



# Synthesis, Characterization, and Electrical and Thermal Stability of Semiconducting $\pi$ -Conjugated Polyazomethines Containing a Tetraphenylthiophene-Oxazole Unit

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A series of polyazomethines (PAM-01, PAM-02, PAM-03) containing various amounts of tetraphenylthiophene-oxazole (TPTP-o) moieties were produced by the polycondensation of a diamine precursor (TPTP-o) with equimolar proportions of two aromatic dialdehydes [isophthalaldehyde (1,3 IPA) and terephthalaldehyde (1,4 TPA)]. The TPTP-o precursor was successfully synthesized in three steps. The synthesized TPTP-o and the polymers (PAM-01, PAM-02, PAM-03) were characterized by ultraviolet–visible (UV–Vis) spectroscopy, FT-IR spectroscopy, x-ray diffraction (XRD), <sup>1</sup>H-NMR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. The effects of the TPTP-o units in the PAM on the insertion with azo linkages were studied with respect to conductivity and thermal stability. The room-temperature DC electrical conductivity of the PAM films was found to range from  $9.59 \times 10^{-7}$  S/cm to  $9.73 \times 10^{-7}$  S/cm. UV absorption at 342 nm confirmed the formation of azo ( $-C=N-$ ) linkages in the polymer, which is helpful for electron conductivity throughout the polymer network. All three PAMs had a glass transition temperature ( $T_g$ ) between 260°C and 267°C, and  $T_{10\%}$  thermal degradation values of thermally stable polyazomethines were in the range of 517–530°C. All three PAMs showed moderate solubility in organic solvents and inherent viscosity of between 0.31 dL/g and 0.35 dL/g. The XRD study indicated that all three PAMs were amorphous in nature, with a broad peak in the vicinity of 20°.

**Key words:** Semiconducting polyazomethines, tetraphenylthiophene-oxazole, XRD, thermogravimetric analysis, ultraviolet

## INTRODUCTION

Conjugated polyazomethines (PAMs) containing different aromatic moieties, having various bulky or pendant groups with a heterocyclic unit in the polymer framework successfully inserted, were investigated to explore the influence of the molecular framework on the electronic and optical

properties of the conjugated polymers.<sup>1</sup> These polymers are recognized as an important applied class of conducting materials for electronic and optoelectronic devices. Conjugated and conducting materials containing polymers have recently attracted significant attention in the development and design of reliable and highly sensitive gas sensors.<sup>2</sup> This type of polymer can be synthesized by chemical or electrochemical doping/de-doping techniques. Aromatic polyazomethines contain azo groups ( $-HC=N-$ ) in their backbones; this azo group replaces their polyvinylene ( $-HC=CH-$ ) equivalents

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and isoelectronic material with their carbon correspondents.<sup>3</sup> Conjugated PAMs are easily synthesized via a simple difunctional molecule condensation reaction, with the elimination of neutral lightweight molecules such as water as the only by-product. These polycondensation reactions can be carried out without the use of a catalyst or harsh reaction conditions,<sup>4,5</sup> providing a more suitable synthetic pathway for the use of polymers in organic electronics applications, because impurities from catalysts can alter the properties of the final device.<sup>6,7</sup> This approach is possible because of the polymer backbone, which contains only azo linkage functional moiety.<sup>8</sup> Research on azomethine synthesis began in 1923, and polyazomethines were first reported in 1950. Polyazomethines are used in fields such as mechanical, chemical, textile, industrial and physical engineering.<sup>9–12</sup> Conjugated polymers have great potential for application in semiconductors, sensors, electrochromic devices, photovoltaic devices, actuators and light-emitting diodes (LEDs). While extended  $\pi$ -conjugation along the polymer chain is essential for the use of such polymers in advanced electronic device fabrication,<sup>5,13–18</sup> alternatively, satisfactory results in the design and synthesis of the polymer backbone for conductivity increases the level of conduction by inserting TPTP-o into the polymer framework. Polyazomethines containing 1,3 IPA- or 1,4 TPA-substituted tetraphenylthiophene-oxazole units have been widely synthesized, displaying unique electronic properties according to their chemical nature and insertion in a polymer chain; for example, high conductivity is scarce on thiophene-oxazole-based polyazomethines.<sup>19</sup>

In the current work, we describe the synthesis of three TPTP-o-based conjugated PAMs. Bulky-heterocyclic ring units containing PAMs were prepared by polycondensation of TPTP-o with equimolar proportions of isophthalaldehyde [IPA (1,3)] and TPA (1,4). The structure–property relationships of the three PAMs were studied. The thermal properties of the synthesized polyazomethines were investigated by DSC and TGA.

## EXPERIMENTAL SECTION

### Reagents and Solvents

Sulfur powder (Sigma-Aldrich, USA); urea, iodine ( $I_2$ ), aluminium trichloride ( $AlCl_3$ ), acetyl chloride,  $Br_2$  solution (> 99.00% purity) (S.D. Fine-Chem Ltd., Maharashtra, India); isophthalaldehyde (1,3 IPA), terephthalaldehyde (1,4 TPA) (Sigma-Aldrich, USA); solvents including tetrahydrofuran (THF), methylene dichloride (DCM), methanol, ethanol, glacial acetic acid, dimethyl sulfoxide (DMSO), *N,N'*-dimethyl acetamide (DMAc), *N*-methyl pyrrolidone (NMP) and *N,N'*-dimethylformamide (DMF) (S.D. Fine-Chem Ltd., Maharashtra, India); lithium chloride (LiCl) (Sigma-Aldrich, USA); *N,N'*-dimethylformamide (DMF), *N*-methyl-2-

pyrrolidinone (NMP) and *N,N'*-dimethyl acetamide (DMAc), were refined by distillation under reduced pressure over barium oxide before being used in the polymerization. Tetrahydrofuran and methylene dichloride were dried using hydrides of sodium and calcium, respectively, before use. Lithium chloride (LiCl) was dehydrated at 180°C in a vacuum oven for 24 h.

### Instruments and Measurements

The UV–Vis and FT-IR spectra for monomers or polyazomethines were recorded using a Beckman DU-640 spectrometer and Nicolet iS-10 Fourier transform mid-infrared spectrometer in the range of 650–4000  $cm^{-1}$ , respectively. The  $^1H$  nuclear magnetic resonance ( $^1H$ -NMR; Bruker 400 MHz) analyses of monomers and polymers were conducted using the solvent DMSO- $d_6$  at room temperature. The AB Sciex APT 5500 mass spectrometer was used to record the mass of the monomers. The solubility tests of the polyazomethines were completed in various solvents using 0.5 mg of sample and 0.5 mL of solvent at 30°C. The inherent viscosity of the polyazomethines was measured with 0.5 g/dL in NMP solution at 30°C using an Ubbelohde suspended level viscometer. XRD scans were recorded on an Ultima IV system with an Ultima IV goniometer.

Prepared polyazomethine or copolyazomethine samples of approximately 100 mg were dissolved in 1 mL formic acid and stirred for 12 h at room temperature to obtain a clear solution. The thin films of polyazomethines were prepared at room temperature by spin coating on a glass plate substrate at 1000 rpm. The temperature-dependent electrical conductivity results were recorded on a Keithley 2400 electrometer device using a four-point probe technique.

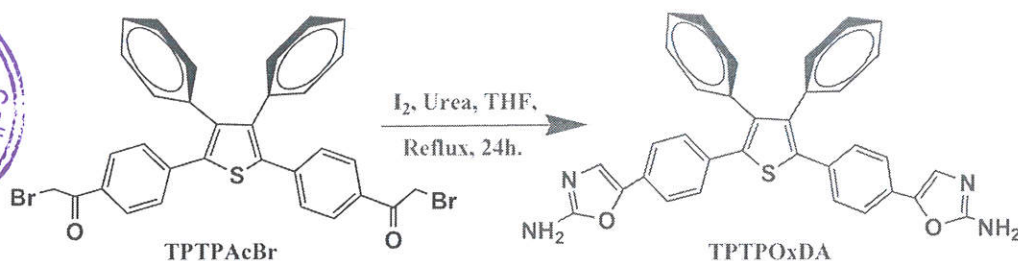
Thermogravimetric analysis was conducted using a Mettler Toledo TGA instrument in the range of 30°C to 900°C. Thermal degradation assessments were carried out using a heating degree scan of 10°C/min in a nitrogen atmosphere with a gas flow rate of 50 mL/min. The DSC scans were analyzed using a Mettler Toledo DSC-1 STARe system in a nitrogen atmosphere (flow rate of 50 mL/min).

### Synthesis Methods

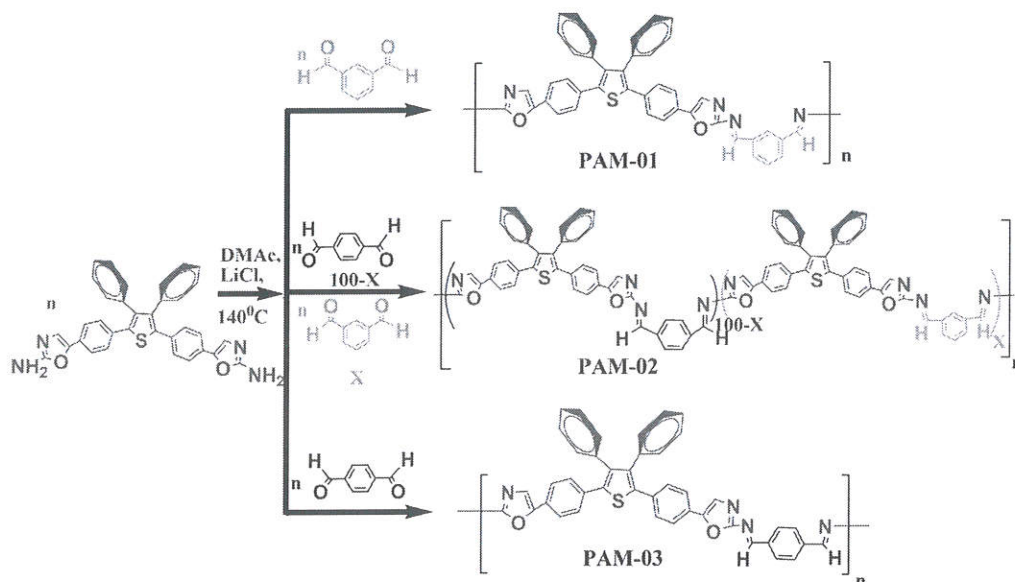
#### Monomer Synthesis

2,5-Bis(4-(1-bromo)acetylphenyl)-3,4-diphenyl thiophene (TPTPAcBr) and intermediates for the TPTP-o diamine monomer were produced in our laboratory using methods described in previous reports.<sup>20–22</sup> The monomer, i.e. TPTP-o, was produced for the first time in our laboratory; the details of the monomer synthesis are depicted in Scheme 1. The precursor (TPTP-o) was characterized using FT-IR, proton magnetic resonance ( $^1H$ -NMR) and mass spectroscopy to confirm its structure.





Scheme 1. Synthetic pathway for the synthesis of 2,5-bis(4-(2-amino-oxazole)phenyl)-3,4-diphenyl thiophene diamine monomer (TPTP-o).



Scheme 2. Synthetic pathway for the synthesis of polyazomethines (PAM-01, PAM-02, PAM-03).

#### 2,5-Bis(4-(2-Amino-Oxazole)Phenyl)-3,4-Diphenyl Thiophene (TPTP-o)

A mixture of TPTPAcBr (5.6 g, 8.88 mmol) and urea (2.42 g, 29.47 mmol) in 70 mL THF in a single-neck 100 mL round-bottom flask was refluxed for 24 h. After reaction completion, the flask was cooled to room temperature, and the clear solution was discharged into a cold sodium hydrogen sulfate solution with continued stirring overnight. The precipitated product was then collected by filtration and recrystallized from hot ethanol as dark yellow crystals, m.p. 246–248°C and yield 85%.

#### Polymer Synthesis

Using the TPTP-o monomer, three polyazomethines were synthesized<sup>23</sup> (Scheme 2). First, 0.552 g (1 mmol) TPTP-o and dry DMAc (3 mL) containing 0.150 g lithium chloride [5 wt.% based on the DMAc] were added to a 100 mL three-neck, round-bottom flask, equipped with magnetic stirrer, reflux condenser, calcium chloride guard tube, and nitrogen gas inlet. The mixture was stirred well at room temperature to obtain a clear solution, and then

0.067 g (0.5 mmol) isophthalaldehyde (IPA) and 0.067 g (0.5 mmol) terephthalaldehyde (TPA) were added. The reaction mixture was stirred overnight at room temperature under a nitrogen atmosphere, after which it was refluxed for 4 h at 140°C and cooled to room temperature, and a sufficient quantity of water was added to precipitate the polymer. The polymer was collected by filtration, washed with water and ethanol, and dried under vacuum at 80°C for 8 h. The polymer yield of was 0.635 g (98%), and its inherent viscosity was 0.35 dL/g. The other two polyazomethines, PAM-01 and PAM-03 (Table I), were similarly prepared (Scheme 2).

## RESULTS AND DISCUSSION

### Synthesis of Monomer

The oxazole heterocyclic ring-enclosed diamine TPTP-o was synthesized (Scheme 1). Ring closure was carried out with urea and iodine and gave 2,5-bis(4-(2-amino-oxazole)phenyl)-3,4-diphenyl thiophene (TPTP-o). The molecular arrangement of the diamine monomer was established by mass, NMR and FT-IR spectroscopy.

Table I. Synthesis of polyazomethines from (TPTP-o)

Polymer code <sup>a</sup>	Diamine mol.%	Dialdehyde mol.%		Yield (%)	Viscosity $\eta_{inh}$ (dL/g) <sup>b</sup>
	TPTP-o	IPA	TPA		
PAM-01	100	100	00	97	0.31
PAM-02	100	50	50	98	0.35
PAM-03	100	00	100	96	0.34

<sup>a</sup>Polymerization was carried out with 1 mmol each of diamine and dialdehyde.

<sup>b</sup>Measured at a concentration of 0.5 g/dL in NMP at 30°C.

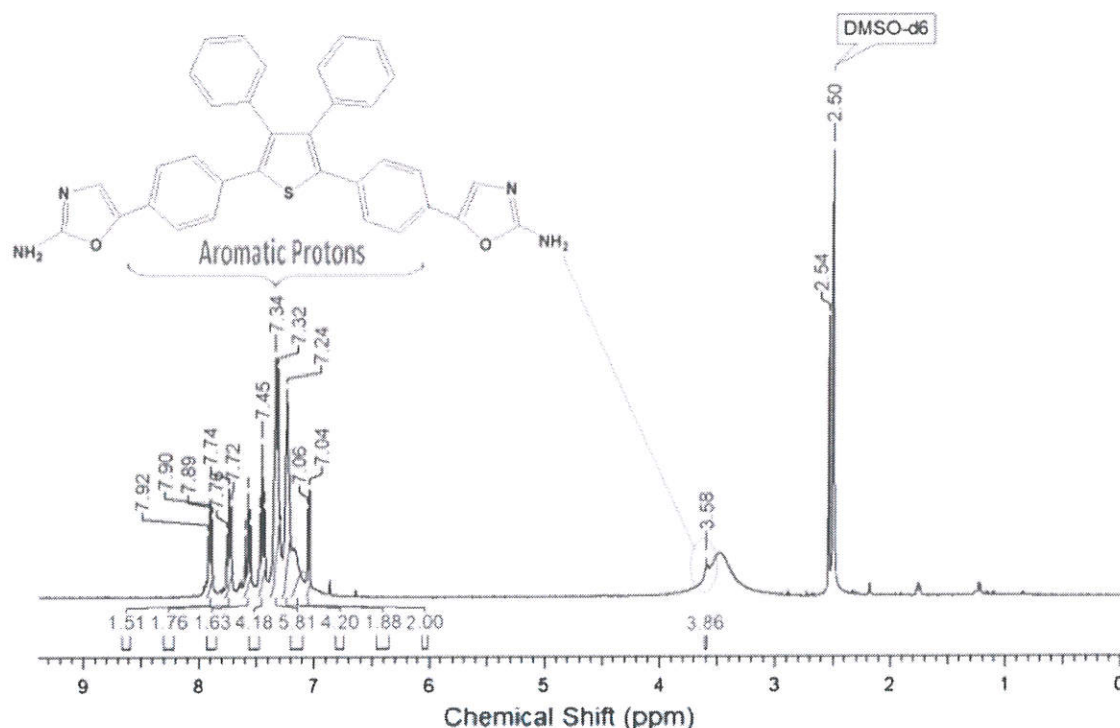


Fig. 1. <sup>1</sup>H-NMR spectra of TPTP-o.

## Synthesis of Polymers

Using TPTP-o, a series of aromatic polyazomethines were fused by direct solution polycondensation using *N,N'*-dimethyl acetamide (3 mL) containing 5 wt.% lithium chloride (Scheme 2). The yields and viscosities are specified in Table I. The inherent viscosity values were between 0.31 dL/g and 0.35 dL/g, representing the production of moderate to fairly high molecular weight polymers. The structural features of the PAMs were characterized by FT-IR and <sup>1</sup>H-NMR spectroscopy.

## Structural Characterization

The <sup>1</sup>H-NMR spectra of the TPTP-o monomer are shown in Fig. 1. The singlet peak at 3.58 ppm (4 H) corresponds to the -NH<sub>2</sub> primary amine protons of

the oxazole ring units. The resonance peaks between 7.40 ppm and 7.92 ppm (16H) are attributed to the aromatic protons of the tetraphenyl moiety. The <sup>1</sup>H NMR analysis clearly indicates that the diketone structure was completely transformed into a diamine structure by cyclization. The FT-IR spectrum of the corresponding monomer (TPTP-o) also supports the successful achievement of complete ring cyclization of the oxazole monomer (Fig. 2). The infrared spectrum shows absorption bands at 3430–3517 cm<sup>-1</sup> corresponding to -NH<sub>2</sub> stretching vibrations. Figure 2 also shows that the TPTP-o was successfully converted into PAMs (PAM-01, PAM-02, PAM-03) using the solution polycondensation method. The IR vibrational assignments of various tetraphenylthiophene-oxazole-based polymers are shown in Fig. 2. The



absorption band corresponding to the  $-\text{C}=\text{N}-$  (azo linkages) stretching vibrations is typically located at  $1694\text{ cm}^{-1}$ . The disappearance of the sharp band at  $1715\text{ cm}^{-1}$  and the broad band at  $3400\text{--}3150\text{ cm}^{-1}$  indicates that all the dialdehyde and diamine groups joined to yield high molecular weight PAMs. The presence of a stretching vibration at  $1602\text{ cm}^{-1}$  is due to the aromatic  $-\text{C}=\text{C}-$  frequency of the phenyl groups, which is in

reasonable agreement with the aromatic type structure of the polymer chain. The broad peak at  $3050\text{ cm}^{-1}$  confirms the aromatic C-H moiety of the polyazomethines chain. The mass spectrum (Fig. 3) was unchanged with the anticipated structure, as the peak at  $m/e$  552 equivalent to the molecular ion of 2,5-bis(4-(2-amino-oxazole)phenyl)-3,4-diphenylthiophene (TPTP-o) is clearly seen. Figure 4 shows the  $^1\text{H-NMR}$  spectrum of PAM-01, and clarifies that the imine proton signal appears at 8.31 ppm, whereas the other protons in the polymer framework display signals further upfield.<sup>24</sup> From this we concluded that the polyazomethines were synthesized with high yield because of the absence of primary amine and dialdehyde proton peaks.

### Solubility and Inherent Viscosity

The solubility of all polyazomethines (PAM-01, PAM-02, PAM-03) was tested qualitatively in numerous solvents, and the results are summarized in Table II. All the polymers were soluble in *N*-methyl pyrrolidone (for PAM-03 only on heating),  $\text{HCOOH}$  (formic acid) and concentrated  $\text{H}_2\text{SO}_4$ . This is because the polymer backbone contains rigid structures (straight chains). On heating, PAM-01 and PAM-02 were soluble in DMAc and DMSO, but were only partially soluble in *m*-cresol and DMF, and were insoluble in chlorinated solvents such as chloroform and dichloromethane.<sup>20,25,26</sup>

The inherent viscosity results were used to inaugurate the formation of side chain packing in the

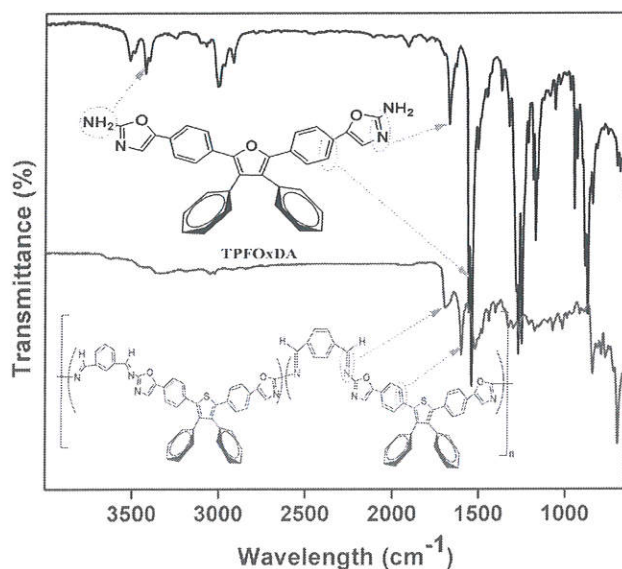


Fig. 2. FT-IR spectrum of TPTP-o and PAM-02.

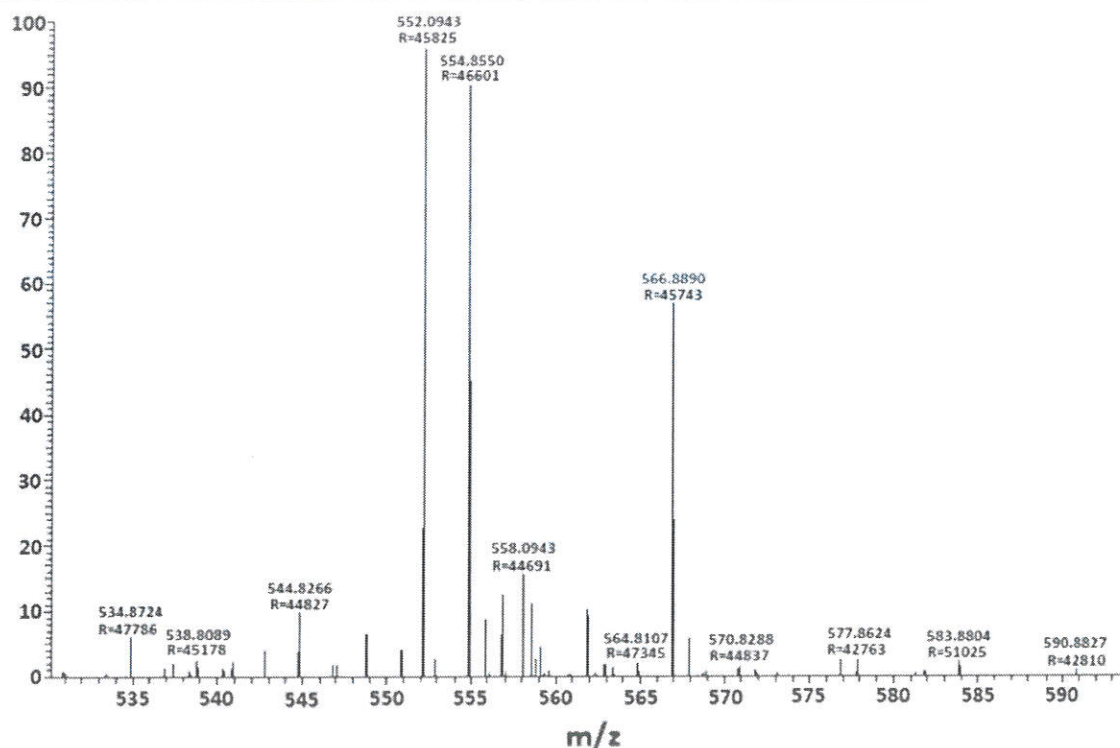


Fig. 3. Mass spectra of TPTP-o.

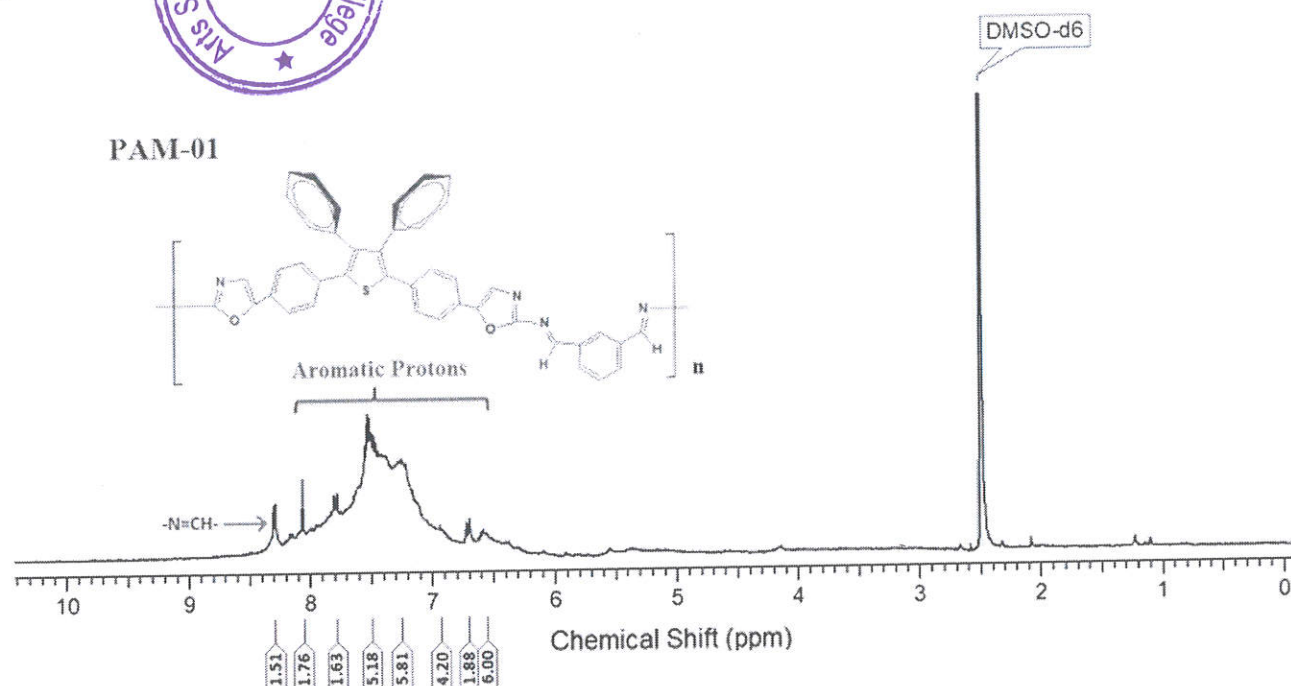


Fig. 4.  $^1\text{H}$ -NMR spectra of PAM-01.

Table II. Solubility of polyazomethines (PAM-01, PAM-02, PAM-03)

Solvents Polymers	DMAc	DMF	NMP	DMSO	m-cresol	Conc. $\text{H}_2\text{SO}_4$	$\text{HCOOH}$	$\text{CHCl}_3$	DCM
PAM-01	+	$\pm$	++	+	$\pm$	++	++	—	—
PAM-02	+	$\pm$	++	$\pm$	—	++	++	—	—
PAM-03	$\pm$	$\pm$	+	$\pm$	—	++	++	—	—

++ Soluble, + soluble on heating,  $\pm$  partly soluble, — insoluble.

polyazomethine matrix. Hence, the inherent viscosity was recorded at  $30^\circ\text{C}$  in *N*-methyl pyrrolidone (0.5 g/dL), with values between 0.31 dL/g and 0.35 dL/g.

### XRD Analysis

XRD was used to check the crystallinity/amorphous nature of the three PAMs (as shown in Fig. 5) in the  $2\theta$  range of  $5^\circ$ – $90^\circ$ .<sup>27</sup> Broad diffraction peaks at  $\sim 12^\circ$  and  $\sim 20^\circ$  ( $2\theta$ ) were observed, indicating that the PAMs were amorphous in nature. The XRD traces allowed us to conclude that the inspected PAMs had an amorphous structure, which was evaluated and was in good agreement with the reported literature.<sup>28,29</sup>

### Electrical Conductivity Study

The DC electrical conductivity performance of polyazomethines (PAMs) was assessed at temperatures from  $40^\circ\text{C}$  to  $200^\circ\text{C}$ , and the acquired data are shown in Fig. 6. It is found that at low temperature,

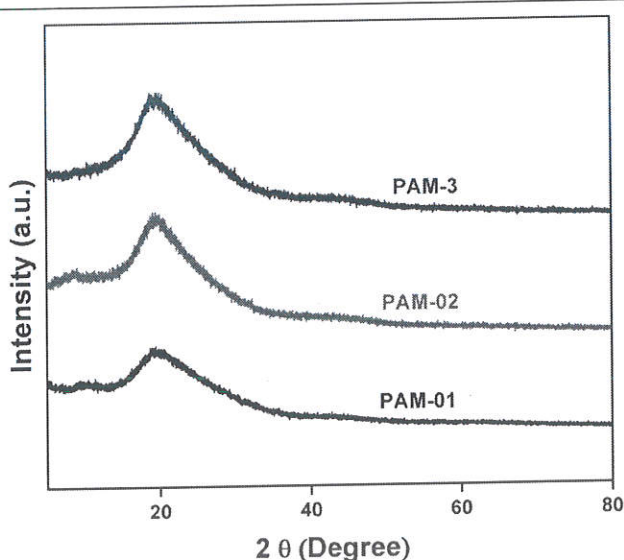


Fig. 5. XRD spectra of PAMs.



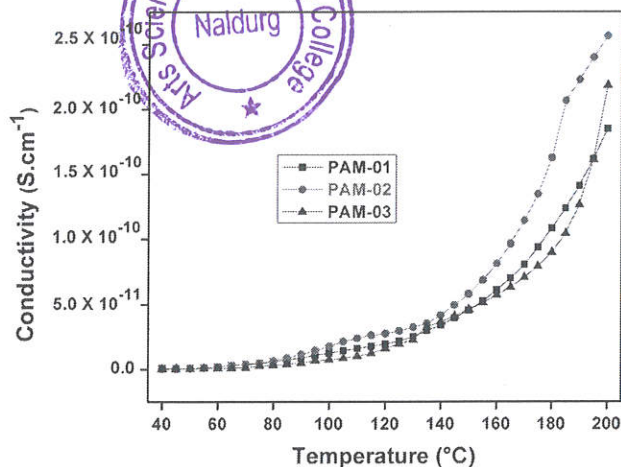


Fig. 6. DC conductivity as a function of temperature for polyazomethines (PAMs).

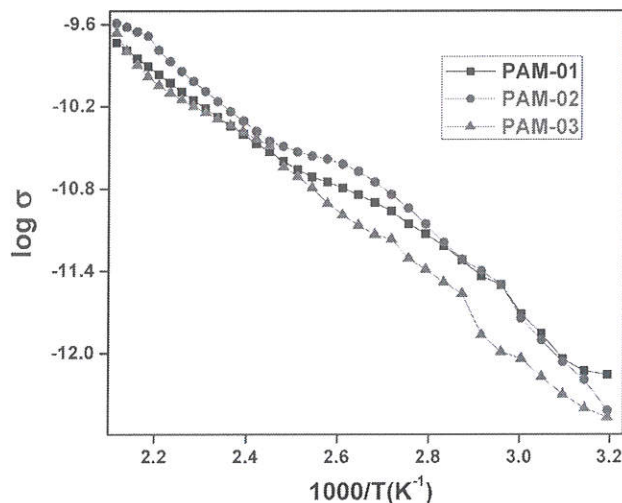


Fig. 7. Temperature-dependent electrical conductivity of polyazomethines (PAMs).

electrical conductivity rises linearly. The sharp rise in current in the temperature range of 40°C to 200°C indicates that there is an influence of thermodynamic alteration in the area of a certain temperature. The effect of temperature on conductivity was correspondingly established by determining the conductivity at different temperatures. Electrical conductivity data revealed that PAM-02 has higher electrical conductivity than PAM-03, whereas PAM-03 has higher conductivity than PAM-01 at 200°C. The increase in conductivity with increasing temperature could be due to thermal activation, molecular orientation, relocation of polymer chains, and conjugation length. The intensification in conductivity with increasing temperature confirmed the semiconducting nature of PAM-01, PAM-02 and PAM-03.

The temperature-dependent conductivity of the PAM films is shown in Fig. 7. The room-temperature DC electrical conductivity of the three

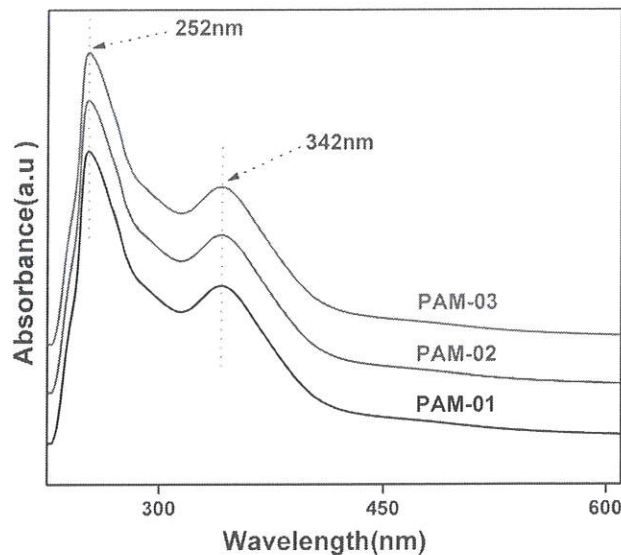


Fig. 8. UV-Vis spectra of PAMs.

polyazomethine films was measured as  $9.73 \times 10^{-7}$  S/cm,  $9.59 \times 10^{-7}$  S/cm and  $9.66 \times 10^{-7}$  S/cm for PAM-01, PAM-02 and PAM-03, respectively. The conductivity increased with increased temperature, which is a distinguishing characteristic of semiconductors. The plot shows that the conductivity of the PAM films increased markedly after the insertion of 1,3 IPA linkages in the polyazomethine matrix. Therefore, the directive of conductivity of the polymers is demonstrated with the benefit of electron density circulation of tetraphenylthiophene-oxazole. The excitation involves the transfer of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the organic semiconductor. The PAM films are of *n*-type semiconducting materials, consuming a huge number of free electron charge carriers accessible to drive conductivity. According to (Scheme 2) the azo ( $-\text{CH}=\text{N}-$ ) group linked in polyazomethines, the increase in conductivity could indicate that a continuous electron transfer is formed between the tetraphenylthiophene-oxazole and the phenyl ring in the polymer chain. Based on these electronic conductivity results, we can confirm that these polymers can be used as semiconducting materials in photovoltaics, electronics, sensors and optoelectronic applications.

### UV-Vis Spectroscopic Analysis

Figure 8 shows the optical absorption spectra of PAM nanofilms on a quartz substrate. The high energy absorption peaks at 252 nm and 342 nm indicate the  $\pi-\pi^*$  and  $n-\pi^*$  electronic transition of the aromatic ( $-\text{C}=\text{C}-$ ) and imine bond  $-\text{C}=\text{N}-$  (azo linkage) of the conjugated polymer backbone. This is attributable to the disclosure in the PAM films, which increases the gradation of orbital junction

Table III. Thermal properties of polyazomethines (PAM-01, PAM-02, PAM-03)

Sr. no.	Polymers	Thermal behavior <sup>a</sup>			Residual wt.% at 900°C	LOI <sup>b</sup>
		$T_g$	$T_i$	$T_d$		
1	PAM-01	260	256	530	33	30.7
2	PAM-02	261	261	524	36	31.9
3	PAM-03	267	268	517	28	28.7

$T_g$  Glass transition temperature,  $T_d$  temperature of 10% decomposition,  $T_i$  initial decomposition temperature.

<sup>a</sup>Temperature at which the onset of decomposition was recorded by TGA at a heating rate of 10°C/min.

<sup>b</sup> Limiting oxygen index.

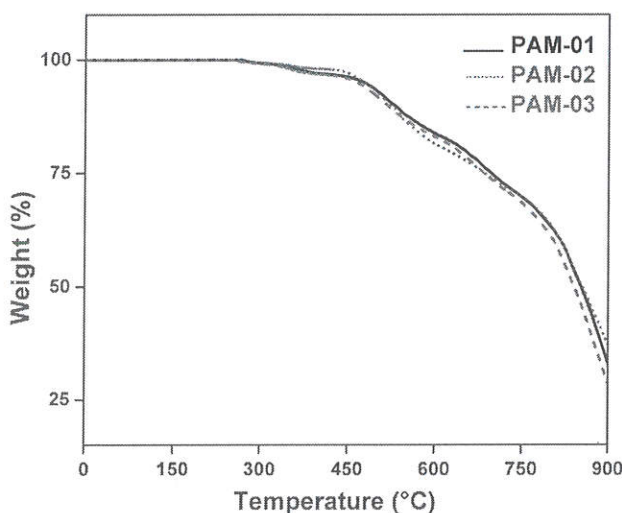


Fig. 9. TGA of polyazomethines (PAM-01, PAM-02, PAM-03).

sandwiched between the  $\pi$  electrons of the heteroaromatic rings, with extended conjugated tetraphenyl thiophene via azo linkages ( $-\text{C}=\text{N}-$ ) in the PAMs.<sup>30,31</sup>

### Thermal Analysis

Thermogravimetric analysis (TGA) and DSC data for the polyazomethines are summarized in Table - III. The TGA curves of the prepared PAMs are also revealed in Fig. 9. According to the TGA results, the initial temperatures ( $T_i$ ) of the synthesized PAM-01, PAM-02 and PAM-03 polymers were 256°C, 261°C and 268°C, respectively. The polyazomethine showed good thermal stability, chemical and mechanical rigidity due to the high heteroaromatic units, as well as the conjugated azo bonds. The general progression evident in the degradation of polymers is the cleavage of weaker bonds first, then the polymer chains, to produce minor components by the breakage of azo bonds. In the case of polyazomethines, fracture by homolytic progression results in aryl nitriles, while heterolytic bond cleavage does not produce such a group. The polyazomethines show a one-step thermal

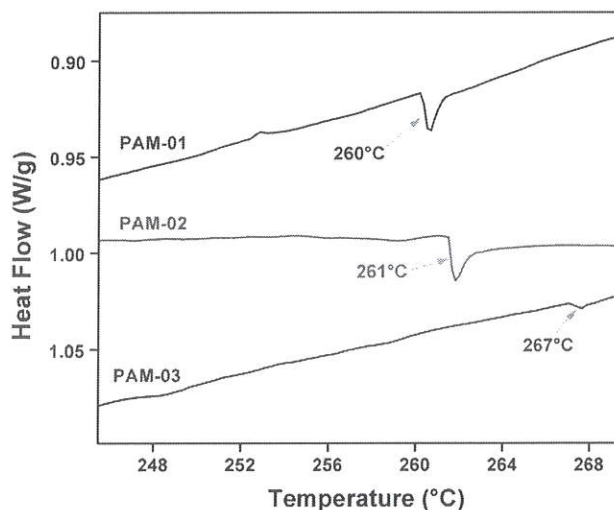


Fig. 10. DSC of polyazomethines (PAM-01, PAM-02, PAM-03).

degradation process. The  $T_{10\%}$  weight loss of the PAM-01, PAM-02 and PAM-03 polymers was found to be 530°C, 524°C and 517°C, respectively, which is good agreement with previous reports.<sup>23,27</sup> According to these results, PAM-03 was the most unstable, while PAM-01 was the most stable. This is due to the collapse of the polymer framework, mostly as a result of the progressive fragmentation of azomethine groups by  $\text{H}-\text{C}=\text{N}-$  bond break. Therefore, it can be concluded that polyazomethine fragmentation follows a homolytic progression. All these polyazomethines also showed a great char yield of 28–36% at 900°C in a nitrogen atmosphere, resulting from their high aromatic content.<sup>23,32–34</sup> Therefore, the higher the aromatic content of a polymer, the higher the char yield. According to this result, all polyazomethines (PAMs) showed excellent thermal stability.

### DSC Results

The glass transition temperature ( $T_g$ ) of polyazomethines was evaluated by DSC traces and is summarized in Table III. Figure 10 shows the DSC heating scans of PAM-01, PAM-02 and PAM-03. The  $T_g$  of the PAMs increased with an increase in the





rigidity of the dialdehydes, the  $T_g$  of PAM-01, PAM-02 and PAM-03 appeared at 260°C, 261°C and 267°C, respectively. With the resulting DSC curves, we conclude that the polyazomethines based on 1,4 TPA linkage have a higher  $T_g$ , due to increasing rigidity, while 1,3 IPA linkages have less rigidity due to m-catenation (bent).

### Flame-Retardant Properties

Generally, components with limiting oxygen index (LOI) higher than 26 show self-extinguishing performance and are considered flame retardant. According to the Van Krevelen and Hoftyzer equation<sup>35,36</sup>:

$$LOI = 17.5 + 0.4 CR$$

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

The LOI values of synthesized PAM-01, PAM-02 and PAM-03 at 900°C were found to be 30.7, 31.9 and 28.7, respectively. The LOI results for the synthesized polyazomethines showing values greater than 28 revealed that these polymers offer good thermal stability and can act as flame-retardant materials.

### CONCLUSIONS

The aim of the current study was the preparation and characterization of TPTP-o diamine-containing PAMs. In addition, we studied the effects of the TPTP-o with varying 1,3 (IPA) and 1,4 (TPA) composition on PAMs, with special attention to thermal and electrical conductivity behavior. The intrinsic viscosity of polyazomethines in NMP solvents was in the range of 0.31–0.35 dL/g. Most of the PAMs exhibited excellent solubility in aprotic organic solvents such as DMAc, DMSO and NMP. These TPTP-o-containing PAMs also exhibited good thermal stability; the  $T_g$  was between 260°C and 267°C by DSC, and the  $T_d$  of all polymers exceeded 517°C in a nitrogen atmosphere. The results of analyses showed that the polyazomethines had different optical, electrical and thermal properties. These polyazomethines could be used to design new types of semiconducting composites or thermally stable materials.

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