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Synthesis and properties of novel aromatic poly(ester amide)s derived from 1,5-bis(4-aminobenzoyloxy)naphthalene and aromatic dicarboxylic acids

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Abstract

A new naphthalene ring-containing bis(ester amine), 1,5-bis(4-aminobenzoyloxy)naphthalene (**2**), was synthesized from the condensation of 1,5-dihydroxynaphthalene with 4-nitrobenzoyl chloride followed by catalytic hydrogenation. A series of naphthalene-containing poly(ester amide)s having inherent viscosities of 0.34–0.82 dl/g were prepared by the direct phosphorylation polyamidation from bis(ester amine) **2** with various aromatic dicarboxylic acids. The poly(ester amide)s derived from terephthalic acid, 4,4′-biphenyldicarboxylic acid, 2,6-naphthalenedicarboxylic acid, and 4,4′-oxydibenzoic acid were semicrystalline and showed less solubility. The other polymers were amorphous and readily soluble in polar organic solvents and gave flexible and tough films via solution casting. Except for four examples, the poly(ester amide)s displayed discernible glass transitions between 190 and 227 °C by differential scanning calorimetry. These poly(ester amide)s did not show significant decomposition below 400 °C in nitrogen or air.

Keywords: Naphthalene units; Bis(ester amine); Poly(ester amide)s

1. Introduction

Wholly aromatic polyamides (aramids) are well known as high-performance polymeric materials with useful properties such as outstanding thermal stability, good chemical resistance, and excellent mechanical properties [1–3]. However, aramids are usually difficult to be processed into articles due to their high glass transition or melting temperatures and limited solubility in common organic solvents caused by the high crystallinity, high rigidity of the polymer backbones, and strong intermolecular interactions through hydrogen bonding. Thus, their applications were restricted in some areas. Processable engineering plastics possessing moderately high softening temperatures and/or solubility in most organic solvents are required for practical use. Therefore, various efforts have focused on the synthesis of soluble and/or thermoplastic polyamides while maintaining the excellent thermal and mechanical properties. The approaches that have been employed to improve the processability of these polymers include the introduction of flexible links [4–6], asymmetric units [7], bulky pendant groups [8–11], and kinked or non-coplanar structures [12–15] into the polymer chain. It has been demonstrated that incorporation of both ether and

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naphthalene units into the polymer backbones may enhance the solubility of aromatic polyamides and polyimides while retaining high thermal stability [16–19]. In continuing our interest in preparing easily processable high-performance polymers bearing naphthalene units, this study deals with the synthesis and basic characterization of novel aromatic poly(ester amide)s derived from the bis(ester amine) bearing naphthalene-1,5-diyl unit, i.e., 1,5-bis(4-aminobenzoyloxy)naphthalene (**2**), and various aromatic dicarboxylic acids. The solubility behaviors and thermal properties of the prepared polymers are compared with those of structurally related ones from 1,5-bis(4-aminophenoxy)naphthalene [16].

2. Experimental

2.1. Reagents and solvents

1,5-Dihydroxynaphthalene (from Acros), 4-nitrobenzoyl chloride (from Acros), 10% palladium on activated carbon (Pd/C, from Fluka), terephthalic acid (**3a**, from Fluka), isophthalic acid (**3b**, from Wako), 5-*tert*-butylisophthalic acid (**3c**, from Aldrich), 4,4′-biphenyldicarboxylic acid (**3d**, from TCI), 2,6-naphthalenedicarboxylic acid (**3e**, from TCI), 4,4′-oxydibenzoic acid (**3f**, from TCI), 4,4′-hexafluoroisopropylidenedibenzoic acid (**3g**, from Chriskev), and 4,4′-sulfonyldibenzoic acid (**3h**, from New Japan Chemical Co.) were used as received. 4,4′-[Isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (**3i**, mp = 276 °C) and 4,4′-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy] dibenzoic acid (**3j**, mp = 318 °C) were synthesized in high purity and high yields via two steps from commercially available reagents [5]. Commercially available reagent-grade anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 8 h prior to use. *N*-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) was also purified by distillation under reduced pressure.

2.2. Monomer synthesis

2.2.1. 1,5-Bis(4-nitrobenzoyloxy)naphthalene (1)

Dinitro-diester **1** was synthesized from the condensation of 1,5-dihydroxynaphthalene with 4-nitrobenzoyl chloride. 1,5-Dihydroxynaphthalene (16 g; 0.1 mol), which was dissolved in 400 ml of dried DMAc, and triethylamine (30 ml; 0.22 mol) were mixed in a 1 l round-bottomed flask. A solution of 4-nitrobenzoyl chloride (39 g; 0.21 mol) in DMAc (100 ml) was then added dropwise over a period of about 1 h. After complete addition, the reaction mixture was stirred at 80 °C for 8 h. The reaction mixture was then poured into 1.5 l of water. The precipitate was collected by filtration, washed thoroughly with water and methanol, and dried. The crude product (43.4 g; 95% yield) was purified by recrystallization from DMF to give 41.5 g (91% yield) of pure dinitro-diester **1** as light yellowish needles; mp = 318 °C (DSC, 10 °C/min).

FT-IR (KBr): 1734 (C=O), 1523, 1348 (NO_2), 1271, 1095 cm^{-1} (C–O–C). Anal. Calcd for $C_{24}H_{14}N_2O_8$ (458.38): C, 62.89%; H, 3.08%; N, 6.11%. Found: C, 62.77%; H, 3.09%; N, 6.05%.

2.2.2. 1,5-Bis(4-aminobenzoyloxy)naphthalene (2)

Bis(ester amine) **2** was synthesized by the catalytic hydrogenation of dinitro-diester **1**. A mixture of 32.4 g (0.07 mol) of dinitro compound **1** and 0.4 g of 10% Pd/C in 600 ml of DMAc was stirred at room temperature under a hydrogen atmosphere until the theoretical amount of hydrogen was consumed. The time taken to reach this stage was about 3 days. The solution was filtered to remove the catalyst, and the obtained filtrate was poured into 2 l of stirring water to give a white precipitate. The yield was 22.5 g (86%); mp = 327 °C (DSC, 10 °C/min).

FT-IR (KBr): 3458, 3359 (NH_2), 1707 (C=O), 1280, 1092 cm^{-1} (C–O–C). ^1H NMR (400 MHz, DMSO-d_6), δ (ppm): 7.98 (d, J = 8 Hz, 4H), 7.78 (d, J = 8 Hz, 2H), 7.60 (t, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 2H), 6.74 (d, J = 8 Hz, 4H), 6.29 (s, NH_2, 4H). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 166.40, 156.07, 148.51, 133.71, 130.02, 127.69, 120.54, 119.94, 114.94, 114.53. Anal. Calcd for $C_{24}H_{18}N_2O_4$ (398.42): C, 72.35%; H, 4.55%; N, 7.03%. Found: C, 71.98%; H, 4.58%; N, 6.91%.

2.3. General poly(ester amide) synthesis

A typical example of polycondensation is as follows. A mixture of 0.498 g (1.25 mmol) of the bis(ester amine) **2**, 0.2778 g (1.25 mmol) of 5-*tert*-butylisophthalic acid (**3c**), 0.2 g of calcium chloride, 2.0 ml of NMP, 0.5 ml of pyridine, and 1.2 ml of TPP was heated with stirring at 110 °C for 3 h. As polycondensation proceeded, the solution became viscous gradually. The resulting highly viscous polymer solution was poured slowly into 250 ml of stirred methanol. The stringy, fiber-like precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100 °C in a vacuum oven. The yield was quantitative. The inherent viscosity of polymer **4c** was 0.55 dl/g, measured at a concentration of 0.5 g/dl in DMAc containing 5 wt.% LiCl at 30 °C. The FT-IR spectrum (film) exhibited characteristic absorptions at 3311 (N–H stretching), 1734 (ester C=O stretching), 1676 (amide C=O stretching), 1530 (N–H bending), and 1261, 1082 cm^{-1} (asymmetrical and symmetrical C–O–C stretching).

2.4. Preparation of poly(ester amide) films

For the organosoluble poly(ester amide)s, the samples were cast into films via solvent casting. A polymer solution was made by dissolving about 0.9 g of the poly(ester amide) sample in 9 ml of DMAc to afford an approximate 10 wt.% solution. The homogeneous solution was poured into a 9-cm diameter glass Petri dish and then placed in a 90 °C oven overnight for the slow release of the cast solvent. The semidried poly(ester amide) 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.

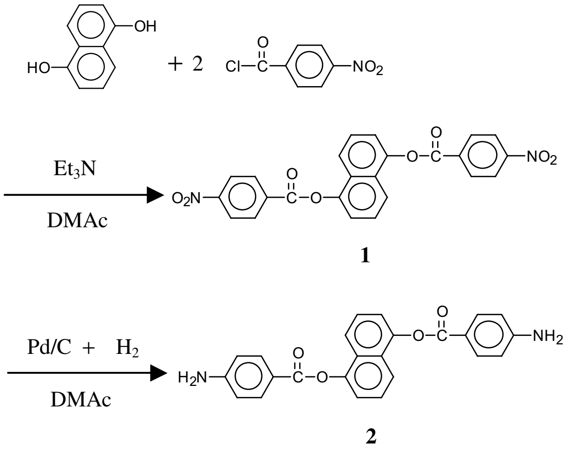
2.5. Measurements

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. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane as the reference, working at 400 and 100 MHz, respectively. The inherent viscosities of the poly(ester amide)s were determined at a concentration of 0.5 g/dl in DMAc containing 5 wt.% LiCl with a Cannon–Fenske 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 Kα radiation. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress–strain behaviors of the poly(ester amide) film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min 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 three replicas was used. Thermogravimetric analyses (TGA) were conducted with a Perkin Elmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film or powder samples heated in flowing nitrogen or air (40 ml/min) at a heating rate of 20 °C/min from 200 to 800 °C. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Pyris 1 DSC at a scanning rate of 20 °C/min from 50 to 400 °C in flowing nitrogen (20 ml/min). Glass transition temperatures (T_gs) were read at the middlepoint 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. Thermomechanical analyses (TMA) were conducted with a Perkin Elmer TMA 7 instrument. The TMA experiments were conducted from 50 to 350 °C at a heating rate of 10 °C/min 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.

3. Results and discussion

3.1. Monomer synthesis

The new bis(ester amine) **2** was successfully synthesized by using hydrogen Pd/C-catalyzed reduction of dinitro-diester **1** resulting from the condensation reaction of 1,5-dihydroxynaphthalene with 4-nitrobenzoyl chloride, as shown in Scheme 1. Elemental, IR, and NMR analyses were used to confirm the structures of compounds **1** and **2**. The elemental analysis values were generally in agreement with the calculated values for the proposed structures. The FT-IR spectra of dinitro-diester **1** and bis(ester amine) **2** are illustrated in Fig. 1. The nitro groups of dinitro-diester **1** showed two characteristic absorption bands at 1523 and 1348 cm^{-1}. After the reduction, the characteristic absorptions of the nitro groups disappeared, and the amino groups showed a pair of N–H stretching absorption bands at 3458 and 3359 cm^{-1}. In the FT-IR spectrum of bis(ester amine) **2**, the characteristic absorption band at 1707 cm^{-1} was assigned to the ester carbonyl group, which is 27 cm^{-1} lower than that of dinitro-diester **1** (1734 cm^{-1}). Conjugation of the amino group substituted at the *para*-position caused the absorption shift. The ^{1}H NMR and ^{13}C NMR spectra of bis(ester amine) **2** are shown in Fig. 2. The assignments of each carbon and proton also are given in the figure, and all the NMR spectroscopic data are consistent with the proposed structure.



Scheme 1. Synthetic route to bis(ester amine) **2**.

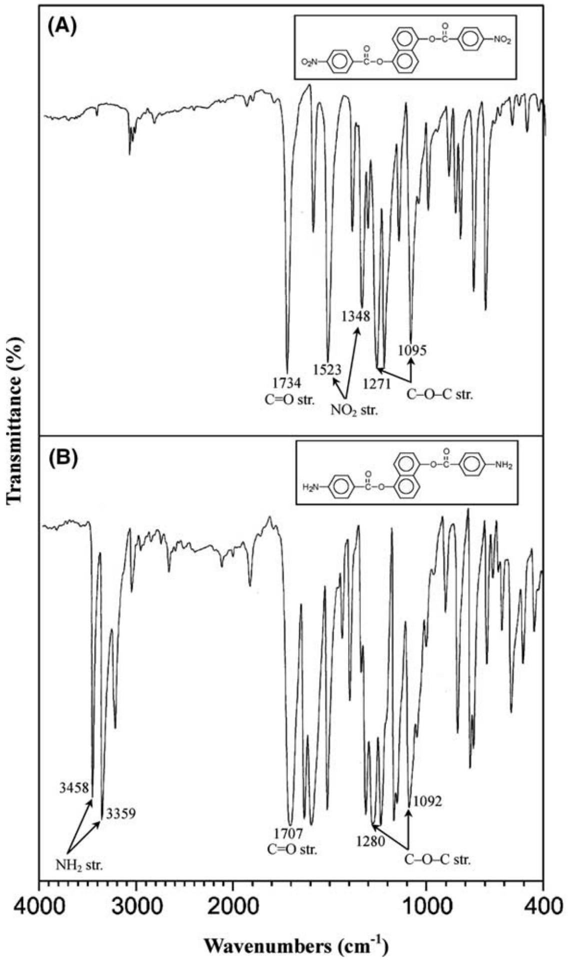


Fig. 1. FT-IR spectra of (A) dinitro-diester **1** and (B) bis(ester amine) **2**.

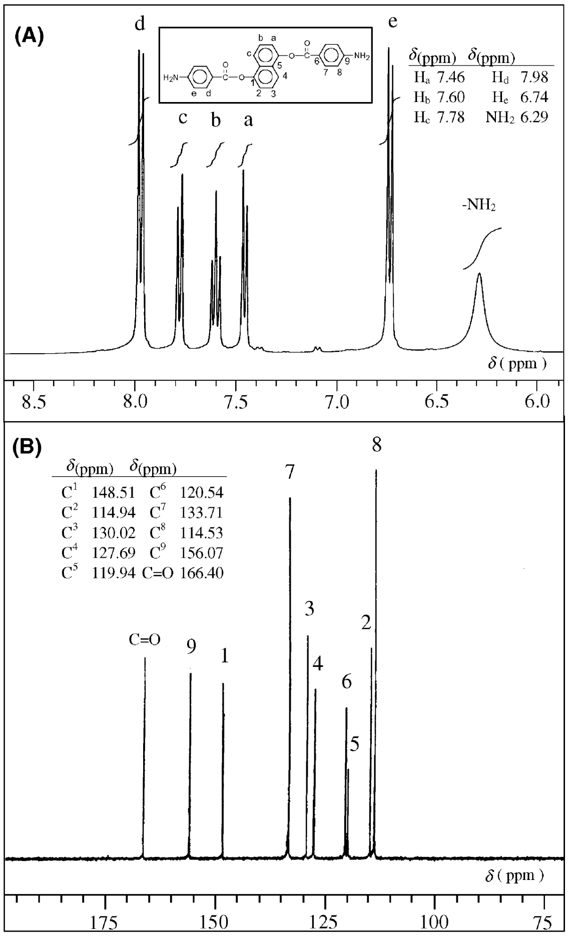
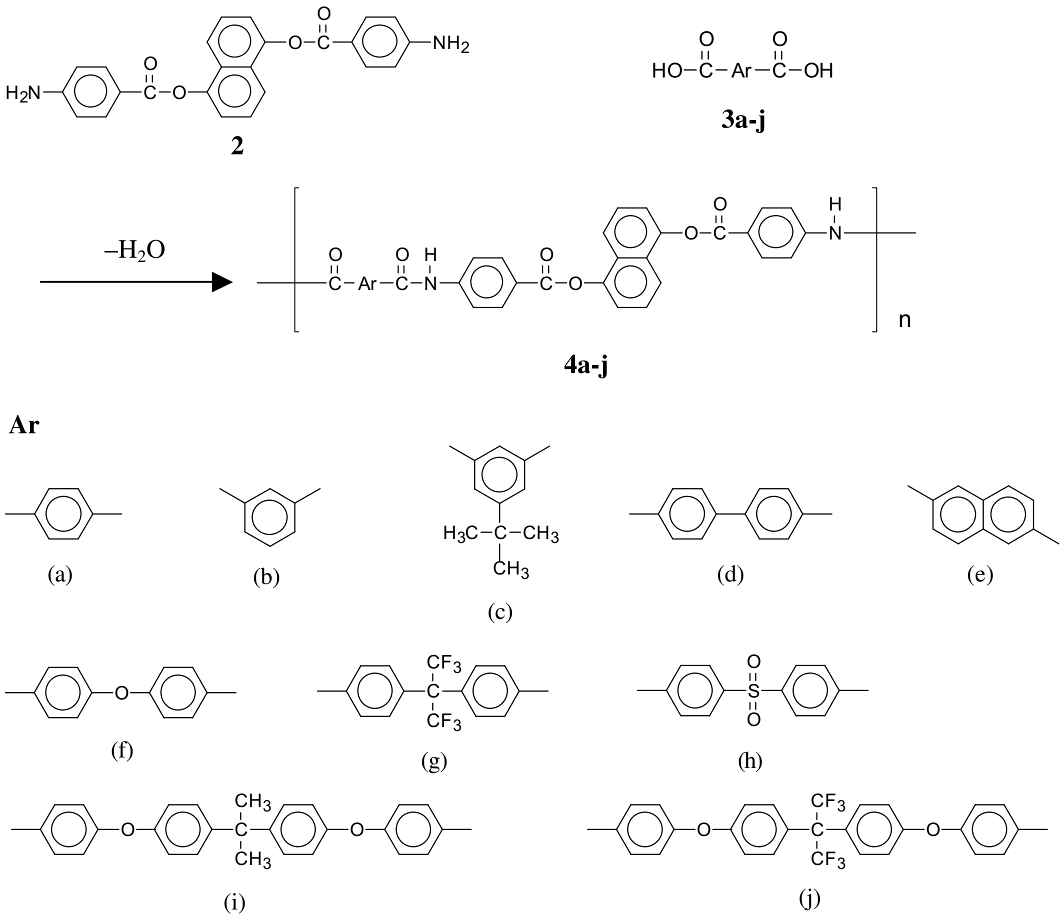


Fig. 2. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of bis(ester amine) **2** in DMSO-d_6.

3.2. Synthesis of poly(ester amide)s

The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids using triphenyl phosphite (TPP) and pyridine as condensing agents has been known to be a convenient method for the preparation of aromatic polyamides on laboratory scale [20]. This method was adopted here to prepare aromatic poly(ester amide)s **4a**–**j** from bis(ester amine) **2** with various aromatic dicarboxylic acids **3a**–**j**, as shown in Scheme 2. Synthesis conditions and inherent viscosities of poly(ester amide)s **4a**–**j** are summarized in Table 1. All the reaction solutions were homogeneously transparent and became highly viscous, except for polymers **4a** and **4d**–**f**, which precipitated from the reaction medium when the reaction systems became viscous. These poly(ester amide)s were obtained in almost quantitative yields with inherent viscosities of 0.34–0.82 dl/g. Except for **4a** and **4d**–**f**, all the poly(ester amide)s could be solution-cast into free-standing films. However, the film of **4i** cracked upon creasing, possibly because of a moderate level of crystallinity. The other films were flexible and creasable.

Structural features of the poly(ester amide)s were verified by FT-IR spectra and elemental analyses. They showed the characteristic absorptions of the amide group at around 3310–3340 cm^{-1} (N–H stretching), 1670–1680 cm^{-1} (amide C=O stretching) and 1530–1550 cm^{-1} (N–H bending). All poly(ester amide)s also exhibited strong characteristic absorption bands at around 1730–1740 cm^{-1} (ester C=O stretching) and 1250–1270, 1080–1090 cm^{-1} (asymmetrical and symmetrical C–O–C stretching) due to the ester groups. A typical FT-IR spectrum of polymer **4c** is illustrated in Fig. 3. The results of the elemental analyses of all poly(ester amide)s are reported in Table 2. The elemental analysis values were generally in agreement with the calculated values for the corresponding recurring units.



Scheme 2. Synthesis of poly(ester amide)s.

3.3. Properties of polymers

3.3.1. X-ray diffraction data

All poly(ester amide)s were characterized by WAXD studies. As can be seen from the diffraction patterns shown in Fig. 4, the polymers that could afford flexible and tough films displayed amorphous patterns. The poly(ester amide)s **4a**, **4d**, and **4e** derived from rigid diacids such as terephthalic acid (**3a**), 4,4′-biphenyldicarboxylic acid (**3d**), and 2,6-naphthalenedicarboxylic acid (**3e**) showed some strong diffraction signals assignable to a semicrystalline polymer. In addition, it is interesting to note that polymer **4f** also displayed a highly crystalline pattern. The WAXD pattern of **4f** indicates that the incorporation of flexible ether linkages does not necessarily reduce the polymer crystallinity dramatically because it may increase the probability of the formation of interchain hydrogen bonding, thus inducing the close packing of chains. Polymer **4i** also can be judged as somewhat crystalline on basis of its WAXD pattern. This result correlated to the slightly brittle nature of its cast film as described earlier. The incorporation of bulky, pendent *tert*-butyl group and sulfonyl and hexafluoroisopropylidene linkages interferes with the dense chain packing. Thus, polymers **4c**, **4g**, **4h** and **4j** revealed an almost completely amorphous diffraction pattern.

3.3.2. Organo-solubility

The solubility of the poly(ester amide)s was determined qualitatively, and the results are reported in Table 3. In general, the semicrystalline polymers revealed a poor solubility. For example, **4a** and **4d**–**f** were insoluble in any of the solvents tested. In contrast, the amorphous poly(ester amide)s exhibited a higher solubility; they were soluble in most polar aprotic solvents. The excellent solubility associated with polymers **4c**, **4g**, **4h** and **4j** can be attributed in part to the presence of *tert*-butyl group and sulfonyl and hexafluoroisopropylidene linking groups along the backbones. The somewhat crystalline polymer **4i** was soluble in NMP and hot DMAc, but insoluble in other solvents tested. In general, the solubility behaviors of the **4** series poly(ester amide)s are

Table 1
Synthesis conditions, inherent viscosities, and film quality of poly(ester amide)s

Polymer code	Amount of reagent used[a]			η_{inh}[c] (dl/g)	Film quality[d]
	NMP (ml)	Pyridine (ml)	$CaCl_2$ (g)		
4a	3	0.8	0.3	0.34	–[e]
4b	2	0.5	0.2	0.59	F
4c	2	0.5	0.2	0.55	F
4d	5 + 5[b]	1.2	0.5	0.65	–
4e	5	1.2	0.5	0.65	–
4f	2.5 + 3	0.8	0.2	0.53	–
4g	3	0.8	0.3	0.59	F
4h	2.5	0.8	0.2	0.58	F
4i	3	0.8	0.3	0.82	B
4j	3	0.8	0.3	0.71	F

[a] Amount of each bis(ester amine) and diacid monomer = 1.25 mmol; TPP = 1.2 ml; reaction temperature = 110 °C; reaction time = 3 h.

[b] "5 + 5" means that an initial amount of 5 ml NMP was used and an additional 5 ml of NMP was added when the reaction solution became too viscous or turbid.

[c] Measured at a concentration of 0.5 g/dl in DMAc containing 5 wt.% LiCl at 30 °C by a Cannon–Fenske viscometer.

[d] Films were cast by slow evaporation of polymer solutions in DMAc. F: flexible; B: brittle, cracked upon creasing.

[e] Insoluble in available organic solvents.

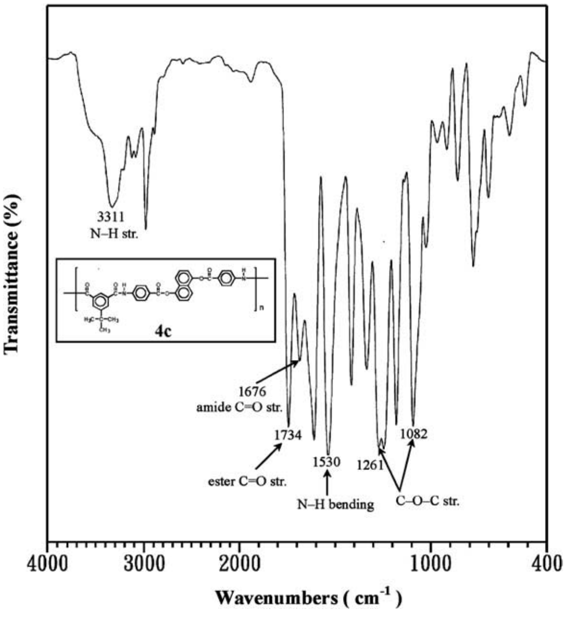


Fig. 3. The thin-film FT-IR spectrum of poly(ester amide) **4c**.

similar to those of the corresponding poly(ether amide)s obtained from 1,5-bis(4-aminophenoxy)naphthalene reported in literature [16].

3.3.3. Tensile properties

As mentioned earlier, all of the amorphous poly(ester amide)s could be solution-cast into flexible and tough films. These films were subjected to tensile test, and their tensile properties are presented in Table 4. These films exhibited ultimate tensile strengths of 72–91 MPa, elongations to break of 9–14%, and initial moduli of 1.9–2.4 GPa, qualifying them as strong and tough materials.

3.3.4. Glass transition and softening temperatures

The thermal properties of the poly(ester amide)s evaluated by DSC, TMA, and TGA are summarized in Table 5. T_g of these polyamides was obtained from the middlepoint temperature of baseline shift on the second DSC heating trace (heating rate = 20 °C/min) after rapid cooling from 400 °C (cooling rate = 200 °C/min). The semicrystalline poly(ester amide)s **4a** and **4d**–**f** showed no discernible T_gs on their DSC curves. The other poly(ester amide)s showed clear T_g between 190 and 227 °C by DSC, generally following the increasing order of chain rigidity, steric hindrance, and polarity of the diacid residues. Poly(ester amide)s **4i** and **4j** had relatively lower T_g values because of their more flexible diacid components. All the semicrystalline poly(ester amide)s showed clear medium-intensity melting endotherms with peak top temperatures at around 346–479 °C on the first DSC heating traces. Typical DSC thermograms of polymer **4i** are illustrated in Fig. 5. Probably due to the presence of flexible ester linkages, the poly(ester amide)s generally exhibited lower T_g values and melting temperatures in comparison with the corresponding poly(ether amide)s reported in literature [16]. The softening temperatures (T_s) (or apparent T_g) of the poly(ester amide) films were determined by the TMA method using a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. A typical TMA thermo-

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

Polymer code	Formula of the repeat unit (formula weight)	C (%)		H (%)		N (%)	
		Calcd	Found	Calcd	Found	Calcd	Found
4a	$C_{32}H_{20}N_2O_6$ (528.52)	72.72	71.43	3.81	4.17	5.30	5.16
4b	$C_{32}H_{20}N_2O_6$ (528.52)	72.72	71.27	3.81	4.16	5.30	5.20
4c	$C_{36}H_{28}N_2O_6$ (584.63)	73.96	71.62	4.83	5.08	4.79	4.59
4d	$C_{38}H_{24}N_2O_6$ (604.62)	75.49	73.49	4.00	4.15	4.63	4.47
4e	$C_{36}H_{22}N_2O_6$ (578.58)	74.73	72.98	3.83	3.94	4.84	4.66
4f	$C_{38}H_{24}N_2O_7$ (620.62)	73.54	72.44	3.90	4.06	4.51	4.21
4g	$C_{41}H_{24}F_6N_2O_6$ (754.64)	65.26	64.20	3.21	3.56	3.71	3.51
4h	$C_{38}H_{24}N_2O_8S$ (668.68)	68.26	66.15	3.62	3.84	4.19	3.95
4i	$C_{53}H_{38}N_2O_8$ (830.89)	76.61	74.56	4.61	4.88	3.37	3.08
4j	$C_{53}H_{32}F_6N_2O_8$ (938.84)	67.81	65.52	3.44	3.57	2.98	2.79

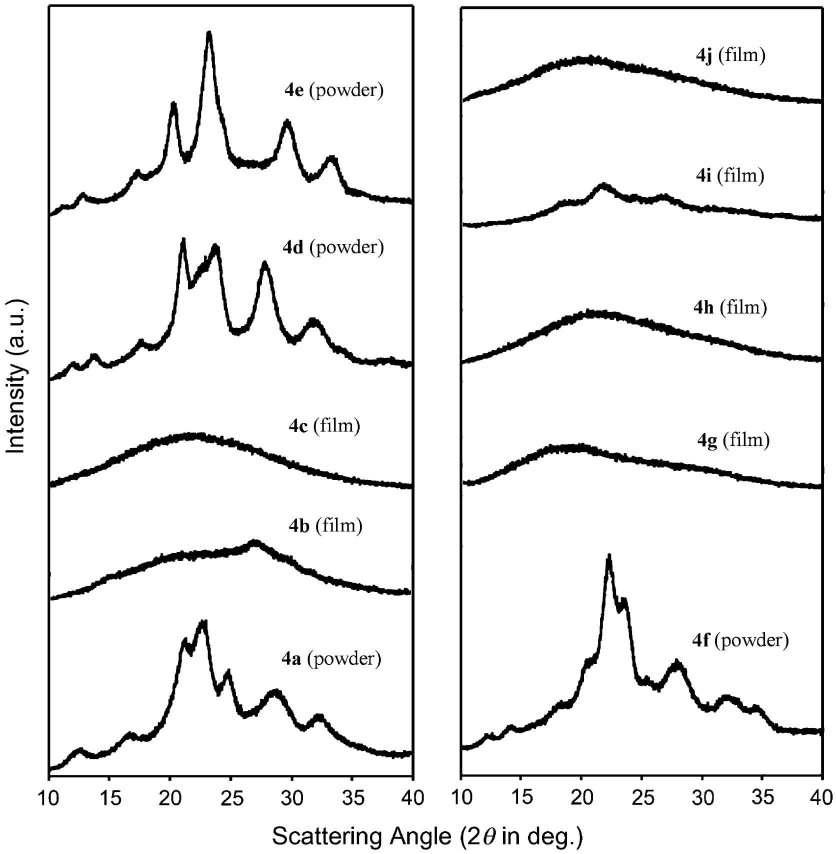


Fig. 4. WAXD patterns of the poly(ester amide)s.

gram of polymer **4c** is illustrated in Fig. 6. As can be seen from Table 5, the T_s values of the flexible poly(ester amide) films were recorded in the range of 181–228 °C. In general, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments. The trend of T_s variation with the chain stiffness is similar to that of T_g observed in the DSC measurements.

3.3.5. Thermal and thermo-oxidative stability

Thermal and thermo-oxidative stabilities of these poly(ester amide)s were evaluated by TGA under both

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

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

[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.

Table 4
Mechanical properties of some poly(ester amide) films

Polymer code	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
4b	91	11	2.4
4c	79	9	2.2
4g	89	14	2.3
4h	72	11	1.9
4j	76	10	2.0

Table 5
Thermal properties of the poly(ester amide)s

Polymer code	T_g (°C)[a]	T_s[b] (°C)	T_d[c] at 5 wt.% loss (°C)		T_d at 10 wt.% loss (°C)		Char yield[d] (%)
			In N_2	In air	In N_2	In air	
4a	–[e] (479)[f]	–[g]	404	399	481	470	56
4b	215	197	384	378	425	424	59
4c	223	228	405	396	437	432	60
4d	– (462)	–	441	440	489	469	56
4e	– (461)	–	442	440	492	477	58
4f	– (418)	–	438	430	471	463	56
4g	227	219	396	409	431	463	57
4h	214	218	386	399	427	443	62
4i	192 (346)	185	416	419	448	455	53
4j	190	181	423	425	447	455	52

[a] Middlepoint 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 **4a** and **4d**–**f** from 50 to 500 °C).

[b] 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.

[c] Decomposition temperature was recorded by TGA at a heating rate of 20 °C/min.

[d] Residual wt.% at 800 °C in N_2.

[e] No discernible transition was observed.

[f] Peak top temperature of the medium-intensity melting endotherm on the first DSC heating trace (rate 20 °C/min) from 50 to 400 °C (for **4a** and **4d**–**f** from 50 to 500 °C).

[g] Not detected.

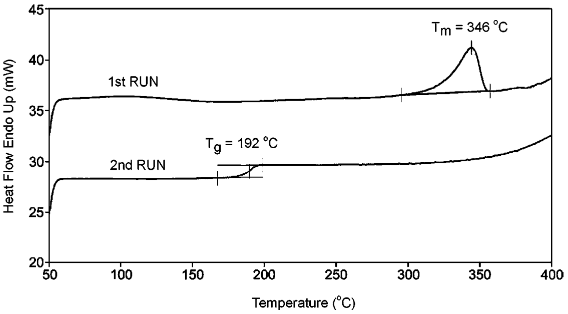


Fig. 5. Typical DSC thermograms of poly(ester amide) **4i** (heating rate = 20 °C/min).

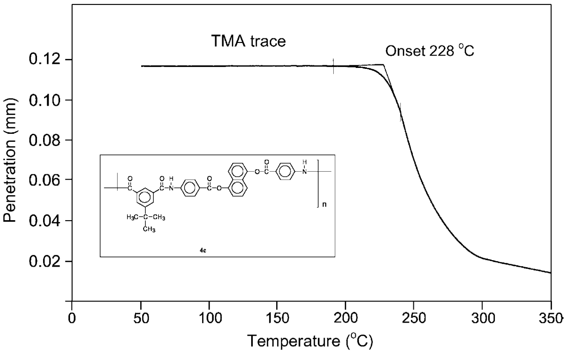


Fig. 6. Typical TMA thermogram of poly(ester amide) **4c** (heating rate = 10 °C/min and applied force = 10 mN).

nitrogen and air atmospheres using 5 and 10 wt.% loss values (T_d) for comparison. The decomposition temperatures (T_ds) at 5 and 10 wt.% loss in nitrogen and in air atmospheres determined from the original TGA thermograms are also summarized in Table 5. All the poly(ester amide)s exhibited good thermal stability with insignificant weight loss up to temperatures of approximately 400 °C in both air and nitrogen atmospheres, and the anaerobic char yields at 800 °C for all polymers were in the range of 52–62 wt.%. The T_d values at 5 wt.% loss for the poly(ester amide)s ranged from 384 to 442 °C in nitrogen and 378 to 440 °C in air, which were lower than those of the analogous poly(ether amide)s [16] because of the less stable ester groups. Typical TGA curves of poly(ester amide) **4c** were reproduced in Fig. 7. All poly(ester amide)s seemed to exhibit a two-stage decomposition behavior at elevated temperatures. The first stage of weight loss starting around 400 °C might be attributed to the early degradation of the less stable ester groups. IR spectra of the solid residues of the polymers after heat treatment were examined. Fig. 8 shows IR spectra of a thin film of **4b** after being heated sequentially in air each for 10 min at 300, 350, 400, and 450 °C. The IR spectra of **4b** after heat treatment at 300 and 350 °C remained almost the same as before heat treatment. After heating at 400 °C for 10 min, a decrease in relative intensities around 1732, 1269, and 1090 cm^{-1} indicates some loss of ester functionalities. After further heating at 450 °C, an obvious decrease in intensities of

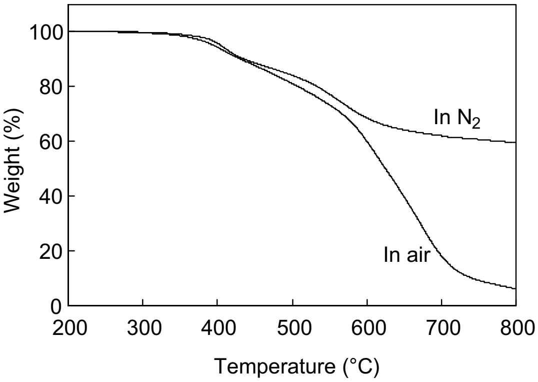


Fig. 7. TGA curves of poly(ester amide) **4c** (heating rate = 20 °C/min).

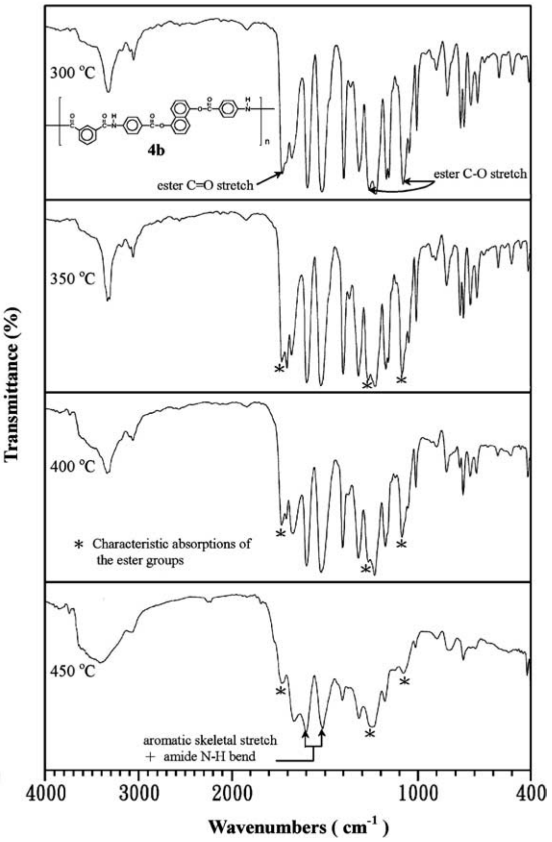


Fig. 8. FT-IR spectra (thin film) of poly(ester amide) **4b** after sequential heating in air at the indicated temperatures, each for 10 min.

the ester absorption bands was observed, while a high content of amide functionalities and aromatic skeletons was still detected.

4. Conclusions

A novel bis(benzoyloxy)naphthalene-containing aromatic bis(ester amine) **2** has been successfully synthesized in high purity and high yields from the condensation reaction of 1,5-dihydroxynaphthalene with 4-nitrobenzoyl chloride and subsequent hydrogen catalytic reduction of the intermediate dinitro compound. A series of naphthalene-containing poly(ester amide)s have been successfully prepared from bis(ester amine) **2** with various aromatic dicarboxylic acids by means of TPP and pyridine. The poly(ester amide)s obtained from some dicarboxylic acids such as terephthalic acid (**3a**), 4,4′-biphenyldicarboxylic acid (**3d**), 2,6-naphthalenedicarboxylic acid (**3e**), and 4,4′-oxydibenzoic acid (**3f**) were semicrystalline and showed less solubility. All of the amorphous poly(ester amide)s 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 amide)s using IR spectroscopy indicated that ester groups are the thermal weak points of these polymers.

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