

# Synthesis and characterization of methoxybenzene-linked polyimides formed by 1,4-addition to bismaleimides

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## Highlights

- Methoxybenzene-linked polyimides were synthesized by 1,4-addition to bismaleimides.
- 1,3-Bis(3,5-dimethoxyphenoxy)propane was newly synthesized as a monomer.
- The synthesized polyimides showed high thermal stability.
- The glass transition temperatures of the polyimides were around 200 °C.

## ABSTRACT

Methoxybenzene-linked polyimides were synthesized by a trifluoromethanesulfonic acid (TfOH)-catalyzed 1,4-addition (Michael addition) reaction. Newly synthesized 1,3-bis(3,5-dimethoxyphenoxy)propane and known 5,5'-oxybis(1,3-dimethoxybenzene) as nucleophilic monomers were reacted with several bismaleimides in the presence of a catalytic amount of TfOH in *m*-cresol. Use of 1,3-bis(3,5-dimethoxyphenoxy)propane afforded polyimides with number average molecular weights ( $M_n$ )s of 8000 to 15000. However, polyimides with  $M_n$  of 4000 or less were obtained when 5,5'-oxybis(1,3-dimethoxybenzene) was employed as a monomer. The synthesized polyimides showed good thermostability as judged by 10% weight loss temperatures between 417 and 441 °C. Their glass transition temperatures were around 200 °C. These polymers featured a wide range of solubility in organic solvents such as *m*-cresol, DMF, pyridine, and chloroform.

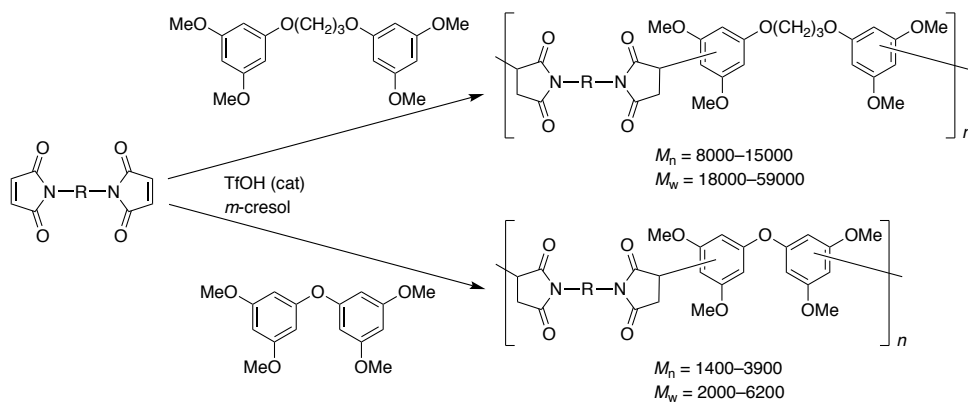
## Keywords

Polyimide

1,3-Bis(3,5-dimethoxyphenoxy)propane

Bismaleimide

## Graphical Abstract



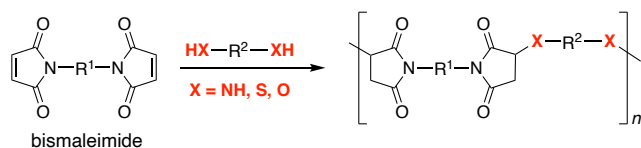
## 1. Introduction

Polyimides synthesized from bismaleimides as monomers have gained considerable attention due to their unique properties [1–4]. A three-dimensional structure bearing the bis(cyclic imide) provides heat resistance, mechanical stability, low thermal expansion, and a low dielectric constant. These properties are advantageous for a wide range of applications in the aeronautical industry and for the production of microelectronics, composites, and so on. Due to the high reactivity of bismaleimide compounds as electron acceptors, polymerizations using Diels–Alder [2,4], ene [2,5,6], and 1,4-addition (Michael addition) reactions [2–4,7] have been extensively studied. In 1,4-addition reactions, diamines, dithiols, and *glycerol* have already been reported as nucleophiles to bismaleimides (Scheme 1A) [2–4,7–14]. Especially, the use of diamines results in the formation of polyaspartimides. Since the pioneering work by Crivello [8], a number of diamines have been installed into polyaspartimides. One notable example is bis(4-aminophenyl)methane, and the use of this diamine produced the commercial Kerimid 601 [11] and Compimide 200 [2], which have been employed as advanced composites with high thermal stability. Other examples are aliphatic secondary diamines [12] and azobenzene-containing aromatic diamines [13].

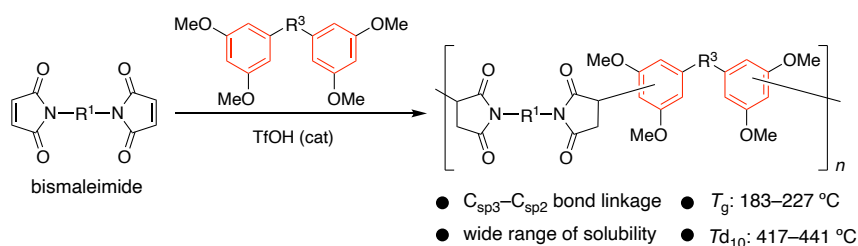
In the present study, we were interested in 1,4-addition reactions of bismaleimides and aromatic rings with high electron density. These reactions are expected to afford a new series of polyimides containing  $C_{sp^3}$ – $C_{sp^2}$  bonds (Scheme 1B) that are completely different from polyimides with  $C_{sp^3}$ – $C_{sp^3}$  bonds formed by Diels–Alder and ene reactions. By introducing methoxybenzenes, which are less polar than amines, the resulting polymers would become less polar. This is expected to result in a lower glass transition temperature and higher solubility in organic solvents of the new polymers compared to those of conventional polyimides synthesized from aromatic bismaleimides and diamines.

Recently we found that the 1,4-addition of 1,3,5-trimethoxybenzene to various maleimides was catalyzed by trifluoromethanesulfonic acid (TfOH) in low polar solvents such as toluene and 1,2-dichloroethane (DCE) (Scheme 2) [15]. On the basis of this result, we planned to synthesize methoxybenzene-linked polyimides by a TfOH-catalyzed 1,4-addition as shown in Scheme 3. First, 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**) as a nucleophilic monomer was newly designed and synthesized. Next, polymerizations of bismaleimides **1a–1c** were conducted either with **2** or 5,5'-oxybis(1,3-dimethoxybenzene) (**4**) [16] to afford new polyimides **3a–3c** or **5a–5c**.

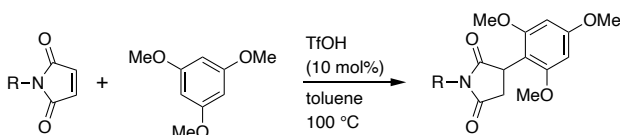
**A) Previous work:** heteroatom nucleophiles as monomers



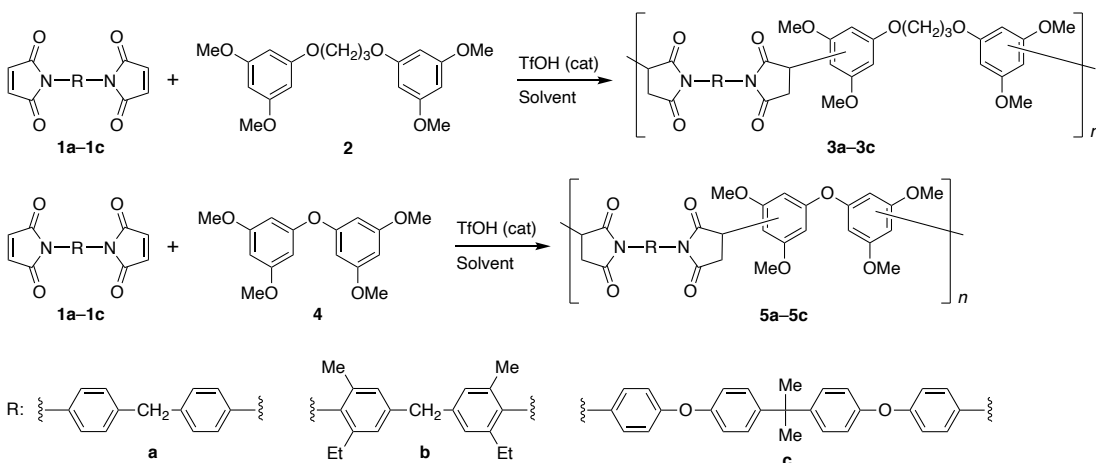
**B) This work:** carbon nucleophiles as monomers



**Scheme 1.** Polymerization by 1,4-addition of nucleophilic monomers to bismaleimides.



**Scheme 2.** 1,4-Addition of 1,3,5-trimethoxybenzene to maleimides.



**Scheme 3.** Synthesis of polyimides from bismaleimides and alkoxybenzenes via 1,4-addition with a catalytic amount of trifluoromethanesulfonic acid.

## 2. Experimental

### 2.1. Materials

Dehydrated solvents [toluene, DMSO, DMF, 1-methyl-2-pyrrolidone (NMP), pyridine, acetone] and potassium phosphate were commercially supplied by Fujifilm Wako Pure Chemical (Osaka, Japan). 1,2-Dichloroethane (DCE) and THF were distilled from CaH<sub>2</sub> prior to use. *m*-Cresol (Sigma-Aldrich, St. Louis, MO, USA), TfOH (Kishida Chemical, Osaka, Japan), NaH (Nacalai, Kyoto, Japan), and CuI (Kishida) were commercially supplied. 1-Bromo-3,5-dimethoxybenzene, 1-bromopropane, 1,3-dibromopropane, 3,5-dimethoxyphenol, *N,N'*-di([1,1'-biphenyl]-2-yl)ethanediamide, *N*-phenylmaleimide, and bis-maleimide derivatives were commercially supplied by Tokyo Kasei Industries (Tokyo). Cyclohexanone (Kanto Chemical, Tokyo, Japan) and chloroform (Wako) were commercially supplied. 5,5'-Oxybis(1,3-dimethoxybenzene) (**4**) was prepared according to the reported method [16,17].

### 2.2. General information on the synthesis of monomers and polymers

Reactions were basically carried out by using the usual Schlenk technique on a dual manifold vacuum–argon system except for entries 1–9 in Table 1, which were optimized for polymerization by using a 12-mL vial (S-5, 19 mm × 70 mm; Nichiden-Rika Glass, Kobe, Japan) with a cap. Thin-layer chromatography (TLC) analysis was conducted by using silica gel 60 F<sub>254</sub> (Merck No. 5715, thickness 0.25 mm; Merck Millipore, Burlington, MA, USA). Normal-phase medium-pressure liquid chromatography (MPLC) was conducted on a Purif-compact purification system (Shoko Science, Tokyo) or on an EPCLC-AI-580S-10V (Yamazaki, Osaka, Japan) using Purif-Pack SI-25 columns (size 60 and 120) or Universal<sup>TM</sup> premium columns (size M).

### 2.3. Synthesis of 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**)

To a stirring mixture of NaH (60% dispersion in oil, 880 mg, 22 mmol) in DMSO (10 mL) under argon was added dropwise a solution of 3,5-dimethoxyphenol (3.39 g, 22 mmol) in DMSO (10 mL) [18]. After the mixture was stirred at 25 °C for 19 h, it was added dropwise to a solution of 1,3-dibromopropane (1.12 mL, 11 mmol) in DMSO (10 mL), and the resulting mixture was stirred at 25 °C for 68 h. The reaction mixture was diluted with EtOAc (100 mL) followed by washing with saturated aq. NaHCO<sub>3</sub> (150 mL). The organic phase was separated and the aqueous phase was back-extracted with EtOAc

(100 mL × 2). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give a crude product, which was purified by normal-phase MPLC (SI-25, size 120, hexane:EtOAc = 99:1 → 78:22) to afford **2** (1.40 g, 37%) as a white solid and 1-allyloxy-3,5-dimethoxybenzene (**6**) (734 mg, 34%) [19] as a colorless syrup.

**2**: *R*<sub>f</sub> 0.37 (4:1 hexane–EtOAc); mp 69.8–71.4 °C; IR (KBr) 541, 684, 824, 839, 929, 951, 1058, 1151, 1199, 1211, 1403, 1432, 1453, 1471, 1601, 2846, 2873, 2909, 2940, 3007 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.23 (quintet, *J* = 6.1 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 2H), 3.76 (s, 4 × OCH<sub>3</sub>, 12 H), 4.11 (t, *J* = 6.1 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 4H), 6.05–6.12 (m, aromatic, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 29.3, 55.5, 64.6, 93.3, 93.6, 160.9, 161.7; HRMS (EI) calcd for C<sub>19</sub>H<sub>24</sub>O<sub>6</sub> [M]<sup>+</sup> 348.1573, found 348.1572.

**6**: *R*<sub>f</sub> 0.60 (4:1 hexane–EtOAc); IR (KBr) 819, 929, 1065, 1151, 1205, 1600 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.77 (s, 2 × OCH<sub>3</sub>, 6H), 4.50 (dt, *J* = 5.4 Hz and 1.5 Hz, CH<sub>2</sub>CH=CH<sub>2</sub>, 2H), 5.29 (dq, *J* = 10.6 Hz and *J* = 1.5 Hz, CH<sub>2</sub>CH=CHH, 1H), 5.42 (dq, *J* = 17.3 Hz and 1.5 Hz, CH<sub>2</sub>CH=CHH, 1H), 6.01–6.14 (m, aromatic and CH<sub>2</sub>CH=CH<sub>2</sub>, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 55.4, 69.0, 93.2, 93.8, 117.8, 133.3, 160.6, 161.6. The IR and NMR spectra of **6** were in accordance with those reported previously [19].

## 2.4. Optimization of polymerization

### 2.4.1. Reaction conditions for entry 1 in Table 1

Prior to the polymerization, a TfOH (106 μL, 1.2 mmol) solution in toluene (10 mL) was prepared in a 20-mL vial (SV-20, 27 mm × 55 mm; Nichiden-Rika Glass). This 120-mM solution (250 μL, 0.03 mmol) was added to a 12-mL vial containing a mixture of 4,4'-bismaleimidodiphenylmethane (**1a**) (107 mg, 0.30 mmol) and 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**) (104 mg, 0.30 mmol) in toluene (0.95 mL). A cap was attached and closed, and the whole mixture was stirred at 100 °C for 24 h. After the mixture was cooled in an ice bath, it was poured into a 50-mL vial containing MeOH (20 mL) with vigorous stirring. **3a** was obtained by filtration and dried under vacuum at 40 °C for 9 h (176 mg, 83%). TLC analysis (3:2 hexane–EtOAc) of the reaction mixture after 1 day showed remaining spots of monomers **1a** and **2**. Therefore, GPC analysis was not conducted.

### 2.4.2. Reaction conditions for entry 12 in Table 1

Prior to the polymerization, a TfOH (1.2 mmol) solution in *m*-cresol (5.0 mL) was prepared in a 20-mL Schlenk tube. This 240-mM solution (420 μL, 0.10 mmol) was added

to another 20-mL Schlenk tube containing a mixture of **1a** (1.0 mmol) and **2** (1.0 mmol) in *m*-cresol (0.25 mL) under argon. A glass stopper with silicon grease was attached and tightly closed, and the whole mixture was stirred at 100 °C for 2.5 h. After the mixture was cooled in an ice bath, CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added and stirred to obtain a homogeneous solution, which was then poured into a 300-mL round-bottom flask containing MeOH (100 mL) with vigorous stirring. **3a** (668 mg, 94%) was obtained by filtration and dried under vacuum at 120 °C for 12 h as a white powder: IR (KBr) 1114, 1150, 1195, 1383, 1513, 1609, 1714, 2941 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 30 mg/0.67 mL) δ 1.91–2.34 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, 2H), 2.66–2.87 (2 × COCHH, 2H), 3.02–3.20 (2 × COCHH, 2H), 3.60–4.25 (4 × OCH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>, and C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 20H), 4.51–4.71 (2 × CHCH<sub>2</sub>CO, 2H), 5.88–6.22 (2 × C<sub>6</sub>H<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>, 4H), 6.80–6.83 (0.06H, vinylic), 7.17–7.36 (2 × C<sub>6</sub>H<sub>4</sub>, 8H); MALDI-TOF MS found [M+Na]<sup>+</sup> = 1436.6 + 706.6 *n* (*n* = 1–9), 1077.8 + 706.8 *n* (*n* = 1–10), 1933.7 + 706.5 *n* (*n* = 1–8). The calculated molecular weight of the repeating unit is 706.7.

### 2.5. Reaction of polymer **3a** with 1,3,5-trimethoxybenzene

To a 12-mL vial containing a solution of 1,3,5-trimethoxybenzene (168 mg, 1.0 mmol) and polymer **3a** (49.7 mg, 2.8 μmol) in DCE (475 μL) was added a 120-mM DCE solution of TfOH (25 μL, 2.8 μmol). A cap was attached and closed, and the whole mixture was stirred at 85 °C for 24 h. After the mixture was cooled by an ice-bath, MeOH (8 mL) was added and the precipitate (24.5 mg) was collected by filtration and dried under reduced pressure. The <sup>1</sup>H NMR spectrum of the collected polymers in CDCl<sub>3</sub> showed the disappearance of the vinyl protons. The MALDI-TOF MS spectrum in the *m/z* range of 6000–10000 is shown in the supplementary data.

### 2.6. Model reaction

#### 2.6.1. Synthesis of 1-(3,5-dimethoxyphenoxy)propane (**8**)

To a stirring mixture of NaH (60% dispersion in oil, 304 mg, 7.6 mmol) in DMSO (5 mL) under argon was added dropwise a solution of 3,5-dimethoxyphenol (771 mg, 5.0 mmol) in DMSO (5.0 mL). After the mixture was stirred at 25 °C for 4 h, a solution of 1-bromopropane (460 μL, 5.1 mmol) in DMSO (5.0 mL) was added dropwise, and then the mixture was stirred at 25 °C for 15 h. The mixture was diluted with EtOAc (50 mL) followed by washing with saturated aq. NaHCO<sub>3</sub> (50 mL × 2). The organic phase was

dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated, and dried under reduced pressure to give a crude product, which was purified by normal-phase MPLC (SI-25, size 120, hexane:EtOAc = 100:0 → 95:5) to afford **8** (515 mg, 53%) [20] as a colorless syrup: *R*<sub>f</sub> 0.47 (9:1 hexane–EtOAc); IR (KBr) 682, 819, 1066, 1151, 1191, 1204, 1472, 1601, 2963 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.03 (t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 3H), 1.79 (sextet, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H), 3.77 (s, 2 × OCH<sub>3</sub>, 6 H), 3.88 (t, *J* = 7.0 Hz, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, 2H), 6.06–6.11 (m, aromatic, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 10.7, 22.7, 55.5, 69.7, 93.0, 93.5, 161.2, 161.6; HRMS (EI) calcd for C<sub>11</sub>H<sub>16</sub>O<sub>3</sub> [M]<sup>+</sup> 196.1099, found 196.1096.

#### 2.6.2. 1,4-Addition of 1-(3,5-dimethoxyphenoxy)propane (**8**) to *N*-phenylmaleimide

A 240-mM TfOH solution in *m*-cresol (420 μL, 0.10 mmol) was added to a 20-mL Schlenk tube containing a mixture of **8** (196 mg, 1.0 mmol) and *N*-phenylmaleimide (173 mg, 1.0 mmol) in *m*-cresol (0.25 mL). A glass stopper with silicon grease was attached and tightly closed, and the whole mixture was stirred at 100 °C for 3 h. After the mixture was cooled in an ice bath, it was diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and neutralized with saturated aq. NaHCO<sub>3</sub> (5 mL). The aqueous phase was back-extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL × 2). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated, and dried under reduced pressure to give a crude product, which was purified by normal-phase MPLC (SI-25, size 60, hexane:EtOAc = 80:20 → 59:41) to afford an inseparable mixture (327 mg, 89%) of **9a** and **9b** as a white solid: *R*<sub>f</sub> 0.53 (1:1 hexane–EtOAc). The ratio of **9a** to **9b** was determined by the integral ratio of the methyl protons of the propyl groups observed by <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> to be 1:1.8. For the <sup>1</sup>H NMR spectra of authentic **9a** and **9b**, see Supplementary data.

#### 2.7. Synthesis of other polymers

All the polymers were obtained after washing with MeOH as in entry 12, Table 1.

##### 2.7.1. Polymer **3b**

**3b** (718 mg, 91%) was obtained in a manner similar to that of entry 12, Table 1, under the following conditions: bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (**1b**) (443 mg, 1.0 mmol), **2** (1.0 mmol), *m*-cresol (0.25 mL), 240 mM solution of TfOH in *m*-cresol (420 μL, 0.10 mmol). **3b**: a white powder; IR (KBr) 803, 1115, 1152, 1196, 1375, 1609, 1714, 2938, 2966 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.06–1.24 (7H), 2.00–2.47 (12H), 2.47–2.60 (2H), 2.94–3.17 (4H), 3.58–3.96 (16H), 4.00–4.36 (4H), 4.65–4.80 (2H), 6.05–6.25 (4H), 6.90–7.07 (5H); MALDI-TOF MS found [M+Na]<sup>+</sup> = 1605.3 + 790.8 *n* (*n* = 1–



10),  $1256.5 + 790.8 n$  ( $n = 1-10$ ). The calculated molecular weight of the repeating unit is 790.9.

#### 2.7.2. Polymer **3c**

**3c** (828 mg, 90%) was obtained in a manner similar to that of entry 12, Table 1 under the following conditions: 2,2'-bis[4-(4-maleimidophenoxy)phenyl]propane (**1c**) (571 mg, 1.0 mmol), **2** (1.0 mmol), *m*-cresol (0.16 mL), 120 mM solution of TfOH in *m*-cresol (840  $\mu$ L, 0.10 mmol). **3c**: a white powder; IR (KBr) 1114, 1151, 1172, 1195, 1239, 1386, 1499, 1595, 1609, 1715, 2965  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.65–1.71 (6H), 2.08–2.20 (1H), 2.20–2.40 (1H), 2.68–2.89 (2H), 3.02–3.22 (2H), 3.65–4.00 (14H), 4.07–4.25 (2H), 4.50–4.71 (2H), 5.90–6.20 (4H), 6.86–7.10 (9H), 7.14–7.34 (overlapped with  $\text{CHCl}_3$ ); MALDI-TOF MS found  $[\text{M}+\text{Na}]^+ = 1861.3 + 918.6 n$  ( $n = 1-6$ ). The calculated molecular weight of the repeating unit is 919.0.

#### 2.7.3. Polymer **5a**

**5a** (398 mg, 61%) was obtained in a manner similar to that of entry 12, Table 1 under the following conditions: **1a** (1.0 mmol), **4** (1.0 mmol), *m*-cresol (0.25 mL), 240 mM solution of TfOH in *m*-cresol (420  $\mu$ L, 0.10 mmol). **5a**: a white powder; IR (KBr) 677, 825, 1151, 1195, 1385, 1514, 1585, 1714, 2840, 2942  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.72–3.38 (4H), 3.54–4.10 (20H), 4.38–4.80 (2H), 6.00–6.40 (6H), 6.78–6.88 (1.2H), 6.96–7.40 (overlapped with  $\text{CHCl}_3$ ); MALDI-TOF MS found  $[\text{M}+\text{Na}]^+ = 1320.4 + 648.7 n$  ( $n = 1-7$ ),  $1611.0 + 648.6 n$  ( $n = 1-4$ ),  $1679.3 + 648.5 n$  ( $n = 1-5$ ). The calculated molecular weight of the repeating unit is 648.7.

#### 2.7.4. Polymer **5b**

**5b** (604 mg, 82%) was obtained in a manner similar to that of entry 12, Table 1 under the following conditions: **1b** (1.0 mmol), **4** (1.0 mmol), *m*-cresol (0.25 mL), 240 mM solution of TfOH in *m*-cresol (420  $\mu$ L, 0.10 mmol). **5b**: a white powder; IR (KBr) 802, 1116, 1151, 1194, 1221, 1375, 1420, 1464, 1482, 1598, 1714, 2938, 2967  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.02–1.26 (7H), 1.96–2.62 (12H), 2.94–3.28 (4H), 3.56–4.01 (18H), 4.52–4.88 (2H), 6.12–6.40 (4.5H), 6.85–6.88 (0.2H), 6.90–7.10 (4.5H); MALDI-TOF MS found  $[\text{M}+\text{Na}]^+ = 1779.5 + 733.0 n$  ( $n = 1-12$ ),  $1488.8 + 732.9 n$  ( $n = 1-11$ ),  $1597.0 + 733.0 n$  ( $n = 1-11$ ). The calculated molecular weight of the repeating unit is 732.8.

#### 2.7.5. Polymer **5c**

**5c** (768 mg, 89%) was obtained in a manner similar to that of entry 12, Table 1 under the following conditions: **1c** (1.0 mmol), **4** (1.0 mmol), *m*-cresol (0.58 mL), 240 mM

solution of TfOH in *m*-cresol (420  $\mu$ L, 0.10 mmol). **5c**: a white powder; IR (KBr) 833, 1151, 1173, 1194, 1241, 1386, 1499, 1597, 1716, 2941, 2966  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.62–1.78 (7H), 2.68–3.40 (4H), 3.58–4.00 (17H), 4.38–4.80 (2H), 6.02–6.42 (5H), 6.82–7.12 (10H), 7.16–7.32 (overlapped with  $\text{CHCl}_3$ ); MALDI-TOF MS found  $[\text{M}+\text{Na}]^+ = 1162.6 + 861.1 n$  ( $n = 1-9$ ),  $1745.3 + 861.1 n$  ( $n = 1-8$ ),  $1853.6 + 861.1 n$  ( $n = 1-8$ ). The calculated molecular weight of the repeating unit is 860.9.

## 2.8. Measurements

Melting points were measured on an MPA 100 apparatus (Stanford Research Systems, Sunnyvale, CA, USA). Infrared (IR) spectra were recorded on a JASCO FT/IR-460 spectrometer (JASCO, Tokyo). Nuclear magnetic resonance (NMR) spectra were measured on a JEOL JNM-ECA500 instrument (JEOL, Tokyo). The concentration of each NMR sample of **7**, **9a**, **9b**, and a mixture of **9a** and **9b** was set at approximately 15 mg/0.67 mL in  $\text{CDCl}_3$ .

The chemical shifts of  $^1\text{H}$  NMR in  $\text{CDCl}_3$  and  $\text{CD}_3\text{CN}$  are expressed in parts per million (ppm) relative to  $\delta$  7.26 and 1.94 [in  $^{13}\text{C}$  NMR, relative to  $\delta$  77.16 and 118.26] [21]. Signal patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. However, these indications are not applied to the signal patterns of the polymers. HRMS measurements were performed on a JEOL JMS-700 (FAB) or JEOL JMS-T100GCV (EI) instrument.

Gel permeation chromatography (GPC) was performed with a JASCO LC-2000Plus system comprising a DG-2080-53 degasser, a PU-2080Plus pump, an AS-2055Plus automatic injector, a CO-2065Plus column oven, and an RI-2031Plus refractive index detector (JASCO). A guard column (Shodex GPC K-D), two GPC columns (Shodex GPC K-806L), and a solvent-peak separation column (Shodex GPC K-800D) were used for the analyses under the following conditions: eluent,  $\text{CHCl}_3$  (>99.0%) stabilized with EtOH (0.5%); flow rate, 1.0  $\text{mL min}^{-1}$ ; temperature, 40  $^\circ\text{C}$ ; injection volume, 100  $\mu\text{L}$ ; concentration of polymer sample, 3  $\text{mg mL}^{-1}$ . The molecular weights were calibrated to polystyrene standards.

MALDI-TOF MS measurements of the polymers were performed on an ultrafleXtreme mass spectrometer (Bruker, Billerica, MA, USA). The instrument was operated in linear positive-ion mode. Samples were prepared by mixing 2  $\mu\text{L}$  of polymers (1 mg in  $\text{CHCl}_3$  (0.2 mL)), 8  $\mu\text{L}$  of dithranol (10 mg in THF (1 mL)) as a matrix, and 1  $\mu\text{L}$  of NaI (2 mg

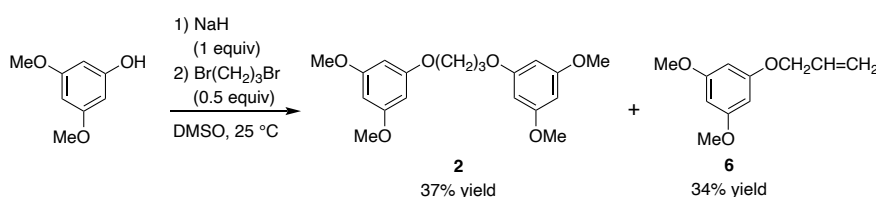
in THF (1 mL)) as a cationizer. The resulting mixtures (1  $\mu$ L) were spotted on the MALDI sample plate, air dried, and analyzed.

Differential scanning calorimetry (DSC) was performed with a DSC7020 (Hitachi High-Tech, Tokyo) to measure glass transition temperatures ( $T_g$ ) at a heating rate of 20  $^{\circ}$ C/min. The DSC measurements were repeated until the DSC profiles were the same. Thermogravimetry/differential thermal analysis (TG/DTA) was performed with a TG/DTA7000 (Hitachi High-Tech) to measure decomposition temperatures with 10% weight loss ( $T_{d10}$ ) under nitrogen or air flow (100 mL/min) at a heating rate of 10  $^{\circ}$ C/min.

### 3. Results and discussion

#### 3.1. Synthesis of monomers

As a novel nucleophilic monomer, 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**) was prepared by the sequential S<sub>N</sub>2 reactions between 3,5-dimethoxyphenol and 1,3-dibromopropane in the presence of sodium hydride (Scheme 4) [18]. The reaction provided compound **2** in 37% yield and olefin byproduct **6** [19] in a similar yield. 5,5'-Oxybis(1,3-dimethoxybenzene) (**4**) (Scheme 3) was synthesized according to the reported method [16,17].



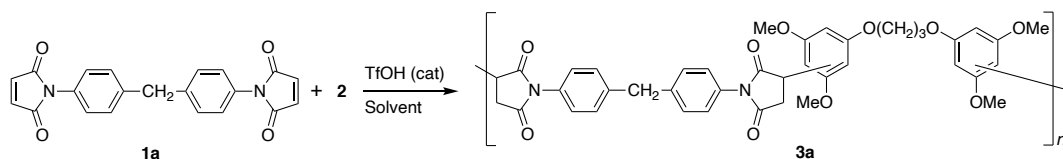
**Scheme 4.** Synthesis of 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**).

#### 3.2. Optimization of polymerization

As shown in Table 1, a combination of 4,4'-bismaleimidodiphenylmethane (**1a**) and 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**) was selected to optimize conditions as a model reaction, focusing on the effects of solvents, monomer concentrations, catalyst loading, and reaction time. The polymerization conditions were basically screened by gel permeation chromatography (GPC) measurements of the polymers. On the basis of our 1,4-addition of 1,3,5-trimethoxybenzene to maleimides [15], the reaction was first performed in toluene under the conditions of [**1a**] = [**2**] = 0.25 M, [TfOH] = 25 mM (10 mol%), and 100 °C (entry 1). TLC analysis of the reaction mixture after 1 day showed remaining spots of monomers **1a** and **2**, indicating that the reaction rate was slow. In addition, a white powder precipitation, probably due to the formation of short oligomers, was observed in the reaction mixture. The low solubility of these products might inhibit the growth of polymers. DCE was examined to enhance the solubility of the growing polymer (entries 2–4). With monomer concentrations of 0.25 M, the product was obtained in 79% yield, and its number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and molar-mass dispersity ( $D_M$ ) were estimated to be  $0.62 \times 10^4$ ,  $6.0 \times 10^4$ , and 9.7, respectively (entry 3). These results suggested that the solubility of the growing polymer was one of the crucial factors in polymerization. Next, the effect of the

concentration was investigated. When the concentrations of the starting materials were doubled, the  $M_n$  value also increased more than twofold, but the  $D_M$  value exceeded 30 (entry 4). The reason for the large increase in  $D_M$  could be the formation of branched polymers, as judged by the GPC chromatogram [22]. Branched polymers could have been formed by 1,4-addition of the intermediary enolates (carboanions) to maleimide moieties due to the lack of sufficient proton sources [12]. On the other hand, when the concentrations were diluted to 0.10 M, the  $M_n$  value decreased with a smaller  $D_M$  value of 4.1 (entry 2).  $M_n$  and  $D_M$  were significantly affected by the monomer concentrations. To obtain longer polymers with low  $D_M$  values, the solvent was changed to *m*-cresol [23], which has frequently been employed for the synthesis of polyaspartimides to protonate enolate intermediate anions [8,24]. With monomer concentrations of 0.25 M, the  $M_n$  value was ca. 4000 with a  $D_M$  value of 1.9 (entry 5). When the concentrations were doubled (entry 6) and the reaction time was increased to 4 days (entry 7), the  $M_n$  values increased while keeping the  $D_M$  values near 2. The concentration and the reaction time were set to 0.5 M and 4 days, respectively, and the effect of catalyst loading was investigated (entries 7–9). When the loading was decreased to 5 mol%, the  $M_n$  value decreased by more than 10% (entry 8). When the catalyst was increased to 20 mol%, the polymer became shorter and the yield decreased dramatically (entry 9). Therefore, the catalyst loading was fixed at 10 mol%. When the scale was increased to threefold that of entry 7, the  $M_n$  value decreased by 20% (entry 10 vs entry 7). Finally, the monomer concentrations were further increased to 1.0 M (entry 11) and 1.5 M (entry 12) to afford longer polymers with approximate  $M_n$  values of  $0.50 \times 10^4$  and  $0.80 \times 10^4$ , respectively. Under the conditions of entry 12, the reaction mixture became too viscous to stir after a few hours, at which point the reaction was stopped. The monomer concentration had a greater effect than the reaction time. Thus, in the combination of **1a** and **2**, we selected entry 12 as the optimized conditions [23]. When applied to other monomers, the concentrations of these optimized conditions were modified because the solubility of the growing polymers depended on the structures (vide infra).

**Table 1.** Polymerization of 4,4'-bismaleimidodiphenylmethane (**1a**) and 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**).<sup>a</sup>



Entry	Solvent	[ <b>1a</b> ] <sup>a</sup> , M	[TfOH], mol%	Temp., °C	Time, d	$M_n \times 10^{-4}$	$D_M$	Yield, %
1 <sup>b</sup>	toluene	0.25	10	100	1	— <sup>c</sup>	— <sup>c</sup>	83
2 <sup>b</sup>	DCE	0.10	10	85	1	0.29	4.1	83
3 <sup>b</sup>	DCE	0.25	10	85	1	0.62	9.7	79
4 <sup>b</sup>	DCE	0.50	10	85	1	1.4	31	89
5 <sup>b</sup>	<i>m</i> -cresol	0.25	10	100	1	0.40	1.9	88
6 <sup>b</sup>	<i>m</i> -cresol	0.50	10	100	1	0.47	2.1	84
7 <sup>b</sup>	<i>m</i> -cresol	0.50	10	100	4	0.55	2.2	84
8 <sup>b</sup>	<i>m</i> -cresol	0.50	5	100	4	0.47	2.2	83
9 <sup>b</sup>	<i>m</i> -cresol	0.50	20	100	4	0.38	2.0	38
10 <sup>d</sup>	<i>m</i> -cresol	0.50	10	100	4	0.44	2.2	92
11 <sup>d</sup>	<i>m</i> -cresol	1.0	10	100	2	0.50	2.3	89
12 <sup>d</sup>	<i>m</i> -cresol	1.5	10	100	0.10	0.80	2.2	94

<sup>a</sup>The reaction was set up using equivalent concentrations of each monomer.

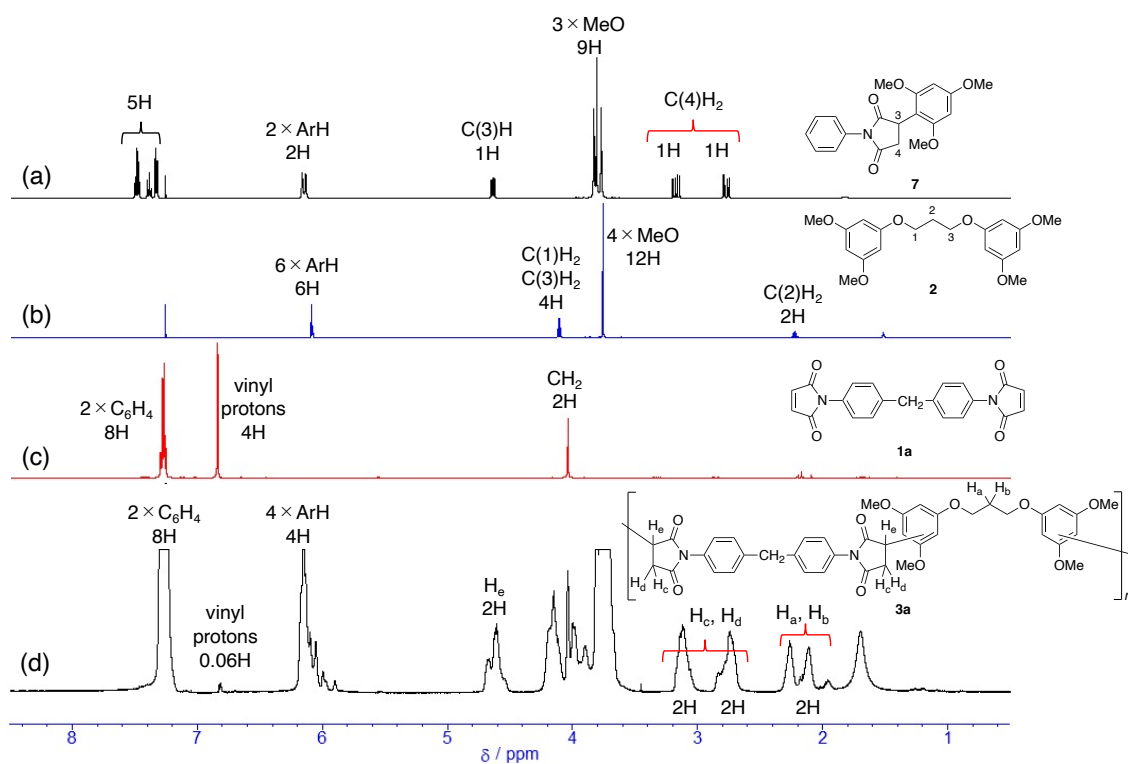
<sup>b</sup>The reaction was conducted in a 12-mL screw vial under air on a 0.30-mmol scale.

<sup>c</sup>Not determined.

<sup>d</sup>The reaction was conducted in a 20-mL Schlenk tube under argon on a 1.0-mmol scale.

### 3.3. Structural determination of polymer **3a**

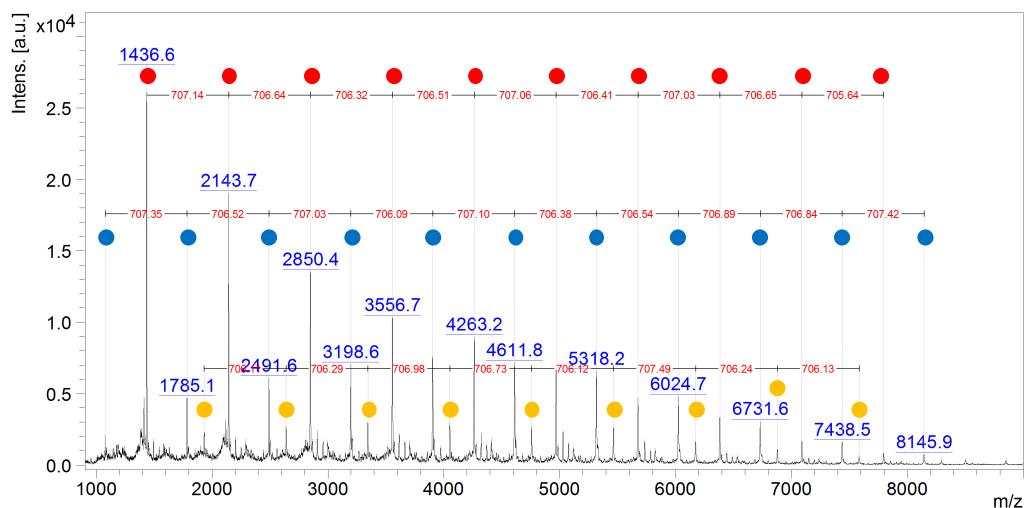
The structure of **3a** obtained in entry 12 of Table 1 was confirmed by  $^1\text{H}$  NMR and MALDI-TOF MS measurements. As shown in Figure 1, the  $^1\text{H}$  NMR spectrum of **3a** was compared with those of *N*-phenyl-3-(2,4,6-trimethoxyphenyl)succinimide (**7**) [15] and two monomers, **2** and **1a**. All the signals of **3a** were broad, and the vinyl protons observed at  $\delta$  6.84 of **1a** almost disappeared in Figure 1 (d), indicating the formation of the polymer. Characteristic aliphatic protons of the newly generated succinimide moieties, labeled  $\text{H}_c$ ,  $\text{H}_d$ , and  $\text{H}_e$ , were observed with the same intensity in the regions of  $\delta$  2.67–2.86, 3.03–3.19, and 4.51–4.71. These chemical shifts are similar to those of protons at the 3- and 4-positions of compound **7**, which suggests that **3a** was formed via the 1,4-addition. Broad aromatic protons were observed in the regions of  $\delta$  5.90–6.19 and 7.19–7.32, which originated from monomers **2** and **1a**, respectively. The integral value of the former was calculated to be 4H, suggesting that the two monomers were polymerized equally on average. The latter showed a signal corresponding to 8H, although it overlapped with the chloroform signal [25]. The methylene protons labeled  $\text{H}_a$  and  $\text{H}_b$  of **3a** were separately observed to be close to the chemical shift of C(2) protons of **2**. The vinyl protons at the end group(s) were observed in the region of  $\delta$  6.80–6.83. The integral ratio of the vinyl protons and  $\text{H}_e$  protons is 1:33, which is consistent with the mass-average degree of polymerization of 25 calculated from  $M_w$  ( $1.8 \times 10^4$ ) and the molecular weight of the building unit (707). This supports the idea that linear polymers were indeed produced. The other protons of **3a** appeared in the region of  $\delta$  3.64–4.24.



**Figure 1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectra of (a) *N*-phenyl-3-(2,4,6-trimethoxyphenyl)succinimide (**7**), (b) 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**), (c) 4,4'-bismaleimidodiphenylmethane (**1a**), and (d) polymer **3a** (30 mg/0.67 mL  $\text{CDCl}_3$ ). The number in front of each “H” indicates the number of protons.

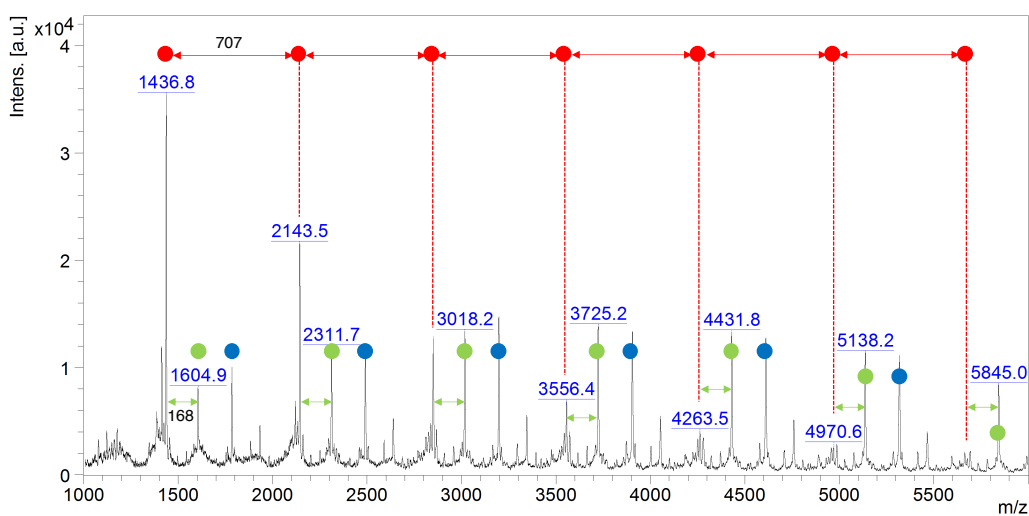


The MALDI-TOF MS spectrum was consistent with the formation of linear polymers with two kinds of end groups originating from the two monomers **1a** and **2** (Figure 2). The following three series of molecular ion peaks were detected as sodium-cationized molecules. The first series of molecular ion peaks, marked by red circles, increased by 706.6 on average, which was consistent with the calculated molecular weight of the repeating structure, and correspond to polymers with a maleimide group at one end and a trialkoxybenzene group at the other. The second series, marked by blue circles, which are weaker in intensity, correspond to polymers with trialkoxybenzene groups at both ends. The third series, marked by orange circles, are considered fragment peaks corresponding to the series of peaks marked by red circles.



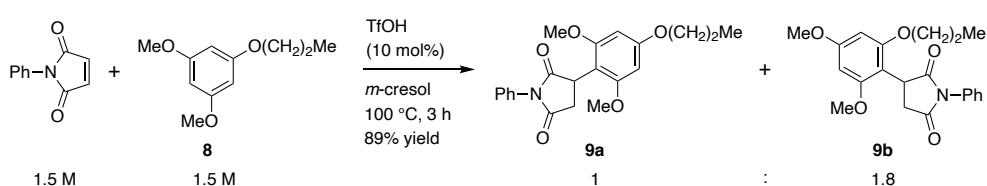
**Figure 2.** MALDI-TOF MS spectrum of polymer **3a**.

It is known that cyclic polymers are formed in step growth polymerizations [26,27]. In our polymerization, cyclic polymers could not accept any nucleophile, while linear polymers having a maleimide moiety at one or both ends are expected to accept nucleophiles such as 1,3,5-trimethoxybenzene ( $F_w = 168.2$ ) [28]. To gain further insights into the formation of cyclic polymers, polymer **3a** was reacted with an excess amount of 1,3,5-trimethoxybenzene in DCE under acidic conditions [15]. The resulting polymers were collected and analyzed by  $^1\text{H}$  NMR and MALDI-TOF MS. The  $^1\text{H}$  NMR spectrum showed that the vinyl protons disappeared, indicating that the 1,4-addition was completed [22]. As shown in Figure 3, new peaks marked with green circles corresponding to 1,3,5-trimethoxybenzene-added polymers were observed at positions where the  $m/z$  increased by 168 over the original peaks marked with red circles on polymer **3a**. The remaining peaks marked with red circles could be assigned to the cyclic polymers. These peaks gradually disappeared toward the high molecular weight region [22].



**Figure 3.** MALDI-TOF MS spectrum of the polymer obtained by addition of an excess amount of 1,3,5-trimethoxybenzene to polymer **3a** with TfOH. The peaks marked with green circles correspond to 1,3,5-trimethoxybenzene-added polymers. The spectrum in the  $m/z$  range of 6000–10000 is shown in the supplementary data.

To estimate the regioselectivity on the benzene ring in the polymerization via the 1,4-addition, a model reaction with *N*-phenylmaleimide and 1-(3,5-dimethoxyphenoxy)propane (**8**) was conducted as shown in Scheme 5. Under the optimized conditions in Table 1, an isomeric mixture of 1,4-adducts, **9a** and **9b** [22], was obtained at a ratio of 1:1.8, reflecting the number of reaction sites. This result suggests that polymer **3a** would be a mixture of various isomers at each benzene ring with the newly formed C–C bonds being found more frequently at the ortho rather than the para.



**Scheme 5.** 1,4-Addition of 1-(3,5-dimethoxyphenoxy)propane (**8**) to *N*-phenylmaleimide in *m*-cresol.

### 3.4. Synthesis of other polymers

Two polymers, **3b** and **3c**, were synthesized from bismaleimides, **1b** and **1c**, with 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**) as shown in Table 2. Although the monomer concentration under the optimized conditions in Table 1 was found to be 1.5 M, we started from 1.0 M because the solubility of the polymer in *m*-cresol might depend on the bismaleimide. When **1b** and **2** were reacted at a concentration of 1.0 M each, **3b** was obtained in a moderate yield with an  $M_n$  value of  $0.28 \times 10^4$ . The  $M_n$  value increased significantly, to  $0.95 \times 10^4$ , when the concentration of the monomers was increased to 1.5 M. In these cases, the  $D_M$  value was around 2. Reaction with **1c** at a concentration of 1.0 M provided polymer **3c** with an  $M_n$  value of  $1.5 \times 10^4$  after only 2.5 h, which indicated that the monomer concentrations were maximized in this case. Here, the  $D_M$  value was calculated to be 3.9, which was larger than those of **3a** and **3b**.

When 5,5'-oxybis(1,3-dimethoxybenzene) (**4**) was employed as a monomer, the  $M_n$  values of polymers **5a–5c** were less than  $0.4 \times 10^4$  (Table 2), probably due to the lower nucleophilicity and flexibility of **4** compared to those of **2**. The monomer concentration was set at 1.5 M for polymers **5a** and **5b**, while a 1.0 M solution of each monomer was employed for polymer **5c**, similar to the case with **3c**.

<sup>1</sup>H NMR and MALDI-TOF MS spectra of **3b**, **3c**, and **5a–5c** were consistent with the structures depicted in Scheme 3. In all the MS spectra, molecular ion peaks of polymers with a maleimide group at one end and a trialkoxybenzene group at the other were clearly detected, as in the spectrum of polymer **3a**. Moreover, additional series of molecular ion peaks were observed for polymers **5a–5c**, probably due to the lower degrees of polymerization compared to those of polymers **3a–3c**: molecular ion peaks of polymers with maleimide moieties at both ends were observed for polymer **5a**, and those of polymers ending with diaryl ether moieties were observed for polymers **5b** and **5c** [22].

**Table 2.** Synthesis of polymers via the 1,4-addition of 1,3-bis(3,5-dimethoxyphenoxy)propane (**2**) or 5,5'-oxybis(1,3-dimethoxybenzene) (**4**) to bismaleimides.<sup>a</sup>

Monomers	Monomer concentration, M	Time, h	Polymer	$M_n \times 10^{-4}$	$D_M$	Yield, %
<b>1b</b> and <b>2</b>	1.0	48	<b>3b</b>	0.28	1.9	75
<b>1b</b> and <b>2</b>	1.5	2.5	<b>3b</b>	0.95	2.1	91
<b>1c</b> and <b>2</b>	1.0	2.5	<b>3c</b>	1.5	3.9	90
<b>1a</b> and <b>4</b>	1.5	24	<b>5a</b>	0.14	1.4	61
<b>1b</b> and <b>4</b>	1.5	2.5	<b>5b</b>	0.39	1.6	82
<b>1c</b> and <b>4</b>	1.0	24	<b>5c</b>	0.26	1.9	89

<sup>a</sup>The reaction was conducted in a 20-mL Schlenk tube in *m*-cresol under argon on a 1.0-mmol scale with the same concentration of each monomer at 100 °C. See Scheme 3 for the linker structure R of bismaleimides **1a–1c**.

### 3.5. Physical properties of polymers

Glass transition temperatures ( $T_g$ ) and decomposition temperatures at 10% weight loss ( $T_{d10}$ ) were measured to investigate the thermal properties of the synthesized polymers, except for polymers **5a** and **5c**, which had lower degrees of polymerization. As shown in Table 3, the  $T_g$  values of polymers **3a–3c** were in the range of 183–192 °C, lower than those of polyaspartimides with a similar  $M_n$  value synthesized from aromatic diamines and bismaleimide **1b** [24]. The flexible methylene chains of **3a–3c** might be attributable to the lower  $T_g$  values. On the other hand, the  $T_g$  value of polymer **5b** was 227 °C, higher than those of **3a–3c**. This is due to the more rigid diphenyl ether moiety in the polymer chain [30]. The  $T_{d10}$  values of the polymers were determined to be higher than 400 °C, which indicates excellent thermal stability [31] because of the presence of stable fragments such as succinimide structures [2] and methoxybenzenes [30]. In addition,  $T_{d10}$  values under nitrogen flow and air flow were almost the same, suggesting that oxidation of the polymers did not occur under air flow [32].

**Table 3.** Thermal properties of polymers.

Polymer	$T_g$ , °C	$T_{d10}$ , °C	
		In N <sub>2</sub>	In air
<b>3a</b> <sup>a</sup>	185	422	417
<b>3b</b> <sup>b</sup>	192	426	425
<b>3c</b>	183	422	419
<b>5b</b>	227	441	441

<sup>a</sup>The polymer sample obtained in entry 12 in Table 1 was used.

<sup>b</sup>The polymer sample with  $M_n$  of 9500 was used.

The solubility of polyimides at room temperature in organic solvents with various solvent polarity index  $E_T(30)$  values [33,34] is shown in Table 4. Most of the polymers were soluble in *m*-cresol; polar aprotic solvents such as DMSO, DMF, NMP, and pyridine; and chlorinated solvents as well as cyclohexanone. Comparing the solubilities of **3a** and **3b**, it is clear that the alkyl groups at the benzene rings of the bismaleimide improve solubility.

**Table 4.** Solubility of polymers.

Solvent	$E_T(30)^a$	Solubility <sup>b</sup>					
		<b>3a</b> <sup>c</sup>	<b>3b</b> <sup>d</sup>	<b>3c</b>	<b>5a</b>	<b>5b</b>	<b>5c</b>
<i>m</i> -cresol	52.4	+	+	+	+	+	+
DMSO	45.1	+	+	+	+	+	+
DMF	43.2	+	+	+	+	+	+
NMP	42.2	+	+	+	+	+	+
acetone	42.2	–	+	–	+	+	–
DCE	41.3	+	+	+	+	+	+
pyridine	40.5	+	+	+	+	+	+
cyclohexanone	39.8	+	+	+	+	+	+
CHCl <sub>3</sub>	39.1	+	+	+	+	+	+
THF	37.4	–	+	+	+	+	+

<sup>a</sup>From references 33 and 34.

<sup>b</sup>Each polymer (2.5 mg) was mixed in a 1-mL microtube (8 mm × 50 mm) with the solvents (1.0 mL) listed at 27–28 °C, and solubility was determined visually: +, dissolved, –, not dissolved.

<sup>c</sup>The polymer sample obtained in entry 12 in Table 1 was used.

<sup>d</sup>The polymer sample with  $M_n$  of 9500 was used.

#### 4. Conclusions

Novel methoxybenzene-linked polyimides were synthesized via 1,4-addition of 1,3-bis(3,5-dimethoxyphenoxy)propane or 5,5'-oxybis(1,3-dimethoxybenzene) to several bismaleimides with a catalytic amount of TfOH. The polymerization conditions were optimized by a combination of 4,4'-bismaleimidodiphenylmethane and newly synthesized 1,3-bis(3,5-dimethoxyphenoxy)propane. To obtain longer polymers with low  $D_M$  values, the use of *m*-cresol as a solvent and high concentrations of the monomers was essential. Polyimides obtained under the optimized conditions had an  $M_n$  value of ca. 8000 with a  $D_M$  value of 2.2. The use of different bismaleimides provided polyimides having  $M_n$  values of 9500 and 15000 with  $D_M$  values of 2.1 and 3.9, respectively. However, polymerization with 5,5'-oxybis(1,3-dimethoxybenzene) as a nucleophilic monomer under the above optimized conditions provided polyimides with  $M_n$  values of less than 4000. In general, the reason for the insufficient molecular weights was likely to be the low solubility of the polymers in *m*-cresol, as judged by the high viscosity of the mixture at the end of the reaction. We think that replacement of *m*-cresol with less polar phenol derivatives as solvents would improve the molecular weights. Our polymerization results indicated that the spacer structure of the nucleophilic monomer could affect the degree of polymerization significantly. The structural determination was performed by  $^1\text{H}$  NMR and MALDI-TOF MS measurements. In addition, the polyimides are a mixture of regioisomers, as judged by the model reaction between 1-(3,5-dimethoxyphenoxy)propane and *N*-phenylmaleimide. These new methoxybenzene-linked polyimides showed a high potential for thermostability: their 10% weight loss temperatures were more than 400 °C. The glass transition temperatures were around 200 °C, and were thus lower than the glass transition temperatures of polyaspartimides. These polymers featured a wide range of solubility in organic solvents such as *m*-cresol, DMF, pyridine, and chloroform, which would be beneficial for polymer processing. Our study provided a new polymerization method and polyimides from bismaleimide and trialkoxybenzenes. Trialkoxybenzenes are components of lignin [35], and therefore, the resulting polymers would show biodegradability. Further applications using our TfOH-catalyzed 1,4-addition are in progress.

### **Acknowledgments**

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### **Supplementary data**

Supplementary data, including the detailed experimental procedures and spectral data related to this article, can be found in online at the journal's homepage.



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