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Synthesis and characterization of processable polyamides containing polar quinoxaline unit in the main chain and evaluation of its hydrophilicity

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ABSTRACT

Here we report a new five polyamides prepared via solution-phase polycondensation under Yamazaki-Higashi conditions to prove the suitability of this method. The synthesized polyamides were characterized by FTIR, ¹H-NMR, differential scanning calorimetry, thermogravimetric analysis, inherent viscosity, solubility and wettability tests. These polyamides were amorphous in nature and they are completely soluble in many organic solvents and they could easily be solution-cast into transparent, flexible films. The as-prepared polymers showed excellent thermal properties. The glass transition temperatures of these polymers are in the range of 251–274 °C under nitrogen atmosphere. The decomposition temperature in nitrogen for a 10% weight-loss temperature is more than 744 °C, and char yield at 900 °C ranged from 43 to 56% in nitrogen. Water contact angles were also tested to know the hydrophilicity of the polyamide films. As-synthesized polyamides showed smallest contact angles indicating hydrophilic surface.

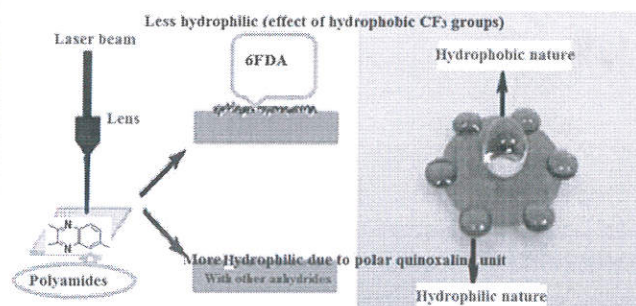
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GRAPHICAL ABSTRACT



1. Introduction

High performance aromatic polyamides are attractive polymers due to their outstanding thermo mechanical properties. To expand the scope of aromatic polyamides by additional optoelectronic features, one may consider by introducing extended π -conjugated systems based on polar heterocycles into the polymer backbone. Pasini et al. synthesized excellent monomeric p-conjugated systems and polymeric architectures.^[1–4] Wholly aromatic polyamides show excellent properties, such as it shows high thermal stability with good electrical behavior and mechanical properties. It was also showed low flammability therefore these polymers find various applications in fields of electronics, adhesives material, composites as well as membranes science.^[5–8] Generally, such aromatic polymers are not processable due to lack of solubility in organic solvents and because of their high

melting temperature, due to the rigid nature of the polymer backbone and present very strong hydrogen bonding in polymer.^[9,10] Therefore, many efforts have been made to increase the processability without reducing their excellent properties by performing structure modification into polymer backbone such as we can achieve good solubility as well as processability by introducing bulky substituents into polymer backbone.^[11–15] The incorporation of pendant groups is one of the well known approach for improving the solubility and thereby the processability. In our previous report we have synthesized the polyamides with introduction of pendant phenyl moiety.^[16] A positive-working photosensitive polymer based on thermal cross-linking and acidolytic cleavage.^[17] In our previous report, we have introduced polar heterocyclic unit into polymer backbone which demonstrate the increases in the solubility of polyamides without

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sacrifices in thermal stability.^[18] The incorporation of asymmetric units^[19,20] as well as bridging substituents in the main polymer chains^[21–23] are also effective for better processability. The introduction of bulky pendant groups into polymeric backbone is also effective option for enhancing the solubility due to decreases hydrogen bonding and would disturb the co-planarity of aromatic units to minimize packing density and crystallinity.^[24–27] In the past few decades, the increasing requirement of the aerospace, automotive, military industries and microelectronic has gave the driving force for the development of new thermally stable polymers to be used in structural applications. Nowadays much effort has been given to the development of aromatic heterocyclic polymers for use as advanced composite matrix, structural adhesives or coatings in high-temperature applications.^[28–31]

In this paper, a new aromatic diamine containing tetraphenyl thiophene moiety with quinoxalines integrated in benzene rings were synthesized and characterized by various spectral techniques. A triphenyl phosphite activated polycondensation (phosphorylation reaction) for the synthesis of polyamides was reported by Yamazaki et al.^[25] A series of new aromatic polyamides were synthesized from 2,5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3,4 diphenyl thiophene (BPAqPDT) with commercial diacids monomers in the presence of NMP, triphenyl phosphite/calcium chloride/pyridine so as to study the effect of introduction of pendant phenyl moiety as well as tetraphenyl thiophene-quinoxaline unit and structure of aromatic diacid chloride into polymer backbone. It has been confirmed that incorporation of tetraphenyl thiophene units having pendant phenyl moiety into the polymer backbone is a successful route to improve the solubility of aramids while retaining high thermal stability.

The structurally rigid aromatic polyamides containing polar unit into the main chain are very interesting in the field of reverse osmosis because such polar units increase the hydrophilicity of the polymeric membrane and allowed for better diffusion of water through the polymeric matrix^[32] so that such rigidity of aromatic polyamides is a critical property for the adequate functioning of the membrane.^[33] Such high stiffness degree is usually associated with high Tg values. The characterization of new polymers such as crystallinity, thermal, contact angle and physical properties are also investigated and discussed.

2. Experimental

2.1. Materials

2,5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3,4 diphenyl thiophene (BPAqPDT) was synthesized according to the method reported elsewhere.^[34] Required chemicals were purchased from commercial sources and used as received. N-Methyl-2-pyrrolidone (NMP) were purified by distillation over P₂O₅ under reduced pressure and stored over 4 Å molecular sieves. LiCl was dried at 180 °C in vacuum oven for 14 hrs.

2.2. Instrumental

The chemical structure of polymers was recorded on a Thermo Nicolet iS-10 Mid Fourier transform infrared (FTIR) spectrometer and ¹H NMR (400-MHz) spectra of monomer was obtained with a Bruker spectrophotometer. Inherent viscosities were measured 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. X-ray diffraction pattern was analyzed by Rigaku x-Ray Diffraction System. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were performed on a Mettler Toledo Thermal Analysis system under a nitrogen atmosphere with a scan rate of 10 °C min⁻¹.

3. Polymerization

3.1. Synthesis of polymers

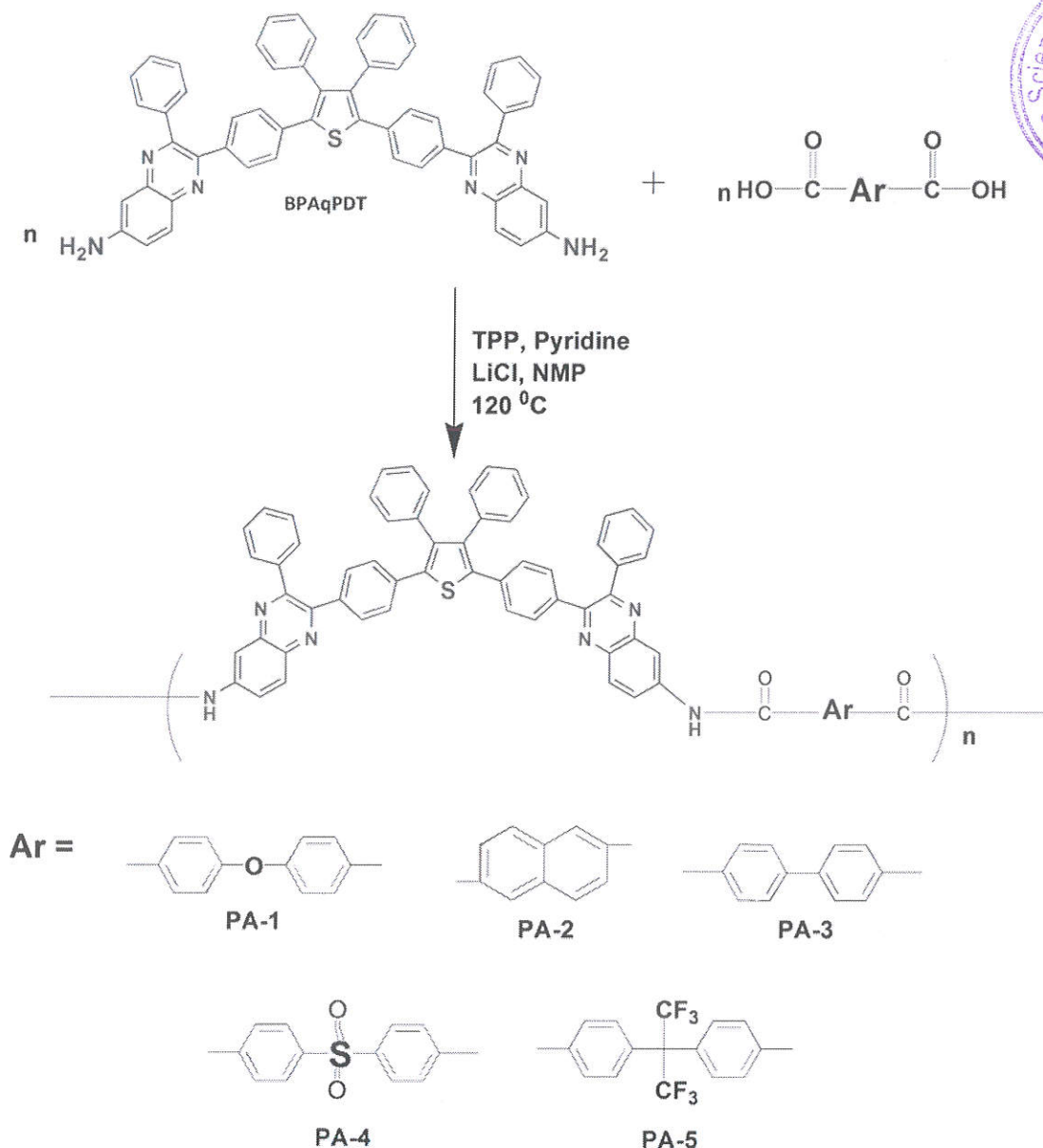
To a completely dried 100 mL, three-necked flask equipped with a mechanical stirring device were charged NMP (8 mL) 2,5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3,4 diphenyl thiophene (BPAqPDT) (0.828 g, 1 mmol), 4,4'-biphenyldicarboxylic acid (0.31 g, 1.25 mmol), lithium chloride (0.54 g), triphenyl phosphite (0.7 mL, 2.64 mmol), and pyridine (2 mL) under nitrogen flow. The mixture was mechanically stirred and heated to 80 °C. After the mixture was completely dissolved, the mixture was heated with stirring at 130 °C for 10 hrs under nitrogen. The resulting viscous polymer solution was poured slowly into 100 mL of methanol with stirring giving rise to a fiberlike precipitate that was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100 °C for 15 hrs. Yield: 99%.

4. Results and discussion

Previously we have reported the synthesis of phenyl substituted thiophene attached with quinoxaline -diamine monomer. It was prepared by FC acylation of tetraphenyl thiophene (TPTP) with phenylacetyl chloride. The oxidation of alpha methyl group of acylated product with SeO₂ to yield tetraketone. Resulting tetraketone undergoes cyclization with 4-nitro-o-phenylenediamine (N-OPD) to form dinitro derivatives of monomer. Diamine monomer was obtained by the catalytic reduction of dinitro with hydrazine monohydrate and Pd/C catalyst. The pure diamine monomer was obtained by recrystallization in ethyl acetate-n-hexane system. The synthesized diamines are valuable building blocks for the preparation of thermally stable aromatic polymers including polyamides (Scheme 1) and polyimides. The better solubility of polyamides has been achieved by the structural modifications of monomer; such as by introducing pendant phenyl groups as well as polar quinoxaline unit.

A new series of aromatic polyamides were prepared by phosphorylation polycondensation of new synthesized diamine with aromatic diacids. The direct polycondensation method was previously reported by Yamazaki et al and it is





Scheme 1. Synthetic route of polyamides from BPAqPDT.

very excellent laboratory technique for the synthesis of polyamides. Throughout all the polymerization reactions were homogeneous. Inherent viscosities of polyamides were in the range 0.53–0.69 dL/g (Table 1) indicating the formation of polymers with moderate molecular weights. The tough and transparent films of polyamides were casted from polymer solutions in DMAc. The formations of polymers were confirmed by FT-IR and NMR spectroscopy. A representative FTIR spectrum of polyamides is shown in Figure 1. The formation of polyamide polymer was confirmed by the –N–H stretching frequency as a broad band between 3,300 and 3,400 cm^{-1} . The carbonyl stretching was appeared approximately at 1,672 cm^{-1} . The ^1H -NMR spectrum of polyamide (PA-3) shown in Figure 2. The amidic proton was appeared at 10.7 ppm. In the diacid unit of polymer, aromatic protons were appearing in the range of 8.39–8.59 ppm and diamine unit of BPAqPDT, aromatic protons were appearing in the

range 6.82–7.87 ppm. Polyamides were tested for solubility at 3 wt. % concentration in various solvents. The results of solubility study were summarized in Table 2. All the polyamides were soluble in polar aprotic solvents like DMAc and NMP. They were also soluble in *m*-cresol and pyridine; whereas previously prepared reference polyamides which were synthesized from rigid diacid monomers like biphenyl dicarboxylic acid (BPDA) and terephthalic acid (TPA) with phenylenediamine which were insoluble in the above all solvents.^[35–37] The increased processability via solubility of polyamides with pendent phenyl groups in polyamides backbone compared with that of reference polyamides could be achieved by presence of heterocyclic quinoxaline unit also. The pendant phenyl groups as well as polar quinoxaline unit along the polymer backbone strongly reduce molecular interactions of stiff chain aromatic polymers forming excellent chain separation effect which stopped their tight chain

packing and exceeded the free volume. The disturbed packing of polymer chains facilitates the diffusion of small molecules of solvent which causes the improvement in solubility.

4.1. X-ray diffraction studies of polymers

X-ray diffractograms of polyamides are shown in Figure 3. The x-ray diffraction study of all synthesized polyamides

showed a broad halo in the middle region ($2\theta = 16-18^\circ$) showing that the polyamides were amorphous in nature.

4.2. Thermal properties of polymers

Thermal properties of polyamides were determined by thermogravimetric analysis (TGA) at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen. The initial decomposition temperature, the temperature at 10% weight loss (T_{10}) and weight residues at 900°C for polyamides are tabulated in Table 3.

Table 1. Synthesis of polyamides from BPAqPDT.

Sr. No.	Polymer code ^a	Diamine mol %	Diacids	Yield (%)	Viscosity ^b dL/g	Film formation
1.	PA-1	100	ODCA	99	0.54	Yes
2.	PA-2	100	NDCA	98	0.53	Yes
3.	PA-3	100	BPDCA	99	0.55	Yes
4.	PA-4	100	SDCA	99	0.69	Yes
5.	PA-5	100	6FDCA	98	0.59	Yes

^aPolymerization was carried out with 1 mmol each of our previously prepared diamine with different diacids.

^bInherent viscosity measured at a concentration of 0.5 g/dL in NMP at 30°C .

Table 2. Solubility of polyamides.

Solvents→ Polymers↓	DMF	DMAc	DMSO	NMP	m-Cresol	Pyridine	THF	CHCl ₃
PA-1	+-	++	+-	++	++	++	+-	--
PA-2	+-	++	+-	++	+	++	+-	--
PA-3	+-	++	+-	++	++	+-	--	--
PA-4	+-	++	+-	++	++	++	+-	--
PA-5	+-	++	+-	++	++	++	+-	--

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

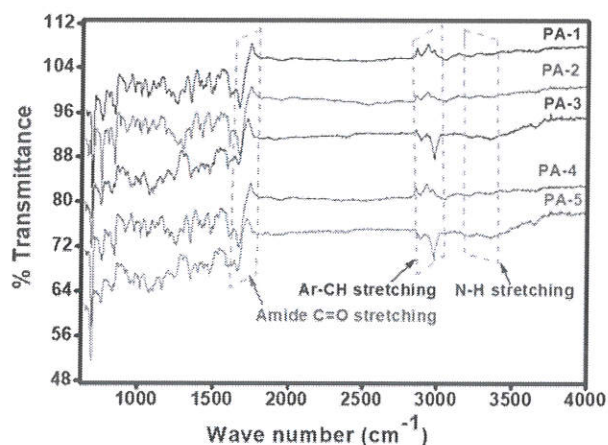


Figure 1. FTIR spectrum of polyamides.

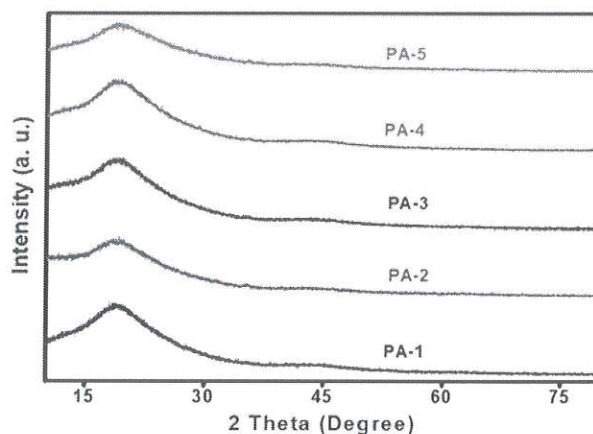


Figure 3. WAXD of polyamides.

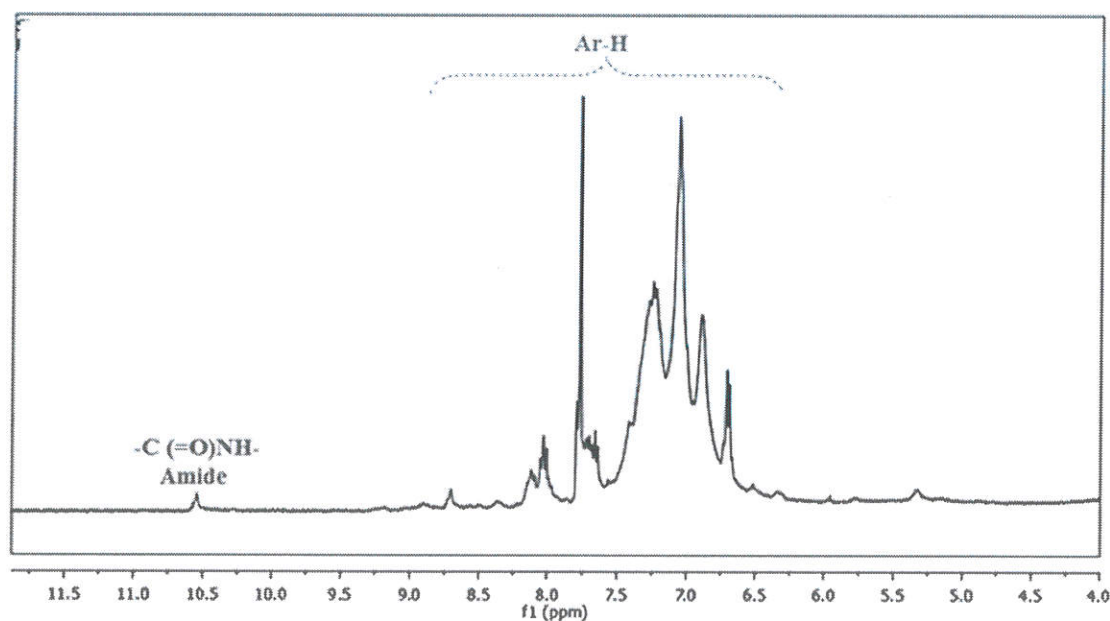


Figure 2. ^1H NMR spectrum of polyamide (PA-3).

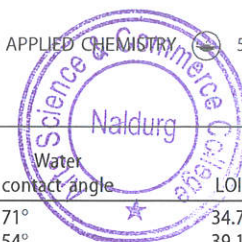


Table 3. Thermal properties and water contact angles of polyimides (PA-1 to PA-5).

Sr. No	Polymer code ^a	Thermal behaviour ^a		Residual Wt % at 900 °C	Glass transition temperature (T _g) °C	Water contact angle	LOI
		T _i °C	T _d °C				
1	PA-1	274	698	43	251	71°	34.7
2	PA-2	268	733	54	272	54°	39.1
3	PA-3	275	744	56	274	48°	39.9
4	PA-4	246	737	51	253	66°	37.9
5	PA-5	236	715	44	267	82°	35.1

^aTemperature at which onset of decomposition was recorded by TG at a heating rate of 10 °C/min.

T_d: Temperature of 10% decomposition; T_i: Initial decomposition temperature.

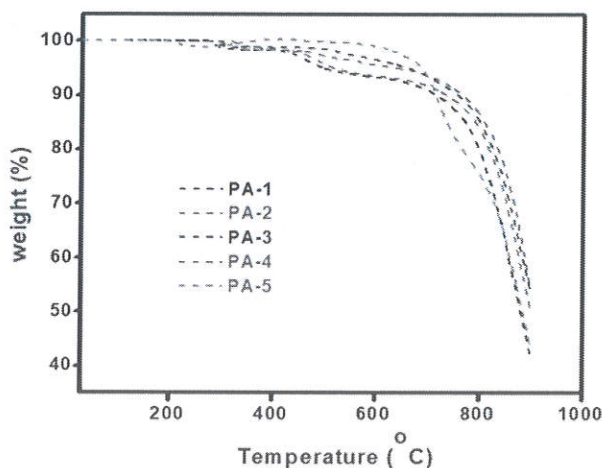


Figure 4. TGA curve of polyamides.

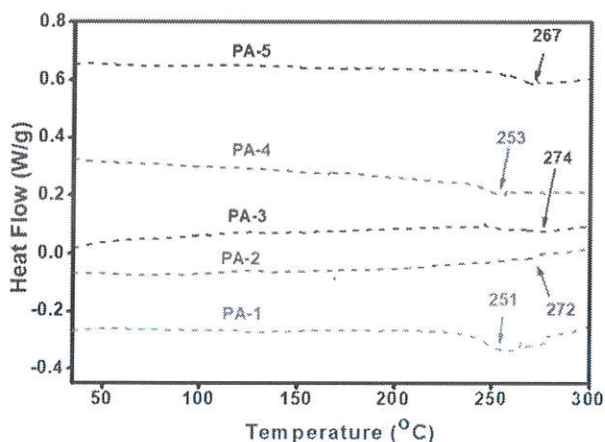


Figure 5. DSC curve of polyamides.

Representative TGA curves of polyamides are shown in Figure 4. The T₁₀ values obtained from TGA curves for polyamides were in the range 698–744 °C indicating their excellent thermal stability. The char yield of polyamides when the polymer was heated to 900 °C, in nitrogen were in the range 43–56%, shows good thermal stability. Glass transition temperatures (T_g) of polyamides were evaluated by DSC at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. DSC curves of polyamides are shown in Figure 5 and the T_g values obtained from second heating scans of polymer samples are listed in Table 3. The T_g values of the synthesized polyamides were in the range 251–274 °C. PA-3 derived from rigid biphenyl-4,4'-dicarboxylic acid exhibited the highest T_g value (274 °C). However, PA-1 derived from 4,4'-oxy(bis benzoic) acid presented the lowest T_g value (251 °C).

4.3. Flame-retardant property

The flame-retardant property by Limiting oxygen index (LOI) Mostly, constituents with limited oxygen index (LOI) upper than 26 shows self-extinguishing performance and are reflected as flame retardant. According to Van Krevelen and Hoftyzer equation^[38]:

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

Where, CR is the percentage of polymer remaining at 900 °C. All polyamides have LOI more than 29 and such polymers can act as flame-retardant materials are summarized in Table 3. The LOI of PA-1, PA-2, PA-3, PA-4 and PA-5 estimated at 34.7, 39.1, 39.9, 37.9, and 35.1, respectively.

4.4. Water contact angle measurement

A famous technique is used to investigate the wettability of a surface of film samples is by contact angle measurements. The films of polyamides were prepared by casting 5% (w/v) N, N dimethylacetamide onto a glass plate and heating at 100 °C for 12 hrs. Then the films were dried in a vacuum oven at 125 °C for 12 hrs. Table 3 also shows contact angles measured for polyamides and the image of the drop (Figure 6) was captured five seconds after placed. 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 their backbone which implies a higher the hydrophobicity and therefore, less wettability.^[39] In our report PA-5 had higher contact angle than PA-1 to PA-4, therefore, the surfaces of PA-1 to PA-4 is the most hydrophilic while PA-5 is less hydrophilic surface. The smallest contact angle values of PA-1 to PA-4 may be due to incorporation of polar quinoxaline unit into the polymer backbone. PA-5 also have polar quinoxaline unit but it is derived from 6FDCA showed less hydrophilic property it is due to the two tri-fluorinated (CF₃) groups, which is migrated to the external surface during the film formation resulting less hydrophilic surface with high fluorine content.^[40] Generally, smallest value of water contact angles i.e. hydrophilic behavior increases the electrochemical performance of supercapacitors, where interfacial contact at electrolyte-electrode is considerably high.^[41,42]

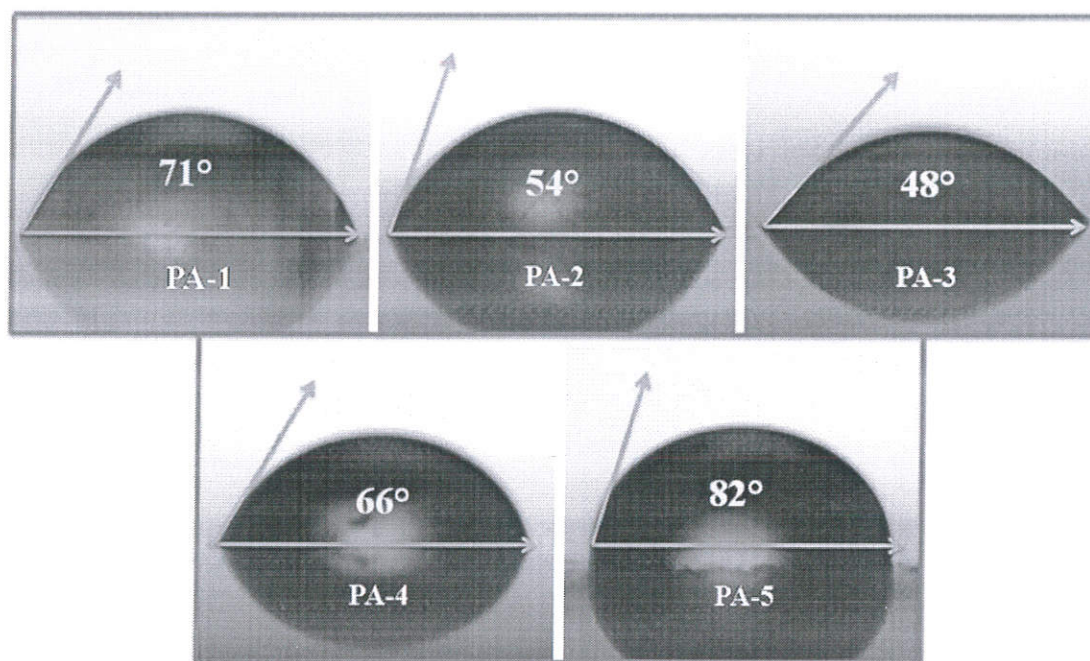


Figure 6. The profiles of a water droplet on the polyamide films.

5. Conclusion

Based on the synthesis of a novel aromatic diamine containing a polar quinoxaline unit and pendant phenyl rings a series of five aromatic polyamides were successfully synthesized by solution-phase polycondensation under Yamazaki-Higashi conditions. Polyamides exhibited excellent thermal stability showed T_{10} values in the range 698–744 °C, and the glass transition temperature values were in the range of 251–274 °C. The obtained polyamides were showed good solubility in polar aprotic solvents, m-cresol, pyridine etc. All polyamides showed the smallest contact angle, indicating the surface is more hydrophilic in nature except PA-5 is less hydrophilic in nature. Hence, based on these properties, future perspective will be able to make composites of these polyamides with nanoparticles to improve electrochemical properties for applications such as supercapacitors, gas sensors and construction etc.

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