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SYNTHESIS AND CHARACTERIZATION OF SOLUBLE POLY (AMIDE-IMIDE)S CONTAINING TETRAPHENYL THIOPHENE MOIETY.

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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 (^{1}H, ^{13}C, DEPT ^{13}C) and Mass spectrometry. A series of novel aromatic poly(amide-imide)s was successfully prepared from BATP and different aromatic dianhydrides using two-step solution polycondensation method. All the poly(amide-imide)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-imide)s were in the range 0.61-0.85 dL/g in DMAc at 30 ± 0.1 °C; indicating moderate to high molecular weight buildup. The poly(amide-imide)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-imide)s were amorphous. The glass transition temperature (T_g) of these poly(amide-imide)s were in the range 198 to 290 °C. The thermogravimetric analysis of all polymers showed no weight loss below 367°C whereas the char yields at 900 °C were in the range 55 to 61 % indicating high thermal stabilities of these polymers. Thus these polymers meet high temperature resistant requirements and are processable (soluble in polar aprotic solvents, Tg: 198-290 °C) so could find applications as special materials in aerospace, military and microelectronics industries. The structure–property correlation among these poly(amide-imide)s is discussed.

KEYWORDS:2,5-Bis-[4”-aminobenzyl)-4’-benzamide]-3,4-diphenyl thiophene; soluble poly(amide-imide)s; thermal stability.

INTRODUCTION:

Aromatic polyimides (PI) have been known for excellent electrical, thermo mechanical properties and chemical resistance[1, 2]. However, the strong interaction and the rigidity of the polymer chains make them insoluble and infusible, which limit its application area. In order to overcome these problems, several approaches such as introduction of flexibilizing groups[3], bulky groups[4,5], cardo groups[6], molecular asymmetry[7] etc. have been reported with varying success via the synthesis of new diamines and dianhydrides or by making copolymers which contain either ester or amide group in polyimides; thereby making poly(ester-imide) or poly(amide-imide). As the results, processable polyimides / modified polyimides have been developed and the most representative one is poly (amide-imide) (PAI).

In the present investigation, we report the synthesis of a series of novel aromatic poly(amide-imide)s from diamine, 2,5-bis-[4”-aminobenzyl)-4’-benzamide]-3,4-diphenyl thiophene (BATP), containing bulky pendant tetraphenyl thiophene group, methylene spacer and preformed amide linkage with five commercially available aromatic dianhydrides using a standard two stage process with thermal imidization of the precursor poly(amic-acid)s. The resulting polymers were characterized by FT-IR Spectroscopy, viscosity measurements, solubility tests, DSC, TGA and XRD.

Experimental:

Monomer Synthesis:

Synthesis of 2,5-Bis-[(4”-nitrobenzyl)-4’-benzamide]-3,4-diphenyl thiophene (BNTP)

In a 250 mL three necked round bottom flask NMP 64 mL, pyridine 16 mL, 2, 5-bis-(4’-aminophenyl)-3, 4-diphenyl thiophene (TPTPDA) 20.9 g (0.05 mol) and 4-nitrophenylacetic acid 18.1 g (0.1 mol) were charged. Triphenyl phosphite 37.2 mL (0.12 mol) was added and the reaction mixture was heated to 110 °C under stirring for 12 h. The reaction mixture was poured into water; the dinitro (BNTP) product was filtered, washed with sodium bicarbonate solution and hot water. Recrystallized from acetone and water mixture gave pure product. Yield: 32.5 g (87.3 %), M.P.: 270-272 °C.

ANAL.: IR : 3313, 1668 and 1597, 1521, 1344 and 2918, 2857 cm^{-1}. Mass: m/e 745 (M+1) ion.

Synthesis of 2, 5-Bis-[(4”-aminobenzyl)-4’-benzamide]-3, 4-diphenyl thiophene (BATP): In a 250 mL three necked round bottom flask a mixture of 7.44 g (0.01 mol) of BNTP, 0.297 g 10 % Pd/C and 110 mL ethanol were placed. The mixture was heated to reflux and 15 mL 99 % hydrazine hydrate was added dropwise 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, the concentrated solution was poured into 200 mL water. Product was filtered, washed with water, recrystallized from ethanol and vacuum dried at 80 °C for 6 h. Yield: 5.10 g (79.1 %), M.P.: 260-262 °C.
ANAL.: IR 3435 and 3396, 3350, 1662 and 1591. Mass: m/e 685 (M+1) ion,

Polymer Synthesis:

Synthesis of the poly (amide-imide), TPI-1 from BATP and BTDA: To a 100 mL flame dried three-necked, round bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet and a calcium chloride guard tube, the diamine, BATP (0.684 g, 1 mmol) and NMP (4.5 mL) were added, stirred to form homogenous solution and cooled to 0 °C in ice bath. To this cold solution, BTDA (0.322 g, 1 mmol) was added in small quantity lots over a period of 1 h. The stirring was continued for additional 2 h at 0 °C and then at room temperature for 12 h under nitrogen atmosphere to afford a highly viscous poly(amic acid) solution.

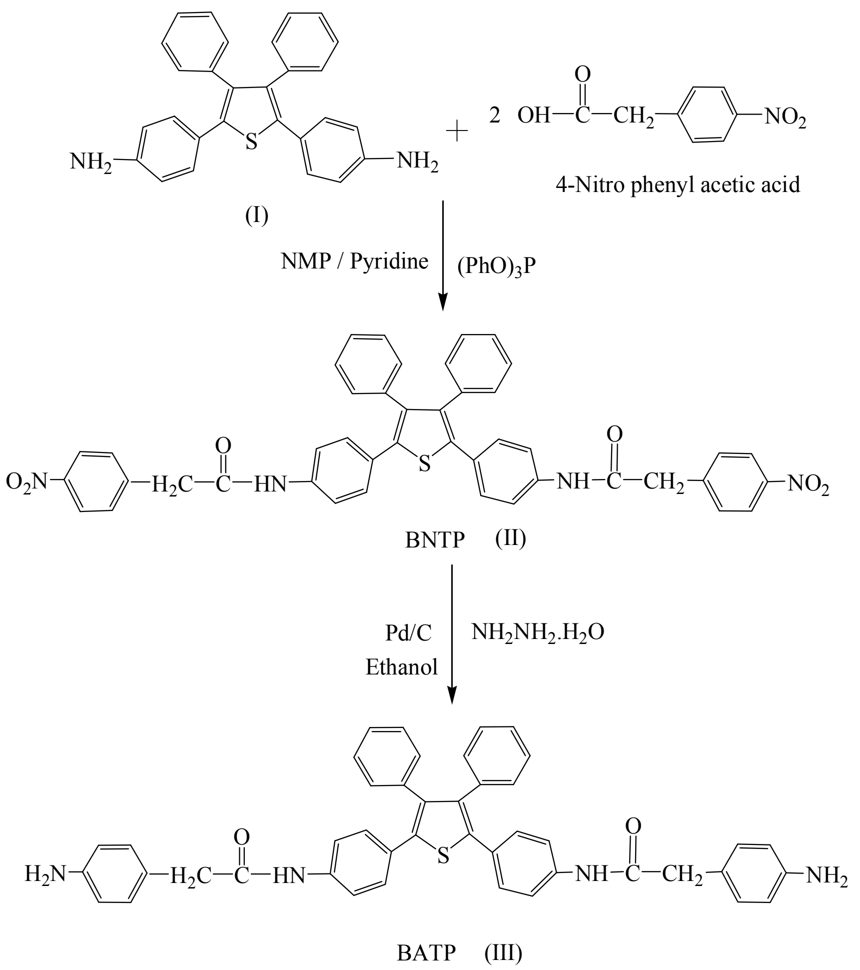
A part of viscous solution was poured into methanol (100 mL) with rapid stirring to precipitate poly(amic acid). The precipitated polymer was filtered, washed with methanol and dried under reduced pressure at 25 °C. Poly(amic acid), PAA, was characterized by FT-IR spectroscopy and inherent viscosity; η_{inh} 0.85 dL/g.

For the thermal imidization, the remaining poly(amic acid) solution was cast onto a clean glass plate and heated (100 °C/ 1 h, 150 °C / 1 h, 200 °C / 1 h and finally at 320 °C / 20 min) to produce a fully imidized polyimide film. Other poly(amide-imide)s, TPI-2 to TPI-5 were synthesized by similar procedure using different dianhydrides.

RESULT AND DISCUSSION:

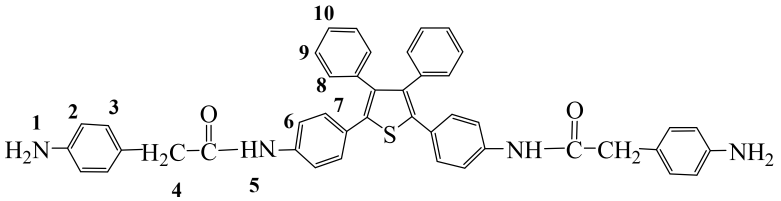
The new diamine BATP was synthesized by reaction of two moles of 4-nitrophenylacetic acid with TPTPDA by Yamazaki’s phosphorylation method, using TPP as a condensing agent to give BNTP; which was converted into BATP by reduction with hydrazine monohydrate and Pd/C (10%) catalyst in ethanol (**Scheme 1**).

The structures of BNTP and BATP were confirmed by IR, NMR (^{1}H and ^{13}C) UV-VIS and mass spectrometry. The ^{1}H 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 (d, 18 H) and δ 7.6 to 8.2 (d, 8 H) were attributed to the aromatic protons. 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 is 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. DEPT ^{13}C NMR of BNBE confirmed the structure.



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

The ^{1}H NMR spectrum of BATP **(Figure 1)** was also consistent with the structure. 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 appeared in the range δ 6.46 to 7.46 as doublets, whereas peak at δ 3.37 ppm is assigned to CH_2 protons. ^{13}C NMR of BATP also showed 16 different peaks corresponding to 16 carbons; of which signal at δ 170.50 is due to amide carbonyl carbon, where as carbon of CH_2 appeared at δ 43.13. All aromatic carbons were appeared in the range 114.27-147.68 δ. In DEPT ^{13}C NMR of BATP was in good agreement of proposed structure.



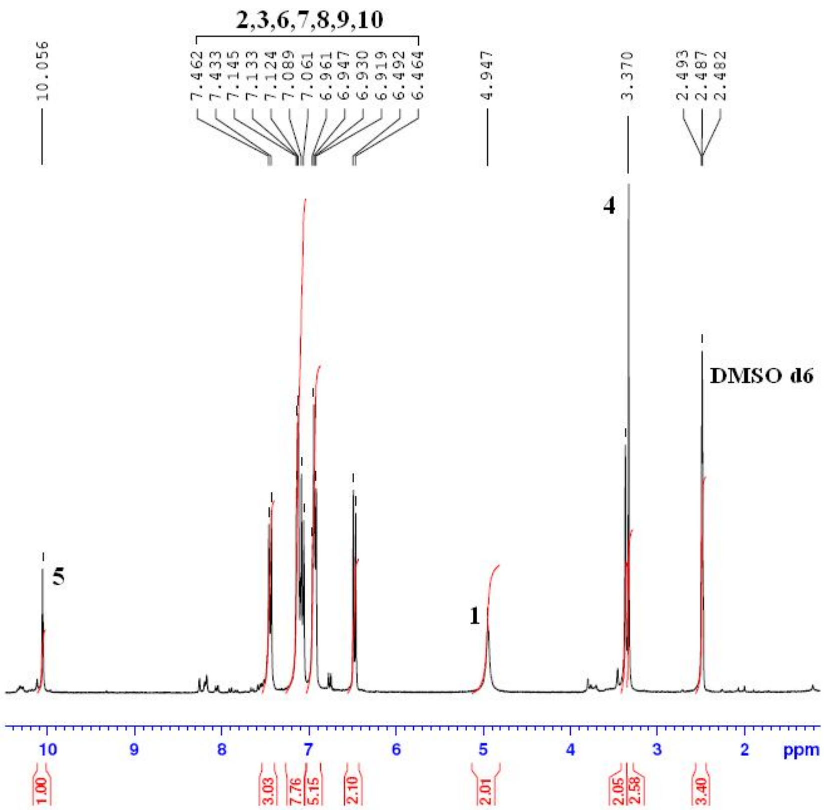
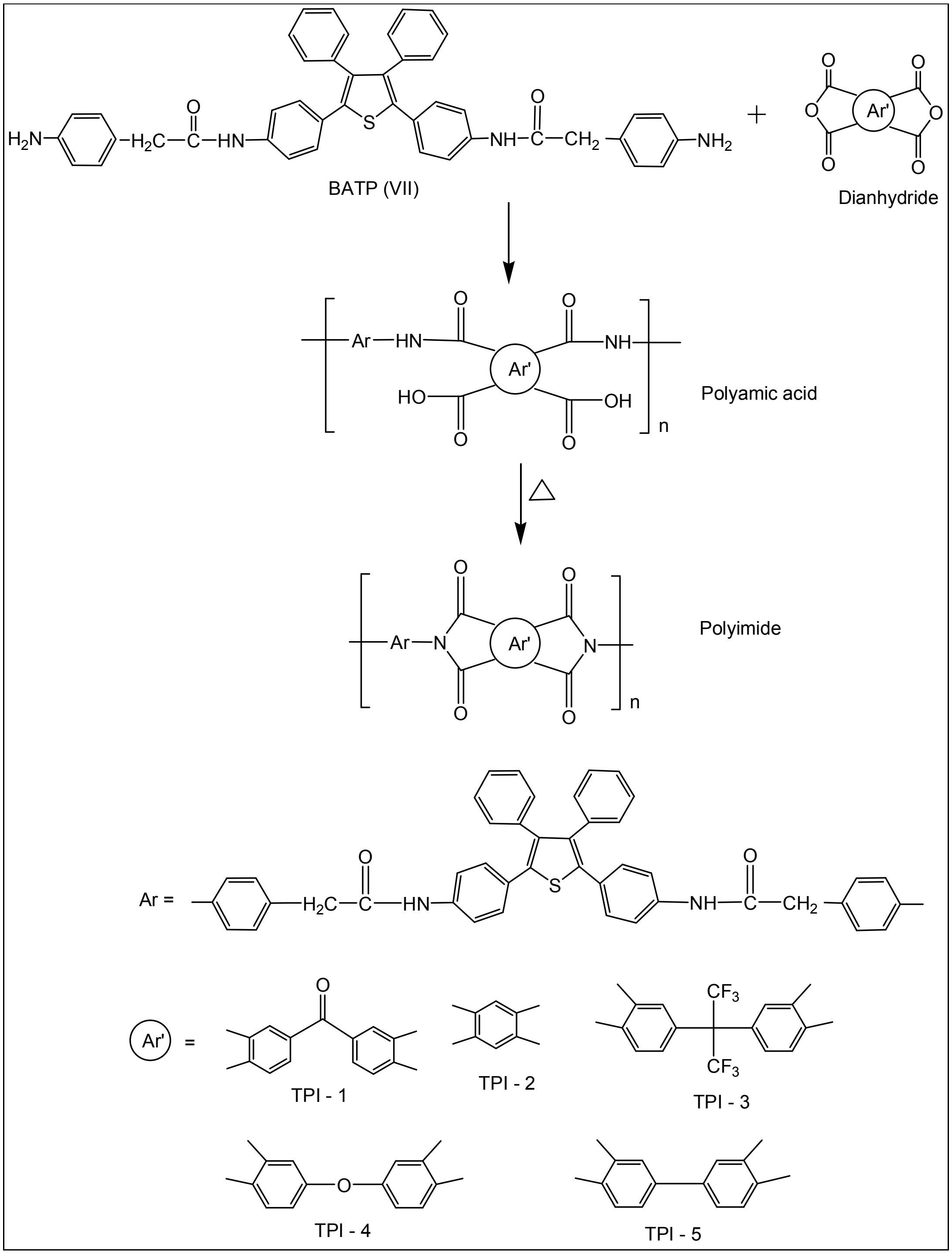


Figure 1 ^{1}H NMR spectrum of BATP

A series of poly(amide-imide)s were synthesized (**Scheme 2**) by the reaction of stoichiometric quantities of BATP and aromatic dianhydrides such as BTDA, PMDA, 6-FDA, ODPA and BPDA using a standard two step process. Step I involved conventional ring-opening polycondensation of BATP with the dianhydrides in NMP at low temperature to form linear open chain poly(amic acid). In the step II the conversion of poly(amic acid) to polyimides was performed by chemical and then thermal process for the subsequent cyclodehydration to form poly(amide-imide)s.



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

The results of synthesis on poly(amide-imide)s are presented in **Table 1**. All the polymers were obtained in the quantitative yields (more than 97 %). The inherent viscosities of these poly(amic acid)s were in the range 0.61 to 0.85 dL/g; indicating the formation of moderate to high molecular weight polymers.

Table 1: Inherent viscosity and Thermal properties of Poly(amide-imide)s

Sr. No.	Polymer Code	Dianhydride	Inherent Viscosity η_{inh}, (dL/g)	T_i (°C)	Residual Wt. (%) at 900 °C	T_g (°C)
1.	TPI-1	BTDA	0.85	367	55	230
2.	TPI-2	PMDA	0.74	383	61	290
3.	TPI-3	6-FDA	0.77	375	58	200
4.	TPI-4	OPDA	0.61	379	60	198
5.	TPI-5	BPDA	0.64	372	59	279

The formation of the polyimides was confirmed by FT-IR spectra. All poly(amide-imide)s showed characteristic imide group absorptions at around 1781 (asymmetrical C=O stretching) and 1720 (symmetrical C=O stretching), 1376 (C-N stretching), 3350-3450 (N-H stretching of preformed amide), 1104 and 720 cm^{-1} (Imide ring deformation). All polyimides showed better solubility in solvents such as NMP, DMAc, DMSO, DMF, hot m-cresol. Improved solubility character can be attributed to the introduction highly phenylated thiophene moiety and aliphatic methylene group in the polymer backbone.

The thermal behavior of these poly(amide-imide)s was evaluated by differential scanning calorimetry / thermogravimetry. The polyimides had glass transition temperatures in the range 198 to 290 °C. All these polyimides showed no weight loss below 367 °C. The polymers showed T_i and T_{10} values in the range 367 to 383 and 438 to 496 °C respectively whereas T_{max} values were between 564 to 599 °C and the char yields at 900 °C were in the range 55 to 61 % indicating the high thermal stability of poly(amide-imide)s. This shows that the introduction of phenyl groups and methylene spacer in to polymer backbone improved solubility without much adverse effect on thermal stability. X-ray diffraction measurements indicated that all poly(amide-imide)s exhibited amorphous nature, which supported the better solubility of these polymers.

CONCLUSION:

The synthesis of novel aromatic diamine monomer, BATP, containing bulky pendant tetraphenyl thiophene group, methylene spacer and preformed amide linkage was performed, characterized and a series of five poly(amide-imide)s was synthesized from BATP and different aromatic dianhydrides using two-step solution polycondensation method. The polymers were soluble in organic solvents and had excellent thermal stability. Thus these poly(amide-imide)s could be considered as new processable high performance polymeric materials.

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