

Synthesis and Characterization of Novel Silane-Containing Aromatic Polyamides from Bis(*p*-aminophenoxy)diphenylsilane and Aromatic Dicarboxylic Acids

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SYNOPSIS

A new silane-containing diamine, bis(*p*-aminophenoxy)diphenylsilane (BAPPS) (I), was prepared by the condensation of *p*-aminophenol with dichlorodiphenylsilane. A series of silane-containing aromatic polyamides was prepared by the direct polycondensation of BAPPS with various aromatic dicarboxylic acids in *N*-methyl-2-pyrrolidinone using triphenyl phosphite and pyridine as condensing agents. The polymers were examined by ¹³C-NMR (nuclear magnetic resonance), infrared (IR) spectra, inherent viscosity, X-ray diffraction, solubility, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The diffraction diagram revealed that polyamides were crystalline or semicrystalline. Almost all of the polyamides were soluble in dimethyl sulfoxide (DMSO), but insoluble in tetrahydrofuran (THF) solvent. The polyamides had glass transition temperatures in the range of 143–194°C. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic polyamides have generally poor processability caused by limited solubility and high melting or softening temperatures.¹ Such high melting transitions result from the sequences of aromatic units, the inherent rigidity of the amide linkage, and interchain hydrogen bonding. Considerable efforts to modify polyamide structures are continuously under way to enhance their processability. For instance, the incorporation of flexible or angular linkages, such as arylene ether (—O—), methylene (—CH₂—), and perfluoroisopropylidene [—C(CF₃)₂—] and/or bulky substituents such as tetraphenylthiophene,^{2–5} into the polymer backbone are conventional strategies. This investigation attempts to incorporate softening siloxane groups within the diamine monomer into a polymer backbone, thereby enhancing solubility

and effectively decreasing the glass transition temperature.⁶

In this article, the bis(*p*-aminophenoxy)diphenylsilane (BAPPS) is prepared by reacting *p*-aminophenol with dichlorodiphenylsilane. The preparation and characterization of silane-containing aromatic polyamides are also described.

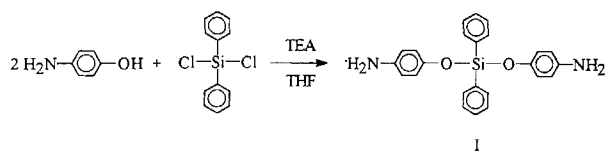
EXPERIMENTAL

Materials

p-Aminophenol (from Merck), dichlorodiphenylsilane (from Aldrich), and triphenyl phosphite (from Riedel de Haën) were used as received. Reagent-grade aromatic dicarboxylic acids, such as isophthalic acid (IIa), 5-*t*-butylisophthalic acid (IIb), 4,4'-sulfonyldibenzoic acid (IIc), 5-nitroisophthalic acid (IId), terephthalic acid (IIe), diphenic acid (IIf), and 2,6-naphthalic acid (IIg), were used without purification.

Reagent-grade calcium chloride and lithium chloride were dried under vacuum at 180°C before

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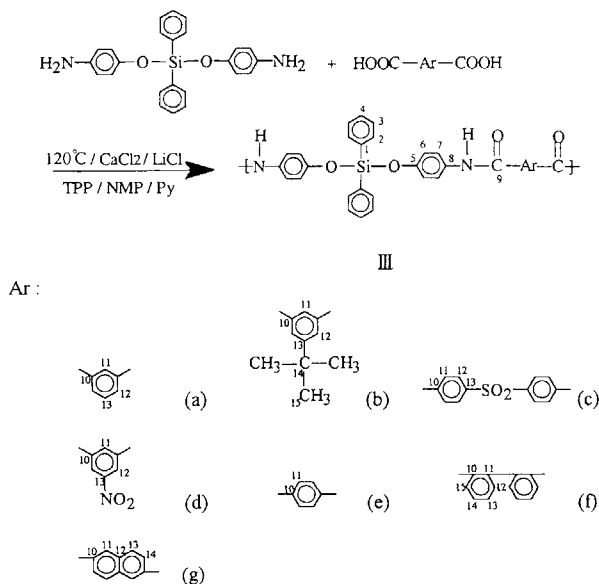
Scheme 1

use. *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), and pyridine (Py) were purified by distilling under reduced pressure over calcium hydride and storing over 4-Å molecular sieves.

Monomer Synthesis

Bis(p-aminophenoxy)diphenylsilane

Bis(*p*-aminophenoxy)diphenylsilane (**I**) was prepared by the condensation of *p*-aminophenol with dichlorodiphenylsilane. A mixture of 43.6 g (0.40 mol) of *p*-aminophenol, 44.5 g (0.44 mol) triethylamine, and 700 mL tetrahydrofuran (THF) were introduced into a three-necked flask to which 50.6 g (0.20 mol) of dichlorodiphenylsilane was added dropwise over a period of 1 h at 75°C. When the addition was completed, the reaction was continued at reflux temperature for another 3 days. The mixture was then filtered to remove salt. The filtrate was concentrated on a rotary evaporator. The residue was dissolved with ether and the precipitated salt was isolated by filtration. The product was crystallized from ether at 0°C to yield brown-yellow



Scheme 2

Table I Observed ^{13}C -NMR Chemical Shifts for Polyamides

Polyamide	Peak Assignments/ppm														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
IIIa	133.68	135.18	129.33	130.68	153.93	122.22	118.72	136.24	164.50	134.91	126.68	130.41	128.53	—	—
IIIb	133.92	134.10	129.22	130.61	154.26	122.47	120.53	135.13	164.92	134.73	124.25	127.59	151.14	34.87	31.11
IIIc	133.81	134.03	129.31	130.31	154.34	122.33	120.60	136.28	163.62	127.63	118.67	129.15	164.08	—	—
III d	133.72	134.03	129.31	130.28	154.28	122.29	118.71	136.63	162.27	136.15	132.48	124.87	148.02	—	—
IIIe	133.68	133.98	129.31	130.50	154.01	122.42	118.71	137.36	164.26	136.09	127.58	—	—	—	—
III f	133.71	134.02	129.53	130.35	154.28	121.54	118.92	136.68	167.61	138.91	129.77	127.78	120.96	128.01	124.15
III g	133.80	134.07	129.28	130.58	153.37	121.74	118.67	136.42	164.82	130.84	122.27	120.02	125.27	121.24	—

Solvent: DMSO- d_6 .

Table II Synthesis of Aromatic Polyamides

Diamine	Diacid	Code	Polymer	
			Yield (%)	η_{inh}^a (dL/g)
I	IIa	IIIa	76.58	0.18
I	IIb	IIIb	42.05	0.13
I	IIc	IIIc	91.05	0.14
I	IId	III d	64.93	0.15
I	IIe	IIIe	75.47	0.15 ^b
I	II f	III f	64.91	0.12
I	II g	III g	95.48	0.21

Diacid and diamine, 3 mmol; triphenyl phosphite, 7.2 mmol; NMP, 6 mL; pyridine, 1.5 mL; temperature, 120°C; CaCl₂, 0.3 g; LiCl, 0.15 g; reaction time, 4 h.

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

^b Measured in DMSO at 30°C for soluble parts.

crystals and dried under reduced pressure at 60°C for 3 days (melting point [mp] 97–99°C). The yield was 48.0 g (60%). The infrared (IR) spectrum (KBr) exhibited absorption peaks at 3423 cm⁻¹ (N—H) and at 1116 cm⁻¹ (O—Si—O).

ANAL. Calculated for C₂₄H₂₂N₂O₂Si: C, 72.22%; H, 5.52%; N, 7.02%. Found: C, 70.85%; H, 5.69%; N, 6.74%.

Polymerization

A typical example of the polycondensation follows.

Polyamide (IIIa) from Diamine (I) and Dicarboxylic Acid (IIa)

A mixture of 1.20 g (3 mmol) of diamine (**I**), 0.5 g (3 mmol) of diacid (**IIa**), and triphenyl phosphite (TPP) (2.24 g, 7.2 mmol) in a mixed solvent of NMP (6 mL) and pyridine (1.5 mL) containing 4 wt % CaCl₂ (0.3 g) and 2 wt % LiCl (0.15 g) was heated at 120°C for 4 h under nitrogen. The obtained polymer solution was slowly poured into 300 mL of acetone with constant stirring; the precipitated polymer was separated by filtration, washed well with acetone, and dried. The yield was 1.21 g (76.6%). The inherent viscosity of the polymer in dimethyl sulfoxide (DMSO) was 0.18 dL g⁻¹, measured at a concentration of 0.5 g dL⁻¹ at 30°C. The IR spectrum (film) exhibited absorptions at 3293 cm⁻¹ (N—H) and 1648 cm⁻¹ (C=O).

All other polymers were prepared using a similar procedure.

Measurements

Melting points were measured on a DuPont 9000 differential scanning calorimeter. An infrared

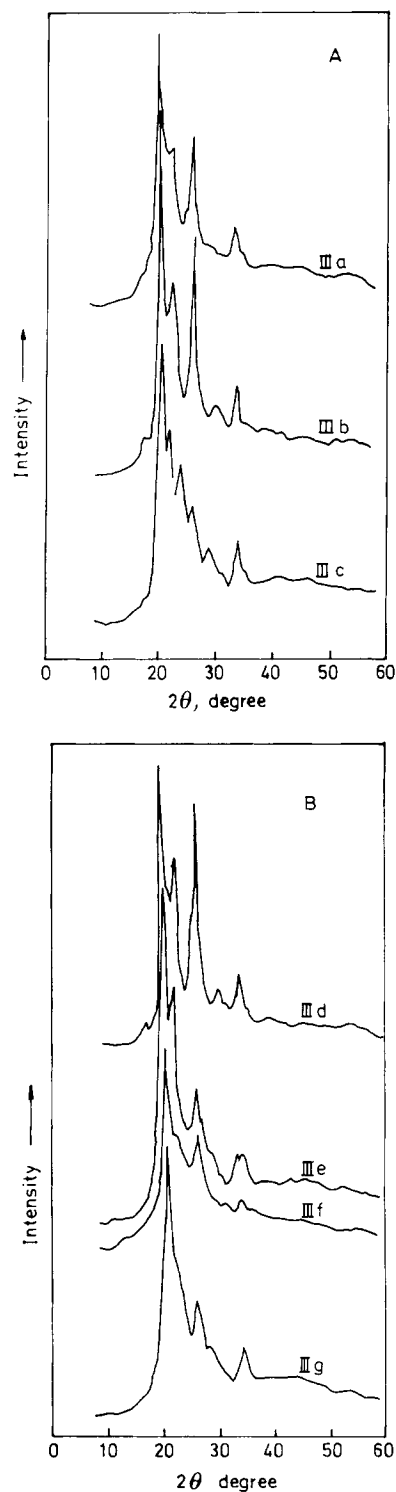


Figure 1 X-ray diffraction patterns of polyamides: (A) **IIIa–IIIc**, (B) **III d–IIIg**.

Table III Solubility of Polyamides

Polymer Code	Solvent ^a							
	DMSO	DMF	NMP	DMAc	Methanol	<i>m</i> -Cresol	Py	THF
IIIa	+	+	+	+	+–	+–	+–	–
IIIb	+	+	+	+	+	+–	+–	–
IIIc	+	–	–	–	–	–	–	–
IIId	+	+	+	+	+	+–	+–	–
IIIe	+–	–	–	–	–	–	–	–
IIIf	+	+	+	+	+	+	+	–
IIIg	+	+–	–	–	–	+–	–	–

Solubility: (+) soluble at room temperature, (+–) partially soluble, and (–) insoluble.

^a DMSO, dimethyl sulfoxide; DMF, *N,N*-dimethyl formamide; NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N,N*-dimethylacetamide; Py, pyridine.

spectrophotometer (Jasco 810) was utilized to identify the polymer structures. Nuclear magnetic resonance (NMR) spectra were measured at 30°C on a Jeol FX-100 NMR spectrometer. Elemental analyses were performed in a Perkin-Elmer model 240 C, H, N analyzer. Inherent viscosities of all polymers were determined at 30°C on solutions of concentration 0.5 g dL⁻¹ in DMSO using a Cannon-Fenske viscometer. Thermogravimetric analysis was measured on an instrument (Perkin-Elmer Thermal Mechanical Analyzer Model TGS-II) with a heating rate of 10°C/min. Differential scanning calorimetry (DSC) analyses were performed on a DuPont 9000 differential scanning calorimeter. The X-ray diffraction diagram was recorded with an X-ray diffractometer (Phillips

Model PW 1710). Measurements were taken of powdered samples.

RESULTS AND DISCUSSION

Monomer Synthesis

Bis(*p*-aminophenoxy)diphenylsilane (**I**) was synthesized by reacting *p*-aminophenol with dichlorodiphenylsilane, as indicated in Scheme 1. Our earlier attempts to prepare **I** by using a high reaction temperature (e.g., toluene reflux temperature) produced a side reaction product (mp 172°C), thereby making the solvent rather difficult to be removed. Hence, a milder method for THF reflux was adopted. The

Table IV Thermal Properties of Polyamides

Polymer Code	T_g^a	T_r^b	IDT ^c (°C)	PDT _{max} ^d (°C)	Char Yield ^e (%)
IIIa	167	200	203	218	51.9
IIIb	171	255	191	231	42.3
IIIc	—	—	237	298	54.2
IIId	174	227	230	260	45.5
IIIe	194	—	222	232	56.2
IIIf	150	205	199	243	46.4
IIIg	126	213	194	292	58.8

^a From DSC measurements conducted at a heating rate of 10°C/min.

^b Rearrangement reaction exotherm in DSC thermogram during heating.

^c Initial decomposition temperature was recorded by TGA at a heating rate of 10°C/min in nitrogen.

^d Maximum polymer decomposition temperature.

^e Char yield at 800°C in nitrogen.

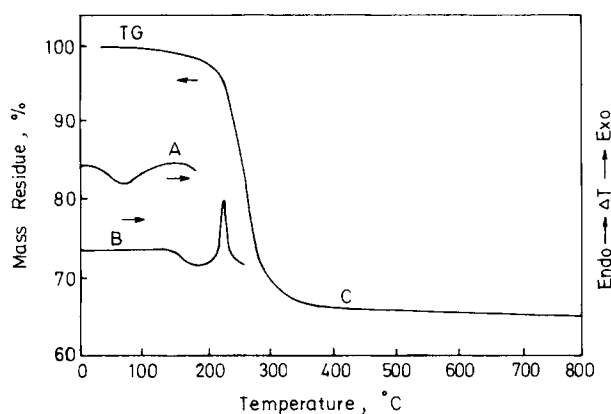


Figure 2 DSC scans of polyamide **IIIId**: (A) first scan, (B) second scan, (C) TG trace.

structure of the product was confirmed by IR, ^1H - and ^{13}C -NMR spectroscopy, and elemental analysis; those results correlated well with the proposed structures. The ^{13}C -NMR spectrum ($\text{DMSO}-d_6$) displayed peaks appearing at 148.30, 140.48, 134.53, 133.62, 130.66, 127.99, 119.53, and 114.81 ppm. The ^1H -NMR spectrum in $\text{DMSO}-d_6$ exhibited signals at 7.66 ppm (*d*, 4H, aromatic ortho to Si), 7.48–7.39 ppm (*t*, 6H), 6.69 ppm (*d*, 4H, aromatic ortho to —O—), 6.44 ppm (*d*, 4H, aromatic ortho to NH_2), and 4.61 ppm (*s*, 4H, NH_2).

Preparation of Polymers

The conventional methods for preparing aliphatic polyamides are not suitable for preparing aromatic polyamides. However, two synthetic methods are available for preparing these polymers: low-temperature polycondensation ($<100^\circ\text{C}$) and direct polycondensation in solution using phosphites, especially in the presence of metal salts.⁷ Most aramides have been synthesized for a long time by low-temperature-solution polycondensation of aromatic diacid chloride with aromatic diamine in polar aprotic solvents. The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids using triphenyl phosphite (TPP) and pyridine as condensation agents has been known to be a feasible method for preparing aromatic polyamides^{2,3,8–12} or polyamide imides^{13,14} on a laboratory scale. This method was employed here to prepare the silane- and phenoxy-containing aramides (**IIIa–IIIg**) based on (**I**), as indicated in Scheme 2. The ^{13}C -NMR chemical shifts of all the polymers are listed in Table I. Table II summarizes the polymerization results. As indicated in Table II, the polyamides were obtained with inherent viscosities of 0.12–0.21 dL g^{-1} . The polyamide

viscosity, less than general aramides, may be due to the weak —Si—O—C— linkage of the polyamide, which resulted in the partial cleavage of polymer chains. This phenomenon had been described in several polymer systems which contain the Si—O—Ph structure, such as poly(oxyaryleneoxydisilane)s¹⁵ and polyimides^{16,17} derived from bis(*p*-aminophenoxy)dimethylsilane or bis(*p*-aminophenoxy)diphenylsilane.

Properties of Polymers

The crystallinity of polyamides was examined by wide-angle X-ray diffraction diagrams obtained in powder form. As shown in Figures 1(A) and 1(B), they all exhibited strong peaks of reflection at around $2\theta = 20, 23,$ and 27° , and a weaker reflection at around 34° . All polymers contained a highly polar hydrogen bond and flexible siloxane single bond that could turn around as a shaft bearing to enhance the stereoregular arrangement. Hence, a combination of hydrogen bond and siloxane single bond tends to produce polymers having a high crystallinity.

The solubility of polymers was tested in various solvents at room temperature; those results are summarized in Table III. All of the polyamides were insoluble in THF. However, all of the polymers except **IIIe** were entirely soluble in DMSO. The polymer **IIIc** containing a sulfonyl group, polymer **IIIe** possessing a *p*-phenylene unit, and polymer **IIIg** with a naphthalene group in their structures showed poor solubility, as indicated in Table III.

Thermal properties of all polyamides were determined by dynamic thermal analysis, including DSC and thermogravimetric analysis (TGA). The thermal behavior and glass transition temperature (T_g) of polymers are summarized in Table IV. The glass transition temperatures of polymers ranged from 126 to 194°C . No discernible T_g value of the aramides **IIIc** was detected from the DSC trace. The use of paraphenyleneamide **IIIe** increased the crystallinity and rigid structure of the polyamide, thereby yielding the highest T_g value. Table IV indicates that the T_g values of these polymers are lower than general aramides. This observation is attributed to the siloxane introduced into structures. However, for all the polymers, no melting endotherm was detected, which is primarily due to the melting temperature being higher than the thermal decomposition temperature.

The thermal stabilities of the polyamides were characterized by thermalgravimetric analyses conducted at a heating rate of $10^\circ\text{C min}^{-1}$. A typical thermal analysis trace of aramide **IIIId** is shown in Figure 2. The results subsequently obtained for all

the materials are summarized in Table IV. The polymers were all unstable in nitrogen. The initial decomposition temperature is 191–237°C; however, more than 42% weight was retained at 800°C. The polymers prepared from 4,4'-sulfonyldibenzoic acid displayed greater thermal stability than those obtained from other dicarboxylic acids. This is primarily due to sulfone units in the main chain. The thermal decomposition of polymers begins at a temperature of 237°C and showed a sudden weight loss at around 298°C.

More experiments are required to understand further the causes of the thermal transition observed for the polymers. These polymers showed interesting thermal behavior. The DSC traces of **III**d are shown in Figure 2(A). The broad endotherm peak for the first run at around 100°C, which was found in all the samples, was due to the evolution of calorimetry showing exotherms which do not appear on scanning the samples, as shown in Figure 2(B). On the basis of these results, the chemical structure of the polymers must have changed during heating to 227°C. However, decomposition of the polymer and the chemical composition of the group seemed to occur simultaneously. From the TGA curve in Figure 2(C), the polymers began to lose weight around 230°C, which correlates well with the exothermic peak observed in the DSC curves [Fig. 2(B)].

CONCLUSIONS

Introduction of a siloxane segment in aromatic polymer backbones resulted in aromatic polyamides, which exhibit crystalline X-ray diffraction patterns. All silane-containing polyamides showed passable solubility in polar solvents. Furthermore, the siloxane group was also the major reason for decreasing the glass transition temperature and thermal stability of these new aramides.

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