

Synthesis and characterization of aromatic polyimides containing tetraphenylfuran-thiazole moiety

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Abstract

2,5-Bis(4-(2-aminothiazole) phenyl)-3,4-diphenyl furan (BATPDF), well prepared in four steps. Novel aromatic polyimides containing tetraphenylfuran-thiazole unit were synthesized via a two-step thermal imidization derived from BATPDF with various commercially available dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydi(phthalic anhydride) (ODPA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). The resulting aromatic PIs were obtained in high yields and moderate inherent viscosities in the range of 0.42–0.48 dL g⁻¹ and were practically amorphous as shown by the X-ray diffraction studies. All the polyimides exhibited excellent solubility in solvents, such as DMAc, NMP, m-cresol and pyridine on heating. PIs showed high glass transition temperatures between 238 and 252 °C. TG of the PIs indicated a 10% mass loss ($T_{10\%}$) in the temperature range of 518–609 °C and char yields at 900 °C under nitrogen atmosphere in the range of 58–65% depending on the dianhydrides monomer used for the synthesis PIs. The structure–property correlation between these polyimides was studied. In view of these polymer's potential applications as thermally stable aerospace, optoelectronics and microelectronics device.

Keywords Polyimides · Tetraphenylfuran-thiazole · Thermal stability · XRD

Introduction

Over many years, with the fast development of different high-tech fields, the performances of the polymer materials are simultaneously put forward to high requirements. As the most successful classes of high temperature polymers, polyimides have been shown to be excellent comprehensive performance and their applications are growing steadily. Polyimides have excellent mechanical properties such as high mechanical strength and excellent electrical properties, high thermal stability as well as good chemical resistance [1–7]. Therefore, polyimides have been widely employed in the fields of the aerospace, microelectronics,

coatings, functional membranes, etc. [8–12]. Aromatic polyimides are well known for their superior resistance to spontaneous pyrolysis and oxidative degradation [13]. Because of their insolubility combined with high softening temperature, they are generally difficult to fabricate [14, 15]. Many studies of new polyimide synthesis have been focused on the preparation of novel diamine or dianhydride having a special structure, such as tetraphenyl-based structure [16–18], neighboring thiazole unit structure [19], high sulfur content structure [20, 21], high symmetrical structure and unsymmetrical structure [22], etc. Compounds having a tetraphenyl and thiazole structure moieties possess high symmetrical structure and have been receiving more attention as a monomer for the synthesis of novel polyimide. In the high-performance polymer materials, the molecular chain comprising tetraphenyl and thiazole may effectively change some properties of the polymer, resulting in high crystallinity, thermal stability and low solubility [23]. Low solubility of the polyimide affects processing and limits its application. Solubility of

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the polyimides has been targeted by several methods, such as introduction of flexible linkages [24–29], bulky pendent substituents [30–32] or aromatic heterocyclic [33–36]. The five-membered heterocyclic or thiazole ring unit is introduced into a containing tetraphenylfuran structure diamine for the synthesis of the polyimide can effectively improve its solubility and processability while not declining positive properties. Over the past two decades, macromolecules containing thiazole, as a heteroaromatic ring containing sulfur atom and one $-C=N-C-$ bond, have been reported on the academic literature and have received commercial attention due to their unique optoelectronic applications [37]. The contribution to thiazole units to high T_g polymers, in which new class of PIs based on the tetraphenylfuran monomers containing thiazole units were developed. It was found that the incorporation of thiazole moieties and bulky pendant group resulted in organic-soluble and high crystallinity with great retaining the thermal stability. On the basis of these considerations, we designed and synthesized a new diamine [2,5-bis(4-(2-aminothiazole) phenyl)-3,4-diphenyl furan, BATPDF] monomer containing thiazole units and bulky tetraphenyl moiety.

In this article, for investigating the structure–property relations of PIs, intermediates of monomer and novel diamine monomer (BATPDF), successfully synthesized. A series of processable aromatic polyimides containing tetraphenylfuran-thiazole unit were synthesized with various aromatic commercial dianhydrides by the usual two-step procedure that included ring-opening polyaddition and subsequent thermal cyclodehydration. Aromatic polyimides are characterized by high glass transition temperature (T_g) along with high decomposition temperatures. The introduction of tetraphenylfuran-thiazole unit into the polymer backbone was expected to increase the glass transition temperature due to the rigid tetraphenyl structure, as well as improve the solubility due to the bulky structure. The structure property relationships of these PIs due to the presence of tetraphenylfuran-thiazole ring are studied by comparison to the reported polymers containing bulky tetraphenyl unit [38, 39].

Experimental

Materials

All materials and solvents were purchased either from Sigma-Aldrich or s d fine. Pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydi (phthalic anhydride) (ODPA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), potassium tertabutoxide, 1,2-

diarylethanone(deoxybenzoin), thiourea, iodine (I_2), aluminum chloride ($AlCl_3$) acetyl chloride. Solvents such as tetrahydrofuran (THF), ethyl acetate, dimethyl sulfoxide (DMSO), dichloromethane (DCM) and toluene were used as received. *N*-methyl-2-pyrrolidone (NMP), *N,N'*-dimethylformamide (DMF) and *N,N'*-dimethylacetamide (DMAc) were purified by distillation over P_2O_5 under reduced pressure and stored over 4 Å molecular sieves. THF and DCM were dried by sodium and calcium hydride, respectively, before use.

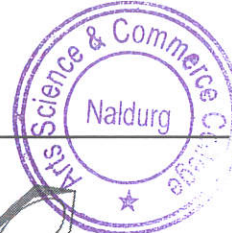
Instruments and measurements

The FTIR spectra were measured by Thermo Nicolet iS-10 Mid Fourier Transform Infrared spectrometer (FTIR) in the 650–4000 cm^{-1} frequency range. The 1H NMR (400 MHz) spectra were measured with a Bruker Spectrometer (Switzerland) using d_6 -DMSO as solvent. The mass spectrum was recorded on MASS Model AB Sciex APT 5500. XRD was recorded on X-Ray diffraction system Ultima IV with ULTIMA IV Goniometer (Japan). Inherent viscosities were measured using an Ubbelohde suspended level viscometer with a 0.5 g dL $^{-1}$ in NMP solution at 30 °C. The TG was recorded using an instrument (Mettler-Toledo TGA, Switzerland) in the temperature range of 30–900 °C. Samples having mass of ca. 5 mg were placed in 100-mL alumina crucibles. Thermal decomposition experiments were carried out using a heating rate of 10 °C min $^{-1}$ in nitrogen atmosphere with a gas flow rate of 50 mL min $^{-1}$. The DSC measurements were performed using a Mettler-Toledo DSC-1 STARe system in nitrogen atmosphere (flow rate of 50 mL min $^{-1}$). Samples of ca. 5 mg were weighed, sealed in aluminum pans, heated to their respective final temperatures that was used for each sample, kept isothermally at that final temperature for 5 min and then cooled. The first heating was done to erase the thermal history of the polyimides. They were then reheated with a heating rate of 10 °C min $^{-1}$. The glass transition temperature (T_g) and melting temperature(T_m) were derived from the second heating traces.

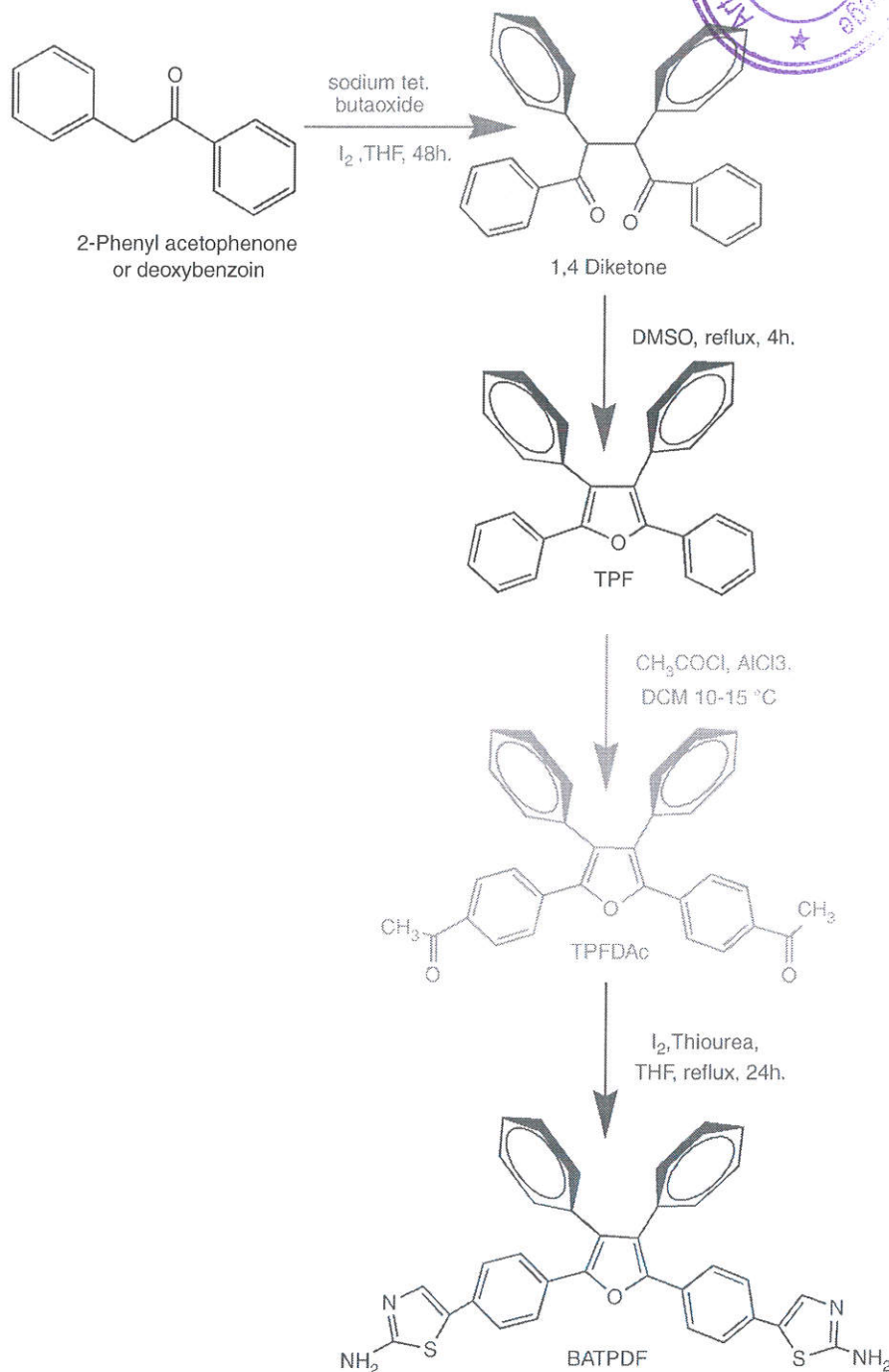
Synthesis methods

Monomer synthesis

2,3,4,5-Tetraphenylfuran (TPF) and intermediates of monomer (Scheme 1) were synthesized in our laboratory according to previous literature reports [40, 41]. By applying some more modification, BATPDF was synthesized for the first time in our laboratory and all the synthetic details of monomer are discussed and the reaction scheme for monomer synthesis is shown in Scheme 1. The monomer (BATPDF) was characterized by using FTIR,



Scheme 1 Synthetic pathway for the synthesis of 2,5-bis(4-(2-aminothiazole) phenyl)-3,4-diphenyl furan diamine monomer



1H -NMR and MASS spectroscopy to confirm their structures.

2,5-Bis(4-acetyl phenyl)-3,4-diphenyl furan (TPFDAc)

In three-neck flask, TPF (6.678 g, 18.05 mmol), anhydrous DCM (50 mL) and $AlCl_3$ (4.783 g, 36.10 mmol) were added under nitrogen atmosphere. The whole mixtures were then cooled to 0 °C by ice-water bath. Acetyl chloride (2.833 g, 36 mmol) was then added drop wise to the stirred

reaction mixture at 0 °C. The reaction was allowed to warm to room temperature and continued for overnight. The resulting mixture was poured into ice water (300 mL), and the organic layer was collected, evaporated to give crude product TPFDAc, and recrystallized from toluene to get pure diacetyl tetraphenylfuran (TPFDAc) as pale yellow needles [42].

M. P. 252–254 °C and yield 70%.

2,5-Bis(4-(2-aminothiazole) phenyl)-3,4-diphenyl furan (BATPDF)

In single-neck 100-mL round-bottom flask, a mixture of (TPFDAc) (4.56 g, 10 mmol), iodine (1.52 g 20 mmol) and thiourea (5.08 g, 20 mmol) in 70 mL THF was refluxed, and completion of the reaction was confirmed by TLC. After completion of reaction cool the flask, this clear solution reaction mass was poured onto cold sodium thio-sulphate solution and precipitated product was collected by filtration and recrystallized from ethyl acetate as brownish-yellow crystals [43].

M. P. 238–240 °C and yield 95–99%.

Polymer synthesis

By using BATPDF, a series of five polyimides were prepared [44].

Synthesis of polyimides (PI-01 to PI-05)

In a 100-mL three-neck round-bottom flask equipped with a magnetic stirrer, nitrogen gas inlet, and calcium chloride guard tube were placed 0.568 g (0.001 mol) of BATPDF in 3.6 mL of *N*-methylpyrrolidone (NMP) and the resulting solution was cooled to 0 °C in ice bath. To this cold solution, 0.218 g (0.001 mol) of solid pyromellitic dianhydride (PMDA) was added in lots over period of 1 h then stirred at 0 °C for 3 h and then for 24 h at room temperature under a nitrogen atmosphere, during this time viscosity of the reaction mixture increased. The viscous polymer solution was poured into methanol to precipitate poly(amic acid), filtered and washed with methanol. The poly(amic acid) was dried under vacuum at 50 °C. The inherent viscosity (η_{inh}) of resultant poly(amic acid) (PI-1) was 0.42 dL g⁻¹ measured in NMP at 30 °C.

The poly(amic acid) was consequently cyclized by thermal imidization, where the polymer was taken in flask and heated step wise under nitrogen flow for 1 h at 100 °C, then 1 h at 150 °C and finally for another 1 h at 200 °C. This process ensured the complete imidization. The overall yield is 99%. The series of polyimides PI-2 to PI-5

(Table 1) was synthesized by utilizing above procedure, where in BATPDF polycondensed with different dianhydrides (Scheme 2).

Results and discussion

Synthesis of monomer

The novel thiazole contained diamine (BATPDF) was synthesized in several steps (Scheme 1).

Carbon–carbon coupling of deoxybenzoin catalyzed by sodium tertabutoxide followed by subsequent addition of iodine to yield 1,2,3,4-tetraphenylbutane-1,4-dione, further cyclization gave 2,3,4,5-tetraphenylfuran (TPF) [38]. Acylation of 2,3,4,5-tetraphenylfuran (TPF) to yield 2,5-bis(4-acetyl phenyl)-3,4-diphenyl furan (TPFDAc) [40]. Finally on cyclization with thiourea and iodine to gave 2,5-bis(4-(2-Aminothiazole) phenyl)-3,4-diphenyl furan (BATPDF). The structure of new diamine monomer was confirmed by FTIR, NMR and mass spectroscopy.

Synthesis of polymers

Furan-thiazole containing aromatic polyimides was synthesized by BATPDF with various aromatic tetracarboxylic dianhydrides (PI-01 to PI-05). The two-step polymerization, shown in Scheme 2, involves ring-opening polyaddition forming soluble polyamic acid and subsequent thermal cyclodehydration [41]. In the first step, the polyaddition in NMP at room temperature afforded polyamic acids with inherent viscosities in the range of 0.42–0.48 dL g⁻¹ (Table 1). In the next step, the thermal conversion was carried out by heating the polyamic acid at 150 °C for 1 h and at 200 °C for 2 h under nitrogen, giving faint yellow to dark red polyimides. The overall yield is 99%. The formation of the polyimides from the polyamic acids was confirmed by means of FTIR and ¹H NMR spectroscopy.

Table 1 Synthesis of polyimides^a from (BATPDF)

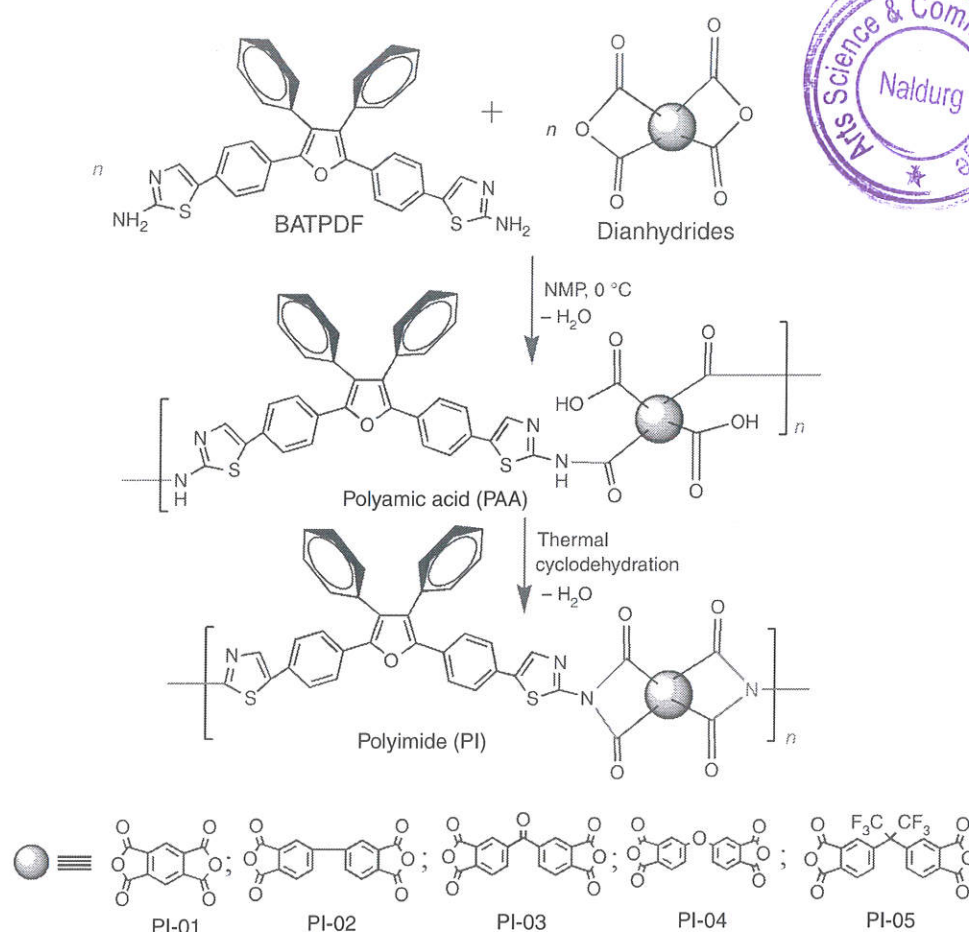
Polymer code ^a	Diamine BATPDF	Dianhydrides	Yield/%	Viscosity ^b η_{inh} /dL g ⁻¹	Film formation
PI-01	BATPDF	PMDA	99	0.42	Yes
PI-02	BATPDF	BPDA	96	0.48	Yes
PI-03	BATPDF	BTDA	98	0.43	Yes
PI-04	BATPDF	OPDA	97	0.44	Yes
PI-05	BATPDF	6FDA	96	0.42	Yes

^aPolymerization was carried out with 1 mmol each of diamine and dianhydrides

^bMeasured at a concentration of 0.5 g dL⁻¹ in NMP at 30 °C



Scheme 2 Synthetic pathway for the synthesis polyimides (PI-01 to PI-05)



Structural characterization

The BATPDF monomer characterized by FTIR spectroscopy, ^1H NMR and Mass spectroscopy.

Figure 1 shows the FTIR spectrum BATPDF. The primary amine ($-\text{NH}_2$) stretching is inspected in the region of at 3350 cm^{-1} . The aromatic $-\text{C}=\text{C}-$ stretching vibrations from the ring standing a band at 1600 cm^{-1} . Peaks accessible completed the range of 3059 cm^{-1} can be recognized to the aromatic $-\text{C}-\text{H}$ stretching vibrations, the peak at $800\text{--}1072\text{ cm}^{-1}$ is distinguishing between the C-S, C-N and bending vibrations, which indicates the presence of a furan-thiazole ring unit. The ^1H NMR spectrum of the monomer (BATPDF) is shown in Fig. 2. The peak at 4.0 ppm, singlet resembles to primary amine, total 4 protons (a) of the thiazole ring units and the remaining all 20 protons (b) in the range of 6.4–7.6 ppm, is signals are attributed to the aromatic protons of the tetraphenyl moiety. The mass spectrum Fig. 3 was consistent with the proposed structure as the peak at m/e 568 corresponding to the molecular ion peak of BATPDF is clearly seen. The other fragmentation peaks at m/e 540, 512, 413 and 385

indicate the fragmentation or loss of 2-amino thiazole units.

Figure 4 shows, IR spectrum of PPA-01, the vibrations displays broad peak at 3350 cm^{-1} could confirm the polyamic acid $-\text{OH}$ group. The formation of polyimides containing furan-thiazole unit was established by the appearance of absorption band at about 1787 and 1727 cm^{-1} ($\text{C}=\text{O}$) and at nearby 1350 cm^{-1} ($\text{C}-\text{N}$) characteristic of imide group in the IR spectra, put forward complete imidization as shown in Fig. 4. The ^1H NMR of polyimide PI-01 in d_6 -DMSO is gathered in Fig. 5. There was a strong separation of the resonance signals matching to the main chain of all aromatic protons in the range of 7.057–8.45 ppm. From the ^1H NMR of PI-01, it is clear that, there is a total conversion of novel diamine BATPDF into corresponding polyamic acids and then into the polyimides. The ^1H NMR spectra are in good agreement with the proposed assembly of the repeating unit of polymer PI-01.

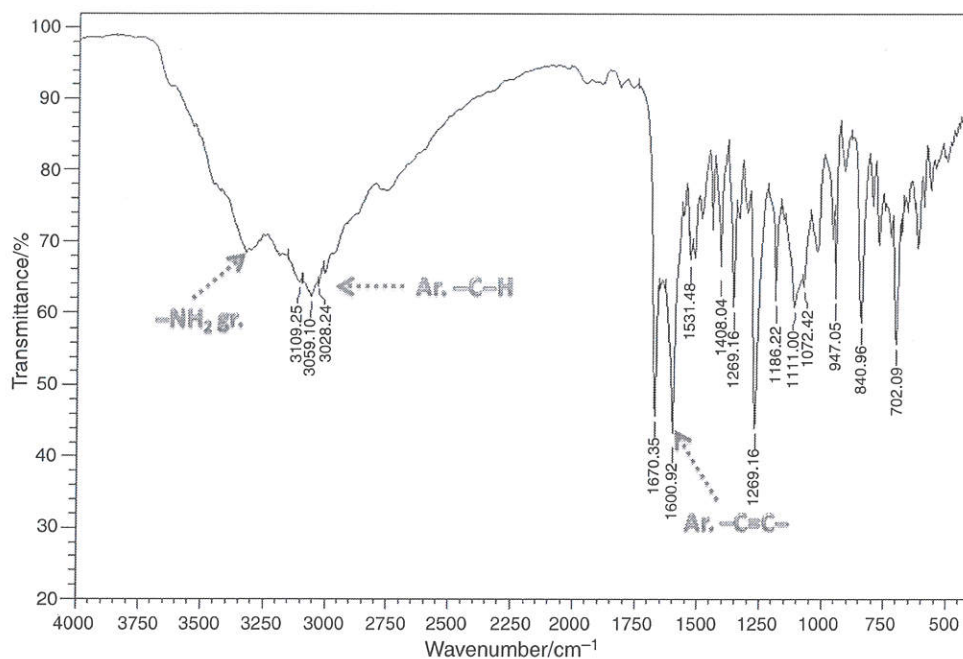
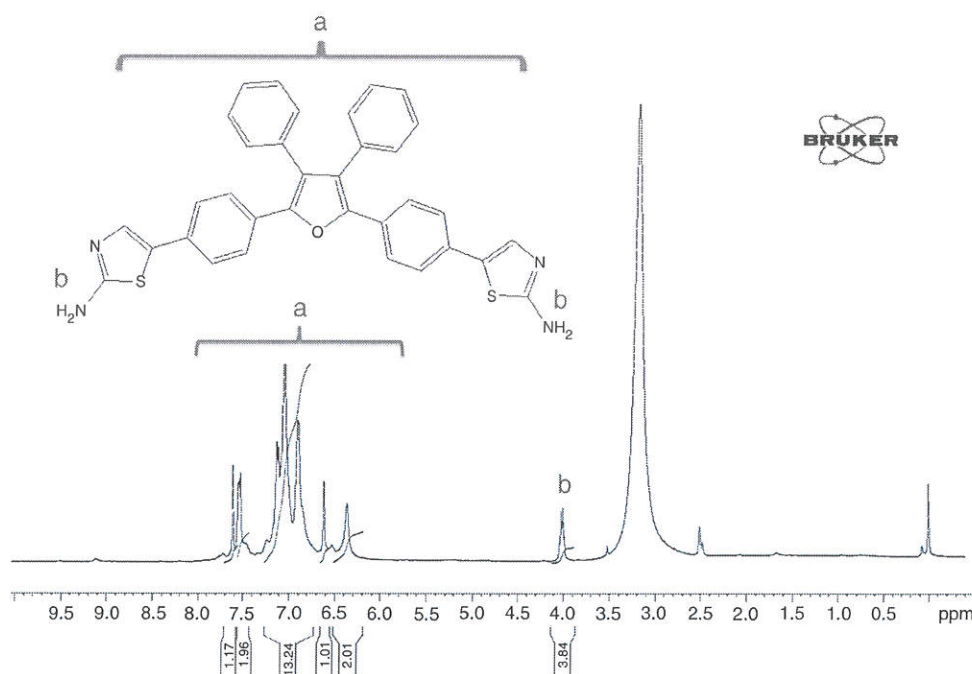


Fig. 1 FTIR spectrum of BATPDF

Fig. 2 ¹H NMR of BATPDF

Solubility and inherent viscosity

Tables 2 and 3 gave qualitative solubility of the tetraphenylfuran-thiazole unit covering polyamic acids (PAA-01 to PAA-05) and polyimides (PI-01 to PI-05), respectively. The concentration of the solubility tests was 1 mass%. Almost all polyamic acids (PAA-01 to PAA-05) were soluble in organic solvents such as DMAc, DMSO,

NMP, DMF, pyridine, m-cresol and insoluble in chlorinated solvent chloroform, THF and so forth. All polyimides were insoluble in organic solvents except NMP, at room temperature. Polyimides such as PI-03, PI-04 and PI-05 having linking clusters were soluble in DMAc, DMSO, DMF, pyridine and m-cresol on heating. On the other hand, polyimides PI-01 and PI-02 having stiff arrangements enlarged, comparatively less soluble. As to compare bulky structures, the solubility of these tetraphenylfuran-thiazole

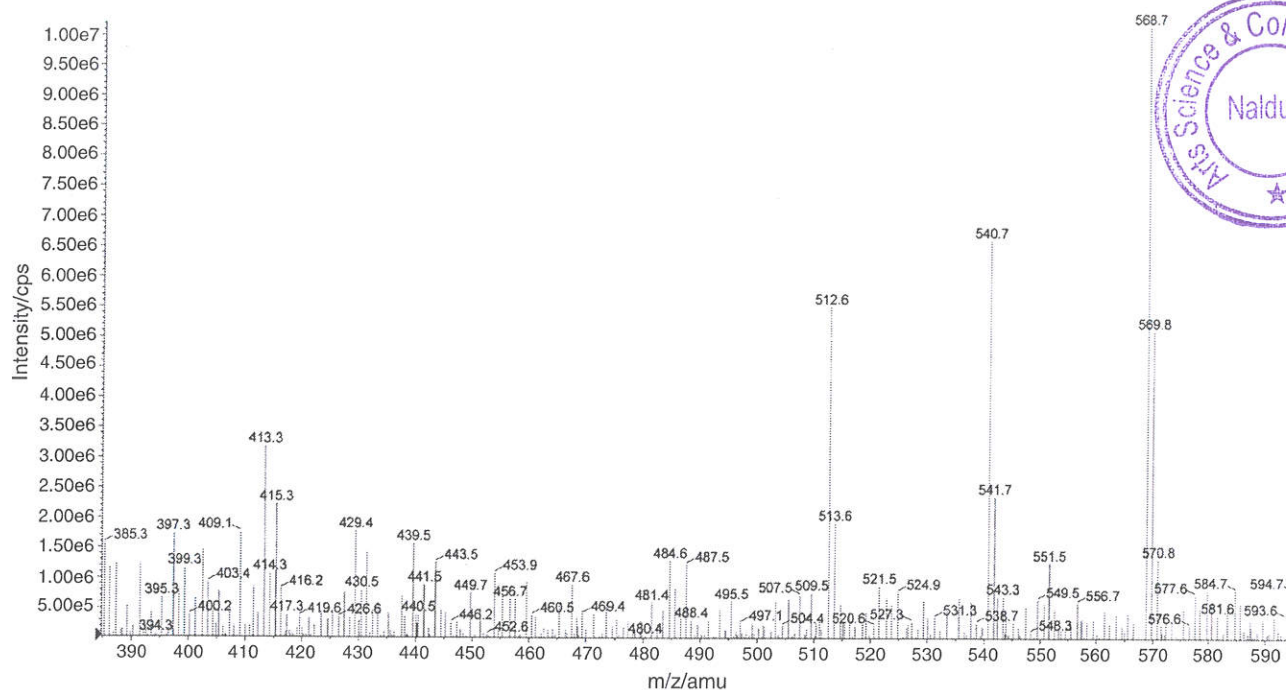
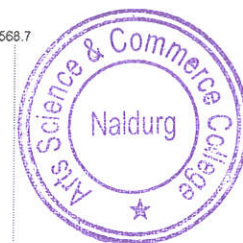


Fig. 3 Mass spectrum of BATPDF

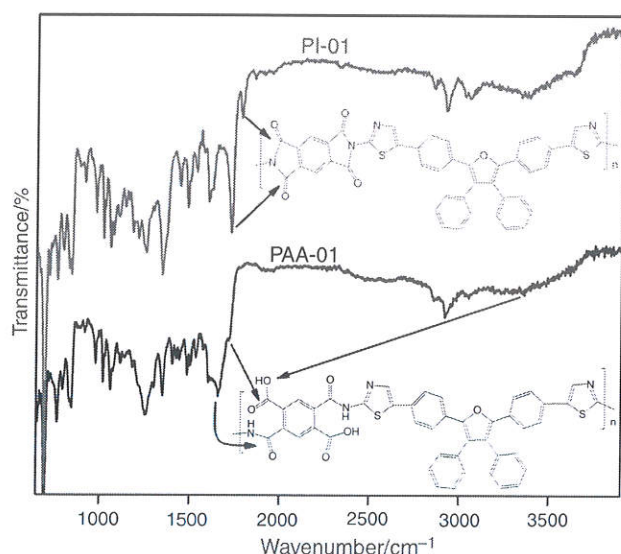


Fig. 4 IR spectrum of PAA-01 and PI-01

constructed polyimides was advanced than that of aromatic polyimides by taking analogous huge structures such as tetraphenylfuran, tetraphenylthiophene, and tetraphenylpyrrole described [38]. The existence of heterocyclic ring units such as thiazole and oxazole diamine constituent of polyimide is estimated to increase the solubility of due to interaction of polar furan-thiazole ring unit with the solvents [19]. The increased solubility of polyimides (PI-01 to PI-05) attributed to their amorphous nature, as shown by X-ray diffractometry.

Inherent viscosity measurements were used to establish an order for constructing molecules or building up of molecules and size of the polyamic acids chain in the series (PAA-01 to PAA-05). As compared with polyimides, polyamic acid shows excellent solubility in organic solvents at room temperature. Thus, the inherent viscosity of polyamic acid was recorded at 30 °C in NMP and values in between 0.42 and 0.48 dL g⁻¹ were obtained.

WAXD analysis

The WAXD patterns of all polyimides are shown in Fig. 6. The polyimides derived from rigid dianhydrides such as PI-02 [3,3',4,4'-biphenyltetracarboxylic dianhydride, (BPDA)] and PI-05 [4,4'-(hexafluoroisopropylidene) diphthalic anhydride, (6FDA)] showed some diffraction signals of medium to low strength assignable to a semicrystalline polymer nature. This for the polymer backbone having molecular regularity of biphenyl unit in PI-02 and for PI-05 due to the presence of two -CF₃. The other polyimides such as PI-01 (PMDA), PI-03 (BTDA) and PI-04 (OPDA) showed amorphous nature. Broad diffraction peaks at ~ 20° (2θ) were observed which confirms the formation of amorphous polymers.

Thermal analysis

Figure 7 shows the TG curve of PI-01 to PI-05 measured at a heating rate of 10 °C min⁻¹. The glass transition

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