

Soluble aromatic polyamides modified by incorporation of 1,2,4-triazole and pentadecyl units into the backbone of polymer

Aslam B. Tamboli, Rajesh G. Bhorkade, Basavraj S. Kalshetti, Shivaji D. Ghodake & Noormahmad N. Maldar

To cite this article: Aslam B. Tamboli, Rajesh G. Bhorkade, Basavraj S. Kalshetti, Shivaji D. Ghodake & Noormahmad N. Maldar (2019): Soluble aromatic polyamides modified by incorporation of 1,2,4-triazole and pentadecyl units into the backbone of polymer, Journal of Macromolecular Science, Part A, DOI: [10.1080/10601325.2019.1602475](https://doi.org/10.1080/10601325.2019.1602475)

To link to this article: <https://doi.org/10.1080/10601325.2019.1602475>



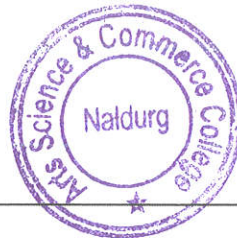
Published online: 02 Aug 2019.



Submit your article to this journal [↗](#)



View Crossmark data [↗](#)



Soluble aromatic polyamides modified by incorporation of 1,2,4-triazole and pentadecyl units into the backbone of polymer

Aslam B. Tamboli, Rajesh G. Bhorkade, Basavraj S. Kalshetti, Shivaji D. Ghodake, and Noormahmad N. Maldar

School of Chemical Science, Solapur University, Solapur, India

ABSTRACT

A new series of soluble aromatic polyamides was synthesized by low temperature solution polycondensation of novel aromatic diamine namely 3,5-bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII) with aromatic diacid chlorides, viz. isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC). The aromaticdiamine (VII) was characterized by elemental analysis, FT-IR, NMR (^1H , ^{13}C), and mass spectrometry. Copolyamides were also synthesized by employing various mole proportions of IPC and TPC with diamine (VII). Inherent viscosities of these polyamides were in the range of 0.50–0.65 dL/g in DMAc, indicating formation of moderate to high molecular weight of polyamides. These polyamides showed good solubility in polar aprotic solvents such as N,N-Dimethyl acetamide (DMAc), N-Methyl 2-pyrrolidone (NMP), N, N, Dimethyl formamide (DMF), and Dimethyl sulphoxide (DMSO), which may be due to incorporation of pendant methoxyphenyl moiety with pentadecyl units. The amorphous morphology of polyamides as evidenced by XRD. These polyamides had lower glass transition temperatures; as determined by DSC, compared to the T_g of conventional aromatic polyamides due to internal plasticization effect of long alkyl pentadecyl group. Polymers showed good thermal stability, with initial decomposition temperature above 300°C.

ARTICLE HISTORY

Received February 2018
Accepted March 2019

KEYWORDS

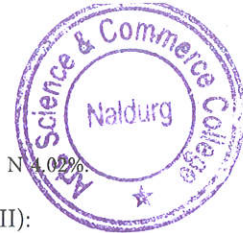
1,2,4-triazole; soluble aromatic polyamides; heat resistant; pentadecyl substituent; cashew nut shell liquid

1. Introduction

Thermally stable high performance polymers are important as they can replace metals and ceramics in several industrial applications. Specifically, some aromatic polyamides exhibit excellent mechanical, electrical and other properties, making them high performance materials.^[1–3] However, their industrial processing is affected by their remarkable intractability caused by the strong molecular interactions through hydrogen bonding of amide groups.^[4] Aromatic polyamides are the class of thermally stable polymers and have good mechanical properties. However these polyamides encounter processing difficulties because of their infusibility and poor solubility in organic solvents due to strong interaction bonding of amide and aromatic hydrogens. To overcome these problems there is need to chemically and structurally modify aromatic polyamides by the incorporation of pendent, cardo, aliphatic chain, halo group, methylene spacer group, flexible ether linkage etc. into the backbone of aromatic polyamide chain. Thuspi-picatenatedKevlar dissolves only in concentrated sulfuric acid from which it has to be processed; Viz. Kevlar^R, Nomex^R. With the aim to reduce the intermolecular bonding energy, many structural modifications have been made in polyamides, such as the incorporation of cardo or flexible units, 1,3-substituted aromatic units, bulky pendant groups or irregular structure in the main chain.^[5] These structural^[6–8] modifications provide increasedinterchain

distance, decreased H-bonding and consequently, higher free volume and solubility, without affecting the thermal properties.^[9–11] Several modified aromatic polyamides based on natural renewable agricultural resources were also reported.

Cashew nut shell liquid (CNSL) based polyamides showed better processability due to the long linear pentadecyl aliphatic substituent group.^[12–14] Similarly cyclic side group such as fluorene or cardo moiety were effective to improve the solubility of the polyamides.^[15,16] Polyamides have wide application in different fields; however, application of polyamides as membrane for gas separation are generally limited. Many strategies have been proposed for the improvement in permeability without affecting the permselectivity of the polymer gas separation membranes, for example polymers chain consisting alternating bulky structural unit and flexible segment gave combination of high selectivity and high permeability. Thus phenylenediamine units, flexible ether, ketone linkages and bulky pendant groups, improved the permeability of the polyamides with high selectivity. For such application these polyamides have to be soluble in organic solvents so that desired polymer film can be obtained. Therefore to explore the similar possible application of polyamides; building block having 1,2,4-triazole heterocyclic moiety containing pendant methoxy, pentadecyl substituted phenyl; derived from renewable agricultural byproductresource CNSL was



investigated.^[17,18] In confirmation of our work on (soluble and processable) derived from CNSL now we report recently on synthesis and characterization of polyamides containing both 1,2,4-triazole unit in main polyamide chain and pendant methoxy phenyl units and pentadecyl group with special properties. This research work is focused on synthesis of long durable polymers which became thermally stable and easily processable. We have worked on sustainable bio-based high-performance polymers. These polyamides were utilized in high energy materials and membrane application for the development of community in the world.

2. Experimental

2.1. Materials

3-Pentadecyl phenol, 10% Pd/C, Isophthaloyl chloride (IPC) and Terephthaloyl chloride (TPC), (Aldrich make), Hydrazine hydrate, Phosphorous penta chloride, 4-Nitro benzoic acid, Thionyl chloride, Toluene (s.d. fine), were utilized as received.

2.1.1. Measurements

The FT-IR spectra of organic compounds and polymers were recorded using Nicolet spectrometer. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained with a Bruker Advance spectrometer at 25 °C using CDCl₃ and DMSO-d₆ as solvent. Polyamides inherent viscosities were obtained with a polyamide concentration of 0.5 g/dL in DMAc solvent at 30 °C using an Ubbelohde suspended level viscometer. Differential scanning calorimetry (DSC) was measured on a Mettler Toledo DSC STAR[®] instrument at heating rate of 20 °C/min. under nitrogen. The glass transition temperatures (T_g) were determined from DSC curves. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo STAR[®] instrument at a heating rate of 10 °C/min under nitrogen. Wide angle X-ray diffraction (WAXD) was measured with a Rigaku X-ray diffractometer using polyamide powder.

2.2. Synthesis of 3, 5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1, 2, 4-triazole (VII) was achieved in six steps on described below

i. Synthesis of 4-Nitro-3-pentadecyl phenol (I)

3-Pentadecyl phenol (20 g, 0.065 mol) was dissolved in chloroform (75 mL) and (5.3 g, 1.2 mmol) fuming nitric acid (sp.gr.1.5) was added to it dropwise with stirring and cooling in an ice bath maintained at 5–10 °C. The reaction mixture was stirred for another 20 minutes at 10 °C; then poured into water, the organic layer was separated by separating funnel. Chloroform solvent was removed by distillation using water aspirator, the residual mass solidified on cooling. After filtration and drying 23 g of red orange solid; mixture of isomeric nitro phenols; was obtained. Product was crystallized 150 mL of petroleum ether (60–80 °C) to get about 10 g of light tan powder of 4-nitro-3-pentadecyl phenol (I). This on further recrystallization from the pet ether gave the purified 4-nitro-3-pentadecyl phenol (I). Yield 8.0 g (71%), m.p 70–71 °C (Lit.m.p. 71 °C.)

Elemental Analysis found: C 72.45, H 10.33, N 4.07%,

Analysis Calculated for C₂₁H₃₅NO₃: C 72, H 10.05, N 4.02%

ii Synthesis of 4-Nitro-3-pentadecyl anisole (II):

In one neck round bottom flask equipped with magnetic stirrer, a mixture of 4-nitro-3-pentadecyl phenol (3.63 g 10 mmol), in dichloromethane (50 mL), sodium hydroxide (0.7 g, 15 mmol) in water (50 mL); the alkylating agent dimethyl sulphate (2.5 mL) (20–30 mmol), and phase transfer catalyst benzyltriethylammoniumchloride (0.1 g, 1 mmol), was agitated with stirring at 30 °C for 12 hrs. The organic layer was then separated and the aqueous layer was extracted thrice (20 mL × 3) with dichloromethane. The organic extract was washed with 2 M aq. ammonia solution to remove residual dimethyl sulphate, the solvent was evaporated and the solid 4-nitro-3-pentadecyl anisole (II) was purified by crystallization from methanol. Yield 2.9 g (85%), m.p. 49 °C.

¹H NMR (in CDCl₃) (ppm), 0.96 (t, 3H), 1.45 (m, 26H), 2.5 (t, 2H), 3.8 (s, 3H), 6.7 (d, 1H), 7.2 (s, 1H), 7.9 (d, 1H).

iii Synthesis of 4-Amino-3-pentadecyl anisole (III)

In three neck round bottom flask (250 mL) equipped with magnetic stirrer, reflux condenser, calcium chloride guard tube, were Placed 4-nitro-3-pentadecyl anisole 3.63 g (0.01 mol), 10% Pd/C (0.2 g), ethanol (50 mL). The reaction mixture was heated to 80 °C and hydrazine hydrate (8 mL), was added dropwise. Stirring and heating the reaction mixture at 80 °C was continued for 8 hrs. Reaction mixture was filtered to remove Pd/C catalyst. Filtrate was cooled to room temperature and poured into the ice cold water to precipitate solid (III), which was filtered, washed with plenty of water, and crystallized from ethanol. Yield 2.4 g, (80%), m.p. 44 °C. ¹H NMR (in CDCl₃) (ppm), 0.96 (t, 3H_d), 1.45 (t, 2H_c), 2.5 (t, 2H_b), 3.5 (s, 2H_a), 3.8 (s, 3H_f), 6.6 (dd, 1H_h), 6.7 (dd, 2H_g), 7.2 (s, 1H_e).

iv Synthesis of bis-(4-Nitro benzohydrazide) (IV).

4-Nitrobenzoyl chloride (20.0 g, 0.108 mol), hydrazine hydrate (8.5 g, 0.17 mol), and NMP (250 mL) were introduced into a two-neck 500 mL R.B. flask and stirred at 30 °C for 5 hrs. The reaction mixture poured into excess of distilled water to precipitate the product. Solid was collected by filtration, washed with ethyl acetate, and dried in a vacuum oven to obtain bis-(4-Nitro benzohydrazide) (IV) which was crystallized from ethanol.

Yield 30 g (95%). m.p. 296 °C, (Lit. Mp. 294 °C). FT-IR (KBr, cm⁻¹): 3200 (-NH), 1347, 1515 (-NO₂), 1614 (-C=O).

v Synthesis of 1, 2-bis-(4-nitrophenyl)chloromethylene hydrazine (V).

Into a 250 mL three neck round bottom flask, mixture of bis-(4-Nitro benzohydrazide) (3.93 g, 12 mmol) and phosphorus pentachloride (6.12 g, 30 mmol) was dissolved in toluene (50 mL) by gentle stirring. Solution were then heated for slow reflux with stirring at 120 °C for 5 hrs. Then solvent was removed under vacuum, and the residue was poured into excess of distilled water. The precipitated solid was collected by filtration, dried and recrystallized from (ethanol and dichloromethane) (3:1) to afford the yellow solid (V) (2.59 g, 60%). m.p. 188 °C.

FT-IR (KBr, cm⁻¹): 1590 (C=N), 1343, 1524 (-NO₂);

Elemental Analysis found: C 45.80, H 2.20, N 15.26%;

Analysis calculated for C₁₄H₈N₄Cl₂O₄: C 45.83, H 2.25, N 15.22%.

vi Synthesis of 3, 5-bis-(4'-Nitrophenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VI)

In 250-mL three-neck round bottom flask fitted with mechanical stirrer and reflux condenser were charged (III) (2.2 g, 6 mmol), (V) (2.4 g, 7.2 mmol), diisopropylamine (1.30 g,

10 mmol) and xylene (65 mL). The reaction contents were heated to 130 °C with stirring for 48 h. After cooling, the solvent was evaporated and the residue was washed with ethyl acetate. The product (VI) was recrystallized from ethanol. Yield 3.5 g (70%) m.p. 120 °C (Lit.m.p.120 °C). FT-IR (KBr, cm^{-1}) 1593 ($\text{C}=\text{N}$), 1346, 1526 ($-\text{NO}_2$).

vii Synthesis of 3, 5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1, 2, 4-triazole (VII):

In a 250 mL three neck round bottom flask, a mixture of (6.47 g, 0.01 mol) (VI), hydrazine hydrate (8 mL), ethanol (80 mL), 10% Pd/C (0.2 g) was refluxed at 80 °C for 24 hrs. The mixture was filtered to remove catalyst and the filtrate was poured into cold water to precipitate the product which was collected by filtration, dried, recrystallized from toluene to give (VII). Yield 4.7 g (80%), mp.103 °C.

Elemental Analysis Found: C 75.82, H 8.54, N 12.06%.

Analysis calculated for $\text{C}_{36}\text{H}_{49}\text{N}_5$: C 76.19, H 8.64, N 12.34%.

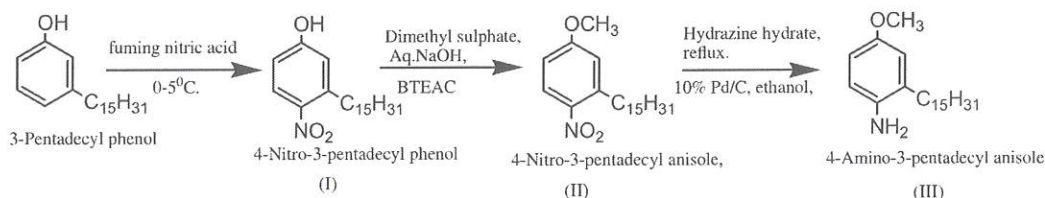
FT-IR (KBr, cm^{-1}): 3369, 3461 ($-\text{NH}_2$). ^1H NMR (CDCl_3 , ppm), 0.96 (t, 3H), 1.2 (m, 26H), 2.03 (t, 2H), 3.7 (s, 4H, NH_2), 3.8 (s, 3H), 6.6 (d, 1H), 6.7 (s, 1H), 7.1(d, 1H), 7.2 (dd, 8H).

^{13}C NMR, (CDCl_3 , ppm) 14.09, 22.67, 28.74, 29.26, 30.68, 55.42, 112.49, 114.62, 115.42, 127.20, 129.39, 130.01, 141.61, 147.61, 154.69, 160.23.

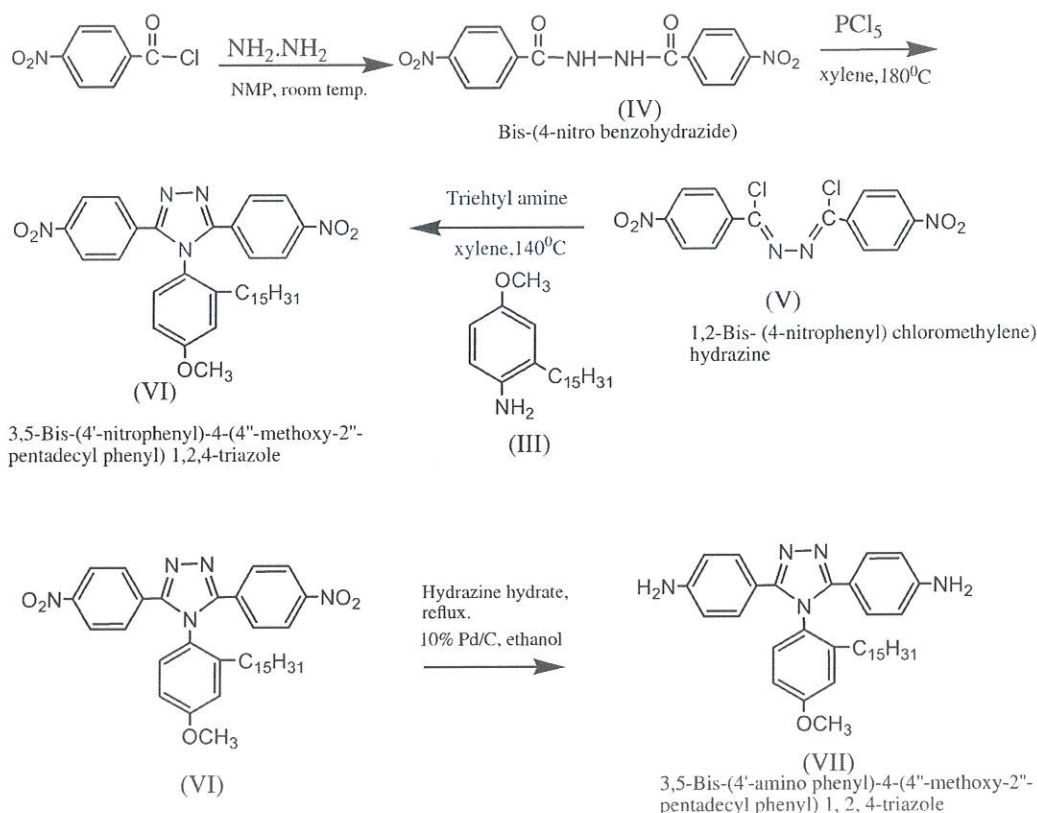
Mass spectrum of (VII) in (Fig. 6) showed (M + 1) peak as strong base peak at 568.

2.3. Synthesis of polyamide PA-1 by low temperature solution polycondensation

In a flame dried 100 mL three neck round bottom flask equipped with a nitrogen gas inlet, magnetic stirrer, were placed diamine (VII) 0.587 g (1 mmol) and dry NMP (4 mL). Mixture was stirred at 30 °C till clear solution was obtained. The solution was cooled to 0 °C in ice salt bath and solidi-sophthaloyl chloride 0.203 g (1 mmol) was added in small portion over period of 10 min; and mixture was further stirred at 0 °C for 1 hr. After 1 hr, triethylamine (0.7 mL) was added and the reaction mixture was stirred at 0 °C for 2 hr, mixture was allowed to attain 30 °C temperature gradually and stirring was continued for 12 hr at this



Scheme 1. Synthesis of 4-amino-3-pentadecyl anisole (III).



Scheme 2. Synthesis of 3,5-bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII).

temperature. The viscous solution was then poured into methanol (250 mL). The fibrous polyamide PA-1 was collected by filtration, washed with water, methanol and dried under vacuum at 80 °C for 6 hrs. Yield 0.685 g (95%). Similarly other polyamides and co-polyamides (PA-2 to PA-5) were prepared.

3. Results and discussion

In present investigation we have synthesized aromatic polyamides containing thermally stable 1, 2, 4-triazole moiety into the main chain of aromatic polyamide and

methoxyphenyl pendant moiety containing flexible linear pentadecyl substituent; so as to improve the solubility of these aromatic polyamides retaining good thermal stability. For this purpose new building block 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1, 2, 4-triazole (VII) was synthesized from renewable agricultural byproduct resource; CNSL. The diamine (VII) was characterized by TLC, FT-IR, NMR (^1H , ^{13}C), and mass spectrometry and elemental analysis.

A new series of soluble aromatic polyamides was synthesized by low temperature solution polycondensation. These aromatic polyamides had good molecular weights

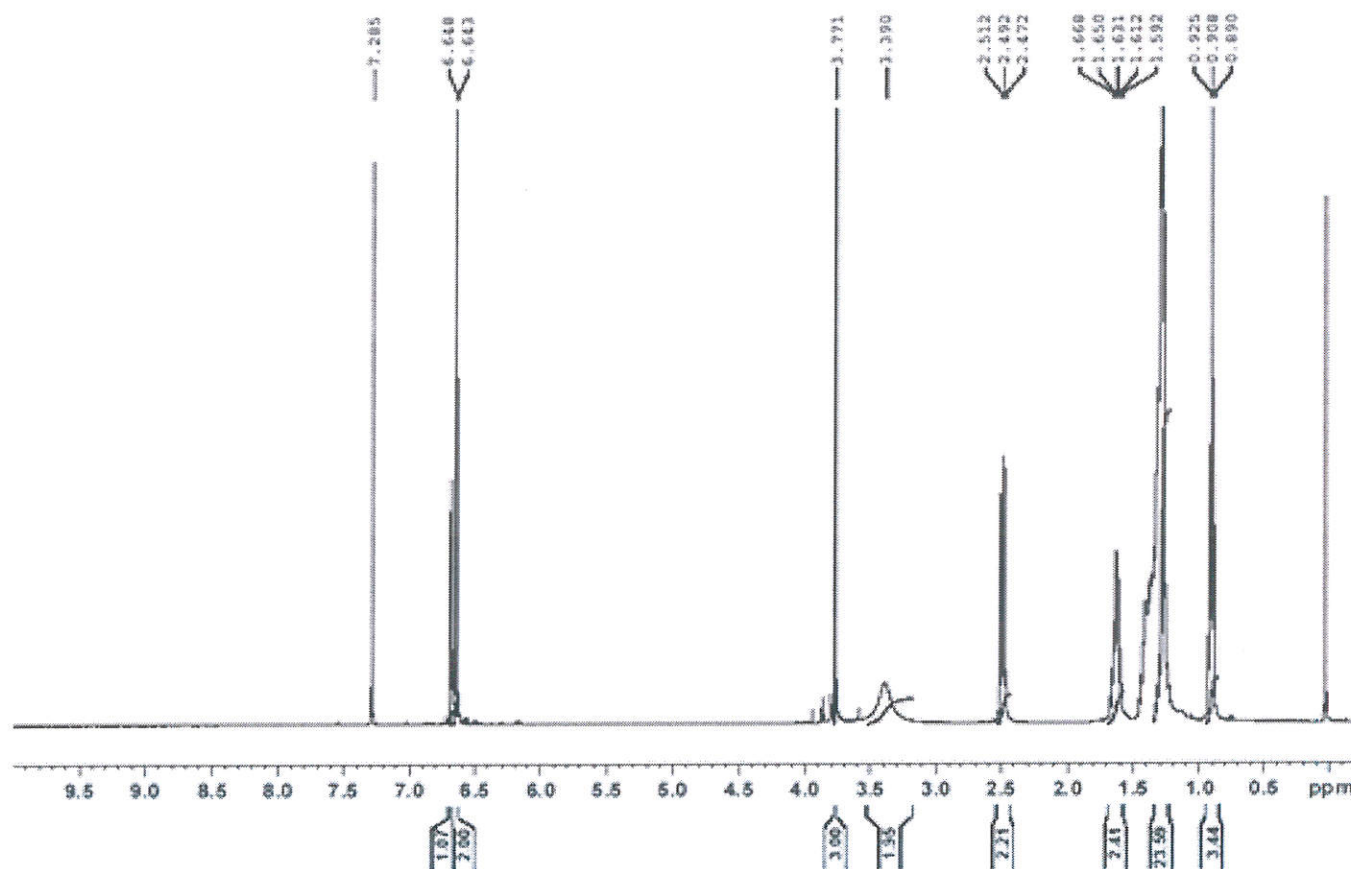


Figure 1. ^1H NMR spectrum of 4-amino-3-pentadecyl anisole (III).

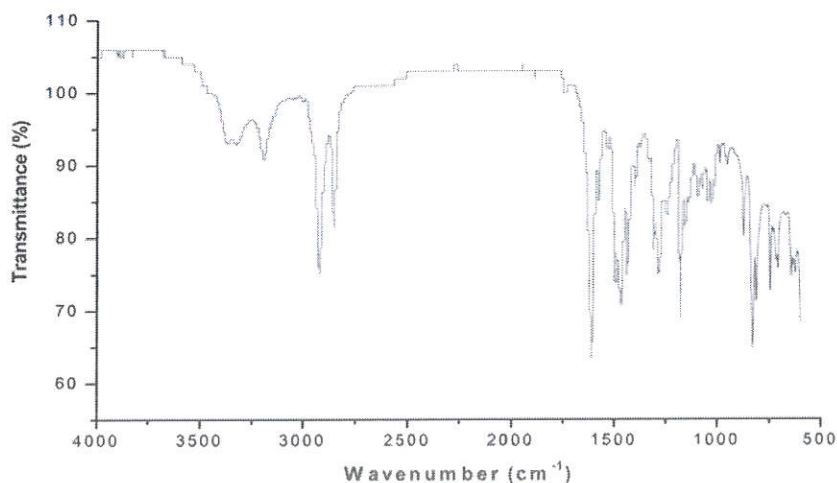


Figure 2. FT-IR spectrum of 3,5-Bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1, 2, 4-triazole (VII).

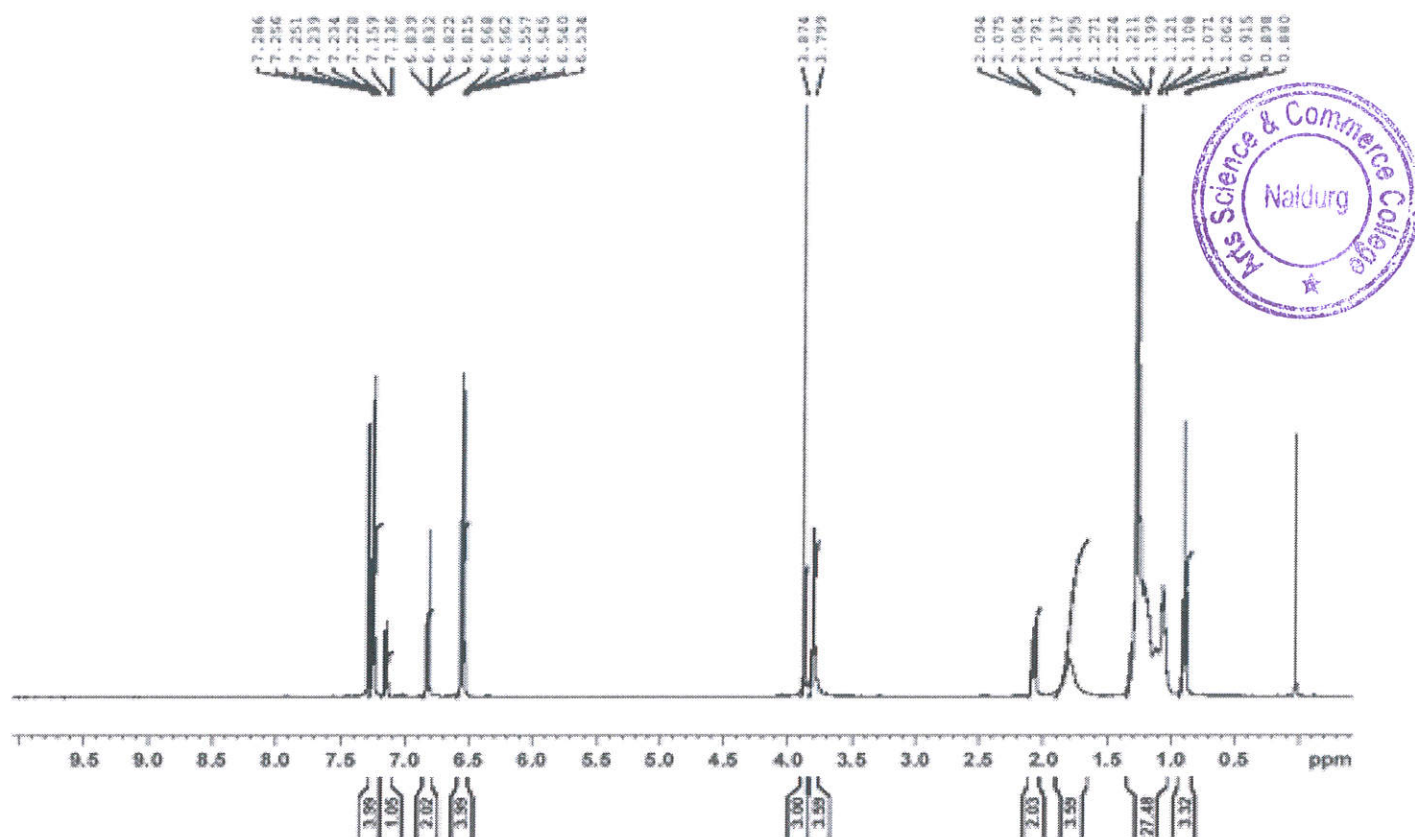


Figure 3. ¹H NMR spectrum of 3,5-Bis-(4'-amino phenyl)-4-(4''-methoxy-2''- pentadecyl phenyl) 1, 2, 4- triazole (VII).

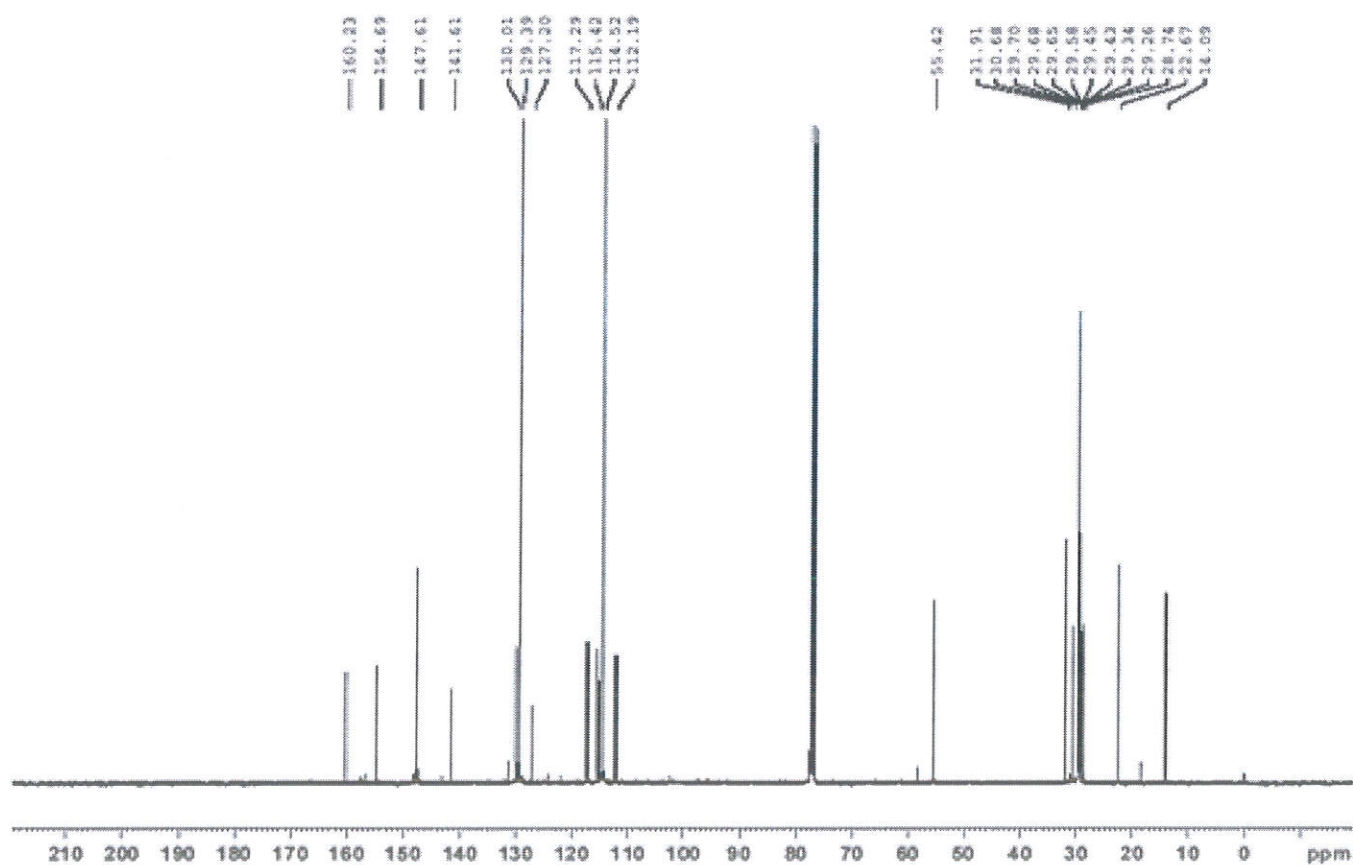


Figure 4. ¹³C NMR spectrum of 3,5-Bis-(4'-amino phenyl)-4-(4''-methoxy-2''- pentadecyl phenyl) 1, 2, 4- triazole (VII).

as reflected by their inherent viscosities in the range 0.50 to 0.65 dL/g; and they showed good solubility in polar aprotic solvents such as N, N, Dimethyl acetamide (DMAc), N-Methyl 2-Pyrrolidone (NMP), N, N, Dimethyl formamide (DMF) and Dimethyl sulphoxide (DMSO). Enhanced solubility of these aromatic polyamides may be due to incorporation of pendant methoxyphenyl moiety containing flexible pentadecyl substituent units leading to amorphous polyamides. Further internal plasticization effect by pentadecyl group helped in lowering T_g of these aromatic polyamides which can help in processing. These soluble aromatic polyamides showed good thermal stability, with initial decomposition temperatures above 350 °C.

3.1. Synthesis 3,5-bis (4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII)

The new aromatic diamine (VII) was successfully synthesized as outlined in Scheme 1 and 2. In order to introduce pendant methoxyphenyl unit with 3-pentadecyl substituent and thermally stable heterocycle 1, 2, 4-triazole; a new diamine namely 3,5-bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII) was synthesized starting from 3-pentadecyl phenol which is obtained from agricultural based cheap renewable byproduct resource. 3-Pentadecyl phenol on nitration, methylation and reduction gave 4-amino-3-pentadecyl anisole (III) (Scheme 1). Further 4-nitro benzoyl chloride on reaction with hydrazine hydrate, Phosphorous pentachloride, gave 1,2-bis-(4-nitrophenyl) chloromethylene) hydrazine (V) (Scheme 2). Then

nucleophilic substitution addition elimination reaction between 4-amino-3-pentadecyl-anisole (III) and 1,2-bis-(4-nitrophenyl chloromethylene) hydrazine (V) formed 3,5-bis-(4'-nitro phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1, 2, 4-triazole (VI) which on catalytic reduction by hydrazine hydrate gave new targeted aromatic diamine (VII)

All the intermediate organic compounds (I) to (VI) and diamine (VII) were characterized by Elemental analysis, TLC, physical constant and FT-IR, NMR (^1H , ^{13}C); mass spectrometry. ^1H NMR of intermediate (III) is shown in Figure 1. The chemical structure of the diamine (VII) was confirmed by FT-IR spectroscopy. FT-IR spectrum of (VII); Figure 1, showed stretching absorptions band at $3330\text{--}3400\text{ cm}^{-1}$ indicating the presence of $-\text{NH}_2$ amine functional group and stretching absorption band at 1593 cm^{-1} indicated $(-\text{C}=\text{N})$, illustrating the complete cyclization to form 1,2,4-triazole moiety in (VII). The stretching absorption at $1200\text{--}1252\text{ cm}^{-1}$ showed the presence of ether linkage; due to methoxy group.

All the intermediate organic compounds (I) to (VI) and final diamine (VII) were characterized by TLC, physical constant and spectroscopically by FT-IR, NMR (^1H , ^{13}C); mass spectrometry and elemental analysis. Typical ^1H NMR of intermediate (III) is shown in Figure 1. The chemical structure of the diamine (VII) was confirmed by FT-IR spectroscopy. FT-IR spectrum of (VII); Figure 2, showed stretching absorptions at $3330\text{--}3400\text{ cm}^{-1}$ indicating the presence of $-\text{NH}_2$ and absorption band at 1593 cm^{-1} indicated $(-\text{C}=\text{N})$, illustrating the complete cyclization to form 1,2,4-triazole moiety in (VII). The stretching absorption at $1200\text{--}1252\text{ cm}^{-1}$ shows the presence of ether linkage;

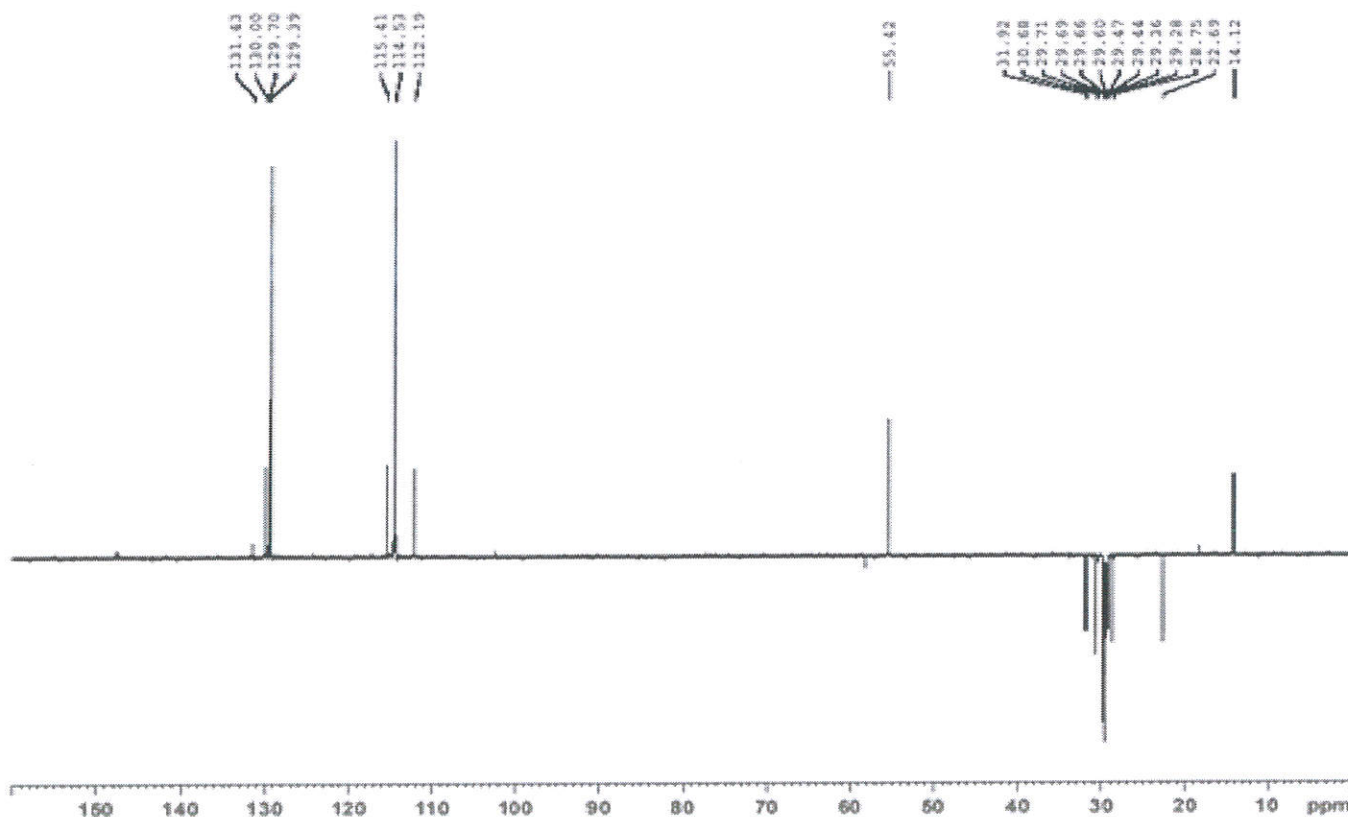


Figure 5. DEPT ^{13}C NMR spectrum of 3,5-bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII).

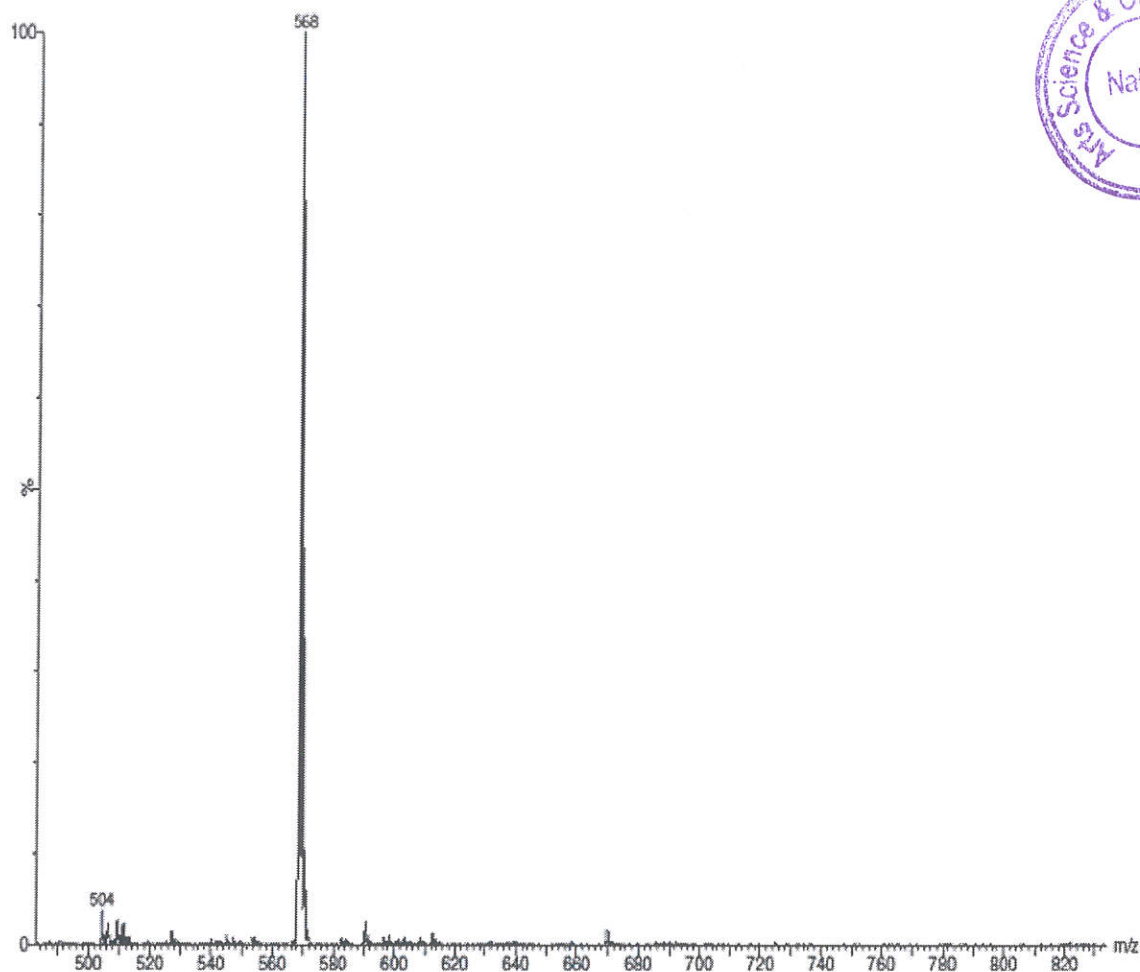
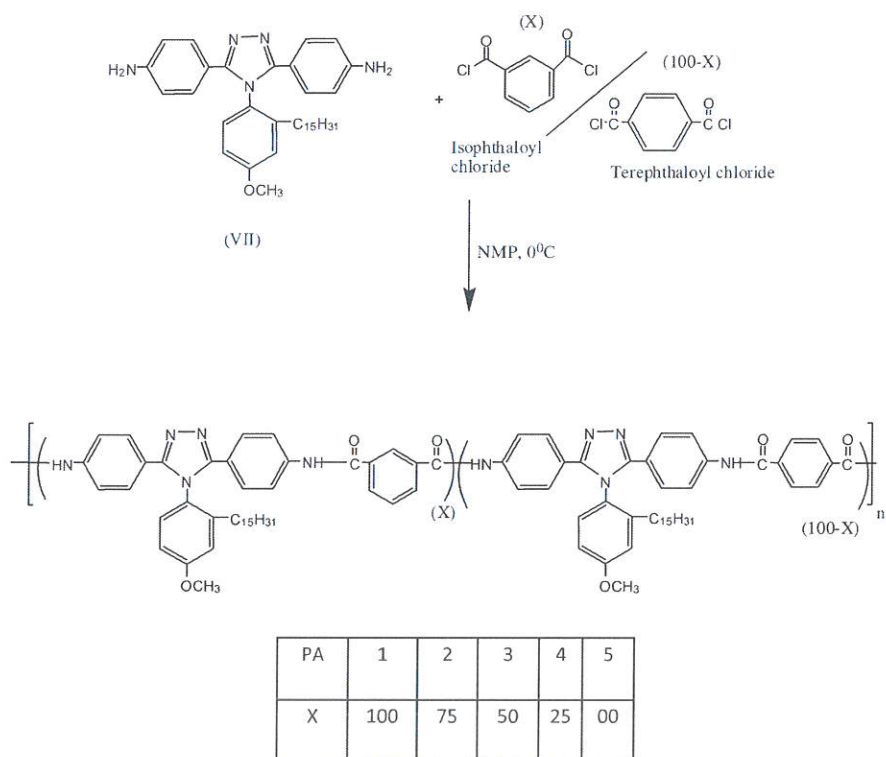
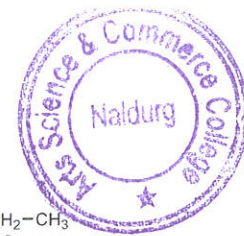


Figure 6. Mass spectrum of 3,5-Bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII).

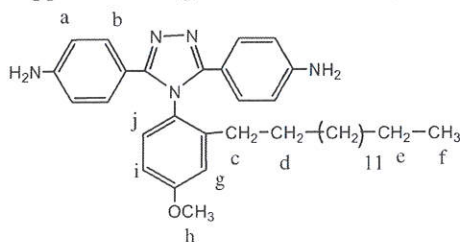


Scheme 3. Polyamide synthesis from aromatic diamine 3,5-Bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII) and IPC/TPC by low temperature solution polymerization.



due to methoxy group. Mass spectrum of (VII) showed (M + 1) peak as strong base peak at 568 indicating molecular formula weight of 567 for diamine(VII), corresponding to molecular formula; $C_{36}H_{49}N_5O$.

The 1H NMR spectrum of (VII); Figure 3; ($CDCl_3$ ppm), signals at 0.96 (t, 3 H, H_f), 1.2 (q, 2 H, H_e), 2.01 (t, 2 H, H_c), 3.7 (s, 2 H, $-NH_2$), 3.8 (s, 3 H, H_g), 6.6 (d, 1 H, H_i), 6.7 (s, 1 H, H_g), 7.1 (d, 1 H, H_j), 7.1 (d, 4 H, H_a), 7.2 (d, 4 H, H_b); support the assigned structure for (VII).



(VII)

^{13}C NMR spectrum of (VII); Figure 4 showed the peak at 154.2 ppm for the triazole ring Carbon ($-C=N$). The ^{13}C DEPT NMR of (VII); Figure 5 ($CDCl_3$, ppm) shows methylene carbons of pentadecyl chain at 14 (C^{13}), 22 (C^{12}), 28 (C^{10}), 29 (C^{11}), 30 (C^8), 31 (C^7). The signal for methoxy group carbon appeared at 55 ppm. Aromatic carbon peaks were in the range 112 to 160 ppm.

The ^{13}C peak at 147 ppm is assigned to carbon directly attached to $-NH_2$; 160 ppm peak is due to carbon attached to $-O-$ group, and carbon signal at 154 ppm is derived from triazole ring carbon involving the $-C=N$ linkage.

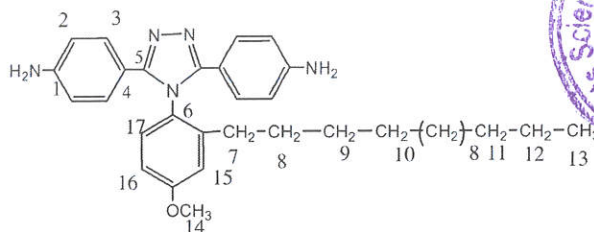
Table 1. Inherent viscosity, yield of polyamides^a from diamine (VII)^b and IPC/TPC.

Serial No.	Polymer code	Mole %		Inherent viscosity ^c (η_{inh}) (dL/g)
		IPC	TPC	
1	PA-1	100	0	0.65
2	PA-2	75	25	0.62
3	PA-3	50	50	0.50
4	PA-4	25	75	0.54
5	PA-5	00	100	0.56

^aPolymerization was carried out with 1 mmol each of aromatic diamine and diacid chloride.

^b3,5-Bis-(4'-amino phenyl)-4-(4''-methoxy-2''-pentadecyl phenyl) 1,2,4-triazole (VII).

^cMeasured with a 0.5% (w/v) polymer solution in DMAc at $30 \pm 0.1^\circ C$.



In DEPT ^{13}C NMR (Figure 5) the peak $-CH_2-$ appeared downside, $-CH-$ carbons remained upside and tertiary carbon peaks disappeared.

Mass spectrum of (VII) in (Figure 6) showed (M + 1) peak as strong base peak at 568 indicating molecular formula weight of 567 for diamine (VII), corresponding to molecular formula; $C_{36}H_{49}N_5O$.

3.2. Polymer synthesis

The synthesis of polymers was carried out by low temperature solution polymerization technique (Scheme 3); reacting aromatic diamine (VII) with isomeric aromatic diacid chlorides namely Isophthaloyl chloride or Terphthaloyl chloride (IPC/TPC). Co-polyamides were also synthesized by reacting aromatic diamine (VII) with various mole proportion of IPC/TPC. All polycondensations proceeded smoothly in solution, however there was precipitation of aromatic polyamide in later stage of polymerization.

4. Polyamide characterization

The data on polyamides is given in Table 1. The inherent viscosities of polyamides were in the range 0.50 to 0.65 dL/g in DMAc solvent at $30 \pm 0.1^\circ C$. Indicating formation of moderate to high molecular weight polyamides.

The FT-IR Spectrum of a representative polyamide PA-1, is shown in Figure 7; which shows characteristic absorption band for N-H stretching at $3350-3340\text{ cm}^{-1}$ and N-H bending at $1665-1650\text{ cm}^{-1}$, the carbonyl stretching frequency of amide at 1650 cm^{-1} , 3039, (aromatic C-H), 2937 cm^{-1} (aliphatic $-CH$ stretching), the sharp bands at $1670-1650$ (amide I) and $1530-1520\text{ cm}^{-1}$ (amide II) confirming formation of amide linkage in polymer.

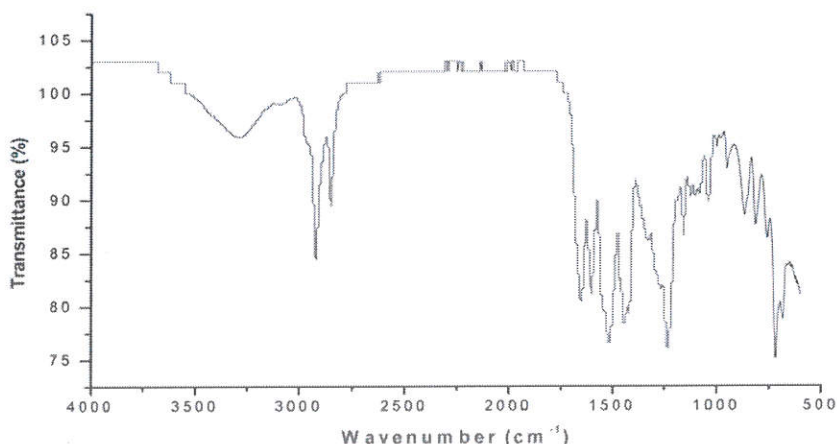


Figure 7. FT-IR spectrum of polyamide PA-1.

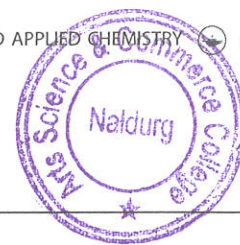


Table 2. Solubility of polyamides PA-1 to PA-5.

Polymer Solvent	PA-1	PA-2	PA-3	PA-4	PA-5
DMAc	++	++	++	++	++
NMP	++	++	++	++	++
DMSO	++	++	++	++	++
DMF	++	++	++	++	++
m-cresol	++	++	++	++	++
CHCl ₃	-	-	-	-	-
Acetone	-	-	-	-	-

Where, ++: soluble at room temperature, -: insoluble at room temperature.

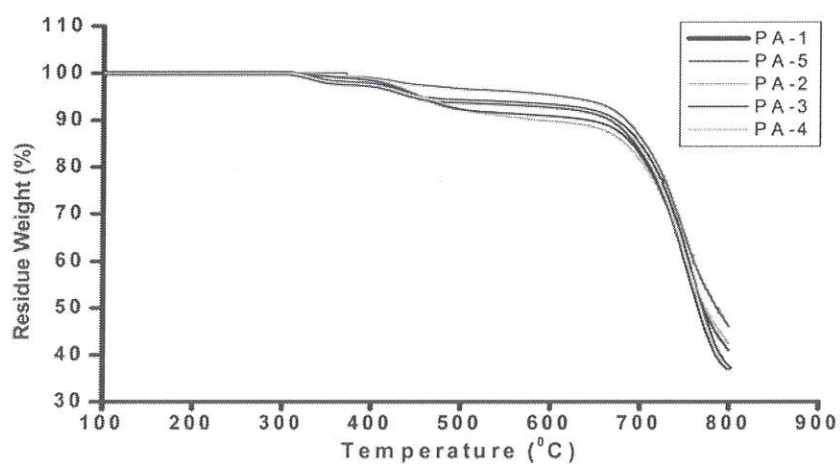


Figure 8. TGA curves of polyamides PA-1 to PA-5.

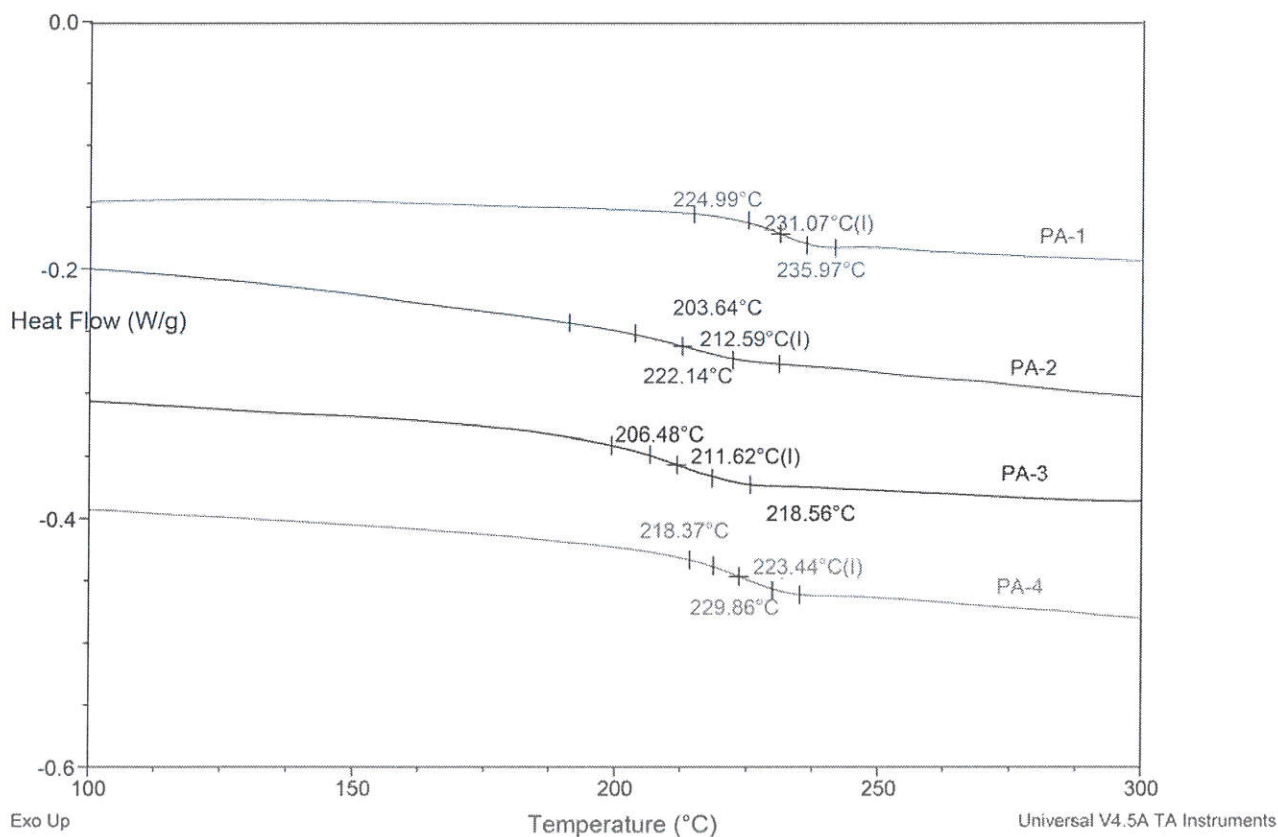


Figure 9. DSC curves of polyamides PA-1 to PA-4.

4.1. Polymer solubility

The solubilities of polyamides were tested in various organic solvents and the results are summarized in Table 2. All the polyamides dissolved readily at room temperature in solvents such as DMAc, NMP, DMSO, DMF and *m*-cresol. Polyamides were insoluble in common organic solvent such as acetone and chloroform. The polyamide shows good solubility probably because of the introduction of pendant methoxyphenyl moiety with long aliphatic pentadecyl substituent units in polymer backbone which disrupted the chain packing close packed structure of the polyamides was possible. This lead to amorphous morphology, which is reflected into the solubility in organic solvents.

4.2. Thermal properties

Thermal properties of polyamides were evaluated by TGA; (Figure 8) and DSC (Figure 9). The Thermal characteristics such as initial decomposition temperature (T_i), 10% weight loss Temperature (T_{10}) and residual weight loss at 800 °C are given in Table 3. No weight loss observed below 350 °C where as T_{10} values were in the range of 390 to 410 °C. All the polyamides showed T_{max} values between 447 to 473 °C and the char yield at 900 °C were in the range 22 to 30%. In general, all these aromatic polyamides exhibited good thermal stability indicating that the pendant alkyl groups do

not affect thermal stability significantly,^[19] as heterocycle 1, 2, 4-triazole and aromatic structure add to thermal stability of polyamides.

DSC of polyamides was performed in nitrogen at a heating rate of 20 °C/min; and DSC curves are shown in Figure 9. The T_g values of the polyamides PA-1 to PA-4 were in the range of 211–231 °C (Table 3.) The T_g were dependent on the stiffness of the polyamide backbone which in turn was dependant on the *m* or *p*-catenated nature of diacid chloride as well on the structure of the aromatic diamine remain constant for PA-1 to PA-4. The polyamide PA-5 synthesized from *p*-catenated rigid diacid chloride TPC did not show the T_g . The T_g of polyamide PA-1 was 231 °C and there was lowering of T_g for PA-2, PA-3 and PA-4 due to random structure because of copolymer effect. Pentadecyl moiety helped in lowering in T_g because of internal plasticization in these polyamides.^[20]

4.2.1. Morphology of polyamides

In order to study the crystalline or amorphous nature of these polyamides, wide angle X-ray diffraction, WAXD, measurements at room temperature, in the region $2\theta = 10$ to 80°, were performed (Figure 10). Wide angle X-ray scattering patterns showed polyamides in nature with a broad halos in the region $2\theta = 15$ to 30°; are amorphous may be due to presence of pendant methoxyphenyl moiety containing long aliphatic substituent on polymer chain which can disrupt the chain regularity and close packing of polyamide chains.

5. Summary and conclusions

A series of thermally stable soluble aromatic polyamides containing heterocyclic 1,2,4-triazole moiety in main polymer chain and pendant methoxyphenyl with pentadecyl substituent was synthesized by low temperature solution polycondensation of new aromatic diamine with IPC/TPC. Diamine (VII) was characterized by spectral techniques and mass spectrometry it was used as building block to obtain

Table 3. Thermal properties of polyamides PA-1 to PA-5.^a

Polyamides	T_g^b (°C)	T_i^c (°C)	T_{10}^d (°C)	T_{max}^e (°C)	Char Yield at 800 °C (%)
PA-1	231	360	410	447	22
PA-2	212	355	410	459	28
PA-3	211	365	390	461	30
PA-4	223	350	420	469	29
PA-5	—	370	420	473	25

^aThermogravimetric analysis at a heating rate of 10 °C/min in nitrogen.

^bGlass transition temperature, determined by Differential Scanning Calorimeter (DSC) at a heating rate of 20 °C/min in nitrogen.

^cInitial decomposition temperature.

^dTemperature at which 10% wt. loss was observed.

^eTemperature at which maximum rate of degradation was observed.

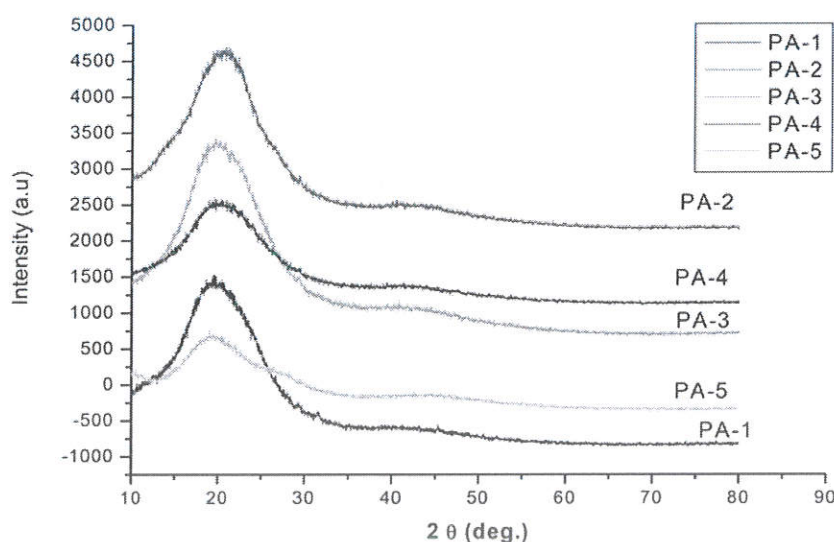
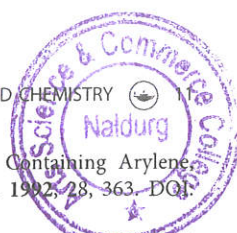


Figure 10. XRD curves of polyamides PA-1 to PA-5.



novel aromatic polyamides. These polyamides exhibited good thermal stability and solubility in polar aprotic solvent such as DMAc, NMP, DMSO, DMF and m-cresol. Transparent and flexible films of polyamides could be cast from DMAc solutions. Thermogravimetric analysis of polyamides under nitrogen showed T_i in the range of 350 to 370 °C indicating their high thermal stability. The lower glass transition temperature of polyamides; determined by Differential Scanning Calorimetry were in the range of 211 to 231 °C and lowering of T_g in these due to internal plasticization effect of long aliphaticpentadecyl chain. Wide angle X-raydiffraction studies of these polyamides revealed broad halos in the region $2\theta = 15$ to 30°; the amorphous nature.

Acknowledgement

Author Mr. A.B. Tamboli is thankful to University Grants Commission (UGC), New Delhi (India) for financial support as JRF and SRF.

References

- [1] Imai, Y.; Maldar, N.N.; Kakimoto, M. Synthesis and Characterization of Soluble Aromatic Polyamides from 2,5-Bis(4-Aminophenyl)-3,4-Diphenylthiophene and Aromatic Diacid Chlorides. *J. Polym. Sci. Part A. Polym. Chem.* **1985**, *23*, 1797.
- [2] Korshak, V.V.; Teplyakov, M.M.; Fedorova, R.D. Synthesis and Investigation of Polybenzimidazoles Containing Alkyl Substituents in Aromatic Nuclei. *J. Polym. Sci. A-1 Polym. Chem.* **1971**, *9*, 1027. DOI: 10.1002/pol.1971.150090417.
- [3] Hsiao, S.-H.; Chu, K.-Y. Synthesis and Properties of Ortho-Linked Aromatic Polyamides Based on 4,4'-(2,3-Naphthalenedioxy) Dibenzoic Acid. *J. Polym. Sci. Part A. Polym. Chem.* **1997**, *35*, 3385. DOI: 10.1002/(SICI)1099-0518(19971130)35:16<3385::AID-POLA6>3.3.CO;2-T.
- [4] Chiriac, C.; Stille, J.K. Polyaramides Containing Sulfone Ether Units. *Macromol.* **1977**, *10*, 712. DOI: 10.1021/ma60057a045.
- [5] Yang, C.P.; Lin, J.H. Syntheses and Properties of Aromatic Polyamides and Polyimides Derived from 9,9-Bis[4-(p-Aminophenoxy)Phenyl]Fluorene. *J. Polym. Sci. A Polym. Chem.* **1993**, *31*, 2153. DOI: 10.1002/pola.1993.080310821.
- [6] Bruma, M.; Mercer, F.; Fitch, J.; Cassidy, P. Synthesis and Characterization of Fluorinated Poly(Imide-Amide-Sulfone)s. *J. Appl. Polym. Sci.* **1995**, *56*, 527. DOI: 10.1002/app.1995.070560501.
- [7] Rao, V.L.; Prabhakaran, P.V. Polyamides Containing Arylene Ether and Ketone Linkages. *Eur. Polym. J.* **1992**, *28*, 363. DOI: 10.1016/0014-3057(92)90255-Z.
- [8] Hamciuc, C.; Hamciuc, E.; Bruma, M.; Klapper, M.; Pakula, T. New Aromatic Poly(Ether-Ketone)s Containing Hexafluoroisopropylidene Groups. *Polym. Bull.* **2001**, *47*, 1. DOI: 10.1007/s002890170014.
- [9] Ubale, V.B.; Patil, A.S.; Maldar, N.N. Polyhydrazides Based on 2,5-Bis(4-Carboxymethylene Phenyl)-3,4-Diphenyl Thiophene. *Euro. Polym. J.* **2007**, *43*, 1038. DOI: 10.1016/j.eurpolymj.2006.10.027.
- [10] Dinari, M.; Haghighi, A. Synthesis and characterization of new heat-resistant polyamides bearing an s-triazine ring under green condition. *J. Polym. Res.* **2017**, *24*, 29.
- [11] Sagar, A.D.; Shingte, R.D.; Wadgaonkar, P.P.; Salunkhe, M.M. Polyamides Containing s-Triazine Rings and Fluorene "Cardo" Groups: synthesis and Characterization. *Eur. Polym. J.* **2001**, *37*, 1493. DOI: 10.1016/S0014-3057(00)00194-4.
- [12] Ghatge, N.D.; Maldar, N.N. Polyimides from Dianhydride and Diamine: structure Property Relations by Thermogravimetric Analysis (t.g.a.). *Polymer* **1984**, *25*, 1353. DOI: 10.1016/0032-3861(84)90390-2.
- [13] Tawade, B.V.; Valsange, N.G.; Wadgaonkar, P.P. Synthesis and characterization of polyhydrazides and poly(1,3,4-oxadiazole)s containing multiple arylene ether linkages and pendent penta-decyl chains. *J. High Perform. Polym.* **2016**, *1*, 888.
- [14] Sayyad, M.M.; Maldar, N.N. Novel poly(arylene ether ether ketone)s containing performed imide unit and pendant long chain alkyl group. *J. Mater. Sci. and Engi. B.* **2009**, *10*, 2016.
- [15] Voirin, C.; Caillol, S.; Sadavarte, N.V.; Tawade, B.V.; Boutevin, B.; Wadgaonkar, P.P. Functionalization of Cardanol: Towards Biobased Polymers and Additives. *J. Polym. Chem.* **2014**, *5*, 3142. DOI: 10.1039/C3PY01194A.
- [16] Mittal, K.L.; editor Polyimide: Synthesis, Characterization and Application, vols. 1-2; New York: Plenum, **1984**.
- [17] Mele, G.; Vasapollo, G. Fine Chemicals and New Hybrid Materials from Cardanol. *Mroc.* **2008**, *5*, 243. DOI: 10.2174/157019308785161611.
- [18] Serna, F.; Garcia, F.; De la Pena, J.L.; Garcia, J.M. Aromatic Polyisophthalamides with Mononitro, Dinitro and Trinitroiminobenzoyl Pendant Groups. *J. High. Perform. Polym.* **2008**, *20*, 19. DOI: 10.1177/0954008307077787.
- [19] Mathew, J. S.; Ph.D. Thesis submitted to University Pune (India) "novel thermally stable polymers from renewable resource (Cashew nut shell liquid) synthesis, characterization and applications".(2001).
- [20] Ghaemy, M.; Behmadi, H.; Alizadeh, R. Synthesis of Organosoluble Polyamides with Bulky Triaryl Imidazole Pendent Group. *Chin. Chem. Lett.* **2009**, *20*, 961. DOI: 10.1016/j.ccl.2009.01.038.

PRINCIPAL
Arts Science & Commerce College
Naldurg, Dist.Osmanabad-413602