Synthesis and Characterization of Polyimide from 4,4'-Diamino diphenyl ether having Substituents at 2,2'-position

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Aromatic polyimides having phenyl groups and trifluoromethyl groups at 2,2'-position of the diphenyl ether moieties have been prepared from bis(4-amino-2-biphenyl)ether (**1**) and bis(4-amino-2-trifluoromethylphenyl)ether (**2**), respectively and various tetracarboxylic dianhydrides by the conventional two-step procedure. The substituents at 2,2'-position of the diphenyl ether had a great influence on the properties of polyimides. In this paper, aromatic polyimides having only one phenyl group at 2,2'-position of the diphenyl ether moieties are prepared from 4,4'-diamino-2-phenyldiphenylether (**3**), and the properties are compared with those of the polyimides from **1** and **2**.

Keyword: polyimide, 4,4'-diamino-2-phenyldiphenylether, bis(4-amino-2-biphenyl)ether, bis(4-amino-2-trifluoromethylphenyl)ether, properties

1. Introduction

Aromatic polyimides are characterized by high glass transition temperatures (T_g) along with high decomposition temperatures and good mechanical properties, and are used in various fields including the aerospace and electric industries [1]. Their one major drawback is that they are insoluble in organic solvents and unprocessable after conversion from polyamic acid, the precursor of polyimide, to the polyimide form. One attractive method to improve solubility is the introduction of bulky phenyl group into the polyimide backbone, and a number of organic soluble polyimides have been successfully prepared without decreasing the thermal properties [2-5]. We have prepared aromatic polyimides from a diamine monomer, **1** and **2**, which had phenyl and trifluoromethyl groups at the 2- and 2'-position of the diphenyl ether moiety, respectively, and compared the properties with those of the corresponding 4,4'-oxydianiline-based polyimides without phenyl group [6-8]. The presence of the substituents had

an influence on the solubility, and almost all the polyimides, even the polyimide from rigid 3,3''',4,4'''-*p*-quinquephenyltetracarboxylic dianhydride, were soluble in organic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc) and *m*-cresol.

In this study, a series of polyimides are synthesized from **3**, and the properties, such as dielectric constants and water absorption, as well as thermal properties and solubility, are measured, compared with those of the polyimides from **1** and **2**, and the structure-property relationships of these polyimides are discussed. Since polyimides from **3** have only one phenyl group at 2,2'-position of the diphenyl ether moiety, the structure is asymmetric. We examined the effects of the asymmetric structure on the polyimide properties. The polyimide from **3** and pyromellitic dianhydride has been synthesized to investigate possibility of heat-resistant composite materials with good processability [9].

2. Experimental

2.1. Materials

Pyromellitic dianhydride **a**, 3,3',4,4'-biphenyltetracarboxylic dianhydride **b**, 3,3',4,4'-benzophenonetetracarboxylic dianhydride **g**, 4,4'-oxydiphthalic dianhydride **h** and 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride **i** were obtained commercially, and purified by sublimation under reduced pressure. 3,3'',4,4''-*p*-Terphenyltetracarboxylic dianhydride **c** was supplied by Hitach Kasei Kogyo Co., Japan. 3,3''',4,4'''-*p*-Quaterphenyltetracarboxylic dianhydride **d** [10], 3,3''',4,4'''-*p*-quinquephenyltetracarboxylic dianhydride **e** [11] and 3,3''',4,4''',6,6'''-*p*-sexiphenyltetracarboxylic dianhydride **f** [12] were prepared as previously reported. 4-Fluoro-3-phenyl nitrobenzene was prepared as previously prepared [6]. NMP was purified by vacuum distillation over calcium hydride.

2.2. Monomer Synthesis

4, 4'-dinitro-2-phenyldiphenylether (**4**)

In a flask, a mixture of 6.85 g (49.3 mmol) of *p*-nitrophenol, 10.7 g (49.3 mmol) of 4-fluoro-3-phenyl nitrobenzene, 6.80 g (49.3 mmol) of potassium carbonate, 160 mL of DMAc and 40 mL of toluene was stirred at 130 °C for 1 h. Then, the reaction temperature was raised to 160 °C, and the mixture was stirred at this temperature for 3 h. The water formed during the reaction was removed by azeotropic distillation using toluene. The reaction mixture was cooled at 80 °C, and the solvent was evaporated under reduced pressure of 15-25 torr. After the residue was washed with 250 mL of water, the pure **4** was obtained by recrystallization from acetic acid. Yield: 10.50 g (63%). The IR spectrum exhibited absorption bands at 1520 cm⁻¹, 1340 cm⁻¹ (NO₂), and 1250 cm⁻¹ (Ar-O-Ar).

¹H NMR spectrum [δ in CDCl₃] showed signals at 6.99 (d, 2H, *J* = 8.7 Hz), 7.20 (d, 1H, *J* = 8.5 Hz), 7.33-7.44 (m, 3H), 7.47-7.53 (m, 2H), 8.18 (d, 2H, *J* = 8.6 Hz), 8.25 (dd, 1H, *J* = 8.6 Hz, *J* = 2.9 Hz) and 8.41 (d, 1H, *J* = 2.9 Hz) ppm.

Anal. Calcd for C₁₈H₁₂N₂O₅: C, 64.29%; H, 3.60%; N, 8.33%, Found: C, 62.115%; H, 3.49%; N, 8.24%.

4,4'-diamino-2-phenyldiphenylether (**3**)

A mixture of 10.50 g (31.2 mmol) of **4** and 0.3 g of 10% Pd/C in 150 mL of *N,N*-dimethylformamide (DMF) was stirred 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 of 15-20 torr. Pure **3** was obtained by distillation under reduced pressure (ceramic heater). Yield: 5.30 g (63%). BP: 260-270 °C (1 Torr). MP: 114-115 °C. The IR spectrum exhibited absorption bands at 3450 cm⁻¹, 3380 cm⁻¹ (NH₂) and 1240 cm⁻¹ (Ar-O-Ar).

¹H NMR spectrum [δ in CDCl₃] showed signals at 6.57 (d, 2H, *J* = 8.7 Hz), 6.61 (dd, 1H, *J* = 8.6 Hz, *J* = 2.9 Hz), 6.70 (d, 2H, *J* = 8.7 Hz), 6.75 (d, 2H, *J* = 2.9 Hz), 6.80 (d, 1H, *J* = 8.6 Hz), 7.23-7.28 (m, H₆), 7.29-7.36 (m, 2H) and 7.47-7.53 (m, 2H) ppm. ¹³C NMR spectrum [δ in DMSO-*d*₆] showed signals at 115.4, 116.2, 117.4, 118.3, 121.2, 126.9, 127.9, 129.1, 134.0, 137.8, 141.0, 142.0, 146.5 and 151.2 ppm.

Anal. Calcd for C₁₈H₁₆N₂O: C, 78.24%; H, 5.84%; N, 10.13%, Found: C, 78.05%; H, 5.66%; N, 9.98 %.

2.3. Polymerization from **3**

Polyimide **PI3a** from **3** and **a**.

In a three-necked flask, 0.545 g (2.50 mmol) of **a** was added to a solution of 0.841 g (2.50 mmol) of **3** in 10.0 mL of NMP in one portion. The mixture was stirred at room temperature for 8 h under nitrogen. A part of the resulting viscous solution was poured into 200 mL of methanol. The precipitated polymer was filtered, washed with methanol and dried under vacuum. The inherent viscosity of polyamic acid **PAA3a** was 0.75 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).

Anal. Calcd for C₂₈H₁₄N₂O₅: C, 73.36%; H, 3.08%; N, 6.11%, Found: C, 73.16%; H, 2.91%; N, 5.85%.

2.4. Measurements

¹H- and ¹³C- NMR spectra were recorded on a JNM-GSX400 FT-NMR spectrometer and IR spectra were recorded on a SHIMADZU spectro Photometer IR 435, respectively. For differential scanning calorimetry (DSC) and thermogravimetry (TG) a Shimadzu DSC-60 and Rigaku thermal analysis station TG 8110 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 at 1.0 Hz at 5 °C min⁻¹.

The contents of water absorption (W_A %) for polyimide films were determined from the relation $(W-W_0)/W_0 \times 100$, where W_0 is the weight of the vacuum-dried films at 100 °C for 12 h, and W denotes the weight of the samples immersed in water at 25 °C for 24 h and subsequently wiped with tissue paper.

The refractive indices of the polyimide films were measured at C-line (656 nm) on Abbe refractometer (Atago NAR 4T).

3. Results and Discussion

3.1. Synthesis of 4,4'-diamino-2-phenyldiphenylether (**3**)

Diamines **3** were synthesized from *p*-nitrophenol and 4-fluoro-3-phenyl nitrobenzene in two steps (Scheme 1). The reaction of *p*-nitrophenol with 4-fluoro-3-phenyl nitrobenzene gave 4,4'-dinitro-2-phenyldiphenylether **4**, and diamine **3** was obtained by hydrogenation of **4** using Pd/C as a catalyst.

Scheme 1. Synthesis of diamines **3**

Chemical structures were confirmed by IR and NMR spectra and elemental analysis. Diamines **3** showed characteristic IR absorption at 3450 and 3380 cm⁻¹ for the amino group, and 1240 cm⁻¹ of ether group. The ¹³C-NMR spectra of **3** had 14 peaks indicating the formation of the desired diamines. Elemental analysis of all the compounds was also in good agreement with calculated results for the proposed structures.

3.2. Polymer synthesis

Aromatic polyimides **PI3x** were synthesized by the usual two-step procedure involving the ring-opening polymerization of the diamine **3** to tetracarboxylic dianhydride (**a-i**) and subsequent thermal cyclodehydration as shown in Scheme 2.

Scheme 2. Synthesis of polyimides **PI3x**

In the first step, ring-opening polymerizations were carried out in NMP at room temperature, leading to the formation of polyamic acids, **PAA3x**, having inherent viscosities of 0.52–0.121 dl g⁻¹ in NMP. In the second step, the thermal conversion of the polyamic acids 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, successively. These polyimides gave tough films.

The formation of polyimides was confirmed by the appearance of IR absorption bands at about 1780 cm⁻¹, 1720 cm⁻¹ and 1360 cm⁻¹ characteristic of an imide group in the IR spectra. Elemental analysis values were in close agreement with the calculated values, also supporting polyimide formation.

3.3. Polymer properties

The thermal behaviors of the polyimide **PI3x** were evaluated by DSC and TG, and values of T_g s and 10% weight loss temperatures (T_{10}) are compared with those of **PI1x** and **PI2x** in Table 1. None of polyimides **PI3x** except **PI3i**, lost weight loss below 470 °C in air and nitrogen. T_{10} values

in air and nitrogen were in the range of 545-575 °C and 593-635 °C, respectively, and almost the same as those of **PI1x**. T_{10} values of **PI2x** were slightly lower than those of **PI1x** and **PI3x**.

Table 1. Thermal properties of aromatic polyimides.

Polyimide	T_g^a (°C)	T_{10}^b (°C)	T_{g10}^c (°C)
PI3a	285	560	615
PI1a	309	563	622
PI2a	300	554	610
PI3b	280	551	614
PI1b	253	550	615
PI2b	281	548	605
PI3c	262	557	625
PI1c	260	560	627
PI2c	281	554	611
PI3d	250	555	613
PI1d	260	560	625
PI2d	282	556	615
PI3e	255	570	637
PI1e	263	568	635
PI2e	277	559	626
PI3f	260	575	635
PI1f	270	580	639
PI2f	285	570	630
PI3g	264	558	614
PI1g	257	560	620
PI2g	256	541	605
PI3h	243	553	609
PI1h	226	558	615
PI2h	234	540	601
PI3i	262	545	593
PI1i	262	544	595
PI2i	273	530	580

^a Determined by DSC.

^b 10% weight loss temperature in air.

^c 10% weight loss temperature in nitrogen.

The polyimides **PI3x** showed T_g s in the range of 243-285 °C without melting in the DSC thermograms corresponding to the amorphous morphology as observed in **PI1x** and **PI2x**. T_g values of **PI3b**, **PI3g** and **PI3h** were slightly higher than those of the corresponding **PI1x**, and those of **PI3d**, **PI3e** and **PI3f** were slightly lower than those of the corresponding **PI1x**. The phenyl groups at 2,2'-position have influences on the rotational flexibility of the diphenyl ether units and the intermolecular interaction among the polyimide chains. The higher T_g values of **PI3b**, **PI3g** and **PI3h** are thought to be due to the lower degree of

the hindrance of intermolecular interaction, and the lower T_g values of **PI3d**, **PI3e** and **PI3f** having longer repeating unit are thought to be due to the lower degree of the hindrance of rotational flexibility as **PI3x** have only one phenyl group at 2,2'-position. The T_g values of **PI2x** which had CF_3 groups, are thought to be the highest due to the lower volume.

Figure 1. Comparison of dynamic mechanical behaviors for polyimides. (a) Polyimide **PI3b**, **PI1b** and **PI2b**. (b) Polyimide **PI3d**, **PI1d** and **PI2d**

Dynamic mechanical behaviors for these polyimides were compared. Temperature dependence of the dynamic storage modulus and $\tan \delta$ curves for **PI3b**, **PI1b** and **PI2b** are shown in Figure 1a, and those for **PI3d**, **PI1d** and **PI2d** are shown in Figure 1b. T_g s were determined as the peak temperatures in the $\tan \delta$ curves, the T_g values of **PI3b**, **PI1b** and **PI2b** were 285 °C, 280 °C and 295 °C, respectively, and those of **PI3d**, **PI1d** and **PI2d** were 260 °C, 275 °C and 285 °C, respectively. The T_g values were slightly higher than those determined by DSC, and the order of increasing the T_g value was in agreement

with the order determined by DSC. For polyimides **PI2b** and **PI2d**, which have trifluoromethyl groups at 2,2'-position of the diphenyl ether moieties, the decrements of storage modulus were larger at the T_g s.

Table 2. Solubility of aromatic polyimides

Polyimide	NMP	DMAc	DMF	<i>m</i> -cresol	pyridine	THF
PI3a	+++	+++	+++	+++	++	--
PI1a	++	++	++	++	++	--
PI2a	+++	+++	+++	-	++	--
PI3b	++	++	++	++	++	--
PI1b	++	++	++	++	++	--
PI2b	++	++	++	++	-	--
PI3c	++	++	++	++	++	--
PI1c	++	-	-	++	++	--
PI2c	++	++	-	++	--	--
PI3d	+++	+++	++	++	++	--
PI1d	++	+	+	+	--	--
PI2d	++	-	-	++	--	--
PI3e	++	+	+	+	--	--
PI1e	++	+	+	+	--	--
PI2e	++	--	--	--	--	--
PI3f	-	--	--	--	--	--
PI1f	-	-	-	--	--	--
PI2f	--	--	--	--	--	--
PI3g	++	++	++	++	++	--
PI1g	++	++	++	++	--	--
PI2g	+++	+++	++	++	--	--
PI3h	++	++	++	++	++	--
PI1h	++	++	++	++	++	-
PI2h	+++	+++	+++	+++	+++	+++
PI3i	+++	+++	+++	+++	+++	--
PI1i	++	++	++	++	++	-
PI2i	+++	+++	+++	+++	+++	+++

THF: tetrahydrofuran

Solubility: +++: soluble at room temperature, ++: soluble on heating, +: precipitation after cooling hot solution, -: partially soluble on heating, --: insoluble.

Table 2 lists out qualitative solubility of polyimides **PI3x**, **PI1x** and **PI2x**. Although **PI2x** were insoluble in organic solvents at room temperature, **PI3a** and **PI3f** were soluble in NMP, DMAc, DMF and *m*-cresol at room temperature, and **PI3d** was also soluble in NMP at room temperature. Almost all the **PI3x** were soluble in NMP on heating, and the effect of asymmetric structure of **PI3x** was observed in the solubility. Almost all the **PI2x** having CF₃ groups at 2,2'-positions were also in NMP on heating, and **PI2a**, **PI2g**, **PI2h** and **PI2i** were soluble in NMP at

room temperature.

The water absorption for polyimides **PI3x** was measured, and the values were compared with those of **PI1x** and **PI2x** (Figure 1-a). The order of increasing water absorption was **PI2x**, **PI1x** < **PI3x**. Water absorption decreased with the increasing number of phenylene units in the case of polyimides prepared from dianhydrides **b**, **c**, **d**, **e** and **f** as previously reported [13], and decreased with decreasing imide content per the repeating unit. The values of water absorption were plotted as a function of the imide group content for all the polyimides, **PI3x**, **PI1x** and **PI2x**, defined as the formula weight (O=C-N-C=O) per that of the repeating unit (Figure 1-b). A positive correlation was observed as previously reported [13,14].

Figure 2. Water absorption of polyimides, **PI3x**, **PI1x** and **PI2x**. (a) Relationship between the polyimide structure and water absorption. (b) Relationship between the imide group content and water absorption.

The refractive indices (n) of polyimides **PI3x** were measured, and dielectric constants (ϵ_{cal}) were estimated using the empirical relationship; $\epsilon_{cal} = 1.1 n^2$ [14, 15] derive from the relationship among velocity of light (C), dielectric constant (ϵ) and magnetic permeability (μ), $C = \frac{1}{\sqrt{\mu\epsilon}}$, and compared with those of **PI1x** and **PI2x** (Figure 3-a). The values of ϵ_{cal} for **PI3x** was in the range of 2.93-3.21, and the value of **PI3i** from 4,4'-(hexafluoroisopropylidene)-diphthalic an-

hydride **i** was the lowest. The values of **PI3x** with the highest imide group contents were the highest, those of **PI2x** having low-polar trifluoromethyl groups were lowest, and the order of ϵ_{cal} was **PI2x** < **PI1x** < **PI3x**. A positive correlation was observed between ϵ_{cal} and the imide group content as in the case of previously reported polyimides (Figure 3-b) [13,16,17], and the change rate of the values to the imide group contents for **PI2x** was the lowest.

Figure 3. Dielectric constants of polyimides, **PI3x**, **PI1x** and **PI2x**. (a) Relationship between the polyimide structure and dielectric constant. (b) Relationship between the imide group content and dielectric constant.

4. Conclusion

Aromatic polyimides **PI3x** having only one phenyl group at 2,2'-position of the diphenyl ether moiety were synthesized, and the properties were compared with those of the polyimides **PI1x** and **PI2x** having phenyl groups and trifluoromethyl

groups at 2,2'-position, respectively. Although the values of water absorption and dielectric constant (ϵ_{cal}) calculated from the refractive indices were larger than those of **PI1x**, the solubility was comparable as that of **PI2x**.

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