

Synthesis and properties of novel aromatic poly(ester–amide)s derived from 1,5-bis(3-aminobenzoyloxy)naphthalene and aromatic dicarboxylic acids

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Abstract: A new naphthalene-ring-containing bis(ester–amine), 1,5-bis(3-aminobenzoyloxy)naphthalene, was prepared from the condensation of 1,5-dihydroxynaphthalene with 3-nitrobenzoyl chloride followed by catalytic hydrogenation. A series of novel naphthalene-containing poly(ester–amide)s was synthesized by direct phosphorylation polyamidation from this bis(ester–amine) with various aromatic dicarboxylic acids. The polymers were produced in high yields and had moderate inherent viscosities of 0.47–0.81 dL g⁻¹. The poly(ester–amide) derived from terephthalic acid was semicrystalline and showed less solubility. Other polymers derived from less rigid and symmetrical diacids were amorphous and readily soluble in most polar organic solvents and could be solution-cast into transparent, flexible and tough films with good mechanical properties. The amorphous poly(ester–amide)s displayed well-defined glass transition temperatures of between 179 and 225 °C from differential scanning calorimetry and softening temperatures of between 178 and 211 °C from thermomechanical analysis. These poly(ester–amide)s did not show significant decomposition below 400 °C in nitrogen or air.

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Keywords: naphthalene units; bis(ester–amine); poly(ester–amide)s

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 process into articles due to their high glass transition (T_g) or melting temperatures and limited solubility in common organic solvents caused by the high crystallinity and high rigidity of the polymer backbones, and strong intermolecular interactions through hydrogen bonding. Thus, their applications have been 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 still 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. These modifications lower the melting temperatures 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 incorporation of both ether and naphthyl units into the polymer backbones may enhance the solubility and processability of aromatic polyamides and polyimides without any significant reduction in thermal stability.^{16–19} In continuing our interest in preparing easily processable high-performance polymers bearing naphthyl units, this present study deals with the synthesis and basic characterization of a series of novel aromatic poly(ester–amide)s derived from a bis(ester–amine) bearing naphthalene-1,5-diyl and *m*-phenylene units, ie, 1,5-bis(3-aminobenzoyloxy)naphthalene (2), with various aromatic dicarboxylic acids. The introduction of ester and *m*-phenylene linkages to the backbone was expected to bring about a reduction in the T_g values and an increase in their solubility in organic solvents.

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EXPERIMENTAL

Materials

1,5-Dihydroxynaphthalene (from Acros), 3-nitrobenzoyl chloride (from Acros) and 10 % palladium on activated carbon (Pd/C, from Fluka) were used as received. Commercially available aromatic dicarboxylic acids, such as terephthalic acid (**3a**, from Fluka), isophthalic acid (**3b**, from Wako), 4,4'-oxydibenzoic acid (**3c**, from TCI), 4,4'-hexafluoroisopropylidenedibenzoic acid (**3d**, from Chriskev) and 4,4'-sulfonyldibenzoic acid (**3e**, from New Japan Chemical Company) were used as received. 4,4'-(Isopropylidene-bis(1,4-phenylene)dioxy)dibenzoic acid (**3f**, mp = 276 °C) and 4,4'-(hexafluoroisopropylidene-bis(1,4-phenylene)dioxy)dibenzoic acid (**3g**, 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 (CaCl₂) 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. *N,N*-Dimethylacetamide (DMAc) (from Tedia), *N,N*-dimethylformamide (DMF) (from Tedia), and dimethyl sulfoxide (DMSO) (from Tedia) were used as received.

Monomer synthesis

1,5-Bis(3-nitrobenzoyloxy)naphthalene (1)

The dinitro-diester **1** was prepared by the condensation of 1,5-dihydroxynaphthalene with 3-nitrobenzoyl chloride. 1,5-Dihydroxynaphthalene (16 g, 0.1 mol), 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 3-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 (43.9 g, 96 % yield) was purified by recrystallization from DMF to give 41.2 g (90 % yield) of the pure dinitro-diester **1** as 'off-white' needles (mp = 251 °C (DSC, 10 °C min⁻¹)).

IR (KBr) (cm⁻¹): 1734 (C=O stretching), 1529, 1348 (NO₂ stretching), 1257, 1122 (C–O–C stretching). Elemental analysis, calculated for C₂₄H₁₄N₂O₈ (458.38): C, 62.89 %; H, 3.08 %; N, 6.11 %. Found: C, 62.86 %; H, 3.16 %; N, 6.06 %.

1,5-Bis(3-aminobenzoyloxy)naphthalene (2)

The bis(ester–amine) **2** was prepared by the catalytic hydrogenation of the dinitro-diester **1**. A mixture of 32.4 g (0.07 mol) of the dinitro compound **1** and 0.4 g of 10 % Pd/C in 500 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 d. The solution was filtered to remove the catalyst, and the obtained filtrate was poured into 1 L of stirred methanol to give a light 'off-white' precipitate. The yield was 24.6 g (87 %); mp = 234 °C (DSC, 10 °C min⁻¹).

IR (KBr) (cm⁻¹): 3460, 3373 (NH₂ stretching), 1726 (C=O stretching), 1215, 1088 (C–O–C stretching). ¹H NMR (400 MHz, (DMSO)-d₆, δ, ppm): 7.82 (d, *J* = 8 Hz, 2H), 7.66 (t, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8 Hz, 2H), 7.42 (d, *J* = 8 Hz, 2H), 7.30 (t, *J* = 8 Hz, 2H), 6.98 (d, *J* = 8 Hz, 2H), 7.53 (s, *J* = 8 Hz, 2H), 5.56 (s, –NH₂, 4H). ¹³C NMR (100 MHz, DMSO-d₆, δ, ppm): 165.18 (C=O), 149.32, 146.72, 129.46, 128.92, 127.77, 126.72, 119.43, 119.29, 118.99, 117.07, 114.56. Elemental analysis, calculated for C₂₄H₁₈N₂O₄ (398.42): C, 72.35 %; H, 4.55 %; N, 7.03 %. Found: C, 72.57 %; H, 4.67 %; N, 7.07 %.

Polymer synthesis

A typical example of the phosphorylation polycondensation reaction employed for the preparation of the poly(ester–amide) **4g** is as follows. A mixture of 0.3984 g (1.0 mmol) of the bis(ester–amine) **2**, 0.5764 g (1.0 mmol) of 4,4'-(hexafluoroisopropylidene-bis(1,4-phenylene)dioxy)dibenzoic acid (**3g**), 0.2 g of calcium chloride, 2.0 mL of NMP, 0.5 mL of pyridine and 1.0 mL of TPP was heated with stirring at 110 °C for 3 h. As the polycondensation proceeded, the solution gradually became viscous. The resulting highly viscous polymer solution was subsequently slowly poured into 250 mL of stirred methanol, giving rise to a 'stringy', fiber-like precipitate which was collected by filtration, washed thoroughly with methanol and hot water and then dried at 100 °C in a vacuum oven. The yield was quantitative. The inherent viscosity of the obtained polymer **4g** was 0.57 dL g⁻¹, measured at a concentration of 0.5 g dL⁻¹ in DMAc containing 5 wt% LiCl at 30 °C. The FT-IR spectrum (film) exhibited characteristic absorptions at 3311 (N–H stretching), 1741 (ester C=O stretching), 1670 (amide C=O stretching), 1502 (N–H bending) and 1244 and 1092 cm⁻¹ (asymmetrical and symmetrical C–O–C stretching). Elemental analysis, calculated for (C₅₃H₃₂F₆N₂O₈)_n (938.84)_n: C, 67.81 %; H, 3.44 %; N, 2.98 %. Found: C, 66.52 %; H, 3.56 %; N, 2.86 %. All of the other poly(ester–amide)s were synthesized by using a similar procedure to that described above.

Preparation of poly(ester–amide) films

For the 'organosoluble' poly(ester–amide)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–amide) 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–amide) 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.

Measurements

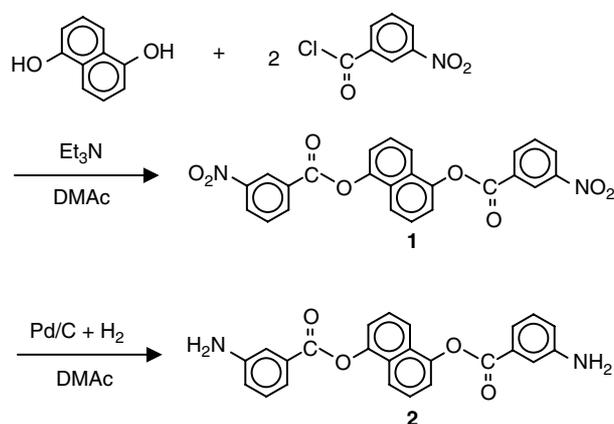
Elemental analysis was carried out on a Heraeus VarioEL-III C, H, N analyser, while infrared spectra were recorded on an Horiba FT-720 Fourier-transform infrared (FT-IR) spectrometer. ¹H and ¹³C NMR spectra were measured on a JEOL EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-*d*₆) as the solvent and tetramethylsilane as the internal reference, operating at 400 and 100 MHz, respectively. The inherent viscosities of the poly(ester–amide)s were obtained at a concentration of 0.5 g dL⁻¹ in DMAc containing 5 wt% LiCl using a Cannon-Fenske 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 columns, Styragel HR-2 and HR-4 (7.8 mm inside diameter × 300 mm), connected in series, were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow-polydispersity 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 CuKα radiation. An Instron universal tester (Model 4400R) with a load cell of 5 kg was used to study the stress–strain behavior of the poly(ester–amide) film samples. A gauge length of 2 cm and a crosshead speed of 5 mm min⁻¹ 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⁻¹), at a heating rate of 20 °C min⁻¹ 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⁻¹ from 50 to 400 °C under flowing nitrogen (20 mL min⁻¹). The 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 trace after rapid cooling from 400 °C at a cooling rate of 200 °C min⁻¹. 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⁻¹ 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.

RESULTS AND DISCUSSION

Monomer synthesis

The new bis(ester–amine) **2** was successfully synthesized by using the hydrogen Pd/C-catalysed reduction of the dinitro–diester **1** resulting from the condensation reaction of 1,5-dihydroxynaphthalene with 3-nitrobenzoyl chloride, as shown in Scheme 1. Elemental analysis, plus IR and NMR spectroscopy were used to confirm the structures of the dinitro compound **1** and diamine monomer **2**. The elemental analysis values were generally in agreement with the calculated values for the proposed structures. The FT-IR spectra of the dinitro–diester **1** and bis(ester–amine) **2** are illustrated in Fig 1. The nitro groups of the dinitro–diester **1** showed two characteristic absorption bands at 1529 (asymmetrical NO₂ stretching) and 1348 (symmetrical NO₂ stretching) 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 3460 (asymmetrical NH₂ stretching) and 3373 (symmetrical NH₂ stretching) cm⁻¹. The characteristic absorptions appearing at 1734 and 1726 cm⁻¹, assigned to the ester carbonyl group, were also apparent in the dinitro–diester **1** and bis(ester–amine) **2**. The structure of the bis(ester–amine) **2** was also identified by high-resolution NMR spectroscopy. The ¹H NMR and ¹³C NMR spectra of the bis(ester–amine) **2** are shown in Fig 2. The assignments of each carbon and proton are also given in this figure, and all the NMR spectroscopic data are consistent with the proposed molecular structure. The ¹H NMR spectrum confirms that the nitro groups have been converted into amino groups by the upfield chemical shift (δ_{H} is decreased) of aromatic protons H_d to H_g (6.98–7.53 ppm) because of the electron-donating property of the amino group and by the signal at 5.56 ppm corresponding to the amino protons.



Scheme 1. Synthetic route used to prepare the bis(ester–amine) **2**.

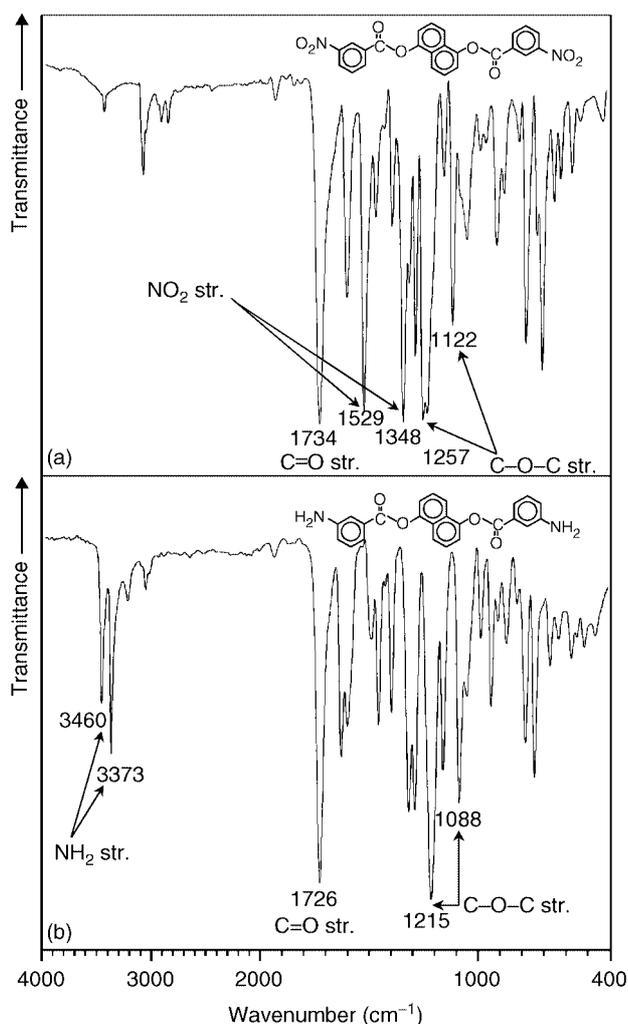


Figure 1. FT-IR spectra of (a) the dinitro–diester **1** and (b) the bis(ester–amine) **2**.

Polymer synthesis

The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids in NMP solution containing dissolved CaCl_2 using triphenyl phosphite (TPP) and pyridine as condensing agents is known to be a convenient method for the preparation of aromatic polyamides on the laboratory scale.²⁰ This method was adopted here to prepare the aromatic poly(ester–amide)s **4a–4g** from the bis(ester–amine) **2** with various aromatic dicarboxylic acids **3a–3g**, as shown in Scheme 2. The synthesis conditions and inherent viscosities of the poly(ester–amide)s **4a–4g** are summarized in Table 1. All of the reaction solutions were homogeneously transparent and became highly viscous, except for polymer **4a**, which precipitated from the reaction medium when the system became viscous, possibly because of a high level of crystallinity and the structural rigidity of the polymer chain. These poly(ester–amide)s were obtained in almost quantitative yields with inherent viscosities in the range $0.47\text{--}0.81\text{ dL g}^{-1}$. Except for polymer **4a**, all of the poly(ester–amide)s could be solution-cast into free-standing films. These films were flexible and creasable, indicative of the formation of

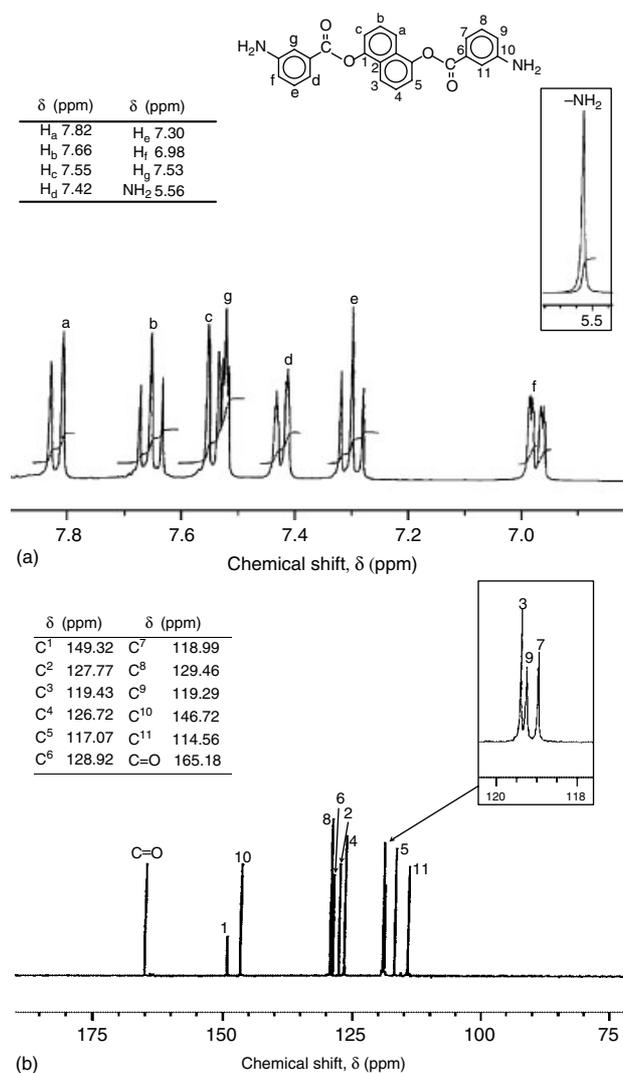
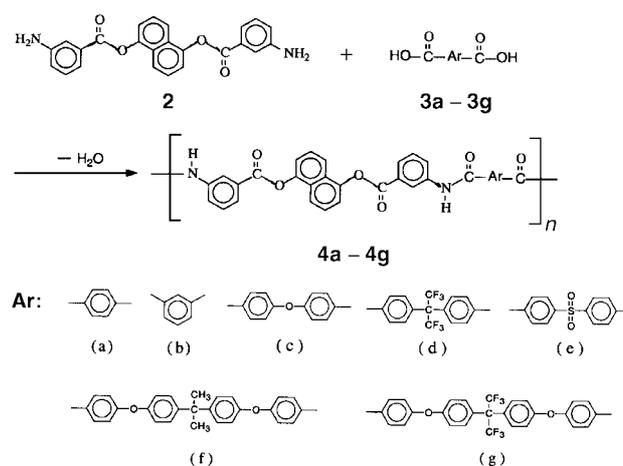


Figure 2. (a) ^1H NMR and (b) ^{13}C NMR spectra of the bis(ester–amine) **2** in $\text{DMSO-}d_6$.



Scheme 2. Synthetic route used to prepare the poly(ester–amide)s.

high-molecular-weight polymers. As can be seen from Table 1, the GPC data obtained for **4d**, **4f** and **4g** indicated that the M_w and M_n values were in the

Table 1. Synthesis conditions, inherent viscosities, film quality and average molecular weights of the poly(ester–amide)s

Polymer	Amount of reagent used ^a			η_{inh}^b (dL g ⁻¹)	Film quality ^c	$M_n^{d,e}$	$M_w^{d,e}$	M_w/M_n^e
	NMP (mL)	Pyridine (mL)	CaCl ₂ (g)					
4a	3	0.8	0.2	0.47	— ^f	—	—	—
4b	1.5	0.5	0.1	0.51	F	—	—	—
4c	2	0.5	0.1	0.52	F	—	—	—
4d	2	0.5	0.2	0.55	F	13 300	21 800	1.64
4e	2	0.5	0.2	0.49	F	—	—	—
4f	3	0.8	0.3	0.81	F	20 800	35 300	1.70
4g	2	0.5	0.2	0.57	F	15 900	28 100	1.77

^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.

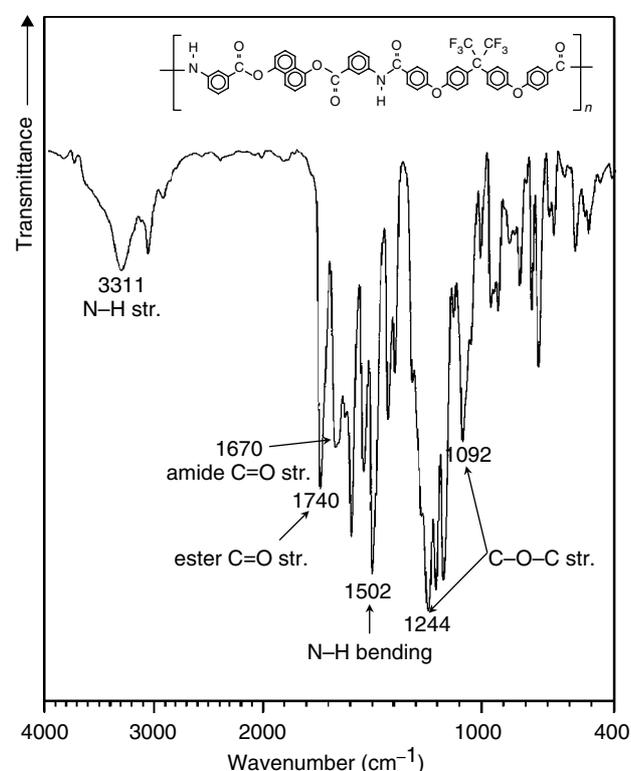
^b Measured at a concentration of 0.5 g dL⁻¹ in DMAc containing 5 wt% LiCl at 30 °C by a Cannon–Fenske viscometer.

^c Films were cast by slow evaporation of polymer solutions in DMAc: F, flexible.

^d Relative to polystyrene standards, using THF as the eluent.

^e Where no data are given, indicates that the polymer(s) are insoluble in THF.

^f Insoluble in available organic solvents.

**Figure 3.** FT-IR spectrum of a thin film of the poly(ester–amide) **4g**.

range of 21 800–35 300 and 13 300–20 800 g mol⁻¹, respectively, on the basis of polystyrene standards.

The structural features of the poly(ester–amide)s were verified by FT-IR spectroscopy and elemental analysis. A typical FT-IR spectrum of polymer **4g** is illustrated in Fig 3. This displays the characteristic IR absorptions of the amide group at around 3310–3340 cm⁻¹ (N–H stretching), 1670–1680 cm⁻¹ (amide C=O stretching) and 1500–1530 cm⁻¹ (N–H bending). All of the poly(ester–amide)s also exhibited strong characteristic absorption bands at around 1730–1740 cm⁻¹ (ester C=O stretching), and at 1240–1270 cm⁻¹

and 1080–1100 cm⁻¹ (asymmetrical and symmetrical C–O–C stretching, respectively) due to the ester groups. The formation of the amide group was also confirmed by the resonance signals of amide protons at around δ 10.6 in the ¹H NMR spectra and amide carbons at around δ 170 in the ¹³C NMR spectra. The results of the elemental analysis of all of the poly(ester–amide)s are reported in Table 2. These data are in good agreement with the proposed structures, with the exception of the % C values, which are always lower than the theoretical ones. This can possibly be attributed to the very aromatic nature of these polymers—such aromatic materials commonly leave small ‘coal-listed’ residues during the standard conditions of microanalysis. Another possible reason may be ascribed to the hygroscopic nature of the amide groups of these polymers.

Properties of the polymers

X-ray diffraction data

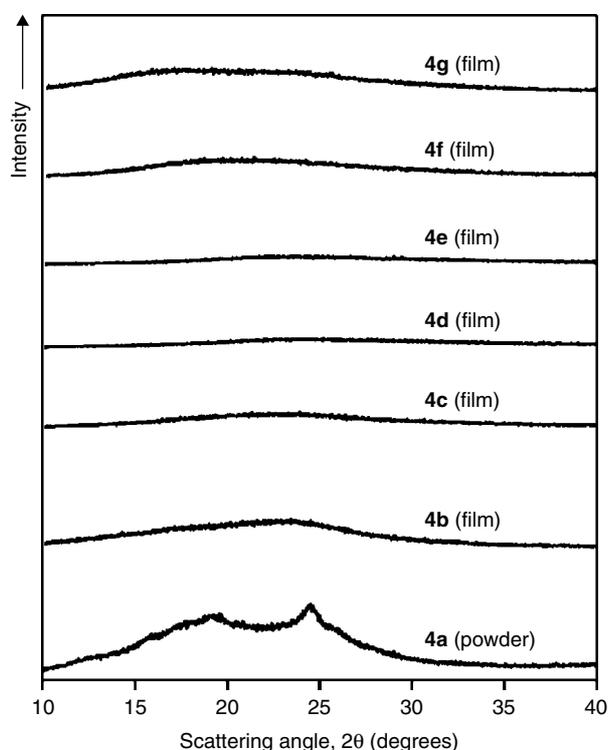
All of the poly(ester–amide)s were characterized by WAXD studies, as can be seen from the diffraction patterns shown in Fig 4. These diffractograms indicate that all of the poly(ester–amide)s, except polymer **4a**, were amorphous. Because of the introduction of an ester group and the *meta*-linked main-chain structure of bis(ester–amine) **2** into the polymer chain, those polymers which could afford flexible and tough films displayed amorphous patterns. The poly(ester–amide) **4a**, derived from the more rigid and symmetrical terephthalic acid (**3a**) showed some strong diffraction signals assignable to a semicrystalline polymer but did not afford a ductile film, even though it had a *meta*-linked main-chain structure.

‘Organosolubility’

The ‘organosolubility’ behavior of these poly(ester–amide)s was tested qualitatively in various organic solvents, and the results are reported in Table 3. In general, the more semicrystalline polymers displayed a lower solubility. For example, polymer **4a** was

Table 2. Elemental analysis data for the poly(ester–amide)s

Polymer	Formula of the repeat unit (Formula weight)	C (%)		H (%)		N (%)	
		Calculated	Found	Calculated	Found	Calculated	Found
4a	C ₃₂ H ₂₀ N ₂ O ₆ (528.52)	72.72	71.63	3.81	4.01	5.30	5.18
4b	C ₃₂ H ₂₀ N ₂ O ₆ (528.52)	72.72	71.57	3.81	3.98	5.30	5.22
4c	C ₃₈ H ₂₄ N ₂ O ₇ (620.62)	73.54	72.55	3.90	4.03	4.51	4.38
4d	C ₄₁ H ₂₄ F ₆ N ₂ O ₆ (754.64)	65.26	64.29	3.21	3.35	3.71	3.62
4e	C ₃₈ H ₂₄ N ₂ O ₈ S (668.68)	68.26	66.95	3.62	3.75	4.19	4.03
4f	C ₅₃ H ₃₈ N ₂ O ₈ (830.89)	76.61	74.76	4.61	4.82	3.37	3.18
4g	C ₅₃ H ₃₂ F ₆ N ₂ O ₈ (938.84)	67.81	66.52	3.44	3.56	2.98	2.86

**Figure 4.** WAXD patterns of the poly(ester–amide)s **4a–4g**.

soluble in hot NMP, hot DMAc and hot DMF, but insoluble in the other solvents tested. In contrast, the amorphous nature of the other polymers was reflected in their excellent solubility. The amorphous poly(ester–amide)s **4b–4g** exhibited a higher solubility in that they were readily soluble in ‘amide-type’ polar solvents, such as NMP, DMAc and DMF, at room temperature and soluble in DMSO and *m*-cresol at room temperature, or on heating. Some of them were even soluble in the ‘less-efficient’ THF at room temperature, eg **4d**, **4f** and **4g**, mainly due to the low cohesive energy and high free volume caused by the introduction of the hexafluoroisopropylidene (6F) groups and/or the multiple flexible units. Especially for **4g**, this polymer was soluble in all of the

Table 3. Solubility behavior of the poly(ester–amide)s

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

^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 of the poly(ester–amide) films

Polymer	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
4b	75	7	1.7
4c	92	9	2.0
4d	75	8	1.8
4e	86	10	1.6
4f	91	12	1.9
4g	94	13	1.9

organic solvents tested, including the less polar *m*-cresol and THF at room temperature. Thus, such excellent solubility makes these polymers potential candidates for practical applications in spin-on and casting processes.

Tensile properties

As previously mentioned, all of the amorphous poly(ester–amide)s could be solution-cast into flexible and tough films. These thin films were of good quality, creasable and suitable for tensile testing, and their tensile properties are presented in Table 4. These films exhibited ultimate tensile strengths to break of 75–94 MPa, elongations to break of 7–13 % and

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

Polymer	T_g (°C) ^a	T_s (°C) ^b	T_d at 5 wt% loss (°C) ^c		T_d at 10 wt% loss (°C) ^c		Char yield (%) ^d
			In N ₂	In air	In N ₂	In air	
4a	— ^e (344) ^f	— ^g	414	409	443	448	65
4b	179	180	383	381	409	421	64
4c	190	178	402	392	431	422	65
4d	225	211	412	414	454	454	56
4e	216	204	419	421	462	461	64
4f	193	181	437	434	479	463	64
4g	207	193	438	439	469	484	57

^a Middle-point temperature of the baseline shift on the second DSC heating trace (rate of 20 °C min⁻¹) from 50 to 400 °C after rapid cooling from 400 °C at a rate of 200 °C min⁻¹.

^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⁻¹. The film samples were heated at 250 °C for 30 min prior to the TMA experiments.

^c Decomposition temperature was recorded by TGA at a heating rate of 20 °C min⁻¹.

^d Residual weight % at 800 °C in N₂.

^e No discernible transition was observed.

^f Peak-temperature of the medium-intensity melting endotherm on the first DSC heating trace (rate of 20 °C min⁻¹) from 50 to 400 °C.

^g Not detected.

initial moduli of 1.6–2.0 GPa, hence qualifying them as strong and tough materials.

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. In the DSC experiments, the poly(ester–amide) **4a** showed a clear medium-intensity melting endotherm with a peak temperature at 344 °C, and no discernible T_g was observed on the heating DSC curve probably because of its semicrystalline nature. The other poly(ester–amide)s showed clear T_g values between 179 and 225 °C by DSC, depending on the chemical structure. A typical DSC thermogram for the representative poly(ester–amide) **4g** is illustrated in Fig 5. None of the polymers, except **4a**, showed a clear melting endotherm in their DSC heating traces. This supports the amorphous nature of these poly(ester–amide)s. In general, the T_g s are affected by several factors, eg molecular packing, chain rigidity, steric hindrance and polarity of the diacid residues. The poly(ester–amide) **4d** exhibited the highest T_g value (225 °C) probably due to the presence of hexafluoroisopropyl groups which result in a

higher steric hindrance to segmental mobility. The second highest T_g value (216 °C) for poly(ester–amide) **4e** is believed to be due to the presence of polar sulfonyl groups which causes an increased intermolecular interaction. The lowest T_g value (179 °C), which was observed for poly(ester–amide) **4b**, derived from the less symmetrical isophthalic acid (**3b**), is probably caused by a reduction in the density of molecular packing. The softening temperature (T_s) values of the flexible poly(ester–amide) films, measured by TMA, were recorded in the range 178–211 °C. A typical TMA thermogram of polymer **4g** is also illustrated in Fig 5. In most cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments. The trend in variation of T_s is similar to that of the T_g observed in the DSC measurements.

Thermal and thermo-oxidative stability

The thermal and thermo-oxidative stabilities of these poly(ester–amide)s were evaluated by TGA under both nitrogen and air atmospheres using the 5 and 10 wt% loss temperatures (T_d) for comparison. The decomposition temperatures (T_d s) at 5 and 10 wt% loss in nitrogen and air atmospheres determined from the original TGA thermograms are also summarized in Table 5. All of the poly(ester–amide)s exhibited good thermal and thermo-oxidative stabilities with insignificant weight losses up to temperatures of approximately 400 °C in both nitrogen and air atmospheres. The amounts of carbonized residues (char yields) at 800 °C in nitrogen for these poly(ester–amide)s were in the range 56–65 wt%. The T_d values at 5 wt% loss for all of the poly(ester–amide)s were recorded in the range 383–438 °C in nitrogen and in the range 381–439 °C in air. There was a large ‘window’ between T_g or T_s and T_d of each polymer, which could be advantageous

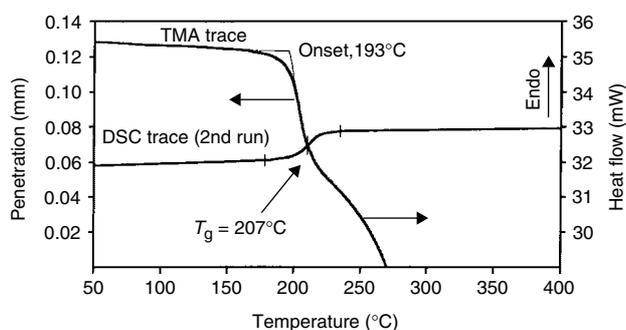


Figure 5. Typical DSC and TMA thermograms of poly(ester–amide) **4g**: DSC, heating rate of 20 °C min⁻¹; TMA, heating rate of 10 °C min⁻¹ and applied force of 10 mN.

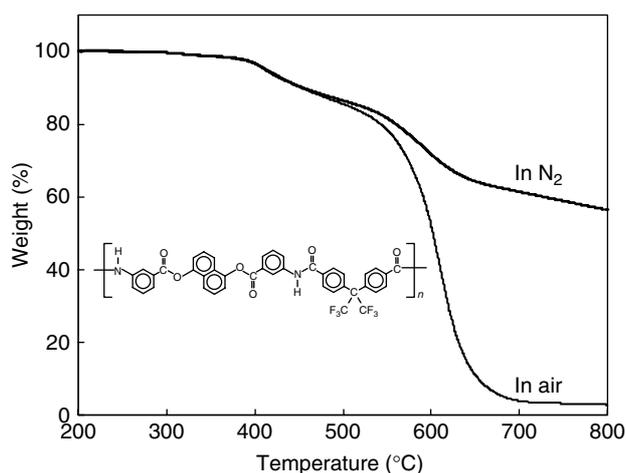


Figure 6. TGA curves of the poly(ester–amide) **4d** in nitrogen and air (heating rates of $20\text{ }^{\circ}\text{C min}^{-1}$).

in the processing of these polymers by thermoforming techniques. A comparison of the TGA behavior in nitrogen and air atmospheres for the representative poly(ester–amide) **4d** is shown in Fig 6. This polymer showed very similar TGA behavior in nitrogen and air atmospheres below $500\text{ }^{\circ}\text{C}$, but when the temperature was increased above $500\text{ }^{\circ}\text{C}$, the polymer showed a rapid weight loss and decomposed almost completely at $700\text{ }^{\circ}\text{C}$ in air. All of the poly(ester–amide)s seemed to exhibit a two-stage decomposition behavior at elevated temperatures. The first stage of weight loss starting around $400\text{ }^{\circ}\text{C}$ might be attributed to the early degradation of the less stable ester groups. The FT-IR spectra of the solid residues of the polymers after heat treatment were examined. Fig 7 shows FT-IR spectra of a thin film of the representative poly(ester–amide) **4e** after being heated sequentially in air, each for 10 min at 300, 350, 400 and $450\text{ }^{\circ}\text{C}$. The FT-IR spectra of **4e** after heat treatment at 300 and $350\text{ }^{\circ}\text{C}$ remained almost the same as that before heat treatment. After heating at $400\text{ }^{\circ}\text{C}$ for 10 min, an obvious decrease in the relative intensities at around 1739 , 1267 and 1095 cm^{-1} indicated some loss of ester functionalities. After further heating at $450\text{ }^{\circ}\text{C}$ for 10 min, the absorption bands of the ester groups almost completely disappeared, while a high content of amide functionalities and aromatic skeletons was still detected. The aforementioned results showed that these poly(ester–amide)s seemed to start to decompose from the weaker ester linkages.

CONCLUSIONS

A novel bis(benzoyloxy)naphthalene-containing aromatic bis(ester–amine) **2** has been successfully prepared in high purity and high yield from the condensation reaction of 1,5-dihydroxynaphthalene with 3-nitrobenzoyl chloride and subsequent catalytic hydrogen reduction of the intermediate dinitro compound. A series of naphthalene-containing poly(ester–amide)s have been successfully synthesized

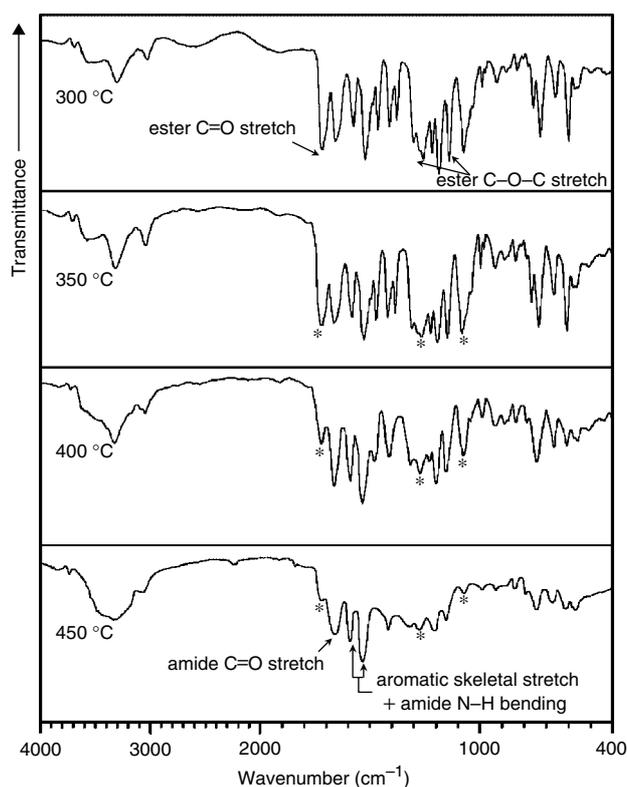


Figure 7. FT-IR spectra (thin-film sample) of the poly(ester–amide) **4e** after sequential heating in air at the indicated temperatures, each for 10 min (*indicates the characteristic absorptions of the ester groups).

from the bis(ester–amine) **2** with various aromatic dicarboxylic acids by means of TPP and pyridine. The poly(ester–amide) **4a** obtained from terephthalic acid (**3a**) was semicrystalline and showed poorer solubility. The other poly(ester–amide)s **4b–4g**, derived from less rigid and symmetrical diacids, were amorphous and displayed good solubility, good film-forming capability, reasonable thermal stability, and moderate T_g or T_s and T_d 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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