

Novel Thermally Stable Poly(ether imide ester)s from 2,6-Bis (4-aminophenoxy) Pyridine

Shahram Mehdipour-Ataei, Ahmad Amirshaghghi

Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran

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ABSTRACT: 2,6-Bis (4-aminophenoxy) pyridine was prepared via reaction of 4-aminophenol with 2,6-dichloropyridine in the presence of potassium carbonate in *N*-methyl-2-pyrrolidone (NMP). This pyridine-based ether diamine was reacted with two moles of trimellitic anhydride to synthesize related diimide-diacid (DIDA). A high temperature solution polycondensation reaction of DIDA with different diols in the presence of triethylamine hydrochloride in dichloroben-

zene resulted in different poly(ether imide ester)s. The monomer and polymers were fully characterized, and the physical and thermal properties of the polymers were studied. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 570–576, 2005

Key words: high performance polymers; polycondensation; polyesters; polyimides

INTRODUCTION

High-performance polymers are an important class of polymers, and their applications are growing steadily. Many studies of new polymer syntheses have been focused on the preparation of high-performance polymers. In general, they show high thermal stability, good chemical resistance, and excellent mechanical properties. Imide polymers and copolymers are a well-established class of polymers that show a good combination of mechanical, electrical, and thermal properties.^{1,2}

Aromatic polyimides are thermally stable polymers that generally show excellent mechanical strength and stability. Due to 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. 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.³ 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.⁴

Aromatic polymers that contain aryl ether linkage generally have greater tractability, lower glass transi-

tion, and greater chain flexibility than their corresponding polymers without these groups in the repeat units.⁵ The improved solubility and lower glass transition temperatures are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation.⁶

Copolycondensation is one of the possible ways for modification of polymer properties.

Modification of the properties of polyimides by incorporation of ester groups has been investigated. Aromatic poly(ester imide)s (PEIs) are an important class of thermally stable polymers, and they have various commercial applications. Their main applications are in coatings for enameled wires, hot melt adhesives, heat resistant films, high strength fibers, and printed circuit boards.^{7–10} Several methods have been reported for the synthesis of PEIs. The most important ones include direct polycondensation of trimellitic anhydride with a mixture of a diamine and a diol,^{11,12} and reaction of a dicarboxylic acid containing a preformed imide group with a diol.^{13–15}

Here we wish to describe the synthesis of novel thermally stable poly(ether imide ester)s via reaction of a dicarboxylic acid containing a preformed imide group with diols. For such investigation and in the first step, reaction of 4-aminophenol with 2,6-dichloropyridine in the presence of potassium carbonate in (NMP) led to preparation of 2,6-bis (4-aminophenoxy) pyridine. Reaction of this ether diamine with trimellitic anhydride resulted in preparation of the related diimide-diacid (DIDA). The DIDA was converted to its diacidchloride (DIDAC) using thionyl chloride. A high temperature solution polycondensation reaction of DIDAC with different diols in the presence of tri-

Correspondence to: S. Mehdipour-Ataei (S.Mehdipour@proxy.ipi.ac.ir).

ethylamine hydrochloride in dichlorobenzene resulted in different aromatic and semiaromatic poly(ether imide ester)s.

EXPERIMENTAL

Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. 2,6-dichloropyridine and trimellitic anhydride were recrystallized from 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. 4-Aminophenol was purified by sublimation under reduced pressure.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FT-IR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in dimethyl sulfoxide (DMSO- d_6) solution using a Bruker Avance DPX 250-MHz instrument (GmbH, Germany). A CHN-O-Rapid Heraeus elemental analyzer performed elemental analyses (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). Differential thermogravimetric (DTG) traces were recorded on a Polymer Lab TGA-1500 (London, UK). The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of 25–300°C at 1 Hz and a heating rate of 5°C/min (Surrey, UK). The value of $\tan \delta$ and the storage modulus versus temperature were recorded for each sample. Inherent viscosities were measured by using an Ubbelohde viscometer in a concentration of 0.5 g/dL in NMP at 30°C. Wide angle X-ray diffraction patterns were performed at room temperature on an X-ray diffractometer (Siemens model D 5000) using Ni-filtered Cu K α radiation (40 kV, 25 mA) with a scanning rate of 3°/min.

Synthesis of 2,6-bis(4-aminophenoxy) pyridine (AP)

Into a 100-mL, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a ni-

trogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer was 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 K₂CO₃ was added to the mixture, and the reaction mixture was heated to 140°C for 6h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165°C by removing 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 (TLC). 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 87.9% (2.58 g).

Synthesis of diimide-diacid (DIDA)

To a solution of 2,6-bis(4-aminophenoxy) pyridine (29.3 g, 0.1 mol) dissolved in 250 mL of NMP in a 500 mL flask, 38.45 g (0.20 mol) of TMA was added. The stirred reaction mixture was heated to 80°C for 2h under N₂. Then, 100 mL of dry toluene was added to the mixture, and it was heated to reflux for about 12h until water was distilled off azeotropically via a Dean-Stark trap.

After cooling the reaction mixture to room temperature, the precipitate was collected by filtration, washed several times with methanol, and dried in a vacuum oven at 100°C. (Yield 91.6%.)

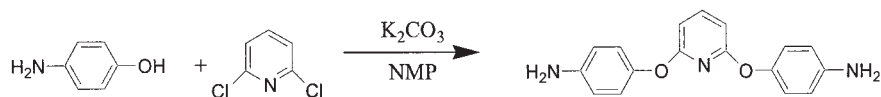
Synthesis of diimide-diacidchloride (DIDAC)

DIDA (9.0 g, 0.014 mol) was refluxed with thionyl chloride (80 mL) and two drops of dry DMF for 4h. Then, the excess of thionyl chloride was removed from the mixture by distillation. The crude product was recrystallized from ether and vacuum dried at 60°C. (Yield 98%.)

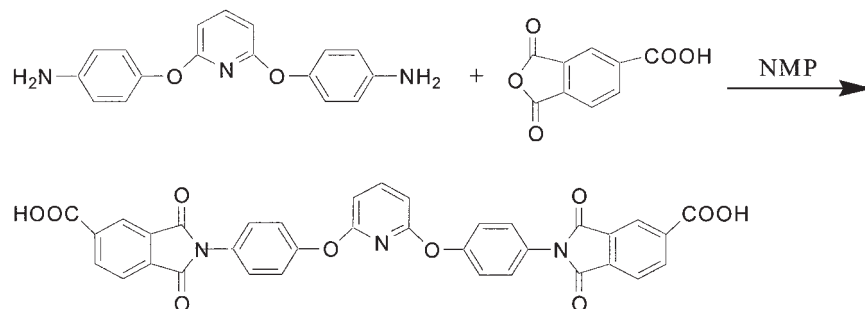
Poly(ether imide ester)s synthesis

A typical synthesis of polyesters was carried out as follows:

In a round-bottomed flask equipped with a stirrer, nitrogen inlet tube, HCl outlet tube, and condenser



Scheme 1 Preparation of diamine (AP).



Scheme 2 Preparation of diimide-diacid (DIDA).

was placed 4.5 mmol of diol, 0.072 g of triethylamine hydrochloride, and 9 mL of 1, 2-dichlorobenzene. The mixture was heated to 180°C under nitrogen flow, and a solution of 4.5 mmol diacid chloride in 9 mL of dichlorobenzene was added dropwise through a funnel. The mixture was heated until the evolution of HCl ceased, a period of about 5 h. After cooling, the polymer was precipitated in hexane and washed with methanol and water successively. (Yields over 78%.)

RESULTS AND DISCUSSION

Aromatic diamines are valuable building blocks for the preparation of high performance polymers, including polyimides, polyamides, and their copolymers. To extend the utility of these high performance polymers, it has been a long desired goal to design and synthesize diamines, which afford special properties to the final polymers.¹⁶ On the other hand, the choice of heterocyclic rings in the main chain of the polymer is to impart certain properties to the polymer. The selection of a pyridine nucleus is based on its high thermal stability derived from its molecular symmetry and aromaticity.¹⁷⁻²⁰

Therefore, structural modifications were considered to impart certain properties to the final polymers. Among these, high thermal stability and improved solubility were the most important goals. Accordingly, these mod-

ifications were: (1) the introduction of a heterocyclic ring along the polymer backbone; (2) the incorporation of flexible or kinked linkages in the backbone; (3) phenylation of the backbone; and (4) relative disruption of symmetry and regularity of the repeating unit.

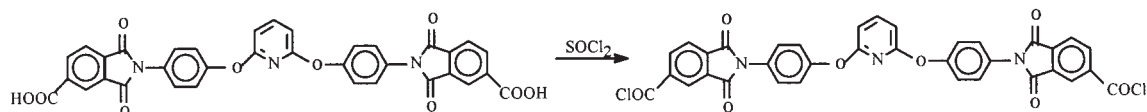
So, a symmetrical pyridine-based ether diamine named 2,6-bis(4-aminophenoxy) pyridine as a building block for the preparation of polymers was synthesized by nucleophilic aromatic substitution reaction of 4-aminophenol with 2,6-dichloropyridine. The reaction was performed in NMP solvent and in the presence of K_2CO_3 (Scheme 1).

Reaction of the obtained diamine with two moles of trimellitic anhydride resulted in preparation of a diacid (DIDA) with preformed imide and ether structures (Scheme 2). The structure of the diamine and the DIDA was characterized by common spectroscopic methods. The FT IR spectrum of the diamine showed characteristic bands at 3300–3450 (–NH stretching of –NH₂), 1450–1600 (C=C stretching and –NH out of plane bending), and 1140 cm^{-1} (–C–O–). Also, bands at 3450 (–OH stretching of –COOH), 3039 (Ar–H), 1782 (imide –C=O symmetrical stretching), 1721 (imide –C=O unsymmetrical stretching), 1597 (C=C), 1384 (imide C–N stretching), and 729 cm^{-1} (–C=O out of plane deformation) were observed in the FT IR spectrum of DIDA. Table I shows the characteristic features of the two substances.

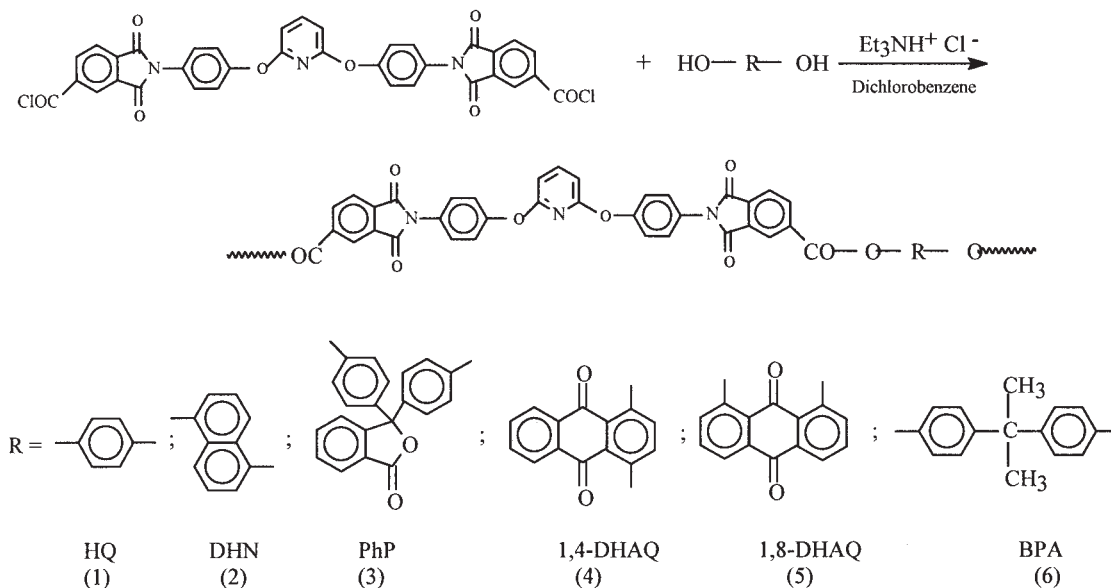
TABLE I
Characteristic Data for Diamine (AP) and Diimide-Diacid (DIDA)

Substrate	IR (KBr-Cm ⁻¹)	NMR ¹ (δ, PPM)	Elemental analysis		Yield (%)
			Calc.	Found	
			C H N	C H N	
AP	3300–3450 1450–1600	3.60s (4H, Amine), 6.34d (2H, Py) 6.63–6.66m (4H, Ph), 6.90–6.93m (4H, Ph), 7.51t (1H, Py)	69.62/5.12/14.33;	69.49/5.19/14.42	87.9
DIDA	3450, 3039 1782, 1721 1597, 1384 729	13.73s(2H, COOH), 8.33d(2H, TMA) 8.01s (2H, TMA), 7.94t (1H, Py) 7.89d (2H, TMA), 7.40d (4H, Ph) 7.23d (4H, Ph), 6.79d (2H, Py)	65.52/2.96/6.55;	65.11/2.77/6.78	91.6

¹ Py: Pyridine; Ph: Phenyl; TMA: Trimellitic anhydride.



Scheme 3 Preparation of diimide-diacidchloride (DIDAC).



Scheme 4 Preparation of poly(ether imide ester)s.

TABLE II
Polymer Characterization

No.	Polymer	IR(KBr, Cm^{-1})	NMR (DMSO- d_6 , δ)	Elemental analysis		η_{inh} (dl/g)	Yield (%)
				Calc. C H N/	Found C H N		
1	DIDAC-HQ	3029,1781,1720, 1586,1383,1217, 720	7.01–8.32/18H, 7.83/1H, 6.69/2H	68.81/2.93/5.87	68.52/3.08/5.39	0.47	90
2	DIDAC-DHN	3026,1779,1719, 1581,1381,1209, 720	7.08–8.40/20H, 7.89/1H, 6.73/2H	70.59/3.00/5.49	70.28/2.86/5.73	0.46	90
3	DIDAC-PhP	3028,1778,1722, 1582,1378,1205, 720	7.10–8.43/26H, 7.88/1H, 6.74/2H	71.50/3.14/3.55	71.84/2.99/4.28	0.40	78
4	DIDAC-1,4-DHAQ	3045,1782,1748, 1723,1585,1383, 1205,719	7.04–8.38/20H, 7.87/1H, 6.70/2H	69.58/2.72/4.97	69.34/2.59/5.06	0.43	90
5	DIDAC-1,8-DHAQ	3042,1780,1745, 1722,1590,1382, 1210,720	7.07–8.35/20H, 7.85/1H, 6.69/2H	69.58/2.72/4.97	69.36/2.94/4.80	0.40	94
6	DIDAC-BPA	3030,2965,1780, 1723,1582,1380, 1208,720	7.02–8.36/23H, 7.85/1H, 6.68/2H, 1.67/6H	72.03/3.72/5.04	71.86/3.55/5.28	0.41	80

To increase the reactivity of the DIDA toward polycondensation, DIDA was converted to its diacidchloride (DIDAC) using thionyl chloride (Scheme 3). The FT IR spectrum of the DIDAC showed characteristic

bands at 3042 (Ar-H), 1810 (acid chloride $-\text{C}=\text{O}$), 1785 (imide $-\text{C}=\text{O}$ symmetrical stretching), 1725 (imide $-\text{C}=\text{O}$ unsymmetrical stretching), 1579 ($\text{C}=\text{C}$), 1380 (imide C-N stretching), and 731 cm^{-1} ($-\text{C}=\text{O}$ out of

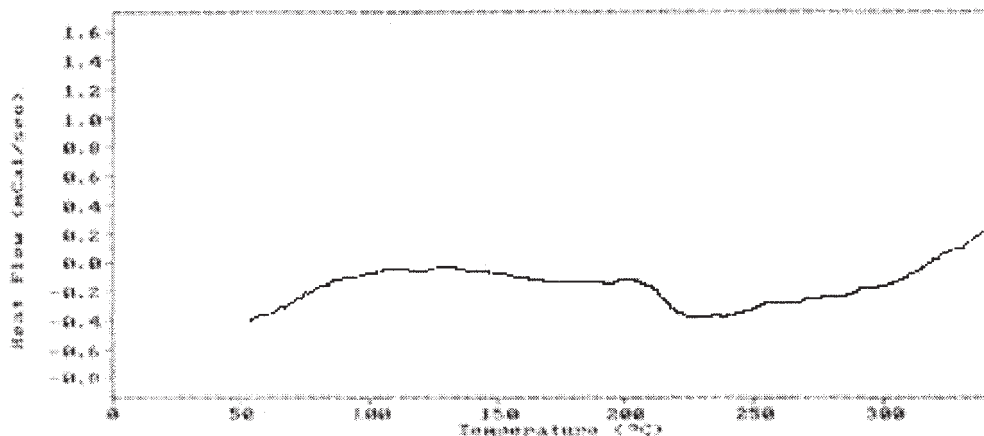


Figure 1 DSC curve of DIDAC-PhP polymer.

plane deformation). The high temperature solution polycondensation of DIDAC with six different diols, including hydroquinone, 1,5-dihydroxy naphthalene, phenolphthalein, 1,4-dihydroxy anthraquinone, 1,8-dihydroxy anthraquinone, and bisphenol A, in the presence of triethylamine hydrochloride in dichlorobenzene resulted in different aromatic and semiaromatic poly(ether imide ester)s (Scheme 4). All the polymers were characterized using IR, NMR, and elemental analysis techniques, and the results are shown in Table II. The inherent viscosity of the polymers as a criterion for evaluation of molecular weights was measured in NMP at a concentration of 0.5gdl^{-1} at 30°C (Table II). These results reveal that the polymers are of reasonable molecular weights.

To study the crystalline characteristics of the polymers, WAXS measurements at room temperature in the region of $2\theta = 5\text{--}70^\circ$ were performed. According to the results, polymers exhibited semicrystalline patterns (about 10–20% crystallinity).

The solubility of the polymers was measured in dipolar aprotic solvents, including NMP, DMAc, DMF, DMSO, and also *m*-cresol. The polymers showed solubility (by heating and stirring) in the range of $0.7\text{--}1.2\text{gdl}^{-1}$. However, the films cast from solutions of polymers were hard and brittle.

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 the polymers (T_g) were in the range of

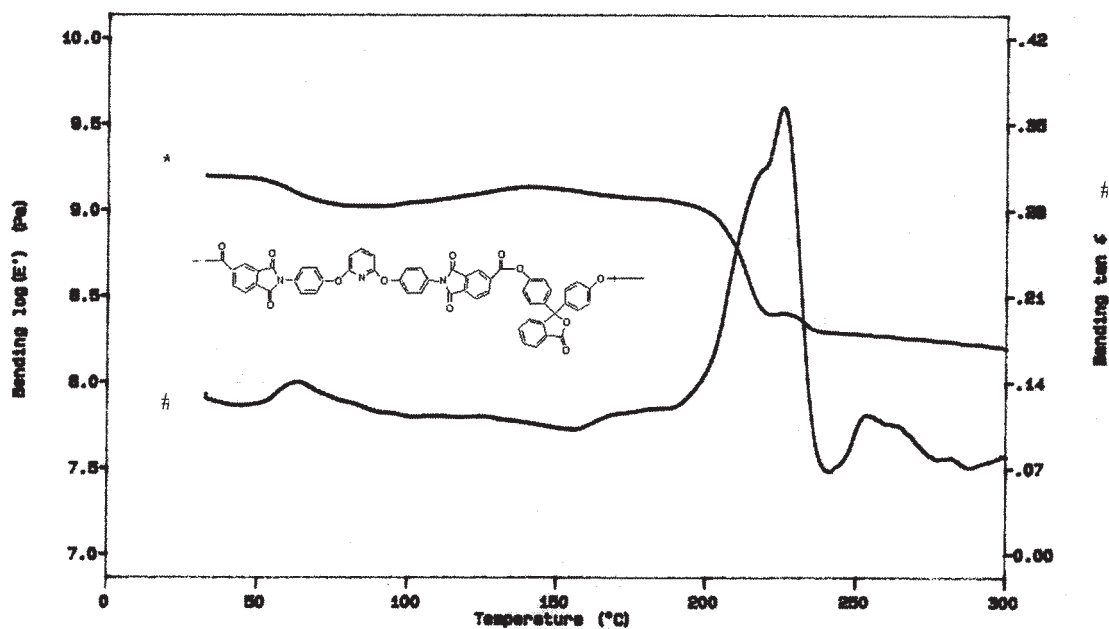


Figure 2 DMTA curve of DIDAC-PhP polymer.

TABLE III
Thermal Analysis Data

No.	T _g (°C)	T ₀ (°C)	T ₁₀ (°C)	T _{max} (°C)	Char yield at 600°C (%)
1	240	215	480	494	64
2	230	210	469	478	63
3	225	200	445	474	60
4	204	180	386	438	53
5	201	176	384	425	55
6	196	169	375	410	45

T_g: glass transition temperature; T₀: initial decomposition temperature; T₁₀: temperature for 10% weight loss; T_{max}: maximum decomposition temperature; Char yield: weight of polymer remained.

196–240°C. It 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 δ in DMTA traces. The representative DSC and DMTA plots are shown in Figures 1 and 2, respectively.

TGA analysis in air at a heating rate of 10°C min⁻¹ was used for evaluation of thermal stability. The temperature for 10% gravimetric loss (T₁₀), which is an important criterion for evaluation of thermal stability, was in the range of 375–480°C. The initial decomposition temperature (T₀) was about 169–215°C. Char yields of the polymers at 600°C were about 45–64%. The obtained results from thermal analyses are collected in Table III, and the representative plot of TGA is shown in Figure 3.

The obtained data showed that these polymers were highly thermally stable polymers and the more rigid ones were more heat resistant. Incorporation of flexible groups from the diol moiety (alkylene group) decreased the thermal stability and increased the solubility of the polymers.

Thus, some approaches, including introduction of imide units, phenylation of the backbone, and retention of symmetry, were used to improve the thermal stability of the polyesters. On the other hand, the presence of a pyridine ring and ether units in the diacid structure, and also incorporation of flexible groups and disruption of symmetry from the diol moieties, were applied to improve the solubility of the polymers.

CONCLUSIONS

A pyridine-based ether diamine as a building block for the preparation of high performance poly (ether imide ester)s was synthesized from nucleophilic aromatic substitution reaction of 4-aminophenol with 2,6-dichloropyridine. Trimellitic anhydride was reacted with this diamine to synthesize a diacid with preformed ether and imide units (DIDA). Using thionyl chloride, DIDA was converted to DIDAC. Poly(ether imide ester)s were prepared via high temperature solution polycondensation of DIDAC with different diols. The prepared polyesters showed high thermal stability (due to the introduction of imide groups, phenylation of the backbone, and retention of symme-

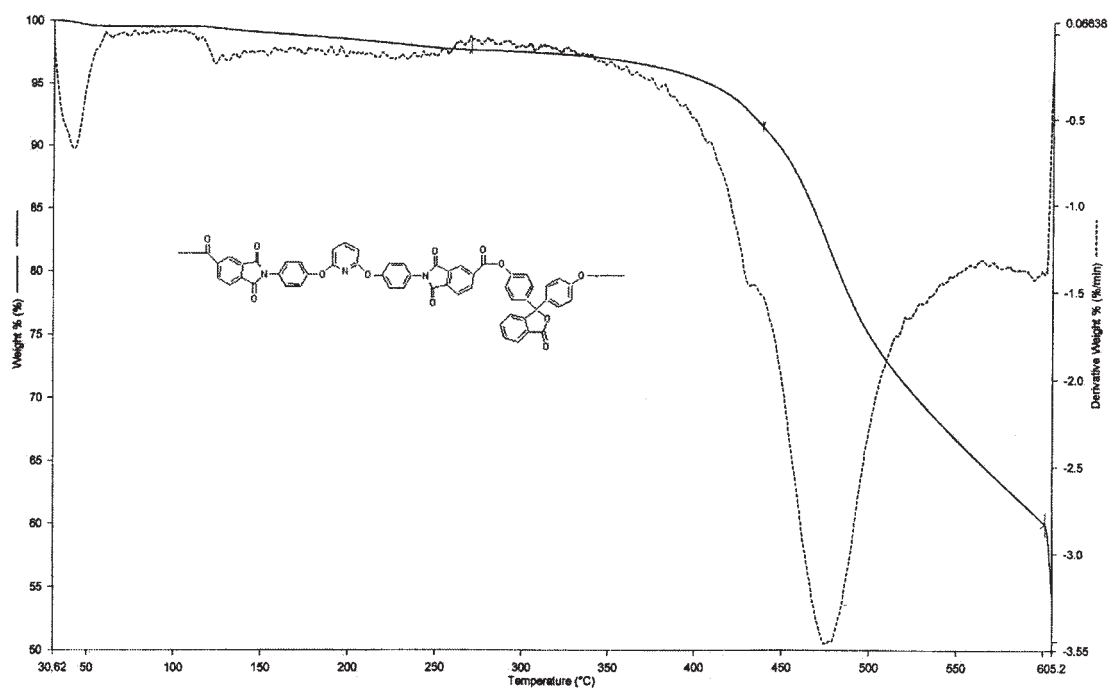


Figure 3 TGA-DTG plot of DIDAC-PhP polymer.

try) and improved solubility (due to incorporation of a pyridine unit and flexible or kinked linkages in the backbone and also relative disruption of symmetry).

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