Synthesis and Characterization of Novel Aromatic Polyimides from Bis(4-amino-2-biphenyl)ether and Aromatic Tetracarboxylic Dianhydrides

Atsushi MORIKAWA,[†] Taka-aki FURUKAWA, and Yukari MORIYAMA

Department of Materials Science, Faculty of Engineering, Ibaraki University,
4-12-1 Nakanarusawa, Hitachi 316-8511, Japan

ABSTRACT: A new phenylated diamine, bis(4-amino-2-biphenyl)ether, was synthesized in five steps starting from 3-chloro-4-fluoronitrobenzene. New aromatic polyimides having phenyl groups at the 2- and 2′-positions of the diphenyl ether moiety were prepared from this diamine and various tetracarboxylic dianhydrides by the conventional two-step procedure that included ring-opening polymerization in NMP and subsequent thermal cyclic dehydration. The polyimides were characterized by differential scanning calorimetry (DSC), thermogravimetry, and dynamic mechanical analysis (DMA). Typical polyimides showed excellent thermal stability, and had glass transition temperature (T_g) above 250 °C. As for the series of polyimides prepared from tetracarboxylic anhydrides having linear phenylene moiety, the introduction of phenyl group at the 2- and 2′-positions of phenyl ether improved thermal and thermo-mechanical properties as well as the solubility of polymers. [DOI 10.1295/polymj.37.759]
KEY WORDS Bis(4-amino-2-biphenyl)ether / Aromatic Polyimide / Differential Scanning Calorimetry / Dynamic Mechanical Analysis / Solubility /

Aromatic polyimides are characterized by high glass transition temperature (T_g) along with high decomposition temperature and good mechanical properties,[1] and are used in various fields including aerospace and electronic industries.[2–7] Thereby, the relationships between structures and properties of polyimides have been extensively investigated, and those of polyimides, derived from 4,4′-oxydianiline (ODA) and various dianhydrides, have been most extensively reported.[8–19] The ODA-based polyimides are known to possess high T_g and excellent mechanical properties in spite of the rotational flexibility at the diphenyl ether units in the polyimides backbone. Such the flexible units are thought to enhance chain mobility and decrease T_g.[8,9] One method to prevent the internal rotation at the diphenyl ether units is expected to be the introduction of bulky substituents into the 2- and 2′-positions of the diphenyl ether moiety. The rotational flexibility at the diphenyl ether units is expected to be decreased due to the steric effect between the substituents.

We conducted the synthesis of a new diamine monomer, bis(4-amino-2-biphenyl)ether, which had phenyl groups at the 2- and 2′-positions of the diphenyl ether moiety, and aromatic polyimides were derived from it. The properties of polyimides, especially thermal properties, thermal mechanical properties and solubility, were discussed, and compared with the corresponding ODA-based polyimides.

EXPERIMENTAL

Materials

Pyromellitic dianhydride(**VIIa**), 3,3′,4,4′-biphenyltetracarboxylic dianhydride(**VIIb**), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride(**VIIc**), 4,4′-oxydiphthalic dianhydride(**VIId**) and 4,4′-(hexafluoroisopropylidene)-diphthalic anhydride(**VIIe**) were obtained commercially, and purified by sublimation under reduced pressure. 3,3″,4,4″-*p*-Terphenyltetracarboxylic dianhydride(**VIIf**) was supplied by Hitachi Kasei Kogyo Co., Japan. 3,3‴,4,4‴-*p*-Quaterphenyltetracarboxylic(**VIIg**) dianhydride, 3,3⁗,4,4⁗-*p*-quinquephenyltetracarboxylic dianhydride(**VIIh**) and 3,3⁗′,4,4⁗′-*p*-sexiphenyltetracarboxylic dianhydride (**VIIi**) were synthesized according to the method reported previously.[16–18] *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were purified by vacuum distillation over calcium hydride. Ethanol was purified by distillation. 3-Chloro-4-fluoronitrobenzene (**I**) and phenylboronic acid were obtained from Tokyo Kasei Kogyo Co., Japan and used without purification. Tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) and sodium hydroxide were obtained from Kanto Kagaku Co., Japan.

Monomer Synthesis

4-Fluoro-3-phenylnitrobenzene (II). To a flask

[†]To whom correspondence should be addressed (E-mail: morikawa@mx.ibaraki.ac.jp).

equipped with a reflux condenser, 17.55 g (100 mmol) of **I**, 12.19 g (100 mmol) of phenylboronic acid, 13.82 g (100 mmol) of potassium carbonate and 120 mL deoxygenated DMF were added. The flask was flushed with nitrogen, and 0.5 g of tetrakis(triphenylphosphine)palladium(Pd(PPh$_3$)$_4$) were added to the reaction mixture. After the mixture was stirred at 90 °C for 8 h, precipitated salts were removed by filtration, and the solvent was removed by distillation under reduced pressure. The residue was distilled under reduced pressure to give pure **II**. Yield: 12.92 g (60%). Bp: 128–135 °C (1 torr). Mp: 47–48 °C. IR spectrum (KBr) exhibited absorption bands at 1525 cm^{-1}, 1348 cm^{-1} (NO$_2$) and 1100 cm^{-1} (Ar–F).
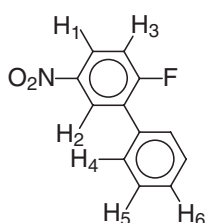
^{1}H Nuclear magnetic resonance (NMR) spectrum [δ in CDCl$_3$] showed signals at 7.30 (dd, 1H, J_{HH} = 9.2 Hz, J_{HF} = 9.2 Hz, H3), 7.41–7.53 (m, 3H, H5 and H6), 7.53–7.59 (m, 2H, H4), 8.18–8.24 (m, 1H, H1) and 8.38 (dd, 1H, J_{HH} = 2.9 Hz, J_{HF} = 6.6 Hz, H2) ppm. ^{13}C NMR spectrum [δ in CDCl$_3$] showed signals at 117.02 (d, J = 25.5 Hz), 124.38 (d, J = 9.6 Hz), 126.41 (d, J = 6.4 Hz), 128.66, 128.74, 128.75, 130.28 (d, J = 15.9 Hz), 133.16, 144.26 (d, J = 3.2 Hz) and 162.96 (d, J = 259.8 Hz) ppm.

Anal. Calcd for C$_{12}$H$_8$NO$_2$F: C, 66.36%; H, 3.71%; N, 6.45%. Found: C, 66.08%; H, 3.50%; N, 6.32%.

4-Ethoxy-3-phenylnitrobenzene (III). To a solution of 7.50 g (34.5 mmol) of **II** in 80 mL of ethanol was added dropwise 1.38 g (34.5 mmol) of sodium hydroxide in 5.0 mL of distilled water at room temperature, and the mixture was refluxed for 12 h. After the mixture was cooled to room temperature, the crude **III** was precipitated. The pure **III** was obtained by recrystallization from ethanol. Yield: 7.95 g (95%). Mp: 110–111 °C. IR spectrum (KBr) exhibited absorption bands at 2985 cm^{-1}, 2930 cm^{-1}, (C–H), 1510 cm^{-1}, 1337 cm^{-1} (NO$_2$) and 1106 cm^{-1} (Ar–O–C$_2$H$_5$).
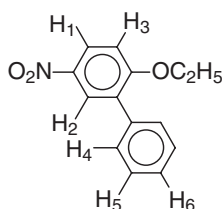
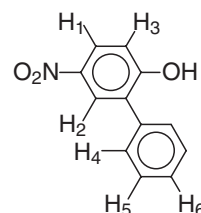^{1}H NMR spectrum [δ in CDCl$_3$] showed signals at 1.41 (t, 3H, J = 7.0 Hz, –CH$_3$), 4.17 (q, 2H, J = 7.0 Hz, –CH$_2$–), 7.00 (d, 1H, J = 8.8 Hz, H3), 7.34–7.47 (m, 3H, H5 and H6), 7.52–7.56 (m, 2H, H4), 8.20 (dd, 1H, J = 8.8 Hz, J = 2.9 Hz, H1) and 8.24 (d, J = 2.9 Hz, H2) ppm. ^{13}C NMR spectrum [δ in CDCl$_3$] showed signals at 14.39, 64.71, 111.29, 124.54, 126.28, 127.69, 128.01, 129.23, 131.10, 136.08, 141.10 and 160.67 ppm.

Anal. Calcd for C$_{14}$H$_{13}$NO$_3$: C, 69.12%; H, 5.39%; N, 5.76%. Found: C, 68.88%; H, 5.20%; N, 5.64%.

4-Hydroxy-3-phenylnitrobenzene (IV). 7.95 g (32.7 mmol) of **III** was heated together with 50.0 g of pyridine hydrochloride at reflux temperature for 30 min. After the reaction mixture became homogeneous, it was poured into water (450 mL). The mixture was 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 distilled under reduced pressure (glass tube oven) to afford pure 4-hydroxy-3-phenylnitrobenzene (**IV**). Yield: 5.22 g (74%). Bp: 210 °C (1 torr). Mp: 125–126 °C. IR spectrum (KBr) exhibited absorption bands at 3550–3100 cm^{-1}, 1496 cm^{-1} and 1327 cm^{-1} (NO$_2$).
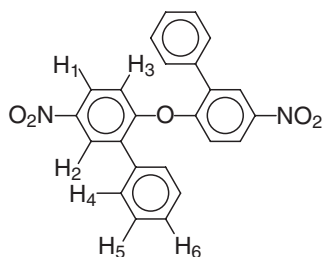

^{1}H NMR spectrum [δ in CDCl$_3$] showed signals at 5.98 (broad s, 1H, –OH), 7.07 (d, 1H, J = 8.8 Hz, H3), 7.44–7.51 (m, 3H, H5 and H6), 7.55 (m, 2H, H4), 8.21 (dd, 1H, J = 8.8 Hz, J = 2.6 Hz, H1) and 8.24 (d, J = 2.6 Hz, H2) ppm. ^{13}C NMR spectrum [δ in CDCl$_3$] showed signals at 116.15, 125.05, 126.06, 128.44, 128.72, 128.95, 129.61, 134.3, 141.45 and 157.84 ppm.

Anal. Calcd for C$_{12}$H$_9$NO$_3$: C, 66.98%; H, 4.22%; N, 6.51%. Found: C, 66.79%; H, 4.11%; N, 6.27%.

Bis(4-nitro-2-biphenyl)ether (V). In a flask, a mixture of 5.26 g (24.2 mmol) of **II**, 5.22 g (24.2 mmol) of **IV**, 3.35 g (24.2 mmol) of potassium carbonate, 30 mL of toluene and 80 mL of DMAc was stirred at 130 °C for 1 h. The water formed during the reaction was removed by azeotropic distillation using toluene. Next, the reaction temperature was raised to 160 °C, and the mixture was stirred at this temperature for 3 h. The reaction mixture was cooled at 80 °C, and the solvent was evaporated under a reduce pressure of 15–25 torr. The residue was washed with 250 mL of water and extracted twice with 200 mL of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated. After the residue was purified by silica gel chromatography eluted by a mixture of dichloromethane and hexane

(6:4), pure **V** was obtained by recrystallization from acetic acid. Yield: 4.28 g (43%). Mp: 143–144 °C. IR spectrum (KBr) exhibited absorption bands at 1520 cm^{-1}, 1344 cm^{-1} (NO$_2$) and 1224 cm^{-1} (Ar–O–Ar).

^{1}H NMR spectrum [δ in CDCl$_3$] showed signals at 7.02 (d, 2H, $J = 8.8$ Hz, H3), 7.33–7.42 (m, 10H, H4, H5 and H6), 8.15 (dd, 2H, $J = 8.8$ Hz, $J = 2.9$ Hz, H1) and 8.30 (d, 2H, $J = 2.9$ Hz, H2) ppm. ^{13}C NMR spectrum [δ in CDCl$_3$] showed signals at 118.82, 124.21, 127.03, 128.44, 128.54, 129.00, 134.24, 134.83, 144.07 and 157.31 ppm.

Anal. Calcd for C$_{24}$H$_{16}$N$_2$O$_5$: C, 69.90%; H, 3.91%; N, 6.79%. Found: C, 69.71%; H, 3.85%; N, 6.68%.

Synthesis of V from II. In a flask, a mixture of 8.69 g (40.0 mmol) of **II**, 5.53 g (40.0 mmol) of potassium carbonate and 50 mL of DMF was stirred at 140 °C for 72 h. The reaction mixture was cooled at 80 °C, and the solvent was evaporated under a reduce pressure of 15–25 torr. The residue was washed with 250 mL of water and extracted twice with 200 mL of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated. After the residue was purified by silica gel chromatography eluted by a mixture of dichloromethane and hexane (6:4), pure **V** was obtained by recrystallization from acetic acid. Yield: 5.63 g (68%). Mp: 143–144 °C. IR spectrum (KBr) exhibited absorption bands at 1520 cm^{-1}, 1345 cm^{-1} (NO$_2$) and 1226 cm^{-1} (Ar–O–Ar).

^{1}H NMR spectrum [δ in CDCl$_3$] showed signals at 7.02 (d, 2H, $J = 8.8$ Hz, H3), 7.33–7.42 (m, 10H, H4, H5 and H6), 8.14 (dd, 2H, $J = 8.8$ Hz, $J = 2.9$ Hz, H1) and 8.30 (d, 2H, $J = 2.9$ Hz, H2) ppm. ^{13}C NMR spectrum [δ in CDCl$_3$] showed signals at 118.83, 124.21, 127.03, 128.44, 128.56, 129.00, 134.24, 134.83, 144.08 and 157.31 ppm.

Anal. Calcd for C$_{24}$H$_{16}$N$_2$O$_5$: C, 69.82%; H, 3.94%; N, 6.75%. Found: C, 69.71%; H, 3.85%; N, 6.68%.

Bis(4-amino-2-biphenyl)ether (VI). A mixture of 4.28 g (10.4 mmol) of **V** and 0.3 g of 10% Pd/C in mL DMF at 60 °C for 12 h under a hydrogen atmosphere. After the Pd/C was removed by filtration, the solvent was evaporated under reduced pressure. The residue was recrystallized from toluene to give a pure **VI**. Yield: 3.08 g (84%). Mp: 204–205 °C. IR spectrum (KBr) exhibited absorption bands at 3375 cm^{-1}, 3354 cm^{-1} (NH$_2$) and 1213 cm^{-1} (Ar–O–Ar).
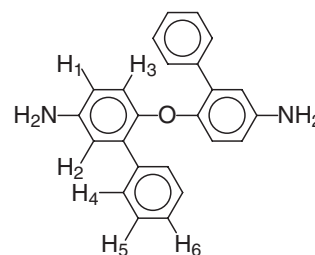
^{1}H NMR spectrum [δ in CDCl$_3$] showed signals at 2.50–3.70 (broad s, 4H, –NH$_2$), 6.57 (dd, 2H, $J = 8.4$ Hz, $J = 2.9$ Hz, H1), 6.69 (d, 2H, $J = 8.4$ Hz, H3), 6.70 (d, 2H, $J = 2.9$ Hz, H2), 7.21–7.33 (m, 6H, H5 and H6) and 7.34–7.42 (m, 4H, H4) ppm. ^{13}C NMR spectrum [δ in CDCl$_3$] showed signals at 115.35, 117.74, 119.57, 126.87, 127.76, 129.16, 133.50, 138.03, 141.01 and 147.42 ppm.

Anal. Calcd for C$_{24}$H$_{20}$N$_2$O: C, 81.79%; H, 5.72%; N, 7.95%. Found: C, 81.51%; H, 5.50%; N, 7.81%.

Polymerization

Polyimide **IXa** from **VI** and **VIIa**. In a three necked flask, 0.433 g (1.99 mmol) of **VIIa** was added to a solution of 0.700 g (1.99 mmol) of **VI** in 8.0 mL of NMP in one portion. The mixture was stirred at room temperature for 6 h under nitrogen. A part of the resulting viscous solution poured into 200 mL of methanol. The precipitated polymer was filtrated, washed with methanol and dried under vacuum. The inherent viscosity of polyamic acid **VIIIa** was 0.87 dlg^{-1} in NMP at 30 °C. The NMP solution was cast onto a glass plate and the solvent was removed at 80 °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 300 °C for 1 h under vacuum. The IR spectrum (film) exhibited absorption band at 1780 cm^{-1} and 1720 cm^{-1} (C=O) and 1360 cm^{-1} (C–N). IR spectrum (film) exhibited absorption bands at 1780 cm^{-1}, 1720 cm^{-1} (C=O) and 1360 cm^{-1} (C–N).

Anal. Calcd for C$_{34}$H$_{18}$N$_2$O$_5$: C, 76.40%; H, 3.39%; N, 5.24%. Found: C, 75.92%; H, 3.35%; N, 5.01%.

Measurement

^{1}H and ^{13}C NMR spectra were recorded on a JNM-GSX400 FT-NMR spectrometer and SHIMADZU spectro Photometer IR 435, respectively. X-Ray diffraction was performed with a Rigaku RAD-B system. For differential scanning calorimetry (DSC) and thermogravimetry (TG) a Shimadzu DSC-60 and Rigaku thermal analysis station TG 8110 were used, respectively, and measurement was 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 at 1.0 Hz at 5 °C min^{-1}.

RESULTS AND DISCUSSION

Monomer Synthesis

New phenylated diamine having phenyl groups at the 2- and 2′-positions of the diphenyl ether moiety, bis(4-amino-2-biphenyl)ether, was synthesized in five steps starting from 3-chloro-4-fluoronitrobenzene **I** according to eq 1. Cross-coupling[20] of **I** with phenylboronic acid yielded 4-fluoro-3-phenyl nitrobenzene **II**. Subsequent reaction of **II** with ethanol in the presence of sodium hydroxide afforded 4-ethoxy-3-phenylnitrobenzene **III**, and **III** was treated with pyridine hydrochloride to give 4-hydroxy-3-phenylnitrobenzene **IV**. The reaction between **IV** and **II** gave bis(4-nitro-2-biphenyl)ether **V**, and bis(4-amino-2-biphenyl)ether **VI** was obtained by hydrogenation of **V** using Pd/C as a catalyst.
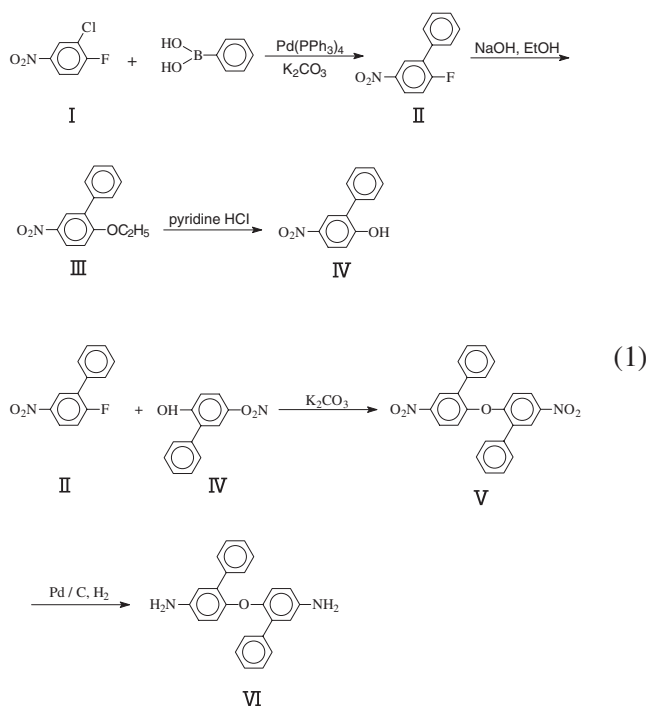
Later, it was found that the compound **V** could be synthesized in one step by treating **II** with potassium carbonate in DMF at 140 °C (see experimental section).


Chemical structures were confirmed by IR, NMR spectra and elemental analysis. In the synthesis of compound **V**, the spin-spin coupling of the protons (H1 and H3) with fluorine atom, which was observed on the ^{1}H NMR spectrum of **II**, disappeared, and the characteristic ether band at 1224 cm^{-1} appeared on the IR spectrum. Compound **VI** showed IR character-istic absorption bond at 3375 and 3354 cm^{-1} of amino group. The ^{13}C NMR spectrum of exhibited 10 peaks due to symmetry, indicating the formation of the postulated diamine (**VI**). Elemental analysis of all the compounds was also in good agreement with calculated results for the proposed structures.

2D-COSY NMR spectra of **IV** and **V** were shown in Figure 1. In the both 2D-COSY NMR spectra, the correlations between the proton of H3 and the protons of H1 and H2 as well as the correlations between the proton of H3 and the phenyl protons (H4, H5, and H6) were observed. However, correlation between the phenyl protons at 2-position and those at 2′-position, which suggested the influence of the phenyl groups on the flexibility of the diphenyl ether, was not observed in the spectrum of **V**. The signals from the phenyl protons of **V** appeared in the field higher than those of **IV**. The higher magnetic field shift might be due to the interaction between the phenyl groups at 2-, and 2′-position.

Polymer Synthesis

Aromatic polyimides (**IXa–h**) were synthesized by the usual two-step procedure involving the ring-opening polymerization of the diamine (**VI**) to tetracarboxylic dianhydrides (**VIIa–h**) and subsequent thermal cyclodehydration as shown in eq 3.
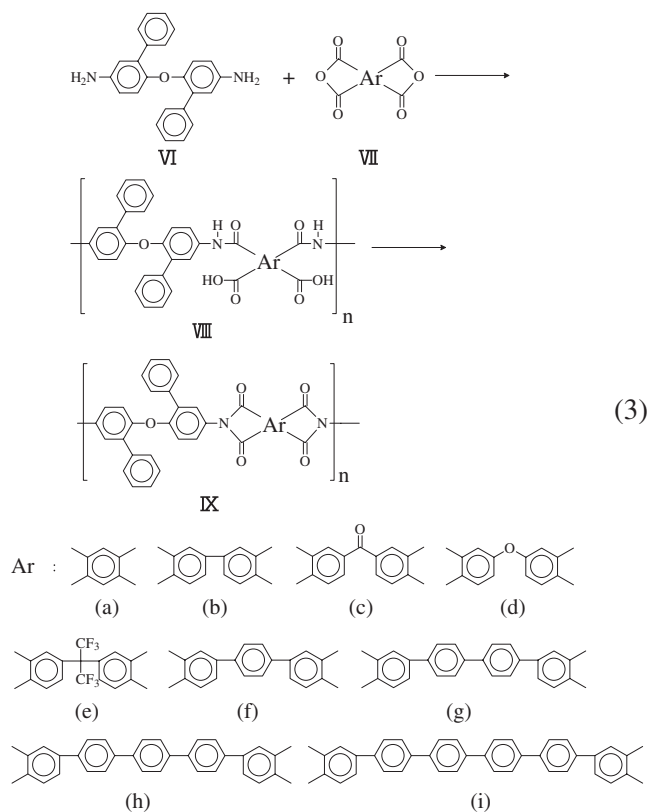
In the first step, ring-opening polymerizations were carried out in NMP at room temperature, leading to the formation of polyamic acids having inherent
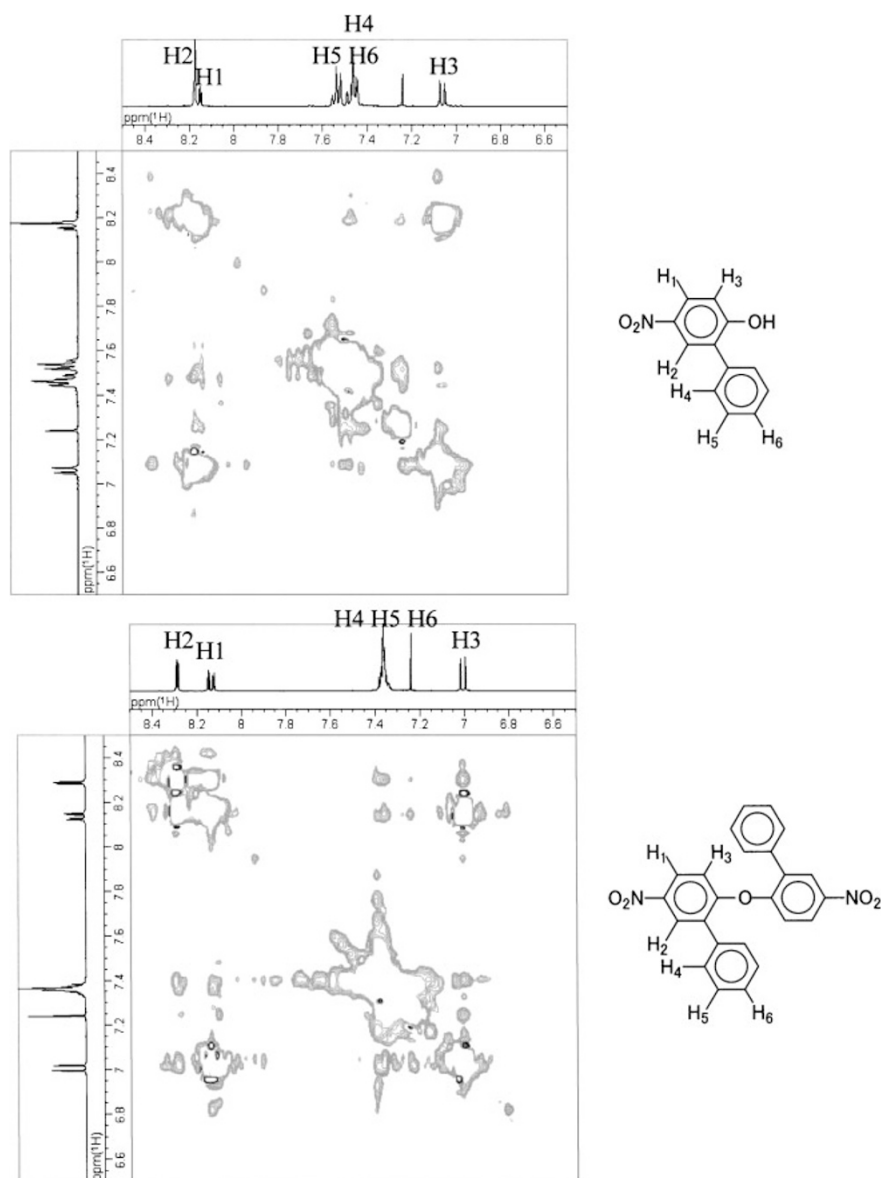
Figure 1. 2D COSY NMR spectra of **IV** and **V**.

viscosities of 0.38–0.92 dlg^{-1} in NMP (Table I). The polymerization proceeded in homogeneous solution in reaction media (NMP), and viscosity of polyamic acid were rather high.

In the second step, the thermal conversion of the polyamic acids to polyimides was performed by heating precursor polymers in the form of film successively at 100 °C for 1 h, 200 °C for 1 h, and finally 300 °C for 1 h under vacuum. These polyimides gave tough films except **IXe**. Polyimide **IXe** was gave only brittle films.

The formation of polyimides were confirmed by appearance of absorption bands at around 1780 cm^{-1} and 1720 cm^{-1} (C=O) and about 1360 cm^{-1} (C–N) characteristic of imide group in the IR spectra. Elemental analysis values were in close agreement with those calculated values, thus also supporting polyimide formation.

Table I. Synthesis of polyamic acid

Dianhydride	Polyamic acid	Yield%	$\eta_{inh}{}^{c}$/dlg^{-1}
VIIa	**VIIIa**[a]	97	0.87
VIIb	**VIIIb**[a]	96	0.55
VIIc	**VIIIc**[a]	92	0.75
VIId	**VIIId**[a]	94	0.74
VIIe	**VIIIe**[a]	88	0.38
VIIf	**VIIIf**[a]	94	0.48
VIIg	**VIIIg**[a]	93	0.58
VIIh	**VIIIh**[a]	94	0.69
VIIi	**VIIIi**[b]	98	0.92

[a]Polymerization was carried out with 2.0 mmol each monomer in 8.0 mL NMP at room temperature for 6 h under nitrogen. [b]Polymerization was carried out with 2.0 mmol each monomer in 12.0 mL NMP at 30 °C for 48 h under nitrogen. [c]Measured at 0.5 gdl^{-1} in NMP at 30 °C.
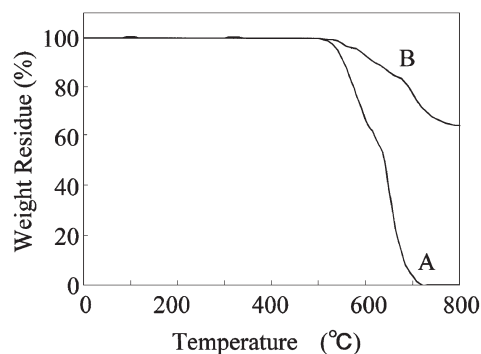
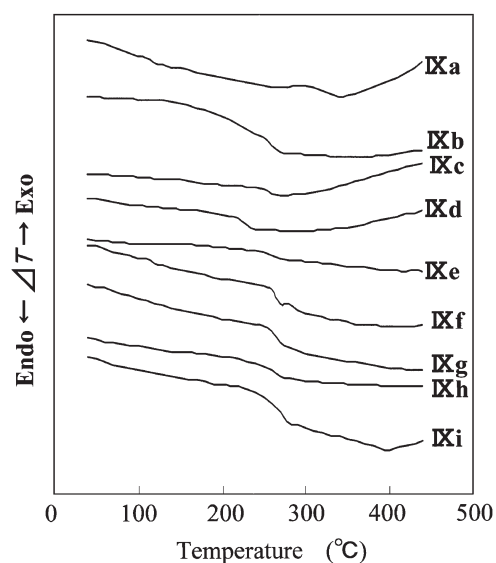**Figure 2.** TG curves of polyimide **IXa**. at heating rate of $10\,°C\,min^{-1}$ in (A) air or (B) nitrogen.

Figure 3. DSC curves for polyimides at heating rate of 10 $°C\,min^{-1}$ in nitrogen.

Table II. Thermal behavior of aromatic polyimides

Polyimides	$T_g{}^a/°C$	$T_{10}{}^b/°C$	$T_{10}{}^c/°C$
IXa	309 (400)[d]	563	622
IXb	253 (234)[d]	550	615
IXc	257 (269)[d]	560	620
IXd	226 (224)[d]	558	615
IXe	262 (294)[d]	544	595
IXf	260 (232)[d]	560	627
IXg	260 (236)[d]	560	625
IXh	263 (243)[d]	568	635
IXi	270 (244)[d]	580	639

[a]Determined by DSC in nitrogen at a heating rate of 10 $°C\,min^{-1}$. [b]Temperature at which 10% weight loss was recorded by TG at a heating rate of $10\,°C\,min^{-1}$ in air. [c]Temperature at which 10% weight loss was recorded by TG at a heating rate of $10\,°C\,min^{-1}$ in N_2. [d]T_g values of the corresponding ODA-based polyimides.
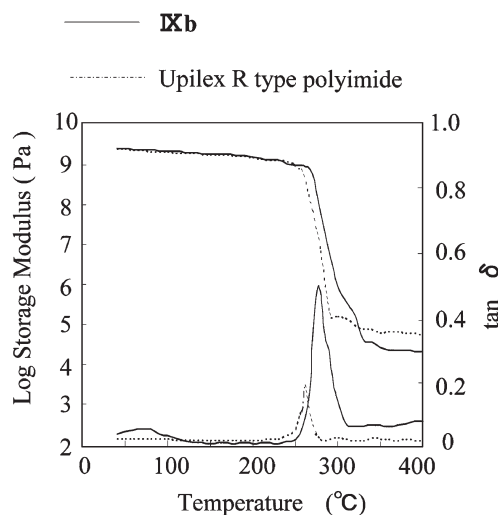

Figure 4. Dynamic mechanical behavior of polyimide **IXb** and polyimide prepared from 4,4′-diaminodiphenyl ether and **VIIb**.

Polymer Properties

Crystallinity of polyimides was estimated by X-ray diffraction. All polymers, even **IXg**, **IXh** and **IXi** which have rigid structure, were amorphous.

Thermal behavior of polyimides was evaluated by TG and DSC. Figures 2 and 3 show TG curves of polyimide **IXa** and DSC curves of all the polyimides, respectively, and glass transition temperature (T_g) and 10% weight loss temperature (T_{10}) are summarized in Table II. T_g of the corresponding ODA-based polyimides without phenyl groups at 2,2′-position of the phenyl ether are also shown in Table II for comparison. None of the present polyimides expect **IXe** lost weight below $470\,°C$ in air or nitrogen, and T_{10} in air and nitrogen were in the range of 544–580 $°C$ and 595–639 $°C$, respectively, and had similar thermal stabilities to polyimides without phenyl groups at 2,2′-position of the phenyl ether. The thermal stability of polyimide **IXe** was reduced.

The present polyimides had T_g in the range of 220–310 $°C$. T_g values of polyimides **IXb**, **IXf**, **IXh** and

IXi having linear phenylene structure were slightly higher than those of the corresponding ODA-based polyimides. However, T_g value of the polyimide **IXa** which was prepared from pyromellitic dianhydride was much lower than the corresponding polyimide based on ODA. This reason is not clear. The high T_g value of the polyimide from ODA and pyromellitic dianhydride was thought to be due to the chain packing originated from high electron affinity of pyromellitic dianhydride.[21,22] The phenyl groups of **IXa** may disturb the chain packing. T_g values of polyimides **IXc** and **IXe** having connecting groups were slightly lower than those of corresponding ODA-based polyimides. It was suggested that the phenyl groups at 2,2′-position of the phenyl ether had a influence on both the chain mobility and chain packing of the polyimides.
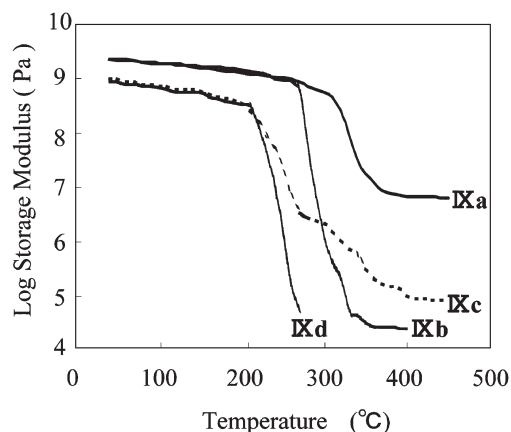
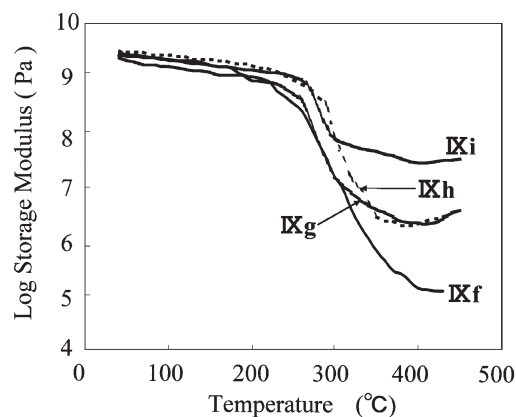**Figure 5.** Storage modulus of polyimides **IXa**, **IXb**, **IXc** and **IXd**.

Figure 6. Storage modulus of polyimides **IXf**, **IXg**, **IXh** and **IXi**.

Table III. Solubility of aromatic polyimides

Polyimide	NMP	DMAc	DMF	m-cresol	Pyridine	THF	Methanol
IXa	++	++	++	++	++	−−	−−
IXb	++	++	++	++	++	−−	−−
IXc	++	++	++	++	++	−−	−−
IXd	++	++	++	++	++	−	−−
IXe	++	++	++	++	++	−	−−
IXf	++	−	−	++	++	−−	−−
IXg	++	+	+	+	−−	−−	−−
IXh	++	+	+	+	−−	−−	−−
IXi	−	−	−	−	−−	−−	−−

Solubility: ++, soluble on heating; +, precipitation after cooling hot solution; −, partially soluble on heating; −−, insoluble.

Figure 4 shows temperature dependence of the dynamic storage modulus (E′) and tan δ for polyimide **IXb** and polyimide (Upilex R type polyimide) prepared from 4,4′-diaminodiphenyl ether and **VIIb**. As shown in T_g values determined by DSC (Table II), regarding the peak temperature in the tan δ curves, polyimide **IXb** showed a T_g at 278 °C, and the corresponding ODA-based polyimide from showed slightly lower T_g at 263 °C. For polyimide **IXb**, E′ decrement at the T_g was larger than that for the Upilex R type polyimide. The effect of the phenyl groups at 2,2′-position was also observed in the dynamic mechanical property of the polyimide.

Figure 5 shows temperature dependence of the dynamic storage modulus for the present polyimides **IXa**, **IXb**, **IXc** and **IXd**, and Figure 6 shows those of polyimides **IXf**, **IXg**, **IXh** and **IXi**. We could not determine the storage modulus of polyimide **IXe** because **IXe** was not obtained as film. The modulus decreased rapidly around 200–250 °C to a very low level (below 10^5 Pa) for **IXb**, **IXc**, and **IXd** without showing a plateau region. As observed in the case of previously prepared polyimides,[16–19] polyimide **IXf**, **IXg**, **IXh** and **IXi** having rigid linear phenylene structure showed a plateau region above 300 °C, the

decrement in the modulus at the glass transition decreased with the number of phenylene units.

Table III lists qualitative solubility of the present polyimides. All the polyimides were insoluble in organic solvents at room temperature. However, almost all the polyimides, even **IXf**, **IXg** and **IXh**, which had rigid structures, were soluble in NMP, DMAc, DMF, and m-cresol on heating. Interestingly, the polyimides except **IXg** and **IXh** never precipitated in spite of insolubility at room temperature when the hot solution was cooled to room temperature. The presence of the phenyl groups at 2,2′-position of the phenyl ether improved the solubility of polyimides drastically. Such the improvement of the solubility by the introduction of bulky substituents were previously reported in many kinds of aromatic polyimides.[23–31]

In conclusion, we successfully improved the solubility of ODA based polyimides by introducing phenyl groups at 2,2′-position of the phenyl ether without decreasing the thermal and thermo-mechanical properties.

REFERENCES

1. P. E. Cassidy, "Thermally Stable Polymer," Marcel Dekker, New York, 1980, chapt. 4.

2. K. L. Mittal, "Polyimides: Synthesis, Characterization, and Applications," Plenum Press, New York, 1984.

3. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev, and L. A. Lauias, "Polyimides: Thermally Stable Polymer," Consultants Bureau, A Division of Plenum Publishing Co., New York, 1987.

4. C. Feger, M. M. Khojasteh, and J. M. MacGrath, "Polyimides: Materials, Chemistry and Characterization," Elsevier, Amsterdam, 1989.

5. M. I. Bessonov and V. A. Zubkov, "Polyamic acid and Polyimides: Synthesis and Transformation and Structure." CRC Press, Boca Raton, FL, 1993.

6. C. Feger, M. M. Khojasteh, and S. E. Molis, "Polyimides: Trends in Materials and Applications," Society of Plastic Engineers, Mid Hudson Section, New York, 1996.

7. M. K. Ghosh and K. L. Mittal, Polyimides: "Fundamentals and Applications," Marcel Dekker, New York, N.Y., 1996.

8. P. M. Hergenrother, *Polym. J.*, **19**, 73 (1987).

9. I. Mita, *Kinouzairyou*, **1**, 1 (1981).

10. M. Hasegawa, N. Sensui, Y. Shindo, and R. Yokota, *Macromolecules*, **32**, 387 (1999).

11. St. A. K. Clair and St. T. L. Clair, *Polym. Mater. Sci. Eng.*, **51**, 62 (1984).

12. St. A. K. Clair, St. T. L. Clair, W. S. Slemp, and K. S. Ezzel, *Proc. 2nd Int. Conf. on Polyimides*, Elleville, NY, 333 (1985).

13. St. A. K. Clair and W. S. Slemp, *SAMPE J.*, **21**, 28 (1985).

14. St. A. K. Clair and St. T. L. Clair, *Polym. Mater. Sci. Eng.*, **55**, 396 (1986).

15. St. A. K. Clair, St. T. L. Clair, and W. P. Winfree, *Polym. Mater. Sci. Eng.*, **55**, 396 (1986).

16. A. Morikawa, *Polym. J.*, **32**, 275 (2000).

17. A. Morikawa and Y. Hosoya, *Polym. J.*, **34**, 544 (2002).

18. A. Morikawa and K. Ono, *Polym. J.*, **32**, 948 (2000).

19. A. Morikawa and K. Ono, *High Perform. Polym.*, **13**, S73 (2001).

20. T. Oh-e, N. Miyaura, and A. Suzuki, *Synlett*, 221 (1990).

21. M. Hasegawa, M. Kochi, I. Mita, and R. Yokota, *Eur. Polym. J.*, **25**, 349 (1989).

22. M. Hasegawa and K. Horie, *Prog. Polym. Sci.*, **26**, 259 (2001).

23. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2189 (1984).

24. H.-J. Jeong, A. Kobayashi, M. Kakimoto, and Y. Imai, *Polym. J.*, **26**, 373 (1994).

25. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 39 (1991).

26. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 1691 (1991).

27. Y. Ohishi, M. Ishida, M. Kakimoto, Y. Imai, and T. Kurosaki, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 1027 (1992).

28. I. K. Spiliopoulos and J. A. Microyannidis, *Macromolecules*, **31**, 1236 (1998).

29. I. K. Spiliopoulos and J. A. Microyannidis, *Macromolecules*, **31**, 515 (1998).

30. A. Morikawa and T. Hatakeyama, *Polym. J.*, **31**, 66 (1999).

31. Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).