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Synthesis and characterization of organosoluble thermally stable polyamides containing spacer methylene linkage and bulky tetraphenylfuran moiety

Yuvraj Patil^a , Jagdish Mahindrakar^b , Sanjay Ankushrao^c, Ramdas Dhokale^a, Vijay Ubale^d, and Anil Ghanwat^b 

^aDepartment of Chemistry, Arts, Science and Commerce College, Naldurg, MS, India; ^bPolymer Research Laboratory, School of Chemical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur, MS, India; ^cDepartment of Chemistry, Vivekanand College, Kolhapur, MS, India; ^dDepartment of Chemistry, DBF Dayanand College of Arts and Science, Solapur, MS, India

ABSTRACT

Thermally stable and organo-soluble polyamides synthesized by polycondensation reaction of diacid monomer, 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) with various commercially available aromatic diamines such as 4,4'-Oxydianiline, 4,4'-methylenedianiline, 4,4'-sulphonyldianiline, 4,4'-Diaminobenzophenone and 4,4'-(hexafluoroisopropylidene)dianiline by using Yamazaki's direct phosphorylation method. A 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) as a new compound containing methylene linkage and bulky moiety of tetraphenylfuran was successfully prepared by a four step reaction. The resulted polymers show excellent thermal stability, good solubility in aprotic polar solvent and inherent viscosities between 0.50 and 0.58 dl/g. Wide angle X-ray diffraction of all these PAs show amorphous nature. Polyamides showed glass-transition temperatures in the range of 169–213 °C indicate that polymers are easily processable. Thermogravimetric analysis of the polyamides indicated a 10% weight loss (T_{10}) in the temperature range of 449–510 °C and char yields at 900 °C under nitrogen atmosphere in the range of 49–58% depending on the diamine monomer used for the synthesis polyamides. The structure-property correlation among these polyamides were discussed. The limiting oxygen indexes of all polyamides are more than 37.1, thus such type polymers of can act as flame retardant materials. These polyamides will be useful for high performance applications.

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Polyamides; tetraphenylfuran; thermally stable; WAXD; LOI

Introduction

Aromatic-aliphatic polyamides are superior high performance class of polymeric material. Aromatic polyamides, or aramids, comprised >90% by amide groups (–CO–NH–) attached directly to two aromatic rings.^[1,2] Outstanding mechanical strength and superior high thermal resistance are the speciality of these aromatic polyamides. Among all the heat resistant materials aromatic polyamides have received particular attention. Some of them are available for use as flame-resistant, high-strength, high-modulus fibers, and high-efficiency semipermeable

CONTACT Yuvraj Patil  patilyuvraj377@gmail.com  Department of Chemistry, Arts, Science and Commerce College, Naldurg 413602 MS, India.

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membranes as well as high-performance plastics.^[3–7] Such brand of outstanding properties of these materials was built-up by the aramids framework which is based on the rigid aromatic amide linkage. These rigid Polyamides (PAs) are difficult to process because they show limited solubility in organic solvents and high melting temperature and glass-transition temperature (T_g). The renowned thermally stable aromatic polyamides have the solemn disadvantage of being unwell soluble in organic aprotic solvents. To condense these polymers processable, there is a requirement to boost their solubility. The usual style of refining the solubility of a polymer comprises the introduction of flexible units into the backbone.^[8–20] Polyamides containing bulky moieties i.e. tetraphenylthiophene tetraphenylfuran and tetraphenylpyrrole units have been reported.^[5,6] They were found to have good thermal stabilities but very poor solubilities. Yamazaki's "phosphorylation" reaction was used for the direct synthesis of polyamides from diacids and diamines.^[18]

The present research deals with the synthesis and characterization of polyamides derived from aromatic-aliphatic diacids, viz. 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) and various commercial available aromatic diamines such as 4,4'-oxydianiline (ODA), 4,4'-methylenedianiline (MDA), 4,4'-sulphonyldianiline (SDA), 4,4'-Diaminobenzophenone (BDA) and 4,4'-(hexafluoroisopropylidene)dianiline (6FDA) by Yamazaki's phosphorylation. The alteration of the polymer backbone by the integration of aliphatic units into the double-strand heterocyclic units improved better-quality of the solubility.

Experimental

Materials

4,4'-Oxydianiline (ODA), 4,4'-methylenedianiline (MDA), 4,4'-sulphonyldianiline (SDA), 4,4'-Diaminobenzophenone (BDA) and 4,4'-(hexafluoroisopropylidene)dianiline (6FDA) were purchased from Sigma Aldrich Company without further purification. Potassium tertabutoxide, 1, 2-diarylethanone (deoxybenzoin), thiourea, iodine (I₂), aluminum chloride (AlCl₃) acetyl chloride of s d fine chemical were used as received. LiCl (Sigma Aldrich) was dried for 24 h at 180 °C under vacuum before use. Solvents such as ethyl acetate, dimethyl sulfoxide (DMSO, s d fine), N, N'-dimethyl acetamide (DMAc, s d fine), triphenyl phosphine (TPP, Sigma Aldrich) and toluene (s d fine), N-methyl-2-pyrrolidone (NMP, s d fine), N, N'-dimethyl foramide (DMF, s d fine), Pyridine (Py, Sigma Aldrich) THF (s d fine) and DCM (s d fine) were used as received.

Measurements

The FTIR spectra were measured by Thermo Nicolet iS-10 Mid Fourier Transform Infrared spectrometer (FTIR) in the 650–4000 cm⁻¹ frequency range. The spectra of monomer were obtained using KBr pellets, recorded at 4 cm⁻¹ resolution with 16 scans and the vibrational transition frequencies were reported in wavenumbers (cm⁻¹). The ¹H NMR (400 MHz) spectra were measured with a Bruker Spectrometer (Switzerland) using dimethyl sulfoxide (DMSO)-d₆ as solvent. The Mass spectrum was recorded on MASS Model AB Sciex API 5500 using Methanol-Acetonitrile as solvent. 200 nanogram/ml sample concentration is prepared. Electrospray ionization method is used for this analysis. XRD was recorded on X-Ray Diffraction system Ultima IV with ULTIMA IV Goniometer (Japan). Inherent viscosities were measured using an Ubbelohde suspended Level Viscometer with a 0.5 g/dL in NMP solution at 30 °C. Molecular weight of polyamide (PA-1) was measured on Thermo-Finnigan make gel permeation chromatograph (GPC) using N-methyl pyrrolidone (NMP) as an eluent at a flow rate of 0.5 mL.min⁻¹ at 30 °C temperature. Sample concentration was 2 mg.mL⁻¹ and Polystyrene was used as calibration standards. The thermogravimetric analysis was recorded

using a TGA instrument (Mettler-Toledo, Switzerland) in the temperature range of 30–900 °C. Samples having mass of ca. 5 mg were placed in 100 mL alumina crucibles. Thermal decomposition experiments were carried out using a heating rate of 10 °C/min in nitrogen atmosphere with a gas flow rate of 50 mL.min⁻¹. The DSC measurements were performed using a Mettler-Toledo DSC-1 STARe system in nitrogen atmosphere (flow rate of 50 mL.min⁻¹). Samples of ca. 5 mg were weighed, sealed in aluminum pans, heated to their respective final temperatures that was used for each sample, kept isothermally at that final temperature for 5 min, and then cooled. Tg values were read at the middle of the transition in heat capacity and were taken from the second heating scan after cooling from 350 °C at a cooling rate of 20 °C/min.

Monomer synthesis

2, 3, 4, 5-Tetraphenylfuran (TPF) and intermediates (Scheme 1) were synthesized in our laboratory according to previous literature reports.^[21,22] All the synthetic details of monomer are discussed below and the reaction scheme for monomer synthesis is shown in Scheme 1. The monomer (BCMPDF) was characterized by FT-IR, ¹H-NMR, ¹³C-NMR and MASS spectroscopy to confirm their structures.

2, 5-Bis (4-acetyl phenyl)-3, 4-diphenyl furan (BAPDF)

In three-neck flask, TPF (6.678 g, 18.05 mmol), anhydrous DCM (50 mL), and AlCl₃ (4.783 g, 36.10 mmol) were added under nitrogen atmosphere. The whole mixtures were then cooled to 0 °C using ice-water bath. Acetyl chloride (2.833 g, 36 mmol) was then added drop wise to the stirred reaction mixture at 0 °C. The reaction was allowed to warm to room temperature and stirring was continued for overnight. The resulting mixture was poured into ice cold water (300 mL), and the organic layer was collected, evaporated to give crude product BAPDF, recrystallized from toluene to get pure yellow crystals of BAPDF.

Yield 3.2g (70%) M.P: 252–254 °C.

2, 5-Bis (4-thioacetomorpholide phenyl)-3, 4-diphenyl furan (BTMPDF)

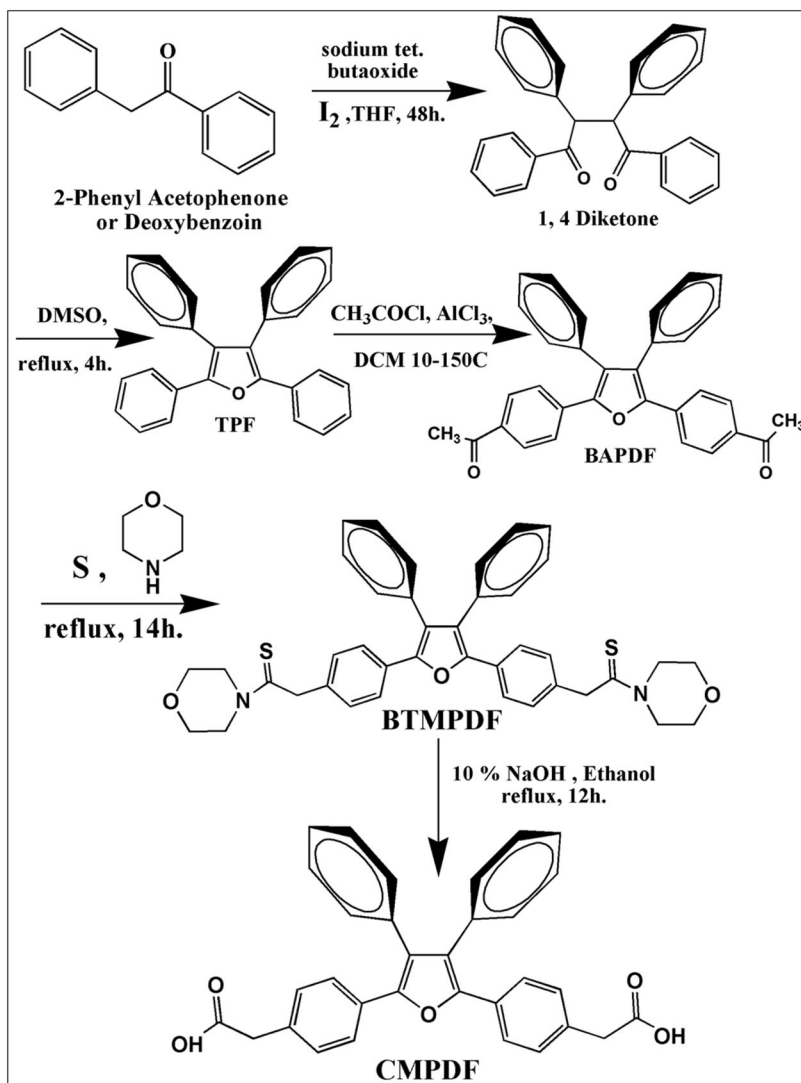
4.42 g (10 mmol) of BAPDF, 0.640 g (20 mmol) sulfur and 1.741 g (1.75 mL, 20 mmol) morpholine added in a 100-mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. This reaction mixture was stirred, gentle reflux to remove complete evolution of hydrogen sulfide and then continued stirred more vigorously for 16 h. Cool, the reaction mixture to room temperature. 200 mL of ethanol was added to obtain a brown buff-color product that was filtered, washed with excess ethanol, and dried.

Yield 5.90 g (88%), M.P.: 140–142 °C.

The IR spectrum exhibited absorption at 1240 cm⁻¹ (C=S).

2, 5-Bis (4-carboxy methylene phenyl)-3, 4-Diphenyl furan (BCMPDF)

A 100 mL round-bottom flask contains a reaction mixture of 6.58 g (BTMPDF, 10 mmol) and 65 mL of 10% ethanolic sodium hydroxide solution. Reaction mixture was refluxed for 12 h with stirring. After the completion of reaction excess ethanol was distilled out under reduced pressure. To these residual product with stirring 150 mL of hot water was added and filtered. The filtrate was acidified by 1:1 hydrochloric acid. The precipitated product was stirred and then filtered,



Scheme 1. Synthetic route for the synthesis of 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) diacid monomer.

washed thoroughly with hot water, and dried. The product was recrystallized from ethanol to get (BCMPDF)

Yield: 3 g (67%), M.P.: 242–240°C.

The IR spectrum of (BCMPDF) exhibited absorption at 2500–3300 cm^{-1} (–COOH), 1704 cm^{-1} (C=O), and 2857–2918 cm^{-1} (C–H aliphatic).

Polymer synthesis

By using the precursor 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) a novel series of five polyamides were synthesized by using Yamazaki's phosphorylation method.

Table 1. Synthesis of polyamides (PA-1 to PA-5).

Polymer ^a code	Diacid BCMPDF	Diamines	Yield (%)	Viscosity ^b η_{inh} (dL/g)	Film formation	Color
PA-1	BCMPDF	ODA	99	0.54	Yes	Yellow
PA-2	BCMPDF	MDA	96	0.50	Yes	Faint yellow
PA-3	BCMPDF	SDA	98	0.58	Yes	Yellow
PA-4	BCMPDF	BDA	97	0.56	Yes	Dark yellow
PA-5	BCMPDF	6FDA	96	0.52	Yes	Yellow

^aPolymerization was carried out with 1 mmol each of diacid and diamines.

^bMeasured at a concentration of 0.5 g/dL in NMP at 30 °C.

Synthesis of polyamides (PA-1 to PA-5)

In a 100-mL three-neck round-bottom flask equipped with magnetic stirrer, reflux condenser, calcium chloride guard tube, and nitrogen gas inlet were placed 0.504 g (1 mmol) 2,5-bis(4-carboxy methylene phenyl)-3,4-diphenyl furan (BCMPDF), 0.200 g (1 mmol) 4,4'-diamino diphenyl ether (ODA), 0.200 g lithium chloride [8 wt % based on solvent *N*-methyl pyrrolidone (NMP) and pyridine mixture], 0.744 g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 mL pyridine, and 2 mL NMP. The mixture was stirred well and temperature was slowly raised to 100 °C. The mixture was heated at 100 °C for 3 h under nitrogen. After cooling, the resulting viscous polymer solution was poured into rapidly stirred 200 mL of methanol. The precipitated polymer was filtered, washed with methanol, and air-dried. The polymer was purified by dissolving in *N,N'*-dimethyl acetamide (DMAc) and reprecipitating in methanol. It was filtered, washed with methanol, and dried under vacuum at 100 °C for 8 h. The yield was 99%, and the inherent viscosity (η_{inh}) of polymer in NMP was 0.54 dL/g. All other polyamides (PA-2 to PA-5), were prepared by similar procedure as mentioned in Table 1 and Scheme 2.

Results and discussion

Synthesis of monomer

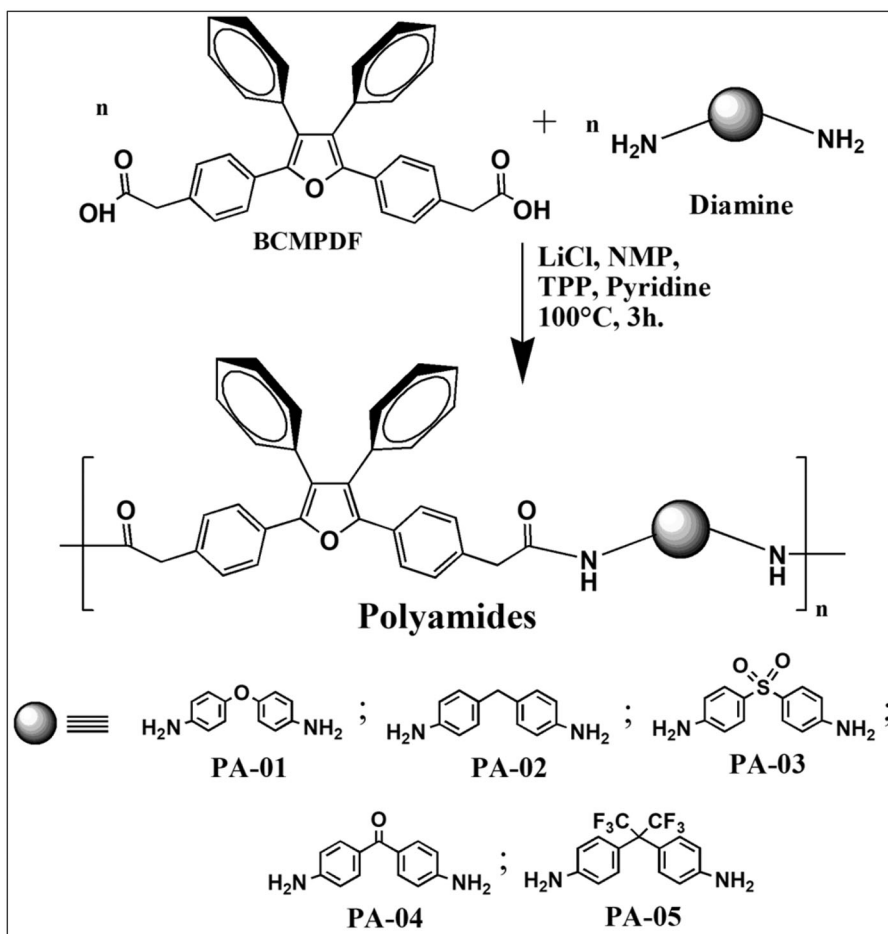
The novel spacer methylene containing diacid 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) was synthesized in several steps (Scheme 1).

Carbon-carbon coupling of deoxybenzoin catalyzed by sodium tertbutoxide followed by subsequently addition of iodine to yield 1, 2, 3, 4-tetraphenylbutane-1, 4-dione, further cyclization gave 2, 3, 4, 5 tetraphenylfuran (TPF). Acylation of TPF yields 2, 5-bis (4-acetyl phenyl)-3, 4-diphenyl furan (BAPDF). Finally BAPDF undergoes Conrad Willgerodt reaction with Kindler variation give 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF). The structure of new diacid precursor was confirmed by FT-IR, ¹H and ¹³C NMR and mass spectroscopy.

Synthesis of polymers

Bulky tetraphenyl furan and spacer methylene containing aromatic-aliphatic polyamides were synthesized by reacting 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) with various commercial aromatic diamines (PA-1 to PA-5). The high temperature solution polymerization, shown in Scheme 2, involves polymerization forming soluble polyamides by using Yamazaki's phosphorylation method.

All the polymers are in yield with inherent viscosities in the range of 0.50–0.58 dL/g (Table 1) giving as faint yellow to dark yellow polyamides (PA-1 to PA-5). The overall yield is 99%. The formation of the polyamides from the diacid monomer was confirmed by means of FT-IR and ¹H NMR spectroscopy.



Scheme 2. Synthetic route of polyamides (PA-1 to PA-5).

Structural characterization

The 2, 5-bis (4-carboxy methylene phenyl)-3, 4-diphenyl furan (BCMPDF) monomer characterized by FT-IR, ^1H and ^{13}C NMR spectroscopy.

In the synthesis of compound BCMPDF, the appearance of the characteristic carbonyl band at 1704 cm^{-1} was observed on the FT-IR spectrum as shown [Figure 1](#). Compound BCMPDF showed IR absorption at $2500\text{--}3300\text{ cm}^{-1}$ characteristic of hydroxyl group of diacid together with the appearance of resonances at $3.50\ \delta$ (4H) due to protons sandwich between carbonyl group and tetraphenylfuran unit on the ^1H NMR spectrum as shown [Figure 2](#). The signals in the range of $7.12\text{--}7.65\ \delta$ of (18H) are attributed to the aromatic protons of phenylene rings whereas signal most downfield at 11.42 are assigned to carboxylic acid proton (2H). The ^{13}C -NMR spectrum of BCMPDF exhibited twelve peaks due to symmetry, indicating the formation of the postulated diacid ([Figure 3](#)).

Polyamide (PA-1) is characterized by FT-IR spectroscopy. The [Figure 1](#) shows polymer synthesis (PA-1), which confirms diacid monomers (BCMPDF) converted into polyamides by using Yamazaki's phosphorylation method. This Spectrum shows strong absorption vibrational peak at around 1658 cm^{-1} for amide carbonyl group. Polyamide linkage contains $-\text{NH}$ group in main framework core which shows vibration peak at around 3302 cm^{-1} . The formation of polyamides

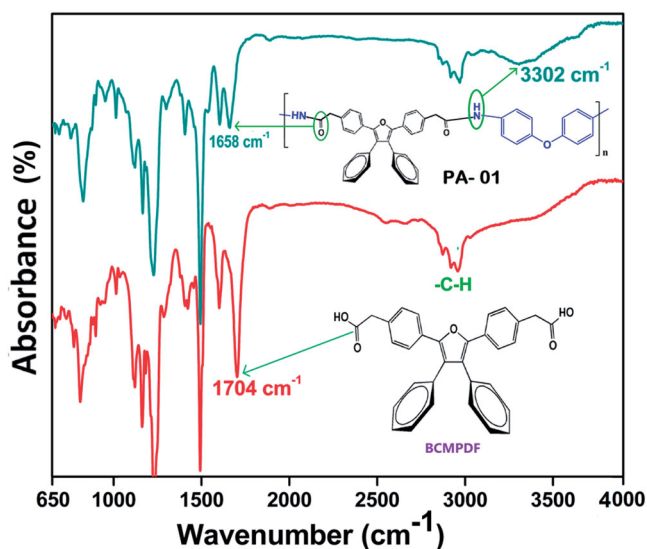


Figure 1. Comparative FT-IR spectrum of BCMPDF with PA-1.

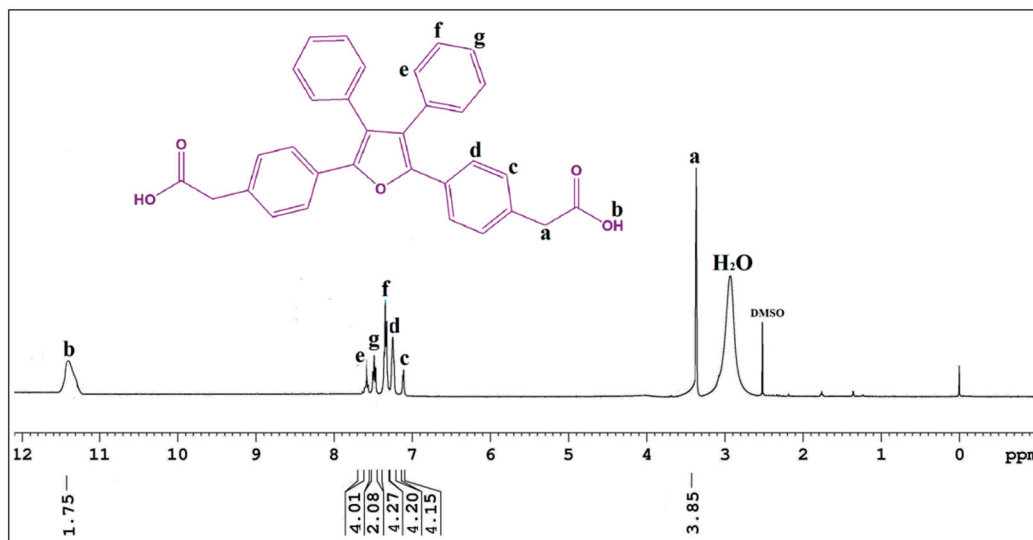


Figure 2. $^1\text{H-NMR}$ spectrum of BCMPDF.

(PA-1) is also characterized by $^1\text{H-NMR}$. As shown in Figure 4 there was a strong separation of the resonance signals of all aromatic and aliphatic protons in the range of 7.14–7.79 δ and 3.9 δ , respectively. Polyamides containing amide linkages $-\text{CONH}$, $-\text{NH}$ group of polyamides shows signal at around 10.34 δ . From the $^1\text{H NMR}$ of PA-1 it clear that, there is a total conversion of novel diacid (BCMPDF) in to corresponding polyamide. The $^1\text{H NMR}$ spectra are in good agreement with the proposed assembly of the repeating unit of polymer PA-1.

The GPC data of polyamide (PA-1) are outlined in Table 2. The results showed that the number-average (M_n) and Weight-average (M_w) values were 39900 and 134800 $\text{g}\cdot\text{mol}^{-1}$ respectively, with respect to polystyrene standards and the ratio M_w/M_n dispersity was 3.38.

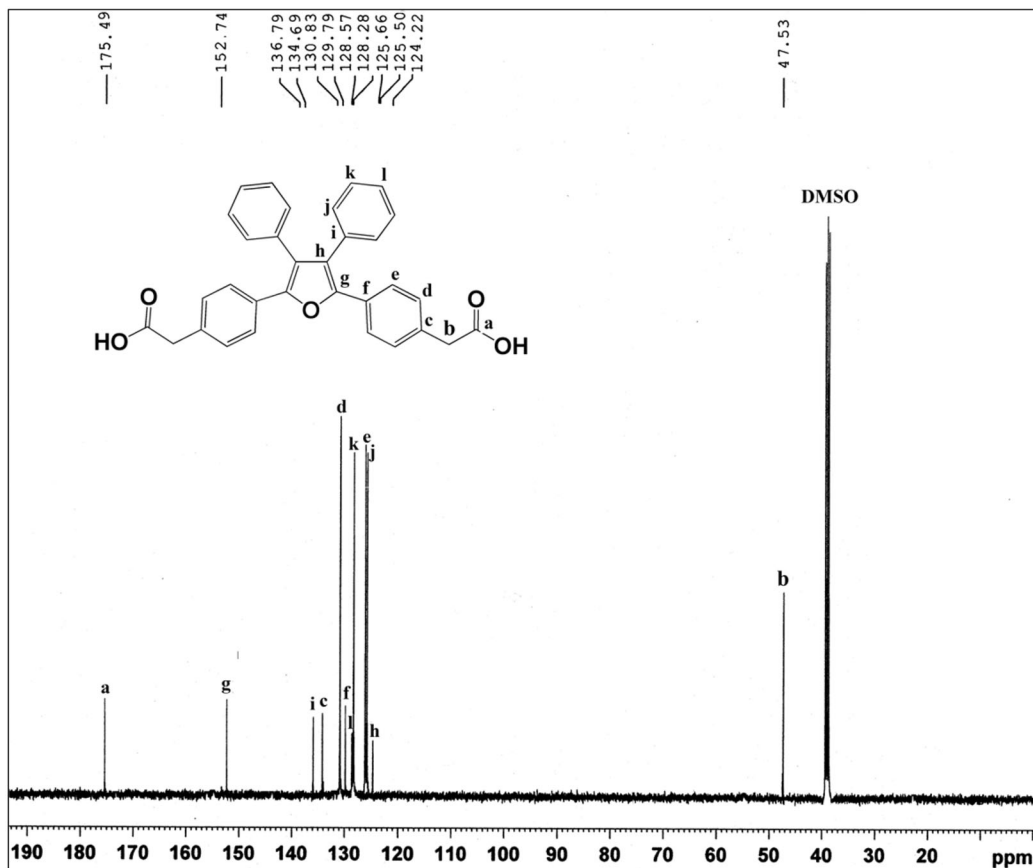


Figure 3. ^{13}C -NMR spectrum of BCMPDF.

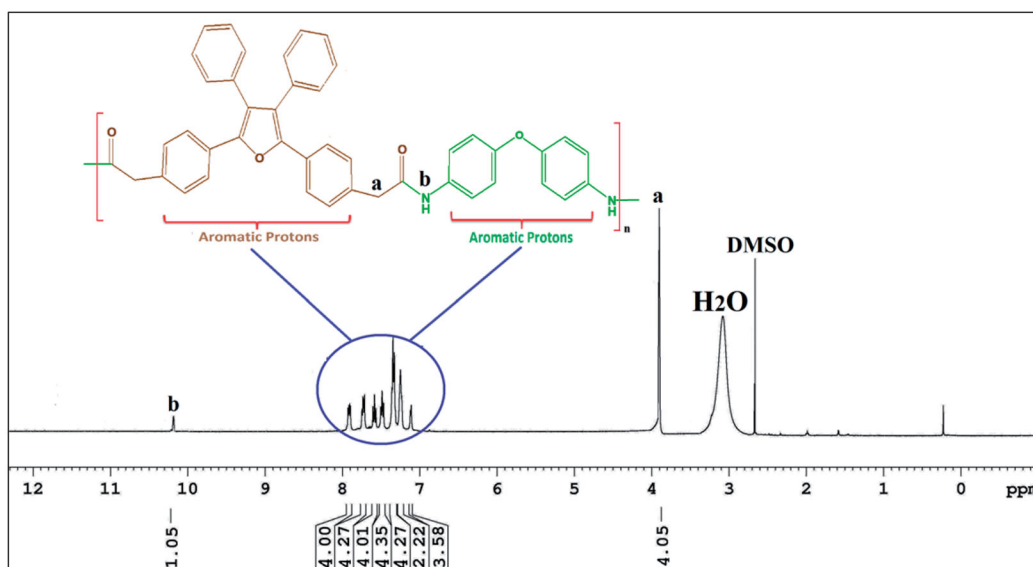


Figure 4. ^1H -NMR Spectrum of PA-1.

Table 2. Weight average molecular weights (Mw), number average molecular weights (Mn) and dispersity index (Mw/Mn) of polyamide (PA-1).

Sr. No.	Polymer code	Mn (g.mol ⁻¹)	Mw (g.mol ⁻¹)	PDI ^a (Mw/Mn)
1	PA-1	39900	134800	3.38

^aThe dispersity index (PDI) of the polyamide (PA-1) samples measured at 30 °C using N-methylpyrrolidone (NMP) as eluent at a flow rate of 0.5 mL.min⁻¹ by GPC.

Table 3. Solubility of polyamides (PA-1 to PA-5).

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

++: Soluble ++: soluble on heating; + -: partly soluble; --: insoluble.

Solubility and inherent viscosity

Table 3 gave qualitative solubility of the bulky tetraphenylfuran and spacer methylene unit covering polyamides (PA-1 to PA-5). The concentration for the solubility tests was 3 wt %. Almost all polyamides (PA-1 to PA-5) were soluble in polar aprotic solvents such as DMAc, NMP, DMF (on heating), DMSO, in pyridine, m-cresol, THF (except PA-3) and Conc. H₂SO₄. While they are insoluble in chlorinated solvent chloroform, etc.

On other hand polyamides PA-1, PA-2, PA-4 and PA-5 having readily more soluble due to the more coordinating polar ether linkages (-O-), flexible methylene linkages (-CH₂-) sandwiched group (C=O) and two-CF₃ unit respectively. PA-3 shows less solubility due to the sandwiched less coordinating insoluble sulfur content sulfonyl group. As compare to bulky structures, the solubility of these bulky tetraphenylfuran and spacer methylene constructed polyamides were advanced than that of aromatic polyamides by taking analogous huge structures such as tetraphenylfuran, tetraphenylthiophene, tetraphenylpyrrole described.^[23]

Inherent viscosity measurements were used to establish an order of constructing molecules or building up of molecules and size of the polyamides chain in the series (PA-1 to PA-5). All these polyamides show excellent solubility in aprotic organic solvents at room temperature except DMF (on heating). Thus, the inherent viscosity of polyamides was recorded at 30 °C in NMP and values in between 0.50 and 0.58 dL/g were obtained as shown in Table 1.

Thermal analysis

The Figure 5 shows the TGA thermograms of PA-1 to PA-5 measured at a heating rate of 10⁰C/min. 10% weight loss temperature of polyamides are summarized in Table 4.

The high thermal stability, chemical and mechanical stiffness for polyamides arises from the aromatic rings (bulky tetraphenylfuran) as well as the amide linkage. The mode elaborate in the degradation of PA-1 to PA-5, smaller units by the cleavage of hetero atom bonds such as C-O, C-N and C-O, homo atomic bond C-C bond. All polyamides (PA-1 to PA-5) show T₁₀ value in the range of 449–510 °C in Nitrogen atmosphere. Amongst these polyamides, the PA-3 and PA-4 exhibits the highest thermal stability with a decomposition temperature of ca. 487 and 510 °C, respectively, this is for the reason that the polymer backbone contains more sandwiched rigid framework of carbonyl center (C=S) and (C=O).^[24] This could be credited to the molecular

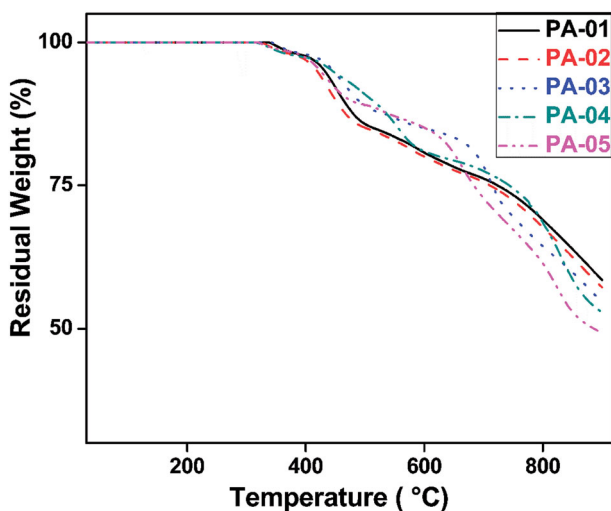


Figure 5. TGA of Polyamides (PA-1 to PA-5).

Table 4. Thermal properties of polyamides (PA-1 to PA-5).

Sr. No.	Polymers	Thermal behaviour ^a			Residual Wt. % at 900 °C	LOI
		T _g	T _i	T _d		
1	PA-1	180	338	462	58	40.7
2	PA-2	183	325	449	57	40.3
3	PA-3	200	343	487	54	39.1
4	PA-4	182	315	510	52	38.3
5	PA-5	178	320	473	49	37.1

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

T_g: glass transition temperature; T_i: initial decomposition temperature; T_d: temperature of 10% decomposition; LOI: limiting oxygen index.

repeating unit of PA-3 and PA-4 which involves stiff rigid polymeric chain framework and hence enhancing its strength and thermal stability. On other hand polyamides such as PA-1, PA-2 and PA-5 with its polymeric framework arrangements containing polar connecting group such as oxy (–O), methylene (–CH₂–) and flexible polar substituted group such as two –CF₃ group which due to which they are slightly lesser strength and thermal stability than PA-3 and PA-4.^[25] In addition, all these polyamides (PA-1 to PA-5) show greater thermal stability without sacrificing other physical properties. Also, all polyamides retained more than 49% weight in nitrogen even at 900 °C.

Here we are comparing the thermal stability of polyamides from tetraphenylfuran with earlier reported polyamide from tetraphenylthiophene^[18] as shown in Figure 6. The thermal stability of bulky tetraphenylfuran with spacer methylene unit based polyamides (PA-1 to PA-5) have greater thermal stability (449–510 °C) with respect to T₁₀ of the structurally related polyamides containing spacer methylene and bulky tetraphenylthiophene components (580–600 °C). These results indicate that high thermal stability of the present polyamides (PA-1 to PA-5). On the basis of T₁₀, these tetraphenyl-furan unit had as higher thermal stability as in order tetraphenylfuran > tetraphenylthiophene. Outcome of synthesized bulky tetraphenylfuran with spacer methylene containing polyimides are very superior in thermal stability with other early reported polyamides. This effect also indicates that the difference in position of substitutions in the aromatic diamines also introduces significant dissimilarities not only in their decomposition temperatures but also in the final char yield.

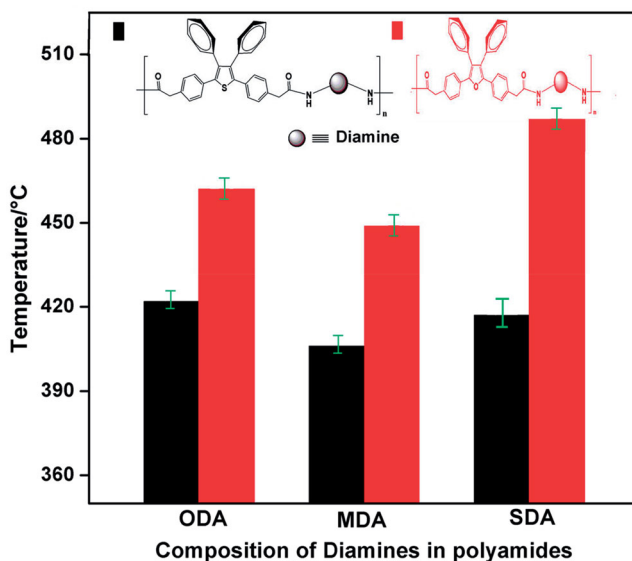


Figure 6. Comparative $T_{10\%}$ weight loss of polyamides containing tetraphenylfuran (PA 01 to PA-05) with tetraphenylthiophene unit.

Flame-retardant property of polyamides (PA-1 to PA-5)

According to Van Krevelen and Hoftyzer's equation,^[26] the char yield can be useful as a conclusive factor for valuing the limited oxygen index (LOI) of polymers using equation,

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

Where, CR is the percentage of polymer remaining at 900 °C.

In general, the material constituents showing LOI values higher than 26 shows self-extinguishing behavior and reflecting as flame retardant. On the basis of the LOI values the resulting polymers can be classified as self-extinguishing materials.

All polyamides have LOI more than 37.1 and such polymers can act as flame-retardant materials are summarized in Table 4. The LOI of all polyamides (PA-1 to PA-5) estimated in the range of 40.7 to 37.1.

DSC results

The DSC plots for PA-1 to PA-5 are presented in Figure 7. The glass transition temperature (T_g) and are summarized in Table 4. The present polyamides had relatively moderate T_g in the range of 169–213 °C. Polyamides PA-1 and PA-2 covered polar and flexible connecting group structures respectively. Among all polyamide PA-3 shows highest T_g values than other polyamides. This is due to the stiff rigid sulfonyl group ($-\text{SO}_2$). On other PA-2 shows excellent T_g curve pattern. This credited to the more spacer methylene groups in polymer frameworks and showing a smooth curve of T_g .^[27] The whole result consideration of bulky tetraphenyl-furan unit with other bulky tetraphenyl unit, the T_g values of the structurally related polyamides decreased as order: tetraphenylthiophene-bearing polyamides (226–273 °C) >the tetraphenylfuran unit centered polyamides (178–200 °C).

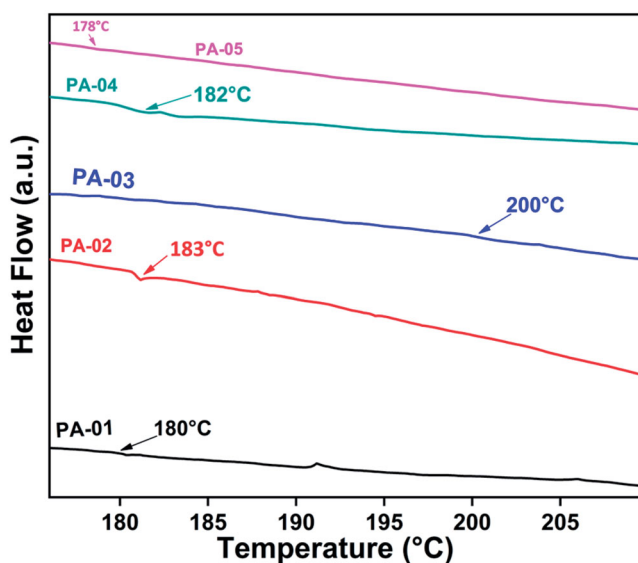


Figure 7. DSC of Polyamides (PA-1 to PA-5).

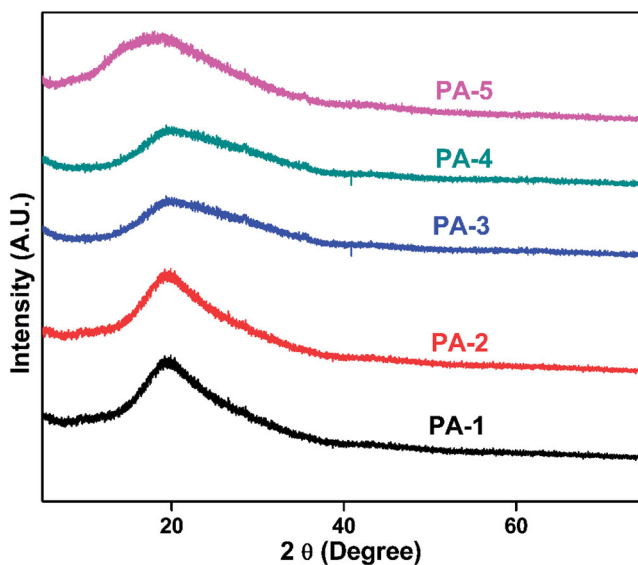


Figure 8. WAXD of Polyamides (PA-1 to PA-5).

WAXD analysis

The WAXD patterns of all polyamides are verified in Figure 8. All the polyamides (PA-1 to PA-5) derived from Polar flexible ($-O-$ and $-CH_2-$), Sandwiched more polar ($C=O$), less polar ($C=S$) and sandwiched polar substituted two $-CF_3$ group showed broad diffraction peaks at $\sim 20^\circ$ (2θ) was observed which confirms the formation of amorphous nature polymers. This amorphous nature of all these polyamides support to solubility and inherent viscosity of polymers.^[27,28] The polymers show no hint for crystallinity.

Conclusions

The new series of aromatic-aliphatic polyamides covering spacer methylene and bulky pendant tetraphenylfuran groups were introduced into the molecular framework of Polyamides via the newly designed diamine monomer and synthesized by the polycondensation of a novel diacid precursor 2, 5-bis (4-carboxymethylene phenyl) 3, 4-diphenyl furan (BCMPDF) and various aromatic diamines by using Yamazaki's phosphorylation method. The structure-property relationships of these polyamides due to the enterprise of bulky substituents and aliphatic spacer methylene were also studied. From the experimental results, it can be concluded that the synergic insertion effects of bulky phenyl substituents such as tetraphenylfuran and aliphatic unit such as methylene, into the polymer backbone was greatly operative for the synthesis of soluble polyamides inventing great $T_{10\%}$ values and adequate T_g analogous to the aromatic-aliphatic polyamides. All the synthesized polyamides have inherent viscosities in range of 0.50 and 0.58 dL/g. Almost all of polyamides were soluble in polar aprotic solvents at room temperature except DMF (on heating). The GPC data of polyamide (PA-1) showed that the number-average (M_n) and Weight-average (M_w) values were $39,900 \text{ g.mol}^{-1}$ and $134,800 \text{ g.mol}^{-1}$ respectively, with respect to polystyrene standards and the ratio M_w/M_n dispersity was 3.38. Synthesized aromatic polyamides (PA-1 to PA-5) are characterized by WAXD; it appraises the insertion effect of precursor on polymer backbone and showing the amorphous nature. They were characterized as high T_g in the range of $178\text{--}200^\circ\text{C}$ and great thermal stability ($449\text{--}510^\circ\text{C}$). It was agreed that the insertion of spacer methylene linkage and bulky pendant tetraphenyl unit is effective for developing novel thermally stable and highly organosoluble polyamides. By consideration of their properties are desired for advanced applications, such as the constituents for superior high thermal resistance.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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ORCID

Yuvraj Patil  <http://orcid.org/0000-0001-9529-1290>

Jagdish Mahindrakar  <http://orcid.org/0000-0001-6435-5212>

Anil Ghanwat  <http://orcid.org/0000-0002-6053-0834>

References

- [1] Morgan, P. W. 1979. Aromatic polyamides. *Chem. Tech.* 9:316.
- [2] Cassidy, P. E. 1980. *Thermally Stable Polymer*. Chapter 4. New York: Marcel Dekker.
- [3] Kuze, K., and S. Miwa. 1968. Kogyo kagaku zasshi. *The Journal of the Society of Chemical Industry, Japan.* 71:443–449.
- [4] Salunkhe, P. H., Y. S. Patil, V. B. Patil, Y. H. Navale, V. P. Ubale, I. A. Dhole, N. N. Maldar, and A. A. Ghanwat. 2018. Synthesis and characterization of conjugated porous polyazomethines with excellent electrochemical energy storage performance. *J Polym. Res.* 25:147.
- [5] Imai, Y., N. Maldar, and M. Kakimoto. 1984. Synthesis and characterization of soluble polyamides from 2, 5-bis (4-aminophenyl)-3, 4-diphenylthiophene and aromatic tetracarboxylic dianhydrides. *J. Polym. Sci. Polym. Chem. Ed.* 22:2189–2196.

- [6] Imai, Y., N. Maldar, and M. Kakimoto. 1984. Synthesis and characterization of soluble aromatic polyazomethines from 2, 5-bis (4-aminophenyl)-3, 4-diphenylthiophene and aromatic dialdehydes. *J. Polym. Sci. Polym. Chem. Ed.* 22:3771–3778.
- [7] Patil, Y. S., P. H. Salunkhe, Y. H. Navale, V. P. Ubale, V. B. Patil, N. N. Maldar, and A. A. Ghanwat. 2018. Synthesis, characterization and conductivity study of co-polyazomethine polymer containing thiazole active ring. *AIP Conf. Proc.* 1989:020034.
- [8] Hergenrother, P. M., and H. H. Levine. 1967. Phenyl-substituted polyquinoxalines. *J. Polym. Sci. A-1 Polym. Chem.* 5:1453–1466.
- [9] Mukamal, H., F. W. Harris, and J. K. Stille. 1967. Diels-alder polymers. III. Polymers containing phenylated phenylene units. *J. Polym. Sci. A-1 Polym. Chem.* 5:2721–2729.
- [10] Patil, Y. S., J. N. Mahindrakar, P. H. Salunkhe, V. P. Ubale, and A. A. Ghanwat. 2018. Synthesis, characterization and structure-property relationships of processable poly(amide-imide)s containing novel Tetraphenylthiophene-Thiazole Diimide-Diacid (TPTPTHDIDA) moiety. *J. Macromol. Sci. Part A.* 55: 572–581.
- [11] Wrasidlo, W., and J. M. Augl. 1969. Phenylated polyquinoxalines from bis(phenylglyoxaloyl)benzene. *J. Polym. Sci. A-1 Polym. Chem.* 7:3393–3405.
- [12] Mahindrakar, J. N., Y. S. Patil, P. H. Salunkhe, S. S. Ankushrao, V. N. Kadam, V. P. Ubale, and A. A. Ghanwat. 2018. Optically transparent, organosoluble poly (ether-amide) s bearing triptycene unit; synthesis and characterization. *J. Macromol. Sci, Part A.* 55:658–667.
- [13] Korshak, V. V., A. L. Rusanov, D. S. Tugushi, and G. M. Cherkasova. 1972. Two stage synthesis of poly (N-phenylbenzimidazoles). *Macromolecules.* 5:807–812.
- [14] Harris, F. W., W. A. Feld, and L. H. Lanier. 1975. Soluble aromatic polyimides from phenylated dianhydrides. *J. Appl. Polym. Sci.* 13: 283–285.
- [15] Ankushrao, S. S., Y. S. Patil, V. P. Ubale, N. N. Maldar, and A. A. Ghanwat. 2017. Synthesis and characterization of thermally stable poly (ether-azomethine) s derived from 1, 1-bis [4-(4-benzaldehyde oxy)-3-methyl phenyl] cyclopentane. *J. Macromol. Sci., Part A.* 54:411–417.
- [16] Thanuja, J., and M. Srinivasan. 1988. Synthesis and characterization of some polyazo(amide-imide)s. *Eur. Polym. J.* 24:1123–1126.
- [17] Salunkhe, P. H., Y. S. Patil, V. N. Kadam, J. N. Mahindrakar, V. P. Ubale, and A. A. Ghanwat. 2019. Synthesis and characterization of processable polyamides containing polar quinoxaline unit in the main chain and evaluation of its hydrophilicity. *J. Macromol. Sci, Part A.* 56:299–305.
- [18] Ubale, V. P., A. D. Sagar, N. N. Maldar, and M. V. Birajdar. 2001. Synthesis and characterization of aromatic-aliphatic polyamides. *J. Appl. Polym. Sci.* 79:566–571.
- [19] Ankushrao, S. S., V. N. Kadam, Y. S. Patil, V. P. Ubale, N. N. Maldar, and A. A. Ghanwat. 2017. Synthesis and characterization of processable heat resistant co-poly (ester-amide)s containing cyclopentylidene moiety. *J. Macromol. Sci, Part A.* 54:124–132.
- [20] Salunkhe, P. H., S. S. Ankushrao, Y. S. Patil, J. N. Mahindrakar, V. N. Kadam, V. P. Ubale, and A. A. Ghanwat. 2018. Processable heat resistant polyamides containing tetraphenyl thiophene having pendant phenyl moiety with heterocyclic quinoxaline unit: Synthesis and characterization. *J. Macromol. Sci, Part A.* 55:377–383.
- [21] Patil, Y. S., P. H. Salunkhe, J. N. Mahindrakar, S. S. Ankushrao, V. N. Kadam, V. P. Ubale, and A. A. Ghanwat. 2019. Synthesis and characterization of aromatic polyimides containing tetraphenylfuran-thiazole moiety. *J. Therm. Anal. Calorim.* 135:3057–3068.
- [22] Jeong, H. W., Y. Oishi, M. Kakimoto, and Y. Imai. 1991. Synthesis and characterization of new soluble aromatic polyimides from 3,4-bis (4-aminophenyl)-2,5-diphenylfuran and aromatic tetracarboxylic dianhydrides. *J. Polym. Sci. A Polym. Chem.* 29:39–43.
- [23] Yoshi, I. 2012. Synthesis of novel organic-soluble high-temperature aromatic polymers. *High Perform. Polym.* 7:337.
- [24] Basutkar, P. H., M. D. Joshi, S. V. Lonikar, N. N. Maldar, and B. B. Idage. 1998. Synthesis and characterization of phenylated aromatic poly (amide-amide)s. *J. Appl. Polym. Sci.* 68:1523–1530.
- [25] Zhao, J., H. Xu, J. Fang, and J. Yin. 2012. Synthesis and characterization of novel aromatic polyamides via Yamazaki-Higashi phosphorylation method. *J. Appl. Polym. Sci.* 126:244–252.
- [26] Krevelen, D. W. 1975. Some Basic Aspects of Flame Resistance of Polymeric Materials. *Polymer.* 16: 615–620.
- [27] Ghanwat, A. A., M. M. Sayyed, P. P. Wadgaonkar, and N. N. Maldar. 2009. Synthesis and thermal properties of soluble silicon containing phenylated aromatic-aliphatic polyamides. *J. Therm. Anal. Calorim.* 98: 539–545.
- [28] Ubale, V. P., A. S. Patil, and N. N. Maldar. 2007. Polyhydrazides based on 2,5-bis(4carboxymethylene phenyl)-3,4-diphenyl thiophene. *Eur. Polym. J.* 43:1038–1045.