

ORIGINAL ARTICLE

Poly(arylene ether ketone)s composed of a 1,8-diaroylenenaphthalene moiety: a non-coplanarly accumulated aromatic-ring repeating unit

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Poly(arylene ether ketone)s composed of a 1,8-diaroylenenaphthalene moiety, which is a non-coplanar accumulated aromatic-ring unit, were successfully synthesized through the nucleophilic aromatic substitution polycondensation of 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene with several arene diols under mild conditions. The polymers show high glass transition temperatures (T_g), poor solubility and good film-forming ability through heat casting.

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INTRODUCTION

Poly(arylene ether ketone)s have received considerable attention because they are among the eminent thermoplastic super-performance engineering polymers that have excellent chemical tolerance.^{1,2} However, the synthetic difficulties resulting from the poor solubility of the intermediate oligomers often restricts their use. During the course of investigations to overcome these problems, the introduction of a crankshaft-shaped moiety has proven to be one of the effective approaches. The twisted accumulated aromatic-ring structures presumably contribute to smooth polymerization without the stable stacking of aligned aromatic rings in the polymer main chains. Such modifications to the chemical structure have also afforded high-molecular-weight wholly aromatic polyketones, that is, poly(arylene ketone)s that are free from ether linkages in the main chain. We have achieved the synthesis of wholly aromatic polyketones³ via the electrophilic aromatic arylation polycondensation using the minute molecular design of acyl-acceptant molecules composed of 2,2'-dioxy-1,1'-biphenylene,⁴ 2,2'-dioxy-1,1'-binaphthylene,⁵ and *o*-terphenylene⁶ moieties.

During the synthetic study of wholly aromatic polyketones, we unexpectedly observed the highly susceptible and selective arylation at the 1- and 1,8-positions of 2,7-dimethoxynaphthalene.^{7,8} Using X-ray crystal structure analyses, the resulting 1-mono- and 1,8-diaroylated naphthalene homologs with various substituents have been shown to contain an accumulated organization of aromatic rings in a non-coplanar arrangement, where the aryl groups are perpendicularly attached to the naphthalene ring and situated in opposite directions.^{9,10} These non-coplanar accumulation features are distinct

from those of the corresponding β -isomers.¹¹ The characteristic congested shapes of these molecules prompted us to trigger the incorporation of the 1,8-diaroyl-2,7-dimethoxynaphthalene moiety into the poly(arylene ether ketone) backbone. When the 1,8-diaroyl-2,7-dimethoxynaphthalene unit is incorporated into the polymer molecule, it is expected to have essentially the same topology of non-coplanar accumulated aromatic-rings spatial organization to that of the crystal of the relating diaroylnaphthalene molecule. In addition, the aromatic polymers synthesized via chain elongation at the 1,8-positions of the naphthalene ring core have rarely been reported¹² in contrast to the analogous aromatic polymers prepared by chain elongation at the 2,6- and 1,5-positions.^{13–17} In this article, we briefly report and discuss the behavior of the polymerization reaction of 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**) during nucleophilic aromatic substitution polycondensation and the several curious properties of the resulting polymers in connection with the unique structure of the 1,8-diaroylenenaphthalene unit.

EXPERIMENTAL PROCEDURE

Measurements

¹H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz) and a JEOL JNM-ECA-500 spectrometer (500 MHz) (JEOL Ltd, Tokyo, Japan). The chemical shifts are expressed in p.p.m. relative to an internal standard of Me₄Si (δ 0.00). ¹³C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (75 MHz) and a JEOL JNM-ECA-500 spectrometer (125 MHz). The chemical shifts are expressed in p.p.m. relative to an internal standard of CDCl₃ (δ 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer (JASCO Corporation, Tokyo, Japan). Elemental analyses were

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performed on a Yanaco CHN CORDER MT-5 analyzer (Yanaco New Science Inc., Kyoto, Japan).

Gel permeation chromatography measurements were performed using a Shodex K-806M column at a flow rate of 0.75 ml min⁻¹ at 40 °C using CHCl₃ as an eluent on a HITACHI L-7100 HPLC pump (Hitachi, Ltd., Tokyo, Japan). The UV absorption was monitored at a wavelength of 254 nm using a HITACHI L-7405 UV-vis HPLC spectrophotometer. The inherent viscosities (η_{inh}) were determined in a NMP (0.3 g dl⁻¹) solution at 30 °C using an Ostwald viscometer. The glass transition temperatures (T_g s) were determined based on the differential scanning calorimetry (DSC) curves. The DSC curves were recorded on a Rigaku DSC-8230 differential scanning calorimeter (Rigaku Corporation, Tokyo, Japan) at a heating rate of 10 K min⁻¹ under nitrogen against the samples that were preheated at the temperature just below the weight-loss-starting temperature followed by quick quenching. The thermal degradation temperatures (T_d s) were determined based on a thermogravimetric analysis (TGA) thermogram. The TGA thermogram was recorded on a Rigaku TG-8120 thermogravimeter at a heating rate of 10 K min⁻¹.

Synthesis of 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (1)

2,7-dimethoxynaphthalene (5 mmol, 0.941 g), 4-fluorobenzoic acid (11 mmol, 1.54 g) and P₂O₅-MsOH¹⁸ (22 ml) were added to a dried 30 ml one-necked flask. After the reaction mixture had been stirred for 1 h at 60 °C, it was poured into ice-cold water (40 ml), and the mixture was extracted using CHCl₃ (30 ml × 3). The combined extracts were washed with aqueous 2 M sodium hydroxide, saturated NaCl (aq) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to yield powdery product **1** (quant.).

1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (1). ¹H NMR δ (300 MHz, CDCl₃): 3.69 (6H, s), 7.02 (4H, dd, J = 8.6 Hz), 7.21 (2H, d, J = 9.3 Hz), 7.71 (4H, dd, J = 8.2, 5.5 Hz), 7.95 (2H, d, J = 9.3 Hz) p.p.m.; ¹³C NMR δ (75 MHz, CDCl₃): 56.28, 111.12, 115.06 (d, J_{C-F} = 21 Hz), 125.46, 129.75, 131.51, 131.64, 132.25, 135.18, 156.24, 165.49 (d, J_{C-F} = 254 Hz), 195.38 p.p.m.; IR (KBr) 1663, 1613, 1596, 1567, 1512, 1504, 1270 cm⁻¹; melting point = 196 °C; C₂₆H₁₈O₄F₂ anal. calcd. for C, 72.22%; H, 4.20%. Found C, 72.05%; H, 4.20%.

Typical procedure for the nucleophilic aromatic substitution polymerization of monomer **1** using diol **2a**

1,8-Bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**, 0.2 mmol, 86.5 mg), diol **2a** (0.2 mmol, 45.6 mg), potassium carbonate (1.0 mmol, 138 mg), and freshly distilled DMAc (0.25 ml) were placed into a 10 ml one-necked flask that was equipped with a condenser. After the reaction mixture had been stirred at 150 °C for 48 h, it was poured into methanol (20 ml) to separate the pale yellow precipitate. The precipitate was collected by filtration with suction and dried in vacuo at 80 °C for 8 h to yield a pale yellow powder of poly(ether ketone) **3a**.

Other reactions were performed using essentially the same procedure as described above.

Poly(ether ketone) 3a. ¹H NMR δ (500 MHz, CDCl₃): 1.65 (6H, s), 3.67 (6H, s), 6.81 (4H, brs), 6.96 (4H, brs), 7.11–7.23 (6H, m), 7.61 (4H, brs), 7.88 (4H, brs) p.p.m.; ¹³C NMR δ (125 MHz, CDCl₃): 31.10, 42.39, 111.29, 113.43, 116.68, 119.90, 121.64, 125.53, 128.31, 131.52, 132.02, 133.47, 146.74, 153.38, 156.16, 161.77, 195.22 p.p.m.; IR (KBr): 1668, 1609, 1592, 1497, 1237, 1269 cm⁻¹; C₄₁H₃₂O₆ anal. calcd. for C, 79.34%; H, 5.20%. Found C, 77.56%; H, 5.16%.

Poly(ether ketone) 3b. ¹H NMR δ (500 MHz, CDCl₃): 3.68 (6H, s), 6.84 (4H, brs), 6.92–7.08 (8H, m), 7.17 (2H, brs), 7.62 (4H, brs), 7.89 (2H, brs) p.p.m.; ¹³C NMR δ (125 MHz, CDCl₃): 56.59, 111.29, 116.35, 120.14, 121.55, 121.95, 125.57, 129.61, 131.57, 132.08, 133.54, 150.97, 154.00, 156.18, 161.98, 195.26 p.p.m.; IR(KBr): 1664, 1595, 1488, 1219 cm⁻¹; C₃₈H₂₆O₇ anal. calcd. for C, 76.76%; H, 4.41%; found C, 74.87%; H, 4.61%.

Poly(ether ketone) 3c. ¹H NMR δ (500 MHz, CDCl₃): 3.72 (6H, s), 6.96 (4H, brs), 7.12–7.20 (6H, m), 7.71 (4H, brs), 7.79 (4H, brs) 7.93 (2H, brs) p.p.m.;

¹³C NMR δ (125 MHz, CDCl₃): 56.54, 111.26, 113.68, 118.26, 118.85, 121.15, 125.58, 129.65, 131.61, 132.39, 133.23, 134.77, 156.29, 159.94, 163.23, 194.27, 195.53 p.p.m.; IR (KBr): 1661, 1589, 1497, 1238 cm⁻¹; C₃₉H₂₆O₇ anal. calcd. for C, 77.22%; H, 4.32%; found C, 75.21%; H, 4.54%.

Poly(ether ketone) 3d. ¹H NMR δ (500 MHz, CDCl₃): 3.69 (6H, s), 6.85 (4H, brs), 7.09 (4H, brs), 7.18 (2H, brs), 7.65 (4H, brs), 7.91 (2H, brs) p.p.m.; ¹³C NMR δ (125 MHz, CDCl₃): 56.57, 111.28, 116.54, 121.50, 121.92, 125.58, 129.62, 131.54, 132.08, 133.69, 151.98, 156.18, 161.73, 195.27 p.p.m.; IR (KBr): 1666, 1597, 1493, 1226 cm⁻¹; C₃₂H₂₂O₆ anal. calcd. for C, 76.48%; H, 4.41%; found C, 76.08%; H, 4.39%.

Poly(ether ketone) 3e. ¹H NMR δ (300 MHz, CDCl₃): 3.68 (6H, s), 6.81–7.02 (4H, m), 7.17 (4H, brs), 7.30 (2H, brs), 7.59–7.73 (4H, m), 7.81 (2H, brs), 7.90 (2H, brs) p.p.m.; ¹³C NMR δ (125 MHz, CDCl₃): 56.56, 111.29, 115.12, 115.76, 117.13, 119.86, 121.48, 125.58, 128.00, 130.09, 131.56, 132.12, 133.85, 135.44, 154.12, 156.23, 161.31, 195.32 p.p.m.; IR (KBr): 1666, 1634, 1594, 1510, 1498, 1228, 1268 cm⁻¹; C₃₆H₂₄O₆ anal. calcd. for C, 78.25%; H, 4.38%; found C, 76.92%; H, 4.58%.

RESULTS AND DISCUSSION

The bis(fluorobenzoyl)naphthalene monomer, 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**), was prepared by the P₂O₅-MsOH-mediated direct condensation of 2,7-dimethoxynaphthalene with 4-fluorobenzoic acid according to the previous study (see Supplementary Charts S1–S3 show ¹H and ¹³C NMR spectra of monomer **1**).⁷ Based on the X-ray crystal structure analysis, the two aryl groups of the bis(4-fluorobenzoyl)naphthalene monomer **1** are asymmetrically bent (Figure 1; Supplementary Figure S1 shows the X-ray crystal structure with the detailed crystal information).¹⁹ The interplanar angles between the naphthalene ring and the two benzene ring planes of monomer **1** are 66.88(7)° and 88.09(6)°, respectively. To our best knowledge,^{9,10,20,21} the 1,8-diaroynaphthalene molecules that have been reported in this study have larger interplanar angles than other homologous molecules, for example, 1,8-diaroynaphthalene without 2,7-methoxy groups.²² These results indicate that the steric environment around the two carbonyl groups in monomer **1** is highly congested.

Table 1 presents the results of the nucleophilic aromatic substitution polymerization of bis(4-fluorobenzoyl)naphthalene monomer **1**

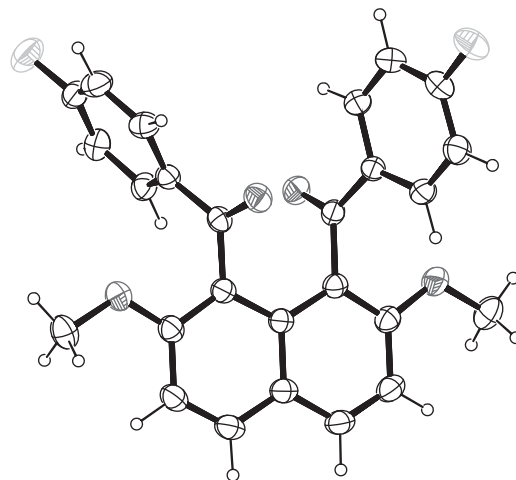
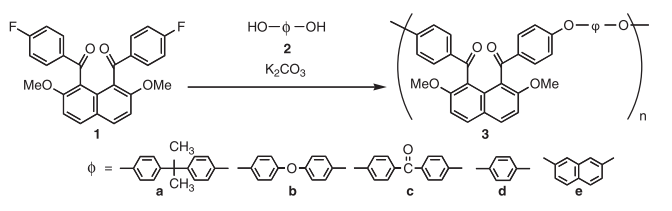


Figure 1 X-ray crystal structure of 1,8-diaroynaphthalene **1**. A full color version of this figure is available at *Polymer Journal* online.

Table 1 Nucleophilic aromatic substitution polycondensation of 1,8-diaroylnaphthalene **1** with diol **2**^a

Entry	Diol	Solvent (ml)	Temperature		Yield (%)	η_{inh} (dl g ⁻¹) ^b	Film-forming ability ^c	
			(°C)	(h)				
1	2a	DMF	0.5	150	24	3a 95	0.15	+
2	2a	DMF	0.25	150	24	3a 92	0.16	+
3	2a	DMF	0.25	150	48	3a 95	0.18	+
4	2a	NMP	0.25	170	6	3a 91	0.13	+
5	2a	DMAc	1.0	150	24	3a 79	0.15	+
6	2a	DMAc	0.5	150	24	3a 86	0.2	+
7	2a	DMAc	0.25	150	24	3a 93	(0.49) ^d	++
8	2a	DMAc	0.25	150	48	3a 97	nd ^e	++
9	2b	DMAc	0.25	150	48	3b 94	nd ^e	++
10	2c	DMAc	0.25	150	48	3c 97	nd ^e	+
11	2d	DMAc	0.25	150	48	3d 100	nd ^e	+
12	2e	DMAc	0.25	150	48	3e 94	nd ^e	+

^aReaction conditions: 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**, 0.2 mmol), diol **2** (0.2 mmol), K₂CO₃ (1.0 mmol), solvent (0.25 ml), under N₂ atmosphere.

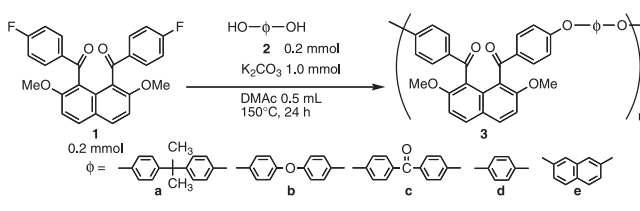
^bDetermined in a NMP solution (0.3 g dl⁻¹) at 30 °C.

^cFilm quality: ++ Flexible; + Brittle.

^dSoluble parts in NMP.

^eInsoluble in NMP and conc. H₂SO₄.

with bisphenol A (**2a**) performed in aprotic polar solvents of DMF, NMP and DMAc. In DMF, the polymerization proceeded slowly (Entry 1). Decreasing the volume of DMF and elongating the reaction time slightly accelerated the chain elongation reaction (Entries 2 and 3). In NMP, the polymerization was retarded, even at rather high reaction temperatures (Entry 4). However, the use of smaller amounts of DMAc achieved smooth polymerization (Entries 5, 6 and 7). In 0.25 ml of DMAc against 0.2 mmol of bis(4-fluorobenzoyl)naphthalene monomer **1**, the reaction solution gradually became viscous, and gelatinous curds were finally formed within 1.5 h (Entries 7 and 8). After reprecipitation, the precipitated mass of polymer **3a** was demonstrated to be insoluble not only in organic solvents but also in conc. H₂SO₄ (Entry 8). Polymer **3**, which was obtained in Entry 7, was partially soluble in chloroform. The molecular weights of the soluble parts were estimated at approximately 10 000 ($n=16$) from the ¹H NMR spectra. However, the insoluble parts easily yielded a transparent flexible film by heat casting. These results led us to conjecture that the chain elongation reaction proceeded satisfactorily and yielded an insoluble high-molecular-weight polymer. Therefore, diols **2b–e** were employed as monomers with bis(4-fluorobenzoyl)naphthalene monomer **1** under similar reaction conditions of Entry 8 (Entries 9–12). The corresponding polymerization proceeded smoothly. The products also showed poor solubility in organic solvents and good film-forming ability by heat casting.

Table 2 Numbers of polymerization estimated by ¹H NMR spectra and molecular weights calibrated by GPC of poly(ether ketone)s **3**^a

Entry	Diol	Product	Yield (%)	n^b	M_n^c
1	2a	3a	86	32	3600
2	2b	3b	95	28–29	5500
3	2c	3c	86	10	2100
4	2d	3d	70	40–41	4600
5	2e	3e	89	19	2000

Abbreviation: GPC, Gel permeation chromatography.

^aReaction conditions: 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**, 0.2 mmol), diol **2** (0.2 mmol), K₂CO₃ (1.0 mmol), DMAc (0.5 ml), 150 °C, 24 h, under N₂ atmosphere.

^bCalculated on the basis of ¹H NMR spectrum.

^cCalibrated on the basis of GPC curve (column: Shodex K-806M. eluent: CHCl₃. UV detector: 254 nm).

Table 3 Thermal properties of poly(ether ketone)s **3**^a

Entry	Polymer	T_g (°C) ^a	T_{d10} (°C) ^b
1	3a	206	366
2	3b	206	382
3	3c	213	373
4	3d	235	401
5	3e	226	391

^aDetermined on the basis of differential scanning calorimetry curves.

^bTemperature where a 10 wt% loss was observed in thermogravimetric analysis thermogram.

Table 2 presents the results of polymerization of bis(4-fluorobenzoyl)naphthalene monomer **1** with several diols **2** performed under gentle reaction conditions, in 0.5 ml of DMAc at 150 °C for 24 h. The products are easily soluble in CHCl₃ (see Supplementary Charts S4–18 show ¹H and ¹³C NMR spectra of the resulting polymers). The numbers of polymerization (n) are determined from the ¹H NMR spectra (The ¹H NMR spectra are available from Supplementary Information) and calibrated by gel permeation chromatography. The n values that were calibrated by gel permeation chromatography are smaller than those estimated from the ¹H NMR spectra. This apparently contradictory observation indicates that the products give small exclusion volumes in CHCl₃, although they have large molecular weights. This result can be explained because the polymer chains are tightly folded by the 1,8-diaroylenenaphthalene units. In other words, the structures of 1,8-diaroylenenaphthalene units provide a greater influence to the spatial organization of the polymer than that of the diol units.

Table 3 summarizes the T_g s and T_d s of the poly(ether ketone)s **3** determined using DSC and TG, respectively. The T_g s rise in the order of poly(ether ketone)s **3a**, **3b** < **3c** < **3e** < **3d**. In addition, the T_d s rise in the order of the poly(ether ketone)s **3a** < **3c** < **3b** < **3e** < **3d**. The difference in the T_g s is relatively small. The T_g s are presumably governed by the restricted rotation of the two adjacent arylene moieties in the 1,8-diaroylenenaphthalene unit. Flexible diol units such as **2a** and **2b** might permit unrestricted rotation of the bonds.

The T_d s likely depend on the structure of the diol units. The sp^3 carbon in the polymer main chain might lower the T_d .

The polymerization behavior and the solubility/thermal elasticity properties of the aromatic poly(ether ketone)s are well explained based on the structural features of the non-coplanar accumulated aromatic-ring repeating units. The polymerization likely proceeds with the folding of the resulting polymer chains at the 1,8-diaroilenaphthalene moieties. The benzene rings in the poly(ether ketone)s (**3**) are coagulated to give accumulation of the mass of the benzene rings such as polystyrene. The concentration of the randomly assembled benzene rings in the poly(ether ketone) (**3**) and polystyrene might be almost equal. However, the mobility of the polymer chain coagulation in the poly(ether ketone)s (**3**) at room temperature is far less than that of polystyrene. During the solution polymerization of monomer **1**, the solvated solvent molecules might be imperfectly squeezed out from the polymer chains until the formation of the less mobile mass of the yielded polyketone (**3**) finally results in the appearance of gelatinous curds. The solvation of the polymer chain of the polyketone (**3**) should be slow to present low solubility after the complete desolvation by reprecipitation. However, the good heat-cast film-forming ability of the polyketone (**3**) is interpreted as follows: Heating of the polymer solid should make the restricted spatial organization of the polymer loosen slightly by rotation of the bonds that are connected to the carbonyl group of the two adjacent aroyl groups in the 1,8-diaroilenaphthalene moiety, which enables the polymer mass to behave as mobile chains of benzene rings, just as in polystyrene melt.

CONCLUSIONS

The nucleophilic aromatic polycondensation of bis(4-fluorobenzoyl)naphthalene monomer **1**, which is a non-coplanar accumulated aromatic-ring molecule, with bisphenols **2** has been successfully achieved in aprotic polar solvents under mild reaction conditions, yielding sufficient amounts of a gelatinoid solid. The solid masses of poly(ether ketone)s **3** obtained via reprecipitation show poor solubility in organic solvents and high film-forming ability through heat casting.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)