

ORIGINAL ARTICLE

Synthesis of trisiloxane-containing alicyclic tetracarboxylic dianhydrides and the characterization of polyimides

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The titular alicyclic tetracarboxylic dianhydrides were synthesized with endo- and/or exo-5-norbornene-2,3-dicarboxylic anhydride and 1,1,3,3,5,5-hexamethyltrisiloxane. The endo-structure tetracarboxylic dianhydride was reported to be a crystal, and could be divided into meso and racemic isomers. By contrast, the exo-structure tetracarboxylic dianhydride was a highly viscous liquid. Polyimides synthesized from these tetracarboxylic dianhydrides and 4,4'-oxydianiline were colorless and organosoluble. The exo-structure polyimide had better mechanical properties and higher glass transition temperatures than the endo-structure polyimides. The elongation at the break of the exo-structure polyimide increased with weight-average molecular weight (Mw) and saturated at 22% when Mw was greater than 88 000. Polyimides synthesized from the meso and racemic isomers of the endo-structure showed the same thermal properties.

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INTRODUCTION

Aromatic polyimides have been used extensively in microelectronics, semiconductors and many other fields, because of their outstanding thermal, electrical and mechanical properties. Recently, however, semi-aromatic or wholly alicyclic polyimides have gained the increasing attention in the optoelectronics field, which requires the colorless and highly transparent polyimides in the near-ultraviolet region.

To derive the above-mentioned polyimides, many alicyclic tetracarboxylic dianhydrides have been synthesized with hydroesterification of unsaturated alicyclic compounds, oxidation of fused alicyclic compounds with nitric acid, hydrogenation of aromatic tetracarboxylic compounds and other methods. However, these methods have the problem of low yield and the necessity of esterification, hydrolysis and dehydration with acetic anhydride before and after the reacting process.

On the other hand, hydrosilylation^{1–5} of endo-5-norbornene dicarboxylic anhydride (endo-NBA) can synthesize the siloxane-containing tetracarboxylic dianhydrides with a one-step reaction and a high yield.

As the most relevant tetracarboxylic dianhydride, 5,5'-(1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diyl)bisbicyclo[2.2.1]heptane-2,3-endo-dicarboxylic anhydride (endo-TriSXDA) was synthesized with endo-NBA and 1,1,3,3,5,5-hexamethyltrisiloxane (HMST). There are two reports concerning the endo-TriSXDA. One of them characterized the polyimides derived from several diamines, and reported that the melting point of the endo-TriSXDA was 133.4–133.9 °C.⁴ However, in the other report, the author showed that the endo-TriSXDA could be

divided into two types of crystals with different melting points: 143.5–144.5 and 119.5–121.5 °C. The former was a fine-needle-like crystal, and was not able to be analyzed by X-ray analysis. The latter was a large single crystal and confirmed to be the racemic isomer.⁵

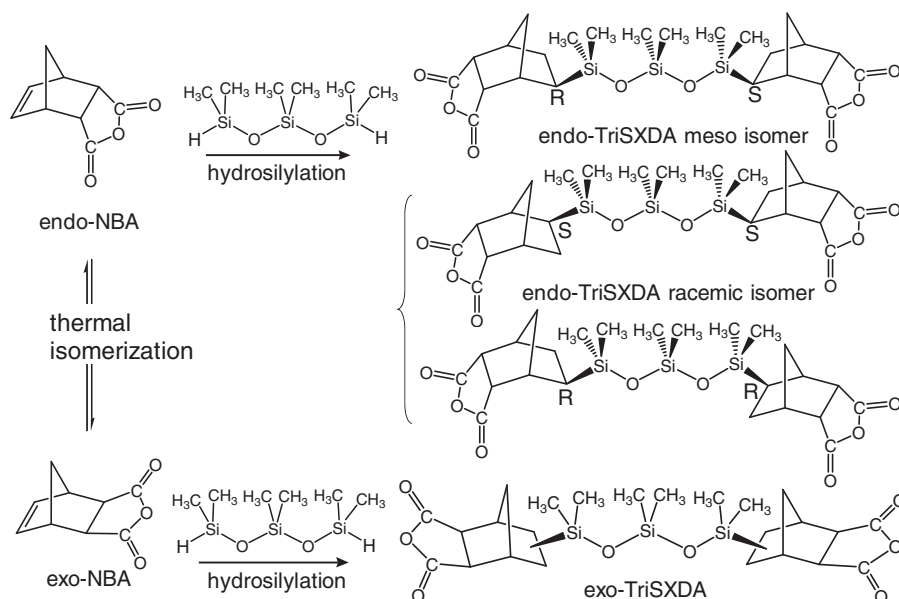
Before the above reports about the endo-TriSXDA, there was a report of the polyimides derived from the DiSXDA (disiloxane-containing endo- and/or exo-norbornane tetracarboxylic dianhydride).⁶ The repeating structural unit of these pentamethyldisiloxane end-capped polyimides, which were synthesized with the disiloxane equilibration reaction, was the same as that of the polyimides derived from DiSXDA and *m*-phenylenediamine. Here, only glass transition temperature (T_g) by differential scanning calorimetry was reported about the properties of these polyimides. In addition, the molecular weight of the polyimide derived from endo-DiSXDA and *m*-phenylenediamine was low, and even the T_g was not reported.

Thus, it is worthwhile to distinguish endo- from exo-structures when synthesizing trisiloxane-containing tetracarboxylic dianhydrides, as shown in Scheme 1. It is also important to clarify the relationship between the structure and properties of polyimides derived from these tetracarboxylic dianhydrides.

EXPERIMENTAL PROCEDURES

Materials

For hydrosilylation to synthesize alicyclic tetracarboxylic dianhydrides, endo-NBA (mp 166.5–167.5 °C), HMST (Shin-Etsu Chem., Tokyo, Japan; LS-8130), Platinum Complex (Sigma-Aldrich, St Louis, MO, USA; Platinum(0)–1,3-



Scheme 1 Synthesis of TriSXDA.

divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylene, 2% Pt) as the catalyst and toluene as the solvent were commercially available and used without being refined. For the synthesis of polyimides, 4,4'-oxydianiline (ODA), 2-hydroxypyridine as the catalyst and 1,2-dichlorobenzene as the solvent were also commercially available and used as commercially formulated. In addition, acetone and methanol were used for precipitating the polyimides, 1-methyl-2-pyrrolidinone was used as the solvent for preparing poly(amic acid), and *N,N*-dimethylacetamide was used as the solvent for preparing polyimide films; these were also commercially available and used as commercially formulated. The exo-NBA (mp 148.0–149.5 °C), which was available through the thermal isomerization of endo-NBA, was synthesized as described in the literature.⁷

Measurements

The melting points of the dicarboxylic anhydrides and tetracarboxylic dianhydrides were measured using a capillary-type apparatus at a heating rate of 2 °C min⁻¹. The viscosity of exo-TriSXDA was measured using a rotational cone-plate-type EH-viscometer by Tokyo Keiki Inc., Tokyo, Japan. The components of hydrosilylation mixture and the purity of tetracarboxylic dianhydrides were determined by gel permeation chromatography (GPC) equipped with polystyrene gel columns (Hitachi Chem., Hitachi-shi, Japan; Gelpack GL-A110, two 500 mm columns in series, with a Mw exclusion limit of ca. 1500), and a Hitachi L-300 RI detector was used with tetrahydrofuran as an eluent at a flow rate of 1.0 ml min⁻¹. Infrared (IR) spectra were obtained with a Varian 3100FT-IR spectrometer (Varian, Palo Alto, CA, USA) by attenuated total reflection (ATR) method. Elemental analyses were performed with an Elementar vario MICRO cube (Elementar, Hanau, Germany). The nuclear magnetic resonance (NMR) spectra were recorded using tetramethylsilane as an internal standard in CDCl₃ on a Bruker BioSpin AV400M (Bruker BioSpin, Rheinstetten, Germany; ¹H NMR: 400 MHz). The number- and weight-average molecular weights (Mn and Mw) of the polyimides were determined by GPC equipped with polystyrene gel columns (Hitachi Chem.; Gelpack GL-R440, GL-R450 and GL-400M in series) and a Hitachi L-300 RI detector, and using tetrahydrofuran at a flow rate of 2.0 ml min⁻¹. The system was calibrated using polystyrene standards at room temperature. A thermomechanical analysis was carried out with a Seiko TMA/SS-6200 (Seiko, Chiba-shi, Japan) in tensile mode at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry was performed with a Seiko DSC-6200 at a heating rate of 10 °C min⁻¹ in air. A thermogravimetric analysis was made with a Seiko TG/DTA-6200 at a heating rate of 10 °C min⁻¹ in air. Ultraviolet–vis spectra of the polyimide films were recorded on a Hitachi U-3310 spectrometer. Mechanical properties were

measured with a Shimadzu AGS-5kNG (Shimadzu, Kyoto, Japan) with a 5 mm min⁻¹ drawing speed. Measurements were performed at ambient conditions for film specimens (10 mm wide, 20 mm long and 20–30 μm thick), and the results of at least five samples were averaged.

Synthesis of tetracarboxylic dianhydrides

Synthesis of meso and racemic isomers of endo-TriSXDA were reported in the previous paper.⁵ The synthesis of exo-TriSXDA is described as follows: exo-NBA (65.66 g, 400 mmol) and toluene (260 g) were placed in a 1 l, four-necked, round-bottomed flask, equipped with a magnetic stirrer, a 50 ml dropping funnel, a nitrogen inlet and a thermometer. When the temperature of the reaction mixture reached to 55 °C, 1.566 g of the Pt catalyst solution (Pt: 0.161 mmol) was added to the flask, and HMTS (41.69 g, 200 mmol) was dripped for 2 h into the flask. The reaction mixture was maintained at 55 °C for 1 h. A GPC analysis confirmed that the reaction had been completed, leaving no exo-NBA, HMTS or their intermediates (because HMTS reacted with one molecule of exo-NBA) in the mixture. After cooling to the room temperature, activated carbon was added to the mixture to decolorize and remove the catalyst. The colorless filtrate had no crystal precipitation. After drying, a highly viscous liquid (99.2 g, 185 mmol, yield: 92.5%) with the viscosity of 38.4 Pa·s at 40 °C was obtained. The purity was 99.5% by GPC analysis.

Results of elemental analysis on C₂₄H₃₆O₈Si₃ (formula weight: 536.79) were as follows: the calculated values of C and H were 53.70% and 6.76%, respectively, and those of measured values were 53.33% and 6.75%, respectively. The ν-values (ATR, cm⁻¹) of the IR spectra of tetracarboxylic dianhydrides were as follows: endo-TriSXDA meso isomer; 1848 and 1772 (C=O), 1258 (Si-CH₃), 1080 and 1063 (Si-O-Si), and 900 (C-O-C), endo-TriSXDA racemic isomer; 1857 and 1777 (C=O), 1255 (Si-CH₃), 1082 and 1048 (Si-O-Si), and 903 (C-O-C), exo-TriSXDA; 1864 and 1774 (C=O), 1257 (Si-CH₃), 1074 and 1034 (Si-O-Si), and 901 (C-O-C). Chemical shift values of ¹H NMR spectra (400 MHz, CDCl₃) were described in Figure 1 and Table 2.

General polymerization procedure and film preparation of polyimides

The polyimides were synthesized with the one-pot method described in the previous paper.⁴ The following were placed into a 100 ml, four-necked, round-bottomed flask, equipped with a mechanical stirrer, a Dean–Stark trap, a nitrogen inlet and a thermometer, along with tetracarboxylic dianhydride (5.368 g, 10.00 mmol), ODA (2.002 g, 10.00 mmol), 2-hydroxypyridine (0.230 g) and 1,2-dichlorobenzene (52.20 g). The mixture was heated at 100 °C

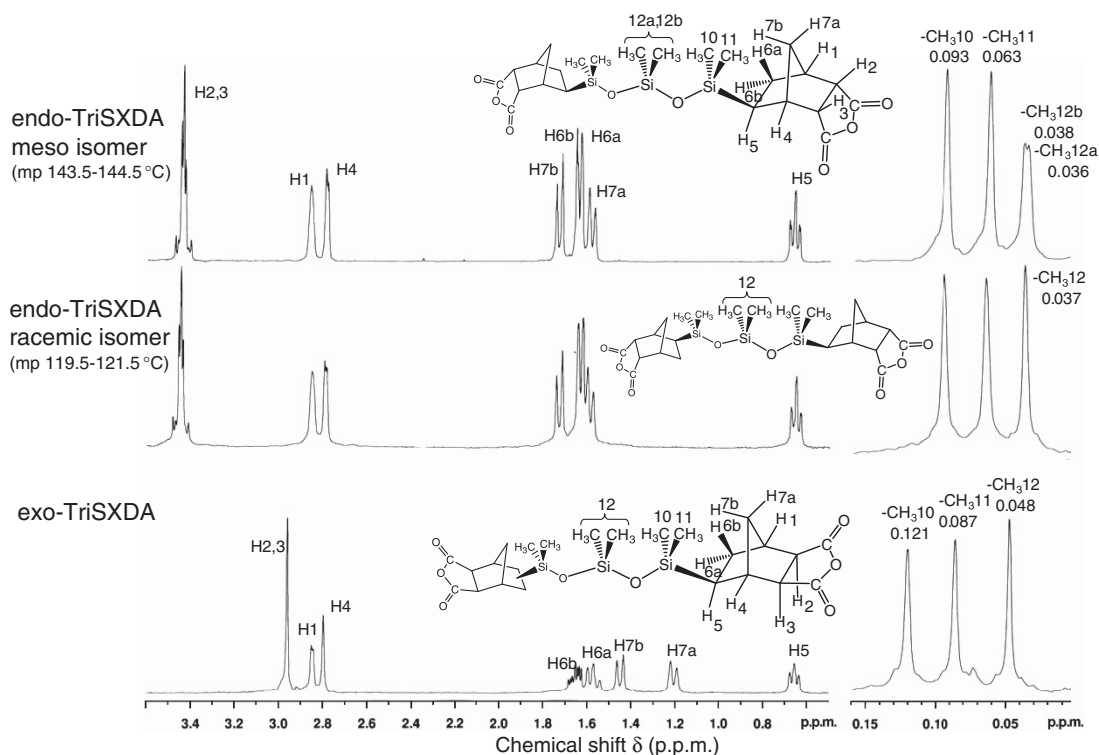


Figure 1 ^1H NMR spectra of the endo- and exo-TriSXDA.

for 30 min until the monomers and the catalyst were fully dissolved. The mixture was then heated to 179 °C and refluxed at this temperature for 4 h.

After being cooled, the solution was poured while being agitated into 500 g of methanol to precipitate a polyimide. The polyimide was then dissolved in acetone (50 g). Methanol was dripped slowly while being agitated into the acetone solution until it separated into two layers. The upper layer was removed by decantation, and methanol was added to the lower layer to precipitate a polyimide. By repeating this procedure, polyimides with the desired molecular weight were prepared.

Next, the prepared polyimide was dissolved in the *N,N*-dimethylacetamide solution. The concentration was 25%. The polyimide film was prepared by casting the solution onto a glass plate and then heating at 65 °C for 30 min, and at 165 °C for 15 min. After cooling, the glass plate was immersed in water and the polyimide film was peeled off in water.

All the polyimides thus synthesized have the same molecular formula, $(\text{C}_{36}\text{H}_{44}\text{N}_2\text{O}_7\text{Si}_3)_x$ and the calculated values of C, H and N were 61.68%, 6.33% and 4.00%, respectively. The results of elemental analyses and molecular weight of the each polyimide were as follows: endo-TriSXDA meso isomer/ODA polyimide: C = 61.17%, H = 6.31% and N = 3.86%; $M_n = 19\,800$ and $M_w = 31\,900$. The endo-TriSXDA racemic isomer/ODA polyimide: C = 61.05%, H = 6.31% and N = 3.92%; $M_n = 15\,700$ and $M_w = 27\,500$. The exo-TriSXDA/ODA polyimide: C = 61.25%, H = 6.26% and N = 3.91%; $M_n = 76\,500$, $M_w = 110\,000$. The ν -values (ATR, cm^{-1}) of each polyimide was as follows: endo-TriSXDA meso isomer/ODA polyimide: 1773 and 1707 (C=O), 1499 (Ph), 1376 and 1168 (C-N-C), 1237 (br, Ph-O-Ph), 1034 (br, Si-O-Si). The endo-TriSXDA racemic isomer/ODA polyimide: 1778 and 1707 (C=O), 1499 (Ph), 1376 and 1168 (C-N-C), 1237 (br, Ph-O-Ph) and 1033 (br, Si-O-Si). The exo-TriSXDA/ODA polyimide: 1775 and 1707 (C=O), 1500 (Ph), 1378 and 1177 (C-N-C), 1239 (br, Ph-O-Ph) and 1034 (br, Si-O-Si). Chemical shift values of ^1H NMR spectra (400 MHz, CDCl_3) were described in Figure 3 and Table 2.

Synthesis of *N*-phenylimide as model compound

N-phenylimide was derived from endo-TriSXDA meso isomer (10 mmol) and aniline (40 mmol), with the same method as that used for polyimide synthesis.

After cooling, the reaction solution was poured into a 1:1 (by weight) mixture of water and methanol. The resultant cloudy upper layer of solution was removed, and the excess aniline and 1,2-dichlorobenzene were removed from the lower pale-yellow layer by vacuum distillation to produce a pale yellowish-brown glassy solid of endo-TriSXDA meso *N*-phenylimide. The yield was 79.6%. The calculated elementary compositions of C, H and N of $\text{C}_{36}\text{H}_{46}\text{N}_2\text{O}_6\text{Si}_3$ were 62.94%, 6.75% and 4.08%, respectively, and the corresponding measured values were 62.13%, 6.69% and 3.92%, respectively. The ν -values (ATR, cm^{-1}) of IR spectrum were as follows: 1773 and 1706 (C=O), 1497 (Ph), 1371 and 1174 (C-N-C), 1256 (Si-CH₃) and 1032 (br, Si-O-Si). Chemical shift values of ^1H NMR spectrum (400 MHz, CDCl_3) were described in Figure 4 and Table 2.

In the same manner, a pale yellowish-brown glassy solid of exo-TriSXDA *N*-phenylimide was produced. The yield was 92.6%. Results of analyses for C, H and N of this compound were 62.30%, 6.69% and 3.97%, respectively. The ν -values (ATR, cm^{-1}) of IR spectrum were as follows: 1773 and 1702 (C=O), 1499 (Ph), 1378 and 1183 (C-N-C), 1256 (Si-CH₃) and 1035 (br, Si-O-Si). Chemical shift values of ^1H NMR spectrum (400 MHz, CDCl_3) were described in Figure 4 and Table 2.

Synthesis of poly(amic acid) as model compound

The synthesis of exo-TriSXDA/ODA poly(amic acid) is described as follows: exo-TriSXDA (6.321 g, 11.78 mmol), ODA (2.358 g, 11.77 mmol) and 1-methyl-2-pyrrolidinone (49.2 g) were placed in a 100 ml, four-necked, round-bottomed flask. The reaction mixture was maintained at 30 °C for 4 h. The solution was poured into water of 300 ml to precipitate a poly(amic acid). A lump of poly(amic acid) was dissolved in acetone (40 g), and then, acetone solution was dripped slowly into water while being agitated. Powdered poly(amic acid) was dried at room temperature for 5 h by vacuum (80 Pa). The yield was 61.6%. The calculated elementary compositions of C, H and N of $(\text{C}_{36}\text{H}_{48}\text{N}_2\text{O}_9\text{Si}_3)_x$ were 58.67%, 6.56% and 3.80%, respectively, and corresponding measured values were 57.85%, 6.49% and 3.74%, respectively. The ν -values (ATR, cm^{-1}) of IR spectrum were as follows: 3324 (br, O-H), 1703 (br, C=O), 1532 (N-H), 1499 (Ph), 1256 (Si-CH₃), 1229 (Ph-O-Ph) and 1035 (br,

Ph and Si-O-Si). The ^1H NMR spectrum (400 MHz, acetone- d_6) is shown in Figure 3.

RESULTS AND DISCUSSION

Synthesis and NMR studies of monomers

The hydrosilylation of endo- and exo-NBA proceeded stoichiometrically without any byproducts, as confirmed by GPC analyses. Comparing the reactivity of endo- and exo-NBA, it was found that the exo-NBA reaction was completed in a shorter period (9 h vs 3 h), despite the latter having half the amount of catalyst (822 p.p.m. vs 402 p.p.m.: molar ratio [Pt]/[NBA]) and a lower reaction temperature (90 °C vs 55 °C). The remarkably higher reactivity of exo-NBA comparing with endo-NBA agreed with the report on the hydrosilylation of endo- and exo-NBA with dimethylchlorosilane under the same conditions, in which the time to complete the reaction for exo-NBA is 30 min or less, in contrast to 48 h for endo-NBA.⁸ According to the another paper, the lower activity of the endo-NBA was due to the charge in the lowest unoccupied molecular orbital (LUMO) and its weak π -acceptor interaction with the platinum atom.⁹

As described in the introduction, the endo-TriSXDA was divided into two types of crystals. The crystal of lower melting point was

confirmed to be the racemic isomer by X-ray analysis, and that of higher melting point was thought to be a meso isomer according to the reaction mechanism. On the contrary, exo-TriSXDA, which was an extremely highly viscous liquid at room temperature, showed no sign of crystallization even after 3 years standing. From the amount of yield, this is presumed to be a mixture of meso and racemic isomers.

Figure 1 shows the ^1H NMR spectra of the tetracarboxylic dianhydrides. The width of the range 0.00–0.15 p.p.m. is scaled up. The attribution of the protons in the figure is based on the results of the Oak Ridge thermal ellipsoid plot program (ORTEP) of X-ray analysis⁵ and analyzing the two-dimensional spectra of incredible natural abundance double quantum transfer experiment (INADEQUATE), heteronuclear single quantum coherence and nuclear overhauser enhancement spectroscopy. The spectra of meso and racemic isomer of endo-TriSXDA were found to be almost the same, and the only difference lies with the methyl group protons of the center silicon in the highest field. The figures attached to these methyl groups represent their chemical shift values. The two methyl groups of the meso isomer are nonequivalent; therefore, these protons were observed as two separate peaks. On the other hand, those of the racemic isomer are equivalent. Therefore, these protons were observed as a single peak.

And then, other results of analyses for the NMR spectra were as follows. The H6a proton (i.e., methylene proton upfield) is in the exo-position of the norbornane ring for endo-TriSXDA, whereas it is in the endo-position for exo-TriSXDA. The two methyl group protons (i.e., $-\text{CH}_310$ and $-\text{CH}_311$) bonded with the side silicon exist near the chiral center (i.e., no. 5 carbon). Therefore, these protons show different chemical shift values. From the relationship between these protons and the norbornane ring protons for the NOESY spectra, it is inferred that the silicon atom does not rotate freely.

Table 1 Results of polymerization and precipitation

Tetracarboxylic dianhydride	Purity (%)	Concentration (%)	Precipitation number	Yield (%)	M_n	M_w	M_w/M_n
Endo-meso	99.6	12.5	1	—	6800	16800	2.49
			2	68	11900	25600	2.15
			4	36	19800	31900	1.61
		15.0	1	95	10900	45600	4.18
			3	54	28400	47000	1.65
			5	40	43000	65500	1.52
Endo-racemic	98.4	12.5	3	50	15700	27500	1.75
			6	18	38900	63000	1.62
			1	—	17300	53300	3.08
		12.5	2	75	25800	57700	2.24
			3	47	35300	63800	1.81
			4	30	44800	72900	1.63
Exo-	99.5	15.0	2	79	30400	56200	1.85
			3	48	55900	88200	1.58
			6	18	76500	110000	1.44
		15.0	8	13	88700	117000	1.32

Preparation of polyimides

The results of polymerization and precipitation are summarized in Table 1. As the repetitions of precipitation using acetone and methanol increased, the yield of polyimides decreased. The relationship between the yield of all polyimides as logarithmic value and the number of precipitations are shown in Figure 2a. A good linear relationship can be seen (correlation coefficient $r = 0.970$). Figure 2b shows the relationship between M_n and polydispersity (M_w/M_n) of polyimides. As the figure indicates, M_n increased with repeated precipitation and M_w/M_n approached toward 1.0. In addition, higher concentration and exo-structure produced the higher M_n polyimides.

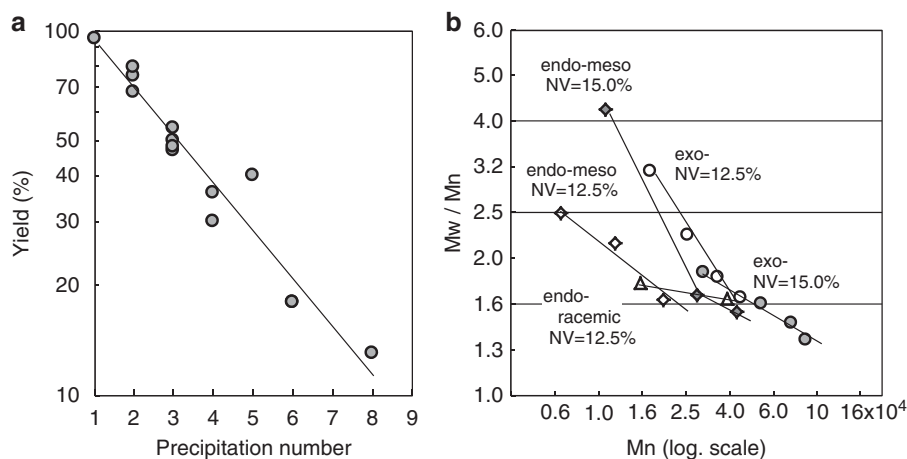


Figure 2 Results of precipitation and M_w of polyimides.

With regards to the film formation of polyimides, endo-polyimides from both meso and racemic isomers maintained the film form until halfway through the drying process. However, when the drying temperature exceeded the T_g , the endo-polyimides developed numerous fine cracks, preventing the formation of films. This is presumably attributable to a change in conformation resulting from molecular movements at temperatures above the T_g . This phenomenon also corresponds to the twisting or distortion of a repeating unit structure, which is inferable via the NMR analysis as mentioned below and the most stable structures of tetracarboxylic dianhydrides from quantum chemical calculation as mentioned in the last section.

Confirmation of imidization

In the IR spectra of three polyimides, the broad absorption near 3300 cm^{-1} based on the O-H stretching vibration of carboxyl group was not observed at all.

Figure 3 shows the ^1H NMR spectra of the polyimides and exo-TriSXDA/ODA poly(amic acid) as contrast. The poly(amic acid) was measured with hexadeuteroacetone as solvent, because it is insoluble in deuteriochloroform. The width of the ranges 0.00–0.20 and 6.6–7.7 p.p.m. is scaled up.

The spectrum of poly(amic acid) is extremely complex compared with the spectra of polyimides. The reason is because of the existence of isomers, which differ in the position where the amide and the carboxyl group joins the norbornane ring. The methyl group protons have the three times higher intensity than the carboxyl group proton and are easy to be observed. However, there is not the methyl group protons coming from poly(amic acid) in the spectra of polyimides. In addition, the existence of the carboxyl group proton

was investigated, but there was not the clear peak in the downfield more than 8 p.p.m.

Thus, it is confirmed that the imidization was completed.

NMR studies of polyimides

The three spectra of the polyimides in Figure 3 were all different to each other. The methyl group protons of the center silicon in the endo-TriSXDA meso isomer/ODA polyimide (endo-meso polyimide) presented two clearly separate peaks. The difference in chemical shift value between the peaks was 0.011 p.p.m., which was larger than the difference for the endo-TriSXDA meso isomer. The methyl group protons of the center silicon in the endo-TriSXDA racemic isomer/ODA polyimide (endo-racemic polyimide) showed the same peak as the endo-TriSXDA racemic isomer. For the exo-TriSXDA/ODA polyimide (exo-polyimide), the H2 and H3 protons were shifted toward the upfield to overlap with the H4 proton, but the methyl group proton showed a different chemical shift value from the endo-polyimides; this was also the case for the tetracarboxylic dianhydride. From these results, it can be concluded that the polyimides maintained the structure of the tetracarboxylic dianhydrides.

The comparison in detail of the chemical shift values of the protons between the tetracarboxylic dianhydrides and the polyimides reveals that the chemical shift values of protons other than the methyl, H2 and H3 protons also changed. The changes in chemical shift values are considered to be a result of the transformation of protons into a polyimide, which causes the change in electronic and magnetic shielding state. To confirm the above-mentioned speculation, N-phenylimides of endo-TriSXDA meso isomer and exo-TriSXDA were synthesized as model compounds. The ^1H NMR spectra and

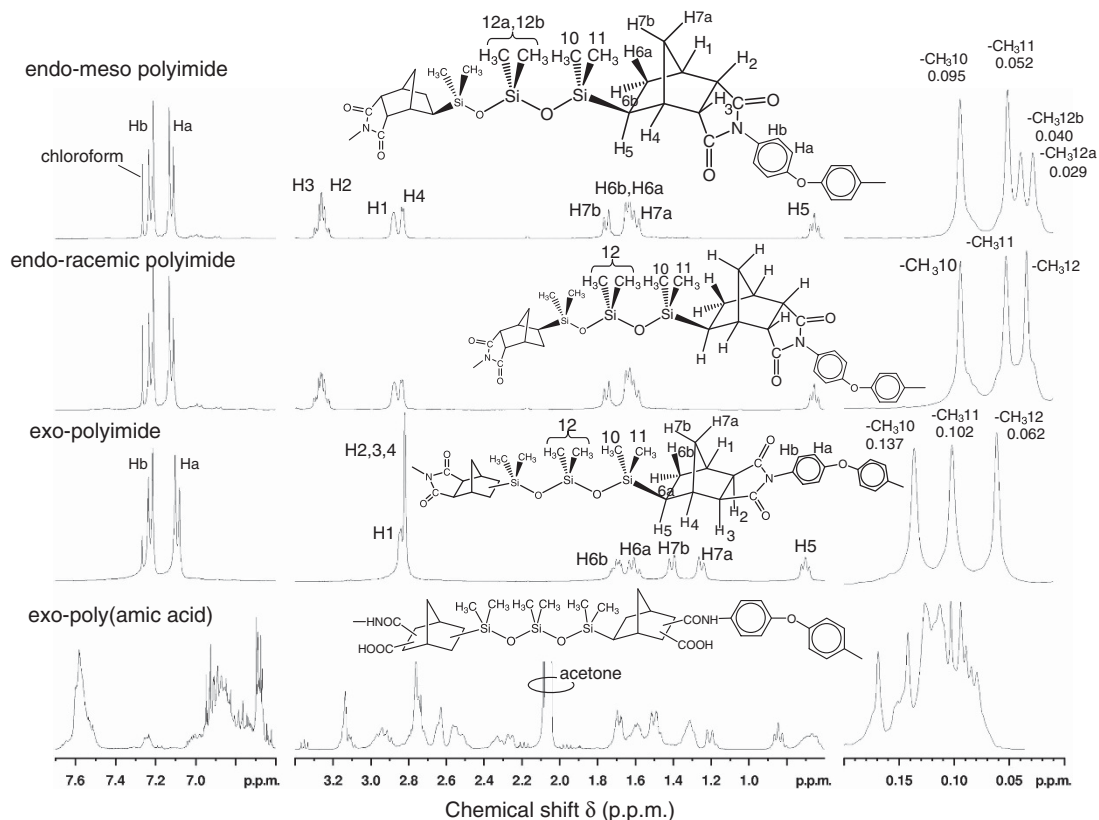


Figure 3 ^1H NMR spectra of the endo-, exo-polyimides and exo-polyamic acid.

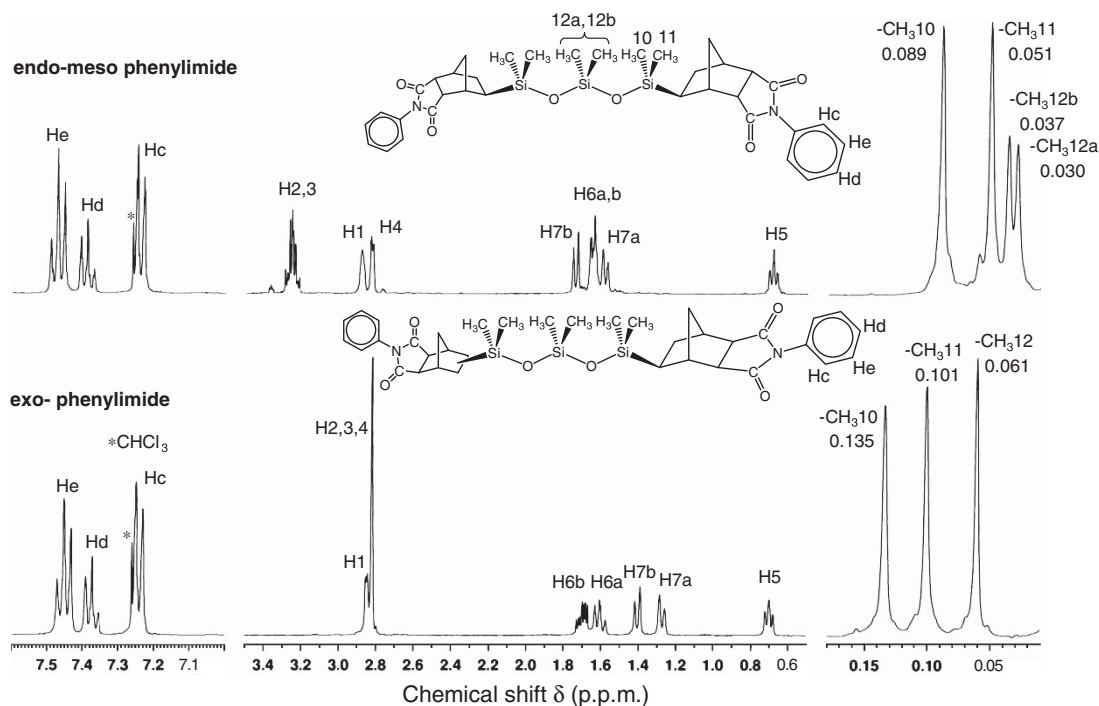


Figure 4 ^1H NMR spectra of endo-meso and exo-phenylimides.

Table 2 Fluctuation of chemical shift values

Proton	Endo-meso					exo-				
	Tetracarboxylic dianhydride	$ \Delta $	Phenylimide	$ \Delta $	Polyimide	Tetracarboxylic dianhydride	$ \Delta $	Phenylimide	$ \Delta $	Polyimide
H1	2.866	0.013	2.879	0.000	2.879	2.847	0.001	2.848	0.006	2.842
H2,3	3.432	0.175	3.257	0.004	3.261	2.961	0.140	2.821	0.001	2.820
H4	2.790	0.036	2.826	0.007	2.833	2.798	0.023			
H5	0.673	0.012	0.685	0.031	0.654	0.657	0.043	0.700	0.002	0.702
H6a	1.641	0.009	1.650	0.019	1.631	1.571	0.034	1.605	0.002	1.607
H6b	1.662	0.001	1.661	0.010	1.651	1.653	0.044	1.697	0.004	1.701
H7a	1.580	0.005	1.585	0.009	1.594	1.207	0.067	1.274	0.022	1.252
H7b	1.736	0.006	1.742	0.012	1.754	1.450	0.045	1.405	0.002	1.407
-CH ₃ 10	0.093	0.004	0.089	0.006	0.095	0.121	0.014	0.135	0.002	0.137
-CH ₃ 11	0.063	0.012	0.051	0.001	0.052	0.087	0.014	0.101	0.001	0.102
-CH ₃ 12a	0.036	0.006	0.030	0.001	0.029	0.048	0.013	0.061	0.001	0.062
-CH ₃ 12b	0.038	0.001	0.037	0.003	0.040					

changes in chemical shift values are shown in Figure 4 and Table 2. Comparing chemical shift values between the N-phenylimide and polyimide of exo-TriSXDA, the value changes occurred only in the H1, H6b and H7a protons. For the endo-TriSXDA meso isomer, however, such changes occurred in most of the protons. Therefore, it can be inferred that the changes in the chemical shift value were caused not only by imidization, or a change in the electronic state, but also by polymerization, which presumably generated twisting or distortion in the structure of the repeating unit of a polyimide. It also explains why endo-polyimides did not show the high molecular weight.

Properties of polyimides

The solubility of the polyimides was tested qualitatively in several solvents and the results are summarized in Table 3. All the polyimides were insoluble in methanol and separated into two separate layers in toluene. However, they dissolved readily in the other solvents.

The T_g by differential scanning calorimetry and the 5% weight loss temperature (Td₅) by thermogravimetric analysis of endo-polyimides are shown in Table 4. There are no differences in the values of thermal properties between the meso and racemic isomers.

The exo-polyimides had good film formability in contrast with endo-polyimides even when M_w was 56 200. Because they are soluble

in acetone, polyimides of various Mw were prepared by repeating the fractional precipitation. Table 5 shows the characteristics of the obtained exo-polyimides.

Many of the characteristic values remain almost unchanged by Mw. However, the value of elongation at break under tensile testing increased with Mw, reaching a constant value when Mw became 88 000 or higher.

Despite the change in elongation with Mw, the value of tensile strength did not change, because the elongation reached the yield point at approximately 7% elongation. In other words, tensile strength is equated with yield strength, and elongation is equated with fracture strain.

As shown in the table, the Tg of the exo-polyimide was 10–15 °C higher than that of the endo-polyimides. This result is contrastive to the previously reported case of the endo- and exo-polyimides, which use DiSXDA and m-phenylenediamine for repeating structural unit,

Table 3 Solubility of polyimides

Unit structure	Mw	Solvents					
		Methanol	Toluene	Acetone	THF	NMP	DMAc
Endo							
Meso	65 500	– ^a	+ / – ^a	++ ^a	++	++	++
Racemic	63 000	–	+ / –	++	++	++	++
Exo	56 200	–	+ / –	++	++	++	++

Abbreviations: THF, tetrahydrofuran; NMP, N-methyl-2-pyrrolidinone; DMAc, N,N-dimethylacetamide.

The qualitative solubility was determined by dissolving 0.1 g of polyimides in 1.0 g of solvent.

^a ++ Soluble at room temperature; + / – phase separate; – insoluble.

Table 4 Thermal properties of the endo-polyimides

Unit structure	Mw	Tg (°C) ^a	Td5 (°C) ^b
Meso	31 900	126	—
	65 500	129	482
Racemic	27 500	131	—
	63 000	126	485

Abbreviation: DSC, differential scanning calorimetry.

^aGlass transition temperature (Tg) was measured by DSC at heating rate of 10 °C min⁻¹ in air.

^bTemperature at which 5 % weight loss was recorded by thermogravimetry at heating rate of 10 °C min⁻¹ in air.

Table 5 Thermal and mechanical properties of the exo-polyimide

Mw	Tg (°C)		CTE ^b (× 10 ⁻⁶ K ⁻¹)	Td5 (°C)	Strength (MPa)	Modulus (GPa)	Elongation (%)
	DSC	TMA ^a					
57 700	140	141	91	466	45	1.64	6.5
56 200	—	140	101	—	41	1.53	6.4
63 800	141	142	94	465	39	1.47	9.7
72 900	142	142	92	456	38	1.46	14
88 200	—	138	102	—	43	1.54	22
110 000	136	140	89	460	43	1.54	21
117 000	143	143	89	460	50	1.42	22

Abbreviations: DSC, differential scanning calorimetry; TMA, thermomechanical analyses; CTE, coefficient of thermal expansion.

^aMeasured by TMA with extension mode applying load of 5 g at heating rate of 10 °C min⁻¹

^bCTE was determined by TMA range 30–100 °C

where the Tg value of 187 °C was the same for the endo- and exo-polyimides.⁶ The reason of the same Tg for endo- and exo-polyimides of m-phenylenediamine may come from the rigid portion joined to dimethylsiloxane chain. Thus, the Tg of the polyimides may be mainly determined by the micro-Brownian motion of the flexible dimethylsiloxane chain.

On the other hand, the polyimides studied in this paper are synthesized from ODA, which has an ether linkage as bent bond. Comparing with polyimides synthesized from m-phenylenediamine mentioned above, the sizes of the rigid portion are small. In contrast to strongly bent rigid portion of endo-polyimide, the rigid portion of the exo-polyimide is extended. As a result, the polymer chain of the exo-polyimide easily takes an extended structure. Thus, the exo-polyimide may have a denser stacked structure compared with endo-polyimides, and the Tg may also become higher due to the effects of the neighboring polymer chain.

The above-mentioned result agrees with the report by Matsumoto *et al.*,¹⁰ in which the values of Tg of polyimide synthesized using either norbornane-2,3-endo; 5,6-exo-tetracarboxylic dianhydride as bent structure and norbornane-2,3-exo; or 5,6-exo-tetracarboxylic dianhydride as extended structure with 1,3-bis(4-aminophenoxy) benzene were evaluated, and the Tg of the latter (225 °C) was reported to be 14 °C higher than that of the former (211 °C).

Also, as shown in Table 5 of mechanical properties, the higher Mw resulted in the higher elongation. The flexible film formability of exo-polyimides may come from the high elongation due to the extended polymer structure. The modulus and elongation in Table 5 are three times higher than endo-polyimide, for which the modulus, strength and elongation were reported to be 0.56 GPa, 52 MPa and 7.9%,⁴ respectively, though another paper reported that the modulus of endo-polyimide estimated from the strength and elongation is 1.6 GPa,¹¹ which is almost the same value in Table 5.

Figure 5 shows the ultraviolet–visible transmission spectra of the polyimides. The films for measurement were prepared by drying on a glass plate at 80 °C for 30 min. The measurement of the endo-meso polyimide was extremely difficult because the film was fragile. The cut-off wavelength was 290 nm for both endo-meso and exo-polyimide films, and they became transparent at above 350 nm. However, the exo-polyimide showed a higher transparency at around 300 nm.

Molecular structure of tetracarboxylic dianhydrides

The above-mentioned essentials are as follows: (1) the synthesizing condition of endo-TriSXDA is more intense than exo-TriSXDA; (2)

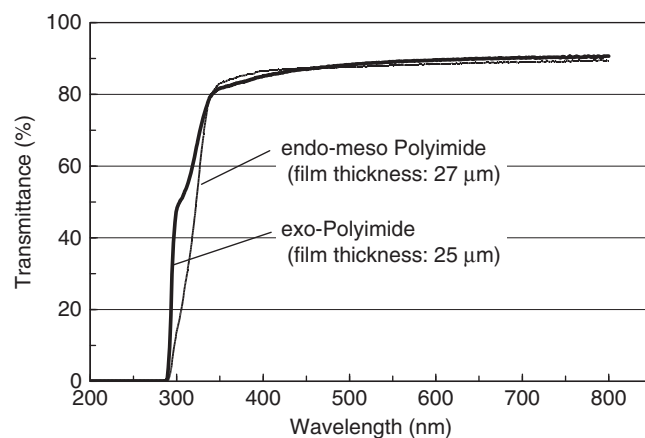


Figure 5 Ultraviolet–vis transmission spectra of polyimides.

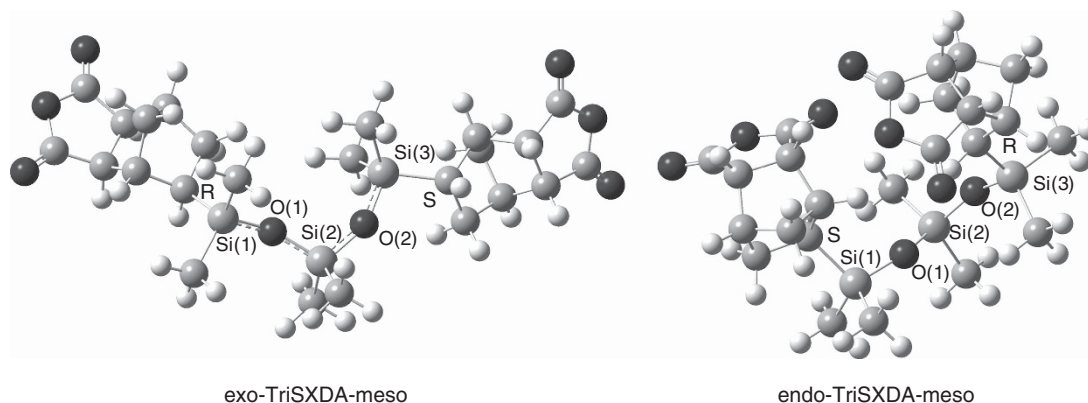


Figure 6 Optimized structures of tetracarboxylic dianhydrides.

the changes in the chemical shift value of endo-polyimide were caused not only by imidization, but also by polymerization; (3) the molecular weight of endo-polyimides is lower than exo-polyimide; (4) the endo-polyimides are inferior to ability to form a film.

It is thought that these results are due to the molecular structure of tetracarboxylic dianhydrides as conveniently illustrated in Scheme 1. To understand the more reasonable structure, the most stable structures were derived from quantum chemical calculation using the Gaussian 09 software implementing the B3LYP functional with the 6-31 G(d) basis set.

Figure 6 shows the each optimized structure of exo- and endo-TriSXDA meso isomer. The two anhydride groups of exo-TriSXDA are located at the ends of molecules, and the molecular structure is extended. On the other hand, the anhydride groups of endo-TriSXDA are located closely, and the molecular structure is spherically shrunk. The structure of endo-TriSXDA is obviously different from that shown in the Scheme 1. Thus, the consideration about the molecular structure is useful to understand the properties of the endo- and exo-polyimides.

CONCLUSION

The exo-TriSXDA synthesized through the hydrosilylation of exo-NBA and HMTS was a highly viscous liquid, but by contrast, endo-TriSXDA from endo-NBA were crystal. Polyimides synthesized from these tetracarboxylic dianhydrides and ODA maintained the original stereo structure. The exo-polyimide had the excellent capability to form film, enabling the measuring of many characteristics. On the other hand, in the case of endo-polyimides, only thermal characteristics were able to be measured because of their poor film-formability. The endo-meso and endo-racemic polyimides showed the same Tg and Td5. In the case of exo-polyimide, most of those values were

constant and irrespective of the Mw value when the Mw exceeded 56 000, except for the elongation at break, which increased with Mw and reached a steady value when Mw exceeded 88 000. Comparing the characteristics of the endo- with exo-polyimide, it was found that the Tg of the latter was higher than the former, and *vice versa* concerning Td5. It can be concluded that the above results are caused by the difference in endo- and exo-TriSXDA structures.

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