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Synthesis, Characterization and Structure–Property Relationships of Processable Poly(amide-imide)s Containing Novel Tetraphenylthiophene-Thiazole Diimide-Diacid (TPTPThDIDA) Moiety

Y. S. Patil^a, J. N. Mahindrakar^a, P. H. Salunkhe^a, V. P. Ubale^b, and A. A. Ghanwat^a

^aPolymer Research Laboratory, School of Chemical Sciences, Solapur University, Solapur, (MS), India; ^bDepartment of Chemistry, DBF Dayanand College of Arts and Science, Solapur, (MS), India

ABSTRACT

The main objective of this research was to study the structure–property relationships to high performance polymers with thermal stability, solubility and viscosity. Hence, a series of novel poly (amide-imide)s (PAIs) was synthesized from a tetraphenylthiophene-thiazole containing diimide-diacid(TPTPThDIDA) monomer with commercially available various aromatic diamines by using Yamazaki's direct phosphorylation reaction. The resulting PAIs were obtained in high yields and inherent viscosities in the range of 0.86–0.96 dL/g. The reinforcement of the heterocyclic thiazole ring unit on the properties of these PAIs was studied by comparison of the corresponding polymers containing tetraphenylthiophene groups. The PAIs exhibited excellent solubility and good thermal stability. PAIs showed high glass-transition temperatures in the range of 267°C–302°C. Thermogravimetric analysis of the PAIs indicated a 10% weight loss (T_{10}) in the temperature range of 609–736°C and char yields at 900°C under nitrogen atmosphere in the range of 73–80% depending on the diamine monomer used for the synthesis PAIs. The LOI of all poly(amide-imide)s were more than 29, thus such type polymers of can act as flame-retardant materials.

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Flame-retardant; Solubility

Introduction

Aromatic polyamides (PAs) and polyimides (PIs) are well accepted as high-performance polymeric plastics are appreciated to the supreme impactive, thermally stable polymers.^[1–4] Nevertheless, their application was inadequate due to their infusibility, insolubility and removal of volatiles components which make them challenging to process. To overwhelmed these difficulties, some copolymers have been proposed-in careful, poly(amide-imide)s (PAIs), which can be linear, soluble, and also stable in distinction to poly(amic acid)s solutions.^[5] This class of polymers seems to be a good finding the middle ground between thermo-stable and processability.^[6–7] Recently, design and synthesis of monomer construction for built up of polymer framework is to advance structurally and revised using PAs and PIs with enhanced solubility and processability through the introduction of aromatic heterocyclic thiophene-thiazole units and bulky tetraphenyl groups into the polymeric framework.^[8–9] It was investigated that the merger between both hydrogen bonded amide groups and polar thiazole rings lead to in poly(amide imide)s (PAIs) with enhanced solubility and processability.^[10] Wholly aromatic poly(amide-imide)s PAIs gain anticipated results. The thermal stability of PAIs are improved by the rigidity of main chain (tetraphenylthiophene) and the processability is

maintained and retained by hetero ring unit (quinoxaline or thiazole) distortion of the main chain regularity.^[11–12]

In this paper, on above considerations we design and well prepared a novel monomer i.e. tetraphenylthiophene-thiazole diimide diacid (TPTPThDIDA) to contain polar thiazole units and bulky tetraphenylthiophene groups. A series of a novel processable poly(amide-imide)s was effectively synthesized from the direct polycondensation of imide group wrapping diacids (TPTPThDIDA) with various commercial available diamines such as ODA, MDA, SDA, DBA and 6FDA via the triphenyl phosphite and pyridine as condensing agents. The structure property relations of these PAIs due to the attendance of tetraphenylthiophene-thiazole components are studied by evaluated with the previously reported polymers containing tetraphenylthiophene groups. Resulting PAIs contained disorderly (imide-imide)-(amide-amide) links with the polymeric framework. Flame retardant property, Solubility, Viscosity, WAXD, TGA and DSC of the polymers will also be studied.

Experimental

Materials

4,4'-Oxydianiline (ODA), 4,4'-methylenedianiline (MDA), 4,4'-sulphonyldianiline (SDA), 4,4'-Diaminobenzophenone

(BDA), 4,4'-(hexafluoroisopropylidene)dianiline (6FDA), Trimellitic anhydride (TMA) and Sulfur were purchased from Sigma Aldrich Company without further purification. Benzyl chloride, thiourea, iodine (I_2), aluminium chloride ($AlCl_3$), acetyl chloride of s d fine chemical were used as received. LiCl (Sigma Aldrich) was dried for 24 h at $180^\circ C$ under vacuum before use. Solvents such as ethyl acetate, dimethyl sulfoxide (DMSO, s d fine), N,N'-dimethyl acetamide (DMAc, s d fine), triphenyl phosphine (TPP, Sigma Aldrich), N-methyl-2-pyrrolidone (NMP, s d fine), N,N'-dimethylformamide (DMF, s d fine), Pyridine (Py, Sigma Aldrich) THF (s d fine) and DCM (s d fine), bromine solution (s d fine), glacial acetic acid (s d fine), were used as received. N-methyl-2-pyrrolidone, N,N'-dimethylformamide and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over $4A^\circ$ molecular sieves.

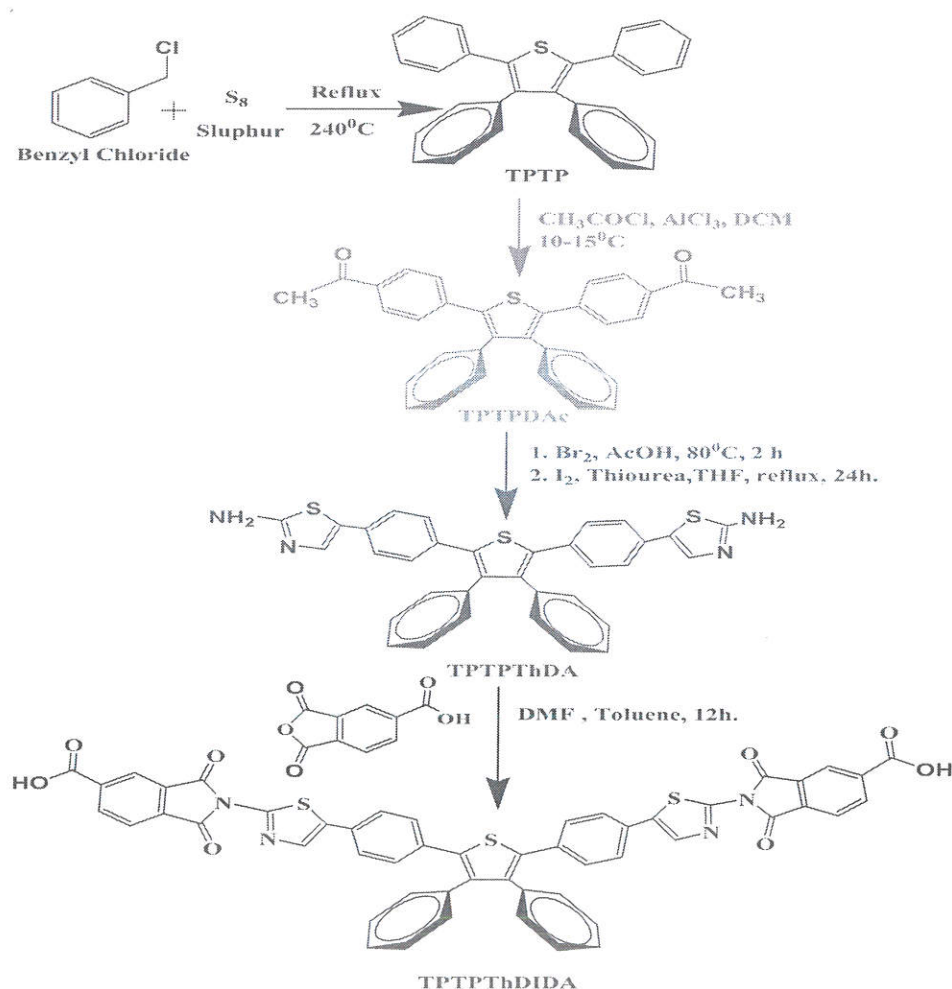
Measurements

The melting points (uncorrected) were measured with an open capillary method. Inherent viscosities were measured with an Ubbelohde suspended-level viscometer with a 0.5 g/dl in NMP solution at $30^\circ C$. The FTIR spectra were

measured on Thermo Nicolet iS-10 Mid Fourier Transform Infrared spectrometer (FTIR) over the range $650\text{--}4000\text{ cm}^{-1}$. The 1H NMR (400 MHz) and ^{13}C NMR spectra were measured on a Bruker Spectrometer (Switzerland). The Mass spectrum was recorded on MASS Model AB Sciex APT 5500. The wide-angle X-ray diffraction (WAXD) measurements were performed on Ultima IV with ULTIMA IV Goniometer (Japan). Thermo-gravimetric analyses (TGA) were conducted with Mettler-Toledo (Switzerland), thermal analyzer under nitrogen and air atmospheres at a heating rate of $10^\circ C\text{ min}^{-1}$. Mettler-Toledo DSC-1 STARe instrument using a heating rate of $10^\circ C\text{ min}^{-1}$ was utilized to measure the glass transition temperatures (T_g s).

Monomer synthesis

The novel tetraphenylthiophene-thiazole diimide-diacid monomer (TPTPThDIDA) and intermediates (Scheme 1) were synthesized according to previous literature reports.^[12–14] All the synthetic details of monomer are discussed below and the reaction scheme for monomer synthesis is shown in Scheme 1. The monomer (TPTPThDIDA) was characterized by FT-IR, 1H -NMR, ^{13}C -NMR and MASS spectroscopy to confirm their structures.



Scheme 1. Synthetic pathway for the synthesis of tetraphenylthiophene-thiazole diimide-diacid monomer (TPTPThDIDA) monomer.

Synthesis of tetraphenylthiophene-thiazole diimide-diacid monomer (TPTPThDIDA)

A 50-mL round-bottom flask was charged with a mixture of TPTPThDA (5.75 g, 10 mmol), trimellitic anhydride (TMA) (4.20 g, 22 mmol), were dissolved in 25 mL of dry DMF. Stirring and heating at 80 °C was continued for 2 h. Then, about 15 mL toluene was added, and the mixture was refluxed for 4 h until virtually 1.2 mL of water was removed by Dean-Stark trap. Continue heating to distill off the lingering toluene. After overnight cooling, the precipitated out diimide-diacid (TPTPThDIDA) were collected by filtration and washed with methanol. It was purified by recrystallized by DMF. The purified product was dried in a vacuum at 100 °C for 24 h to afford a light yellow solid. Yield: 75%; mp. 346–348 °C.

IR (KBr) 3385–2480 (broad), 1786, 1737, 1708, 1631, 1494, 1334, 1284, 1251, 1147, 723 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6); δ 7.05–7.12 (t, 2H, $J=7.4$ Hz), 7.14–7.2 (d, 4H, $J=7.4$ Hz), 7.22–7.34 (d, 4H, $J=7.4$ Hz), 7.88–7.91 (d, 4H, $J=7.4$ Hz), 7.94–7.96 (d, 4H, $J=7.4$ Hz), 8.12–8.17 (d, 2H, $J=7.8$ Hz), 8.19 (d, 2H, $J=7.8$ Hz), 8.35 (s, 2H), 8.44 (s, 2H) 12.43 (broad, 2H, C(O)O–H);

^{13}C NMR (400 MHz, DMSO- d_6); δ 113.88, 123.85, 124.35, 125.98, 127.12, 128.06, 129.00, 130.44, 131.63, 132.74, 133.16, 134.40, 135.92, 136.89, 137.44, 140.01, 150.10, 151.59, 162.27, 164.07, 164.13, 165.65 ppm.

Synthesis of poly(amide imide)s (PAIs-01)

Tetraphenyl-thiazole containing PAIs were synthesized by condensation reaction of DIDA with various aromatic diamines (PAI-01 to PAI-05) as expounded in Scheme 2.

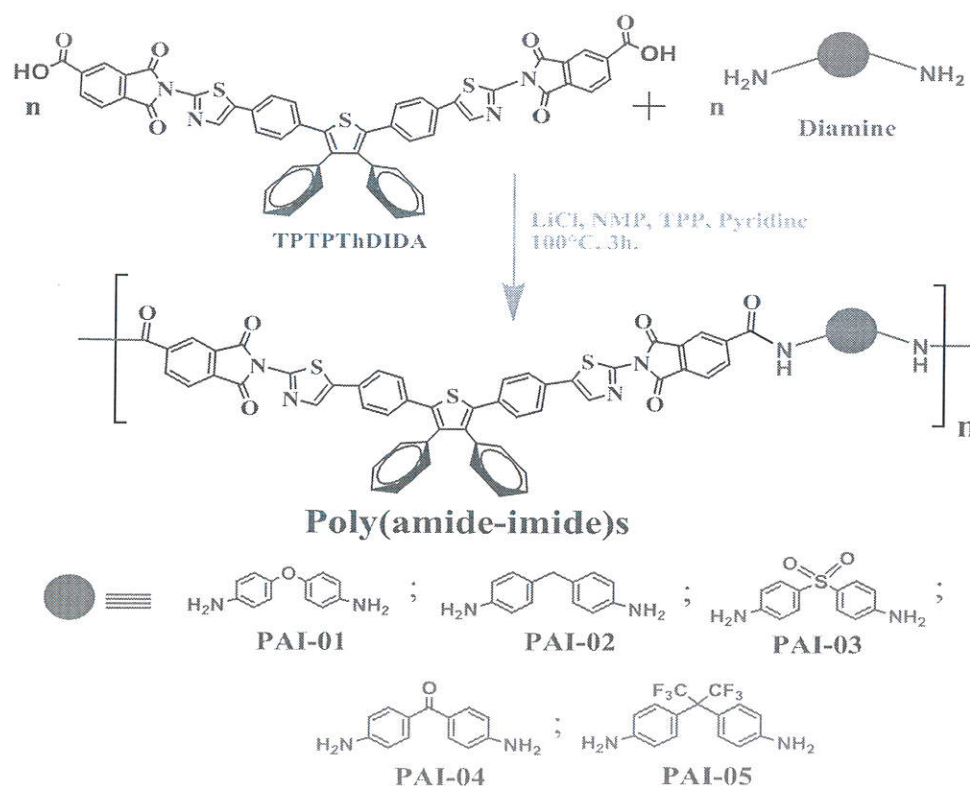
A typical polycondensation procedure for the PAI-1 is described as follows. A mixture of 0.932 g (1 mmol) of TPTPThDIDA, 0.200 g (1 mmol) of 4,4'-oxydianiline (ODA), lithium chloride (0.25 g), triphenyl phosphite (TPP, 0.5 mL), pyridine (0.5 mL) and NMP (2.0 mL) was heated at 110 °C for 3 h, under nitrogen atmosphere with stirring. As the polycondensation proceeded, the reaction mixture of complex slowly converted into highly viscous polymeric materials. After the completion of reaction, these polymeric materials were slowly discharged into methanol (200 mL) under speedy stirring. The product was filtered and washed with hot water and methanol thoroughly. It was finally dried under vacuum at 100 °C overnight. The yield was 99.00%, and the inherent viscosity (η_{inh}) of polymer in NMP was 0.90 dL/g.

IR (KBr): 3392, 3058, 1769, 1715, 1680, 1594, 1499, 1339, 1262, 1197, 975, 877, 830 and 716 cm^{-1} . All other poly(amide-imide)s (PAIs-02 to PAIs-05) was also prepared using similar procedures (Scheme 2).

Results and Discussion

Monomer synthesis

Bulky tetraphenylthiophene and polar thiazole unit containing diimide-diacid monomers were synthesized and predictable to be fighting fit for highly processable polymers. All this well enhanced properties are significant to attain a stunning appreciative result by means of structure-property relationships. Therefore, in the current research work, a new monomer containing bulky- polar i.e. tetraphenylthiophene-thiazole diimide-diacid monomer (TPTPThDIDA) was prepared by condensation of 2,5-bis



Scheme 2. Synthetic pathway for the synthesis poly(amide-imide)s (PAI-01 to PAI-05).

(4-(2-aminothiazole) phenyl)-3,4-diphenyltetraphenyl thiophene (TPTPThDA) with two moles equivalent of TMA was refluxed in DMF-Toluene azeotropically (Scheme 1). The structure of TPTPThDIDA monomer confirmed by FTIR, ^1H NMR, ^{13}C NMR and MASS. The Figure 1 shows FTIR spectrum of TPTPThDIDA, the distinctive broad peak groupings of carboxylic acid and sharp peak of cyclic imide groups 3385–2480 (broad) and 1786, 1737 cm^{-1} respectively. The acid carbonyl sharp peaks at 1708 cm^{-1} . The resonance signals of trimellitimido unit protons of TPTPThDIDA (as shown in Figure 2g, h, and i) are observed in between 8.12–8.35 ppm i.e. downfield regions in the ^1H NMR spectrum of TPTPThDIDA. The sandwiched phenyl aromatic protons (d, e) and thiazole protons (f) are accredited 7.88–7.91 and 7.94–7.96 respectively. The signals integrated in Figure 2 at 7.05–7.34 ppm are attributed to the protons of outside aromatic two phenyl rings (a, b and c). All the integrated peak area as shown in Figure 2 is in agreement with the assignment. In the ^{13}C NMR spectrum (Figure 3a and b) of TPTPThDIDA, twenty two signals are observed, which are consistent with the estimated structure. Aromatic Signals in the range of 113.88–151.59 ppm. The carbonyl carbons of carboxylic acid and imide groups resonate in the downfield at 165.65, 164.13 and 164.07 ppm, respectively. The peak around 162.27 ppm is for imine carbon. In Addition for the structure confirmation mass spectrum (Figure 4) investigate the molecular weight of monomer. The molecular ion (m/z) peaks at 932.83 originate to the TPTPThDIDA.

Polymer synthesis

The foremost purpose of the presented work was an adverse the effects of polar thiazole and bulky tetraphenylthiophene

units on the polymer properties. For that reason, we designed and synthesized a series of tetraphenylthiophene-thiazole framework containing PAIs based on a novel diimide-diacid (TPTPThDIDA) monomer (Scheme 2). The processable polycondensations of PAI-1–PAI-5 is synthesized by using Yamazaki's direct phosphorylation reaction method^[15–16] (NMP, LiCl, TPP, and pyridine) in high yields. During polymerization of PAI-1 and PAI-5, the reaction mixtures became highly viscous. Synthetic conditions, mole ratio of difunctional monomers and inherent viscosities of these polymers (PAI-1 to PAI-5) are summarized in Table 1. The structural elucidations of the PAIs were clarified by FTIR and ^1H NMR techniques. The FTIR spectra (Figure 5) of PAIs-2 offered a distinctive absorption bands for the imide ring of carbonyl (stretching) at about 1769 cm^{-1} and 1715 cm^{-1} , 1339 cm^{-1} (C–N stretching). The absorption of amide group seems at nearby 3392 cm^{-1} (N–H stretching) and 1680 cm^{-1} (C=O stretching). Figure 6 illustrated a specific ^1H NMR spectrum for PAI-1, in which all the protons are in good clearance with the suggested structure. The formation of amide linkages in PAIs is attributed to resonance signals in the most downfield region at about 9.51 ppm.

Solubility and Inherent Viscosity

The Table 2 provided qualitative solubility of the bulky tetraphenylthiophene and polar thiazole units covering poly(amide-imide)s (PAIs-1 to PAIs-5). Almost all PAIs were soluble in organic solvents such as NMP, DMSO, DMAc, pyridine and DMF (on heating). While they are partly soluble in m-cresol, DMF (PAI-3) and insoluble in chlorinated solvent chloroform, THF, and so forth. On other hand it was proven that bulky and polar groups in

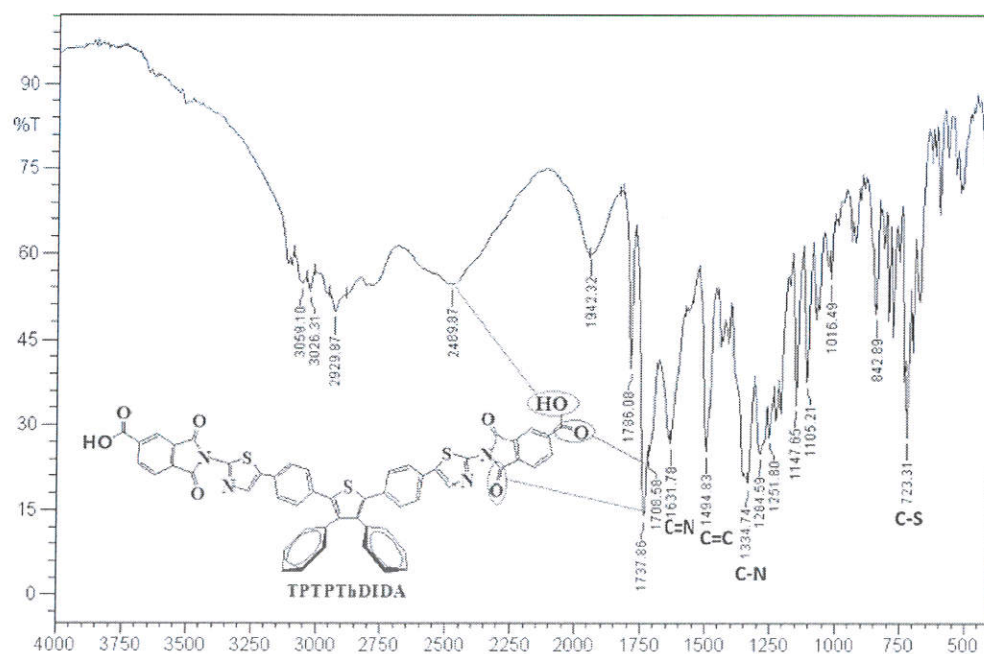


Figure 1. FT-IR spectrum of TPTPThDIDA.

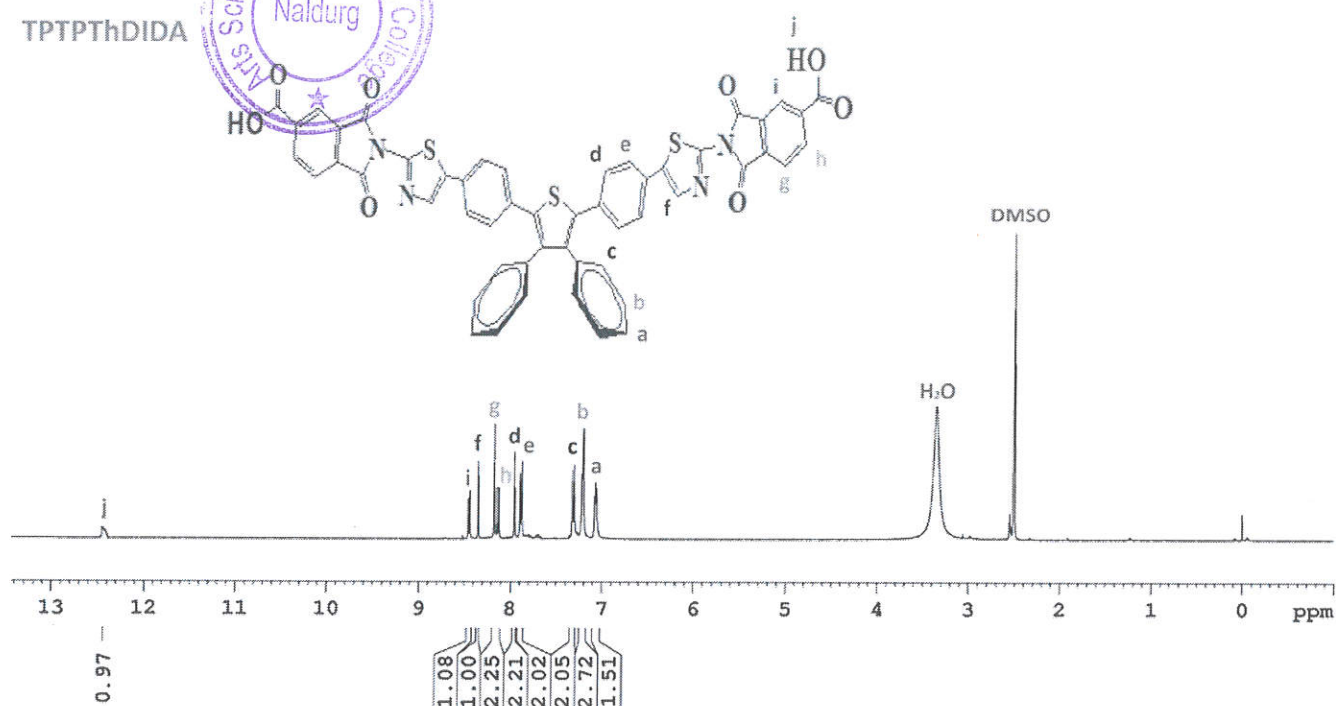


Figure 2. ^1H -NMR Spectrum of TPTPhDIDA.

the polymer framework can enhance the solubility and processability of aromatic polyamides and polyimides, lacking any substantial deteriorating in thermal stability. As shown in Table 2, all the PAIs partaking polar thiazole ring and bulky tetraphenylthiophene groups discovered outstanding solubility in acceptable and vastly polar solvents. The solubility behaving depends upon the commercial diamines. Considering the polymeric chemical structures in Scheme 2, the appearance of highly flexible ether linkages (PAI-1) and methylene linkages (PAI-2) in the polymeric framework charged to enlarged elasticity and troubled the planarity of aromatic units, resultant in diminution of the close packing. Hence, these polymers were found to be highly soluble in aprotic organic solvents. Other PAI-3 and PAI-4 having connecting polar (SO_2 , $\text{C}=\text{O}$) groups shows moderate to high solubility in organic solvents except (DMF on heating) respectively. While the PAI-5 shows remarkably in addition of two polar $-\text{CF}_3$ groups with bulky tetraphenylthiophene polar thiazole units. As compare to bulky structures, the solubility of these bulky and polar tetraphenylthiophene-thiazole constructed poly(amide-imide)s (PAIs) were advanced than that of aromatic polyamides by compelling with huge structures such as tetraphenylthiophene^[17] and 2,5-Bis(4-trimellitimidophenyl)-3,4-diphenylthiophene described.^[8]

Inherent viscosity measurements were used to establish an order of constructing molecules or building up of molecules and size of the PAIs chain in the series (PAI-01 to PAI-05). All these poly(amide-imide)s shows excellent solubility in organic solvents at room temperature except DMF (on heating). Thus, the inherent viscosity of poly(amide-imide)s was recorded at 30°C in NMP and values in between 0.86 and 0.96 dL/g were obtained as shown in Table 1.^[18]

Thermal Analysis

The Figure 7 shows the TGA thermograms of PAI-01 to PAI-05 measured at a heating rate of $10^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) and 10% weight loss temperature of these polymers are tabulated in Table 3. The high thermal stability, chemical and mechanical stiffness for poly(amide-imide)s arises from the aromatic rings (bulky tetraphenylthiophene) as well as the imide-imide and amide-amide linkages.^[19] The degradation of polymeric chain to yield smaller units by the cleavage of heteroatom bonds such as $\text{C}-\text{O}$, $\text{C}-\text{N}$, $\text{C}-\text{F}$ and $\text{C}-\text{O}$, homoatomic bond $\text{C}-\text{C}$ bond. All poly(amide-imide)s (PAI-01 to PAI-05) showed T_{10} values in N_2 atmosphere in the range of 609 – 736°C . Amongst these poly(amide-imide)s, the PAI-03 and PAI-04 exhibits the supreme thermal stability with a disintegration temperature of ca. 736°C and 688°C respectively, this is for the reason that the polymer backbone contains more bulky and polar groups tetraphenylthiophene-thiazole and sandwiched rigid connecting framework of carbonyl centers ($\text{C}=\text{S}$) and ($\text{C}=\text{O}$). On other hand poly(amide-imide)s such as PAI-01, PAI-02 and PAI-05 with its molecular arrangements containing polar connecting group such as ether, methylene and flexible polar substituent groups such as two $-\text{CF}_3$ group which chains moderately slanted towards along the axis and hence have slightly lesser strength and thermal stability than PAI-03 and PAI-04.^[20–21] Also, all PAIs retained more than 73% in weight nitrogen even at 900°C . In addition, all these poly(amide-imide)s (PAI-01 to PAI-05) shows greater thermal stability even with the introduction to polar thiazole ring units with bulky tetraphenylthiophene groups without sacrificing other physical properties. On comparing the thermal stability of bulky tetraphenylthiophene with polar thiazole ring units based poly(amide-imide)s (PAI-01 to PAI-05) has greater thermal stability (609 – 736°C) with respect to the T_{10} of

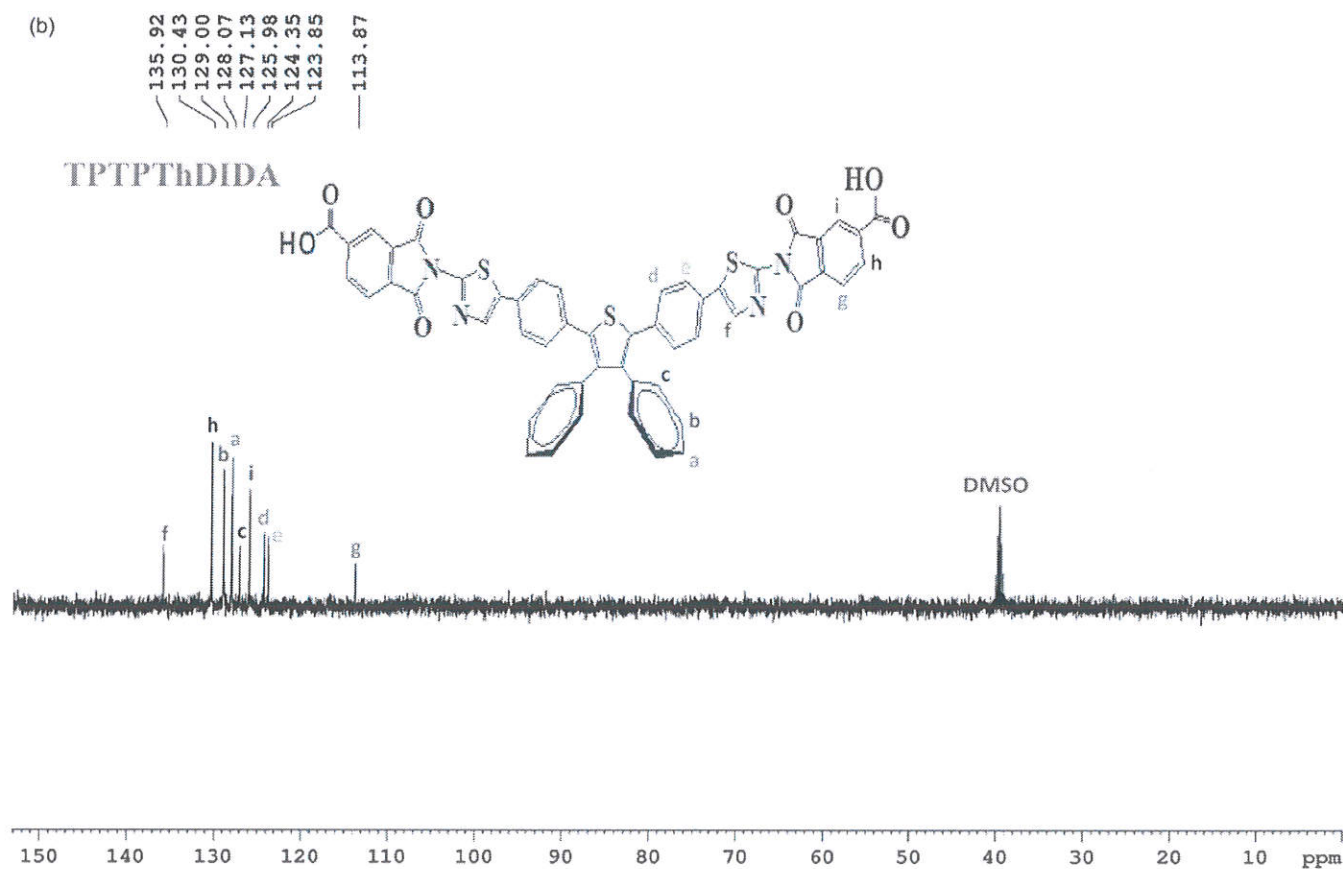
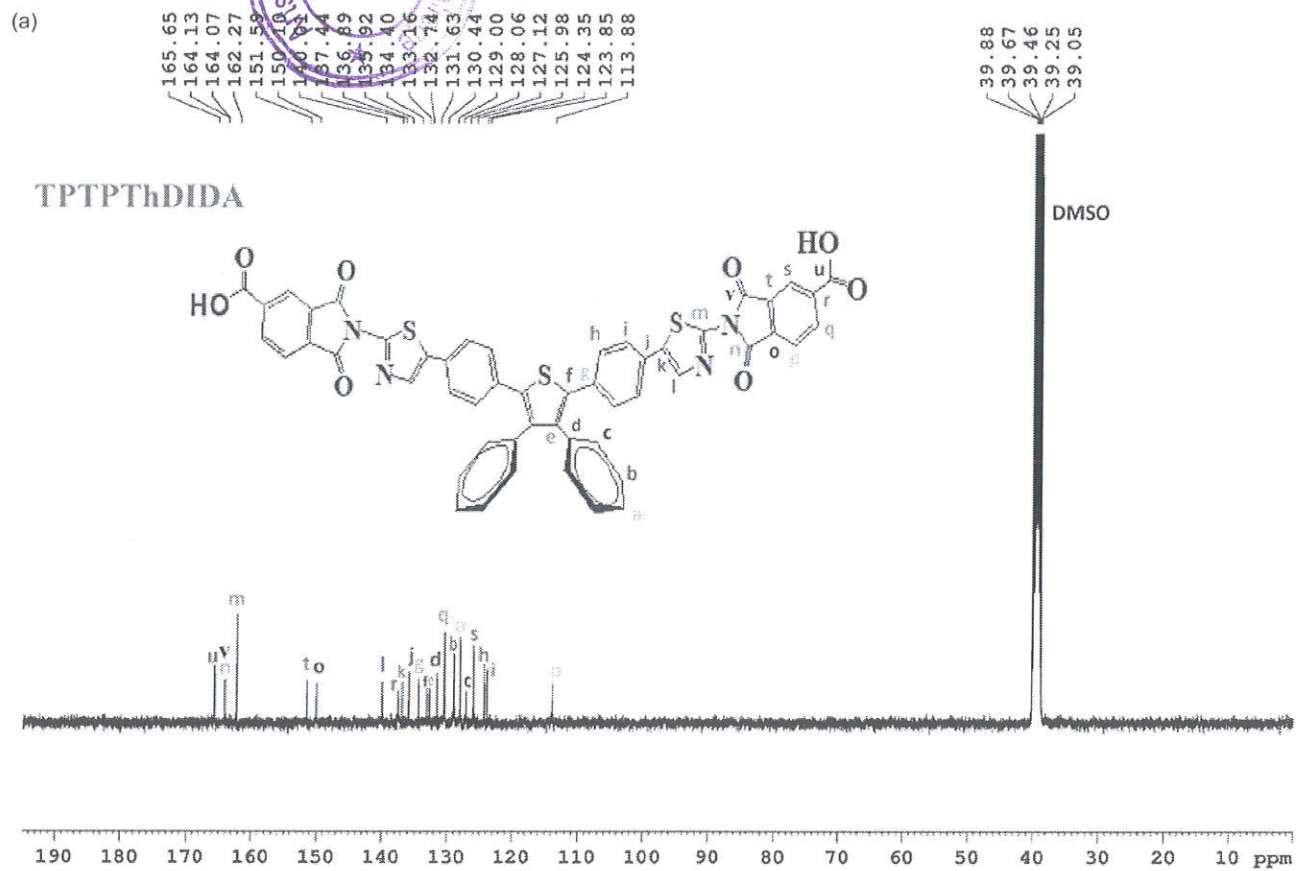


Figure 3. (a) ^{13}C -NMR Spectrum of TPTPThDIDA, (b) DEPT Spectrum of TPTPThDIDA.

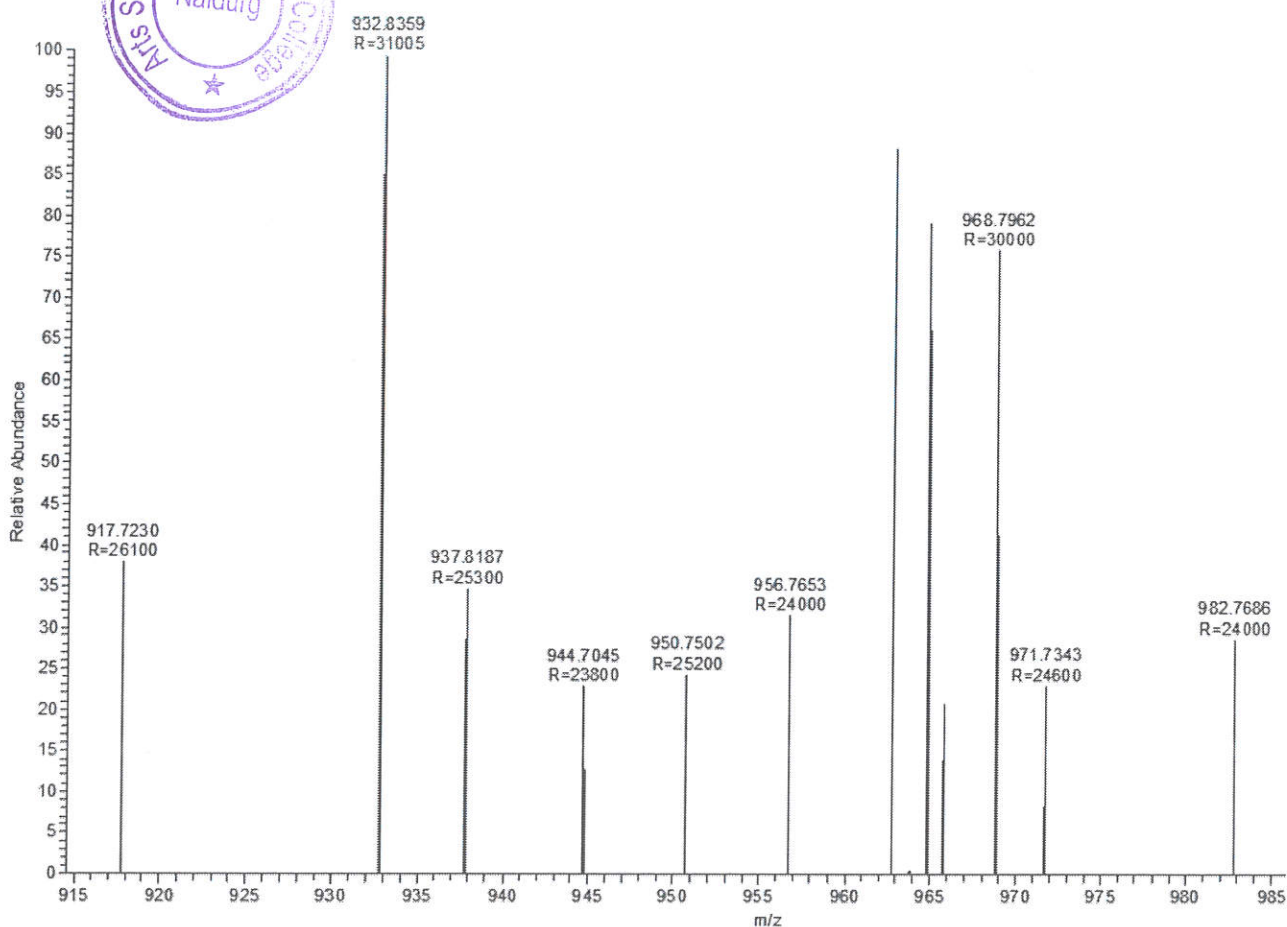


Figure 4. MASS Spectrum of TPTPTHIDA.

Table 1. Synthesis of Poly(amide-imide)s from (TPTPTHIDA).

Polymer ^a Code	Diacid CMPDF	Diamines	Yield (%)	Viscosity ^b η_{inh} (dL/g)	Flim Formation	Color
PAI-01	TPTPTHIDA	ODA	99	0.90	Yes	Yellow
PAI-02	TPTPTHIDA	MDA	96	0.86	Yes	Faint yellow
PAI-03	TPTPTHIDA	SDA	98	0.96	Yes	Yellow
PAI-04	TPTPTHIDA	BDA	97	0.92	Yes	Yellow
PAI-05	TPTPTHIDA	6FDA	96	0.88	Yes	Faint yellow

^aPolymerization was carried out with 1mmol each of diacid and diamines.

^bMeasured at a concentration of 0.5 dL/g in NMP at 30 °C.

the structurally bulky related poly(amide-imide)s containing tetraphenylthiophene unit i.e. 2,5-Bis(4-trimellitimidophenyl)-3,4-diphenylthiophene (550–596 °C). These results indicate that high thermal stability of the present poly(amide-imide)s (PAI-01 to PAI-05). Inference of prepared bulky polar tetraphenylthiophene-thiazole containing poly(amide-imide)s is very magnificent in thermal stability with other early reported poly(amide-imide)s.^[8,17] The introduction effect of polar thiazole rings not only in their decomposition temperatures but also in the final char yield.

DSC Study

The DSC plots of PAI-01 to PAI-05 are presented in Figure 8. The glass transition temperature (T_g) is shortened in Table 3. The DSC results investigated that for every sample there is no indication of crystallization and

melting processes, assist the amorphous nature of these entire poly(amide-imide)s. As outlined in Figure 8 and Table 3, the highest T_g values of these aromatic poly(amide-imide)s was in the range of 267–302 °C. As expected, the T_g values depended on the structure of the diamine component and decreased with increasing flexibility of the polymer backbones. Poly(amide-imide)s PAI-01 and PAI-02 covered polar (ether) and flexible (methylene) group structures respectively. Among all poly(amide-imide)s PAI-02 shows the highest T_g values than other poly(amide-imide)s containing sandwiched connecting groups such as PAI-03(C=S), PAI-04(C=O) and PAI-05(-CF₃). This credited higher T_g values because the tetraphenyl moieties reduced the mobility of polymer chains with increasing the chain flexibility by spacer methylene linkages followed by the flexible substituent (-CF₃) below that polar ether linkages (-O-) in polymer frameworks leading smooth T_g curve.^[22–23]

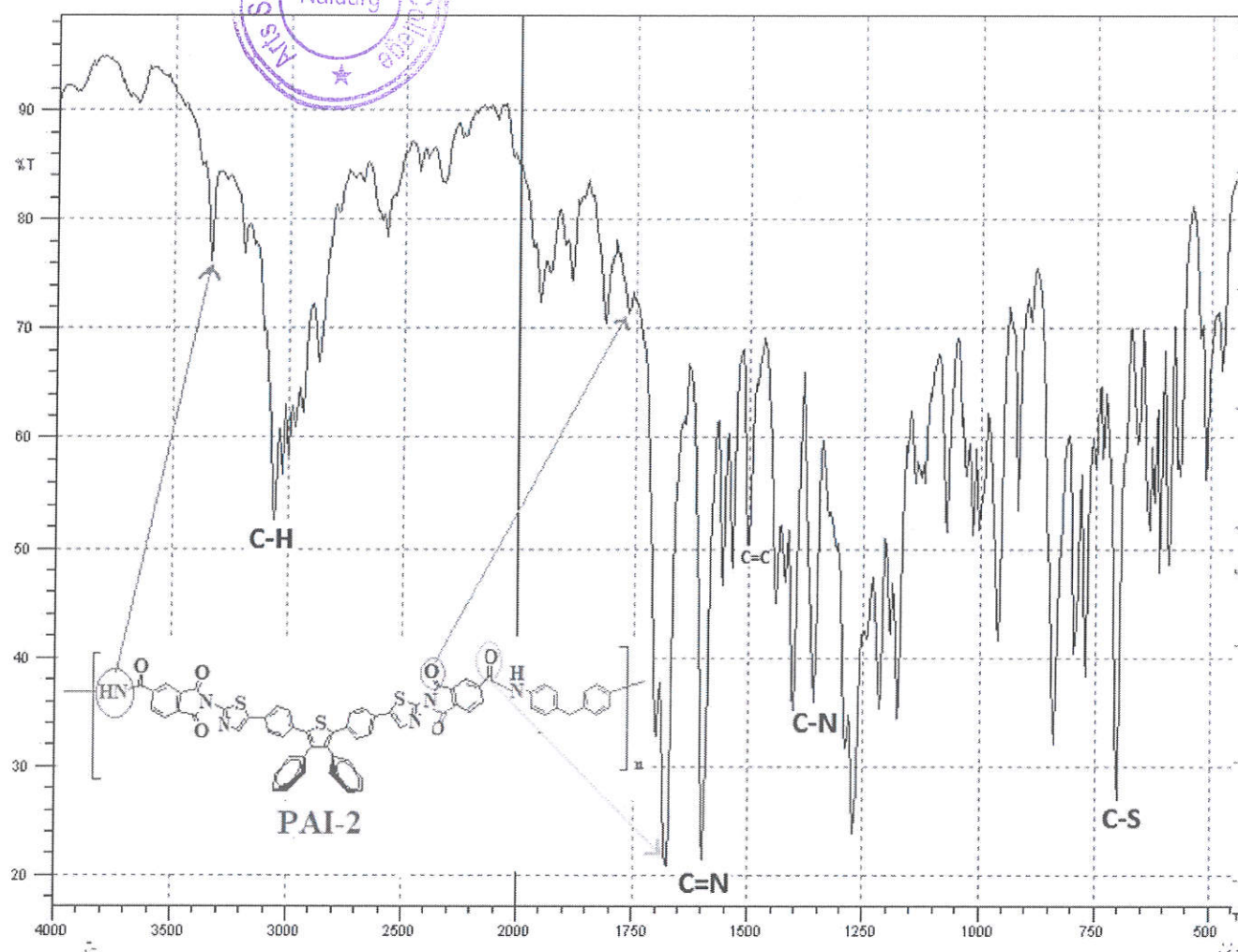


Figure 5. FT-IR Spectrum of Poly(amide-imide)s PAI-2.

Poly(amide imide)s (PAI-1)

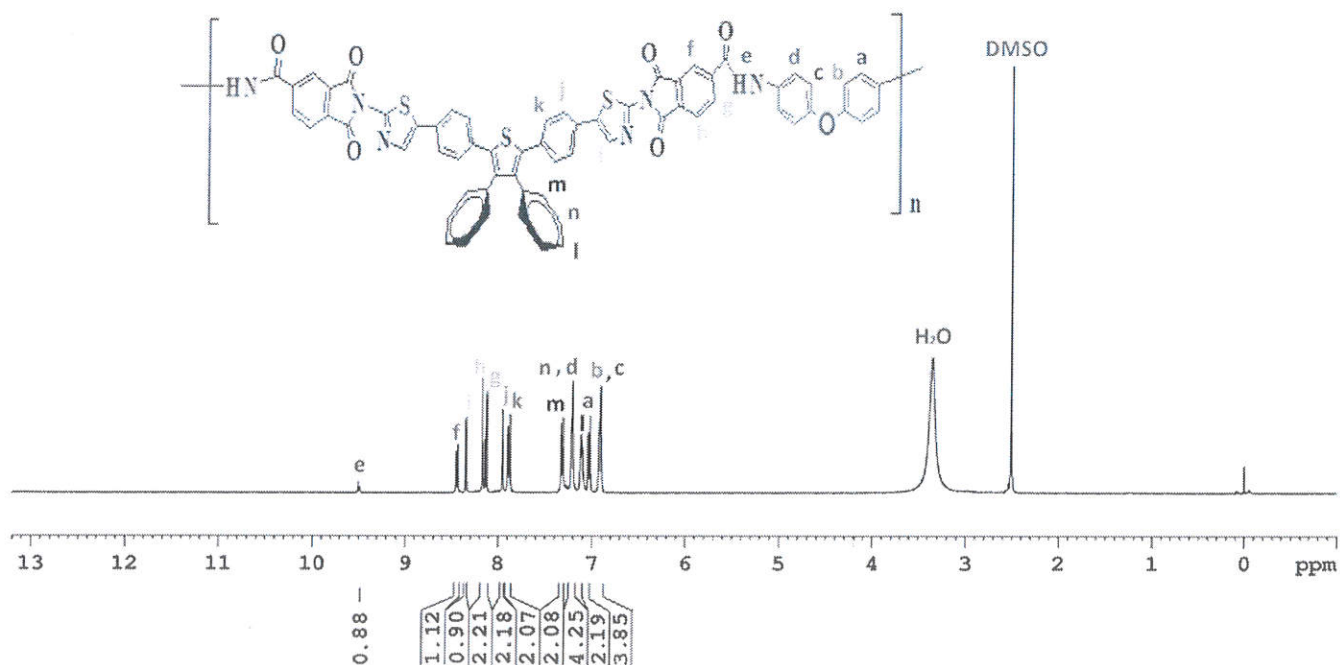
Figure 6. ¹H-NMR spectra of Poly(amide-imide)s PAI-1.

Table 2. Solubility of Poly(amide-imide)s (PAI-01 to PAI-05).

Solvents	DMAC	NMP	DMF	DMSO	Pyridine	Conc. H ₂ SO ₄	m-cresol	CHCl ₃	THF
PAI-01	++	++	+	++	+	++	+-	-	-
PAI-02	++	++	+	+	++	++	+	-	-
PAI-03	+	+	+-	++	+	++	+-	-	-
PAI-04	++	++	+	++	++	++	+	-	-
PAI-05	++	++	+	++	++	++	++	-	-

++ Soluble + soluble on heating +- partly soluble -Insoluble.

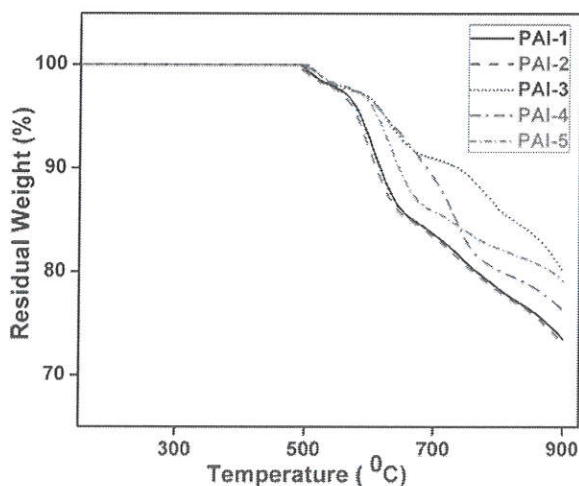


Figure 7. TGA of Poly(amide-imide)s (PAI-1 to PAI-5).

Table 3. Thermal properties of Poly(amide-imide)s (PAI-01 to PAI-05).

Sr. No.	Polymers	Thermal Behaviour ^a			Residual Wt % at 900°C	LOI
		T _g	T _i	T _d		
1	PAI-01	295	491	615	73	29.2
2	PAI-02	302	485	609	73	29.2
3	PAI-03	267	499	736	80	32.0
4	PAI-04	272	493	688	76	30.4
5	PAI-05	300	503	644	79	31.6

^aTemperature at which onset of decomposition was recorded by TG at a heating rate of 10°C/min.T_g - Glass transition temperature.T_i - Initial decomposition temperature T_d - Temperature of 10% decomposition.

LOI - Limiting oxygen index.

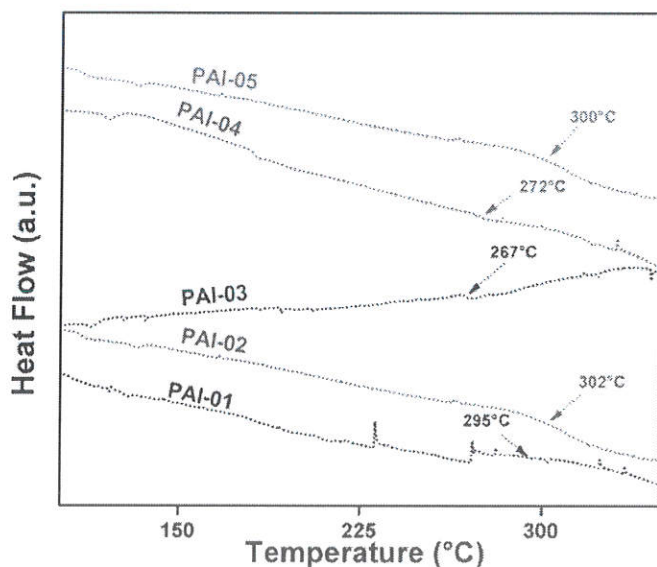


Figure 8. DSC of Poly(amide-imide)s (PAI-1 to PAI-5).

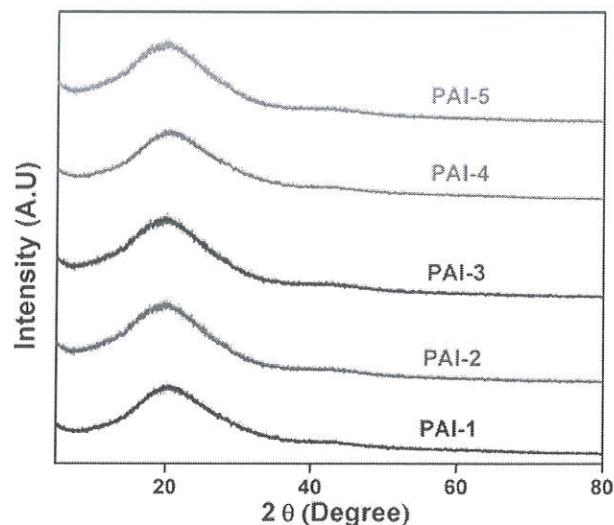


Figure 9. WAXD of Poly(amide-imide)s (PAI-01 to PAI-05).

Flame-retardant Property by Limiting oxygen index (LOI)

Mostly, constituents with limited oxygen index (LOI) upper than 26 shows self-extinguishing performance and are reflected as flame retardant. According to Van Krevelen and Hoftyzer equation^[24]:

$$\text{LOI} = 17.5 + 0.4\text{CR}$$

where CR is the percentage of polymer remaining at 900°C.

All poly(amide-imide)s has LOI more than 29 and such polymers can act as flame-retardant materials are summarized in Table 3. The LOI of PAI-1, PAI-2, PAI-3, PAI-4 and PAI-5 estimated at 29.2, 29.2, 32, 30.4 and 31.6 respectively.

WAXD Analysis

The wide-angle X-ray diffraction (WAXD) patterns of all poly(amide-imide)s are confirmed in Figure 9. All the polyamides (PAI-01 to PAI-05) derived from Polar flexible (-O- and -CH₂-), connecting Sandwiched more polar (C=O), less polar (C=S) and polar substituted two -CF₃ group showed broad halo at ~20° (2θ) was observed which confirms that the polymers are amorphous in nature. This due to the presence of bulky tetraphenyl unit all over the polymeric framework which slowed down chain packing effectiveness and diminished the intermolecular forces, consequently affected a decline in crystallinity. This amorphous nature of all these poly(amide-imide)s supported to solubility and inherent viscosity of polymers.^[25-26]

Conclusions

The new series of diimide-diamide containing aromatic poly(amide-imide)s covering polar thiazole and bulky tetraphenyl groups were introduced into the molecular framework of PAIs via the newly developed diimide-diacid monomer. This advanced monomer synthesized by the imide cyclo-condensation reaction of a novel tetraphenylthiophene-thiazole diimide-diacid precursor (TPTPhDIDA) and various aromatic diamines by using Yamazaki's


phosphorylation method. The structure-property relationships of these PAIs due to the enterprise of bulky tetraphenyl unit and polar thiazole rings unit were also studied and well established with respect to the Solubility, inherent viscosity, and morphology of polymers (WAXD) and most advanced in thermal properties. From all the experimental results, it can be concluded that the synergic insertion effects of polar-bulky tetraphenylthiophene-thiazole units, into the polymeric framework was greatly operative for the synthesis of highly processable poly(amide-imide)s inventing great T_{10} values and high T_g to the analogous PAIs. They were characterized as high T_g in the range of 267–302 °C and great thermal stability (509–736 °C). All the PAIs synthesized had inherent viscosities in range of 0.86 and 0.96 dL/g. Almost all of these poly(amide-imide)s was soluble in polar solvents at room temperature except DMF (on heating). Synthesized aromatic PAIs are characterized by WAXD; it appraises the insertion effect of precursor to polymer backbone and showing the amorphous nature. By all consideration of their properties are desired for advanced applications, such as the constituents for superior high thermal resistance. By LOI these poly(amide-imide)s behaving as flame-retardant materials. Thus, these PAIs could live on the unforgivable environments of many high-tech applications.

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ORCID

P. H. Salunkhe  <http://orcid.org/0000-0001-5735-0421>

A. A. Ghanwat  <http://orcid.org/0000-0002-6053-0834>

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 Arts Science & Commerce College
 Naldurg, Dist. Osmanabad-413602