Synthesis and Properties of Polyimides from Bis[4-(Aminophenoxy)phenyl] Ether and Aromatic Dianhydrides Having Various Numbers of Phenylene Units

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Aromatic polyimides **PI-3e-PMDA** and **PI-3e-m** (**m** = 0–4) with 3 ether linkages per monomer unit were prepared from bis[4-(4-aminophenoxy)phenyl] ether (**1**) and various tetracarboxylic dianhydrides, pyromellitic dianhydride (**PMDA**), 3,3',4,4'-biphenylteracarboxylic dianhydride (**DA-0**), 3,3'',4,4''-*p*-terphenylteracarboxylic dianhydride (**DA-1**), 3,3''',4,4'''-*p*-quarterphenylteracarboxylic dianhydride (**DA-2**), 3,3''''4,4''''-*p*-quinquephenylteracarboxylic dianhydride (**DA-3**), and 3,3'''''4,4'''''-*p*-sexiphenylteracarboxylic dianhydride (**DA-4**), by a conventional two-step procedure that included ring-opening polymerization in 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), and compared on the basis of the number (**m**) of phenylene units. **PI-3e-PMDA** and **PI-3e-m** (**m** = 0–4) had glass transition temperatures (T_g) at 280 °C and 210–230 °C, respectively, and T_g values were not dependent on **m**. The storage modulus (E') of **PI-3e-m** decreased at about 200 °C, after which a rubbery plateau region was seen, followed by a further decrease at about 330 °C. The DMA results for the annealed **PI-3e-PMDA** and **PI-3e-m** (**m** = 0–4) were also compared and discussed on the basis of **m**.

Keywords: Bis[4-(4-Aminophenoxy)phenyl] ether, 3,3'',4,4''-*p*-Terphenylteracarboxylic dianhydride, 3,3''',4,4'''-*p*-Quarterphenylteracarboxylic dianhydride, 3,3''''4,4''''-*p*-Quinquephenylteracarboxylic dianhydride, 3,3'''''4,4'''''-*p*-Sexiphenylteracarboxylic 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 [3] with various aromatic diamines [4–13]. 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 [14–16]. The T_g values were not dependent on **m**, but depended on the structure of the diamine as reported in the literature [17]. The rotational barrier of the connecting group in the diamine moiety was reported to play a determining role in the value of

T_g . In the temperature dependence of the 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 in the polyimides from **DA-2**, **DA-3** and **DA-4**. The decrease in modulus was smaller with increasing **m**. In polyimides from diamines with more ether linkage, unique DMA behavior was observed. The polyimides **PI-5e-m** (**m** = 0–4) from bis{4-[4-(4-aminophenoxy)phenoxy]phenyl} ether with 5 ether linkages showed a two-step decrease in the storage modulus at T_g and the melting region, and exhibited adhesion when heated at the melting region [13]. The polyimides from **DA-3** and 1,4-bis(4-amino-2-phenylphenoxy)

benzene and 4,4'-bis(4-amino-2-phenylphenoxy) biphenyl having two ether linkages showed two rubbery plateau regions above the T_g , and two $\tan \delta$ peak temperatures [9].

In this study, polyimides **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$) were synthesized from **PMDA** and **DA-m** ($m = 0-4$) and bis [4-(4-aminophenoxy)phenyl] ether (**1**) with 3 ether linkages, and the properties were compared on the basis of the number of phenylene units (m). The temperature dependence of the storage modulus for **PI-3e-m** ($m = 2-4$) annealed at 320 °C exhibited unique behavior.

2. Experimental

2.1. Materials

Bis[4-(4-aminophenoxy)phenyl] ether (**1**) was prepared as previously reported [18]. **PMDA** and **DA-0** were obtained commercially, and purified by sublimation under reduced pressure. **DA-1** was supplied by Hitach Kasei Kogyo Co., Japan, and purified by recrystallization from acetic anhydride. **DA-2** [1], **DA-3** [2], and **DA-4** [3] were prepared as previously reported. NMP was purified by vacuum distillation over calcium hydride.

2.2. Polymer synthesis

2.2.1. PI-3e-PMDA

In a three-necked flask, **PMDA** (0.436 g, 2.0 mmol) was added in one portion to a solution of **1** (0.769 g 2.0 mmol) in 10 mL of NMP. 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 filtered, 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} and 1720 cm^{-1} (C=O) and 1360 cm^{-1} (C-N).

Anal. Calcd for $\text{C}_{34}\text{H}_{18}\text{N}_2\text{O}_7$: C, 72.08%; H, 3.20%; N, 4.94%. Found: C, 71.80%; H, 2.98%; N, 4.65%.

2.2.2. PI-3e-2

In a three-necked flask, **DA-2** (0.670 g, 1.5 mmol) was added in one portion to a solution of **1** (0.577 g 1.5 mmol) in 10 mL of NMP. 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 filtered, 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} and 1720 cm^{-1} (C=O) and 1360 cm^{-1} (C-N).

Anal. Calcd for $\text{C}_{52}\text{H}_{30}\text{N}_2\text{O}_7$: C, 78.58%; H, 3.80%; N, 3.52%. Found: C, 78.20%; H, 3.35%; N, 3.43%.

2.3. Measurements

IR spectra were recorded on a Shimadzu spectrometer IR 435. Reflection mode wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature in the range of $2\theta = 5-60^\circ$ with a sampling step of 0.1° and a scan rate $10^\circ \text{ min}^{-1}$ 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. Dynamical mechanical analysis (DMA) at 1.0 Hz and thermomechanical analysis were performed with the Advanced Rheometric Expansion System at $5^\circ \text{C min}^{-1}$.

3. Results and discussion

3.1. Polymer synthesis

Aromatic polyimides were synthesized by the 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 1.

In the first step, ring-opening polymerizations were carried out in NMP at room temperature, leading to the formation polyamic acids [**PAA-3e-PMDA**, **PAA-3e-m** ($m = 0-4$)] having inherent viscosities of 0.87-1.31 dLg^{-1} in NMP (Table 1). In the second step, the thermal conversion of the polyamic acids was performed by heating the precursor polymers in the form of films successively at 100 for 1 h, 200 for 1 h, and finally 300 for 1 h under vacuum. These polyimides produced tough films.

The formation of the polyimides was confirmed by the appearance of IR absorption bands at about

Scheme 1. Synthesis of polyimides **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$).

Table 1. Synthesis of **PAA-3e-PMDA** and **PAA-3e-m** ($m = 0-4$).

Dianhydride	Polyamic acid	Yield / %	η_{inh} / dLg ⁻¹ ^c
PMDA	PAA-3e-PMDA ^a	95	1.20
$m = 0$	PAA-3e-0 ^a	96	1.31
$m = 1$	PAA-3e-1 ^a	96	0.96
$m = 2$	PAA-3e-2 ^b	94	0.87
$m = 3$	PAA-3e-3 ^b	96	1.08
$m = 4$	PAA-3e-4 ^b	96	1.22

^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 1.5 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.

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.

3.2. Polymer properties

The thermal properties of the polyimides were evaluated by DSC and TG, and transition temperatures and 10% weight loss temperature (T_{10}) are shown in Table 2. No polyimides exhibited a weight loss below 470 °C in air or nitrogen. T_{10} values in air and nitrogen were in the range of 535–568 °C and 585–600 °C, respectively, and were slightly higher with increasing m . In DSC measurements (Fig. 1), **PI-3e-PMDA** showed T_g at 280 °C, while **PI-3e-m** ($m = 0-4$) did not show T_g clearly. **PI-3e-0** and **PI-3e-1** showed exothermic crystallization peaks at around 270 °C followed by endothermic peaks at around 370 °C. **PI-3e-2** and **PI-3e-3** clearly showed endothermic peaks at around 410 °C due to their higher crystallinity. In the WAXD patterns for these polyimides, **PI-3e-0**, **PI-3e-1**, **PI-3e-3**, **PI-3e-4** showed slightly intense diffraction peaks at around $2\theta = 20^\circ$, which were assigned to crystalline polymers (Fig. 2 (a)). **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$) were insoluble in organic solvents even upon heating similar to **PI-5e-PMDA** and **PI-5e-m** ($m = 0-4$) [13].

The dynamic mechanical properties of these polyimides were also compared. The T_g values were observed as the $\tan \delta$ peak temperature (Fig. 3).

Fig. 1. DSC curves for **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$).

Table 2. Thermal properties of **PI-3e-PMDA** and **PI-3e-m (m = 0-4)**.

Polyimide	$T_g / ^\circ\text{C}^a$	$T_g / ^\circ\text{C}^b$	$T_m / ^\circ\text{C}^b$	$T_{10} / ^\circ\text{C}^c$	$T_{10} / ^\circ\text{C}^d$	$T_g / ^\circ\text{C}^e$
PI-3e-PMDA	280	-- ^f	-- ^f	535	585	285
PI-3e-0	230	250-280	320-380	545	590	230
PI-3e-1	230	250-290	340-385	550	590	230
PI-3e-2	210	-- ^f	370-400 400-430	560	595	340
PI-3e-3	220	-- ^f	390-440	568	600	230
PI-3e-4	210	-- ^f	370-430	560	600	240

^a Tan δ peak temperature was recorded by DMA at a heating rate $5 ^\circ\text{C min}^{-1}$.^b Determined by DSC in nitrogen at a heating rate of $10 ^\circ\text{C min}^{-1}$.^c Temperature at which 10% weight loss was recorded by TG at a heating rate of $10 ^\circ\text{C min}^{-1}$ in air.^d Temperature at which 10% weight loss was recorded by TG at a heating rate of $10 ^\circ\text{C min}^{-1}$ in nitrogen.^e Tan δ peak temperature of annealed polyimide film was recorded by DMA at a heating rate of $5 ^\circ\text{C min}^{-1}$.^f Not detected by DSC. Fig. 2. X-ray diffraction patterns for **PI-3e-PMDA** and **PI-3e-m (m = 0-4)** before annealing (a) and after annealing (b).

The T_g values for **PI-3e-PMDA** and **PI-3e-0**, **PI-3e-1**, **PI-3e-2**, **PI-3e-3** and **PI-3e-4** were $280 ^\circ\text{C}$, $230 ^\circ\text{C}$, $230 ^\circ\text{C}$, $210 ^\circ\text{C}$, $220 ^\circ\text{C}$, and $210 ^\circ\text{C}$, respectively (Table 1), which were slightly higher than those for **PI-5e-PMDA** and **PI-5e-m (m = 0-4)** [13], and the T_g values were not dependent on m . The value for **PI-3e-PMDA** was the highest due to intermolecular charge transfer [19], similar to the case for previously reported polyimides from dianhydrides having various numbers of phenylene units [1-16].

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' value for amorphous **PI-3e-PMDA** decreased at around $350 ^\circ\text{C}$ to about 10^7 Pa, and the E' value at $400 ^\circ\text{C}$ was higher than that for **PI-5e-PMDA** due to fewer ether linkages [13]. The E' value for **PI-3e-m (m = 0-4)**

decreased at a T_g of $200 ^\circ\text{C}$, after which a rubbery plateau region was seen, followed by an additional decrease at about $330 ^\circ\text{C}$. The E' value for **PI-3e-m (m = 0-4)** was about 10^4 Pa at $400 ^\circ\text{C}$, which was lower than that for **PI-5e-m (m = 0-4)** despite having fewer ether linkages. However, **PI-3e-m (m = 0-4)** did not show adhesion properties when heated at $400 ^\circ\text{C}$ as did **PI-5e-PMDA** and **PI-5e-m (m = 0-4)** [13]. The decrease in E' was thought to be due to melting and was accompanied by an endothermic process in the DSC measurements.

In the DSC measurement, **PI-3e-0** and **PI-3e-1** showed exothermic peaks at 250 – $280 ^\circ\text{C}$ and 250 – $290 ^\circ\text{C}$, respectively, and ordered structures such as crystals were thought to be formed above T_g . **PI-3e-0** and **PI-3e-1** films were annealed at $300 ^\circ\text{C}$ for 30 min. **PI-3e-m (m = 2-4)** did not show any clear exothermic peaks in DSC measurements, but were annealed at $320 ^\circ\text{C}$, a temperature at which E' did

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

not show additional decreases, for 30 min. **PI-3e-PMDA** was also annealed at 320 °C. The DMA properties of the annealed polyimide films are shown in Fig. 4. **PI-3e-m** ($m = 0-4$) showed higher E' values in the rubbery plateau region above T_g than those before annealing. The E' value for **PI-3e-2** was higher than those for **PI-3e-3** and **PI-3e-4**, in contrast to the previously reported polyimides [1-16] from dianhydrides having various numbers of phenylene units, for which the E' value was higher with increasing phenylene units (m). **PI-3e-m** ($m = 2-4$) did not show an additional decrease in E' at about 330 °C, which was observed before annealing. The T_g values (the $\tan \delta$ peak temperatures) for **PI-3e-m** ($m = 2-4$) were higher than those before annealing. In particular, that for **PI-3e-2** was 340 °C, 130 °C higher, and higher than those of **PI-3e-m** ($m = 3,4$). The increment of E' value in the plateau region for **PI-3e-m** ($m = 0-4$) and the higher T_g values for **PI-3e-m** ($m = 2-4$) were thought to be due to the development of ordered structures. The WAXD patterns for the annealed **PI-3e-m** ($m = 0-4$) were sharper, and the peak intensity for the annealed **PI-3e-2** greatly increased (Fig. 2-(b)). The disappearance of the decrease in E' observed for the annealed **PI-3e-m** ($m = 2-4$) was regarded as a shift of the melting region to above 450 °C. Such a shift due to the development of a crystalline structure was observed for poly[(3,3'-dioxiphenyl)diphenylene pyromellitimide] [20].

Figure 5 shows the thermochemical analysis results for annealed **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$). The elongations due to the glass transition for **PI-3e-m** ($m = 2-4$) were much smaller than those for **PI-3e-m** ($m = 0-1$), and **PI-3e-2** barely elongated. Remarkable elongations at about 330 °C for **PI-3e-m** ($m = 2-4$) were not observed,

Fig. 4. Dynamic mechanical properties of annealed **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$).

which reflected the DMA results. The elongations for **PI-3e-m** ($m = 2-4$) in the temperature range 50-450 °C were about 0.7%, and as short as those for the polyimides [16] from **DA-m** ($m = 1-3$) and *p*-phenylenediamine, even though **PI-3e-m** ($m = 2-4$) had three flexible ether linkages in the repeating unit.

Fig. 5. Thermomechanical analysis of annealed **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$).

4. Conclusion

Polyimides **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$) were synthesized from bis [4-(4-aminophenoxy)phenyl] ether and aromatic dianhydrides 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 (the $\tan \delta$ peak temperatures) for **PI-3e-PMDA** and **PI-3e-m** ($m = 0-4$) were 280 °C and 210-230 °C, respectively. The storage modulus (E') for **PI-3e-m** ($m = 0-4$) decreased at about 200 °C, after which a rubbery plateau region was seen, followed by a further decrease at about 330 °C. After the polyimides were annealed, the E' values for the plateau region

were higher, **PI-3e-m** (**m** = **2-4**) did not show any further decrease in E' at about 330 °C, and the T_g values of **PI-3e-m** (**m** = **2-4**) were higher, with **PI-3e-2** being 340 °C (130 °C higher).

References

1. A. Morikawa, *Polym. J.*, **32** (2000) 275.
2. A. Morikawa and Y. Hosoya, *Polym. J.*, **34** (2002) 544.
3. A. Morikawa and K. Ono, *Polym. J.*, **32** (2000) 948.
4. A. Morikawa, T. Furukawa, and Y. Moriyama, *Polym. J.*, **37** (2005) 759.
5. A. Morikawa, T. Furukawa, and Y. Moriyama, *High Perform. Polym.*, **18** (2006) 593.
6. T. Okabe and A. Morikawa, *High Perform. Polym.*, **20** (2008) 53.
7. A. Satoh and A. Morikawa, *High Perform. Polym.*, **22** (2010) 412.
8. T. Okabe and A. Morikawa, *High Perform. Polym.*, **22** (2010) 799.
9. A. Morikawa, F. Miyata, and J. Nishimura, *High Perform. Polym.*, **24** (2012) 783.
10. A. Morikawa, S. Nabeshima, A. Satoh, and Y. Moriyama, *J. Photopolym. Sci. Technol.*, **26** (2013) 367.
11. S. Nabeshima and A. Morikawa, *High Perform. Polym.*, **27** (2015) 772.
12. A. Morikawa, C. Karube, and Y. Sakaki, *High Perform. Polym.*, **28** (2016) 1201.
13. A. Umezawa and A. Morikawa, *J. Photopolym. Sci. Technol.*, **32** (2019) 489.
14. A. Morikawa and K. Ono, *High. Perform. Polym.*, **13** (2001) S73.
15. A. Morikawa, "High Performance Polymers and Engineered Plastics", V. Mittal, Ed., Wiley, Salem, **7** (2011) 205.
16. Y. Hosoya and A. Morikawa, *J. Photopolym. Sci. Technol.*, **32** (2019) 495.
17. J. de Abajo and J. G. de la Campa, "Processable Aromatic Polyimides", in "Advances in Polymer Science", **140** (1999) 23, Springer-Verlag Berlin Heidelberg.
18. T. J. Dingemans, E. Mendes, J. J. Hinkley, E. S. Weiser, and T. L. StClair, *Macromolecules*, **41** (2008) 2474.
19. S. Ando, T. Matsuura, and S. Sakaki, *Polym. J.*, **29** (1997) 69.
20. S. P. Ma, S. Yuasa, M. Tsuji, K. Sakurai, and T. Takahashi, *Kobunshi Ronbunshu*, **51** (1994) 329 (in Japanese).