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Scientific paper

Synthesis and Characterization of Multicolor Luminescent and Thermally Stable Thioureas and Polythioamides

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Abstract

Two new polythioamides were prepared through the polycondensation reaction between thiourea monomers and terephthaloyl dichloride, while the thiourea monomers were synthesized by the interaction of aromatic (4,4'-diaminophenylsulfone) or alicyclic (1,2-cyclohexanediamine) diamine with ammonium thiocyanate. The elemental composition of polythioamides was confirmed through CHN microanalysis. The structure and properties of thiourea monomers and polythioamides were determined through proton NMR, UV-Vis, FT-IR spectroscopy, fluorescence, TGA/DTA and SEM. The polythioamides indicated high thermal stabilities which were assessed from their T_{max} (temperature indicating highest rate of weight loss) values (670 °C and 346 °C) observed in their DTG graphs. The thioureas and polythioamides were fluorescent and showed multicolor (violet, green, yellow, orange and red) emissions at different excitation wavelengths. All the synthesized compounds were also tested for their antifungal and antibacterial functions and showed antibacterial activity against *Salmonella typhi*, *Bacillus subtilis* and *Staphylococcus aureus*, and antifungal activity against *Candida albicans*.

Keywords: polythioamides, thioureas, thermal stability, multicolor fluorescence emissions, antimicrobial functions

1. Introduction

In comparison to the wide literature on sulfur containing polymers, the work on the polymers containing thioamide functional group called polythioamides is limited.[1] The polythioamides are analogous to polyamides in which oxygen of the carbonyl group (C=O) is replaced by the sulfur (C=S). The stability of polythioamides is also similar to polyamides, however their melting points and glass transition temperatures are lower as compared to their homologous polyamides.[2–4] The thiocarbonyl group in polythioamides decreases hydrogen bonding which may increase their solubility in common solvents such as chloroform.[5] In recent years, interest in the synthesis of polythioamides has been increasing because of their unique qualities such as high refractive index and luminescence behavior.[6,7] The polythioamides have an ability to selectively adsorb valuable metals such as platinum(IV), gold(III) and palladium(II),[8,9] and toxic metals like mercury(II), lead(II) and chromium(III) from wastewater systems.[10–12] The interest of researchers is increasing towards the preperation and applications of antifungal, antibacterial and antiviral polymeric food packaging after Covid-19 pandemic for reducing the harmful effects of various microrganisms on human health.[13] A number of polythioamide antibiotics have been designed and studied based on Closthioamide (the first polythioamide antibiotic from a strictly anaerobic bacterium Clostridium cellulolyticum) architecture.[14–17] Different methods have been adopted for the synthesis of polythioamides, one of them being the condensation reaction between bis(dithioesters) or dithioesters with diamines, but the formation of harmful methanethiol during the synthesis of bis(dithioesters) or dithioesters restricts the employment of this method.[4,18] The conversion of polyamides to polythioamides (thionation reaction) through Lawesson reagent is an alternative technique, however this reaction is usually carried out in toluene at 100 °C and suffers from incomplete conversion and hydrolytic degradation.[1,5] Multicomponent polymerization (MCP) is a new and powerful technique for the preparation of functional polymers due to its operational simplicity and high efficiency.[19] The

Willgerodt-Kindler reaction is a useful procedure for the preparation of polythioamides which involves polycondensation of dialdehydes and diamines in attendance of elemental sulfur.[20–22] The corresponding polythioamides were obtained in high yield through polycondensation using isophthalaldehyde and terephthalaldehyde, while polymerization was not achieved with phthalaldehyde due to steric effect. The polycondensation with the use of aliphatic primary diamines and cyclic secondary diamines resulted in good yields of polythioamides, while no polymeric product was obtained with acyclic secondary diamines, whereas aromatic diamines provided insoluble polymers.[21] A catalyst free MCP of aliphatic diamines, aromatic diynes, dicarboxylic acids and elemental sulfur have been reported which resulted in high molecular weight luminescent polythioamides.[7,23] Recently, a series of high refractive index polythioamides were prepared through straight polymerization of primary aliphatic diamines with elemental sulfur at 110 °C without using catalyst, the yield and molecular weight of the resulted polymer was high and they also indicated good thermal stability.[6]

In the present work two (one new) thiourea monomers were synthesized by the interaction of aromatic or aliphatic diamine with ammonium thiocyanate, and two new polythioamides were prepared through polycondensation between thiourea monomers with terephthaloyl dichloride. The monomers and polymers were obtained in good yield (70–92%). The structural design of one of the synthesized polythioamides contains aromatic rings of dapsone while other contains aliphatic rings of cyclohexane, the purpose of these structural changes was to study their influence on the properties (solubility, fluorescence, antimicrobial activities and thermal stability) of polythioamides.

2. Experimental

2. 1. Chemicals

4,4'-diaminodiphenyl sulfone (97%, Sigma-Aldrich, USA), ammonium thiocyanate (≥97.5%, Sigma-Aldrich, USA), 1,2-cyclohexanediamine (99%, Merck, Darmstadt, Germany), chloroform (anhydrous, ≥99%, Merck, Darmstadt, Germany), ethanol (95%, Merck, Darmstadt, Germany), tetrahydrofuran (anhydrous, ≥99%, Merck, Darmstadt, Germany), sodium bicarbonate (ACS reagent, ≥99.7%, Merck, Darmstadt, Germany), activated charcoal (powder extra pure, Merck, Germany), hydrochloric acid (ACS reagent, 37%, Merck, Germany), sodium hydroxide (reagent grade, ≥98%, pellets (anhydrous), Sigma-Aldrich, Seelze), terephthaloyl chloride (99%, Alfa-Aesar, Germany), acetone (ACS reagent, ≥99.5%, Sigma-Aldrich, Germany), N,N-Dimethylformamide (≥99.8%, AnalaR BDH, England), dimethyl sulfoxide (≥99.9%, AnalaR BDH, England), and distilled water were used.

2. 2. Equipment

The melting points of the synthesized thioureas and polythioamides were measured on Gallenkamp Apparatus (U.K.) with build-in thermometer. The solubility of thiourea monomers and polythioamides was tested in different solvents by adding 5 mg of each compound in 2 mL of solvent and mixed well. If precipitates were observed at the bottom of the tube, the contents were heated at 60–70 °C for 5 min. A change in the contents of solid mass in the solvent was noted. The E.I. mass spectra of thiourea monomers were obtained on mass spectrometer JEOL JMS-600H (Japan) at HEJ Research Institute of Chemistry, Karachi University, Sindh, Pakistan. The CHN analysis of the polythioamides was carried out on elemental analyzer EA111O at Elemental Microanalysis Ltd, Devon, EX20 1UB(UK). The ^{1}HNMR spectra of thioureas and polythioamides were documented on spectrometer BRUKER AVANCE-NMR 400 MHz. Tetramethylsilane was employed as internal standard and dimethylsulfoxide-d_6 (DMSO-d_6) as deuterated solvent. The FT-IR spectroscopy of thioureas and polythioamides was performed on FT-IR spectrometer Thermo Scientific™ Nicolet™ iS10 equipped with ATR (attenuated total reflectance) and Software OMNIC™ within 4000–600 cm^{-1}. The UV-Vis spectra of thioureas and polythioamides were performed in solvent DMSO within 190–800 nm, with 1 cm^3 quartz cuvettes on UV-1800 Shimadzu double beam spectrophotometer with software UV Probe. The emission spectra of thioureas and polythioamides were recorded on Shimadzu RF-5301PC Series (Japan) spectrofluorometer, using 1cm quartz cuvette and the solvent was DMSO. The surface morphologies of the thiourea and polythioamides were recorded at Center of Pure and Applied Geology, Sindh University, Jamshoro, Pakistan on Scanning Electron Microscope JEOL JSM-6490 LV or on JEOL JSM-5910 with accelerating voltage 15 kV at Centralized Resource Laboratory (CRL), Peshawar University, Pakistan. The were measured through the SEM images of the synthesized thiourea monomers and polythioamides by using ImageJ software. The TGA (thermogravimetric analysis) and DTA (Differential thermal analysis) graphs of thioureas and polythioamides were recorded in the nitrogen atmosphere with flow rate 20 mL/min on Perkin Elmer Pyris Diamond Series (USA) thermal analyzer particle area, diameter and pore surface area. The sample (3.10–8.26 mg) was placed on ceramic pan and then heated from 40–800 °C with 20 °C/min heating rate and the reference material was alumina. Antibacterial functions of thioureas and polythioamides were examined against various species of bacteria (*Escherichia coli*, *Salmonella typhi, Staphylococcus aureus*, *Bacillus subtilis* and *Pseudomonas aeruginosa*) by microplate alamar blue assay through 96 well plate method and using Ofloxacin as standard drug, 2 to 4 mg of compound

(thioureas and polythioamides) was dispersed in DMSO solvent to make concentration 50 or 200 μg/mL. The Mueller-Hinton Agar (MHA) was utilized as medium for bacterial growth and incubation time was 18 to 20 hrs. The % inhibition by the compound (thioureas and polythioamides) against bacterial strains was estimated from reported procedure and the formula is given as Eq. 1.[24-27]

$$\%\ inhibition = \frac{(\varepsilon_{ox})\lambda_2 A\lambda_1 - (\varepsilon_{ox})\lambda_1 A\lambda_2}{(\varepsilon_{red})\lambda_1 A'\lambda_2 - (\varepsilon_{red})\lambda_2 A'\lambda_1} \times 100 \quad (1)$$

Where ε_{ox} is the molar extinction coefficients of dye Alamar blue in its oxidized (blue) form, ε_{red} is the molar extinction coefficients of dye Alamar blue in its reduced (pink) form, A is the test well absorbance, A' is negative control well absorbance, λ_1 is 570 nm and λ_2 is 600 nm. The antifungal functions of thioureas and polythioamides were evaluated by agar tube dilution method against various species of fungi (*Aspergillus niger*, *Candida albicans*, *Fusarium lini*, *Trichophyton rubrum* and *Microsporum canis*), drug Amphotericin B was employed as standard for *Aspergillus niger* and drug Miconazole as standard for other strains. For fungal growth SDA (Sabouraud dextrose agar) medium was utilized, 12 mg of the compound (thioureas and polythioamides) was dispersed in DMS0 solvent to make 200 μg/mL concentration. The period of the incubation was seven days at a temperature of 27 °C. The % inhibition by the compounds (thioureas and polythioamides) against fungal strains was calculated through the formula given as Eq. 2.[25–27]

$$\%\ Inhibition\ = 100 - \frac{linear\ growth\ in\ test\ \ (mm)}{linear\ growth\ in\ control\ (mm)} \times 100 \quad (2)$$

2. 3. Synthesis of Thiourea Monomers

The monomers 1,2-cyclohexanebis(thiourea) (CBT) and 4,4'-diphenylsulfonebis(thiourea) (SBT) were synthesized by following a literature procedure.[28] The thiourea monomer CBT is new while thiourea SBT is already reported.[29]

In a typical synthesis, 4,4'-diaminodiphenyl sulfone (dapsone) or 1,2-cyclohexanediamine (0.01 mol), 45 ml of deaerated water, pinch of activated charcoal and 10 ml of concentrated. HCl were added to a 250 ml round-bottom flask assembled with magnetic agitator. The mixture was heated at 50 °C under consistent stirring for 20 minutes. Then the contents were filtered and relocated to another 250 ml round-bottom flask assembled with a thermometer, magnetic agitator and condenser, ammonium thiocyanate (0.04 mol) was also added into it. The reaction mixture was refluxed at 90 °C for 48 hours. The resulting granular product was allowed to cool naturally until it reached room temperature, filtered and then washed with hot water. The product was recrystallized with 50 ml of DMSO/water (1:1 by volume) and then dried. In case of thiourea monomer (CBT) derived from 1,2-cyclohexanediamine, the product was not precipitated in the reaction flask, therefore the contents of the flask were transferred in a 250 ml beaker having cold water and permitted for precipitates formation. The resultant compound was filtered and washed with hot water, but it dissolved in the hot water during washing, therefore few drops of 0.1 N sodium hydroxide were added to the product solution in water and as a result precipitates were reappeared. The resulting amount was filtered and then dried. The synthetic reactions for thiourea monomers are given in Figure 1.

2. 3. 1. 4,4'-diphenylsulfonebis(thiourea) (SBT)

Melting point, m.p. mp 80–100 °C, yield = 72%, $C_{14}H_{14}N_4O_2S_3$, MS *m/z* (relative intensity %) 291(12.2), 151(1.0), 75(1.4), 60(1.0). ^{1}HNMR (400 MHz, DMSO-d_6) δ ppm 10.39 (t, *J* 22.4 Hz, 2H, NH), 7.86 (qu, *J* 8.8 Hz, 2H, Ph), 7.74 (qu, *J* 8.8 Hz, 1H, Ph), 7.66 (d, *J* 8.4 Hz, 1H, Ph), 7.59 (d, *J* 8.4 Hz, 1H, Ph), 7.50 (t, *J* 8.8 Hz, 1H, Ph), 7.42 (d, *J* 8.4 Hz, 1H, Ph), 6.58 (m, *J* 8.8 Hz, 1H, Ph), 6.10 (d, *J* 15.6 Hz, 2H, NH_2), 5.94 (s, 2H, NH_2). ^{1}HNMR of this compound is also reported in literature.[28,29] FT-IR, cm^{-1} (rela-

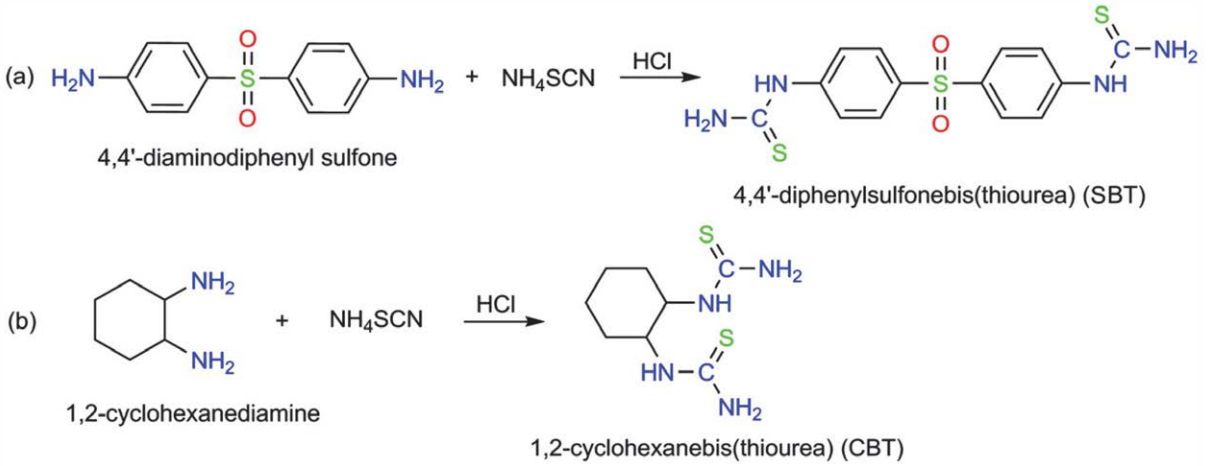

Figure 1. Reactions for the preparation of thiourea monomers: **a** SBT and **b** CBT.

tive magnitude) 3333(w), 2050(w), 1624(w), 1588(s), 1526(m), 1493(m), 1402(w), 1289(m), 1249(m), 1182(w), 1142(s), 1102(s), 1071(w), 1011(m), 949(w), 829(m), 716(m), 679(m). UV (DMSO), λ_{max} (ε, L mole^{-1} cm^{-1}) 258 (185767), 294 (148613), 311 nm (191695).

2. 3. 2. 1,2-cyclohexanebis(thiourea) (CBT)

Melting point mp 110 °C, yield = 70%, $C_8H_{16}N_4S_2$, ^{1}HNMR (400 MHz, DMSO-d_6), δ ppm 8.53 (s, 2H, NH), 6.09 (s, 2H, NH_2), 5.38 (s, 2H, NH_2), 1.98 (t, *J* 6 Hz, 2H, CH), 1.74 (t, *J* 12 Hz, 4H, CH_2), 1.59 (d, *J* 6.4 Hz, 2H, CH_2), 1.37-1.05 (m, 2H, CH_2). FT-IR, cm^{-1} (relative magnitude) 3315(w), 2930(m), 2857(w), 2058(m), 1568(s), 1470(m), 1380(m), 1338(m), 1311(w), 1288(w), 1261(w), 1154(w), 1076(w), 1039(w), 1007(w), 934(w), 820(w), 707(w). UV (DMSO), λ_{max} (ε, L mole^{-1} cm^{-1}) 283 (178.8), 307 nm (145.4).

2. 4. Synthesis of Polythioamides

Two novel polythioamides poly-4,4'-diphenylsulfonebis(carbamothioyl)benzamide (PSB) and poly-1,2-cyclohexanebis(carbamothioyl)benzamide (PCB) were prepared by following a slightly modified literature procedure.[30]

Thiourea monomer (SBT or CBT) (0.01 mol) was dissolved to make concentrated solution in DMF, and 1 M aqueous sodium hydroxide solution (approx. 5–10 ml) was combined slowly until the solution remained clear, then the solution was transferred to 250 ml round-bottom flask assembled with magnetic agitator and ice bath. Terephthaloyl dichloride (0.01 mol) was dispersed alone in DMF and then combined with the help of dropping funnel to the flask containing thiourea solution with constant stirring. The constituents of the flask were stirred continuously for 2 h in ice bath. The mixture was then poured to a 500 ml beaker having cold distilled water for the production of precipitates. The resulting compound was filtered and then dried at room temperature. In case of polythioamide (PCB) derived from thiourea CBT, the product was not precipitated in water, therefore few drops of 0.1 N sodium bicarbonate solution was added into it, but precipitates were not formed, then polymer-water solution was concentrated up to half of its original volume, which resulted to precipitates formation. The product was gathered

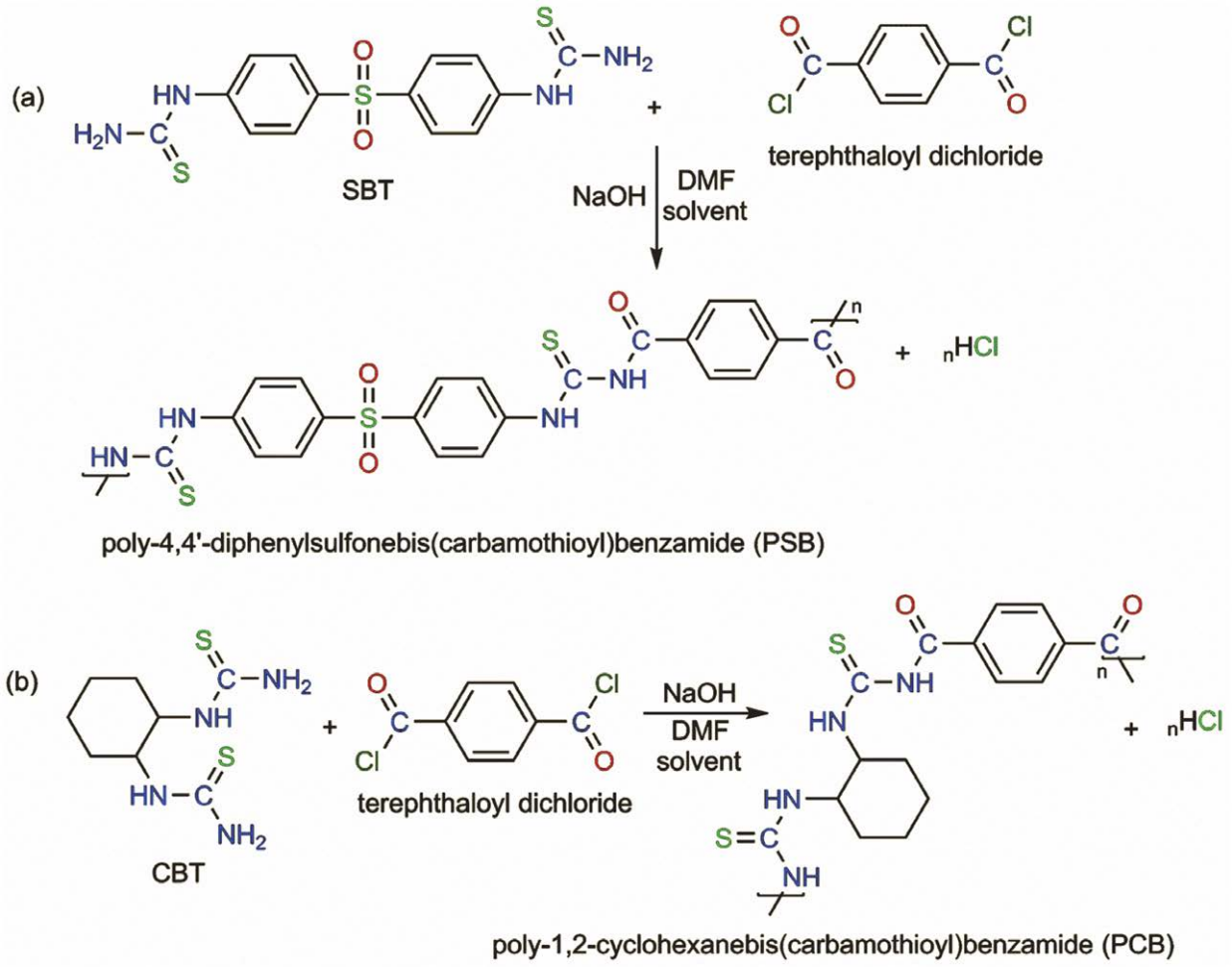

Figure 2. Reactions for the preparation of polythioamides: **a** PSB and **b** PCB.

through filtration and dried up at room temperature. The reactions for the preparation of polythioamides are given in Figure 2.

2. 4. 1. poly-4,4'-diphenylsulfonebis(carbamothioyl)benzamide (PSB)

Melting point. mp 275–300 °C, yield 92%, Anal. Calcd for $(C_{22}H_{16}N_4O_4S_3)_n$: % C 53.22, H 3.22, N 11.29. Found: %C 52.87, H 3.56, N 11.06. ^{1}HNMR (400 MHz, DMSO-d_6), δ ppm 13.18 (t, *J* 62.4 Hz, 1H, NH), 10.66 (t, *J* 36 Hz, 1H, NH), 8.03 (s, 8H, Ph), 7.94 (s, 2H, Ph), 7.85 (q, *J* 8.8 Hz, 2H, Ph), 7.76 (d, *J* 8.4 Hz, 2H, Ph), 7.71 (t, *J* 4.0 Hz, 2H, Ph), 7.51 (t, *J* 8.8 Hz, 2H, Ph), 7.43 (d, *J* 8.4 Hz, 1H, Ph), 7.33 (d, *J* 8.0 Hz, 1H, Ph), 6.59 (sext, *J* 4.4 Hz, 2H, Ph), 6.11 (s, 2H, Ph), 2.88 (s, 1H, CHO end on), 2.70 (s, 1H, CHO end on). FT-IR, cm^{-1} (relative magnitude) 3344(w), 2819(w), 2544(w), 1660(s), 1590(m), 1529(w), 1509(w), 1494(w), 1423(w), 1387(w), 1282(s), 1252(m), 1182(w), 1142(s), 1102(s), 1071(w), 1019(w), 934(w), 880(w), 831(w), 782(w), 729(m), 681(w). UV (DMSO), λ_{max} (1% absorptivity) 294 (3120), 309 nm (3455).

2. 4. 2. poly-1,2-cyclohexanebis(carbamothioyl) benzamide (PCB)

mp > 360 °C, yield 74%, Anal. Calcd for $(C_{16}H_{18}N_4O_2S_2)_n$: % C 53.03, H 4.97, N 15.46. Found: % C 52.43, H 4.62, N 14.87. ^{1}HNMR (400 MHz, DMSO-d_6) δ ppm 13.26 (s, 2H, NH), 8.03 (s, 4H, Ph), 2.89 (s, 1H, CH), 2.72 (s, 1H, CH). FT-IR, cm^{-1} (relative magnitude) 3100(w), 3060(w), 2812(w), 2536(w), 1673(s), 1574(m), 1509(m), 1422(m), 1279(s), 1136(w), 1112(m), 1019(w), 930(m), 879(m), 780(m), 727(s) 672(w). UV (DMSO), λ_{max} (1% absorptivity) 285 nm (92.8).

3. Results and Discussion

3. 1. Melting Point

The melting points of polythioamides PSB (275–300 °C) and PCB (above 360 °C) were higher than their corresponding thiourea monomers SBT (80–100 °C) and CBT (110 °C) respectively, which indicates their formation, because melting points of the polymers are generally higher than their corresponding monomers due to their high molecular weights.

3. 2. Synthesis

The synthetic reactions for the synthesis of thiourea monomers (SBT and CBT) and polythioamides (PSB and PCB) with their structures are given in Figure 1 and Figure 2 respectively. Two (one new) thiourea monomers SBT and CBT were synthesized by the reaction of ammonium thiocyanate with 4,4'-diaminodiphenyl sulfone (also called dapsone) or 1,2-diaminocyclohexane respectively. The yield of thiourea monomers was SBT = 72% and CBT = 70%. Two new polythioamides PSB and PCB were prepared through polycondensation reaction of thiourea monomers SBT or CBT with terephthaloyl dichloride respectively. The resulting polythioamides were acquired in high yield (PSB = 92% and PCB = 74%). The structures of thioureas (SBT and CBT) and polythioamides (PSB and PCB) were confirmed through different characterization methods, and all the results supported the formation of these compounds.

3. 3. E.I Mass Spectrum

The E.I mass spectrum of thiourea monomer SBT recorded fragment ion peak at m/z 291 for $[NH_2.CS.NH.C_6H_4{\cdot}SO_2{\cdot}C_6H_4]^+$ with a loss of fragment corresponding to $[NH_2.CS.NH]^+$ from molecular ion peak (M^+) and also indicated fragment ion peaks at m/z 151, 75 and 60 for $[NH_2{\cdot}CS{\cdot}NH{\cdot}C_6H_4]^+$, $[NH_2{\cdot}CS{\cdot}NH]^+$ and $[NH_2{\cdot}CS]^+$ respectively (supplementary Figs. S1a, b).

3. 4. Solubility

The solubility of thioureas (SBT and CBT) and polythioamides (PSB and PCB) was tested in DMSO, DMF, THF, chloroform, acetone, ethanol and water. All the compounds were not soluble in water. The thiourea monomer SBT was soluble in all the organic solvents except ethanol while thiourea CBT was fully soluble in DMSO and DMF at room temperature, soluble on heating in ethanol and partially soluble in acetone, chloroform and THF. The polythioamides PSB and PCB were fully soluble in DMSO and DMF without heating, while insoluble in other solvents.

3. 5. ^{1}HNMR Spectroscopy

The ^{1}HNMR spectra of thiourea monomers (SBT and CBT) and polythioamides (PSB and PCB) were recorded in DMSO-d_6 solvent and all the compounds showed two strong residual protons signals at δ ppm 3.3 and 2.49 due to solvent impurities. The thiourea monomer SBT showed triplet at δ ppm 10.39 for –NH, doublets and multiplets within δ ppm 7.86–6.58 for C–H aromatic protons, while doublet and singlet at δ ppm 6.10 and 5.94 respectively were for NH_2 protons (supplementary Fig. S2). The thiourea monomer CBT indicated proton signal at δ ppm 8.53 for –NH, proton signals at δ ppm 6.09 and 5.38 for –NH_2, and range of signals within δ ppm 1.05–1.98 for aliphatic –CH_2 protons due to cyclohexane. The polythioamide PSB indicated –NH proton signals at δ ppm 13.18 and 10.66, range of proton signals within δ ppm 8.03–6.11 for C–H aromatic protons and signals at δ ppm 2.88 and 2.70 for –CHO end on groups. (Figure 3). The polythioamide PCB showed –NH proton signal at δ ppm 13.26, and

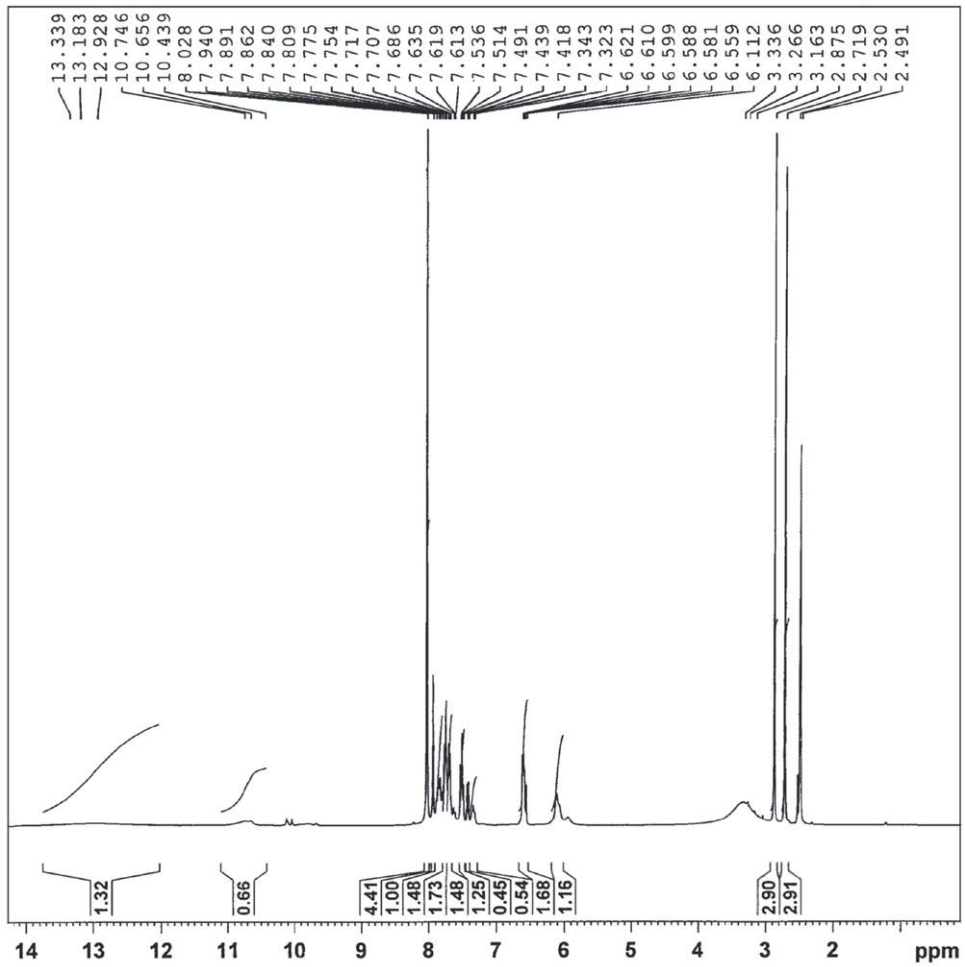

Figure 3. [1]HNMR spectrum of polythioamide PSB.

–CH_2 aliphatic proton signals at δ ppm 2.89 and 2.72 due to cyclohexane. These results supported the formation of thioureas and polythioamides. Similar [1]HNMR assignments are reported for related thioureas and polythioamides.[12,28,29]

3. 6. FTIR Spectroscopy

The FTIR spectra of thiourea monomers SBT and CBT indicated bands of medium intensity at 3333 and 3311 cm^{-1} respectively for υ N-H, thiourea CBT indicated two peaks at 2930 cm^{-1} and 2858 cm^{-1} for aliphatic υ CH_2 due to cyclohexane, thiourea SBT indicated bands at 1624, 1588 and 1526 cm^{-1} due to υ C=C of aromatic rings and bending vibration of N–H while CBT showed band at 1568 cm^{-1} due to bending vibration of N–H, both SBT and CBT indicated one weak band at 1071 and 1076 cm^{-1} for υ C=S respectively (Figure 4a and supplementary Fig. S3a). The FT-IR spectra of polythioamide PSB indicated one feeble band at 3344 cm^{-1} while polythioamide PCB indicated two feeble bands at 3100 and 3060 cm^{-1} for υ N–H, polythioamide PCB indicated band at 2812 for υ CH_2 aliphatic owing to cyclohexane, both PSB and PCB indicated one strong band at 1660 and 1673 cm^{-1} for υ C=O respectively, PSB indicated four bands within 1590–1494 cm^{-1} while PCB displayed two bands at 1574 and 1509 cm^{-1} due to υ C=C in aromatic rings (Figure 4b and supplementary Fig. S3b). Similar FT-IR assignments are described for related thioureas and polythioamides.[12,28]

3. 7. UV-Vis Spectroscopy

The UV-Visible spectra of thiourea monomers and polythioamides were recorded in DMSO solvent. Molar absorptivity (ε) (L $mole^{-1}$ cm^{-1}) was calculated for thiourea monomers, while 1% absorptivity was calculated for polythioamides because molecular weights of polythioamides were unknown. The UV-Vis spectra of thiourea SBT indicated three absorption bands, the first two bands at 258 and 294 nm with molar absorptivity 185767 and 148613 L $mole^{-1}$ cm^{-1} respectively were for π – π* transitions within aromatic rings of dapsone while the third band at 311 nm with molar absorptivity 191695 L $mole^{-1}$ cm^{-1} was for π – π* transition involving C=S pi-bond and lone pair of nitrogen (Figure 5a). The thiourea CBT indicated two bands, the first at 283 nm with molar absorptivity 178.8 L $mole^{-1}$

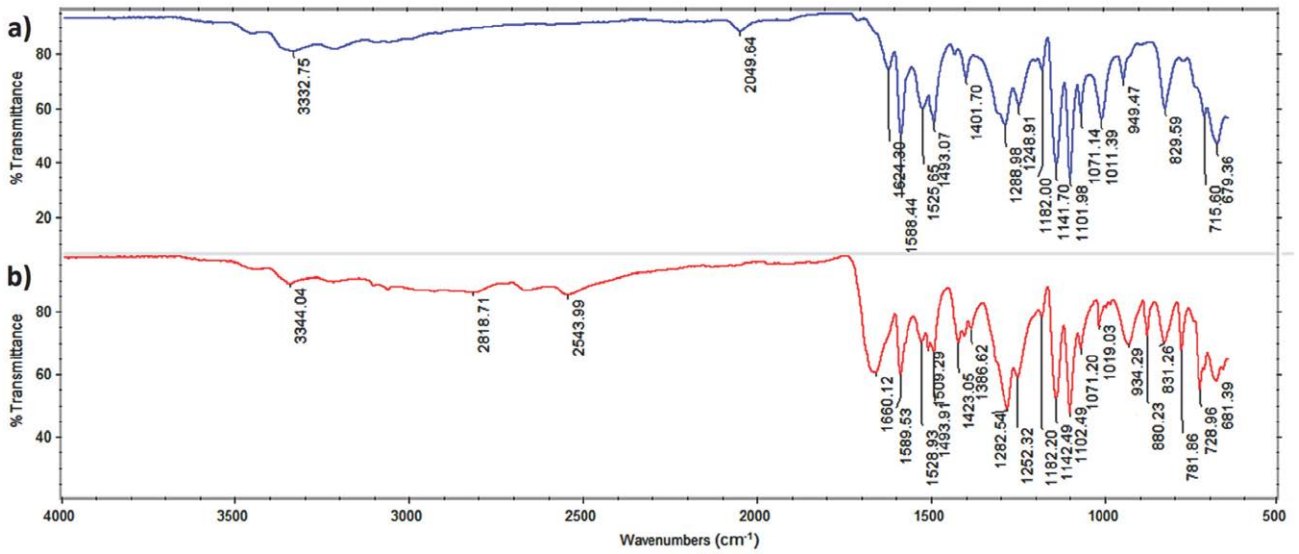

Figure 4. FT-IR spectra of **a** thiourea monomer SBT and **b** its corresponding polythioamide PSB.

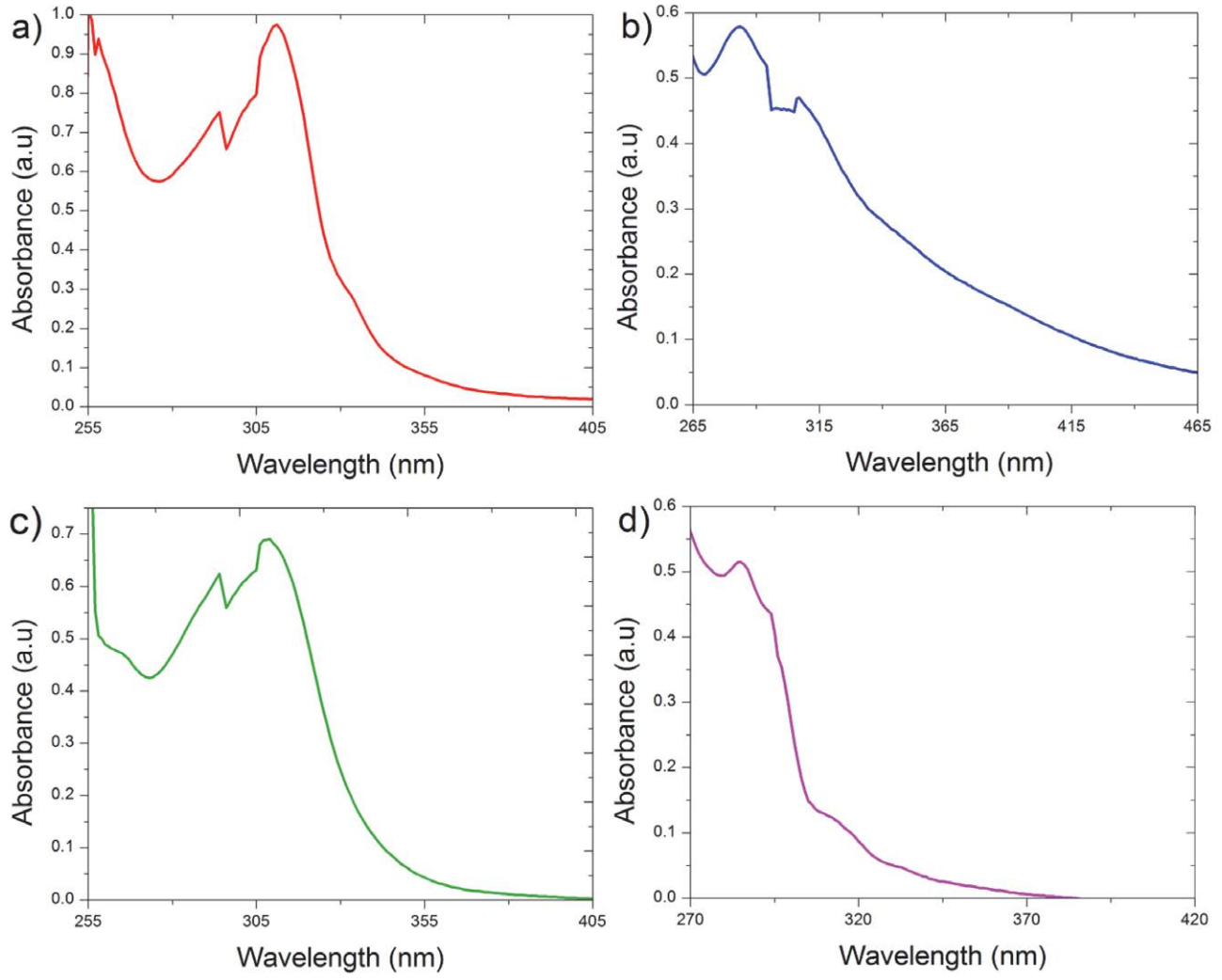

Figure 5. UV-Vis spectra of **a** thiourea SBT, **b** thiourea CBT, **c** polythioamide PSB and **d** polythioamide PCB.

cm^{-1} was for π – π* transitions within nitrogen lone pair and C=S pi-bond**,** while second band at 307 nm with molar absorptivity 145.4 L $mole^{-1}$ cm^{-1} was for n – π* transition within non-conjugated C=S group and lone pair of sulfur (Figure 5b). The polythioamide PSB indicated two bands, the first band at 294 nm with 1% absorptivity 3120 was for π – π* transitions within aromatic rings of dapsone and the next band at 309 nm with 1% absorptivity 3455 was for π – π* transition engaged in aromatic ring and amide group (Figure 5c). The polythioamide PCB indicated only single band at 285 nm with 1% absorptivity 92.8 for π – π* transition within aromatic ring and amide group (Figure 5d). Similar UV-Vis specifications are described for related compounds.[5,29]

3. 8. Fluorescence Spectroscopy

The emission spectra of thiourea monomers (SBT and CBT) and polythioamides (PSB and PCB) were recorded in DMSO solvent and all the compounds showed fluorescence color emissions. The Stokes shifts (λ_{em}–λ_{ex}) were also estimated for their emission in visible region, which is the wavelength difference between positions of λ_{max} (band maxima) in emission and λ_{max} in absorption spectra. The results of spectrofluorometric measurements are provided in Table 1. The thiourea monomer SBT indicated violet (408 nm) and red (686 nm) light emissions at excitation 258 nm, violet light (411 nm) emission at excitation 294 nm, and violet (414 nm) and green (532 nm) light emissions at excitation 311 nm (Figure 6a-c). The thiourea CBT indicated violet (417 nm), yellow (565 nm) and red (659 nm and 677 nm) light emissions at excitation 283 nm, and violet (417 nm), orange (616 nm) and red (683 nm) light emission at excitation 307 nm (Figure 6d, e). The polythioamide PSB indicated violet light (416 nm) emissions at excitations 309 and 294 nm (Figure 7a, b), while polythioamide PCB indicated yellow (571 nm) and red light (660 nm) emissions at excitation 285 nm (Figure 7c). The thiourea monomer SBT, polythioamide PSB and polythioamide PCB indicated fluorescence emissions due to the presence of aromatic rings in conjugation with the hetero atoms (nitrogen, oxygen and sulfur) in their structures.[25,26,31–33] However, thiourea monomer CBT indicated multi-color fluorescence emissions, despite the absence of aromatic rings in its structure, these unexpected fluorescence emissions were observed due to the presence of closely assembled hetero atoms (nitrogen and sulfur) containing lone pair of electrons. The emission maxima of the compounds depends upon the formation of molecular aggregates through hydrogen bonding and n → π* interaction between thioamide groups.[1,7,33] The polythioamide PSB showed smaller Stokes shifts (107 and 122 nm) as compared to polythioamide PCB (286 and 375 nm), which indicates its lower vibrational relaxations and strong inter-

Table 1. Spectrofluorometric studies of thiourea monomers (SBT and CBT) and polythioamides (PSB and PCB) in DMSO solvent.

S. No	Compound	Concentration (μg/ml)	λ_{ex} (nm)	λ_{em} (nm)	Relative emission intensity	Color of emission	Stokes shift (nm) (λ_{em}–λ_{ex}) of visible region
1	SBT	166.6	258	408	24	violet	150
				686	0.9	red	428
			294	411	23.12	violet	117
			311	414	20	violet	103
				532	2.22	green	221
2	PSB	166.6	294	416	15.3	violet	107
			309	416	16	violet	122
3	CBT	416.6	283	350	1016	–	–
				417	167	violet	134
				565	66	yellow	282
				659	118	red	376
				677	119	red	394
			307	344	463	–	–
				417	211	violet	110
				616	39	orange	309
				683	41.5	red	376
4	PCB	166.6	285	340	642	–	–
				571	6.9	yellow	286
				660	57.5	red	375

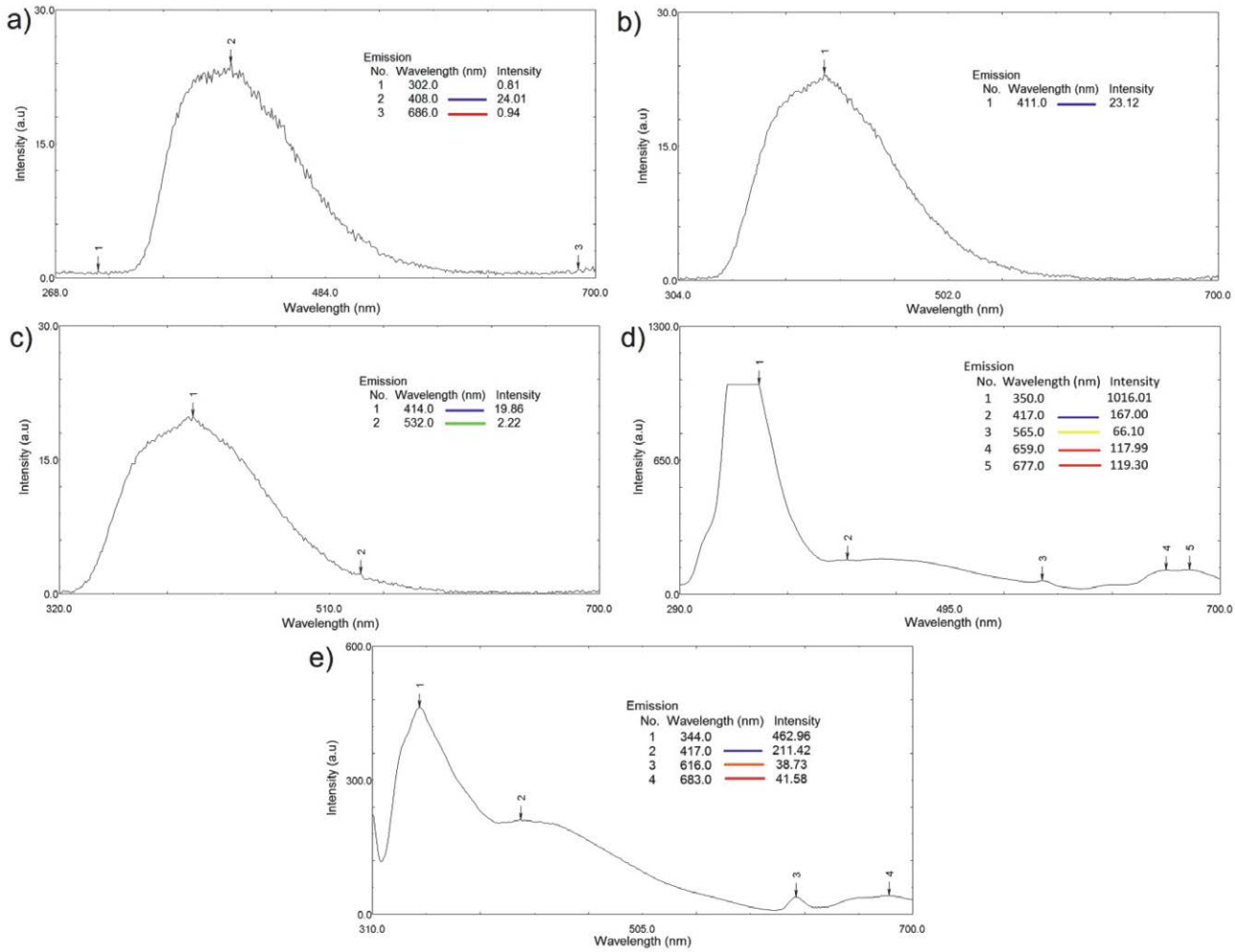

Figure 6. Emission spectra of thiourea monomers SBT and CBT: **a** SBT at excitation 258 nm **b** SBT at excitation 294 nm **c** SBT at excitation 311 nm **d** CBT at excitation 283 nm and **e** CBT at excitation 307 nm.

molecular packing due to the existence of large number of rigid aromatic rings in PSB structure,[34,35] while polythioamide PCB contains flexible rings of cyclohexane in addition to aromatic rings, the presence of cyclohexane rings makes its structure less rigid.

3. 9. Scanning Electron Microscopy

The SEM image of thiourea monomer SBT noted at 500 μm indicated rugged surface morphology (Figure 8a) and the SEM image of its corresponding polythioamide PSB recorded at 20 μm also revealed rugged surface with intermittent gaps. The average area covered by these gaps was 19.8 μm^2 (Figure 8b). Polythioamide PSB can be employed as an adsorbent material because of the presence of these gaps. The SEM images of thiourea CBT recorded from 10 μm to 1 μm showed clusters of needle shaped crystalline particles of different lengths. The average length of these particles was 3.12 μm, the mean diameter of these particles was 0.21 μm and the average area of the interparticle voids (empty spaces between particles) was 1.15 μm^2 (Figure 9a, b). The SEM images of its resulting polythioamide PCB recorded from 10 μm to 1 μm displayed irregular shaped non-porous particles. The average length of these particles was 23.16 μm, the average area of these particles was 314 μm^2 and the average area of the interparticle voids was 31 μm^2 (Figure 9c, d). The existence of interparticle voids in thiourea CBT and polythioamide PCB makes them potentially effective adsorbent materials by providing greater surface area for adsorption and by facilitating the accessibility of adsorbates to the active sites within the material. The surface morphology of the polythioamide PSB showed larger interparticle voids as compared to its corresponding monomer CBT. The variations between the surface morphology of thiourea monomers (SBT and CBT) and their derived polythioamides (PSB and PCB) were due to the inclusion of $–COC_6H_5CO–$ moiety in the structures of polythioamides. The synthesized polythioamides can be applied as adsorbents due to the presence of interparticle voids.

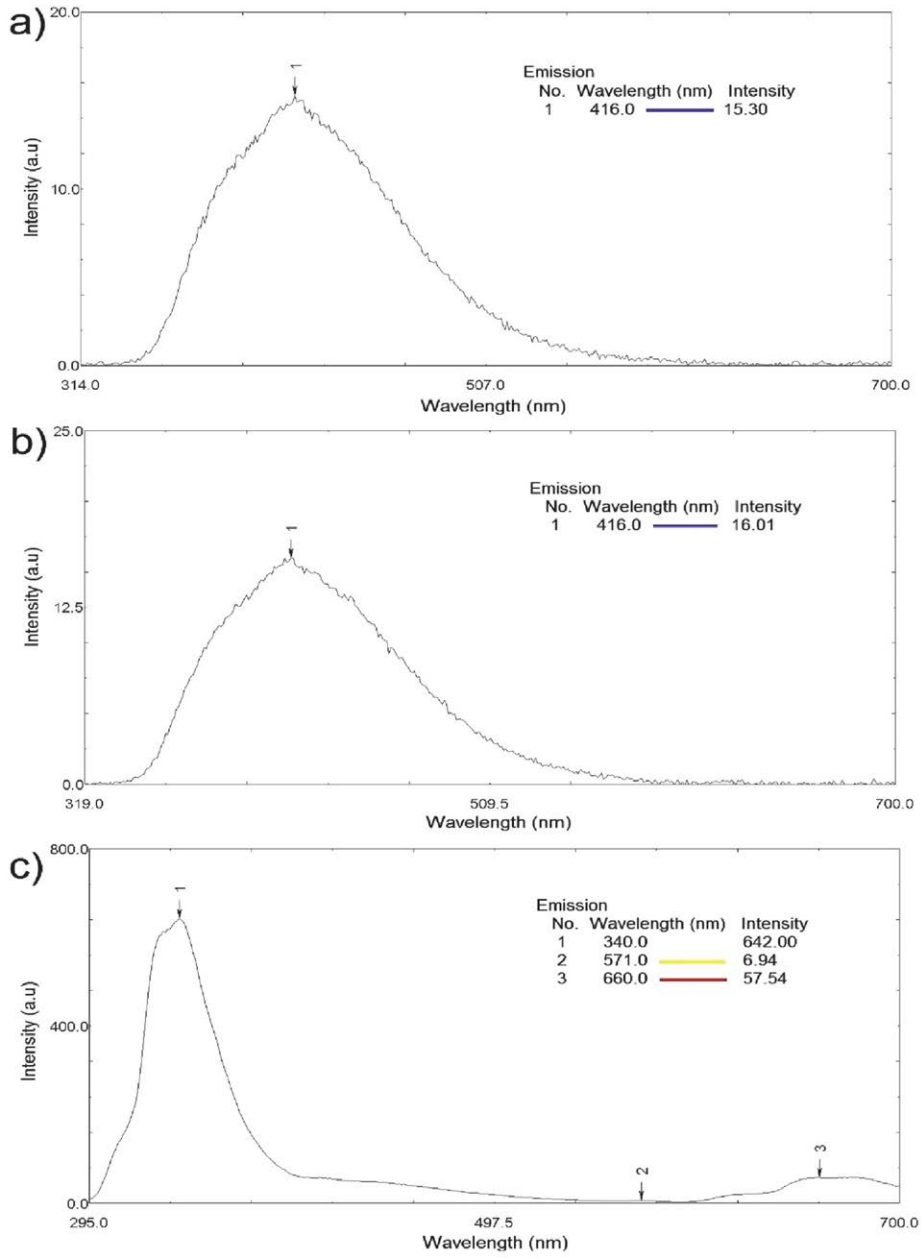

Figure 7. Emission spectra of polythioamides PSB and PCB: **a** PSB at excitation 294 nm **b** PSB at excitation 309 nm and **c** PCB at excitation 285 nm.

3. 10. Thermal Analysis

The TGA/DTA graphs of the compounds were recorded in nitrogen atmosphere and all the results are given in Table 2. The thermal stability of the compounds was estimated from the T_{max} (temperature indicating highest rate of weight loss) value obtained from their DTG graphs. TGA of thiourea SBT recorded four stages of wt. loss (weight loss) with 5% wt. loss within 38–190 °C due to the loss of water and volatile organic solvents, 13% wt. loss within 191–311 °C was due a thioamide ($NH_2C{=}S$) group, 36% wt. loss within 312–475 °C owing to loss of thioamide groups, leaving behind $C_6H_5SO_2C_6H_5$ and 46% wt. loss within 476–770 °C due to complete loss in weight. DTG indicated T_{onset} at 188 °C and T_{max} was noted at 448 °C. DTA of SBT indicated an endotherm at 221 °C for vaporization/decomposition, exotherm at 367 °C for vaporization/decomposition, endotherm at 510 °C for vaporization/decomposition and a large exotherm at 687 °C for decomposition (Figure 10a). TGA of polythioamide PSB showed three stages of wt. loss, 24% wt. loss indicated within 132–325 °C may be due to decomposition of HN–C(=S)NH–/–C(=O)C_6H_5C(=O) groups, 28% wt. loss within 326-513˚C may be attributed to the decomposition of –C_6H_5–(O=S=O)–C_6H_5–/–HN–C(=S)NH–C(=O)C_6H_5C(=O)- and 39% wt. loss within 514–689 °C due to complete decomposition. DTG indicated T_{onset} at 132

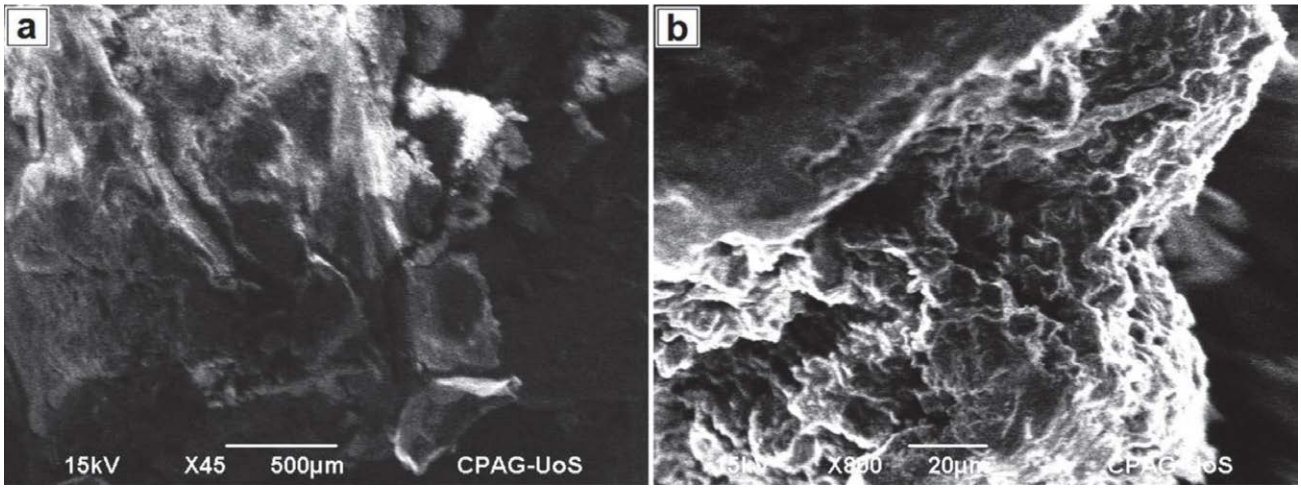

Figure 8. SEM images of thiourea monomer SBT and its corresponding polythioamide PSB: **a** SBT at 500 µm and **b** PSB at 20 µm.

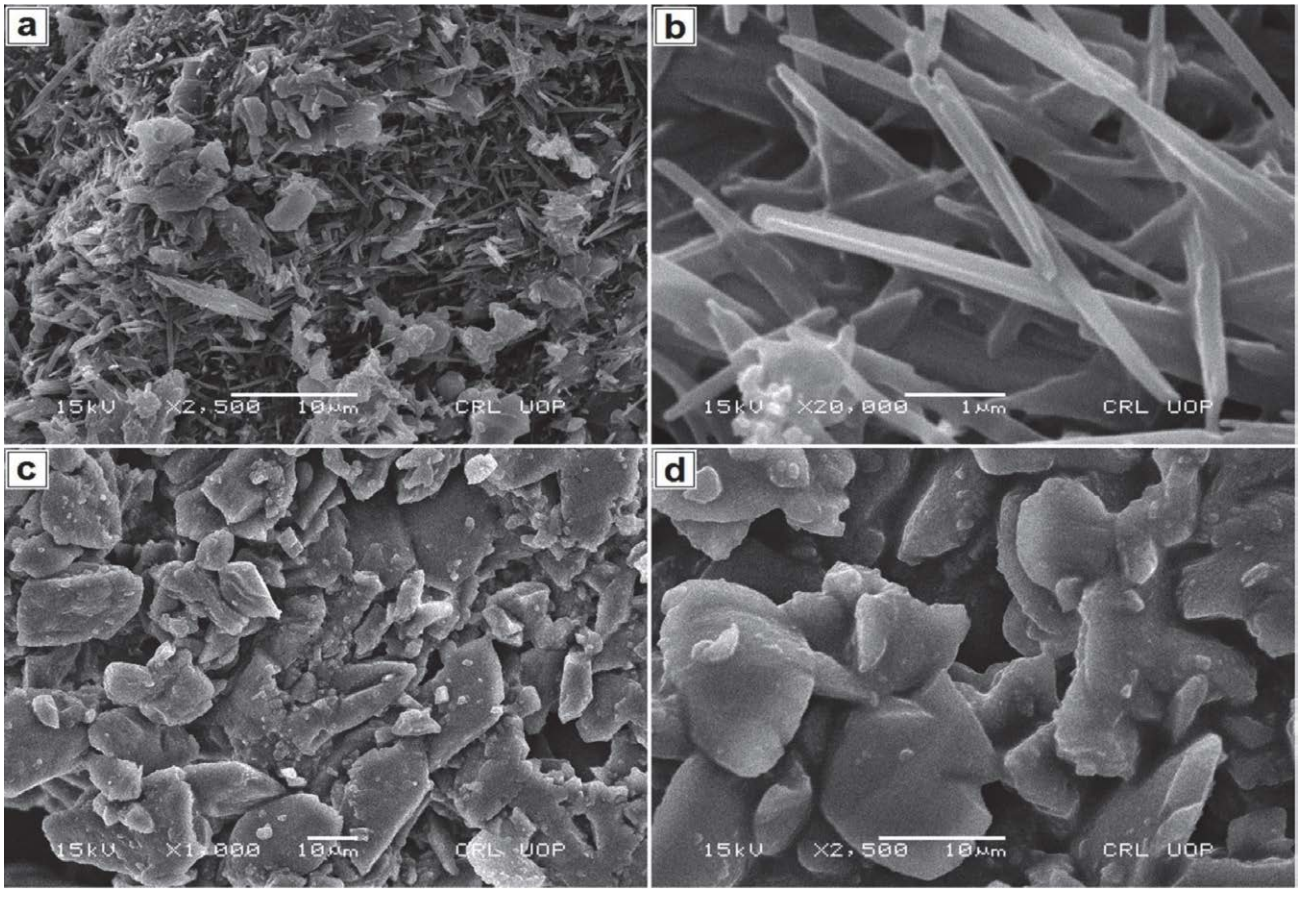

Figure 9 SEM images of thiourea monomer CBT and its derived polythioamide PCB: **a** CBT at 10 µm, **b** CBT at 1 µm and **c, d** PCB at 10 µm.

Table 2. Thermal analysis results of polythioamides (PSB and PCB).

Compound	TGA			DTG		DTA	
	Stages of weight loss			T_{onset} °C	T_{max} °C	Endo °C	Exo °C
	I	II	III				
	Weight loss % (temperature range°C)						
PSB	24 (138–325)	28 (326–513)	39(514–689)	132	670	296	449, 660
PCB	65 (205–353)	5 (354–498)	–	262	346	345, 427	209, 368, 470

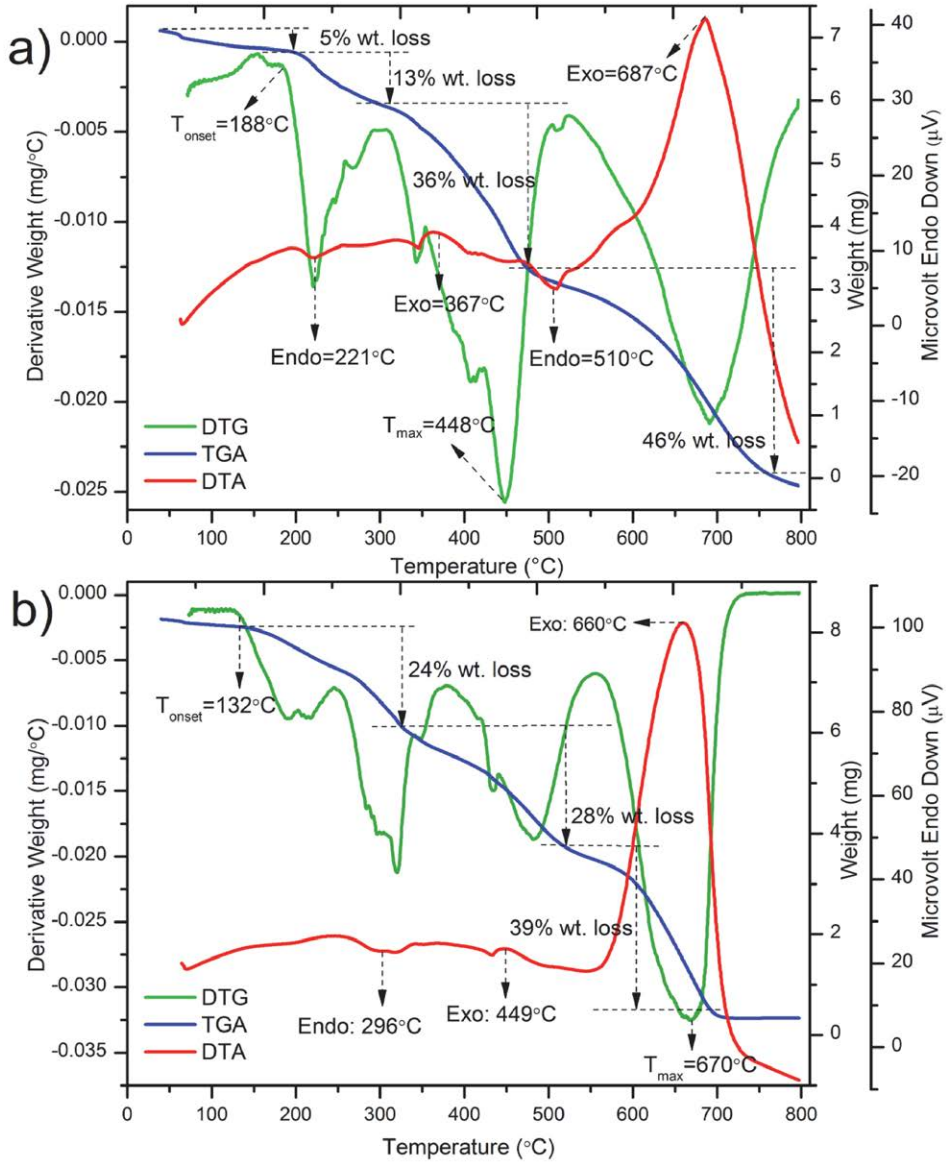

Figure 10. TGA/DTG/DTA graphs of **a** thiourea SBT and **b** polythioamide PSB.

°C and T_{max} was found at 670 °C. The T_{max} value of polymer PSB was higher than the monomer SBT. DTA of polythioamide PSB displayed small endotherm at 296 °C for melting, exotherm at 449 °C for vaporization/decomposition and one large decomposition exotherm at 660 °C (Figure 10b). TGA of polythioamide PCB recorded two stages of wt. loss with 65% wt. loss within 205–353 °C due to decomposition of $-C_6H_5-/-HN-C(=S)NH-C(=O)C_6H_5C(=O)$ and 5% wt. loss within 354–498 °C due to complete decomposition. DTG showed T_{onset} at 262 °C and T_{max} at 346 °C. DTA of PCB indicated an exotherm at 209 °C for vaporization, endotherm at 345 °C for vaporization/decomposition, exotherm at 368 °C owing to vaporization/decomposition, endotherm at 427 °C because of melting, and an exotherm at 470 °C due to decomposition (supplementary Fig. S4).

3. 11. Antimicrobial Activities

The synthesized thiourea monomers (SBT and CBT) and polythioamides (PSB and PCB) were tested for their antibacterial and antifungal functions against various strains of bacteria and fungi. All the compounds showed antibacterial function against *Salmonella typhi*, *Bacillus subtilis* and *Staphylococcus aureus*, while no activity was reported for *Escherichia coli* and *Pseudomonas aeruginosa*. The results of antibacterial assay are presented in Table 3. All the compounds showed antifungal activity against *Candida albicans*. The thiourea SBT, polythioamide PSB, thiourea CBT and polythioamide PCB indicated 20%, 15%, 15% and 20% inhibition against *Candida albicans* respectively. The polythioamide PCB showed 20% inhibition against *Fusarium lini*, while others (SBT, PSB and CBT)

did not indicate inhibition against *Fusarium lini*. The synthesized compounds did not show inhibition against *Aspergillus niger*, *Trichophyton rubrum* and *Microsporum canis*.

Table 3. Results of antibacterial functions of thiourea monomers and polythioamides.

Compound	% inhibition of thioureas (SBT and CBT) and polythioamides (PSB and PCB) against bacterial strains compared with Ofloxacin (standard drug)		
	Salmonella typhi	***Bacillus subtilis***	***Staphylococcus aureus***
SBT	7.5%	18.5%	3.7%
PSB	7.4%	13%	11%
CBT	12%	9.6%	27.5%
PCB	1.85%	7.4%	10%
Ofloxacin	94.09%	92.57%	83.01%

4. Conclusion

Two new polythioamides (PSB and PCB) were synthesized through polycondensation reaction of thiourea monomers (SBT and CBT) with terephthaloyl dichloride. The synthesized compounds were achieved in high yield (70–92%). The polythioamides PSB and PCB were completely soluble in DMSO and DMF without heating. The structures of thiourea monomers and polythioamides were analyzed and confirmed by different characterization techniques. All the synthesized thioureas and polythioamides were thermally stable and indicated multicolor fluorescence emission, therefore they can be employed as heat-resistant and fluorescent materials in different industrial and engineering fields. The antibacterial activities of the synthesized thioureas and polythioamides were found within the range of 1.85–27.5% against *Salmonella typhi*, *Bacillus subtilis* and *Staphylococcus aureus*. All the synthesized compounds indicated 15 or 20% antifungal activity against *Candida albicans* and the polythioamide PCB also indicated 20% antifungal activity against *Fusarium lini*.

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Povzetek

Pripravili smo dva nova politioamida s polikondenzacijsko reakcijo med monomeri tiosečnine in tereftaloil dikloridom. Monomere tiosečnine smo sintetizirali z reakcijo med aromatskim (4,4'-diaminofenilsulfona) ali alicikličnim (1,2-cikloheksandiamin) diaminom z amonijevim tiocianatom. Elementno sestavo politioamidov smo potrdili z mikroanalizo CHN. Struktura in lastnosti monomerov tiosečnine in politioamidov so bile določene s protonsko NMR, UV-VIS, FT-IR spektroskopijo, fluorescenco, TGA/DTA in SEM. Politioamidi so pokazali visoko toplotno stabilnost, ki je bila ocenjena na podlagi njihovih vrednosti T_{max} (temperatura, ki kaže najvišjo stopnjo izgube teže; 670 °C in 346 °C), opaženih v DTG grafih (derivativne termogravimetrije). Tiosečnine in politioamidi so fluorescirali in pokazali večbarvne (vijolične, zelene, rumene, oranžne in rdeče) emisije pri različnih valovnih dolžinah vzbujanja. Vse sintetizirane spojine so bile testirane tudi na podlagi njihovih protiglivičnih in antibakterijskih funkcij in so pokazale antibakterijsko delovanje proti *Salmonella typhi*, *Bacillus subtilis* in *Staphylococcus aureus* ter protiglivično delovanje proti *Candidi albikans*.