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Research Article

Novel flame retardant poly(thiourea-sulfone-imide)s for high temperature applications: synthesis and characterization

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Abstract: The synthesis and polymerization of a novel diamine monomer, 1,1-(sulfonylbis (4,1-phenylene)) bis (thiourea) (SPT), with various aromatic dianhydrides were carried out. In addition, the fabrication of poly(thiourea-sulfone-imide)s (PTSIs) with noble thermal properties and flame retardancy was conducted. The structures of SPT and polymers were characterized by FT-IR, ¹H NMR, and ¹³C NMR spectroscopy along with elemental analysis. Crystallinity, organosolubility, inherent viscosity, and gel permeation chromatographic measurements were taken as well. The amorphous nature was exhibited by PTSIs containing C=S and $-SO_2$ - moieties in the backbone that were readily soluble in highly polar organic solvents. The inherent viscosities of PTSIs were 0.89–1.13 dL g⁻¹ and molecular weights were 87,000–96,550 g mol⁻¹, respectively. Their thermal stability was studied in terms of temperature at 10% weight loss, which ranged between 478 and 526 °C under inert atmosphere. Polyimides had a glass transition temperature around 253–268 °C depending on the dianhydrides used. The flame retardant properties of PTSIs were studied in terms of limiting oxygen index values and were measured in the range of 50–56.

Key words: Poly(thiourea-sulfone-imide)s, crystallinity, flame retardancy, GPC measurements

1. Introduction

Aromatic polyimides have been acknowledged as high performance polymers having excellent potential for use in electronic devices, aerospace composites, aircraft wire, and cable coatings and materials for gas separation membranes, thanks to their high inherent thermal and thermo-oxidative and dimensional stability, marvelous electrical and mechanical properties, and high radiation and solvent resistance.¹⁻⁵ In contrast, their insoluble nature and high softening temperatures have often restricted their use for such applications. Chain rigidity, strong intermolecular interactions, and chain packing ability are the significant reasons for the insoluble and nonmelting character of solely aromatic polyimides.^{6,7} The incorporation of bulky substituents,⁸⁻¹³ flexible linkages, fluoro groups,¹⁴ and noncoplanar¹⁵ and nonsymmetric moieties¹⁶ into the rigid polymer backbone are the most successful ways to overcome the above-mentioned problems without sacrificing the inherent characteristics of these polymers.

The introduction of thiourea moieties into the backbone of polymer functions as indispensable scaffolds in material chemistry belonging to electroluminescent organic dyes.^{17,18} Thiourea containing polymers are

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important in agricultural and pharmaceutical chemistry and the presence of coordination sites acts as a support for immobilized catalysts.^{19–21} In advance technological applications, they are applied in the field of anion sensing waste recovery of anions through solid-phase extraction and anion membrane for purification and synthetic purposes.^{22,23} Thiourea-based polymers can be used as coordinating resins for selective binding of heavy metal cations such as Hg(II) and Pb(II) from acidic as well as neutral solutions. Thus, they are promising materials for the elimination of environmentally toxic Hg(II) and Pb(II) cations.^{24,25}

Several efforts have been made to fabricate fire-resistant polymers by using monomers containing sulfur, nitrogen, phosphorous, sulfone, and boron units and consequently the flame retardancy of sulfur-containing groups has been investigated.^{26,27} An efficient way to improve thermal stability and flame retardancy is to introduce thiourea and sulfone linkages in the backbone of a polymer. In this connection, we have explored the nonflammability and thermal stabilization of poly(thiourea-sulfone-imide)s (PTSIs) originating from the presence of SO₂ and C=S linkages. This paper presents the synthesis of polyimides with better processability and solubility from a novel aromatic monomer, 1,1-(sulfonylbis(4,1-phenylene))bis(thiourea)(SPT), containing 1 sulfone and 2 thiourea groups. It was especially considered a potential monomer for polyimides, imparting solubility and better thermal stability. The structure property relationship of thiourea substituted polymers was investigated by synthesizing polyimides from SPT and 4 commercially available dianhydrides through a 2-stage process. Hence SPT was found to be a suitable candidate to produce processable PTSIs with excellent thermal stability.

2. Experimental

2.1. Materials

Bis(4-aminophenyl) sulfone, acetic anhydride (Ac $_2$ O; 98%), pyridine (99.8%), pyromellitic dianhydride (PMDA; 97%), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA; 98%), 4,4'-oxydiphthalic anhydride (ODPA; 98%), 4,4-(hexafluoroisopropylidene)diphthalic anhydride (6FDA; 99%) and N,N'-dimethylacetamide (DMAc; 99%) were purchased from Aldrich and were utilized without further purification. Ammonium thiocyanate (98%), N, N'-dimethylformamide (DMF; 99%), and tetrahydrofuran (THF; 99.5%) were purchased from Fluka. N-methylpyrrolidone (NMP; 99%) and dimethylsulfoxide (DMSO; 99%) were provided by Merck.

2.2. Measurements

The recording of NMR spectra was done at room temperature using a BRUKER spectrometer operating at 300.13 MHz for ¹H NMR and at 75.47 MHz for ¹³C NMR. Deutrated dimethyl sulfoxide (DMSO-d₆) was used as solvent for analysis with tetramethylsilane as an internal reference. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra (400–4000 cm⁻¹) of monomers and polymers were recorded at room temperature on a Bio-Rad Excalibur FTIR, model FTS 3000 MX. Melting points were recorded on an Electrothermal 1A9000 series digital melting point apparatus. Inherent viscosities were measured with a Gilmount falling ball viscometer (Vemon Hills, IL, USA). Thermal and differential scanning calorimetry (DSC) analyses were carried out with a PerkinElmer TGA-7 (Waltman, MA, USA) and Netzsch DSC-404C (Selb, Germany). Elemental analysis was carried out with a PerkinElmer CHNS/O 2400. Wide-angle X-ray diffractograms were obtained with an X'Pert PRO 3040/60 diffractometer (Eindhoven, Netherlands). Moisture absorption was determined through the weighing of the changes in dried pellets before and after immersion in distilled water at 25 °C for 24 h. A VISCOTEK TDA MODEL 300 calibrated with a mixture of polystyrene

standards and GPC software was used to determine the number-average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity of the polyimides. Dimethylformamide (DMF) with 0.1% lithium bromide (LiBr) was used as an eluent at a flow rate of 0.5 mL/min at 70 °C. A refractive index detector was used. Tensile properties of the polyimide films were measured according to ASTM D638 standard. Tensile testing was performed on an Instron model 4301 universal testing machine having a crosshead speed of 5 mm min⁻¹ at 25 °C. The dielectric constant of the polyimide films was determined on an Agilent 4291B instrument at a frequency of 100 MHz at 25 °C.

A Stanton Redcroft FTA flammability unit (nitrogen gas, oxygen gas, and precision pressure regulator systems) was used to determine the limiting oxygen index (LOI) of the PTSIs. LOI values were measured according to ASTM D2863, which is a method to determine the minimum concentration of oxygen in an oxygen/nitrogen mixture that will support a flaming burn in the specimen.

2.3. Synthesis of 1,1-(sulfonylbis(4,1-phenylene))bis(thiourea) (SPT)

Bis(4-aminophenyl)sulfone 2.48 g (0.01 mol), 16 mL of concentrated hydrochloric acid, ammonium thiocyanate 1.52 g (0.02 mol), and 120 mL of deaerated water were thoroughly mixed and heated in a porcelain dish for 2–3 h on a steam bath and allowed to cool to room temperature.³⁴ The mixture was then again evaporated gradually to dryness over 8–10 h. The product obtained was boiled with a small quantity of charcoal in ethanol, filtered, and cooled. Finally, 1,1-(sulfonyl*bis*(4,1-phenylene))*bis*(thiourea) thus obtained was recrystallized from methanol and dried under vacuum at 70 °C for 24 h. Yield: 86%. Melting point: 157–158 °C.

Elemental analysis: $C_{14}H_{14}N_4O_2S_3$ (MW = 366.48) in wt % Calc. C = 45.88, H = 3.85, N = 15.29, S = 26.25 and found to be C = 46.12, H = 3.58, N = 15.02, S = 26.68. FT-IR: \bar{v} (cm⁻¹): 3452–3329 (N-H stretching), 1598 (N-H bending), 1412 (C-N stretching), 1327 (SO₂ asymmetric stretching), 1134 (C=S), 1112 (symmetric stretching), ¹H NMR (DMSO-d₆, δ , ppm and J, Hz): 4.1 (s, 4H, H_a) 9.95 (s, 2H, H_b), 7.78 (d, 4H, H_c,), 7.95 (d, 4H, H_d). ¹³C NMR (DMSO-d₆, δ , ppm): 164.3 (C₁), 144.8 (C₂), 120.5 (C₃), 130.2 (C₄), 135.3 (C₅).

2.4. Preparation of polymers

The synthesis of the polyimides was carried out in a 100-mL 2-necked round-bottom flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a calcium chloride drying tube charged with 0.01 mol of the diamine (SPT) and 50 mL of dry NMP. The mixture was stirred at 0 °C for 0.5 h. Subsequently, 0.01 mol of the dianhydride was added and the mixture was again stirred at 0 °C for 1 h. The stirring was continued at room temperature for 24 h. Poly (amic acid) was precipitated by pouring the contents of the flask into 200 mL of a water-methanol (3:1) mixture. The precipitate was then filtered, washed with hot water, and dried overnight under vacuum at 70 °C.

The conversion of poly (amic acid) into polyimide was achieved through chemical cyclization.¹⁸ For this purpose, a 100-mL 2-necked round bottom flask equipped with a magnetic stirrer and a nitrogen gas inlet tube was charged with 1.0 g of poly (amic acid) and 5 mL of dry DMAc. The mixture was stirred and 5 mL of acetic anhydride and 2.5 mL of pyridine were added. After that, the mixture was stirred for 0.5 h and then slowly heated to 80 °C and held for 6 h at the same temperature. The mixture was then cooled and poured into water. The precipitate thus obtained was filtered, washed with hot water and methanol, and dried overnight under vacuum at 120 °C.

The spectral data of synthesized PTSIs validate their expected structures. FTIR: 1786 and 1721 cm⁻¹ (typical of imide carbonyl asymmetric and symmetric stretching), 1361 cm⁻¹ (C-N stretching), 1097 and 723 cm⁻¹ (imide ring deformation). ¹H NMR (DMSO-d₆, δ , ppm and J, Hz): 7.75–7.96 (2 doublets corresponding to the aromatic protons of SPT diamine unit), 10.02–10.1 (singlet assigned to N-H), other signals in the aromatic region are due to aromatic protons of the anhydride unit.

3. Results and discussion

3.1. Synthesis of monomers and polymers

The main objective of this study was the preparation of highly soluble and processable polyimides without sacrificing their thermal and physical properties. A novel monomer containing their linkage and its polymers was designed and synthesized successfully. Characterization of the structure of SPT was done by elemental analysis, and FTIR, ¹H NMR, and ¹³C NMR spectroscopy. Figure 1 presents the FTIR spectrum of SPT, where the absorption bands in the region of $3452-3329 \text{ cm}^{-1}$ show the presence of NH₂ (N-H asymmetric and symmetric stretching); those at 1598 cm⁻¹ (N-H bending), 1412 cm⁻¹ (C-N stretching), and 1134 cm⁻¹ (C=S) confirm the presence of a thioamide group.



Figure 1. FTIR spectrum of SPT.

The ¹H NMR spectrum of SPT (Figure 2) showed 2 singlets at 4.1 and 9.95 ppm, which were assigned to the -NH- group attached to the aromatic ring and the $-NH_2$ group of thioimide, respectively. Two doublets at 7.95 and 7.78 ppm were assigned to aromatic protons directly attached to adjacent ipso carbon to sulfone and thioamide group, respectively. The ¹³C NMR spectrum of SPT also supported the proposed structure as presented in Figure 3. A signal at 164.3 ppm was assigned to thioamide carbon and another downfield signal at 144.8 ppm was assigned to the aromatic carbon directly attached to the nitrogen atom. The structure of SPT was also confirmed by elemental analysis, which was in good agreement with the calculated values.

A good agreement of all the spectroscopic data was noted with the expected structure. Thus, the diamine building blocks were successfully transmitted to the polyimides, resulting in the design and synthesis of an entirely unique aromatic diamine with built-in thiourea and sulfone units.



Figure 3. ¹³C NMR spectrum of SPT.

Highly soluble PTSIs were prepared from SPT and 4 commercially available dianhydrides, i.e. BPDA, PMDA, ODPA, and 6FDA, through a 2-step chemical imidization as shown in the Scheme. A chemical method of polymerization was followed because of its advantages over thermal imidization. Thermally imidized polyimides show poor solubility and the reason might be the presence of intermolecular crosslinking produced during the thermal imidization process.⁴¹ Hence polyimides were synthesized by reacting stoichiometric amounts of SPT monomer with aromatic dianhydrides in NMP. Stirring at 0-5 °C for 24 h yields poly(amic acid)s and then heating at 80 °C in a mixture of Ac₂O/pyridine leads to the corresponding polymers.

The chemical structures of the polyimides were confirmed by spectroscopic techniques and elemental analysis; the results are reported in Table 1. Inherent viscosities, yields, M_w , M_n , and polydispersities of PTSIs were also investigated. The FTIR spectra of the polyimides shown in Figure 4 exhibit characteristic





Figure 4. FTIR spectra of PTSIs.

absorption bands of the 5-membered imide ring around $1783-1777 \text{ cm}^{-1}$, $1724-1716 \text{ cm}^{-1}$ (typical of imide carbonyl asymmetric and symmetric stretching), $1363-1359 \text{ cm}^{-1}$ (C-N stretching), $1103-1097 \text{ cm}^{-1}$, and $734-723 \text{ cm}^{-1}$ (imide ring deformation). In the ¹H NMR spectra, the characteristic singlet of the amino group at 4.1 ppm disappeared and the singlet corresponding to the thioamide proton of SPT at 9.95 ppm shifted downfield around 10.01-10.08 ppm due to the electron-withdrawing effect of carbonyl functionality of dianhydride. These observations authenticated the successful synthesis of polyimides.

Polymer	Composition of	Frequency (cm ⁻¹)	¹ H NMR (DMSOd ppm)	Elemental analysis			
	repeating unit	Frequency (cm)	$\Pi MIR(DMSOd_6, ppm)$	С	Н	Ν	S
SPT-BPDA	$C_{30}H_{16}N_4O_6S_3\\$	1783, 1724, 1363, 1097, 731	7 79/4H 7 96/4H 8 06/2H	Calc. 57.68	2. 58	8.97	15.40
			8.1/2H,8.2/2H,10.04/2H	Found 57.84	2.77	9.17	15.21
SPT-PMDA	$C_{24}H_{12}N_4O_6S_3$	1778, 1719, 1359, 1101, 723	7.77 <i>4</i> H, 7.95/4H, 8.87/2H,	Calc. 52.55	2.20	10.21	17.54
			10.08/2H	Found 52.67	2.57	10.68	17.91
SPT-ODPA	$C_{30}H_{16}N_4O_7S_3\\$	1777,1716, 1360,1103, 734	7.75/4H, 7.94/4H, 8.05/2H,	Calc. 56.24	2.52	8.57	15.01
			8.11/2H, 8.21/2H, 10.02/2H	Found 56.69	2.57	8.45	15.18
SPT-6FDA	$C_{33}H_{16}F_6N_4O_6S_3\\$	1781, 1722, 1361, 1097, 733	7.76/4H,7.92/4H, 8.02/2H,	Calc. 51.16	2.08	7.23	12.42
			8.12/2H, 8.2/2H 10.1/2H	Found 51.48	2.14	7.39	12.27

 Table 1. Polymer characterization.

3.2. Organosolubility

The solubilities of the PTSIs synthesized by chemical imidization were investigated in various organic solvents by dissolving 30 mg of the polymer in 1 mL of solvent (3% w/v) at different temperatures. The results are reported in Table 2. The PTSIs are soluble in polar aprotic solvents (DMSO, DMF, DMAc, and NMP) at room temperature. However, they are soluble on heating in less polar solvents like m-cresol and are slightly soluble in common solvents such as THF but not SPT-BPDA. The solubility of these polyimides depends on their chemical structure and is in the order SPT-6FDA > SPT-ODPA > STP-PMDA > SPT-BPDA. PTSIs obtained from ODPA and 6FDA are highly soluble due to the presence of a more flexible and bent chain structure. The presence of ether and hexafluoroisopropylidine units in SPT-ODPA and SPT-6FDA, respectively, increases their solubility at room temperature. This improvement in solubility might be attributed to the presence of a bulky trifluoromethyl group, which increased the disorder in the chains, hindered the dense chain packing, and increased the free volume, reducing the interchain interactions and causing better solvent molecule penetration into the polymer chain. Moreover, the solubility behavior of 6FDA- and ODPA-based polyimides may also be credited to the capability of hydrogen bonding.³⁵ However, PTSIs with BPDA and PMDA have lower solubility, which may be due to the rigidity of their aromatic structure and dense chain packing.

In general, the superior solubility of PTSIs is due to the presence of C=S and $-SO_2$ -, because sulfone groups have very different bond angles (around 106°) as compared to aromatic ether (around 121°) groups. Thus the presence of a kinked sulfone group in the polymer backbone might increase the intermolecular freedom and polymer polar solvent interactions, resulting in improved solubility in organic polar solvents.³⁶

Polymer	DMSO	DMF	NMP	DMAc	m-Cresol	THF	H_2SO_4
SPT-BPDA	+++	+++	+ + +	+ + +	_	—	++
SPT-PMDA	+++	+++	+ + +	+ + +	+	+	++
SPT-ODPA	+++	+++	+ + +	+ + +	++	+	+ + +
SPT-6FDA	+++	+++	+++	+ + +	++	+	+ + +

Table 2. Solubility of the polymers.

Qualitative solubility was determined at 3.0% (w/v) + + + = soluble at room temperature; ++ = soluble on heating; + = slightly soluble on heating; - = insoluble

3.3. Moisture absorption of polyimides

The moisture absorption behavior of polyimides is dependent on their chemical structures, which increases the dielectric constant and decreases the mechanical strength.²⁸ In addition, the corrosion of integrated circuits and ionization of ionic impurities are due to the presence of moisture content. The moisture uptake of PTSIs was determined by using the following equation:

Moisture absorption (%) =
$$(W/W_o - 1) \times 100$$
,

where W is the weight of the sample after immersion in water at 25 °C for 24 h and W_o is the weight of the sample dried in a vacuum oven for 24 h. PTSIs exhibited relatively low moisture absorption due to the hydrophobic nature of thiourea moiety. The moisture absorption behavior of PTSIs is illustrated in Table 3, which shows that SPT-6FDA absorbs the least moisture due to synergy in the hydrophobic nature of thiourea and fluorine moieties.

3.4. Viscometry and molecular weight analysis

The inherent viscosities of thiourea-based polyimides were measured in NMP at 30 °C and the results are summarized in Table 3. The inherent viscosities were found to be in the range of 0.89–1.13 dL/g, indicating the formation of medium to high molecular weight polymers.^{37,38} As expected, SPT-6FDA having a hexafluoroisopropylidene group displayed the lowest η_{inh} among all the polyimides. This is because the presence of these bulky groups in the polymer backbone hinders the close packing of the polymer chain. PTSIs with rigid BPDA and PMDA units presented higher inherent viscosity due to higher chain stacking efficiency. GPC measurements were carried out to determine weight average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity values. M_n and M_w values were found in the range of 54,037–61,497 and 87,000–96,550 with respect to polystyrene standards, respectively. The ratio of M_w/M_n was about 1.57–1.61. BPDA-derived polyimides showed the highest values of M_n and M_W among these polymers and 6FDA-derived polyimides had the lowest ones. GPC results validated that the diamine monomer, SPT, bearing thiourea and sulfone linkages had very good polymerization activity to form polyimides with reasonable η_{inh} M_n and M_w .

3.5. X-ray diffraction

The crystallinity of PTSIs was examined by X-ray diffraction in the region of $2\theta = 5-50^{\circ}$, using the polyimide powdered samples. The results are shown in Figure 5. Regardless of the anhydrides employed, all of the PTSIs exhibited amorphous patterns in the WAXD analysis. The X-ray diffraction curve of polyimide based on SPT-BPDA and SPT-PMDA exhibit a broad peak at around 20° . This might be interpreted as the region

of crystallinity. Polyimides based on SPT-ODPA and SPT-6FDA appear amorphous as expected, because the presence of flexible linkages induces looser chain packing. Furthermore, the improved solubility of these polyimides is a reflection of their entirely amorphous nature.

n dI /a	\mathbf{M}_n	M_w	M_w/M_n	Water	Yield
η _{inh} αL/g	(g/mol)	(g/mol)		uptake $(\%)$	(%)
1.13	$61,\!497$	$96,\!550$	1.57	0.19	83
1.1	59,248	93,612	1.58	0.17	87
0.93	56,062	89,700	1.6	0.22	87
0.89	$54,\!037$	87,000	1.61	0.11	92
	$\frac{\eta_{inh} dL/g}{1.13}$ 1.1 0.93 0.89	$\begin{array}{c} & {\rm M}_n \\ ({\rm g/mol}) \\ \hline 1.13 & 61,497 \\ 1.1 & 59,248 \\ 0.93 & 56,062 \\ 0.89 & 54,037 \end{array}$	$\begin{array}{c c} \eta_{inh} \mathrm{dL/g} & \begin{array}{c} \mathrm{M}_n & \mathrm{M}_w \\ (\mathrm{g/mol}) & (\mathrm{g/mol}) \end{array} \\ 1.13 & 61,497 & 96,550 \\ 1.1 & 59,248 & 93,612 \\ 0.93 & 56,062 & 89,700 \\ 0.89 & 54,037 & 87,000 \end{array}$	$\begin{array}{c c} & M_n & M_w & M_w/M_n \\ \hline & (g/mol) & (g/mol) \\ \hline 1.13 & 61,497 & 96,550 & 1.57 \\ \hline 1.1 & 59,248 & 93,612 & 1.58 \\ \hline 0.93 & 56,062 & 89,700 & 1.6 \\ \hline 0.89 & 54,037 & 87,000 & 1.61 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 3. Inherent viscosity^a, M_n, M_w, polydispersity, and yield of polymers.

^{*a*}Measured in NMP at a concentration of 0.3 g dL⁻¹ at 30 °C.



Figure 5. XRD pattern of PTSIs.

3.6. Mechanical and electrical properties

All the polyimides resulted in clear, flexible, and tough films after processing. The mechanical properties such as tensile strength and tensile modulus as well as elongation at break for these polyimides films were notable. The tensile strength of polyimide films varied between 119 and 127 MPa, elongation at breakage was found to be 7%–13%, and tensile moduli ranged between 2.31 and 2.67 GPa. These values are comparable to those of commercially available polyimides including Ultern 1000 (tensile strength, 105 MPa; tensile modulus, 3.0 GPa; elongation at break, 60%) and Ultern 6000 (tensile strength 103 MPa; tensile modulus, 3.03 GPa, elongation at break, 30%).³⁹

The dielectric constants values of the polyimide films were also determined and the results are summarized in Table 4. The dielectric constant values are dependent on chemical structure and might also be affected by molecular packing efficiency. Polyimide films with low molecular packing lead to a decrease in the number of polar groups in a unit volume. Polyimide films based on SPT-6FDA and SPT-ODPA have the lowest dielectric constant due to the presence of bulky $-C(CF_3)_2$ - groups, which cause variation in hydrophobicity, free volume, and total polarizability.²⁹ SPT-ODPA has ether linkages leading to a decrease in dipole number density. Furthermore, dielectric constant varies with frequency and it can be attributed to the polarization mechanism.

Water absorption has a very strong effect on the dielectric constant of polyimides. The absorbed water can ionize the ionic impurities and deteriorate the mechanical properties of polymeric materials. As discussed earlier (Table 3), the water uptake values ranged between 0.11 and 0.22 in a decreasing order of SPT-6FDA < SPT-PMDA < SPT-0DPA. SPT-6FDA has the smallest value because the hexafluoroisopropylidene

group acts as hydrophobic hindrance in the polyimide. The low water uptake and dielectric constant of SPTbased polyimides suggest a potential utility of these materials in the microelectronics industry.

Dolumon	Tensile strength	Tensile modulus	Elongation at	Dielectric constant
Polymer	(MPa)	(GPa)	breakage (%)	at 100 MHz
SPT-6FDA	119	2.31	11	2.89
SPT-ODPA	120	2.55	9	3.04
SPT-PMDA	125	2.63	6.2	3.1
SPT-BPDA	127	2.67	7	3.21

Table 4. Mechanical and electrical properties of polyimides.

3.7. Thermal stability of polymers

Thermal properties of the PTSIs were investigated using TGA and DSC at a heating rate of 10 $^{\circ}$ C min⁻¹. The results are shown in Table 5. The thermal stability of the polyimides was determined in terms of temperature at 10% weight loss (T₁₀), maximum degradation temperature (T_{max}), and residual weight at 800 °C. Thermograms of the polymers are similar to each other and no significant weight loss below 480 °C was observed (Figure 6a). The PTSIs exhibit T₁₀ in the range 478–526 °C, T_{max} of 571–605 °C, and char yields of polyimides at 800 °C were about 48%-54%. A comparison of maximum degradation temperature and residual weight at 800 $^{\circ}$ C of the synthesized polyimides revealed that the polyimide derived from BPDA had the maximum degradation temperature and residual weight at 800 °C compared to those derived from PMDA, ODPA, and 6FDA. A very rigid dianhydride monomer and impenetrable polymer chain packing might be the reasons. The 10% weight loss above 450 $^{\circ}$ C showed the effectiveness of the introduction of diacid BPDA for improving the thermal stability of the polyimides. The rigid BPDA unit and increased chain stiffness can be credited for this increase in thermal stability. On the other hand, diverse packing density of the polymer aggregation and the interaction of the polymer chain can be the causes for the lower thermal stability of the polyimides containing the flexible units than those with the BPDA and PMDA unit.²⁶ Reduction in the chain interactions, poor packing of the polymer chain, and lower thermal stability are due to the presence of bulky CF_3 groups.

The glass transition temperatures of PTSIs were about 253–268 °C (Table 5). T_g was taken as the midpoint of the change in the slope of the baseline in the DSC curve (Figure 6b). The Tg values of the polyimides depend on the structure of the polymer and decrease with the increase in flexibility of the polyimide backbone.²⁵ ODPA- and 6FDA-based polyimides showed lower Tg values than those derived from BPDA and PMDA due to the presence of flexible linkages between the phthalimide units, leading to intrasegmental mobility and also disrupting intersegmental chain packing. SPT-BPDA showed the highest tag because of the presence of the highly rigid biphenyl unit.

The flame retardant properties of the PTSIs were studied in terms of char yields and LOI values (Table 5). It is interesting to note the dependence of thermal stability on the polymer structure and the introduction of sulfone and thiourea linkages into the main chain. It has also been reported that the weight of thermal residue up to 700 °C or higher is related to flame retardancy of a polymer.⁴⁰ In addition, the absence of significant weight loss up to 500 °C shows that the PTSIs have high fire resistance and thermal stability. Increasing char yield at 800 °C could limit the production of combustible gases and thermal conductivity of the polymers, consequently limiting the polymer's flammability.^{30,31} LOI values of PTSIs were found in the range of 50–56. These values are larger than those reported for phosphorous-containing and other flame retardant polyimides.^{32,33} Moreover,

the LOI values of PTSIs are higher than those without thiourea moiety in the polymer backbone as reported in our previous studies.⁴⁰ There appears to be a correlation between LOI and polymer structure. The introduction of sulfur-containing thiourea and sulfone groups is found to significantly increase the flame retardancy of the polyimides without reducing their thermal stability. Hence, the thiourea functionality in the PTSIs backbones renders these polymers flame retardant.

Polymer	Specific heat capacity	$T_g(^{\circ}C)$	$T_{10} (^{\circ}C)^{b}$	$T_{max} (^{\circ}C)^{c}$	LOI	\mathbf{Y}_c at		
	at 200 °C (J $g^{-1}K^{-1})^a$	-				800 °C (%) ^d		
SPT-BPDA	1.7888	268	526	605	56	54		
SPT-PMDA	1.7299	262	510	592	54	51		
SPT-ODPA	1.6472	258	487	577	50	49		
SPT-6FDA	1.5787	253	478	571	53	48		
^a Monotomouth by DSC at a heating rate of $10 ^{\circ}\text{C/min}$								

ſable	5.	Thermal	analysis	data	of	PTSIs	in	\mathbf{a}	nitrogen	flow
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^{*a*}Measurement by DSC at a heating rate of 10 $^{\circ}$ C/min.

^bTemperature for 10% weight loss.

 $^c\mathrm{Maximum}$ decomposition temperature obtained from differential curves.

^dChar yield (weight of the polymer remaining).



Figure 6. TGA curves of PTSIs obtained at heating rate of 10 $^{\circ}$ C min⁻¹ in an inert atmosphere of nitrogen (a). DSC thermograms of PTSIs obtained at a heating rate of 10 $^{\circ}$ C min⁻¹ under nitrogen flow (b).

4. Conclusion

A series of novel PTSIs containing flexible C=S and $-SO_2$ - moieties were synthesized from SPT and aromatic dianhydrides using 2-step chemical imidization. In this way, SPT was used as starting material for the synthesis of new highly thermally stable and high molecular weight PTSIs.

In general, the synthesized polyimides showed excellent solubility and medium to high inherent viscosity as well as molecular weight. These polyimides exhibited an amorphous nature and a fine balance of properties (thermal stability and solubility). PTSIs were observed to have excellent electrical properties with dielectric constants of 2.89–3.21 and outstanding mechanical properties with tensile strengths of 119–127 MPa and tensile modulus values of 2.31–2.67 GPa. Thus, the introduction of thiourea and sulfone groups into the main chain of PTSIs was successful and SPT diamine monomer can be considered as a candidate for the fabrication of processable as well as heat resistant materials. These pronounced favorable properties of PTSIs make them attractive for the electronics and aerospace industries. The reasons for such stability in these polymers might originate primarily from their chemical structure, which is composed of units usually known to be highly flame retardant, such as sulfur containing thiourea and sulfone moieties.

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