Synthesis of Wholly Alicyclic Polyimides from N-Silylated Alicyclic Diamines and Alicyclic Dianhydrides

Yasufumi Watanabe, Yoshimasa Sakai, Yuji Shibasaki, Shinji Ando, and Mitsuru Ueda*

Department of Organic & Polymeric Materials, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku, Tokyo 152-8552, Japan

Yoshiyuki Oishi and Kunio Mori

Department of Applied Chemistry and Molecular Science, Faculty of Engineering, Iwate University, Morioka, Iwate 020-8551, Japan

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ABSTRACT: A new synthetic method to give wholly alicyclic polyimides with high molecular weights has been developed. The polymerization of cyclobutanetetracarboxylic dianhydride (**1a**) or bicyclo[2.2.1]-heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride (**1b**) with various N-silylated alicyclic diamines (**2**) was carried out in *N*,*N*-dimethylacetamide (DMAc) at room temperature, giving poly(amic acid trialkylsilylester)s (**3**) as precursor polymers that were hydrolyzed to poly(amic acid)s (**4**) with inherent viscosities up to 0.99 dL/g. Both polyimide precursors were readily converted to corresponding polyimides (**5**) by thermal treatment. These polyimides are readily soluble in polar aprotic solvents such as 1-methyl-2-pyrrolidone, *N*,*N*-dimethylacetamide and dimethyl sulfoxide at room temperature, and showed high thermal stability (T_{d10} = 420−445 °C in N_2) and excellent transparency at wavelengths above 250 nm. The average refractive index of the polyimide **5aa** was 1.498, and the dielectric constant estimated from the refractive index was 2.47.

Introduction

Polyimides (**PIs**) are a class of polymers used extensively in microelectronics because of their outstanding key properties such as thermoxidative stability, high mechanical strength, and excellent electrical properties.[1] They are used as interlayer dielectrics in integrated circuit fabrication. Recently, semiaromatic **PIs** have been used in the applications as optoelectronics and interlayer dielectric materials thanks to the better colorless transparency and the lower dielectric constant compared with conventional fully aromatic polyimides.[2−13] They hardly form inter- or intramolecular charge-transfer complexes, which increase the dielectric constant and lower the transparency. Moreover, alicyclic structures are effective to decrease a molecular density because of their bulkiness, giving **PIs** with a low dielectric constant.

The synthesis of wholly aliphatic or alicyclic **PIs** is rather difficult.[14−17] The polymerization of dianhydrides with aliphatic or alicyclic diamines gives poly(amic acid)s (**PAAs**), which make salts of **PAAs** with the free diamines having a high basicity. This salt formation prevents the formation of high molecular weight **PAAs**. To remedy this problem, solution imidization and acid chloride methods were reported.[18,19]

In a previous paper,[20] we reported the synthesis of aromatic polyimides from N,N′-bissilylated aromatic diamines and aromatic tetracarboxylic dianhydrides. Quite recently, we have reported briefly the successful synthesis of wholly alicyclic **PIs** with relatively high molecular weights (η_{inh} = 0.74 dL/g) by the polymerization of cyclobutanetetracarboxylic dianhydride (**1a**) with N-trimethylsilylated alicyclic diamines (**2**).[21] The reaction of carboxylic anhydrides with N-silylated amines produces amide-silylesters which do not form salts with amines.

In this paper, we report the detailed preparation and properties of various wholly alicyclic **PIs** from several alicyclic dianhydrides (**1**) and N-silylated alicyclic diamines (**2**).

Experimental Section

Materials. 1-Methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), triethylamine (TEA), and toluene were purified by the usual manner, and stored under an atmosphere of N_2. 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (**1a**) was purified by recrystallization from acetic anhydride and dried at 150 °C before use. Bicyclo-[2.2.1]heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride (**1b**) was heated to 90 °C in acetic anhydride and toluene, stirred for 1 h, filtered, and then dried at 90 °C for 1 h prior to use. 5-Amino-1,3,3-trimethyl-cyclohexane- methylamine and 2,5(2,6)-bis(aminomethyl)bicyclo[2.2.1]heptane were purified by distillation. Other reagents and solvents were used as received.

5-Trimethylsilylamino-*N*-trimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (2a). A 300-mL three-necked round-bottomed flask equipped with a magnetic stirrer, a nitrogen inlet, a 10 mL pressure-equalizing dropping funnel, and a no-air stopper was charged with 5-amino-1,3,3-trimethylcyclohexanemethylamine (10.6 g, 60.0 mmol) and toluene (150 mL) under an N_2 stream. To this solution was added trimethylchlorosilane (13.5 g, 120 mmol) at 5 °C, and the solution was stirred for 30 min. Then, TEA (12.1 g, 120 mmol) was added dropwise to this solution through the funnel. White

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* To whom correspondence should be addressed. E-mail: mueda@polymer.titech.ac.jp.

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HCl·TEA salt precipitated immediately. The reaction was kept for another 2 h at 5 °C and then 24 h at 60 °C. The reaction mixture was filtered and concentrated at reduced pressure. The crude product was distilled under reduced pressure to give **2a** as a clear oil. The yield was 10.1 g (52%): bp 88−94 °C (0.75 Torr). IR (NaCl): $\nu = 3409$ (N−H), 1249 (Si−CH$_3$), 836 (Si−CH$_3$) cm^{-1}. Anal. Calcd for ($C_{16}H_{38}N_2Si_2$): C, 61.07; H, 12.17; N, 8.90. Found: C, 60.99; H, 12.32; N, 9.12.

2,5(2,6)-Bis(*N*-trimethylsilylaminomethyl)bicyclo[2.2.1]-heptane (2b). This compound was prepared as described above using 2,5(2,6)-bis(aminomethyl)- bicyclo[2.2.1]heptane in place of 5-amino-1,3,3-trimethylcyclohexanemethylamine.

The yield of **2b** was 48% as a clear oil: bp 106−110 °C (0.75 Torr). IR (NaCl): $\nu = 3405$ (N−H), 1249 (Si−CH$_3$), 836 (Si−CH$_3$) cm^{-1}. Anal. Calcd for ($C_{15}H_{34}N_2Si_2$): C, 60.33; H, 11.48; N, 9.38. Found: C, 59.95; H, 11.14; N, 9.66.

5-*tert*-Butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (2c). This compound was prepared as described above using *tert*-butyldimethylchlorosilane in place of trimethylchlorosilane. The yield of **2c** was 82% as a clear oil: bp 120−123 °C (0.15 Torr). IR (NaCl): $\nu = 3405$ (N−H), 1253 (Si−*tert*-Butyl), 829 (Si−*tert*-Butyl) cm^{-1}. Anal. Calcd for ($C_{22}H_{50}N_2Si_2$): C, 66.26; H, 12.64; N, 7.02. Found: C, 66.07; H, 12.32; N, 7.26.

4,4′-Methylenebis(*N*,*N*′-*tert*-butyldimethylsilylcyclohexylamine) (2d). This compound was prepared as described above using 4,4′-methylenebis(cyclohexylamine) in place of 5-amino-1,3,3-trimethylcyclohexanemethylamine. The yield of **2d** was 50% as a clear oil: bp 144 °C (0.02 Torr). IR (NaCl): $\nu = 3397$ (N−H), 1249 (Si−*tert*-Butyl), 829 (Si−*tert*-Butyl) cm^{-1}. Anal. Calcd for ($C_{25}H_{54}N_2Si_2$): C, 68.42; H, 12.40; N, 6.38. Found: C, 68.13; H, 12.11; N, 6.37.

Poly(amic acid trialkylsilylester)s (3). A flame-dried 25 mL flask was charged with **2a** (0.899 g, 2.86 mmol) and DMAc (3.41 g) under nitrogen. 1,2,3,4-Cyclobutanetetracarboxylic dianhydride **1a** (0.560 g, 2.86 mmol) was added to this solution at 25 °C in one portion. The solution was stirred at this temperature for 1 h under nitrogen. The inherent viscosity of the resulting polymer solution was 0.99 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. IR (KBr): $\nu = 1708$ (C=O, silylester), 1654 (C=O, amide) cm^{-1}.

Poly(amic acid)s (4). The solution of polymer **3** was poured into a 0.2 wt % aqueous HCl solution. The precipitate was filtered off, washed with water, and dried under vacuum.

IR (KBr): $\nu = 1727$ (C=O, carboxylic acid), 1646 (C=O, amide) cm^{-1}. Anal. Calcd for $(C_{18}H_{26}N_2O_6 \cdot 0.8H_2O)_n$: C, 56.77; H, 6.88; N, 7.36. Found: C, 56.76; H, 6.51; N, 7.36.

Poly(imide)s (5). The polyimide film was prepared by casting the solution of polymer **3** on a silicon wafer at room temperature and then by heating at 100, 150, 200, and 250 °C for 0.5 h and 300 °C for 1 h under nitrogen atmosphere.

IR (KBr): $\nu = 1770$ and 1708 (imide C=O), 1361 (C−N) cm^{-1}. Anal. Calcd for $(C_{18}H_{22}N_2O_4 \cdot 0.1H_2O)_n$: C, 65.08; H, 6.74; N, 8.43. Found: C, 64.54; H, 6.58; N, 8.40.

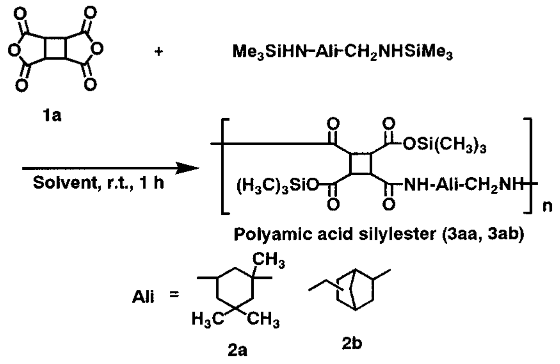
Measurements. The infrared spectra were recorded on a Horiba FT-720 spectrophotometer. ^{1}H NMR spectra were obtained using a Bruker DPX300 (300 MHz) spectrometer. The UV−visible spectra of polyimide films were recorded on a Jasco V-560 spectrophotometer. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed with a Seiko TG/DTA 6300 and DSC 6200, respectively. Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using TOSO HPLC (HLC-8120GPC) equipped with a TOSO TSK gel column (TSKgel GMHHR-M, TSKgel GMHHR-L) at 40 °C in DMF with LiBr. Refractive indices of polyimide films formed on quartz substrates were measured at a wavelength of 1.320 μm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly-polarized laser light with parallel (TE: transverse electric) and perpendicular (TM: transverse magnetic) polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thickness of the samples were determined.

Calculations. A density functional level of theory (B3LYP) with an extended basis set with polarization functions (6-31G-(d,p)), which is implemented in the "Gaussian-98" (Revision A.7) program, was used to calculate molecular orbital energies of dianhydrides. The geometric structures of computed compounds were fully optimized under no constraints prior to the calculations of molecular orbital energies.

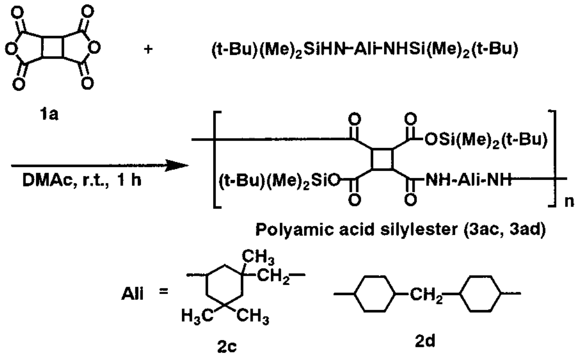
Results and Discussion

Synthesis of Poly(amic acid trialkylsilyl esters) (3). As alicyclic dianhydrides (**1**), 1,2,3,4-cyclobutanetetracarboxylic dianhydride (**1a**) and bicyclo[2.2.1]-heptane-2-methanecarboxylic-3,5,6-tricarboxylic-2,3:5,6-dianhydride (**1b**) were employed**.** On the other hand, N-trimethylsilylated alicyclic diamines (**2**), 5-trimethylsilylamino-*N*-trimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (**2a**) and 2,5(2,6)-bis(*N*-trimethylsilylaminomethyl)bicyclo[2.2.1]heptane (**2b**) were prepared by the reactions of corresponding diamines with trimethylchlorosilane in the presence of TEA.

To determine optimal conditions for polymerization, the polymerization of **1a** with N-silylated diamines **2a** or **2b** was studied in detail. The ring-opening polyaddition was performed with 1 mmol of monomers in a solvent at room temperature for 1 h [eqs 1 and 2]



(1)



(2)

Table 1 summarizes the effects of solvent on the inherent viscosity of polymer **3**. Polymerizations of **2a** or **2b** with **1a** proceeded rapidly in a homogeneous solution without salt formation and were completed in 1 h, giving colorless and viscous polymer solutions. The polymers with inherent viscosities ranging between 0.71 and 0.99 dL/g were obtained in DMAc.

On the basis of these results, the polymerization of **2a** or **2b** with **1b** was performed in DMAc at room temperature. Polymers **3ba** or **3bb** obtained after 24 h showed very low inherent viscosities of 0.09 and 0.12 dL/g. The polymerization was carried out at 60 °C again, but no discernible effect on the inherent viscosity was observed (Table 2). This result would be explained by a low reactivity of **1b** compared to that of **1a**. Ando et al.[22] have reported that the acylation rate constants of

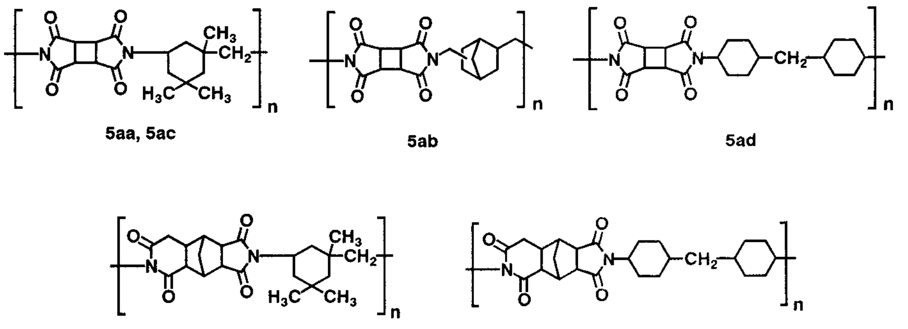


Figure 1. Structures and numbers of wholly alicyclic polyimides synthesized in this study.

Table 1. Synthesis of Wholly Alicyclic Poly(amic acid silyl esters)[a]

dianhydride	diamine	solvent	polymer	inherent viscosity (dL/g)[b]
1a	**2a**	DMAc	**3aa**	0.99 (0.74)[c]
1a	**2b**	DMAc	**3ab**	0.71
1a	**2c**	DMAc	**3ac**	0.51
1a	**2d**	DMAc	**3ad**	0.64
1a	**2a**	NMP	**3aa**	0.60
1a	**2b**	NMP	**3ab**	0.59
1a	**2a**	DMSO	**3aa**	0.72
1a	**2b**	DMSO	**3ab**	0.53

[a] Polymerization was carried out with 1.0 mmol of each monomer in the solvent at room temperature for 1 h under nitrogen. [b] Measured at a concentration of 0.5 g/dL in each solvent at 30 °C. [c] Inherent viscosity of poly(amic acid).

Table 2. Synthesis of Poly(amic acid silyl esters)[a]

monomers	reaction temp, °C	reaction time, h	polymer	η_{inh}[b]
1b + **2a**	room temp	24	**3ba**	0.09
1b + **2b**	room temp	24	**3bb**	0.12
1b + **2a**	60	24	**3ba**	0.10

[a] Polymerization was carried out with 1.0 mmol of each monomer in the solvent at each temperature for 24 h under nitrogen. [b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

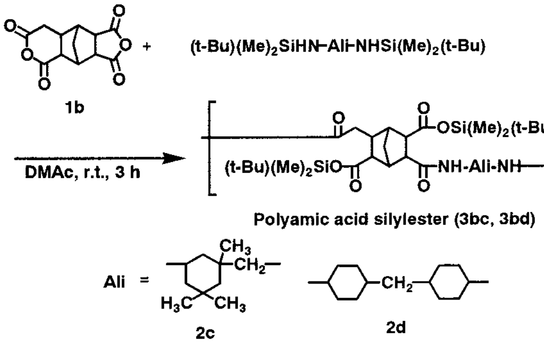
Table 3. Synthesis of Poly(amic acid silyl esters)[a]

dianhydride	diamines	polymer	η_{inh}[b]
1b	**2c**	**3bc**	0.35
1b	**2d**	**3bd**	0.29

[a] Polymerization was carried out with 1.0 mmol of each monomer in the solvent at room temperature for 3 h under nitrogen. [b] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

dianhydrides can be inferred from the molecular orbital energies of the lowest unoccupied molecular orbital (ϵ_{LUMO}), electron affinities, and ^{13}C chemical shifts of carbonyl carbons. The calculated value of ϵ_{LUMO} for **1a** (−1.87 eV) is considerably lower than that for **1b** (−1.37 eV), which indicates that the former has higher acylation reactivity than the latter. The calculated value of ϵ_{LUMO} for bicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydrides that has the same skeletal structure as that of **1b** but contains two five-membered anhydride ring is −1.53 eV. This value is closer to ϵ_{LUMO} of **1b** rather than that of **1a**. Hence, the lower reactivity of **1b** is mainly ascribed to the skeletal norbornane structure, though the introduction of six-membered anhydride ring further reduces the acylation reactivity.

N-Trimethylsilylated alicyclic diamines, which are labile in polar aprotic solvents, might be hydrolyzed to original diamines. Thus, more stable *N*-*tert*-butyldimethylsilylated alicyclic diamines, 5-*tert*-butyldimethylsilylamino-*N*-*tert*-butyldimethylsilyl-1,3,3-trimethylcyclohexanemethylamine (**2c**), 4,4′-methylenebis(*N*,*N*′-*tert*-butyldimethylsilylcyclohexylamine) (**2d**) were prepared. The polymerization was carried out in DMAc at room temperature for 3 h. The results are summarized in Table 3. The polymers **3bc** and **3bd** with inherent viscosities ranging between 0.29 and 0.35 dL/g were produced (eq 3). Trimethylsilylated diamines show higher reactivity than *tert*-butyldimethylsilylated diamines as can be seen in the synthesis of **3aa** and **3ac** in Table 1. The inherent viscosity of **3aa** increased rapidly compared to that of **3ac**.



(3)

Polymers **3** were readily converted to poly(amic acid)s (**4**) by pouring the solution of polymers **3** into a 0.2 wt % aqueous HCl solution at room temperature.

Polymer Characterization. Polymers **3** were identified as the expected poly(amic acid trialkylsilyl ester)s by IR spectroscopy. The IR spectra showed characteristic amide and silyl ester absorptions at 1658 and 1708 cm^{-1}. On the other hand, three characteristic absorptions for amide, carboxyl, and hydroxyl groups were observed at 1650, 1720, and 3000−3700 cm^{-1} for polymers **4**. Furthermore, elemental analyses also supported the formation of the expected polymers **4**.

Polymers **3** were soluble in THF, chloroform, and polar aprotic solvents such as NMP, DMAc, and DMSO at room temperature. The solubility of polymers **4** is lower compared to that of polymers **3**, but polymers **4** were still soluble in polar aprotic solvents at room temperature.

The molecular weight of **3bc** having an inherent viscosity of 0.35 dL/g was determined by means of GPC. The chromatogram indicated that the M_{n} and M_{w} values were 29 000 and 64 000, respectively, with respect to polystyrene standards, and the ratio $M_{\mathrm{w}}/M_{\mathrm{n}}$ was 2.2.

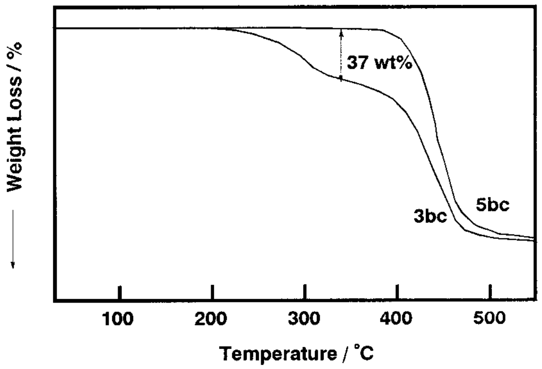
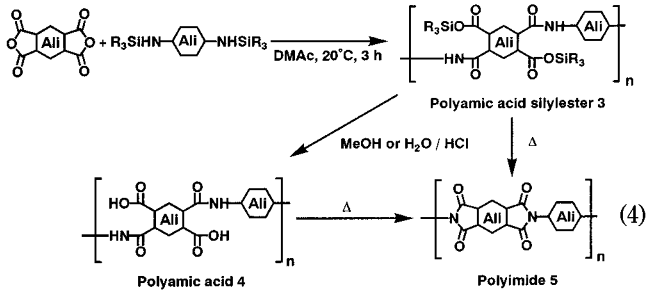


Figure 2. TGA curves of **3bc** and **5bc**.

These polyimide precursors **3** and **4** were converted to the corresponding polyimides (**5**) by thermal treatment. The structures and the abbreviations of the polyimides are illustrated in Figure 1 (eq 4).



(4)

The traces of thermogravimetry for polymer **3bc** and the corresponding polyimide **5bc** are shown in Figure 2. A rapid weight loss for **3bc** was observed at 200−350 °C. In this range, the weight loss was 37%, which is in good agreement with the value of weight loss calculated from the elimination of *tert*-butyldimethylsilanol due to the imidization.

The IR spectrum of thermally treated polymer **5bc** film (100 °C for 30 min, 150 °C for 30 min, 250 °C for 30 min, and 300 °C for 1 h) is shown in Figure 3, where characteristic imide absorptions at 1778 and 1704 cm^{-1} are visible and the absorption due to the carboxylic acid silyl esters at 1708 cm^{-1} had completely disappeared. Furthermore, the structure of polymer **5bc** was also confirmed by elemental analysis.

Table 4. Thermal Properties of Polyimides[a]

polymer	T_g (°C)[b]	T_s (°C)[c]	T_d(5%) (°C)[d]	T_d(10%) (°C)[e]
5aa	*f*	361	415	425
5ab	300	380	435	445
5ac	*f*	368	410	421
5ad	*f*	378	430	440
5bc	*f*	364	409	421
5bd	*f*	367	415	428

[a] Determined by TG at heating rate of 10 °C/min under N_2. [b] Glass transition temperature (T_g) measured by DSC at heating rate of 20 °C/min under N_2. [c] Starting temperature of decomposition. [d] Temperature at 5% weight loss. [e] Temperature at 10% weight loss. [f] Not detected.

Table 5. Refractive Indices and Birefringence of Wholly Alicyclic Polyimides Films

polyimide	d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	Δn[e]	ϵ[f]
5bc	5.3	1.5174	1.5170	1.5173	0.0004	2.53
5aa	6.5	1.4977	1.4977	1.4977	0.0000	2.47

[a] Film thickness. [b] The in-plane refractive indices. [c] The out-of plane refractive indices. [d] Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$. [e] Birefringence; $\Delta n = n_{TE} - n_{TM}$. [f] Optically estimated dielectric constant; $\epsilon = 1.10{n_{AV}}^2$.

Thermal properties of the polyimides evaluated by the TG technique have been listed in Table 4. The 10% weight loss temperatures (T_{d10}) in nitrogen were observed at 420−445 °C, respectively. These results show that the thermal stability is lower than that of aromatic polyimides, whereas it is enough for microelectronics applications.

The transmission UV−vis spectrum of the **5aa** and **5bc** film is shown in Figure 4. The wholly alicyclic polyimide films exhibit cutoffs at 230 and 235 nm, respectively. These values are close to those of other alicyclic polyimides (234 nm). Although a small absorption due to the carbonyl n−π* is observed around 260 nm, these films are entirely colorless. A cutoff wavelength is defined here as the point where the transmittance becomes below 1% in the spectrum.

Dielectric Constant of Polyimide 5. As listed in Table 5, the average refractive indices (n_{AV}) of the polyimides **5bc** and **5aa** were determined as 1.5173 and 1.4977, respectively. A dielectric constant (ϵ) of material at optical frequencies can be estimated from the refractive index n according to Maxwell's equation, $\epsilon \doteqdot n^2$. The ϵ around 1 MHz has been evaluated as $\epsilon \doteqdot 1.10{n_{AV}}^2$, including an additional contribution of approximately

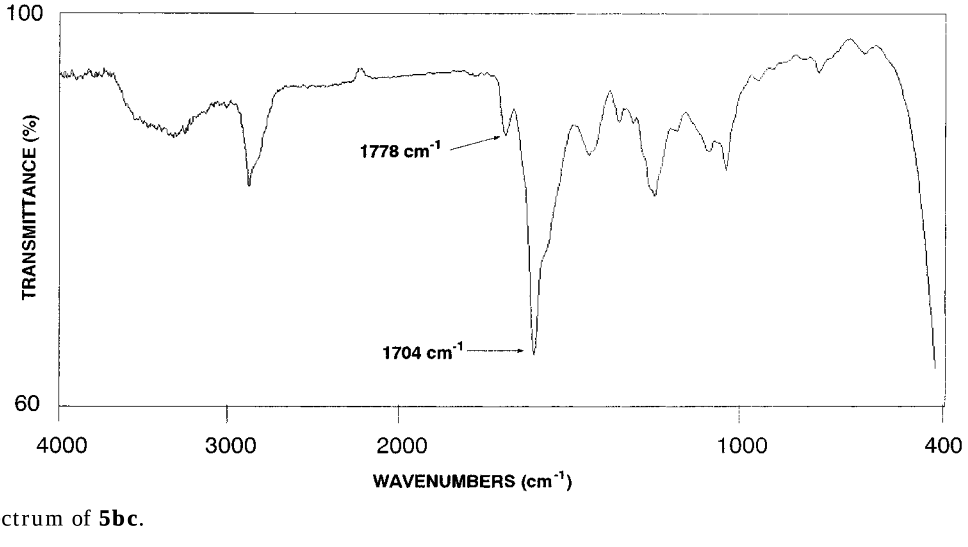


Figure 3. IR spectrum of **5bc**.

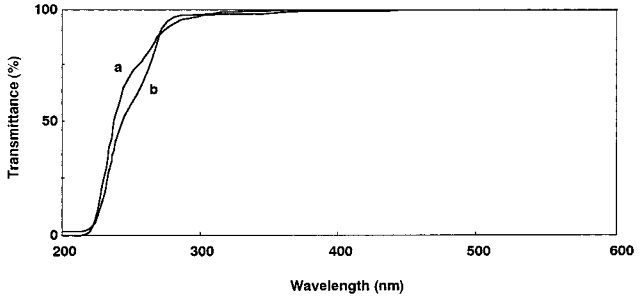


Figure 4. UV−vis spectra of wholly alicyclic polyimide films: (a) polyimide **5bc**; (b) polyimide **5aa**.

10% from the infrared absorption.[14,23] The n_{AV} of 1.5173 and 1.4977 can be translated into dielectric constants of 2.53 and 2.47, respectively. These values are slightly lower than the optically estimated ϵ of an alicyclic polyimide (2.55)[16] and a fluorinated semiaromatic polyimide (2.6)[14] and significantly lower than that of a semiaromatic polyimide (2.83).[16] In addition, the in-plane/out-of-plane birefringences (Δn) of the two polyimides were estimated as 0.0004 and 0.0000, respectively. These negligibly small birefringence implies that these polymers have low polarizability anisotropy and the polymer chains are randomly oriented in the film. The absence of birefringence was also reported for an alicyclic polyimide.[16]

Conclusions

The ring-opening polyaddition of N-trialkylsilylated alicyclic diamines **2** with alicyclic tetracarboxylic dianhydrides **1** in DMAc at room temperature afforded poly(amic acid trialkylsilyl esters) **3** with high molecular weights ($\eta_{inh} = 0.99$ dL/g), because polymers **3** have good solubility in organic solvents and do not undergo any side reactions such as salt formation with N-silylated diamine. Polymers **3** were easily hydrolyzed to corresponding poly(amic acid)s **4**. The films of polymers **3** and **4** were converted to transparent films of the wholly alicyclic polyimides **5** with the elimination of *tert*-butyldimethylsilanol and H_2O by thermal treatment, respectively. Polyimides **5** are transparent over 250 nm and have good thermal stability with the 10% weight loss temperature around 430 °C. The wholly alicyclic polyimides synthesized in this study exhibit low refractive indices, and the estimated dielectric constant is as low as 2.47. Thus, the N-silylated diamine method is considered to be a versatile and promising route for synthesis of a variety of high molecular weight wholly alicyclic polyimides.

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