

# Synthesis and properties of novel aromatic poly(ester-imide)s bearing 1,5-bis(benzoyloxy)naphthalene units

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## Abstract

Two series of new aromatic poly(ester-imide)s were prepared from 1,5-bis(4-aminobenzoyloxy)naphthalene (*p*-1) and 1,5-bis(3-aminobenzoyloxy)naphthalene (*m*-1), respectively, with six commercially available aromatic tetracarboxylic dianhydrides 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 0.41–0.84 and 0.66–1.37 dl/g, respectively. All the *para*-series and most of the *meta*-series poly(ester-imide)s were semicrystalline and showed less solubility. Two of the *meta*-series poly(ester-imide)s derived from less rigid dianhydrides were amorphous and readily soluble in polar aprotic solvents, and they could be solution-cast into transparent and tough films with good mechanical properties. The *meta*-series polymers derived from rigid dianhydrides were generally semicrystalline and showed less solubility. Except for one example, the *meta*-series poly(ester-imide)s displayed discernible  $T_g$ s in the range 239–273 °C by DSC. All of these two series poly(ester-imide)s did not show significant decomposition below 450 °C in nitrogen or in air.

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**Keywords:** Naphthalene units; Bis(ester-amine)s; Poly(ester-imide)s

## 1. Introduction

Aromatic polyimides are well known as high-performance polymeric materials and 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 ( $T_g$ ) or melting temperatures caused by the high intermolecular interactions and rigidity of the polymer backbones. This makes it impossible for most polyimides to be directly processed in their imidized forms; thus, their applications have been restricted in some 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 been focused on the preparation of

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soluble and/or thermoplastic polyimides, while still maintaining the excellent thermal and mechanical properties. Typical approaches have been employed to improve the processability of these polyimides include the incorporation of flexible links [3–5], bulky pendant or cardo groups [6–9], kinked or unsymmetrical structures [10–18], and spiro-skeletons [19–23] into the polymer chain. These modifications lower the melting temperature and lead to soluble and amorphous polymers. In general, amorphous polymers have a lower softening temperature ( $T_s$ ) and improved solubility with respect to their crystalline analogues. It has been demonstrated that incorporating of both ether and naphthyl units into the polymer backbones may enhance the solubility and processability of aromatic polyimides without any significant reduction in thermal stability [24–30]. In a continuation of our interest in preparing easily processable high-performance polymers bearing naphthyl units, the present study deals with the synthesis of novel aromatic poly(ester-imide)s derived from 1,5-bis(4-aminobenzoyloxy)naphthalene (*p*-**1**) and 1,5-bis(3-aminobenzoyloxy)naphthalene (*m*-**1**), respectively, with various aromatic tetracarboxylic dianhydrides. The solubility behaviors, film-forming ability, crystallinity and thermal properties of the poly(ester-imide)s were investigated to illustrate the effect of the incorporation of 1,5-bis(benzoyloxy)naphthalene units.

## 2. Experimental

### 2.1. Reagents and solvents

The bis(ester-amine) monomers *p*-**1** (mp = 327 °C) and *m*-**1** (mp = 234 °C) were prepared by the condensation reaction of 1,5-dihydroxynaphthalene with 4-nitrobenzoyl chloride and 3-nitrobenzoyl chloride, respectively, followed by Pd/C-catalyzed hydrogenation of the intermediate dinitro-diester. The synthetic details and characterization data of these two bis(ester-amine)s have been reported in our previous publications [31,32]. 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**, mp = 241–243 °C) (Hoechst Celanese) were heated at 250 °C for 3 h in vacuo for ring closure. *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 synthesis of the poly(ester-imide) *m*-**4c** was used as an example to illustrate the general synthetic route used to produce the poly(ester-imide)s. To a solution of 0.5529 g (1.39 mmol) of the bis(ester-amine) *m*-**1** in 9.5 ml of CaH<sub>2</sub>-dried DMAc in a 50-ml flask, 0.4471 g (1.39 mmol) of dianhydride BTDA 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(ester-amic acid) solution. The inherent viscosity of the resultant poly(ester-amic acid) *m*-**3c** was 0.75 dl/g, measured in DMAc at a concentration of 0.5 g/dl at 30 °C. The poly(ester-amic acid) was subsequently chemically cyclized in solution to give the poly(ester-imide) *m*-**4c**. A mixture of 2 ml of pyridine and 5 ml of acetic anhydride was added into the preceding poly(ester-amic acid) solution, and the reaction mixture was stirred at room temperature for 1 h and then heated at 100 °C for 2 h. The resultant poly(ester-imide) solution was poured into 200 ml of methanol to give a light yellow precipitate, which was collected by filtration, washed thoroughly with methanol, and dried at 100 °C in a vacuum oven. The yield was almost quantitative. The FT-IR spectrum (thin film) exhibited characteristic absorptions at 1782 cm<sup>-1</sup> (imide asymmetrical C=O stretching), 1725–1735 cm<sup>-1</sup> (imide symmetrical and ester C=O stretching), 1371 cm<sup>-1</sup> (C–N stretching), 1236, 1090 cm<sup>-1</sup> (asymmetrical and symmetrical C–O–C stretching), and 717 cm<sup>-1</sup> (imide ring deformation). Elemental analysis, calculated for (C<sub>41</sub>H<sub>20</sub>N<sub>2</sub>O<sub>9</sub>)<sub>n</sub> (684.62)<sub>n</sub>: C, 71.93%; H, 2.94%; N, 4.09%. Found: C, 70.67%; H, 3.04%; N, 3.98%. All of other poly(ester-imide)s were synthesized by using a similar procedure as above.

### 2.3. Preparation of poly(ester-imide) films

For the organosoluble poly(ester-imide)s, the samples were cast into films by using the solvent-casting technique. A polymer solution was made by dissolving about 0.9 g of the poly(ester-imide) sample in 9 ml of DMAc to afford an approximately 10 wt% solution. After the polymer was completely dissolved, the homogeneous solution was poured into a 9-cm diameter glass Petri dish and then placed in an oven overnight (at 90 °C) to enable slow evaporation of the cast solvent. The semi-dried poly(ester-imide) film was stripped off from the glass substrate and further dried in vacuo at 160 °C for 8 h. The obtained films, about 0.1 mm in thickness, were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analysis.

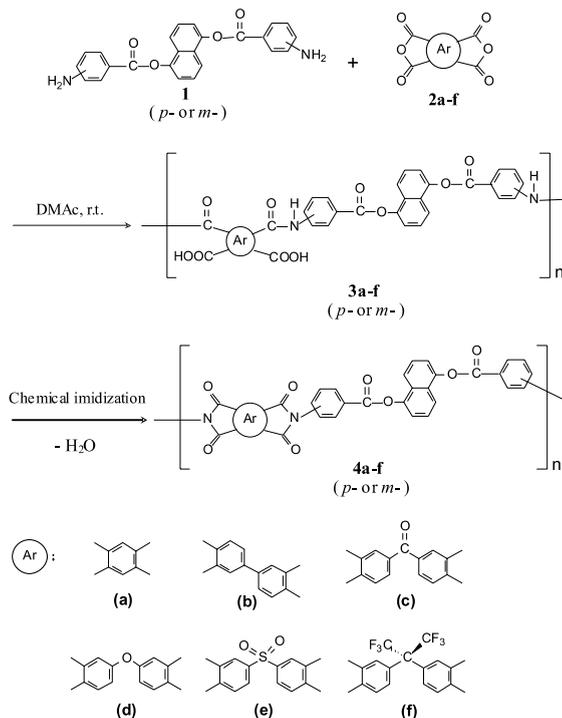
## 2.4. Measurements

Elemental analysis was carried out on 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 poly(ester-imide)s were obtained at a concentration of 0.5 g/dl in DMAc with an Ubbelohde viscometer at 30 °C. 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-K $\alpha$  radiation. An Instron universal tester (Model 4400 R) with a load cell of 5 kg was used to study the stress–strain behavior of the poly(ester-imide) film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were employed in 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 replicas was used. Thermogravimetric analysis (TGA) was conducted with a Perkin–Elmer Pyris 1 TGA instrument. These experiments were carried out on approximately 6–8 mg film or powder samples heated under flowing nitrogen or air (40 ml/min) at a heating rate of 20 °C/min from 200 to 800 °C. Differential scanning calorimetry (DSC) analysis was performed on a Perkin–Elmer Pyris 1 DSC instrument, at a scanning rate of 20 °C/min from 50 to 400 °C under flowing nitrogen (20 ml/min). The glass transition temperatures ( $T_g$ s) were read at the mid-point of the transition in the heat capacity and were taken from the second heating trace after rapid cooling from 400 °C at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was performed with a Perkin–Elmer TMA 7 instrument. The TMA experiments were conducted from 50 to 300 °C at a heating rate of 10 °C/min using a penetration probe of 1.0 mm in diameter under an applied constant load of 10 mN. The softening temperatures ( $T_s$ ) were taken as the onset temperatures of the probe displacement on the TMA traces.

## 3. Results and discussion

### 3.1. Polymer synthesis

Two series of poly(ester-imide)s *p-4a–f* and *m-4a–f* were prepared from the bis(ester-amine)s *p-1* and *m-1*, respectively, with various commercially available aromatic tetracarboxylic dianhydrides **2a–f** by the conventional two-stage synthetic method involving a ring-opening polyaddition and subsequent chemical cyclodehydration, as shown in Scheme 1. An equimolar amount of bis(ester-amine) and dianhydride monomers were used in all cases. As shown in Table 1, the inherent



Scheme 1. Synthesis of poly(ester-imide)s.

viscosities of the intermediate poly(ester-amic acid)s were in the range of 0.41–0.84 dl/g for *p-3a–f* and 0.66–1.37 dl/g for *m-3a–f* in DMAc. We had tried thermal cyclodehydration of the poly(ester-amic acid)s; however, highly brittle polyimide films were usually obtained. It may be suggested that the ester linkages in the polymer chain may be hydrolyzed during imidization at elevated temperatures. Therefore, the precursor poly(ester-amic acid)s obtained were chemically cyclized in solution to give the poly(ester-imide)s. The poly(ester-imide)s *m-4e* and *m-4f* could be solution-cast into transparent, flexible, and strong films, indicative of the formation of high-molecular-weight polymers. The inherent viscosities of the organosoluble poly(ester-imide)s *m-4e* and *m-4f* were 0.48 and 0.46 dl/g, respectively, as measured in DMAc at 30 °C. However, the other poly(ester-imide)s precipitated during chemical imidization and were insoluble in most organic solvents, possibly because of a high level of crystallinity or the structural rigidity of the polymer chain. Thus, no attempts were made to cast them into films.

The IR spectra supported the formation of poly(ester-imide)s. A typical set of FT-IR spectra for the poly(ester-amic acid) *m-3c* and poly(ester-imide) *m-4c* is shown in Fig. 1. All of the poly(ester-amic acid)s revealed characteristic absorption bands at around 1650 cm<sup>-1</sup> (amide and acid C=O stretching) and in the region of 2500–3500 cm<sup>-1</sup> (O–H and N–H stretching).

Table 1  
Inherent viscosities and elemental analysis of the poly(ester-imide)s

Polymer code	$\eta_{inh}^a$ (dl/g)	Formula of the repeat unit (formula weight)	C (%)		H (%)		N (%)	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>p-4a</i>	0.84	C <sub>34</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> (580.51)	70.35	69.10	2.78	2.84	4.83	4.88
<i>p-4b</i>	0.41	C <sub>40</sub> H <sub>20</sub> N <sub>2</sub> O <sub>8</sub> (656.61)	73.17	72.13	3.07	3.17	4.27	4.26
<i>p-4c</i>	0.69	C <sub>41</sub> H <sub>20</sub> N <sub>2</sub> O <sub>9</sub> (684.62)	71.93	70.92	2.94	2.99	4.09	4.02
<i>p-4d</i>	0.65	C <sub>40</sub> H <sub>20</sub> N <sub>2</sub> O <sub>9</sub> (672.61)	71.43	70.67	3.00	3.11	4.16	4.06
<i>p-4e</i>	0.52	C <sub>40</sub> H <sub>20</sub> N <sub>2</sub> O <sub>10</sub> S (720.67)	66.67	65.56	2.80	2.88	3.89	3.83
<i>p-4f</i>	0.77	C <sub>43</sub> H <sub>20</sub> F <sub>6</sub> N <sub>2</sub> O <sub>8</sub> (806.63)	64.03	63.44	2.50	2.63	3.47	3.50
<i>m-4a</i>	1.37	C <sub>34</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> (580.51)	70.35	69.25	2.78	2.89	4.83	4.75
<i>m-4b</i>	0.75	C <sub>40</sub> H <sub>20</sub> N <sub>2</sub> O <sub>8</sub> (656.61)	73.17	72.57	3.07	3.16	4.27	4.14
<i>m-4c</i>	0.75	C <sub>41</sub> H <sub>20</sub> N <sub>2</sub> O <sub>9</sub> (684.62)	71.93	70.67	2.94	3.04	4.09	3.98
<i>m-4d</i>	0.78	C <sub>40</sub> H <sub>20</sub> N <sub>2</sub> O <sub>9</sub> (672.61)	71.43	70.53	3.00	3.09	4.16	4.08
<i>m-4e</i>	0.70 (0.48) <sup>b</sup>	C <sub>40</sub> H <sub>20</sub> N <sub>2</sub> O <sub>10</sub> S (720.67)	66.67	65.69	2.80	2.90	3.89	3.81
<i>m-4f</i>	0.66 (0.46) <sup>b</sup>	C <sub>43</sub> H <sub>20</sub> F <sub>6</sub> N <sub>2</sub> O <sub>8</sub> (806.63)	64.03	63.31	2.50	2.58	3.47	3.46

<sup>a</sup> Inherent viscosity of the poly(amic acid), measured at a concentration of 0.5 g/dl in DMAc at 30 °C.

<sup>b</sup> Inherent viscosity of the chemically imidized polyimide.

The disappearance of the amic acid bands indicates a virtually complete conversion of the poly(ester-amic acid) precursor into the poly(ester-imide). The characteristic absorption bands of the imide rings appeared near 1780 and 1730 cm<sup>-1</sup> (typical of imide carbonyl asymmetrical and symmetrical stretching), 1370 cm<sup>-1</sup> (C–N stretching), and 720 cm<sup>-1</sup> (imide ring deformation). All of the poly(ester-amic acid)s and poly(ester-imide)s also exhibited strong characteristic absorption bands at around 1720–1740 cm<sup>-1</sup> (ester C=O stretching) and 1230–1270, 1070–1090 cm<sup>-1</sup> (asymmetrical and symmetrical C–O–C stretching) due to the ester groups. The elemental analysis results of the poly(ester-imide)s are also compiled in Table 1. The found values are generally in good agreement with the calculated values for the proposed formulas.

### 3.2. Properties of the polymers

#### 3.2.1. X-ray diffraction data

Morphological information of the poly(ester-imide)s was obtained by WAXD studies. The WAXD patterns of all the poly(ester-imide) samples prepared via both thermal and chemical imidization routes are shown in Fig. 2. In most cases, the degree of crystallinity of these samples depended on the imidization methods. In general, the chemical imidization method can yield a material with a higher degree of crystallinity than that obtained from the thermal imidization method. This implies that imidization of the poly(amic acid) in solution may allow it to obtain a more favourable conformation for packing. The poly(ester-imide)s *m-4e* and *m-4f* derived from DSDA and 6FDA showed amorphous patterns because of the introduction of *meta*-linked main chain structure of bis(ester-amine) *m-1* into the polymer chain; thus they could be solution-cast into flexible and

tough films. All of the thermally imidized poly(ester-imide)s showed highly brittle films, even though they showed amorphous patterns, probably due to hydrolysis of the ester linkages occurring during thermal imidization. In addition, it is interesting to note that the chemically imidized polymers *p-4e* and *p-4f* seemed to display a higher packing density than their corresponding *meta*-analogues, according to their WAXD patterns.

#### 3.2.2. Organo-solubility

The solubility behavior of these poly(ester-imide)s was tested qualitatively in various organic solvents, and the results are reported in Table 2. In general, the semicrystalline polymers revealed a lower solubility. For example, polymers *p-4a–e* and *m-4a–c* were insoluble in all of the organic solvents tested. In general, the solubility of the *p*-series poly(ester-imide)s was similar to those of the corresponding poly(ether-imide)s reported in literature [30]. The poly(ester-imide) *p-4f* was only soluble in NMP at room temperature and *m*-cresol on heating. The poly(ester-imide) *m-4d* was only soluble in NMP and *m*-cresol on heating. The poly(ester-imide)s *m-4e* and *m-4f* exhibited a higher solubility; they were readily soluble in the amide-type polar solvents such as NMP, DMAc, and DMF at room temperature and soluble in DMSO and *m*-cresol on heating. The poly(ester-imide) *m-4f* even was soluble in less efficient THF at room temperature mainly due to the low cohesive energy and high free volume caused by the introduction of the hexafluoroisopropylidene (6F) groups. Thus, polymers *m-4e* and *m-4f* could be solution-cast, in their fully imidized form, to flexible and strong films. These films exhibited ultimate tensile strengths to break of 100–120 MPa, elongations to break of 10–13%, and initial moduli of 1.9–2.1 GPa, qualifying them as strong and tough materials. When comparing the solubility

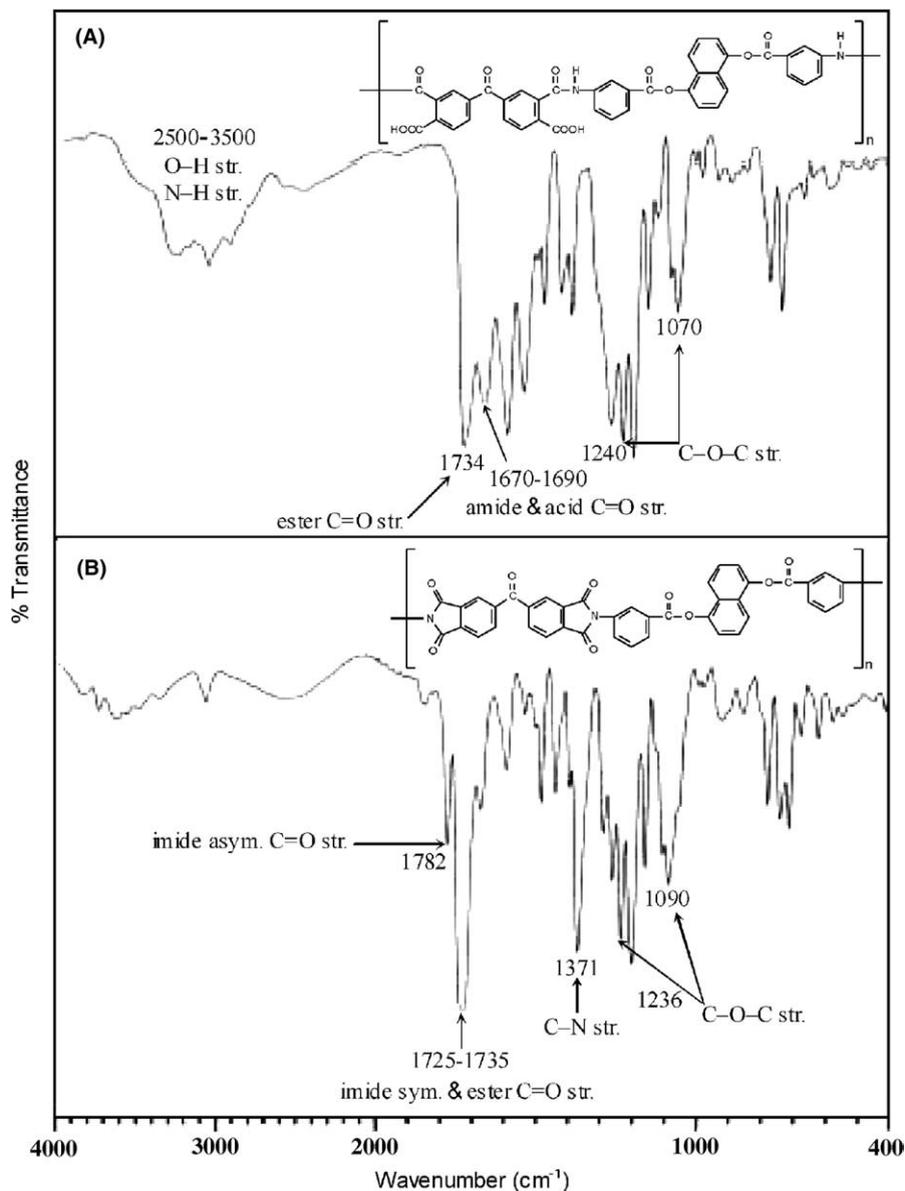


Fig. 1. The thin-film FT-IR spectra of (A) the poly(ester-amic acid) precursor *m-3c* and (B) the poly(ester-imide) *m-4c*.

behaviors of the analogous pairs of *m-4d-f* and *p-4d-f*, one can see a clear effect of the *meta*-catenation on increasing the solubility of these polymers.

### 3.2.3. Glass transition and softening temperatures

Some thermal behavior data of the poly(ester-imide)s obtained by DSC, TMA, and TGA are summarized in Table 3. In the DSC experiments,  $T_{gs}$  of the polymers were obtained from the mid-point temperature of baseline shift on the second DSC heating trace (heating rate = 20 °C/min) after rapid cooling from 400 to 50 °C (cooling rate = 200 °C/min). The first run was

aimed to eliminate any possible volatiles such as the absorbed moisture and the residual solvent in the samples. A typical DSC thermogram for the representative poly(ester-imide) *m-4f* is illustrated in Fig. 3. All the *p*-series poly(ester-imide)s and *m-4a* showed no discernible  $T_{gs}$  on their DSC curves probably due to their semicrystalline nature or rigid backbones. The poly(ester-imide)s *p-4a*, *p-4d*, *p-4f*, and *m-4a* showed clear medium-intensity melting endotherms with peak top temperatures at around 419–484 °C on the first DSC heating traces. The other poly(ester-imide)s showed clear  $T_{gs}$  of between 239 and 273 °C by DSC, generally

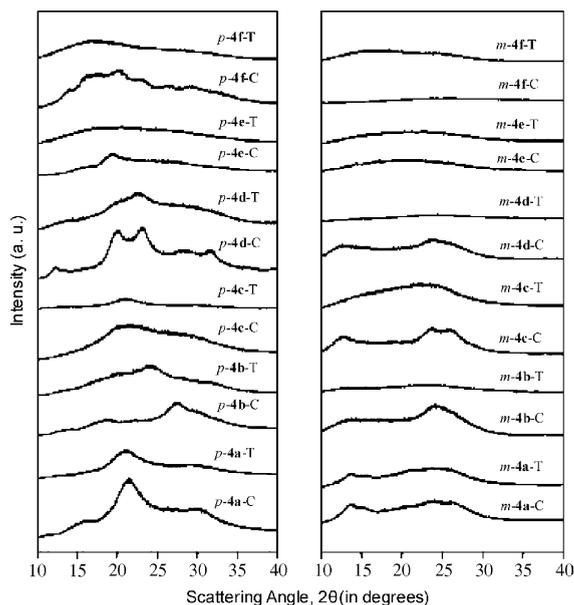


Fig. 2. WAXD patterns of the poly(ester-imide)s *p-4a–f* and *m-4a–f* (C: chemical imidization; T: thermal imidization).

following the increasing order of chain rigidity and steric hindrance. The lowest  $T_g$  value (239 °C) was observed for the poly(ester-imide) *m-4d* derived from ODPa because of the decreased rotational barrier caused by the

Table 2  
The solubility behavior of the poly(ester-imide)s

Polymer code	Solubility <sup>a</sup>					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
<i>p-4a</i>	–	–	–	–	–	–
<i>p-4b</i>	–	–	–	–	–	–
<i>p-4c</i>	–	–	–	–	–	–
<i>p-4d</i>	–	–	–	–	–	–
<i>p-4e</i>	–	–	–	–	–	–
<i>p-4f</i>	+	–	–	–	+h	–
<i>m-4a</i>	–	–	–	–	–	–
<i>m-4b</i>	–	–	–	–	–	–
<i>m-4c</i>	–	–	–	–	–	–
<i>m-4d</i>	+h	–	–	–	+h	–
<i>m-4e</i>	+	+	+	+h	+h	–
<i>m-4f</i>	+	+	+	+h	+h	+

+ : 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.

<sup>a</sup> Qualitative solubility tested with 10 mg of sample in 1 ml of the solvent.

flexible ether linkage between two phthalimide units. The softening temperatures ( $T_s$ ) (or apparent  $T_g$ ) of the flexible poly(ester-imide) films were determined by the TMA method with a loaded penetration probe. They

Table 3  
Thermal properties of the poly(ester-imide)s

Polymer code	$T_g^a$ (°C)	$T_s^b$ (°C)	$T_d^c$ at 5 wt% loss (°C)		$T_d$ at 10 wt% loss (°C)		Char yield <sup>d</sup> (%)
			In N <sub>2</sub>	In air	In N <sub>2</sub>	In air	
<i>p-4a</i>	– <sup>c</sup> (484) <sup>f</sup>	– <sup>g</sup>	531	527	560	552	58
<i>p-4b</i>	–	–	530	524	558	553	61
<i>p-4c</i>	–	–	511	505	536	533	59
<i>p-4d</i>	– (450)	–	509	508	535	543	58
<i>p-4e</i>	–	–	481	478	501	500	54
<i>p-4f</i>	– (419)	–	496	462	521	492	49
<i>m-4a</i>	– (454)	–	477	468	507	509	57
<i>m-4b</i>	273	–	500	491	524	540	56
<i>m-4c</i>	251	–	496	487	519	522	55
<i>m-4d</i>	239	–	501	478	518	522	52
<i>m-4e</i>	253	240	452	457	467	479	51
<i>m-4f</i>	243	230	456	453	481	488	51

<sup>a</sup> Mid-point temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) from 50 to 400 °C after rapid cooling from 400 °C at –200 °C/min (for *p-4a–f* and *m-4a* from 50 to 500 °C).

<sup>b</sup> Softening temperature was measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min. The film samples were heated at 300 °C for 30 min prior to the TMA experiments.

<sup>c</sup> Decomposition temperature was recorded by TGA at a heating rate of 20 °C/min.

<sup>d</sup> Residual weight % at 800 °C in N<sub>2</sub>.

<sup>e</sup> No discernible transition was observed.

<sup>f</sup> Peak-temperature of the medium-intensity melting endotherm on the first DSC heating trace (rate 20 °C/min) from 50 to 500 °C.

<sup>g</sup> Not detected.

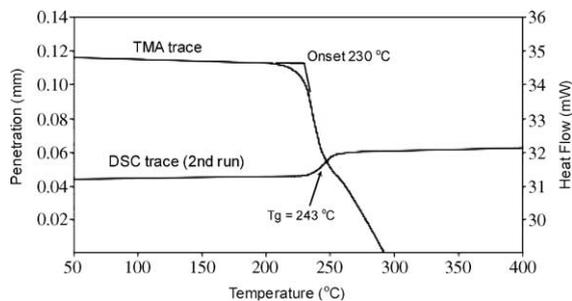


Fig. 3. Typical DSC and TMA thermograms of the poly(ester-imide) *m-4f* (for DSC, heating rate = 20 °C/min; for TMA, heating rate = 10 °C/min and applied force = 10 mN).

were read as the intersection of the extrapolation of the baseline from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of the poly(ester-imide) *m-4f* is also shown in Fig. 3. As can be seen from Table 3, the  $T_s$  values of the flexible poly(ester-imide) films were recorded at 240 °C for *m-4e* and 230 °C for *m-4f*.

### 3.2.4. Thermal and thermo-oxidative stability

The thermal and thermo-oxidative stabilities of these poly(ester-imide)s were evaluated by TGA under both nitrogen and air atmospheres using 5 and 10 wt% loss temperatures ( $T_d$ ) for comparison. The decomposition temperatures ( $T_{d5}$ ) at 5% and 10% weight loss in nitrogen and air atmospheres determined from the original TGA thermograms are also summarized in Table 3. All of the poly(ester-imide)s exhibited good thermal and thermo-oxidative stabilities with insignificant weight losses up to temperatures of approximately 450 °C in both nitrogen and air atmospheres. The amounts of carbonized residues (char yields) at 800 °C in nitrogen for these poly(ester-imide)s were in the range 49–61 wt%.

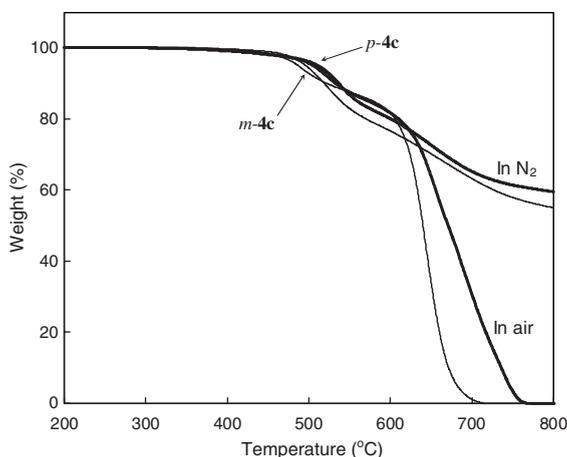


Fig. 4. TGA curves of the poly(ester-imide)s *p-4c* and *m-4c* in nitrogen and air (heating rate = 20 °C/min).

The  $T_d$  values at 5% weight loss for the *p*-series poly(ester-imide)s ranged from 481 to 531 °C in nitrogen and 462–527 °C in air. Probably due to the presence of less stable ester linkages, the *p*-series poly(ester-imide)s generally exhibited lower  $T_d$  values in comparison with the analogous poly(ether-imide)s reported in literature [30]. The  $T_d$  values at 5% weight loss for the *m*-series poly(ester-imide)s were recorded in the range 452–501 °C in nitrogen and 453–491 °C in air. Typical TGA curves of the poly(ester-imide)s *p-4c* and *m-4c* were reproduced in Fig. 4. All of the poly(ester-imide)s seemed to exhibit a two-stage decomposition behavior at elevated temperatures. The first stage of weight loss starting at around 450 °C might be attributed to the early degradation of the less stable ester groups.

## 4. Conclusions

Two series of 1,5-bis(benzoyloxy)naphthalene-containing poly(ester-imide)s were prepared from the bis(ester-amine)s *p-1* and *m-1*, respectively, with various aromatic tetracarboxylic dianhydrides via a conventional two-stage process. The intermediate poly(ester-amic acid) precursors exhibited moderately high molecular weights. Thermal cyclodehydration of the poly(ester-amic acid) films at elevated temperatures resulted in highly brittle poly(ester-imide) products. Most of the chemically imidized poly(ester-imide)s revealed a semi-crystalline nature and were insoluble in most organic solvents. Only two poly(ester-imide)s *m-4e* and *m-4f* were amorphous and displayed good solubility and film quality. These two polymers showed excellent thermal stability and moderate  $T_g$  or  $T_s$  values suitable for thermoforming processing. Thus, they exhibit a good combination of properties required for high-performance materials and demonstrate a promising potential for future applications.

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