Synthesis and Properties of Polyimides from Aromatic Dianhydrides Having Various Number of Phenylene Units and Bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} Ether

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A new *para*-substituted aromatic ether diamine, bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether **1**, was synthesized in four steps starting from 4,4'-dibromodiphenyl ether. New aromatic polyimides, with 5 ether linkages per monomer unit, were prepared from this diamine and various tetracarboxylic dianhydrides, pyromellitic dianhydride (**PMDA**), 3,3',4,4'-biphenyltetracarboxylic dianhydride (**DA-0**), 3,3'',4,4''-*p*-terphenyltetracarboxylic dianhydride (**DA-1**), 3,3''',4,4'''-*p*-quarterphenyltetracarboxylic dianhydride (**DA-2**), 3,3''',4,4''''-*p*-quinquephenyltetracarboxylic dianhydride (**DA-3**), and 3,3''',4,4''''-*p*-sexiphenyltetracarboxylic dianhydride (**DA-4**), by a conventional two-step procedure that included ring-opening polymerization in *N*-methylpyrrolidone (NMP) and subsequent thermal cyclic dehydration. The polyimides were characterized by wide-angle X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetry (TG), and dynamic mechanical analysis (DMA). **PI-PMDA** from **PMDA** and **PI-m** (**m** = **0-4**) from **DA** (**m** = **0-4**) had glass transition temperatures (T_g) at 290 °C and 200-210 °C, respectively. The thermal properties, adhesion properties heated at 400 °C, dielectric constants (ϵ) and water absorption of the polyimides were compared and discussed on the basis of the number (**m**) of phenylene units in the dianhydrides.

Keywords: Bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether,
3,3'',4,4''-*p*-Terphenyltetracarboxylic dianhydride,
3,3''',4,4'''-*p*-Quarterphenyltetracarboxylic dianhydride,
3,3''',4,4''''-*p*-Quinquephenyltetracarboxylic dianhydride,
3,3''',4,4''''-*p*-Sexiphenyltetracarboxylic dianhydride

1. Introduction

We previously synthesized dianhydrides **DA-m** having various numbers (**m**) of phenylene units, **DA-2** [1], **DA-3** [2], and **DA-4** [3]. These were used to prepare aromatic polyimides containing *p*-quarterphenyl [1], *p*-quinquephenyl [2] and *p*-sexiphenyl units [3] with commercially available aromatic diamines, such as 4,4'-oxydianiline, 3,4'-oxydianiline, 4,4'-diaminodiphenyl methane, *m*-phenylenediamine, *p*-phenylenediamine, and 4,4'-bis(4-aminophenoxy) biphenyl, and diamines which authors had synthesized [4-8].

The properties were compared with those of polyimides from **DA-0** and **DA-1**, and discussed on the basis of the number (**m**) of phenylene units [9,10]. The T_g values depended on the connecting group and the structure of the diamine moiety, and were not dependent on **m**. The rotational barrier of the connecting group in the diamine moiety played a determining role in the value of T_g [11,12]. In the temperature dependence of storage modulus E' , a high modulus glassy region was followed by a decrease in modulus at the T_g , and rubbery plateau regions were observed above the T_g s in the polyimides from **DA-2**,

DA-3, and **DA-4**. The decrease in modulus was smaller with increasing **m**. Unique dynamic mechanical behaviors were observed in the polyimides from **DA-m** and 1,4-bis(4-amino-2-phenylphenoxy) benzene and 4,4'-bis(4-amino-2-phenylphenoxy) biphenyl having two ether linkages in the diamine. The only polyimides from **DA-3** showed two rubbery plateau regions above the T_g , and two tan peak temperatures [13]. In this study, polyimides **PI-m** were synthesized from **DA-m** and bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether with more ether linkages, and the properties were compared on the basis of the number (**m**) of phenylene units. **PI-m** with more **m** would yield behavior comparable to polyphenylene-*block*-polyethers.

2. Experimental

2.1. Materials

4-Methoxyphenol, 4,4'-dibromodiphenyl ether, 4-fluoronitrobenzene, **PMDA** and **DA-0** were obtained commercially, and **PMDA** and **DA-0** were purified by sublimation under reduced pressure. **DA-1** was supplied by Hitachi Kasei Kogyo Co., Japan, and purified by recrystallization from acetic anhydride. **DA-2** [1], **DA-2** [2], and **DA-2** [3] were prepared as previously reported. NMP was purified by vacuum distillation over calcium hydride.

2.2. Monomer synthesis

2.2.1. Bis [(4-methoxyphenoxy) phenyl] ether (**2**)

Potassium *tert*-butoxide (22.44 g, 0.2 mol) was added to a solution of 4-methoxyphenol (24.83 g, 0.2 mol) in NMP (200 mL) at 20 °C. After stirring at 20 °C for 0.5 h, the temperature was raised to 150 °C to remove *tert*-butanol formed during the reaction. After stirring for an additional 2 h, 4,4'-dibromodiphenyl ether (26.24 g, 0.08 mol) and copper iodide (1.5 g) were added, and the reaction mixture was stirred at 180 °C for 12 h. The reaction mixture was cooled to 80 °C, and the solvent was evaporated under a reduced pressure of 15-25 torr. The residue was washed with 400 mL of water and extracted twice with 200 mL of dichloromethane. The combined extracts were dried over anhydrous magnesium sulfite, and the solvent was evaporated. Pure **2** was obtained after recrystallization from toluene. Yield: 18.9 g (57%); mp 137-138 °C. The IR spectrum exhibited absorption bands at 2950 cm^{-1} , 2900 cm^{-1} (C-H), and 1240 cm^{-1} (Ar-O-C).

The ^1H NMR spectrum [δ in CDCl_3] showed signals at 3.80 (s, 6H), 6.87 (d, 4H, $J = 8.8$ Hz), 6.90-6.95 (m, 8H), and 6.97 (d, 4H, $J = 8.7$ Hz). The ^{13}C NMR spectrum [δ in CDCl_3] showed signals at 55.7, 114.9, 119.2, 119.8, 120.3, 150.9, 152.9, 153.9 and 155.8 ppm.

Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_5$: C, 75.35%; H, 5.35%. Found: C, 75.15%; H, 5.20%.

2.2.2. Bis[(4-hydroxyphenoxy) phenyl] ether (**3**)

2 (8.29 g, 0.02 mol) was heated with pyridine hydrochloride (80.0 g) at 260 °C for 30 min. After the reaction mixture became homogeneous, it was poured into water (1000 mL). The precipitated compound was collected by filtration and dried in vacuo. Pure **3** was obtained after recrystallization from toluene. Yield: 6.11 g (79%); mp 171-172 °C. The IR spectrum exhibited absorption bands at 3300-3600 cm^{-1} (-OH) and 1230 cm^{-1} (Ar-O-).

The ^1H NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 6.76 (d, 4H, $J = 8.8$ Hz), 6.85 (d, 4H, $J = 8.8$ Hz), 6.90 (d, 4H, $J = 8.8$ Hz), 6.96 (d, 4H, $J = 8.8$ Hz), and 9.10 (s, 2H). The ^{13}C NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 115.9, 118.4, 119.3, 119.9, 148.4, 151.8, 153.2 and 153.4 ppm.

Anal. Calcd for $\text{C}_{24}\text{H}_{18}\text{O}_5$: C, 74.60%; H, 4.70%. Found: C, 74.37%; H, 4.49%.

2.2.3. Bis{4-[4-(4-nitrophenoxy)phenoxy]-phenyl} ether (**4**)

In a flask, a mixture of **3** (5.80 g, 15 mmol), 4-fluoronitrobenzene (4.80 g, 34 mmol), potassium carbonate (4.70 g, 34 mmol), toluene (15 mL), and *N,N*-dimethylacetamide (30 mL) was stirred at 130 °C for 1 h. Next, 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 to 80 °C, and the solvent was evaporated under a reduced pressure of 15-25 torr. The residue was washed with 400 mL of water and extracted twice with 200 mL of dichloromethane. The combined extracts were dried over anhydrous magnesium sulfite, and the solvent was evaporated. Pure **4** was obtained after recrystallization from toluene. Yield: 7.54 g (80%); mp 145-146 °C. The IR spectrum exhibited absorption bands at 1520 cm^{-1} , 1340 cm^{-1} (-NO₂), and 1240 cm^{-1} (Ar-O-Ar).

The ^1H NMR spectrum [δ in CDCl_3] showed signals at 7.00 (d, 4H, $J = 8.8$ Hz), 7.00-7.50 (m,

16H), and 8.20 (d, 4H, $J = 8.8$ Hz). The ^{13}C NMR spectrum [δ in CDCl_3] showed signals at 116.5, 119.6, 119.9, 120.4, 121.8, 122.6, 125.8, 149.5, 152.2, 153.2, 155.0 and 163.5 ppm.

Anal. Calcd for $\text{C}_{36}\text{H}_{24}\text{N}_2\text{O}_9$: C, 68.79%; H, 3.85%; N, 4.46%. Found: C, 68.52%; H, 3.70%; N, 4.38%.

2.2.4. Bis{4-[4-(4-aminophenoxy)phenoxy]-phenyl} ether (**1**)

A mixture of **4** (6.29 g, 10 mmol) and 10% Pd/C (0.4 g) in *N,N*-dimethylformamide (70 mL) 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. The residue was recrystallized from toluene to give pure **1**. Yield: 4.21 g (74%); mp 175-176 °C. The IR spectrum exhibited absorption bands at 3390 cm^{-1} , 3230 cm^{-1} ($-\text{NH}_2$), and 1240 cm^{-1} (Ar-O-Ar).

The ^1H NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 4.80 (s, 4H), 6.58 (d, 4H, $J = 8.8$ Hz), 6.74 (d, 4H, $J = 8.8$ Hz), 6.89 (d, 4H, $J = 8.8$ Hz), 6.97 (d, 4H, $J = 8.8$ Hz), and 6.96-7.03 (m, 8H). The ^{13}C NMR spectrum [δ in $\text{DMSO}-d_6$] showed signals at 114.7, 117.9, 119.2, 119.49, 119.54, 120.0, 144.8, 146.1, 151.1, 152.1, 152.7 and 154.2 ppm.

Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_5$: C, 76.04%; H, 4.96%; N, 4.93%. Found: C, 76.16%; H, 4.80%; N, 4.75%.

2.2.5. PI-3

In a three-necked flask, **DA-3** (0.523 g, 1.0 mmol) was added to a solution of **1** (0.569 g, 1.0 mmol) in 10.0 mL of NMP in one portion. The mixture was stirred at room temperature for 12 h under nitrogen. Part of the resulting viscous solution was poured into 200 mL of methanol. The precipitated polymer was filtrated, washed with methanol and dried under vacuum. The NMP solution was cast onto a glass plate and the solvent was removed at 70 °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 bands at 1780 cm^{-1} , 1720 cm^{-1} (C=O), and 1360 cm^{-1} (C-N).

Anal. Calcd for $\text{C}_{70}\text{H}_{42}\text{N}_2\text{O}_9$: C, 79.69%; H, 4.01%; N, 2.66%. Found: C, 79.30%; H, 3.85%; N, 2.44%.

2.3. Measurements

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX400 FT-NMR spectrometer and IR spectra were recorded on a Shimadzu spectrophotometer IR 435. Reflection mode wide-angle X-ray diffraction (WAXD) measurements were performed in the range of $2\theta = 5$ -60° on a Rigaku RAD-B system with a radiation source of $\text{CuK}\alpha$. For differential scanning calorimetry (DSC) and thermogravimetry (TG), a Shimadzu DSC-60 and Rigaku thermal analysis station TG 8110 were used, respectively. Dynamic mechanical analysis (DMA) was performed with the Advanced Rheometric Expansion System at 1.0 Hz at a heating rate of 5 °C min^{-1} from room temperature to 500 °C. Dielectric constants of the polyimide films were measured by the hollow resonance method at 10 GHz.

The contents of water absorption (W_A %) for the polyimide films were determined from the equation $(W-W_0)/W_0 \times 100$, 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.

3. Results and discussion

3.1. Synthesis of Bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether

Diamine **1** was synthesized in four steps from 4,4'-dibromodiphenyl ether (Scheme 1). The reaction of 4,4'-dibromodiphenyl ether with potassium *p*-methoxyphenolate yielded bis [(4-methoxyphenoxy) phenyl] ether **2**, which was treated with pyrisine hydrochloride to give bis [(4-hydroxyphenoxy)phenyl] ether **3**. The reaction between **3** and 4-fluoronitrobenzene gave bis {4-[4-(4-nitrophenoxy)phenoxy]-phenyl} ether **4**. Bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether **1** was obtained by hydrogenation of **4** using Pd/C as a catalyst.

Chemical structures were confirmed by IR and NMR spectroscopies and elemental analysis. Diamine **1** showed characteristic IR absorptions at 3390 cm^{-1} and 3230 cm^{-1} for the amino group, and 1240 cm^{-1} for the ether group. The ^{13}C NMR spectrum of **1** had 12 peaks due to symmetry, 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.

Scheme 1. Synthesis of bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether **1**.

3.2. Polymer synthesis

Aromatic polyimides **PI-m** were synthesized by the usual two-step procedure involving the ring-opening polymerization of diamine **1** to tetracarboxylic dianhydride [**PMDA**, **DA-m** (**m** = **0-4**)] and subsequent thermal cyclodehydration as shown in Scheme 2.

In the first step, ring-opening polymerization were carried out in NMP at room temperature, leading to the formation of polyamic acids, **PAA-m**, having inherent viscosities of 0.79-1.60 dLg⁻¹ in NMP (Table 1). In the second step, the thermal conversion of polyamic acids was performed by heating the precursor polymers in the form of films 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.

Scheme 2. Synthesis of polyimides **PI-PMDA** and **PI-m** (**m** = **0-4**).

The formation of the 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. Elemental analysis values were in close agreement with the calculated values, also supporting polyimide formation.

3.3. Polymer properties

The crystal structures of the polyimides were evaluated by WAXD. The WAXD patterns of

Table 1. Synthesis of **PAA-PMDA** and **PAA-m** (**m** = **0-4**).

Dianhydride	Polyamic acid	Yield / %	η_{inh}^c / dLg ⁻¹
PMDA	PAA-PMDA ^a	97	1.35
DA-0	PAA-0 ^a	98	1.42
DA-1	PAA-1 ^a	97	0.79
DA-2	PAA-2 ^a	96	0.97
DA-3	PAA-3 ^b	97	0.92
DA-4	PAA-4 ^b	98	1.60

^a Polymerization was carried out with 2.0 mmol of each monomer in 10 mL NMP at room temperature for 12 h under nitrogen.

^b Polymerization was carried out with 1.0 mmol of each monomer in 10 mL NMP at room temperature for 12 h under nitrogen.

^c Measured at 0.5 g dL⁻¹ in NMP at 30 °C.

PI-PMDA and **PI-m** (**m** = **0-4**) are shown in Fig. 1. **PI-2**, **PI-3** and **PI-4** showed intensive diffraction peaks at 2θ = 15-30°, which were assigned to crystalline polymers. The peak intensities decreased with decreasing **m**, and **PI-0** were semicrystalline polymers. Diffraction peaks for **PI-PMDA** were not observed.

Fig. 1. X-ray diffraction patterns of **PI-PMDA** and **PI-m** (**m** = **0-4**).

The thermal behaviors of the polyimides were evaluated by DSC and TG, and transition temperatures and 10% weight loss temperatures (T_{10}) are shown in Table 2. No polyimides had weight loss below 470 °C in air and nitrogen. T_{10} values in air and nitrogen were in the range of 520-545 °C and 575-595 °C, respectively, and were slightly higher with increasing **m**.

In DSC measurement (Fig. 2), **PI-PMDA** exhibited only one T_g at 280 °C, and was amorphous. **PI-0** and **PI-1** showed T_g at around 160 °C followed by exothermic crystallization peak at 220-310 °C and endothermic peak at 320-380 °C. **PI-2**, **PI-3** and **PI-4** showed T_g s at 170-180 °C followed by endothermic peaks at 370-450 °C prior to thermal decomposition, though exothermic peaks were not observed. The

Table 2. Thermal properties of **PI-PMDA** and **PI-m (m = 0-4)**.

Polyimide	$T_g / ^\circ\text{C}^a$	$T_c / ^\circ\text{C}^a$	$T_m / ^\circ\text{C}^a$	$T_{10} / ^\circ\text{C}^b$	$T_{10} / ^\circ\text{C}^c$	$T_g / ^\circ\text{C}^d$	$T_g / ^\circ\text{C}^e$
PI-PMDA	280	-- ^f	-- ^f	520	580	290	290
PI-0	160	225-270	323-362	523	575	203	200
PI-1	164	228-308	336-376	527	583	209	200
PI-2	168	-- ^f	376-420	534	590	210	220
PI-3	176	-- ^f	400-436	543	593	210	210
PI-4	180	-- ^f	404-450	545	595	210	230

^a Determined by DSC in nitrogen at heating rate of $10\text{ }^\circ\text{C min}^{-1}$. ^b Temperature at which 10% weight loss was recorded by TG at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in air. ^c Temperature at which 10% weight loss was recorded by TG at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in nitrogen. ^d Glass transition temperature of polyimide film determined as $\tan \delta$ peak temperature by DMA. ^e Glass transition temperature of annealed polyimide film determined as $\tan \delta$ peak temperature by DMA. ^f Not detected by DSC.

results of the DSC measurements agreed with the WAXD results. The T_g values were slightly higher with increasing **m** except for **PI-PMDA**. The value of **PI-PMDA** was the highest due to intramolecular charge transfer [14].

Fig. 2. DSC curves of **PI-PMDA** and **PI-m (m = 0-4)**.

Dynamic mechanical behaviors for these polyimides were also compared (Fig. 3). T_g s were observed as $\tan \delta$ peak temperatures. The T_g values of **PI-PMDA**, **PI-0**, **PI-1**, **PI-2**, **PI-3**, and **PI-4** were $290\text{ }^\circ\text{C}$, $203\text{ }^\circ\text{C}$, $209\text{ }^\circ\text{C}$, $210\text{ }^\circ\text{C}$, $210\text{ }^\circ\text{C}$, and $210\text{ }^\circ\text{C}$, respectively. The T_g values determined by mechanical DMA were higher than those determined by DSC. The temperature-dependent storage modulus, E' , for the polyimides is described as follows. A high-modulus glassy region was followed by a decrease in the modulus at T_g . The E' of amorphous **PI-PMDA** decreased rapidly at around $300\text{ }^\circ\text{C}$ to a very low level (below 10^4 Pa). The E' of **PI-m** showed an additional decrease. The E' of all **PI-m** decreased at around $200\text{ }^\circ\text{C}$ to the 10^7 Pa level, after which a rubbery plateau region was seen, followed by a further decrease at around $320\text{--}350\text{ }^\circ\text{C}$. The E' of **PI-0** and **PI-1** decreased to a very low level (below 10^4 Pa), and those of **PI-2**, **PI-3**, and **PI-4** decreased to $5.1 \times 10^4\text{ Pa}$, $1.8 \times 10^5\text{ Pa}$ and $1.0 \times 10^6\text{ Pa}$ at $400\text{ }^\circ\text{C}$, respectively. The rubbery plateau region of **PI-2**,

PI-3, and **PI-4** were longer than those of **PI-0** and **PI-1**.

Fig. 3. Dynamic mechanical behaviors of **PI-PMDA** and **PI-m (m = 0-4)**.

On the basis of the above results, the adhesion properties of the polyimides were studied. The adhesion test was evaluated by the shear adhesive strength of copper plates through the polyimide films heated at $400\text{ }^\circ\text{C}$. The polyimides film was placed between copper plates and heated at $400\text{ }^\circ\text{C}$ for 10 minutes, then cooled to room temperature. Since the plates were adhered through the polyimide, the shear adhesive strength was measured according to JIST 6850 [15,16] and the results are shown in Table 3. **PI-PMDA** and **PI-m (m = 0-1)** exhibited shear adhesive strengths of more than 50 MPa , and those of **PI-2**, **PI-3**, and **PI-4** were lower with increasing **m**, reflecting the E' at $400\text{ }^\circ\text{C}$. No adhesion properties were in the previous polyimides from other diamines [1-3], suggesting that **PI-PMDA** and **PI-m (m = 0-4)** showed such adhesion properties due to their five rotational ether linkages in the diamine unit. In the DSC measurement, **PI-0** and **PI-1** showed exothermic peaks at $225\text{--}270\text{ }^\circ\text{C}$ and $228\text{--}308\text{ }^\circ\text{C}$, respectively, and ordered structures such as crystals were thought to be formed above T_g . **PI-0** and **PI-1** films were annealed at $320\text{ }^\circ\text{C}$ for 30 min. Though **PI-PMDA** and **PI-m (m = 2-4)** films did not show exothermic peaks, their films were annealed at $350\text{ }^\circ\text{C}$, respectively, for 30 min.

DMA behaviors of the annealed polyimides films are shown in Fig. 4. The T_g values as $\tan \delta$ peak temperatures were almost the same as those before annealing (Table 2). The decrease in the storage modulus above the T_g was smaller than that before annealing, and the storage modulus values became higher to the level of 10^8 - 10^9 from 10^6 - 10^7 . **PI-2** maintained a high storage modulus up to 320 °C, showed high shear adhesive strength, and was suggested to be a high-resistant adhesive polyimide.

Table 3. Shear adhesive strength (MPa) of polyimides.

PI-PMDA	PI-0	PI-1	PI-2	PI-3	PI-4
62	54	52	44	13	5

Fig. 4. Dynamic mechanical behaviors of annealed **PI-PMDA** and **PI-m** ($m = 0-4$).

Table 4. The water absorption (W_A) and dielectric constants (ϵ) for **PI-PMDA** and **PI-m** ($m = 0-4$).

	PI-PMDA	PI-0	PI-1	PI-2	PI-3	PI-4
W_A	1.21	1.05	0.90	0.78	0.62	0.40
ϵ	3.00	3.00	2.94	2.89	2.83	2.80

Table 4 shows the water absorption (W_A) and dielectric constants (ϵ) for the polyimides. W_A and ϵ were 0.40-1.21% and 2.80-3.00, respectively. These values were lower than those of 4,4'-oxydianiline-based polyimides [17] due to the lower imide content per repeating unit [7,18], and decreased with increasing m .

4. Conclusion

Polyimides were synthesized from bis {4-[4-(4-aminophenoxy)phenoxy]phenyl} ether and aromatic dianhydride having various numbers (m) of phenylene units and their properties were compared on the basis of the number (m) of phenylene units in the dianhydrides. The T_g values of **PI-PMDA** and **PI-m** ($m = 0-4$) were 290 °C and 203-210 °C as

the $\tan \delta$ peak temperatures, respectively. The E' of **PI-PMDA** decreased rapidly at around 270-310 °C to a very low level (below 10^4 Pa). The E' of all **PI-m** ($m = 0-4$) decreased at around 200 °C to the 10^7 Pa level, after which a rubbery plateau region was seen, followed by a further decrease at around 300 °C. The E' values at 400 °C were higher with increasing m , and **PI-PMDA** and **PI-m** ($m = 0-1$) exhibiting high shear adhesive strengths. The strengths of **PI-2**, **PI-3** and **PI-4** were lower with increasing m . The water absorption and the dielectric constants were also lower with increasing m .

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