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ORIGINAL PAPER

Synthesis and characterization of novel thermally stable aromatic and semiaromatic polyamides derived from thiourea-based flexible diacid dichlorides

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Abstract New diacid dichlorides bearing phenyl thiourea groups were prepared by a facile synthetic approach and characterized using spectroscopic and elemental analyses. A series of novel aromatic and semiaromatic polyamides were prepared via a condensation route from the synthesized diacid dichlorides with 4,4′-oxydianiline. The polymers were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and their physical properties, including their solution viscosities, solubilities and thermal properties, were studied too. Polyamides with phenyl thiourea moieties in the backbone showed good solubilities in amide solvents such as DMAc, DMF, DMSO, and NMP. All of the synthesized polymers had η_{inh} values of 0.042–0.053 dm^3/g, and were obtained in quantitative yield. GPC measurements of the synthesized polyamides indicated M_{w} values of 64,759–86,172. The crystallinity of the polymers was evaluated via their X-ray diffraction patterns. Their glass transition temperatures were found to be 218–229 °C. Furthermore, thermogravimetric analysis indicated that the polymers were thermally stable in the range 300–398 °C in a N_2 atmosphere.

Keywords Phenyl thiourea groups · Polyamides · Diacid dichloride · IR spectroscopy · NMR spectroscopy · Condensation

Introduction

Polyamides that are stable at high temperatures and have a favorable balance of physical and chemical properties are increasingly in demand as performance materials for industrial and aerospace applications [1, 2]. However, difficulties are encountered when processing these polymers into articles due to their high melting and glass transition temperatures and their limited solubilities in common organic solvents. Processable engineering plastics possessing moderately high softening temperatures and solubilities in some organic solvents are required for practical use. Aromatic polyamides have generally proven to be difficult in this respect, since they show a tendency to decompose during or even before melting, and have limited solubility [3–6]. Consequently, efforts to chemically modify the compositions of these materials are being made with the objective of improving their processability. The major factors that account for the low solubility of aromatic polyamides are molecular order and strong interchain attractive forces—mainly hydrogen bonding, which enhances the molecular packing. Consequently, it is acknowledged that the incorporation of bulky pendant groups is beneficial to solubility, because this approach separates the chains, weakens hydrogen bonding, and lowers chain packing, while gaining free volume. Accordingly, bulky side groups restrict molecular mobility, so that the overall observable effect is a rise in the glass transition temperature and an improvement in the solubility (processability) [7–12]. Furthermore, it has been shown that the incorporation of flexible linkages into the main polymer chain greatly enhances molecular mobility and provides better solubility, but it decreases thermal transitions and stability [13, 14]. For this reason, a number of attempts have been made to enhance the processability of polyamides without

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incurring any significant reduction in thermal stability [15–17].

The introduction of the thiourea group into the polyamide backbone as a flexibilizing agent is a relatively unexplored area. The thiourea group introduces additional features like biomedical activity [18], corrosion inhibition [19–22], organic thermal stabilization [23], and semiconductivity [24, 25]. Moreover, thiourea-based coordinating polymers have been synthesized that can potentially be used to bind to noble metals [26]. In this study, the deliberate incorporation of phenyl thiourea groups into the polymer backbone enhanced the solubility and processability of polyamides without any significant reduction in thermal stability. It was shown that thiourea moieties undermine the packing efficiency of polyamides by forming flexible intermolecular hydrogen-bonding networks. This prompted us to synthesize a new series of polyamides bearing both carbonyl and thiocarbonyl moieties, with the objective of obtaining new multifunctional polymers. Thus, poly(thiourea amides) possess multiple hydrogen-bonding interactions because thiocarbonyl is capable of participating in weaker intermolecular hydrogen bonds (C=S···H) than amide carbonyl (C=O···H). The present work aimed to create processable polyamides with improved solubility while conserving the thermal stability of the polyamides at a high level. Aromatic and semiaromatic (aromatic–aliphatic) polyamides with phenyl thiourea groups in the backbone were successfully synthesized from two wholly aromatic diacid dichlorides [isophthaloyl bis(3-(3-chlorocarbonylphenyl)thiourea) and terephthaloyl bis(3-(3-chlorocarbonylphenyl)thiourea)] and two semiaromatic [adipoyl bis(3-(3-chlorocarbonylphenyl) thiourea) and sebacoyl bis(3-(3-chlorocarbonylphenyl) thiourea)] diacid dichlorides using a solution polycondensation [27] procedure. All monomers and polymers were characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR. Attention was focused upon polymer properties such as thermal stability, thermal properties, crystallinity, solubility behavior, inherent viscosity, as well as molecular weight.

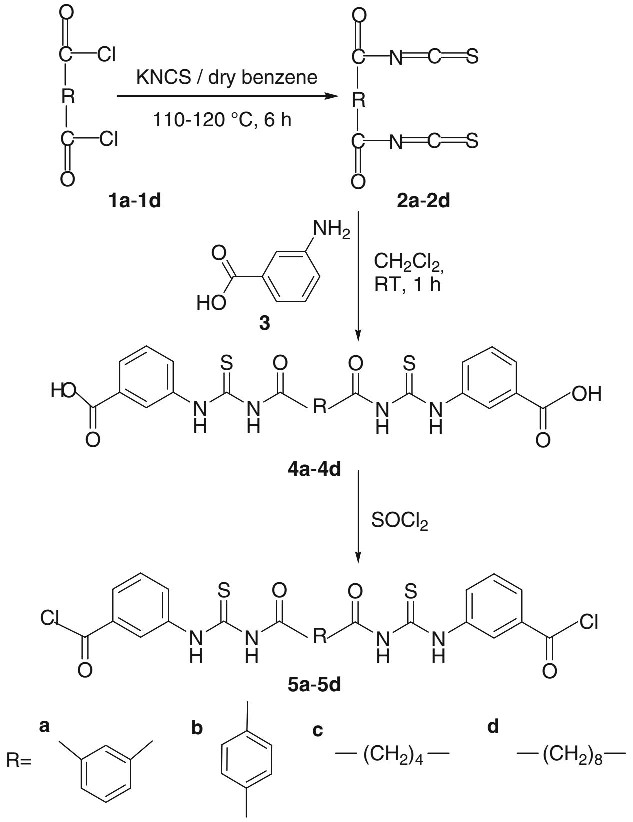
Results and discussion

Monomer and polymer synthesis

The new aromatic and semiaromatic polyamides **7a–7d** containing thiourea units were synthesized from new diacid dichloride monomers (Scheme 1). Initially, the synthesis of dicarboxylic acids **4a–4d** was accomplished using diisothiocyanate compounds **2a–2d**, which on treatment with thionyl chloride yielded corresponding diacid dichlorides **5a–5d**. The synthetic route leading to **7a–7d** is depicted in Scheme 2. The basic reaction employed here is the condensation [27] of an aromatic acid chloride and an amine, which is generally known to be fast and quantitative.

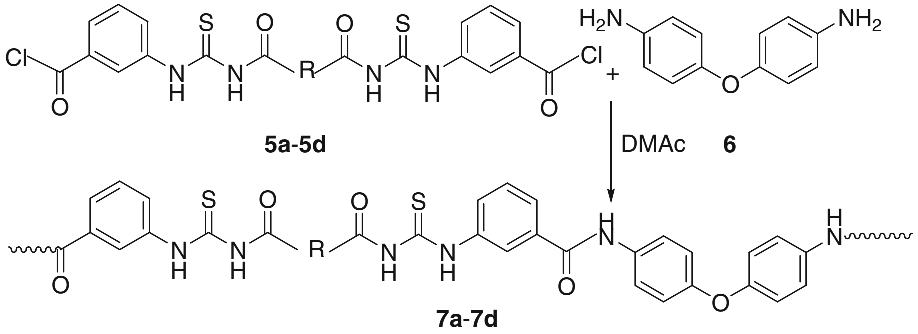
The main objective of this study is to produce modified polyamides with improved solubility and processability without deteriorating their thermal properties. The polymerization technique used in this work is relatively simple, and produced polymers in satisfactorily high yields and with fairly good η_{inh} values and molecular weights (M_w). Generally, these polymers were yellow in color owing to the presence of phenylthiourea groups in the polymer backbone. The structures of the synthesized polyamides were investigated by FT-IR and NMR spectroscopic techniques. The thermal stabilities, T_g values, and crystallinities of **7a–7d** were also studied using the corresponding techniques, as described below.

The main structural modification of **7a–7d** was the introduction of thiourea linkages in polymers backbones to augment their solubilities while retaining their thermal stabilities. These thiourea moieties interrupted their intermolecular hydrogen bonding, and degraded their stacking efficiency. Hence, multiple hydrogen-bonding interactions (C=S···H and C=O···H) were observed in the poly(thiourea amides), as depicted in Scheme 3 [28]. Moreover, previous research suggested that thioureas have improved

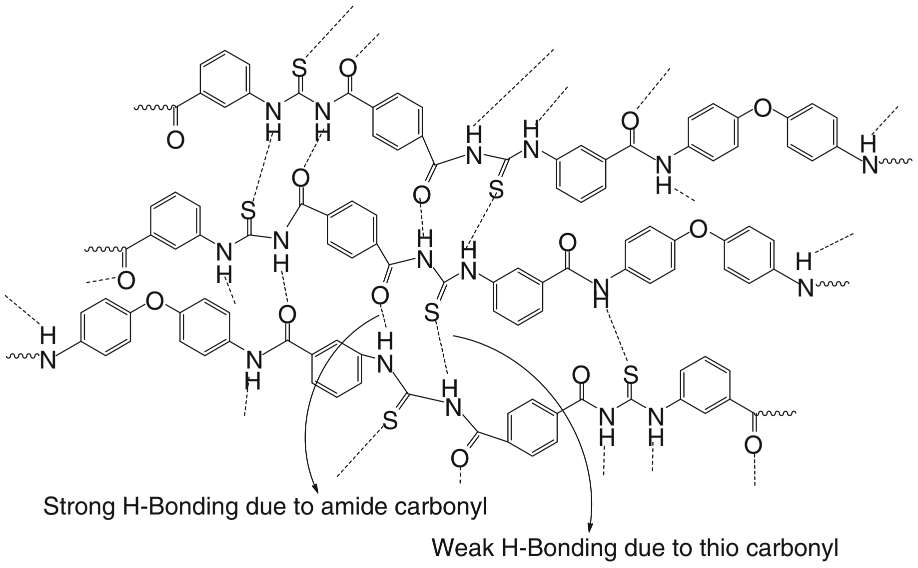


Scheme 1

Scheme 2



Scheme 3



properties as hydrogen-bond donors, form more flexible hydrogen-bonding networks, and show a lower tendency to self-associate than the corresponding urea analogs. Concisely, the introduction of the C=S units into polyamides **7a**–**7d** led to enhanced solubility and a relatively high T_g owing to the resulting reduction in segmental mobility as well as the increased steric hindrance. Thus, a vigilant investigation revealed that the introduction of C=S groups in order to increase the solubility and processability of polyamides was successful.

Table 1 Solubility characteristics of the polyamides

Polymer	Solvent					
	NMP	DMAc	DMF	DMSO	THF	*m*-Cresol
7a	++	++	++	++	−	+−
7b	++	++	++	++	−	+−
7c	++	++	++	++	−	+−
7d	++	++	++	++	−	+−

Solubility: ++ soluble at room temperature; +− partially soluble at room temperature, − insoluble

Organosolubility

All of the investigated polymers were found to be highly soluble in common organic polar solvents such as DMAc, DMSO, NMP, and DMF at room temperature (Table 1). The solubility was evaluated with 15 mg of the polymer in 1 cm^3 of the solvents at room temperature. In general, high solubility is desirable for polymer processing. The good organosolubility of the polyamides can be attributed to the presence of the flexible thiourea groups in the polymer framework. Furthermore, the presence of the flexible ether group in the diamine moiety also had a beneficial effect on the solubilities of the polyamides. It was also established that the semiaromatic polyamide **7d** with the longest alkyl chain dissolved much more quickly at room temperature than the aromatic polyamides **7a** and **7b** which have rigid chain structures. The solubilities of the polymers follow the order:

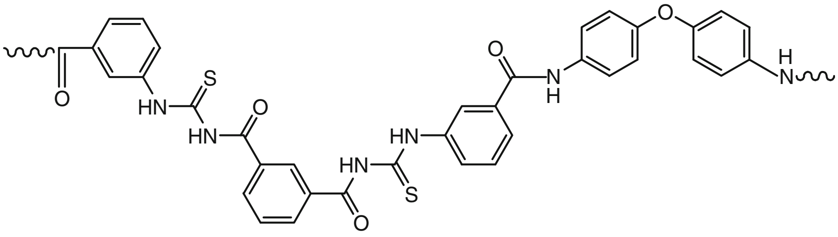
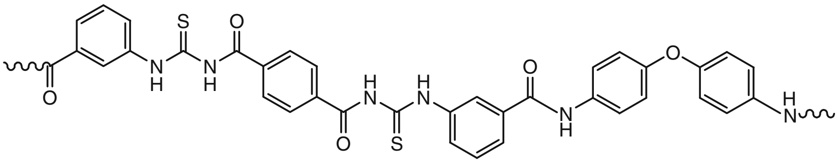
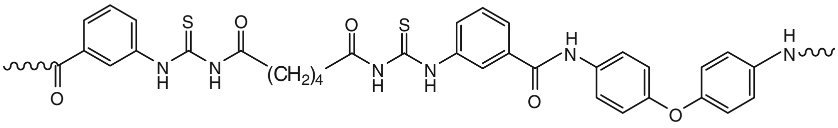
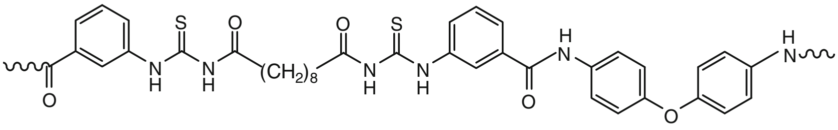
7**d** > 7**c** > 7**a** > 7**b**.

Regardless of the nature of the solvent used, it was perceived that **7a**—with all *m*-linkages—appeared to be rapidly soluble when compared with **7b**, which contains both *m*- and *p*-linkages. In addition, **7b** formed viscous solutions, even at low concentrations. This behavior indicates that the *p*-oriented type of polymer possesses increased rigidity, packing efficiency, and hydrogen bonding. Likewise, it was observed that the incorporation of flexible thiourea units into the polymer backbone causes a decrease in crystallinity and enhances the solubility and processability of aromatic as well as semiaromatic polyamides.

Viscometry and molecular weight

The η_{inh} values of polyamides measured at a concentration of 0.5 g/100 cm^3 in DMSO at 30 °C were about 0.042–0.053 dm^3/g (Table 2). It was found that the aromatic polyamides possess higher η_{inh} values, which indicates that their polymer chains are more rigid. On the other hand, η_{inh} decreased with the incorporation of alkyl groups into the diacid dichlorides **5c** and **5d** when compared with **7a** and **7b**. Accordingly, the polyamide **7b** with *p*-linkages yielded the highest η_{inh} (0.053 dm^3/g), whereas **7d**, which has the longest alkyl chain, produced the lowest viscosity of 0.042 dm^3/g. Furthermore, the polyamide **7a**, which only has *meta* linkages, had an intermediate η_{inh} value of 0.050 dm^3/g (i.e., in-between these two extreme values). The higher inherent viscosity value of the *p*-oriented type of polymer was attributed to its higher rigidity and its increased interchain hydrogen bonding, which are associated with higher chain symmetry and packing efficiency. Additionally, GPC measurements during the molecular weight analysis of **7a**–**7d** supported the above arguments. The weight-average M_w values and the polydispersity indices determined by GPC are specified in Table 2. The M_w values of about 86,172–64,759 indicate that **7a**–**7d**, which bear C=S moieties, have fairly high molecular weights. Correspondingly, **7b**, which has *p*-oriented rigid

Table 2 η_{inh} and M_w values as well as the yields of **7a**–**7d**

Polymer	η_{inh} (dm^3/g)	M_w	M_w/M_n	Yield (%)
 **7a**	0.050	82,789	1.42	94
 **7b**	0.053	86,172	1.35	96
 **7c**	0.044	71,763	1.43	95
 **7d**	0.042	64,759	1.45	95

units in the backbone, exhibited the highest M_w value of 86,172.

Thermal analyses

The DSC and TGA techniques were used to study the thermal behaviors and thermal properties of **7a–7d** (Table 3). These properties were followed in N_2 at a heating rate of 10 °C/min. The T_g values (where T_g taken as the midpoint of the change in slope of the baseline) of **7a–7d** were between 218 and 229 °C, and the representative DSC curves are shown in Fig. 1.

It appeared that the T_g values of **7a–7d** were dependent on the chemical structures of the diacid dichlorides **5a–5d**. In view of this, **7b** exhibited the highest T_g value because of the *p*-oriented aromatic nature of its rigid polymer backbone. On the other hand, **7d**, which was derived from the aliphatic diacid dichloride **5d**, showed the lowest T_g value due to its long, flexible alkyl groups. As a general rule, when the crystallinity of a polymer increases, its heat resistance also increases. For this reason, these results were also corroborated by X-ray diffraction patterns of **7a–7d**. Polyamide **7b**, which has high thermal properties, displayed a crystalline pattern, whilst **7c** and **7d** showed amorphous behavior (Fig. 4).

Table 3 Thermal analysis data of **7a–7d**

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Y_c at 600 °C (%)
7a	222	338	380	552	59
7b	229	350	398	576	66
7c	219	282	319	530	49
7d	218	274	300	528	40

T_g glass transition temperature, T_0 initial decomposition temperature, T_{10} temperature required for a 10% weight loss, T_{max} maximum decomposition temperature, Y_c char yield; weight of polymer remaining

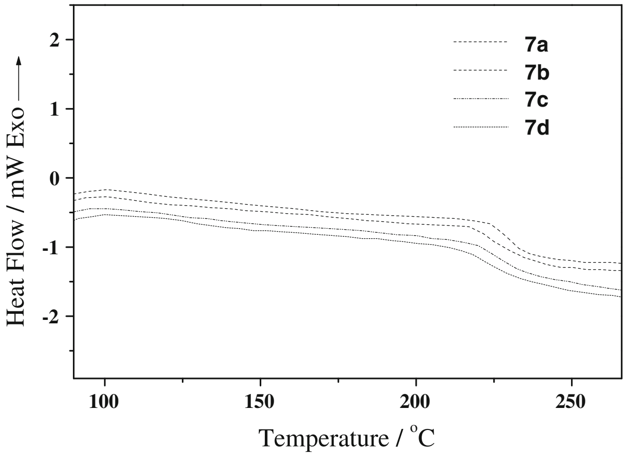


Fig. 1 DSC thermograms of **7a–7d** obtained at a heating rate of 10 °C/min in N_2

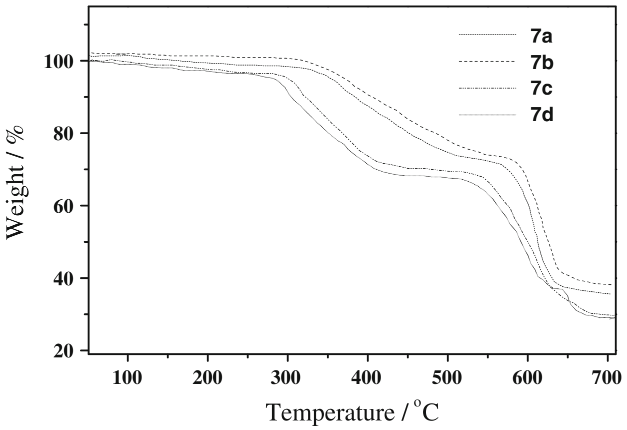


Fig. 2 TGA curves of **7a–7d** obtained at a heating rate of 10 °C/min in N_2

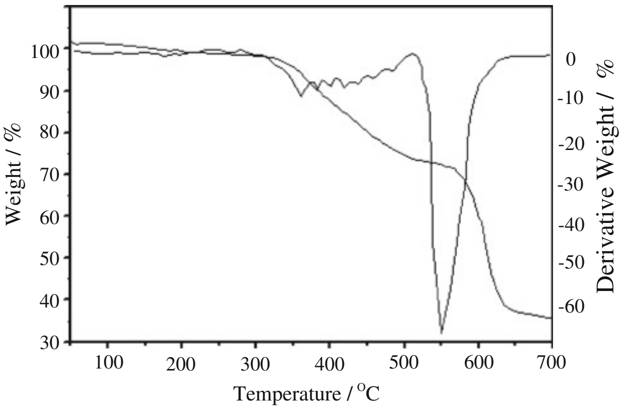


Fig. 3 TGA and DTG thermograms of **7a**

According to the TGA data, the initial decomposition temperatures (T_0) were about 274–350 °C, and the temperatures for 10% gravimetric loss (T_{10}, which is an important indicator of thermal stability) were in the range of 300–398 °C (Fig. 2). Subsequently, the maximum decomposition temperatures (T_{max}) were about 528–576 °C, and the char yields of **7a–7d** (600 °C) were around 40–66%. T_{max} values for **7a–7d** were evaluated from DTG thermograms, as illustrated in Fig. 3.

Moreover, **7a–7d** illustrated a double-step decomposition pattern from 300 to 600 °C, indicating a complex degradation mechanism. Apparently, the flexible thiourea group and the electrophilic oxygen atom in **6** allow looser molecular packing, resulting in improved solubility in organic solvents without degrading the thermal properties of **7a–7d**.

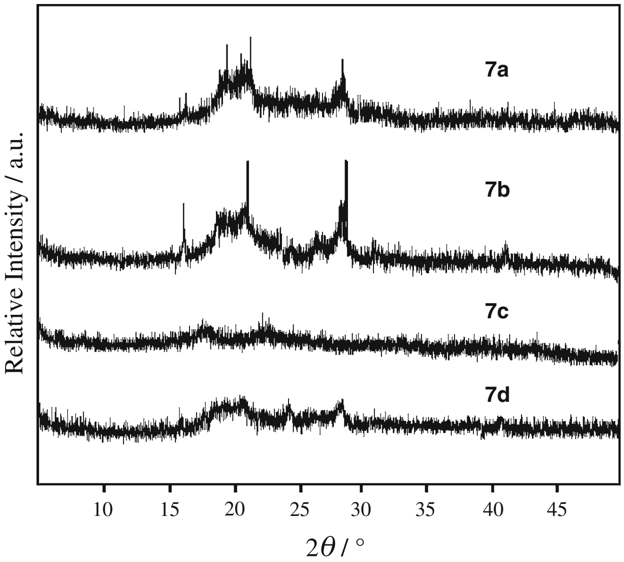


Fig. 4 X-ray diffraction patterns of **7a**–**7d**

X-ray diffraction

X-ray diffraction scans with 2θ ranging from 5° to 50° for powder specimens were obtained for the synthesized polyamides (Fig. 4). Certain sharp peaks were observed in the X-ray diffractrogram of **7b** in the region $2\theta = 16–30°$. The crystalline morphology of **7b** may be related to the rigidity of the *p*-phenylene structure, a hypothesis supported by its higher thermal stability. However, the XRD pattern for **7a** revealed small crystalline peaks at around 20° and 28°, which demonstrated a small degree of crystallinity. Nevertheless, the semiaromatic polyamides **7c** and **7d** showed almost amorphous behavior. This is because the presence of an aliphatic group in addition to the flexible ether group in **6** reduce intermolecular forces between the polymer chains, causing a decrease in crystallinity. On the whole, new wholly aromatic polyamides gave crystalline patterns, whereas semiaromatic polyamides showed amorphous behaviour.

Conclusions

The design and synthesis of the novel diacid dichlorides **5a**–**5d** that could be used in the preparation of thermally stable polyamides with improved solubility was our main aim. Consequently, **5a**–**5d** were successfully prepared in high yield from dicarboxylic acids **4a**–**4d** in the presence of $SOCl_2$. In the present study, a series of aromatic and semiaromatic polyamides **7a**–**7d** were synthesized by solution polycondensation of diacid dichlorides containing phenyl thiourea units and commercially available diamines. A nice balance of properties (thermal stability versus solubility) was observed for these polyamides. The incorporation of thiourea groups into the polymer backbones in order to enhance the solubility and processability of the polyamides without significantly reducing the thermal stability was achieved. The properties of the polymers were strongly affected by their structures; the incorporation of aliphatic units in the place of aromatic ones within the polymers greatly affected their physical and thermal properties. In general, it was established that the introduction of *p*-phenylene rings led to polymers with higher thermal stabilities, η_{inh} values, and molecular weights. These properties indicated the regularity of the supermolecular packing occurring within the bulk of polymer in addition to the collinear arrangement of the *p*-phenylene units, which permits the establishment of stronger interchain hydrogen bonding. On the other hand, semiaromatic polyamides with aliphatic contents exhibited lower thermal stabilities, η_{inh} values, and molecular weights, indicating an overall flexibility of the polymer chains. Therefore, **5a**–**5d** can be considered candidates for the preparation of soluble and heat-resistant polyamides. Furthermore, this novel series of multifunctional poly(thiourea amides) can be exploited as potentially excellent candidates in supramolecular chemistry due to their specific interactions with biologically important anions [32, 33], in addition to their potential use as ideal supports for immobilized enzymes and to bind to noble metals.

Experimental

Materials

3-Aminobenzoic acid (**3**, 97%), isophthaloyl chloride (**1a**, 98%), terephthaloyl chloride (**1b**, 99%), potassium thiocyanate (98%), and dimethylformamide (DMF, 99%), all procured from Fluka, were used. *N*-Methylpyrrolidone (NMP, 99%), dimethyl sulfoxide (DMSO, 99%), and benzene (99%) were purchased from Merck. 4,4′-Oxydianiline (**6**, 97%), adipoyl chloride (**1d**, 98%), sebacoyl chloride (**1c**, 92%), and *N*,*N*-dimethylacetamide (DMAc, 99%), all obtained from Aldrich, were used as received.

Measurements

IR spectra of the monomers and polymers were obtained at room temperature at a resolution of 4 cm^{-1} using an Excalibur Series FTIR spectrometer, model No. FTSW 300 MX, manufactured by Bio-Rad. NMR spectra were recorded at room temperature using a Bruker spectrometer operating at 300.13 MHz for ^1H and at 75.47 MHz for ^{13}C NMR. The solvent used in the analysis was DMSO-d_6. Elemental analysis was performed using a PerkinElmer

2400 CHN elemental analyzer; found values agreed favorably with calculated ones. Inherent viscosity (η_{inh}) was measured in DMSO at 30 °C with an Ubbelohde viscometer for polymer solutions at concentrations of 0.5 g/100 cm^3. Gel permeation chromatography (GPC) analysis was carried out with Waters Alliance GPCV2000 for molecular weight determination. Polystyrene was employed as the standard and THF was used as an eluent. The eluents were monitored with a refractive index (RI) detector. Qualitative solubility was determined with 15 mg of polymer in 1 cm^3 of various solvents at room temperature. Thermal stability of the polyamides was determined by Mettler Toledo TGA/SDTA 851^e thermogravimetric analyzer using 1–5 mg of the sample in an Al_2O_3 crucible at a heating rate of 10 °C/min under a nitrogen atmosphere at a gas flow rate of 30 cm^3/min. Differential scanning calorimetry (DSC) was performed to obtain glass transition temperatures by a Mettler Toledo DSC 822^e differential scanning calorimeter, using 5–10 mg of samples encapsulated in aluminum pans and heated at a rate of 10 °C/min under a nitrogen atmosphere. X-ray diffraction patterns were obtained at room temperature on an X-ray diffractometer (3040/60 X'pert PRO) using Ni-filtered Cu Kα radiation (40 kV, 30 mA) at a scanning rate of 0.04°/s.

Monomer synthesis

General procedure for the preparation of diisothiocyanates **2a–2d**

A saturated solution of 40 g potassium thiocyanate (0.41 mol) in 300 cm^3 boiling ethanol was poured into 1.5 dm^3 of diethylether, forming a fine white powder. The solid was collected by filtration and washed with 300 cm^3 of diethylether. Finely powdered potassium isothiocyanate was isolated after drying in vacuum at 110 °C for 10 h.

A mixture of 1 mol diacid dichloride **1a–1d**, 194 g of finely pulverized and thoroughly dried potassium isothiocyanate (2 mol), and 500 cm^3 of dry benzene was refluxed for 6 h at 110–120 °C. The mixture was subsequently filtered twice through a Buchner funnel. The salt was removed by filtration and the excess of benzene was evaporated in a vacuum oven at 80 °C [29].

General procedure for the synthesis of diacids **4a–4d**; example **4b**

A solution of **2b** (2.48 g, 0.01 mol; synthesized as described above) in 50 cm^3 of dichloromethane was cooled to 0 °C followed by the addition of 2.74 g (0.02 mol) of 3-aminobenzoic acid (**3**) with continuous stirring for 1 h under an inert atmosphere [29, 30]. The solution was then washed with 1% HCl, distilled water, and brine. The solvent was removed by filtration and dried under vacuum, yielding the solid product. The crude product was then recrystallized from methanol. Diacid **4b** (1.00 g, 0.002 mol) was dissolved in 20 cm^3 of a 1:1 mixture of acetone:ethanol. The sample was titrated with 0.1 M KOH solution using phenolphthalein as indicator, so the acid value was calculated potentiometrically. Diacid **4b** was found to be 95% pure. The other dicarboxylic acids **4a**, **4c**, and **4d** were prepared by the same procedure but using the appropriate diisothiocyanate **2a**, **2c**, and **2d** instead.

3,3′-[(1,3-Phenylene)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid] (**4a,** $C_{24}H_{18}N_4O_6S_2$)
Dirty white solid; yield 94%; FTIR (KBr): $\bar{\nu}$ = 3,399 (O–H), 3,345 (N–H), 3,108, 1,703 (acid C=O), 1,687 (amide C=O), 1,587, 1,413 (C–N), 1,156 (C=S) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 6.80 (d, 2H, ArH), 7.22 (t, 2H, ArH), 7.33 (s, 2H, ArH), 7.49 (d, 2H, ArH), 7.62 (t, 1H, ArH), 8.20 (d, 2H, ArH), 8.64 (s, 1H, ArH), 9.40 (s, 2H, ArNH), 10.42 (s, 2H, amide NH), 12.04 (s, 2H, OH) ppm; ^{13}C NMR (DMSO-d_6): δ = 126.30, 129.07, 131.69, 137.01, 124.90, 125.10, 129.10, 130.60, 130.91, 134.31, 169.01 (amide C=O), 169.4 (acid C=O), 181.30 (C=S) ppm.

3,3′-[(1,4-Phenylene)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid] (**4b,** $C_{24}H_{18}N_4O_6S_2$)
Dirty white solid; yield 95%; FTIR (KBr): $\bar{\nu}$ = 3,404 (O–H), 3,291 (N–H), 3,068, 1,704 (acid C=O), 1,686 (amide C=O), 1,586, 1,413 (C–N), 1,186 (C=S), 804, 878 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 6.91 (d, 2H, ArH), 7.23 (t, 2H, ArH), 8.01 (d, 2H, ArH), 8.31 (s, 2H, ArH), 8.74 (s, 4H, *p*-ArH), 9.45 (s, 2H, ArNH), 10.44 (s, 2H, amide NH), 12.06 (s, 2H, OH) ppm; ^{13}C NMR (DMSO-d_6): δ = 125.01, 126.30, 129.77, 131.70, 134.50, 139.01, 128.32, 139.60, 169.01 (amide C=O), 169.4 (acid C=O), 182.90 (C=S) ppm.

3,3′-[(Butane-1,4-diyl)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid] (**4c,** $C_{22}H_{22}N_4O_6S_2$)
Light brown solid; yield 95%; FTIR (KBr): $\bar{\nu}$ = 3,394 (O–H), 3,335 (N–H), 3,101, 2,916, 1,701 (acid C=O), 1,686 (amide C=O), 1,586, 1,412 (C–N), 1,155 (C=S) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 2.18 (t, 4H, CH_2), 1.57 (m, 4H, CH_2), 6.79 (d, 2H, ArH), 7.20 (t, 2H, ArH), 7.31 (s, 2H, ArH), 7.47 (d, 2H, ArH), 9.39 (s, 2H, ArNH), 10.40 (s, 2H, amide NH), 12.00 (s, 2H, OH) ppm; ^{13}C NMR (DMSO-d_6): δ = 25.10, 35.51, 126.10, 124.81, 129.01, 130.41, 131.59, 136.90, 169.39 (acid C=O), 175.30 (amide C=O), 181.20 (C=S) ppm.

3,3′-[(Octane-1,8-diyl)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid] (**4d,** $C_{26}H_{30}N_4O_6S_2$)
Light brown solid; yield 94%; FTIR (KBr): $\bar{\nu}$ = 3,391 (O–H), 3,329 (N–H), 3,100, 2,911, 1,701 (acid C=O), 1,685 (amide C=O), 1,586, 1,413 (C–N), 1,154 (C=S) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 2.18 (t, 4H, CH_2), 1.57 (m, 4H, CH_2), 1.29 (m, 8H, CH_2), 6.78 (d, 2H, ArH), 7.19 (t, 2H, ArH), 7.30 (s, 2H, ArH), 7.45 (d, 2H, ArH), 9.39 (s, 2H, ArNH), 10.38 (s, 2H,

amide NH), 11.98 (s, 2H, OH) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 26.02$, 28.72, 29.03, 36.21, 124.71, 126.01, 129.03, 130.36, 131.49, 136.89, 169.36 (acid C=O), 175.29 (amide C=O), 181.11 (C=S) ppm.

General procedure for the synthesis of diacid dichlorides **5a**–**5d**; example **5b**

Diacid dichloride **5b** was prepared by reacting an excess of thionyl chloride and **4b** at 35 °C for 7 days [31]. The crude product was recrystallized from acetone. A sample (1.0 g, 1.7 mmol) was dissolved in 20 cm^3 of a 1:1 mixture of acetone. Then the sample was titrated with 0.1 M KOH solution using phenolphthalein as indicator, and the acid value was calculated potentiometrically. Diacid dichloride **5b** was found to be 94% pure. The other diacid dichlorides **5a**, **5c**, and **5d** were prepared and analyzed by the same methods.

3,3′-[(1,3-Phenylene)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid chloride]
(**5a,** $C_{24}H_{16}Cl_2N_4O_4S_2$)
Gray solid; yield 94%; FTIR (KBr): $\bar{\nu} = 3{,}285$ (N–H), 3,088, 1,782 (acid chloride C=O), 1,686 (amide C=O), 1,590, 1,413 (C–N), 1,154 (C=S) cm^{-1}; ^{1}H NMR (DMSO-d_6): $\delta = 6.73$ (d, 2H, ArH), 7.11 (t, 2H, ArH), 7.17 (s, 2H, ArH), 7.33 (d, 2H, ArH), 7.52 (t, 1H, ArH), 8.19 (d, 2H, ArH), 8.54 (s, 1H, ArH), 9.19 (s, 2H, ArNH), 10.14 (s, 2H, amide NH) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 125.12$, 129.02, 130.90, 134.31, 126.01, 127.41, 129.43, 133.11, 133.60, 137.41, 167.90 (acid chloride C=O), 169.43 (amide C=O), 181.32 (C=S) ppm.

3,3′-[(1,4-Phenylene)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid chloride]
(**5b,** $C_{24}H_{16}Cl_2N_4O_4S_2$)
Gray solid; yield 94%; FTIR (KBr): $\bar{\nu} = 3{,}283$ (N–H), 3,076, 1,783 (acid chloride C=O), 1,689 (amide C=O), 1,592, 1,412 (C–N), 1,155 (C=S), 678, 804, 871 cm^{-1}; ^{1}H NMR (DMSO-d_6): $\delta = 6.97$ (d, 2H, ArH), 7.30 (t, 2H, ArH), 8.08 (d, 2H, ArH), 8.28 (s, 2H, ArH), 8.78 (s, 4H, ArH), 9.19 (s, 2H, ArNH), 10.14 (s, 2H, amide NH) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 128.32$, 139.89, 125.01, 129.93, 131.68, 133.86, 135.07, 137.01, 167.63 (acid chloride C=O), 169.50 (amide C=O), 181.31 (C=S) ppm.

3,3′-[(Butane-1,4-diyl)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid chloride]
(**5c,** $C_{22}H_{20}Cl_2N_4O_4S_2$)
Dark brown solid; yield 94%; FTIR (KBr): $\bar{\nu} = 3{,}323$ (N–H), 3,106, 2,899, 1,786 (acid chloride C=O), 1,687 (amide C=O), 1,595, 1,412 (C–N stretch), 1,154 (C=S stretch) cm^{-1}; ^{1}H NMR (DMSO-d_6): $\delta = 2.18$ (t, 4H, CH_2), 1.57 (m, 4H, CH_2), 6.71 (d, 2H, ArH), 7.10 (t, 2H, ArH), 7.15 (s, 2H, ArH), 7.30 (d, 2H, ArH), 9.14 (s, 2H, ArNH), 10.13 (s, 2H, amide NH) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 35.51$, 25.03, 125.91, 127.31, 129.32, 133.01, 133.42, 137.21, 167.85 (acid chloride C=O), 175.33 (amide C=O), 181.21 (C=S) ppm.

3,3′-[(Octane-1,8-diyl)bis(carbonyliminocarbonothioylimino)]bis[benzoic acid chloride]
(**5d,** $C_{26}H_{28}Cl_2N_4O_4S_2$)
Dark brown solid; yield 95%; FTIR (KBr): $\bar{\nu} = 3{,}253$ (N–H), 3,107, 2,896, 1,785 (acid chloride C=O), 1,686 (amide C=O), 1,594, 1,413 (C–N), 1,155 (C=S) cm^{-1}; ^{1}H NMR (DMSO-d_6): $\delta = 1.29$ (m, 8H, CH_2), 1.57 (m, 4H, CH_2), 2.18 (t, 4H, CH_2), 6.65 (d, 2H, ArH), 7.06 (s, 2H, ArH), 7.12 (t, 2H, ArH), 7.22 (d, 2H, ArH), 9.10 (s, 2H, ArNH), 10.11 (s, 2H, amide NH) ppm; ^{13}C NMR (DMSO-d_6): $\delta = 26.03$, 28.73, 29.03, 36.22, 123.41, 124.81, 129.02, 130.90, 137.11, 137.13, 171.31 (acid chloride C=O), 175.31 (amide C=O), 181.21 (C=S) ppm.

General procedure for the synthesis of polyamides **7a**–**7d**; example **7b**

A 100 cm^3 two-necked round-bottom flask equipped with a dropping funnel and gas inlet tube was charged with a solution of 0.1 g **6** (0.5 mmol) in 12 cm^3 DMAc. Triethylamine (0.1 g, 1 mmol) was added to the solution and 0.28 g **5b** (0.5 mmol) dissolved in 5 cm^3 DMAc were added dropwise to the solution at 0 °C under N_2 with constant stirring for 5 h and then at room temperature overnight in a N_2 atmosphere. The solution was subsequently poured into water, and the yellow precipitate of **7b** was filtered off and washed with distilled water. Eventually, the obtained product was dried in vacuum at 80 °C for 24 h. This method was also used for the preparation of **7a**, **7c**, and **7d** using **5a**, **5c**, and **5d** and **6**. Yields of polymers are given in Table 2.

Poly[imino-1,4-phenyleneoxy-1,4-phenyleneiminocarbonyl-1,3-phenyleneiminocarbonothioyliminocarbonyl-1,3-phenylenecarbonyliminocarbonothioylimino-1,3-phenylenecarbonyl] (**7a**, $(C_{36}H_{26}N_6O_5S_2)_n$)
FTIR (KBr): $\bar{\nu} = 3{,}300$ (N–H), 3,100, 1,663 (amide C=O), 1,596, 1,412 cm^{-1}(C–N), 1,262 (C–O), 1,124 (C=S) cm^{-1}; ^{1}H NMR (DMSO-d_6): $\delta = 6.39$ (d, ArH ODA unit), 6.64 (d, ArH ODA unit), 7.00 (s, ArH), 7.21(d, ArH), 7.43 (t, ArH), 7.83 (d, ArH), 8.20 (d, ArH), 8.64 (s, ArH), 9.39 (Ar NH), 10.36 (amide NH) ppm.

Poly[imino-1,4-phenyleneoxy-1,4-phenyleneiminocarbonyl-1,3-phenyleneiminocarbonothioyliminocarbonyl-1,4-phenylenecarbonyliminocarbonothioylimino-1,3-phenylenecarbonyl] (**7b**, $(C_{36}H_{26}N_6O_5S_2)_n$)
FTIR (KBr): $\bar{\nu} = 3{,}283$ (N–H), 3,077, 1,669 (amide C=O), 1,597, 1,417 (C–N), 1,258 (C–O), 1,121 (C=S stretch) cm^{-1}; ^{1}H NMR (DMSO-d_6): $\delta = 6.38$ (d, ArH

ODA unit), 6.67 (d, ArH ODA unit), 7.01 (s, ArH), 7.12 (d, ArH), 7.33 (t, ArH), 7.62 (d, ArH), 8.16 (s, *p*-ArH), 9.39 (Ar NH), 10.42 (amide NH) ppm.

Poly[imino-1,4-phenyleneoxy-1,4-phenyleneiminocarbonyl-1,3-phenyleneiminocarbonothioyliminocarbonyl-1,4-butanediylphenylenecarbonyliminocarbonothioyl-imino-1,3-phenylenecarbonyl] (**7c**, $(C_{34}H_{30}N_6O_5S_2)_n$) FTIR (KBr): $\bar{\nu} = 3{,}337$ (N–H), 3,149, 1,666 (amide C=O), 1,588, 1,418 (C–N), 1,258 (C–O), 1,154 (C = S) cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 1.57$ (m, CH_2), 2.18 (m, CH_2), 6.36 (d, ArH ODA unit), 6.70 (d, ArH ODA unit), 6.99 (s, ArH), 7.18 (d, ArH), 7.32 (t, ArH), 7.73 (d, ArH), 9.29 (Ar NH), 10.31 (amide NH) ppm.

Poly[imino-1,4-phenyleneoxy-1,4-phenyleneiminocarbonyl-1,3-phenyleneiminocarbonothioyliminocarbonyl-1,8-octanediylcarbonyliminocarbonothioylimino-1,3-phenylenecarbonyl] (**7d**, $(C_{38}H_{38}N_6O_5S_2)_n$) FTIR (KBr): $\bar{\nu} = 3{,}360$ (N–H), 3,043, 1,668 (amide C=O), 1,593, 1,417 (C–N), 1,263 (C–O), 1,156 (C=S) cm^{-1}; ^1H NMR (DMSO-d_6): $\delta = 1.29$ (m, CH_2), 1.82 (m, CH_2), 2.34 (m, CH_2), 6.32 (d, ArH ODA unit), 6.68 (d, ArH ODA unit), 7.03 (s, ArH), 7.29 (d, ArH), 7.52 (t, ArH), 7.81 (d, ArH), 9.23 (Ar NH), 10.29 (amide NH) ppm.

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