition temperatures (T_0) of PTAM 2a-d were about 404–419°C and decomposition temperatures at 10% weight loss (T_{10}) stayed within the range of 413–431°C. Among all polyamides, PTAM 2b having symmetric p-phenylene units illustrated highest values of T_0 (419°C) along with T_{10} (431°C). Incidentally high T_0 and T_{10} of PTAM 2a-d can also be elucidated by their high $\eta_{inh.}$ PTAM 1a-d revealed succeeding highest T_{10} values (410–430°C) among PTAMs, owing to the presence of unsymmetrical isophthaloyl units. In contrast, PTAM 3a-d containing aliphatic spacers

TABLE III
η_{inh}, M_w, Polydispersity, and Yields of PTAMs

Polymer	Structure	Yield %	η_{inh} dL/g	$M_w \times 10^2$	M_w/M_n
PTAM 1a		95	1.52	723	1.62
PTAM 1b		95	1.54	752	1.68
PTAM 1c		95	1.48	687	1.70
PTAM 1d		94	1.45	668	1.65
PTAM 2a		96	1.54	806	1.72
PTAM 2b		96	1.56	851	1.75
PTAM 2c		96	1.49	707	1.83
PTAM 2d		95	1.47	698	1.75
PTAM 3a		95	0.94	643	1.82
PTAM 3b		95	0.96	652	1.88
PTAM 3c		94	0.93	636	1.86
PTAM 3d		94	0.92	607	1.79

presented lower values of T_0 about 305–338°C and T_{10} nearly 310–354°C. Apparently, such behavior of polyamides was attributed to higher free volume determined by CH$_2$ groups. The fact was rational since poly(thiourea-amide)s derived from AC (PTAM 3a-d) were rapidly soluble at room tempera-ture relative to corresponding wholly aromatic PTAMs. Moreover, X-ray patterns of PTAM 3a-d did not show any crystalline reflection, rather the typical halo of amorphous materials was observed. The char yields of polymers were about 46–68% at 600°C, which was indicative of excellent thermal stability.

TABLE IV
Thermal Analyses Data of Different PTAMs Samples

Polymer	T_g (ºC)	T_0 (ºC)	T_{10} (ºC)	T_{max} (ºC)	Y_c at 600ºC (%)
PTAM 1a	244	409	420	570	64
PTAM 1b	248	417	430	574	67
PTAM 1c	242	405	414	564	52
PTAM 1d	240	403	410	560	50
PTAM 2a	254	411	420	572	66
PTAM 2b	258	419	431	576	68
PTAM 2c	252	408	415	566	53
PTAM 2d	248	404	413	561	51
PTAM 3a	239	326	342	567	63
PTAM 3b	241	338	354	569	65
PTAM 3c	236	311	320	550	49
PTAM 3d	232	305	310	544	46

Same trend was pursued in the char yields of PTAMs, as can be seen in the case of thermal properties (T_0 and T_{10}). Thus, higher char yields of PTAM 2a-d (51–68%) were ascribed to the presence of high *p*-aromatic content in backbones whereas aromatic–aliphatic poly(thiourea-amide)s owned somewhat lower char yields. Glass-transition temperatures (T_g) of PTAMs were observed in the range of 232–258°C. DSC curves for PTAM 1a-d, PTAM 2a-d, and PTAM 3a-d are shown in Figures 9–11 respectively. The T_g values were found to be dependent on the structures of diacid chloride components. PTAM 2a-d derived from TPC, thus exhibited high T_g of 248–258°C. Furthermore, moderately high T_g of PTAM 1a-d, were undoubtedly due to the presence of *m*-oriented moieties. On the other hand, low T_g around 232–241°C were displayed by PTAM 3a-d. This behavior was also corroborated by their reasonably low η_{inh}, since, flexible CH_2 sequences endowed polymers with higher molecular mobility. In due course, thermal data herein articulated that presence of thiourea units outstandingly enhanced the solubility with out desecrating thermal properties of PTAMs.
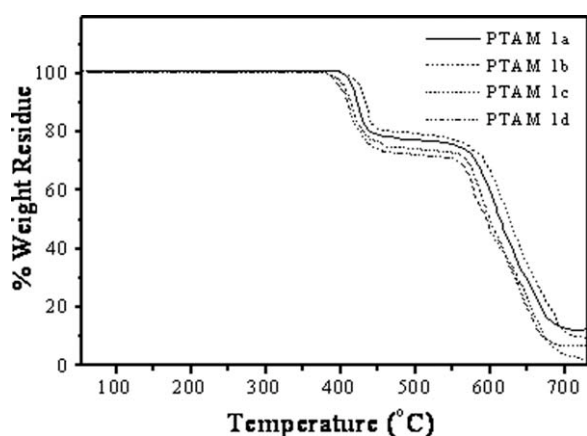

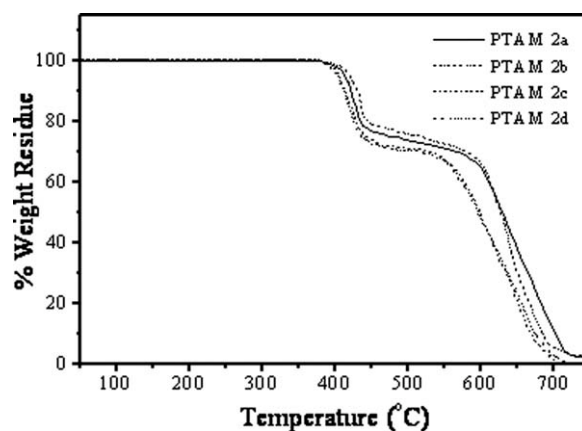**Figure 7** TGA curves of PTAM 2a-d at a heating rate of 10°C/min in N$_2$.

X-ray diffraction

Crystallinity of PTAMs was examined through X-ray diffractograms. As illustrated in Figure 12, PTAM 1a-d composed of *m*-phenylene rings in polymer backbone encompassed certain degree of crystallinity. Correspondingly, PTAM 1a displayed diffraction peaks near 19° and 26°. PTAM 1b and PTAM 1c also gave crystalline order close to 20° and 19°, respectively. On the other hand, overall crystalline character presented by PTAM 2a–c (Fig. 13), was carefully attributed to rigid and symmetrical *p*-oriented moieties in the polymer chains. For that reason, among all PTAMs, the crystalline morphology was executed by PTAM 2a-d, also reflected in their highest thermal stability. Accordingly, PTAM 2b showed several sharp crystal peaks about 2θ = 16–28 on account of better polymer chain packing. At the same time, as PTAM 2a showed moderately crystalline peaks around 18° and 25°. Small crystal peaks were observed in X-ray diffractogram of PTAM 2c as well. Quite the opposite, PTAM 2 d and PTAM 3 d were practically amorphous accredited to the
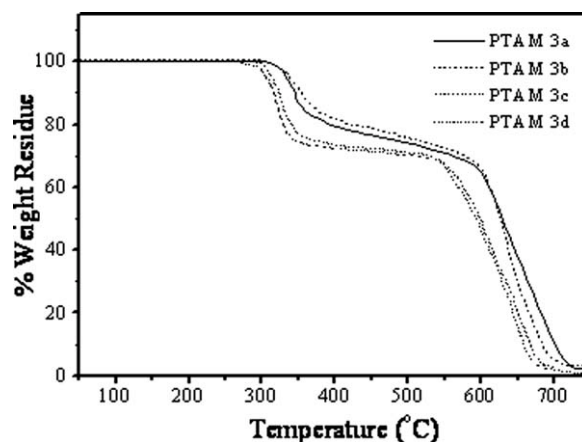

Figure 6 TGA curves of PTAM 1a-d at a heating rate of 10°C/min in N$_2$.

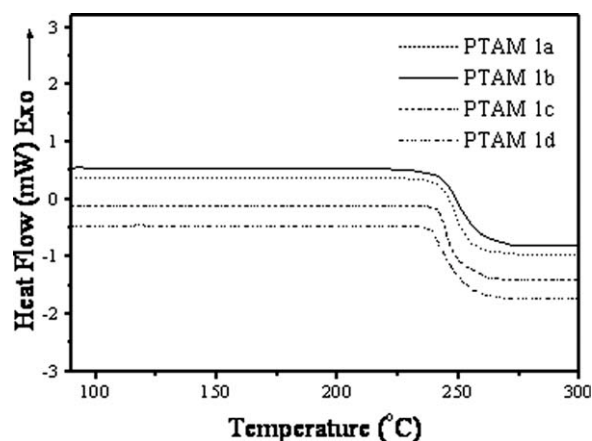**Figure 8** TGA curves of PTAM 3a-d at a heating rate of 10°C/min in N$_2$.

Figure 9 DSC thermograms of PTAM 1a-d at heating rate of 10°C/min in N_2.

presence of thiourea units along with aliphatic spacers in polymer backbone. Furthermore, PTAM 3a-d were all amorphous (Fig. 14) owing to flexible (C=S and CH_2) units that significantly increased disorder in chains, thus, instigated lesser chain packing. It follows that, XRD studies specified poor crystallinity of aromatic–aliphatic poly(thiourea-amide)s. Ultimately, these results were also corroborated by thermal analysis wherein wholly aromatic PTAMs demonstrated superior thermal stability and elevated T_g values.

Solid–liquid extraction of toxic metal ions by poly(thiourea-amide)s

Poly(thiourea-amide)s containing host units for both cations and anions were designed for the extraction of salts through hydrogen-bonding interactions (ion-dipole) between the host moieties and metal ions/ counter ions. Solid–liquid extraction transpires instantaneously when a solid phase is in contact with the solution containing guest molecules, only if
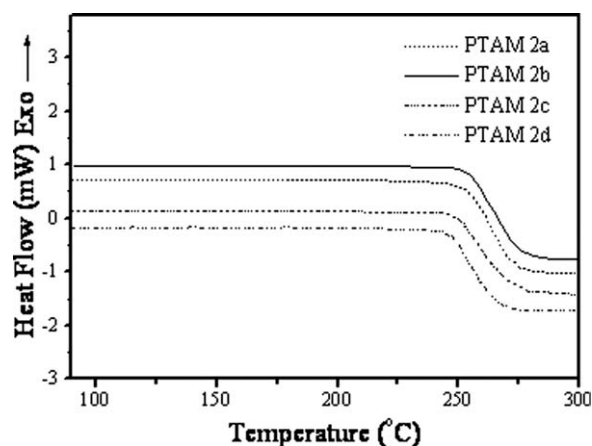

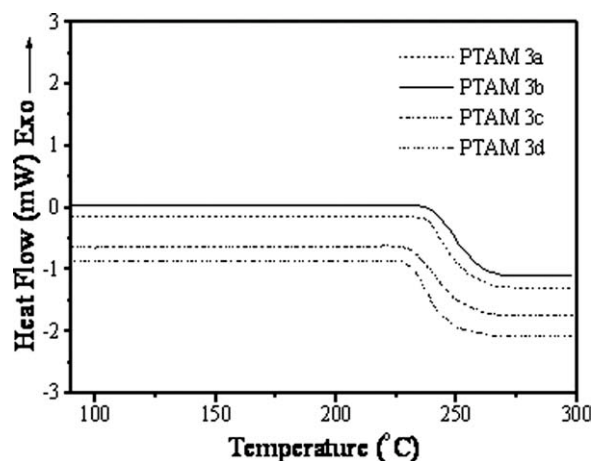**Figure 10** DSC thermograms of PTAM 2a-d at heating rate of 10°C/min in N_2.

Figure 11 DSC thermograms of PTAM 3a-d at heating rate of 10°C/min in N_2.

the solid phase owns certain ability to interact selectively with the introduced guest particles. Poly (thiourea-amide)s having thiourea moieties act as host molecules for anions and cations dissolved in water. Simple mechanism operates in this case, i.e., thiourea group functions as an ion receptor unit due to the formation of weak bonds between hydrogen of thiourea group and the ions. Since, thiourea units are expected to act as soft bases having high affinity for soft acids such as heavy metal ions. Similar weak interactions are also formed between the cations and amide carbonyl in addition to aromatic rings (electron-rich). This mechanism inevitably predicts the partial displacement of highly favorable hydrogen-bonding interaction of water with the polar groups. In this way, salts can be extracted from water by the formation of weak interactions between the ions and poly(thiourea-amide)s in aqueous environment. Eventually, the solid polyamide phases can be washed with water after extraction to concentrate or
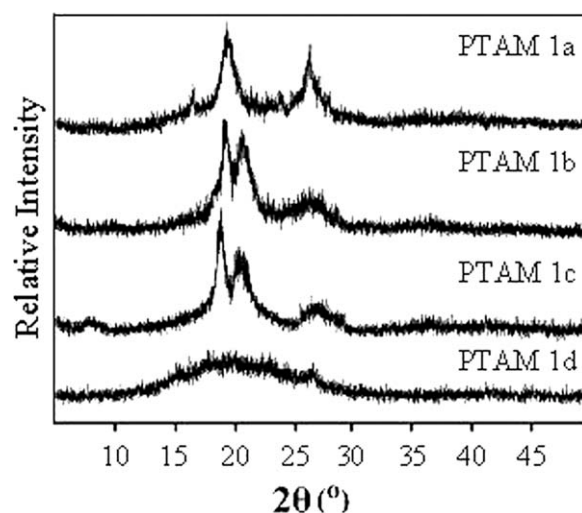

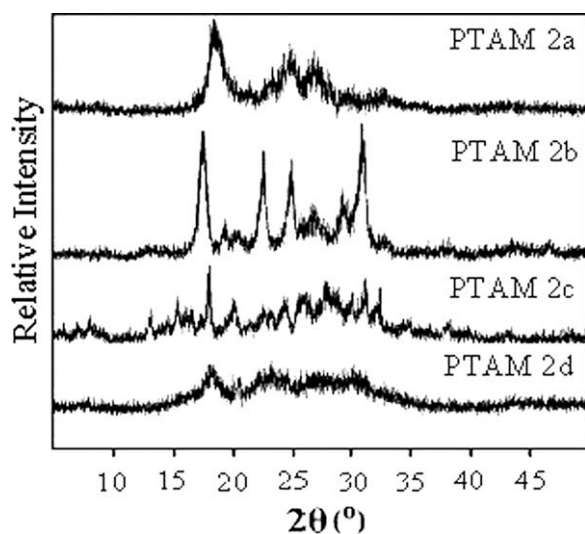**Figure 12** X-ray diffraction patterns of PTAM 1a-d.

Figure 13 X-ray diffraction patterns of PTAM 2a-d.

remove the cations to reuse the extractant polyamide phases.

The efficacy and selectivity of thiourea units for the extraction of environmentally toxic heavy metal ions was studied in terms of distribution coefficient (K_d') and solid−liquid extraction selectivity ($\alpha_{S,L}$).[27,28] Accordingly, K_d' is the measure of the capacity of material to extract cations under competitive conditions, where %E is extraction percentage; V is volume of the solution (liters), and n the molar amount of polymer structural units [eq. (1)].

$$Kd' = \left(\frac{\%E}{100 - \%E}\right)\left(\frac{V}{n}\right). \qquad (1)$$

On the other hand, $\alpha_{S,L}$ is the ratio of two distribution coefficients [eq. (2)]. Hg^{2+} cation was taken as the reference, as it has the highest distribution coefficient ($K_d'_{M2}$).

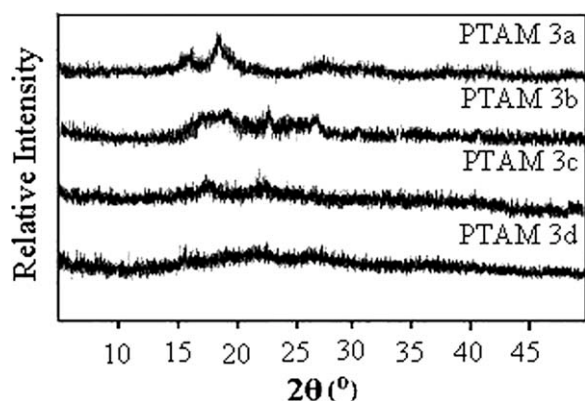$$\alpha_{S,L} = \frac{Kd_{M1}}{Kd_{M2}} = \frac{Kd'_{M1}}{Kd'_{M2}}. \qquad (2)$$

Figure 14 X-ray diffraction patterns of PTAM 3a-d.

TABLE V
Solid–Liquid Extraction of Various Metal Cations from Aqueous Solution by Solid PTAM 1a and 2a

Salt	%E		K_d'/L mol^{-1}		$\alpha \times 10^3$	
	PTAM 1a	PTAM 2a	PTAM 1a	PTAM 2a	PTAM 1a	PTAM 2a
$Cr(NO_3)_3$	29	29	15	15	6	6
$Fe(NO_3)_3$	30	30	16	16	6	6
$Cu(NO_3)_2$	35	35	21	21	8	8
$ZnCl_2$	24	24	13	13	5	5
$Co(NO_3)_2$	35	35	21	21	8	8
$Cd(NO_3)_2$	36	36	21	21	8	8
$Ni(NO_3)_2$	34	34	20	20	8	8
$Pb(NO_3)_2$	98	98	26×10^2	26×10^2	1×10^3	1×10^3
$Hg(NO_3)_2$	99	99	27×10^2	27×10^2	1×10^3	1×10^3

Table V illustrates the solid−liquid extraction results for the elimination of several cations from aqueous solution using PTAM 1a and 2a as extractants. These poly(thiourea-amide)s were selected for study owing to their *meta*-phenylene polymer spine having less rigid structure. Consequently, extraction levels for the tested metal cations were in the range of 24–36%, except for Pb^{2+} and Hg^{2+} showing extraction levels close to 100% from aqueous solution. Such high extraction level of lead and mercury cations by solid poly(thiourea-amide)s depicts their future applications in various industries such as decontamination of water, for selective cation transport membranes and in other sensing materials. Under this assertion, several useful polyamides for the elimination or detection of environmentally damaging cations, anions, and neutral molecules, have been synthesized. It has been reported that urea group[27] also imparts hydrophilicity to polymers and is an efficient host unit for anions, which facilitates the preparation of solid polymer phases to be used as extractants for toxic cations. Nevertheless, the polyamides with urea groups gave moderate results; up to 30% of lead could be extracted from water to the polyamide solid phase. Another series of polyamides having pendant crown structures,[29] exhibited fine selectivity for the extraction of Pb^{+2} from aqueous and organic media in similar type of extraction experiments, has been prepared. However, the novel poly(thiourea-amide)s synthesized in the current effort possess much higher efficiency towards the elimination of environmentally toxic ions, when compared to the reported polyamides.

CONCLUSIONS

New series of novel diamines, BAPTa-d, were synthesized from dinitro functionalized compounds BNPTa-d. These BAPTa-d were effectively used as condensation monomers in polymerization with diacid chlorides giving 12 novel poly(thiourea-

amide)s. A convenient synthetic route was utilized to produce three series of aromatic and aromatic–aliphatic PTAMs. Nice balance of properties (thermal stability versus solubility) was observed in PTAMs. Consequently, the combination of amide and thiourea groups along the backbone endowed the current polymers with some special characteristics, such as excellent solubility, high glass transition temperatures, and thermal resistance along with high molecular masses. In a nutshell, novel diamines (BAPTa-d) can be advantageously considered as forthcoming candidates for the production of soluble and heat resistant poly(thiourea-amide)s possessing high M_w. Moreover, poly(thiourea-amide)s are efficient hosts for toxic heavy metal cations, thus making these polymers effective solid extracting phases for the extraction and elimination of lead and mercury cations from water media (elimination of nearly 100% of Pb^{2+} and Hg^{2+} cations).

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