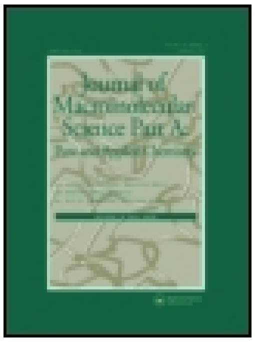

Journal of Macromolecular Science, Part A
Pure and Applied Chemistry

ISSN: 1060-1325 (Print) 1520-5738 (Online) Journal homepage: http://www.tandfonline.com/loi/lmsa20

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To cite this article: P. H. Salunkhe, S. S. Ankushrao, Y. S. Patil, J. N. Mahindrakar, V. N. Kadam, V. P. Ubale & A. A. Ghanwat (2018): Processable heat resistant polyamides containing tetraphenyl thiophene having pendant phenyl moiety with heterocyclic quinoxaline unit: Synthesis and characterization, Journal of Macromolecular Science, Part A, DOI: 10.1080/10601325.2018.1444418

To link to this article: https://doi.org/10.1080/10601325.2018.1444418

JOURNAL OF MACROMOLECULAR SCIENCE, PART A: PURE AND APPLIED CHEMISTRY
2018, VOL. 0, NO. 0, 1–7
https://doi.org/10.1080/10601325.2018.1444418

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Processable heat resistant polyamides containing tetraphenyl thiophene having pendant phenyl moiety with heterocyclic quinoxaline unit: Synthesis and characterization

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ABSTRACT

A series of new polyamides containing tetraphenyl thiophene having pendant phenyl moiety with heterocyclic quinoxaline unit were synthesized by using the solution polycondensation method of novel diamine monomer V with isopthaloyl chloride (IPC) and terpthaloyl chloride (TPC) in various mole proportions. These novel polymers were characterized by FT-IR, solubility, inherent viscosity, thermal analysis and X-ray diffraction studies. Inherent viscosities of these polymers were in the range 0.66 to 1.44 dL/g indicating moderate to high molecular weight built-up. These polymers exhibited solubility in various solvents such as DMAc, NMP, pyridine, m-cresol etc. X-ray diffraction pattern of polymers showed that introduction of pendant phenyl moiety would disturb the chain regularity and packing, leading to amorphous nature. Thermal analysis by TGA and DSC showed excellent thermal stability of polymers. The structure -property correlation among these polyamides were studied, in view of these polymer's potential applications as processable high temperature resistance materials.

ARTICLE HISTORY
Received January 2018
Revised and
Accepted February 2018

KEYWORDS
Co-polymerization; heat resistant; polyamides; processable; thermal properties

1. Introduction

Wholly aromatic polyamides (aramids) are highly thermally stable polymers for high temperature resistance with a favourable balance of physical, chemical properties[1–3] and mechanical properties.[4] The design of suitable polymeric materials is an increasingly important research area due to demands for applications as biomedical, pharmaceutical, agricultural surgical implants and scaffolds for tissue engineering.[5] The aromatic polyamides are well known for their excellent thermal stability, and they find use in various high temperature resistance applications especially as strong fibre and tough films industrial and aerospace applications. However aromatic polymers are difficult to fabricate because of their limited solubility in common organic solvents.[6–10] The introduction of pendant moiety is one of the well known approach for improving the solubility and thereby the processability. Imai et al. synthesized the polyamide, with introduction of pendant groups such as phenyl moiety. The introduction of polar groups in the polymer increased the solubility[11] and also introducing bulky substituents and bulky pendant groups into polymer chain, which leads to a reduction in crystallinity[12–14] such modifications lower the glass transition temperature and lead to soluble and amorphous polymers which may often found many applications in the fields of gas membranes, films, coatings and engineering plastics,[15] polymer blends, and composites.[16,17] The introduction of bulky pendant groups can decrease hydrogen bonding and inter chain interactions in polyamides and generally disturb the co-planarity of aromatic units to minimize packing density and crystallinity.[18–21] The introduction of cardo group in polymer backbone is also enhancing the solubility of polymer.[22] This should enhance solubility.[23,24] Generally, it is more convenient to synthesize the modified aramids with the structural modification of diamine monomers, followed by the polycondensation reaction with available aromatic dicarboxylic acids or their derivatives.

In the present investigation, a new aromatic conjugated diamine containing tetraphenyl thiophene moiety with quinoxaline integrated in one benzene ring (V) was synthesized and characterized by various spectral techniques. A series of polyamides was synthesized from (V) by low temperature solution polycondensation method with different mol proportion of IPC and TPC. The polymers were characterized by inherent viscosity, solubility, FT-IR spectra, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray diffraction so as to study the effect of introduction of pendant phenyl moiety as well as tetraphenyl thiophene unit and structure of aromatic diacid chloride into polymer backbone. It has been demonstrated that incorporation of both phenyl and tetraphenyl thiophene units into the polymer backbone is a

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successful route to improve the solubility of aramids while retaining high thermal stability.

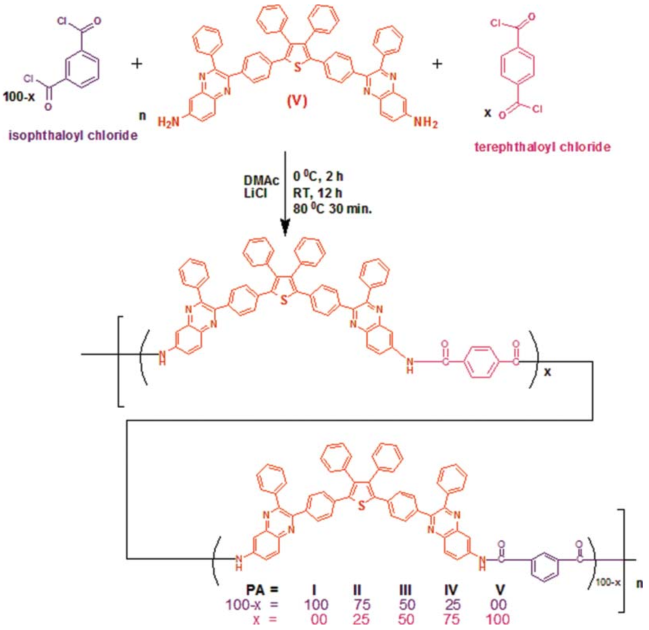
2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and used as received unless stated otherwise. Solvents such as toluene, glacial acetic acid, ethanol, and THF were used as received. N, N'-dimethylacetamide (DMAc) were purified by distillation over P_2O_5 under reduced pressure and stored over 4 angstroms (Å) molecular sieves. Dichloromethane (DCM) was dried by sodium and calcium hydride respectively before use. LiCl was dried at 180°C in vacuum oven for 14 hrs.

2.2. Instrumental

The chemical structure of polymers and monomer was recorded on a Thermo NicoletiS-10 Mid Fourier transform infrared (FTIR) spectrometer in the 500–4000 cm^{-1} frequency range, ^1H NMR (400-MHz) spectra of monomer was obtained with a Bruker spectrophotometer. Chemical shifts (delta values) are given as parts per million with tetramethylsilane (TMS) as an internal standard. Inherent Viscosity measurements can be done 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 (XRD) of polymers was recorded on Rigaku X-ray Diffraction System with ULTIMA IV Goniometer. 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}. Differential scanning calorimetry was performed on a Mettler Toledo DSC at a heating rate of 10°C min^{-1}.

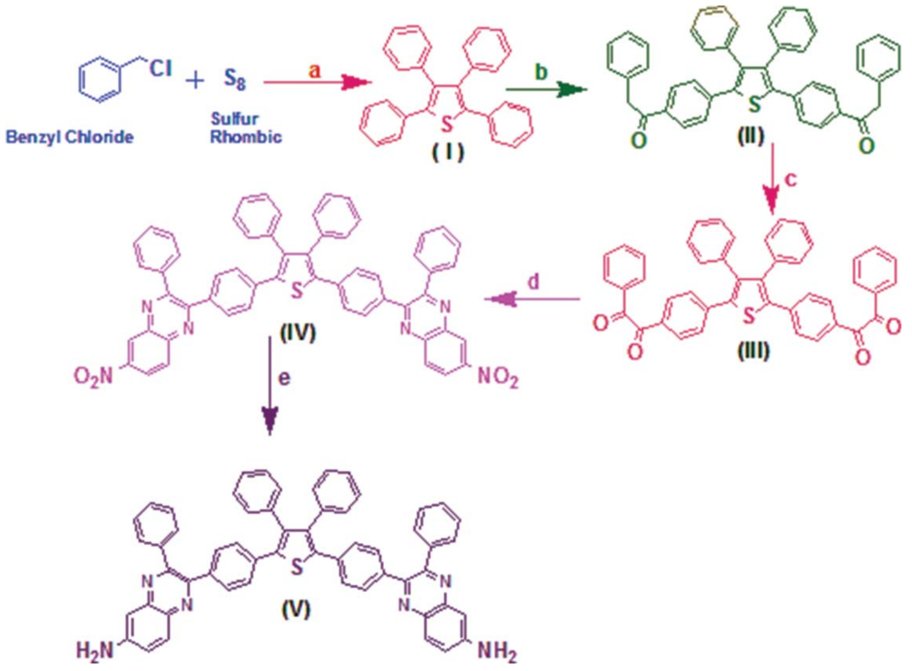


Scheme 2. Synthesis route of polyamides (PA-I to PA-V) from new diamine (V).

2.3. Preparation of monomer

2.3.1. 2, 3, 4, 5-Tetraphenylthiophene (TPTP) (I)

Tetraphenyl thiophene (I) was prepared according to a literature procedure (25). TPTP (I) was recrystallized from dichloromethane – methanol system to give white needles (yield: 51%, mp: 184 -186°C).



Scheme 1. Synthetic route of 2, 5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (V) monomer.
Reagents and conditions:
Reflux, 240° C, 3 days. b) $PhCH_2COCl$, $AlCl_3$, DCM, 10-15° C. c) SeO_2, glacial acetic acid, reflux 12 hrs. d) 4-Nitro-o-phenylene diamine, glacial acetic acid, reflux 4 hrs. e) H_2, Pd/C Hydrazine hydrate, mixture of EtOH - THF, 80° C.

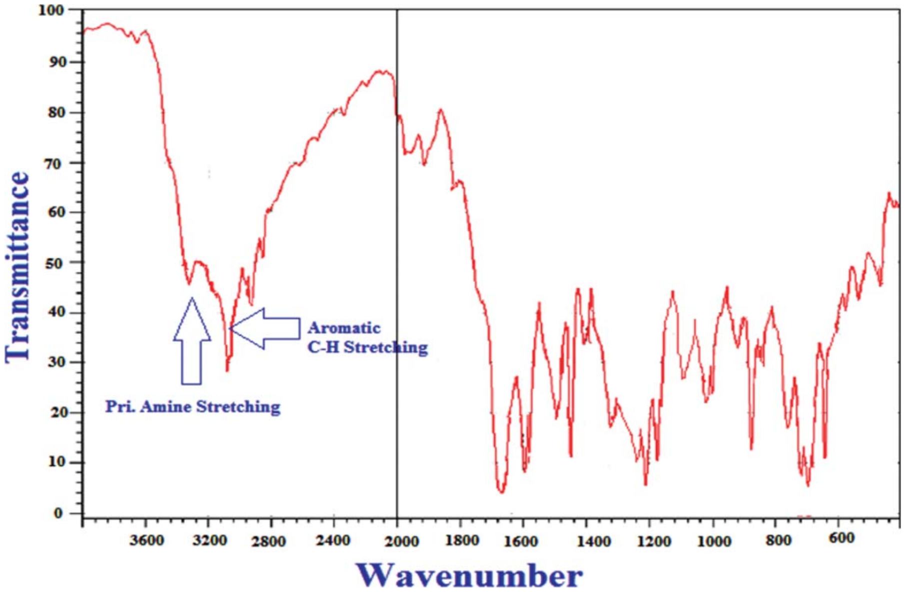


Figure 1. FT-IR spectrum of new diamine (V).

2.3.2. 2, 5-Bis [(4-carbonylbenzyl) phenyl] – 3, 4-diphenyl thiophene (II)

TPTP (I) (20 g, 0.05 mol), anhydrous DCM (300 mL), and $AlCl_3$ (13.3 g, 0.1 mol) were added to a three-neck flask under nitrogen atmosphere. The whole mixture was then cooled to 0°C by ice-water bath. Phenylacetyl chloride (15.5 g, 0.1 mol) was then added drop wise to the stirred reaction mixture at 0°C. The reaction was allowed to warm to room temperature and continued for overnight. The resulting mixture was poured into ice water (1000 mL) and the organic layer was collected, evaporated to give crude product (II). Recrystallized from toluene to get pure (II) as pale yellow needles yield: 14.9 g (46.33%) mp: 226–230°C. FT-IR cm^{-1}: 1682 ($>C = O$ in conjugation with $C = C$), 1595,1510 ($>C = C$ conjugation with $C = O$), 2921 (aromatic C-H stretch).

2.3.3. 2, 5-Bis-[(4- benzoylcarbonyl) phenyl] -3-4 diphenyl thiophene (III)

In a 250 mL round bottom flask equipped with reflux condenser and magnetic stirrer were placed 2.77 g (0.025 mol) selenium dioxide and 20 mL of glacial acetic acid and 3.12 g (0.005 mol) of (II) was added in the reaction flask at 60°C. The reaction mixture stirred at reflux temperature for 24 hrs followed by hot filtration. The clear yellow filtrate was concentrated to about 25 mL and then filtered. The yellow residue was washed with acetic acid (5 mL) dried in air and recrystallized from a mixture of ethyl acetate and hexane to give yellow crystals of (III) yield 2.90 g (88.95%), mp.140°C. ^1H-NMR: (400 MHz, $CDCl_{3-}$ ppm) δ: 7.99 d (4H) J = 8.4 HZ, 7.85 d (4H) J = 8.4 Hz, 7.71-7.66 m (2H), 7.53 t (4H) J = 8.4 & 1.6 Hz, 7.38 d (4H) J = 8.8 Hz, 7.21-7.15 m (6H), 6.98 d (4H) J = 8.0 Hz.

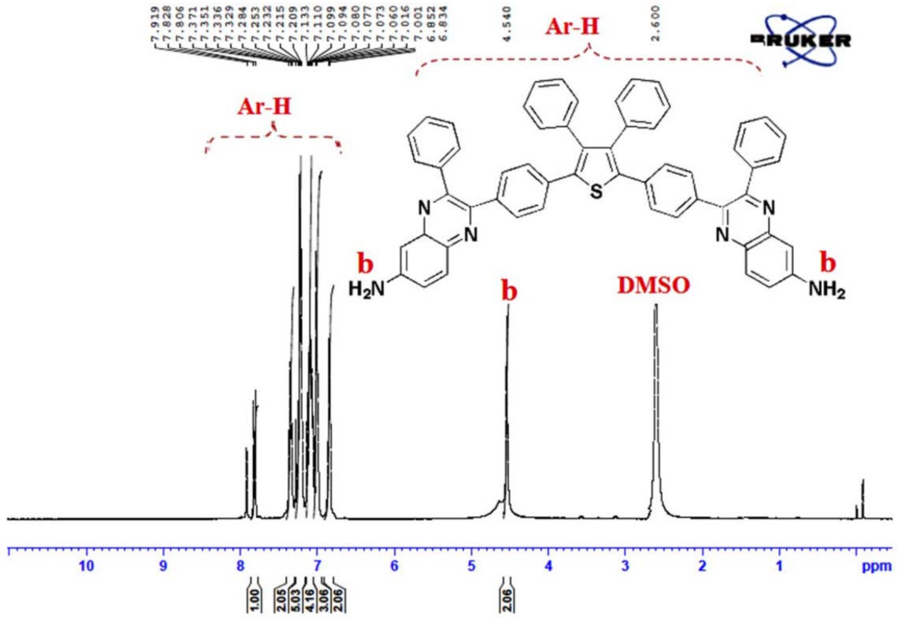


Figure 2. ^1H – NMR of new diamine (V).

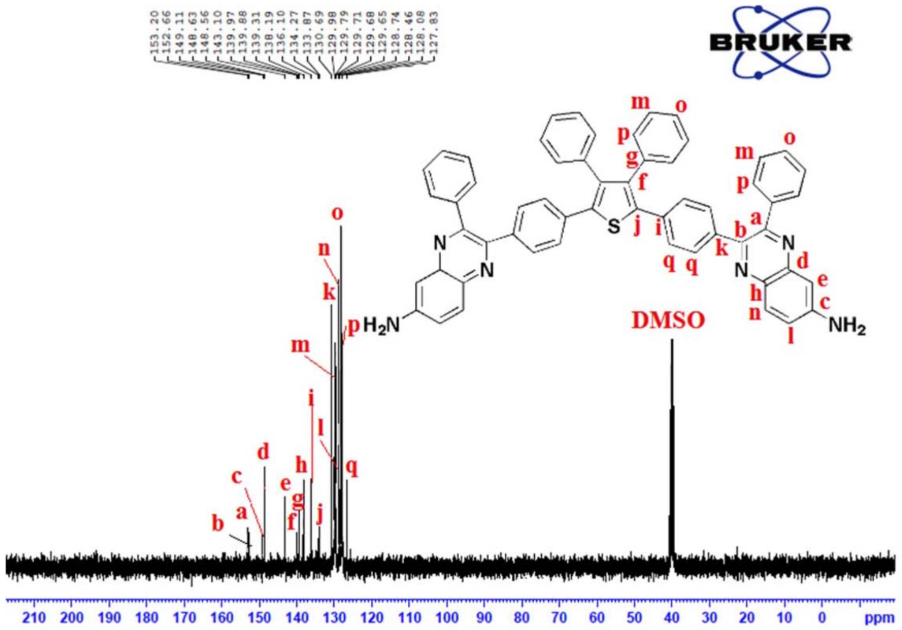


Figure 3. ^{13}C spectrum of new diamine (V).

2.3.4. 2, 5 Bis [4-(2-phenyl-7-nitroquinoxaline) phenyl] 3, 4 diphenyl thiophene (IV)

In a 100 mL two necked round bottom flask equipped with a condenser and stirrer bar, a mixture of 6.5 g (0.009 mol) of (III), 2.75 g (0.018 mol) diamino-4-nitrobenzene and 250 mL glacial acetic acid was refluxed for 4 hrs. Upon cooling, the precipitated yellow solid was collected by filtration and washed with mixture of ethanol/water (1:1, v/v). The crude product was recrystallized from toluene to give yellow crystals of (IV). Yield 6.30 g (92.78%) mp.260°C. ^{1}H-NMR: (400 MHz, DMSO -d_6) δ: 8.92 s (1H), 8.48 d (1H) J = 9.2 Hz, 8.24 d (1H) J = 8.8 Hz, 7.47 d (2H) J = 6.4 Hz, 7.40-7.30 m (5H), 7.14 d (2H) J = 8.4 Hz,7.08 d (3H) J = 5.2Hz, 6.90 d (2H) J = 5.2 Hz.

2.3.5. 2, 5 Bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (V)

In a 100 mL two necked round bottom flask equipped with a reflux condenser, a dropping funnel, and a magnetic stirrer bar, a mixture of 5.6 g (0.0063 mol) IV, 0.5 g of 10% Pd/C, 200 mL 1:1 mixture of absolute ethanol-tetrahydrofuran (THF) and 9.45 mL hydrazine monohydrate was heated at reflux temperature for 16 hrs. The reaction solution was filtered while hot to remove the catalyst. Upon cooling, the filtrate was poured into water to form yellow precipitate was isolated by filtration and then recrystallized from mixture of ethyl acetate and hexane and dried. The yield was 4.2 g (80.45%) mp.230°C. ^{1}H-NMR: (400 MHz, DMSO -d_6) δ: 7.82 d (1H) J = 8.8 Hz, 7.35 d (2H) J = 8.0 Hz, 7.28-7.21 m (5H), 7.13-7.06 m (4H), 7.01 d (3H) J = 6.84 d (2H) J = 7.2 Mz, 4.54 Broad s (2H, NH_2).

2.4. Synthesis of polyamides

In a 100 mL three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet, a calcium chloride guard tube and a thermowell were placed 0.826 g (0.001 mol) 2, 5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (V) and 3 mL dry DMAc was added to the flask. The mixture was stirred under nitrogen atmosphere till the dissolution was complete. The reaction flask was cooled to 15°C with the help of ice–salt mixture. 0.203 g (0.001 mol) isopthaloyl chloride was added in two lots and stirring was continued for 2 h at 0°C. Then the mixture was stirred for 12 h at room temperature; and then neutralized with 0.075 g (0.00104 mol) lithium carbonate and heated at 80°C, for 20 min. It was then degassed under vacuum and the polymer was precipitated by adding reaction mixture to excess of rapidly stirred methanol. The precipitated polymer was filtered, washed with water and finally with methanol. It was dried at 80°C under vacuum for 6 h. The yield of polymer (PA-I) was 99% and inherent viscosity of polymer was 0.66 dL/g.

Table 1. Synthesis of polyamides from new diamine (V).

Sr. No.	Polymer code	Diamine (V) mol %	Diacid chlorides mol % IPC	Diacid chlorides mol % TPC	Yield (%)	Viscosity[b]	Film formation
1	PA-I	100	100	00	99	0.66	Yes
2	PA-II	100	75	25	97	0.77	Yes
3	PA-III	100	50	50	100	1.44	Yes
4	PA-IV	100	25	75	98	1.17	Yes
5	PA-V	100	00	100	99	1.29	Yes

[a] Polymerization was carried out with 1 mmol each of diamine (V) with IPC and/or TPC.

[b] Measured at a concentration of 0.5 g/dL in NMP at 30°C.

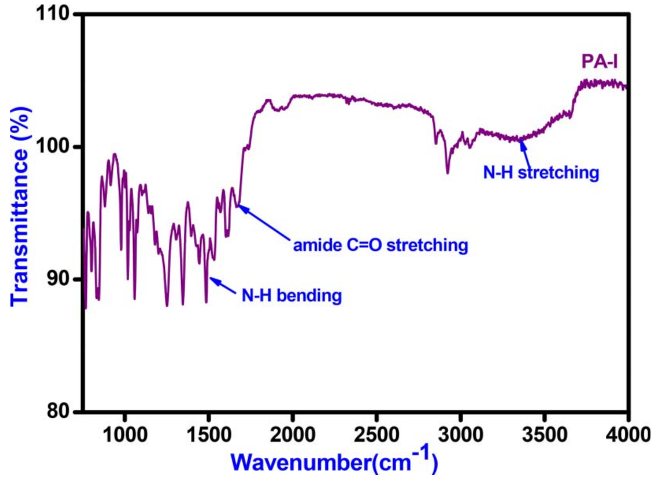


Figure 4. FT- IR spectrum of PA-I.

3. Results and discussion

The synthetic route (Scheme 1 and Scheme 2) towards new monomer and polymer only requires six steps and uses commercially available raw material. In the present investigation the phenylated thiophene containing diamino quinoxaline integrated in benzene ring monomer prepared by friedel craft acylation of tetra phenyl thiophene with phenyl acetyl chloride fallowed by oxidation of alpha methyl group with selenium dioxide to yield 1, 2 diketone and it undergoes cyclization with 4-nitro-o-phenylenediamine to yield phenylated thiophene containing quinoxaline dinitro compound. Then, the diamine was obtained on the catalytic reduction of intermediate dinitro-compound with hydrazine monohydrate and Pd/C catalyst in refluxing mixture of ethanol and THF in high yields. The pure new diamine was obtained by recrystallization from ethyl acetate and n-hexane system. Diamines are valuable building blocks for the preparation of thermally stable aromatic polymers including polyimides. Copolymerization is an effective approach to enhance the solubility and processability (26–29). Although most soluble polymers have been prepared by combinations of the structural modifications, it does appear that a pendant moiety is a necessary prerequisite for enhancing solubility.

The 2, 5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (V) monomer characterized by FTIR spectroscopy, ^{1}H NMR and ^{13}C spectroscopy. The FT-IR spectrum of new diamine monomer is showed in figure 1. The primary amine (-NH$_2$) stretching are identified approximately at 3373 cm^{-1}. The aromatic C = C stretching vibrations from the ring present a band at 1540 cm^{-1}. Low intensity peak presented over the range of 2924 cm^{-1} can be attributed to the aromatic C-H stretching vibrations, the peak at 600–800 cm^{-1} is characteristic of the C-S bending vibrations, which indicates the presence of a thiophene ring. The proton NMR spectrum of 2, 5 bis [4-(2-phenyl-7-aminoquinoxaline) phenyl] 3, 4 diphenyl thiophene (V) monomer (Figure 2) showed the NMR signal (b) at 4.54 δ, corresponding to an primary amine (2H) group of the amino quinoxaline and remaining all 17 protons (a) are aromatic in the range of 6.9 to 7.82 δ. ^{13}C NMR spectrum of new diamine monomer showed 17 signals for different carbons in monomer (figure 3). All the spectroscopic data values were in good agreement with the proposed structures.

Table 2. Solubility behaviour of polyamides (PA-I to PA-V).

Solvents									
Polymers	DMF	DMSO	DMAc	NMP	m-Cresol	Pyridine	H$_2$SO$_4$	THF	CHCl$_3$
PA-I	+-	+-	++	++	++	++	++	–	–
PA-II	+-	+-	++	++	++	++	++	–	–
PA-III	+-	+-	++	++	++	++	++	–	–
PA-IV	+-	+-	++	++	++	++	++	–	–
PA-V	+-	+-	++	++	++	++	++	–	–

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

4. Polymerization

4.1. Synthesis of polyamides

A new series of aromatic polyamides were synthesized (Scheme 2) by condensation of new diamine (V) with IPC and/or TPC in different mol proportion by low temperature solution polycondensation in DMAc. The polymerization preceded smoothly giving highly viscous solution. The resulting polymers were precipitated by pouring the viscous polymer solutions in methanol. The mol %, yields and viscosity data of polyamides was presented in Table 1. All the polymers were obtained in excellent yields (97 to 100%). The inherent viscosities of polymers were in the range of 0.66 to 1.44 dL/ g; indicating the formation of moderate to reasonably high molecular weight polymers.

The structural features of the polyamides were characterized by FT-IR spectroscopy (figure 4). The infrared spectrum of polymer PA-I showed characteristics absorption at 3350 cm^{-1} (N-H stretching), 1502 cm^{-1} (N-H bending), 1678 cm^{-1} (amide C = O stretching). The proton NMR spectrum of PA-I (Figure 5) showed the signals at 10.93 and 10.96 δ, corresponding to formation of a symmetrical amide linkage of polyamide from synthesized new diamine monomer with IPC / TPC. Remaining signals for aromatic protons were appeared in the range of 6.9 to 8.72 δ. A solubility characteristic of polyamides is tabulated in Table 2. The solubility of polymers was determined in different organic solvents. It is observed that polyamides synthesized from new diamine (V), exhibited better and partial solubility in various polar aprotic solvents such as N, N-dimethyl sulphoxide (DMSO), N, N-dimethyl formamide (DMF). All the polyamides (PA-I to PA-V) completely soluble in N, N-dimethyl acetamide (DMAc), N-methylpyrrolidone (NMP), pyridine, m-cresol and Conc. H$_2$SO$_4$ etc. All the polymers were insoluble in THF, CHCl$_3$. Thus, better solubility of these polyamides as expected; can be attributed to the introduction of pendant phenyl moieties, in the polymer backbone.

Thermal behaviour of polymers was evaluated by means of dynamic thermogravimetry and differential scanning calorimetry. Table 3 incorporates the thermal data such as initial decomposition temperature (T$_i$), 10% Wt. loss temperature (T$_{10}$) and residual weight at 900°C. The thermal stability of the polyamides was studied by thermogravimetric analysis (Figure 6) at a heating rate of 10°C/min in nitrogen atmosphere. The initial weight loss (T$_i$), temperature at which 10% weight loss (T$_{10}$) and char yields at 900°C were determined from the original

Table 3. Thermal properties of polyamides (PA-I to PA-V).

Sr.No	Polymers	Thermal Behaviour[a]		Residual Wt% at 900°C	Glass Transition Temperature (Tg)
		T_i	T_d		
1	PA- I	356	578	70	158
2	PA- II	352	574	68	166
3	PA- III	355	577	68	197
4	PA- IV	348	737	71	229
5	PA- V	357	635	72	—

[a] Temperature at which onset of decomposition was recorded by TG at **a** heating rate of 10^{0}C/min.
T_d – Temperature of 10% decomposition T_i _ Initial decomposition temperature.

thermograms. T_i values range in between 348 to 357°C. T_{10} values range between 574 to 737°C, respectively. Residual weight loss at 900°C was in the range of 68 to 72%. This shows that the introduction of highly phenylated linkage with heterocyclic quinoxaline unit into a polymer backbone improves solubility without having much affected on thermal stability.

The polyamides had glass-transition temperatures in the range of 158–229°C (figure 7). The glass-transition temperature

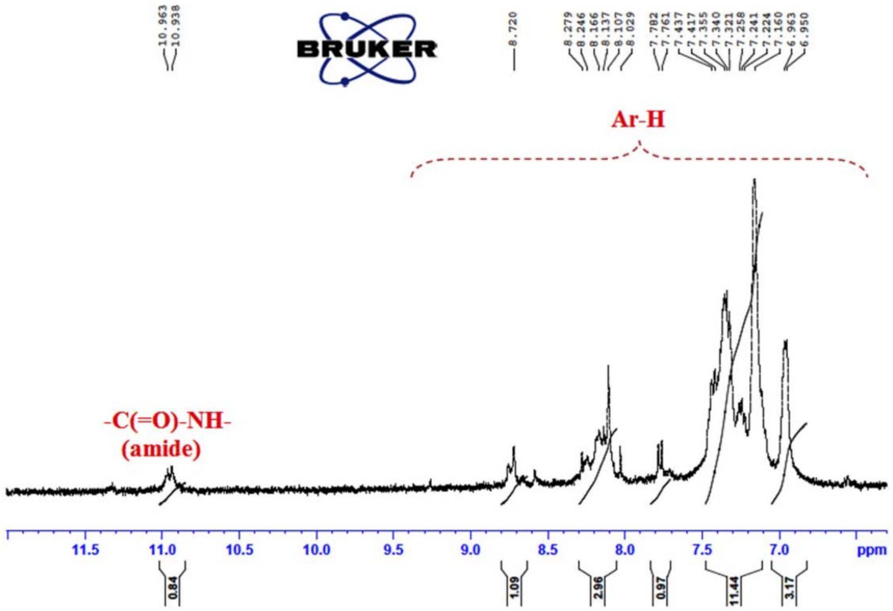


Figure 5. ^{1}H NMR of PA-I.

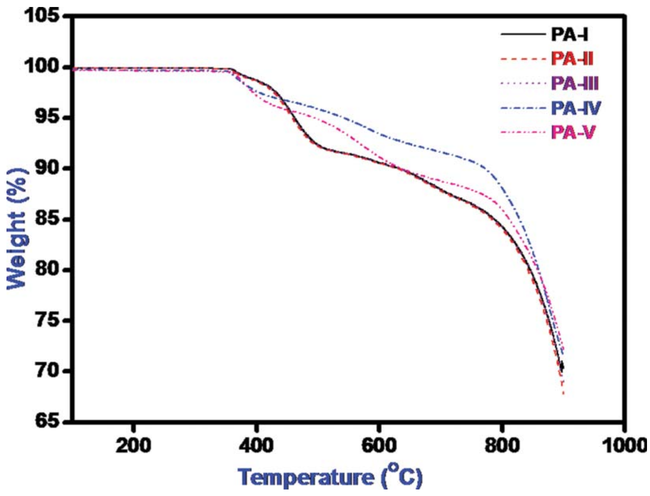


Figure 6. TGA curve of polyamides.

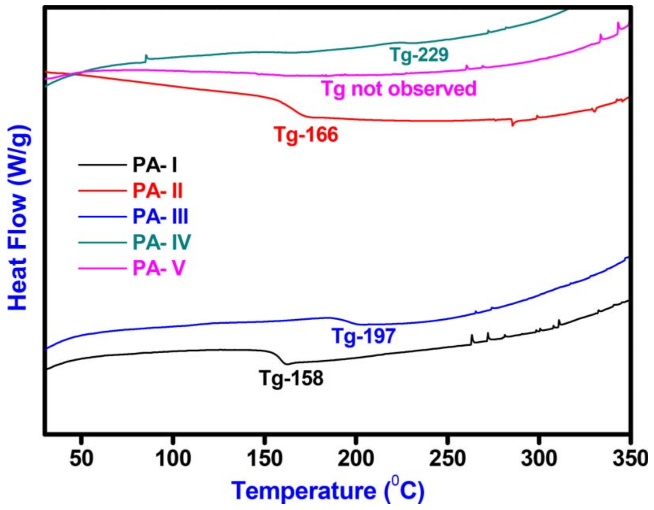


Figure 7. DSC curve of polyamides.

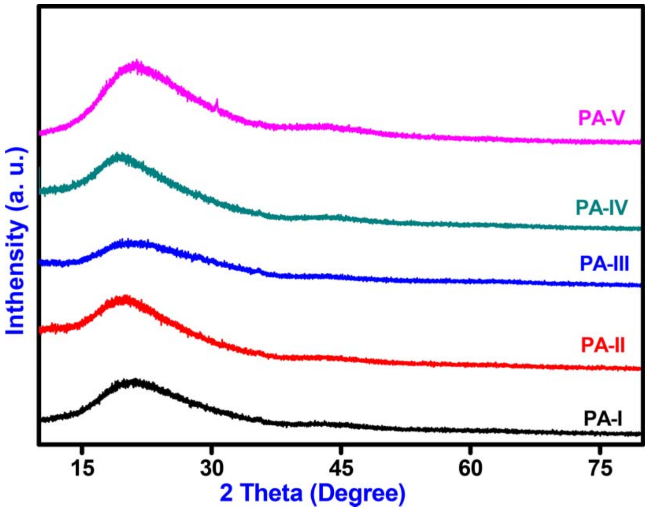


Figure 8. WAXD of Polyamides PA-I to PA-V.

of PA-I was 158°C and of PA-II was 166°C. This shows that m-catenation lowers the glass-transition temperature. Similarly Tg value of PA-III shows 197°C. PA-IV and PA-V do not show Tg values because of their rigid structures due to p substitution.

All the polyamides were characterized by wide-angle X-Ray diffraction (WAXD) studies (Figure 8). It is observed that PA-II, PA-IV and PA-V polymers exhibit amorphous nature but PA-I polymer exhibit more amorphous in nature. More enhancements in amorphous nature of polymer PA-III additionally may be attributed due to the random placement of monomers, caused by combination of two monomers (TPC and IPC) in copolymerization with novel monomer containing pendent phenyl ring, which reduces the orderly arrangement of polymer chains resulting in reduced crystallinity and leading to amorphous nature.

5. Conclusion

A series of novel aromatic polyamides containing quinoxaline units and tetraphenyl thiophene moiety with phenyl pendant group in the polymer backbone were synthesized with the aim of improving the solubility and processability of polymers. The inherent viscosities of these polymers range from 0.66 to 1.44 dL/g. Most of these polymers are amorphous and partly soluble or completely soluble in many organic solvents, such as DMAc, NMP, m-cresol pyridine and H_2SO_4 etc. The Td's for 10% weight loss in nitrogen range from 574 to 737°C and had glass-transition temperatures in the range of 158–229°C depending on the exact polymer structure. Hence, based on these properties, future perspective will be to make composites of these polyamides with nanoparticles to improve electrochemical properties for applications such as supercapacitors, construction, etc.

Acknowledgments

The author AAG thanks to University Grant Commission, New Delhi for financial assistance in the form of major research project. (Scheme No. UGC-MAJOR-MRP-CHEM-2013- 39804).

References

[1] Mohite, S. S.; Maldar, N. N.; Marvel, C. S. *J. Polym. Sci. Polym. Chem.* 1988, *26*, 2777.
[2] Sudhakar, S.; Mahajan, B.; Sarwade, D.; Maldar, N. N. *Polym. Bull.* 1990, *24*, 143.
[3] Basutkar, P. H.; Joshi, M. D.; Lonikar, S. V.; Maldar, N. N.; Idage, B. B. *J. App. Polym. Sci.* 1998, *68*, 1523.
[4] Wang, Y. J.; Liu, X. L.; Huang, Z. Z.; Jiang J. W.; Sheng, S. R. *J. Macromol. Sci, Part A.* 2017, *54*, 534–542.
[5] Hassan, H.; El-Husseiny, A.; Abo-Elfadl, A.; El-Faham, A.; Albericio, F. *J. Macromol. Sci, Part A.* 2012, *49*, 41–54.
[6] Yang, H. H.; '*Aromatic high strength fibers*', John Wiley and Sons Publication: New York, 1989.
[7] Maglio, G.; Paiumbo, R.; Vignola, M. C. *Macromol. Chem. Phy.* 1995, *196*, 775.
[8] Sowrirajulu, B.; Muthusamy, S. *J. Polym Res.* 2007, *14*, 261.
[9] Shadpour, S.; Zahra, M.; Rafiee, Z.; *Polym. Adv. Technol.* 2008, *19*, 1474.
[10] Guey, S. L.; Hung, Yi. L. *Macromolecules.* 2009, *42*, 125.
[11] Joshi, M D; Basutkar, P H; Lonikar, S V; Maldar, N N; Idage, B B; *J Appl Polym. Sci.* 1998, *68*, 1523.
[12] Chang, G.; Lao, X.; Zhang, L.; Lin, R. *Macromolecules.* 2007, *40*, 8625.
[13] Imai, Y.; Maldar, N. N.; Kakimoto, M. J. *J. Polym. Sci. Polym. Chem.* 1985, *22*, 2189.
[14] Jadhav, S.; Maldar, N.; Vernekar, S.; *P. Polym. Int.* 1993, *32*, 5–11.
[15] Espeso, J. F.; De la. Campa, J.G.; Lozano, A. E.; De Abaso, J. *J. Polym. Sci. Polym. Chem.* 2000, *38*, 1014.
[16] Chen, Y.; Wang, B.; Zhao, L.; Dutta, P.; Winston Ho, W. *J. Membr. Sci.* 2015, *495*, 415–423.
[17] Zhao, L.; Chen, Y.; Wang, B.; Sun, C.; Chakraborty, S.; Ramasubramanian, K.; Dutta, P.K.; Winston Ho, W.S. *J. Membra. Sci.* 2016, *498*, 1–13.
[18] Yamazaki, N.; Higashi, F.; Kawabata, J. *J. Polym. Sci. Polym. Chem.* 1974, *12*, 2149.
[19] Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. Polym. Chem.* 1975, *13*, 1373.
[18] Ghaemy, M.; Barghamadi, M. *J. Appl. Polym. Sci.* 2008, *110*, 1730.
[20] Basutkar, P. H.; Joshi, M. D.; Lonikar, S. V.; Maldar, N. N.; Idage, B. B. *J. Appl. Polym. Sci.* 1998, *68*, 1523.
[21] Joshi, M. D.; Lonikar, S. V.; Maldar N. N.; Wadgaonkar, P. P. *J. Macromol. Sci, Part A.* 1997, *34*, 1077–1083.
[22] Ankushrao, S.; Kadam, N.; Patil, Y.; Ubale, P.; Maldar, N.; Ghanwat, A., *J. Macromol. Sci, Part A.* 2017, *54*, 124–132.
[23] Liou, G. S.; Hsiao, S. H. *J. Polym. Sci. Part A: Polym. Chem.* 2002, *40*, 459.
[24] Shockravi, A.; Abouzari, E.; Atabaki, F.; *Euro. Polym. J.* 2009, *45*, 1599.
[25] Imai, Y.; Maldar, N. N.; Kakimoto, M.; *J. Polym. Sci. Part A: Polym. Chem.* 1985, *23*, 1797–1803.
[26] Serbezeanu, D.; Vlad-Bubulac, T.; Hamciuc, C. *Mater. Plastic.* 2011, *48*, 7–11.
[27] Aducci, J.; Chapoy, L.L.; Jonsson, G.; Kops, J.; Shinde, B.M. *Polym. Eng. Sci.* 1983, *28*, 2069.
[28] Aducci, J.; Chapoy, L.L.; Jonsson, G.; Kops, J.; Shinde, B.M. *Polym. Eng. Sci.* 1981, *21*, 712.
[29] Ghanwat, A.; Sayyad, M.; Wadgaonkar, P.; Maldar, N.; *J. Therm. Anal Calorim.* 2009, *98*:539–545.