

NOTES

## Synthesis of Optically Active Aromatic Poly(ether ketone)s via Nucleophilic Aromatic Substitution Polymerization

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2,2'-Disubstituted 1,1'-binaphthyls such as BINAP have axial asymmetry and have been applied to asymmetric organic reactions.<sup>1</sup> Polymeric binaphthylene derivatives are requisite for recyclable asymmetric organic catalysts and materials. There have been several reports on polymers containing 2,2'-disubstituted 1,1'-binaphthylene units in the main chains, *e.g.* polyphenylenes, polycarbonates, polyamides, polyarylates, and polyimides.<sup>2–8</sup> On the other hand, aromatic polyketones such as poly(ether ketone), *i.e.*, PEEK<sup>®</sup> have much attention in the field of high-performance materials.<sup>9–12</sup> We have also studied on the syntheses of wholly aromatic polyketones *via* electrophilic aromatic substitution acylation polymerization<sup>13–18</sup> or *via* nickel-complex mediated aromatic coupling polymerization.<sup>19–23</sup> However, there have been no reports on the syntheses of aromatic polyketones containing 2,2'-disubstituted 1,1'-binaphthylene units. Introduction of these optically active units to aromatic polyketones would contribute to creation of novel types of high-performance chiral reagents and materials.

In this paper, we would like to report successful synthesis of aromatic poly(ether ketone)s containing 2,2'-dimethoxy-1,1'-binaphthyl-6,6'-ene unit in the main chains *via* regioselective bis(4-fluorobenzylation) of (*S*)-2,2'-dimethoxy-1,1'-binaphthyl (**1**) and the nucleophilic aromatic substitution polymerization of the resulting bis(fluorobenzyloxy) binaphthyl (**3**) with aromatic diols **4**.

## EXPERIMENTAL

### General

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-AL300 (H, 300 MHz; C, 75 MHz). Chemical shifts are expressed in ppm relative to internal standards of Me<sub>4</sub>Si (H;  $\delta$ , 0.00) and CDCl<sub>3</sub> (C;  $\delta$ , 77.0). IR measurement was recorded on a JEOL FR/IR-5300. Inherent viscosities ( $\eta_{inh}$ ) were determined in a concentrated H<sub>2</sub>SO<sub>4</sub> (0.3 g dL<sup>-1</sup>) solution at 30 °C using an Ostwald viscometer. Glass transition temperatures ( $T_g$ 's) were determined on the basis of DSC curves. DSC curves were recorded on a SEIKO DSC-200 differential scanning calorimeter with a heating rate of 10 K min<sup>-1</sup> under nitrogen. Thermal degradation temperature ( $T_d$ ) was determined on the basis of a TGA thermogram. The TGA thermogram was recorded on a SEIKO TG/DTA-200 thermogravimeter with a heating rate of 10 K min<sup>-1</sup>. P<sub>2</sub>O<sub>5</sub>-MsOH mixture was prepared according to Eaton's procedure.<sup>24</sup>

### 6,6'-Bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (**3**)

2,2'-Dimethoxy-1,1'-binaphthyl (**1**, 0.2 mmol, 63 mg) and 4-fluorobenzoic acid (**2**, 0.4 mmol, 56 mg) were placed to a two-necked flask under nitrogen atmosphere. To the flask, P<sub>2</sub>O<sub>5</sub>-MsOH (0.4 mL) was added. The reaction mixture was stirred for 24 h at rt or 60 °C. The reaction mixture was poured into water slowly. The mixture was extracted with chloroform three times and the extracts were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent

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was removed under reduced pressure. Recrystallization from chloroform/ethanol afforded a white powder of binaphthyl **3** quantitatively.

IR  $\nu$  (KBr): 1655, 1599, 1477, 1277, 1249  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 3.83 (3H, s), 7.17 (2H, d,  $J = 8.4$  Hz), 7.19 (4H, t,  $J = 8.4$  Hz), 7.54 (2H, d,  $J = 8.8$  Hz), 7.69 (2H, d,  $J = 8.8$  Hz), 7.90 (4H, dd,  $J = 5.4, 8.4$  Hz), 8.09 (2H, d,  $J = 8.8$  Hz), 8.30 (2H, s) ppm.  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 56.6, 115.4, 118.8, 125.4, 126.3, 127.7, 131.5, 132.5, 132.6, 134.3, 136.0, 157.1, 166.1, 195.0 ppm. Anal. Calcd. for  $\text{C}_{36}\text{H}_{24}\text{F}_2\text{O}_4$ : C, 77.41%; H, 4.33%. Found: C, 77.42%; H, 4.23%.

*Polymerization of 6,6'-Bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (3) with Arenediol (2) through Nucleophilic Aromatic Substitution Reaction*

To a two-necked flask, 6,6'-bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (**3**, 0.2 mmol), aromatic diol (**4**, 0.2 mmol), and potassium carbonate (1.0 mmol) were placed. Freshly distilled NMP (0.5 mL) was added to the flask. The mixture was stirred at 170 °C for 6 h. Reaction mixture was poured into 5 wt % sodium hydroxide solution and the mixture was extracted with  $\text{CHCl}_3$  three times. The combined extracts were washed with water and dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The precipitates were collected by suction filtration and dried *in vacuo* at 120 °C to give a pale yellow solid of polymer **5**.

**Polyketone 5a**: IR  $\nu$  (KBr): 1651, 1595, 1493, 1226  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 3.81 (6H, s), 7.07 (4H, d,  $J = 8.4$  Hz), 7.14 (4H, s), 7.18 (2H, d,  $J = 8.7$  Hz), 7.52 (2H, d,  $J = 8.7$  Hz), 7.68 (2H, d,  $J = 8.7$  Hz), 7.88 (4H, d,  $J = 8.4$  Hz), 8.08 (2H, d,  $J = 8.7$  Hz), 8.31 (2H, s) ppm.  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 56.6, 114.4, 117.0, 118.9, 121.6, 125.3, 126.5, 127.8, 131.4, 132.1, 132.4, 132.6, 132.9, 135.9, 152.1, 156.9, 161.4, 195.2 ppm. Anal. Calcd. for  $(\text{C}_{42}\text{H}_{28}\text{O}_6)_n$ : C, 80.24%; H, 4.49%. Found: C, 79.69%; H, 4.43%.

**Polyketone 5b**: IR  $\nu$  (KBr): 1651, 1487, 1217  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 3.81 (6H, s), 7.02–7.11 (12H, m), 7.17 (2H, d,  $J = 8.4$  Hz), 7.51 (2H,

d,  $J = 8.4$  Hz), 7.67 (2H, d,  $J = 8.4$  Hz), 7.86 (4H, d,  $J = 8.1$  Hz), 8.07 (2H, d,  $J = 8.4$  Hz), 8.30 (2H, s) ppm.  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 56.6, 114.4, 116.8, 118.9, 120.1, 121.6, 125.3, 126.5, 127.8, 131.4, 132.0, 132.4, 132.9, 135.9, 151.0, 154.0, 156.9, 161.7, 195.2 ppm. Anal. Calcd. for  $(\text{C}_{48}\text{H}_{32}\text{O}_7)_n$ : C, 79.99%; H, 4.47%. Found: C, 79.23%; H, 4.33%.

**Polyketone 5c**: IR  $\nu$  (KBr): 1659, 1589, 1495, 1240  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 3.82 (6H, s), 7.11–7.21 (10H, m), 7.51–7.56 (2H, m), 7.67–7.71 (2H, m), 7.84–7.93 (8H, m), 8.06–8.12 (2H, m), 8.33 (2H, s) ppm.  $^{13}\text{C}$  NMR (75 MHz)  $\delta$  ( $\text{CDCl}_3$ ): 56.6, 114.5, 118.6, 118.7, 118.8, 125.4, 126.4, 127.8, 131.5, 132.2, 132.3, 132.4, 132.6, 133.8, 136.0, 157.0, 159.6, 159.9, 194.1, 195.1 ppm. Anal. Calcd. for  $(\text{C}_{49}\text{H}_{32}\text{O}_7)_n$ : C, 80.31%; H, 4.40%. Found: C, 79.92%; H, 4.22%.

## RESULTS AND DISCUSSION

6,6'-Bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl ((*S*)-**3**) was prepared *via* electrophilic aromatic substitution reaction of optically pure 2,2'-dimethoxy-1,1'-binaphthyl ((*S*)-**1**) with 4-fluorobenzoic acid (**2**) in  $\text{P}_2\text{O}_5$ -MsOH.<sup>25</sup>

Binaphthyl (*S*)-**3** was treated with hydroquinone (**4a**) in the presence of  $\text{K}_2\text{CO}_3$  in DMAc, DMF, and NMP at 150–170 °C. Degree of polymerization was estimated by measurement of inherent viscosity in a concentrated  $\text{H}_2\text{SO}_4$  solution and the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$ . The results are shown in Table I.

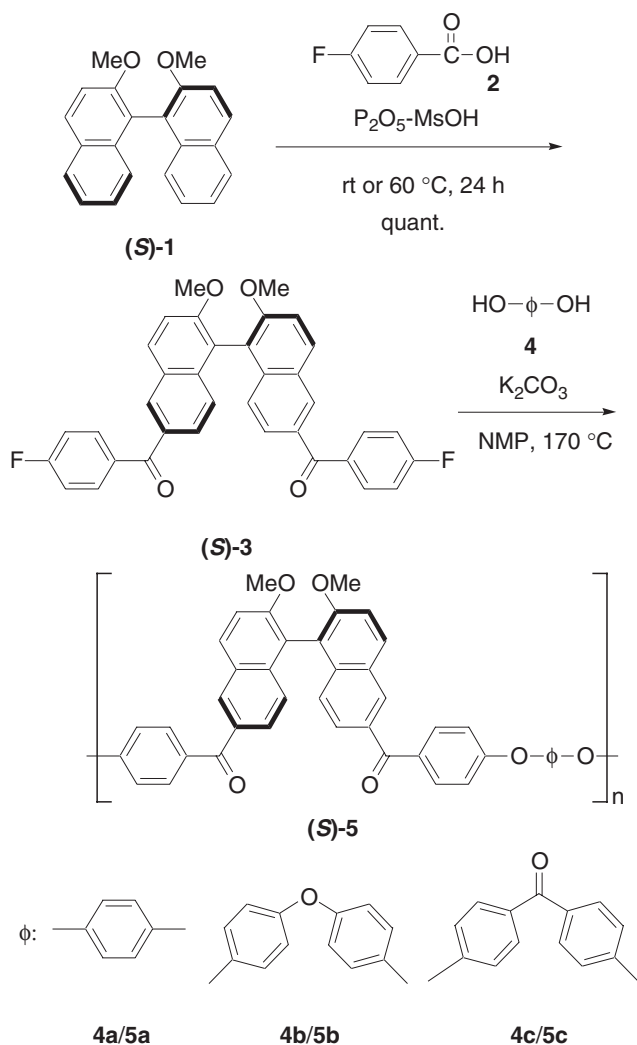
Among solvents screened, NMP was the most suitable to obtain high-molecular-weight poly(ether ketone)s. High basicity and high boiling point of the solvent are probably requisite for sustainable nucleophilic aromatic substitution polymerization. However, the slight residual signals of end groups were observed in the  $^1\text{H}$  NMR spectrum, which indicates that the polymer is a tetramer and/or a pentamer on average.

Table II shows the results of polymerization of optically active binaphthyl **3** with several aromatic diols **4**. When 4,4'-oxybisphenol (**4b**) was employed instead of hydroquinone (**4a**), the corresponding polyketone (**5b**) was obtained. The polyketone (**5b**) was a much

**Table I.** Nucleophilic aromatic substitution polymerization of hydroquinone (**4a**) with 6,6'-bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl ((*S*)-**3**)

Run	Solvent/mL	Temp./°C	Time/h	Yield/%	$\eta_{\text{inh}}/\text{dLg}^{-1}$	Film <sup>a</sup>
1	DMAc/0.5 mL	150	48	72	0.15	–
2	DMF/0.5 mL	150	48	94	0.20	+
3	NMP/0.5 mL	170	6	92	0.29	++
4	/1 mL	170	6	69	0.21	++

Reaction conditions: hydroquinone (**4a**), 0.2 mmol; (*S*)-**3**, 0.2 mmol;  $\text{K}_2\text{CO}_3$ , 1.0 mmol;  $\text{N}_2$ . <sup>a</sup>++, flexible; +, brittle; – not obtained.


**Scheme 1.**

more flexible film than polyketone **5a**. No residual signals assignable to end groups were observed in the  $^1\text{H}$  NMR spectrum of polymer **5b**. In addition, the inherent viscosity of the polyketone (**5b**) was 0.80 dL/g. These results indicate that sufficiently high-molecular-weight polyketone (**5b**) is obtained. On the other hand, polyketone **5c** obtained in the reaction of 4,4'-hydroxybenzophenone (**4c**) has almost the

same degree of polymerization as polyketone **5a**.

The specific rotation values of the resulting poly(ether ketone)s ((*S*)-**5a–c**) are shown in Table II. No drastic difference in specific rotation was observed between polymers **5a–c** and monomer (*S*)-**3a**, *i.e.*,  $76^\circ$ . Though the polymerization at high temperature has the danger of racemization, the product after stirring a DMAc solution of monomer (*S*)-**3a** and  $\text{K}_2\text{CO}_3$  at  $170^\circ\text{C}$  for 6 h had the same specific rotation value as the starting material, which indicates that no racemization occurs during polymerization.

CD spectra of polyketones (*S*)-**5a–c** and monomer (*S*)-**3** in  $\text{CHCl}_3$  are shown in Figure 1. Monomer (*S*)-**3** exhibited bisignate Cotton effects at 283 and 328 nm. However, the CD spectrum of polyketone **5a** showed a drastic decrease in intensity and those of polyketones **5b** and **5c** showed no Cotton effects. These undesirable results indicate that polyketones have no specific secondary structures such as helix. More rigid backbones than polyketones **5** will be requisite for control of secondary structures.

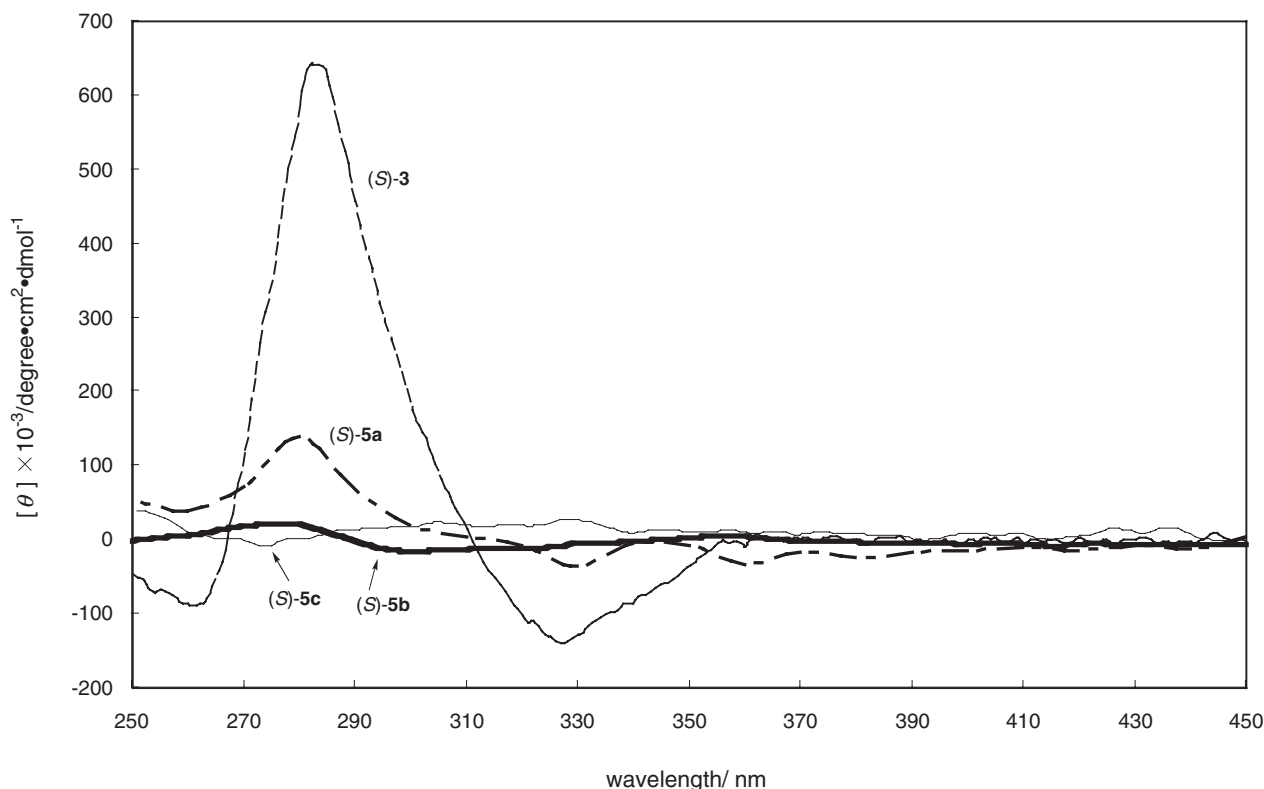
The thermal characteristics of the poly(ether ketone)s (**5**) are also shown in Table II. Glass transition temperatures are  $147\text{--}180^\circ\text{C}$ . Introduction of polar functional groups such as carbonyl and ether units raises glass transition temperatures of the polyketones. In TGA measurements, polyketones **5** were thermally stable to *ca.*  $400^\circ\text{C}$  and started to decompose gradually. The temperatures are almost the same as those where 2,2'-dimethoxy-5,5'-biphenylene-containing wholly aromatic polyketones start to decompose.<sup>15</sup> The similar thermal behavior suggests that the thermal decomposition in both polymers occur with cleavage of methoxy groups situated at 2,2'-positions as a start.

In conclusion, polymerization of 6,6'-bis(4-fluorobenzoyl)-2,2'-dimethoxybinaphthyl **3** with aromatic diol **4** in the presence of  $\text{K}_2\text{CO}_3$  proceeds with sustainable reactivity and excellent regioselectivity, giving the corresponding aromatic polyketones (**5**) containing axial asymmetry. Among aromatic polyketones screened, the polyketone derived from 4,4'-oxybiphenol was the highest-molecular-weight one.

**Table II.** Synthesis of optically active aromatic poly(ether ketone)s (*S*)-**5** via nucleophilic aromatic substitution polymerization of aromatic diols **4** with (*S*)-**3**

Run	Diol <b>4</b>	Product <b>5</b>	Yield/%	$\eta_{\text{inh}}/\text{dL g}^{-1}$ <sup>a</sup>	Film <sup>b</sup>	$[\alpha]_{\text{D}}^{25}/\text{deg}^{\text{c}}$	$T_{\text{g}}/^\circ\text{C}^{\text{d}}$	$T_{\text{d}10}/^\circ\text{C}^{\text{e}}$
1	<b>4a</b>	<b>5a</b>	92	0.29	++	+34	147	403
2	<b>4b</b>	<b>5b<sup>f</sup></b>	97	0.80	++	+31	170	404
3	<b>4c</b>	<b>5c</b>	88	0.35	++	+29	180	403

Reaction conditions: aromatic diol **4**, 0.2 mmol; (*S*)-6,6'-bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (**3**), 0.2 mmol;  $\text{K}_2\text{CO}_3$ , 1.0 mmol; NMP, 0.5 mL;  $170^\circ\text{C}$ ; under  $\text{N}_2$ . <sup>a</sup>Determined in a concentrated  $\text{H}_2\text{SO}_4$  solution (0.3 g/dL) at  $30^\circ\text{C}$ . <sup>b</sup>++, obtained as a flexible film. <sup>c</sup> $[\alpha]_{\text{D}}^{25}$  was measured in a  $\text{CHCl}_3$  solution (0.3 g/dL). <sup>d</sup>Determined on the basis of DSC curves. Heating rate: 10 K/min. <sup>e</sup>Temperature where a 10 wt % loss was recorded by TG. <sup>f</sup> $M_{\text{n}}$ : 20400.  $M_{\text{w}}$ : 118000.  $M_{\text{w}}/M_{\text{n}}$ : 5.80. Determined by GPC using narrow molecular weight PS as standards (column: Shodex KD-806M. eluent:  $\text{CHCl}_3$ . UV detector: 300 nm).



**Figure 1.** CD spectra of polyketones **5a–c** and monomer **3** in  $\text{CHCl}_3$  ( $c$ : ca.  $10^{-5}$  mol/L).

The exclusion of flexible ether bonds from the main chains, *i.e.*, wholly aromatic polyketones, will lead to the control of secondary structures of polymers.

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