

Synthesis and properties of polyimides containing long phenylene units

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Abstract:

Rigid aromatic polyimides **PI-Ar-m**, which were characterized by having long phenylene units, were synthesized from 3,3'',4,4''-*p*-quaterphenyltetracarboxylic dianhydride (**DA-2**), 3,3''',4,4''''-*p*-quinquephenyltetracarboxylic dianhydride (**DA-3**) and 3,3''''',4,4''''''-*p*-sexiphenyltetracarboxylic dianhydride (**DA-4**). In this study, the properties were compared with those of polyimides prepared from 3,3'',4,4''-*p*-terphenyltetracarboxylic dianhydride (**DA-1**) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (**DA-0**) on the basis of the number (**m**) of phenylene units. Almost all the polyimides were insoluble in organic solvents, and the glass transition temperature (T_g) values were not dependent on **m**. In addition, polyimides **PI-Ar-Z** were prepared from a bent / distorted Z-type sexiphenyltetracarboxylic dianhydride (**DA-Z**), isomer of **DA-4**, and the properties were compared with those of **PI-Ar-4**.

Keywords: 3'',4,4''-*p*-quaterphenyltetracarboxylic dianhydride, 3,3''',4,4''''-*p*-quinquephenyltetracarboxylic dianhydride, 3,3''''',4,4''''''-*p*-sexiphenyltetracarboxylic dianhydride, Z-type sexiphenyl tetracarboxylic dianhydride

1. INTRODUCTION

Aromatic polyimides are characterized by high T_g as well as high decomposition temperature and good mechanical properties, and used in various fields including the aerospace and electric industries. Therefore the relationships between the structures and properties of polyimides have been extensively investigated. A polyimide (**PI-PP-0**) [1] from 3,3',4,4'-biphenyltetracarboxylic dianhydride (**DA-0**) and *p*-phenylenediamine showed excellent properties, a high T_g , high thermos-oxidative stability, high modulus and strength, high chemical resistance, and low linear coefficient on thermal expansion (CTE) etc. **PI-PP-1** [1] from 3,3'',4,4''-*p*-terphenyltetracarboxylic dianhydride (**DA-1**) and *p*-phenylenediamine have higher T_g and lower CTE than **PI-PP-0**. **DA-1** has one more phenylene unit than **DA-0**, and more rod-like. We synthesized dianhydride **DA-m** (**m** = 2, 3, 4) [2-4] having more phenylene units than **DA-1**, and there were used to prepare aromatic polyimides containing *p*-quaterphenyl, *p*-quinquephenyl, and *p*-sexiphenyl units with various aromatic diamines, such as 4,4'-oxydianiline (**ODA**), 4,4'-methylenedianiline (**MDA**), *p*-phenylenediamine (**PP**) and 4,4'-bis(4-aminophenoxy) biphenyl (**BAPB**). In this study, the properties were compared with those of polyimides prepared from **DA-1** and **DA-0** on the basis of the number (**m**) of phenylene units, and the effect of phenylene groups on the polyimide property was examined. The isomer effect on the basis of properties **PI-Ar-Z** [5] from **DA-Z**, a isomer of **DA-4**, was also examined.

2. EXPERIMENTAL

2.1. Materials

DA-0, ODA, MDA, PP and BAPB were obtained commercially, and purified by sublimation under reduced pressure. *N*-methyl-2-pyrrolidone (NMP) was purified by vacuum distillation over calcium hydride. **DA-1** was supplied by Hitachi Kasei Kogyo Co., Japan. **DA-2** [2], **DA-3** [3], **DA-4** [4] and **DA-Z** [5] were synthesized to the method reported previously.

2.2. Synthesis of polyimide by two-step procedure

In a three-necked flask, 2.5 mmol of dianhydride was added to a solution of 2.5 mmol of diamine in 15 mL of NMP in one portion. The mixture was stirred at room temperature for about 24 h under nitrogen. The NMP solution was cast onto a glass plate and the solvent was removed at 70 °C. The thermal cyclodehydration of polyamic acid was performed by successive heating at 100 °C for 1h, 200 °C for 1 h and finally 300 °C for 1 h under vacuum. The IR spectrum (film) exhibited absorption bands at 1780 cm⁻¹ and 1720 cm⁻¹ (C=O) and 1360 cm⁻¹ (C-N).

2.3. Synthesis of polyimide by one-step procedure

In a flask equipped a condenser, 1.0 mmol of dianhydride, 1.0 mmol of diamine and 3 mL of dried toluene were added to 10 mL of *m*-cresol in one portion. The mixture was stirred at 130 °C for 30 min and at 190 °C for 6 h under 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. 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 70 °C, the residue was dried under reduced pressure at 200 °C for 6 h to yield a tough film. The IR spectrum (film) exhibited absorption bands at 1780 cm⁻¹ and 1720 cm⁻¹ (C=O) and 1360 cm⁻¹ (C-N).

2.4. Measurements

IR spectra were recorded on a Shimadzu Spectrometer IR 435. For differential scanning calorimetry (DSC) and thermogravimetry (TG), 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. Dynamical mechanical analysis (DMA) were performed with the Advanced Rheometric Expansion System at 1.0 Hz at 5 °C min⁻¹. X-ray diffraction was performed with Smart Lab-SP/IUA (Rigaku). Densities of polyimides films were measured using a density-gradient tube prepared from carbon tetrachloride and heptane. The refractive indices of the polyimide films were measured at C-line (656 nm) on Abbe refractometer (Atago NAR 4T, Atago Corporation, Tokyo, Japan).

3. RESULTS AND DISCUSSION

3.1. Polyimides from rod- like **DA-m** (m = 2, 3, 4)

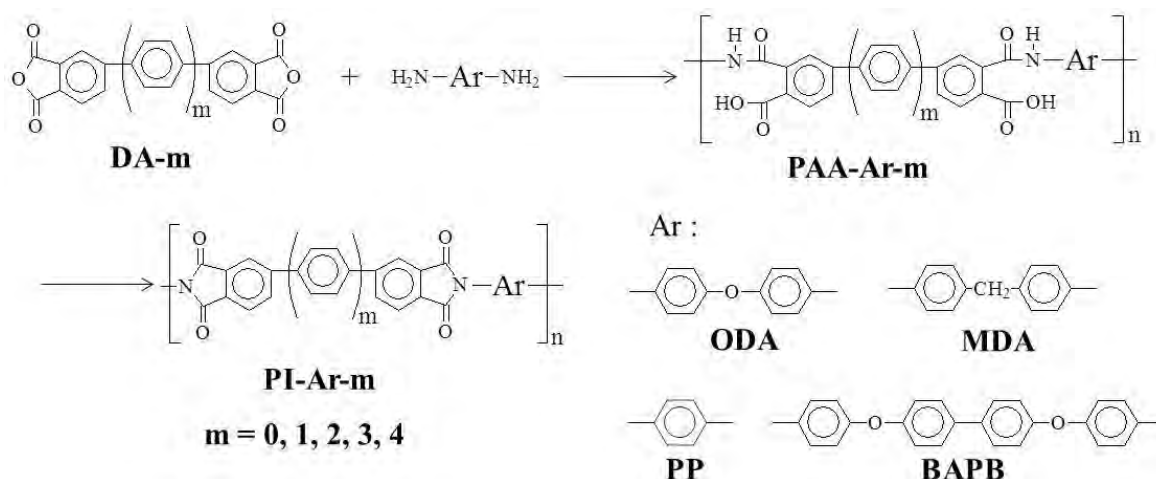
Aromatic polyimides were synthesized by the two-step procedure³⁻⁵ involving the ring-opening polymerization of diamines to tetracarboxylic dianhydride **DA-m** (m = 2, 3, and 4) and subsequent thermal cyclodehydration as shown in Scheme 1.

In the first step, ring-opening polymerizations were carried out in NMP at room temperature, leading to the formation of polyamic acids having inherent viscosities of 0.53-1.69 dLg⁻¹ in NMP. The polymerization of **PAA-Ar-2** was carried out with 1.5 mmol each monomer in 7.0 mL NMP at room temperature for 5 h, and the polymerization of **PAA-Ar-3** was carried out with 1.0 mmol each monomer in 10 mL NMP at room temperature for 5 h. The polymerization of **PAA-Ar-4** was carried out with 1.25 mmol each monomer in 30 mL NMP at 30 °C for 24 h. The reaction concentration was lower with increasing **m**. Polyamic acid **PAA-PP-4** from **DA-4** was precipitated during polymerization due to low solubility, as that inherent viscosity of **PAA-PP-4** could not be measured.

In the second step, thermal conversion of the polyamic acid was performed by heating precursor

polymer in the form of films successively at 100 °C for 1h, 200 °C for 1 h and finally 300 °C for 1 h under vacuum. These polyimides except **PI-PP-4** gave tough films. The thermal conversion **PAA-PP-4** was performed in the form of the powder.

The formation of polyimides was confirmed by the appearance of IR absorption bands at about 1780, 1720 (C=O) and 1360 cm⁻¹ (C-N) characteristic of imide groups. Elemental analysis values were in close agreement with the calculated values, also supporting the polyimide formation.



Scheme 1. Preparation of **PI-Ar-m** from **DA-m**.

The thermal behaviors of polyimides were evaluated by DSC and TG, and 10% weight loss temperatures (T_{10}) and transition temperatures (T_g) were shown in Table 1. None of the polyimides lost weight below 480 °C in air or nitrogen. T_{10} values of **PI-Ar-m** in air and nitrogen were in the range of 550-600 °C and 600-645 °C, respectively, and increased slightly with increasing **m**.

In the DSC measurement, **PI-Ar-2** showed T_g around 220-282 °C followed by exothermic crystallization around 275-470 °C above their T_g s. The polyimides except **PI-PP-2** exhibited broad endothermic peaks prior to their decomposition. **PI-Ar-3** except **PI-BAPB-3** showed T_g around 243-263 °C followed by exothermic crystallization around 326-371 °C above their T_g s. **PI-BAPB-3** showed T_g at 233 °C without exothermic peak. **PI-Ar-4** showed T_g around 232-281 °C followed by exothermic peak around 325-455 °C above their T_g s. The T_g values were dependent on the structure of the diamine moiety, and not dependent on **m**. It is reported that the rotational barrier of the connecting group in the diamine moiety play a determining role in the value of T_g [6]. The T_g values decreased in the order of **PI-PP-m** > **PI-MDA-m** > **PI-ODA-m** > **PI-BAPB-m**.

Table 1. Thermal properties of **PI-Ar-m** (**m** = 2, 3, 4).

Polyimide	T_g (°C) ^a	T_{exo} (°C) ^a	T_{end} (°C) ^a	T_{10} (°C) ^b	T_{10} (°C) ^c
PI-ODA-2	236	275-297	415-456	585	638
PI-MDA-2	252	300-322	420-462	570	600
PI-PP-2	282	345-470	- ^d	600	645
PI-BAPB-2	220	276-322	413-465	575	612
PI-ODA-3	243	326-341	- ^d	575	635
PI-MDA-3	260	326-363	- ^d	560	605
PI-PP-3	263	332-371	- ^d	565	637
PI-BAPB-3	233	- ^d	- ^d	550	610

PI-ODA-4	244	377-421	-	d	585	640
PI-MDA-4	244	330-385	-	d	580	637
PI-PP-4	281	385-450	-	d	595	645
PI-BAPB-4	232	325-455	-	d	580	635

^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 air.

^d None detected up to 470 °C.

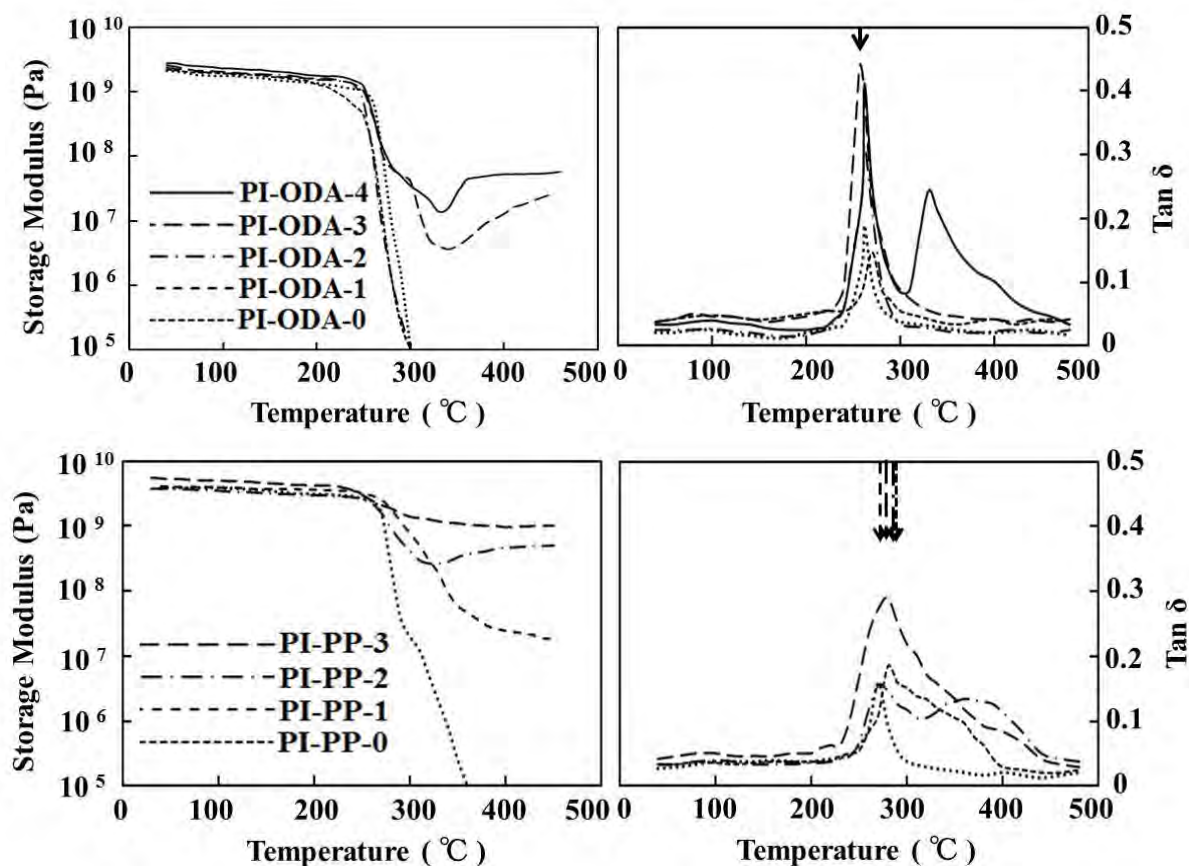


Figure 1. Dynamic mechanical behaviors of **PI-ODA-m** ($m = 0, 1, 2, 3, 4$) and **PI-PP-m** ($m = 0, 1, 2, 3$).

The DMA of the polyimides was performed, and the DMA of **PI-ODA-m** and **PI-PP-m** are shown in Figure 1. DMA of polyimides from **DA-0** and **DA-1** are also shown in Figure 1 for comparison. T_g were observed as $\tan \delta$ peak temperatures, which was shown with an arrow, the values of **PI-ODA-m** and **PI-PP-m** were 257-270 °C and 270-280 °C and were almost in agreement with the results from DSC. In the temperature dependence of storage modulus E' , a high modulus glassy region was followed by a decrease of modulus at the T_g . The decrease of modulus was smaller with increasing m . The previous **PI-PP-0** and **PI-PP-1** prepared by imidation at 400 °C were reported to have much higher T_g values [1]. All **PI-ODA-m** and **PI-PP-m** films were annealed at 400 °C for 30 min for comparison, and the DMA was performed (Figure 2). T_g values defined as $\tan \delta$ peak temperature, which was shown with an arrow, were 269-290 °C and 310-380°C in **PI-ODA-m** and **PI-PP-m**, respectively, and higher than those before annealing. The increment of **PI-PP-m** was

higher than that of **PI-ODA-m**, and the value of **PI-PP-0** was 110 °C higher as well. The decreases of modulus at the T_g was smaller than those before annealing.

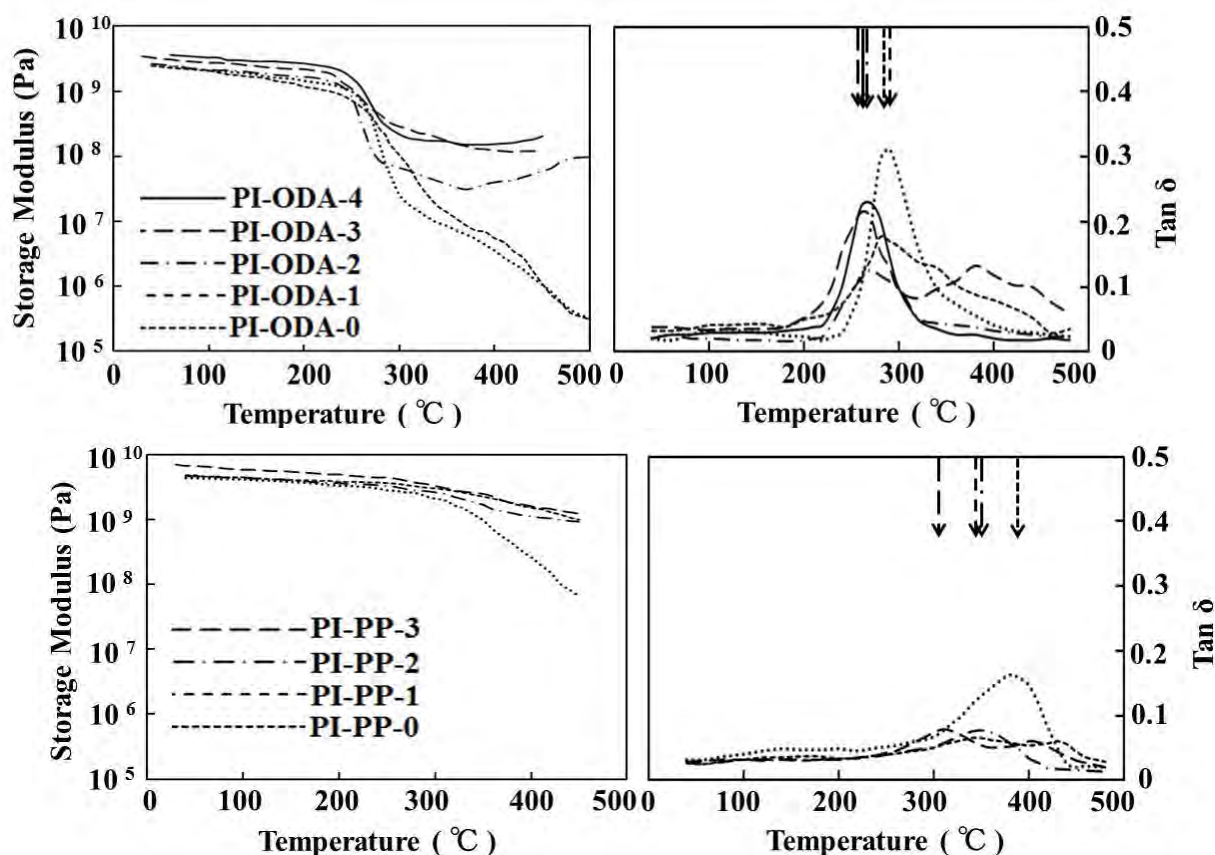


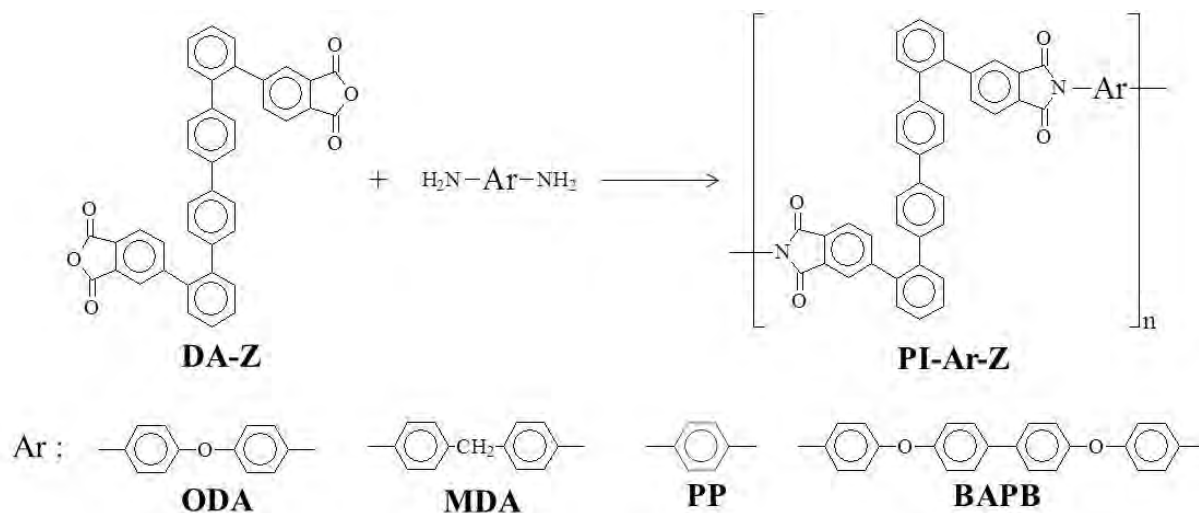
Figure 2. Dynamic mechanical behaviors of **PI-ODA-m** ($m = 0, 1, 2, 3, 4$) and **PI-PP-m** ($m = 0, 1, 2, 3$) annealed at 400 °C for 30 min .

3.2. Polyimides from a bent/ distorted **DA-Z**

Linkages along the polymer backbone, such as *p*- and *m*-linkages, are known to influence the polymer properties, and the effect of such linkages in the dianhydride moiety on polyimide properties have been examined in polyimides from BPDAs [7]. Polyimides were synthesized from a Z-type sexiphenyltetracarboxylic dianhydride, isomer of **DA-4**, and their properties were compared with those of polyimides from **DA-4** [5].

Aromatic polyimides were synthesized by the conventional two-step procedure [5]. The viscosities of polyamic acids were rather low (0.11-0.17 dLg⁻¹), and the polyimides could not be obtained as a film. The viscosities of the thermally converted polyimides were in the range 0.14-0.49 dLg⁻¹ in NMP, which is higher than those of the polyamic acids (Table 3). Polymerizations likely proceeded during imidation, and were also examined by a one-step procedure [5] as shown in Scheme 2. 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

0.84-1.21 dLg⁻¹ in NMP, and much higher than those of the polyimides prepared by the two-step procedure (Table 2). The formation of polyimides was confirmed by the appearance of IR absorption bands at about 1780, 1720 (C=O) and 1360 cm⁻¹ (C-N) characteristic of imide groups. Elemental analysis values were in close agreement with the calculated values, also supporting the polyimide formation.



Scheme 2. Preparation of **PI-Ar-Z** from **DA-Z**.

Table 3. Preparation of **PI-Ar-Z**.

Polyamic acid ^a	Yield (%)	η_{inh} (dlg ⁻¹) ^b	η_{inh} (dlg ⁻¹) ^c	Polyimide ^d	Yield (%)	η_{inh} (dlg ⁻¹) ^e
PAA-ODA-Z	94	0.17	0.32	PI-ODA-Z	96	1.15
PAA-MDA-Z	95	0.16	0.49	PI-MDA-Z	97	1.21
PAA-PP-Z	95	0.13	0.45	PI-PP-Z	96	0.84
PAA-BAPB-Z	97	0.16	0.28	PI-BAPB-Z	97	0.92

^a Polymerization was carried out with 1.00 mmol of each monomer 8 ml 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.

^d Polymerization was carried out with 1.00 mmol of each monomer 10 ml *m*-cresol at 190 °C.

^e Inherent viscosity of polyimide. Measured at 0.5 g dL⁻¹ in NMP at 30 °C.

The thermal behaviors of polyimides were evaluated by DSC, DMA and TG, and T_{10} and T_g were shown in Table 4. T_g values determined as tan δ peak temperature in DMA were also added in Table 4. None of the polyimides lost weight below 480 °C in air or nitrogen. T_{10} values of **PI-Ar-m** in air and nitrogen were in the range of 575-590 °C and 635-640 °C, respectively, and had thermal stabilities similar to the corresponding **PI-Ar-4**. **PI-Ar-Z** showed T_g without exothermic and endothermic peak in DSC thermograms, indicating amorphous morphology. **PI-Ar-Z** had a T_g in the range of 270 and 345 °C (Table 4), and the values were higher than those of **PI-Ar-4**. In particular, the T_g values of

PI-PP-Z was 65 °C higher than that of **PI-PP-4**. Rotation of aromatic rings around the C-C bond in **DA-Z** was more restricted than that in **DA-4**, and the bent / distorted Z type structure restricted the internal rotation at flexible connecting linkage.

Table 4. Thermal properties of **PI-Ar-Z**.

Polyimide	T_g (°C) ^a	T_g (°C) ^b	T_{10} (°C) ^c	T_{10} (°C) ^d
PI-ODA-Z	290	290	580	640
PI-MDA-Z	295	310	575	635
PI-PP-Z	345	390	590	640
PI-BAPB-Z	270	275	575	635

^a Determined by DSC in nitrogen at a heating rate of 10 °C min⁻¹.

^b Determined by dynamic mechanical analysis (tan δ peak temperature) at a heating rate of 5 min⁻¹.

^c Temperature at which 10% weight loss was recorded by 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 air.

The DMA of the polyimides was performed, and Figure 3 compares the DMAs for **PI-ODA-Z** and **PI-ODA-4**, and the DMAs for **PI-PP-Z** and **PI-PP-3**. Since **PI-PP-4** was not obtained as a film, DMA of **PI-PP-3** film was used instead. T_g values defined as tan δ peak temperatures (Table 4) were higher than those of the corresponding **PI-Ar-4**, which was in agreement with the results determined by DSC. In the temperature dependence of storage modulus E' , a high modulus glassy region was followed by a decrease of storage modulus at the T_g . The decrease temperatures of **PI-ODA-Z** and **PI-PP-Z** were higher than those of **PI-ODA-4** and **PI-PP-3**, respectively, and the decrease of **PI-ODA-Z** and **PI-PP-Z** at the T_g were larger.

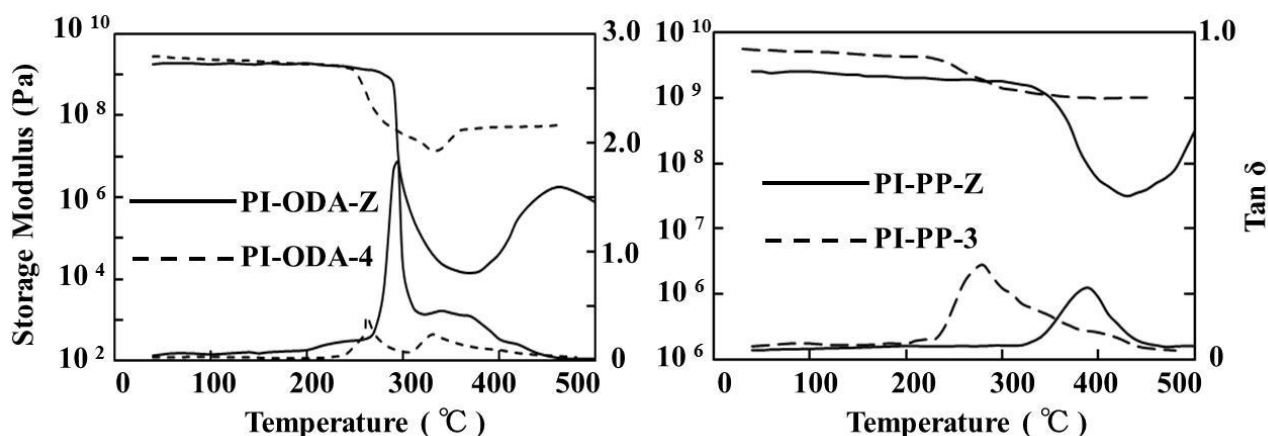


Figure 3. Comparison of dynamic mechanical behaviors between **PI-Ar-Z** and **PI-Ar-m**. (a) **PI-ODA-Z** and **PI-ODA-4** and (b) **PI-PP-Z** and **PI-PP-3**.

Table 5 compares the quantitative solubilities and densities for **PI-Ar-Z** and **PI-Ar-4**. **PI-Ar-Z** except **PI-MDA-Z**, and **PI-PP-Z** were soluble in polar solvents at room temperature, and **PI-MDA-Z** and **PI-PP-Z** were soluble in polar solvents upon heating, in contrast to **PI-Ar-4**, which were insoluble even upon heating. The Z-type structure had a significant influence on the solubility of polyimides from sexiphenyltetracarboxylic dianhydride. The higher solubility is presumably due to the free volume. The densities of **PI-Ar-Z** films were 1.27-1.31, lower than those (1.32-1.35) of the

PI-Ar-4 and free volume fraction suggested to be larger.

Table 5. Solubilities and densities of **PI-Ar-Z**.

Polyimide	NMP	DMAc	DMF	m-cresol	Pyridine	THF	Methanol
PI-ODA-Z	+++	+++	+++	+++	++	--	--
PI-MDA-Z	++	++	++	+++	-	--	--
PI-PP-Z	++	++	++	++	-	--	--
PI-BAPB-Z	+++	+++	+++	+++	+++	--	--

Abbreviations: NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide, DMF; N,N-dimethylformamide; THF, tetrahydrofuran.

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

The refractive indices (n) of polyimide film **PI-ODA-Z**, **PI-DPM-Z**, **PI-PP-Z** and **PI-BAPB-Z** were measured, and the dielectric constants (ϵ_{cal}) were estimated using an empirical relationship, $\epsilon_{\text{cal}} = 1.1 \times n^2$. The values of **PI-ODA-Z**, **PI-DPM-Z**, **PI-PP-Z** and **PI-BAPB-Z** were 2.74, 2.73, 2.78 and 2.73, respectively, lower than those of **PI-Ar-4**. The values of **PI-ODA-4**, **PI-DPM-4** and **PI-DAPB-4** were 2.90, 2.88 and 2.87, respectively. The free volume may also have an effect on the dielectric constant.

4. CONCLUSIONS

Rigid aromatic polyimides **PI-Ar-m** were synthesized from 3,3'',4,4''-*p*-quaterphenyltetracarboxylic dianhydride (**DA-2**) 3,3'',4,4''''-*p*-quinquephenyltetracarboxylic dianhydride (**DA-3**) and 3,3''''',4,4''''''-*p*-sexiphenyltetracarboxylic dianhydride (**DA-4**), the properties were compared with those of polyimides prepared from 3,3'',4,4''-*p*-terphenyltetracarboxylic dianhydride (**DA-1**) and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (**DA-0**), and the effect of phenylene groups on the polyimide property was examined. T_g values of the polyimides were not dependent on **m** of phenylene units, whereas there was a decrease in the modulus above T_g with increasing **m**. Polyimides containing bent / distorted sexiphenyl unit were synthesized from Z-type sexiphenyltetracarboxylic dianhydride by a one-step procedure. The T_g values were higher than those of **PI-Ar-4**, and the decrease in the storage modulus at the T_g was larger than that of **PI-Ar-4**. **PI-Ar-Z** were soluble, and showed lower dielectric constant (ϵ) than **PI-Ar-4**, and Z-type sexiphenylene structure affect the polyimide properties.

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