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Synthesis and characterization of heat resistant, pyridine-based polyimides with preformed ether and ester groups

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Abstract

A pyridine-based diamine as a building block for the preparation of heat resistant polyimides was prepared. Reaction of 1,5-dihydroxy naphthalene with 4-nitrobenzoyl chloride resulted in preparation of 5-hydroxy-1-naphthyl-4-nitrobenzoate (HNNB). 5-Hydroxyl-1-naphthyl-4-aminobenzoate (HNAB) was prepared via reduction of nitro group of HNNB. The diamine with built-in ether and ester groups was synthesized by nucleophilic substitution reaction of HNAB with 2,6-dichloropyridine in the presence of K_2CO_3. The obtained diamine was fully characterized and its polycondensation reaction with different aromatic dianhydrides led to preparation of novel heat resistant poly (ether ester imide)s. All the polymers were characterized and their physical and thermal properties were studied.

Keywords: Diamine; Polycondensation; Poly(ether ester imide)s; Heat resistant

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1. Introduction

Aromatic polyimides are heat resistant polymers that generally show excellent mechanical strength and stability. Due to the increased performance characteristics demanded on polymers in various fields including the aerospace, automobile, and microelectronic industries, the use of these aromatic polymers in growing steadily [1]. However, one of the drawbacks to the employment of these high performance polymers is the difficulty in processing due to their high melting temperatures or high glass transition temperatures [2]. Strong interaction between polyimide chains and their rigid structure are the main reasons for these behaviors.

Therefore, some significant synthetic efforts, in the area of high-temperature resistant polymers, have been focused on improving their processability and solubility through the design and synthesis of new monomers [3].

Copolycondensation is one of the possible ways for modification of polymer properties. Thus, for the processing of polyimides many copolyimides, such as poly(amide-imide)s, poly(sulfone-imide)s, poly(ether-imide)s, poly(ester-imide)s and other copolymers have been prepared [4–8]. Aromatic polymers that contain aryl ether linkage generally have greater tractability, lower glass transition, and greater chain flexibility than their corresponding polymers without these groups in the repeat units [9]. The improved solubility and lower

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glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation [10].

The choice of heterocyclic rings in the main chain of the polymer is to impart certain properties to the polymer. The selection of pyridine nucleus is based on its high thermal stability derived from its molecular symmetry and aromaticity [11,12].

According to our interest to prepare novel pyridine-based diamines and related polymers [13–17], here we wish to report the synthesis of a pyridine-based, ether ester diamine (PEED) and resulting heat resistant polyimides. PEED was synthesized through three successive steps. First, reaction of 1,5-dihydroxy naphthalene with 4-nitrobenzoyl chloride yielded HNNB. The nitro group of HNNB was reduced to amino group using hydrazine and Pd/C to afford HNAB. Finally, PEED was prepared through nucleophilic aromatic substitution reaction of HNAB (two moles) with 2,6-dichloropyridine (one mole) in *N*-methyl-2-pyrrolidone (NMP) in the presence of K_2CO_3. Two step polycondensation reactions of the PEED with aromatic dianhydrides including pyromellitic dianhydride (PMDA), benzophenonetetracarboxylic dianhydride (BTDA), and hexaflouroisopropylidene diphthalic anhydride (6FDA) resulted in preparation of fully aromatic poly(ether ester imide)s.

2. Experimental

2.1. Materials

All needed chemicals were purchased either from Merck or Aldrich Chemical Co. 2,6-dichloropyridine was recrystallized from aqueous ethanol. Dianhydrides were dried in a vacuum oven at 110 °C for 5 h. NMP, *N*,*N*-dimethylacetamide (DMAc), and toluene were vacuum distilled over calcium hydride.

2.2. Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). The ^{1}H-NMR spectra were recorded in DMSO-d_6 solution using a Bruker Avance DPX 250 MHz (GmbH, Germany). The mass spectra were recorded on a Shimadzu GC-MS-QP 1100-EX (Tokyo, Japan). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded in air at a heating rate of 10 °C/min on a Stanton Redcraft STA-780 (London, UK). Inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 30 °C by using an Ubbelohde viscometer.

2.3. Monomer synthesis

Synthesis and characteristic data of 5-hydroxy-1-naphthyl-4-nitrobenzoate (HNNB), 5-hydroxy-1-napthyl-4-aminobenzoate (HNAB), and pyridine-based ether ester diamine (PEED) were completely described in our pervious manuscript [18].

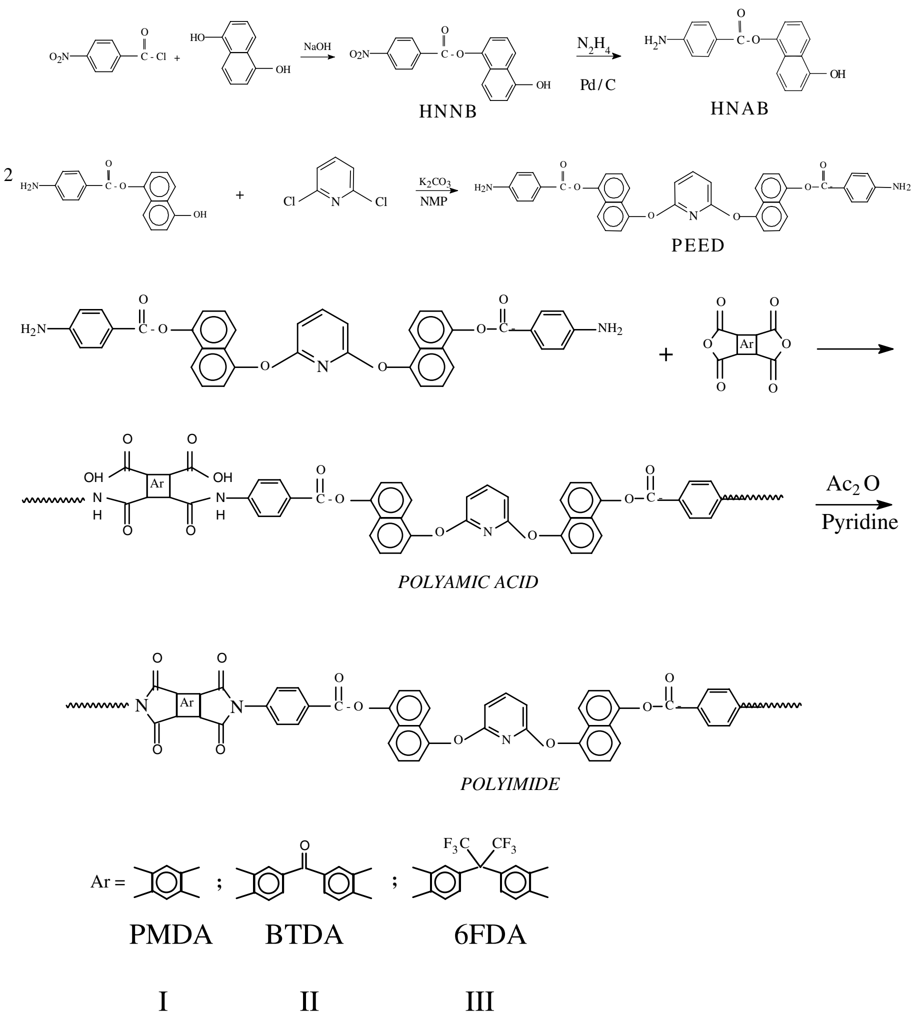
2.4. Polyimide synthesis

The synthesis of polyimide typically was carried out as follows: A 100-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 2 mmol of the diamine (PEED) and 15 mL of dry NMP. The mixture was stirred at 0 °C for 0.5 h. Then 2 mmol of dianhydride was added and the mixture was stirred at 0 °C for 1 h. The temperature was raised to room temperature and the solution was stirred for 24 h. Poly(amic acid) was precipitated by pouring the flask content into 200 mL of a 3:1 volume mixture of water and methanol. Then it was filtered, washed with hot water and dried overnight under vacuum at 40 °C. (Yields over 91%.) Chemical cyclization was applied for conversion of poly(amic acid) to polyimide: Into a 100-mL, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a reflux condenser was placed 1.0 g of poly(amic acid) and 5 mL of dry DMAc. The mixture was stirred and then 5 mL of acetic anhydride and 2.5 mL of pyridine were added. The mixture was stirred for 0.5 h and then slowly heated to 140 °C and held for 6 h at the same temperature. After that the mixture was cooled and poured into water, it then was filtered, washed with hot water and methanol, and dried overnight under vacuum at 120 °C. (Yields over 93%).

3. Results and discussion

Preparation of modified polyimides with improved solubility and processability without sacrificing their thermal and physical properties was the main aim of this study. Accordingly, the design and synthesis of new monomer and resulting polyimides with structural modifications were considered. These modifications were included: (1) the introduction of heterocyclic ring along the polymer backbone; (2) the incorporation of flexible or kinked linkages in the backbone; (3) the introduction of ester group in the main chain; (4) phenylation of backbone; and (5) relative disruption of symmetry and regularity of the repeating unit.

Therefore, a pyridine-based diamine (PEED) with built-in ether and ester units as a building block for preparation of polyimides were synthesized via three steps (Scheme 1). Nucleophilic reaction of 1,5-dihydroxy



Scheme 1. Preparation of poly(ether ester imide).

naphthalene with 4-nitrobenzoyl chloride in the presence of NaOH resulted in preparation of HNNB. Then, hydrazine hydrate and Pd/C catalyst was used to reduce the nitro group of HNNB to amino group and HNAB was obtained. Since the pyridine derivatives undergo nucleophilic substitution reaction easily [19] thus for the preparation of novel diamine, nucleophilic aromatic substitution reaction of two moles of HNAB with 2,6-dichloropyridine in the presence of potassium carbonate in NMP was performed.

Therefore, a novel pyridine-based diamine was designed and prepared in such a way that it contained rigid phenyl, naphthyl, and ester group to increase the thermal stability of the final polyimides. Also incorporation of pyridine ring [20], ether, and bulky naphthyl groups for increasing of the solubility and processability were considered.

Two step polycondensation reaction of the diamine with aromatic dianhydrides (PMDA, BTDA, and 6FDA) resulted in preparation of their polyamic acids and then fully aromatic poly(ether ester imide)s were prepared using chemical cyclization (Scheme 1).

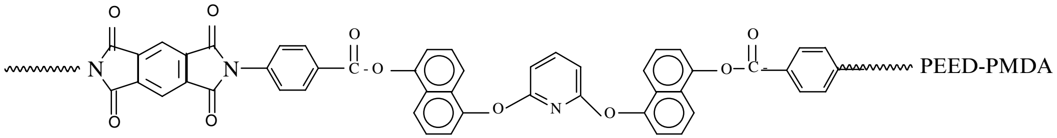
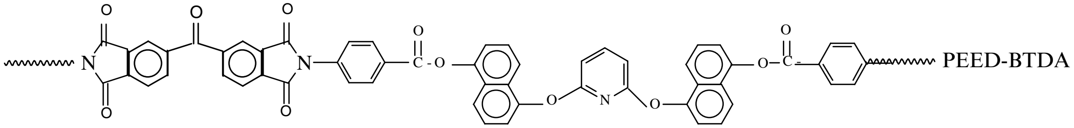
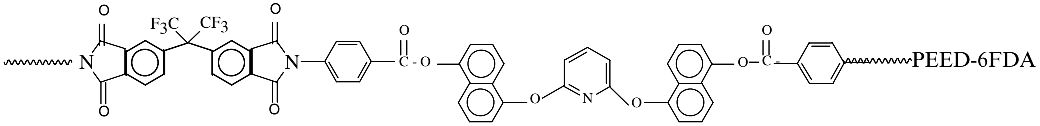
Instrumental techniques including IR, NMR and elemental analysis were performed for the characterization of the polyimides. The results were shown in Table 1.

The inherent viscosity of the polymers was measured at a concentration of 0.5 g/dL in NMP at 30 °C. The viscosity of polyimides, as a good criterion for estimation of molecular weight, was in the range of 0.32–0.36 g/dL that revealed reasonable molecular weights (Table 2). The solubility of the fully aromatic poly(ether ester imide)s in dipolar aprotic solvents such as NMP, *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) was about

Table 1
Polymers characterization data

No.	Structure	IR (KBr-Cm^{-1})	NMR(DMSO-d$_6$,δ,PPM)	Elemental analysis					
				Calc.			Found		
				C	H	N	C	H	N
I	PEED-PMDA	1769, 1718, 1649, 1589, 1501, 1390, 1210, 729	5.70(2H), 6.70(4H), 7.28(4H), 7.78(4H), 7.80(1H), 7.86(4H), 8.16(4H), 9.02(2H)	72.15	3.09	5.15	71.89	2.94	5.38
II	PEED-BTDA	1768, 1713, 1650, 1590, 1503, 1392, 1211, 726	5.68(2H), 6.69(4H), 7.26(4H), 7.76(4H), 7.78(1H), 7.82(4H), 8.13(4H), 8.16(2H), 8.25(2H), 8.59(2H)	73.12	3.18	4.57	72.88	2.97	4.86
III	PEED-6FDA	1772, 1716, 1650, 1588, 1502, 1393, 1213, 727	5.67(2H), 6.68(4H), 7.23(4H), 7.71(2H), 7.75(4H), 7.77(1H), 7.80(4H), 8.13(4H), 8.18(2H), 8.26(2H)	66.86	2.81	4.03	66.39	2.99	3.89

Table 2
Specifications of the polymers

No.	Structure	Yield (%)	$\eta_{\text{Inh.}}$[a] (dL/g)
I	 PEED-PMDA	83	0.36
II	 PEED-BTDA	80	0.33
III	 PEED-6FDA	81	0.32

[a] Measured at a concentration of 0.5 g/dL in NMP at 30 °C.

Table 3
The solubility behavior of the polymers[a]

Polymer solvent	NMP	DMAc	DMF	DMSO	Pyridine	THF	Dioxane
I	+	+	+	+	–	–	–
II	+	+	+	+	–	–	–
III	+	+	+	+	–	–	–

[a] Solubility: +, soluble on heating; –, insoluble.

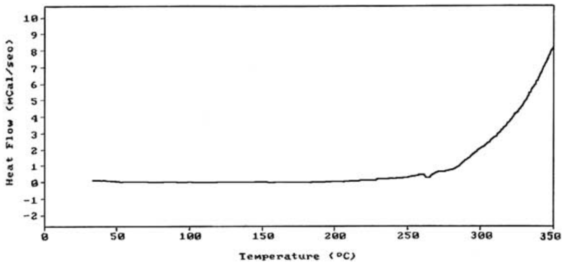


Fig. 1. DSC curve of PEED-PMDA.

1.35 g/dL (Table 3). Improving the solubility of the polyimides could be attributed to the presence of flexible ether groups, bulky naphthyl groups, and pyridine polar ring on the polymer chain.

DSC and TGA techniques were used to study the thermal behaviors and thermal properties of the polyimides. They were taken in air at a heating rate of 10 °C/min. The glass transition temperature of polyimides that was taken as the midpoint of the change in slope of the baseline was found in the range of 235–265 °C and the representative DSC curve after heating, cooling, and re-heating is shown in Fig. 1. According to the TGA data the initial decomposition temperatures (T_0) were about 293–314 °C and the temperatures for 10% gravimetric loss (T_{10}), which is an important evidence for thermal stability, were in the range of 420–435 °C. The maximum decomposition temperature (T_{max}) was in the range of 507–527 °C and also char yields of the polyimides at 600 °C were about 45–50% (Table 4). The representative TGA (weight % vs. temperature) curve is shown in Fig. 2. Phenylation of back-

Table 4
Thermal properties data

No.	T_g (°C)	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 600 °C (%)
I	265	314	435	527	50
II	250	301	423	505	45
III	235	293	420	507	46

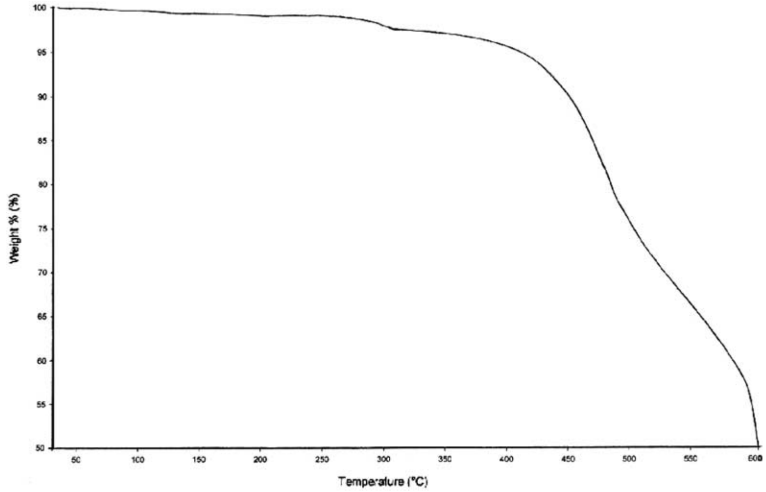


Fig. 2. TGA curve of PEED-PMDA.

bone and incorporation of ester group were effective factors in increasing of the thermal stability of the polyimides.

4. Conclusions

A pyridine-based diamine with preformed ether and ester units was prepared via three step reactions: HNNB was prepared by reaction of 4-nitrobenzoyl chloride with 1,5-dihydroxy naphthalene. The nitro group in HNNB was reduced to amino group and HNAB was produced. For the synthesis of pyridine-based ether ester diamine, the HNAB was reacted with 2,6-dichloropyridine in the presence of K_2CO_3. Novel poly(ether ester imide)s were prepared via two step polycondensation reactions of the diamine with aromatic dianhydrides. The polyimides were fully characterized and their physical and thermal properties were studied. These polymers showed nice balance of properties including high thermal stability and improved solubility. Structural modifications including incorporation of pyridine, ether, ester, and bulky groups were important modifications for preparation of these aromatic polyimides.

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