Synthesis and Properties of Novel Aromatic Poly(ester imide)s Bearing Naphthalene-2,7-diyl units

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Abstract: Two series of 2,7-naphthalenediyl units-containing homo- and copoly(ester imide)s were prepared from 2,7-bis(4-aminobenzoyloxy)naphthalene and 2,7-bis(3-aminobenzoyloxy)naphthalene, respectively, with six commercially available aromatic tetracarboxylic dianhydrides and their mixtures via a conventional two-stage synthesis that included ring-opening polyaddition to give poly(amic acid)s followed by chemical imidization to polyimides. The intermediate poly(amic acid)s obtained in the first stage had inherent viscosities of 0.59∼1.15 and 0.51∼1.20 dL g^{-1}, respectively. Some of the poly(ester imide)s derived from less rigid dianhydrides had excellent solubility in polar aprotic solvents such as N-methyl-2-pyrrolidone and N,N-dimethylacetamide and could be solution-cast into transparent, flexible, and tough films. The poly(ester imide)s derived from rigid dianhydrides such as pyromellitic dianhydride (PMDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) were semicrystalline and showed less solubility. Except for some examples, most of the poly(ester imide)s displayed discernible glass-transition temperatures (T_gs) between 233 and 295°C in the differential scanning calorimetry traces. These poly(ester imide)s showed insignificant decomposition below 450°C in nitrogen or air. The investigation of the thermal decomposition of the poly(ester imide)s using pyrolysis-gas chromatography/mass spectrometry (pyrolysis–GC/MS) indicated that a dramatic breakage of the ester linkages occurred at around 450°C, which initiated the polymer chain scission.

1. INTRODUCTION

Aromatic polyimides are widely used in the semiconductor and electric packaging industry because of their outstanding thermal and chemical stability, good insulation properties with low dielectric constant, and excellent mechanical properties [1, 2]. However, one of the problems with most polyimides is their insolubility in most organic solvents and high glass-transition or softening temperatures caused by the high stiffness of the polymer backbones. This makes it impossible for most polyimides to be directly processed in their imidized forms; thus, their applications are limited in

many fields.   Processable engineering plastics possessing moderately high softening temperatures and/or solubility in some organic solvents are required for practical use. Therefore, various efforts have focused on the synthesis of soluble and/or thermoplastic polyimides while maintaining the excellent thermal and mechanical properties.   Typical approaches of the chemical structure modification to increase the processability of these polyimides were to introduce kinks of flexible linkages, non-coplanar units, or bulky pendant groups into backbones of the polyimides [3–14].   It has been demonstrated that incorporating both ether and naphthyl units into the polymer backbones is a successful route to improve the solubility of polyimides while retaining high thermal stability [15–20].   Very recently, we have reported poly(ester amide)s based on the diamino-diesters bearing naphthalene-2,7-diyl unit, i.e. 2,7-bis(4-aminobenzoyloxy)naphthalene (*p*-**1**) and 2,7-bis(3-aminobenzoyloxy)naphthalene (*m*-**1**) [21]. In continuing our interest in preparing easily processable high-performance polymers bearing naphthyl units, the present study deals with the synthesis and basic characterization of novel aromatic homo- and copoly(ester imide)s derived from the diamino-diesters *p*-**1** and *m*-**1**, respectively, with various aromatic tetracarboxylic dianhydrides or their mixtures. The solubility behaviors and thermal properties of the poly(ester imide)s obtained from the diamino-diester *p*-**1** were compared with those of structurally related poly(ether imide)s from 2,7-bis(4-aminophenoxy)naphthalene [22]. Because the understanding of the thermal decomposition behavior of a polymer is of crucial importance in its end use application, the thermal decomposition of the resultant poly(ester imide)s was also investigated by using pyrolysis–gas chromatography/mass spectrometry GC/MS analysis.

2. EXPERIMENT

2.1. Materials

2,7-Bis(4-aminobenzoyloxy)naphthalene (*p*-**1**, mp 272–273°C) and 2,7-bis(3-amino-benzoyloxy)naphthalene (*m*-**1,** mp 161–162°C) were prepared by the condensation reaction of 2,7-dihydroxynaphthalene with 4- and 3-nitrobenzoyl chloride and subsequent Pd/C-catalyzed hydrogenation of the intermediate dinitro-diesters. The synthetic details and characterization data of these two diamino-diesters have been reported in a previous publication [21].   Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA; **2a**, mp 284–286°C) (Aldrich) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; **2c**, mp 225–226°C) (Aldrich) were purified by recrystallization from acetic anhydride.   3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA; **2b**, mp 298–300°C) (Oxychem), 4,4′-oxydiphthalic dianhydride (ODPA; **2d**, mp 226–227°C) (Oxychem), 3,3′,4,4′-Diphenylsulfonetetracarboxylic dianhydride (DSDA; **2e**, mp 287-288°C) (New Japan Chemical Co.), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **2f**, 241–243°C) (Hoechst Celanese) were heated in vacuo at 250°C for 3 h prior to use. *N,N*-Dimethylacetamide (DMAc) (Fluka) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2.2. Polymer synthesis

The poly(ester imide)s were synthesized from various dianhydrides and either the diamino-diester p-**1** or m-**1** via a two-step method. The synthesis of the poly(ester imide) p-**4f** was used as an example to illustrate the general synthetic route used to produce the polyimides. To a solution of 0.4728 g (1.18 mmol) of the diamino-diester p-**1** in 9.5 mL of CaH$_2$–dried DMAc in a 50-mL flask, 0.5272 g (1.18 mmol) of dianhydride 6FDA was added in one portion. Thus, the solid content of the solution is approximately 10 wt%. The mixture was stirred at room temperature overnight (for about 24 h) to afford a viscous poly(amic acid) solution. The inherent viscosity of the resultant poly(amic acid) p-**3f** was 0.70 dL g^{-1}, measured in DMAc at a concentration of 0.5 g dL^{-1} at 30°C. The poly(amic acid) was subsequently chemically cyclized in solution to give the polyimide. A mixture of 2 mL of pyridine and 5 mL of acetic anhydride was added into the preceding poly(amic acid) solution, and the reaction mixture was stirred at room temperature overnight and at 100°C for 2 h. The resultant homogeneous poly(ester imide) solution was poured into 200 mL of methanol to give a light yellow fibrous precipitate, which was collected by filtration, washed thoroughly with methanol, and dried at 100°C in a vacuum oven. The yield was quantitative. The inherent viscosity of the poly(ester imide) p-**4f** was 0.54 dL g^{-1} in DMAc at a concentration of 0.5 g dL^{-1} at 30°C. The FT-IR spectrum (film) exhibited characteristic absorptions at 1783 cm^{-1} (imide asymmetrical C = O stretching), 1733 cm^{-1} (imide symmetrical C = O stretching), 1726 cm^{-1} (ester C = O stretching), 1367 cm^{-1} (C–N stretching), and 1262, 1142 cm^{-1} (asymmetrical and symmetrical C–O–C stretching). ELEM. ANAL. Calculated. for $(C_{43}H_{20}F_6N_2O_8)_n$ $(806.63)_n$: C, 64.03 %; H, 2.50 %; N, 3.47 %. Found: C, 63.34 %; H, 2.56 %; N, 3.56 %.

2.3. Film preparation

For the organosoluble poly(ester imide)s, the samples were cast into films via solvent casting. A solution of polymer was prepared by dissolving about 0.8 g of the poly(ester imide) sample in 8 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish that was placed in a 90°C oven overnight to remove most of the solvent. The semidried film was stripped off from the glass substrate and further dried in vacuo at 160°C for 8 h. The obtained films had about 0.1 mm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

2.4. Measurements

Elemental analyses were run in a Heraeus VarioEL-III C, H, N analyzer. Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared (FT-IR) spectrometer. The inherent viscosities of the polymers were measured at a concentration of 0.5 g dL^{-1} in DMAc with an Ubbelohde viscometer at 30°C. Gel permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive-index detector. Two Waters 5-μm Styragel HR-2 and HR-4 columns

(7.8-mm inside diameter $\times$ 300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow polystyrene standards. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25°C) on a Shimadzu XRD 6000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu-Kα radiation. An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress–strain behaviors of the polyimide film samples. A gauge length of 2 cm and a crosshead speed of 5 mm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick), and an average of at least five individual determinations was used. Thermogravimetric analyses (TGA) were conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (40 cm^3 min^{-1}) at a heating rate of 20°C min^{-1} from 200 to 800°C. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a scanning rate of 20°C min^{-1} from 50 to 400°C in flowing nitrogen (20 cm^3 min^{-1}). Glass transition temperatures (T_gs) were read at the mid-point of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400°C at a cooling rate of 200°C min^{-1}. Thermomechanical analyses (TMA) were conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 50 to 350°C at a heating rate of 10°C min^{-1} using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s) were taken as the onset temperature of probe displacement on the TMA traces. Pyrolysis–GC/MS analyses were run in a Frontier Laboratories model PY-2020iD Double-Shot Pyrolyzer coupled to a Hewlett Packard 6890 series gas chromatograph linking to a Hewlett Packard 5973 mass selective detector. The pyrolysis temperatures were respectively set at 350, 400, 450 and 500°C. The pyrolysis gases from the poly(ester imide) were introduced directly into GC/MS analysis system. The GC column is a F-Lab UA5-30M-0.25F metal capillary column (30 m $\times$ 0.25 mm i.d. with a coated film thickness of 0.25 μm). The Pyrolyzer can also be operated under evolved gas analysis (EGA) mode to provide total ions and individual ions emission abundance verse temperature or time. The EGA curve was generated by detecting evolved gases obtained by continuously heating a sample at a heating rate of 20°C min^{-1} from 50 to 700°C. The evolved gases for EGA mode were introduced directly into MS analysis system through a F-Lab UADTM-2.5M deactivated metal capillary tube (2.5 m $\times$ 0.15 mm i.d. with a coated film thickness < 0.01 μm). Thus, all evolved gases for the EGA model were detected without any separation. Data analyses were searched to match the database of Wiley275.L Mass Spectra Library.

3. RESULTS AND DISCUSSION

3.1. Polymer synthesis

Two series of homopoly(ester imide)s p-**4a-f** and m-**4a-f** were prepared from the diamino-diesters p-**1** and m-**1**, respectively, with various commercially available aromatic tetracarboxylic dianhydrides **2a-f** by the conventional two-stage synthetic
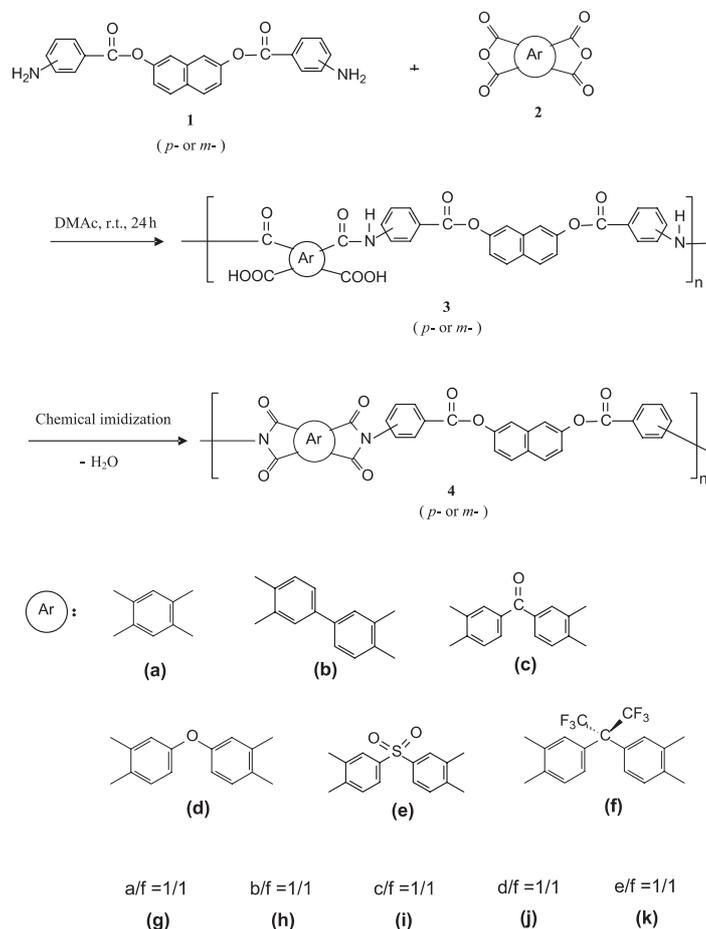
Scheme 1. Synthesis of poly(ester mide)s.

method involving a ring-opening polyaddition and subsequent chemical cyclodehydration (Scheme 1). An equimolar amount of diamino-diester and dianhydride monomers were used in all cases. Two series of random copoly(ester imide)s p-**4g-k** and m-**4g-j** were also prepared from p-**1** and m-**1**, respectively, with equimolar mixtures of 6FDA and another dianhydride. As shown in Table 1, the inherent viscosities of the intermediate poly(amic acid)s were in the range of $0.59\sim1.15$ dL g^{-1} for p-**3a-k** and $0.51\sim1.20$ dL g^{-1} for m-**3a-j** in DMAc. The GPC chromatogram of p-**4f** indicated that the M_w and M_n values were about 45 500 and 39 500, respectively, relative to standard polystyrene. In the case of its meta analogue m-**4f**, the M_w and M_n values were about 44 500 and 37 000, respectively. We had tried thermal cyclodehydration of the poly(amic acid)s; however, highly brittle polyimide films were usually obtained. It may be suggested that the ester linkages

Table 1. Inherent viscosities and tensile properties of the poly(ester imide)s.

Polymer code	η_{inh} of poly(amic acid) (dL g^{-1})[a]	η_{inh} of polyimide (dL g^{-1})[a]	Tensile properties of poly(ester imide) films		
			Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
p-**4a**	1.15	–[b]	–[c]	–	–
p-**4b**	0.82	–	–	–	–
p-**4c**	0.88	–	–	–	–
p-**4d**	0.80	–	–	–	–
p-**4e**	0.59	–	–	–	–
p-**4f**	0.70	0.54	95	10	2.1
p-**4g**	0.80	–	–	–	–
p-**4h**	0.73	–	–	–	–
p-**4i**	0.61	–	–	–	–
p-**4j**	0.66	0.51	91	7	2.3
p-**4k**	0.65	0.45	113	9	2.3
m-**4a**	1.20	–	–	–	–
m-**4b**	0.70	–	–	–	–
m-**4c**	0.90	–	–	–	–
m-**4d**	0.74	–	–	–	–
m-**4e**	1.05	0.74	103	10	2.1
m-**4f**	0.72	0.43	101	9	2.1
m-**4g**	0.77				
m-**4h**	0.51				
m-**4i**	0.55	0.51	101	10	2.1
m-**4j**	0.55	0.49	91	12	1.9

Notes:

[a] Inherent viscosity was measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 °C.

[b] Insoluble in DMAc.

[c] No available samples.

in the polymer chain may be hydrolyzed during imidization at elevated temperatures. Therefore, the precursor poly(amic acid)s obtained were chemically cyclized in solution to give the poly(ester imide)s. Some of the poly(ester imide)s such as p-**4f**, p-**4j-k**, m-**4e-f** and m-**4i-j** could be cast into transparent, flexible, and strong films from DMAc solutions, indicative of high molecular weight polymers. The inherent viscosities of the organosoluble poly(ester imide)s were recorded in the range of 0.43~0.74 dL g^{-1}, as measured in DMAc at 30°C. However, the other poly(ester imide)s precipitated during chemical imidization and were insoluble in any available organic solvents, possibly because of a higher level of crystallinity or structural rigidity.

The formation of the poly(ester imide)s was confirmed with FT-IR spectroscopy and elemental analysis. A typical set of FT-IR spectra for poly(amic acid) p-**3f** and poly(ester imide) p-**4f** are shown in figure 1. All poly(amic acid)s revealed characteristic absorption
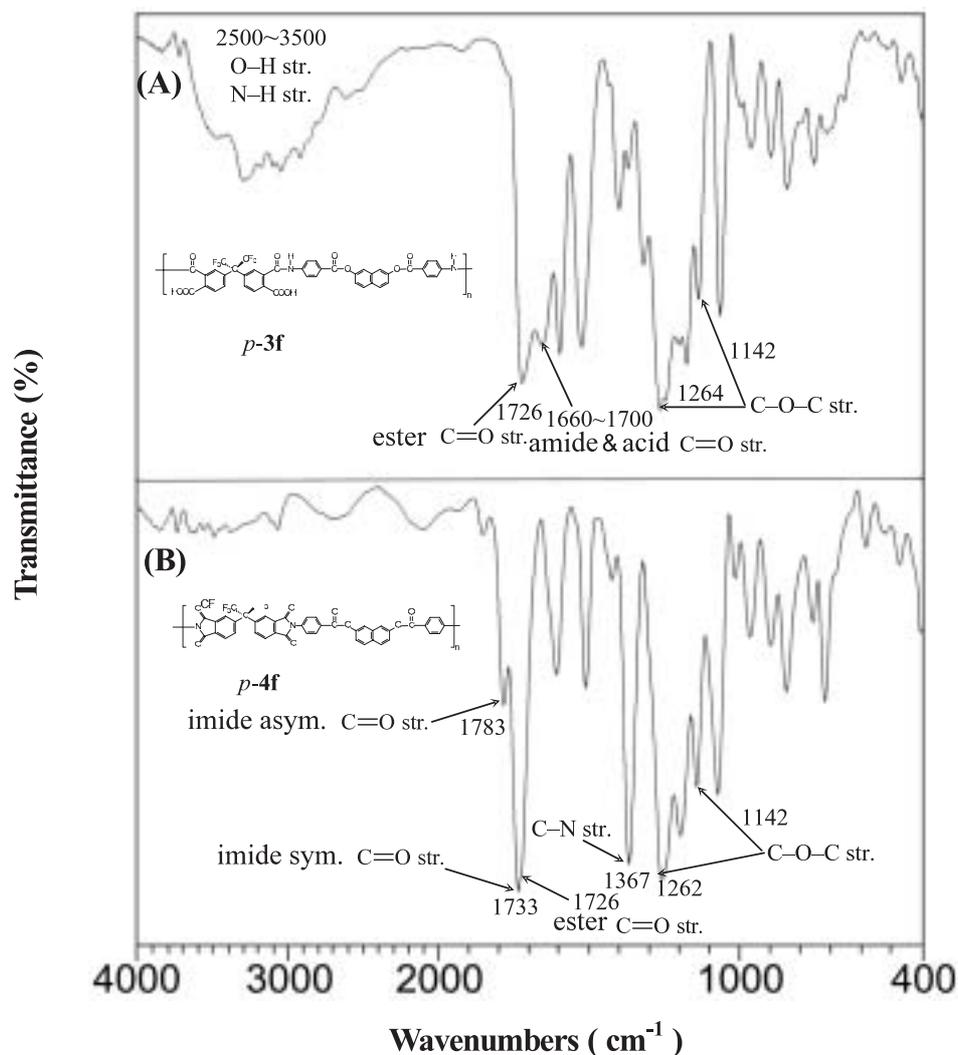
Figure 1. IR spectra of (A) poly(amic acid) precursor p-**3f** and (B) poly(ester imide) p-**4f**.

bands at around 1660~1700 cm^{-1} and 2500~3500 cm^{-1}. The disappearance of the amic acid bands indicates a virtually complete conversion of the poly(amic acid) precursor into the polyimide. The characteristic absorption bands of the imide rings appeared at around 1780 and 1730 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretching), 1370 cm^{-1} (C–N stretching), and 1070 and 720 cm^{-1} (imide ring deformation). All poly(amic acid)s and poly(ester imide)s also exhibited strong absorptions at around 1730 cm^{-1} (ester C=O stretching) and 1260, 1140 cm^{-1} (asymmetrical and symmetrical

Table 2. The elemental analyses of the poly(ester imide)s.

Polymer code	Formula of the repeat unit (Formula weight)	C (%)		H (%)		N (%)	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
p-**4a**	$C_{34}H_{16}N_2O_8$ (580.51)	70.35	69.31	2.78	2.81	4.83	4.84
p-**4b**	$C_{40}H_{20}N_2O_8$ (656.61)	73.17	72.34	3.07	3.11	4.27	4.24
p-**4c**	$C_{41}H_{20}N_2O_9$ (684.62)	71.93	71.02	2.94	3.03	4.09	4.18
p-**4d**	$C_{40}H_{20}N_2O_9$ (672.61)	71.43	70.57	3.00	3.11	4.16	4.28
p-**4e**	$C_{40}H_{20}N_2O_{10}S$ (720.67)	66.67	65.61	2.80	2.86	3.89	3.83
p-**4f**	$C_{43}H_{20}F_6N_2O_8$ (806.63)	64.03	63.34	2.50	2.56	3.47	3.56
m-**4a**	$C_{34}H_{16}N_2O_8$ (580.51)	70.35	69.28	2.78	2.85	4.83	4.85
m-**4b**	$C_{40}H_{20}N_2O_8$ (656.61)	73.17	71.94	3.07	3.13	4.27	4.22
m-**4c**	$C_{41}H_{20}N_2O_9$ (684.62)	71.93	70.99	2.94	2.96	4.09	3.93
m-**4d**	$C_{40}H_{20}N_2O_9$ (672.61)	71.43	70.66	3.00	3.02	4.16	4.05
m-**4e**	$C_{40}H_{20}N_2O_{10}S$ (720.67)	66.67	65.72	2.80	2.88	3.89	3.96
m-**4f**	$C_{43}H_{20}F_6N_2O_8$ (806.63)	64.03	63.51	2.50	2.58	3.47	3.57

C–O–C stretching) due to the ester groups. The results of the elemental analyses of all homopoly(ester imide)s p-**4a-f** and m-**4a-f** are reported in table 2. The elemental analysis values were generally in good agreement with the calculated values for the proposed structures.

3.2. Properties of the polymers

3.2.1. X-ray diffraction data

All the poly(ester imide)s were characterized by wide-angle X-ray diffraction (WAXD) studies. As can be seen from the diffraction patterns shown in figure 2, the homopoly(ester imide)s (*p*- or *m*-**4a-d**) derived from PMDA, BPDA, BTDA and ODPA displayed some diffraction signals of medium intensity assignable to a semicrystalline polymer. The homopoly(ester imide)s (*p*- or *m*-**4f**) derived from 6FDA showed amorphous patterns. It is interesting to note that polymer *p*-**4e** derived from DSDA also displayed a slightly semicrystalline pattern, whereas its corresponding meta analogue (*m*-**4e**) displayed a nearly completely amorphous pattern. The copoly(ester imide)s (*p*- or *m*-**4g-h**) derived from equimolar PMDA/6FDA and BPDA/6FDA still revealed similar semicrystalline WAXD patterns as those of the PMDA and BPDA homopolymers. However, the copoly(ester imide)s *p*-**4j-k** and *m*-**4j** derived from equimolar ODPA/6FDA and DSDA/6FDA displayed amorphous patterns. In addition, it is interesting to note that polymer *p*-**4i** derived from BTDA/6FDA seemed to display a higher packing density than its corresponding meta analogue (*m*-**4i**), according to their WAXD patterns. In general, the poly(ester imide)s that could afford flexible and tough films as listed in table 1 showed amorphous patterns.

3.2.2. Organo-solubility

The solubility properties of the poly(ester imide)s are reported in table 3. In general, the semicrystalline polymers revealed a poor solubility. With the exception of polymers *p*-**4f**, *m*-**4e**, and *m*-**4f**, all the homopoly(ester imide)s were insoluble in almost all of the organic solvents tested. The excellent solubility of poly(ester imide)s *p*-**4f** and *m*-**4f** may be due to the low cohesive energy caused by the hexafluoroisopropylidene (6F) group. Because the homopoly(ester imide)s derived from 6FDA showed excellent solubility, the copoly(ester imide)s based on equimolar mixtures of 6FDA and another dianhydride were also prepared, and their solubility was investigated. The resultant copoly(ester imide)s *p*-**4g-h** and *m*-**4g-h** derived from equimolar PMDA/6FDA and BPDA/6FDA, respectively, were still insoluble in all the solvents tested. However, the copoly(ester imide)s from other combinations such as ODPA/6FDA, DSDA/6FDA, and BTDA/6FDA showed an enhanced solubility. For example, copoly(ester imide)s *p*-**4j** and *p*-**4k** were soluble in polar solvents such as *N*-methyl-2-pyrrolidone (NMP), DMAc, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) at room temperature or on heating, and copoly(ester imide)s *m*-**4i** and *m*-**4j** were soluble in all the organic solvents including less polar *m*-cresol and THF at room temperature. When comparing the solubility behaviors of the analogous pairs of *m*-/*p*-**4e**, **4i**, and **4j**, one can see a clear effect of the meta-catenation on increasing the solubility of these polymers.
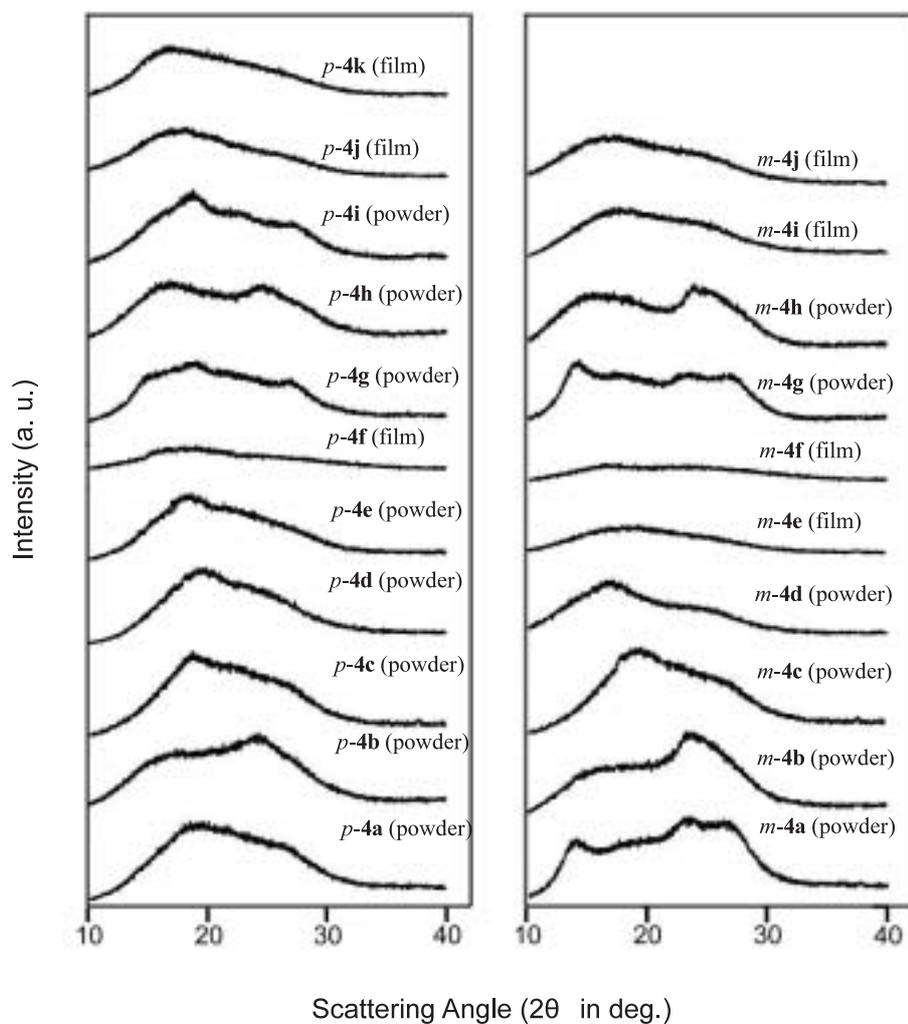
Figure 2. Wide-angle X-ray diffractograms of the poly(ester imide)s *p*-**4a-k** and *m*-**4a-j**.

3.2.3. Tensile properties

As mentioned earlier, most of the amorphous poly(ester imide)s could be solution-cast into flexible and tough films. The amorphous poly(ester imide)s *p*-**4f**, *p*-**4j-k**, *m*-**4e-f** and *m*-**4i-j** afforded good-quality and creasable films with a light color. These films were subjected to tensile test, and their tensile properties are also presented in table 1. These

Table 3. The solubility behaviors of the poly(ester imide)s.

Polymer code	Solubility[a]					
	NMP	DMAc	DMF	DMSO	m-Cresol	THF
p-**4a**	–	–	–	–	–	–
p-**4b**	–	–	–	–	–	–
p-**4c**	–	–	–	–	–	–
p-**4d**	–	–	–	–	–	–
p-**4e**	+	–	–	–	–	–
p-**4f**	+	+	+	+	+	+
p-**4g**	–	–	–	–	–	–
p-**4h**	–	–	–	–	–	–
p-**4i**	+h	–	–	–	–	–
p-**4j**	+h	+h	+h	+h	+h	–
p-**4k**	+	+	+	+h	+h	–
m-**4a**	–	–	–	–	–	–
m-**4b**	–	–	–	–	–	–
m-**4c**	–	–	–	–	+	–
m-**4d**	–	–	–	–	+h	–
m-**4e**	+	+	+	+	+h	–
m-**4f**	+	+	+	+	+	+
m-**4g**	–	–	–	–	–	–
m-**4h**	–	–	–	–	–	–
m-**4i**	+	+	+	+	+	–
m-**4j**	+	+	+	+	+	+

Notes:

[a] Qualitative solubility tested with 10 mg of sample in 1 mL of the solvent. +, soluble at room temperature; +h, soluble on heating at 100°C; –, insoluble even on heating.   NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

films exhibited ultimate tensile strengths of 91~113 MPa, elongations to break of 7~12%, and initial moduli of 1.9~2.3 GPa qualifying them as strong and rigid materials.

3.2.4. Glass transition and softening temperatures

The glass-transition temperatures (T_gs) of these poly(ester imide)s were obtained from the mid-point temperature of baseline shift on the second DSC heating trace (heating rate = 20°C min^{-1}) after rapid cooling from 400°C (cooling rate = 200°C min^{-1}). A typical DSC thermogram of poly(ester imide) p-**4f** is illustrated in figure 3. Five of the poly(ester imide)s, i.e., p-**4a-b**, p-**4g-h**, and m-**4a**, showed no discernible T_gs on their DSC curves probably due to their semicrystalline nature or rigid backbones. The other poly(ester imide)s showed clear T_gs between 233 and 295°C by DSC, generally following the
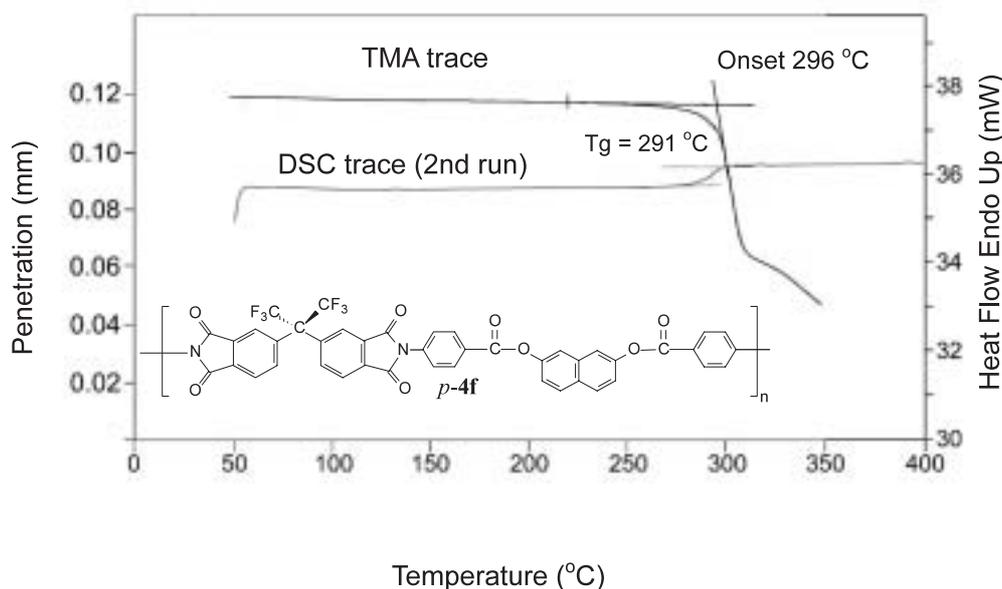
Figure 3. Typical DSC and TMA thermograms of the poly(ester imide) p-**4f** (For DSC, heating rate = 20°C min^{-1}; for TMA, heating rate = 10°C min^{-1} and applied force = 10 mN).

increasing order of chain rigidity and steric hindrance. The poly(ester imide)s containing ODPA moieties showed lower T_gs because of the decreased rotational barrier caused by the flexible ether linkage between two phthalimide units. The p-**4** series poly(ester imide)s showed higher T_gs as compared to the corresponding m-**4** series counterparts because of the difference in symmetry between para and meta catenations. When compared with the corresponding poly(ether imide)s p-**4'** as reported previously [22], the p-**4** series of poly(ester imide)s exhibited an enhanced T_gs possibly because of the increased interchain interactions caused by the ester groups. The softening temperatures (T_s) (or apparent T_g) of the poly(ester imide) films were measured by the TMA method using a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of the poly(ester imide) p-**4f** is also shown in figure 3. As can be seen from table 4, the T_s values of the poly(ester imide) films were recorded in the range of 264∼296°C for the p-series and 231∼264°C for the m-series. In general, the T_s values obtained by TMA are comparable with the T_g values measured by the DSC experiments. The trend of T_s variation with the chain stiffness was similar to that of T_g observed in the DSC measurements.
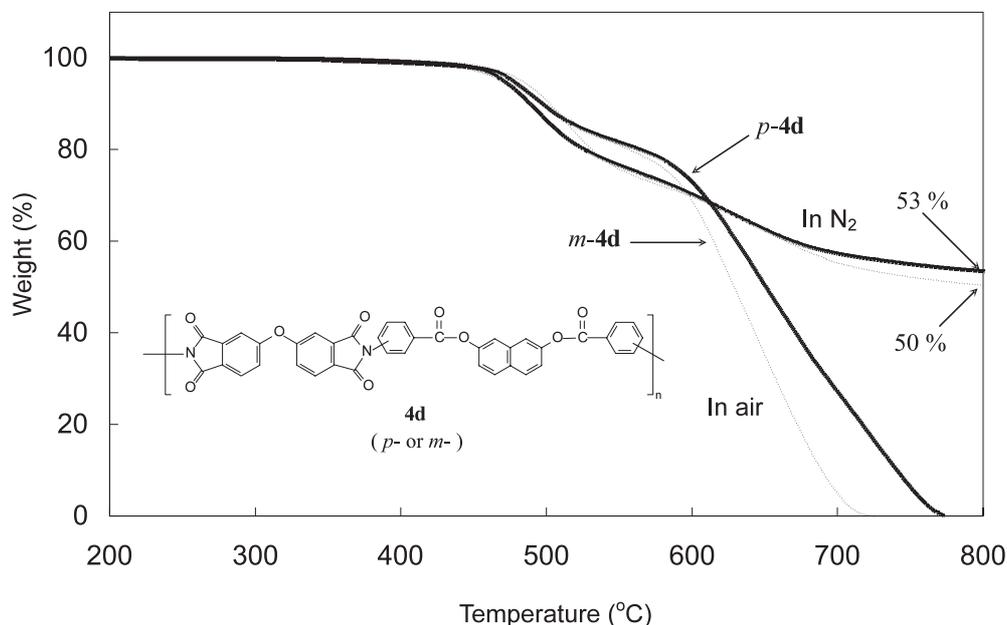
Figure 4. TGA thermograms of the poly(ester imide)s *N*-**4d** and , -**4d** at a heating rate of 20⁻C min′ ¹.

3.2.5. Thermal and thermo-oxidative stability

Thermal and thermo-oxidative stabilities of these poly(ester imide)s were evaluated by TGA measurements in both air and nitrogen atmospheres. The decomposition temperatures (μ_1s) at 5 and 10% weight loss in nitrogen and in air atmospheres determined from the original TGA thermograms are also summarized in table 4. All poly(ester imide)s exhibited good thermal stability with insignificant weight loss up to temperatures of approximately 450°C in nitrogen or air atmosphere, and the anaerobic char yields at 800°C for all polymers were in the range of 48×54 wt%. The μ_1 values at 5% weight loss for the *D*-series poly(ester imide)s ranged from 453 to 492°C in nitrogen and 444 to 482°C in air, which were lower than those of the analogous poly(ether imide)s [22] because of the less stable ester groups. The μ_1 values for the *p*-series poly(ester imide)s stayed in the range of 451 to 497°C in nitrogen and 447 to 475°C in air. Typical TGA curves of the poly(ester imide)s *D*-**4d** and *p* -**4d** were reproduced in figure 4. These poly(ester imide)s exhibited obvious weight loss starting at around 450°C that might be attributed to the early degradation of the less stable ester groups.

Table 4. Thermal properties of the poly(ester imide)s.

Polymer code	μ_2 (°C)[3]	μ_4^n (°C)	μ_1^s at 5 % wt loss (°C)		μ_1 at 10 % wt loss (°C)		Char yield[1] (%)
			In N_0	In air	In N_0	In air	
D-**4a**	–[6]	–[8]	471	468	497	495	50
D-**4b**	– (272)[w]	–	482	489	505	515	54
D-**4c**	290 (265)	–	456	460	477	483	54
D-**4d**	260 (252)	–	470	477	489	497	53
D-**4e**	295 (289)	–	466	444	486	471	48
D-**4f**	291 (280)	296	490	466	513	503	53
D-**4g**	–	–	469	478	503	518	53
D-**4h**	–	–	492	482	517	509	55
D-**4i**	286	–	456	457	484	490	53
D-**4j**	265	264	453	448	482	479	52
D-**4k**	286	276	464	445	489	489	50
p -**4a**	–	–	471	475	491	499	51
p -**4b**	282	–	459	454	478	484	55
p -**4c**	250	–	487	467	509	501	53
p -**4d**	236	–	483	471	502	499	50
p -**4e**	264	264	451	447	463	468	50
p -**4f**	255	251	485	472	508	506	53
p -**4g**	272	–	497	468	513	501	53
p -**4h**	253	–	489	467	514	498	54
p -**4i**	241	242	455	452	481	476	53
p -**4j**	233	231	458	467	483	496	54

Notes:

[3] Middlepoint temperature of baseline shift on the second DSC heating trace (rate 20°C min′ [g]) after rapid cooling from 400°C at –200°C min′ [g].

[i] Softening temperature was measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10°C min′ [g]. The film samples were heated at 300°C for 30 min prior to the TMA experiments.
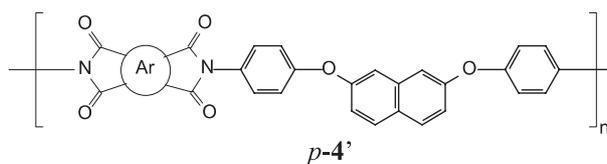
[n] Decomposition temperature was recorded by TGA at a heating rate of 20°C min′ [g].

[1] Residual weight % at 800°C in N_0.

[6] No discernible transition was observed.

[8] Not detected.

[2] Values in parentheses are reported a_2s of analogous poly(ether imide)s (D-4ˉ) having the corresponding –Ar– unit as in the D-**4** series (see ref. 22).

p-**4'**

3.2.6. Pyrolysis behavior

Preliminary investigation on the thermal decomposition mechanisms of these poly(ester imide)s was carried out by using pyrolysis-GC/MS. The EGA curve can indicate the thermal characteristic of a sample. As can be seen from figure 5, the EGA behavior of a representative poly(ester imide) p-**4a** corresponded to the TGA behavior. The EGA curves of the individual ions at m/z 160, 44, 144, and 223 are shown in figure 6. Typical pyrograms of the poly(ester imide) p-**4a** instantly heated at 350, 400, 450 and 500°C are illustrated in figure 7. Structure assignments of the relevant pyrolysis compounds were based on their major mass fragments. Table 5 lists four major pyrolysis products of p-**4a** in pyrolysis-GC/MS at 450 and 500°C in helium. As can be seen from figure 7, the most abundant pyrolysis compound evolved at 350∼500°C was due to 2,7-dihydroxynaphthalene (m/z 160). The evolution of 2,7-dihydroxynaphthalene from the decomposition of the ester groups started at around 350°C and reached a greater intensity at around 450°C. The other thermal degradation compounds evolved at around 450°C were mainly due to carbon dioxide (m/z 44), 2-naphthol (m/z 144), and N-phenylphthalimide (m/z 223). It can be noticed that 2,7-dihydroxynaphthalene was evolved exclusively within the pyrograms at 350 and 400°C, indicating that the ester bonds are apparently the weakest units of the poly(ester imide) p-**4a**. Further studies that may allow a detailed schematization of the thermal degradation pathways involved in the degradation of these poly(ester imide)s are in progress.

4. CONCLUSION

Two series of 2,7-bis(benzoyloxy)naphthalene-containing homo- and copoly(ester imide)s were prepared from the diamino-diesters p-**1** and m-**1**, respectively, with various aromatic tetracarboxylic dianhydrides or their mixtures via a conventional two-stage process. The poly(ester imide)s obtained from dianhydrides PMDA, BPDA, BTDA, and ODPA were generally semicrystalline and showed a less solubility. The 6FDA homopoly(ester imide)s and most of the copoly(ester imide)s containing the 6FDA component displayed good solubility, good film-forming capability, reasonable thermal stability, and moderate T_g or T_s values suitable for thermoforming processing. Investigation of the thermal degradation of the poly(ester imide)s using pyrolysis-GC/MS indicated that ester groups are the thermal weak points of these polymers.

NOTE

1. Author to whom correspondence should be addressed: e-mail: shhsiao@ttu.edu.tw
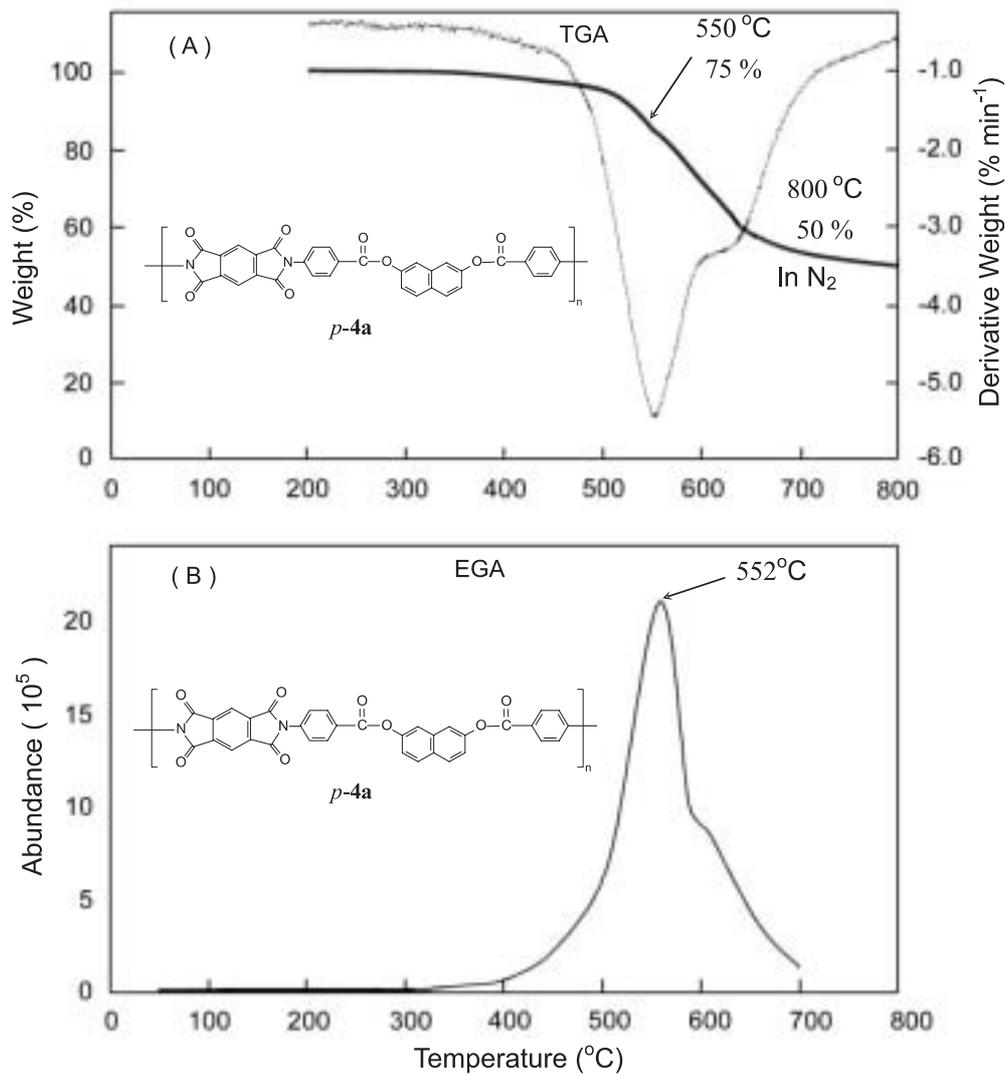
Figure 5. (A) TGA thermogram from 200 to 800°C in nitrogen and (B) EGA curve of total ions of the poly(ester imide) *N*-**4a** from 50 to 700°C at a heating rate of 20°C min' ¹ in helium.
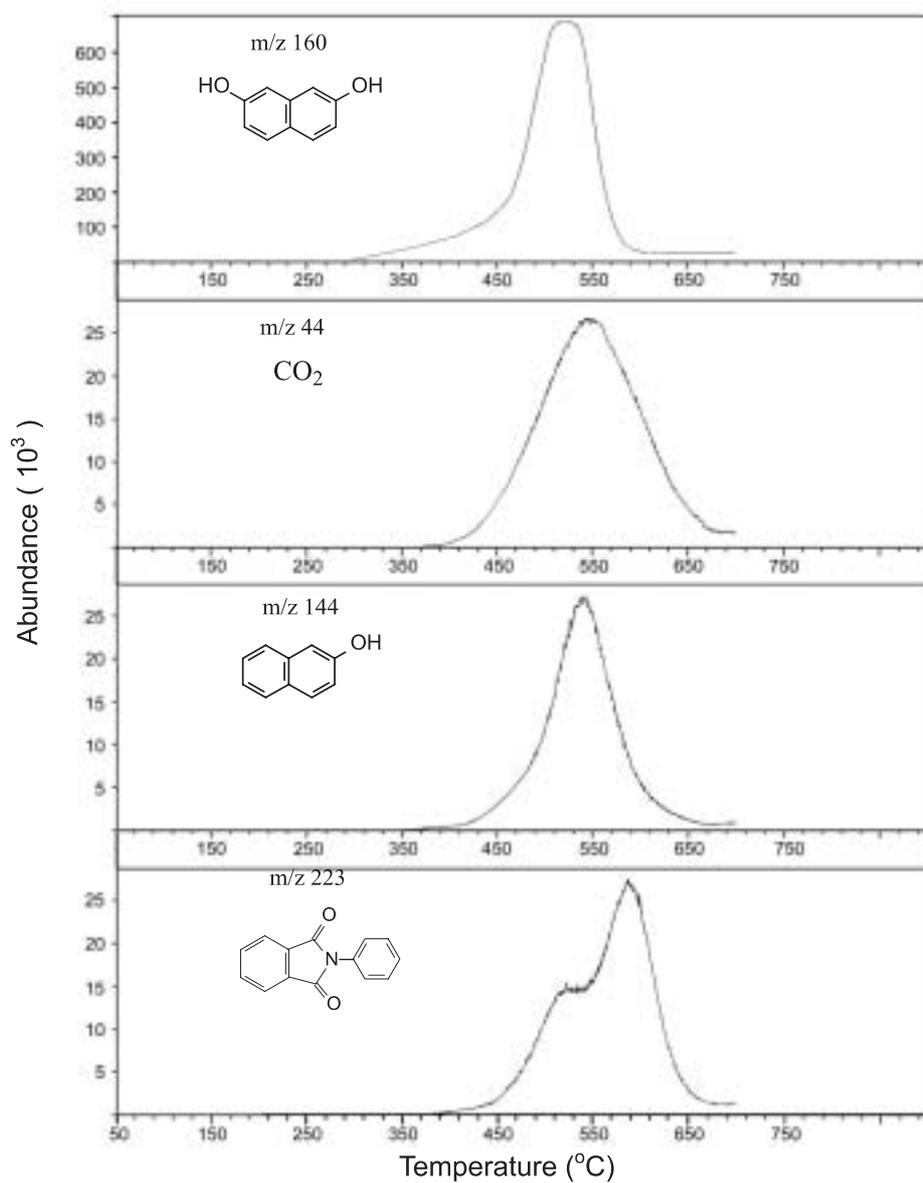
Figure 6. EGA curves of the individual ions at m/z 160, 44, 144, and 223 of the poly(ester imide) *N*-**4a** when it was heated from 50 to 700 °C at a heating rate of 20 °C min⁻¹ in helium.
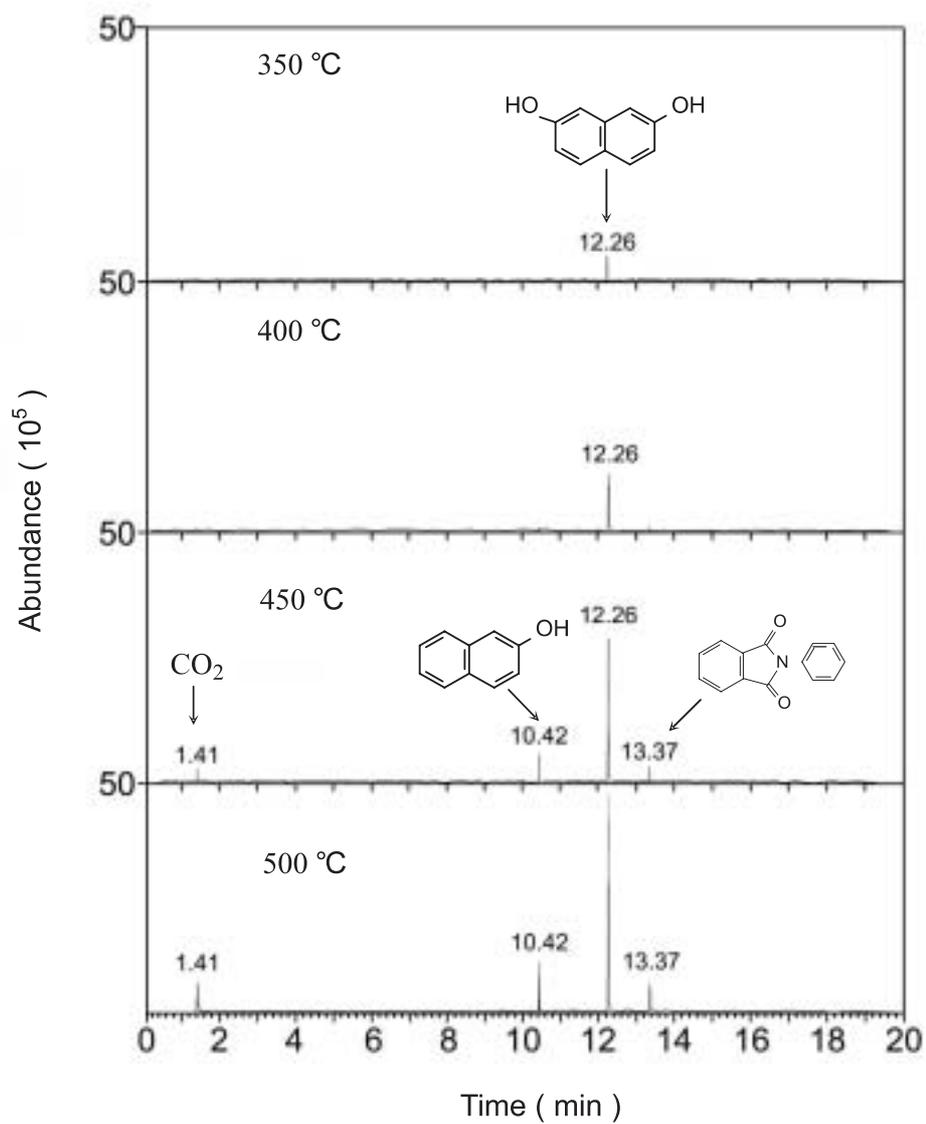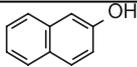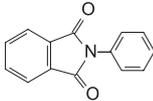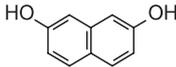
Figure 7. Pyrograms obtained in the pyrolysis-GC/MS of the poly(ester imide) *N*-**4a** at 350, 400, 450, and 500 °C in helium.

Table 5. Identification of the pyrolysis products in pyrolysis-GC/MS of p-**4a** at 450 and 500°C in Helium.

Retention time (min)	Compound	Structural formula	Major mass fragments	Quality (Library searched)
	CO_2			
1.41	Carbon dioxide		44	90
10.42	2-Naphthol		115,144	96
12.26	2,7-Naphthalenediol		77, 103, 131, 160	94
13.37	N-phenylphthalimide		76, 104, 179, 223	93

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