

HEAT-RESISTANT PYRIDINE-BASED POLY(ETHER-ESTER)S: SYNTHESIS, CHARACTERIZATION AND PROPERTIES

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Abstract A pyridine-based diacid was synthesized *via* nucleophilic substitution reaction of 4-hydroxy benzoic acid with 2,6-dichloropyridine in the presence of potassium carbonate. The diacid was characterized using FT-IR and ¹H-NMR spectroscopic methods and also with elemental analysis. Polycondensation reaction of the diacid with different diols including 1,4-dihydroxy benzene, 1,5-dihydroxy naphthalene, bis-phenol A and bis-phenol-P resulted in preparation of pyridine-based poly(ether-ester)s. The polymers were characterized and their physical and thermal properties including inherent viscosity, molecular weight, solubility, thermal stability, thermal behavior and crystallinity were studied. They revealed high heat-resistance and improved solubility in polar solvents. Structure-property relations for the prepared polyester were also studied.

Keywords: Polyester; Polymer synthesis and characterization; Thermal properties; Structure-property relations.

INTRODUCTION

Heat-resistant or thermally stable materials are one of the noteworthy areas within polymer science which have been recognized for about 60 years and their applications are growing progressively. The most significant categories of these polymers are polyimide, polyamide, polyarylate and their copolymers. Polyarylates belong to the class of high-performance engineering plastics, and they show good thermal and mechanical properties and have various commercial applications^[1, 2]. Their main applications are in coatings for enameled wires, hot melt adhesives, heat resistant films, high strength fibers and printed circuit boards^[3–6]. Some of them with special properties find particular applications, for example optical activity polyesters are among these groups. Preparation of optically active polymers has become of vast interest due to their chiral structure, which may contribute a significant position in the molecular arrangement and assembly that is essential for optoelectronics supramolecular structure^[7, 8].

However, because of their limited solubility in organic solvents and their high melting or high glass transition temperatures, polyarylates are generally difficult to be processed by virtue of their rigid structures. Introduction of bulky and pendent units, presence of flexible ether or alkyl units and also disruption of symmetry are important methods to overcome this drawback^[9–12].

Therefore, a great deal of attempts has been devoted to improve the processing characteristics of these relatively intractable polymers. Thus, efforts in this area include introducing flexible segments into the polymer chain, replacing symmetrical aromatic rings with unsymmetrical ones which lead to a reduction in crystallinity, introducing bulky pendant groups to minimize crystallization and forming a noncoplanar structure, thereby making crystallization impossible^[13–18].

Here we wish to describe the synthesis of a diacid. The diacid was prepared in such a way that it contained

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Received February 24, 2012; Revised April 7, 2012; Accepted April 12, 2012

doi: 10.1007/s10118-013-1192-0

pyridine unit and ether flexible groups. New types of pyridine-based heat resistant poly(ether-ester)s were prepared *via* polycondensation reactions of the diacid with four different diols. The structures of the prepared poly(ether-ester)s were confirmed, and their physical and thermal properties were studied. Structure-property relations for these polyesters were also investigated. Presence of flexible ether units and polar pyridine rings from one side caused improved solubility, and incorporation of aromatic rings and avoid of weak linkages from another side led to high heat-resistant of these new poly(ether-ester)s. Therefore, the main problem of heat-resistant polymers that is improving of solubility without too much sacrificing of thermal stability was properly overcome.

EXPERIMENTAL

Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF) and toluene were distilled over calcium hydride under reduced pressure. 1,4-Dihydroxy benzene, 1,5-dihydroxy naphthalene, bis-phenol A and bis-phenol-P were purified by recrystallization.

Instruments

Infrared measurements were performed on a Bruker-IFS 48 FT-IR spectrometer (Ettlingen, Germany). The ¹H-NMR spectra were recorded in DMSO-*d*₆ solution using a Bruker Avance DPX 250 MHz (GmbH, Germany). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Thermogravimetric analysis (TGA) was recorded on a Stanton Redcraft STA-780 (London, UK). Inherent viscosities were measured at a concentration of 0.5 g/dL in DMF at 30°C by using an Ubbelohde viscometer. 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 scanning rate of 3 (°)/min. The weight-average molecular weight (*M_w*) was determined by gel permeation chromatography (GPC). GPC was performed on a Waters 150-C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as solvent.

Synthesis of Diacid

Into a 100 mL, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath and a magnetic stirrer were placed 0.012 mol (1.79 g) of 2,6-dichloro pyridine, 12 mL of dry NMP, 7 mL of dry toluene and 0.022 mol (3.55 g) of 4-hydroxy benzoic acid. Then 2.20 g of K₂CO₃ 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 removing more toluene and kept at the same temperature for 18 h. During this time, progress of the reaction was monitored by thin-layer chromatography (TLC). The resulting reaction mixture was cooled and poured into water. Then it was washed repeatedly with water. The obtained diacid was dried in a vacuum oven at 60°C (yield 78%).

IR (KBr): ν 2650–3250, 1692, 1434–1588, and 1288 cm⁻¹; ¹H-NMR (DMSO-*d*₆, δ): 13.06 (s, 2H, COOH), 7.89 (t, 1H, pyridine), 7.68 (d, 4H, phenyl), 7.50 (d, 2H, pyridine), 7.38 (d, 4H, phenyl); elemental analysis calculated for C₁₉H₁₃NO₆ (M.W. = 351): C, 64.96%; H, 3.70%; N, 3.99%; found: C, 65.05%; H, 3.63%; N, 4.04%.

Synthesis of Poly(ether-ester)s

A typical procedure was as follows: A mixture of 11.5 mmol of *p*-toluenesulfonyl chloride, 1.0 mL of dry DMF and 4.0 mL of pyridine was stirred at room temperature for 30 min. Then 0.002 mol of diacid was added to the mixture and stirring was continued. After solidification of the mixture, it was heated to 80°C for 10 min. Diol (0.002 mol) was dissolved in 5.0 mL of pyridine and was added to the mixture during 10 min. The reaction

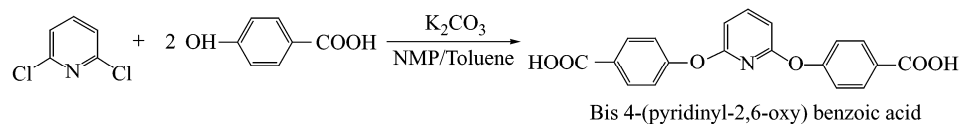
mixture was heated to 120°C for 2 h. After cooling, the reaction mixture was poured into a large amount of water with stirring. The obtained precipitate was filtered and washed several times with methanol and hot water. Then it was dried at 90°C under vacuum overnight.

RESULTS AND DISCUSSION

Aromatic polyesters were developed as high performance polymers which possess good thermal properties, excellent mechanical properties and high glass transition temperatures. However, their main problem which limits their applications is their low solubility and therefore difficult processability. Structural modifications such as the introduction of a bulky pendant substituent, non-coplanar biphenylene moieties and flexible spacers have been reported to improve the solubility and to lower the phase transition temperatures^[19–24].

Among these, the inclusion of flexible or angular linkages into the polymer backbone is one of the most effective approaches. Introducing flexible units into polyester chains or substituents in the dicarboxylic acid and diols leads to low transition temperatures. In general, 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. 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^[25, 26].

The main objective of this study was focused on improving the solubility of the novel polyesters without sacrificing thermal stability *via* synthesis of a diacid. Therefore, for the preparation of a flexible diacid containing ether units, 2,6-dichloro pyridine was reacted with 4-hydroxybenzoic acid (Scheme 1). This reaction was performed in the presence of K₂CO₃ *via* nucleophilic aromatic substitution of hydroxyl groups with chlorine. Thus, a diacid containing ether and pyridine units was prepared which was characterized using conventional FT-IR, and ¹H-NMR spectroscopic methods and also elemental analysis technique. Table 1 shows the obtained characterization data, and Figs. 1 and 2 show the FT-IR and ¹H-NMR spectra of the diacid.



Scheme 1 Preparation of diacid

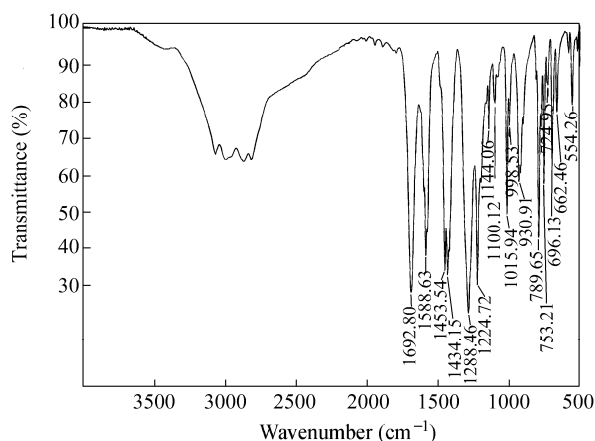


Fig. 1 FT-IR spectrum of diacid

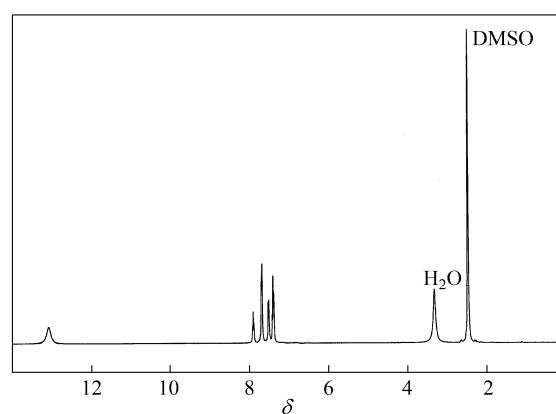


Fig. 2 ¹H-NMR spectrum of diacid

Table 1. Diacid characterization data

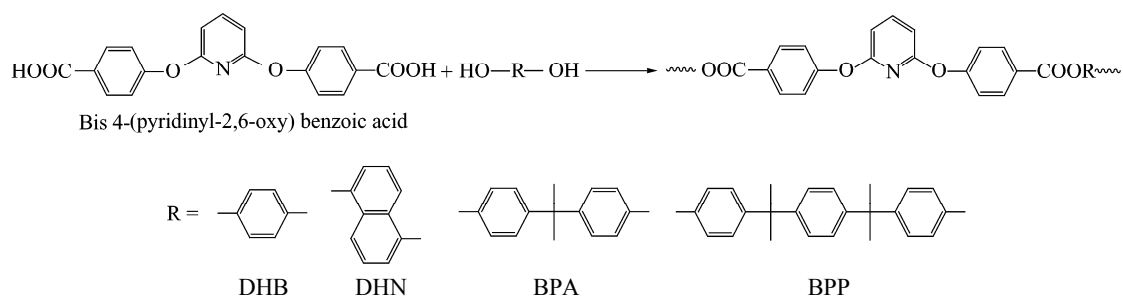
Monomer	FT-IR (KBr, cm^{-1})	$^1\text{H-NMR}$ (DMSO- d_6 , δ)	Elemental analysis					
			Calc.			Found		
			C	H	N	C	H	N
Diacid	2650–3250 (OH)	13.06 (s, COOH, 2H)						
	1692 (C=O)	7.89 (t, pyridine, 1H)						
	1434–1588 (C=C)	7.68 (d, phenyl, 4H)	64.96	3.70	3.99	65.05	3.63	4.04
		7.50 (d, pyridine, 2H)						
	1288 (C–O)	7.38 (d, phenyl, 4H)						

Poly(ether ester)s were prepared *via* polycondensation reactions of the diacid with four different diols including 1,4-dihydroxy benzene (DHB), 1,5-dihydroxy naphthalene (DHN), bis-phenol A (BPA) and bis-phenol-P (BPP) in the presence of *p*-toluenesulfonyl chloride in DMF and pyridine (Scheme 2). The prepared polymers were characterized using conventional methods including FT-IR and $^1\text{H-NMR}$ spectroscopic methods and also elemental analysis technique, and the results are collected in Table 2. The representative FT-IR and $^1\text{H-NMR}$ spectra are shown in Figs. 3–6, respectively.

Table 2. Polymer characterization data

Polymer	IR (KBr, cm^{-1})	NMR ¹ (DMSO- d_6 , δ)	Elemental analysis		
			C	H	N
Diacid-DHB	3050 (aromatic CH)	8.14 (t, py, 1H)			
	1736 (C=O)	7.75 (d, phenyl, 4H)	Calc.	70.59	3.53
	1426–1587 (C=C)	7.56 (d, py, 2H)			3.29
	1261 & 1173 (C–O)	7.41 (d, phenyl, 4H)	Found	70.36	3.40
		7.28 (d, phenyl, 4H)		3.40	3.51
Diacid-DHN		8.16 (t, py, 1H)	Calc.	73.26	3.58
	3052 (aromatic CH)	7.78 (d, phenyl, 4H)			2.95
	1738 (C=O)	7.70 (d, naphthyl, 2H)			
	1424–1588 (C=C)	7.57 (d, py, 2H)			
	1260 & 1181 (C–O)	7.44 (d, phenyl, 4H)	Found	73.06	3.72
Diacid-BPA		7.30 (dd, naphthyl, 2H)			2.83
		6.97 (d, naphthyl, 2H)			
	3056 (aromatic CH)	8.11 (t, py, 1H)	Calc.	75.14	4.60
	2963 (aliphatic CH)	7.72 (d, phenyl, 4H)			2.58
	1738 (C=O)	7.54 (d, py, 2H)			
Diacid-BPP	1425–1582 (C=C)	7.38 (d, phenyl, 4H)			
	1265 & 1203 (C–O)	7.23 (d, phenyl, 4H)	Found	75.02	4.71
		7.09 (d, phenyl, 4H)			2.69
		1.56 (s, methyl, 6H)			
	3055 (aromatic CH)	8.10 (t, py, 1H)	Calc.	78.06	5.29
Diacid-BPP	2965 (aliphatic CH)	7.69 (d, phenyl, 4H)			2.12
	1737 (C=O)	7.52 (d, py, 2H)			
	1427–1585 (C=C)	7.35 (d, phenyl, 4H)			
	1262 & 1205 (C–O)	7.20 (d, phenyl, 4H)			
		7.07 (d, phenyl, 4H)	Found	78.00	5.15
		7.01 (d, phenyl, 4H)			2.25
		1.54 (s, methyl, 12H)			

¹Py = Pyridine



Scheme 2 Preparation of poly(ether ester)s

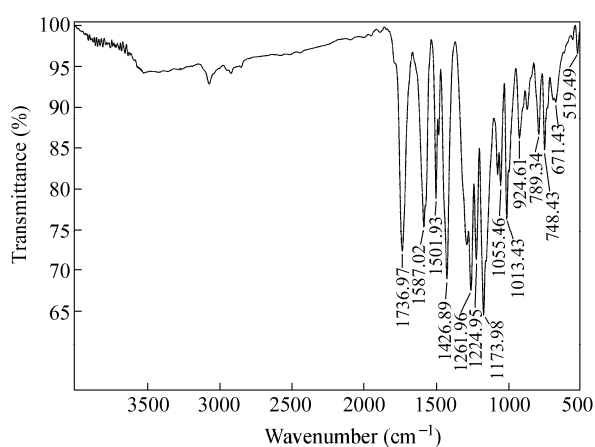


Fig. 3 FT-IR spectrum of DHB-based polyester

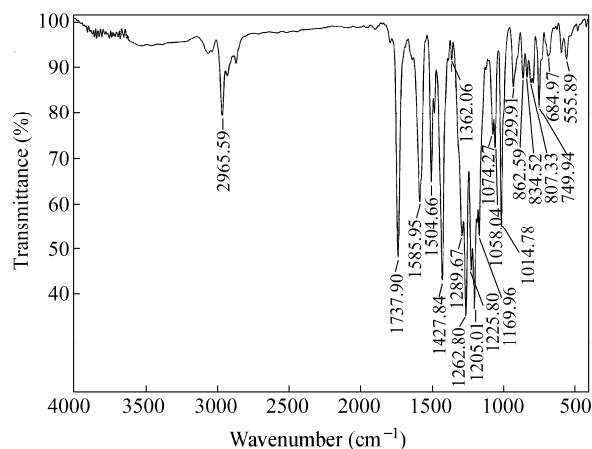
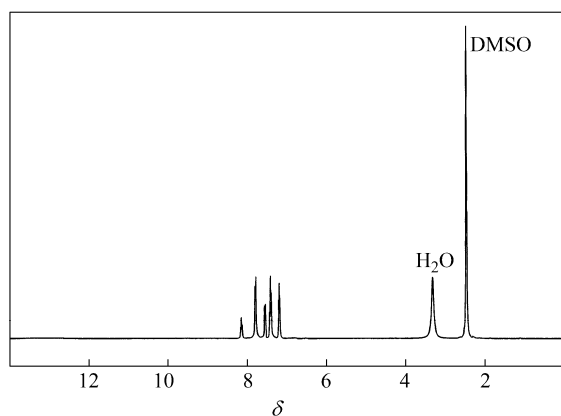
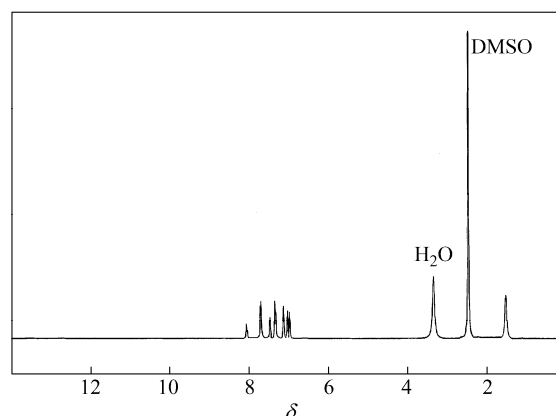


Fig. 4 FT-IR spectrum of BPP-based polyester

Fig. 5 ¹H-NMR spectrum of DHB-based polyesterFig. 6 ¹H-NMR spectrum of BPP-based polyester

The inherent viscosity of the polymers as a criterion for evaluation of molecular weights was in the range of 0.47–0.52 dLg⁻¹ measured in DMF at a concentration of 0.5 g dL⁻¹ at 30°C (Table 3). The weight average molecular weights (M_w), the number average molecular weights (M_n), and polydispersity index were determined by GPC collected in Table 3. These results reveal that the polymers comprised reasonable molecular weights.

Table 3. Yield, viscosity and molecular weights of polymers based on GPC data

Polymer	Yield (%)	η_{inh} (dL/g)	M_w	M_n	PDI
Diacid-DHB	92	0.52	51100	36500	1.40
Diacid-DHN	88	0.47	49500	30500	1.62
Diacid-BPA	91	0.49	50400	33600	1.50
Diacid-BPP	90	0.50	50500	34100	1.48

The solubility of the polymers in dipolar aprotic solvents such as NMP, DMAc, DMF, dimethylsulfoxide (DMSO), and also in *m*-cresol was in the range of 1.65–2.40 g/dL. Also, they were partially soluble in THF and pyridine by heating. The order of solubility was as follows:

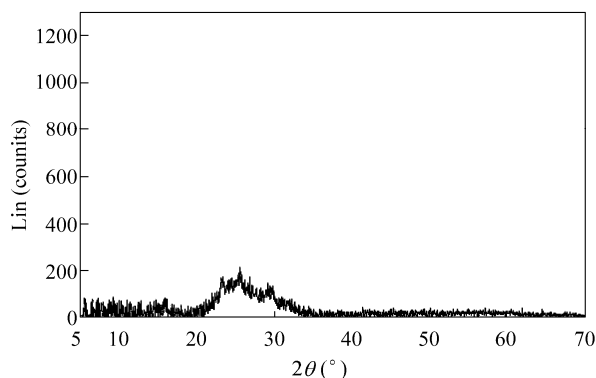
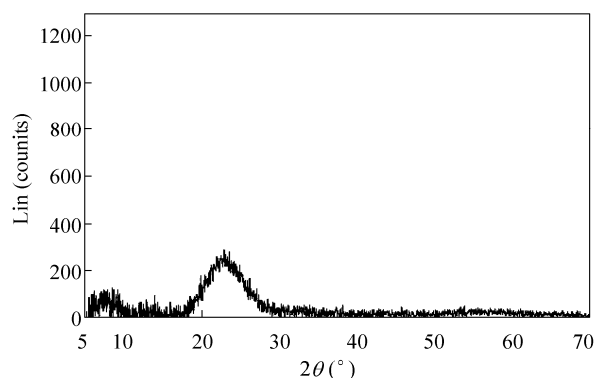
$$\text{Diacid-BPP} > \text{Diacid-BPA} > \text{Diacid-DHN} > \text{Diacid-DHB}$$

Incorporation of ether and pyridine units into the backbone of polymers, in addition to the presence of alkyl and bulky groups in the polyesters was the main reasons for improving the solubility of the polymers. Flexible groups like ether and alkyl groups provided more free volume due to the low internal rotational energy about these bonds. Presence of polar pyridine units caused more dipole-dipole interaction between polymer and polar solvents. Bulky naphthyl group afforded reduction of interaction between polymeric chains, increasing of free volume, and subsequently penetration of solvent into the polymeric chains.

WAXS measurements at room temperature in the region of $2\theta = 5^\circ$ – 70° were performed in order to study the crystalline characteristics of the polymers. According to the results, polymers were almost amorphous, and the presence of flexible groups intensified this character according to the following order:

$$\text{Diacid-BPP} > \text{Diacid-BPA} > \text{Diacid-DHN} > \text{Diacid-DHB}$$

Typical WAXS curves are given in Figs. 7 and 8.

**Fig. 7** WAXD pattern of DHB-based polyester**Fig. 8** WAXD pattern of BPP-based polyester

Thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) in air at a heating rate of 10 K/min. The polymers did not show any major weight losses below 270°C and their initial decomposition temperatures (T_0) were about 265–305°C. The temperature for 10% gravimetric loss (T_{10}), an important criterion for evaluation of thermal stability, was in the range of 420–460°C and also the weight of polymers remained (char yield) at 600°C was about 38%–53%. Maximum decomposition temperatures (T_{max}) of the polymers were in the range of 460–480°C (Table 4), and the representative TGA curves are shown in Figs. 9 and 10.

Table 4. Thermal stability data

Polymer	T_0 (°C)	T_{10} (°C)	T_{max} (°C)	Char yield at 600°C (%)
Diacid-DHB	305	460	480	53
Diacid-DHN	295	445	472	50
Diacid-BPA	273	425	465	42
Diacid-BPP	265	420	460	38

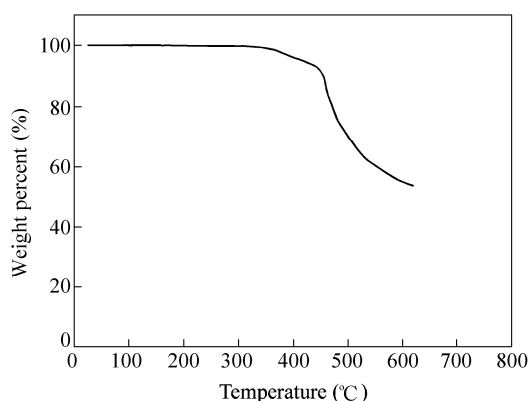


Fig. 9 TGA curve of DHB-based polyester

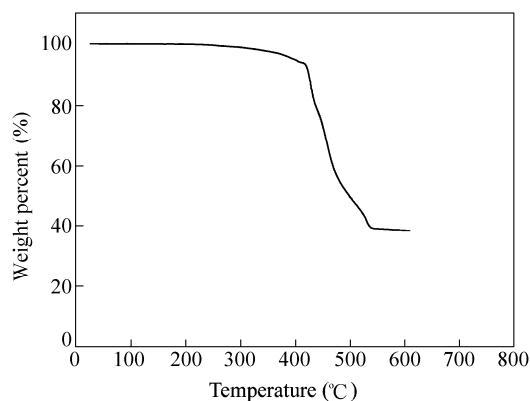


Fig. 10 TGA curve of BPP-based polyester

The most rigid and symmetric polymer (DHB-based polymer) showed the highest thermal stability, and the most flexible polymer (BPP-based polymer) revealed the lowest thermal stability among the prepared polyesters.

CONCLUSIONS

A diacid containing pyridine unit and flexible spacers (ether groups) was prepared *via* substitution reaction of two moles of 4-hydroxy benzoic acid with 2,6-dichloropyridine. Polycondensation reactions of the diacid with different aromatic diols resulted in preparation of a series of poly(ether ester)s. Presence of flexible ether, methylene and bulky groups from one side and ester and aromatic units from the other side offered a nice balance of properties including improved solubility and high thermal stability in these poly(ether ester)s.

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