

Preparation and Properties of Novel Thermally Stable Pyridine-Based Poly(amide imide amide)s

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Received 28 July 2010; accepted 10 October 2010

DOI 10.1002/app.33572

Published online 18 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The 2,6-bis(4-nitrobenzamido)pyridine was prepared via reaction of 2,6-diaminopyridine with two moles of 4-nitrobenzoyl chloride in the presence of propylene oxide. Catalytic reduction of nitro groups of 2,6-bis(4-nitrobenzamido)pyridine with hydrazine yielded 2,6-bis(4-aminobenzamido)pyridine. Reaction of this diamine with two moles of trimellitic anhydride afforded a diacid with preformed amide and imide structures. Poly(amide imide amide)s were prepared by direct polycondensation reactions of the diacid with different diamines in the presence of triphenyl phosphite. All the precursors and

polymers were fully characterized using common spectroscopic methods and elemental analysis and physical properties of the polymers including solution viscosity, thermal stability, thermal behavior, and solubility were studied. According to the obtained results the polymers showed high thermal stability and enhanced solubility. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 299–308, 2011

Key words: thermal properties; synthesis; polyamides; polycondensation; structure–property relations

INTRODUCTION

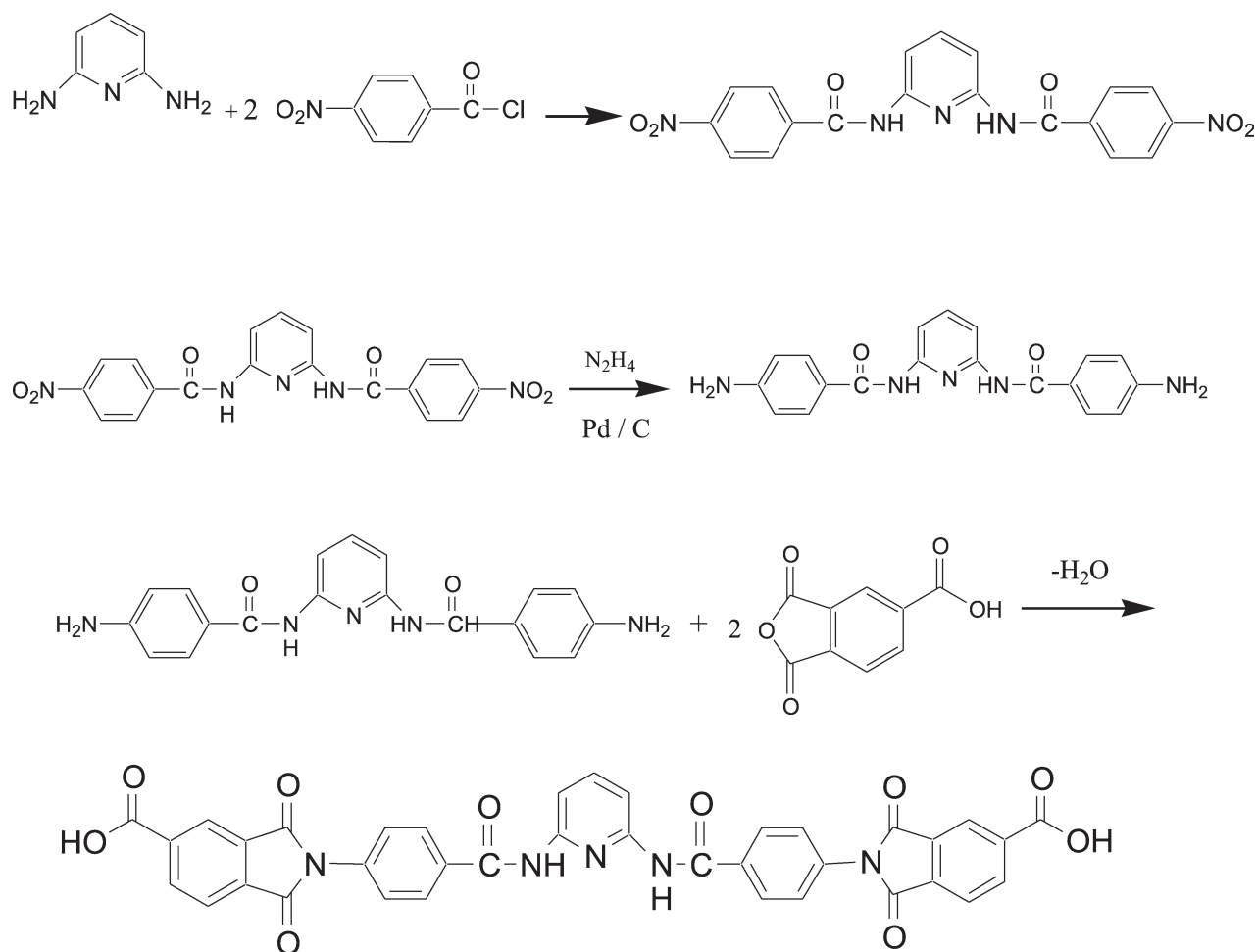
Aromatic diamines are valuable building monomers for the preparation of different types of high-performance polymers including polyamides, polyimides, and their copolymers. Aromatic polyamides are one of the most important classes of high-performance polymers because of their outstanding mechanical properties, thermal and oxidative stability, chemical resistance, and low flammability. Because of these properties, they are of major commercial and industrial importance.^{1,2} However, the weak solubility and high softening or melting temperature resulted from high stiffness and intermolecular hydrogen bonding between amide groups lead to difficult solubility and processability of these polymers.³ Some important synthetic attempts in the area of thermally stable polymers have been focused on enhancing their processability and solubility through the design and synthesis of new monomers.^{4–7}

Introduction of flexible bonds and polar units into the backbone of polyamides have been recognized as efficient methods for improving solubility while maintaining thermal stability of them.

On the other hand, copolycondensation is one of the possible ways for modification of polymer properties. Modification of the properties of polyamides by incorporation of imide groups and more hydrogen-bonded amide groups has been investigated and poly(amide imide amide)s have been studied extensively.^{8–13} The incorporation of rigid segments in the polymer chain is an effective method to enhance the thermal stability. Thermal resistance of polyimides is higher than that of polyamides, but polyamides have better solubility and processability than polyimides. Poly(amide imide amide)s are known as valuable polymers among high-performance polymers due to the fact that they combine and inherit desirable features from both polyamides and polyimides.^{14–17} Poly(amide imide amide) can be synthesized by polycondensation of various monomers containing anhydride, carboxylic acid, or aromatic amino groups with preformed units.

Specific properties could be incorporated into the main chain of the synthetic polymer by imparting aromatic heterocyclic rings into the polymer.¹⁸ Among different aromatic heterocyclic rings, pyridine has remarkable situation because of its high thermal stability derived from its molecular symmetry and aromaticity. Also its higher polarity in comparison to benzene makes the final polymer more polar and therefore increases interaction of polar solvents with backbone of polymer resulting in improved solubility.^{19–21}

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Scheme 1 Synthesis of DA.

This article describes the synthesis of a novel diacid with preformed amide and imide units via three-step reactions: (a) nucleophilic substitution reaction of 4-nitrobenzoyl chloride with 2,6-diaminopyridine and (b) subsequent reduction of their nitro groups, and (c) final reaction of the prepared diamine with trimellitic anhydride (TMA). The diacid with built-in amide and imide units was prepared and reacted with different commercially available diamines through Yamazaki polycondensation method to prepare poly(amide imide amide)s with good thermal stability and improved solubility.

EXPERIMENTAL

Materials

All chemicals were purchased either from Merck or Aldrich Chemical. The 2,6-diaminopyridine, 4,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl methane, 4,4'-diaminodiphenyl ether, *p*-phenylene diamine, and trimellitic anhydride were recrystallized from benzene, ethanol, water, ethanol, ethanol, and

tetrahydrofuran (THF), respectively. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and toluene were purified by distillation over calcium hydride under reduced pressure.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer from KBr pressed samples. The ^1H NMR spectra were recorded in dimethyl sulfoxide ($\text{DMSO}-d_6$) solution using a Bruker Avance DPX 400-MHz instrument. A CHN-O-Rapid Heraeus elemental analyzer performed elemental analyses. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 instrument in air at a heating rate of $10^\circ\text{C min}^{-1}$. Differential thermogravimetric (DTG) traces were recorded on a Polymer Lab TGA-1500. The dynamic mechanical measurements were recorded on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of room temperature to 350°C at

TABLE I
Characterization of Substrates

Substrate	IR (KBr, cm^{-1})	H-NMR (DMSO- d_6 , δ , ppm)	Elemental analysis						Yield (%)
			calcd			found			
			C	H	N	C	H	N	
BNBP	3353, 1694	10.97 s (2H, NH)	56.02, 3.19, 17.20			56.18, 3.10, 17.28			88.6
	1604, 1586	8.32 d (4H, Phenyl)							
	1522, 1351	8.15 d (4H, Phenyl)							
BABP	3370–3332	7.87–7.89 m (3H, Pyridine)	65.71, 4.90, 20.17			65.80, 5.01, 20.09			87.6
	3223, 1673	9.85 s (2H, NH)							
	1601, 1585	7.77–7.79 m (3H, Pyridine)							
		7.69 d (4H, Phenyl)							
		6.55 d (4H, Phenyl)							
DA	3415, 1778	5.80 s (4H, Amine)	63.88, 3.02, 10.07			64.02, 2.91, 9.95			85.8
	1729, 1668	13.89 s (2H, COOH)							
	1588, 1375	10.66 s (2H, NH)							
	1290, 722	8.42 dd (2H, Phenyl)							
		8.31 s (2H, Phenyl)							
		8.15 d (4H, Phenyl)							
		8.09 d (2H, Phenyl)							
		7.90 m (3H, Pyridine)							
	7.63 d (4H, Phenyl)								

1 Hz and a heating rate of 5°C min^{-1} . The value of $\tan \delta$ and the storage modulus versus temperature were recorded for each sample. Inherent viscosities were measured with an Ubbelohde viscometer.

Synthesis of 2,6-bis(4-nitrobenzamido)pyridine (BNBP)

A 250 mL, two-necked, round bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 0.03 mol (3.375 g) of the 2,6-diamino pyridine and 90 mL of NMP. The mixture was stirred at 0°C for 0.5 h. Then about 43 mL of propylene oxide and 0.07 mol (13.635 g) of 4-nitrobenzoyl chloride was added and the mixture was stirred at 0°C for 50 min. The temperature was raised to room temperature and the solution was stirred for 20 h. The 2,6-bis(4-nitrobenzamido)pyridine was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water and methanol successively, and dried overnight under vacuum at 50°C (yield = 88.6%).

Synthesis 2,6-bis(4-aminobenzamido)pyridine (BABP)

About 0.0123 mmol (5.0 g) of the 2,6-bis(4-nitrobenzamido)pyridine (BNBP), 0.32 g of Pd/C 10%, and 63 mL of ethanol were introduced into a two-necked flask to which a mixture of 25 mL of hydrazine monohydrate and 20 mL ethanol was added dropwise over a period of 2 h at 85°C . After the complete addition, the reaction was continued at reflux temperature for another 18 h. Then, 25 mL of tetrahy-

drofuran was added to the suspension to redissolve the precipitated product and refluxing was continued for 3 h. The mixture was filtered to remove the Pd/C and the filtrate was poured into water. The product was filtered off, washed with hot water, and dried (yield = 87.6%).

Synthesis of diacid (DA)

To a solution of 2,6-bis(4-aminobenzamido)pyridine (0.347 g, 0.1 mol) dissolved in 250 mL of NMP in a 500-mL flask, 3.84 g (0.20 mol) of TMA was added. The stirred reaction mixture was heated to 80°C for 2 h under N_2 . Then 100 mL of dry toluene was added to the mixture and it was heated to reflux for about 12 h until water was distilled off azeotropically via a Dean-Stark trap. Diacid was precipitated by pouring the flask content into 200 mL of 3 : 1 (v/v)

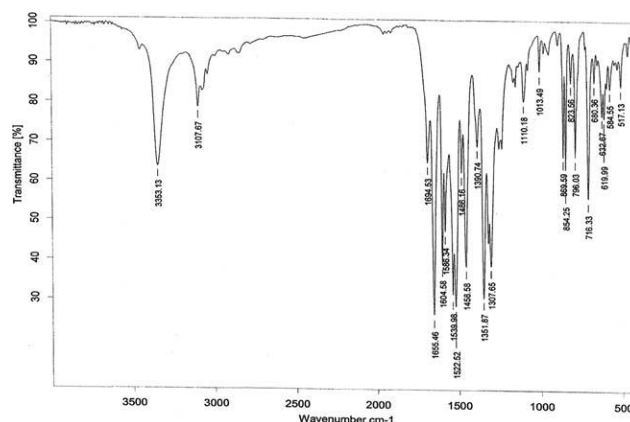


Figure 1 FTIR spectrum of BNBP.

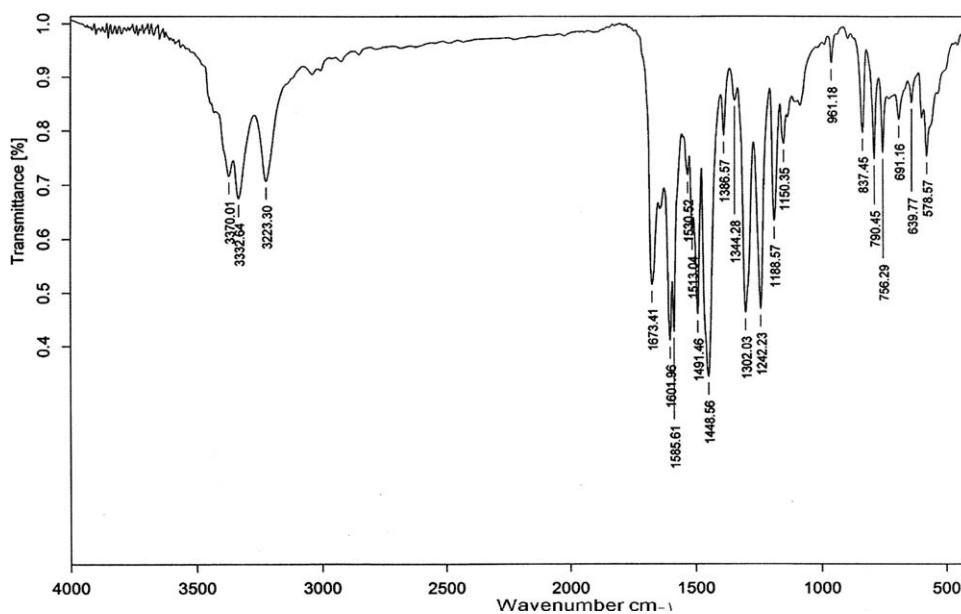


Figure 2 FTIR spectrum of BABP.

mixture of water and methanol. It was then filtered and dried overnight in vacuum oven at 100°C (yield = 85.8%).

Polymer synthesis

A typical procedure was as follows. A mixture of 1.6 mmol of diamine, 1.6 mmol (1.03 g) of diacid (DA), 0.72 g of calcium chloride, 1.6 mL of triphenyl phosphite, 1.6 mL of pyridine, and 8 mL of NMP was

refluxed for 3 h. After cooling, the reaction mixture was poured into a large amount of methanol with stirring. The obtained precipitate was filtered and washed with methanol and hot water. Then it was dried at 110°C under vacuum overnight.

RESULTS AND DISCUSSION

Generally, most approaches to obtain soluble and thermally stable polymers have involved the

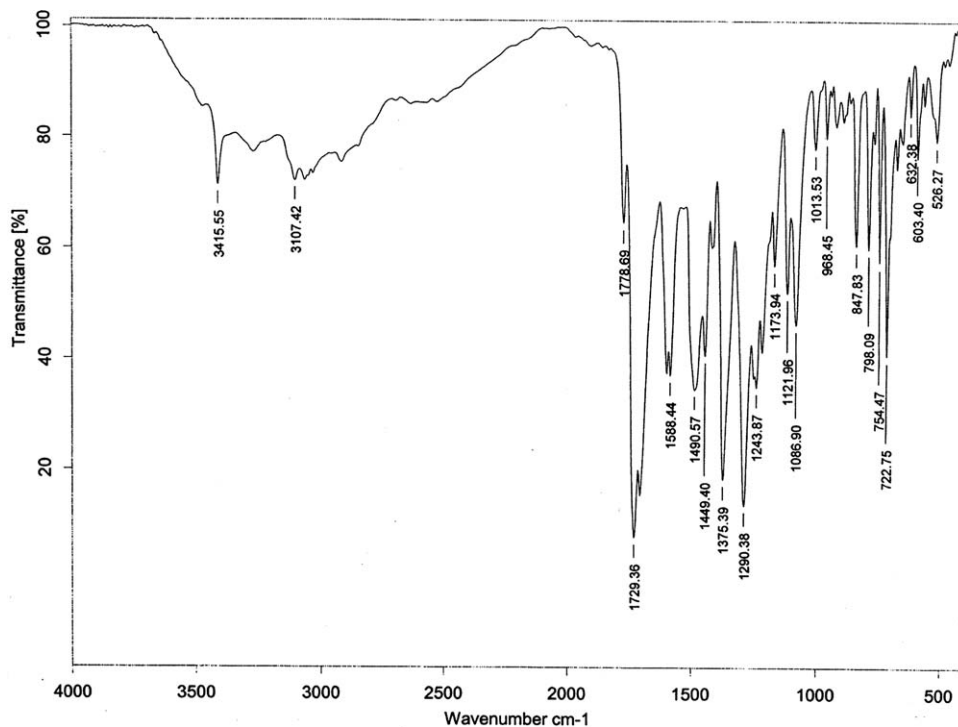


Figure 3 FTIR spectrum of DA.

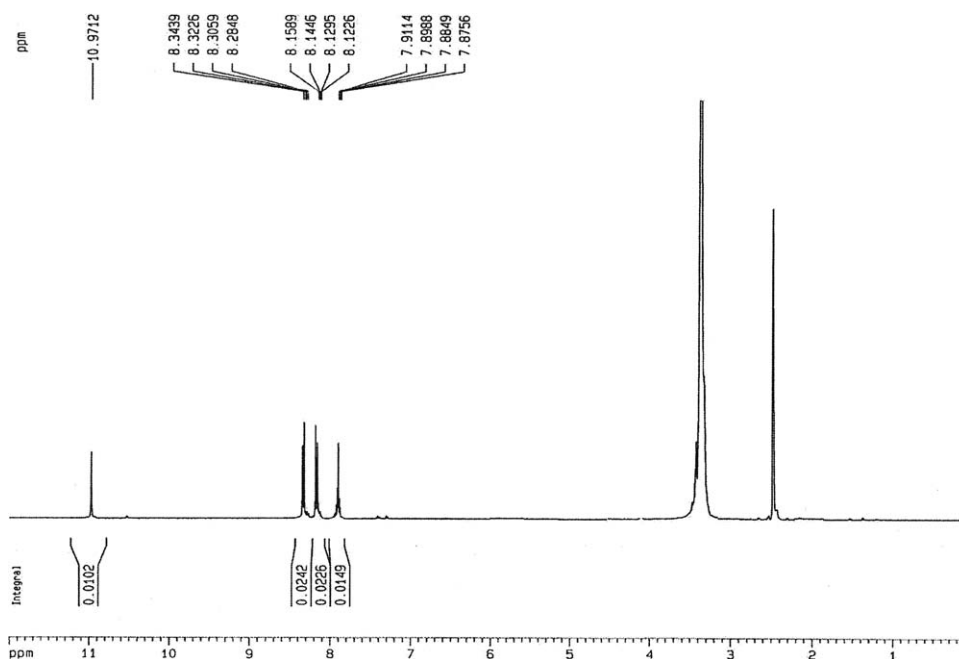


Figure 4 ^1H NMR spectrum of BNBP.

following modifications: (a) the introduction of a large polar or nonpolar substituent along the polymer backbone; (b) the incorporation of flexible or kinked linkages in the backbone, and (c) the disruption of symmetry and regularity of the repeating unit through copolymerization.^{22–28}

Preparation of novel aromatic polyamides with high thermal stability and improved solubility was the objective of this study. Preparation of thermally stable poly(amide imide amide)s based on the reaction of a novel diacid with preformed amide and imide units with different diamines using triphenyl

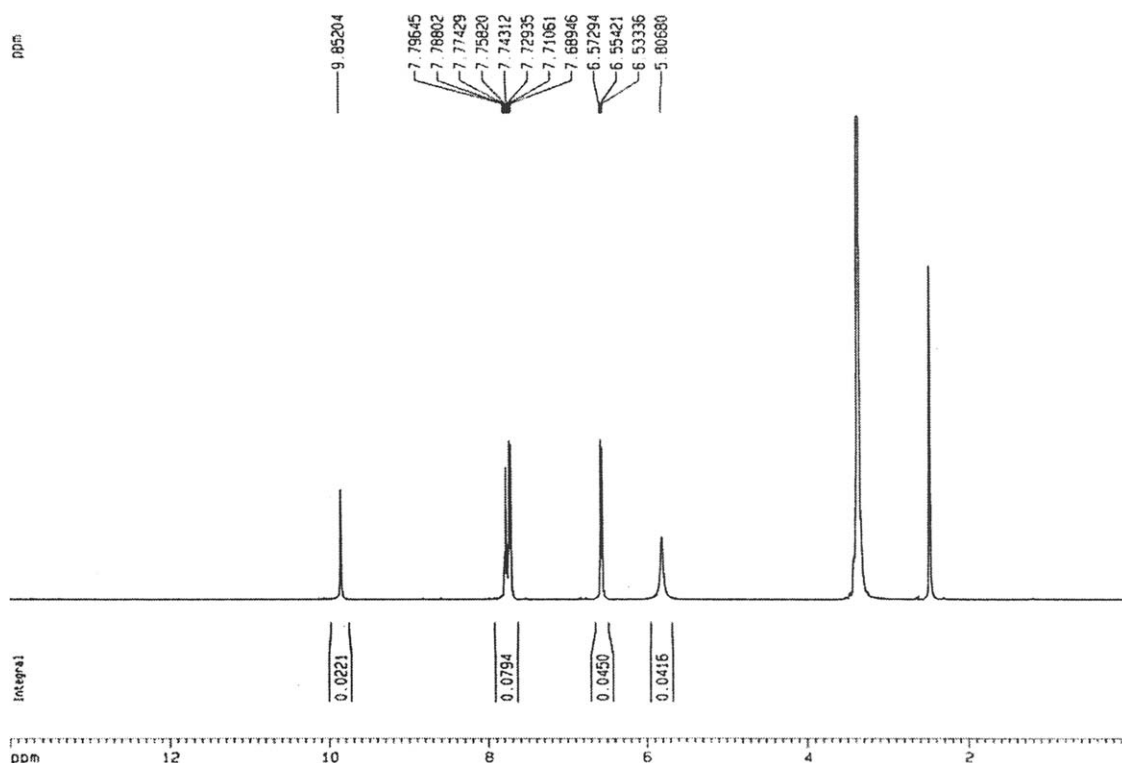


Figure 5 ^1H NMR spectrum of BABP.

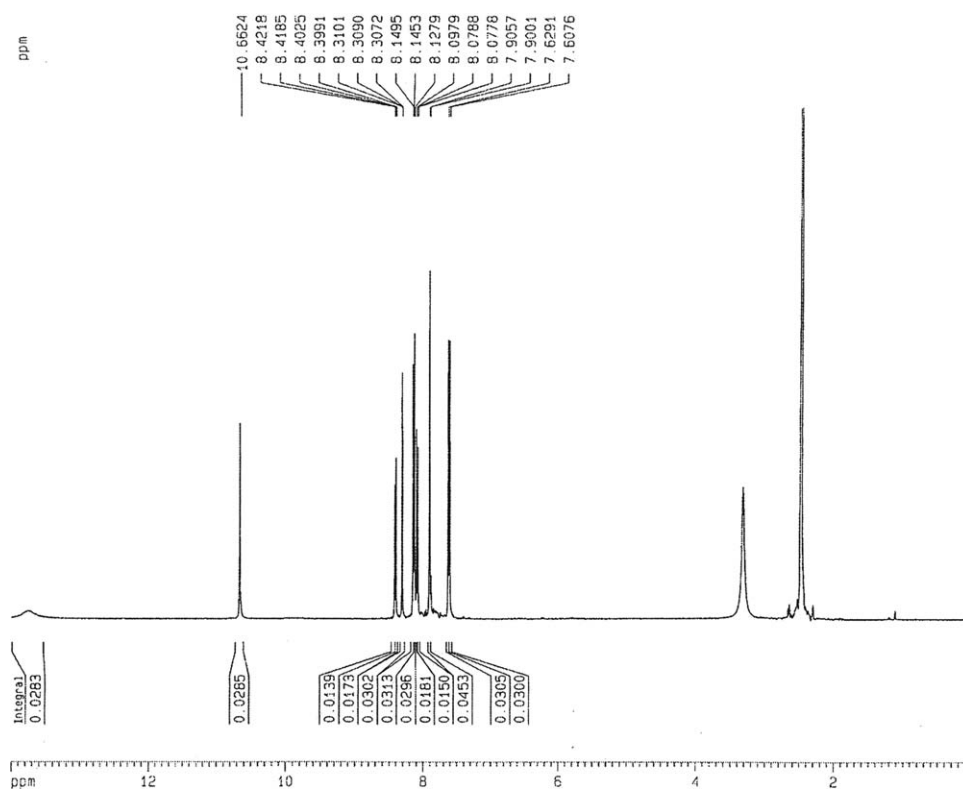
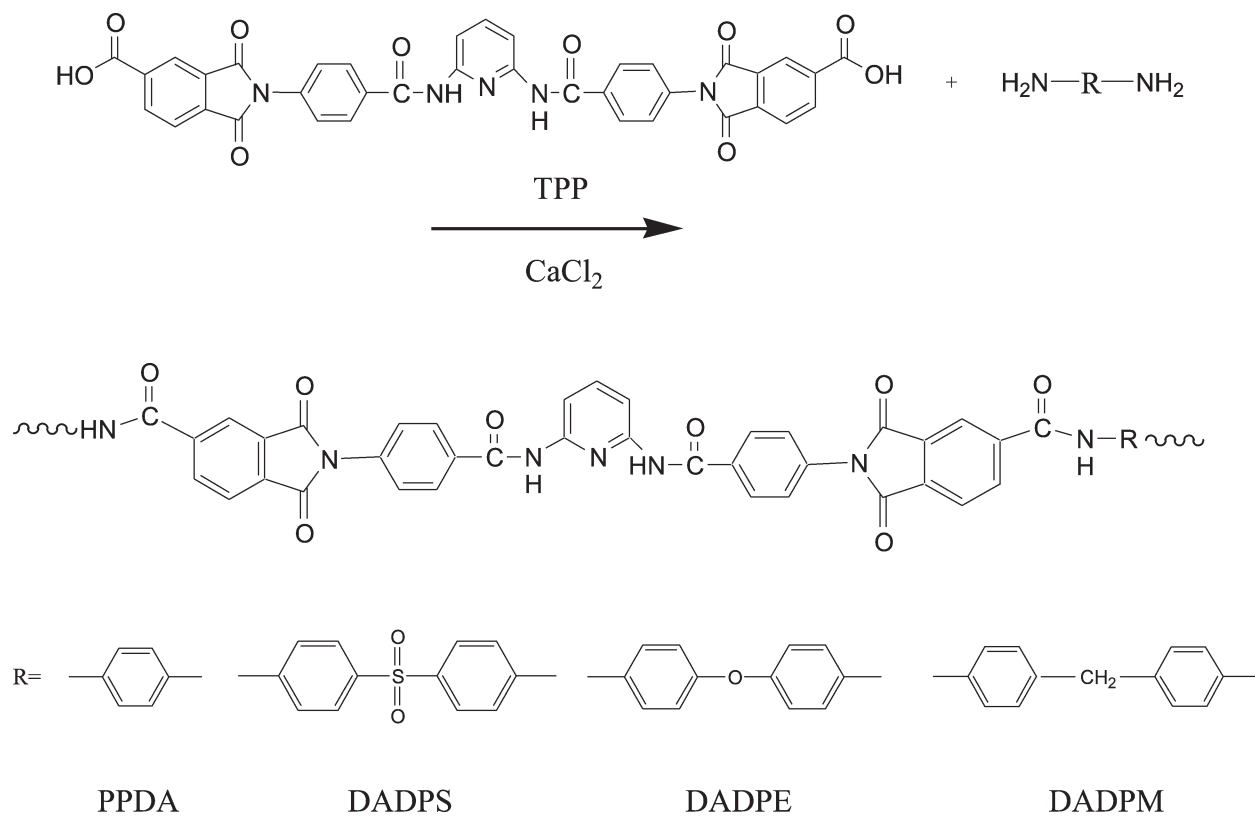


Figure 6 ^1H NMR spectrum of DA.



Scheme 2 Preparation of polymer.

TABLE II
Characterization of Polymers

Polymer	IR (KBr, m^{-1})	NMR (DMSO- d_6 , ppm)	Elemental analysis						Inherent viscosity (dL/g)	Yield (%)
			calcd			found				
			C	H	N	C	H	N		
DA-PPDA	3413, 1779 1723, 1662 1602, 1363 717	10.72 (2H), 10.64 (2H) 8.53 (2H), 8.44 (2H) 8.13 (6H), 7.90 (3H) 7.81 (4H), 7.62 (4H)	67.27, 3.26, 12.78	67.15, 3.11, 12.95	0.53	84.7				
DA-DADPS	3416, 1779 1722, 1670 1590, 1369 1317, 1103 719	10.98 (2H), 10.68 (2H) 8.52 (2H), 8.43 (2H) 8.14 (6H), 8.05 (4H) 7.96 (4H), 7.90 (3H) 7.63 (4H)	64.83, 3.20, 10.80	64.69, 3.04, 10.96	0.54	85.1				
DA-DADPE	3367, 1779 1721, 1655 1602, 1369 1222, 723	10.73 (2H), 10.67 (2H) 8.54 (2H), 8.44 (2H) 8.16 (6H), 7.91 (3H) 7.81 (4H), 7.65 (4H) 7.06 (4H)	68.45, 3.38, 11.41	68.21, 3.52, 11.20	0.57	83.9				
DA-DADPM	3419, 1779 1727, 1647 1600, 1363 719	10.69 (2H), 10.58 (2H) 8.52 (2H), 8.42 (2H) 8.13 (6H), 7.90 (3H) 7.72 (4H), 7.63 (4H) 7.21 (4H), 3.90 (2H)	70.01, 3.62, 11.43	69.89, 3.80, 11.30	0.58	84.3				

phosphite via polycondensation reaction was considered. In this way, 2,6-bis(4-nitrobenzamido)pyridine (BNBP) was synthesized by nucleophilic aromatic substitution reaction of 4-nitrobenzoyl chloride with 2,6-diaminopyridine in 2 : 1 ratio. The reaction was performed in NMP solvent and in the presence of an acid scavenger (propylene oxide). Catalytic reduction of nitro groups of 2,6-bis(4-nitrobenzamido)pyridine with hydrazine using Pd/C catalyst led to preparation of 2,6-bis(4-aminobenzamido)pyridine (BABP). Reaction of the obtained diamine with trimellitic anhydride resulted in preparation of a diacid (DA) with preformed amide and imide structures (Scheme 1). Structure of the BNBP, BABP, and DA was confirmed by FTIR and ^1H NMR spectroscopy and also elemental analysis (Table I). The NO_2 asymmetric and symmetric stretching bands in the FT-IR spectrum of BNBP were appeared at 1522 and 1351 cm^{-1} , respectively. By conversion of nitro groups to amino groups these absorption bands were disappeared and amine bands at 3370–3332 cm^{-1} (N-H stretching) were appeared. Also shift of the amide C=O stretching band from 1694 cm^{-1} in BNBP to 1673 cm^{-1} in BABP due to electron-donating character of NH_2 groups was another reason for conversion of BNBP to BABP. Appearance of amine peak at 5.80 ppm in the ^1H NMR of BABP and shift of other peaks to higher chemical fields were other criteria for amine formation. Elemental analyses were also confirmed the structures of BNBP and BABP.

In the FTIR spectrum of the DA characteristic bands at 3415 cm^{-1} ($-\text{OH}$ stretching of $-\text{COOH}$), 1778 cm^{-1} (imide $-\text{C=O}$ unsymmetrical stretching), 1729 cm^{-1} (imide $-\text{C=O}$ symmetrical stretching), 1668 cm^{-1} (amide

$-\text{C=O}$), 1375 cm^{-1} (imide C-N stretching), 1290 cm^{-1} (acid $-\text{C-O}$), and 722 cm^{-1} (imide $-\text{C=O}$ out-of plane deformation) were appeared. Presence of four imide absorption bands and also acidic band in the FTIR spectrum of DA confirmed the proposed structure of diacid. Existence of a broad peak at 13.89 ppm due to acidic OH group, appearance of three additional peaks at 8.42, 8.31, and 8.09 ppm from trimellitimide moieties, and disappearance of amine peaks at 5.80 ppm in the ^1H NMR of DA were proven the diacid structure. The found results of elemental analysis of diacid showed good agreement with calculated results (Table I). Figures 1–3 shows the FTIR spectra and Figures 4–6 ^1H NMR spectra of BNBP, BABP, and DA, respectively.

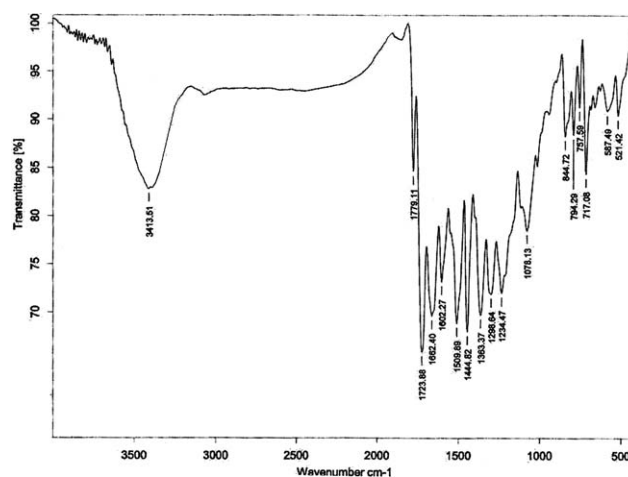


Figure 7 FTIR spectrum of DA-PPDA polymer.

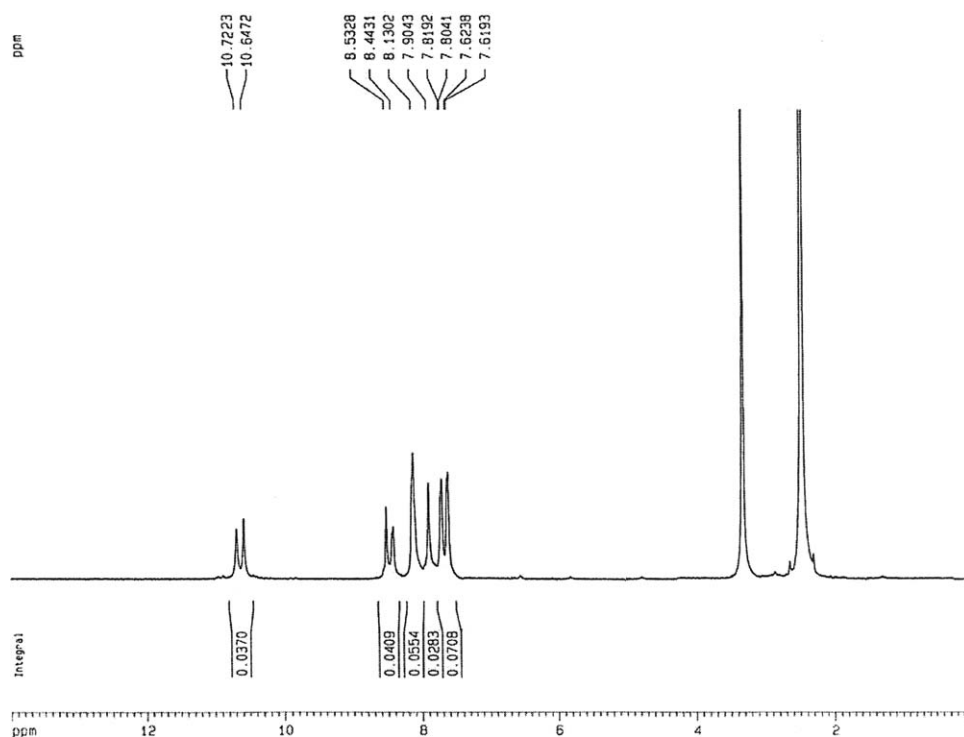
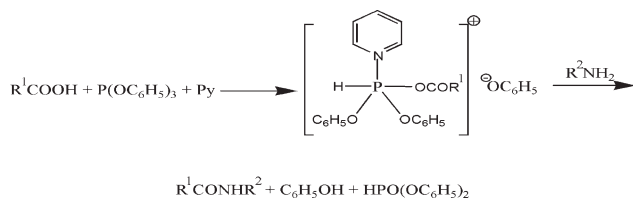


Figure 8 ^1H NMR spectrum of DA-PPDA polymer.

For the preparation of polymers direct method of polyamidation was used. In fact, polycondensation reaction of the DA with different aromatic diamines including *p*-phenylene diamine (PPDA), 4,4'-diaminodiphenyl sulfone (DADPS), 4,4'-diaminodiphenyl methane (DADPM), and 4,4'-diaminodiphenyl ether (DADPE) in NMP by the Yamazaki method using triphenyl phosphite and pyridine as condensing agents, yielded poly(amide imide amide)s (Scheme 2). Yamazaki reaction has been proposed to proceed via an acyloxy *N*-phosphonium salt of pyridine formed by dephenoxylation of triphenyl phosphite that followed by attack of amine group to the carbonyl group of ester (aminolysis) according to the following scheme^{29,30}:



All the polymers were characterized using FTIR, ^1H NMR, and elemental analysis techniques. The FTIR spectra of the polymers showed characteristic bands at 3419–3367 cm^{-1} ($-\text{NH}$), 1779 cm^{-1} (imide I $-\text{C}=\text{O}$), 1727–1721 cm^{-1} (imide II $-\text{C}=\text{O}$), 1670–1647 cm^{-1} (amide I $-\text{C}=\text{O}$), 1369–1363 cm^{-1} (imide C–N), and 723–717 cm^{-1} (imide $-\text{C}=\text{O}$ out-of-plane). Accordingly, all characteristic peaks confirming preparation of poly(amide imide amide)s were observed

in the FTIR spectra. Also ^1H NMR of polymers proved the proposed structures via disappearance of acidic proton peak of DA monomer at 13.89 ppm and appearance of NH amidic peak. Additionally, a reasonable agreement was observed between calculated and found values in elemental analysis of polymers. The results are brought together in Table II and the representative FTIR and ^1H NMR spectra of one polymer are shown in Figures 7 and 8, respectively.

Since the inherent viscosity could be considered as a suitable criterion for evaluation of molecular weight, the inherent viscosity of the polymers was measured in NMP at a concentration of 0.5 g dL^{-1} at 30°C (Table II). It was in the range of 0.53–0.58 dL g^{-1} that revealed reasonable molecular weight for the polymers. The solubility of the polymers was measured in dipolar aprotic solvents including NMP, DMAc, DMF, DMSO, and *m*-cresol. The

TABLE III
Thermal Analysis Characteristic Data

Polymer	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{MAX} (°C)	Char yield at 600°C (%)
DA-PPDA	270	325	445	534	62
DA-DADPS	235	315	421	538	57
DA-DADPE	225	309	415	522	52
DA-DADPM	218	300	405	520	47

T_g , glass transition temperature; T_0 , initial decomposition temperature; T_{10} , temperature for 10% weight loss; T_{MAX} , maximum decomposition temperature.

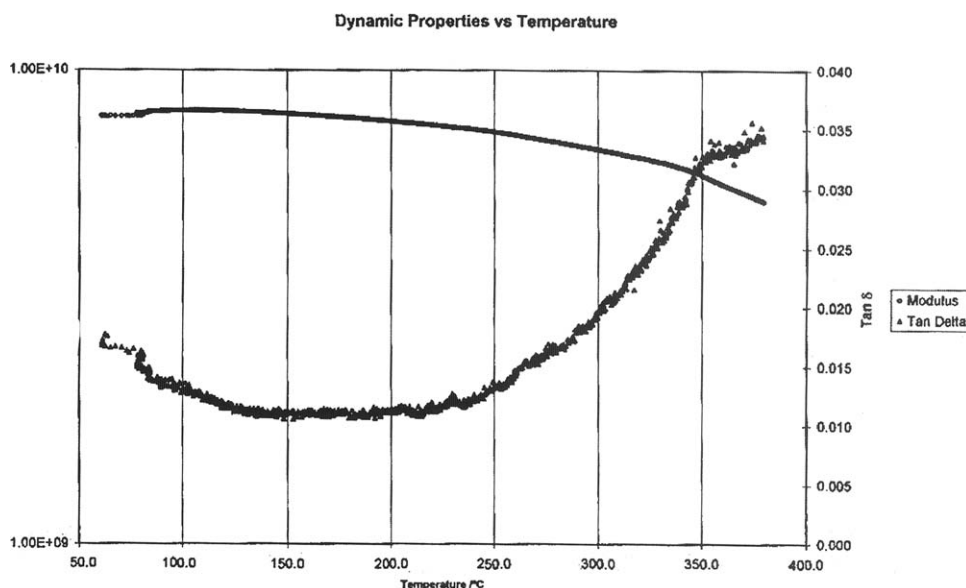


Figure 9 DMTA curve of DA-PPDA polymer.

solubility of the polymers (by heating and stirring) was in the range of 1.1–1.4 g dL⁻¹. The solubility of the polymers was mainly attributed to the incorporation of pyridine polar group and also flexible methylene, ether, and sulfone groups.

To study the thermal behavior and thermal stability of the polymers, analysis techniques including DSC, TGA, and DMTA were used. The glass transition temperatures of polymers (T_g) were in the range of 218–270°C. The T_g was taken as the midpoint of the change in slope of the baseline in DSC traces and also from decreasing in the storage modulus with increasing of $\tan \delta$ in DMTA traces. Thermogravimetric analysis was used for evaluation of thermal stability. The temperature for 10% gravimetric loss (T_{10}) which is an important criterion for evaluation of thermal stability was in the range of 405–445°C. Char yields of the polymers at 600°C were about 47–62%. The obtained results from thermal analyses are collected in Table III and the representative plots of DMTA and TGA curves are shown in Figures 9 and 10, respectively. It is quite clear that the polymer derived from fully aromatic diamine (PPDA-derived polymer) was more thermally stable than polymers derived from aromatic diamines with flexible moieties. Therefore, phenylation of backbone, incorporation of imide units, avoidance of any weak linkages, and retention of symmetry were the main factors used to enhance the thermal stability of the polymers.

Comparison of the prepared poly(amide imide amide)s with similar polymers showed that presence of amide units in the structure of DA affected some properties of final polymers. The glass transition temperature and thermal stability of DA-based polymers were lower than previously reported 2,6-diaminopyridine-based polyimides and 2,6-bis(4-amino-

phenoxy) pyridine-based polyimides.^{7,31} This was related to the fact that polyimides are more rigid than similar poly(amide imide amide)s and therefore show higher thermal stability.

CONCLUSIONS

A diacid (DA) containing amide and imide units was prepared from 2,6-diaminopyridine using three successive reactions. Nucleophilic reaction of 2,6-diaminopyridine with 4-nitrobenzoyl chloride led to preparation of BNPB and subsequent reduction of its nitro groups yielded BABP compound. This diamine was reacted with trimellitic anhydride and the new diacid (DA) was obtained. Polycondensation reactions of DA with different diamines via Yamazaki method yielded different poly(amide imide amide)s. Polymers showed high thermal stability that resulted from phenylation of backbone, incorporation of imide units, avoidance of any weak linkages, and retention of symmetry in the backbone of the polyamides. On the other hand, enhanced

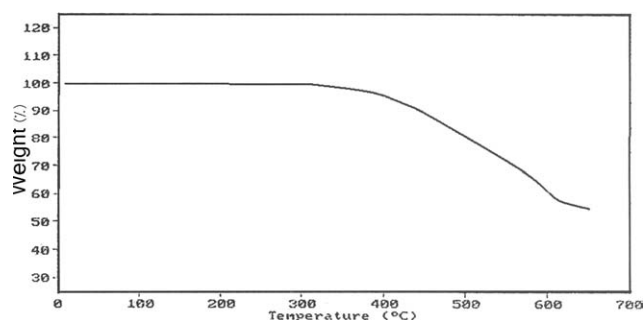


Figure 10 TGA curve of DA-PPDA polymer.

solubility of the polymers in polar aprotic solvents was related to the presence of pyridine polar unit and also existence of methylene, ether, and sulfone flexible groups in the backbone.

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