Synthesis and Characterization of Novel Soluble Triphenylamine-Containing Aromatic Polyamides Based on *N*,*N*′-Bis(4-aminophenyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine

GUEY-SHENG LIOU,[1] SHENG-HUEI HSIAO,[2] MINA ISHIDA,[3] MASAAKI KAKIMOTO,[3] YOSHIO IMAI[3]

[1]Department of Applied Chemistry, National Chi Nan University, 1 University Road Puli, Nantou Hsien 545, Taiwan, Republic of China

[2]Department of Chemical Engineering, Tatung University, Taipei 104, Taiwan, Republic of China

[3]Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

ABSTRACT: A new triphenylamine-containing aromatic diamine, *N*,*N*′-bis(4-aminophenyl)-*N*,*N*′-diphenyl-1,4-phenylenediamine, was prepared by the condensation of *N*,*N*′-diphenyl-1,4-phenylenediamine with 4-fluoronitrobenzene, followed by catalytic reduction. A series of novel aromatic polyamides with triphenylamine units were prepared from the diamine and various aromatic dicarboxylic acids or their diacid chlorides via the direct phosphorylation polycondensation or low-temperature solution polycondensation. All the polyamides were 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 good mechanical properties. They had useful levels of thermal stability associated with relatively high glass-transition temperatures (257–287 °C), 10% weight-loss temperatures in excess of 550 °C, and char yields at 800 °C in nitrogen higher than 72%. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 2810–2818, 2002

Keywords: aromatic polyamides; triphenylamine unit; solubility; thermal properties; high performance polymers

INTRODUCTION

Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, rigidity of the backbone and strong hydrogen bonding results in high melting or glass-transition temperatures (T_g's) and limited solubility in most organic solvents.[1,2] 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.[3–11] 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 impossible. Gen-

erally, one of the successful approaches to increase the solubility and processability of polyamides without sacrificing high thermal stability is the introduction of bulky pendant phenyl groups into polymer backbone. Our previous studies have revealed that the highly phenylated aromatic diamines such as 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene,[12,13] 3,4-bis(4-aminophenyl)-2,5-diphenylfuran,[14] 3,4-bis(4-aminophenyl)-2,5-diphenylpyrrole,[15] 1,1-bis(4-aminophenyl)-2,2-diphenylethylene,[16] and 4,4′-diaminotriphenylamine[17,18] were used for the preparation of soluble high-temperature aromatic polyimides and polyamides. In a continuation of these studies, this work deals with the synthesis and basic characterization of novel soluble aromatic polyamides derived from N,N'-bis(4-aminophenyl)-N,N'-diphenyl-1,4-phenylenediamine, a triphenylamine-containing diamine monomer extended from N,N'-diphenyl-1,4-phenylenediamine. The incorporation of bulky, propeller-shaped triphenylamine moieties would interrupt the intermolecular hydrogen bonding of the polyamides and generally disturb the coplanarity of the aromatic unit to reduce stacking efficiency and crystallinity. This should enhance solubility while maintaining a high T_g through decreased segmental mobility resulting from steric hindrance. In addition, these triphenylamine-containing polyamides may be applied in organic electroluminescent elements because light-emitting triarylamine derivatives[19,20] and triarylamine-containing polymers[21,22] are reputed to be hole-transporting layer materials and are showing increasing potential as active components for a wide range of electronic and optoelectronics devices.

EXPERIMENTAL

Materials

N,N'-Diphenyl-1,4-phenylenediamine (**1**) [from Tokyo Chemical Industry (TCI)], 4-fluoronitrobenzene (from TCI), and 10% Pd/C (from Lancaster or Fluka) were used without further purification. Commercially available aromatic dicarboxylic acids such as terephthalic acid (**4a**) (TCI), isophthalic acid (**4b**) (TCI), 2,6-naphthalenedicarboxylic acid (**4c**) (TCI), 4,4′-biphenyldicarboxylic acid (**4d**) (TCI), 4,4′-oxydibenzoic acid (**4e**) (TCI), and 4,4′-sulfonyldibenzoic acid (**4f**) (New Japan Chemical Co.) were used as received. Terephthaloyl chloride (**5a**) (TCI) and isophthaloyl chloride (**5b**) (TCI) were purified by distillation under re-

duced pressure before use. Other aromatic diacid chlorides were prepared by the reaction of the corresponding aromatic dicarboxylic acids with thionyl chloride in the presence of a few drops of N,N-dimethylformamide (DMF) as a catalyst. 2,6-Naphthalenedicarbonyl chloride (**5c**) and 4,4′-biphenyldicarbonyl chloride (**5d**) were purified by sublimation, whereas 4,4′-oxydibenzoyl chloride (**5e**) and 4,4′-sulfonyldibenzoyl chloride (**5f**) were purified by distillation.[23] Dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride. Hydrazine monohydrate, triphenyl phosphite (TPP), pyridine, and propylene oxide were used as received.

Monomer Synthesis

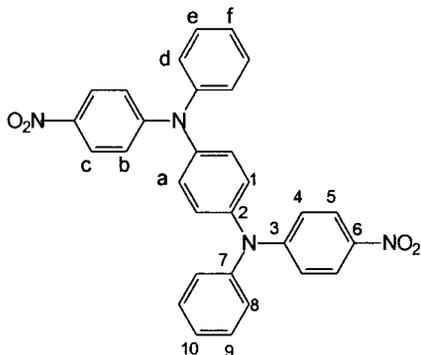#### N,N′-Bis(4-nitrophenyl)-N,N′-diphenyl-1,4-phenylenediamine (2)

Compound **2** was prepared by the condensation of 4-fluoronitrobenzene with N,N'-diphenyl-1,4-phenylenediamine (**1**) in a dipolar solvent in the presence of a base. There are two typical synthetic procedures.

Method A. A mixture of 32.50 g (0.125 mol) of **1**, 35.42 g (0.251 mol) of 4-fluoronitrobenzene, 35.88 g (0.260 mol) of anhydrous potassium carbonate, and 300 mL of NMP was heated with stirring at 170 °C for 24 h. After cooling to room temperature, the mixture was poured into 2 L of water, and the precipitated brown solid was collected by filtration and washed thoroughly with water and methanol. After recrystallization from acetonitrile, 33.30 g (yield: 53%) of dinitro compound **2** were obtained as orange-red needles.

Method B. A mixture of 6.00 g (0.250 mol) of sodium hydride in 300 mL of DMSO was stirred at room temperature. To the mixture 32.54 g (0.125 mol) of **1** and 35.28 g (0.250 mol) of 4-fluoronitrobenzene were added in sequence. The mixture was heated with stirring at 100 °C for 6 h and then precipitated into 2 L of saturated NaCl aqueous solution. Recrystallization from acetonitrile yielded 47.1 g of the desired dinitro compound **2** as orange-red crystals in 75% yield.

mp: 178–179 °C [differential scanning calorimetry (DSC), at a scan rate of 2 °C/min]. IR (KBr): 1342, 1583 cm^{-1} (—NO$_2$). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.09 (d, J = 7.2 Hz, 4H, Hc), 7.48

(two overlapped AB doublets, J = 7.2 Hz, 4H, He), 7.32 (d, J = 7.2 Hz, 4H, Hd), 7.31 (t, J = 7.2 Hz, 2H, Hf), 7.29 (s, 4H, Ha), 6.89 (d, J = 7.2 Hz, 4H, Hb). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 153.08 (C^3), 144.73 (C^7), 142.29 (C^6), 139.20 (C^2), 130.27 (C^9), 127.83 (C^1), 126.89 (C^8), 126.33 (C^{10}), 125.54 (C^5), 117.25 (C^4). ELEM. ANAL. Calcd. for $C_{30}H_{22}N_4O_4$ (502.56): C, 71.70%; H, 4.41%; N, 11.15%. Found: C, 71.24%; H, 4.41%; N, 11.09% (see Structure 1).

N,N′-Bis(4-aminophenyl)-N,N′-diphenyl-1,4-phenylenediamine (3)

Hydrogen Pd/C-Catalyzed Reduction. A mixture of 30.15 g (0.06 mol) of the obtained dinitro compound **2**, 3.0 g of palladium 10 wt % on activated carbon (Pd/C), and 300 mL of DMF was stirred at 40 °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 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 toluene to afford 14.92 g (yield: 56%) of white-beige crystals.

Hydrazine Pd/C-Catalyzed Reduction. In a 500-mL round-bottom flask, 30.15 g (0.06 mol) of dinitro compound **2** and 0.4 g of 10% Pd/C were dissolved/suspended in 300 mL of ethanol. After addition of 30 mL of hydrazine hydrate, the solution was stirred at reflux temperature for 10 h. After cooling to room temperature, 200 mL of DMF were then added to the suspension solution to dissolve the solid product. The solution was filtered to remove catalyst, and the filtrate was poured into 500 mL of water. The crude product was purified by recrystallization from toluene to give 15.92 g (60%) of diamine **3** as white-beige crystals.

mp: 261-262 °C (DSC, 2 °C/min). IR (KBr): 3465, 3374 cm^{-1} (—NH$_2$). ^{1}H NMR (400 MHz, DMSO-d_6, δ): 5.01 (s, 4H, —NH$_2$), 6.56–7.17 (m, 22H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 148.36, 145.93, 141.98, 135.25, 128.79, 127.81, 123.70, 119.86, 119.72, 114.87. ELEM. ANAL. Calcd. for $C_{30}H_{26}N_4$ (442.56): C, 81.42%; H, 5.92%; N, 12.66%. Found: C, 81.17%; H, 5.87%; N, 12.54%.

General Polymer Synthesis

Typical procedures for the synthesis of triphenylamine-containing polyamide **6a** are as follows.

Direct Polycondensation via the Phosphorylation Reaction

A mixture of 0.553 g (1.25 mmol) of diamine **3**, 0.208 g (1.25 mmol) of terephthalic acid (**4a**), 0.3 g of calcium chloride, 0.9 mL of TPP, 1.2 mL of pyridine, and 5 mL of NMP was heated with stirring at 105 °C for 3 h. The polymer solution was poured slowly into 300 mL of stirring methanol giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C; yield: 0.711 g (99%). The inherent viscosity of the obtained polyamide **6a** was 0.54 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.

Low-Temperature Solution Polycondensation

A solution of 1.106 g (2.5 mmol) of diamine **3** in 10 mL of NMP was cooled to about −10 °C on a dry ice–acetone bath. After, 0.8 mL of propylene oxide was added to the mixture, and then 0.508 g (2.5 mmol) of terephthaloyl chloride (**5a**) were added. The mixture was stirred at −10−0 °C for 6 h. The polymer solution was trickled slowly into 300 mL of methanol giving rise to a stringy, fiberlike precipitate that was refluxed in methanol for 12 h. The yield of the polymer was 1.42 g (99%), and the inherent viscosity was 0.56 dL/g as measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.

IR (film): 3310 (N—H stretching), 1657 cm^{-1} (amide carbonyl). ELEM. ANAL. Calcd. for $(C_{38}H_{28}N_4O_2)_n$ (572.42)$_n$: C, 79.70%; H, 4.93%; N, 9.78%. Found: C, 76.99%; H, 4.64%; N, 9.43%.

Preparation of Films

A solution of polymer was made by dissolving about 0.7 g of the polyamide sample in 10 mL of

DMAc or NMP. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight to remove most of the solvent; then the semidried film was further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 90–120 μm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Measurements

IR spectra were recorded with a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were performed by a PerkinElmer model 2400 CHN analyzer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL EX 400 spectrometer with perdeuteriodimethyl sulfoxide (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 concentrated sulfuric acid, DMAc 5 wt % LiCl, or NMP with 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 with 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. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined with gel permeation chromatography (GPC) on the basis of polyoxyethylene calibration on a Jasco apparatus (eluent: DMF). 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 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.
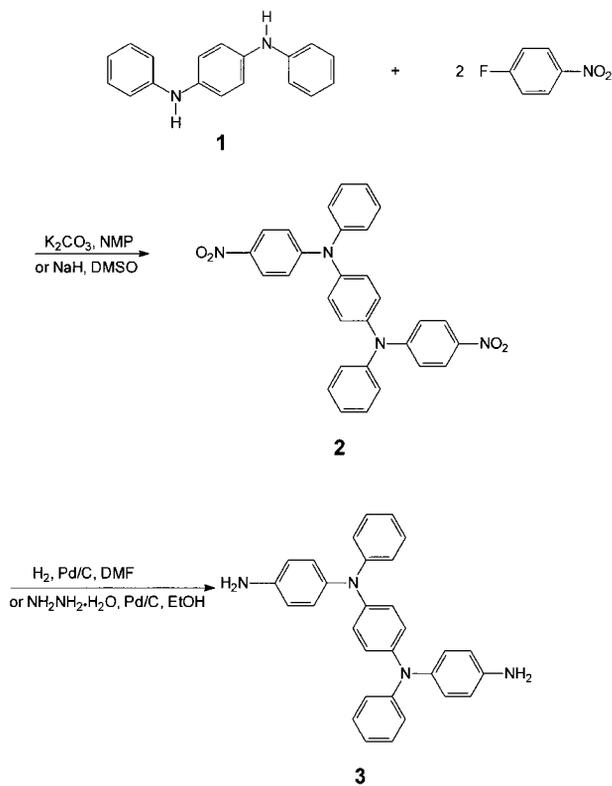

Scheme 1

RESULTS AND DISCUSSION

Monomer Synthesis

The new triphenylamine-containing aromatic diamine monomer, **3**, was successfully synthesized by hydrogen or hydrazine Pd/C-catalyzed reduction of the dinitro compound **2** resulting from the condensation reaction of **1** with 4-fluoronitrobenzene in the presence of potassium carbonate or sodium hydride according to the synthetic routes outlined in Scheme 1. The aromatic fluoro-displacement reaction of 4-fluoronitrobenzene with the amine ion of **1** treated by sodium hydride was generally more preferrable than that with potassium carbonate for the preparation of dinitro compound **2** with a higher yield. Elemental analysis, IR, and ^{1}H and ^{13}C NMR spectroscopic techniques were used to identify the structures of the intermediate dinitro compound **2** and the diamine monomer **3**. The IR spectra of dinitro compound **2** gave two nitro group characteristic bands at 1583 (antisymmetrical stretching) and 1342 cm^{-1} (symmetrical stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed
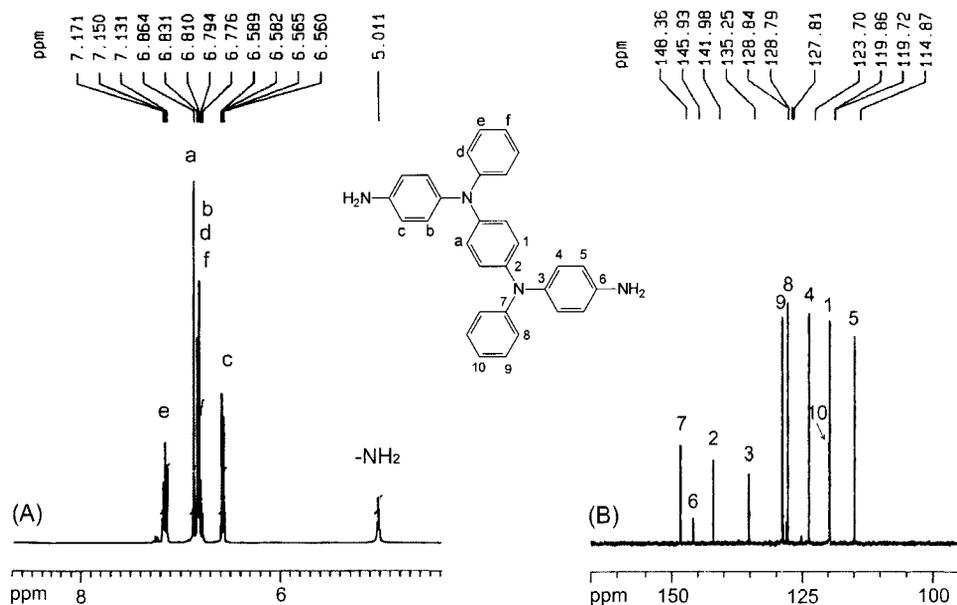
Figure 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of diamine **3** in DMSO-d_6.

a typical N—H stretching absorption pair at 3465 and 3374 cm^{-1}. The structures of **2** and **3** were also confirmed by high-resolution NMR spectra. The ^{1}H and ^{13}C NMR spectra of diamine **3** are given in Figure 1. 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 completely converted into amino groups by the high field shift of aromatic protons Hc from 8.1 to 6.6 ppm and by the signal at 5.0 ppm corresponding to the amino protons.

Polymer Synthesis

Both the direct polycondensation technique[24] and the low-temperature solution polycondensation technique[25] were used for the synthesis of the triphenylamine-containing polyamides **6a–f** as shown in Scheme 2 from various combinations of monomers. First, the polyamides were prepared by high-temperature direct polycondensation of diamine **3** with various aromatic dicarboxylic acids (**4a–f**) with triphenyl phosphite and pyridine as condensing agents. All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. All the polymers precipitated in a tough fiberlike form when slowly pouring the resulting polymer solutions under stirring into methanol. As shown in Table 1, the polyamides prepared by

this method had inherent viscosities in the range of 0.43–0.73 dL/g measured in concentrated sulfuric acid and 0.50–1.64 dL/g in DMAc 5 wt % LiCl. In addition, the polyamides were also pre-
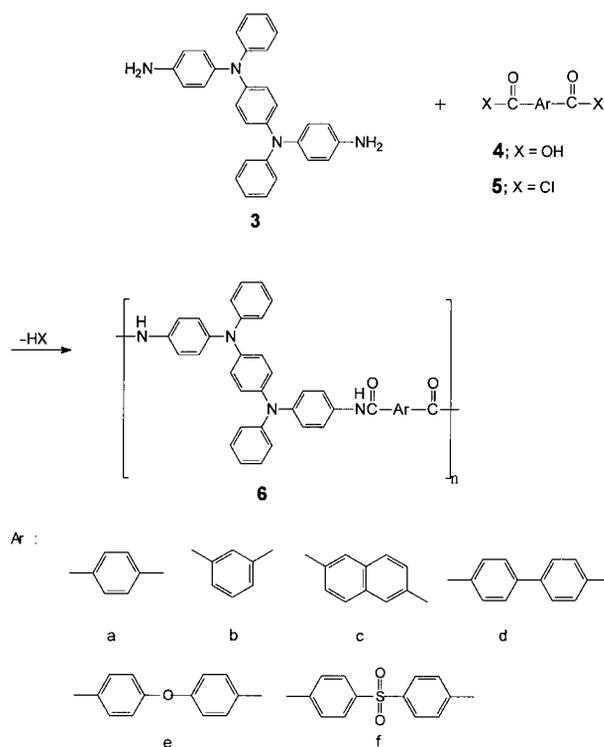
Scheme 2

Table 1. Inherent Viscosities and Elemental Analysis of Polyamides

Polymer Code	Method of Preparation[a]	η_{inh}^{b} (dL/g)	Elemental Analysis							
			Calcd. (%)				Found (%)			
			C	H	N	S	C	H	N	S
6a	A	0.54 (1.10)[c]	79.70	4.93	9.78		76.99	4.64	9.43	
	B	0.56								
6b	A	0.43 (0.50)[c]	79.07	4.93	9.78		77.33	4.81	9.61	
	B	0.55 (0.45)[d]								
6c	A	0.65 (0.87)[c]	81.01	4.86	9.00		79.01	4.63	8.82	
	B	1.05								
6d	A	0.73 (1.64)[c]	81.46	4.97	8.64		79.97	4.83	8.36	
	B	0.72								
6e	A	0.54 (0.62)[c]	79.50	4.85	8.43		78.19	4.96	8.18	
	B	0.58 (0.49)[d]								
6f	A	0.53 (0.50)[c]	74.14	4.52	7.86	4.50	71.23	4.57	7.68	4.84
	B	0.62								

[a] A: Direct polycondensation; polymerization was carried out with 1.25 mmol of each diamine and diacid monomer with 2.5 mmol (about 0.9 mL) of triphenyl phosphite and 1.2 mL of pyridine in 5 mL of NMP containing 0.3 g of calcium chloride at 105 °C for 3 h. B: Low-temperature polycondensation; polymerization was carried out with 2.5 mmol of each diamine and diacyl chloride monomer in 10 mL of NMP and 25 mmol of propylene oxide as an acid acceptor at $-10–0$ °C for 6 h.
[b] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.
[c] Measured in DMAc 5 wt % LiCl.
[d] Measured in NMP.

pared by the low-temperature solution polycondensation from diamine **3** and various diacid chlorides (**5a**–**f**) in NMP cooled by an ice–acetone bath with propylene oxide as the HCl scavenger. As summarized in Table 1, the inherent viscosities of the polymers obtained via the acid chloride route stayed in the range of 0.55–1.05 dL/g. In most cases, the inherent viscosities of the polymers obtained via the low-temperature solution polycondensation method are comparable to or higher than those of the polymers produced via the phosphorylation method. All the polymers except polyamide **6c** could be solution cast into flexible and tough films, indicative of the formation of high molecular weight polymers. The GPC chromatogram of polyamide **6b** obtained via the acid chloride route indicated that the M_w and M_n values were 150,000 and 60,000, respectively, relative to standard polyoxyethylene, and the polydispersity ratio of M_w/M_n was 2.5. In the case of another polyamide **6f**, the M_w and M_n values were 130,000 and 56,000, respectively, and the M_w/M_n ratio was 2.4.

The IR spectra of the polymers, which showed characteristic amide absorptions at 3400–3300 and 1650 cm^{-1}, supported the formation of the polyamides. The elemental analysis values of

these polyamides are listed in Table 1. In all cases, however, the carbon and nitrogen analysis values were lower than the calculated values for the proposed structures. This probably relates to higher char yields of these polymers at elevated temperatures, discussed subsequently.

Properties of Polymers

The X-ray diffraction studies of the triphenylamine-containing polyamides indicated that all the polymers were essentially amorphous. The solubility behavior of these polymers was tested qualitatively, and the results are listed in Table 2. All the polyamides except polymer **6c** derived from rigid and symmetrical diacid (**4c**) were soluble in polar solvents such as DMAc and NMP. Even polyamides **6a** and **6d** obtained from rigid monomers such as terephthalic acid (**4a**) and 4,4′-biphenyldicarboxylic acid (**4d**) were also organic soluble. Polyamides **6b**, **6e**, and **6f** with more-flexible linkages in the diacid moieties were also soluble in DMF, DMSO, and *m*-cresol. All the polymers were practically insoluble in tetrahydrofuran, chloroform, and methanol. Their high solubility and amorphous nature can be attributed to the introduction of a bulky, twisted, three-

Table 2. Solubility and Mechanical Properties of Polyamides

	Solubility[a]						Tensile Properties of the Polymer Films[b]		
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Tensile Strength (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
6a	+h	+h	+h	−	−	−	103	9	2.7
6b	+	+	+	+	+	−	95	10	2.4
6c	+h	−	−	−	−	−			
6d	+	+	−	−	−	−	115	8	2.9
6e	+	+	+	+	+h	−	100	11	2.4
6f	+	+	+	+	+	−	91	8	2.3

[a] +, Soluble at room temperature; +h, soluble on heating; and −, insoluble even on heating.
[b] Films were cast by the slow evaporation of polymer solutions in DMAc. The film specimens were dried *in vacuo* at 160 °C for 8 h prior to the tensile test.

dimensional triphenylamine unit along the polymer backbone. Thus, the excellent solubility makes these polymers potential candidates for practical applications in spin-on and casting processes.

As previously mentioned, except **6c**, all polyamides could be solution cast into smooth, flexible, and tough films. These films were subjected to tensile testing, and the results are also given in Table 2. The tensile strengths, elongations to break, and initial moduli of these films were in the ranges of 91–115 MPa, 8–11%, and 2.3–2.9 GPa, respectively.

The thermal stability of these polyamides was examined by TGA. Typical TGA curves of a representative polymer **6a** in both air and nitrogen atmospheres are shown in Figure 2. Some thermal-behavior data determined from original thermograms are tabulated in Table 3. In general, all the polyamides exhibited good thermal stability with insignificant weight loss up to 400 °C in nitrogen. The 10% weight-loss temperatures of
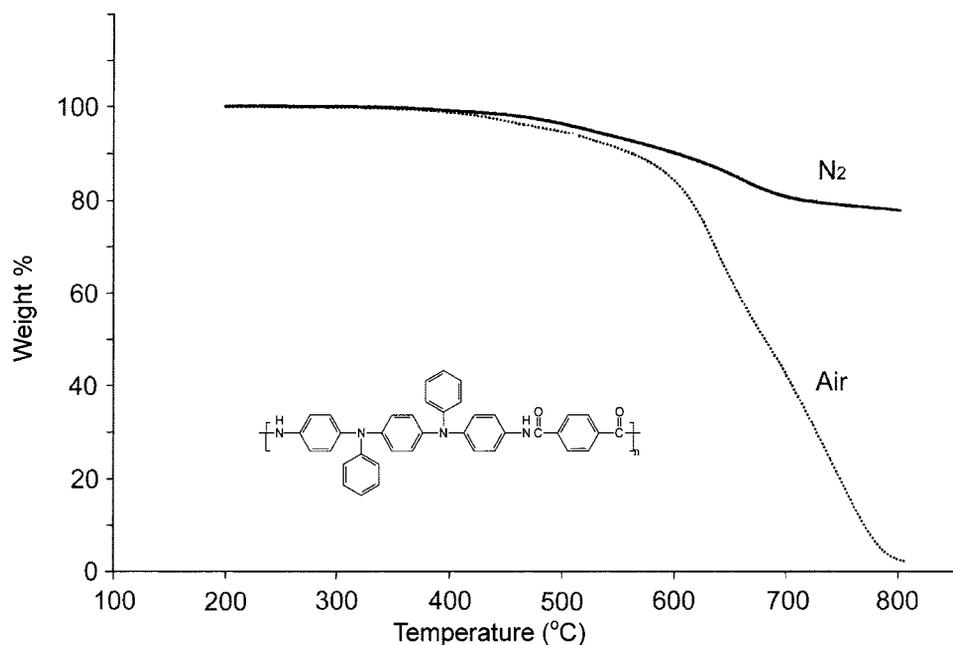
Figure 2. TGA thermograms of polyamide **6a** at a scan rate of 20 °C/min.

Table 3.   Thermal Properties of Polyamides

| Polymer	T_g (°C)[a]	T_s (°C)[b]	T_d at 5% Weight Loss (°C)[c]		T_d at 10% Weight Loss (°C)[c]		Char Yield (wt %)[d]
			N₂	Air	N₂	Air	
6a	278 (297)[c]	274	520	489	600	561	78
6b	265 (281)	270	523	503	568	554	78
6c	287 (312)	282	479	503	569	561	76
6d	282	282	485	481	562	559	72
6e	257	256	512	495	582	573	75
6f	277 (313)	278	511	503	558	553	75

[a] Glass-transition temperature, taken as the midpoint temperature of the baseline shift on the DSC heating trace (scan rate = 20 °C /min) after preheating at 300 °C for 30 min.
[b] Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace 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, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm³/min.
[d] Residual weight percentage at 800 °C in nitrogen.
[e] Values in parentheses are reported T_g's of analogous polyamides (**6′**) having the corresponding –Ar= unit as in the **6** series (see ref. 17).
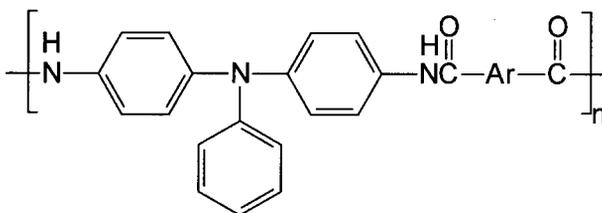
6'

the polyamides in nitrogen and air were recorded in the range of 558–600 and 553–573 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 70% 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 polyamides. The influence of residual solvent or the absorbed moisture and history of thermal annealing is sometimes observed in the DSC and TMA scans. Thus, all the polymers were heated at 300 °C for 30 min prior to the DSC and TMA experiments. The T_g's of all the polymers could be easily measured in the DSC thermograms; they were observed in the range of 257–287 °C and decreased with decreasing rigidity and symmetry of the dicarboxylic acids. When compared with the corresponding polyamides **6′** as reported previously,[17] the **6** series of polyamides exhibited a decreased T_g possibly because of the increased flexibility or free volume caused by the introduction of one more triphe-

nylamine group in the repeat unit. All the polymers showed no clear melting endotherms up to the decomposition temperatures on the DSC thermograms. This result supports the amorphous nature of these triphenylamine-containing polymers. The softening temperatures (T_s's) (may be referred to as apparent T_g) of the polymer film samples were determined by the TMA method with a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. 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 or T_s and the decomposition temperature of each polymer, which could be advantageous in the processing of these polymers by the thermoforming technique.

CONCLUSIONS

A new triphenylamine-containing diamine, N,N′-bis(4-aminophenyl)-N,N′-diphenyl-1,4-phenylene-

diamine, has been synthesized in good yields and high purity from readily available reagents. A series of high molecular weight polyamides have been readily prepared from the diamine and various aromatic dicarboxylic acids or their diacid chlorides via the direct phosphorylation polycondensation or low-temperature solution polycondensation. Because of the presence of the bulky triphenylamine unit, all the polymers were amorphous, had good solubility in many polar aprotic solvents, and exhibited excellent thin-film-forming ability. Good solubility, moderate T_g or T_s values suitable for molding, and good thermal stability and mechanical properties make these triphenylamine-containing polyamides as promising processable high-performance polymeric materials.

REFERENCES AND NOTES

1. Cassidy, P. E. Thermally Stable Polymers; Marcel Dekker: New York, 1980.
2. Yang, H. H. Aromatic High-Strength Fibers; Wiley: New York, 1989.
3. Imai, Y. High Perform Polym 1995, 7, 337.
4. Imai, Y. React Funct Polym 1996, 30, 3.
5. Imai, Y.; Maldar, N. N.; Kakimoto, M. J Polym Sci Polym Chem Ed 1985, 23, 1797.
6. Liou, G. S.; Hsiao, S. H. J Polym Sci Part A: Polym Chem 2001, 39, 1786.
7. Hsiao, S. H.; Li, C. T. Macromolecules 1998, 31, 7213.
8. Liou, G. S. J Polym Sci Part A: Polym Chem 1998, 36, 1937.
9. Eastmond, G. C.; Paprotny, J.; Irwin, R. S. Polymer 1999, 40, 469.
10. Yang, C. P.; Hsiao, S. H.; Yang, H. W. Macromol Chem Phys 1999, 200, 1528.
11. Espeso, J. F.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. J Polym Sci Part A: Polym Chem 2000, 38, 1014.
12. Imai, Y.; Maldar, N. N.; Kakimoto, M. J Polym Sci Polym Chem Ed 1984, 22, 2189.
13. Imai, Y.; Kakimoto, M. Polym Plast Technol Eng 1989, 28, 371.
14. Jeong, H. J.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1991, 29, 39.
15. Jeong, H. J.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1991, 29, 1691.
16. Xie, M.; Oishi, Y.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1991, 29, 55.
17. Oishi, Y.; Takado, H.; Yoneyama, M.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1990, 28, 1763.
18. Oishi, Y.; Ishida, M.; Kakimoto, M.; Imai, Y.; Kurosaki, T. J Polym Sci Part A: Polym Chem 1992, 30, 1027.
19. Imai, K.; Shinkai, M.; Kakimoto, T.; Shirota, Y. U.S. Patent 5,256,945, 1993.
20. Imai, K.; Kakimoto, T.; Shirota, Y.; Inada, H.; Kobata, T. U.S. Patent 5,374,489, 1994.
21. Wu, A.; Kakimoto, M.; Imai, Y. Supramol Sci 1996, 3, 3.
22. Lu, J.; Hlil, A. R.; Sun, Y.; Hay, A. S. Chem Mater 1999, 11, 2501.
23. Liou, G. S.; Maruyama, M.; Kakimoto, M.; Imai, Y. J Polym Sci Part A: Polym Chem 1993, 31, 2499.
24. Yamazaki, N.; Matsumoto, M.; Higashi, F. J Polym Sci Polym Chem Ed 1975, 13, 1373.
25. Morgan, P. W. Condensation Polymers by Interfacial and Solution Methods; Interscience: New York, 1965.