Synthesis and Properties of New Soluble Aromatic Polyamides and Polyimides on the Basis of *N,N′*-Bis(3-aminobenzoyl)-*N,N′*-diphenyl-1,4-phenylenediamine

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ABSTRACT: A new *N*-phenylated amide (*N*-phenylamide) unit containing aromatic diamine, *N,N′*-bis(3-aminobenzoyl)-*N,N′*-diphenyl-1,4-phenylenediamine, was prepared by the condensation of *N,N′*-diphenyl-1,4-phenylenediamine with 3-nitrobenzoyl chloride, followed by catalytic reduction. Two series of organosoluble aromatic poly(*N*-phenylamide-imide)s and poly(*N*-phenylamide-amide)s with inherent viscosities of 0.58–0.82 and 0.56–1.21 dL/g were prepared by a conventional two-stage method and the direct phosphorylation polycondensation, respectively, from the diamine with various aromatic dianhydrides and aromatic dicarboxylic acids. All polyimides and polyamides are amorphous and readily soluble in many organic solvents such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. These polymers could be solution cast into transparent, tough, and flexible films with high tensile strengths. These polyimides and polyamides had glass-transition temperatures in the ranges of 230–258 and 196–229 °C, respectively. Decomposition temperatures of the polyimides for 10% weight loss all occurred above 500 °C in both nitrogen and air atmospheres. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 2564–2574, 2002

Keywords: polyimides; polyamides; *N*-phenylated amide linkage; *N,N′*-bis(3-aminobenzoyl)-*N,N′*-diphenyl-1,4-phenylenediamine; solubility; thermal properties; high performance polymers

INTRODUCTION

Wholly aromatic polyimides and polyamides (aramids) are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong intermolecular interactions through hydrogen bonding (in polyamides) and charge-transfer complex formation (in polyimides) result in high melting or glass-transition temperatures (T_g's) and limited solubility in most organic solvents.[1–4] These properties make them generally intractable or difficult to process, thus restricting their applications. Therefore, a great deal of effort has been expended to try to improve the processing characteristics of the relatively intractable polymers.[5–12] These studies include introducing flexible segments into the polymer chain; replacing symmetrical aromatic rings by unsymmetrical ones, which leads to a reduction in crystallinity; introducing bulky pendant groups to minimize crystallization; and forming a non-coplanar structure, thereby making crystallization

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impossible. Generally, one of the successful approaches to increase solubility and processability of polyimides and polyamides without sacrificing high thermal stability is the introduction of bulky pendant phenyl groups into polymer backbone. Some organic-soluble polyimides or polyamides have been demonstrated using highly phenylated tetracarboxylic dianhydrides[13,14] or highly phenylated aromatic diamines.[15–21] On the other hand, an alternative method for increasing solubility and lowering T_g's of aramids is the incorporation of *N*-alkyl or aryl substitutents along the backbone.[22–25] It has been demonstrated that *N*-phenylated aramids obtained from *N*,*N*′-diphenyl-1,4-phenylenediamine and aromatic diacid chlorides showed better solubility and melt-processing characteristics as compared with analogous unsubstituted aramids. It has also been concluded that the *N*-phenylated aramids are promising as high-performance plastics than the *N*-methyl substituted aramids because of a minor detrimental effect on the thermal stability caused by the *N*-phenyl substitution.[23,24] In this article, we report the synthesis of novel aromatic polyimides and polyamides derived from a new aromatic diamine, *N*,*N*′-bis(3-aminobenzoyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine, that combines the highly phenylated structure and hydrogen-free amide linkage. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers were also investigated.

EXPERIMENTAL

Materials

N,*N*′-Diphenyl-1,4-phenylenediamine (**1**) (from TCI), 3-nitrobenzoyl chloride (from Fluka), and 10% Pd/C (from Lancaster) were used without further purification. Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA) (**4a**) (Aldrich), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**4c**) (Aldrich), 4,4′-oxydiphthalic dianhydride (**4d**) (Oxychem), and diphenylsulfone-3,3′,4,4′-tetracarboxylic dianhydride (**4e**) (New Japan Chemical Co.) were purified by recrystallization from acetic anhydride. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) (**4b**) (Oxychem) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**4f**) (Hoechst Celanese) were purified by vacuum sublimation. Terephthalic acid (**6a**) (TCI), isophthalic acid (**6b**) (TCI), 4,4′-biphenyldicarboxylic acid (**6c**) (TCI), 1,4-naphthalenedicarboxylic acid (**6d**) (Wako), 2,6-naphthalenedicarboxylic acid (**6e**) (TCI), 4,4′-oxydibenzoic acid (**6f**) (TCI), 4,4′-sulfonyldibenzoic acid (**6g**) (New Japan Chemical), and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**6h**) (Chriskev) were used as received. *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and *N*-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride. Triphenyl phosphite (TPP), pyridine, and triethylamine were used as received.

Monomer Synthesis

Synthesis of N,N′*-Bis(3-nitrobenzoyl)-*N,N′*-diphenyl-1,4-phenylenediamine (2)*

N,*N*′-diphenyldiamine **1** (26.04 g, 0.10 mol), which was dissolved in 250 mL of DMF, and triethylamine (0.22 mol) were introduced into a 500-mL flask equipped with a nitrogen inlet. After the reaction solution was cooled to 0–5 °C, 3-nitrobenzoyl chloride (40.84 g, 0.22 mol) was added incrementally over 1 h, and the reaction mixture was maintained at room temperature for 10 h. The mixture was poured into 2 L of water, and the precipitated yellow solid was collected by filtration and washed thoroughly with water and methanol. The yield of the product was 50.4 g (90% yield). The crude product was recrystallized from DMF twice to afford 39.1 g (70% yield) of light yellow crystals.

mp: 280–281 °C [differential scanning calorimetry (DSC), at a scan rate of 2 °C/min]. IR (KBr): 1306, 1525 (—NO$_2$), 1652 cm^{-1} (amide carbonyl). Elem. Anal. Calcd. for $C_{32}H_{22}N_4O_6$ (558.55): C, 68.81%; H, 3.97%; N, 10.03%. Found: C, 68.54%; H, 3.93%; N, 10.12%.

Synthesis of N,N′*-Bis(3-aminobenzoyl)-*N,N′*-diphenyl-1,4-phenylenediamine (3)*

A mixture of the obtained dinitro compound (27.9 g), 10% Pd/C (1.4 g), and 300 mL of DMF was stirred at 50 °C under a hydrogen atmosphere until the theoretical amount of hydrogen was consumed. The time taken to reach this stage was about 2 days. The solution was filtered to remove catalyst, and the obtained filtrate was poured into 2 L of stirring water, giving rise to a precipitate that was isolated by filtration. The crude product was recrystallized from DMF/methanol to afford 19.9 g (80% yield) of off-white crystals.

mp: 265–266 °C (DSC, 2 °C/min). IR (KBr): 3435, 3354, 3232 (—NH_2), 1633 cm^{-1} (amide carbonyl). ^1H NMR [400 MHz, dimethyl sulfoxide (DMSO-d_6), δ]: 5.13 (d, 4H, —NH_2), 6.40–7.32 (m, 22H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 170.26, 148.17, 143.59, 141.48, 136.56, 128.99, 127.96, 127.67, 127.47, 126.21, 116.02, 115.35, 113.87. ELEM. ANAL. Calcd. for $C_{32}H_{26}N_4O_2$ (498.58): C, 77.09%; H, 5.25%; N, 11.24%. Found: C, 76.94%; H, 5.29%; N, 11.28%.

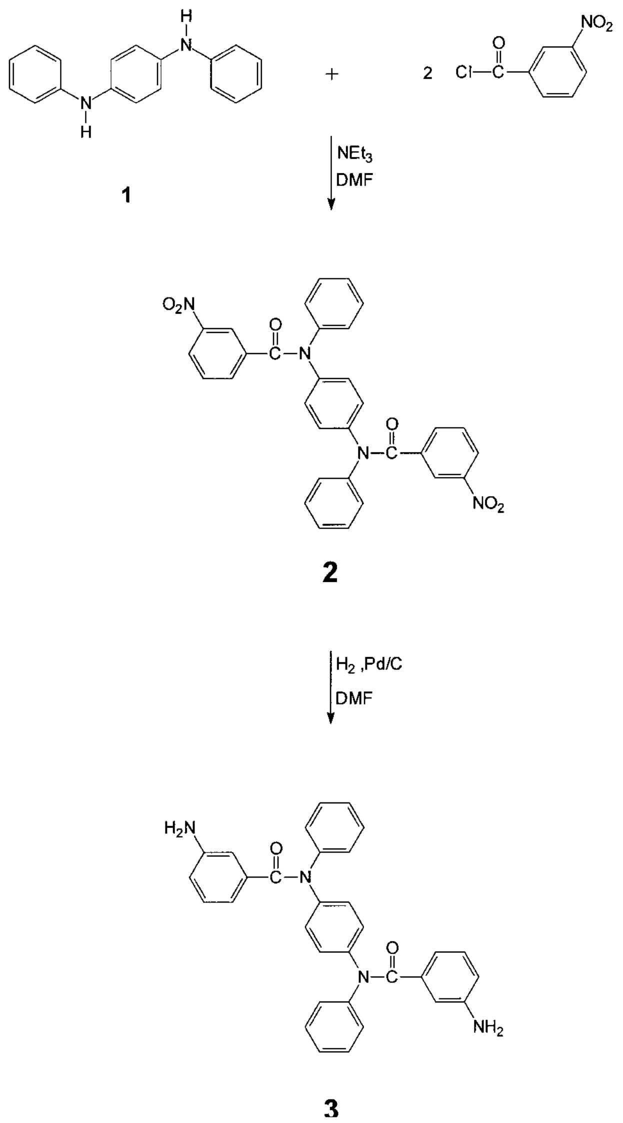
General Poly(*N*-phenylamide-imide) Synthesis

Synthesis of poly(*N*-phenylamide-imide) (**5b**) is described as a typical procedure. Monomer **3** (0.6289 g, 1.26 mmol) was dissolved in 9.5 mL of CaH_2-dried DMAc in a 50-mL round-bottom flask. Then, BPDA (0.3711 g, 1.26 mmol) was added to the diamine solution in one portion. Thus, the solid content of the solution was approximately 10 wt %. The mixture was stirred at room temperature for about 3 h to yield a viscous polyamic acid solution. The inherent viscosity of the resulting polyamic acid was 1.13 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The intermediate polyamic acid was subsequently chemically cyclized in solution to give the polyimide. A mixture of acetic anhydride (5 mL) and pyridine (2 mL) was added into the preceding polyamic acid solution, and the reaction mixture was stirred at room temperature overnight and at 100 °C for 2 h. The polymer precipitated during cyclization. After cooling to room temperature, the polymerization mixture was poured into 200 mL of methanol to remove solvent from the powdery yellow polymer (**5b**), which was isolated by filtration and dried at 120 °C under vacuum [yield: 0.95 g, about quantitative; inherent viscosity = 0.79 dL/g (DMAc, 0.5 g/dL, 30 °C)].

IR (film): 1776, 1732 (imide C═O stretch), 1662 (amide C═O stretch), 1276–1375 (broad, imide + amide C—N stretch), 1107, 742 cm^{-1} (imide-ring deformation). ELEM. ANAL. Calcd. for $(C_{48}H_{28}N_4O_6)_n$ $(756.77)_n$: C, 76.18%; H, 3.73%; N, 7.40%. Found: C, 75.20%; H, 3.80%; N, 7.32%.

General Poly(*N*-phenylamide-amide) Synthesis

The synthesis of polymer **7a** is used as an example to illustrate the general synthetic route used to produce the poly(*N*-phenylamide-amide)s. A mixture of 0.748 g (1.5 mmol) of diamine **3**, 0.249 g (1.5 mmol) of terephthalic acid (**6a**), 0.3 g of calcium chloride, 1.1 mL of TPP, 1.2 mL of pyridine, and 6 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was trickled slowly into 300 mL of methanol giving rise to a stringy precipitate that was washed thoroughly with hot water and methanol, collected by filtration, and dried under vacuum at 100 °C [yield: 0.93 g (99%)]. The inherent viscosity of the obtained polymer **7a** was 0.96 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.



Scheme 1. Synthesis of dinitro and diamino compounds.

IR (film): 3311 (N—H stretch), 1655 (amide carbonyl), 1545 cm^{-1} (N—H bend). ELEM. ANAL. Calcd. for $(C_{40}H_{28}N_4O_4)_n$ $(628.68)_n$: C, 76.42%; H, 4.49%; N, 8.91%. Found: C, 74.78%; H, 4.49%; N, 8.91%.

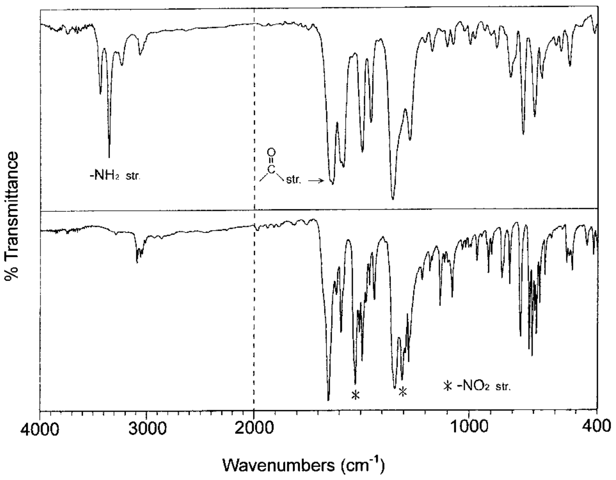


Figure 1. IR spectra of dinitro compound **2** and diamine **3**.

Film Preparation

A solution of polymer was made by dissolving about 0.8 g of the polyimide or polyamide sample in 10 mL of DMAc or NMP. The homogenous 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 were about 90–120 μm in thickness and used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run in a PerkinElmer model 2400 CHN analyzer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX 400 spectrometer using DMSO-d_6 as the solvent and tetramethylsilane as the internal reference. The inherent viscosities were determined at a concentration of 0.5 g/dL in DMAc using a Cannon-Fenske viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on 3–5-mg samples heated in flowing nitrogen or air (30 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC in flowing nitrogen (20 cm^3/min) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10 °C/min with a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered Cu Kα radiation (40 kV, 15 mA), and the scanning rate was 2°/min. Measurements were performed with film specimens of about 0.1 mm in thickness. An Instron Universal Tester model 1130 with a load cell of 5 kg was used to examine the stress-strain behavior of the samples at a crosshead speed of 5 mm/min. Measurements were performed at room

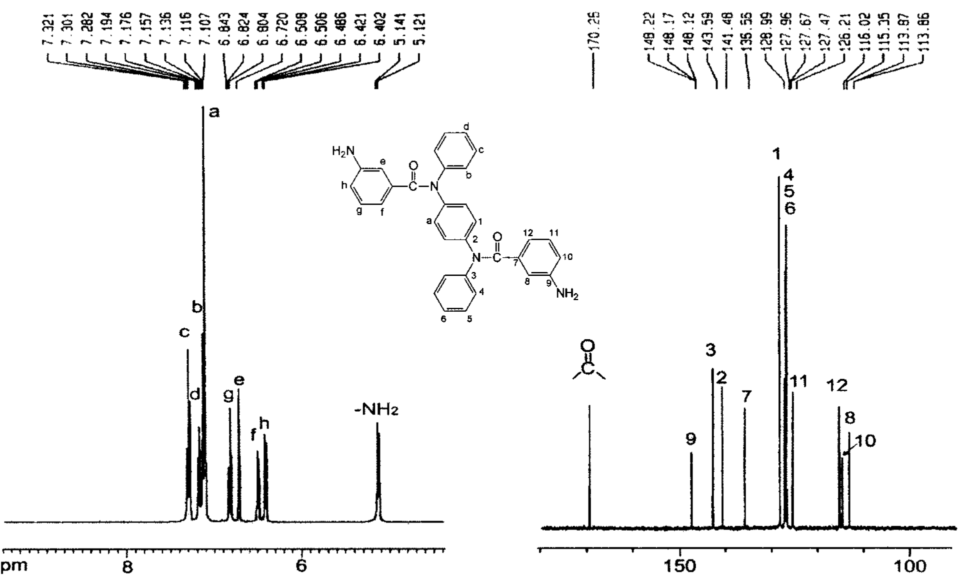
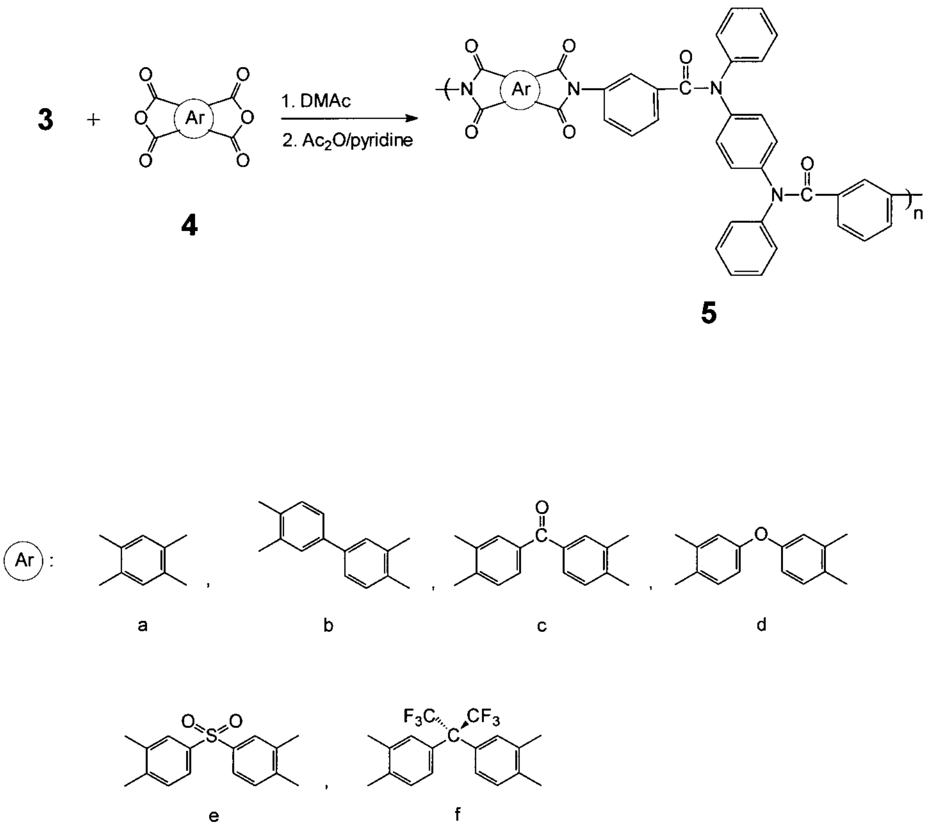


Figure 2. ^{1}H and ^{13}C NMR spectra of diamine **3** in DMSO-d_6.



Scheme 2. Synthesis of poly(*N*-phenylamide-imide)s.

temperature with film specimens (0.5 cm width, 6 cm length, and ca. 0.1 mm thickness), and an average of at least five individual determinations was used.

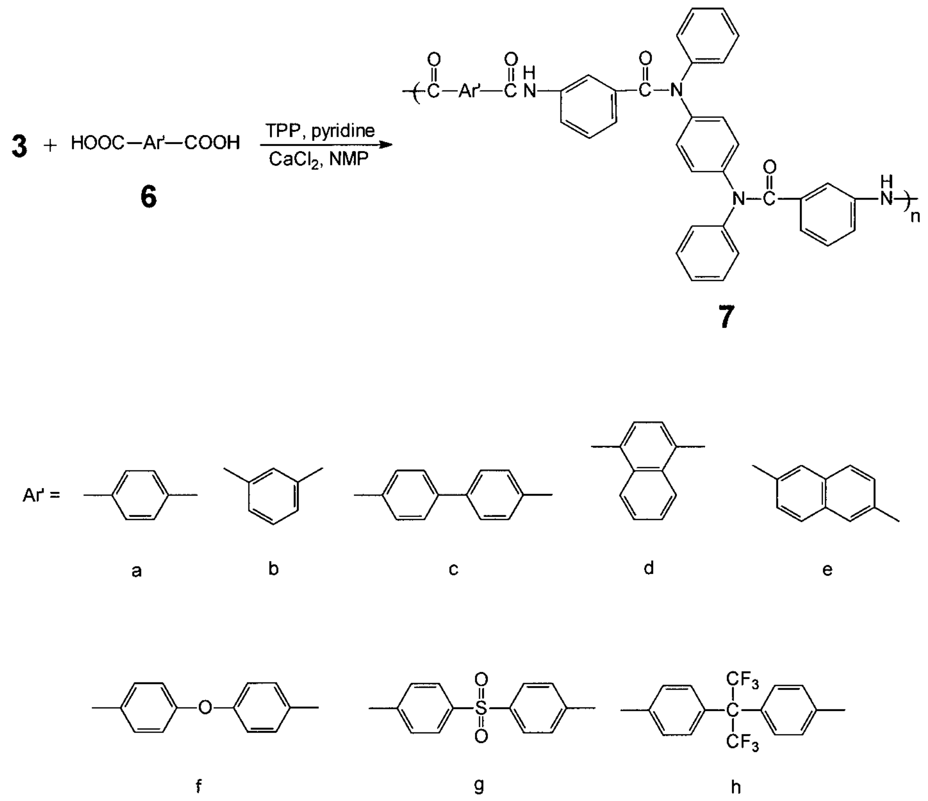
RESULTS AND DISCUSSION

Monomer Synthesis

The new *N*-phenylamide-containing aromatic diamine monomer, *N*,*N*′-bis(3-aminobenzoyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine (**3**), was prepared by hydrogen Pd/C-catalyzed reduction of dinitro compound **2** resulting from the condensation reaction of *N*,*N*′-diphenyl-1,4-phenylenediamine (**1**) with 3-nitrobenzoyl chloride as shown in Scheme 1. IR and elemental analysis identified the structures of dinitro compound **2** and diamine monomer **3**. The IR spectra of dinitro compound **2** and diamine **3** are illustrated in Figure 1. The nitro group of compound **2** gave two characteristic bands at 1525 (asymmetrical stretch) and 1306 cm^{-1} (symmetrical stretch). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed N—H stretching bands at 3435, 3354, and 3232 cm^{-1}. The characteristic absorptions appearing at 1653 and 1633 cm^{-1}, assigned to the amide carbonyl group, were also apparent in dinitro compound **2** and diamine **3**. The structure of the diamine monomer was also confirmed by high-resolution NMR spectra. Figure 2 shows ^{1}H and ^{13}C NMR spectra of diamine **3**. Assignments of each carbon and proton are also given in the figure, and these spectra agree with the proposed molecular structure. The ^{1}H NMR spectrum confirms that the nitro groups have been converted into amino groups by the high field shift of aromatic protons He to Hh (6.4–6.8 ppm) and by the signal at 5.1 ppm corresponding to the amino protons.

Polymer Synthesis

A series of new *N*-phenylamide-containing polyimides **5a–f** having inherent viscosities in the range of 0.54–0.82 dL/g were synthesized by a conventional two-stage process that involves the preparation of polyamic acids from diamine **3**



Scheme 3. Synthesis of poly(*N*-phenylamide-amide)s.

with various aromatic tetracarboxylic dianhydrides **4a–f** in DMAc at room temperature, followed by chemical imidization of the polyamic acid precursors using acetic anhydride and pyridine (Scheme 2). According to the Yamazaki–Higashi phosphorylation polyamidation technique,[26] partly *N*-phenylated polyamides **7a–h** were prepared by the direct polycondensation of diamine **3** with various aromatic dicarboxylic acids **6a–h** in NMP solution containing dissolved $CaCl_2$, using TPP and pyridine as condensing agents (Scheme 3). All the reaction solutions were homogeneously transparent and became highly viscous, indicative of the formation of high molecular weights. As shown in Table 1, polyimides **5a–f** and polyamides **7a–h** were obtained with inherent viscosities of 0.54–0.82 and 0.56–1.21 dL/g, respectively. The film of polyimide **5a** derived from PMDA cracked upon creasing probably because of the structural rigidity of the polymer chain. All the other polymers had sufficiently high molecular weights to permit the casting of tough and flexible films.

The formation of polyimides and polyamides was confirmed with elemental analysis and IR spectroscopy. Figure 3 demonstrates a typical set of FTIR spectra for polyimide **5a** and polyamide **7a**. The partly *N*-phenylated polyamide **7a** displayed a broad absorption peak centered at 3300 cm^{-1} as a result of the hydrogen-bonded N—H stretching vibration and an absorption peak at 1545 cm^{-1} resulting from N—H deformational vibration. These peaks were absent, and only the amide I band at 1655 (C=O stretch) was present in the spectrum of the completely *N*-phenylated polymer **5a**. Polymer **5a** also exhibited strong bands at 1778 and 1732 cm^{-1} that are commonly attributed to the asymmetrical and symmetrical stretching vibrations of imide carbonyl groups; the absorptions at 1150 and 720 cm^{-1} are possibly due to imide-ring deformation.

Properties of the Polymers

The solubility behavior of these *N*-phenylamide-containing polyimides and polyamides was determined for the film samples in excess solvents. As listed in Table 1, because of the introduction of bulky *N*-phenylated amide likages and *m*-phenylene units into diamine **3**, all its derived poly-

Table 1. Inherent Viscosities, Solubility Behavior, and Tensile Properties of Poly(*N*-phenylamide-imide)s **5a–f** and Poly(*N*-phenylamide-amide)s **7a–h**

		Solubility[b]						Tensile Properties of the Polymer Films[c]		
Polymer	η_{inh}[a] (dL/g)	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
5a	0.58	+	+	+	+	+	−			
5b	0.79	+	+	+h	+h	+	−	89	6	2.13
5c	0.71	+	+	+	+	+	−	84	7	2.00
5d	0.54	+	+	+	+	+	−	83	7	1.98
5e	0.62	+	+	+	+	+	−	83	6	2.09
5f	0.82	+	+	+	+	+	−	83	6	2.19
7a	0.96	+	+	+	+	+	−	104	7	2.37
7b	0.73	+	+	+	+	+	−	85	6	2.49
7c	1.21	+	+	+	+	+	−	68	4	2.25
7d	0.56	+	+	+	+	+	−	94	6	2.42
7e	1.00	+	+	+	−	+	−	88	5	2.50
7f	0.79	+	+	+	+	+	−	107	8	2.45
7g	0.71	+	+	+	+	+	−	91	6	2.32
7h	0.71	+	+	+	+	+	−	76	5	2.22

[a] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

[b] +, soluble at room temperature; +h, soluble on heating; and −, insoluble even on heating.

[c] Films were cast by the slow evaporation of polymer in DMAc. The film specimens were dried *in vacuo* at 160 °C for 6 h prior to the tensile test.

imides **5a–f** and polyamides **7a–h** were readily soluble in polar solvents such as DMAc, NMP, DMF, and even in less-polar *m*-cresol. Even polyimide **5a** and polyamides **7a**, **7c**, and **7e** obtained from rigid monomers such as PMDA (**4a**), terephthalic acid (**6a**), 4,4′-biphenyldicarboxylic acid (**6c**), and 2,6-naphthalenedicarboxylic acid (**6e**) also showed very good solubility. The solubility of these *N*-phenylamide-containing polyimides and polyamides was significantly enhanced as compared with conventional aromatic polyimides and polyamides, and this could be attributed to the bulky phenyl side-chain effect and lack of hydrogen-bond-forming hydrogen of the *N*-phenylamide units, which help to prevent the close packing of chains in these series polymers. Thus, the excellent solubility makes these polymers potential candidates for practical applications in spin-coating and casting processes.

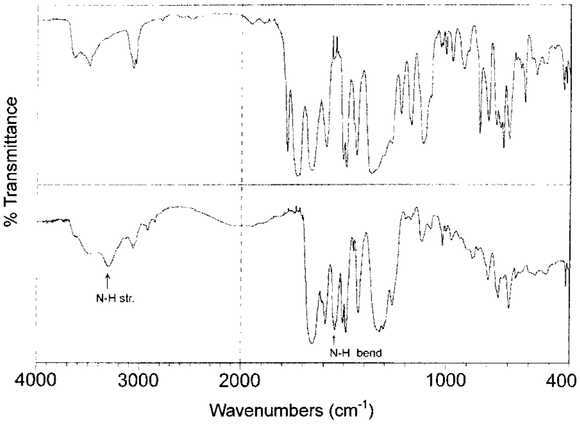


Figure 3. IR spectra of polymers **5a** (top) and **7a** (bottom).

The wide-angle X-ray diffraction studies of the polymers were performed with film specimens. The results revealed that all of the *N*-phenylamide-containing polymers, even those obtained from PMDA, terephthalic acid, 4,4′-biphenyldicarboxylic acid, and 2,6-naphthalenedicarboxylic acid, were completely amorphous. This is reasonable because the presence of the packing-disruptive bulky *N*-substituted phenyl structure resulted in increased chain distances and decreased interchain interactions because of the absence of the hydrogen-bonded N—H group. Thus, the amorphous nature of these polymers was also reflected in their excellent solubility.

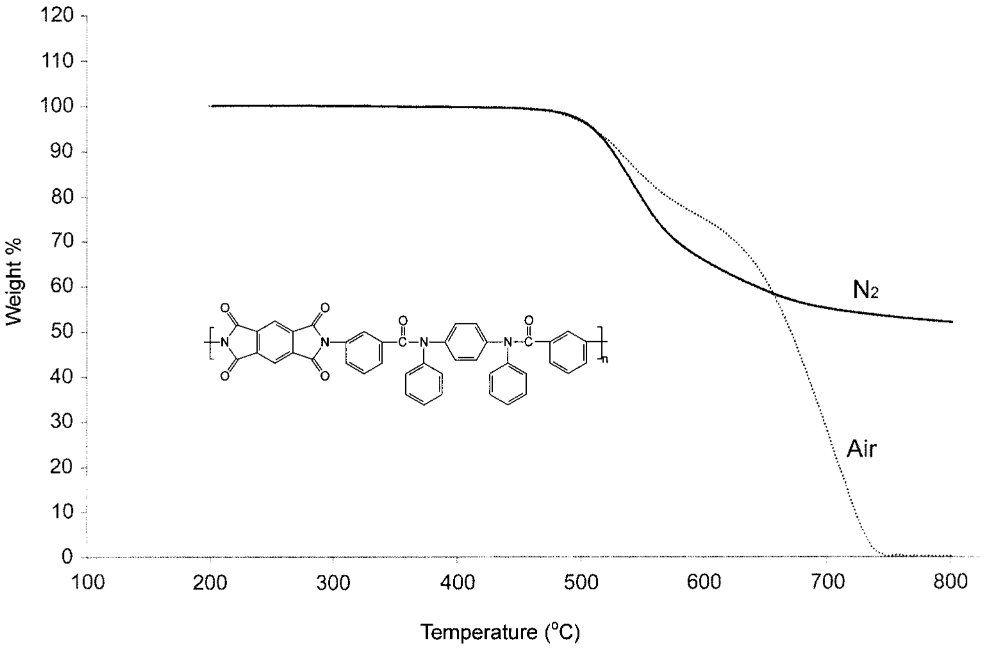


Figure 4. TGA thermograms of poly(*N*-phenylamide-imide) **5a** at a scan rate of 20 °C/min.

As mentioned previously, except polyimide **5a**, all polyimides and polyamides could be solution cast into smooth, flexible, and tough films. These films were subjected to tensile testing, and the results are given in Table 1. The tensile strengths, elongations to break, and initial moduli of these films were in the ranges of 76–107 MPa, 5–8%, and 1.98–2.50 GPa, respectively.

The thermal stability of these polyimides and polyamides was analyzed by TGA. Typical TGA curves of representative polymers **5a** and **7h** in both air and nitrogen atmospheres are shown in Figures 4 and 5, respectively. Some thermal-be-

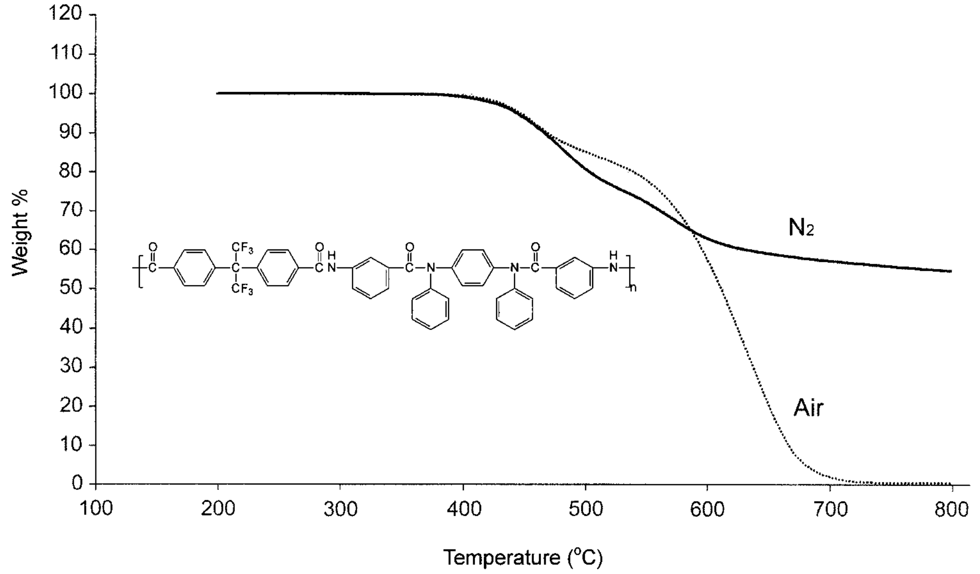


Figure 5. TGA thermograms of poly(*N*-phenylamide-amide) **7h** at a scan rate of 20 °C/min.

Table 2. Thermal Properties of the Polymers

Polymer	T_g[a] (°C)	T_s[b] (°C)	T_d at 5 wt % Loss (°C)[c]		T_d at 10 wt % Loss (°C)		Char Yield[d] (wt %)
			N_2	Air	N_2	Air	
5a	258	264	509	509	525	530	51.8
5b	246	250	535	513	552	544	57.5
5c	237	240	526	518	541	538	54.2
5d	224	230	533	526	549	544	52.6
5e	246	249	493	495	507	516	49.7
5f	241	241	534	543	548	564	59.9
7a	222	207	429	422	456	443	60.8
7b	196	192	423	424	447	447	61.4
7c	218	206	433	439	455	462	61.4
7d	211	197	420	409	440	439	58.5
7e	220	192	436	441	459	460	58.9
7f	204	204	430	437	454	458	59.3
7g	201	208	422	432	452	459	56.7
7h	229	237	443	446	465	468	54.4

[a] The samples were heated from 50 to 400 °C with a heating rate of 20 °C/min and rapidly cooled to 50 °C at −200 °C/min in nitrogen. The midpoint of baseline shift on the subsequent DSC heating trace (20 °C/min) was defined as T_g.

[b] Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace. The film samples were heated at 250 °C for 30 min prior to the TMA test.

[c] Recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 40 cm^3/min.

[d] Residual weight percentage at 800 °C in nitrogen.

havior data determined from original thermograms are tabulated in Table 2. In general, all the polyamides and polyimides exhibited good thermal stability with insignificant weight loss up to 400 and 450 °C, respectively, in nitrogen and air. The 10% weight-loss temperatures of the polyamides and polyimides in nitrogen or air were recorded in the ranges of 439–468 and 507–564 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 50% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content.

DSC and TMA were used to evaluate the thermal transitions of these polyimides and polyamides. The influence of residual solvent or the absorbed moisture and history of thermal annealing is sometimes observed in the first heating scan of DSC. These polymers were first heated to approximately 400 °C at 20 °C/min and then rapidly quenched to room temperature at a cooling rate of approximately −200 °C/min to form predominantly amorphous samples so that the T_g's of all the polymers could be easily measured in the DSC charts of the subsequent heating trace. The T_g values of the polyimides **5a–f** and polyamides **7a–h** were observed in the ranges of 224–258 and 196–229 °C, respectively, following the decreasing order of chain flexibility and steric hindrance of the dianhydrides and dicarboxylic acids. The T_g's of the **5** series polymers were about 20–40 °C higher than those of the **7** series polymers as a result of the difference in rigidity between imide rings and amide links. All polymers showed no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result supports the amorphous nature of these *N*-phenylamide-containing polymers. The softening temperatures (T_s) (may be referred as apparent T_g) of the polymer film samples were determined by the TMA method using a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. A typical TMA thermogram for polymer **5c** is illustrated in Figure 6. In most cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments. There is a large window between T_g and T_s and the decomposition temperature of each polymer, which could be advantageous in the processing of these polymers.

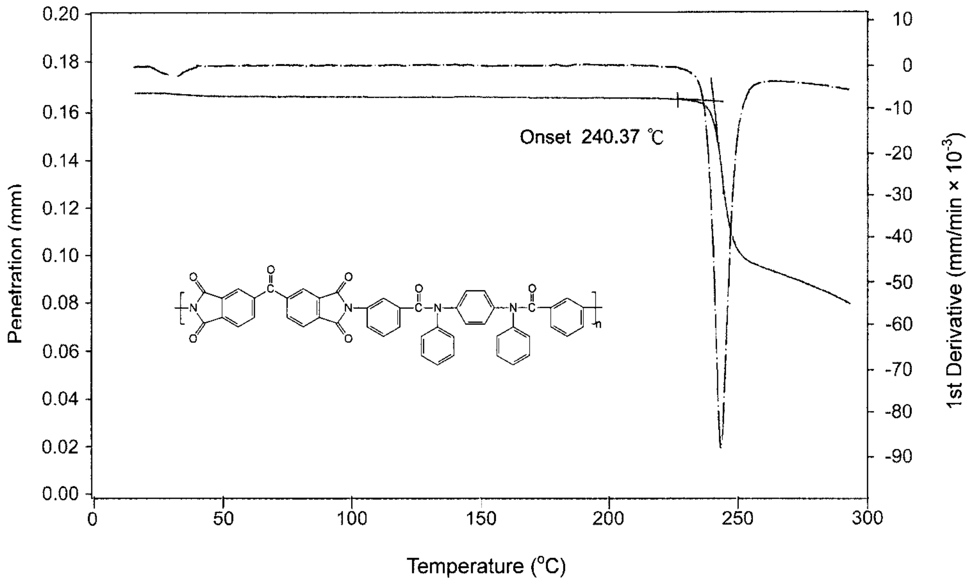


Figure 6. TMA thermograms of poly(*N*-phenylamide-imide) **5c** at a scan rate of 10 °C/min.

CONCLUSIONS

A new *N*-phenylamide-containing diamine, *N*,*N*′-bis(3-aminobenzoyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine, has been synthesized in high yield and high purity from readily available reagents. Two series of high molecular weight polyimides and polyamides have been readily prepared from various combinations of aromatic dianhydrides or dicarboxylic acids with the diamine via the two-stage method and the direct phosphorylation polycondensation, respectively. Because of the presence of the bulky *N*-phenyl-substituted amide unit, all polymers were amorphous and had excellent solubility in many polar aprotic solvents and could be cast into transparent, tough, and flexible films. Excellent solubility, moderate T_g or T_s values, and good thermal stability make these *N*-phenylamide-containing polyimides and polyamides promising high-performance polymeric materials.

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