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ORIGINAL ARTICLE

Synthesis and characterization of novel aromatic polyimides from Z-type sexiphenyltetracarboxylic dianhydride and aromatic diamines

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A Z-type sexiphenyltetracarboxylic dianhydride, 3,3′′′′′,4,4′′′′′-1,1′:2′,1′′:4′′,1′′′:4′′′,1′′′′:2′′′′,1′′′′′-sexiphenyltetracarboxylic dianhydride (1), was synthesized in seven steps from diethyl 4-bromophthalate. New aromatic polyimides (PI1x) containing the Z-type sexiphenyl unit were synthesized from 1 and various aromatic diamines (x) by both conventional two- and one-step procedures. The inherent viscosities of PI1x produced by the one-step procedure were 0.23–1.21, which is much higher than those of the polyimides produced by the two-step procedure. The polyimides PI1x were characterized by X-ray diffraction, differential scanning calorimetry, thermogravimetry and dynamic mechanical analysis (DMA). The structure–property relationships of the polyimides PI1x were compared with those of the polyimides (PI2x) previously prepared from rigid 3,3′′′′′, 4,4′′′′′-p-sexiphenyltetracarboxylic dianhydride (2), which is an isomer of 1. The glass transition (T_g) temperatures were much higher (270–345 °C) than those of the corresponding PI2x, and the decrease in the storage modulus at T_g was larger than that of the corresponding PI2x. The polyimides PI1x showed lower dielectric constants (ε) and were soluble in polar organic solvents at room or elevated temperature in contrast with PI2x. The Z-type structure significantly influences the properties of polyimides containing sexiphenylene units.
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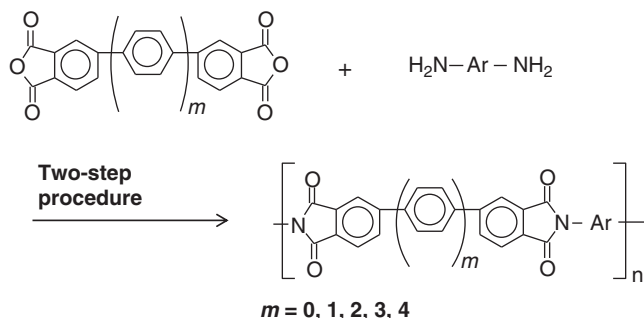
INTRODUCTION

Aromatic polyimides are characterized by high glass transition (T_g) values along with high decomposition temperatures and advantageous mechanical properties. They are used in various fields, including the aerospace and electric industries.[1] Therefore, the relationships between the structures and properties of polyimides have been investigated extensively, and the factors that influence various properties of polyimides have been clarified as follows.[2–6] The high T_g is due to the large enthalpy change and small entropy change at the T_g.[2] The thermomechanical properties are influenced by conformation;[2] processability and solubility are influenced by free volume;[3,4] and the dielectric properties are influenced by the polarization of imide groups and free volume.[5–7] Because these factors are greatly dependent on the polyimide structure, the relationships between structures and properties of polyimides have been examined more systematically.[8–14]

As shown in Scheme 1, we have synthesized aromatic polyimides from p-quaterphenyltetracarboxylic dianhydride ($m = 2$),[15] p-quinquephenyltetracarboxylic dianhydride ($m = 3$)[16] and p-sexiphenyltetracarboxylic dianhydride (2) ($m = 4$).[17] The properties of

these polyimides were compared with those of polyimides from 3,3′′,4,4′′-p-terphenyltetracarboxylic dianhydride ($m = 1$) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA; $m = 0$) and discussed on the basis of the number (m) of phenylene units.[18–23] T_g values were independent of m, while storage moduli were higher and the decrement at the T_g decreased with increasing m. The T_g values of the polyimides (PI2x) from 2 were not so high, and the polyimides PI2x were insoluble in organic solvents even upon heating.

In this study, polyimides PI1x were synthesized from a Z-type sexiphenyltetracarboxylic dianhydride 1, an isomer of 2, and their properties were compared with those of polyimides PI2x prepared from 2. Linkages along the polymer backbone, such as p- and m-linkages, are known to influence the polymer properties,[4] and the effects of such linkages in the dianhydride moiety on polyimide properties have been examined in polyimides from BPDAs.[24–27] There are three types of isomers in BPDA: 3,3′,4,4′-BPDA (s), 2,3,3′,4′-BPDA (a), and 2,2′,3,3′-BPDA (i). The T_g values of the polyimides from these dianhydrides increased in the order of s-polyimide < a-polyimide < i-polyimide, and the order of solubility in

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Scheme 1 Preparation of polyimides with various numbers of 1,4-phenylene units.

N-methyl-2-pyrrolidone (NMP) was s-polyimide < a-polyimide < i-polyimide. These results could be explained in terms of the restriction of the internal rotation around the biphenyl linkage and the free volumes in the polyimides. As the difference in linearity from **1** and **2** is much larger than that among the three types of BPDAs, the properties of polyimides **PI1x** are expected to be considerably different from those of the polyimides **PI2x**.

EXPERIMENTAL PROCEDURE
Materials
2-Methoxyphenylboronic acid (**3**), tetrakis(triphenylphosphine)palladium (Pd(PPh$_3$)$_4$), 4,4′-diaminodiphenyl ether (**a**), 4,4′-diaminodiphenylmethane (**b**), *m*-phenylenediamine (**c**) and *p*-phenylenediamine (**d**) were purchased from Wako Pure Chemical Industries (Osaka, Japan). 4,4′-Bis(4-aminophenoxy)biphenyl (**e**) and 3,4′-diaminodiphenyl ether (**f**) were purchased from Tokyo Kasei Kogyo (Tokyo, Japan). The diamines were purified by sublimation under reduced pressure. Diethyl 4-bromophthalate (**4**)[15] and bis-(trimethylene)-4,4′-biphenylene diboronate (**5**)[28] were prepared as previously reported. NMP was purified by vacuum distillation over calcium hydride.

Monomer synthesis
Diethyl 4-(2-methoxyphenyl)phthalate (6). The following were added to a flask equipped with a reflux condenser: 25.0 g (83 mmol) of **3**, 12.8 g (83 mmol) of **4**, 12.4 g (90 mmol) of potassium carbonate and 150 ml of deoxygenated toluene. The system was flushed with nitrogen, and 0.5 g of Pd(PPh$_3$)$_4$ was added to the reaction mixture. After the mixture was stirred at 90 °C for 8 h, the salts were removed by filtration, and the solvent was evaporated. The residue was distilled under reduced pressure to yield pure liquid **6**. Yield: 19.9 g (73%). BP: 233–240 °C (1 Torr).

The infrared (IR) spectrum (NaCl) exhibited absorption bands at 3040–2970 (C-H) and 1720 cm^{-1} (C=O).
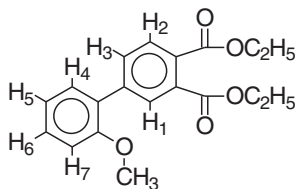
The ^{1}H nuclear magnetic resonance (NMR) spectrum (δ in CDCl$_3$) showed signals at 1.35 (t, 3H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 1.37 (t, 3H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 3.82 (s, 3H, -OCH$_3$), 4.35 (q, 2H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.37 (q, 2H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 6.96–7.01 (m, 1H, H7), 7.02–7.07 (m, 1H, H5), 7.30–7.33 (m, 1H, H6), 7.33–7.39 (m, 1H, H4), 7.67–7.70 (dd, 1H, $J = 8.1$ Hz, $J = 2.2$ Hz, H3), 7.78 (d, 1H, $J = 8.1$ Hz, H2) and 7.85 (d, 1H, $J = 2.2$ Hz, H1).

The ^{13}C NMR spectrum (δ in CDCl$_3$) exhibited peaks at 14.1, 55.4, 61.6, 61.9, 115.9, 125.4, 126.8, 128.6, 128.7, 129.4, 129.7, 130.0, 131.7, 133.8, 145.8, 160.1, 167.3 and 168.2 p.p.m.

Analysis calculated for C$_{19}$H$_{20}$O$_5$: C, 69.50%; H, 6.14%. Found: C, 69.42%; H, 6.20%.

4-(2-Hydroxyphenyl)phthalic acid (7). To synthesize 4-(2-hydroxyphenyl)phthalic acid (**7**), 19.7 g (60 mmol) of **6** was heated together with 70 g of pyridine hydrochloride for 30 min at reflux temperature (260 °C). After the reaction mixture became homogeneous, it was poured into water (1000 ml). The precipitated solid was collected by filtration, washed thoroughly with water and dried under vacuum. The crude product was used in the next reaction without further purification. Yield: 13.9 g (90%).

The IR spectrum (KBr) exhibited absorption bands at 3400–3000 (OH) and 1700 cm^{-1} (C=O).
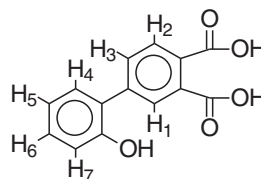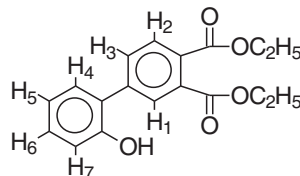

The ^{1}H NMR spectrum (δ in DMSO-d_6) showed signals at 6.85–6.90 (m, 1H, H7), 6.94–7.00 (m, 1H, H5), 7.19–7.26 (m, 1H, H6), 7.26–7.36 (m, 1H, H4), 7.69–7.78 (m, 2H, H2 and H3) and 7.81 (d, $J = 2.2$, H1).

The ^{13}C NMR spectrum (δ in DMSO-d_6) exhibited peaks at 114.1, 125.6, 126.2, 128.2, 128.7, 129.8, 130.2, 130.8, 131.6, 132.9, 144.6, 156.9, 167.4 and 167.6 p.p.m.

Diethyl 4-(2-hydroxyphenyl)phthalate (8). To synthesize diethyl 4-(2-hydroxyphenyl)phthalate (**8**), 13.7 g (53 mmol) of **7**, 250 ml of absolute ethanol and 0.2 ml of sulfuric acid were added to a flask, and the mixture was heated at reflux for 60 h. After the mixture was cooled, it was washed twice with 100 ml of 10 wt% sodium carbonate solution and extracted three times with 100 ml of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was purified by silica gel column chromatography eluted by dichloromethane. Yield: 12.2 g (73%). Mp: 70–71 °C.

The IR spectrum (KBr) exhibited absorption bands at 3400–3000 (OH), 3020–2970 (C-H) and 1730 cm^{-1} (C=O).

The ^{1}H NMR spectrum (δ in CDCl$_3$) showed signals at 1.35 (t, 3 H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 1.37 (t, 3H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.34 (q, 2H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.37 (q, 2H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 5.60 (s, 1H, OH), 6.94–6.97 (m, 1H, H7), 6.95-7.01 (m, 1H, H5), 7.22-7.27 (m, 1H, H6), 7.22-7.30 (m, 1H, H4), 7.68-7.72 (dd, 1H, $J = 8.1$ Hz, $J = 2.2$ Hz, H3), 7.83 (d, 1H, $J = 8.1$ Hz, H2) and 7.86 (d, 1H, $J = 2.2$ Hz, H1).

The ^{13}C NMR spectrum (δ in CDCl$_3$) exhibited peaks at 14.1, 61.6, 61.9, 115.9, 124.9, 126.5, 128.5, 128.7, 129.4, 129.8, 130.5, 131.4, 134.5, 144.8, 156.4, 167.3 and 168.3 p.p.m.

Analysis calculated for C$_{18}$H$_{18}$O$_5$: C, 68.78%; H, 5.77%. Found: C, 68.51%; H, 5.92%.

3′,4′-Di(ethoxycarbonyl)biphenyl-2-triflate (9). A solution of 12.7 g (45 mmol) of trifluoromethanesulfonyl anhydride in 70 ml of dichloromethane was added dropwise to a solution of 11.3 g (36 mmol) of **8** and 10 ml of pyridine in 150 ml of dichloromethane at 0 °C. After stirring at 20 °C for 2 h, the mixture was poured into ice water. The organic layer was collected, and the aqueous layer was extracted twice with 50 ml of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate. After evaporation of the

solvent, the residue was purified by silica gel column chromatography eluted by dichloromethane. Yield: 14.3 g (89%). Mp: 66–67 °C.

The IR spectrum (KBr) exhibited absorption bands at 3400–3000 (OH), 3020–2970 (C-H), 1730 (C=O), 1420 (S=O) and 1215 cm^{-1} (C-F).
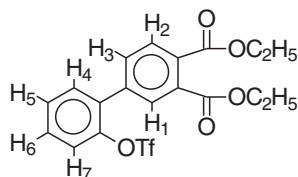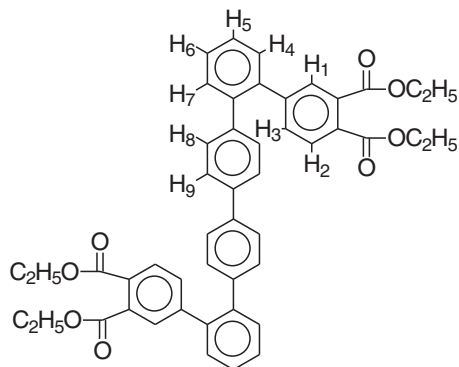

The ^{1}H NMR spectrum (δ in CDCl$_3$) showed signals at 1.35 (t, 3H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 1.37 (t, 3H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.34 (q, 2H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.37 (q, 2H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 7.40–7.46 (m, 1H, H7), 7.46–7.51 (m, 3H, H4, H5 and H6), 7.62–7.67 (dd, 1H, $J = 8.1$ Hz, $J = 2.2$ Hz, H3), 7.82 (d, 1H, $J = 2.2$ Hz, H1) and 7.83 (d, 1H, $J = 8.1$ Hz, H2).

The ^{13}C NMR spectrum (δ in CDCl$_3$) exhibited peaks at 14.2, 61.8, 61.9, 118.8 (q, $J = 320$ Hz), 122.0, 127.5, 128.2, 129.1, 129.3, 129.7, 131.3, 133.4, 134.1, 139.7, 142.1, 149.6, 167.0 and 167.5 p.p.m.

Analysis calculated for C$_{19}$H$_{17}$O$_7$F$_3$S: C, 51.12%; H, 3.84%. Found: C, 50.85%; H, 3.93%.

Tetraethyl 3,3'''',4,4'''''-1,1':2',1'':4'',1''':4''',1'''':2'''',1'''''-sexiphenyltetracarboxylate (10). In total, 13.6 g (30.5 mmol) of **9**, 4.83 g (15 mmol) of **5**, 4.55 g (33 mmol) of potassium carbonate and 150 ml of deoxygenated *N,N*-dimethylformamide were added to a flask equipped with a reflux condenser. The system was flushed with nitrogen, and 0.5 g of Pd(PPh$_3$)$_4$ was added to the reaction mixture. After the mixture was stirred at 90 °C for 8 h, the salts were removed by filtration, and the solvent was evaporated. The residue was purified by silica gel column chromatography eluted by dichloromethane. Yield: 6.27 g (56%). Mp: 182–183 °C.

The IR spectrum (KBr) exhibited absorption bands at 3020–2970 (C-H) and 1720 cm^{-1} (C=O).

The ^{1}H NMR spectrum (δ in CDCl$_3$) showed signals at 1.35 (t, 6H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 1.37 (t, 6H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.35 (q, 4H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 4.37 (q, 4H, $J = 7.0$ Hz, -CH$_2$CH$_3$), 7.18 (d, 4H, $J = 8.8$ Hz, H8), 7.20-7.25 (m, 2H, H5), 7.42-7.52 (m, 12H, H2, H4, H6, H7 and H9), 7.52-7.57 (dd, 2H, $J = 8.1$ Hz, $J = 2.2$ Hz, H3) and 7.62 (d, 2H, $J = 2.2$ Hz, H1).

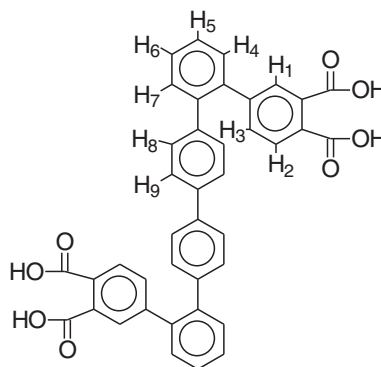The ^{13}C NMR spectrum (δ in CDCl$_3$) exhibited peaks at 14.2, 61.7, 61.8, 126.8, 127.2, 127.4, 127.6, 127.7, 127.8, 129.2, 129.8, 130.4, 132.1, 133.5, 138.2, 139.4, 139.9, 140.8, 143.7, 167.2 and 168.0 p.p.m.

Analysis calculated for C$_{48}$H$_{42}$O$_8$: C, 77.19%; H, 5.67%. Found: C, 76.95%; H, 5.81%.

3,3'''',4,4'''''-1,1':2',1'':4'',1''':4''',1'''':2'''',1'''''-Sexiphenyltetracarboxylic acid (11). At 190 °C, 5.97 g (8 mmol) of **10** was dissolved in 350 ml of 2-(2-methoxyethoxy)ethanol. A solution of 1.92 g (48 mmol) of sodium hydroxide in 20 ml of water was added, and the mixture was heated at this temperature

for 2 h to yield a white precipitate. The reaction mixture was concentrated under reduced pressure, and a solution of 1.92 g (48 mmol) of sodium hydroxide in 400 ml of water was added. The system was then heated at reflux temperature for 2 h. After being cooled to room temperature, the solution was acidified by 6 M hydrochloric acid. The precipitated **11** was collected and dried under vacuum. The crude product was used in the next reaction without further purification. Yield: 4.77 g (94%).

The IR spectrum (KBr) exhibited absorption bands at 3400–3000 (OH) and 1705 cm^{-1} (C=O).

The ^{1}H NMR spectrum (δ in DMSO-d_6) showed signals at 7.20 (d, 4H, $J = 8.8$ Hz, H8), 7.26–7.31 (m, 2H, H5), 7.46–7.56 (m, 12H, H3, H4, H6, H7 and H9), 7.65 (d, 2H, $J = 2.2$ Hz, H1) and 7.70 (d, 2H, $J = 8.1$ Hz, H2).

The ^{13}C NMR spectrum (δ in DMSO-d_6) exhibited peaks at 125.7, 126.2, 126.5, 126.7, 126.8, 127.0, 127.8, 130.5, 130.9, 132.5, 133.7, 137.2, 138.1, 139.3, 141.6, 146.8, 167.4 and 167.8 p.p.m.

3,3'''',4,4'''''-1,1':2',1'':4'',1''':4''',1'''':2'''',1'''''-Sexiphenyltetracarboxylic dianhydride (1). At reflux temperature (260 °C), 4.76 g (7.5 mmol) of **11** was heated together with 200 ml of diphenyl ether for about 1 h. The reaction mixture became homogeneous and was cooled to 150 °C. After the diphenyl ether was evaporated under reduced pressure, the residue was twice recrystallized from toluene to yield pure **1**. Yield: 3.52 g (78%). Mp: 188–189 °C.

The IR spectrum (KBr) exhibited absorption bands at 1850 (C=O) and 1780 cm^{-1} (C=O).
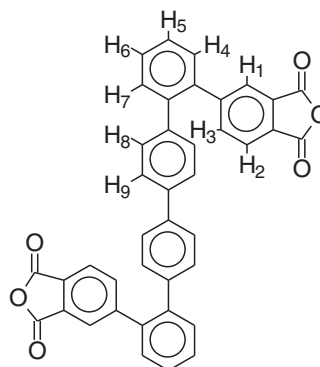
The ^{1}H NMR spectrum (δ in CDCl$_3$) showed signals at 7.14–7.17 (d, 4 H, $J = 8.8$ Hz, H8), 7.42–7.58 (m, 12 H, H4, H5, H6, H7 and H9), 7.60–7.64 (dd, 1 H, $J = 8.1$ Hz, $J = 2.2$ Hz, H3), 7.81 (d, 1 H, $J = 8.1$ Hz, H2) and 7.88 (d, 1 H, $J = 2.2$ Hz, H1).

The ^{13}C NMR spectrum (δ in CDCl$_3$) exhibited peaks at 122.5, 125.8, 126.6, 126.8, 127.0, 127.4, 127.9, 129.4, 131.4, 132.1, 134.0, 136.7, 138.2, 139.7, 141.7, 147.2, 167.2 and 168.0 p.p.m.

Analysis calculated for C$_{40}$H$_{22}$O$_6$: C, 80.26%; H, 3.70%. Found: C, 80.03%; H, 3.90%.

Polymerization using a two-step procedure

Before polymerization, dianhydride **1** was treated *in vacuo* at 270 °C for 30 min. In a three-necked flask, 0.598 g (1.0 mmol) of **1** was added to a solution of 0.2 g (1.0 mmol) of 4,4′-oxydianiline (**a**) in 8.0 ml of NMP in one portion. The mixture was stirred at room temperature for 24 h under nitrogen. The NMP solution was poured into 300 ml of methanol. The precipitated polymer was filtered, washed with methanol and dried under vacuum. The inherent viscosity of polyamic acid **PAA1a** was 0.17 dl g^{-1} in NMP at 30 °C. The thermal cyclodehydration of the polyamic acid was performed by successive heating at 100 °C for 1 h, 200 °C for 1 h and finally at 300 °C for 1 h under vacuum. Yield: 0.72 g (94%).

The IR spectrum (KBr) exhibited absorption bands at 1780 (C=O), 1720 (C=O) and 1360 cm^{-1} (C-N).

Analysis calculated for $C_{52}H_{30}N_2O_5$: C, 81.88%; H, 3.96%; N, 3.67%. Found: C, 81.42%; H, 4.15%; N, 3.52%.

Polymerization by one-step procedure

Before polymerization, dianhydride **1** was treated *in vacuo* at 270 °C for 30 min. In a flask equipped with a condenser, 0.598 g (1.0 mmol) of **1**, 0.2 g (1.0 mmol) of **a** and 3 ml of dried toluene as an azeotropic agent were added to 10 ml of *m*-cresol. The mixture was stirred at 130 °C for 30 min and at 190 °C for 6 h under a nitrogen atmosphere. The resulting viscous solution was poured into 300 ml of methanol. The precipitated polymer was filtered, washed with methanol and dried under vacuum. The inherent viscosity of polyimide **PI1a** was 1.15 dl g^{-1} in NMP at 30 °C. All the polyimide powders were dissolved in 12 ml of NMP, and the solution was cast onto a glass plate. After the solvent was removed at 80 °C, the residue was dried under reduced pressure at 200 °C for 6 h to yield a tough film.

The IR spectrum (KBr) exhibited absorption bands at 1780 (C=O), 1720 (C=O) and 1360 cm^{-1} (C-N).

Analysis calculated for $C_{52}H_{30}N_2O_5$: C, 81.88%; H, 3.96%; N, 3.67%. Found: C, 81.57%; H, 4.14%; N, 3.49%.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a JNM-GSX400 FT-NMR spectrometer (JEOL, Tokyo, Japan) and IR spectra were recorded on a Shimadzu spectrophotometer IR 435 (Shimadzu Corporation, Kyoto, Japan). X-ray diffraction was measured with a Rigaku RAD-B system (Rigaku Corporation, Tokyo, Japan), using Cu Kα radiation at room temperature in the range of $2\theta = 5$–$60°$ with a sampling step of 0.1° and a scan rate of 10° min^{-1}. For differential scanning calorimetry (DSC) and thermogravimetry, a Shimadzu DSC-60 (Shimadzu Corporation) and Rigaku thermal analysis station TG 8110 (Rigaku Corporation) were used, respectively, and measurements were made at a heating rate of 10 °C min^{-1} in air or nitrogen. Dynamic mechanical analysis (DMA) was performed with the Advanced Rheometric Expansion System (TA Instruments—Waters LLC, New Castle, DE, USA) at 1.0 Hz at a heating rate of 5 °C min^{-1} from room temperature to 500 °C. Mechanical properties were measured with a Shimadzu Autograph precision universal tester (Shimadzu Corporation) at a strain rate of 10% min^{-1}. Densities of polyimide films were measured using a density-gradient tube prepared from carbon tetrachloride and heptane. Five specimens (7×7 mm^2) per polyimide film were measured, and the maximum and minimum values are reported in Table 4. The refractive indices of the polyimide films were measured at C-line (656 nm) on an Abbe refractometer (Atago NAR 4T, Atago Corporation, Tokyo, Japan). Transmission spectra of polyimide films (ca. 40 m) were measured with a Shimadzu UV–vis-NIR (Shimadzu Corporation) scanning spectrophotometer.

RESULTS AND DISCUSSION

Monomer synthesis

3,3′′′′′,4,4′′′′′-1,1′:2′,1′′:4′′,1′′′:4′′′,1′′′′:2′′′′,1′′′′′-Sexiphenyltetracarboxylic dianhydride (**1**) was synthesized with reactions involving the extension of the unit using 2-methoxyphenylboronic acid (**3**), as previously reported (Scheme 2).[17] Cross-coupling of **3** and **4** using Pd(PPh$_3$)$_4$ as a catalyst yielded **6**, which was treated with pyridine

hydrochloride to yield **7** and then converted to diethyl ester **8**. Afterwards, **8** was converted to triflate **9** using trifluoromethanesulfonyl anhydride, and cross-coupling of **9** with diboronate **5** yielded tetraethyl sexiphenyltetracarboxylate **10**. Hydrolysis of **10** afforded tetracarboxylic acid **11**, which was converted to tetracarboxylic dianhydride **1** by heating in diphenyl ether.

The chemical structures were confirmed by IR and NMR spectroscopy and elemental analysis.

Compound **1** exhibited IR absorption at 1850 and 1780 cm^{-1}, which is characteristic of a carboxylic anhydride. The ^{13}C NMR spectrum of **1** exhibited 18 peaks due to symmetry, indicating the formation of the desired tetracarboxylic dianhydride. Elemental analyses of all compounds were in good agreement with the calculated results for the proposed structures.

Polymer synthesis

Aromatic polyimides **PI1a–PI1f** were synthesized by a conventional two-step procedure that included ring-opening polyaddition of aromatic diamines **a–f** to **1** and thermal cyclodehydration, as shown in Scheme 3. The ring-opening polyadditions were carried out in NMP at room temperature, leading to the formation of polyamic acids with inherent viscosities of 0.11–0.17 dl g^{-1} in NMP. Although the polymerizations proceeded in homogeneous solution, the viscosities of the polyamic acids were rather low compared with those of polyimides **PI2x** from **2**. Thermal conversion of the polyamic acids to polyimides was then performed by heating the precursor polymers in powder form successively at 100 °C for 1 h, 200 °C for 1 h and 300 °C for 1 h under vacuum. The polyimides **PI1x** were soluble in organic solvents, and the inherent viscosities of the polyimides formed were in the range of 0.14–0.49 dl g^{-1} in NMP (Table 1), which is higher than those of the polyamic acids. Polymerization likely proceeded during imidation. Polymerizations were also examined by a one-step procedure. The polymerizations were carried out in *m*-cresol at 130–190 °C, leading to the formation of polyimides. The water formed during the reaction was removed as an azeotrope to promote polymerization. The reactions proceeded homogeneously in *m*-cresol, and no precipitation occurred when the hot solutions were cooled to room temperature. The inherent viscosities were in the range of 0.23–1.21 dl g^{-1} (Table 2) and those of **PI1a**, **PI1b**, **PI1d** and **PI1e** were much higher than those of the polyimides produced by the two-step procedure. A similarly higher viscosity of the polyimides produced by the one-step procedure than by the two-step procedure was reported in the preparation of polyimides from 3,6-diphenylpyromellitic dianhydride.[29] Based on molecular modeling, the authors reported some steric hindrance from the phenyl groups, restricting the formation of the tetrahedral intermediate necessary for addition of the amine. In the present polymerization, the lower viscosities of the polyimides by the two-step procedure may be due to steric hindrance of the 1,4-phenylene group. This influence was thought to be smaller in the one-step procedure, because the polymerization was carried out at a higher temperature (190 °C). Polyimides with high viscosities could not be prepared from diamines **c** and **f**. The reason for this failure is still unclear but may be partially attributed to the trend of forming cyclic oligomers in the polymerization of diamines **c** and **f** with a narrow V-shaped angle between the two amino groups. The polyimide **PI1a**, **PI1b**, **PI1d** and **PI1e** films were obtained by casting the NMP solutions onto a glass plate and removing the solvent. The obtained films were dried at 200 °C for 6 h under vacuum. The formation of polyimides was confirmed by the appearance of IR absorption bands at approximately 1780 and 1720 (C=O) and 1360 cm^{-1} (C-N), which is characteristic
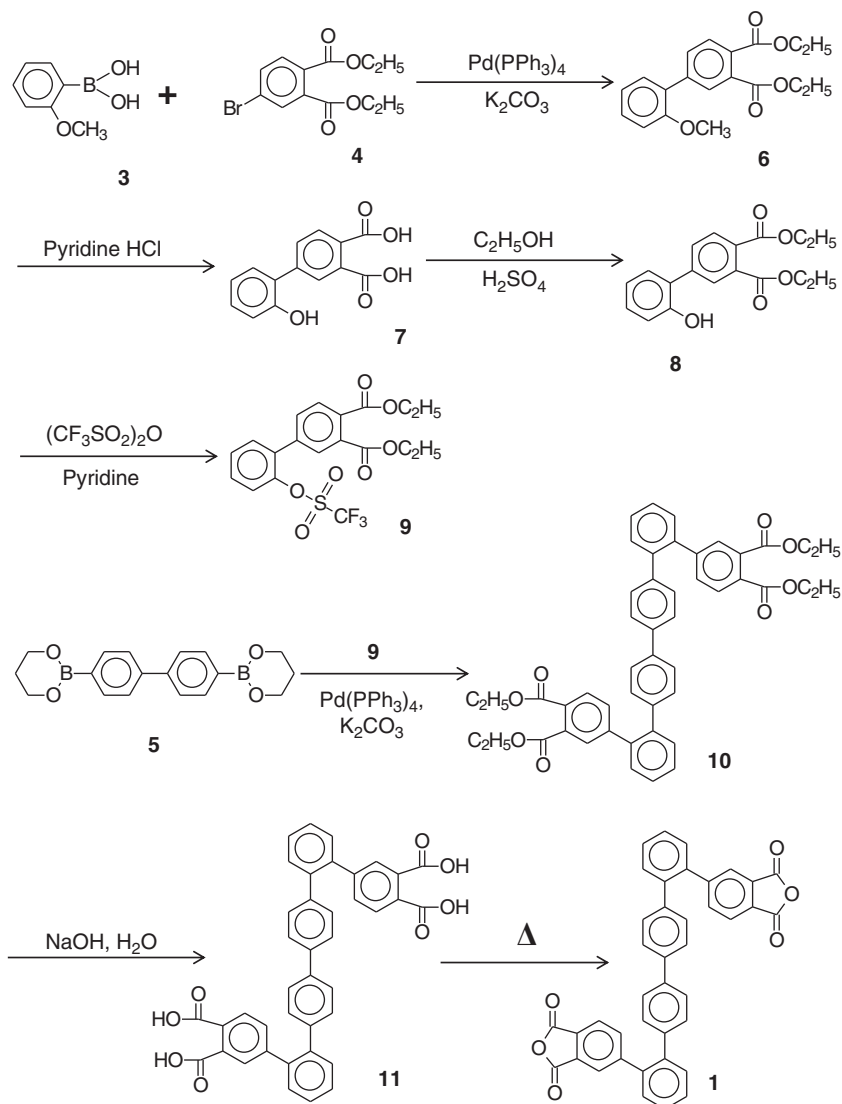
Scheme 2 Synthesis of tetracarboxylic dianhydride **1**.

of an imide group. The values from elemental analysis were in close agreement with the calculated values, further supporting polyimide formation.

The polyimide films, **PI1a**, **PI1b**, **PI1d** and **PI1e**, were transparent and yellow in color. The transparencies of the **PI1x** films were compared with those of the **PI2x** films. The transmission spectra of the **PI1a** and **PI2a** films are shown in Figure 1, and the cutoff wavelength is defined here as the point at which the transmittance decreases below 10% in the spectrum. The cutoff wavelength of the **PI1a** film was 423 nm, which is shorter than that (438 nm) of the **PI2a** film, and the **PI1a** film exhibited higher transmittance in the 400–450 nm region. The cutoff wavelengths of **PI1b**, **PI1d** and **PI1e** films were 421, 430 and 425 nm, respectively, while those of the **PI2b** and **PI2e** films were 440 and 442 nm, respectively. The cutoff wavelengths of the **PI1x** films were shorter than those of **PI2x**, indicating that the λ_{max} values of the **PI1x** films were smaller than those of the **PI2x** films. The calculated λ_{max} values for the optimized model compounds (Figure 2) of **PI1x** and **PI2x** were 355 and 373 nm, respectively.

Polymer properties

The crystallinity of the polyimides was estimated by wide-angle X-ray diffraction. All polymers were amorphous.

The thermal properties of the polyimides were evaluated by DSC, thermogravimetry and DMA. The T_g and 10% weight loss temperatures (T_{10}) are summarized in Table 3. The T_g and T_{10} of the rigid polyimides **PI2x**[17] are also shown in Table 3 for comparison. The T_{10} values of **PI1c** and **PI1f** were lower due to lower inherent viscosities. None of the polyimides **PI1a**, **PI1b**, **PI1d** and **PI1e** lost weight below 480 °C in air or nitrogen. The T_{10} values in air and nitrogen of **PI1a**, **PI1b**, **PI1d** and **PI1e** were in the ranges of 575–590 and 635–640 °C, respectively. All **PI1x**, except **PI1c** and **PI1f**, had thermal stabilities similar to the corresponding polyimides **PI2x**.

The polyimides **PI1x** showed T_g values without melting in the DSC thermograms, indicating amorphous morphology. **PI1x** had a T_g between 270 and 345 °C (Table 3), and the values were higher than those of the corresponding **PI2x**. In particular, the T_g value of **PI1d** was 65 °C higher than that of the corresponding **PI2d**. The higher T_g
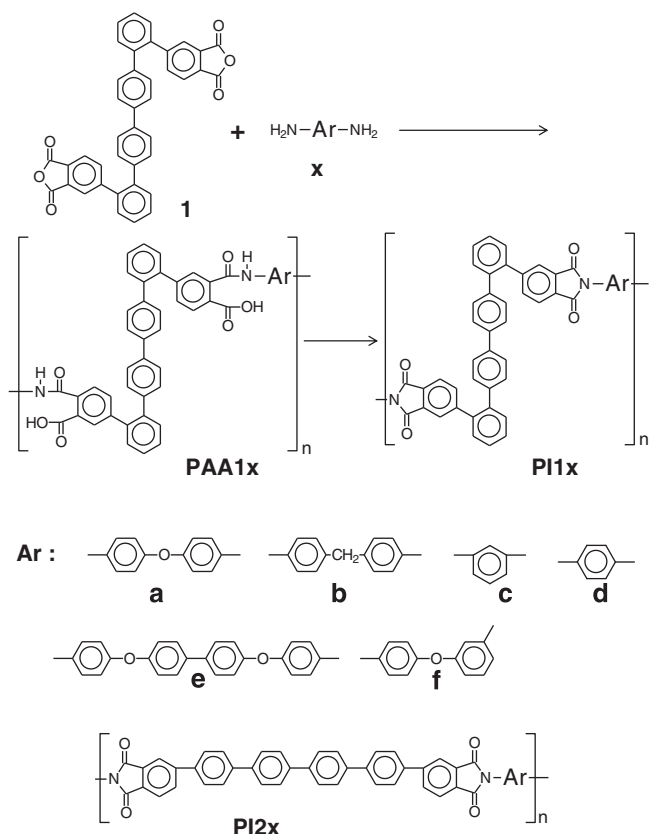
Scheme 3 Synthesis of polyimides **PI1x** and structure of polyimides **PI2x**.

Table 2 Synthesis of polyimides by one-step procedure

Diamine	Polyimide[a]	Yield (%)	η_{inh} $(dlg^{-1})^b$
a	PI1a	96	1.15
b	PI1b	97	1.21
c	PI1c	94	0.23
d	PI1d	96	0.84
e	PI1e	97	0.92
f	PI1f	96	0.33

[a]Polymerization was carried out with 1.00 mmol of each monomer in 10 ml m-cresol of 190 °C for 6 h under nitrogen.
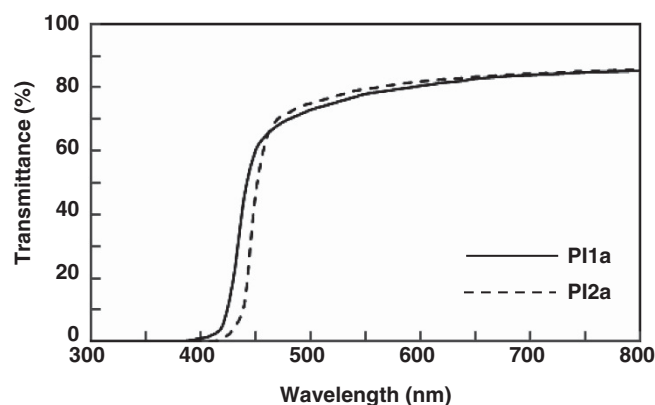[b]Measured at 0.5 g dl^{-1} in NMP at 30 °C.

Figure 1 Comparison of the transmission spectra of polyimide films of **PI1a** and **PI2a**.

Table 1 Synthesis of polyamic acids and conversion to polyimides

Diamine	Polyamic acid[a]	Yield (%)	η_{inh} $(dlg^{-1})^b$	η_{inh} $(dlg^{-1})^c$
a	PAA1a	94	0.17	0.32
b	PAA1b	95	0.16	0.49
c	PAA1c	95	0.11	0.14
d	PAA1d	95	0.13	0.45
e	PAA1e	97	0.16	0.28
f	PAA1f	96	0.11	0.15

[a]Polymerization was carried out with 1.00 mmol of each monomer in 8 mml NMP at room temperature for 24 h under nitrogen.
[b]Inherent viscosity of polyamic acid. Measured at 0.5 g dl^{-1} in NMP at 30 °C.
[c]Inherent viscosity of polyimide. Measured at 0.5 g dl^{-1} in NMP at 30 °C.

can be explained by the difficulty of internal rotation around the biphenyl linkages and the conformational change during rotational motion, which were both reported as causes of the higher T_g values of a-BPDA- and i-BPDA-based polyimides compared with s-BPDA-based polyimides.[24–27] Figure 2 shows the optimized structures of bis(N-phenylimide)s of 1 and 2, which are model compounds of **PI1x** and **PI2x**, respectively. The dihedral angles between the aromatic rings around the C_1-$C_{1'}$, $C_{2'}$-$C_{1''}$ and $C_{4''}$-$C_{1'''}$ bonds in the model compound of **PI1x** are denoted as ω_{11}, ω_{12} and ω_{13}, respectively, and those around the C_1-$C_{1'}$, $C_{4'}$-$C_{1''}$ and $C_{4''}$-$C_{1'''}$ bonds in the model compound of **PI2x** are denoted as ω_{21}, ω_{22} and ω_{23}, respectively. Density functional theory calculations in the gas phase were carried out as implemented in the Gaussian09W package of

quantum chemical programs. The optimized ω_{11}, ω_{12} and ω_{13} were 50, 51 and 35°, respectively, and the optimized ω_{21}, ω_{22} and ω_{23} were all 36°. The potential energies were estimated as a function of ω, and the difference between the maximum and minimum values (the optimized structure) was defined as the energy barrier for rotation of the aromatic rings around the C-C bond. The values for ω_{11}, ω_{12} and ω_{13} in the model compound of **PI1x** were 26, 27 and 2.2 kcal mol^{-1}, respectively, and those for ω_{21}, ω_{22} and ω_{23} in the model compound of **PI2x** were 2.2, 2.2 and 2.1 kcal mol^{-1}, respectively. The energy barriers for rotation in the model compound of **PI1x** were much higher than those in the model compound of **PI2x** due to the approach of the hydrogen atom in the 6-position to the hydrogen atom in the 2″-position. Thus, internal rotations around the biphenyl linkages in polyimide **PI1x** were suggested to be more restricted. Based on the optimized structures of the model compounds, a larger conformational change was also suggested to be required in the internal rotation around flexible connecting groups, such as -O- and -CH$_2$-, in **PI1x**.

DMA of **PI1x** was performed, and T_g values were observed as tan δ peak temperatures (Table 3). The T_g values of **PI1x** were higher than those of the corresponding **PI2x**, which was in agreement with the result determined by DSC. Polyimides **PI1c** and **PI1f** were not obtained as films. Figure 3a compares the DMAs for **PI1a** and **PI2a**, and Figure 3b compares the DMAs for **PI1d** and the polyimide from 3,3″″,4,4″″-p-quinquephenyltetracarboxylic dianhydride (**QPDA**)[16] and **d**. Because **PI2d** was not obtained as a film,[17] the polyimide from **QPDA** and **d** was used as a rigid polyimide for comparison. The T_g value of the polyimide from **QPDA** and **d** was almost equal to that of **PI2d**, and polyimides from **QPDA** showed

Table 3 Comparison of thermal properties of polyimides PI1x with those for PI2x

Polyimides	T_g (°C)[a]	T_g (°C)[b]	T_{10} (°C)[c]	T_{10} (°C)[d]
PI1a	290	290	580	640
PI2a	244	262	585	640
PI1b	295	310	575	635
PI2b	244	265	580	637
PI1c	320	—[e]	560	585
PI2c	237	275	590	600
PI1d	345	390	590	640
PI2d	280	—[e]	595	645
PI1e	270	275	575	635
PI2e	232	252	580	635
PI1f	310	—[e]	560	610
PI2f	248	270	580	630

[a]Determined by differential scanning calorimetry in nitrogen at a heating rate of 10 °C min^{-1}.
[b]Determined by dynamic mechanical analysis (tan δ) at a heating rate of 5 °C min^{-1}.
[c]Temperature at which 10% weight loss was recorded by thermogravimetry (TG) at a heating rate of 10 °C min^{-1} in air.
[d]Temperature at which 10% weight loss was recorded by TG at a heating rate of 10 °C min^{-1} in nitrogen.
[e]Not obtained as film.

dynamic mechanical behaviors similar to those of **PI2x**, exhibiting a plateau region above 300 °C; the decrement in the storage modulus E' at the T_g was small. In the temperature dependence of storage modulus, a high modulus glassy region was followed by a decrease of modulus at the T_g. The decrease temperatures of **PI1a** and **PI1d** were higher than those of the corresponding rigid polyimides, and the decreases of **PI1a** and **PI1d** at the T_g s were larger. The same results were observed in DMA of **PI1b** and **PI1e**. Rotation around the biphenyl linkages and flexible connecting groups in the polyimides was intense above T_g and resulted in conformational changes. The larger decreases of E' for the Z-type polyimides were possibly due to the larger conformational change of **PI1x**, which is expected from the optimized structures of the model compounds. The E' value below T_g of **PI1d** was much lower than that of the polyimide from **QPDA** and **d**. The higher E' of the polyimide was possibly due to the crystallization of the rigid quinquephenylene unit.

The tensile properties of the **PI1x** films were evaluated from the stress–strain curves; the typical stress–strain curves of **PI1x** and **PI2x** films are shown in Figure 4. The stress–strain curve of **PI1d** was compared with that of the polyimide film from **QPDA** and **d**. The tensile values, tensile strength/elongation at break/tensile modulus of
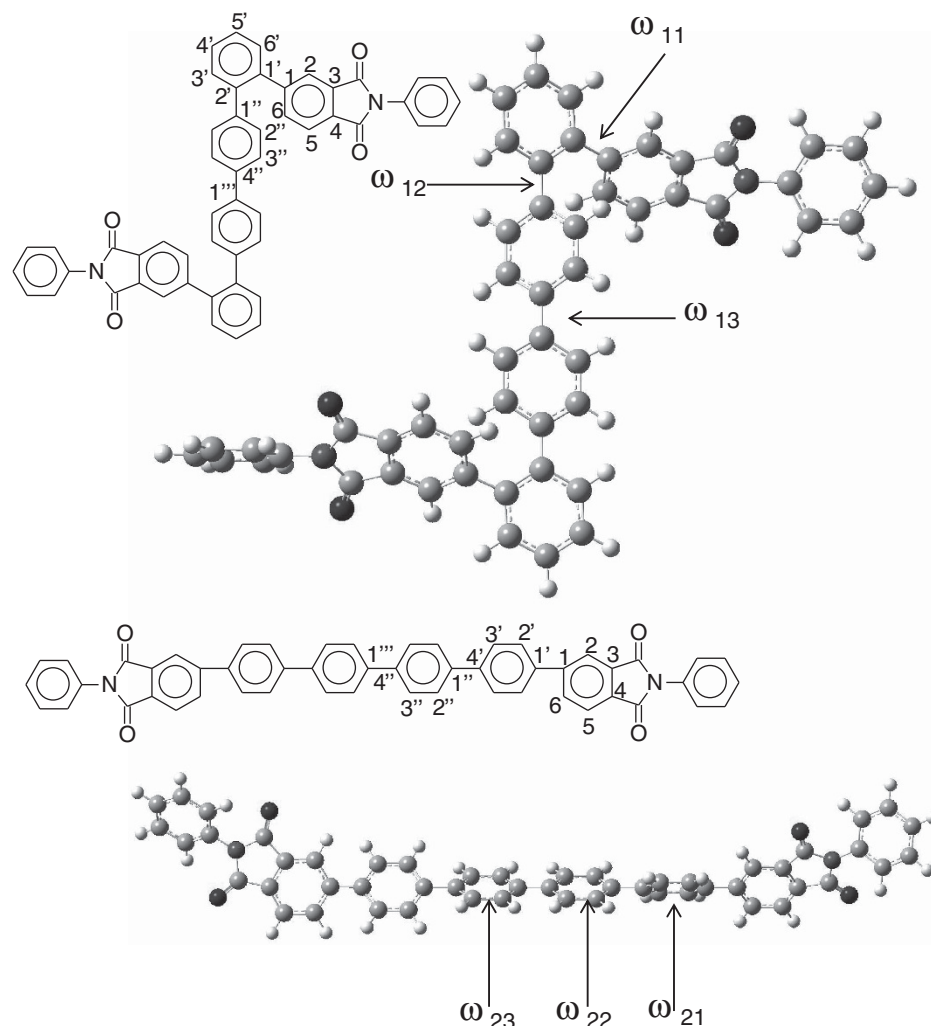
Figure 2 Optimized structures of model compounds corresponding to **PI1x** and **PI2x**. A full color version of this figure is available at *Polymer Journal* online.
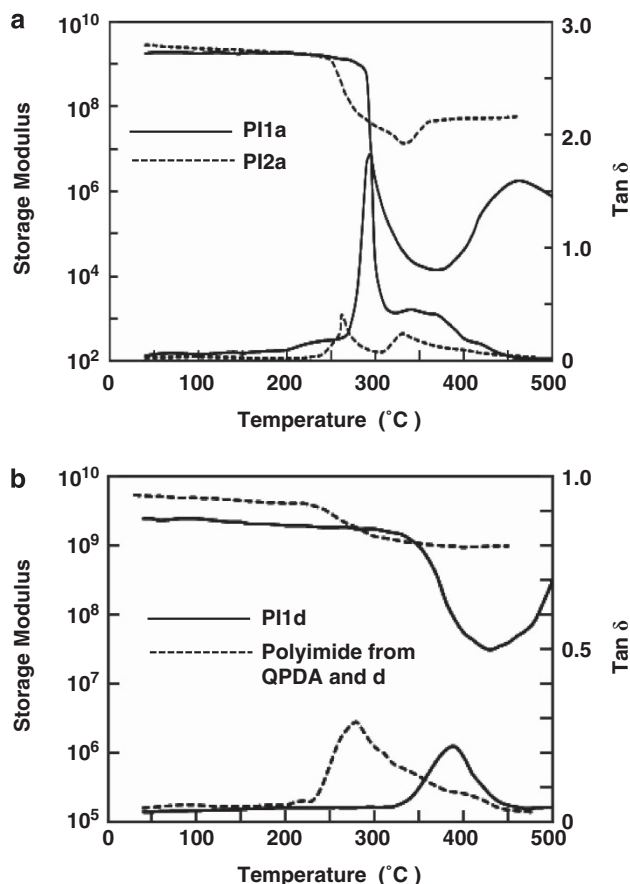
Figure 3 Comparison of the dynamic mechanical behaviors of polyimides **PI1x** and those of **PI2x**. (**a**) **PI1a** and **PI2a** and (**b**) **PI1d** and polyimide from **QPDA** and **d**.
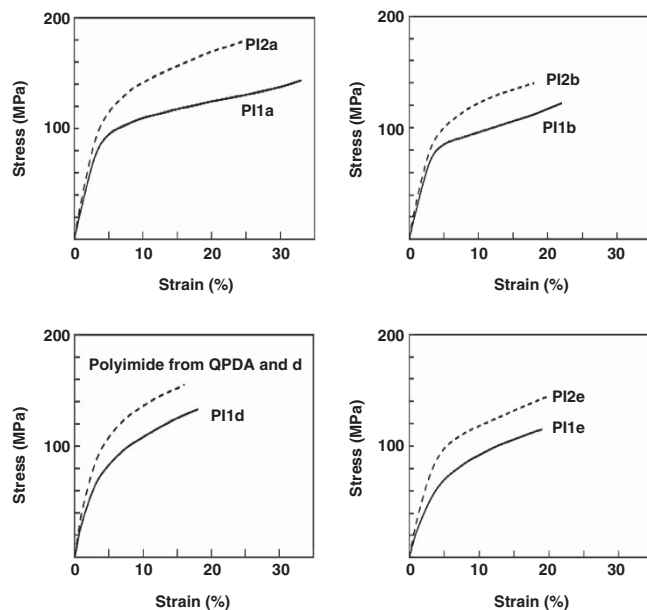

Figure 4 Comparison of the stress–strain curves for polyimides **PI1x** and those for **PI2x**.

Table 4 Comparison of solubilities and densities of polyimides **PI1x** with those for **PI2x**

	NMP	DMAc	DMF	m-Cresol	Pyridine	THF	Methanol	Film density (g cm^{-3})
PI1a	+ + +	+ + +	+ + +	+ + +	+ +	− −	− −	1.28–1.31
PI2a	− −	− −	− −	− −	− −	− −	− −	1.33–1.35
PI1b	+ +	+ +	+ +	+ + +	−	− −	− −	1.28–1.30
PI2b	− −	− −	− −	− −	− −	− −	− −	1.32–1.34
PI1c	+ + +	+ + +	+ + +	+ + +	+ + +	+ +	− −	a
PI2c	−	− −	− −	− −	− −	− −	− −	1.33–1.36
PI1d	+ +	+ +	+ +	+ +	−	− −	− −	1.33–1.34
PI2d	− −	− −	− −	− −	− −	− −	− −	a
PI1e	+ + +	+ + +	+ + +	+ + +	+ + +	− −	− −	1.27–1.30
PI2e	+	− −	− −	− −	− −	− −	− −	1.30–1.32
PI1f	+ + +	+ + +	+ + +	+ + +	+ + +	+ +	− −	a
PI2f	− −	− −	− −	− −	− −	− −	− −	1.36–1.38

Abbreviations: NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; THF, tetrahydrofurane.
Solubility: + + +, soluble at room temperature; + +, soluble on heating; +, precipitation after cooling hot solution; −, partially soluble on heating; − −, insoluble.
aNot obtained as film.

the **PI2a** film, were approximately 180 MPa/25%/3.2 GPa, while those of the **PI1a** film were 144 MPa/33%/2.9 GPa. The tensile strength and tensile modulus of **PI1x** were lower than those of **PI2x**, and the elongation at break was larger.

Table 4 compares the qualitative solubilities and densities for polyimides **PI1x** and corresponding polyimides **PI2x**. Solubility tests were conducted by stirring the polyimide films or powders in solvents at 30 °C for 12 h at a solid content of approximately 3 wt%. Insoluble polyimides were heated at approximately their boiling temperature for a few minutes, followed by cooling to room temperature. All polyimides **PI1x** except **PI1b** and **PI1d** were soluble in polar solvents such as NMP, N,N-dimethylacetamide, N,N-dimethylformamide and m-cresol at room temperature, and **PI1b** and **PI1d** were soluble in polar solvents upon heating, in contrast to polyimides **PI2x**,[17] which were insoluble even upon heating. The Z-type structure had a significant influence on the solubility of the polyimides from sexiphenyltetracarboxylic dianhydride. The higher solubility is presumably due to the free volume. The densities of **PI1x** films, except **PI1d**, were 1.27–1.31 g cm^{-2}, lower than those of the **PI2x** films, and the free volume fraction (the ratio of free volume to the sum of free volume and the van der Waals volumes of the polyimide) was suggested to be larger.

The refractive indices (n) of polyimide films **PI1a**, **PI1b**, **PI1d** and **PI1e** were measured, and the dielectric constants (ε_{cal}) were estimated using an empirical relationship, $\varepsilon_{cal} = 1.1 \times n^2$.[7,30] The ε_{cal} were compared with those of the corresponding **PI2x**. The values of **PI1c**

and **PI1f** could not be measured, as they were not obtained as films. The values of ε_{cal} for **PI1a**, **PI1b**, **PI1d** and **PI1e** were 2.74, 2.73, 2.78 and 2.73, respectively, lower than those of **PI2x**. The values of **PI2a**, **PI2b** and **PI2e** were 2.90, 2.88 and 2.87, respectively. The free volume may also have an effect on the dielectric constant. The dielectric constant of polyimide from pyromellitic dianhydride and 4,4′-diaminodiphenyl ether was reported to be 3.22 (10 GHz), while that of the polyimide from pyromellitic dianhydride and 3,3′-diaminodiphenyl ether was reported to be 2.84. The lower dielectric constant was likely due to the larger free volume.[7]

CONCLUSION

We have examined the synthesis of new polyimides **PI1x** from a Z-type tetracarboxylic dianhydride, 3,3′′′′′,4,4′′′′′-1,1′:2′,1′′:4′′,1′′′:4′′′, 1′′′′:2′′′′,1′′′′′-sexiphenyltetracarboxylic dianhydride (**1**) and compared their properties with those of polyimides **PI2x** that were previously prepared from rigid 3,3′′′′′, 4,4′′′′′-*p*-sexiphenyltetracarboxylic dianhydride (**2**). Polyimides **PI1x** produced by a one-step procedure had higher inherent viscosities than those produced by a two-step procedure. The T_g temperatures of **PI1x** were higher than those of polyimides **PI2x**, and the decrease in the storage modulus at the T_g was larger than that of **PI2x**. Polyimides **PI1x** showed higher solubilities and lower dielectric constants (ε) than **PI2x**, and the Z-type sexiphenylene affected the polyimide properties.

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