Synthesis and Properties of Novel Aromatic Polyimides Derived from Bis(p-aminophenoxy)methylphenylsilane

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SYNOPSIS

A novel siloxane-containing diamine, bis(p-aminophenoxy)methylphenylsilane (BAMPS), was synthesized from the condensation of dichloromethylphenylsilane with p-aminophenol in the presence of triethylamine. A series of BAMPS-based aromatic polyimides were prepared from BAMPS and various aromatic tetracarboxylic dianhydrides by the usual two-step procedure including ring-opening polyaddition to poly(amic acid)s and subsequent cyclodehydration to polyimides. The inherent viscosities of poly(amic acid)s III_a–III_f ranged from 0.09 to 0.36 dL g^{-1} in N,N-dimethylacetamide at a concentration of 0.5 g dL^{-1} at 30°C. The inherent viscosities of polyimides were between 0.06 and 0.32 dL g^{-1} in various solvents at 30°C. Polyimides, especially IV_c and IV_f, were soluble in a wide range of organic solvents such as N-methyl-2-pyrrolidinone, concentrated H_2SO_4, N,N-dimethylacetamide, N,N-dimethylformamide, and dimethyl sulfoxide. The polyimides were characterized by elementary analysis, IR spectra, TGA, and DSC. They also had glass transition temperatures ranging from 128 to 181°C. The 10% mass loss temperature was recorded in the range of 404–443°C in nitrogen and of 315–339°C in oxygen. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides have become an increasingly important class of materials for their outstanding physical properties and are widely used, especially in aerospace and electrical/electronic applications.[1-6] Polyimides usually have very bulky and rigid backbone structures, which means that they also have very high glass transition temperatures, and are often insoluble in most organic solvents in their fully imidized form, making them extremely difficult to fabricate. In the literature, a considerable effort has been spent on combining siloxanes with polyimides, which afforded new copolymers possessing good solubility, a low dielectric constant, low water absorption, and an excellent adhesive property.[7-16] More recently, a photosensitive siloxane-containing polyimide derived from bis(p-aminophenoxy)dimethylsilane was also prepared.[17,18] It is of interest to synthesize a new monomer, which contains a siloxane bond for the

sake of soluble aromatic polyimides. The present article describes the synthesis and characterization of novel polyimides derived from bis(p-aminophenoxy)methylphenylsilane (BAMPS) and various tetracarboxylic dianhydrides. Both chemical and thermal cyclodehydrations were performed in this article. Percent imidizations of polyimides were examined. The solubilities and thermal properties were also investigated and are discussed.

EXPERIMENTAL

Materials

Dichloromethylphenylsilane and p-aminophenol (from Merck) were used as received. Triethylamine (TEA, from Riedel-de Haen) was dried over sodium before use. Reagent-grade aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA, II_a, from TCI), 3,3′4,4′-biphenyltetracarboxylic dianhydride (BPDA, II_b, from CHRISKEV), 4,4′-oxydiphthalic anhydride (ODPA, II_c, from CHRISKEV), 3,3′,4,4′-benzophenonetetra-
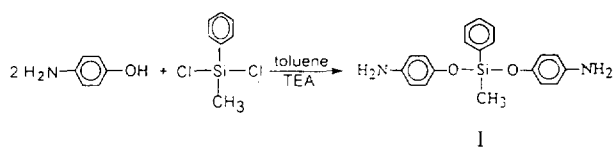
Scheme 1

carboxylic dianhydride (BTDA, **II$_d$**, from TCI), 4,4′-sulfonyldiphthalic anhydride (SDPA, **II$_e$**, from New Japan Chemical Co.), and 4,4′-hexafluoroisopropylidenebisphathalic anhydride (6FDA, **II$_f$**, from CHRISKEV) were recrystallized from acetic anhydride before use. N,N-Dimethylacetamide (DMAc) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Acetic anhydride was purified by vacuum distillation.

Preparation of BAMPS

Dichloromethylphenylsilane (8.12 mL, 50 mmol) was added dropwise to a well-stirred slurry mixture of p-aminophenol (10.92 g, 100 mmol), anhydrous triethylamine (15.26 g, excess 10%), and 200 mL fresh distilled toluene at room temperature in a 500 mL three-necked flask which was dried, purged with nitrogen, and fitted with a mechanical stirrer and a condenser. After the addition, the mixture was then heated to a gentle reflux and was continuously stirred for 24 h. The color of the slushy mixture was slightly yellow at first, then it gradually turned brown. When its color turned deep brown, the mixture was cooled to room temperature. The white by-product triethylhydroammonium chloride salt was filtered off quickly to minimize contamination of the product by hydrolysis when the salt is exposed to
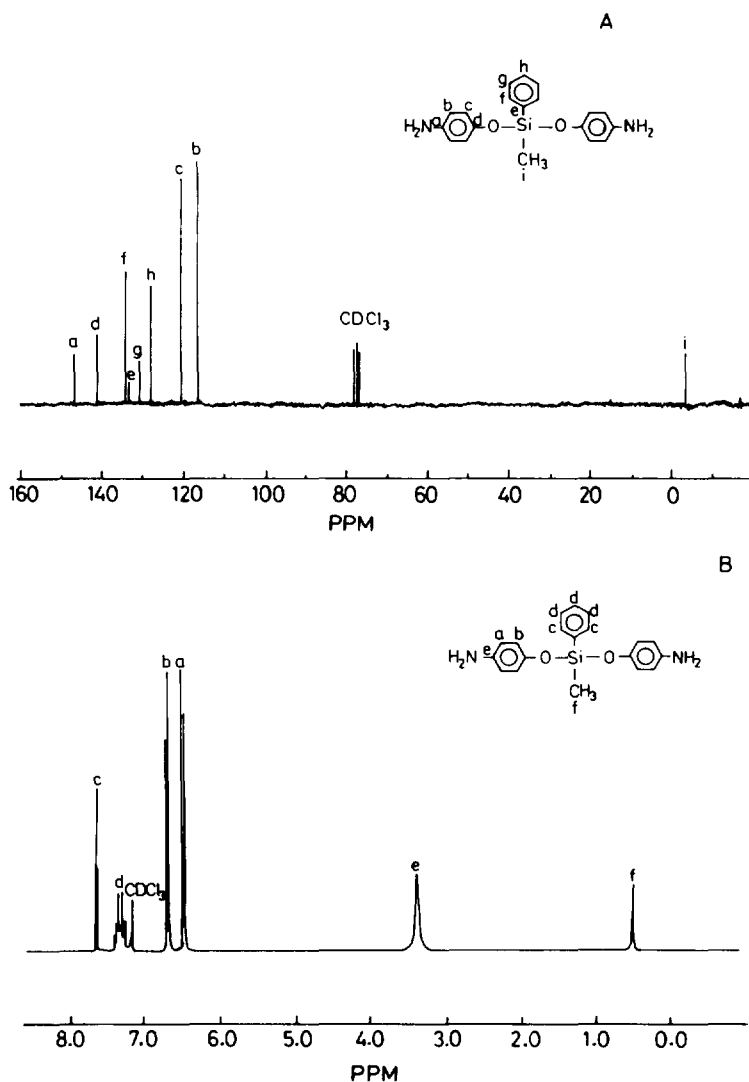

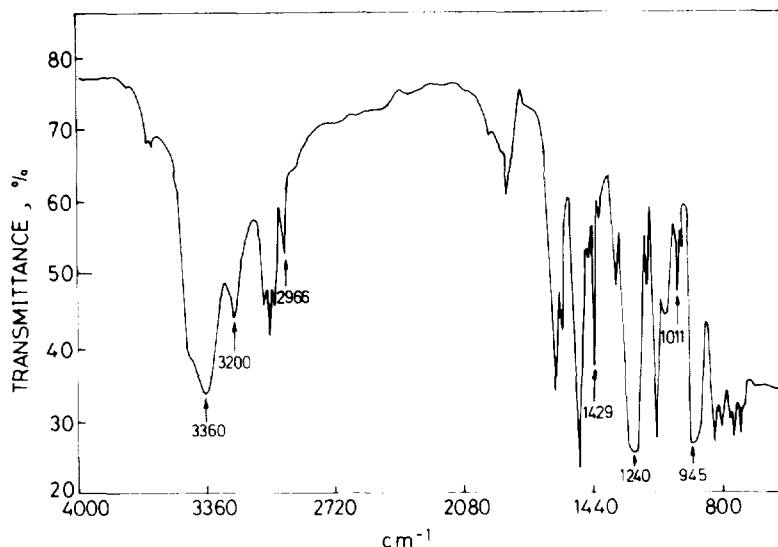**Figure 1** NMR spectra of BAMPS: (A) ^{1}H-NMR; (B) ^{13}C-NMR.

Figure 2   FTIR of BAMPS.

moisture. The viscous crude product, 16.25 g, was recovered after removing the solvent using an evaporator. The crude product was then dissolved in chloroform and filtered. The solvent of the filtrate was removed and the residue was finally dried in a vacuum at 50°C. The final product was a viscous brown oil. Yield = 15.87 g; 94.5%. The monomer was characterized by ^{1}H-NMR(CDCl$_3$ δ/ppm): 0.48
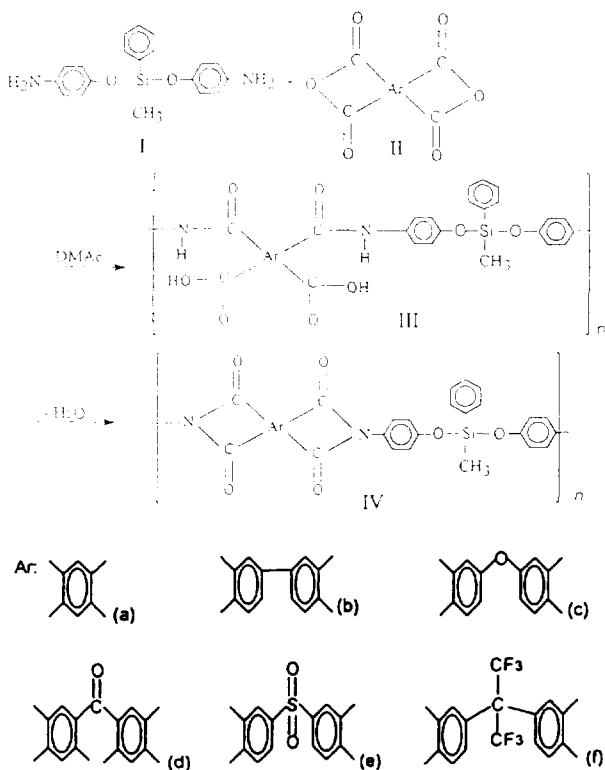

Scheme 2

(s, 3H, Si — CH$_3$), 3.40 (s, 4H, — NH$_2$), 6.52 (d, 4H, aminophenoxy), 6.75 (d, 4H, aminophenoxy), 7.39 (m, 3H, Si—Ph), 7.69 (d, 2H, Si — Ph). ^{13}C-NMR(CDCl$_3$ δ/ppm): -3.78, 116.1, 120.2, 126.5, 127.8, 130.3, 133.4, 134.0, 140.9. IR (ν/cm^{-1}): 3200 and 3360 (— NH$_2$), 2966 and 1240 (Si — CH$_3$), 1429 (Si — Ph), 1011 (Si — O), 945 (Si — O — Ph).

ANAL.: Calcd for C$_{19}$H$_{20}$N$_2$O$_2$Si: C, 64.75%; H, 5.91%; N, 8.28%. Found: C, 64.23%; H, 5.95%; N, 8.34%.

Polymerization

Polyimide (IV$_e$) from BAMPS (I) and SDPA (II$_e$) by Chemical Conversion Method

A typical example of polymerization is as follows: To a constantly stirred solution of BAMPS (3.36 g, 10 mmol) in 54 mL of DMAc, SDPA (3.58 g, 10 mmol) was added in four portions of 90, 5, 3, and 2% within 30 min under an argon atmosphere at room temperature. The solution was stirred and maintained at 50°C overnight; then, the poly(amic acid) was obtained. A mixture of acetic anhydride and pyridine (volume ratio 2 : 1) was added slowly to the obtained poly(amic acid) at 50°C and the resulting solution was held at 105°C for 4 h. In all cases except 6FDA, polymers precipitated during the reaction period. The polymer solution was poured into methanol. The precipitates were collected by filtration, washed thoroughly with methanol and hot water, and dried at 100°C in a vacuum. The inherent viscosity of the chemically imidized polyimide (IV$_e$) in the DMAc solution with a 0.5 g dL^{-1} concentration at 30°C was 0.32 dL g^{-1}. All other polyimides were prepared by the same procedure as above.

Table I Preparation of BAMPS-based Polyimides

Tetracarboxylic Dianhydride	Poly(amic acid)[a]		Polyimide[b]					
	Code	η_{inh}^{c} (dL g^{-1})	Code	η_{inh}^{e} (dL g^{-1})	Elemental Analysis			
						C%	H%	N%
II_a	III_a	0.10	IV_a	0.07	Found	66.77	3.37	5.35
					Calcd	(67.20)	(3.47)	(5.40)
II_b	III_b	0.16	IV_b	0.06	Found	68.78	3.60	4.78
					Calcd	(70.72)	(3.70)	(4.71)
II_c	III_c	0.09	IV_c	0.12[d]	Found	66.87	3.45	4.83
					Calcd	(68.85)	(3.61)	(4.59)
II_d	III_d	0.12	IV_d	0.08	Found	69.01	3.46	4.55
					Calcd	(69.46)	(3.54)	(4.50)
II_e	III_e	0.36	IV_e	0.32[c]	Found	61.99	3.32	4.26
					Calcd	(63.83)	(3.34)	(4.26)
II_f	III_f	0.16	IV_f	0.08[d]	Found	58.89	2.88	3.88
					Calcd	(60.81)	(2.93)	(3.73)

[a] Polymerization was carried out with equimolar quantities of BAMPS and aromatic dianhydrides to obtain 10 mass % poly(amic acid) solutions.

[b] Obtained by chemical cyclization from the corresponding poly(amic acid)s.

[c] Measured in DMAc at a concentration of 0.5 g dL^{-1} at 30°C.

[d] Measured in DMSO at a concentration of 0.1 g dL^{-1} at 30°C.

[e] Measured in concd H$_2$SO$_4$ at a concentration of 0.5 g dL^{-1} at 30°C.

Polyimide (IV_e) from BAMPS (I) and SDPA (II_e) by Thermal Conversion Method

The poly(amic acid) solutions were prepared by the same procedure as that of the chemical conversion method. The poly(amic acid) solutions obtained were then cast on KBr and the solvent was removed at 80°C for 1 h. Imidization was carried out by thermal cyclodehydration of the poly(amic acid) film by sequential heating at 150, 180, 230, and 250°C for 15 min each.

Measurements

Elemental analyses were run in a Perkin-Elmer Model 240 C, H, N analyzer. An infrared spectrophotometer (Bio-Rad FTS 165) was utilized to identify the structures of these polymers. ^{1}H- and ^{13}C-NMR spectra were measured at room temperature on a Bruker 300 MHz NMR spectrometer. Inherent viscosities of all polymers were determined at 30°C on solutions at a concentration 0.1 or 0.5 g dL^{-1} in DMSO, DMAc, or concentrated sulfuric acid according to their solubilities using a Ubbelohode viscometer. Since polyimides (IV_a, IV_b, and IV_c) were insoluble in DMAc even at a concentration of 0.1 g dL^{-1} at 30°C, inherent viscosities of these polyimides were measured in concentrated H$_2$SO$_4$ of 0.5 g dL^{-1}. Thermogravimetric data were obtained on a DuPont 9900 in flowing nitrogen (100 cm^3

min^{-1}) at a heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter in flowing nitrogen (30 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}.

RESULTS AND DISCUSSION

Monomer Synthesis

BAMPS, a new siloxane-containing oily diamine, was synthesized via direct condensation of p-aminophenol and dichloromethyl–phenylsilane in the presence of triethylamine (Scheme 1). The structure of this diamine was confirmed by elementary analysis, IR, and ^{1}H- and ^{13}C-NMR spectroscopy and the results were in good agreement with the proposed structures (Scheme 1). The ^{1}H- and ^{13}C-NMR spectra of BAMPS are shown in Figure 1, and the IR spectrum, in Figure 2 (vide supra).
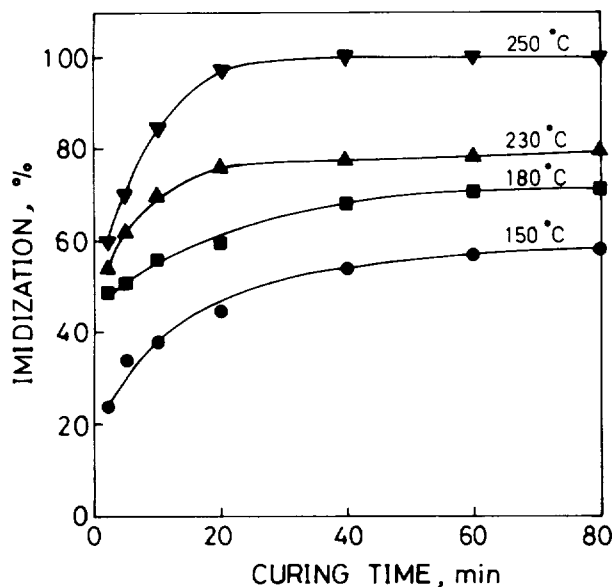
Preparation of Polymers

To obtain high molar mass poly(amic acid)s, it was necessary to remove the moisture from the reaction system. The process of monomer addition in a polar solvent plays an important role for the preparation of poly(amic acid)s from aromatic diamine and dianhydrides[1,19,20] (Scheme 2). BAMPS was first dis-
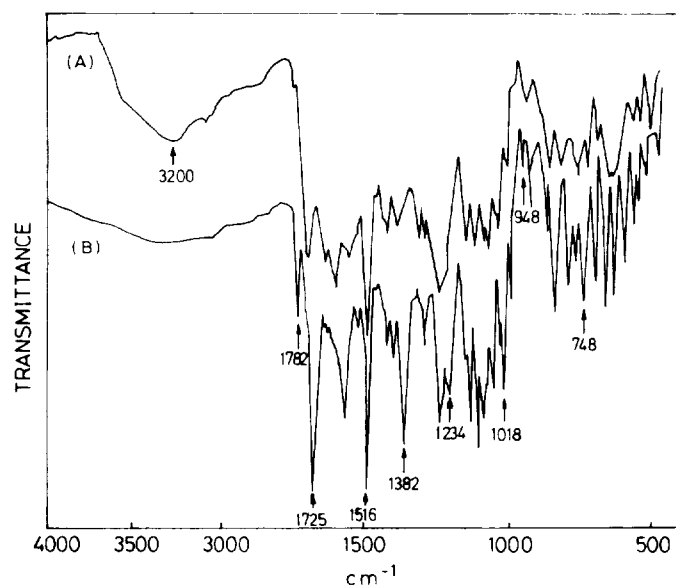
Figure 3   (A) IR spectra of poly(amic acid) **III_e** and (B) the corresponding polyimide **IV_e** by thermal cyclodehydration.

solved in DMAc; then, dianhydride was added in four portions of 90, 5, 3, and 2% within 30 min. By means of this addition process, the viscosity of poly(amic acid)s was found to be increased effectively.[20] The inherent viscosities of all poly(amic acid)s together with those of the corresponding polyimides are summarized in Table I. The poly(amic acid)s had inherent viscosities in the range $0.09-0.36$ dL g^{-1}. Among them, the poly(amic acid) **III_e** exhibited the highest inherent viscosity. The inherent viscosities of the polyimides measured in DMSO, DMAc, or concentrated

Figure 4   Percent imidizations of polyimides **IV_a** versus time at various temperatures.

H_2SO_4 ranged from 0.06 to 0.32 dL g^{-1} (Table I). The inherent viscosity values of siloxane-containing polyimides were found to be lower than the usual aromatic polyimides.[19,20] This phenomenon had been described in several polymer systems which contain the Si — O — Ph structure, such as polyoxy-aryleneoxydisilanes[21] and polyimides[18] derived from bis(p-aminophenoxy)dimethylsilane. Table I also lists the results of elemental analysis, which were generally in good agreement with their respective structures for hydrogen and nitrogen, while values are below the theoretical ones for carbon, which is a phenomenon common to high-temperature polyimides.[22]

Figure 3 shows the IR spectra of the representative poly(amic acid) **III_e** and the corresponding polyimide **IV_e** by thermal cyclodehydration. The poly(amic acid) revealed characteristic absorptions at around 3200 and 1550–1650 cm^{-1}. These bands disappeared entirely after cyclodehydration, while the absorption of the imide ring appeared at 1782 and 1725 (asymmetrical C $=$ O stretching), 1382 (C — N stretching), 748 (ring deformation), 1234 (Si — CH$_3$), 1018 (Si — O), and 948 cm^{-1} (Si — O — Ph). The thermal conversion of poly(amic acid) to polyimide was monitored by IR spectroscopy. The IR films were prepared by casting 5 mass % poly(amic acid) solutions in DMAc onto KBr and heated at 80°C in a hot-air oven for about 1 h. These films were subsequently dried and imidized by various controlled thermal treatments in IR spectroscopy equipped with a hot stage under a nitrogen atmosphere. The degree of imidization was analyzed by FTIR by the band ratio method.[23] The

Table II   Solubility of BAMPS-based Polyimides

| Polymer | Solvent[a] | | | | | | | |
	DMAc	NMP	DMF	conc.H$_2$SO$_4$	THF	Toluene	m-Cresol	DMSO
IV$_a$	+−	+−	+−	++	+−	+−	+−	+−
IV$_b$	+−	+−	+	++	+	+−	++	+−
IV$_c$	+−	+	+	++	+−	+−	+−	+
IV$_d$	+−	+−	+−	++	+−	+−	+−	+−
IV$_e$	++	+−	+−	++	+−	+	+	++
IV$_f$	++	++	++	++	++	++	++	++

Polyimides obtained by chemical cyclohydration from poly(amic acid)s.

[a] ++, soluble at room temperature; +, soluble on heating; +−, partial soluble on heating; −, insoluble. Abbreviations: DMAc, N,N-dimethylacetamide; NMP, N-methyl-2-pyrrolidinone; DMF, N,N-dimethyl-formamide; DMSO, dimethyl sulfoxide.

absorption peak at 1782 cm^{-1} of the asymmetric carbonyl stretching was ratioed with a reference peak at 1516 cm^{-1} (aromatic stretching).

The percent imidization of poly(amic acid) was calculated by the following equation:

Percent imidization

$$= \frac{[A(1)/A(2)]_t - [A(1)/A(2)]_{t=0}}{A(1)/A(2)]_{t=\infty} - [A(1)/A(2)]_{t=0}}$$

where $A(1)$ = the absorbance of the imide peak at 1782 cm^{-1}, $A(2)$ = the absorbance of the standard reference at 1516 cm^{-1}, and t = 0 was taken as the time after the poly(amic acid) solution was cast on KBr and was heated to 80°C for 1 h. The curing time $t = \infty$ was taken as the time beyond which no further changes in the imide peak at 250°C occurred.

The percent imidizations of polyimides IV$_a$ vs. time at various temperatures are shown in Figure 4. When the poly(amic acid) III$_a$ was cured at 150°C for 80 min, the imide peak absorbance approached approximately 55% of its final size. The percent imidization increased with the increasing curing temperatures until 250°C. The percent imidization would not increase at any other curing temperature beyond 250°C.

Properties of Polyimides

The solubility of BAMPS-based polyimides IV$_a$–IV$_f$ are summarized in Table II. The present polyimides show better solubilities as compared to the other usual aromatic polyimides derived from aromatic dianhydrides. The reason may be explained by the presence of a siloxane-containing bond in the
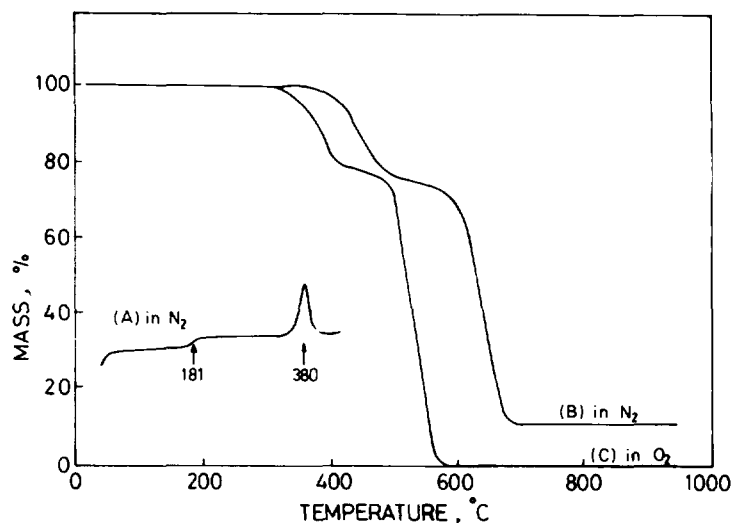
Figure 5   Thermal analysis traces (TGA and DSC) of polyimide IV$_d$: (A) DSC running at a heating rate of 20°C min^{-1} in nitrogen; TGA at a heating rate of 10°C min^{-1} under both (B) nitrogen and (C) oxygen.

Table III   Thermal Properties of Polyimides

Polyimide	T_g[a] (°C)	T_m[a] (°C)	$T_d^{10\%}$[b] (°C) In N_2	$T_d^{10\%}$[b] (°C) In O_2	R_{950}[b] (%) In N_2	R_{950}[b] (%) In O_2
IV$_a$	137	—	431	392	24.4	0
IV$_b$	—	—	441	369	11.1	0
IV$_c$	—	—	436	347	2.6	0
IV$_d$	181	380	443	365	12.3	0
IV$_e$	164	—	433	320	2.5	0
IV$_f$	128	—	404	315	5.1	0

[a] Glass transition temperature (T_g) and melting point (T_m) were measured by DSC at a heating rate of 20°C min^{-1}.

[b] Temperature at 10% mass loss $(T_d^{10\%})$ and residual mass % at 950°C (R_{950}) were recorded by TGA at a heating rate of 10°C min^{-1}.

polymer backbone. Polyimides **IV$_c$–IV$_f$** which possess ether, ketone, sulfone, and fluorine exhibit higher solubilities than those of **IV$_a$** and **IV$_b$** in polar solvents. These agree with the results in the literature.[20] Among these polyimides, **IV$_c$** and **IV$_f$** are found to be highly soluble in a wide range of solvents such as DMAc, NMP, DMF, THF, concentrated H_2SO_4, and DMSO at room temperature. Besides, the poor solubility of polyimide **IV$_a$** in all solvents in Table II, except concentrated H_2SO_4, may be due to its rigid structure.

The thermal behaviors of these polyimides were examined using both differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurement was conducted with a heating rate of 20°C min^{-1}. In all cases, the samples were quenched from elevated temperature to room temperature to produce a detectable glass transition step. TG analyses were performed at a heating rate of 10°C min^{-1} under both nitrogen and oxygen. A typical thermal analysis trace (both DSC and TGA) of polyimide **IV$_d$** is shown in Figure 5.

The DSC heating curve showed the single glass transition temperature (T_g) at 181°C and a melting peak at 380°C. The TGA curves, either in nitrogen or in oxygen, exhibited two-stage degradation processes. The results obtained for all the polyimides are summarized in Table III. The T_g of these polyimides ranging from 128 to 181°C were relatively low compared to the usual aromatic polyimides derived from similar dianhydrides.[20] This may be attributed to the flexible — O — Si — O — linkage of the polyimides. All polyimides show a similar two-stage decomposition behavior characterized by no mass loss below 360°C in nitrogen and 250°C in oxygen. The temperatures where 10% mass loss occurred were in the range 404–443°C in nitrogen and 315–392°C in oxygen, depending on the dianhy-

drides used. The amounts of carbonized residue of all polyimides at 950°C were in the range 2–24% in nitrogen and 0% in oxygen.

CONCLUSIONS

A series of new polyimides, derived from bis(p-aminophenoxy)methylphenylsilane and the various aromatic tetracarboxylic dianhydrides, were successfully synthesized. The inherent viscosities of polyimides were between 0.06 and 0.32 dL g^{-1} in various solvents at 30°C. These polyimides, containing a siloxane unit, obviously have increased the solubility in many polar solvents but have decreased the glass transition temperatures as compared to other aromatic polyimides. The present aromatic polyimides are considered as the new soluble polymeric materials. The introduction of O — Si — O linkage to the polymer backbone could be a good choice to improve the solubilities of bulky and rigid polyimides.

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