

Nickel Complex-Mediated Synthesis of Optically Active Wholly Aromatic Polyketones Bearing 2,2'-Dimethoxy-1,1'-binaphthyl-6,6'-ene Units

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ABSTRACT: 6,6'-Bis(chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyls **2a** and **2b** are prepared *via* P₂O₅-MsOH mediated regioselective diaryoylation of 2,2'-dimethoxy-1,1'-binaphthyl (**1**). NiBr₂/Zn-mediated aromatic coupling polymerization of 6,6'-bis(chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyls **2** yields the corresponding wholly aromatic polyketones. When optically active bis(chlorobenzoylated) binaphthyls (**2**) are employed, optically active wholly aromatic polyketones **3** with large specific rotations, excellent thermal resistance, and excellent solubility to organic solvents are obtained. [DOI 10.1295/polymj.37.736]

KEY WORDS 2,2'-Dimethoxybinaphthyl / Nickel Complex-Mediated Aromatic Coupling Polymerization / Wholly Aromatic Polyketone / Excellent Solubility / Optically Active Polyketones /

There have been a lot of reports on aromatic polyketones, which have attracted much attention for their excellent physical and chemical resistance.^{1–8} On the other hand, there have been only a few reports on wholly aromatic polyketones, *i.e.*, aromatic polyketones *without* ether bonds in the main chains.^{8–13} Electrophilic aromatic aryoylation reaction⁸ and aromatic coupling reaction^{9–12} are presumed to be the useful protocols for syntheses of wholly aromatic polyketones.

We have already reported that AlCl₃-mediated Friedel–Crafts type polymerization^{14–16} and phosphorus oxide–methanesulfonic acid mixture (P₂O₅–MsOH) mediated direct condensation polymerization¹⁷ using 2,2'-dimethoxybiphenyl proceed with sustainable reactivity and high regioselectivity at 5,5'-positions, giving wholly aromatic polyketones with high-molecular-weights. In addition, we have also succeeded in the synthesis of 2,2'-dimethoxy-5,5'-biphenylene-containing wholly aromatic polyketones *via* NiBr₂/Zn-mediated aromatic coupling polymerization.^{18–20}

As the application of wholly aromatic polyketones, we planned the synthesis of wholly aromatic polyketones bearing 2,2'-dimethoxy-1,1'-binaphthyl-6,6'-ene units instead of 2,2'-dimethoxybiphenylene ones. Introduction of aromatic units with large dihedral angle between two naphthalene rings, *e.g.* 2,2'-dialkoxy-1,1'-binaphthylene units, probably weakens intermo-

lecular interaction such as π,π -stacking during polymerization, which will realize further sustainable polymerization. In addition, the polymer skeletons have axial chirality and will be widely applied as ligands for asymmetric transition metal catalysts.²¹ Introduction of optically active ligands on the chemical-resistant polymer backbones would be effective for creation of a novel type of polymeric ligands. There have been several reports on the syntheses of polymers such as polyarylenes, polycarbonates, polyamides, and polyimides containing 2,2'-disubstituted 1,1'-binaphthylene units.^{22–28} However, there have been no reports on wholly aromatic polyketones containing axially chiral units such as 2,2'-dimethoxy-1,1'-binaphthylene units in main chains.

Preliminary, we have reported the regioselective diaryoylation²⁹ of 2,2'-dimethoxy-1,1'-binaphthyl proceeds at 6,6'-positions with the aid of P₂O₅–MsOH as a condensing reagent and a solvent. This motivated us to synthesize 2,2'-dimethoxy-1,1'-binaphthylene-containing wholly aromatic polyketones.

In this paper, we would like to report NiBr₂/Zn-mediated aromatic coupling polymerization of 6,6'-bis(chlorobenzoylated) 2,2'-dimethoxy-1,1'-binaphthyls, which are prepared through regioselective bis(chlorobenzoylation) of 2,2'-dimethoxy-1,1'-binaphthyl.

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EXPERIMENTAL

General

¹H NMR spectra were recorded on a JEOL JNM-AL300 (300 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me₄Si (δ , 0.00). ¹³C NMR spectra were recorded on a JEOL JNM-AL300 (75 MHz). Chemical shifts are expressed in ppm relative to internal standard of CDCl₃ (δ , 77.0). IR measurement was recorded on a JEOL FT/IR-5300. Specific rotations were measured in CHCl₃ ($c = 0.05 \text{ g dL}^{-1}$) using a JASCO DIP-1000 digital polarimeter.

Gel permeation chromatography (GPC) measurements were carried out at a flow rate of 1.0 mL min^{-1} at 40 °C using CHCl₃ as an eluent on a Shimadzu SPD-6A equipped with a UV detector (300 nm) and a Shodex GPC KD-806M column. Inherent viscosities (η_{inh}) were determined in a concentrated H₂SO₄ (0.3 g dL^{-1}) 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 Rigaku DSC-8230 differential scanning calorimeter with a heating rate of 10 K min^{-1} under nitrogen. Thermal degradation temperature (T_d) was determined on the basis of a TGA thermogram. The TGA thermogram was recorded on a Rigaku TG-8120 thermogravimeter with a heating rate of 10 K min^{-1} .

P₂O₅-MsOH was prepared according to Eaton's procedure.³⁰

Preparation of Bis(chlorobenzoylated) 2,2'-Dimethoxy-1,1'-binaphthyl (2)

To a reaction mixture of 4- or 3-chlorobenzoic acid (1.5 mmol) and 2,2'-dimethoxy-1,1'-binaphthyl (**1**, 0.50 mmol) placed in a round flask, P₂O₅-MsOH (1.5 mL) was added and the reaction mixture was stirred at 60 °C for 24 h. Water was added to the reaction mixture and the aqueous mixture was neutralized with aqueous sodium hydroxide and extracted with ether for three times. The combined extracts were washed with aqueous 0.1 M potassium hydroxide and brine successively and dried over anhydrous magnesium sulfate. After removal of solvent, the residue was purified by recrystallization from ethanol/chloroform to give the pure product as a dark brown solid.

6,6'-Bis(4-chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (2a). mp 214.5–215 °C (CHCl₃/ethanol). IR ν (KBr): 1651, 1612, 1478, 1092 cm⁻¹. ¹H NMR δ (CDCl₃): 3.83 (6H, s), 7.18 (2H, d, $J = 8.4 \text{ Hz}$), 7.48 (4H, d, $J = 8.7 \text{ Hz}$), 7.54 (2H, d, $J = 8.4 \text{ Hz}$), 7.69 (2H, dd, $J = 1.8, 8.4 \text{ Hz}$), 7.81 (4H, d, $J = 8.7 \text{ Hz}$), 8.09 (2H, d, $J = 8.4 \text{ Hz}$), 8.29 (2H, d, $J = 1.8 \text{ Hz}$) ppm. ¹³C NMR δ (CDCl₃): 56.5, 114.4, 118.7,

125.4, 126.2, 127.7, 128.6, 131.4, 131.6, 132.2, 132.5, 136.0, 136.4, 138.5, 157.1, 195.2 ppm. *Anal.* Calcd. for C₃₆H₂₄Cl₂O₄: C, 73.10%; H, 4.09%. Found: C, 72.93%; H, 4.25%.

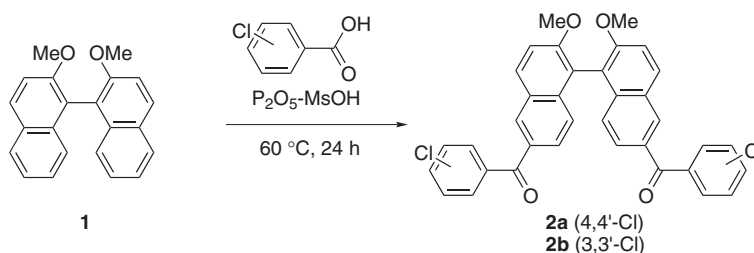
6,6'-Bis(3-chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (2b). mp 131.5–133.5 °C (CHCl₃/ethanol). IR ν (KBr): 1655, 1471, 1064 cm⁻¹. ¹H NMR δ (CDCl₃): 3.83 (6H, s), 7.19 (2H, d, $J = 8.4 \text{ Hz}$), 7.45 (2H, t, $J = 8.4 \text{ Hz}$), 7.55 (2H, d, $J = 8.4 \text{ Hz}$), 7.57 (2H, d, $J = 8.7 \text{ Hz}$), 7.70 (2H, dd, $J = 8.7, 1.5 \text{ Hz}$), 7.72 (2H, d, $J = 8.7 \text{ Hz}$), 7.83 (2H, t, $J = 1.5 \text{ Hz}$), 8.11 (2H, d, $J = 8.7 \text{ Hz}$), 8.31 (2H, d, $J = 1.5 \text{ Hz}$) ppm. ¹³C NMR δ (CDCl₃): 56.6, 114.4, 125.5, 126.2, 127.7, 128.0, 129.6, 129.8, 131.7, 132.0, 132.7, 134.5, 136.2, 139.9, 140.2, 148.4, 157.2, 198.8 ppm. *Anal.* Calcd. for C₃₆H₂₄Cl₂O₄: C, 73.10%; H, 4.09%. Found: C, 72.82%; H, 4.28%.

NiBr₂/Zn-Mediated Aromatic Coupling Polymerization

6,6'-Bis(4-chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (2a, 0.4 mmol, 236 mg), NiBr₂ (0.2 mmol, 43.7 mg), triphenylphosphine (0.4 mmol, 105 mg), 2,2'-bipyridyl (0.2 mmol, 31.2 mg), and Zn (1.2 mmol, 78.5 mg) were placed in a two-necked round flask and to this mixture, freshly distilled DMAc (0.8 mL) was added *via* a syringe. The reaction mixture was stirred at 100 °C for 2 h. The mixture was diluted with DMAc and the solution was poured dropwise into a hydrochloric acid/methanol solution (2 M) with stirring to separate out a solid. The solid was filtrated and washed with methanol. The precipitates were dried under reduced pressure at 80 °C to give polymer **3a**. Polymer **3b** was synthesized according to this procedure.

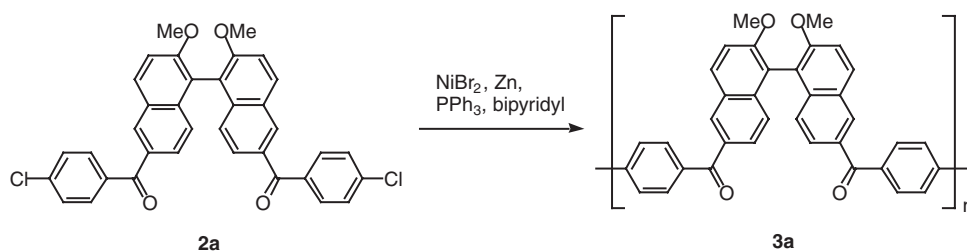
Polymer 3a. IR ν (KBr): 1651, 1616, 1477 cm⁻¹. ¹H NMR δ (CDCl₃): 3.83 (6H, pseudo s), 7.20 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 7.55 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 7.76–7.81 (6H, m), 7.98 (4H, pseudo d, $J = 9.0 \text{ Hz}$), 8.11 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 8.38 (2H, pseudo s) ppm. ¹³C NMR δ (CDCl₃): 56.6, 114.4, 118.7, 125.4, 126.4, 127.2, 127.7, 130.7, 131.6, 132.5, 132.6, 136.0, 137.5, 143.6, 157.1, 196.0 ppm. *Anal.* Calcd. for (C₃₆H₂₄O₄)_n: C, 83.06%; H, 4.65%. Found: C, 82.58%; H, 4.61%.

Polymer 3b. IR ν (KBr): 1655, 1616, 1475 cm⁻¹. ¹H NMR δ (CDCl₃): 3.78 (6H, pseudo s), 7.20 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 7.47 (2H, pseudo d, $J = 11.0 \text{ Hz}$), 7.57 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 7.75 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 7.83 (4H, pseudo t, $J = 11.0 \text{ Hz}$), 8.04 (2H, pseudo d, $J = 9.0 \text{ Hz}$), 8.11 (2H, pseudo s), 8.35 (2H, pseudo s) ppm. ¹³C NMR δ (CDCl₃): 56.5, 114.3, 118.7, 125.4, 126.4, 127.7, 128.5, 128.9, 129.3, 130.8, 131.6, 132.3, 132.8, 136.0, 138.9, 140.5, 157.1, 196.2 ppm. *Anal.* Calcd. for (C₃₆H₂₄O₄)_n: C, 83.06%; H, 4.65%. Found: C, 82.65%; H, 4.78%.

Table I. Bis(chlorobenzoylation) of 2,2'-dimethoxy-1,1'-binaphthyl (**1**)

Run	Chlorobenzoic acid	Time/h	Yield/%
1	4-Cl	24	90
2	3-Cl	4	86

Reaction conditions: 2,2'-dimethoxy-1,1'-binaphthyl (**1**), 0.5 mmol; chlorobenzoic acid, 1.5 mmol; P₂O₅-MsOH, 1.5 mL.

Table II. NiBr₂/Zn-mediated aromatic coupling polymerization of 6,6'-bis(4-chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (**2a**)

Run	Solvent	Temp./°C	Time/h	Yield/%	η_{inh}/dLg^{-1a}	Film ^b
1	THF	reflux	2	0	—	—
2	DMAc	100	2	24	0.37	—
3	NMP	100	2	91	0.18	—
3	DMF	100	2	98	0.59 ^c	+
4		120	2	98	0.26	—
5		80	2	91	0.13	—
6		100	1	98	0.39	—
7			4	88	0.18	—

Reaction conditions: 6,6'-bis(4-chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (**2a**), 0.4 mmol; NiBr₂, 0.2 mmol; NiBr₂/PPh₃/bipyridyl = 1/2/1; Solvent, 0.8 mL; N₂ atmosphere. ^aInherent viscosity was determined in a conc. H₂SO₄ solution (0.3 g/dL) at 30 °C. ^b+, obtained as a flexible film. —, failure in film forming. ^cM_n was determined as 12,000 by GPC calculation (Column: Shodex, GPC KD-806M. Eluent: CHCl₃, UV detector: 300 nm).

RESULTS AND DISCUSSION

Preparation of 6,6'-Bis(chlorobenzoylated) 2,2'-Dimethoxy-1,1'-binaphthyls **2a,b**

When 3 equimolar amounts of *p*- or *m*-chlorobenzoic acid was treated with 2,2'-dimethoxy-1,1'-binaphthyl (**1**) in the presence of P₂O₅-MsOH, regioselective diarylation reaction proceeded to afford 6,6'-bis(chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyls (**2**), the monomers for nucleophilic aromatic substitution polymerization, in good yields. Two methoxy groups situated at 2,2'-positions probably enhance the reactivity and regioselectivity at 6,6'-positions sterically and electrically.

NiBr₂/Zn-Mediated Aromatic Coupling Polymerization

Bis(4-chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl (**2a**) was treated with 50 mol % of NiBr₂, 310 mol % of Zn, 100 mol % of PPh₃, and 50 mol % of 2,2'-bipyridyl in several solvents.

Table II shows the results of the polymerization. The degree of polymerization was estimated by measurement of inherent viscosity in a concentrated H₂SO₄ solution. Among solvents screened, DMF was the most suitable for sustainable polymerization. In particular, when the reaction was performed at 100 °C for 2 h, the highest molecular weight polyketone was obtained. In addition, there was no signal assignable to protons of chlorobenzoyl groups in the ¹H NMR

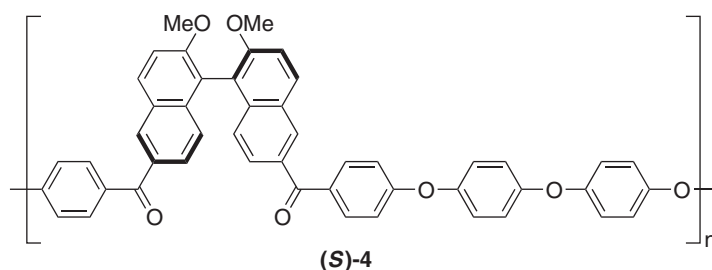
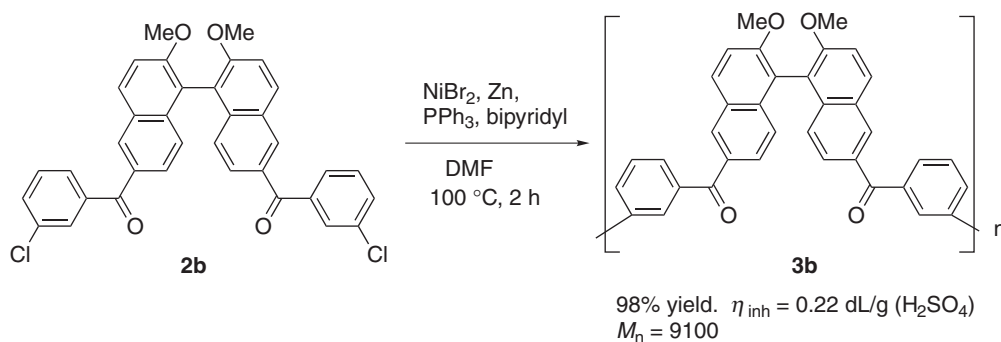


Figure 1. Structure of optically active poly(ether ketone) (S)-4.

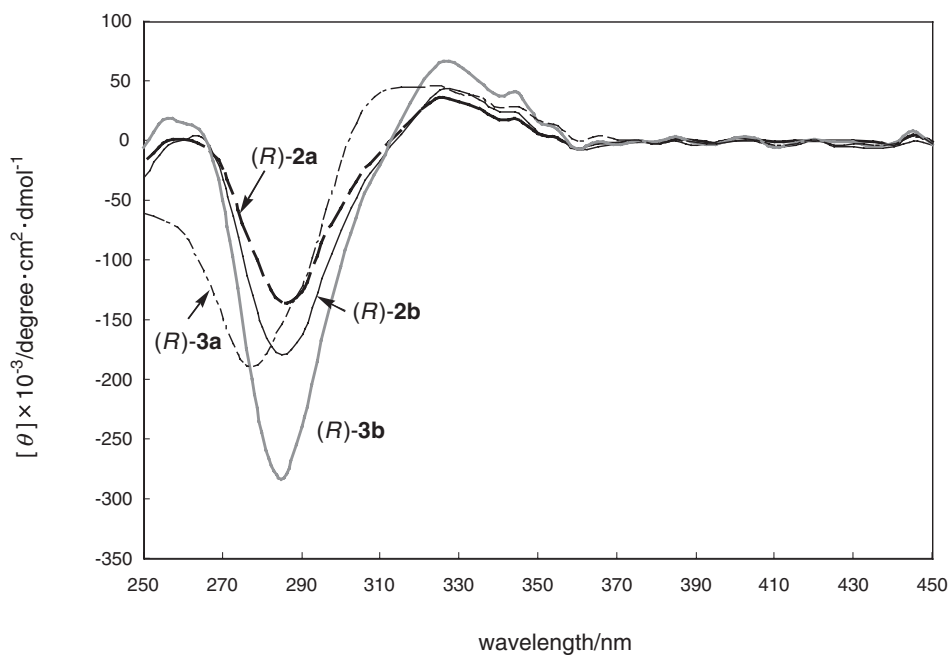


Figure 2. CD spectra of polyketones (R)-3a/3b and monomer (R)-2a/2b.

spectra of these polyketones.

Polymerization of regioisomeric monomer **2b** was also performed under the optimized reaction conditions in the polymerization of monomer **2a**. In the same manner, polymerization proceeds to give the corresponding wholly aromatic polyketone (**3b**).

Next, optically active wholly aromatic polyketones (**R**)-**3a** and (**R**)-**3b** were prepared as the same as usual from (**R**)-2,2'-dimethoxy-1,1'-binaphthyl. Specific

rotations and circular dichroism (CD) spectra of polyketones (**R**)-**3a** and (**R**)-**3b** are shown in Table III and Figure 2.

The resulting polyketones (**R**)-**3a** and (**R**)-**3b** show much larger specific rotations than monomers (**R**)-**2a/2b** and aromatic poly(ether ketone) **4**, which is synthesized *via* nucleophilic aromatic substitution polymerization of (*S*)-6,6'-bis(4-fluorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyl with 4,4'-oxybiphenol.³¹

Table III. Specific rotations and thermal properties of optically active wholly aromatic polyketones (*R*)-**3a**, (*R*)-**3b** and poly(ether ketone) (*S*)-**4**

Run	Polyketone	$[\alpha]_D^{25}/\text{deg}^a$	$T_g/^\circ\text{C}$	$T_d/^\circ\text{C}^b$
1	(<i>R</i>)- 3a	-427 ^c	167	458
2	(<i>R</i>)- 3b	-346 ^d	160	416
3	(<i>S</i>)- 4	+31	170	404

^aOptical rotations were measured in CHCl₃ (c = 0.05 g/dL).

^bTemperature where a 10 wt% loss was recorded by TG.

^cMonomer (*R*)-**2a**; $[\alpha]$: -41°. ^dMonomer (*R*)-**2b**; $[\alpha]$: -37°.

Specific rotation of polyketone **3a** is larger than that of polyketone **3b**, which is due to high rigidity of *p,p*-biphenylene units compared with *m,m*-biphenylene ones, presumably. CD spectra of polyketones **3** show an increase in intensity of the Cotton effects compared with monomers **2**. In addition, (*S*)- and (*R*)-**3** exhibit mirror-image Cotton effects. These results probably suggest that wholly aromatic polyketones **3** hold regular secondary structures such as helix on the basis of introduction of rigid polymer backbones, *i.e.*, exclusion of flexible ether bonds from main chains.

Thermal behaviors of the resulting wholly aromatic polyketones (**3**) are examined. DSC curve shows that glass transition temperature of polyketone **3a** is 167 °C and that of polyketone **3b** is 160 °C. T_g values of polyketones **3** are lower by *ca.* 50 °C than those of wholly aromatic polyketones containing 2,2'-dimethoxybiphenylene units.^{14–17} This is probably because 2,2'-dimethoxy-1,1'-binaphthylene units have weaker intermolecular interaction on the basis of larger dihedral angle between biaryls than 2,2'-dimethoxybiphenylene ones. The TGA thermogram shows that the resulting polyketones keep the weight up to *ca.* 400 °C and they begin to decompose gradually. The thermal behavior is similar to those of wholly aromatic polyketones containing 2,2'-dimethoxybiphenylene units. This similarity suggests that thermal degradation of these polyketones **3** and **4** occurs motivated by cleavage of sp³ carbon-oxygen bonds of methoxy groups.

CONCLUSIONS

6,6'-Bis(chlorobenzoyl)-2,2'-dimethoxy-1,1'-binaphthyls **2** were prepared in good yields with the aid of P₂O₅-MsOH. NiBr₂/Zn-mediated aromatic coupling polymerization yielded high molecular weight polyketones **3**. Application of optically active 2,2'-dimethoxy-1,1'-binaphthyls enabled us to formulate a novel type of optically active wholly aromatic polyketones with excellent thermal resistance, and excellent solubility to organic solvents.

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