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Synthesis, Characterization and Thermal Properties of Aromatic Fluorinated Polyamide bearing Pendant Pentadecyl Chain

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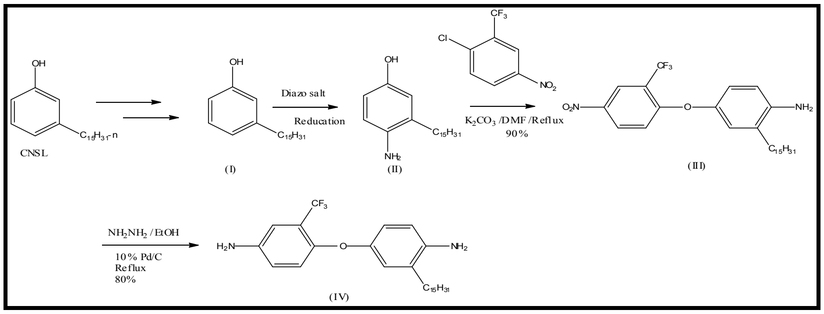
ABSTRACT

Synthesis of a new aromatic fluorinated diphenyl diamine ether type monomer with pendant pentadecyl chain group, viz. 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) and it's derived polyamide. The aromatic polyamide was synthesized from condensation of diamine with terephthalloyl chloride (TPC) and isophthalloyl chloride (IPC) and its equimolar mixture via interfacial polycondensation method. The resulting polyamides were characterized by inherent viscosity *measurement, solubility, FT-IR, thermal properties and XRD. At room temperature all polyamides were readily soluble in polar aprotic solvents. The polyamide shows inherent viscosity in the range between 0.30-0.63 dL* g^{-1} *in N-methyl-2-pyrrolidone (NMP) at 30°C. The polyamides showed useful levels of thermal stability with glass transition temperature* (T_g) *in the range of 150-175°C and no 10% weight-loss below 448°C and amorphous in nature.*

Graphical Abstract



Synthesis of 4-(4-amino-2-(trifluoromethyl)phenoxy)-2-pentadecylaniline (ATPP) (IV)

Keywords: Polyamide, Trifluoromethyl, Pentadecyl chain, Thermal properties.

INTRODUCTION

Aromatic Polyamides (PA) are constantly attracting much interest due to their outstanding thermal and mechanical resistance [1, 2]. Aromatic polyamides were first introduced for commercial applications in the early 1960s, with a meta-aramid fiber invented as trade name Nomex®. While para-aramids introduced for commercial applications in the early 1973s, as trade name Kevlar®. Their properties arise from their aromatic structure and amide linkages, which result in stiff rod-like macromolecular chains that interact with each other via strong and highly directional hydrogen bonds. These bonds create high-level intermolecular packing and cohesive energy. Due to their rigid chemical structure they exhibit extremely high transition temperatures viz. T_g and T_m that may lie above their decomposition temperatures. These polymers are sparingly soluble in common organic solvents and that restricts their solution processability. Several approaches have been taken by many researchers to improve the processability of polyamides by structural modification without compromising thermal stability employ the introduction of flexible or non-symmetrical linkages in the polymer backbone or the incorporation of bulky substituent as pendant groups in to the polymer backbone [3-8], can be used to modify the polymer properties, either by lowering the inter-chain interaction or by reducing the stiffness of the polymer chain [9-14].

Among the various structural modification methods mentioned above, the appendance of flexible side chain along the polymer backbone is a particularly interesting approach [15], since the peculiar structure of the main chain of such polymers is not altered by the attachment of flexible side chains. It is reported that the use of monomers bearing pendent flexible groups greatly reduces strong molecular interactions of stiff-chain aromatic polymers, producing an effective chain separation effect. Along with flexible side chain the introduction of trifluoromethyl (–CF_3) groups in the polyamide structure endows remarkable improvements in several properties compared to non fluorinated polyamides [16, 17]. Introduction of fluorinated groups into the polyamides improves their electrical insulating properties, gas permeability, flame resistance, environmental stability, and optical transparency and lowers their dielectric constant and water uptake values and also exhibits higher or comparable thermal property compared to that of non fluorinated polymers.

Thus our aim in the present studies was to make use of one or more of the structural modifications mentioned above, to have a cumulative effect on the properties of the resulting polymers. For this purpose our synthetic research interest was directed towards designing monomers with features that disturb structural regularity and chain packing hence imparting improved processability to the polymers. The intention of our research was to utilize CNSL as a starting material to design and synthesize bifunctional monomer. CNSL, an agricultural by-product abundantly available in the country, is unique in that it contains a phenolic moiety with an unsaturated meta alkyl 15-carbon side chain, the alkyl chain act as internal plasticizer which improve the processability. The meta- linkage introduces "kinks" to the main chain which decrease the rigidity of the polymer backbone and inhibit packing, thus reducing the interchain interactions leading to enhanced solubility. Along with flexible side chain introduction of fluorine in the form of trifluoromethyl groups (-CF_3) in polymer lead to great benefits for improving polymer properties are very attractive for applications in advanced technologies [18-20]. The present work was undertaken to synthesis and characterization of new aromatic diamine; 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV); and novel polyamides therefrom, ATPP was synthesized by condensation of 4-Amino -3-pentadecyl phenol (4-ATHA) (II) with 5-Chloro-2-nitro benzotrifluoride. Therefore, the polyamides prepared from ATPP containing pendent pentadecyl chains and trifluoromethyl groups with aromatic acid chlorides *viz.* terphthalloyl chloride (TPC) and isophthalloyl chloride (IPC), to examine the effect of incorporation of these substitutions on the polymer properties such as solubility, inherent viscosity, thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) and XRD studies.

MATERIALS AND METHODS

All reagents were purchased from Sigma-Aldrich, Spectrochem and Thomas Beaker (India) and used as received unless otherwise noted. 3-Pentadecyl phenol, 5-Chloro-2-nitro benzotrifluoride, palladium-10 % on activated carbon (Pd-C, 10 wt %), NMP, DCM were purified by distillation and dried by standard procedure before use. Sulfanilic acid, hydrazine hydrate (99 %), ethanol, acetic acid, sodium dithionite, sodium hydroxide, sodium carbonate, sodium Nitrite, Terphthalloyl chloride (TPC) and isophthalloyl chloride (IPC) were purified by recrystallization in dry hexane.

Measurements: Melting points were recorded on Thomas Hover melting apparatus by open capillary method and are uncorrected. NMR spectra were recorded on Bruker 400 MHz spectrometer at resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C measurement using $CDCl_3$ as a solvent. The solubility of polyamides was determined at 3 wt % concentration in polar aprotic solvents. Inherent viscosity of polyamides was measured with 0.5 % (w/v) solution of polyamide in NMP at 30±0.1°C using an Ubbelhode suspended level viscometer. FT-IR spectra were recorded using polyamide on ATR attachment Bruker Tenser 37 spectrophotometer. Thermo gravimetric analysis was performed on Shimadzu 60H system at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Sample weight taken was ~5-7 mg. DSC analysis was carried out on Metteler Toledo instruments DSC-3 at a heating rate of 10°C min^{-1} in nitrogen atmosphere. X-Ray diffraction patterns of polyamides were obtained on a Rigaku Ultima-IV X-ray diffractometer at a tilting rate of 20°C min^{-1}. Polyamide powder was used for X-ray measurements. Elemental analyses were performed on Thermo FLASH EA 1112 series elemental analysis.

Synthesis of monomer and intermediate

Synthesis of 4-(4-nitro-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (NTPP) (III) [22]: Into a 500 mL three neck round bottom flask equipped with a nitrogen gas inlet, a reflux condenser and a magnetic stirrer were placed 4-amino-3-pentadecyl phenol (II) [21] (20.0 g, 63 mmol), 5-Chloro-2-nitro benzotrifluoride (14.5 g, 63 mmol), potassium carbonate (8.98 g, 65 mmol) and DMF (100 mL). The reaction mixture was refluxed for 6 h under dry nitrogen gas stream. The reaction mixture was then allowed to cool to room temperature and poured into water. The precipitated product was filtered, dried and recrystallized from ethanol. Yield: 28.97 g (90%); M.P. 62-63°C, FT-IR (ATR, cm^{-1}):3452, 3370 (-N-H stretch), 1619, 1260 (-C-O-C stretch), 1530 (-NO_2 asymmetric stretch), 1345 (-NO_2 symmetric stretch), 1592 (aromatic C=C stretch), ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.58 (s, 1H, Ar-H), 8.29 (s, 1H, Ar-H), 6.79 (m, 4H, Ar-H), 3.70 (s, 2H, -NH_2), 2.50 (t, 2H, Ar-CH_2), 1.29-1.50 (m, 26H, $(CH_2)_{13}$), 0.90 (t, 3H, -CH_3), The elemental analysis calculated for $C_{28}H_{39}F_3N_2O_3$: C, 66.12; H, 7.73; N, 5.51 %, Found: C, 66.24; H, 7.41.24; N, 5.74 %.

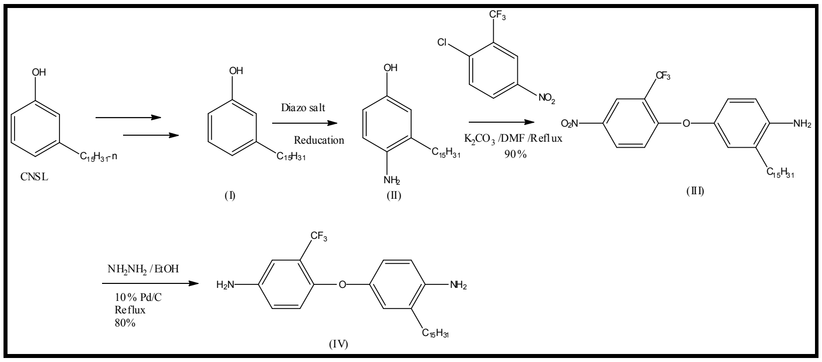
Synthesis of 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) [22]: Into a 250 mL three neck round bottom flask equipped with a dropping funnel and a reflux condenser were charged 4-(4-nitro-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (III) (5.0 g, 9.8 mmol), palladium charcoal (3 wt %) and ethyl alcohol (70 mL). The reaction mixture was heated to 70°C and hydrazine hydrate (39.7 mL, 0.79 mol) was added drop-wise over a period of 15 min and refluxed for 6 hrs. The reaction mixture was filtered while hot and the solvent was distilled on a rotary evaporator to obtain the crude diamine (IV), which was recrystallized from ethanol. Yield 3.99 g (85%); M.P. 78-79°C, FT-IR (ATR, cm^{-1}):3396, 3306, and 3196 (-N-H stretch), 1632, 1260 (-C-O-C stretch), ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 6.79-7.38 (m, 6H, Ar-H), 3.59 (s, 4H, -NH_2), 2.45 (t, 2H, Ar-CH_2), 1.29-1.50 (m, 26H, $(CH_2)_{13}$), 0.93 (t, 3H, -CH_3), ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 150.68, 144.84, 144.83, 130.50, 123.94, 121.62, 121.42, 119.24, 118.88, 115.53, 113.32, 33.17, 31.65, 29.95, 29.26, 28.58, 22.94, 22.57, 14.02, The elemental analysis calculated for $C_{28}H_{41}F_3N_2O$: C, 70.26; H, 8.63; N, 5.85 %, Found: C, 70.20; H, 8.42; N, 5.85 %.

Synthesis of polyamides: In a 100 mL three neck round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube were placed ATPP 0.478 g. (1 mmol), NaOH 0.080 g (2 mmol) dissolved in 12.5 mL water and cooled to 0°C in ice bath. To the reaction mixture, TPC/IPC 0.203 g (1 mmol) in DCM 8 mL was introduced all at once and stirred for 30 min at 0°C. The stirring was (vigorously) continued at 30°C for an hour when viscous solution was obtained. Solution was poured into excess of hexane to precipitate the polyamide. Polymer was filtered and washed with water and dried under vacuum at 80°C 1 mm^{-1} Hg for 10 h. Yield: 0.61 gm (95%). A similar procedure was followed for the synthesis of PA-2 to PA-5 polyamides.

RESULTS AND DISCUSSION

Synthesis of 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV): A new unsymmetrical aromatic diamine *viz.*, 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) was synthesized in three steps starting from 3-pentadecylphenol (3-PDP) (I) which in turn is obtainable from CNSL a renewable cheap agricultural resource material (Scheme 1).

4-ATHA was converted to 4-(4-nitro-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (NTPP) (III) by reacting with 5-Chloro-2-nitro benzotrifluoride in presence of potassium carbonate catalyst. FT-IR spectrum of NTPP figure 1 exhibited absorption bands at 1530 and 1345 cm^{-1} corresponding to the asymmetric -NO_2 stretching and symmetric -NO_2 stretching, respectively.



Scheme 1 Synthesis of (ATPP) (IV)

The reduction of NTPP using hydrazine hydrate / Pd-C (10 wt %) reagent system afforded the desired 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP); which was characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral techniques. FT-IR spectrum of ATPP figure 2 showed absorption bands at 3200, 3320 and 3400 cm^{-1} corresponding to the –N-H stretching of amino group.

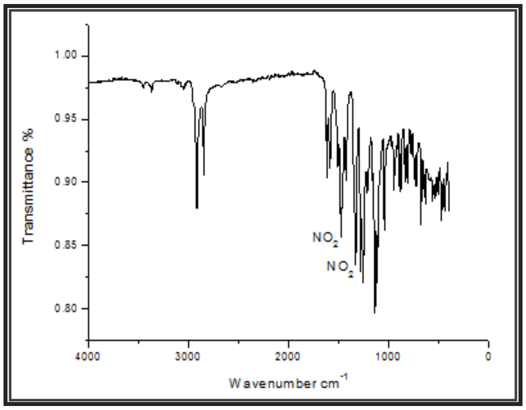


Figure 1 FT-IR spectrum of NTPP (III)

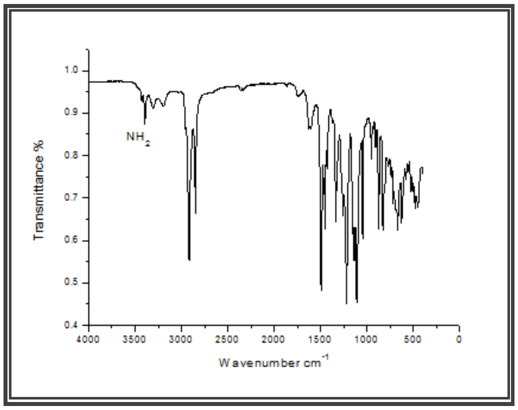


Figure 2 FT-IR spectrum of ATPP (IV)

The structure of NTPP (III) and ATPP (IV) was also confirmed by ^{1}H-NMR and ^{13}C-NMR spectrum respectively. The spectra of these compounds are illustrated in figure 3-5. The assignment of each proton and carbon are also given in the figures and these spectra are in good agreement with the molecular structures.

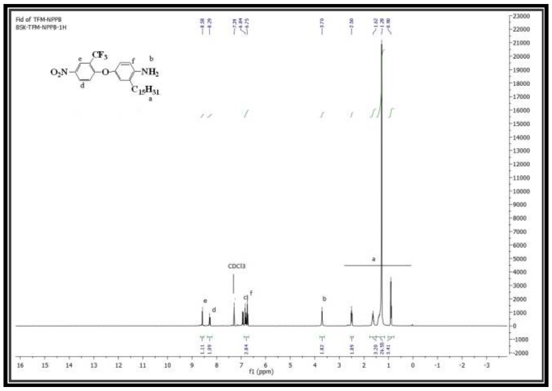


Figure 3 ^{1}H-NMR spectrum of NTPP (III)

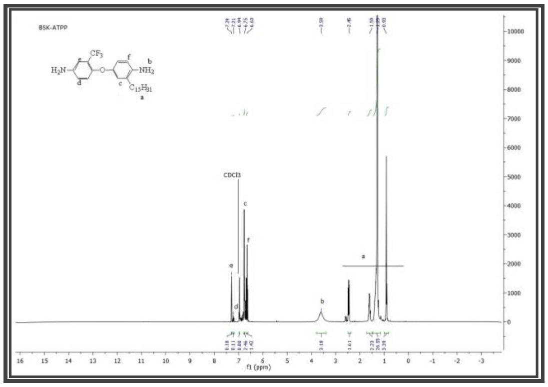


Figure 4 ^{1}H-NMR spectrum of ATPP (IV)

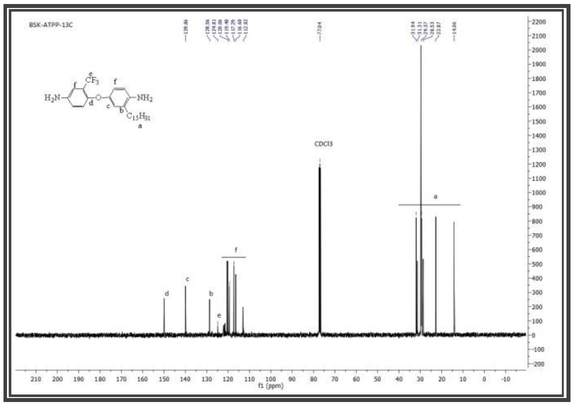
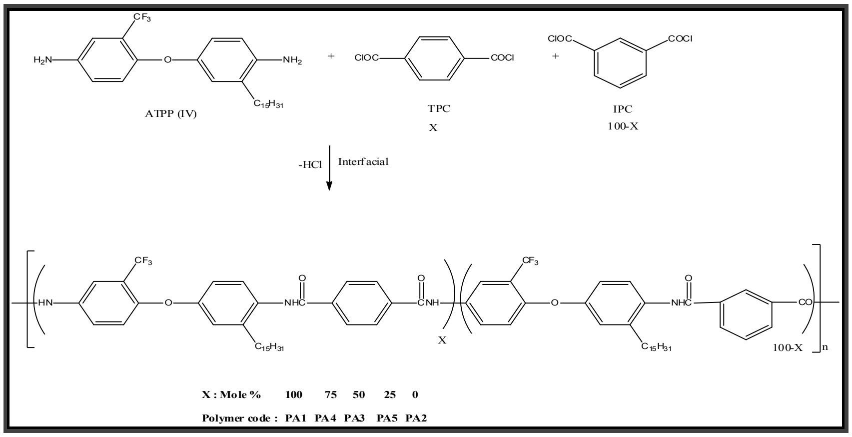


Figure 5. ^{13}C-NMR spectrum of ATPP (IV)

Synthesis of polyamides: In the interfacial polycondensation method the monomers were dissolved and reacted at interface of two phases, i.e. in a pair of immiscible liquids one of which is preferably water. The water phase contained the diamine and an inorganic base to neutralize the byproduct acid. The organic phase contained the acid chloride in an organic solvent such as dichloromethane. The two phase system was stirred vigorously to obtain high M_W polymers. Scheme 2 illustrates synthesis of polyamides from 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) and aromatic terphthalloyl chloride (TPC) / isophthalloyl chloride (IPC).



Scheme 2. Synthesis of polyamide based on (ATPP) (IV) and TPC/IPC

The results of polymerization are summarized in Table 1. All the reaction mixtures were homogeneous throughout the course of polymerization.

Table 1 Polyamide series yield and viscosity

Polyamide code	TPC Mole %	IPC Mole %	Yield (%)	η_{inh} [a] dL g-1
PA-1	100	0	97	0.63
PA-2	0	100	95	0.30
PA-3	50	50	95	0.78
PA-4	75	25	96	0.47
PA-5	25	75	97	0.49

a- η_{inh} was measured with 0.5 % (w/v) solution of polyamide in NMP at 30±0°C

Inherent viscosities of polyamides were in the range 0.30-0.63 dL g $^{-1}$ table 1 indicating formation of medium to reasonably high molecular weight polymers.

Structural characterization: The formation of polyamides was confirmed by FT-IR. A representative FT-IR spectrum of polyamide based on 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) and TPC/IPC is reproduced in figure 6.

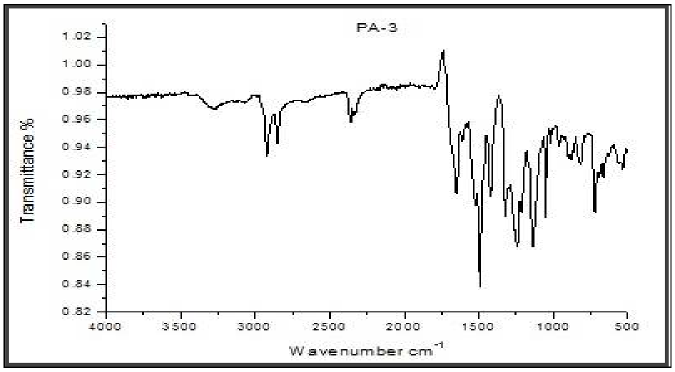


Figure 6. FT-IR spectrum of PA-3 based on (ATPP) (IV) and TPC/IPC

Polyamide formation was characterized by the –NH stretching frequency as a broad band around 3276 cm^{-1}. Due to the hydrogen bonding, the C=O stretching vibration band shifted to lower wave number and appeared at 1649 cm^{-1}.

Solubility measurements: Solubility of polyamides was tested in various organic solvents at 3 wt % concentration and data is summarized in table 2.

Table 2. Solubility data of polyamides derived from (ATPP) (IV) and TPC/IPC

Polyamide code / Solvent	PA1	PA2	PA3	PA4	PA5
NMP	++	++	++	++	++
DMAc	++	++	++	++	++
DMF	+-	++	++	++	++
Pyridine	++	++	++	++	++
m-Cresol	+-	++	++	+-	+-
Conc. H_2SO_4	++	++	++	++	++

+ + soluble at room temp., + - soluble heating, - - not soluble.

Polyamides were soluble in NMP, DMAc, DMF, pyridine, m-cresol, and conc. H_2SO_4 either at room temperature or upon heating whereas reference polyamides derived like Kevlar® and Nomex® type polyamide with ODA were insoluble [23-26]. The improved solubility of polyamides containing pendent pentadecyl chains and trifluoromethyl groups compared with that of reference polymers could be attributed to the presence of pentadecyl chains and trifluoromethyl groups. The pendent pentadecyl chains along and trifluoromethyl groups the polymer backbone greatly reduce strong molecular interactions of stiff chain aromatic polymers producing an effective chain separation effect which prevents their tight chain packing and increases the free volume. The disturbed packing of macromolecular chains facilitated the diffusion of small molecules of solvent which leads to improvement in solubility.

X-ray diffraction studies: X-ray diffractograms of polyamides derived from 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) and TPC/IPC are shown in **figure 7**.

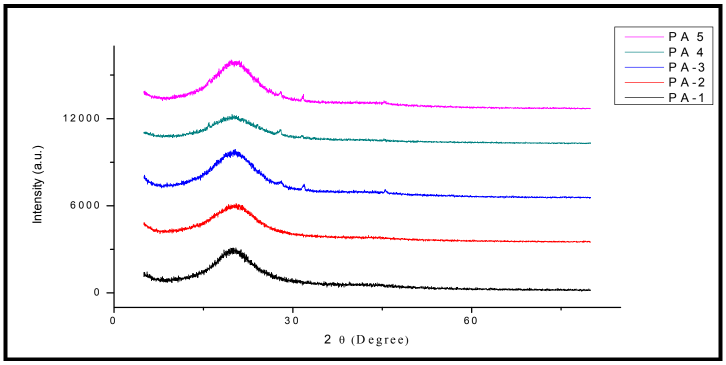


Figure 7. X-ray diffraction patterns of polyamides derived ATPP) (IV) and TPC/IPC

X-ray diffractograms of all polyamides PA-1 to PA-5 exhibited a broad peek at the wide angle region 2θ ≈ 20° indicating that these polyamides were amorphous in nature. This result could be explained in terms of the presence of the pendent pentadecyl chain and trifluoromethyl groups in the polymer backbone which hindered packing of the polymer chains and decreased the intermolecular forces, subsequently causing a decrease in crystallinity.

Thermal properties: Thermal stability of polyamides was determined by thermogravimetric analysis (TGA) at a heating rate of 10°C min^{-1} under nitrogen atmosphere. TG curves of polyamides PA-1 to PA-5 are shown in figure 8.

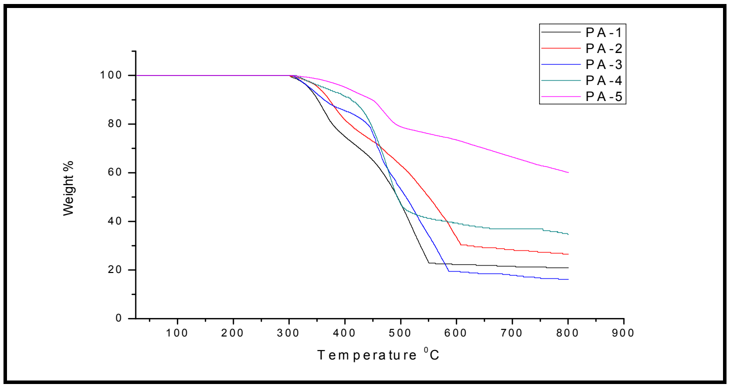


Figure 8 TGA of polyamides derived from (ATPP) (IV) and TPC/IPC

Initial decomposition temperature T_i of polymers was in the range 301 to 312°C. The temperature at 10 % weight loss (T_{10}) and the weight residues at 800°C were determined from thermograms data is given in table 3.

Table 3 Thermal properties of polyamides derived from (ATPP) (IV) and TPC/IPC

Polyamide code	T_i (°C)	T_{10} (°C)	T_g (°C)	Weight residue at 800°C (%)
PA-1	301	351	175	20
PA-2	301	371	153	26
PA-3	307	361	154	16
PA-4	312	410	150	34
PA-5	308	448	157	60

T_{10} values obtained from TGA curves for polyamides were in the range 351-448°C indicating their good thermal stability. The weight residue of polyamides at 800°C in nitrogen was in the range 20-60 %. The two stage weight loss observed from thermograms indicating the initial weight loss was due to aliphatic chain. It is also observed in DTA curve. The second stage weight loss or stability is due to trifluoromethyl group in the polymer chain. The increased thermal and oxidative stability is due to trifluoromethyl group, however due to long pentadecyl alkyl chain somewhat lowering in T_i is observed in polymer chain.

Glass transition (T_g) temperature of the polyamides was evaluated by differential scanning calorimetery (DSC). T_g values were obtained from second heating scans of polyamide samples at a heating rate of 10°C / minute. DSC curves are reproduced in figure 9 and T_g values are given in table 3.

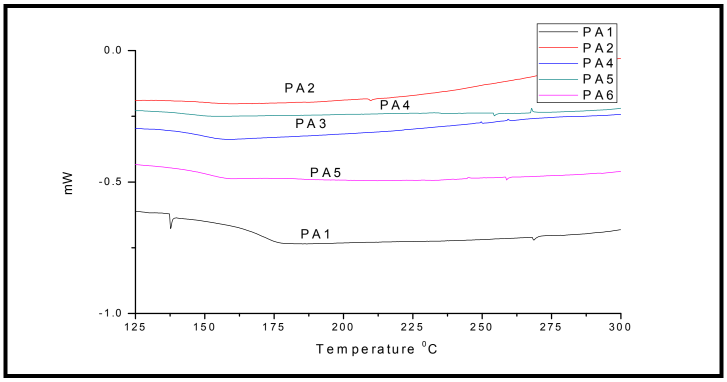


Figure 9. DSC of polyamides derived from (ATPP) (IV) and TPC/IPC

T_g of polyamides PA-1 to PA-5 containing pendent pentadecyl chains and $-CF_3$ group were in the range 150-175°C. The decreasing order of T_g corresponds to an decreasing in the rigidity of the polyamide. For example, PA-I derived from TPC exhibited highest T_g value (175°C) among the series of these polyamides. Polyamides containing pendent pentadecyl chains and $-CF_3$ group showed lower glass transition temperature in comparison with those for Kevlar® and Nomex® type polyamide with ODA [23-26], which possess a T_g at 275°C, This result is reasonable and can be attributed to the fact that pendent pentadecyl chains to the polymer backbone, act as an internal plasticizer, and increase segmental mobility, thus resulting in a reduction in the T_g. A large difference in T_g and decomposition temperature of these polyamides offers a broad processing window.

APPLICATION

Polyamides were soluble in NMP, DMAc, DMF, etc., it indicates that the incorporation of pendent flexible pentadecyl chains and $-CF_3$ group lead to a significant improvement in solubility of polyamides.

CONCLUSIONS

A series of new polyamides PA-1 to PA-5 containing pendent pentadecyl chains and $–CF_3$ group was synthesized by the interfacial polycondensation of 4-(4-amino-2-(trifluoromethyl) phenoxy)-2-pentadecylaniline (ATPP) (IV) and TPC/IPC. Inherent viscosities of polyamides were in the range 0.30-0.63 dL g^{-1}indicating formation of medium to reasonably high molecular weight polymers. These polyamides were soluble in NMP, DMAc, DMF, etc. This indicates that the incorporation of pendent flexible pentadecyl chains and $–CF_3$ group lead to a significant improvement in solubility of polyamides. Wide angle X-ray diffraction patterns indicated that these polyamides containing pendent pentadecyl chains and $–CF_3$ group were amorphous in nature, which is also reflected into solubility in polar aprotic organic solvent. T_{10} values for these polyamides were in the range 351-448°C indicating good thermal stability of polyamides. T_g values of these polyamides were in the range 150-175°C. The depression in T_g values of polyamides could be attributed to the presence of pendent pentadecyl chains and $–CF_3$ group. A large difference in T_g and initial decomposition temperature of these polyamides offers a broad processing window.

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