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ORIGINAL ARTICLE

Nanosized palladium-catalyzed Suzuki–Miyaura coupling polymerization: synthesis of soluble aromatic poly(ether ketone)s

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Nanosized palladium species, which were prepared *in situ* from $Pd(OAc)_2$, PPh_3 and Bu_4NOAc in 1,4-dioxane, were suitable for the synthesis of 1,1′-binaphthyl-2,2′-dioxy-bearing aromatic poly(ether ketone)s 5. The resulting poly(ether ketone)s 5 are soluble in typical organic solvents, such as $CHCl_3$, tetrahydrofuran and *N,N*-dimethylformamide. Glass transition temperatures (T_g′s) of poly(ether ketone)s 5 are in the range of 188–224 °C. Temperatures where 10% weight losses of poly(ether ketone)s 5 occur under N_2 flow are in the range of 445–480 °C.
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INTRODUCTION

Aromatic poly(ether ketone)s, which consist of aromatic, carbonyl and ether units, have drawn considerable attention owing to their outstanding chemical and physical stability.[1–3] General synthetic methods of aromatic poly(ether ketone)s are mainly (i) nucleophilic aromatic substitution polymerization of aromatic difluorides with aromatic diols, (ii) electrophilic aromatic substitution polymerization of highly electron-rich aromatics with aromatic dicarboxylic acids/acid dichlorides and (iii) transition metal-catalyzed aromatic coupling polymerization, such as $NiBr_2$/Zn-mediated aromatic homo-coupling polymerization of aromatic dichlorides.[2,3] Almost all of the reported aromatic poly(ether ketone)s have been synthesized through nucleophilic aromatic substitution polymerization owing to high conversion, easy treatment and wide application. As ether bonds are inevitably formed through this polymerization, they behave as flexible units and lower the thermal stability of the resulting polymers. On the other hand, aromatic carbonyl bonds are formed in electrophilic aromatic substitution polymerization. However, selection of polymerizable and regioselective electron-rich arenes is extremely limited. Although aromatic–aromatic bonds are formed in $NiBr_2$/Zn-mediated aromatic homo-coupling polymerization, strict treatment against oxygen and moisture during polymerization is required for smooth polymerization.

We have reported the synthesis of several aromatic polyketones using these three methods.[4–11] Among these studies, it has been revealed that aromatic polyketones containing twisted aromatic ring-assembly units show both excellent thermal stability and sufficient solubility to typical organic solvents, affording flexible and thermally stable polymer films. In particular, introduction of 1,1′-binaphthyl-6,6′-diyl units to polyketone backbones was effective for the development of aromatic polyketones with both high T_g and sufficient solubility through these three methods.[8–11]

The Suzuki–Miyaura cross-coupling reaction is one of the most useful protocols for aromatic–aromatic bond formation reactions and has been applied for the synthesis of a lot of π-conjugated organic materials, including polymers.[12–15] Although it has the advantage of high conversion and easy treatment, it has scarcely been applied to the synthesis of aromatic polyketones. In particular, Suzuki–Miyaura coupling reaction of bis(halobenzoyl)-type monomers requires long reaction times, probably because of lower reactivity based on carbonyl groups.[15]

Recently, we presented a preliminary report on the successful synthesis of aromatic poly(ether ketone)s through nanosized palladium-catalyzed[16–26] Suzuki–Miyaura coupling polymerization of 2,2′-bis(iodobenzoyl)-1,1′-binaphthyls with aromatic diboric acid pinacol esters.[27] In this article, we would like to discuss the nanosized palladium-catalyzed Suzuki–Miyaura coupling polymerization from the viewpoints of the scope and limitations of monomer structures and detail an investigation of reaction conditions.

EXPERIMENTAL PROCEDURE

Materials

(*S*)-BINOL (**1**, $[\alpha]_D^{25}$: −33 °), triphenylphosphine and trimethyl borate were purchased from Kanto Chemical Co. Ltd. (Tokyo, Japan). $Pd(OAc)_2$, potassium carbonate and pinacol were purchased from Wako Pure Chemical Industries

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(Osaka, Japan). Bu_4NOAc and MS4A were purchased from Aldrich (St Louis, MO, USA). These reagents were used as received. 1,4-Dioxane was purchased from Kanto Chemical Co. Ltd. and was used after distillation in the presence of CaH_2. Dimethylformamide was purchased from Kanto Chemical Co. Ltd. and was used after distillation in the presence of CaH_2 under reduced pressure.

4-Fluoro-4′-iodobenzophenone (**2A**) and related halobenzophenones **2B–2E** were prepared through $AlCl_3$-mediated Friedel–Crafts acylation reaction of fluorobenzene with the corresponding halobenzoyl chloride. Diboric acid pinacol esters **4m** and **4p** were prepared through esterification of the corresponding diboric acids with pinacol. The diboric acids were prepared through lithiation of the corresponding dibromide followed by transmetallation by trimethyl borate and acidic workup.

Instruments

^{1}H-NMR spectra were recorded on a JEOL ECX-400 (JEOL, Tokyo, Japan, 400 MHz) and a JEOL AL-300 (300 MHz). Chemical shifts are expressed in p.p.m. relative to the internal standard of Me_4Si ($\delta = 0.00$). ^{13}C-NMR spectra were recorded on a JEOL ECX-400 (100 MHz) and a JEOL AL-300 (75 MHz). Chemical shifts are expressed in p.p.m. relative to the internal standard of $CDCl_3$ ($\delta = 77.0$). Infrared (IR) measurement was recorded on a JEOL FTIR-4100 and a Horiba FT-210 (Horiba, Kyoto, Japan). Molar rotations ($[\Phi]_{25}^{D}$) were estimated on the basis of the measurement in a $CHCl_3$ solution (1 g dl^{-1}) using a JASCO DIP-1000 digital polarimeter (JASCO, Tokyo, Japan). Circular dichroism measurement was performed in a $CHCl_3$ solution (6.6×10^{-5} mol l^{-1}) using a JASCO J-720WI. Gel permeation chromatography 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 JASCO PU-2080 equipped with a Ultraviolet detector (254 nm) and a Shodex K-804L column (Shodex, Tokyo, Japan). Glass transition temperatures (T_g) were estimated on the basis of differential scanning calorimetry thermograms. The differential scanning calorimetry thermograms were recorded on a PerkinElmer DSC-4000 differential scanning calorimeter with a heating rate of 10 K min^{-1} (Waltham, MA, USA). Thermal degradation temperatures (T_d) were estimated on the basis of thermogravimetric analysis thermograms. The thermogravimetric analysis thermograms were recorded on a PerkinElmer TGA 4000 thermogravimeter with a heating rate of 10 K min^{-1}.

Synthesis of diiodide 3P(I), 3M(I) 3O(I), dibromide 3P(Br) and dichloride 3P(Cl)

To a 50-ml two-necked flask, (*S*)-BINOL (**1**, 1.14 g, 4.0 mmol), 4-fluoro-4′-iodobenzophenone (**2A**, 4.54 g, 14 mmol), anhydrous potassium carbonate (1.66 g, 12 mmol) and freshly distilled dimethylformamide (5 ml) were added. The mixture was stirred at 150 °C for 24 h. The reaction mixture was poured into water in a beaker. The precipitate was collected by suction filtration and extracted with $CHCl_3$ three times. The combined extracts were dried over anhydrous $MgSO_4$. After removal of the drying reagent, $CHCl_3$ was removed under reduced pressure. The crude product was purified by silica gel column chromatograph (hexane:chloroform = 1:1) to yield diiodide **3P(I)** in 71% yield (2.55 g) as a white powder. A series of dihalides **3** were also prepared in the same manner.

Diiodide **3P(I)**: Yield: 71%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 6.79 (4H, d, $J = 8$ Hz), 7.27–7.33 (6H, m), 7.36 (4H, d, $J = 8$ Hz), 7.45 (2H, t, $J = 8$ Hz), 7.52 (4H, d, $J = 8$ Hz), 7.78 (4H, d, $J = 8$ Hz), 7.91 (2H, d, $J = 8$ Hz), 7.95 (2H, d, $J = 8$ Hz) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 99.7, 117.4, 120.0, 122.9, 125.5, 126.0, 127.1, 128.3, 130.4, 131.0, 131.2, 131.3, 132.0, 134.2, 137.2, 137.6, 151.1, 161.6 and 194.2 p.p.m. IR ν (KBr): 1648, 1587, 1500 and 1240 cm^{-1}. HRMS-FAB (*m/z*) For $C_{46}H_{28}I_2O_4$: Calcd [M$^+$]: 898.0082. Found: 898.0096. $[\alpha]_D^{25}$: −24 °. $[\Phi]_D^{25}$: −216 °.

Diiodide **3M(I)**: Yield: 61%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 6.81(4H, d, $J = 8$ Hz), 7.17(2H, t, $J = 8$ Hz), 7.27–7.35(6H, m), 7.45(2H, t, $J = 8$ Hz), 7.55(4H, d, $J = 8$ Hz), 7.58(2H, d, $J = 8$ Hz), 7.85(2H, d, $J = 8$ Hz), 7.91(2H, d, $J = 8$ Hz), 7.96(2H, d, $J = 8$ Hz), 7.97(2H, s) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 94.2, 117.4, 120.1, 123.0, 125.5, 126.0, 127.1, 128.3, 129.0, 130.0, 130.4, 131.0, 131.1, 132.2, 134.1, 138.4, 140.0, 140.9, 151.1, 161.7 and 193.6 p.p.m. IR ν (KBr): 1654, 1587, 1500 and 1243 cm^{-1}. HRMS-FAB (*m/z*) for $C_{46}H_{28}I_2O_4$: Calcd [M$^+$]: 898.0082. Found: 898.0096. $[\alpha]_D^{25}$: −38 ° $[\Phi]_D^{25}$: −341 °.

Diiodide **3O(I)**: Yield: 83%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 6.77 (4H, d, $J = 8$ Hz), 7.13 (2H, t, $J = 8$ Hz), 7.20–7.34 (6H, m), 7.38–7.47 (6H, m), 7.54 (4H, d, $J = 8$ Hz), 7.85–7.96 (6H, m) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 92.3, 117.7, 119.9, 122.8, 125.5, 125.9, 127.1, 127.9, 128.3, 128.4, 130.0, 130.3, 131.0, 132.5, 134.1, 139.7, 144.2, 151.8, 162.2 and 195.9 p.p.m. IR ν (KBr): 1664, 1585, 1500 and 1243 cm^{-1}. $[\alpha]_D^{25}$: −32 °. $[\Phi]_D^{25}$: −287 °.

Dibromide **3P(Br)**: Yield: 83%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 6.68 (4H, d, $J = 8$ Hz), 7.30 (4H, d, $J = 8$ Hz), 7.32 (2H, t, $J = 8$ Hz), 7.46 (2H, t, $J = 8$ Hz), 7.49–7.57 (12H, m), 7.91 (2H, d, $J = 8$ Hz), 7.95(2H, d, $J = 8$ Hz) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 117.4, 120.0, 122.9, 125.5, 126.0, 127.1, 127.2, 128.3, 130.4, 131.0, 131.2, 131.4, 131.6, 132.0, 134.1, 136.6, 151.1, 161.6 and 194.2 p.p.m. IR ν(KBr): 1654, 1587, 1500, 1245 and 1068 cm^{-1}. HRMS-FAB (*m/z*) for $C_{46}H_{28}Br_2O_4$: Calcd [M$^+$]: 802.0356. Found: 802.0362. $[\alpha]_D^{25}$: −49 °. $[\Phi]_D^{25}$: −393 °.

Diiodide **3P(Cl)**: Yield: 90%. ^{1}H-NMR δ (300 MHz, $CDCl_3$): 6.80 (4H, d, $J = 8.7$ Hz), 7.29–7.35 (6H, m), 7.39–7.48 (6H, m), 7.53 (4H, d, $J = 8.7$ Hz), 7.59 (4H, d, $J = 8.4$ Hz), 7.92 (2H, d, $J = 8.4$ Hz), 7.96 (2H, d, $J = 8.7$ Hz) p.p.m. ^{13}C-NMR δ (75 MHz, $CDCl_3$): 117.3, 119.8, 122.8, 125.3, 125.8, 126.9, 128.2, 128.5, 130.2, 130.9, 131.1, 131.2, 131.9, 134.0, 136.1, 138.5, 151.0, 161.4 and 194.0 p.p.m. IR ν(KBr): 1656, 1590, 1243 and 1090 cm^{-1}. HRMS-FAB (*m/z*) for $C_{46}H_{28}Cl_2O_4$: Calcd [M$^+$]: 714.1366. Found: 714.1379. $[\alpha]_D^{25}$: −4.1 °. $[\Phi]_D^{25}$: −29 °.

Synthesis of aromatic polyketones 5

To a dried 30-ml two-necked flask equipped with a reflux condenser, palladium acetate (4.5 mg, 20 μmol) and triphenylphosphine (10.5 mg, 40 μmol) were added. Tetrabutylammonium acetate (603 mg, 2.0 mmol), pottasium carbonate (276 mg, 2.0 mmol), molecular sieves 4A (70 mg), diiodide **3P(I)** (180 mg, 0.2 mmol), boric acid pinacol ester **4m** (77.9 mg, 0.2 mmol) and 1,4-dioxane (1.0 ml) were added to this flask. After stirring at 100 °C for 1 h, the reaction mixture was poured into 150 ml of MeOH/aqueous HCl(v/v = 9/1) in a beaker. The precipitant was washed with water and acetone. The solid was dissolved in $CHCl_3$ and filtrated by celite. After removal of $CHCl_3$ under reduced pressure, polyketone **5Pm** was obtained in 90% yield (140.4 mg). Other polyketones were synthesized in the same manner.

Polyketone **5Pm**: ^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.84 (6H, s), 6.60 (1H, s), 6.83 (4H, d, $J = 8$ Hz), 7.22–7.35 (10H, m), 7.38–7.51 (3H, m), 7.51–7.74 (8H, m), 7.84–8.00 (4H, m) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 56.0, 96.2, 117.5, 120.0, 122.3, 122.9, 125.4, 126.0, 127.0, 128.3, 129.3, 129.9, 130.4, 131.0, 132.0, 132.2, 132.8, 134.2, 135.9, 142.1, 151.4, 157.7, 161.3 and 195.1 p.p.m. IR ν (KBr): 1654, 1600, 1498, 1234 and 1203 cm^{-1}. $[\alpha]_D^{25}$: −5.8 ° $[\Phi]_D^{25}$: −45 °.

Polyketone **5Pp**: Yield 91%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.78(6H, s), 6.85(4H, d, $J = 8$ Hz), 6.98(2H, s), 7.26–7.36(10H, m), 7.40–7.48(2H, m), 7.60-7.70(4H, m), 7.73(4H, d, $J = 8$ Hz), 7.86–7.99(4H, m) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 56.5, 114.7, 117.5, 120.0, 122.9, 125.4, 126.0, 127.0, 128.3, 129.4, 129.8, 130.0, 130.3, 131.0, 131.9, 132.2, 134.2, 136.5, 142.2, 150.9, 151.4, 161.3 and 195.0 p.p.m. IR ν (KBr): 1654, 1600, 1498, 1236, 1211 cm^{-1}. $[\alpha]_D^{25}$: −5.9°. $[\Phi]_D^{25}$: −46°.

Polyketone **5Mm**: Yield 49%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.75(6H, s), 6.57(1H, s), 6.81(4H, d, $J = 8$ Hz), 7.19–7.44(6H, m), 7.50–7.68(11H, m), 7.78–7.93(8H, m) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 55.9, 96.0, 117.5, 120.0, 122.3, 122.9, 125.4, 125.9, 127.0, 128.1, 128.3, 130.3, 131.0, 131.9, 132.3, 132.7, 133.1, 134.1, 137.7, 138.0, 151.4, 157.2, 161.3 and 195.4 p.p.m. IR ν (KBr): 1654, 1585, 1500, 1232 and 1203 cm^{-1}. $[\alpha]_D^{25}$: −6.6 °. $[\Phi]_D^{25}$: −51 °.

Polyketone **5Mp**: Yield 63%. ^{1}H-NMR δ (400 MHz, $CDCl_3$): 3.71(6H, s), 6.84(4H, d, $J = 8$ Hz), 6.94(2H, s), 7.22–7.32(4H, m), 7.34–7.43(4H, m), 7.46(2H, t, $J = 8$ Hz), 7.61(2H, d, $J = 8$ Hz), 7.67(4H, d, $J = 8$ Hz), 7.72(2H, d, $J = 8$ Hz), 7.82–7.95(6H, m) p.p.m. ^{13}C-NMR δ (100 MHz, $CDCl_3$): 56.5, 114.6, 117.4, 120.0, 122.9, 125.4, 125.9, 127.0, 128.1, 128.3, 128.7, 129.8, 130.3, 130.8, 130.9, 131.8, 132.3, 133.2, 134.2, 137.8, 138.3, 150.7, 151.3, 161.4 and 195.3 p.p.m. IR ν (KBr): 1654, 1587, 1500, 1234 and 1211 cm^{-1}. $[\alpha]_D^{25}$: −4.5 °. $[\Phi]_D^{25}$: −35 °.

RESULTS AND DISCUSSION

Preparation of monomers 3

According to our previous papers,[4,9] three regioisomeric diiodides **3M(I)**, **3P(I)** and **3O(I)** were prepared *via* nucleophilic aromatic substitution reaction of (*S*)-BINOL (**1**) with 4-fluoroiodobenzophenones **2A-C**,

which are prepared through Friedel–Crafts acylation of fluorobenzene with iodobenzoyl chloride in the presence of $AlCl_3$, in moderate yields (Scheme 1). The corresponding dibromide **2D** and dichloride **2E** were also prepared in the same procedure.

Optimization of reaction conditions—polymerization between monomer 3P(I) and 4m

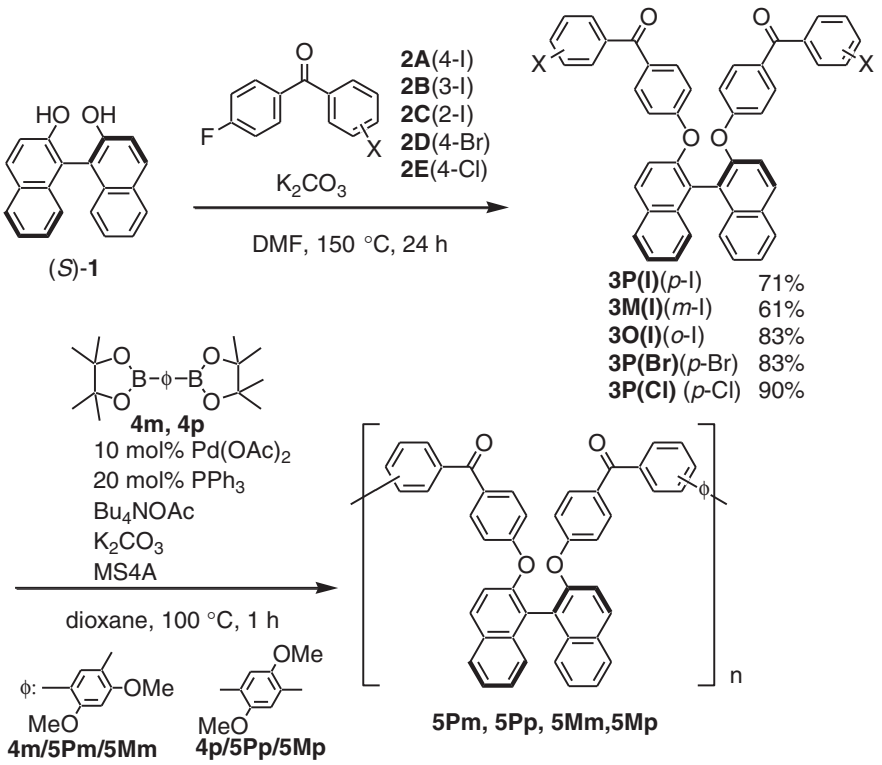
Polymerization of monomer **3P(I)** with diboric acid pinacol ester **4m** was conducted under the various reaction conditions. The results are shown in Table 1. When the nanosized palladium catalyst,[16] which was prepared *in situ* from $Pd(OAc)_2$, PPh_3 and Bu_4NOAc in 1,4-dioxane, was employed, smooth and rapid polymerization proceeded to give poly(ether ketone) **5Pm**. As shown in runs 1–3, 10 mol% $Pd(OAc)_2$ ($=20\,\mu$mol) against the monomers (0.2 mmol, respectively) were the most suitable to obtain high-molecular-weight polymers. When 20 mol% catalyst was employed, the molecular weights of the resulting polymer slightly decreased, probably owing to aggregation of nanosized palladium under concentrated conditions (run 3). Even during polymerization in the presence of 10 mol% catalyst, it seems that active nanosized palladium species are gradually deactivated by slow aggregation. Consequently, prolongation of reaction time gave no effects on increase in molecular weights. When Bu_4NOAc, was not added, that is, under general palladium catalyst system (conditions B), only low-molecular-weight polymer was obtained even after stirring for 6 h (run 4). Use of a more polar solvent, that is, dimethylformamide was also ineffective under the general palladium catalyst system (run 5). On the other hand, addition of Bu_4NBr was also effective to enable smooth polymerization (run 6). When $Pd(PPh_3)_4$ was employed instead of $Pd(OAc)_2$/$2PPh_3$, the moderate-molecular-weight polymer was obtained. Consequently, the $Pd(OAc)_2$/PPh_3/Bu_4NOAc system (run 2) was determined as the optimized reaction conditions.

Synthesis of aromatic poly(ether ketone)s 5

At first, polymerization of the corresponding dibromide **3P(Br)** and dichloride **3P(Cl)** with diboric acid pinacol ester **4m** was carried out under the above optimized conditions. Although the corresponding poly(ether ketone) **5Pm** was obtained, the molecular weights of the polymers derived from **3P(Br)** and **3P(Cl)** were lower than those derived from **3P(I)**. In the case of dibromide **3P(Br)** and dichloride **3P(Cl)**, the oxidation addition step proceeds slower as imagined, affording lower-molecular-weight polymer. However, it could be evaluated that the nanosized palladium-catalyzed polymerization of dichloride **3P(Cl)** proceeded moderately (Table 2).

Next, polymerization of *m*-substituted and *o*-substituted diiodides, **3M(I)** and **3O(I)**, were also performed. When *m*-substituted diiodide **3M(I)** was used, poly(ether ketone)s **5Mm** and **5Mp** with lower molecular weights were obtained. When *o*-substituted diiodide **3O(I)** was used, no polymerization proceeded and only diiodide **3O(I)** was recovered. These reactions demonstrate that steric hindrance around reactive halogens influences the reactivity in the transmetallation step and the *o*-substitution structure is more disadvantageous.

All of the poly(ether ketone)s **5Pm**, **5Pp**, **5Mm** and **5Mp** were soluble in typical solvents as shown in Table 3. Among these polymers, poly(ether ketone)s **5Mm** and **5Mp**, which are derived from *m*-substiutited diiodide **3M(I)**, were more soluble than **5Pm** and **5Pp.** The difference of the solubility is probably because of not only the decrease of molecular weights but also the bent structures based on *m*-substitution compared with linear ones based on *p*-substitution.



Scheme 1 Suzuki–Miyaura coupling polymerization of dihalides **3** with diboric acid pinacol esters **4m** and **4p**.

Table 1 Nanosized palladium-catalyzed Suzuki–Miyaura coupling polymerization of diiodide 3P(I) with diboric acid pinacol ester 4m

Run	*Conditions*	*$Pd(OAc)_2$ (μmol)*	*Time (h)*	*Yield (%)*	*Mn*[a]	*Mw*[a]	*Mw/Mn*[a]
1	A[b]	10	1	82	8900	16500	1.85
2	A[b]	20	1	90	10100	16600	1.64
3	A[b]	40	1	90	7000	15300	2.19
4	B[c]	40	6	83	3200	8400	2.58
5	C[d]	40	6	42	4600	10000	2.15
6	D[e]	20	1	79	10800	21300	1.96
7	E[f]	20	1	87	6200	14700	2.36

[a]Estimated by gel permeation chromatography (eluent; $CHCl_3$) based on polystyrene standards.
[b]Reaction conditions A: monomer **3P(I)** and **4m** (0.2 mmol, respectively), palladium acetate, PPh_3 (twice against $Pd(OAc)_2$), potassium carbonate (2 mmol), Bu_4NOAc (2 mmol), MS4A (70 mg) and 1,4-dioxane (1 ml), reflux, 1 h.
[c]Reaction conditions B: Bu_4NOAc and MS4A were not added against conditions A.
[d]Reaction conditions C: In replace of dioxane, dimethylformamide was used. Other reaction conditions are the same as conditions B.
[e]Reaction conditions D: In replace of Bu_4NOAc, Bu_4NBr was used. Other reaction conditions are the same as conditions A.
[f]Reaction conditions E: In replace of $Pd(OAc)_2$ and $2PPh_3$, $Pd(PPh_3)_4$ was used. Other reaction conditions are the same as conditions A.

Table 2 Synthesis of aromatic poly(ether ketone)s 5[a]

3	*4*	*5*	*Yield/%*	M_n[b]	M_w[b]	M_w/M_n[b]
3P(I)	**4m**	**5Pm**	90	10100	16600	1.64
3P(Br)	**4m**	**5Pm**	51	2100	7000	3.33
3P(Cl)	**4m**	**5Pm**	60	1500	4900	3.28
3P(I)	**4p**	**5Pp**	91	5400	16700	3.09
3M(I)	**4m**	**5Mm**	49	2100	7600	3.59
3M(I)	**4p**	**5Mp**	63	3200	10500	3.27
3O(I)	**4m**	—	0[c]	—	—	—

[a]Reaction conditions: monomer **3** and **4** (0.2 mmol, respectively), palladium acetate (20 μmol), PPh_3 (40 μmol), potassium carbonate (2 mmol), Bu_4NOAc (2 mmol), MS4A (70 mg) and 1,4-dioxane (1 ml), reflux, 1 h.
[b]Eatimated by gel permeation chromatography (eluent; $CHCl_3$) based on polystyrene standards.
[c]No polymerization.

Table 3 Solubility of aromatic poly(ether ketone)s 5[a]

5	*MeOH*	*$CHCl_3$*	*THF*	*DMSO*	*DMF*	*NMP*
5Pm	−	+ +	+ −	+ −	+ +	+ +
5Pp	−	+ +	+ −	+	+ +	+ +
5Mm	−	+ +	+ +	+ +	+ +	+ +
5Mp	−	+ +	+ +	+ +	+ +	+ +

Abbreviations: DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; NMP, *N*-methylpyrrolidinone; THF, tetrahydrofuran.
[a](+ +), soluble at room temperature; (+), soluble on heating; (+ −), partially soluble; (−), insoluble.

Table 4 Thermal and optical properties of aromatic poly(ether ketone)s 5

5	*T_g (°C)*[a]	*T_{d10} (°C)*[b]	*$[\alpha]_D^{25}$ (degree)*[c]	*$[\Phi]_D^{25}$ (degree)*[c]
5Pm	224	445	−5.8	−45
5Pp	205	465	−5.9	−46
5Mm	188	480	−6.6	−51
5Mp	191	475	−4.5	−35

[a]Determined on the basis of differential scanning calorimetry (DSC) curves. Heating rate: $10\,K\,min^{-1}$.
[b]Temperature where a 10% weight loss occurs. Heating rate: $10\,K\,min^{-1}$.
[c]Measured in a $CHCl_3$ solution ($1\,g\,dl^{-1}$).

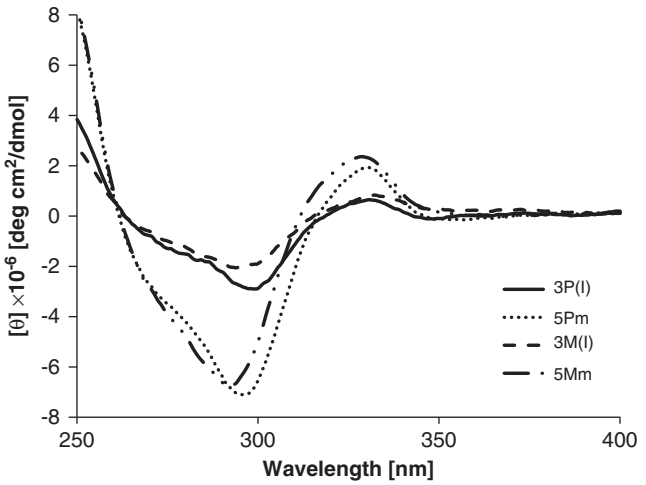


Figure 1 Circular dichroism spectra of monomers **3** and poly(ether ketone)s **5**.

Thermal properties

Thermogravimetric analysis of poly (ether ketone)s **5** proved that they have excellent thermal stability. No loss of the weights in the temperature ranging up to ca. 450 °C under N_2 flow was observed. These thermal behaviors are similar to the polyketones bearing methoxy groups, which indicates that the cleavage of O-CH_3 bonds occurs firstly during thermal degradation.

Glass transition temperatures (T_g) of poly(ether ketone)s **5** are in the range of 188–224 °C, which are higher than those of PEEK (143 °C) and almost all of the reported aromatic poly(ether ketone)s including our previous works.[4–10] The excellent thermal stability and sufficient solubility depend on non-coplanar structures of 1,1′-binaphthyl-2,2′-diaryoxy units, which give suitable suppression of the free rotation and the π,π-stacking to polymer main chains. In addition, the exclusion of flexible ether units from the main chains is another factor to increase T_g.

Optical properties

Optical rotation of poly (ether ketone)s **5** was measured in a 1-g dl^{-1} $CHCl_3$ solution. Specific rotation [α] and molar rotation [*Φ*] of poly (ether ketone)s **5** are shown in Table 4. There is only negligible difference among these values. Figure 1 shows circular dichroism spectra of monomers **3P(I)** and **3M(I)** derived from (*S*)-**1**, and poly(ether ketone)s **5Pm** and **5Mm** derived from the (*S*)-monomers. Although larger cotton effects in the spectra of **3M(I)** and **5Mm** were observed than those of **3P(I)** and **5Pm**, there are no differences between the diiodides and the corresponding polymers. These results probably indicate that the poly(ether ketone)s **5** hold no specific regular secondary structures.

CONCLUSIONS

Nanosized palladium species, which are easily prepared *in situ* from $Pd(OAc)_2$, PPh_3 and Bu_4NOAc in 1,4-dioxane, were suitable for Suzuki–Miyaura cross-coupling polymerization of diiodides **3** and aromatic diboric acid pinacol esters **4** to synthesize 1,1′-binaphthyl-2,2′-diaryloxy-bearing aromatic poly(ether ketone)s **5**. This catalyst was able to be applied to polymerization of aromatic dibromide and

even aromatic dichloride. Addition of ammonium salt, that is, Bu_4NOAc and Bu_4NBr, was requisite for smooth polymerization. The resulting poly(ether ketone)s **5** are soluble in typical organic solvents, such as $CHCl_3$, tetrahydrofuran and dimethylformamide. Poly(ether ketone)s **5** are optically active on the basis of optically active 1,1′-binaphthyl-2,2′-oxy units. Glass transition temperatures (T_g′s) of poly(ether ketone)s **5** are in the range of 188–224 °C. Temperatures where 10% weight losses of poly(ether ketone)s **5** occur under N_2 flow are in the range of 445–480 °C.

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