

# Preparation of Novel Pyridine-Based, Thermally Stable Poly(ether imide)s

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**ABSTRACT:** Two aromatic, pyridine-based ether diamines were prepared by the nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine in *N*-methyl-2-pyrrolidone as a solvent. Polycondensation reactions of the obtained diamines with pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, and hexafluoroisopropylidene diphthalic anhydride resulted in six pyridine-based, thermally stable poly(ether imide)s. The prepared monomers

and polymers were characterized by common spectroscopic methods. The physical and thermal properties of the polymers, including the thermal behavior, thermal stability, solubility, and solution viscosity, were studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 22–26, 2004

**Key words:** polyimides; polycondensation; high performance polymers; thermal properties

## INTRODUCTION

Aromatic polyimides are thermally stable polymers that generally show excellent mechanical strength and stability. Because of the increased performance characteristics demanded of polymers in various fields, including the aerospace, automobile, and microelectronic industries, the use of these aromatic polymers is growing steadily.<sup>1</sup> However, one of the drawbacks of these high-performance polymers is difficulty in processing due to their high melting temperatures or high glass-transition temperatures ( $T_g$ 's).<sup>2</sup> 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.<sup>3</sup>

Aromatic polymers that contain aryl ether linkages generally have greater tractability, lower glass transitions, and greater chain flexibility than their corresponding polymers without these groups in the repeat units.<sup>4</sup> The improved solubility and lower  $T_g$ 's are attributed to the flexible linkages, which provide a polymer chain with a lower energy of internal rotation.<sup>5</sup>

The heterocyclic rings in the main chain of a polymer impart certain properties to the polymer. The selection of a pyridine nucleus is based on its high thermal stability, which is derived from its molecular symmetry and aromaticity.<sup>6,7</sup>

As part of our continuing interest in the preparation of thermally stable polymers,<sup>8–14</sup> we describe the synthesis and characterization of two pyridine-based diamines. The polycondensation reactions of 2,6-bis(4-aminophenoxy) pyridine (AP) and 2,6-bis(5-amino-1-naphthoxy) pyridine (AN) with aromatic dianhydrides afforded thermally stable poly(ether imide)s.

## EXPERIMENTAL

### Materials

Dianhydrides, 2,6-dichloropyridine, *N*-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), toluene,  $K_2CO_3$ , methanol, pyridine, and acetic anhydride were obtained from Merck Chemical Co. 4-Aminophenol and 5-amino-1-naphthol were purchased from Aldrich Chemical Co. Dianhydrides were dried in a vacuum oven at 110°C for 5 h. NMP, DMAc, and toluene were purified by vacuum distillation over calcium hydride.

### Instruments

Infrared measurements were performed on a Bruker IFS 48 FTIR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in a dimethyl sulfoxide ( $DMSO-d_6$ ) or chloroform ( $CDCl_3$ ) solution with a Bruker Avance DRX 250-MHz instrument (GmbH, Germany). A Heraeus CHN-O rapid elemental analyzer (Wellesley, MA) was used for the elemental analyses. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Differential thermogravimetry traces were recorded on a Polymer

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Lab TGA-1500 (Surrey, UK). The dynamic mechanical measurements were performed on a Polymer Laboratories MK-II dynamic mechanical thermal analyzer (Surrey, UK) at 1 Hz and at a heating rate of 5°C/min. The value of  $\tan \delta$  and the storage modulus versus the temperature were recorded for each sample. The inherent viscosities ( $\eta_{inh}$ ) were measured with an Ubbelohde viscometer.

### Monomer synthesis

#### Synthesis of the AP diamine

Into a 100-mL, three-necked, round-bottom flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer were placed 0.01 mol of 2,6-dichloropyridine, 25 mL of dry NMP, 15 mL of dry toluene, and 0.021 mol of 4-aminophenol. Then, 0.0315 mol of  $K_2CO_3$  was added to the mixture, and the reaction mixture was heated to 140°C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C by the removal of more toluene and kept at the same temperature for 20 h. During this time, the progress of the reaction was monitored by thin-layer chromatography. The resulting reaction mixture was cooled and poured into water. Then, 100 mL of 3% NaOH was added to the mixture, and the mixture was washed repeatedly with a 3% NaOH solution and water. The obtained diamine was dried in a vacuum oven at 60°C. The yield of the reaction was about 88% (2.58 g).

IR (KBr,  $\nu$ ): 3300–3450 (N—H), 1450–1600 (C=C), about 1140  $cm^{-1}$  (—O—).  $^1H$ -NMR ( $CDCl_3$ ,  $\delta$ ): 3.60 (s, 4H, amine), 6.34 (d, 2H, pyridine ring), 6.63–6.66 (m, 4H, benzene ring), 6.90–6.93 (m, 4H, benzene ring), 7.51 (t, 1H, pyridine ring). ELEM. ANAL. Calcd. for  $C_{17}H_{15}N_3O_2$ : C, 69.62%; H, 5.12%; N, 14.33%. Found: C, 69.49%; H, 5.19%; N, 14.42%.

#### Synthesis of the AN diamine

The aforementioned procedure was applied to the synthesis of the diamine. However, 5-amino-1-naphthol was used instead of 4-aminophenol. The yield of the reaction was about 92% (3.61 g).

IR (KBr,  $\nu$ ): 3300–3400 (N—H), 1400–1600 (C=C), about 1150  $cm^{-1}$  (—O—).  $^1H$ -NMR ( $DMSO-d_6$ ,  $\delta$ ): 5.83 (s, 4H, amine), 6.50 (d, 2H, pyridine), 6.71 (d, 2H, naphthyl ring), 7.01–7.29 (m, 8H, naphthyl ring), 7.75 (t, 1H, pyridine), 7.94 (d, 2H, naphthyl ring). ELEM. ANAL. Calcd. for  $C_{25}H_{19}N_3O_2$ : C, 76.33%; H, 4.83%; N, 10.69%. Found: C, 76.24%; H, 4.79%; N, 10.74%.

### Polyimide synthesis

A two-step method was used for the preparation of the polyimides. A typical procedure for the prepara-

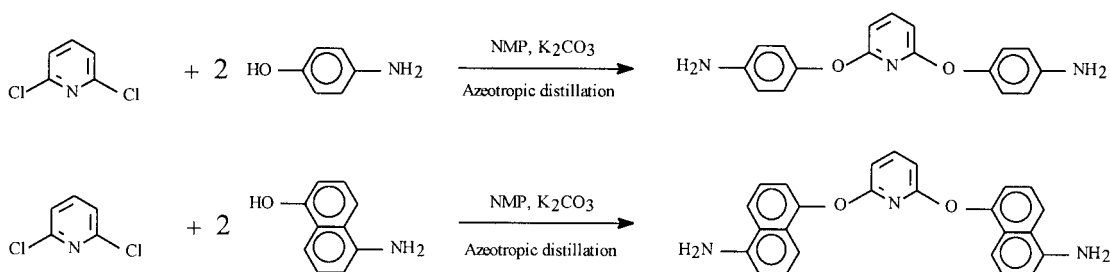
tion of poly(amic acid) was as follows. A 100-mL, two-necked, round-bottom flask equipped with a magnetic stirrer, a nitrogen gas inlet tube, and a calcium chloride drying tube was charged with 1.5 mmol of the prepared diamine and 12 mL of dry NMP. The mixture was stirred at 0°C for 0.5 h, 1.5 mmol of the 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 the flask content being poured into 200 mL of a 3:1 (v/v) mixture of water and methanol; it was then filtered and dried overnight *in vacuo* at 40°C, and yields greater than 85% were obtained. Chemical cyclization for the conversion of poly(amic acid) to polyimide was applied: into a 100-mL, two necked, round-bottom flask equipped with a magnetic stirrer, an  $N_2$  gas inlet tube, and a reflux condenser were 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 was slowly heated to 140°C and held for 6 h at the same temperature. Afterward, the mixture was cooled and poured into water; it was filtered, washed with hot water, and dried overnight *in vacuo* at 120°C. Yields greater than 87% were obtained.

## RESULTS AND DISCUSSION

The preparation of modified polyimides with improved solubility and processability without the sacrifice of their thermal and mechanical properties was the main aim of this study. Accordingly, the design and synthesis of the monomers and polymers involved some structural modifications. These modifications included (1) the introduction of a heterocyclic ring along the polymer backbone, (2) the incorporation of flexible or kinked linkages into the backbone, (3) the phenylation of the backbone, and (4) a relative disruption of the symmetry and regularity of the repeating unit.

Therefore, two diamines, used as building blocks for the preparation of polyimides, were synthesized. A nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine afforded AP and AN, respectively. The reactions were carried out in NMP (used as a solvent) and in the presence of potassium carbonate (Scheme 1).

The structures of the prepared diamines were fully characterized by common spectroscopic methods. The reaction of the obtained diamine with aromatic dianhydrides provided poly(amic acid)s, with which, after subsequent chemical dehydration, the related poly(ether imide)s were prepared (Scheme 2). Conventional spectroscopic methods were used to character-



**Scheme 1** Preparation of ether diamines.

ize the structures of the poly(ether imide)s, and the results are collected in Table I.

Although there are a few reports on using aminophenoxy pyridine diamine as a monomer for the preparation of some polymers,<sup>15,16</sup> here studied a series of polyimides based on aminophenoxy and aminonaphthoxy pyridine diamines and compared the structure-property relations.

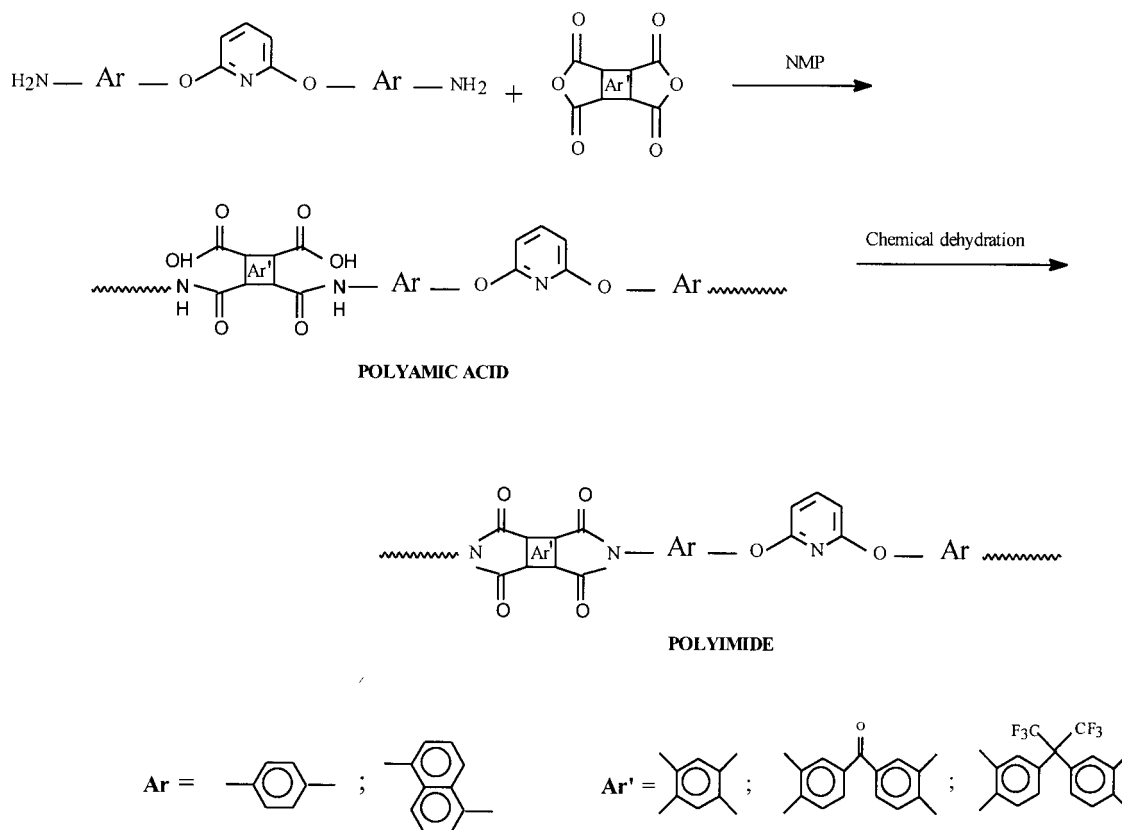
The  $\eta_{inh}$  values of the polyimides were about 0.38–0.45 dL/g, indicating moderate molecular weights (Table I).

To study the thermal behavior of the polymers, we recorded dynamic mechanical thermal analysis (DMTA) traces. The softening point was not detected

for the polyimides. However, the storage modulus of the polymers decreased, and  $\tan \delta$  went through a maximum in the range of 215–253°C. This property was attributed to  $T_g$  of the polymers.

An exotherm transition starting around 236–312°C was observed for the polymers assigned to thermal degradation. Also, DSC traces were recorded, and the obtained results confirmed the DMTA results.

A thermal stability evaluation of the polyimides was carried out by TGA in air at a heating rate of 10°C/min. The polymers started to lose weight, because of thermal degradation, in the range of 236–312°C. This was the initial decomposition temperature (IDT), denoted  $T_0$  in Table II. The temperature for 10%



**Scheme 2** Preparation of poly(ether imide)s.

TABLE I  
Reactants and Properties of the Poly(ether imides)

Reactant	IR (KBr; $\text{cm}^{-1}$ )	NMR (DMSO- $d_6$ ; $\delta$ )	Elemental analysis						$\eta_{\text{inh}}^a$ (dL/g)
			Calcd			Found			
			C	H	N	C	H	N	
AP-PMDA	1780, 1724, 1377, 1165, 725	8.32/2H, 7.58/1H, 7.54/4H, 6.90/4H, 6.37/2H	68.21	2.74	8.84	68.34	2.84	8.75	0.43
AP-BTDA	1782, 1718, 1375, 1161, 726	8.16/2H, 8.13/2H, 7.88/2H, 7.56/1H, 7.51/4H, 6.87/4H, 6.35/2H	70.47	2.94	7.25	70.32	3.02	7.38	0.38
AP-6FDA	1786, 1728, 1377, 1146, 728	7.99/2H, 7.68/2H, 7.61/2H, 7.57/1H, 7.53/4H, 6.88/4H, 6.35/2H	61.63	2.42	5.99	61.94	2.64	5.79	0.40
AN-PMDA	1780, 1725, 1375, 1148, 726	8.76/2H, 8.34/2H, 8.31/2H, 7.79/2H, 7.77/1H, 7.73/2H, 7.48/2H, 6.76/2H, 6.54/2H	73.04	2.96	7.30	73.34	3.04	7.15	0.45
AN-BTDA	1782, 1724, 1376, 1153, 721	8.72/2H, 8.32/2H, 8.15/2H, 8.11/2H, 7.85/2H, 7.77/2H, 7.74/1H, 7.70/2H, 7.45/2H, 6.72/2H, 6.51/2H	74.23	3.09	6.18	74.51	2.99	6.34	0.41
AN-6FDA	1786, 1730, 1378, 1145, 722	8.71/2H, 8.31/2H, 7.95/2H, 7.77/2H, 7.74/1H, 7.71/2H, 7.68/2H, 7.60/2H, 7.46/2H, 6.73/2H, 6.52/2H	65.92	2.62	5.24	65.78	2.84	5.78	0.45

PMDA = pyromellitic dianhydride; BTDA = benzophenonetetracarboxylic dianhydride; 6FDA = hexafluoroisopropylidene diphthalic anhydride.

<sup>a</sup> Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

gravimetric loss ( $T_{10}$ ) was an important criterion for the evaluation of thermal stability in these thermally stable polymers. It was around 418–475°C, which indicated high thermal stability in these polymers. Maximum decomposition temperature ( $T_{\text{max}}$ ) of the polymers was derived from TGA curve. The results are collected in Table II.

The IDT temperatures of the polymers were not too high. This may be attributed to the presence of heterocyclic groups in the backbone and the polar nature of the polymers. Because of these features, the polymers did not exclude moisture and solvents completely even after drying in a vacuum oven, and so they showed relatively low IDTs. However,  $T_g$ ,  $T_{10}$ ,

and char yields of the polymers were good criteria for the estimation of the thermal stability. Therefore, on the basis of the thermal analysis data, it was concluded that the prepared polyimides were highly thermally stable polymers.

According to the results, polyimides derived from AP had higher thermal stability than corresponding polyimides based on the AN diamine. This was a result of the symmetry and regularity of the aminophenoxy group in comparison with the aminonaphthoxy group.

The polymers were soluble in dipolar aprotic solvents such as NMP, DMAc, dimethylformamide, and DMSO and also in a less efficient solvent (*m*-cresol) in

TABLE II  
Thermal Data of the Polyimides

Polymer	$T_g$ (°C)	$T_0$ (°C)	$T_{10}$ (°C)	$T_{\text{max}}$ (°C)	Char yield at 600°C (%)
AP-PMDA	253	312	475	578	65
AP-BTDA	238	306	462	552	62
AP-6FDA	235	300	470	553	60
AN-PMDA	237	254	432	535	64
AN-BTDA	219	238	420	525	52
AN-6FDA	215	236	418	552	58

PMDA = pyromellitic dianhydride; BTDA = benzophenonetetra carboxylic dianhydride; 6FDA = hexafluoroisopropylidene diphthalic anhydride.

the range of 0.8–1.4 g/dL. However, the aminonaphthoxy-derived polymers were more soluble than the aminophenoxy-derived polymers. This was another effect of the symmetry and its relative disruption of the properties of the polymers in addition to the effect of flexible groups being added.

Films of the polymers were cast from NMP (used as a solvent) with temperature programming (1 h at 100°C, 1 h at 200°C, and 0.5 h at 300°C). Almost all the polymer films were brittle.

### CONCLUSIONS

Two pyridine-based ether diamines were prepared by a nucleophilic aromatic substitution reaction of 4-aminophenol and 5-amino-1-naphthol with 2,6-dichloropyridine. Six different thermally stable poly(ether imide)s were prepared by a two-step polycondensation reaction of the diamines with aromatic dianhydrides. The introduction of an ether linkage, the phenylation of the backbone, the presence of a heterocyclic pyridine ring, and the relative disruption of the symmetry (a less symmetrical structure for the aminonaphthoxy group than for the aminophenoxy group) were used to improve the solubility of the polyimides without a remarkable sacrifice of thermal stability. A study of polyureas and their synthesis from the prepared diamines is in progress.

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