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Synthesis of Aromatic Polyimides from *N,N'*-Bis(trimethylsilyl)-Substituted Aromatic Diamines and Aromatic Tetracarboxylic Dianhydrides

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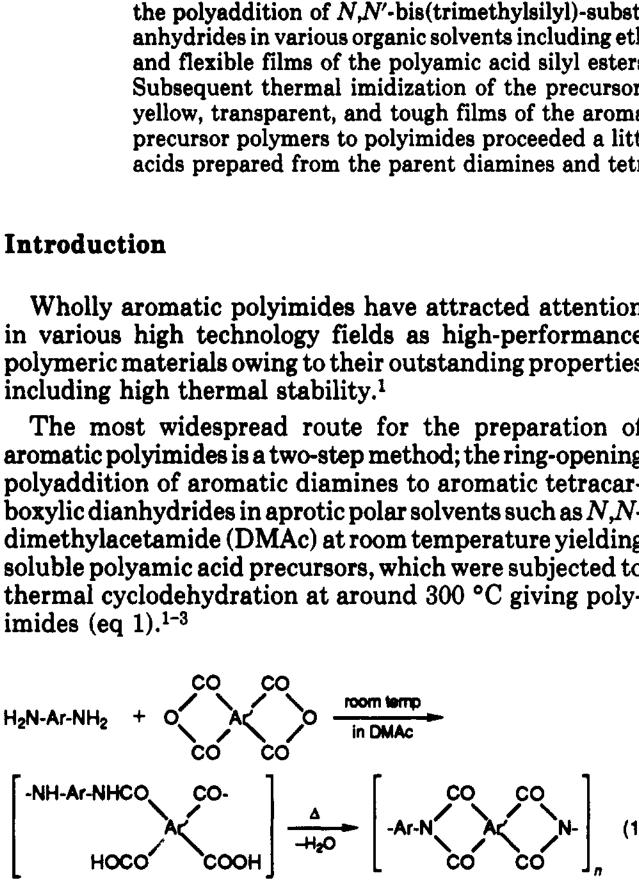
ABSTRACT: Aromatic polyamic acid trimethylsilyl esters of high molecular weights were synthesized by the polyaddition of *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines to aromatic tetracarboxylic dianhydrides in various organic solvents including ethers and hydrocarbons at room temperature. Transparent and flexible films of the polyamic acid silyl esters were obtained by casting directly from these solutions. Subsequent thermal imidization of the precursor polymers with the elimination of trimethylsilanol gave yellow, transparent, and tough films of the aromatic polyimides. The thermal conversion of the silylated precursor polymers to polyimides proceeded a little more rapidly than that of the corresponding polyamic acids prepared from the parent diamines and tetracarboxylic dianhydrides.

Introduction

Wholly aromatic polyimides have attracted attention in various high technology fields as high-performance polymeric materials owing to their outstanding properties including high thermal stability.[1]

The most widespread route for the preparation of aromatic polyimides is a two-step method; the ring-opening polyaddition of aromatic diamines to aromatic tetracarboxylic dianhydrides in aprotic polar solvents such as *N,N*-dimethylacetamide (DMAc) at room temperature yielding soluble polyamic acid precursors, which were subjected to thermal cyclodehydration at around 300 °C giving polyimides (eq 1).[1-3]



(1)

Recently, we demonstrated a novel synthetic route, N-silylated diamine method, for the synthesis of various types of aromatic polymers such as aromatic polyamides,[4-8] polybenzoxazoles,[9] polyureas,[10] and polyamines[11] by using *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines.

The N-silylated diamine method has been applied to the synthesis of polyimides. The first synthesis of aromatic polyimides by this method was disclosed by Boldebuck and Klebe in the patent literature in 1967.[12] Korshak and his group reported the synthesis of aliphatic–aromatic polyimides from *N,N'*-bis(trimethylsilyl)hexamethylenediamine and aromatic tetracarboxylic dianhydrides in 1983.[13] Recently, we utilized this method for the synthesis of random and block copolyimides from N-silylated aromatic diamines and aromatic tetracarboxylic dianhydrides.[14] The present article deals with detailed discussions on the synthesis of polyimides by the N-silylated diamine method: the polyaddition of N-silylated aromatic diamines to aromatic tetracarboxylic dianhydrides yielding polyamic acid silyl esters and subsequent thermal imidization to polyimides.

Experimental Section

Materials. *N*-(Trimethylsilyl)aniline (**1**), *N,N'*-bis(trimethylsilyl)bis(4-aminophenyl) ether (**5a**), *N,N'*-bis(trimethylsilyl)bis(4-aminophenyl)methane (**5b**), *N,N'*-bis(trimethylsilyl)-*m*-phenylenediamine (**5c**), and *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (**5d**) were prepared according to the method reported elsewhere.[7,10] Phthalic anhydride (**2**), pyromellitic dianhydride (**6a**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**6b**), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**6c**) were purified by sublimation before use. Solvents used for the reactions were purified by distillation.

Model Reaction. Phthalanilic Acid 4 from 1 and 2. To a solution of 0.827 g (5.0 mmol) of **1** in 8 mL of tetrahydrofuran (THF) was added 0.741 g (5.0 mmol) of **2** with stirring under nitrogen at 20 °C. Stirring was continued at that temperature for 6 h. To this solution was added 20 mL of methanol. The solvent was evaporated from the solution under reduced pressure, and the resulting white solid was collected, washed with hexane, and dried. The yield was 1.14 g (95%): mp 167–169 °C (lit.[15] mp 169 °C); IR (KBr) 3320 (N—H), 1715 (acid C═O), 1640 cm^{-1} (amide C═O).

Polymerization. Polyimide 9aa from 5a and 6a. In a three-necked flask equipped with a mechanical stirrer and nitrogen inlet and outlet tubes, 1.723 g (5.0 mmol) of **5a** was dissolved in 12.5 mL of DMAc. To this solution was added 1.091 g (5.0 mmol) of **6a**. The solution was stirred at 10–15 °C for 1 h and then at 40 °C for 6 h under nitrogen. A portion of the reaction solution was poured into methanol. The precipitated polyamic acid **8aa** was collected and dried under vacuum at room temperature for 24 h. The inherent viscosity of the polyamic acid in DMAc was 1.65 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. A film of polyamic acid silyl ester **7aa** was obtained by casting the reaction solution under nitrogen atmosphere. The film was dried at room temperature for 24 h, at 60 °C for 12 h, and at 100 °C for 12 h under vacuum. Thermal cyclization of the precursor polymer in the form of a film was performed by heating at 150 °C for 6 h and 200 °C for 6 h under vacuum and then at 300 °C for 2 h under nitrogen, affording polyimide **9aa**. IR (film) 1770, 1720 (C═O), 1370 (C—N), 720 cm^{-1} (imide ring). Anal. Calcd for $(C_{22}H_{10}N_2O_5)_n$: C, 69.11; H, 2.64; N, 7.33. Found: C, 68.67; H, 2.55; N, 7.38.

Polyimide 9da from 5d and 6a. A mixture of 1.263 g (5.0 mmol) of **5d** and 1.091 g (5.0 mmol) of **6a** in 10 mL of DMAc was stirred at 10–15 °C for 1 h and then at 40 °C for 6 h under nitrogen.

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The inherent viscosity of the polyamic acid **8da**, derived from polyamic acid silyl ester **7da**, was 1.21 dL·g^{-1} in DMAc. The film of polyimide **9da** was prepared by heating the film of **7da** at 160 °C for 6 h and 200 °C for 6 h under vacuum and then at 300 °C for 2 h under nitrogen. IR (film) 1775, 1715 (C=O), 1355 (C—N), 720 cm^{-1} (imide ring). Anal. Calcd for $(C_{16}H_6N_2O_4)_n$: C, 66.21; H, 2.08; N, 9.65. Found: C, 65.13; H, 2.00; N, 9.35.

Polyamic Acid Silyl Ester 7aa from 5a and 6a. A mixture of 1.723 g (5.0 mmol) of **5a** and 1.091 g (5.0 mmol) of **6a** in 16.7 mL of THF was stirred at 10–15 °C for 1 h and then at 40 °C for 6 h under nitrogen. A transparent and colorless film of polyamic acid silyl ester **7aa** was cast directly from the polymer solution on a glass plate under nitrogen and dried at room temperature for 2 days under vacuum. IR (film) 3260 (N—H), 2950 (CH_3), 1700 (ester C=O), 1650 (amide C=O), 1235, 845, and 755 cm^{-1} $(SiCH_3)$. Anal. Calcd for $(C_{28}H_{30}N_2O_7Si_2)_n$: C, 59.76; H, 5.37; N, 4.98. Found: C, 58.30; H, 5.16; N, 5.03.

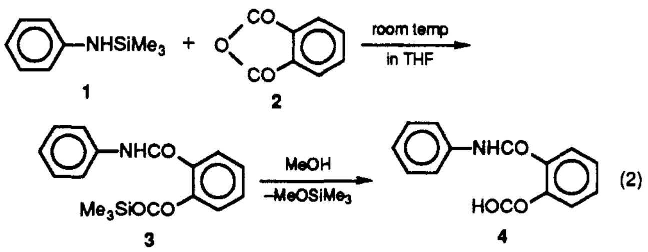
Polyamic Acid 8aa from Polyamic Acid Silyl Ester 7aa. In order to obtain polyamic acid **8aa**, a film of **7aa** was soaked in methanol for 12 h at room temperature. The polymer was dried at room temperature for 24 h under vacuum. The inherent viscosity of the polymer was 0.96 dL·g^{-1} in DMAc, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. IR (KBr) 3260 (N—H), 1715 (acid C=O), 1650 cm^{-1} (amide C=O). Anal. Calcd for $(C_{22}H_{14}N_2O_7)_n$: C, 63.16; H, 3.37; N, 6.70. Found: C, 63.17; H, 3.35; N, 6.62.

Polyimide 9aa from Polyamic Acid Silyl Ester 7aa. The film of **7aa** obtained from the THF solution was heated at 60 °C for 12 h, at 100 °C for 1 h, at 200 °C for 1 h, and then at 300 °C for 2 h under nitrogen, giving a yellow, transparent, and tough film of polyimide **9aa**. IR (film) 1770, 1720 (C=O), 1370 (C—N), 720 cm^{-1} (imide ring). Anal. Calcd for $(C_{22}H_{10}N_2O_5)_n$: C, 69.11; H, 2.64; N, 7.33. Found: C, 68.69; H, 2.50; N, 7.40.

Measurements. IR spectra were recorded on a JEOL FT/IR-3 spectrometer. Thermogravimetry (TG) was performed with a Simadzu thermal analyzer TGA-30M at a heating rate of 10 K·min^{-1} in nitrogen. Wide-angle X-ray diffraction patterns were obtained for polymer film specimens at room temperature on a Rigakudenki XG X-ray diffraction apparatus with nickel-filtered Cu Kα radiation (35 kV, 20 mA).

Results and Discussion

Model Reaction. Before polyimide synthesis, the model reaction of *N*-(trimethylsilyl)aniline (**1**) with phthalic anhydride (**2**) was investigated (eq 2).



The reaction was carried out in THF at 20 °C and then quenched with methanol. The reaction afforded phthalanilic acid (**4**) in an excellent yield. In this reaction, the trimethylsilylamino group of **1** was reactive enough toward the carboxylic anhydride to form phthalanilic acid silyl ester (**3**). The silylated product, which was not isolated, could readily be desilylated with methanol to give **4**.

Polymer Synthesis. To optimize the reaction conditions, the polyaddition of N-silylated bis(4-aminophenyl) ether **5a** to pyromellitic dianhydride **6a** leading to polyamic acid **8aa**, via desilylation of polyamic acid silyl ester **7aa** with methanol, was investigated (eq 3).

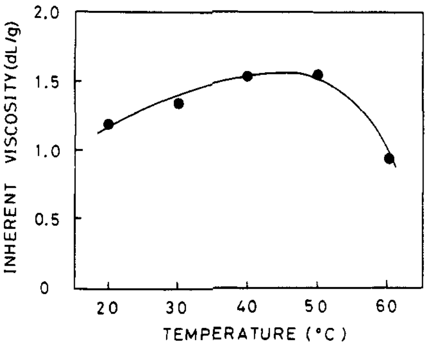
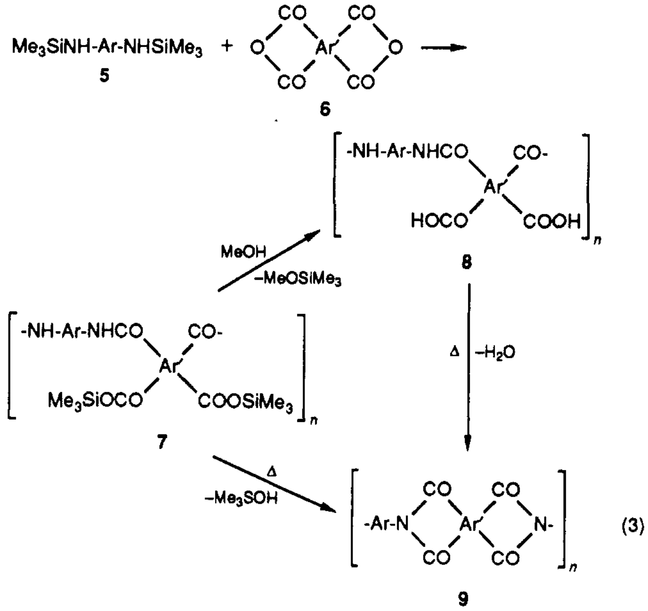
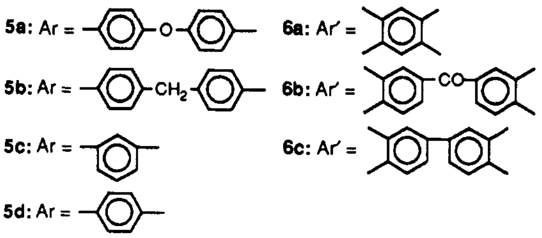


Figure 1. Effect of reaction temperature on inherent viscosity of polyamic acid **8aa** derived from polyamic acid silyl ester **7aa** formed by the polyaddition of **5a** with **6a** at a monomer concentration of 0.3 mol·L^{-1} in DMAc for 6 h.





The effect of reaction temperature on inherent viscosity of the polyamic acid was examined in DMAc at temperatures between 20 and 60 °C (Figure 1). The inherent viscosity increased gradually as the reaction temperature increased to 50 °C and the highest viscosity around 1.5 dL·g^{-1} was obtained at that temperature.

Table I summarizes the solvent effect on the polyaddition. Since these N-silylated aromatic diamines dissolved quite readily in a wide range of organic solvents, compared with the corresponding aromatic diamines, the solution polyaddition could be carried out in various solvents. The polymerizations in amide-type solvents such as DMAc and *N*-methyl-2-pyrrolidone (NMP), which were generally used for conventional polyaddition, gave polyamic acids readily having high inherent viscosities of 1.4–1.6 dL·g^{-1}. In addition, regardless of the dielectric constant of the solvents, the polyaddition in bis(methoxyethyl) ether, THF, chloroform, and 1,4-dioxane proceeded in

Table I
Synthesis of Polyamic Acid 8aa from 5a and 6a in Various Solvents[a]

		polymer		
solvent	dielectric const	yield, %	η_{inh},[b] dL·g^{-1}	remarks[c]
1,4-dioxane	2.2	97	0.90	S
toluene	2.4	96	0.92	P
chloroform	4.7	99	1.20	S
tetrahydrofuran	7.4	91	1.39	S
bis(methoxyethyl) ether		98	1.10	S
N-methyl-2-pyrrolidone	32.0	99	1.46	S
nitrobenzene	34.6	95	0.81	P
acetonitrile	37.5	96	0.88	P
N,N-dimethylacetamide	37.8	99	1.65	S

[a] Polymerization was carried out with 5.0 mmol of each monomer in 12.5 mL of DMAc at 10–15 °C for 1 h and then 40–45 °C for 6 h under nitrogen. [b] Measured at a concentration of 0.5 g·dL^{-1} at 30 °C. [c] Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation.

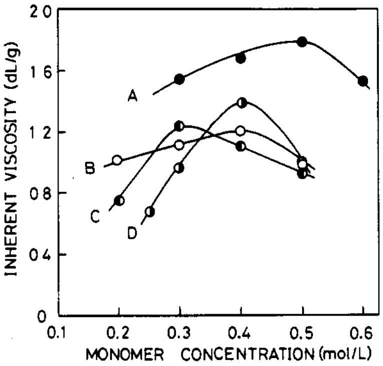


Figure 2. Effect of monomer concentration on inherent viscosity of polyamic acid **8aa** derived from polyamic acid silyl ester **7aa** formed by the polyaddition of **5a** with **6a** at 10–15 °C for 1 h and then 40–45 °C for 6 h in (A) DMAc, (B) chloroform, (C) bis(methoxyethyl) ether, and (D) THF.

homogeneous solution giving polyamic acids with inherent viscosities above 0.9 dL·g^{-1}. The other solvents such as acetonitrile, nitrobenzene, and toluene also afforded the polymer with inherent viscosities in the range of 0.8–0.9 dL·g^{-1}, despite the fact that precipitation of the polymer occurred during the polymerization. Thus, it was found that the polyamic acid silyl ester prepared by polyaddition had good solubility in various solvents including not only amide solvents but also low boiling point solvents such as THF and chloroform.

Figure 2 explains the effect of monomer concentration on inherent viscosity of the polymer. When DMAc was used as the polymerization solvent, the inherent viscosity of the polymer increased with increasing monomer concentration, reaching a maximum of 1.77 dL·g^{-1} at 0.5 mol·L^{-1}. The lower inherent viscosity of the polyamic acid obtained at a higher reactant concentration (0.6 mol·L^{-1}) is attributable to reduced reactant mobility due to the onset of gelation, which takes place before the viscosity reaches a higher value. In the case of other solvents such as chloroform, bis(methoxyethyl) ether, and THF, the gelation occurred at around 0.5 mol·L^{-1} and the highest viscosity of the polymer was obtained in the concentration range 0.3–0.4 mol·L^{-1}. These results indicated that amide solvents such as DMAc and NMP were good solvents for the polymer and hence were the most effective solvents for the polyaddition, affording the polyamic acid silyl esters with higher molecular weight.

The polyadditions of both benzophenonetetracarboxylic dianhydride (**6b**) and biphenyltetracarboxylic dianhydride (**6c**) also proceeded in homogeneous solution in DMAc, bis(methoxyethyl) ether, and THF, and the resulting polyamic acids had high inherent viscosities above 0.9 dL·g^{-1} (Table II).

Table II
Synthesis of Polyamic Acids 8 from 5a and 6[a]

		polymer			
monomer	solvent	8	yield, %	η_{inh},[b] dL·g^{-1}	remarks[c]
6a	*N,N*-dimethylacetamide	**8aa**	99	1.77	S
6a	bis(methoxyethyl) ether	**8aa**	98	0.92	S
6a	tetrahydrofuran	**8aa**	91	0.97	S
6b	*N,N*-dimethylacetamide	**8ab**	99	1.25	S
6b	bis(methoxyethyl) ether	**8ab**	98	1.05	S
6b	tetrahydrofuran	**8ab**	99	1.21	S
6b	toluene	**8ab**	99	0.95	P
6c	*N,N*-dimethylacetamide	**8ac**	99	1.28	S
6c	bis(methoxyethyl) ether	**8ac**	98	1.13	S
6c	tetrahydrofuran	**8ac**	95	0.95	S

[a] Polymerization was carried out with 5.0 mmol of each monomer in 10 mL of solvent at 10–15 °C for 1 h and then 40–45 °C for 6 h. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [c] Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation.

Table III
Synthesis of Polyamic Acids[a]

monomers			polymer		
5	6	solvent	8	η_{inh},[b] dL·g^{-1}	remarks[c]
5b	**6a**	*N,N*-dimethylacetamide	**8ba**	1.18	S
5c	**6a**	*N,N*-dimethylacetamide	**8ca**	0.67	S
5d	**6a**	*N,N*-dimethylacetamide	**8da**	1.21	S
5d	**6a**	bis(methoxyethyl) ether	**8da**	0.99	P
5d	**6a**	bis(methoxyethyl) ether[d]	**8da**	0.78	P
5d	**6a**	tetrahydrofuran	**8da**	0.86	P
5d	**6b**	*N,N*-dimethylacetamide	**8db**	0.97	S
5d	**6b**	bis(methoxyethyl) ether	**8db**	0.82	S
5d	**6b**	tetrahydrofuran	**8db**	0.72	S
5d	**6c**	*N,N*-dimethylacetamide	**8dc**	1.07	S
5d	**6c**	bis(methoxyethyl) ether	**8dc**	0.87	P
5d	**6c**	tetrahydrofuran	**8dc**	0.90	P

[a] Polymerization was carried out with 5.0 mmol of each monomer in 10 mL of solvent at 10–15 °C for 1 h and then 40–45 °C for 6 h under nitrogen. [b] Measured at a concentration of 0.5 g·dL^{-1} in DMAc at 30 °C. [c] Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation. [d] Polymerization was carried out with in 16.7 mL of solvent.

Table III summarizes the results of the polyaddition of various N-silylated aromatic diamines to various aromatic tetracarboxylic dianhydrides. A variety of high molecular weight polyamic acids with inherent viscosities ranging between 0.6 and 1.2 dL·g^{-1} were successfully prepared in homogeneous solution. Although the polymerizations of N-trimethylsilylated *p*-phenylenediamine (**5d**) with **6a** and **6c** proceeded with polymer precipitation in bis(methoxyethyl) ether and THF due to more rigid nature of polymer backbone, polymers **7da** and **7dc** were found to have high inherent viscosities.

The formation of polyamic acid silyl esters **7** as well as polyamic acids **8** (derived from **7**) was confirmed by means of IR spectroscopy and elemental analysis. The IR spectrum of **7aa** (Figure 3A) obtained from **5a** and **6a** in THF exhibited absorption bands due to the N–H bond and the amide carbonyl group at 3260 and 1650 cm^{-1}, respectively, and the methyl and carbonyl of trimethylsilyl ester at 2950 and 1700 cm^{-1}, respectively. In addition, the other absorptions due to the trimethylsilyl group appeared at 1235, 845, and 755 cm^{-1}. The results of the elemental analysis were in good agreement with the calculated values of the proposed structure of polymer **7aa**. The IR spectrum of the **7aa** film (Figure 3B) soaked

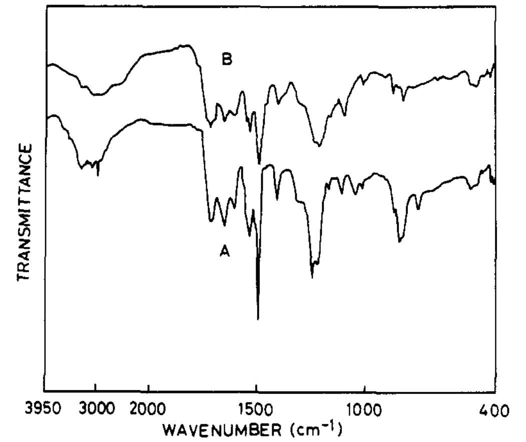


Figure 3. IR spectra of (A) polyamic acid silyl ester **7aa** obtained from **5a** and **6a** in THF and (B) polyamic acid **8aa** derived from **7aa** by the desilylation with methanol.

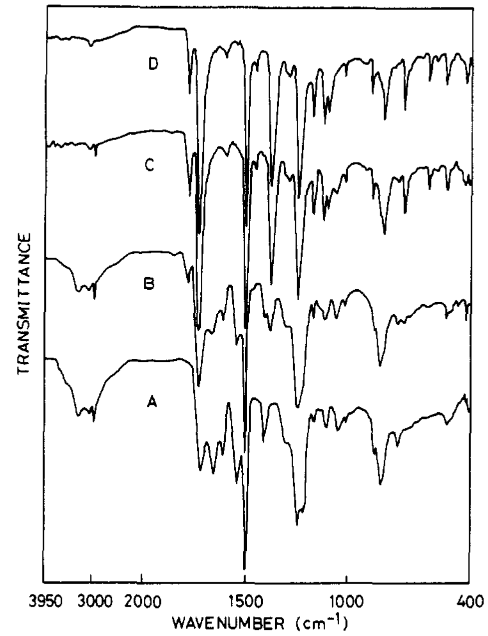


Figure 4. IR spectra of polyamic acid silyl ester **7aa** cured at (A) room temperature, (B) 150 °C for 1 h, (C) 200 °C for 1 h, and then (D) 260 °C for 1 h under nitrogen.

in methanol showed that the absorption at 1715 cm^{-1} due to the carboxyl group appeared and the absorption corresponding to the trimethylsilyl group disappeared. Elemental analysis data also confirmed the formation of polyamic acid **8aa**.

In the second stage, the silylated precursor polymers were subjected to thermal imidization to convert them to polyimides. The film of **7aa** obtained from **5a** and **6a** in THF was heated stepwise. As the imidization temperature increased, the IR spectra (Figure 4) exhibited a gradual increase in intensity of the imide absorption bands at 1770, 1720, 1370, and 720 cm^{-1} and a decrease of the absorptions at 3260 cm^{-1} (N—H) and 1650 cm^{-1} (C=O) of the amide moiety and 2950 cm^{-1} (CH$_3$) of the trimethylsilyl group. It has been known that the heat treatment of polyamic acids often resulted in the formation of side products such as anhydride, isoimide, and intermolecular imide, which exhibited absorptions in the ranges 1880–1850, 1820–1800, and 1750–1670 cm^{-1}, respectively.[16-17] According to our observations, the IR spectra of the heat-treated film (Figure 4) gave no evidence for the formation of these side products. The IR spectrum and elemental analysis were consistent with the chemical structure of the corresponding polyimide.

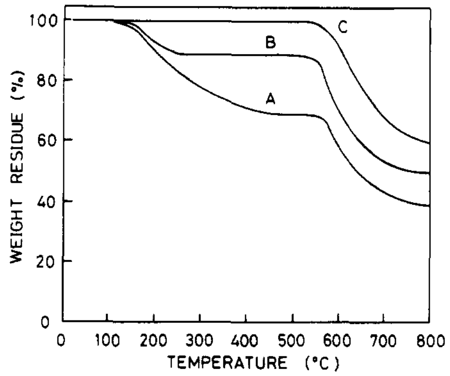


Figure 5. TG curves for (A) polyamic acid silyl ester **7aa**, (B) polyamic acid **8aa**, and (C) polyimide **9aa** at a heating rate of 10 K·min^{-1} in nitrogen.

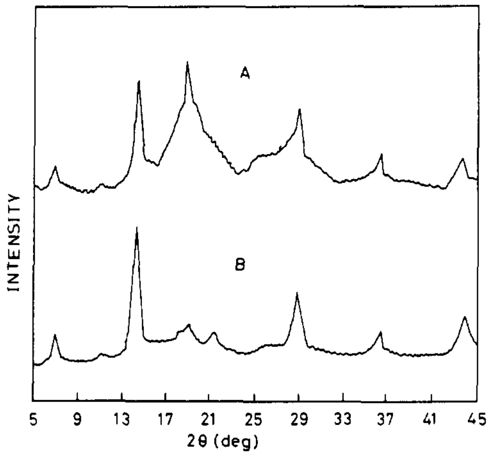


Figure 6. X-ray diffraction diagrams of polyimides **9da** obtained by (A) the conventional method and (B) the N-silylated diamine method.

Polymer Characterization. The thermal behavior of the polymers was studied by using TG technique. Figure 5 shows typical TG curves for silylated polyamic acid **7aa** (obtained from **5a** and **6a** in THF), as well as those of polyamic acid **8aa** and polyimide **9aa** (both were derived from **7aa**), in nitrogen at a heating rate of 10 K·min^{-1}. The TG curve of the film of **7aa** (curve A) revealed that the weight loss started at around 130 °C and came to an end at about 450 °C. The weight loss of 31% on the basis of thermal cyclization of **7aa** agreed quite well with the calculated value (32%) of the amount of trimethylsilanol eliminated from **7aa**. The polyamic acid **8aa** lost 9% of its weight on the basis of thermal cyclodehydration to polyimide **9aa** (curve B). The polyimide obtained by the preparative route did not lose weight up to 520 °C, and 10% weight loss was observed at 590 °C in nitrogen (curve C).

The crystal nature of polyimides obtained by two different methods was evaluated by X-ray diffraction studies. Poly[*N*,*N*′-(*p*-phenylene)pyromellitimide] (**9da**), obtained by a conventional diamine method from *p*-phenylenediamine and **6a**, is well-known as a highly crystalline polymer (Figure 6A). As shown in Figure 6B, the N-silylated diamine method starting from **5d** and **6a** gave a transparent film with low crystallinity. Bulkiness of the trimethylsilyl group of the silylated precursor polymer may reduce close-packing ability of the precursor polymer chains, and hence the loose packing may remain mostly unchanged in the polyimide chains after the thermal cyclization.

The tensile properties of the polyimide films were evaluated from the stress–strain curves. The tensile

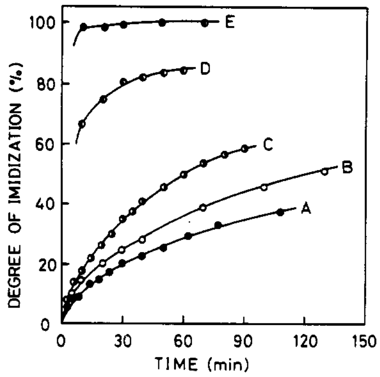


Figure 7. Time dependence of degree of imidization of polyamic acid silyl ester **7aa**, obtained from **5a** and **6a** in THF, at (A) 170 °C, (B) 180 °C, (C) 190 °C, (D) 200 °C, and (E) 240 °C.

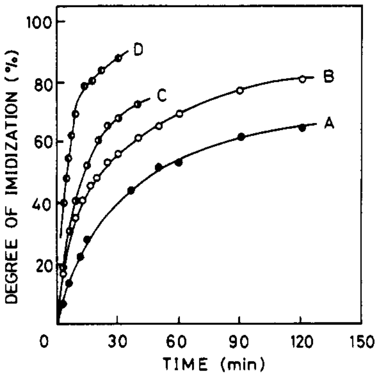


Figure 8. Time dependence of degree of imidization of polyamic acid silyl ester **7aa**, obtained from **5a** and **6a** in DMAc, at (A) 160 °C, (B) 170 °C, (C) 180 °C, and (D) 190 °C.

strength, elongation at break, and tensile modulus of the film of polyimide **7aa** prepared by the N-silylated diamine method were 147 MPa, 88%, and 2.0 GPa, respectively. These values are almost the same as those of the polyimide film prepared by a conventional method.[14]

Imidization Studies. The progress of the thermal imidization was monitored with films of polyamic acid silyl ester **7aa** by using IR technique under nitrogen atmosphere. The absorption at 1380 cm^{-1} was used to follow the appearance of the imide moiety.[16] The degree of imidization (x) was calculated using eq 4,[18] where $A(1370)$

$$x\,(\%) = \frac{[A(1370)/A(1490)]_t - [A(1370)/A(1490)]_{t=0}}{[A(1370)/A(1490)]_{t=\infty} - [A(1370)/A(1490)]_{t=0}} \times 100 \quad (4)$$

stands for the absorbance of imide peak at 1370 cm^{-1} and $A(1490)$ is the absorbance of standard reference peak at 1490 cm^{-1}.

Figures 7 and 8 show the degree of imidization plotted against heating time at different temperatures. The degree of imidization of the film of **7aa** obtained by casting from the THF solution increased with an increase in heating temperature (Figure 7). The completion of imidization of the silylated precursor polymer was achieved at 240 °C. The thermal conversion of the film obtained by casting from the DMAc solution proceeded more rapidly at a lower temperature (Figure 8). This may be due to the presence of a trace amount of residual DMAc in the film, which was known to assist the polymer chains to achieve a favorable orientation for ring closure and enhance the rate of imidization.[19] In addition, it is noteworthy that the thermal conversion of the silylated precursor polymer prepared in DMAc to polyimide proceeded a little more rapidly than that of the parent polyamic acid prepared by the conventional diamine method from bis(4-aminophenyl) ether and **6a** in DMAc (Figure 9).

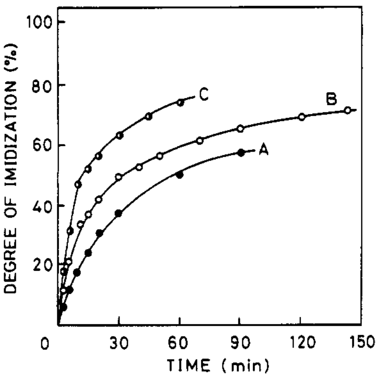


Figure 9. Time dependence of degree of imidization of polyamic acid **8aa**, obtained from bis(4-aminophenyl) ether and **6a** in DMAc, at (A) 170 °C, (B) 180 °C, and (C) 190 °C.

Table IV
First-Order Rate Constants for the Imidization of Polyamic Acid Derivatives

	rate constant (k), min^{-1}		
temp, °C	**7aa**[a]	**7aa**[b]	**8aa**[c]
160		2.17 × 10^{-2}	
170	4.96 × 10^{-3}	3.73 × 10^{-2}	1.93 × 10^{-2}
180	7.33 × 10^{-3}	5.78 × 10^{-2}	3.56 × 10^{-2}
190	1.09 × 10^{-2}	1.24 × 10^{-1}	6.39 × 10^{-2}

[a] Prepared by the polyaddition of **5a** with **6a** in THF. [b] Prepared by the polyaddition of **5a** with **6a** in DMAc. [c] Prepared by the polyaddition of bis(4-aminophenyl) ether with **6a** in DMAc.

The conversion of the silylated precursor polymer to polyimide in the initial stage should be regarded as a first-order reaction, because it proceeds between two functional groups belonging to the same precursor fragment. Accordingly, if the degree of imidization is x at heating time t, the rate of imidization dx/dt can be expressed as in eq 5, where k is the first-order rate constant. This expression

$$dx/dt = k(100 - x) \quad (5)$$

is transformed into eq 6.

$$\ln\,[100/(100 - x)] = kt \quad (6)$$

A linear relationship was obtained for the half-logarithmic plots by substituting the experimental data into eq 5. This clearly indicated that the thermal imidization process could be described by first-order kinetics.[19]

The first-order rate constants (k) were calculated for each temperature and are listed in Table IV. The rate constants for the thermal imidization of three kinds of precursor polymers increased in the following order: **7aa** (prepared in THF) < **8aa** (prepared in DMAc) < **7aa** (prepared in DMAc). The Arrhenius plots generated from the derived first-order rate constants gave the activation energy (E_a) and frequency factor (A) (Figure 10). The activation parameters such as activation enthalpy (ΔH^*), activation entropy (ΔS^*), and Gibbs free energy (ΔG^*) were calculated from the method of transition state and are summarized in Table V. The results suggested that control of the imidization rate resided in the activation enthalpy rather than in the activation entropy for the imidization of polyamic acid **8aa** and polyamic acid trimethylsilyl ester **7aa**. Thus, the enhanced rate of imidization of the polyamic acid trimethylsilyl ester may be explained

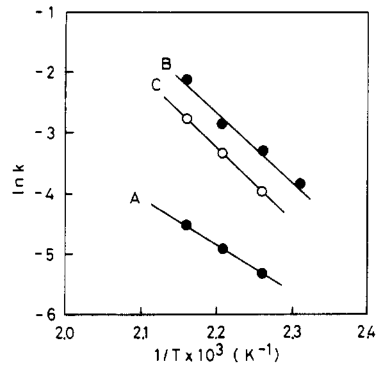


Figure 10. Arrhenius polts for the imidization of (A) polyamic acid silyl ester **7aa** obtained from **5a** and **6a** in THF, (B) polyamic acid silyl ester **7aa** obtained from **5a** and **6a** in DMAc, and (C) polyamic acid **8aa** obtained from bis(4-aminophenyl) ether and **6a** in DMAc.

Table V
Activation Parameters for the Thermal Imidization of Polyamic Acid Derivatives at 180 °C

polymer	E_a, kcal·mol⁻¹	A	ΔH^*, kcal·mol⁻¹	ΔS^*, cal·K⁻¹·mol⁻¹	ΔG^*, kcal·mol⁻¹
7aa[a]	15.7	2.68×10^5	14.8	−36.6	31.4
7aa[b]	22.3	3.96×10^9	21.4	−17.5	29.3
8aa[c]	23.9	1.19×10^{10}	23.0	−15.3	29.9
8aa[d]	26.4	3.23×10^{11}	25.5	−8.7	29.4

[a] Prepared by the polyaddition of **5a** with **6a** in THF. [b] Prepared by the polyaddition of **5a** with **6a** in DMAc. [c] Prepared by the polyaddition of bis(4-aminophenyl) ether with **6a** in DMAc. [d] Obtained by Kreuz et al.[19]

by low intramolecular forces due to the decrease of hydrogen bonding in the growing polyimide molecule.

Conclusion

The polyaddition of *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines to aromatic tetracarboxylic dianhydrides in various organic solvents including ethers and hydrocarbons at room temperature afforded polyamic acid trimethylsilyl esters of high molecular weights, because both N-silylated aromatic diamines and silylated polyamic acid precursors have good solubility in organic solvents due to lack of hydrogen bonding, compared with the parent aromatic diamines and polyamic acids. Colorless, transparent, and flexible films of the silylated precursor polymers were prepared by casting from the polymer solutions. Desilylation of the silylated polymers with an alcohol like methanol proceeded smoothly, affording the corresponding polyamic acids. The films of the silylated precursors were converted by subsequent thermal treatment to yellow, transparent, and tough films of the aromatic polyimides with the elimination of trimethylsilanol. The rate of imidization of the silylated polymers was a little faster than that of the polyamic acids prepared by the conventional method using the parent diamines and tetracarboxylic dianhydrides. The characteristics such as chemical resistance, thermal stability, and tensile properties of the polyimide films prepared by the N-silylated diamine method were almost the same as those of the polyimide films obtained by a conventional method.

Thus, the N-silylated diamine method is considered to be a versatile and promising route for the synthesis of a variety of high molecular weight aromatic polyimides.

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