

Synthesis and Characterization of Novel Polyamide-imides Containing Thioether Linkages, Thiazole, and Nitrophenyl Units with High Solubility and Processability for Optical Film Applications

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Editor's note: Polyamide-imides (PAIs) are remarkable polymers that merge the beneficial properties of both polyamides and polyimides, making them suitable for various applications. Jalali synthesized a novel diimide-diacid monomer and utilized it to develop several sulfur-containing PAIs with high processability and solubility for optical film applications.

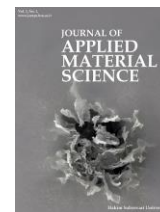
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Synthesis and Characterization of Novel Polyamide-imides Containing Thioether Linkages, Thiazole, and Nitrophenyl Units with High Solubility and Processability for Optical Film Applications

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Abstract

In this study, a novel diimide-diacid (DIDA) monomer featuring thiazole rings, nitrophenyl groups, and a thioether linkage has been introduced. Subsequently, several new sulfur-containing polyamide-imides (PAIs) were developed through the polycondensation reaction of DIDA with various aromatic diamines. This was achieved using a direct polycondensation method that employs triphenyl phosphite and pyridine. The resulting polymers were obtained in high yields, with inherent viscosities ranging from 0.73 to 0.92 dL/g. All synthesized polymers are amorphous and exhibit excellent solubility, easily dissolving in amide-type polar aprotic solvents such as *N*-methyl-2-pyrrolidone, dimethyl sulfoxide, *N,N*-dimethylacetamide, and dimethylformamide. Additionally, they can dissolve in less polar solvents like tetrahydrofuran, pyridine, and acetone. This solubility makes them promising candidates for the development of optical films, particularly given their confirmed high optical properties. The polymers also demonstrate good thermal stability, with a 10% weight loss occurring at temperatures ranging from 332.17 °C to 402.18 °C in a nitrogen atmosphere. Furthermore, the char yield of the synthesized polymers, defined as the percentage of solid residue remaining after heating from room temperature to 800 °C under nitrogen, ranges from 49.61% to 56.71%.

Keywords: Soluble polymer; Thioether linkage; Thiazole; Processible polymer; Polyamide-Imide.

1. Introduction

PAIs (Polyamide Imides) are high-performance polymers that combine the exceptional properties of both polyimides and polyamides. They exhibit excellent mechanical performance, outstanding thermal stability, and good processability [1]. Due to their high thermal stability, PAIs are promising candidates for various

studies and industrial applications. For example, they are used to create coatings for optical fiber sensors in large-scale applications [2]. Compared to polyimides (PIs), PAIs have several advantages, including thermal and hydrolytic stability [2].

PAIs have a wide range of optical applications, ranging from protective coatings to flexible display devices [1-3]. PAIs and their nanocomposites have outstanding thermal

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and mechanical properties [3], making them ideal for the development of protective coatings of optical fibers [2], thermally stable alternative materials for glass substrates [3], and flexible displays [4-6].

Sulfur-containing polymers, on the other hand, are unique polymers that have attracted significant interest in recent years [7, 8]. The incorporation of sulfur into the polymer backbone can improve thermal stability, mechanical properties, processability, solubility in common organic solvents, and flame resistance [9]. Several types of sulfur-containing polymers have been extensively studied, including poly(methacrylates) [10], epoxy resins [11], poly(arylene sulfide)s [12, 13], polyurethanes [14], polyamides (PAs) [15-18], PIs [19, 20], and thiol-containing cross-linked polymers [9].

Sulfur-containing PIs have high chemical and oxidative resistance, thermal stability, good mechanical properties, and inherently high refractive indices stemming, owing to their polarizable chains [21, 22]. However, despite their exceptional properties, most polyimides suffer from limitations such as poor solubility in common organic solvents, low processability due to high processing temperatures, deep colors, poor optical dispersion, and birefringence resulting from their rigid structures [23]. Consequently, extensive research has been conducted to improve the processability of polyimides while preserving their thermal stability [24, 25]. Strategies such as introducing flexible linkages, non-coplanar groups, bulky polar or non-polar pendant substituents, and heterocyclic units into the polymer backbone have attracted great research interest [26, 27]. In addition, copolymerization PAs and PIs can also lead to the synthesis of polymers that combine the beneficial properties of both polyamides and polyimides, as well as excellent thermal stability and good processability [1].

Thiazole ring as a sulfur-containing five-member hetero aromatic unit with one $-C=N-C-$ bond, and a rigid structure has received considerable attention in academic studies and optoelectronic applications, with the preceding description introducing the thiazole ring into the polymer structure can improve the thermal stability, solubility of the polymer, processability, and refractive index of polymer with increasing in sulfur content (Sc) while maintaining low molar volumes. Thiazole-containing polymers have widespread electrical and optical applications from this we can point to their application in transistors [28], polymer

semiconductors [29, 30], electroluminescent devices [31], and non-linear optical (NLO) applications [32]. However, the design, synthesis, and properties study of high-refractive-index polymers (high-n) with thiazole units and high SC had not been done before our previous works [19, 33]. In these works, a new class of PAs and PAIs was introduced in which the monomers were designed with thioether bridges and thiazole units. The results demonstrate that the incorporation of both thiazole unit and thioether linkages resulted in organic-soluble and heat-resistant polymers [19, 33].

The solubility of polymers is directly affected by their chain structure. Replacing a hydrogen atom in the structure of a polymer with another group with higher polarity is a strategy to improve the solubility and processability of polymers [34]. The nitro group has higher polarity than hydrogen and the replacement of one of the hydrogen atoms of the phenyl ring by this group in organic monomers can lead to a significant enhancement in the solubility and processability of PAI polymers [34].

The present work introduces a novel DIDA monomer with thiazole ring, thioether-linkage, and nitrophenyl groups. Using this novel DIDA, a series of new PAIs is synthesized by polycondensation reaction of DIDA with aromatic diamines. The rigid thiazole units improved thermal stability. The bulky pendant nitrophenyl unit is expected to increase the processability and solubility of prepared polymers in conventional organic solvents concerning the reported analogous polymers containing phenyl groups [35]. Also, the flexible thioether linkage can improve the solubility and processability of synthesized polymer films by increasing the flexibility of the polymers. The structure-property relationships of the synthesized PAIs, such as the solubility, thermal resistance, inherent viscosity, moisture uptake, and morphological structure and crystallinity of the PAIs are also investigated in detail.

2. Experimental

2.1. Materials

5,5'-Thiobis(2-amino-4-nitrophenyl-thiazole) (DA) was synthesized following the established method described in the literature [36] and was subsequently recrystallized from a *N,N*-dimethylformamide (DMF, MERCK)/water mixture. Triphenyl phosphite (TPP, MERCK) and trimellitic anhydride (TMA, MERCK) were used

without any additional purification. *N*-methyl-2-pyrrolidone (NMP, MERCK) and pyridine (Py, Fluka) were purified by distillation under reduced pressure over calcium hydride prior to use and were stored over 4 Å molecular sieves. Lithium chloride (LiCl, MERCK) was dried for 18 hours at 180°C under vacuum before its application. Both 1,4-phenylenediamine (MERCK) and 1,3-phenylenediamine (MERCK) were purified via vacuum sublimation. Additionally, 4,4'-oxydianiline (MERCK), 4,4'-diaminodiphenyl sulfone (MERCK), and 3,3'-diaminodiphenyl sulfone (MERCK) were purified by recrystallization from methanol. All other commercially available reagents and solvents were also used without further purification.

2.2. Monomer synthesis

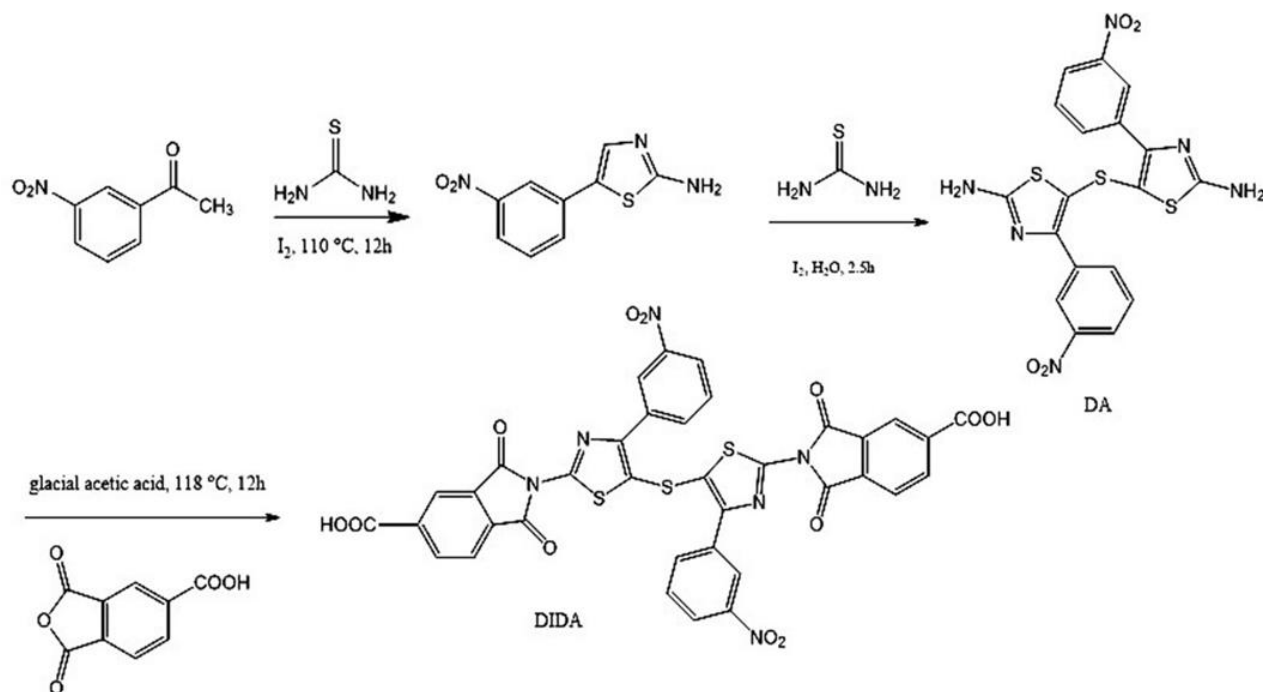
For the synthesis of DIDA (Scheme 1), a 250-mL round-bottom flask was charged with a mixture of diacetylene (DA) (2.362 g, 5 mmol), trimethylamine (TMA) (1.921 g, 10 mmol), and glacial acetic acid (50 mL). The heterogeneous mixture was refluxed for 12 hours and subsequently allowed to cool to room temperature. The reaction mixture was then slowly transferred into 500 mL of water and the resulting precipitate was collected by filtration, boiled in

methanol, and recrystallized from a solvent system of *N,N*-dimethylformamide (DMF)/water (v/v = 5:1). Finally, the product was dried under vacuum at 100°C for 24 hours, yielding a light-yellow solid.

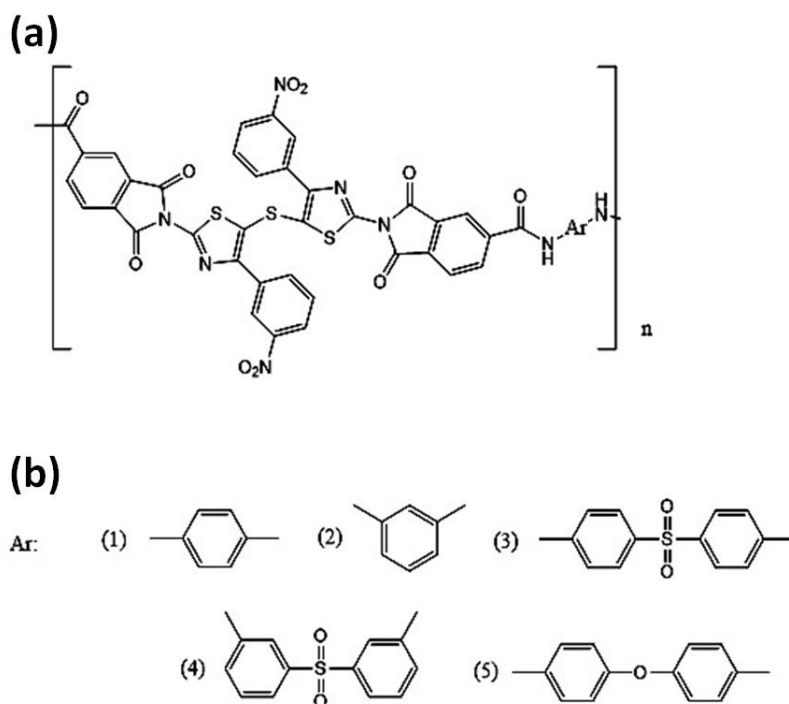
Yield: 90%; melting point: 349-350°C; IR (KBr) 3400–2600 cm⁻¹ (broad), 1792, 1732, 1703, 1529, 1346, 1296, 1227, 1169, 724, 695 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆); δ 7.691–7.745 (t, 1H, J = 8.1 Hz), 8.025–8.051 (d, 1H, J = 7.8 Hz), 8.230–8.273 (dd, 2H were overlapped), 8.301 (s), 8.376–8.403 (d, 1H, J = 8.1 Hz), 8.625 (s), 13.5 (broad, 2H, C(O)O-H); ¹³C NMR (75 MHz, DMSO-d₆); δ 119.59, 124.90, 124.69, 128.02, 128.64, 128.92, 131.34, 132.33, 134.06, 136.29, 137.24, 153.99, 155.60, 163.24, 163.31, 165.61 ppm; Analysis calculated for (C₃₆H₁₆N₆O₁₂S₃)_n: C, 52.68; H, 1.97; N, 10.24. Found: C, 52.71; H, 2.00; N, 10.20.

2.3. Synthesis of polymers and film preparation

The polymerization reactions were carried out using the DIDA monomer and several aromatic diamines (1–5 in Scheme 2). The synthesis process for PAI-3 is detailed as follows: A mixture was prepared by combining 0.820 g (1 mmol) of DIDA, 0.108 g (1 mmol) of 4,4'-Diaminodiphenylsulfone, 0.3 g of LiCl, 0.6 mL of TPP, 0.5 mL of pyridine, and 3 mL of NMP in a suitable



Scheme 1. Synthesis of DIDA.



Scheme 2. (a) The general repeating unit of PAIs and (b) five aromatic diamines (labeled as Ar in panel a) used for the synthesis of different PAIs in this study.

round-bottom flask. This mixture was then reacted at 120 °C for 6 hours under a nitrogen atmosphere. During the polymerization, the viscosity of the mixture gradually increased and hence, 1 mL of NMP was added to the reaction mixture after 1 h. The resulting mixture was then slowly transferred into 200 mL of methanol while stirring vigorously. After filtration, the mixture was washed with 200 mL of hot water and 100 mL of methanol, then dried under vacuum at 100 °C overnight. For further purification, the polymer was dissolved in DMAc, the solution was filtered, and then the polymer was precipitated into methanol.

IR (KBr): 3358, 3099, 1791, 1729, 1683, 1591, 1532, 1496, 1400, 1435, 1350, 1321, 1255, 1182, 1152, 1107, 1075, 911, 837, 743, 722, 693, 594, 566 cm^{-1} . Elemental Analysis calculated for $(\text{C}_{48}\text{H}_{24}\text{N}_8\text{O}_{12}\text{S}_4)_n$: C, 55.76%; H, 2.44%; N, 10.84%. Found C, 55.64%; H, 2.62%; N, 10.70%.

2.4. Measurements

The $^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra were recorded on a Bruker DRX 300 AVANCE instrument at a temperature of 25 °C. Fourier transform infrared (FTIR) spectra were obtained using potassium

bromide (KBr) pellets on a Perkin-Elmer FT Spectrum RX1, covering a range of 400–4000 cm^{-1} . Elemental analysis was performed with a Perkin-Elmer 2004 (II) CHN analyzer. Melting points (uncorrected) were measured via an Electrothermal Engineering LTD 9200 apparatus. Inherent viscosities ($\eta_{\text{inh}} = \ln \eta_r/c$) were determined at a concentration of 0.5 g/dL using an Ubbelohde suspended-level viscometer at 30 °C, with *N,N*-dimethylacetamide (DMAc) as the solvent. Wide-angle X-ray diffraction (WAXD) measurements were taken at ambient temperature using a Philips PW 1800 diffractometer, equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.5401 \text{ \AA}$). The scanning rate was maintained at 0.08 °/s over a 2θ range of 4–80°. Thermogravimetric analyses (TGA) were conducted using a Du Pont 2000 thermal analyzer under a nitrogen atmosphere, with a heating rate of 10 °C/min.

3. Results and discussion

3.1. DIDA Monomer Characterization

The synthesis of a new DIDA monomer, which contains thiazole heteroaromatic rings, nitrophenyl groups, and a thioether linkage, is illustrated in Scheme

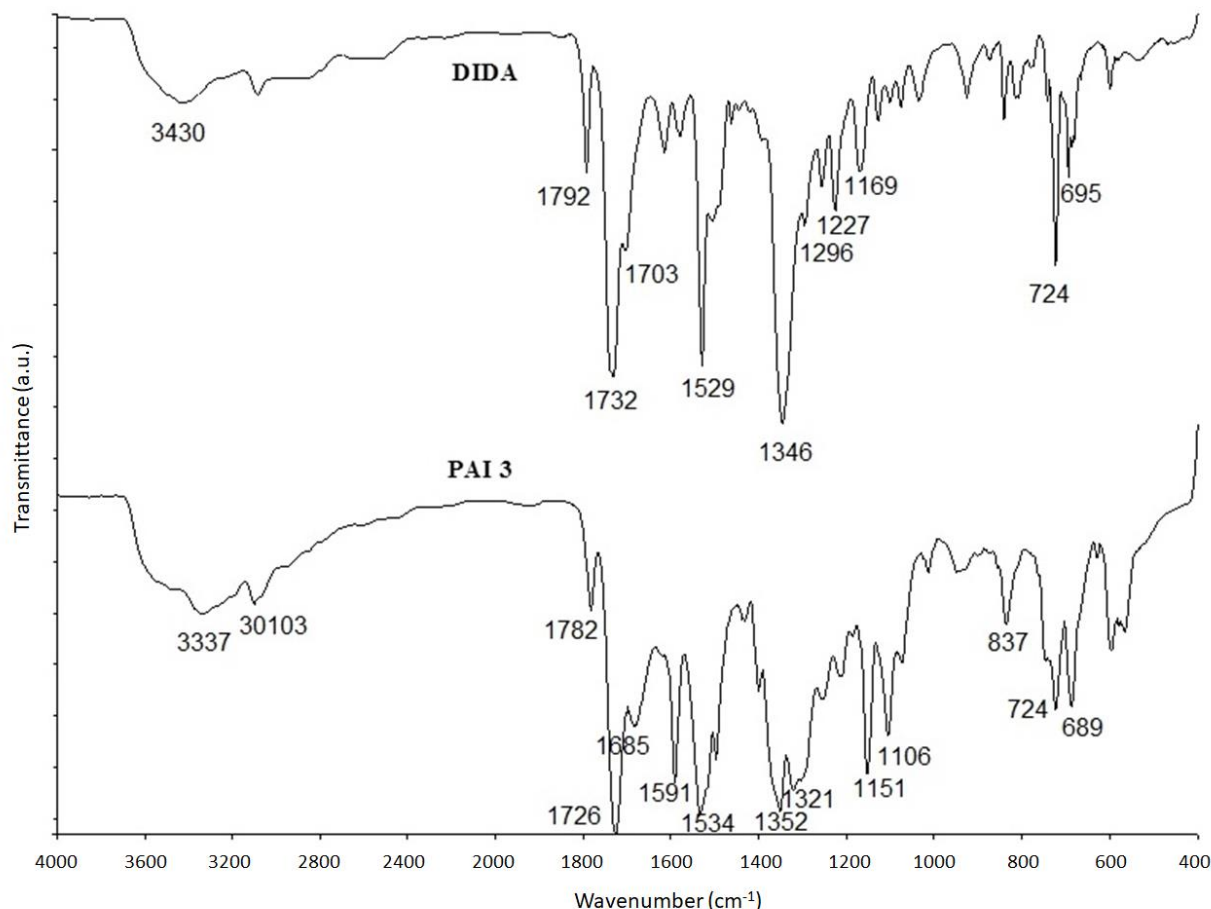


Figure 1. FTIR spectra of DIDA and PAI-3.

1. The DIDA was synthesized by polycondensation of DA with two-mole equivalents of TMA in refluxed glacial acetic acid. FTIR, $^1\text{H-NMR}$, $^{13}\text{CNMR}$, and elemental analysis confirmed the structure of the DIDA monomer. The FTIR spectrum of DIDA (Figure 1) displayed distinct spectral features indicative of carboxylic acid and cyclic imide functionalities. Notable absorption bands were observed in the range of 2400–3400 cm^{-1} , which correspond to C(O)O-H stretching vibrations. Additionally, peaks at 1792 cm^{-1} and 1732 cm^{-1} were observed, representing the asymmetrical and symmetrical C=O stretching vibrations of the imide group [37, 38]. Absorption bands at around 1346 cm^{-1} and 1529 cm^{-1} were also observed, corresponding to the symmetrical and asymmetrical stretching vibrations of nitro functionalities [39], confirming the presence of nitro substituents in the molecular structure of DIDA.

$^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra were also used to further confirm the successful synthesis of DIDA, as shown in Figures 2 and 3, respectively. In the $^1\text{H-NMR}$ spectrum of DIDA (Figure 2), downfield resonance signals at 8.025–8.051 ppm (d, $J = 7.8$ Hz), 8.301 ppm (s), and 8.376–8.402 ppm (d, $J = 7.8$ Hz) correspond to the protons of the trimellitimido moiety (c, a, and b protons in Figure 2b), supported by conjugation effects from the carboxylic acid and imide structure [19]. The nitrophenyl aromatic protons were detected at 7.691–7.745 ppm (f proton), 8.230–8.273 ppm (e and g protons), and 8.625 ppm (e proton).

The $^{13}\text{C-NMR}$ spectrum (Figure 3) revealed eighteen distinct carbon signals, consistent with the expected molecular structure. The carbonyl carbons of the carboxylic acid and imide groups resonate downfield at 172.00, 163.73, and 163.69 ppm. Elemental analysis

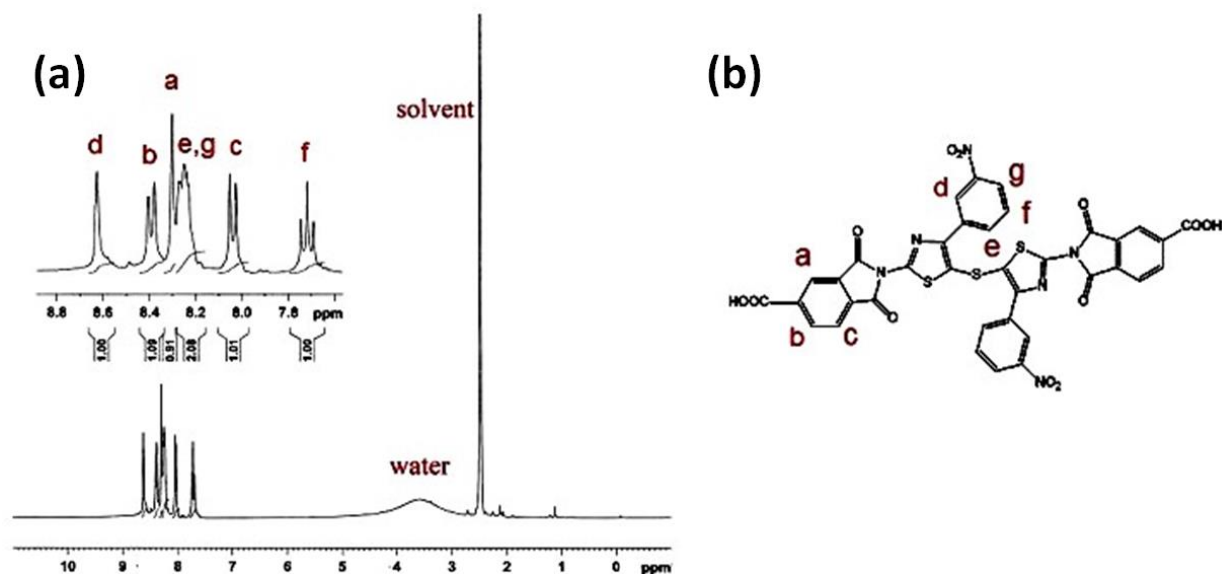


Figure 2. (a) The ^1H -NMR spectrum and (b) the proton assignments in the structure of synthesized DIDA.

results for DIDA also aligned with the calculated values for the proposed structure.

3.2. Structural characterization of synthesized PAIs

The Yamazaki-Higashi phosphorylation polycondensation method involves the reaction of aromatic diamines with aromatic dicarboxylic acids, utilizing TPP and Py as

condensing agents. This classic technique has been widely used for preparing aromatic polyamides (PAs) on a laboratory scale [40]. One of the main advantages of this method over the diacid chloride preparation approach is that it avoids the boring work-up process and is less sensitive to moisture [41]. Additionally, it effectively synthesizes polymers with moderate to high degrees of polymerization. We have previously employed

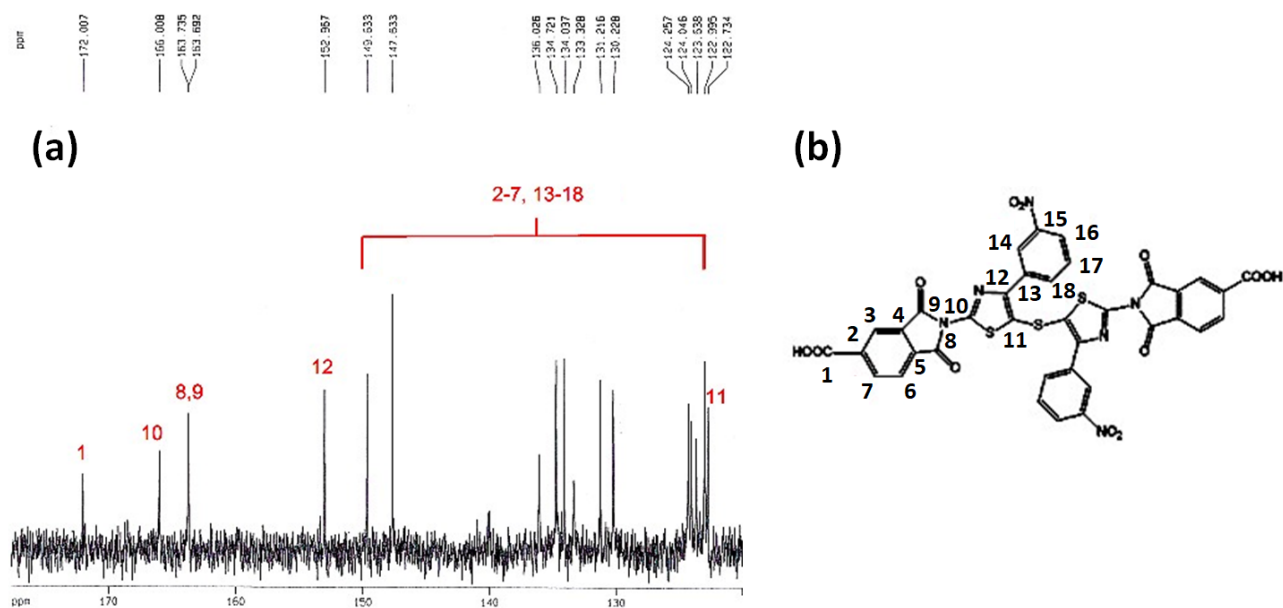


Figure 3. (a) The ^{13}C -NMR spectrum and (b) the carbon assignments in the structure of synthesized DIDA.

Table 1. Synthetic conditions and inherent viscosities of PAIs

Polymer code	Amounts used			η_{inh} (dL/g)
	NMP (ml)	Py (ml)	LiCl (g)	
PAI-1	3+1	0.5	0.3	0.92
PAI-2	3	0.5	0.25	0.81
PAI-3	3+1	0.5	0.3	0.75
PAI-4	3	0.6	0.3	0.73
PAI-5	3	0.5	0.25	0.86

Notes: DIDA and diamine monomers= 1.0 mmol; TPP= 0.6mL; temperature= 120 °C; time= 6 h; 3+1: 3 mL initial and 1 mL additional.

this method in our research [19, 35], and the results demonstrated that these polymers exhibit excellent thermal stability, high refractive indices, and relatively good optical transparency.

In this study, a series of novel thiazole-containing PAIs with bulky pendant nitrophenyl groups and thioether linkages were synthesized using different functional groups (groups 1 to 5 for the synthesis of PA-1 to PA-5 in Scheme 2). All polycondensation reactions were carried out in freshly dried NMP, resulting in a homogeneous solution. The synthesis conditions and the inherent viscosities of the PAIs are reported in Table 1. The inherent viscosities of the polymers ranged from 0.73 to 0.92 dL/g, as measured in DMAc solutions.

The structural features of these PAIs were confirmed through elemental analysis, FTIR, and ^1H NMR spectroscopy. The results of the elemental analysis and moisture uptake of the PAIs are summarized in Table 2. Although the elemental analysis values generally aligned with the calculated values for the PAIs, the hygroscopic nature of the amide groups led to the

observed carbon values being lower than those predicted for the proposed structures [42].

The FT-IR spectrum of PAI-3 revealed characteristic absorption bands associated with the imide ring and amide bonds, as shown in Figure 1. The imide ring shows stretching vibrations of the carbonyl groups at approximately 1780 cm^{-1} (asymmetric C=O stretching vibrations) and 1720 cm^{-1} (symmetric C=O stretching vibrations) [24, 37, 38]. Additionally, the C-N stretching vibrations are observed around 1380 cm^{-1} , while the imide ring deformation occurs at about 1092 cm^{-1} and 725 cm^{-1} . The amide group displays absorption peaks at around 3300 cm^{-1} (N-H stretching vibrations) and 1670 cm^{-1} (C=O stretching vibrations) [43]. These results confirm that the PAIs possess the expected chemical structures. Figure 4 illustrates a typical ^1H NMR spectrum for PAI-3, where all the proton signals align well with the proposed structure. A notable resonance peak appears in the downfield region at approximately 11.04 ppm, further supporting the formation of amide linkages.

Table 2. Elemental analysis and moisture uptake results of DIDA and PAIs

Sample code	Formula (Formula weight)		Elemental analysis (%)			Moisture uptake (%)
			C	H	N	
DIDA	$(\text{C}_{36}\text{H}_{16}\text{N}_6\text{O}_{12}\text{S}_3)_n$ (820.73)	Calculated	52.68	1.97	10.24	-
		Measured	52.71	2.00	10.20	
PAI-1	$(\text{C}_{42}\text{H}_{21}\text{N}_8\text{O}_{10}\text{S}_3)_n$ (839.86) _n	Calculated	56.44	2.37	12.54	1.40
		Measured	56.31	2.49	12.41	
PAI-2	$(\text{C}_{42}\text{H}_{21}\text{N}_8\text{O}_{10}\text{S}_3)_n$ (839.86) _n	Calculated	56.44	2.37	12.54	1.47
		Measured	56.35	2.53	12.43	
PAI-3	$(\text{C}_{48}\text{H}_{25}\text{N}_8\text{O}_{12}\text{S}_4)_n$ (1034.01) _n	Calculated	55.76	2.44	10.84	1.5
		Measured	55.61	2.56	10.69	
PAI-4	$(\text{C}_{48}\text{H}_{25}\text{N}_8\text{O}_{12}\text{S}_4)_n$ (1034.01) _n	Calculated	55.76	2.44	10.84	1.68
		Measured	55.72	2.55	10.72	
PAI-5	$(\text{C}_{48}\text{H}_{25}\text{N}_8\text{O}_{11}\text{S}_3)_n$ (985.95) _n	Calculated	58.47	2.56	11.37	1.38
		Measured	58.32	2.67	11.25	

Notes: Moisture uptake (%) = $[(W-W_0)/W_0] \times 100$; W and W_0 are the polymer weight after 72h at 25 °C and after drying at 100 °C for 12 h under vacuum, respectively.

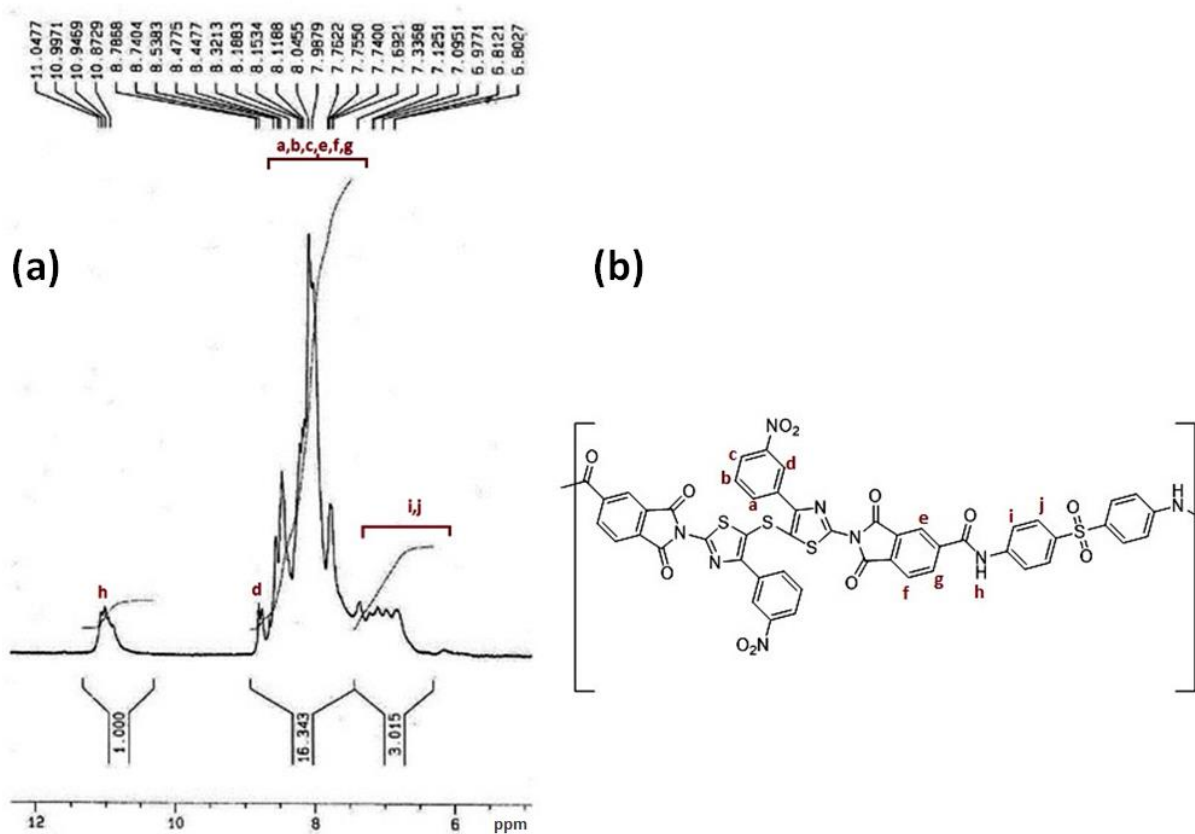


Figure 4. (a) The $^1\text{H-NMR}$ spectrum and (b) the proton assignments in the structure of the PAI-3 in DMSO-d_6 .

3.3. Solubility and microstructure of PAI films

The solubility of a polymer constitutes a critical determinant that influences its processability across various applications. Recently, several studies focused on the design and synthesis of polymers exhibiting a high refractive index, characterized by favorable solubility and processability, achieved through the incorporation of flexible thioether linkages within the polymer backbones [19, 33]. Furthermore, the incorporation of bulky moieties into either the polymer backbone or pendant groups can significantly enhance the solubility and processability of aromatic polyamides and polyimides, with a minimal decrease in thermal stability [19, 33].

The new DIDA monomer introduced in this work features thioether linkages and bulky pendant nitrophenyl rings. To assess the solubility of PAIs synthesized using this new DIDA, 0.05 g of each polymer was dissolved in 1 mL of various solvents,

including N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAC), dimethylformamide (DMF), tetrahydrofuran (THF), pyridine, acetone, and chloroform at 25 °C for 24 h. As summarized in Table 3, all PAIs displayed excellent solubility in both moderately and highly polar solvents. The solubility varied based on the specific diamine used.

The presence of highly flexible ether linkages in the backbone of PAI-5, derived from 4,4'-oxydianiline, increased flexibility and disrupted the planarity of the aromatic units in this polymer. This alteration led to decreased close packing in the polymer chains. Consequently, PAI-5 was soluble not only in highly polar solvents like NMP, DMSO, DMAC, and DMF but also in moderately polar solvents such as acetone and chloroform when heated. In addition, a comparison with the solubility of PAIs containing methyl pendant groups was also reported in Table 3 [19, 35]. As observed in Table 3, PAIs with pendant nitrophenyl groups demonstrate better solubility compared to those with

Table 3. Solubility of synthesized PAIs

Polymer code	Solvent							
	NMP	DMSO	DMAc	DMF	THF	Pyridine	Acetone	Chloroform
PAI-1	++ (+)	++ (+)	+ (+)	++ (+)	± (±)	± (-)	- (-)	- (-)
PAI-2	++ (++)	++ (+)	+ (+)	++ (+)	± (S)	± (±)	± (-)	- (-)
PAI-3	++ (++)	++ (+)	+ (+)	++ (+)	± (±)	± (±)	- (-)	- (-)
PAI-4	++ (++)	++ (+)	+ (+)	++ (+)	± (±)	++ (±)	± (-)	- (-)
PAI-5	++ (++)	++ (++)	++ (++)	++ (++)	++ (+)	++ (+)	+ (+)	+ (±)

Notes: (++) Soluble at room temperature (polymer concentration: 0.05 g/mL), (+) soluble after heating, (±) partially soluble, (S) swelling, (-) insoluble; Data in parentheses is those reported in the literature for PAIs containing methyl pendant groups [19]; NMP: *N*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

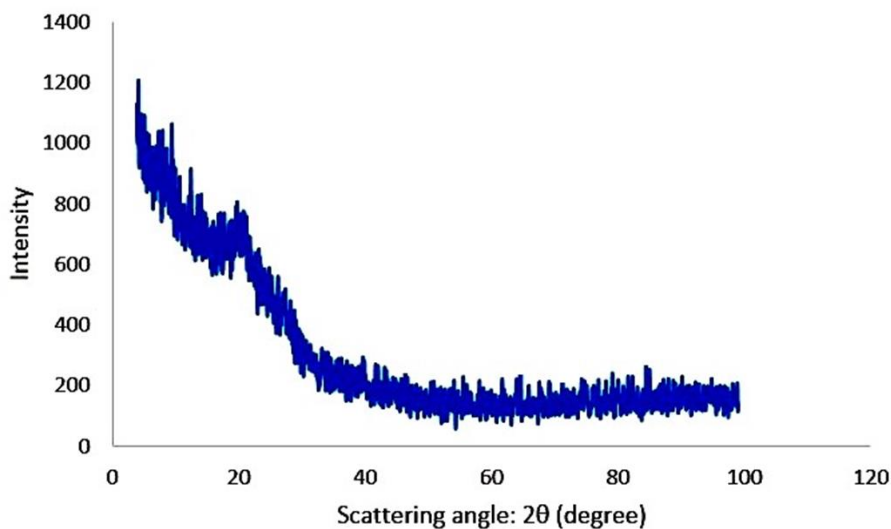
pendant methyl groups [19]. The bulky pendant Nitrophenyl groups disrupted the regularity and close packing of polymer chains.

The morphological structure and crystallinity of the synthesized PAI-1 were assessed using WAXD, as shown in Figure 5. PAI-1. The crystalline structure affects the refractive index and birefringence of the polymers applicable in optical industries and acts as a defect interrupting the guiding light [44, 45]. The diffractogram of the PAI-1 revealed a broad halo between $2\theta = 15^\circ$ and 25° , with no distinct peak features, indicating that the synthesized polymer is fully amorphous. This amorphous nature can be attributed to the presence of pendant nitrophenyl groups in the polymer backbone, which reduces the symmetry and regularity of the backbone. This reduction weakens the intermolecular forces, such as hydrogen bonding

between the polymer chains, thereby hindering chain packing efficiency. As a result, the intermolecular forces diminish, leading to lower crystallinity. The excellent solubility in organic solvents and favorable film-forming properties of these PAIs contribute to their amorphous structure.

3.4. Thermal properties of synthesized PAIs

The thermal and thermo-oxidative stabilities of the polymers were evaluated using thermogravimetric analysis (TGA) under a nitrogen atmosphere, as shown in Figure 6. One of the key metrics for assessing the thermal stability of the polymers is the temperature of 10 wt.% loss occurs (T_{10}). Moreover, char yield can provide important information on the structure of polymers. These two thermal characteristics were extracted from Figure 6 and summarized in Table 4. All synthesized

**Figure 5.** WAXD pattern of PAI-1.

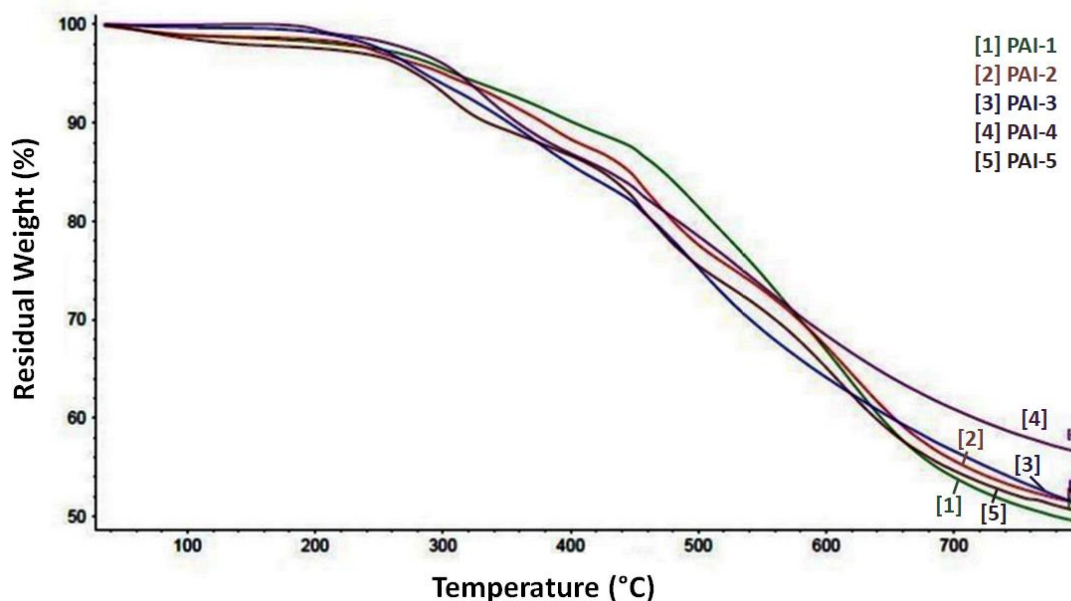


Figure 6. TGA results of the synthesized PAIs (heating rate: 10 °C/min under N₂).

PAIs demonstrated good thermal stability, exhibiting no significant weight loss below 330 °C. The T₁₀ values for the PAIs ranged from 332 to 402 °C in nitrogen. Additionally, the residual weight of all the PAIs at 800 °C under N₂ was greater than 49%. As anticipated, these polymers maintained excellent thermal stability, even with the incorporation of flexible thioether linkages and pendant nitro phenyl groups, enabling them to withstand elevated processing temperatures.

Table 4. The thermal stability results of synthesized PAIs

Polymer	T ₁₀ (°C)	Char Yield at 800 °C (%)
PAI-1	402.18	49.61
PAI-2	372.01	51.49
PAI-3	342.06	51.51
PAI-4	351.98	56.71
PAI-5	332.17	50.68

4. Conclusions

In this study, a new non-coplanar DIDA monomer featuring bulky nitrobenzene rings and thiazole groups linked by thioether was synthesized and polymerized with various aromatic diamines to produce a series of sulfur-containing PAIs. As anticipated, the combined effects of the non-coplanar structure, nitro units, and

flexible thioether bridges in the DIDA monomer contributed to the good solubility of the resulting PAIs in a range of organic solvents. These polymers exhibited high thermal and thermo-oxidative stability. Analysis of X-ray diffractograms and solubility data suggests that the non-coplanar structure and flexible linkages prevent the polyamide-imide chains from packing closely together, giving the polymers an amorphous nature and enhancing their solubility. Synthesized polymers can be used in the fabrication of high-performance optical films for various applications.

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Conflict of Interest

The author declares no conflict of interest.

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