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Synthesis, characterization, wettability study and thermal behaviour of aromatic polyimides containing tetraphenylthiophene-quinoxaline unit.

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ABSTRACT

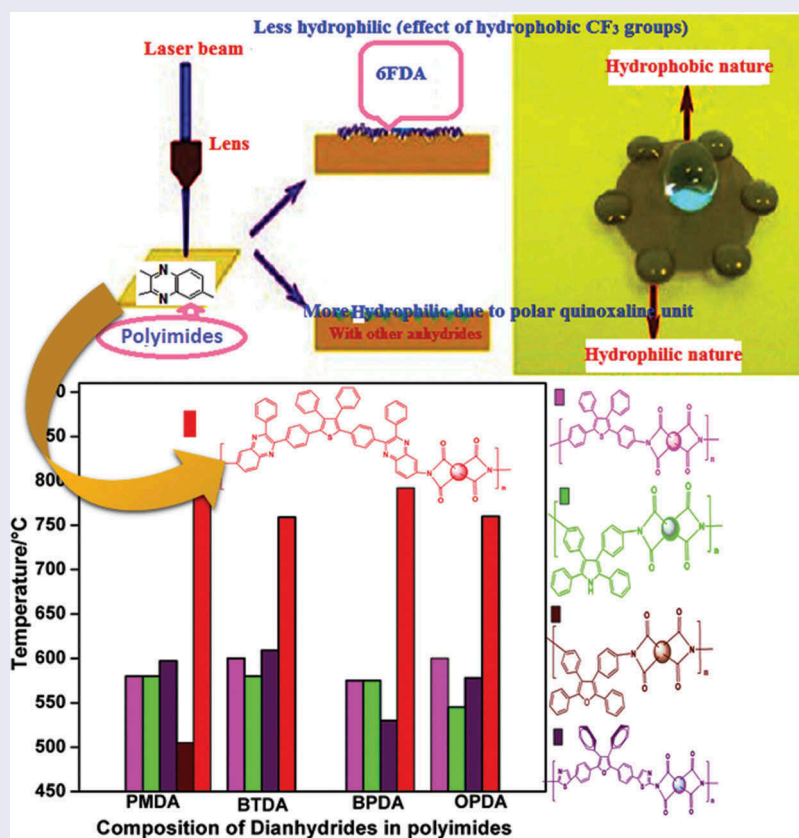
A new series of aromatic polyimides were synthesised by solution polycondensation of diamine monomer with different dianhydrides via the conventional two-step method. On comparison with tetraphenyl components related previous reports, synthesized polyimides containing heterocyclic tetraphenylthiophene-quinoxaline unit showed outstanding thermal properties. Synthesized polyimides showed high glass transition temperatures between 244–274°C. The structure-property correlations among these polyimides were also studied. Also, these polyimides were displayed excellent hydrophilicity except PI-V with the contact angles in the range of 50.4–93.6°. Such hydrophilic polyimide films can be used as polymer electrolytes in ion conduction applications and batteries.

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Films; Polycondensation; Polyimides; thermal properties; structure-property relations



1. Introduction

The aromatic polyimides (PIs) are high performance polymers which comprises the imide rings and

aromatic groups. Aromatic polyimides have widespread applications in the fields of optoelectronic properties, microelectronic field, aerospace science and automobile

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industries due to their outstanding chemical stability, high heat resistance, and physical and mechanical properties.^[1–3] Nevertheless, polyimides also showed some shortcomings; with polyimides have strong attractive forces, dense molecular packing, and chain rigidity affecting in difficulty for processing and have less solubility in common organic solvents.^[4] Henceforth, many hard works have been taken to improve the solubility of PIs and preserve thermal stability by introducing rigid heterocyclic moieties, bulky pendent groups, non-coplanar structures and hyper branched structure into the polymer backbones.^[5–7] One of the attractive methods typically used such as the introduction of bulky pendant phenyl groups into the polymer backbone which improve solubility.^[8] Earlier some studies on new polyimide synthesis have been focused on the preparation of novel diamine or dianhydride monomers having a special structure, such as bulky tetraphenyl based structure^[9,10] covering thiazole unit in the main chain^[11] and also having high sulphur content as well as triptycene unit.^[12–14] A few different polyimides having high glass transition temperatures and having good solubility have been successively prepared by using aromatic diamines containing tetraphenyl thiophene unit.^[15,16] Also, combination of nitrogen atoms in the polyimide's backbone generates a polarized bond, which also improves the thermal properties, wettability as well as solubility of polymers. This is due to increase the dipole-dipole interactions in the polyamides and solvents.^[17,18] For example, Wang et al. described that introduction of bulky moieties or groups^[19,20] into molecular structures are also creative methods to progress the thermal stability, electrical properties, and optical transparency of the polymers. The introduction of polar groups in the polyamides as well as polyimides improved the solubility and introducing bulky substituents and bulky pendant groups into polymer chain, which leads to a decrease in crystallinity^[21] such variations lower the glass transition temperature and lead to soluble and amorphous polymers^[22–25] which may often found many applications in the fields of gas membranes, films, coatings and engineering plastics.^[26] Compounds having a tetraphenyl and 'N' rich quinoxaline unit have highly 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 containing tetraphenyl and heterocyclic quinoxaline may proficiently change some properties of the polymer, ensuing in high crystallinity, excellent thermal stability and low solubility. Moreover, structurally rigid aromatic heterocyclic

polymers comprising polar groups into the main or side chain of the polymers are very fascinating in the field of optoelectronic as well as reverse osmosis because it raises the hydrophilicity of the polymeric membrane and permitted improved diffusion of water through the polymeric matrix.^[27–29] Structural rigidity of asprepared polymer is a serious property for the acceptable functioning of the membrane.^[30] Such high stiffness degree is usually associated with high T_g values.

In this study a series of novel aromatic polyimides (PIs) covering tetraphenyl thiophene with heterocyclic polar quinoxaline units and bulky pendent phenyl groups into main chains were designed and synthesized to progress the solubility, excellent thermal properties and hydrophilicity of polymers. In this study novel diamine monomer, 2, 5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (BPAqPDT) was synthesized, and then it was used to synthesise a series of PIs with different dianhydrides such as 4,4'-oxydiphthalic anhydride (OPDA), 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA), 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA), pyromellitic dianhydride (PMDA), and (4,4'-hexafluoroisopropylidene) diphthalic anhydride (6FDA). Synthesized polyimides were studied for solubility parameters, inherent viscosity measurements, thermal properties via thermogravimetry as well as differential scanning calorimetry and x-ray diffraction. Meanwhile, the effect of polar quinoxaline unit on its surface wetting properties was also studied.

2. Experimental

2.1. Materials

2, 5 Bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (BPAqPDT) was synthesized conferring to our method reported elsewhere.^[31] All essential chemicals were bought from commercial sources and used as received unless stated otherwise. Solvents such as toluene, glacial acetic acid, ethanol, and tetrahydrofuran (THF) were used as received. N, N'-dimethylacetamide (DMAc) were purified by distillation over P₂O₅ under reduced pressure and stored over 4 angstroms (Å) molecular sieves. LiCl was dried at 180°C in vacuum oven for 14hrs.

2.2. Characterizations

The chemical structure of monomer and polymers were recorded on a Thermo Nicoletis-10 Mid Fourier transform infrared (FTIR) spectrometer in the 500–4000 cm⁻¹ frequency range. Inherent viscosity

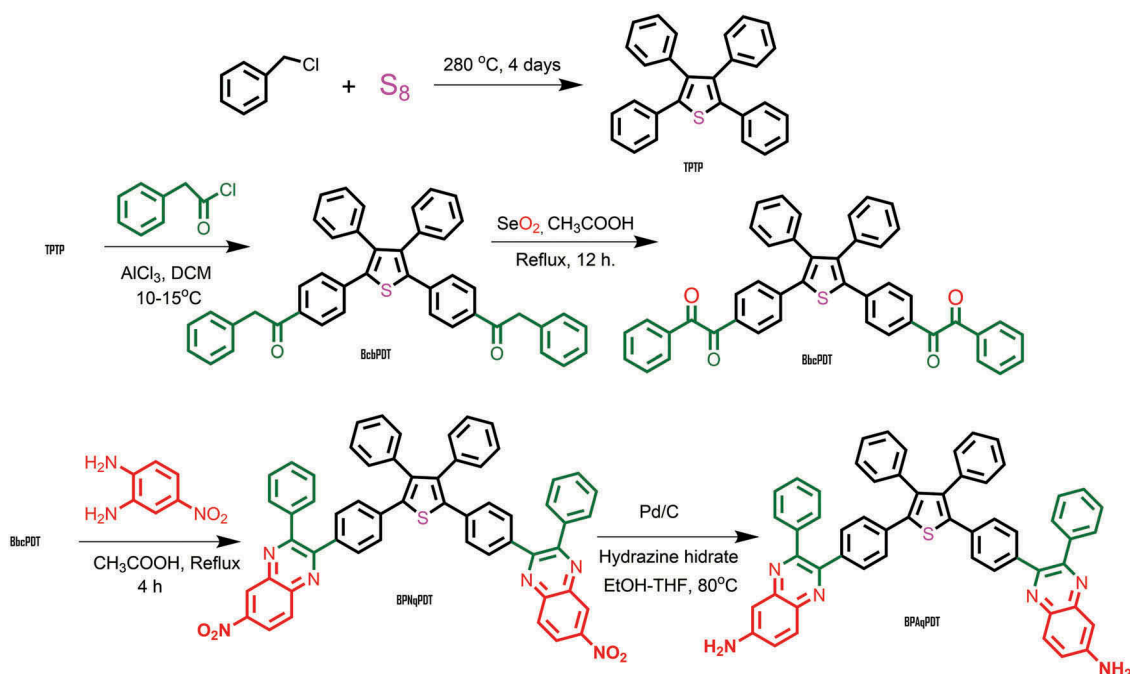
measurements can do with 0.5% (W/V) solution of polymers at 30°C using Ubbelohde suspended level viscometer. The solubility of polymers was determined at 3% concentration in different solvents at room temperature. The X-ray diffraction study of prepared polymers was recorded on Rigaku X-ray diffraction system. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo thermal analysis system under a nitrogen atmosphere with a scan rate of 10°C min⁻¹ in N₂ environment. Differential scanning calorimetry was performed on a Mettler Toledo DSC at a heating rate of 10°C min⁻¹ in N₂ environment. Gel permeation chromatography (GPC) analysis was done by using N-methyl pyrrolidone (NMP) as eluent at a flow rate of 0.5 mL min⁻¹. A differential refractometer was used as a detector. The tool of GPC was standardized by using a mixture of polystyrene standards. The static contact angle on the film for water was tested by JY-PHb contact angle analysis instrument at the room temperature. The static contact angle is the contact angle with which the contact area between liquid and solid is not changed from the outside during the measurement, in contrast to the dynamic contact angle which is produced in the course of wetting (advancing angle) or de-wetting (receding angle). With real solids, liquids and ambient conditions, the contact angle can vary as a function of time and location. Inhomogeneities and changes of wetting over time can therefore be detected by means of the static contact angle. If, on the other hand, the effect of location and time is to be minimized, then the advancing angle is usually measured.

2.3. Synthesis of polyimides

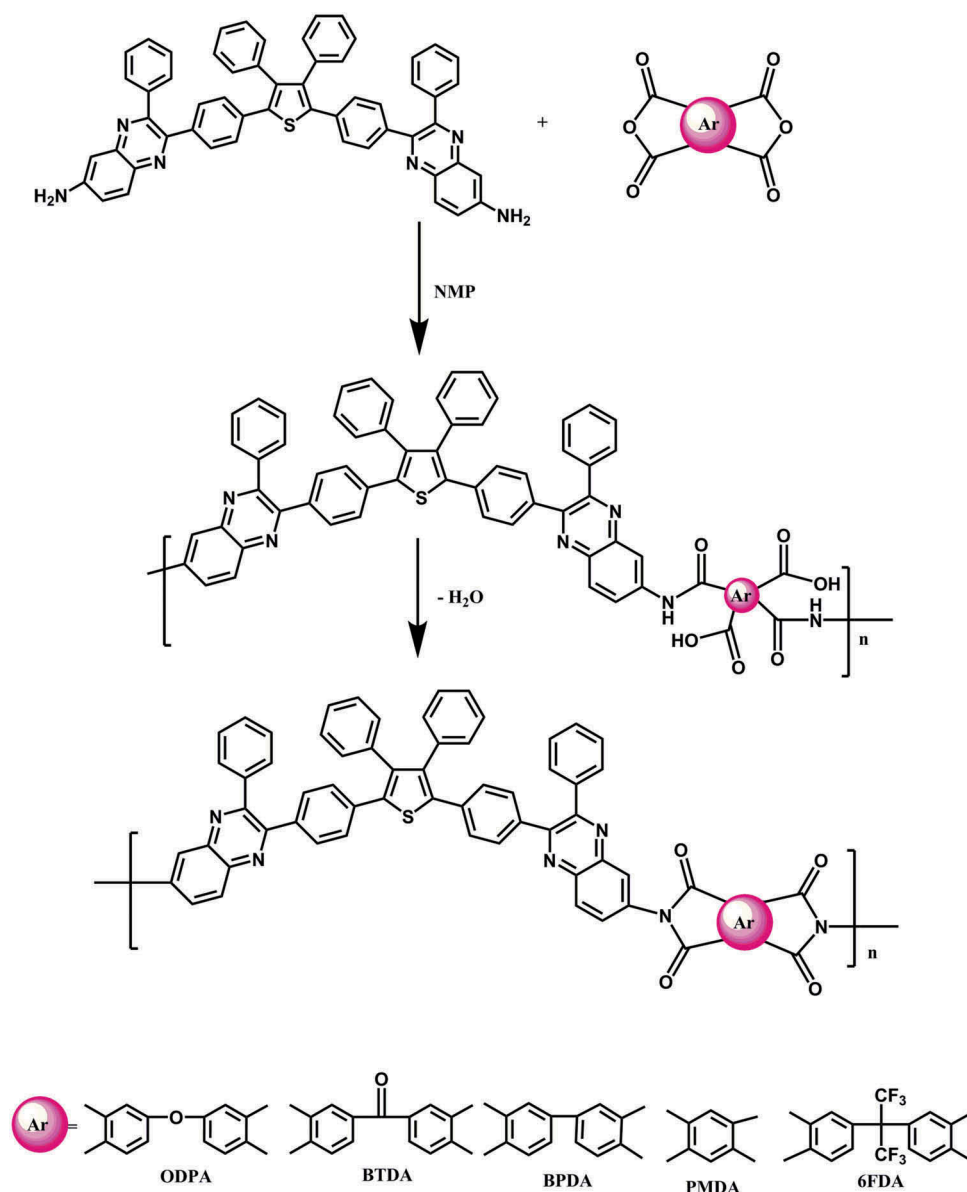
In a 100 mL three neck round bottom flask equipped with a magnetic needle, nitrogen gas inlet and calcium chloride guard tube were placed 0.826 g (0.001 mol) BPAqPDT in 3.6 mL of N-methylpyrrolidone (NMP) and the resulting solution was cooled to 0°C in ice bath. To this cold solution, 0.218 g (0.001 mol) of solid pyromellitic dianhydride (PMDA) was added in lots over 1 hour. Stirred at 0°C for 3 h and 24 h at room temperature under a nitrogen atmosphere, during which 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 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 hour of each at temperature: 150°C, 200°C, 250°C and finally for another 1 hour at 300°C. This process ensured the complete imidization. The overall yield is 99%. The series of other polyimides was synthesized by utilizing above procedure, where in BPAqPDT polycondensation with different dianhydrides. The Inherent viscosity (η_{inh}) of resultant polyamide IV was 0.57 dL.g⁻¹ measured in NMP at a concentration of 0.5 g.dL⁻¹ at 30°C.

2.4. Result and discussion

The route of synthesis to monomer as well as polymers (Scheme 1 and 2) involves six steps and requires commercially obtainable raw material. The



Scheme 1. Synthesis of BPAqPDT.



Scheme 2. Synthetic route of polyimides from BPAqPDT.

heterocyclic tetraphenylthiophene-quinoxaline unit in diamine synthesized by Fridal Craft acylation reaction of tetraphenylthiophene by using phenylacetyl chloride. The resulted product undergoes oxidation with selenium dioxide to yield tetraketone intermediate. Cyclization of tetraketone with 4 nitro *o*-phenylenediamine to yield dinitro compound. Then 2, 5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (BPAqPDT) was prepared on the catalytic reduction of dinitro compound with hydrazine monohydrate and Pd/Charcoal as a catalyst to produce good thermally stable polymers. The pure BPAqPDT was found by recrystallization of crude BPAqPDT from ethyl acetate and *n*-hexane system. Synthesized diamine monomer are valued

building blocks for the preparation of thermally stable aromatic polymers such as polyimides. The composition of monomers yields, and viscosities of polymers are listed in Table 1.

Table 1. Synthesis of polyimides prepared from BPAqPDT (V).

Sr. No.	Polymer code ^a	BPAqPDT (mol %)	Dianhydrides	Viscosity ^b ($\eta_{inh}/dL\ g^{-1}$)	Film formation
1.	PI-I	100	OPDA	0.33	Yes
2.	PI-II	100	BTDA	0.43	Yes
3.	PI-III	100	BPDA	0.39	Yes
4.	PI-IV	100	PMDA	0.57	Yes
5.	PI-V	100	6FDA	0.40	Yes

^a Polymerization was carried out with 1 mmol each of diamine (BPAqPDT) with different dianhydrides.

^b Measured at a concentration of 10 mg of polymer in 1 mL NMP at 30°C.

2.5. Synthesis and structural characterizations of polyimides (PIs)

Thermal imidization was generally selected to prepare for PIs. As shown in Scheme 2, a series of polyimides were prepared from BPAqPDT and commercially available aromatic dianhydrides, such as OPDA, BTDA, BPDA, PMDA, and 6FDA via conventional two-step thermal imidization. The prepared diamine was mixed in NMP and when proper dissolution of diamine, the equimolar amount of dianhydride monomers was added to the reaction mixture. After completing the addition, the solution was stirred for 24 h at room temperature, and then formed viscous poly (amic-acid) solution. The formations of PAA and PIs were confirmed by FTIR spectroscopy which is showed in Figures 1 and 2 respectively. The complete conversion of the polyamic acid to imide ring was demonstrated by the corresponding C = O stretching of carboxylic acid and C = O amide stretching together by the appearance of absorption bands at about 1775 cm^{-1} (asymmetrical C = O stretching), 1721 cm^{-1} (symmetrical C = O stretching), 1380 cm^{-1} (C-N stretching), and 720 cm^{-1} (C = O bending) consistent to the characteristic of imide bands. The GPC data of polyimides are outlined in Table 2. The results showed that the Mn values were between 9.9×10^4 and 2.40×10^5 with respect to polystyrene standards, respectively, and the ratio Mw/Mn was between 2.16 and 3.15.

2.6. Polymer viscosity and solubility

Inherent viscosity measurements can be done with 0.5% (W/V) solution of polymers at 30°C using Ubbelohde suspended level viscometer and the results are outlined in Table 1. The resulting inherent viscosity values of PIs were

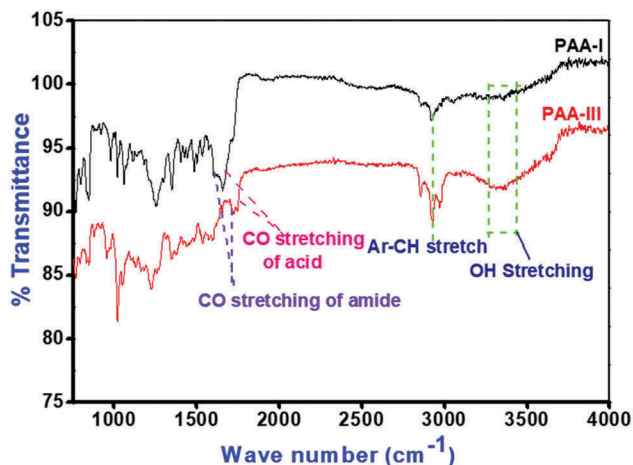


Figure 1. FT-IR spectra of poly(amic-acid)s prepared from BPAqPDT.

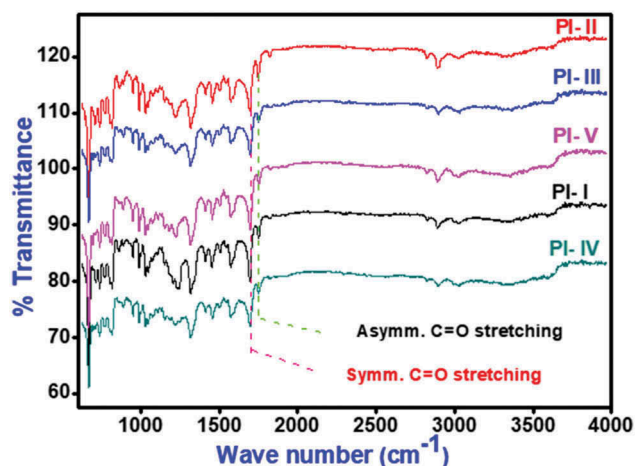


Figure 2. FT-IR spectra of polyimides (PIs) prepared from BPAqPDT.

Table 2. Weight average molecular weights (Mw), Number average molecular weights (Mn) and polydispersity indices (Mw/Mn) of polyimides.

Sr. No.	Polyimides	Mw x 10 ⁵	Mn x 10 ⁵	PDI ^a (Mw/Mn)
1.	PI-I	5.72	1.88	3.04
2.	PI-II	6.87	2.39	2.87
3.	PI-III	3.12	0.99	3.15
4.	PI-IV	4.72	2.18	2.16
5.	PI-V	6.69	2.40	2.78

^a The polydispersity index (PDI) of the polyimide samples measured at 30°C using N-methylpyrrolidone (NMP) as eluant at a flow rate of 0.5 mL/min by GPC.

in the range of $0.33\text{--}0.57\text{ dLg}^{-1}$, which showed polymers formed with moderate to high molecular weight. As shown in Table 3, It was observed that PI-I originated from OPDA and PI-V originated from 6FDA not only showed greater solubility at room temperature in high boiling point solvents, such as DMF, DMSO, NMP, m-cresol and pyridine but also they were partially soluble in low-boiling-point solvents CHCl_3 and THF mainly due to the bulky pendent phenyl groups, which disturbed the packing density of polymeric chains, then made the solvents penetrate easily. However, PI-IV originated from PMDA showed less solubility in organic solvents which may be due to the relative rigidity of pyromellitic structure in the polymer chain. PI-III prepared from BPDA was soluble in NMP, m-cresol and H_2SO_4 , as well as partially soluble in DMF, DMSO, DMAc, pyridine and insoluble in CHCl_3 , THF due to the rigidity of biphenyl structure and may be due to the higher molecular weight of polyimide polymer, thereby leading to weak in solubility. PI-II based on BTDA was soluble on heating in DMF, DMSO, DMAc, NMP, m-cresol and was partially soluble in pyridine THF and CHCl_3 it may be due to the incorporation of the relative flexible carbonyl groups

Table 3. Solubility of polyimides (PIs).

Solvents → Polymers ↓	DMF	DMAc	DMSO	NMP	m-Cresol	Pyridine	H ₂ SO ₄	THF	CHCl ₃
PI-I	++	++	++	++	++	++	++	+-	+-
PI-II	+	+	+	+	+	+	++	-	-
PI-III	+-	+-	+-	++	++	+-	++	-	-
PI-IV	+-	+-	+-	++	++	+-	++	-	-
PI-V	++	++	++	++	++	++	++	+-	+-

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

in the polyimide backbone. All polymers could only be dissolved in concentrations of >2% (w/v) in concentrated sulphuric acid after isolation.

2.7. Thermal properties

The thermal behaviour of the polyimides analysed by DSC and TG and is concise in Table 4. DSC revealed that fast cooling from 300°C to room temperature formed predominantly amorphous samples, so that glass transition temperature (T_g) of the polyimides could be simply read in the second heating. As shown in Figure 3, the T_g values of PIs were in the range of 244–274°C. The increasing value of glass transition temperature (T_g) generally interrelated with the dihydride component. As predictable, PI-IV prepared from PMDA showed the maximum glass transition temperature (274°C) because of the introduction of rigid pyromellitic units. However, PI-I based on OPDA showed the lowermost T_g (244°C), which may be due to the presence of phenyl pendant moieties in the polymer backbone. As shown in Figure 4, the thermal stabilities of the polyimides were evaluated by thermogravimetry (TG). From the TG curves, these polyimides did not exhibit weight loss before the scanning temperature reached up to 302°C in nitrogen atmosphere, representative that there is no thermal decomposition happened. As shown in Table 4, the onset decomposition starting temperatures of the resulting PIs were in range of 302–339°C and the temperatures at T_{10%} mass loss were in range of 759–797°C in nitrogen atmosphere respectively. In addition, the residual weight at 900°C for the polyimides was in

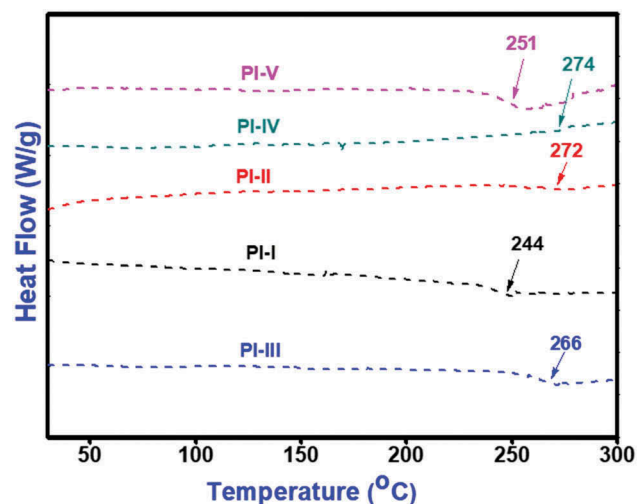


Figure 3. DSC curves of polyimides (PIs).

range of 70–79% in nitrogen atmosphere which concluded that all the PIs have outstanding thermal stability and it may be due to the outcome of the introduction of rigid imide rings, heterocyclic quinoxaline units, and bulky pendent phenyl groups into the polyimide backbone.

The difference between the prepared polyimides and previously reported polyimides showed in Figure 5, the thermal stability of synthesized tetraphenyl-quinoxaline unit based polyimides (PI-I to PI-V) with respect to T_{10%} mass loss temperature of the structurally consistent polyimides comprising heterocyclic (thiophene, furan and pyrrole) bulky tetraphenyl components was in the following order. The tetraphenylthiophene-quinoxaline unit based polyimide's (759–797°C) > tetraphenylfuran-

Table 4. Thermal properties and water contact angles of polyimides (PI-I to PI-V).

Sr. No	Polymers	Thermal Behaviour ^a		Residual Wt % at 900°C ^b	LOI	Glass Transition Temperature ^c T _g /°C	Water contact angle (°)
		T _i /°C	T _{10%} /°C				
1	PI- I	339	760	77	48.3	244	71.0
2	PI- II	318	759	73	46.7	272	56.6
3	PI- III	314	792	79	49.1	266	50.4
4	PI- IV	324	797	76	47.9	274	68.1
5	PI- V	302	781	70	45.4	251	93.6

^aTemperature at which T_i or T_{10%} mass loss was recorded by TG at heating rate of 10°C min⁻¹ under N₂.

^bMass percentage of material left after TG analysis at a maximum temperature of 900 °C.

^cGlass transition temperature was recorded at a heating rate of 10°C.min⁻¹ in a nitrogen atmosphere

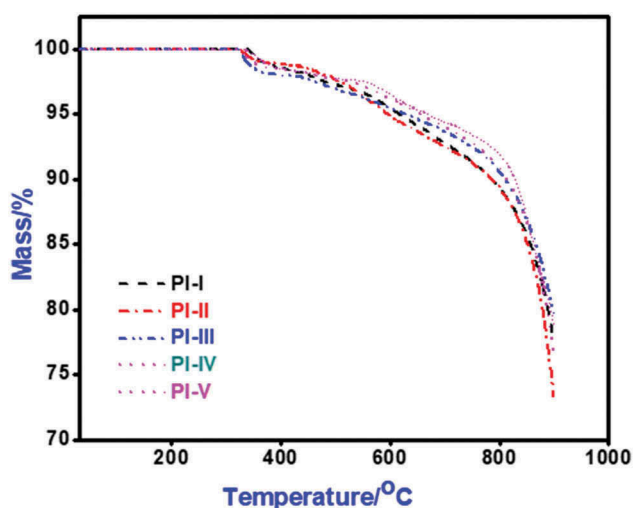


Figure 4. TGA curves of polyimides (PIs).

thiazole unit centered polyimides^[32] (T_i - 251 to 265°C and T_d - 530–609°C) > tetraphenylthiophene-bearing polyimides^[33] (T_i - Not reported, T_d -580–600°C) > the tetraphenyl pyrrole containing polyimides^[34], (T_i -Not reported, T_d -545–580°C) > the tetraphenyl furan-based polyimides^[35], (T_i - Not reported, T_d -505°C for PMDA). These above outcomes specify high thermal stability of the asprepared polyimides (PI-I to PI-V) based on above comparison, $T_{10\%}$ mass loss. These tetraphenylthiophene-quinoxaline unit had as higher thermal stability than tetraphenylfuran-thiazole unit > tetraphenylthiophene > tetraphenyl furan-based polyimides, which was the most thermally stable polymer in the aromatic polyimide having similar bulky tetraphenyl unit.^[35] It is concluded that the synthesized tetraphenylthiophene-quinoxaline unit containing polyimides are outstanding thermal stability than other previously

reported polyimides^[32–35] and these observations also representing that the variance position of substitutions in the aromatic rings or incorporation of heterocyclic units into polymeric backbones showed significant discrepancies not only in their initial and final decomposition temperatures but also in their final char yield.

2.8. Flame-retardant property

Flame-retardant property by limiting oxygen index (LOI) typically, 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^[36],

$$\text{LOI} = 17 : 5 + 0.4\text{CR}$$

Where, CR is the percentage of polymer remaining at 900°C. All polyimides have LOI more than 29 and such polymers can act as flame-retardant materials and are summarized in Table 4. The LOI of PI-I, PI-II, PI-III, PI-IV and PI-V estimated at 48.3, 46.7, 49.1, 47.9 and 45.4 respectively.

2.9. Wide-angle x-ray diffraction (WAXD)

As shown in Figure 6, the crystallinity of polyimides film was characterised by wide-angle X-ray diffraction. The broad peaks were observed, results the asprepared polyimides were amorphous polymers and it was clarified by the pendent phenyl groups reduced the intermolecular forces between the polyimides results reduction in crystallinity^[37] also the pendant phenyl groups into the polymeric backbones disturb the chain regularity as well as packing in polymer, to get amorphous nature.

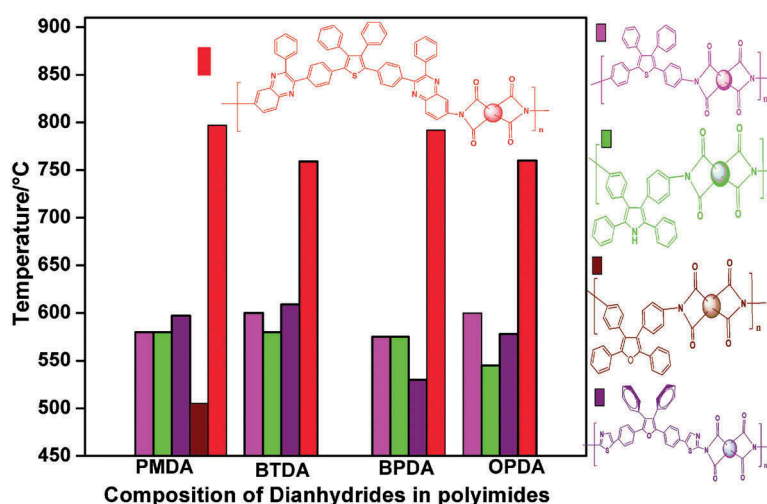


Figure 5. Comparative thermal stability of polyimides containing tetraphenylthiophene-quinoxaline unit (PI-I to PI-V) with other tetraphenyl bulky aromatic polyimides.

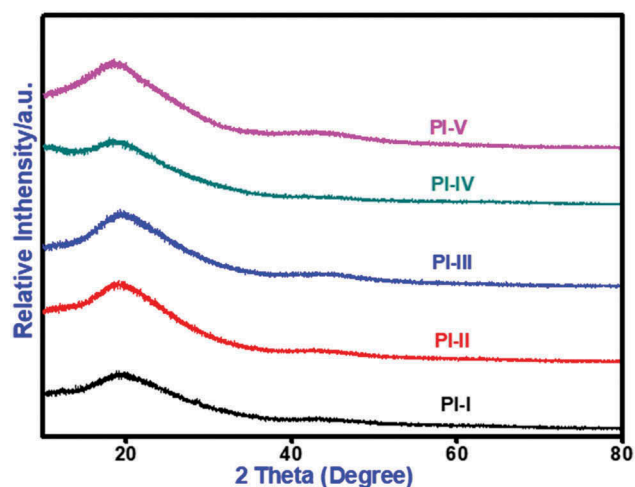


Figure 6. Wide-angle X-ray diffraction patterns of polyimides (PIs).

Meanwhile, no melting peaks were observed except glass transition temperatures in Figure 4, which also agreed with the analysis results of wide-angle X-ray diffraction.

2.10. Surface wettability properties of the polyimide films

A famous technique is used to investigate the wettability of a surface of film samples is by contact angle measurements. Dense films were prepared from all polyimides by casting 10% (w/v) N, N dimethylacetamide polymer solutions onto a glass plate and heating at 75°C overnight. Then, the films were stripped off and were dried in a vacuum oven at 100°C overnight and at 150°C for 48 h. Generally, fully aromatic polymer had hydrophobic nature and explained to these results should be sought in the capability that has the chain for adopting different conformations and molecular packing and from this point of view the number of aromatic rings increases in polymeric backbone which implies a higher the hydrophobicity and therefore, less wettability.^[38] But in our report, the smallest contact angle values of PI-I to PI-IV may be due to incorporation of polar quinoxaline unit into the polymer backbone. The incorporation of the polar heterocyclic quinoxaline unit into the polyimide backbone which rises the molecular polarity and it will affect the surface polarity of the polyimides. This means that the polar quinoxaline moiety in the polyimide backbone resulted in the hydrophilic enhancement. The results in Figure 7 and Table 4 showed that all the polyimides film showed hydrophilic nature except PI-V. Obviously, PI-V originated from 6FDA showed somewhat hydrophobic property it may be due to

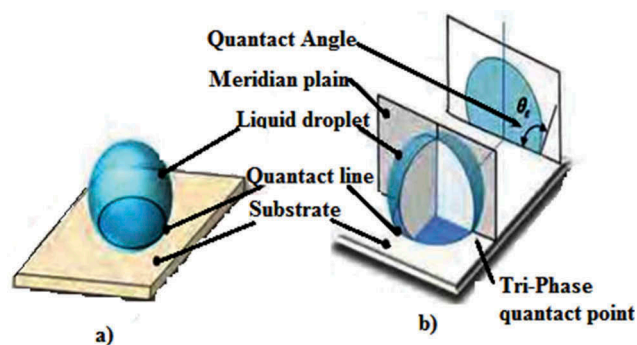


Figure 7. The profiles of a water droplet on the polyimides (PIs) films.

the two fluorinated (CF_3) groups, which is migrated to the external surface during the film formation resulting more hydrophobic surface with high fluorine content. Generally, low water contact angle value (hydrophilic behaviour) also increases the electrochemical performance, where interfacial contact at electrolyte-electrode is considerably high.^[39,40] The main features of the liquid droplet and it is put in contact with a surface presented in Figure 8. The hydrophilicity is used to achieve a desired effect in many applications. A hydrophilic coating allows formation of closely adherent layers of water with lubricity in biological systems and its ability to oppose oil adsorption in anti-graffiti coatings.

3. Conclusion

A series of novel polyimides (PIs) containing polar quinoxaline units and pendant phenyl moieties were prepared from novel aromatic diamine with various commercial aromatic dianhydrides such as OPDA, BTDA, BPDA, PMDA and 6FDA via two step procedure. All the PIs showed high thermal stability with the T_i at 302–339°C and $T_{10\%}$ mass loss temperature at 759–797°C in nitrogen atmosphere and all the PIs presented good solubility and outstanding hydrophilicity. X-ray diffraction pattern of polyimides showed that introduction of pendant phenyl moiety would disturb the chain regularity and packing, leading to amorphous nature. The GPC results showed that the number average molecular weight values were in between 9.9×10^4 and 2.40×10^5 with respect to polystyrene standards, respectively, and the ratio M_w/M_n was between 2.16 and 3.15 and Inherent viscosities of these polymers were in the range 0.33 to 0.57 dL/g indicating moderate to high molecular weight built-up. The structure-property correlation among these polyimides were studied, in view of these polyimides are desirable for application on

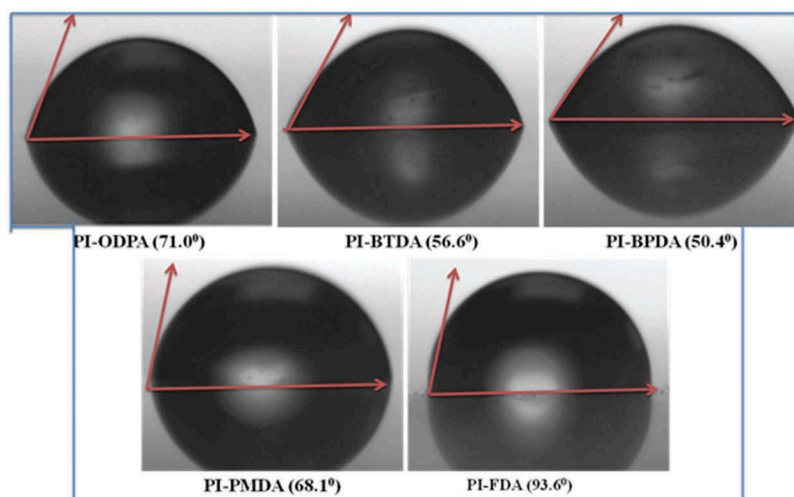


Figure 8. The profiles of a water droplet on the polyimides (PIs) films.

space solar cells and thermal control coating systems. The outstanding comprehensive performances of these polymers also give them potential applications in the areas of electrochemical supercapacitors, optoelectronics, anti-fog coatings and so on.

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