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Article

## Fabrication of Poly(*p*-phenylenebenzobisoxazole) Film Using a Soluble Poly(*o*-alkoxyphenylamide) as the Precursor

Takahiro Fukumaru,<sup>†</sup> Yusuke Saegusa,<sup>†</sup> Tsuyohiko Fujigaya,<sup>\*,†,‡</sup> and Naotoshi Nakashima<sup>\*,†,‡,§</sup>

<sup>†</sup>Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka Nishi-ku, Fukuoka 819-0395, Japan

<sup>‡</sup>International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka Nishi-ku, Fukuoka 819-0395, Japan

<sup>§</sup>JST-CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

**Supporting Information** 



ABSTRACT: Poly(*p*-phenylenebenzobisoxazole) (PPBO) is a polymer having the most excellent thermal properties among the organic polymers reported to date, and the design and the preparation of PPBO with the desired shape and form are expected to provide novel PPBO-based devices and materials in the fields of automobiles, aerospace, microelectronics, etc. We here describe the fabrication and characterization of PPBO films via the solution-casting and successive thermal conversion of its precursor, alkyl-substituted hydroxypolyamides (poly(*o*-alkoxyphenylamide)s) that were synthesized by a low-temperature polycondensation reaction of dialkoxydiaminobenzene with terephthaloyl chloride in *N*-methylpyrrolidone. The formation mechanism of the thermal conversion was carefully investigated based on the analyses of the results using TGA, IR, pyrolysis gas chromatography mass spectrometry (Py-GC/MS), and evolved gas analysis GC/MS (EGA-GC/MS) measurements. A transparent PPBO precursor film provided a PPBO film after thermal treatment at 250 °C for 6 h and then at 300 °C for 6 h under vacuum. The obtained PPBO film showed excellent mechanical properties (tensile strength = 76 MPa, Young's modulus = 2.7 GPa) as well as a high thermal stability (temperature of 5 wt % loss = 670 °C). Such outstanding mechanical and thermal properties would significantly contribute to fulfill the requirements for next generation extreme materials/devices.

#### **1. INTRODUCTION**

Aromatic polymers with excellent mechanical and thermal properties<sup>1</sup> have been manufactured and widely utilized in the aerospace, protective clothing, electrical insulation, industrial filters, etc.<sup>2</sup> Further improvement in the properties of such polymers has been strongly requested, and indeed, significant efforts have been made to develop such high performance polymer materials. Among all the reported organic polymers containing heat-resistant polymers with ladder-like rigid structures, poly(p-phenylenebenzobisoxazole) (PPBO),<sup>3</sup> commercialized as Zylon (PPBO fiber),<sup>4</sup> shows the highest mechanical properties (Young's modulus: 270 GPa) and thermal stabilities (decomposition temperature: 650 °C) (coefficient of thermal expansion:  $-6 \text{ ppm K}^{-1}$ ). Such outstanding mechanical and thermal properties would significantly contribute to fulfill the requirements for next generation extreme materials/devices. However, the insolubility of the PPBO in organic solvents as well as the absence of a glass transition below its decomposition temperature due to its rigid structure prevents the fabrication of PPBO with a desired shape such as film, pellet, etc.

One possible approach to prepare the PPBO film is the use of a strong acid, such as poly(phosphoric acid), that dissolves the PPBO.<sup>5,6</sup> However, the use of such an acid is

environmentally unfriendly and unfavorable in a view of manufacturing. Thus, the fabrication of PPBO without using strong acids is highly requested.

Another approach is to develop a PPBO precursor that is soluble in organic solvents and thus is able to convert a PPBO precursor film to the PPBO film by a thermally induced ring-closing reaction of the *o*-hydroxyphenyl amide to form the benzoxazole structure.<sup>7–10</sup> Since the solubility of poly(*o*-hydroxyphenyl amide) (prePPBO; Figure 1, R = H) was found to be extremely low, we recently developed a prePPBO derivative containing the *tert*-butyldimethylsilyl (TBS) group as a soluble PPBO precursor (TBS-prePPBO) as shown in Figure 1 (R = TBS) and successfully converted the precursor into PPBO by heat treatment.<sup>11</sup> We revealed that the TBS-prePPBO showed an excellent solubility in organic solvents by introducing the TBS group and allowed easy fabrication of a film by the solution casting method. The obtained PPBO film showed the highest thermal resistivity among any of the other polymeric materials, and thus the polymer is a promising alternative to other

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alkyl-prePPBO

Figure 1. Chemical structures of prePPBO.

alkyl

polymer materials.<sup>11</sup> However, especially in the field of microelectronics, generation of an organosilicon moiety during the fabrication is avoided in order to prevent the contamination of the devices, and thus a PPBO precursor free from the silyl moiety is strongly requested.

In this paper, we describe the development of a novel soluble PPBO precursor functionalized with an alkyl group instead of TBS as a substitution group of poly(o-hydroxyphenyl amide) (R = alkyl in Figure 1). Especially, the formation mechanism of the thermal conversion from the *o*-alkoxyphenylamide<sup>12,13</sup> to the benzoxazole structure has not yet been studied, and the structural dependency of the alkyl group (methyl vs isopropyl) was investigated based on the TGA, IR, pyrolysis gas chromatography mass spectrometry (Py-GC/MS), and evolved gas analysis GC/MS (EGA-GC/MS) techniques. Finally, we evaluated the mechanical and thermal properties of the fabricated freestanding PPBO films from the novel PPBO precursor films prepared in this study.

#### 2. EXPERIMENTAL SECTION

**2.1. Materials.** 1,5-Difluoro-2,4-dinitrobenzene and terephthaloyl chloride were purchased from TCI. Terephthaloyl chloride was purified by recrystallization from *n*-hexane, and the other reagents were used as received. Palladium on carbon (Pd/C, 10%), potassium hydroxide (KOH), and triethylamine were purchased from Aldrich and used as received. Potassium carbonate ( $K_2CO_3$ ), ethyl acetate (EtOAc), methanol, 2-propanol, sulfuric acid ( $H_2SO_4$ ), methanesulfonic acid, NMP, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) were purchased from Wako Pure Chemical Co. and used as received. 1,5-Dimethoxy-2,4-dinitrobenzene, 4,6-dimethoxy-1,3-diaminobenzene (1), and 4,6-diisopropoxy-1,3-diaminobenzene (2) were synthesized according to the literature.<sup>14</sup> 1,5-Diisopropoxy-2,4-dinitrobenzene was synthesized according to the literature<sup>15</sup> (for details, see the Experimental Section in the Supporting Information).

**2.2.** Synthesis of PPBO Precursor (Me-prePPBO). Under a nitrogen atmosphere, 1 (0.168 g, 1.0 mmol) was dissolved in NMP (4.0 mL) and then cooled to 0 °C, to which terephthaloyl chloride (0.203 g, 1.0 mmol) and triethylamine (0.3 mL, 2.0 mmol) were added. After a few minutes, the solution changed to a gel, to which NMP (46 mL) was added followed by stirring at 100 °C for 24 h. The obtained solution was poured into 800 mL of methanol to produce a precipitate, which was filtered and rinsed several times with methanol. The obtained solid was rinsed with methanol at 90 °C using a Soxhlet extractor and then dried at 80 °C for 24 h in a vacuum to give a brown powder (0.254 g, yield 85%). The inherent viscosity of the obtained polymer measured at the concentration of 0.5 dL g<sup>-1</sup> in H<sub>2</sub>SO<sub>4</sub> at

30 °C was 0.46 dL g<sup>-1.</sup> <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ ,  $\delta$  ppm): 9.69 (s, 2H, NH–C=O), 8.07 (s, 4H,Ar–H), 7.81 (s, 1H, Ar–H), 6.87 (s, 1H, Ar–H), 3.89 (s, 6H, CH<sub>3</sub>). IR (ATR,  $\nu$ , cm<sup>-1</sup>): 3422 ( $\nu$  N–H), 2939 ( $\nu$  CH<sub>3</sub>), 1651 (amide I type), 1524 (amide II type). Anal. Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 64.41; H, 4.73; N, 9.39. Found: C, 66.74; H, 6.13; N, 7.74. EA analysis on Me-prePPBO do not agree with the calculated ones, which suggests that Me-prePPBO contains many end groups, such as amine and carboxylic acid moieties.

2.3. Synthesis of PPBO Precursor (iPr-prePPBO). Under a nitrogen atmosphere, 2 (0.224 g, 1.0 mmol) was dissolved in NMP (4.0 mL) and then cooled to 0 °C, to which terephthaloyl chloride (0.203 g, 1.0 mmol) and triethylamine (0.3 mL, 2.0 mmol) were added, and then the mixture was stirred at 0 °C for 24 h. The solution was poured into 80 mL of methanol to produce a precipitate, which was filtered and rinsed several times with methanol. The obtained solid was rinsed with methanol at 90 °C using a Soxhlet extractor and then dried at 80 °C for 24 h in a vacuum to produce a green powder (0.336 g, yield 95%). The inherent viscosity of the obtained polymer measured at a concentration of 0.5 dL  $g^{-1}$  in  $\rm H_2SO_4$  at 30  $^{\circ}C$  was 1.21 dL g<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, DMSO- $d_{6}$ ,  $\delta$  ppm): 9.60 (s, 2H, NH-C=O), 8.14 (s, 4H, Ar-H), 8.08 (s, 1H, Ar-H), 6.94 (s, 1H, Ar–H), 4.73 (m, 2H, C–H), 1.37 (d, 13H, CH<sub>3</sub>). IR (ATR,  $\nu$ , cm<sup>-1</sup>): 3419 (v N-H), 2976 (v CH-CH<sub>3</sub>), 1667 (amide I type), 1520 (amide II type). Anal. Calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub> + 1.33 H<sub>2</sub>O: C, 63.48; H, 5.81; N, 7.40. Found: C, 63.48; H, 4.72; N, 9.19.

**2.4.** Fabrication of Free-Standing PPBO Films. The *i*PrprePPBO (100 mg) was dissolved in NMP (2 mL) at 140 °C for 2 h. The solution was then filtered through cotton followed by solution casting on a glass substrate to obtain a film, which was dried at 60 °C for 1 h, 70 °C for 1 h, 80 °C for 1 h, 100 °C for 1 h, and finally at 120 °C for 1 h. The film was peeled off the glass substrate by immersing the substrate in water. The obtained film was dried at 80 °C for 24 h under vacuum and subsequently heated in a vacuum at 250 °C for 6 h and then at 300 °C for 6 h. The intrinsic viscosity of the obtained polymer film measured in methanesulfonic acid at 30 °C was 1.68 dL g<sup>-1</sup>. IR (ATR,  $\nu$ , cm<sup>-1</sup>): 1617 ( $\nu$  C=N), 1361 ( $\nu$  C-N), 1054 ( $\nu$  C-O). Anal. Calcd for C<sub>14</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub> + 0.084 H<sub>2</sub>O: C, 71.79; H, 3.15; N, 10.94. Found: C, 71.80; H, 2.56; N, 11.96.

**2.5. Measurements.** The inherent viscosity measurements were carried out using an Ostwald viscometer. The <sup>1</sup>H NMR spectra and FT-IR spectra were measured using an AV 300 M spectrometer (Bruker Biospin) and a Spectrum 65 FT-IR (PerkinElmer) spectrometer equipped with an ATR apparatus at a resolution of 4 cm<sup>-1</sup>, respectively. The mechanical properties of the films were measured at 25 °C using an EZ-S (Shimadzu) at the displacement rate of 1.0 mm min<sup>-1</sup>.

**2.6. TG Analysis.** A thermogravimetric analysis (TGA) was carried out using an EXSTAR TG/DTA 6300 (SII Nanotechnology). The temperature program was 30–900 °C at the heating rate of 10 °C min<sup>-1</sup> under flowing N<sub>2</sub> (200 mL min<sup>-1</sup>), and for the isothermal TGA, the temperature program was 30–250, 30–300, 30–350, 30–400, and 30–450 °C at the heating rate of 10 °C min<sup>-1</sup> under flowing N<sub>2</sub> (200 mL min<sup>-1</sup>) and holding the temperature (250, 300, 350, 400, and 450 °C) for 6 h under flowing N<sub>2</sub> (200 mL min<sup>-1</sup>).

**2.7. Py-GC/MS Analysis.** A multifunctional double-shot pyrolyzer PY-2020iD (Frontier Lab.) mounted on a GC-MS-QP-2010Plus (Shimadzu) was used under flowing He as the carrier gas. A coated stainless steel tube (HP-5MS, length = 30 m, inner diameter = 0.25 mm, film thickness = 0.25  $\mu$ m) (Agilent Tech.) was used as the GC/MS column. The GC oven was programmed at 40 °C at the heating rate of 10 °C min<sup>-1</sup> to 300 °C. The injection port was in the constant linear velocity mode at 80 kPa with the split ratio = 1/30.





#### Scheme 2. Synthesis of PPBO via PPBO Precursor (Poly(dialkoxyphenylamide)



Figure 2. FT-IR spectra of Me-prePPBO (upper) and *i*Pr-prePPBO (lower).

The mass spectrometer was operated in the EI mode with the mass range of 30-550 amu. The pyrolysis temperature program was 200-450 °C at the heating rate of 10 °C min<sup>-1</sup>.

**2.8. EGA-GC/MS Analysis.** The evolved gas analysis-mass spectrometry (EGA-MS) measurements were carried out in a multifunctional double-shot pyrolyzer directly coupled with an ion source of MS via a deactivated and coated stainless steel transfer tube (Ultra ALLOY-DTM, length = 2.5 m, inner diameter = 0.15 mm). The oven column temperature was isothermally maintained at 350 °C, and the temperature of the pyrolyzer was programmed from 200 to 800 °C at the heating rate of 10 °C min<sup>-1</sup> under a flowing He carrier gas. The injection port was in the constant linear velocity mode at 80 kPa with the split ratio of 1/100. The mass spectrometer was operated in the EI mode with the mass range of 10–600 amu.

#### 3. RESULTS AND DISCUSSION

**3.1.** Synthesis of PPBO Precursor. 4,6-Dialkoxy-1,3diaminobenzene (1: R = methyl; 2: R = isopropyl in Scheme 1) synthesized based on the literature<sup>14,15</sup> (Scheme 1) was reacted with terephthaloyl chloride in the presence of triethylamine as a base<sup>16</sup> in NMP at 0 °C to form the corresponding poly-(*o*-alkoxyphenylamide)s (Me-prePPBO; R = Me, *i*Pr-prePPBO; R = isopropyl in Scheme 2) that acts as the PPBO precursors. We have also conducted the polycondensation reaction in the absence of triethylamine, while in such conditions, we obtained the polymer with a low viscosity.

We noticed that the reaction mixture immediately turned to a gel in the case of 1, while the reaction of 2 with terephthaloyl chloride became a viscous solution. Since the gel was dissolved at 100 °C after the addition of a large amount of NMP, the gel was not a chemically cross-linked gel, but a physical gel. We assumed the interchain packing of Me-prePPBO through an amide bond and the  $\pi$ - $\pi$  stacking induced the physical crosslinking, whereas the isopropyl group serves to prevent the stacking of *i*Pr-prePPBO in order to facilitate the reaction. As a matter of fact, the inherent viscosity of Me-prePPBO was only 0.46 dL g<sup>-1</sup> in sulfuric acid at 30 °C, while that of



Figure 3. <sup>1</sup>H NMR spectra of Me-prePPBO (a) and *i*Pr-prePPBO (b).



**Figure 4.** TGA curves of Me-prePPBO (blue line) and *i*Pr-prePPBO (red line). TGA curve of prePPBO is shown for comparison (black line).

*i*Pr-prePPBO reached as high as 1.21 dL  $g^{-1}$ , indicating the smooth reaction for 2.

Figure 2 shows the IR spectra of Me-prePPBO (upper) and *i*Pr-prePPBO (lower). The characteristic peaks of the amide bonding that appeared at 1640 (amide I) and 1550 cm<sup>-1</sup> (amide II) were clearly observed. The <sup>1</sup>H NMR spectra of Me-prePPBO (Figure 3a) and *i*Pr-prePPBO (Figure 3b) were measured, and the integration ratio of the methyl and aromatic



**Figure 5.** (a) Weight change of the Me-prePPBO under different isothermal conditions (250, 300, 350, 400, and 450 °C) for 6 h in a nitrogen atmosphere. The temperature programs of each experiment are also shown in the figure. (b) Total weight loss of the Me-prePPBO at different isothermal conditions (250, 300, 350, 400, and 450 °C) for 6 h under a nitrogen atmosphere. (c) Weight change of the *i*Pr-prePPBO at different isothermal condition (250, 300, 350, 400, and 450 °C) for 6 h under a nitrogen atmosphere. The temperature programs of each experiment are also shown in the figure. (d) Total weight loss of the *i*Pr-prePPBO at different isothermal conditions (250, 300, 350, 400, and 450 °C) for 6 h under a nitrogen atmosphere. The temperature programs of each experiment are also shown in the figure. (d) Total weight loss of the *i*Pr-prePPBO at different isothermal conditions (250, 300, 350, 400, and 450 °C) for 6 h under a nitrogen atmosphere. The temperature programs of each experiment are also shown in the figure. (d) Total weight loss of the *i*Pr-prePPBO at different isothermal conditions (250, 300, 350, 400, and 450 °C) for 6 h under a nitrogen atmosphere.



Figure 6. (a) FT-IR spectra of Me-prePPBO at different isothermal conditions (250, 300, 350, 400, and 450  $^{\circ}$ C) for 6 h under a nitrogen atmosphere. FT-IR spectra of Zylon and Me-prePPBO are shown for comparison. (b) FT-IR spectra of *i*Pr-prePPBO at different isothermal conditions (250, 300, 350, 400, and 450  $^{\circ}$ C) for 6 h under a nitrogen atmosphere. FT-IR spectra of Zylon and *i*Pr-prePPBO are shown for comparison.

protons were methyl:aromatic = 6:6 and 13:6 for Me-prePPBO and *i*Pr-prePPBO, respectively, guaranteeing that the hydroxyl groups were fully functionalized by the alkyl group after the

polymerization. Notably, these alkyl groups enable the PPBO precursor to be quite soluble into organic solvents, such as NMP and DMSO, which is in sharp contrast to the prePPBO

(R = H in Figure 1) which showed an extremely low solubility in organic solvents and was only soluble in acid.<sup>11</sup>

**3.2. Thermal Conversion of PPBO Precursor to PPBO.** Figure 4 shows the TGA curves of the PPBO precursors measured at 10 °C min <sup>-1</sup> under flowing nitrogen together with that of the prePPBO. A large weight loss starting at around 350 and 320 °C for Me-prePBO (blue line in Figure 4) and *i*Pr-prePBO (red line in Figure 4), respectively, was observed. Based on the weight loss of the prePPBO in a similar temperature range assignable to the ring-closing dehydration,<sup>17–19</sup> the weight losses for Me-prePPBO and *i*Pr-prePPBO in the temperature ranges are attributed to the ring-closing reaction of the *o*-alkoxyphenylamide.<sup>12,13</sup>

**3.3. Isothermal Characterization of PPBO Precursor.** To explore the behavior of the thermal ring-closing reaction of the poly(*o*-alkoxyphenylamide)s, the weight changes of the Me-prePPBO and *i*Pr-prePPBO upon isothermal heating under flowing nitrogen were monitored, and the IR spectra were measured after heating (Figures 5 and 6 and Tables 1 and 2). We found that the heating at 250 °C for 6 h produced small changes in the weight as well as the IR spectra for both polymers. Interestingly, upon heating at 300 °C, a gradual decrease in the weight was observed only for *i*Pr-prePPBO, while Me-prePPBO showed a weight loss of only ~1.3 wt % after heating for 6 h. This difference corresponds well with the difference in the starting temperature of the weight reduction in the TGA (Figure 4). Upon heating at 350 °C, significant weight losses were observed for both polymers and the total weight

### Table 1. Weight Loss of the Me-prePPBO after Specified Isothermal Treatments

temp [°C]	weight loss of $(a)^a$ [%]	weight-loss of $(b)^b$ [%]	total weight loss <sup>c</sup> [%]
250	0.73	0.56	1.29
300	0.84	3.38	4.22
350	1.67	19.96	21.63
400	12.70	12.61	25.31
450	30.9	4.60	35.5

<sup>*a*</sup>Weight loss of (a) is a weight loss of the Me-prePPBO during raising temperature from room temperature to specified temperature. <sup>*b*</sup>Weight loss of (b) is a weight loss of the Me-prePPBO holding the temperature for 6 h. <sup>*c*</sup>Total weight loss is a sum of weight loss of (a) and (b).

losses after heating for 6 h were 21.6% and 29.7% for Me-prePPBO and *i*Pr-prePPBO, respectively, both of which agreed well with the calculated value, i.e., 21.5% for Me-prePPBO and 33% for *i*Pr-prePPBO as indicated in Figure 5 (dotted line). Notably, the IR spectra of Me-prePPBO and *i*Pr-prePPBO after heating at 350 °C for 6 h exhibited the characteristic peaks that newly appeared at around 1620, 1360, and 1054 cm<sup>-1</sup> assignable to the C=N, C-N, and C-O vibration of the benzoxazole ring, respectively, which are quite similar to that of Zylon (Figure 6). Since these peaks were not observed for both polymers after heating at 300 °C for 6 h, heating at 350 °C was found to be the minimum temperature necessary to obtain the PPBO structure.



Figure 7. (a) Py-GC/MS Pyrogram of Me-prePPBO upon heating at 300–500 °C under helium. Chemical structures of each peak are presented in the box. (b) EGA-GC/MS chromatogram of total ions of Me-prePPBO from 200 to 450 °C at the heating rate of 10 °C min<sup>-1</sup>. Ion chromatograms of water, methanol (A), and decomposition compounds of dimethyl terephthalate (B–E) are also shown. (c) Magnified ion chromatograms of water, methanol, and decomposition compounds of dimethyl terephthalate around 300–450 °C.

 Table 2. Weight Loss of the *i*Pr-prePPBO after Specified

 Isothermal Treatments

temp [°C]	weight loss of $(a)^a$ [%]	weight loss of $(b)^b$ [%]	total weight loss <sup>c</sup> [%]
250	0.23	4.72	4.95
300	0.13	19.66	19.79
350	1.51	28.26	29.77
400	29.97	5.66	32.63
450	29.97	2.76	32.74

<sup>*a*</sup>Weight loss of (a) is a weight loss of the *i*Pr-prePPBO during raising temperature from room temperature to specified temperature. <sup>*b*</sup>Weight loss of (b) is a weight loss of the *i*Pr-prePPBO holding the temperature for 6 h. <sup>*c*</sup>Total weight loss is a sum of weight loss of (a) and (b).

However, we noticed that the total weight loss of MeprePPBO ( $\sim$ 36%) after heating at 400 and 450 °C for 6 h was greater than that of the calculated value (21.5%). On the other hand, when *i*Pr-prePPBO was heated at 400 and 450 °C for 6 h, the total weight loss ( $\sim$ 33%) was still very close to the calculated value (34%). These results suggested that unexpected side reactions occurred for Me-prePPBO but an ideal ring-closing reaction underwent for *i*Pr-prePPBO.

**3.4.** Analysis of Outgas during Ring-Closing Reaction. To further study the reaction mechanism of Me-prePPBO and *i*Pr-prePPBO upon the ring-closing reaction, pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) and real time EGA-GC/MS were carried out. The Py-GC/MS is a useful method to analyze the fragments from the sample during heating. Figure 7a is the Py-GC/MS pyrogram of the Me-prePPBO showing the mass of the outgas collected in the range from 300 to 500 °C at the heating rate of 10 °C min<sup>-1</sup> under helium (for Py-GC/MS pyrograms from 500 to 750 °C, see Supporting Information, Figure S1). Outgases consisting of methanol (m/z = 31) (denoted A in Figure 7) and the fragments from the dimethyl terephthalate (denoted B-E in Figure 7) were obtained. Real-time EGA-GC/MS spectrometry measurements were conducted in order to monitor the amount of the chemicals of interest evolved from the sample as an outgas. The results of the Me-prePPBO upon heating from 200 to 450 °C at the heating rate of 10 °C min<sup>-1</sup> under helium are shown in Figure 7b (for EGA-GC/MS spectrometry from 200 to 800 °C, see Supporting Information, Figure S2). It was revealed that water, methanol, and B-E were detected at around 375 °C, at which temperature a high weight loss (>21.4%) was observed in the TGA (blue line in Figure 4). Unexpectedly, very large peaks from the fragment of dimethyl terephthalate were also observed and the major outgas component was not methanol, but water (Figure 7c).

Figure 8a shows the Py-GC/MS pyrogram of the *i*PrprePPBO upon heating from 200 to 450 °C (for Py-GC/MS pyrograms from 450 to 800 °C, see Supporting Information, Figure S3). The detected MS peaks were identified as propene (m/z = 41) (denoted L), acetone (m/z = 43) (denoted M), isopropanol (m/z = 45) (denoted N), and fragments from the



Figure 8. (a) Py-GC/MS Pyrogram of *i*Pr-prePPBO upon heating at 200–450 °C under helium. Chemical structures of each peak are presented in the box. (b) EGA-GC/MS chromatogram of total ions of *i*Pr-prePPBO from 200 to 450 °C at the heating rate of 10 °C min<sup>-1</sup>. Ion chromatograms of water, propene (L), acetone (M), *i*Pr-OH (N), and the fragments of from the diisopropoxy aniline (O and P) are also shown. (c) Magnified ion chromatograms of water, propene, and isopropanol around 300–450 °C.

diisopropoxy aniline (denoted O and P in Figure 8). It is noted that the MS profile is much simpler than that of Me-prePPBO. Figure 8b shows the real time EGA-GC/MS chromatograms of water, propene, isopropanol, O, and P produced from the iPrprePPBO upon heating from 200 to 450 °C (for EGA-GC/MS spectrometry from 200 to 800 °C, see Supporting Information, Figure S4). The peak ranges at around 350 °C were close to the temperature range of the high weight loss ( $\sim$ 33%) in the TGA (red line in Figure 4) and were slightly lower than that of MeprePPBO. Unlike the behavior of Me-prePPBO, the main outgas was derived from the leaving group, such as propene, water, and isopropanol, and the main chain fragments were suppressed. We assumed that the isopropyl group on iPrprePPBO is first cleaved to the secondary carbocation and formed propene via an E1 elimination to produce a proton, and the generated proton is involved in the dehydration that occurs to form a benzobisoxazole ring. The lower temperature of the dehydration in iPr-prePPBO compared to Me-prePPBO is explained by the higher stability of the secondary carbocation than the primary carbocation. On the basis of the above discussions, we considered that one of the key reaction causing the excess weight loss of Me-prePPBO observed in Figures 5a,b was thermally induced cleavage of benzamide bonding, leading to the backbone decomposition because the benzonitrile derivative attributed to the product from the cleavage of benzamide<sup>20</sup> was detected only from Me-prePPBO in Py-GC/MS (compound **D** in Figure 7). The different behavior can be well explained by considering the different temperature of the benzoxazole formation for Me- (ca. 375 °C) and *i*Pr-prePPBO (ca. 350 °C) (see Figures 4, 7, and 8). We considered that the formation of thermally stable benzoxazole ring for *i*Pr-prePPBO (ca. 350 °C) prior to the cleavage of benzamide occurred around 375 °C (Figure 7c) is crucial to avoid the decomposition of the backbone.

The systematic studies to reveal more detail mechanisms of the ring-closing reaction to produce *o*-alkoxyphenylamide structures are currently undergoing using the model monomers, and the results will be reported in a subsequent paper.

**3.5.** Fabrication and Characterization of a Free-Standing PPBO Film. The higher solubility of *i*Pr-prePPBO allows us to fabricate its films by the solution-cast method. A hot NMP solution of the *i*Pr-prePPBO was cast on a glass plate, and the obtained film was peeled off the substrate by immersing it in water (Figure 9a).

Thermal conversion of the iPr-prePPBO film into the PPBO film was carried out under a vacuum condition. Under the vacuum condition, different from heating under a flowing inert gas (Figure 6), the characteristic peaks due to the benzoxazole formation at 1620, 1360, and 1054  $\text{cm}^{-1}$  assignable to the C=N, C-N, and C-O, respectively, were clearly observed after heating at 250 °C for 6 h and subsequent heating at 300 °C for 6 h (Figure 9b). Figure 9c shows a photograph of the PPBO film prepared from the iPr-prePPBO film after the heat treatment under vacuum. After heating, we found the weight of the film decreased by 35%, which agreed well with the calculated value ( $\sim$ 34%). In addition, the film thickness decreased by ca. 33% from 30 to 20  $\mu$ m upon heating. Both results strongly indicated that the leaving group was successfully eliminated from the film unlike TBS-prePPBO, in which the silyl compound remained in the resulting PPBO film (see Supporting Information, Figure S5). Indeed, the residue observed for the PPBO film prepared from TBS-prePPBO after the heating to 900 °C was not observed for the PPBO film prepared from the



**Figure 9.** (a) Photograph of the *i*Pr-prePPBO film. (b) FT-IR spectra of the *i*Pr-prePBO film before and after heat treatment at 250 °C for 6 h and 300 °C for 6 h under vacuum. FT-IR spectrum of Zylon is shown for comparison. (c) Photograph of the *i*Pr-prePPBO film after heating at 250 °C for 6 h and 300 °C for 6 h under vacuum.

*i*Pr-prePPBO (see Supporting Information, Figure S6). It was noted that the obtained films after heating at 350 and 400  $^{\circ}$ C for 1 h were very brittle.

Table 3 summarizes the results of the tensile tests for the free-standing *i*Pr-prePPBO film and the PPBO films.

Table	3.	Mec	hanical	Properties	of th	1e <i>i</i> Pr-p	rePPBO	and
РРВС	) <b>F</b>	ilms						

sample	tensile strength [MPa]	tensile modulus [GPa]	elongation [%]
<i>i</i> Pr-prePPBO	$59 \pm 0.8$	$1.5 \pm 0.1$	$11.6 \pm 1.7$
РРВО	76 ± 12	$2.7 \pm 0.3$	$3.5 \pm 0.8$

The tensile strength and tensile modulus of the PPBO film were 76 MPa and 2.7 GPa, respectively, and the tensile strength was greater than that of the PPBO films prepared from the TBS-prePPBO (tensile strength was 42  $MPa^{11}$ ). In addition, the obtained PPBO film showed an excellent thermal stability up to 670 °C in a nitrogen atmosphere (Figure 10) comparable to that of the previously reported PPBO film.<sup>11</sup> Such a mechanically tough and thermally stable film without organosilyl materials could serve as a promising material not only for aerospace applications but also for microelectronics as well.



Figure 10. TGA curve of PPBO film from the *i*Pr-prePPBO film under flowing nitrogen.

#### 4. CONCLUSIONS

In summary, in this study, we designed and synthesized a novel PPBO precursor, poly(o-alkoxyphenylamide). We found that the alkoxy unit allows the PPBO precursor to be soluble into organic solvents and allows the fabrication of fine films by the solution casting method. On the basis of a detailed thermal analysis using EGA and GC/MS, we revealed that the structure of the alkyl group affected not only the ring-closing reaction temperature but also the reaction behavior. For Me-prePPBO, the thermal cleavage of the methoxy unit occurred at around 375 °C followed by not only the benzoxazole formation but also the decomposition of the backbone due to the cleavage of benzamide bonding (ca. 375 °C), while the decomposition of the backbone was significantly suppressed for *iPr-prePPBO* after the thermal cleavage of the isopropoxy unit occurred at around 350 °C. Such a thermal stability of backbone structure for *i*Pr-prePPBO is due to the smooth benzoxazole formation based on the facile cleavage of the isopropyl group. After optimizing the thermal treatment conditions, a free-standing PPBO film was successfully fabricated from the *i*Pr-prePPBO film by heating at 250 °C for 6 h and 300 °C for 6 h under vacuum. We found that the PPBO film from the precursor exhibited high mechanical and thermal resistive properties. The excellent solubility of the precursor enables the preparation of the composite material. Such a silyl-free PPBO including their composites are highly attractive for the next-generation electronic applications and also promising for automobile and aerospace applications as well.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental procedures for the reaction of 1 and 2, Py-GC/MS pyrograms and EGA-GC/MS chromatograms of total ions of Me-prePPBO and *i*Pr-prePPBO, FT-IR spectrum of the residue from the PPBO prepared from the TBS-prePPBO after heating, and TGA curves of the PPBO films prepared the *i*Pr-prePPBO and TBS-prePPBO. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### Corresponding Authors

\*Tel +81-92-802-2840; Fax +81-92-802-2840; e-mail fujigaya-tcm@mail.cstm.kyushu-u.ac.jp (T.F.).

\*Tel +81-92-802-2840; Fax +81-92-802-2840; e-mail nakashima-tcm@mail.cstm.kyushu-u.ac.jp (N.N.).

#### Notes

The authors declare no competing financial interest.

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