

Preparation and Characterization of Organosoluble Polyimides Based on 1,1-Bis[4-(3,4-aminophenoxy)phenyl]cyclohexane and Commercial Aromatic Dianhydrides

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ABSTRACT: A bis(ether amine) **III-A** containing a cyclohexane cardo group, 1,1-bis[4-(4-aminophenoxy)phenyl]cyclohexane, was synthesized and used as a monomer to prepare polyimides **VI-A** with six commercial dianhydrides via three different procedures. The intermediate poly(amic acid)s had inherent viscosities of 0.83–1.69 dL g⁻¹ and were thermally or chemically converted into polyimides. Polyimides were also prepared by high-temperature direct polymerization in *m*-cresol and had inherent viscosities higher than the thermally or chemically cyclodehydrated ones. To improve the solubility of polyimides, six copolyimides were also synthesized from bis(ether amine) **III-A** with a pair of dianhydrides, which contained 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride or 4,4'-hexafluoroisopropylidenediphthalic anhydride. Series **VI-A** polyimides were characterized by the good physical properties of their film-forming ability, thermal stability, and tensile properties. A comparative study of the properties, with the corresponding polyimides derived from 2,2-bis[4-(4-aminophenoxy)phenyl]propane, is also presented. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2750–2759, 2001

Key words: copolymerization; high-performance polymers; polyimides; thermal properties

INTRODUCTION

Aromatic polyimides have found wide usage as films, as coatings, in gas separation, and as complex materials due to their outstanding thermal behavior combined with their excellent mechanical and electrical properties, gas-separation capability, and radiation resistance.^{1,2} However, their combination of properties made rigid aromatic

polyimides essentially difficult to fabricate in the melt or with a solvent. Broad applications of these polyimides have generally been reduced by the limited solubility in common solvents. Thus, they must be processed as their unstable precursors [poly(amic acid)s]. There has been considerable research carried out and aimed at developing aromatic polyimides that are processed in the fully imidized form.^{3–7} Introduction of flexible chains (ether linkage) or bulk groups (cardo group) into polyimides could make their polymer backbones more flexible and decrease the packing density of polymers, so that their solubility in organic solvents are improved significantly without an unacceptable loss of thermal properties.^{8–15}

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Therefore, the preparation of soluble and/or thermoplastic polyimides has been a major research interest. To accomplish this goal, many attempts have been made with the aim of synthetic modification. Bis(ether amine) and its polymers with cardo-based aromatics were developed by our laboratory.^{16–21} In addition to bulky non-linear monomers, pendent aromatic cardo groups can also be used to disrupt crystallinity and obtain almost completely amorphous polymers. These polymers were found to have good thermal stabilities, and they could be processed easily by dissolving them in polar organic solvents. The polymers with aliphatic cardo groups, such as the cyclohexane group, could be prepared from 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC) by polycondensation as well as bisphenol A to form polyarylates, polyethers, and polycarbonates, etc.^{22–24} Although 1,1-bis[4-(4-aminophenoxy)phenyl]cyclohexane (BAPC) prepared from BHPC has been reported, and is used in epoxy resins as the curing agent, etc.,^{25–27} clear reports for the syntheses of polyimides are not available. The present study focused on the syntheses and characterizations of polyimides **VI-A** with the cyclohexyl cardo unit by three different methods, and their properties are compared with polyimides **VI-B** having an isopropyl unit. Polyimides with poor solubility could be improved by copolymerization by mixing with a molar ratio of dianhydrides during copolymerization.

EXPERIMENTAL

Materials

BHPC (**I**, from TCI), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**III-B**, from Chriskev Corp.), and *p*-chloronitrobenzene (from TCI, Tokyo, Japan) were used as received. Pyromellitic dianhydride (**VI_a**, PMDA, from TCI), 3,3',4,4'-biphenyltetracarboxylic dianhydride (**IV_b**, BPDA, from Chriskev, Leawood, KS), 4,4'-oxydiphthalic anhydride (**IV_c**, ODPDA, from Chriskev), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (**IV_d**, BTDA, from Chriskev), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (**IV_e**, DSDA, from New Japan Chemical Co., Osaka, Japan), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (**IV_f**, 6FDA, from Chriskev) were recrystallized from acetic anhydride prior to use. Hydrazine monohydrate, *N,N*-dimethylformamide (DMF, from Fluka, Tokyo, Japan), *N,N*-dimethylacetamide (DMAc, from Fluka), and

N-methyl-2-pyrrolidone (NMP, from Fluka) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Synthesis of 1,1-Bis[4-(4-aminophenoxy)phenyl]cyclohexane (**III-A**)

Bis(ether amine) **III-A** (mp 157°C) was synthesized through nucleophilic substitution reaction of BHPC (**I**) and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction with a 10% Pd—C catalyst and hydrazine hydrate according to our previous study.²⁸

IR (KBr): 3460 and 3360 (primary N—H stretching), 3040 (aromatic C—H stretching), 2932 and 2858 (aliphatic C—H stretching), 1623 (N—H bending), 1502 (aromatic C=C stretching), 1231 (C—N stretching), and 833 cm⁻¹ (N—H out-of-plane bending).

ANAL. Calcd for C₃₀H₃₀N₂O₂ (450.58):C, 79.97%; H, 6.71%; N, 6.22%. Found: C, 79.91%; H, 6.72%; N, 6.20%.

Synthesis of Polyimides

Two-stage Polymerization

Typical examples of the synthesis of the series **VI-A(C)** and **VI-A(T)** are as follows: To a solution of 0.90 g (2.0 mmol) of bis(ether amine) **III-A** in 12.6 mL of dried DMAc in a 50-mL flask, 0.72 g (2.0 mmol) of **VI_e** was added in one portion. The mixture was stirred at room temperature for 1 h to afford a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) **V-A_e** was 1.42 dL g⁻¹, as measured in DMAc at a concentration of 0.5 g dL⁻¹ at 30°C.

- Chemical cyclodehydration: A 1.0-mL mixture of acetic anhydride and pyridine (volume ratio = 2:1) was added to 6.8 g of a poly(amic acid) solution **V-A_e**. The mixture was stirred at 80–100°C for 1 h. The polymer solution was poured into methanol. The fibrous precipitate **VI-A_e(C)** was collected by filtration, washed thoroughly with methanol, and dried at 100°C. The inherent viscosity of the polymer in DMAc was 0.97 dL g⁻¹, measured at a concentration 0.5 g dL⁻¹ at 30°C. The polymer was further baked at 250°C for 30 min to ensure complete cyclization of imide groups.
- Thermal cyclodehydration: The solution of

poly(amic acid) **V-A_e** was spread onto a glass plate, which was placed in an 80°C oven for 1 h to remove the solvent. The semidried poly(amic acid) film was sequentially heated at 120°C for 10 min, 150°C for 10 min, 180°C for 10 min, 210°C for 10 min, and 250°C for 30 min. By soaking in water, a flexible polyimide film of **VI-A_e(T)** was self-stripped off the glass surface. The inherent viscosity of the resulting polyimide in DMAc was 0.76 dL g⁻¹, measured at a concentration 0.5 g dL⁻¹ at 30°C.

Polymerization by Direct Heating in *m*-Cresol

A typical example of polycondensation of series **VI-A(m)** is as follows: To a solution, of **III-A** (0.45 g, 1.0 mmol) in 8.0 mL of *m*-cresol, the dianhydride **IV_e** (0.36 g, 1.0 mmol) was added. The reaction solution was stirred for another 0.5 h at 60°C. The reaction temperature was increased by sequential heating for 15 min at 120, 160, and 180°C. Finally, the reaction mixture was heated at 200°C for 1 h to provide **VI-A_e(m)**. The inherent viscosity of the polyimide in NMP was 1.35 dL g⁻¹, measured at a concentration 0.5 g dL⁻¹ at 30°C.

Characterization

Melting points were measured in capillaries on a Yamato mp apparatus (Model MP-21) without correction. Elemental analyses were run on a Perkin-Elmer Model 2400 C, H, N analyzer. IR spectra were recorded on a Jasco FTIR-7000 Fourier-transform infrared spectrometer. Inherent viscosities were measured with a Cannon-Fenske viscometer at 30°C. Solubilities were determined at 1% (w/w) concentration. Differential scanning calorimetry (DSC) traces were measured on a Sinku Riko 7000 differential scanning calorimeter coupled to a basic component TA 7000 thermal analyzer at the rate of 20°C min⁻¹ in flowing nitrogen (30 cm³ min⁻¹).

Thermogravimetry analysis (TGA) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100; experiments were carried out on 10 ± 2-mg samples heated in flowing nitrogen or air (50 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. An Instron universal tester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the polymer films. A gauge length of 2 cm and a strain rate of 5 cm min⁻¹ were used for this study. Measurements

were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.5 mm thick) and an average of at least five individual determinations was used.

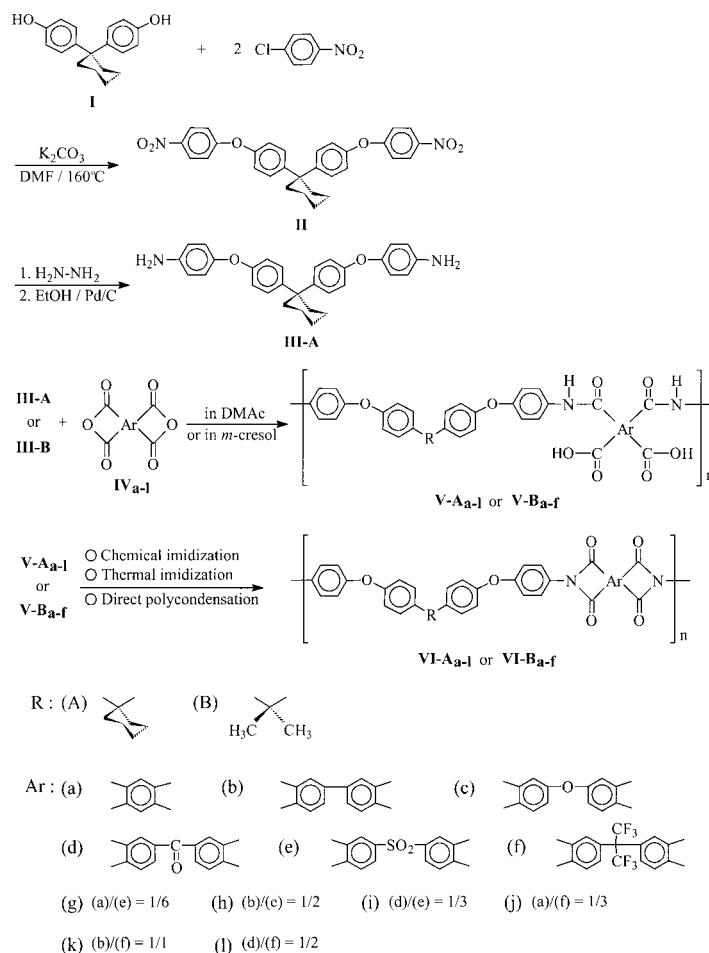
RESULTS AND DISCUSSION

Polymer Synthesis

The cyclohexane-based bis(ether amine) **III-A** was prepared according to the synthetic routes outlined in Scheme 1. An intermediate dinitro compound **II** was synthesized by nucleophilic aromatic halogen displacement of *p*-chloronitrobenzene with BHPC (**I**) in the presence of anhydrous potassium carbonate in DMF. The cyclohexanediamine **III-A** was readily obtained by the catalytic hydrogenation of the intermediate dinitro compound **II** using hydrazine hydrate and Pd/C as the reducing agent in refluxing ethanol. The yield was high (99%) and the purity was also high enough for the preparation of polymers with high molecular weights. As shown in the Experimental section, IR and elemental analysis confirmed the structure of the diamine **III-A**.

In Scheme 1, the cyclohexane cardo-containing polyimides **VI-A_{a-f}** were prepared from bis(ether amine) **III-A** and various aromatic tetracarboxylic dianhydrides **IV_{a-f}** by three different methods. The **VI-A(T)** and **VI-A(C)** were produced using a conventional two-step method. The poly(amic acid)s **V-A** were first synthesized by a ring-opening addition reaction in the DMAc solvent system. For **VI-A(T)**, the poly(amic acid)s were cast and baked into polyimide films by stepwise heating in an air-flowing high-temperature oven. For **VI-A(C)**, the poly(amic acid)s could be converted to the corresponding polyimides by means of chemical imidization using acetic anhydride and pyridine. For comparison, polyimides **VI-B** were also prepared from bis(ether amine) **III-B** with dianhydrides **IV_{a-f}** by the above two same processes. In addition, polymers **VI-A(m)** were obtained utilizing a direct one-step polycondensation in *m*-cresol. The poly(amic acid)s were prepared in the *m*-cresol solvent system; then, polyimides **VI-A(m)** were cyclized by direct heating of poly(amic acid)s in *m*-cresol at 200°C for 1 h.

As shown in Table I, the poly(amic acid) precursors **V-A_{a-1}** exhibited inherent viscosities ranging from 0.83 to 1.69 dL g⁻¹. These poly(amic acid)s were dehydrated to form polyimides that for **VI-A(T)** could afford free-standing films by


Scheme 1 Synthetic process.

solution casting and that for **VI-A(C)** could be stringy using the condensation agent (Py/Ac₂O). The polyimides **VI-A(T)** and **VI-A(C)** exhibited inherent viscosities in the ranges 0.44–0.76 and 0.55–1.34 dL g⁻¹, respectively. The polyimides prepared by chemical dehydration could supply higher molecular weight than could those by thermal dehydration. However, polyimides **VI-A(m)**, which used the direct heating one-step method in *m*-cresol without any catalyst, gave the highest inherent viscosities, ranging from 0.87 to 2.76 dL g⁻¹. The poly(amic acid)s **V-B** also exhibited inherent viscosities ranging from 0.64 to 2.02 dL g⁻¹, indicating medium to high molecular weight. Except for **VI-B_{e,f}**, almost all the other polymers **VI-B** were insoluble in organic solvents. When the inherent viscosities of polymers **VI-B_{a-d}** were measured in concentrated H₂SO₄, the obtained values were very low (approximately 0.1 dL g⁻¹). This may be because polymers were decomposed in concentrated H₂SO₄; therefore, their inherent

viscosities could not be determined in the imidized form. Furthermore, **VI-B_{e,f}(C)** still showed higher inherent viscosities than those of **VI-B_{e,f}(T)**. The elemental analyses of all polyimides listed in Table II were generally in good agreement with the respective structures for hydrogen and nitrogen, while the carbon analysis data were slightly lower than were the theoretical values, a phenomenon common for heat-resistant polymers.^{29,30}

Properties of Polymers

The solubilities of the polyimides and copolyimides were tested qualitatively, and the results are summarized in Table III. With the exception of **VI-A_a** containing PMDA, all the **VI-A** series polymers were soluble in *m*-cresol, but only the polyimides **VI-B_{e,f}** from DSDA or 6FDA in the **VI-B** series showed comparable solubilities in contrast to the **VI-A** series polyimides. **VI-A_{b-d}** also had

Table I Inherent Viscosities of Poly(amic acid)s and Polyimides

Poly(amic acid)s		Polyimides		
Polymer Code	η_{inh}^a (dL g ⁻¹)	Polymer Code	η_{inh}^a (dL g ⁻¹)	Remark ^b
V-A_a	1.60	VI-A_a(C)	—	Turbid
		VI-A_a(T)	—	Flexible
V-A_b	1.48	VI-A_b(C)	0.99 ^c	Gel
		VI-A_b(T)	0.74 ^c	Flexible
		VI-A_b(m)	2.12	Stringy
V-A_c	0.87	VI-A_c(C)	0.60 ^c	Gel
		VI-A_c(T)	0.45 ^d	Flexible
		VI-A_c(m)	2.76 ^c	Stringy
V-A_d	0.83	VI-A_d(C)	0.55 ^d	Turbid
		VI-A_d(T)	0.44 ^d	Flexible
		VI-A_d(m)	0.87 ^d	Stringy
V-A_e	1.42	VI-A_e(C)	0.97	Homogeneous
		VI-A_e(T)	0.76	Flexible
		VI-A_e(m)	1.35 ^c	Stringy
V-A_f	1.69	VI-A_f(C)	1.34	Homogeneous
		VI-A_f(T)	0.70	Flexible
		VI-A_f(m)	1.50 ^c	Stringy
V-A_g	1.33	VI-A_g(C)	0.84	Stringy
V-A_h	1.28	VI-A_h(C)	0.84	Stringy
V-A_i	1.09	VI-A_i(C)	0.94	Stringy
V-A_j	1.11	VI-A_j(C)	0.92	Stringy
V-A_k	1.42	VI-A_k(C)	1.07	Stringy
V-A_l	1.38	VI-A_l(C)	0.83	Stringy
V-B_a	1.62	VI-B_a(C)	—	Turbid
		VI-B_a(T)	—	Flexible
V-B_b	2.02	VI-B_b(C)	—	Gel
		VI-B_b(T)	—	Flexible
		VI-B_b(m)	—	Flexible
V-B_c	0.77	VI-B_c(C)	0.48 ^c	Gel
		VI-B_c(T)	—	Flexible
V-B_d	0.64	VI-B_d(C)	—	Turbid
		VI-B_d(T)	—	Flexible
V-B_e	1.23	VI-B_e(C)	0.96	Homogeneous
		VI-B_e(T)	0.80	Flexible
V-B_f	1.82	VI-B_f(C)	1.44	Homogeneous
		VI-B_f(T)	1.05	Flexible

^a Measured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C.

^b Appearance of the polyimide solution during chemical cyclodehydration, film quality of thermal cyclodehydration, and the polymer product of *m*-cresol polycondensation when precipitated in stirred methanol.

^c Measured at a concentration of 0.5 g dL⁻¹ in NMP at 30°C.

^d Measured at a concentration of 0.5 g dL⁻¹ in *m*-cresol at 30°C.

better solubility in NMP than that of **VI-B_{b-d}**. Therefore, the organosolubility of polyimides containing the cyclohexane cardo structure was better than that of the isopropyl group-bearing polyimides. From the results in Table III, the solubilities of polyimides, which were prepared from **III-A** and various dianhydrides, were in the order of **VI-A_f** > **VI-A_e** > **VI-A_b** > **VI-A_c** > **VI-A_d**

> **VI-A_a**, depending on the structure of dianhydride component. Polyimides with 6FDA and DSDA had the best solubility, polyimide with PMDA exhibited the poorest solubility, and the remaining polyimides had limited solubility which might be insufficient for processing.

Because four of the polyimides **VI-A** showed limited solubility, we investigated the possibility

Table II Elemental Analysis of Polyimides

Polymer Code	Formula (Molecular Weight)		Elemental Analysis (%)		
			C	H	N
VI-A_a	$(C_{40}H_{28}N_2O_6)_n$ (632.67) _n	Calcd	75.94	4.46	4.43
		Found	74.95	4.63	4.39
VI-A_b	$(C_{46}H_{32}N_2O_6)_n$ (708.77) _n	Calcd	77.95	4.55	3.95
		Found	76.30	4.39	3.74
VI-A_c	$(C_{46}H_{32}N_2O_7)_n$ (724.77) _n	Calcd	76.23	4.45	3.87
		Found	75.36	4.52	3.74
VI-A_d	$(C_{47}H_{32}N_2O_7)_n$ (736.78) _n	Calcd	76.62	4.38	3.80
		Found	75.46	4.42	3.80
VI-A_e	$(C_{46}H_{32}N_2O_8S)_n$ (772.83) _n	Calcd	71.49	4.17	3.62
		Found	70.42	4.31	3.63
VI-A_f	$(C_{49}H_{32}N_2O_6F_6)_n$ (858.79) _n	Calcd	68.53	3.76	3.26
		Found	67.75	3.83	3.30
VI-B_a	$(C_{37}H_{24}N_2O_6)_n$ (592.61) _n	Calcd	74.99	4.08	4.73
		Found	73.85	4.36	4.83
VI-B_b	$(C_{43}H_{28}N_2O_6)_n$ (668.71) _n	Calcd	77.23	4.22	4.19
		Found	76.24	4.32	4.17
VI-B_c	$(C_{43}H_{28}N_2O_7)_n$ (684.70) _n	Calcd	75.43	4.12	4.09
		Found	74.47	4.35	4.00
VI-B_d	$(C_{44}H_{28}N_2O_7)_n$ (696.72) _n	Calcd	75.85	4.05	4.02
		Found	74.75	4.18	4.00
VI-B_e	$(C_{43}H_{28}N_2O_8S)_n$ (732.76) _n	Calcd	70.48	3.85	3.82
		Found	69.38	3.98	3.80
VI-B_f	$(C_{46}H_{28}N_2O_6F_6)_n$ (818.73) _n	Calcd	67.48	3.45	3.42
		Found	66.85	3.55	3.38

The polyimides are thermally imidized samples.

of preparing soluble polyimides by carrying out the copolymerization of dianhydrides of both high- and low-solubility polyimides with **III-A**. DSDA and 6FDA, containing the sulfonyl and hexafluoroisopropyl groups, were first each mixed with the rest of the dianhydrides at varying molar ratios before reacting with **III-A**. The obtained copolyimides **VI-A_{g-1}(C)** could be modified into easily soluble polymers, and their solubilities could be changed arbitrarily, depending on the change in the matching proportion. Among these copolymers, copolyimide **VI-A_g**, which was formed from those mixed by rigid PMDA (**IV_a**) and DSDA (**IV_e**), needed a larger molar ratio of **IV_a:IV_e** to reach 1:6, so that **VI-A_g** could dissolve easily in the test solvents. When 6FDA (**IV_f**), which led to easily soluble polyimides even in halogenated hydrocarbons like CH₂Cl₂ and CHCl₃, replaced DSDA in the copolymerization reaction, the resulting copolymer **VI-A_j** exhibited good solubility with a lower molar ratio than that of **VI-A_g**.

Polyimides **VI-A(C)**, **VI-A(T)**, and **VI-A(m)** revealed different solubilities due to different synthesis methods. **VI-A(m)**, obtained from the *m*-cresol system, showed better solubility than that of the others. This may be attributable to the slower imidization rate of **VI-A(m)**, which avoided formation of intermolecular links of poly(amic acid)s during direct polycondensation. The solubilities of **VI-A(T)**, formed through thermal cyclodehydration, also were poorer than were those of **VI-A(C)** formed through chemical cyclodehydration. This may be due to the films, through thermal cyclodehydration, being denser, so that the dissolving rates were slower than were those obtained through chemical cyclodehydration. Furthermore, the fast rate of thermal cyclization might produce crosslinks under the solid-state baking conditions, so that **VI-A(T)** exhibited the lowest solubility among the three methods.

Good-quality and creasable polyimide films could be made through thermal cyclodehydration.

Table III Solubility Behavior of Polyimides

Polymer Code	Solvent ^a								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	THF	CH ₂ Cl ₂	CHCl ₃
VI-A _a (C)	-	-	-	-	-	-	-	-	-
VI-A _a (T)	-	-	-	-	-	-	-	-	-
VI-A _b (C)	+	+h	-	-	+	-	-	-	-
VI-A _b (T)	+	-	-	-	+	-	-	-	-
VI-A _b (<i>m</i>)	+	+	-	-	+	+	-	-	-
VI-A _c (C)	+	-	-	-	+	-	-	-	-
VI-A _c (T)	+h	-	-	-	+	-	-	-	-
VI-A _c (<i>m</i>)	+	+h	-	-	+	+	-	-	-
VI-A _d (C)	+h	-	-	-	+	-	-	-	-
VI-A _d (T)	-	-	-	-	+	-	-	-	-
VI-A _d (<i>m</i>)	-	-	-	-	+	-	-	-	-
VI-A _e (C)	+	+	+	+	+	+	+	-	-
VI-A _e (T)	+	+	+	+	+	+	-	-	-
VI-A _e (<i>m</i>)	+	+	+	+	+	+	+	+	+
VI-A _f (C)	+	+	+	+	+	+	+	+	+
VI-A _f (T)	+	+	+	+	+	+	+	+	+
VI-A _f (<i>m</i>)	+	+	+	+	+	+	+	+	+
VI-A _g (C)	+	+	+	+	+	+	-	-	-
VI-A _h (C)	+	+	+	+	+	+	-	-	-
VI-A _i (C)	+	+	+	+	+	+	-	-	-
VI-A _j (C)	+	+	+	+	+	+	+	+	+
VI-A _k (C)	+	+	+	+	+	+	+	+	+
VI-A _l (C)	+	+	+	+	+	+	+	+	+
VI-B _a (C)	-	-	-	-	-	-	-	-	-
VI-B _a (T)	-	-	-	-	-	-	-	-	-
VI-B _b (C)	-	-	-	-	-	-	-	-	-
VI-B _b (T)	-	-	-	-	-	-	-	-	-
VI-B _c (C)	+	-	-	-	+	-	-	-	-
VI-B _c (T)	-	-	-	-	-	-	-	-	-
VI-B _d (C)	-	-	-	-	-	-	-	-	-
VI-B _d (T)	-	-	-	-	-	-	-	-	-
VI-B _e (C)	+	+	+	+	+	+	-	-	-
VI-B _e (T)	+	+	+	+	+	+	-	-	-
VI-B _f (C)	+	+	+	+	+	+	+	+	+
VI-B _f (T)	+	+	+	+	+	+	+	+	+

+, Soluble at room temperature; +h, soluble on heating; -, insoluble even on heating.

^a NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine; THF: tetrahydrofuran.

These films were subjected to a tensile test, and their tensile properties are summarized in Table IV. The tensile strength of **VI-A** was in the range of 80–110 MPa and was larger than that of **VI-B**, between 76 to 99 MPa. In series **VI-A**, only **VI-A_d** appeared to have a yield point on the stress–strain curve; however, four polymers in series **VI-B** exhibited yield strengths from 82 to 106 MPa. Both the elongations to break or the initial moduli of polymers **VI-B** were close to or larger than those of polymers **VI-A**. From the above

results, the **VI-B** films had stronger and tougher properties than those of the **VI-A** films. This can be due to the presence of the hindered cyclohexane cardo group in polyimides **VI-A**. The introduction of the large pendent unit seems to cause a decrease of both strength and toughness due to the decreased packing density of the molecular chain, which was strongly affected by the intermolecular interactions. However, the **VI-A** series was strong and tough enough for useful polymer materials.

Table IV Tensile Properties of Polyimide Films

Polymer Code	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
VI-A_a	—	80	9	1.83
VI-A_b	—	109	13	1.75
VI-A_c	—	105	12	1.72
VI-A_d	117	110	12	2.18
VI-A_e	—	105	13	1.88
VI-A_f	—	108	10	1.94
VI-B_a	82	76	26	1.90
VI-B_b	—	99	37	2.16
VI-B_c	93	91	11	2.05
VI-B_d	95	89	16	2.22
VI-B_e	—	94	7	2.38
VI-B_f	106	96	26	2.10

Polyimide films obtained by the thermal cyclodehydration method.

Thermal properties of all the polyimides were evaluated by thermogravimetry (TG) and DSC. The thermal behavior data of all the polymers are summarized in Table V. DSC measurements were conducted with a heating rate of 20°C min⁻¹ in nitrogen. Quenching from elevated temperatures (approximately 400°C) to room temperature in air gave predominantly amorphous samples so that

the glass transition temperatures (T_g) of most polyimides could be easily measured in the second heating traces of DSC. As shown in Table V, no discernible T_g was observed for **VI-A_a** and **VI-B_a** synthesized from rigid PMDA, and the T_g values of the rest of the polyimides stayed in the range of 230–266 g⁻¹. Polyimides **VI-A** displayed T_g values comparable with corresponding polyimides

Table V Thermal Properties of Polyimides

Polymer Code	TGA			
	DSC	Decomposition Temperature ^b (°C)		Weight Percent Residue at 800°C in N ₂
	T_g^a (°C)	In Nitrogen	In Air	
VI-A_a	—	525	503	48
VI-A_b	262	549	533	58
VI-A_c	230	532	536	54
VI-A_d	240	526	495	58
VI-A_e	266	538	533	45
VI-A_f	252	535	527	56
VI-B_a	—	552	548	55
VI-B_b	252	567	561	62
VI-B_c	232	552	554	55
VI-B_d	237	551	551	63
VI-B_e	263	522	525	47
VI-B_f	250	556	549	59

Thermally imidized samples.

^a From the second heating traces of DSC measurements conducted with a heating rate of 20°C min⁻¹ in nitrogen.

^b Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20°C min⁻¹.

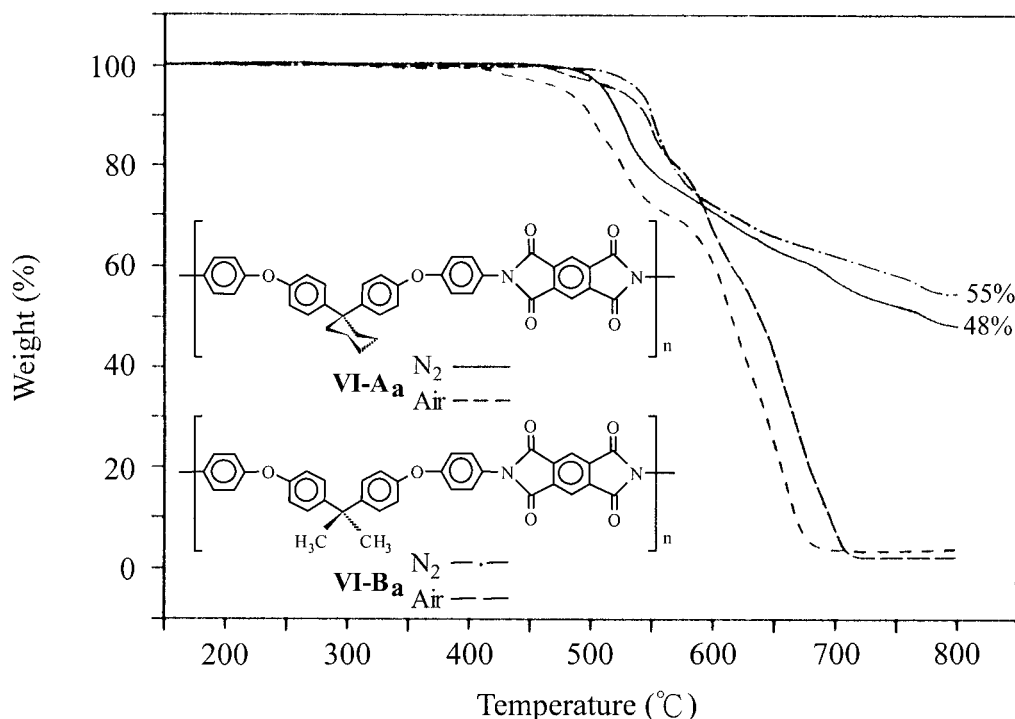


Figure 1 TGA curves of polyimides **VI-A_a** and **VI-B_a** at a heating rate of $20^{\circ}\text{C min}^{-1}$.

VI-B, indicating that the aliphatic cardo ring did not affect significantly the polymer glass transition temperature. The T_g values depended upon the structure of the dianhydride component. As expected, polyimides **VI-A_c** and **VI-B_c** derived from ODPa showed the lowest T_g values in both series because of the presence of a flexible ether bridge between the phthalimide units, and polyimides **VI-A_{b,e}** and **VI-B_e**, derived from BPDA and DSDA, exhibited higher T_g values due to the rigid biphenyl unit and polar sulfonyl group, respectively.

The thermal stability of the polyimides was characterized by TG analysis conducted at a heating rate of $20^{\circ}\text{C min}^{-1}$. The temperatures for 10% weight loss (T_{10}), in nitrogen and air atmospheres, were determined from original thermograms and are also tabulated in Table V. Figure 1 shows typical TG curves for the representative polyimides **VI-A_a** and **VI-B_a** in nitrogen and air atmospheres. Almost all polyimides showed similar decomposition behavior and did not degrade noticeably below 400°C in air or nitrogen. When the temperature exceeded 570°C , the degradation rate in nitrogen slowed; however, the rate in air remained fast. The T_{10} values of series **VI-A** stayed in the range from 525 to 549°C in nitrogen and from 495 to 536°C in the air, which are rea-

sonable values considering the aliphatic content of these polyimides. The anaerobic char yields, of these cardo group-containing polyimides in a nitrogen atmosphere, were in the range of 45–58% even at 800°C . On comparing the thermal properties of polymers **VI-A** with their analogous **VI-B**, the T_{10} values of almost all polyimides **VI-A** were slightly lower than were those of the **VI-B** series in both air and nitrogen atmospheres, and the **VI-B** series polyimides left higher char yields at 800°C in nitrogen. The lower thermal stability of series **VI-A** may be accounted for by their higher percentages of less stable aliphatic segments. In addition, the degradation seems to start by the breaking of the pendant aliphatic groups and, hence, the structure of the dianhydride does not seem to influence the thermal stability.

CONCLUSIONS

A series of novel polyimides was synthesized from commercial dianhydrides and bis(ether amine) **III-A** containing the cyclohexylidene cardo group. Dianhydrides PMDA, BPDA, ODPa, and BTDA with diamine **III-A** gave low-solubility polyimides, but easily soluble copolyimides were synthesized by copolymerizing diamine **III-A** with a

mixture of these dianhydrides and DSDA (or 6FDA). Polyimides, synthesized by direct polymerization in *m*-cresol, had higher inherent viscosities and better organosolubilities than those from thermal or chemical cyclodehydration of poly(amic acid)s in two steps. The polyimides showed a reasonable level of thermal stability and exhibited moderate glass transition temperatures, which are advantageous in the processing of these polymers.

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