

Pyridine-Thiourea Based High Performance Polymers: Synthesis and Characterization^{*}

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Abstract A novel diamine monomer, pyridine-2, 6-bis((4-aminophenyl)thioureido)carbonyl (PATC) was synthesized efficiently and polymerized with various aromatic dianhydrides. Consequently, poly(pyridine thiourea-imide)s (PPTIs) with good thermal properties and flame retardancy were fabricated. The structures of PATC and PPTIs were characterized by FTIR, ¹H-NMR, ¹³C-NMR spectroscopy along with elemental analysis, crystallinity, organosolubility, inherent viscosity and gel permeation chromatographic measurements. PPTIs containing C=S, CONH and *meta* substituted pyridine moieties in the polymer backbone showed amorphous nature and were readily soluble in highly polar organic solvents and even in less polar solvents such as tetrahydrofuran (THF). Polymers had inherent viscosities in the range of 0.91–1.16 dL/g and molecular weight was found between 68000–77000 g/mol. The electrical properties of the PPTIs were estimated in terms of dielectric constant over a range of frequencies. Their thermal stability was determined by 10% weight loss temperature found in the range of 519–563 °C under inert atmosphere. The glass transition temperature of the polyimides varied between 247 °C and 267 °C. The flame retardant properties of PPTIs were investigated in terms of limiting oxygen index (LOI) which was found in the range of 38.26–39.95. Introduction of thiourea in the polymer backbone is an effective way to improve the thermal stability and flame retardancy. Thus PATC can be considered as an excellent candidate for the synthesis of high performance polymers.

Keywords: Poly(pyridine thiourea-imide)s; Crystallinity; Flame retardancy; GPC measurements.

INTRODUCTION

Aromatic poly(amide-imide)s are classified as meta aramid family. It is naturally non-flamable, which is permanent characteristic to its chemical structure including a high proportion of aromatic structures and combined double bonds. In the past decade, the demand for polyamide-imide (PAI) and other high-temperature resistant polymeric materials has grown steadily because of their outstanding mechanical properties and excellent thermal and oxidative stability^[1, 2]. They have an excellent resistance to cold acids, even when immersed for a fairly long period in concentrated and dilute alkalis at ambient temperature. They also withstand most organic solvents (except highly polar and phenol-based solvents), chlorine bleach, detergents and water vapours^[3]. PAIs are well-known for their low thermal expansion coefficient and dielectric constant. In microelectronics, PAIs have been widely used as an inter-dielectric material, and in the large-scale integrated circuit industry, as an electrical insulation for conventional appliances^[4–6]. Compared with pure polyimide and polyamide, PAIs exhibit better processability and heat-resistant properties. The application of PAIs as a wire-coating material with thermal-resistant properties has attracted increasing interest^[7–9]. However, their

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applications are restricted because of their poor solubility in organic solvents and extremely high glass transition temperatures that make them very difficult to be processed by spin coating or thermoforming techniques. Much effort has been made to create structurally modified aromatic polymers having increased solubility and processability with retention of their high thermal stability. It is known that the solubility of polymers is often increased when flexible bonds such as $[-O-]$, $[-SO_2-]$, $[-CH_2-]$, $[-C(CF_3)_2-]$, $[-CSNH-]$, $CONH-$ ^[10], bulky pendent groups^[11, 12], large pendent groups or polar constituents such as heterocyclic segments are incorporated into the polymer backbone due to the varying crystallinity and intermolecular interactions^[13–15]. If the heterocyclic moiety is carefully chosen, it is possible to promote solubility without affecting thermal and mechanical properties to any great extent^[16–22].

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 pyridine-containing polymers has been investigated^[22]. An efficient way to improve thermal stability and flame retardancy is to introduce pyridine and thiourea linkages in the backbone of a polymer^[23–26]. In this connection, we have explored the nonflammability and thermal stabilization of poly(pyridine thiourea-imide)s (PPTIs) originating from the presence of pyridine and C=S linkages. This paper presents the synthesis of polyimides with better processability and solubility from a novel aromatic monomer, pyridine-2, 6-*bis*((4-aminophenyl)thioureido)carbonyl (PATC), containing pyridine and 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 PATC and commercially available dianhydrides through a two-stage process. Hence PATC was found to be a suitable candidate to produce processable PPTIs with excellent thermal stability as well as low flammability.

In this article, the ability of pyridine-2, 6-*bis*((4-aminophenyl)thioureido)carbonyl to influence the chain flexibility of aromatic polyimide and improve the solubility has been studied. The incorporation of *meta* substituted pyridine ring, amide and thioamide groups into the polymer backbone improves the solubility of the resulting polyimides without scarifying their thermal and thermooxidative stability. Keeping in view these properties, this paper presents the synthesis and characterization of a novel diamine monomer to prepare novel polyimides with good processability and thermal stability. The results obtained from thermal analyses, XRD, η_{inh} , GPC and solubility proved that introduction of such flexible linkages could impart processability to polyimides without worsening the inherent properties of the resulting polyimides.

EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich, Fluka or Merck. 4-Nitroaniline ($\geq 99\%$), pyridine-2, 6-dicarbonyl dichloride (97%), acetic anhydride (Ac_2O ; 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%), acetone ($\geq 99.5\%$) and *N,N'*-dimethylacetamide (DMAc; 99%) obtained from Aldrich were used as received. 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.

Measurements

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. Solvent used for analysis was deuterated dimethyl sulfoxide ($DMSO-d_6$) with tetramethylsilane as an internal reference. IR spectra ($400-4000\text{ cm}^{-1}$) 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 obtained with a Gilmount falling ball viscometer (Vemon Hills, Illinois). Thermal and differential scanning calorimetry (DSC) analyses were carried out with a Perkin Elmer TGA-7 (Waltman, Massachusetts) and a Netzsch DSC-

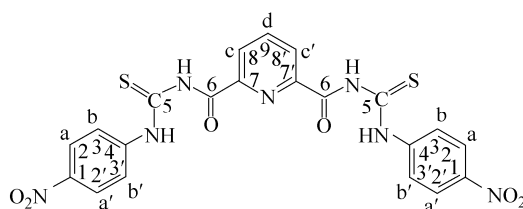
404C (Selb, Germany). Elemental analysis was carried out with a Perkin Elmer CHNS/O 2400. Wide-angle X-ray diffractograms were obtained with an X'Pert PRO 3040/60 diffractometer (Eindhoven, Netherland). Moisture absorption was determined through the weighing of the changes in dried pellets before and after immersion in boiling water for 6 h. Viscotek TDA Model 300 was used to determine the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity of the polyimides using dimethylformamide (DMF) with 0.1% lithium bromide (LiBr) as an eluent at 70 °C through a Polymer Laboratories PL Gel mixed A column set and a refractive index detector.

A Stanton Redcroft FTA flamibility unit (nitrogen gas, oxygen gas and precision pressure regulator systems) was used to determine the limiting oxygen index (LOI) of the polyimides. 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 specimen.

Synthesis of Pyridine-2,6-bis((4-nitrophenyl)thioureido)carbonyl (PNTC)

A solution of pyridine-2,6-dicarbonyl dichloride (0.01 mol, 2.04 g) in anhydrous acetone (75 mL) and 2.5% tetrabutylammonium bromide (TBAB) in dry acetone was added dropwise to the suspension of ammonium thiocyanate (0.02 mol, 1.52 g) in dry acetone (75 mL). The reaction mixture was refluxed for 2–3 h. A solution of (0.02 mol, 2.76 g) of 4-nitroaniline in 60 mL of dry acetone was added to the reaction mixture after cooling it to room temperature. The resulting reaction mixture was refluxed for 4–5 h. Hydrochloric acid (0.1 mol/L, 500 mL) was added to the reaction mixture and left it for precipitation for 24 h. Light yellow precipitate was filtered, washed with hot water and recrystallized from dichloromethane: tetrahydrofuran (1:3) mixture and dried under vacuum at 70 °C for 24 h. Yield: 83%. Melting point: 189–191 °C.

Elemental analysis for $C_{21}H_{15}N_7O_6S_2$ ($M_w = 525.52$) in wt% Calc. C = 48, H = 2.88, N = 18.66, S = 12.20 and found to be C = 47.83, H = 3.06, N = 18.57, S = 12.13. FTIR: ν (cm^{-1}): 1681 (C=O, amide), 1601 (C=N, stretch), 1417 (C=C, stretching vibration of aromatic), 1526 (asymmetric stretching of NO_2), 1321 (symmetric stretching of NO_2), 1241 (C=S). ^1H -NMR (DMSO- d_6 , δ and J , Hz): 12.23 (2H, br s, CSNH), 10.86 (2H, br s, CONH), 8.39–8.36 (4H, d, $J_{ab} = J_{a'b'} = 8.7$), 7.68–7.65 (4H, d, $J_{ba} = J_{b'a'} = 9$), 8.21–8.19 (2H, d, $J_{cd} = J_{c'd} = 8.4$), 7.94–7.91 (1H, t, $J_{dc} = J_{d'c'} = 8.2$). ^{13}C -NMR (DMSO- d_6 , δ): 171.13 (2C, C_5 , C_5), 162.77 (2C, C_6 , C_6), 149.64 (2C, C_1 , C_1), 124.91 (4C, C_2 , C_2 , C_2 , C_2), 112.13 (4C, C_3 , C_3 , C_3 , C_3), 142.74 (2C, C_4 , C_4), 140.24 (2C, C_7 , C_7), 126.89 (2C, C_8 , C_8), 122.32 (1C, C_9).

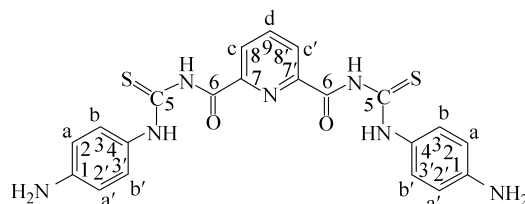


Synthesis of Pyridine-2,6-bis((4-aminophenyl)thioureido)carbonyl (PATC)

The nitro compound (PNTC), 2.63g (5mmol) and 10% palladium on carbon (Pd-C) (0.16 g, 8 wt%) catalyst were added to ethanol (80 mL) and the mixture was charged in a Parr hydrogenation apparatus equipped with a mechanical stirrer. After 6 h at 80–85 °C and 1.38 MPa of hydrogen pressure, the conversion of dinitro to diamine was checked by TLC (ethylacetate: *n*-hexane 1:1 *V/V*). When the reaction was completed, the solution was filtered to remove Pd-C, concentrated and crude diamine was isolated. The diamine was recrystallized from tetrahydrofuran to obtain dark brown crystals of PATC and dried under vacuum at 70 °C for 24 h. Yield: 91%. Melting point: 167–168 °C.

Elemental analysis for $C_{21}H_{19}N_7O_2S_2$ ($M_w = 465.55$) in wt% Calc. C = 54.18, H = 4.11, N = 21.06, S = 13.78 and found to be C = 53.89, H = 4.23, N = 21.15, S = 13.89. FTIR: ν (cm^{-1}): 3456, 3361 (N–H stretching), 1683 (C=O, amide), 1617 (C=N, stretch), 1411 (C=C, stretching vibration of pyridine), 1234 (C=S). ^1H -NMR (DMSO- d_6 , δ and J , Hz): 12.07 (2H, br s, CSNH), 10.18 (2H, br s, CONH), 6.62–6.60 (4H, d, $J_{ab} = J_{a'b'}$).

= 8.8), 7.66–7.64 (4H, d, $J_{ba} = J_{b'a'} = 9$), 8.18–8.16 (2H, d, $J_{cd} = J_{c'd} = 8.6$), 7.92–7.90 (1H, t, $J_{dc} = J_{dc'} = 8.3$), 4.73 (4H, s, NH_2). ^{13}C -NMR (DMSO- d_6 , δ): 170.64 (2C, C_5 , C_5), 161.19 (2C, C_6 , C_6), 147.45 (2C, C_1 , C_1), 112.89 (4C, C_2 , C_2 , C_2 , C_2), 114.17 (4C, C_3 , C_3 , C_3 , C_3), 141.18 (2C, C_4 , C_4), 139.13 (2C, C_7 , C_7), 125.81 (2C, C_8 , C_8), 119.17 (1C, C_9).

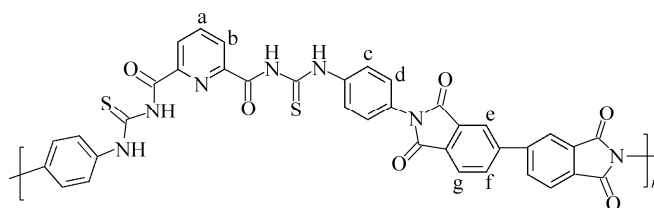


Preparation of Polymers

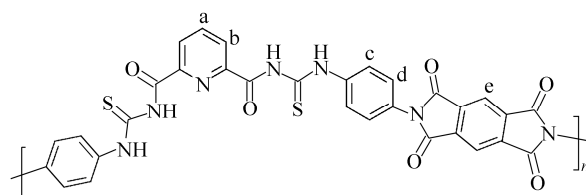
The synthesis of the polyimides typically was carried out in a 100 mL two-necked round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and a calcium chloride drying tube charged with 0.01 mol of the diamine (PATC) and 50 mL dry NMP. The mixture was stirred at 0 °C for 0.5 h. Subsequently, 0.01 mol of 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.

Chemical cyclization was applied for the conversion of poly(amic acid) to polyimide^[27]. For this purpose, a 100 mL two-necked round bottomed 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. The mixture was stirred for 0.5 h and slowly heated to 80 °C and then held for 6 h at the same temperature. The mixture was 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^[28].

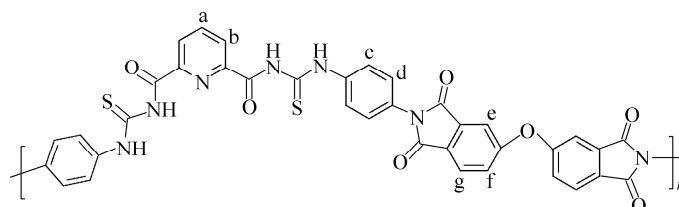
Elemental analysis for the polyimide PATC-BPDA ($\text{C}_{37}\text{H}_{21}\text{N}_7\text{O}_6\text{S}_2$) in wt% Calc. C = 61.40, H = 2.92, N = 13.52, S = 8.86 and found to be C = 61.57, H = 2.77, N = 13.67, S = 9.01. FTIR: ν (cm^{-1}): 1782 (imide, asymmetric C=O stretching), 1721 (imide, C=O symmetric Stretching), 1364 (imide ring vibration axial) and 733 (imide ring deformation). ^1H -NMR (DMSO- d_6 , δ and J , Hz): 7.89 (1H, t, H_a) 7.13 (4H, d, H_d) 7.68 (4H, d, H_c) 8.08 (2H, d, H_g) 8.18 (2H, d, H_e) 8.13 (2H, dd, H_f) and 8.24 (2H, d, H_b).



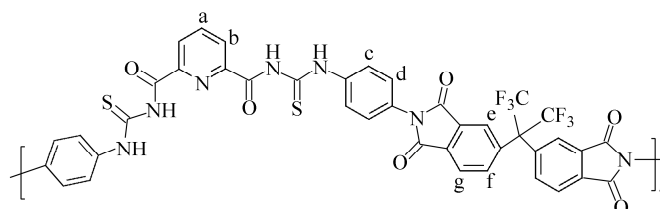
Elemental analysis the polyimide PATC-PMDA ($\text{C}_{31}\text{H}_{17}\text{N}_7\text{O}_6\text{S}_2$) in wt% Calc. C = 57.49, H = 2.65, N = 15.14, S = 9.90 and found to be C = 57.66, H = 2.57, N = 15.16, S = 9.97. FTIR: ν (cm^{-1}): 1777 (imide, asymmetric C=O stretching), 1716 (imide, C=O symmetric Stretching), 1358 (imide ring vibration axial) and 721 (imide ring deformation). ^1H -NMR (DMSO- d_6 , δ and J , Hz): 7.93 (1H, t, H_a) 7.17 (4H, d, H_d) 7.71 (4H, d, H_c), 10.08 (2H, d, H_e) and 8.87 (2H, d, H_b).



Elemental analysis for the polyimide PATC-ODPA ($C_{37}H_{21}N_7O_7S_2$) in wt% Calc. C = 60.07, H = 2.87, N = 13.25, S = 8.67 and found to be C = 59.79, H = 2.77, N = 13.45, S = 8.78. FTIR: ν (cm^{-1}): 1779 (imide, asymmetric C=O stretching), 1717 (imide, C=O symmetric stretching), 1365 (imide ring vibration axial) and 733 (imide ring deformation). ^1H -NMR (DMSO- d_6 , δ and J , Hz): 7.89 (1H, t, H_a) 7.21 (4H, d, H_d) 7.76 (4H, d, H_c), 8.11 (2H, d, H_g) and 8.21 (2H, d, H_b), 8.08 (2H, d, H_f), 8.05 (2H, d, H_e).



Elemental analysis for the polyimide PATC-6FDA ($C_{40}H_{21}F_6N_7O_6S_2$) in wt% Calc. C = 54.98, H = 2.42, N = 11.22, S = 7.34 and found to be C = 55.18, H = 2.39, N = 11.33, S = 7.29. FTIR: ν (cm^{-1}): 1781 (imide, asymmetric C=O stretching), 1722 (imide, C=O symmetric stretching), 1361 (imide ring vibration axial) and 733 (imide ring deformation). ^1H -NMR (DMSO- d_6 , δ and J , Hz): 7.79 (1H, t, H_a) 7.17 (4H, d, H_c) 7.73 (4H, d, H_d), 8.12 (2H, d, H_g), 8.2 (2H, d, H_b), 8.08 (2H, d, H_f) and 8.02 (2H, d, H_e).

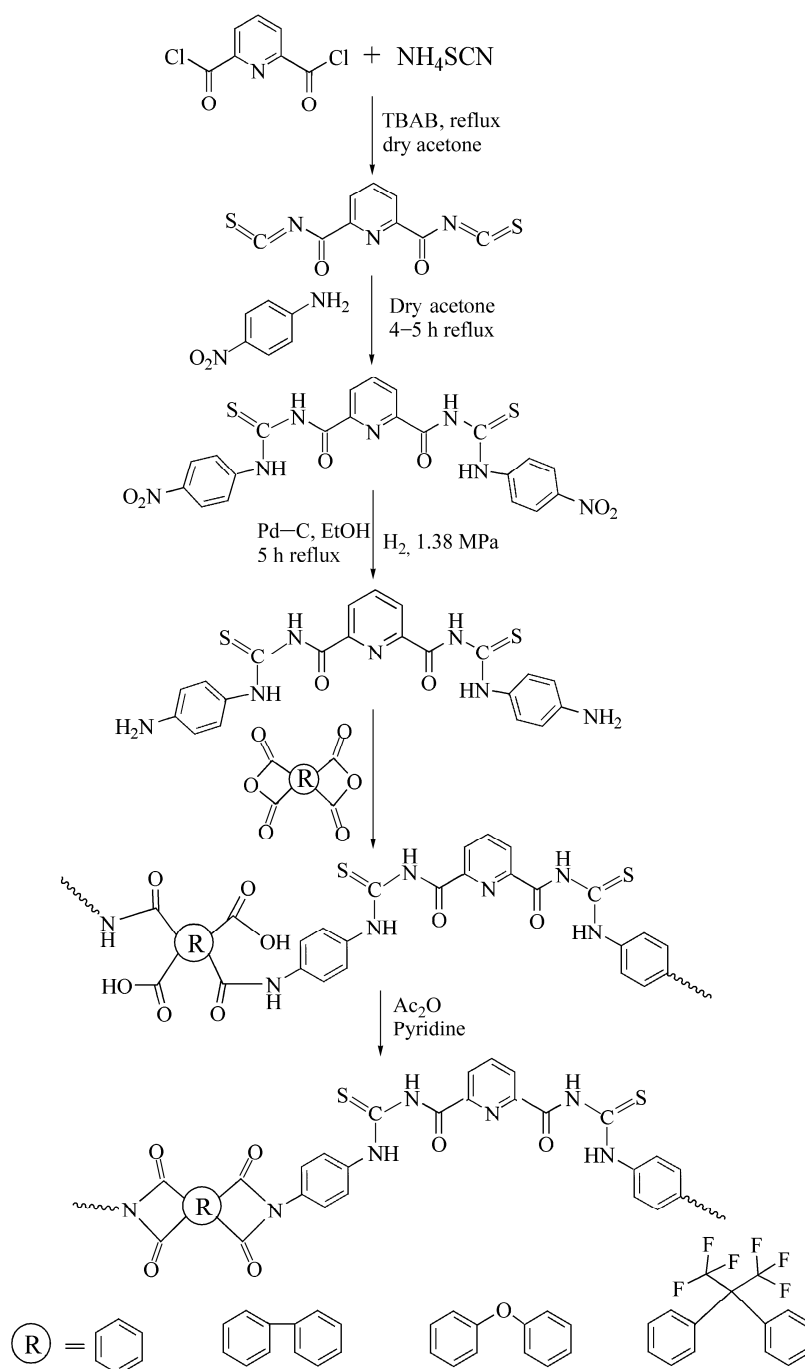


RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

The main aim of this study was the preparation of soluble and processable polyimides without scarifying their thermal and physical properties. The novel diamine monomer containing pyridine amide and thiouamide linkages was synthesized in two steps according to the well-known method as shown in Scheme 1. In first step isothiocyanate was synthesized from 2, 6-dicarbonyldichloride and ammonium thiocyanate in the presence of tetrabutylammonium bromide (TBAB) as phase transfer catalyst^[22]. This isothiocyanate was then treated with 4-nitroaniline to synthesize PNTC. The dinitro (PNTC) was reduced to diamine (PATC) in the presence of hydrogen using Pd-C catalyst. Monomers PNTC and PATC were characterized by elemental analysis, FTIR, ^1H -NMR and ^{13}C -NMR spectroscopy. FTIR spectrum of PNTC showed characteristic absorption bands around 1526 and 1321 cm^{-1} due to asymmetric and symmetric stretching vibrations of nitro groups. Where as absorption band corresponding to C=S was observed at 1241 cm^{-1} (Fig. 1a). After reduction, the absorption bands corresponding to nitro groups disappeared and characteristic absorption of amino groups appeared at 3456 and 3361 cm^{-1} as shown in the FTIR spectrum of PATC (Fig. 1b).

The monomers were further characterized by ^1H - and ^{13}C -NMR spectroscopy. In the ^1H -NMR spectrum of PNTC a doublet observed at δ = 8.39 was assigned to protons directly attached to the carbon atoms adjacent to nitro carrying carbon atoms. Two broad singlets observed at δ = 12.23 and 10.86 in ^1H -NMR spectrum of PNTC were assigned to CSNH and CONH protons respectively. The appearance of a new singlet at δ = 4.73 in the ^1H -NMR spectrum of PATC supported the change of functionality to amine as shown in Fig. 2. Moreover, a doublet observed in the up field region at δ = 6.62 was assigned to the protons directly attached to the ipso carbon to which the amino group was attached. All the spectroscopic data and elemental analysis results were in good agreement with the expected structure.



Scheme 1 Synthesis of PATC diamine and polyimides

As diamines are building blocks in the preparation of polyimides and features of diamine will transmit in the polyimides. So, a novel fully aromatic diamine with built-in pyridine, amide and thioamide units was designed and synthesized. The synthesized polyimides were characterized by different analytical and spectroscopic techniques. Spectral data of synthesized polyimides validate their structures. In FTIR spectra absorption bands around 1793 and 720 cm⁻¹ corresponded to symmetric and asymmetric imide C=O stretching.

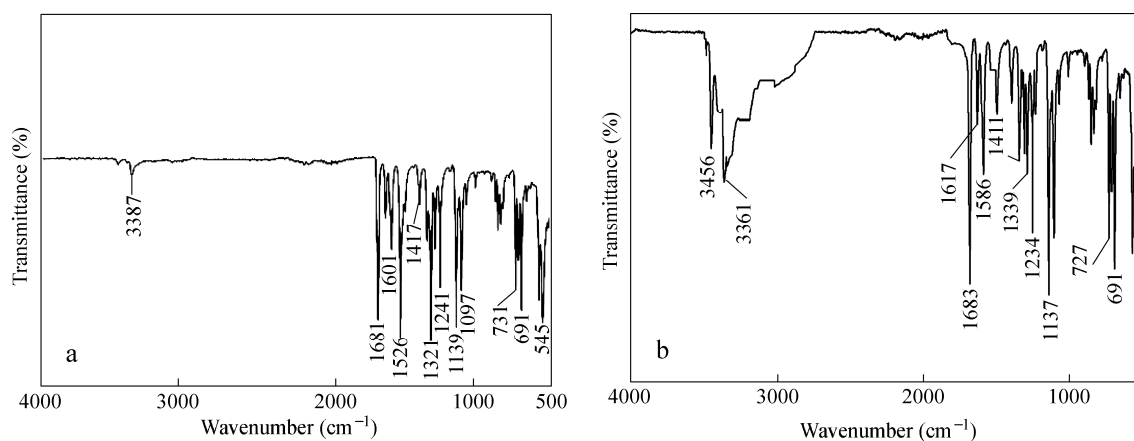


Fig. 1 FTIR spectrum of PNTC (a) and PATC (b)

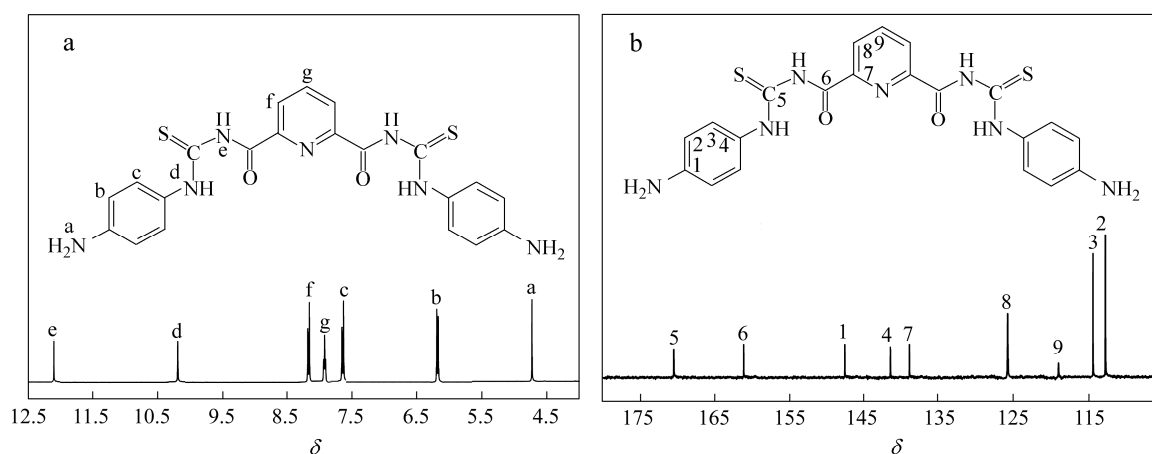


Fig. 2 ¹H-NMR spectrum (a) and ¹³C-NMR spectrum (b) of PATC

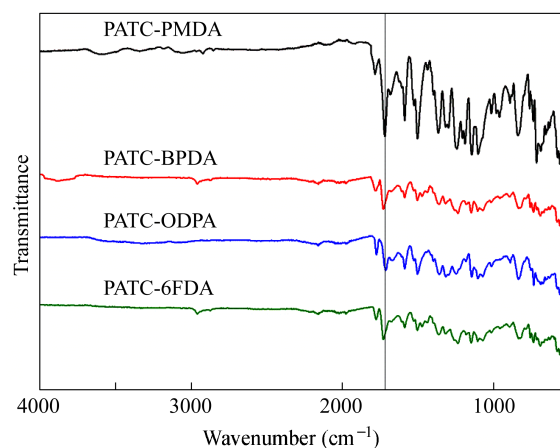


Fig. 3 FTIR spectra of polyimides synthesized from PATC

Another absorption band due to imide ring deformation was observed around 1090 cm⁻¹. The FTIR spectra of polyimides are shown in Fig. 3. In ¹H-NMR the signals between in the range of δ = 7.13–8.18 corresponding to the aromatic protons of (PATC) diamine unit and singlets at 10.11 and 12.13 are assigned to CONH and CSNH

respectively, other signals in the aromatic region are due to aromatic protons of anhydride unit. In addition, the aromatic protons resonating at the *ortho* position to the amino group also shifted down field around $\delta = 6.75$ due to the deshielding effect of the imide group.

Organosolubility

The solubilities of polyimides (PIs) 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 PIs were soluble in polar aprotic solvents (DMSO, DMF, DMAc and NMP) and even in less polar solvent such as *m*-cresol. They also exhibited solubility in common solvents such as THF, chloroform and toluene on heating. The solubility of these polyimides depends on their chemical structure and are in the order PATC-6FDA > PATC-ODPA > PATC-PMDA > PATC-BPDA. PIs obtained from PATC are highly soluble due to the presence of more flexible and bent chain structure. The presence of ether and hexafluoroisopropylidene units in PATC-ODPA and PATC-6FDA respectively increases their solubility at room temperature. However, PPTIs with BPDA and PMDA have lower solubility. It may be due to rigidity of structure and dense chain packing. In case of 6FDA, the bulky hexafluoroisopropylidene groups could result in low molecular packing due to steric hinderance. Moreover, the solubility trend of polyimides derived from 6FDA and ODPA is attributed to the ability of the hydrogen bonding resulting in the improvement of polymer solubility^[29].

The presence of heterocyclic *meta* substituted pyridine ring, amide and thioamide also contributes to the superior solubility of the resulting PIs, by reducing the chain-chain interactions and close packing of macromolecules^[30]. Consequently, the penetration of small solvent molecules between the polymer chains is facilitated.

Viscometry and Molecular Weight Analysis

The inherent viscosities of the pyridine based polyimides were measured in NMP at 30 °C, and results are collected in Table 1. The inherent viscosities were found in the range of 0.91–1.16 dL/g indicating the formation of reasonably high molecular weight polymers^[31, 32]. The results demonstrated that the PPTIs which have rigid units (BPDA, PMDA) displayed the highest η_{inh} due to higher chain symmetry and packing efficiency. However, the η_{inh} decreased with the incorporation of bulky groups such as hexafluoroisopropylidene in the polymer backbone which serve as “molecular spacers” and hinder the molecular chain packing. In addition, the aforementioned discussion is supported by the GPC measurements. The number and weight-average molecular weight (M_n , M_w) and the polydispersity index determined by the GPC are shown in Table 3. M_n and M_w of PATC based polyimides were found in the range of 41700–49700 and 67500–76500 g/mol respectively, showing that the resulting polyimides are of reasonably high molecular weights. The polydispersity index of the resulting polyimides was ranged between 1.51 and 1.62. GPC results validated that diamine monomer, PATC bearing *meta* substituted pyridine ring, amide and thioamide linkages had a very good polymerization activity to form polyimides with good η_{inh} , M_n and M_w .

Table 1. Inherent viscosity^a, M_w , M_n , polydispersity and yield of polymers

Polymer	η_{inh} (dL/g)	M_w (g/mol)	M_n (g/mol)	Polydispersity	Yield (%)
PATC-BPDA	1.16	76550	49708	1.54	85
PATC-PMDA	1.14	73612	48750	1.51	89
PATC-ODPA	0.98	69700	43562	1.6	86
PATC-6FDA	0.91	67566	41709	1.62	91

^a Measured in NMP at a concentration of 0.3 g/dL at 30 °C

X-ray Diffraction

Crystallinity of polyimides was examined by X-ray diffraction in the region of $2\theta = 5^\circ$ – 50° , using the polyimide powder obtained as samples. The results are shown in Fig. 4. The polyimide PATC-BPDA and PATC-PMDA show some crystalline character and exhibit a characteristic peaks around 20° , which indicates a little of crystalline morphologies in the resulting polyimide. These might be related to the more efficient packing of the polymer chains containing biphenyl units. The polyimides based on PATC-ODPA and PATC- 6FDA show

amorphous patterns, and this is because the presence of flexible ether linkages and bulky hexafluoroisopropylidene groups induces looser chain packing and reveals a large decrease in crystallinity. Regardless of the anhydrides employed, the presence of kinky —NHCS and —NHCO groups and *meta* substituted pyridine ring in the polymer repeat units might inhibit the polymer chain packing and interactions, therefore resulting in lack of crystallinity. In addition, the amorphous nature of polyimides is also reflected by their improved solubility.

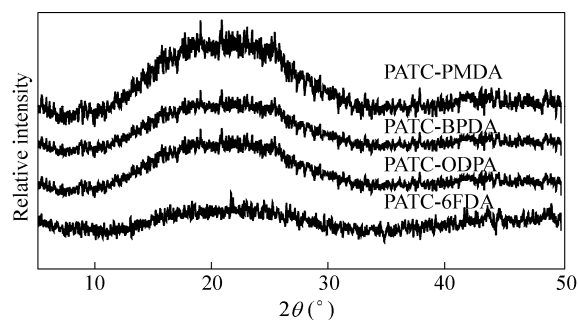


Fig. 4 Wide-angle X-ray diffractograms of the polymers

Mechanical Properties and Water Uptake

The polyimide films were subjected to tensile tests, and the results including tensile strength, Young's modulus and elongation at break are reported in Table 2. The Young's modulus is the gradient of the straight line representing the elastic behavior of the material. The polyimides derived from PMDA and BPDA have higher value of tensile strength, Young's modulus and lower value of strain at break which could be attributed to the rigid polymer backbone. However, 6FDA and ODPA based polyimides showed higher values of elongation at break due to flexibilizing effect of hexafluoroisopropylidene and ether linkages^[33, 34]. The tensile strength of polyimide films varied between 125 MPa and 133.5 MPa, elongation at break was found to be 5.2%–7.92% and tensile moduli ranged between 2.74 GPa and 3 GPa. These values are comparable to those of commercially available polyimides including Ultem 1000 (tensile strength, 105 MPa; tensile modulus, 3.0 GPa; elongation at break, 60%) and Ultem 6000 (tensile strength 103 MPa; tensile modulus, 3.03 GPa, elongation at break, 30%)^[35].

Table 2. Mechanical properties and water uptake of polymers

Polymer	Max. stress (MPa) ± 0.3	Max. strain (%) ± 0.02	Young's modulus (GPa) ± 0.2	Water uptake (%)
PATC-PMDA	133.5	5.2	3	0.18
PATC-BPDA	133.8	5.6	2.94	0.19
PATC-ODPA	131	7.4	2.79	0.23
PATC-6FDA	125	7.92	2.74	0.16

The moisture uptake of the polyimide films was measured according to ASTM D570-63 standard by immersing in boiling water at 100 °C for 6 h. The moisture uptake of the polyimide films depends upon several factors including the chemical structure, introduction of fluorinated and other functional groups, the geometrical packing of polymer chains and film processing parameters. The polyimides synthesized from 6FDA showed low moisture absorption (hydrophobicity) as compared to other polyimides credited to the higher fluorine content in the repeating unit. However, the higher moisture absorption of PATC-ODPA might be due to hydrogen bonding^[36].

Electrical Properties

The dielectric constant values of the polyimide films were measured over a range of frequency (1 MHz to 5 MHz), and the results are summarized in Table 3. These results illustrated that the dielectric constant value of each polyimide film was quite different, depending on its chemical structure. It might be affected by the

molecular packing efficiency and low molecular packing order which can lead to decrease in the number of polar groups in unit volume. The polyimides synthesized from 6FDA have lower dielectric constant values owing to the presence of bulky CF_3 groups^[37, 38].

Table 3. Dielectric constants of the polyimides at various frequencies

Polymer	1 MHz	2 MHz	3 MHz	4 MHz	5 MHz
PATC-PMDA	3.29	3.28	3.23	3.21	3.05
PATC-BPDA	3.27	3.25	3.22	3.17	3.03
PATC-ODPA	3.26	3.22	3.19	3.13	3.01
PATC-6FDA	3.22	3.19	3.14	3.11	2.99

The bulky hexafluoroisopropylidene groups $[-\text{C}(\text{CF}_3)_2-]$ in PATC-6FDA could result in a low molecular packing due to steric hindrance. In addition, the strong electronegativity of fluorine results in very low polarizability of the C—F bonds under the influence of an applied field which consequently lowers the dielectric constant^[39].

The dielectric constants decreased gradually with the increase in frequency due to the variations in the dipolar polarizable units with frequency for each polyimide. This behavior could be accredited to the dependence of the polarization mechanism *i.e.*, the reduction in dielectric constant values is due to the slower response of dipoles, which are unable to follow the rapidly varying ac field^[40].

Thermal Properties

The effect of introducing the thiourea and pyridine moieties on the thermal properties of polymers was investigated by thermogravimetric analysis. The results are reported in Table 4 and thermograms are shown in Fig. 5. The thermal stability of the polyimides was evaluated in terms of temperatures at 5%, 10%, weight loss and residual weight at 800 °C. The results shed light on the fact that the polyimides synthesized from PMDA demonstrated a higher thermal stability, which owed to the inclusion of the rigid PMDA units in the polymer backbone. However, the introduction of the hexafluoroisopropylidene units appeared to reduce the packing density of molecular chains, which have a strong impact on the intermolecular interactions^[41, 42]. Consequently, this imparts reduction in the thermal stability of the 6FDA-based polyimides. The residual weight of the polyimides synthesized from PATC varied between 49.4% and 55%. The glass transition temperature of the polyimides decreased with increasing flexibility of their backbone according to the structure of a particular dianhydride. The PMDA-derived polyimide exhibited the highest T_g owing to the highly rigid pyromellitimide unit. The T_g values of the polyimides were found in the range of 247–267 °C. These values are comparable to those reported in literature of *meta* substituted pyridine based polyimides containing *meta* substituted pyridine and amide linkages in the polymer backbone (204.5–237.4 °C and 244–283 °C)^[43, 44].

Table 4. Thermal behavior of the polyimides under nitrogen flow

Polymer	Specific heat capacity at 200 °C ^a (J/g·K)	Thermal stability ^b				T_g ^g (°C)	LOI ^h
		T_5 ^c (°C)	T_{10} ^d (°C)	T_{max} ^e (°C)	Char yield ^f (wt%)		
PATC-PMDA	1.4186	490	563	581	55	267	39.95
PATC-BPDA	1.5643	467	552	573	52.7	258	39.18
PATC-6FDA	1.7783	455	537	566	50.21	251	38.51
PATC-ODPA	1.8191	443	519	551	49.4	247	38.26

^a Measured by DSC under nitrogen at a heating rate of 10 K/min;

^b Measured by TGA under nitrogen at a heating rate of 10 K/min;

^c Temperature at 5% weight loss;

^d Temperature at 10% weight loss;

^e Maximum degradation temperature obtained from differential curves;

^f Residual mass (wt%) at 800 °C;

^g Glass transition temperature (T_g) measured by DSC at heating rate of 10 K/min;

^h Limiting oxygen index > 25 denotes self-extinguishing

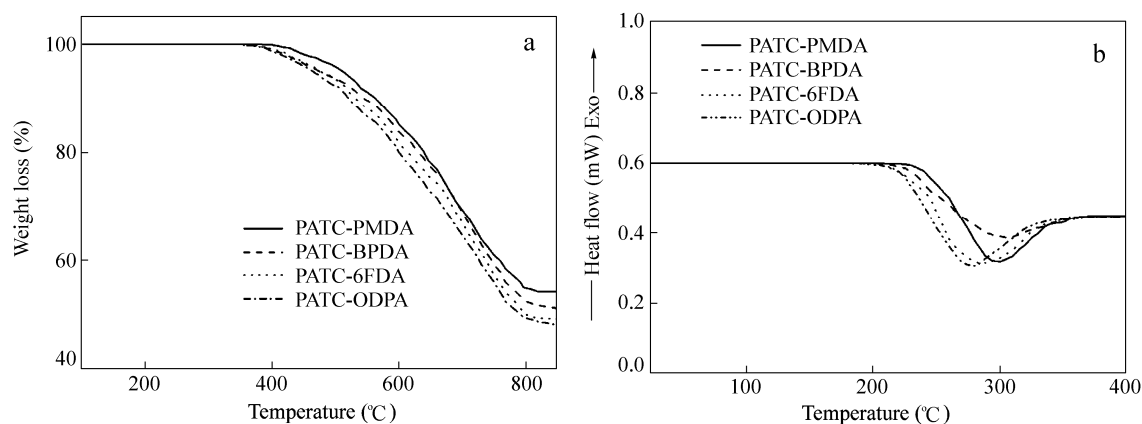


Fig. 5 (a) TGA curves of PPTIs obtained at heating rate of 10 K/min in an inert atmosphere of nitrogen and (b) DSC thermograms of PPTIs obtained at a heating rate of 10 K/min under nitrogen flow

The flame-retardant properties of the polyimides were studied in terms of LOI values and were found in the range of 38.26–39.95. Higher LOI values showed that these polyimides have a higher intrinsic fire resistance and thus could limit the production of combustible gases^[45]. This in turn decreases the exothermicity of the pyrolysis reaction and thermal conductivity, consequently limiting the polyimide's flammability. The introduction of the thiourea moiety in the polymer backbone increases the flame retardancy of the polyimides without reducing their thermal stability^[46].

CONCLUSIONS

A new pyridine-containing aromatic diamine monomer, pyridine-2, 6-bis((4-aminophenyl) thioureido)carbonyl (PATC) containing flexible linkages such as CONH, CSNH and *meta* substituted pyridine ring, was successfully synthesized and characterized, which was employed in polycondensation with various aromatic dianhydrides, to prepare a series of pyridine-containing polyimides. Experimental results indicate that the resulting diamine monomer PATC has good polymerizability, and therefore, strong and tough polyimide films can be obtained. The novel polyimides obtained have relatively high T_g values, excellent thermal stability in nitrogen, as well as good solubility not only in polar aprotic solvents but also in some low-boiling-point solvents such as THF. Meanwhile, the films also possess low water uptake of less than 1%. The dielectric constant of the polyimides measured over a range of frequencies (1 MHz–5 MHz) were found between 2.99 and 3.29. In addition, the polyimide films manifest excellent mechanical properties, with Young's modulus of 2.74–3 GPa. Therefore, the designation of the polymers succeeded in improving the solubility of aromatic polyimides without the loss of thermal stability and mechanical properties of the polymers. Thus, these polyimides are considered to be new promising processable high performance polymer materials.

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