

Synthesis and Properties of Novel Triphenylamine-Containing Aromatic Polyimides

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ABSTRACT

A series of new triphenylamine-containing aromatic polyimides 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. The precursor poly(amic acid)s obtained in the first stage had inherent viscosities between 0.71 and 1.86 dL/g. Except for the polyimide from pyromellitic dianhydride, all the other polyimides dissolved in NMP, and several polyimides also showed good solubility in other organic solvents. All the polyimides 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 glass transition temperatures (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%.

Keywords: aromatic polyimides; triphenylamine unit; solubility; thermal properties.

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 due to 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 to increase 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 to date about aromatic polyimides having 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 previous publication.¹⁴ As the continuation to 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.

The present work deals with 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-phenylenediamine¹⁵ with aromatic tetracarboxylic dianhydrides through a two-step method. It is quite likely that the triphenylamine-containing polyimides will possess electro- and photochemical properties as well as high thermal stability due to the triphenylamine conjugated system. Thus, these triphenylamine-containing poly(amine-imide)s may be applied in organic electroluminescent elements, since light-emitting triarylamine derivatives¹⁶⁻¹⁸ and triarylamine-containing polymers^{19,20} are reputed to be a hole-transporting layer material 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**), 4-fluoronitrobenzene, hydrazine monohydrate and 10% Pd/C were used without further purification. *N,N'*-Bis(4-amino phenyl)-*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.¹⁵ Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA) (**4a**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (**4c**), 4,4'-oxydiphthalic dianhydride (ODPA) (**4d**), and 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA) (**4e**) were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) (**4b**) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (**4f**) were purified by vacuum sublimation. 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 CaH₂-dried DMAc in a 50-mL round-bottomed 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 poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 1.09 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30°C. The poly(amic 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 poly(amic 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 (C₄₇H₂₈N₄O₅)_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

Poly(amic acid) **5c** was prepared by the same procedure described above. The precursor poly(amic 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 above poly(amic 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** which was collected by filtration, washed thoroughly with methanol, and dried at 120 °C under vacuum.

RESULTS AND DISCUSSION

Polymer Synthesis

The two-step procedure was used for the synthesis of the triphenylamine-containing aromatic poly(amine-imide)s **6a-f** as shown in Scheme 1. The results of the synthesis 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 poly(amic acid)s **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 poly(amic 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 poly(amic 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. It is worth mentioning that the sulfuric acid solutions of these polymers appeared 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 poly(amic acid) precursors using acetic anhydride and pyridine.

The formation of poly(amine-imide)s was confirmed by means of IR spectroscopy and elemental analysis, with some deviation in carbon analysis being noticed between the calculated and observed values.

Properties of Polymers

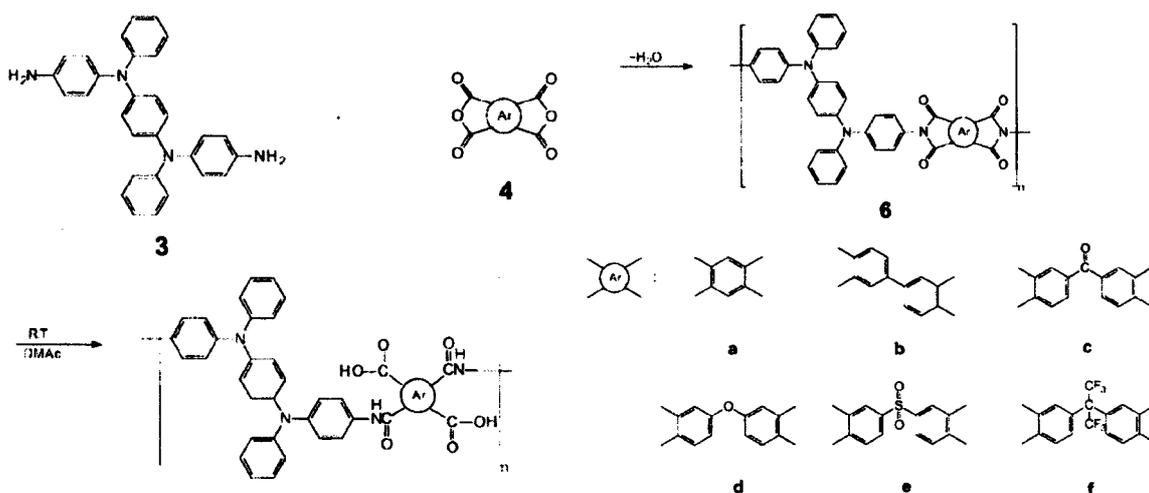
The color of poly(amine-imide) films depends markedly on the chemical structure of dianhydride components. Thus, the films of poly(amine-imide)s **6a-d** were from dark red to almost black, while the films of poly(amine-imide)s **6e** and **6f** had pale brown color. The dark red to almost black color of the films can be attributed to charge transfer complexing between electron donating triphenylamine unit and strongly electron accepting pyromellitimide or phthalimide unit. As mentioned above, all the aromatic poly(amine-imide)s could afford flexible and tough films. These films were subjected to tensile testing, and the tensile strengths, 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 was studied qualitatively, and the results are listed in Table 2. 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 ODPDA, 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 the present polymers potential candidates for practical applications in spin-on and casting processes. In addition, the poly(amine-imide)s prepared by the chemical imidization procedure had better solubility compared with those by the thermal imidization method. 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 resulted in some degree of ordering due to molecular aggregation of polymer chain segments.

Thermal properties of these poly(amine-imide)s are summarized in Table 2. All of the poly(amine-imide)s showed 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 in air were recorded in the range of 559-627 °C 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) 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 2),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 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) (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. In all cases, the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments (Table 2). It can be noticed that 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 thermoforming technique.

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Scheme 1. Synthesis of polyimides by two-step method.

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

Tow-Step Method		One-Step Method	
Poly(amic acid)		Polyimide	
Code	η_{inh}^a (dL/g)	Code	η_{inh}^b (dL/g)
5a	1.86	6a	0.50
5b	1.10	6b	0.45
5c	1.09	6c	0.48
5d	0.71	6d	0.30
5e	0.91	6e	0.27 (0.36) ^a
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.

Table 2. 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% wt loss (°C) ^c		T_d at 10% wt 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

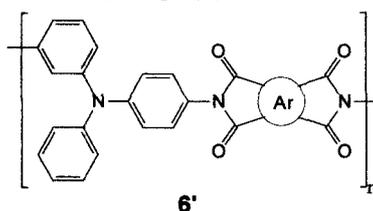
^a Glass transition temperature, taken as the midpoint temperature of the baseline shift on the DSC heating trace (scan rate = 20 °C/min) after quenching from 400 °C.

^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_g s of analogous poly(amine-imide)s (**6'**) as in the **6** series (see ref. 14).

**Table 3.** 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 4. Solubility of Aromatic Poly(amine-imide)s^a

Polymer	Method of Preparation ^b	Solvent ^c						
		NMP	DMAc	DMF	DMSO	<i>m</i> -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