NOTE

Synthesis and Properties of New Aromatic Poly(amine-imide)s Derived from *N,N'*-Bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine

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INTRODUCTION

Wholly aromatic polyimides are well accepted as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, the technological applications of rigid polyimides are limited by processing difficulties because of high melting or glass-transition temperatures (T_g's) and limited solubility in most organic solvents.[1,2] To overcome such a difficulty, polymer-structure modification becomes necessary.[3–9] One of the successful approaches for increasing solubility and processability of polyimides without sacrificing high thermal stability is the introduction of bulky pendant phenyl groups into polymer backbone.[10–13] Nevertheless, little is known about aromatic polyimides having a phenyl-pendant aromatic amine unit in the polymer backbone, that is, poly(amine-imide)s. The only example was the poly(amine-imide)s derived from 4,4'-diaminotriphenylamine in our previous publication.[14] As a continuation of the study, we have designed new triphenylamine-containing poly(amine-imide)s having 1,4-phenylene backbone to elucidate the effect of backbone structure on properties of poly(amine-imide)s.

This work explores the synthesis and basic characterization of new aromatic poly(amine-imide)s containing the triphenylamine unit by the polymerization of *N,N'*-bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylene-diamine[15] with aromatic tetracarboxylic dianhydrides by a two-step method or with aromatic tetracarboxylic dithioanhydrides via a one-step method. It is quite likely that the triphenylamine-containing polyimides will possess electro- and photochemical properties as well as high thermal stability because of the triphenylamine conjugated system. Thus, these triphenylamine-containing poly(amine-imide)s may be applied in organic electroluminescent elements because light-emitting triarylamine derivatives[16–18] and triarylamine-containing polymers[19,20] are reputed to be a hole-transporting layer material and show 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 Industries (TCI)], 4-fluoronitrobenzene (from

TCI), hydrazine monohydrate, and 10% Pd/C (from Lancaster or Fluka) were used without further purification. *N,N'*-Bis(4-aminophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (**3**) (mp: 261–262 °C) was synthesized by hydrogen or hydrazine Pd/C-catalyzed reduction of *N,N'*-bis(4-nitrophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (**2**) resulting from the condensation of **1** with 4-fluoronitrobenzene in the presence of potassium carbonate or sodium hydride. Details of the synthesis and characterization data of the dinitro intermediate **2** and diamine **3** have been described in a preceding article.[15] Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA) (**4a**) (Aldrich), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (**4c**) (Aldrich), 4,4′-oxydiphthalic dianhydride (ODPA) (**4d**) (Oxychem), and 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA) (**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 (6FDA) (**4f**) (Hoechst Celanese) were purified by vacuum sublimation. Pyromellitic dithioanhydride (**7a**), 3,3′,4,4′-biphenyltetracarboxylic dithioanhydride (**7b**), 3,3′,4,4′-benzophenonetetracarboxylic dithioanhydride (**7c**), and diphenylsulfone-3,3′,4,4′-tetracarboxylic dithioanhydride (**7d**) were prepared by the reaction of the corresponding aromatic tetracarboxylic acids with sodium sulfide according to a previously reported procedure.[14,21] Dimethyl sulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP) were purified by distillation under reduced pressure over calcium hydride.

General Polymer Synthesis

Typical procedures for the synthesis of triphenylamine-containing poly(amine-imide) **6c** are as follows.

Two-Step Method via Thermal Imidization Reaction

Monomer **3** (0.5787 g, 1.31 mmol) was dissolved in 9.5 mL of CaH$_2$-dried DMAc in a 50-mL round-bottom flask. Then BTDA (0.4213 g, 1.31 mmol) was added to the diamine solution in one portion. Thus, the solid content of the solution is 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 1.09 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The polyamic acid **5c** film was obtained by casting from the reaction polymer solution onto a glass plate and drying at room temperature overnight under vacuum. The polyamic acid in the form of film was converted to polyimide **6c** by successive heating under vacuum at 100 °C for 1 h, 200 °C for 1 h, and then 300

°C for 1 h. The inherent viscosity of poly(amine-imide) **6c** was 0.48 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.

IR (film): 1780, 1730 (imide C=O stretching), 1380 (imide C-N stretching), and 725 cm^{-1} (imide-ring deformation). ELEM. ANAL. Calcd. for $(C_{47}H_{28}N_4O_5)_n$ $(728.76)_n$: C, 77.46%; H, 3.87%; N, 7.69%. Found: C, 78.21%; H, 3.97%; N, 8.27%.

Two-Step Method via Chemical Imidization Reaction

Polyamic acid **5c** was prepared by the same procedure described previously. The precursor 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 **5c** solution, and the reaction mixture was stirred at room temperature overnight and at 100 °C for 2 h. After cooling to room temperature, the polymerization mixture was poured slowly into 300 mL of stirred methanol giving rise to a fibrous precipitate of poly(amine-imide) **6c** that was collected by filtration, washed thoroughly with methanol, and dried at 120 °C under vacuum.

One-Step Thioanhydride Method

To a solution of 0.8851 g (2 mmol) of diamine **3** in 10 mL of NMP, 0.7087 g (2 mmol) of **7c** was added at room temperature. The mixture was heated with stirring at 140 °C for 6 h under nitrogen atmosphere. About half-volume of the reaction solution was poured into 300 mL of methanol. The precipitated polymer was collected by filtration, and dried at 100 °C for 12 h and 200 °C for 1 h under vacuum. The film of poly(amine-imide) **6c** was cast directly from the reaction solution onto a glass plate and dried under vacuum at room temperature for 24 h, 100 °C for 12 h, and 200 °C for 1 h. The inherent viscosity of poly(amine-imide) **6c** was 0.37 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30 °C.

IR (film): 1780, 1730 (imide C=O stretching), 1380 (imide C-N stretching), and 725 cm^{-1} (imide-ring deformation). ELEM. ANAL. Calcd. for $(C_{47}H_{28}N_4O_5)_n$ $(728.76)_n$: C, 77.46%; H, 3.87%; N, 7.69%. Found: C, 75.51%; H, 3.70%; N, 7.77%.
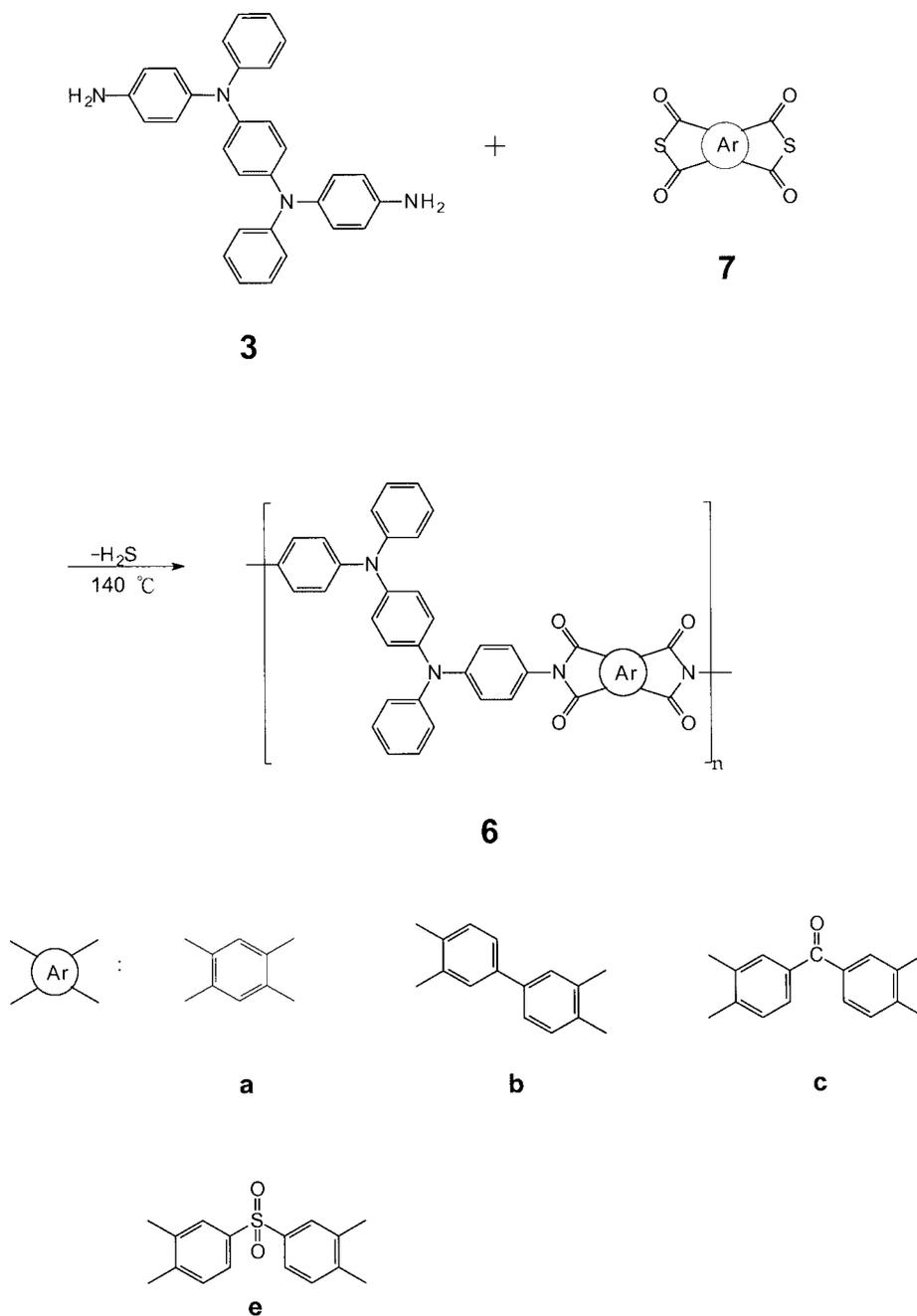
Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were performed by a PerkinElmer model 2400 CHN analyzer. The inherent viscosities were determined at a concentration of 0.5 g/dL in concentrated sulfuric acid or DMAc using a Cannon-Fenske or an Ubbelohde viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Ex-
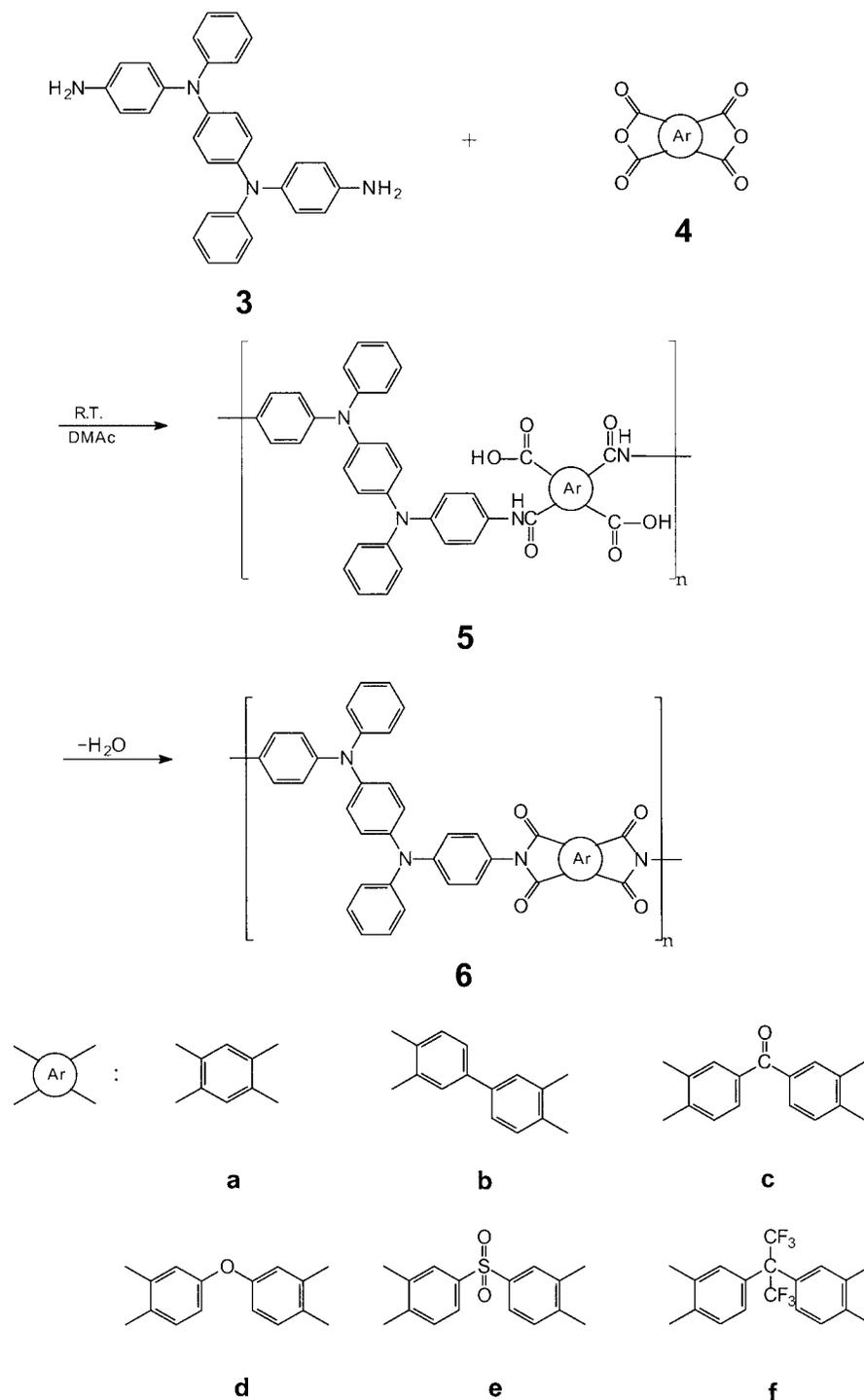
Scheme 1. Synthesis of polyimides by two-step method.

periments were carried out on 3–5-mg samples heated in flowing nitrogen or air (30 mL/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC in flowing nitrogen (20 mL/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 scan-

3

7

6

Ar :

a   **b**   **c**

e

Scheme 2. Synthesis of polyimides by one-step method.

ning 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 5 kg was used to measure 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 wide, ca. 0.1 mm thick, and 2 cm gauge length), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

Both the two-step procedure and the one-step thioanhydride method[14,21] were used for the synthesis of the triphenylamine-containing aromatic poly(amine-imide)s **6a–f** as shown in Schemes 1 and 2 from various combinations of monomers. The results of the synthesis

Table 1. Synthesis of Aromatic Poly(amine-imide)s

Two-Step Method				One-Step Method	
Polyamic acid		Polyimide		Polyimide	
Code	$\eta_{inh}{}^a$ (dL/g)	Code	$\eta_{inh}{}^b$ (dL/g)	Code	$\eta_{inh}{}^b$ (dL/g)
5a	1.86	**6a**	0.50	**6a**	0.25
5b	1.10	**6b**	0.45	**6b**	0.30
5c	1.09	**6c**	0.48	**6c**	0.37
5d	0.71	**6d**	0.30	—	—
5e	0.91	**6e**	0.27 (0.36)^a	**6e**	0.27
5f	1.14	**6f**	0.28 (0.68)^a	—	—

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

are summarized in Table 1. First, the poly(amine-imide)s were prepared by the two-step method starting from diamine **3** with various aromatic tetracarboxylic dianhydrides **4a–f** in which the first step was the formation of polyamic acids **5a–f** (Scheme 1) through the ring-opening polyaddition reaction. All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. As shown in Table 1, the polyamic acid precursors **5a–f** exhibited inherent viscosities ranging from 0.71 to 1.86 dL/g and could afford free-standing films by solution casting, indicative of the formation of high-molecular-weight polymers. The second imidization step was carried out via thermal cyclodehydration of polyamic acid films by sequential stage-by-stage heating to 300 °C under vacuum. The resulting poly(amine-imide)s had inherent viscosities of 0.27–0.50 dL/g measured in concentrated sulfuric acid. The sulfuric acid solutions of these polymers appeared to be a deep blue color and could be diluted with water without polymer precipitation occurring. Poly(amine-imide)s **6e** and **6f** were soluble in DMAc; therefore, the characterization of inherent viscosity in DMAc was also carried out without difficulty, and the values were 0.36 and 0.68 dL/g, respectively. Certainly, the poly(amine-imide) samples also could be obtained by chemical imidization of the polyamic acid precursors using acetic anhydride and pyridine.

In addition, the one-step thioanhydride method[14,21] was also adopted here to prepare aromatic poly(amine-imide)s **6** (Scheme 2). The poly(amine-imide)s were produced with inherent viscosities in the range of 0.25–0.37 dL/g (in concentrated sulfuric acid), comparable to those obtained by the two-step method. The polymerization of diamine **3** with dithioanhydrides **7c** and **7e** in NMP at 140 °C proceeded in homogeneous solution, producing poly(amine-imide)s **6c** and **6e**, respectively. These homogeneous poly(amine-imide) solutions could be used directly for the preparation of transparent films by solution casting. However, in the cases of poly-(amine-imide)s **6a** and **6b**, precipitation occurred during the reaction because of insolubility of the resulting polymers. The formation of poly(amine-imide)s by both methods was confirmed by means of IR spectroscopy and elemental analysis, with some deviation in carbon analysis noticed between the calculated and observed values.

Properties of Polymers

The color of poly(amine-imide) films depends markedly on the chemical structure of dianhydride components. Thus, the films of poly(amine-imide)s **6a–d** were from dark red to almost black, whereas the films of poly-(amine-imide)s **6e** and **6f** had a pale brown color. The dark red to almost black color of the films can be attributed to charge-transfer complexing between the electron-donating triphenylamine unit and the strongly electron-accepting pyromellitimide or phthalimide unit. As mentioned previously, all the aromatic poly(amine-imide)s could afford flexible and tough films. These films were subjected to tensile testing, and the results are given in Table 2. The tensile strengths,

Table 2. Mechanical Properties of Poly(amine-imide) Films Prepared by Two-Step Thermal Imidization Method

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
6a	98	9	2.6
6b	100	6	2.3
6c	128	9	2.2
6d	116	7	2.5
6e	118	6	2.5
6f	115	8	2.1

Table 3. Solubility of Aromatic Poly(amine-imide)s[a]

Polymer	Method of Preparation[b]	Solvent[c]						
		NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Chloroform
6a	Two-step(T)	−	−	−	−	−	−	−
	Two-step(C)	±	−	−	−	−	−	−
	One-step	±	±	±	±	±	±	±
6b	Two-step(T)	+h	−	−	−	+h	−	+h
	Two-step(C)	+	−	−	−	+	−	+
	One-step	±	±	±	±	+h	±	+
6c	Two-step(T)	+h	−	−	+h	+h	−	−
	Two-step(C)	+	+h	+h	+h	+	−	+
	One-step	+h	+h	±	±	+h	±	±
6d	Two-step(T)	+h	+h	−	+h	+h	−	−
	Two-step(C)	+	+h	−	+h	+	±	+
6e	Two-step(T)	+h	+	+	+h	+h	−	±
	Two-step(C)	+	+	+	+h	+	−	+
	One-step	+	+	+	±	+h	+	+
6f	Two-step(T)	+	+	+	+h	+h	+	+
	Two-step(C)	+	+	+	+	+	+	+

[a] Solubility: +, soluble at room temperature; +h, soluble on heating; ±, partially soluble or swelling; −, insoluble even on heating.
[b] (T): thermal imidization; (C): chemical imidization.
[c] Abbreviation of solvents: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; THF, tetrahydrofuran.

elongations to break, and initial moduli of these films were in the ranges of 98–128 MPa, 6–9% and 2.1–2.6 GPa, respectively.

The X-ray diffraction studies of the poly(amine-imide)s indicated that all the polymers were essentially amorphous. The solubility behavior of the poly(amine-imide)s obtained by the two-step method, through thermal and chemical imidization, and the one-step thioanhydride method was investigated qualitatively, and the results are listed in Table 3. All of the poly(amine-imide)s except polymer **6a** derived from rigid and symmetrical PMDA were soluble at least in NMP. Poly-(amine-imide)s derived from the dianhydrides having flexible bridging groups, such as ODPA, BTDA, DSDA, and 6FDA, exhibited higher solubility and were soluble even in less polar solvents such as chloroform and tetrahydrofuran. The enhanced solubility and amorphous nature can be attributed to the introduction of bulky, twisted, three-dimensional triphenylamine unit along the polymer backbone. Thus, the good solubility makes these polymers potential candidates for practical applications in spin-on and casting processes. In addition, the poly(amine-imide)s prepared by the one-step method had better solubility as compared with those by the two-step thermal imidization method, whereas they had almost the same solubility as that of the poly(amine-imide)s obtained by the two-step chemical imidization procedure. Thus, the difference in solubility of poly(amine-imide)s obtained by different

methods could be ascribed to morphological change of the polymers during heat treatment resulting in some degree of ordering from molecular aggregation of the polymer chain segments.

Thermal properties of these poly(amine-imide)s are summarized in Table 4. All of the poly(amine-imide)s exhibited a similar TGA pattern with no significant weight loss below 500 °C in air or nitrogen atmosphere. The 10% weight-loss temperatures of the poly(amine-imide)s in nitrogen and air were recorded in the range of 559–627 and 576–616 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 63% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The glass-transition temperatures (T_g's) of all the polymers were observed in the range of 263–332 °C by DSC and decreased with decreasing rigidity and symmetry of the tetracarboxylic dianhydride used. When compared with the analogous poly(amine-imide)s **6′**, as reported previously (Table 4),[14] the **6** series of poly(amine-imide)s showed a decreased T_g possibly because of the increased conformational flexibility or free volume caused by the introduction of one more triphenylamine group in the repeat unit. All the polymers indicated 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 re-

Table 4. Thermal Properties of Aromatic Poly(amine-imide)s Prepared by Two-Step Thermal Imidization

| 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]
			N$_2$	Air	N$_2$	Air	
6a	332	325	602	590	625	616	71
6b	291 (331)[e]	293	600	577	627	611	77
6c	274 (302)	274	591	567	617	596	69
6d	263 (287)	263	590	563	614	599	68
6e	290 (320)	292	532	538	559	577	63
6f	284 (310)	282	573	543	600	576	67

[a] Glass-transition temperature, taken as the midpoint temperature of the baseline shift on the DSC heating trace (scan rate = 20 °C/min) after quenching from 400 °C.
[b] Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace at a heating rate of 10 °C/min.
[c] Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas flow rate of 30 mL/min.
[d] Residual weight percentage at 800 °C in nitrogen.
[e] Values in parentheses are reported T_gs of analogous poly(amine-imide)s (6′) having the corresponding dianhydride residue as in the 6 series (see ref. 14).

6'
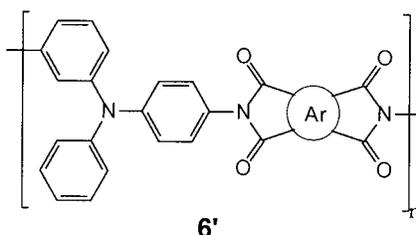
ferred as apparent T_g) of the polymer film samples were determined by the TMA method with a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. In all cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments (Table 4). 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 series of new triphenylamine-containing aromatic poly(amine-imide)s have been successfully synthesized either by a conventional two-step process from N,N'-bis(4-aminophenyl)-N,N'-diphenyl-1,4-phenylenediamine with various aromatic tetracarboxylic dianhydrides or by the one-step thioanhydride method from the diamine with aromatic tetracarboxylic dithioanhydrides. In the two-step process, the precursor polyamic acids obtained in the first stage had inherent viscosities between 0.71 and 1.86 dL/g. Except for the poly(amine-imide) from pyromellitic dianhydride, all the other poly(amine-imide)s dissolved in NMP, and several poly(amine-imide)s also exhibited good solubility in other organic solvents. All the poly(amine-imide)s were amorphous in nature as evidenced by X-ray diffractograms. These polymers could afford tough and flexible films with good mechanical properties. They had useful levels of thermal stability associated with relatively high T_g's (274–332 °C), 10% weight-loss temperatures above 560 °C in both nitrogen and air atmospheres, and char yields at 800 °C in nitrogen higher than 63%.

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