2,2′-Bis(4-benzoylphenoxy)biphenyl: A Novel Efficient Acyl-acceptant Monomer Yielding Wholly Aromatic Polyketones *via* Friedel–Crafts Type Polymerization with Arenedicarbonyl Chloride

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ABSTRACT: The biphenyl derivative having two benzoylphenoxy groups at 2,2′-positions (**1**), is proved to be an efficient acyl-acceptant monomer for AlCl$_3$-mediated Friedel–Crafts acylation polymerization. Diaroylation of biphenyl **1** with 4-chlorobenzoyl chloride (**2a**) in the presence of AlCl$_3$ readily proceeds with continuous reactivity and high regioselectivity at 5,5′-positions to give the diaroylated biphenyl (**3a**) in good yields. Further, polymerization of monomer **1** with several arenedicarbonyl chlorides (**4a–c**) affords the corresponding wholly aromatic polyketones (**6**) with high molecular weights. These wholly aromatic polyketones are soluble in various organic solvents such as chloroform, THF, and so on. The superior heat resistibility of the resulting polyketones (**6**) is probably attributed to their characteristic polymer structures, *i.e.*, all of the carbons involved in the polymer molecules have sp^2 hybrid orbitals.
KEY WORDS   2,2′-Bis(4-benzoylphenoxy)biphenyl / Novel Acyl-Acceptant Monomer / Friedel–Crafts Acylation Polymerization / Thermal Resistibility /

There are only a few reports on the synthesis of wholly aromatic polyketones, *i.e.*, aromatic polyketones where no ether linkages are included in the main chains.[1,2] Recently, we have succeeded in the synthesis of wholly aromatic polyketones *via* electrophilic aromatic substitution polymerization[3–7] and *via* nickel complex-mediated aromatic coupling polymerization.[8–10] As the ketonic carbonyl groups deactivate the arene rings against electrophilic aromatic substitution, electrophilic aroylation polycondensation between arenes and arenedicarboxylic acids is substantially difficult. For this reason, to perform polymerization in such manner especially needs activation of the intermediating aroylated arene in a unique fashion. During the course of our synthetic study on wholly aromatic polyketones, it has been disclosed that 2,2′-dimethoxybiphenyl is an excellent acyl-acceptant monomer having continuous reactivity and high regioselectivity in AlCl$_3$-mediated Friedel–Crafts-type polymerization. In 2,2′-dimethoxybiphenyl molecule, the properly situated methoxy groups activate the biphenyl electrically sufficiently, preventing the electrical deactivation of the still non-substituted aryl group in the biphenylene unit. These methoxy groups also make the dihedral angle between two aromatic rings in biphenylene unit suitably twisted, restraining the aggregation to precipitate the oligomeric intermediates in the early stage of polymerization. The resulting polyketone holds its weight constant till 450 °C in nitrogen and it starts to decompose about this temperature. Probably, scission of sp^3 carbon–oxygen bond of 2,2′-dimethoxybiphenylene units occurs at the temperature.[6] On the basis of such consideration, we have planned the improved molecular designing by exhaustive exclusion of sp^3 carbon–oxygen bond from the polymer backbone. In this course, change of the repeating units from 2,2′-dimethoxybiphenylene units into 2,2′-diaryloxybiphenylene ones has been undertaken. As the aryloxy unit introduced alternately, we have a choice of 4-benzoylphenoxy group based on the following consideration: 1) electron-donating effect of two aryloxy groups situated at 2,2′-positions favors sustainable and regioselective electrophilic aromatic acylation on both phenylene rings in the biphenylene units and 2) introduction of the electron-deficient groups, *i.e.*, aromatic ketonic groups, onto the phenoxy units in the side chains suppresses electrophilic aromatic substitution on the *side chains*.

In this paper, we would like to report the preparation of 2,2′-(4-benzoylphenoxy)biphenyl (**1**) and AlCl$_3$-mediated Friedel–Crafts type acylation polymerization of the biphenyl (**1**) with arenedicarbonyl chlorides to afford wholly aromatic polyketones with high thermal resistibility.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on a JEOL JNM-A500 (500 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me$_4$Si (δ, 0.00).

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^{13}C NMR spectra were recorded on a JEOL JNM-A500 (125 MHz). Chemical shifts are expressed in ppm relative to internal standard of CDCl$_3$ (δ, 77.0). IR measurement was recorded on a JEOL FR/IR-5300. Gel permeation chromatography (GPC) measurements were carried out at a flow rate of 1.0 mL min^{-1} at 40 °C using CHCl$_3$ as an eluent on a Shimadzu SPD-6A equipped with a UV detector (340 nm) and a Shodex GPC KD-806M column. Inherent viscosities (η_{inh}) were determined in a concentrated H$_2$SO$_4$ (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 SEIKO DSC-200 differential scanning calorimeter with a heating rate of 10 K min^{-1} under nitrogen. Thermal degradation temperatures (T_d) were 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^{-1}.

Preparation of 2,2′-Bis(4-benzoylphenoxy)biphenyl 1

To a two-necked flask, 4-fluorobenzophenone (5 mmol, 1.0 g), 2,2′-biphenol (2.5 mmol, 0.46 g), and potassium carbonate (7.5 mmol, 0.93 g) were placed. Toluene (10 mL) and *N,N*-dimethylacetamide (10 mL) were added to the flask. The mixture was refluxed for 24 h. After reflux, the reaction mixture was poured into 5 wt% sodium hydroxide solution dropwise and the mixture was extracted with CHCl$_3$ three times. The combined extracts were washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure. The residue was purified by recrystalization from methanol. IR ν (KBr): 1655, 1599, 1501, 1233 cm^{-1}. ^{1}H NMR (500 MHz) δ (CDCl$_3$): 6.86 (4H, d, $J = 9.0$ Hz), 7.04 (2H, dd, $J = 2.8, 8.0$ Hz), 7.19 (2H, d, $J = 8.0$ Hz), 7.32 (2H, dt, $J = 2.0, 7.5$ Hz), 7.42 (6H, dd, $J = 2.0, 8.0$ Hz), 7.52 (2H, t, $J = 7.5$ Hz), 7.67–7.70 (8H, m) ppm. ^{13}C NMR (125 MHz) δ (CDCl$_3$): 117.1, 120.0, 120.4, 128.1, 129.3, 129.6, 130.0, 131.6, 132.0, 132.1, 132.2, 137.8, 153.0, 161.3, 195.3 ppm. Anal. Calcd. for C$_{38}$H$_{26}$O$_4$: C, 83.50 %; H, 4.79 %. Found: C, 83.74 %; H, 5.02 %.

AlCl$_3$-mediated Friedel–Crafts Type Acylation Polymerization

Acyl-acceptant monomer **1** (0.4 mmol, 218 mg) and arenedicarbonyl dichloride **4a–c** (0.4 mmol) were placed to a two-necked flask under nitrogen atmosphere. To the flask, 1,2-dichloroethane (2.0 mL) was added with a syringe. AlCl$_3$ (3.6 mmol, 480 mg) was added by portions to the solution. The reaction mixture was stirred for 1 h at 5 °C, warmed up to 15 °C, and stirred further for 24 h at RT. The reaction was quenched by addition of methanol to separate out white precipitates. The precipitates were collected by suction filtration and dried *in vacuo* at 120 °C to give a white solid of polymer **6a–c**.

Polyketone 6a. IR ν (KBr): 1657, 1589, 1493, 1252 cm^{-1}. ^{1}H NMR (500 MHz) δ (CDCl$_3$): 7.01 (4H, d, $J = 8.0$ Hz), 7.07 (2H, d, $J = 8.5$ Hz), 7.43 (4H, t, $J = 7.5$ Hz), 7.55 (2H, t, $J = 6.5$ Hz), 7.69 (4H, d, $J = 8.0$ Hz), 7.75 (4H, d, $J = 8.0$ Hz), 7.82 (2H, dd, $J = 1.0, 8.5$ Hz), 7.85 (4H, s), 8.01 (2H, s) ppm. ^{13}C NMR (125 MHz) δ (CDCl$_3$): 118.1, 118.6, 128.3, 128.5, 129.6, 129.8, 132.2, 132.4, 132.5, 132.6, 133.3, 133.4, 134.4, 137.4, 140.6, 158.0, 159.4, 194.1, 195.1 ppm. Anal. Calcd. for (C$_{46}$H$_{28}$O$_6$)$_n$: C, 81.64 %; H, 4.17 %. Found: C, 81.22 %; H, 4.12 %.

Polyketone 6b. IR ν (KBr): 1657, 1595, 1493, 1238 cm^{-1}. ^{1}H NMR (500 MHz) δ (CDCl$_3$): 6.99 (4H, d, $J = 8.5$ Hz), 7.03 (2H, d, $J = 8.5$ Hz), 7.42 (4H, t, $J = 7.0$ Hz), 7.53 (3H, t, $J = 7.0$ Hz), 7.68 (4H, d, $J = 8.0$ Hz), 7.73 (4H, d, $J = 8.5$ Hz), 7.79 (2H, d, $J = 8.5$ Hz), 7.95 (2H, d, $J = 7.5$ Hz), 8.01 (2H, s), 8.27 (1H, s) ppm. ^{13}C NMR (125 MHz) δ (CDCl$_3$): 118.0, 118.7, 128.3, 128.5, 129.8, 132.4, 132.5, 133.3, 133.4, 134.3, 137.4, 137.9, 157.9, 159.4, 194.0, 195.1 ppm. Anal. Calcd. for (C$_{46}$H$_{28}$O$_6$)$_n$: C, 81.64 %; H, 4.17 %. Found: C, 81.47 %; H, 4.48 %.

Polyketone 6c. IR ν (KBr): 1657, 1591, 1495, 1252 cm^{-1}. ^{1}H NMR (500 MHz) δ (CDCl$_3$): 7.02 (4H, d, $J = 9.0$ Hz), 7.09 (2H, d, $J = 8.5$ Hz), 7.44 (4H, t, $J = 7.5$ Hz), 7.55 (2H, t, $J = 7.0$ Hz), 7.70 (4H, d, $J = 7.5$ Hz), 7.76 (4H, d, $J = 8.5$ Hz), 7.85 (2H, dd, $J = 2.0, 8.5$ Hz), 7.89 (8H, s), 8.03 (2H, s) ppm. ^{13}C NMR (125 MHz) δ (CDCl$_3$): 118.0, 118.7, 128.3, 128.5, 129.8, 132.4, 132.5, 133.3, 133.4, 134.3, 137.4, 137.9, 157.9, 159.4, 194.0, 195.1 ppm. Anal. Calcd. for (C$_{53}$H$_{32}$O$_7$)$_n$: C, 81.53 %; H, 4.13 %. Found: C, 81.27 %; H, 4.29 %.

RESULTS AND DISCUSSION

Preparation of Acyl-acceptant Monomer 1

The acyl-acceptant monomer, 2,2′-(4-benzoylphenoxy)biphenyl (**1**), was prepared *via* nucleophilic aromatic substitution reaction of 2,2′-biphenol and 4-fluorobenzophenone in the presence of potassium carbonate for 24 h in DMAc/toluene (84 % yield).

Reactivity of Acyl-acceptant Monomer 1

We preliminarily investigated the reactivity of the resulting acyl-acceptant monomer (**1**) in the reaction with a monofunctional acyl donor compound. Table I shows the results of diaroylation of monomer **1** with 4-chlorobenzoyl chloride (**2a**) or 4-chlorobenzoic acid

Table I. Reaction of 2,2′-bis(4-benzoylphenoxy)biphenyl (1) with *p*-chlorobenzoic acid derivatives[a]

Run	2/mmol	Reagent	Temp. (°C)	Yield (%)[c] 3a	3b
1[b]	2a/0.8	AlCl₃, 1.8 mmol	RT	0	63
2[b]	2a/0.8	AlCl₃, 3.6 mmol	RT	92	0
3[b]	2a/0.4	AlCl₃, 3.6 mmol	RT	13	72
4[d]	2b/0.8	P₂O₅–MsOH 1.4 mL	120	50	50
5	2b/0.8	P₂O₅–MsOH, 1.4 mL	120	52	48

[a]Reaction conditions: biphenyl 1; 0.4 mmol, Reaction time; 24 h. [b]Solvent, 1,2-dichloroethane; 2.0 mL. [c]^{1}H NMR yield. [d]Reaction time, 8 h.

(2b). When 4.5 equimolar amounts of AlCl₃ were subjected, the monosubstituted product (3b) was obtained chemoselectively and regioselectively (Run 1). Though the production of the monosubstituted product (3b) means low ability for the *second* aroylation of monomer 1, it has been solved by treatment of biphenyl 1 with 9 equimolar amounts of AlCl₃ to give the disubstituted product (3a) as a single product in a high yield (Run 2). In this way, it has been disclosed that 2,2′-bis(4-benzoylphenoxy)biphenyl (1) has a sufficient reactivity for Friedel–Crafts diaroylation in the presence of excess AlCl₃. On the contrary, direct condensation of biphenyl 1 with carboxylic acid 2b in P₂O₅–MsOH[5,6,11–13] gave mixtures of monosubsituted and disubstituted products.

Polymerization of Acyl-acceptant Monomer 1 with Terephthaloyl Chloride

Table II shows the results of polymerization of 2,2′-bis(4-benzoylphenoxy)biphenyl (1) with terephthaloyl chloride (4a) in the presence of AlCl₃. Among solvents screened, 1,2-dichloroethane is the most suitable for this polymerization. The structures of the polyketones were confirmed on the basis of ^{1}H NMR spectra. The signal at 7.19 ppm which is assignable to the protons at 5,5′-positions of monomer 1 clearly disappears in the ^{1}H NMR spectrum of the product. This indicates
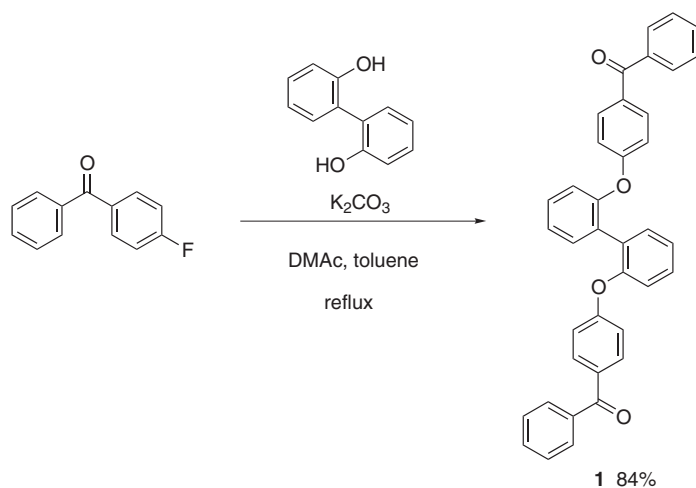
Scheme 1.
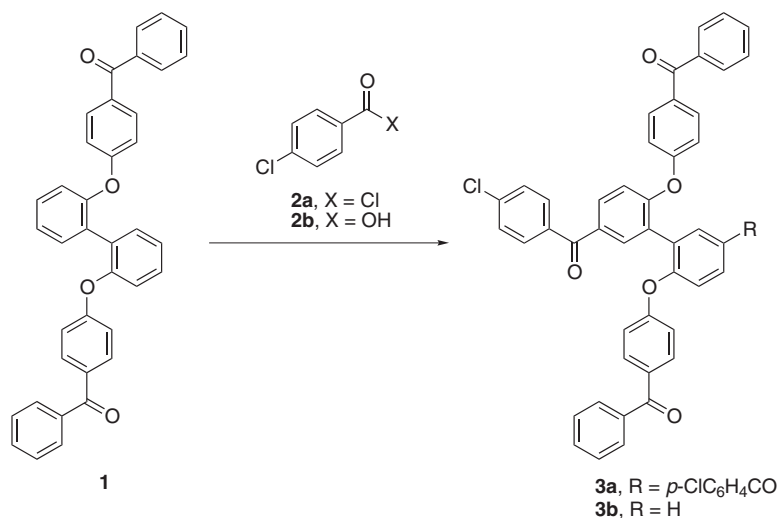
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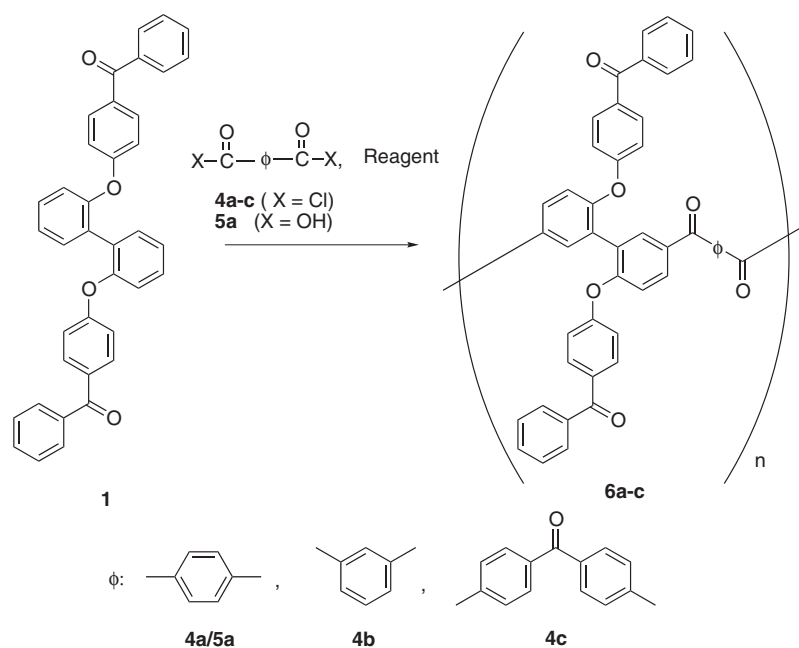
Scheme 3.

Table II. Polymerization of 2,2′-bis(4-benzoylphenoxy)biphenyl (**1**) with terephthalic acid derivatives **4a/5a**[a]

Run	4a/5a	Reagent/solvent	Temp. (°C)	Time (h)	Yield (%)	M_n[b]
1[c]	**4a**	AlCl₃/ClCH₂CH₂Cl	RT	20	84	13000
2[c]	**4a**	AlCl₃/ClCH₂CH₂Cl	RT	30	84	17000
3[c]	**4a**	AlCl₃/C₆H₅NO₂	RT	20	0	—
4[c]	**4a**	AlCl₃/CHCl₃	RT	20	83	3400
5[d]	**5a**	P₂O₅–MsOH	120	40	40	4000

[a]Monomer **1**, 0.4 mmol; terephthaloyl chloride (**4a**)/terephthalic acid (**5a**), 0.4 mmol. [b]Calibrated on the basis of GPC curve (column: Shodex KD-806M. eluent: CHCl₃. UV detector: 340 nm.) [c]AlCl₃, 3.6 mmol; Solvent, 2 mL. [d]P₂O₅–MsOH, 1.2 mL.

Table III. Polymerization of 2,2′-bis(4-benzoylphenoxy)biphenyl (**1**) with arenedicarbonyl chloride **4**[a]

Run	4	Time (h)	Yield (%)	M_n[b]	η_{inh} (dL g⁻¹)[c]	T_g (°C)	T_d (°C)[d]
1	**4a**	30	84	17000	0.382	159	525
2	**4b**	60	72	12000	0.362	158	510
3	**4c**	60	75	15000	0.318	163	500

[a]Reaction conditions: monomer **1**, 0.4 mmol; arenedicarbonyl chloride **4**, 0.4 mmol. AlCl₃, 3.6 mmol, ClCH₂CH₂Cl, 2 mL. [b]Calibrated on the basis of GPC curve (column: Shodex KD-806M. eluent: CHCl₃. UV detector: 340 nm.) [c]Determined in a concentrated H₂SO₄ solution (0.3 g dL⁻¹) at 30 °C. [d]Temperature where a 5 wt% weight loss was recorded by TG.

that regioselective dual aroylation at the 5,5′-positions of monomer **1**, *i.e.*, polymerization, proceeded. The resulting polyketone is soluble in CHCl₃. Such solubility is distinct from that of 2,2′-dimethoxybiphenylene-containing polyketones we have already synthesized, which is soluble only in concentrated H₂SO₄. Further elongation of reaction time, however, incurs the precipitates during polymerization in 1,2-dichloroethane and the precipitates were insoluble even in trifluoroacetic acid and concentrated H₂SO₄. When reaction time was elongated to 60 h, the component soluble in CHCl₃ was only 2 %. On the other hand, there is no difference in IR spectra between the soluble and insoluble components. On the basis of these observations, insolubilization is possibly due to either high molecular weight or cross-linked structure.

Synthesis and Characterization of Wholly Aromatic Polyketones 6a–c

Table III shows the results of the AlCl₃-mediated polymerization of monomer **1** with other arenedicarbonyl chlorides **4b** and **4c**. The same reaction behaviors were observed in the reaction of other dicarbonyl chlorides, yielding the corresponding polyketones. When isophthaloyl chloride (**4b**) was employed, elongation of reaction time incurred no precipitation of insoluble component but no further polymerization occurred. On the other hand, when 4,4′-benzophenonedicarbonyl chloride (**4c**) was allowed to react, a trace amount of the component insoluble to any solvent was obtained. As the structures of acyl chlorides **4a** and **4c** are probably stretched, the resulting polymers should be rigid and easy to separate out. On the contrary, the characteristically bent structures of *m*-phenylene units presumably results in high solubil-

ity of the polyketones derived from isophthaloyl chloride (**4b**).

Polyketones **6a–c** shows a 5 % weight loss in the TGA thermograms under nitrogen at *ca.* 500 °C. These properties are superior to those of the 2,2′-dimethoxybiphenylene-containing wholly aromatic polyketones we have already reported.[7] Probably, exclusion of sp^3 carbon–oxygen bond raises heat resistibility. T_g's of polyketones **6a–c** were determined to be *ca.* 160 °C on the basis of the DSC curves. These values are lower than those of 2,2′-dimethoxybiphenylene-containing wholly aromatic polyketones.[3,7] In addition, any polyketones thus obtained showed no melting point.

CONCLUSION

2,2′-Bis(4-benzoylphenoxy)biphenyl (**1**) has an excellent acyl-accepting reactivity in electrophilic aromatic substitution so that high-molecular-weight wholly aromatic polyketones are readily yielded. The obtained polyketones show excellent solubility to organic solvents and have high heat resistibility.

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