
SYNTHESIS AND CHARACTERIZATION OF NOVEL POLY (AMIDE-AMIDE)S CONTAINING BULKY TETRAPHENYL THIOPHENE UNIT.



Avinash S. Patil

Department of General Science, Brahmaveddada Mane
Institute of Technology, Solapur, India.

ABSTRACT:

A novel aromatic diamine, 2,5-bis-[4''-aminobenzyl]-4'-benzamide]-3,4-diphenyl thiophene (BATP) containing bulky tetraphenyl thiophene group, methylene spacer and preformed amide linkage was synthesized and characterized by FT-IR, NMR (^1H , ^{13}C , DEPT ^{13}C) and Mass spectrometry. A series of novel aromatic-aliphatic poly(amide-amide)s was successfully prepared from BATP and different aliphatic / aromatic diacids using Yamazaki's phosphorylation method. Triphenyl phosphite was used as a condensing agent. All the poly(amide-amide)s were obtained in very good yields and were characterized by FT-IR Spectroscopy, viscosity measurements, solubility tests, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The inherent viscosities (η_{inh}) of these poly(amide-amide)s were in the range 0.32-0.57 dL/g in DMAc at 30 ± 0.1 °C; indicating moderate to high molecular weight buildup. The poly(amide-amide)s were readily soluble in aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethyl sulphoxide (DMSO), N,N-dimethylformamide (DMF), pyridine etc. which is supported by the XRD results showing that the poly(amide-amide)s were amorphous. The glass transition temperature (T_g) of these poly(amide-amide)s were in the range 237 to 244 °C. The thermogravimetric analysis of all polymers showed no weight loss below 312°C whereas the char yields at 900 °C were in the range 44 to 62 % indicating high thermal stabilities of these polymers. Thus these polymers meet high temperature resistant requirements and are processable (soluble in polar aprotic solvents, T_g : 237-244 °C) so could find applications as special materials in aerospace, military and microelectronics industries. The structure-property correlation among these polyamides is discussed.

KEYWORDS: 2,5-Bis-[4''-aminobenzyl]-4'-benzamide]-3,4-diphenyl thiophene; Yamazaki's phosphorylative polycondensation, soluble poly(amide-amide)s; thermogravimetric analysis (TGA), structure-property relations.

INTRODUCTION

During the development of a new, synthetic polymer many factors need to be taken into consideration that will allow the production of a material with the desired chemical and physical properties. One factor that is often highly influential upon polymer design is the ease of processability. Clearly, materials that are easier to process will also be more commercially viable. The properties those determine how facile a polymeric material is to process are mainly glass transition temperature (T_g) and solubility, especially in common and environmentally acceptable solvents.

Aromatic polyamides have found use in a wide variety of applications since they possess many desirable characteristics, such as excellent mechanical properties, good thermal stability and high solvent resistance.¹⁻⁴ However, they have traditionally been difficult to process due to their high T_g values and poor solubility in organic solvents. Research has therefore been directed towards the preparation of high temperature polymers which are melt-processable or possess good solubility properties. The successful approaches employed to improve processability, without causing any detrimental effect upon any of the other mechanical and thermal properties include, introduction of flexible bridging units⁵⁻⁷, cardo groups^{8,9}, pendant phenyl groups^{10,11}, unsymmetrical¹²⁻¹⁴ and alicyclic units¹⁵⁻¹⁷, within the macromolecular backbone. These structural modifications could increase the overall chain flexibility, lower the T_g and enhance solubility.

In continuation of our efforts to obtain processable high performance polymers¹⁸⁻²⁰ in the present investigation a novel aromatic diamine, 2,5-bis-[4''-aminobenzyl]-4'-benzamide]-3,4-diphenyl thiophene (BATP) containing bulky tetraphenyl thiophene group, methylene spacer and preformed amide linkage was synthesized and characterized by FT-IR, NMR (¹H, ¹³C, DEPT ¹³C) and Mass spectrometry. A series of novel aromatic-aliphatic poly(amide-amide)s was successfully prepared from BATP and different aliphatic / aromatic diacids using Yamazaki's phosphorylation method. All the poly(amide-amide)s were characterized by FT-IR Spectroscopy, viscosity measurements, solubility tests, DSC, TGA and XRD.

EXPERIMENTAL

Materials

Commercially available sulphur was purified by dissolving sulphur with calcium oxide in water and the filtrate was precipitated with conc. hydrochloric acid. Benzyl chloride was fractionally distilled. N-Methyl-2-pyrrolidone (NMP), N, N-dimethyl acetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves 4 Å. Pyridine was refluxed over potassium hydroxide pellets under nitrogen, distilled and stored over 4 Å molecular sieves. 4-Nitrophenylacetic acid, terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were synthesized and purified by reported procedure. Lithium chloride (LiCl) was dried under vacuum at 150 °C for 6 h. Triphenyl phosphite (Merck) was used as received.

Measurements

All melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. The transmission IR spectra of polymers were recorded as a KBr pellet on a Perkin-Elmer 883 IR spectrophotometer. ¹H-NMR spectra and ¹³C-NMR spectra were recorded on a Bruker NMR spectrophotometer (400 MHz) in DMSO-d₆. Mass spectra were recorded on IIMS 30 double beam mass spectrometer. Inherent viscosity measurements were made with a 0.5% (w/v) polyamide solution in DMAc at 30 ± 0.1 °C using suspended level Ubbelohde viscometer. The solubility of polymers was determined at 3 wt % concentration in various solvents at room temperature or on warming if needed. Differential scanning calorimetry (DSC) analysis was performed on Q10 TA Instrument at a heating rate of 20 °C/min and thermogravimetric analysis (TGA) was performed on TGA Q5000 at a heating rate of 10 °C/min under a flow of nitrogen gas. Wide angle X-ray diffraction (WAXD) measurements were made in the powder form of polyamides on Jeol JDX-8030 X-ray diffractometer with nickel filtered CuK α ($\lambda = 1.5418$ Å)

Monomer Synthesis

The novel diamine, 2,5-bis-[(4''-aminobenzyl)-4'-benzamide]-3,4-diphenyl thiophene (BATP) was synthesized starting from benzyl chloride and sulphur.

Synthesis of 2,5-Bis-[(4''-nitrobenzyl)-4'-benzamide]-3,4-diphenyl thiophene (BNTP) (II): A 250 mL three necked round bottom flask equipped with a water condenser, a calcium chloride guard tube, a magnetic stirrer, a nitrogen gas inlet and a thermowell was flame dried under flow of nitrogen gas. N-Methyl-2-pyrrolidone (NMP) 64 mL, pyridine 16 mL, 2, 5-bis-(4'-aminophenyl)-3, 4-diphenyl thiophene (I)²¹ 20.9 g (0.05 mol) and 4-nitrophenylacetic acid 18.1 g (0.1 mol) were charged. Triphenyl phosphite (TPP) 37.2 mL (0.12 mol) was added and the reaction mixture was heated to 110 °C under stirring, where reaction mixture was maintained for 12 h. The reaction mixture was then cooled and poured into excess water, to precipitate the dinitro (BNTP) product (II), which was filtered, washed with sodium bicarbonate solution and then with hot water. It was dried under vacuum at 80 °C, and recrystallized from aqueous acetone to get pure (II).

Yield: 32.5 g (87.3 %), M.P.: 270-272 °C.

IR (KBr pellet): 3313 (-NH stretch), 1668 (amide I, C=O stretching) and 1597 (CONH, amide II, N-H deformation), 1521 and 1344 (NO₂), 2918, 2857 cm⁻¹(in plane and out of plane stretching vibrations of methylene group). Mass: m/e 745 corresponding to (M+1) ion, 581 (loss of -COCH₂PhNO₂ group).

Synthesis of 2, 5-Bis-[(4''-aminobenzyl)-4'-benzamide]-3, 4-diphenyl thiophene (BATP) (III): In a 250 mL three necked round bottom flask equipped with a water condenser and a magnetic stirrer, a mixture of 7.44 g (0.01 mol) BNTP (II), 0.297 g 10 % Pd/C and 110 mL ethanol were placed. The mixture was heated to reflux and 15 mL 99 % hydrazine monohydrate was added dropwise through dropping funnel over 1 h. After additional 4 h. of refluxing, the resulting clear, dark solution was filtered while hot to remove Pd/C and the filtrate was subjected to distillation to remove part of solvent. The concentrated solution was poured into 200 mL water with stirring, giving out an off white product, which was filtered, washed with water till free from hydrazine hydrate. The product was recrystallized from ethanol and vacuum dried at 80 °C for 6 h. Yield: 5.10 g (79.1 %), M.P.: 260-262 °C.

IR (KBr pellet): 3435 and 3396 (-NH₂), 3350 (-NH), 1662 (amide I, C=O stretching) and 1591 (CONH, amide II, N-H deformation). Mass: m/e 685 corresponding to (M+1) ion, 551(loss of -COCH₂PhNH₂ group).

Polymer Synthesis: Poly(amide-amide) [TYPA-1] from III and adipic acid by Yamazaki's phosphorylation method.

In a 100 mL three necked round bottom flask equipped with a reflux condenser, a magnetic stirrer, a calcium chloride guard tube and a nitrogen gas inlet were placed 0.684 g (1mmol) 2, 5-Bis-[(4''-aminobenzyl)-4'-benzamide]-3, 4-diphenyl thiophene (BATP) (III), 0.146 g (1mmol) adipic acid, 0.2 g lithium chloride [8 wt % based on solvent N-methyl pyrrolidone (NMP) and pyridine mixture] and 0.744 .g (0.63 mL, 2.4mmol) triphenyl phosphite (TPP), 0.5 mL pyridine and 3 mL NMP. The mixture was stirred well and temperature was slowly raised to 100 °C over a period of 30 min. and the mixture maintained at 100 °C for 3 h. After cooling, the resultant viscous solution was poured into rapidly stirred methanol 200 mL. The precipitated polymer (TYPA-1) was filtered, washed with methanol and dried under vacuum at 100 °C for 8h. The yield was 99 % and the inherent viscosity of polymer in DMAc was 0.44 dL/g.

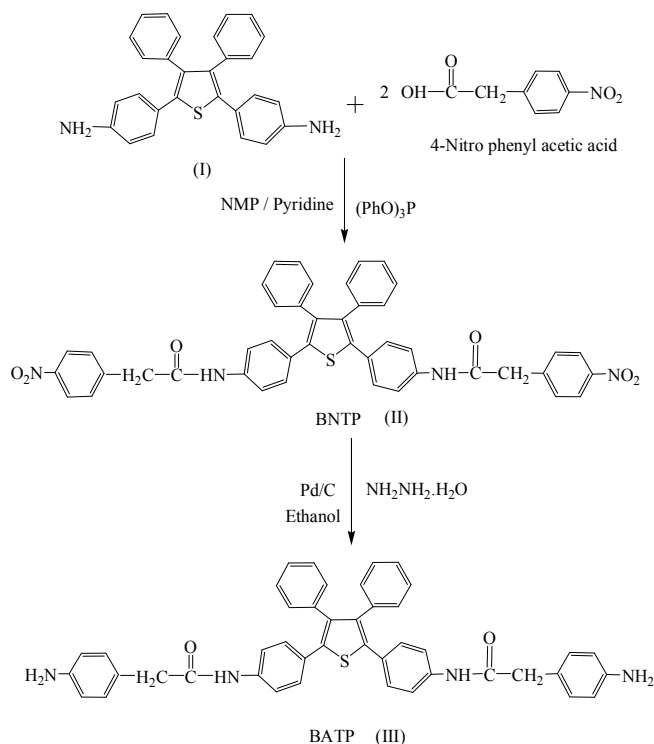
All other polyamides i.e. TYPA-2 to TYPA-6 were synthesized by a similar procedure with different aliphatic/ aromatic diacids.

RESULTS AND DISCUSSION

The new aromatic diamine BATP (III) containing preformed amide and methylene linkage; in addition to tetraphenyl thiophene moiety was synthesized as shown in **Scheme 1**. In order to

introduce methylene and amide linkage in the aromatic diamine monomer, 4-nitrophenylacetic acid was taken as one of the starting material. Reaction of two moles of 4-nitrophenylacetic acid with 2,5-bis-(4'-aminophenyl)-3,4-diphenyl thiophene (I) by Yamazaki's phosphorylation method, using triphenyl phosphite (TPP) as a condensing agent afforded 2,5-Bis-[(4''-nitrobenzyl)-4'-benzamide]-3,4-diphenyl thiophene (BNTP) (II). This dinitro compound BNTP (II) was converted into the novel aromatic diamine 2,5-Bis-[(4''-aminobenzyl)-4'-benzamide]-3,4-diphenyl thiophene (BATP) (III) by reduction with hydrazine monohydrate and Pd/C (10%) catalyst in ethanol.

The structures of BNTP and BATP were confirmed by FT-IR, NMR (^1H and ^{13}C) and mass spectrometry. IR spectrum of BNTP showed characteristic absorption bands at 1521 and 1344 cm^{-1} corresponding to NO_2 group. The ^1H NMR spectrum is consistent with the structure of BNTP in which signal at δ 9.52 (s) was due to amide NH proton. The NMR signals in the range δ 6.9 to 7.6 (18 H) were attributed to the aromatic protons of tetraphenyl moiety and the signals in the range δ 7.6 to 8.2 (d, 8 H) are assigned to aromatic protons of nitro substituted phenylene unit. The sharp signal at δ 3.8 (singlet) was assigned to CH_2 protons. ^{13}C NMR of BNTP showed 16 different peaks corresponding to 16 carbons; of which signal at δ 167.72 was due to carbonyl carbon of amide group, where as carbon of CH_2 appeared at δ 43.17. All aromatic carbons were in the range of 118.72-146.98. In the DEPT ^{13}C NMR of BNTP, peak of $-\text{CH}_2-$ appeared as negative signal at downside and $-\text{CH}-$ carbon remained upside and tertiary carbon peaks disappeared.



Scheme 1 Synthesis of 2,5-bis-[(4''-aminobenzyl)-4'-benzamide]-3,4-diphenyl thiophene (BATP)

The infrared spectrum of BATP showed characteristic absorption bands at 3435 and 3396 cm^{-1} due to $-\text{NH}_2$ group with corresponding disappearance of absorption bands at 1521 and 1344

cm^{-1} of NO_2 group indicating complete reduction of nitro functionality to amine. The ^1H NMR spectrum (**Figure 1**) is also consistent with the structure of BAPT in which signals at δ 4.94 (s, broad) and δ 10.05 (s) are related to NH_2 (amino group) and NH protons (amide group) respectively. Aromatic protons of tetraphenyl moiety (18 H) and phenyl ring with amino group (8 H) appeared in the range δ 6.46 to 7.46, whereas peak at δ 3.37 was assigned to CH_2 protons.

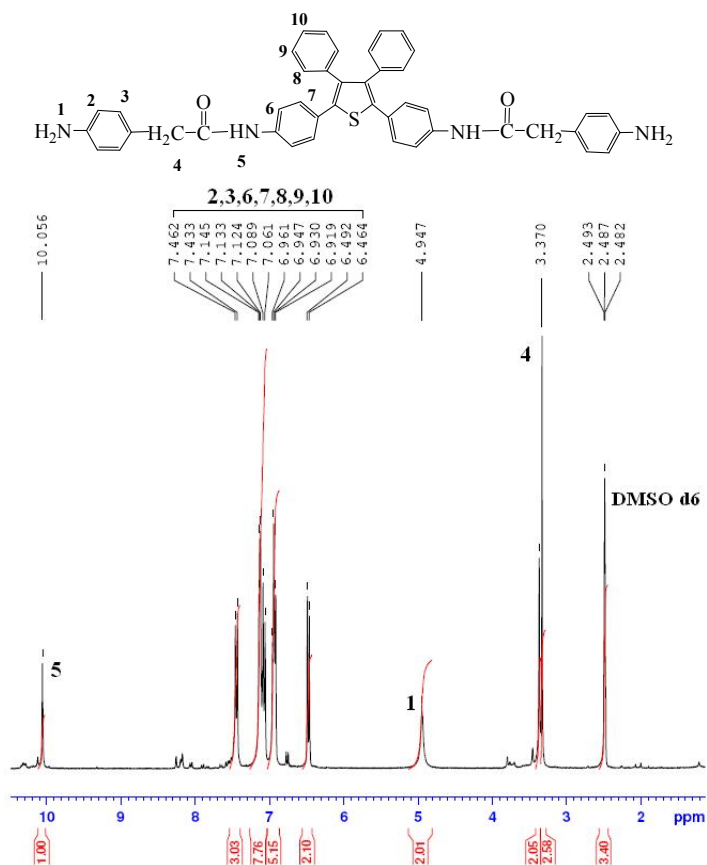


Figure 1 ^1H NMR spectrum of BAPT

^{13}C NMR of BAPT (**Figure 2**) also showed 16 different peaks corresponding to 16 carbons; of which signal at δ 170.50 was assigned to amide carbonyl carbon, where as carbon of CH_2 appeared at δ 43.13. All aromatic carbons were in the range of 114.27-147.68; of which tertiary carbons appeared at 147.68 ($\text{C}-\text{NO}_2$), 139.49, 139.18, 137.61, 136.51 and 128.55 where as CH aromatic were at δ 130.91, 129.86, 129.51, 128.39, 127.30, 123.09, 119.28 and 114.27. This was confirmed by DEPT ^{13}C NMR of BAPT, where in peak of $-\text{CH}_2-$ appeared downside, $-\text{CH}-$ carbons remained upside at δ 130.91, 129.86, 129.51, 128.39, 127.30, 123.09, 119.28 and 114.27 and tertiary carbon peaks disappeared.

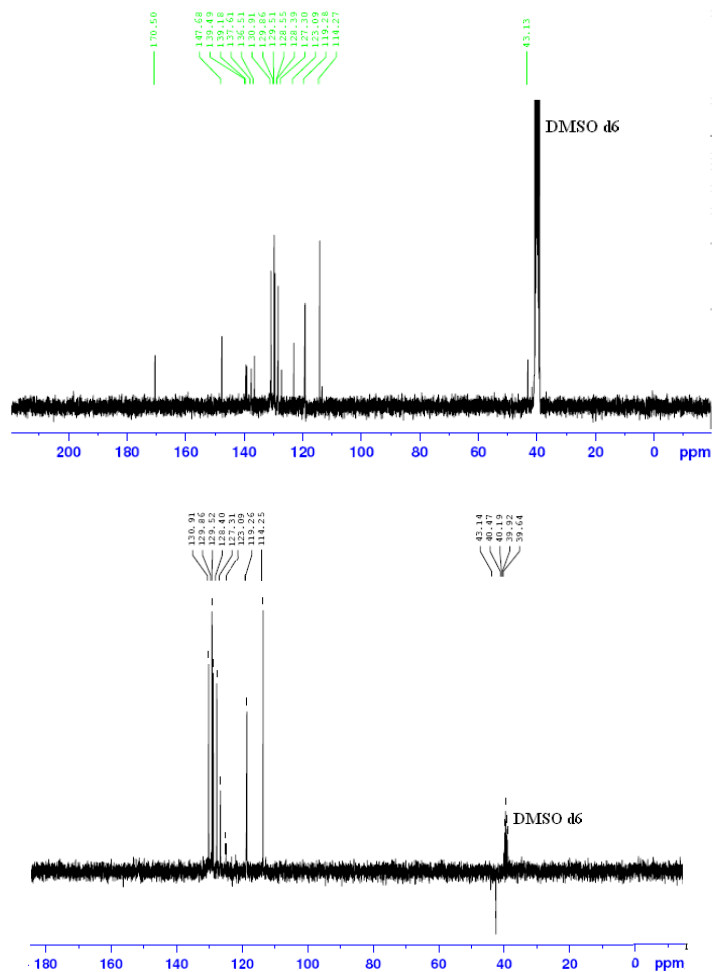


Figure 2 ^{13}C NMR and DEPT ^{13}C NMR spectra of B ATP

Conventionally; aromatic polyamides are prepared by the polycondensation of diacid chlorides with diamine in the presence of an acid acceptor in a polar aprotic solvent. However, preparation; purification and storage of diacid chlorides are troublesome. Hence the direct polycondensation of diacid as reported by Yamazaki²² was used in the synthesis of polyamides from B ATP. A series of novel aromatic – aliphatic poly(amide-amide)s bearing tetraphenyl thiophene moiety, preformed amide and methylene linkage was successfully prepared by polymerization of B ATP with different aliphatic / aromatic diacid by the Yamazaki's procedure (**Scheme 2**). Triphenyl phosphite was used as the condensing agent, wherein the mixture of NMP and pyridine (4:1 by volume), containing 8 wt. % anhydrous lithium chloride, was employed as solvent. The polymerization was carried out at 100 °C for 3 h under nitrogen. The polymerization preceded smoothly giving viscous solutions. The resulting polymers were precipitated by pouring the viscous solution in methanol.

Table 1 Yield, inherent viscosity of Poly(amide-amide)s^a from BATP^b and different diacids

Serial No.	Polymer Code	Diacid	Yield (%)	Inherent Viscosity ^c η_{inh} , (dL/g)
1.	TYP A-1	Adipic acid	99	0.44
2.	TYP A-2	Azelic acid	99	0.54
3.	TYP A-3	Sebasic acid	98	0.54
4.	TYP A-4	Isophthalic acid	98	0.53
5.	TYP A-5	Terephthalic acid	99	0.57
6.	TYP A-6	4, 4' Oxy bis (benzoic acid)	98	0.32

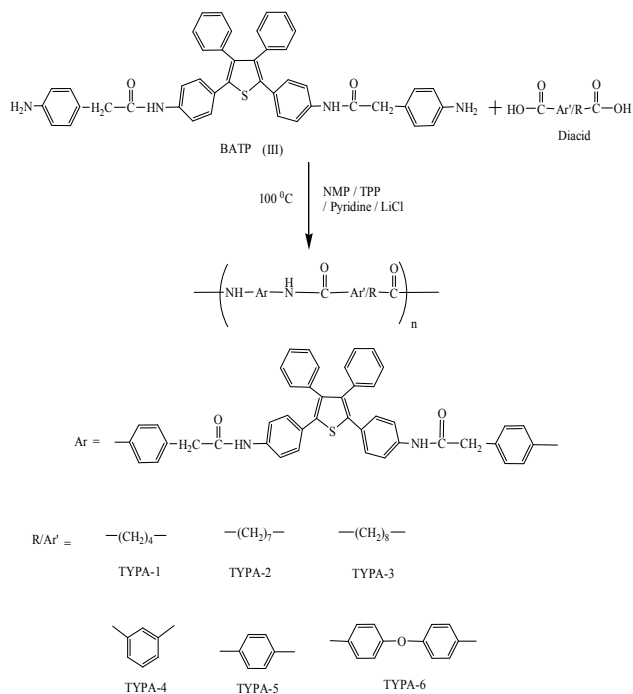
^a Polymerization was carried out with 1 mmole each of BATP and diacid.

^b BATP, 2, 5-Bis-[(4''-aminobenzyl)-4'-benzamide]-3, 4-diphenyl thiophene.

^c Measured with a 0.5 % (w/v) polymer solution in DMAc at 30 ± 0.1 °C.

The yields and viscosities of all poly(amide-amide)s are summarized in **Table 1**. All the polymers were obtained in almost quantitative yields (more than 98 %). The inherent viscosities were in the range 0.32 to 0.57 dL/g in DMAc indicating moderate to high molecular weight build up. Inherent viscosity of polyamide TYP A-5 based on TPA was highest among the series.

The formation of the poly(amide-amide)s was confirmed by FT-IR spectroscopy. All polyamides showed characteristic amide absorption bands at 3286-3298 cm⁻¹(amide -NH stretching), 1660-1667 (amide-I, C=O stretching) and 1595-1599 cm⁻¹ (amide-II,-NH deformation).



Scheme 2 Synthesis of Poly(amide-amide)s from B ATP and various diacids

Solubility characteristics of all poly(amide-amide)s were determined in different organic solvents with 3% polymer concentration. All polyamides showed better solubility (**Table 2**) in organic solvents such as NMP, DMAc, DMSO, DMF, m-cresol and pyridine. Improved solubility character can be attributed to the introduction of bulky highly phenylated thiophene moiety in addition to preformed amide and aliphatic methylene group in the polymer backbone which hindered chain packing and formed amorphous polymers. All polymers were insoluble in solvents like CHCl_3 , DCM, acetone and THF etc.

Table 2 Solubility of Poly(amide-amide)s from B ATP.

Polymer → Solvent ↓	TYPA-1	TYPA-2	TYPA-3	TYPA-4	TYPA-5	TYPA-6
DMAc	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	++	++	++	++
DMF	++	++	++	++	++	++
Pyridine	++	++	++	++	+ -	++
m-cresol	++	++	+	++	+	++
H_2SO_4	++	++	++	++	++	++

(++): Soluble at room temperature (+): Soluble on heating
(+ -) : Partially soluble (--) : Insoluble

The thermal behavior of these polyamides was evaluated by differential scanning calorimetry and thermogravimetry. The thermal stability has been probed by traditional analysis, namely thermogravimetric analysis (TGA) at 10 °C / min heating rate in nitrogen to evaluate the degradation occurring via weight loss. The DSC curves of all poly(amide-amide)s are shown in **Figure 3** whereas TG curves are shown in **Figure 4**. **Table 3** incorporates the thermal data such as glass transition temperature (T_g), initial decomposition temperature (T_i), 10% weight loss temperature (T_{10}), temperature of maximum rate of decomposition (T_{max}) and residual weight at 900 °C.

The polyamides had glass transition temperatures in the narrow range 237 to 244 °C. This close range of T_g s probably indicated that the T_g s of these polyamides were mainly dependent on diamine structure and had no major contribution from diacid units.

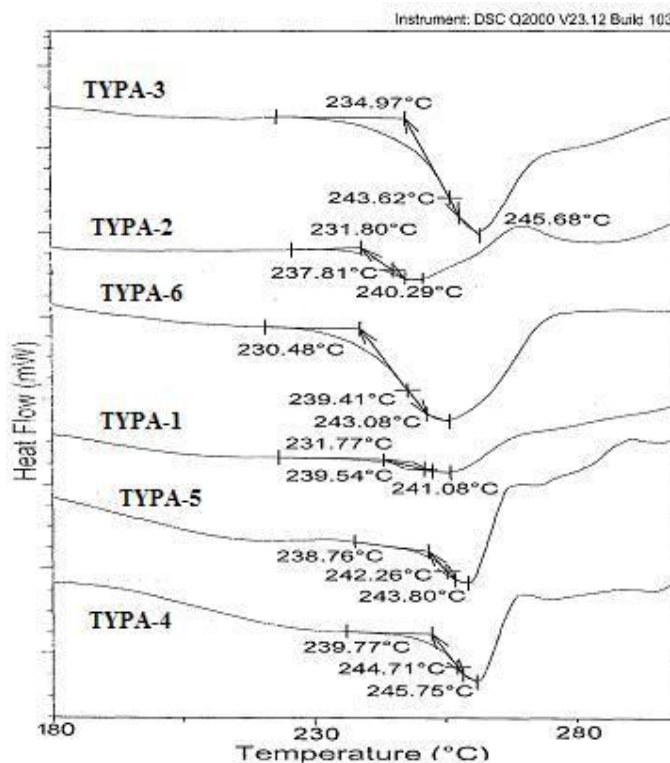


Figure 3 DSC curves of Poly(amide-amide)s TYPA-1 to TYPA-6

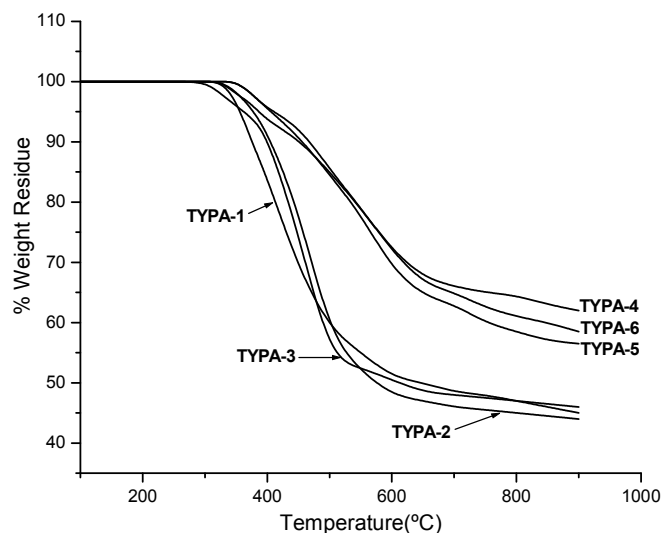


Figure 4 TG curves of Poly(amide-amide)s TYPA-1 to TYPA-6

Table 3 Thermal properties^a of Poly(amide-amide)s from BATP.

Polymer code	^b T _i (°C)	^c T ₁₀ (°C)	^d T _{max} (°C)	Residual Wt. (%) at 900 °C	^e T _g (°C)
TYPA-1	325	375	498	45	239
TYPA-2	329	405	470	44	237
TYPA-3	312	409	465	46	243
TYPA-4	350	466	555	62	244
TYPA-5	342	457	530	56	242
TYPA-6	325	452	531	58	239

^a Thermogravimetric analyses were conducted at a heating rate of 10 °C / min under nitrogen.

^b Temperature at which weight loss initiated.

^c Temperature at which 10 % weight loss was observed.

^d Temperature at which maximum rate of weight loss was observed.

^e Determined by DSC measured at a heating rate 20 °C/min

All these polyamides showed a similar pattern of decomposition with no weight loss below 312 °C. The polymers showed T_i and T₁₀ values in the range 312 to 350 and 375 to 466 °C respectively whereas T_{max} values between 465 to 555 °C and the char yields at 900 °C were in the range 44 to 62 %, meaning that they are excellent in performance as a high-temperature polymer. The aromatic polyamides (TYPA-4 to TYPA-6) showed char yields of 56 to 62 % when heated to 900 °C under nitrogen atmosphere, whereas the char yield values of aliphatic- aromatic polyamides (TYPA-1 to TYPA-3) ranged from 44 to 46 %. The increase in char yields of the aromatic polyamides

was most obviously due to the higher content of aromatic groups which has good char concentration.

A comparative study of thermal data from TGA of polyamides TYPA-1 to TYPA-3 and TYPA-4 to TYPA-6 showed that the latter polyamides (aromatic) commence to slowly lose weight with T_{10} and T_{max} values of 452 to 466 °C and 530 to 555 °C respectively; which are naturally on higher side than T_{10} (375 to 409 °C) and T_{max} (465 to 498 °C) values of polyamides TYPA-1 to TYPA-3 due to the thermally labile flexible methylene groups, which are much inferior in thermal resistances, present in aliphatic diacid component in the TYPA-1 to TYPA-3 polyamides. Such decrease in thermal resistance is observed commonly in many rigid aromatic polymers with flexible aliphatic chains. The higher thermal stability of these polyamides may be attributed to the highly phenylated thiophene unit and preformed amide linkages and this shows that the introduction of highly phenylated thiophene unit into polymer backbone improved solubility without much effect on thermal stability.

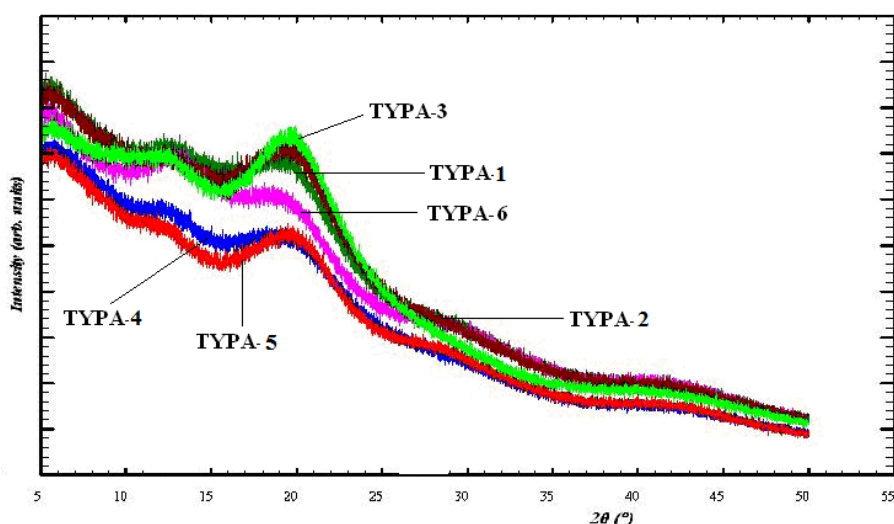


Figure 5 WAXD curves of Poly(amide-amide)s TYPA-1 to TYPA-6

To study the morphology of poly(amide-amide)s X-ray diffraction measurements were performed, and X-ray diffraction patterns of all polyamides are shown in **Figure 5**. It was observed that all polymers exhibited amorphous nature, which supported the better solubility of these polymers.

CONCLUSION

The synthesis of novel aromatic diamine monomer, B ATP, containing bulky tetraphenyl thiophene unit, methylene spacer and preformed amide linkage was successfully synthesized and characterized by FT-IR, NMR (^1H , ^{13}C , DEPT ^{13}C) and Mass spectrometry. A series of six poly(amide-amide)s was synthesized from B ATP and different diacids using Yamazaki's phosphorylation method. Triphenyl phosphite was used as condensing agent. All the polyamides were characterized by IR spectroscopy, inherent viscosity, solubility, XRD and thermal analysis. Because of the presence of a tetraphenyl thiophene moiety, aliphatic methylene spacer in addition to preformed amide linkage, the polyamides exhibited better solubility without having much of an effect on thermal stability. Thus these polyamides could be considered as new processable high performance polymeric materials to be used in a wide range of applications.

REFERENCES

1. Yang, H. H.; *Aromatic High-Strength Fibers*, Wiley, New York, 1989.
2. Liaw, D. J.; Wang, K. L. *J Polym Sci Polym Chem* 1996, 34, 1209.
3. Bellomo, M. R.; Di Pasquale, G.; La Rosa, A.; Pollicino, A.; Siracusa, G. *Polymer* 1996, 37, 2877.
4. Zulfiqar, S.; Ishaq, M.; Ahmad, Z.; Sarwar, M. I. *Polym Adv Technol* 2008, 19, 1250.
5. Scariah, K. J.; Krishnamurthy, V. N.; Rao, K. V. C.; Srinivasan, M. *J Macromol Sci Chem* 1985, 22, 1753.
6. Mahajan, S. S.; Sarwade, B. D.; Maldar, N. N. *Polym Bull* 1990, 24, 143.
7. Patil, A. S.; Sayyad, M. M.; Bhairamadgi, N. S.; Han, S. H.; Maldar, N. N. *Polym Bull* 2010, DOI 10.1007/s00289-010-0344-4
8. Hsiao, S. H.; Yang, C. P.; Chuang, M. H.; Lin, S. J. *J Polym Sci Polym Chem* 1999, 37, 4510.
9. Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. *J Polym Sci Polym Chem* 2000, 38, 74.
10. Kakimoto, M.; Negi, Y.; Imai, Y. *J Polym Sci Polym Chem* 1985, 23, 1787.
11. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem* 1985, 23, 1797.
12. Cheng, L.; Jian, X. G.; Mao, S. Z. *J Polym Sci Polym Chem* 2002, 40, 3489.
13. Pal, R. R.; Patil, P. S.; Salunkhe, M. M.; Maldar, N. N.; Wadgaonkar, P. P. *Eur Polym J* 2009, 45, 953.
14. In, I.; Kim, S. Y. *Polymer* 2006, 47, 547.
15. Matsumoto, T.; Kurosaki, T. *Macromolecules* 1995, 28, 5468.
16. Yang, C. P.; Su, Y. Y.; Hsiao, F. Z. *Polymer* 2004, 45, 7529.
17. Sheng, S. R.; Pei, X. L.; Huang, Z. Z.; Liu, X. L.; Song, C. S. *Eur Polym J* 2009, 45, 230.
18. Ubale, V. P.; Ghanwat, A. A.; Wadgaonkar, P. P.; Maldar, N. N.; *J Macromol Sci Part A Pure Appl Chem* 2008, 46, 1.
19. Ubale, V. P.; Sagar, A. D.; Maldar, N. N.; Birajdar, M. V. *J Appl Polym Sci* 2001, 79, 566.
20. Patil, V. B.; Sayyed, M. M.; Mahajan, P. A.; Wadgaonkar, P. P.; Maldar, N. N. *J Polym Res* 2010, DOI 10.1007/s10965-010-9448-7.
21. Imai, Y.; Maldar, N. N.; Kakimoto, M. *J Polym Sci Polym Chem* 1984, 22, 2189.
22. Yamazaki, N.; Masumoto, M.; Higashi, F. *J Polym Sci Polym Chem* 1975, 13, 1373.