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Synthesis of Aromatic Polyketones Bearing 1,1′-Binaphthyl-2,2′-dioxy Units through Suzuki–Miyaura Coupling Polymerization

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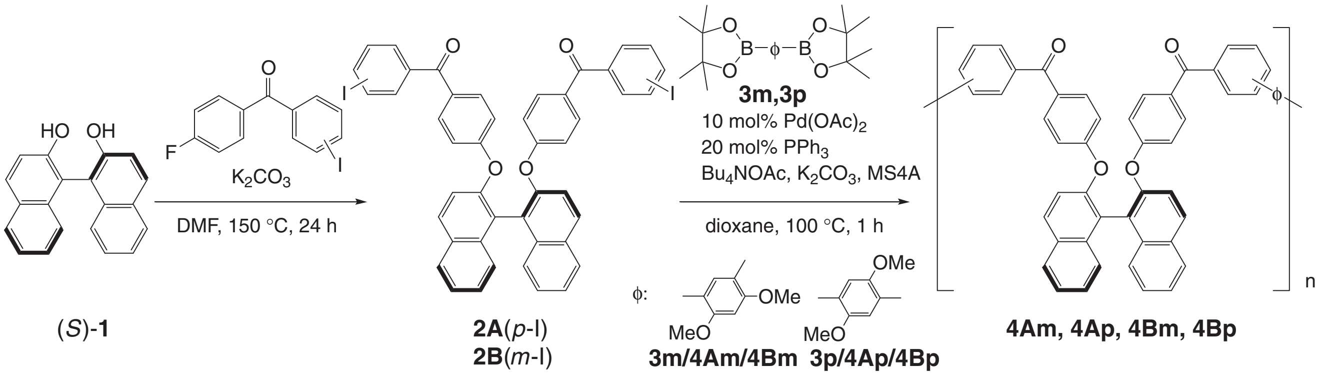
Palladium nanocluster-catalyzed Suzuki–Miyaura coupling polymerization of 2,2′-bis(iodobenzoylphenoxy)-1,1′-binaphthyls **2** with aromatic diboric acid diesters **3** proceeded smoothly, affording 1,1′-binaphthyl-2,2′-dioxy-bearing aromatic polyketones **4**. The resulting polyketones **4** have excellent thermal stability and solubility in typical organic solvents.

Aromatic polyketones, which consist of aromatics and carbonyl groups, receive much attention from the viewpoint of excellent chemical and thermal stability, high mechanical strength, and so on.[1] We have reported the synthesis of several aromatic polyketones.[2–4] During our studies, it has been disclosed that aromatic polyketones bearing 2,2′-diaryloxy-5,5′-biphenylene,[2] *o*-terphenylene,[3] and 2,2′-dimethoxy-1,1′-binaphthyl-6,6′-diyl[4] units in the main chains are very soluble in typical organic solvents. The excellent solubility originates in introduction of suitably-twisted aromatic ring-assemblies to the main chains. In particular, introduction of 1,1′-binaphthyl units improved both solubility and thermal stability of the resulting polyketones. The Suzuki–Miyaura coupling reaction is one of the most important tools for bond formation reactions between aromatic rings in terms of high conversion and easy treatment.[5] However, the Suzuki–Miyaura coupling polymerization[6] has been less applied to the synthesis of aromatic polyketones than nucleophilic aromatic substitution polymerization and homocoupling polymerization.[2–4] Recently, nanosized palladium has been applied to the cross-coupling reaction, in which nanopalladium plays a role as a reservoir of the ligandless, naked active species.[7,8] Facile synthesis of aromatic polyketones with high molecular weight through the Suzuki–Miyaura coupling is expected by adopting the nano-palladium catalyst system. In this communication, we would like to report the synthesis of aromatic polyketones through the Suzuki–Miyaura coupling polymerization catalyzed by the nano-palladium species developed by us.[8]

Regioisomeric diiodide **2A** and **2B** were prepared through nucleophilic aromatic substitution reaction of (*S*)-1,1′-bi-2-naphthol (**1**) with 4-fluoro-4′/3′-iodobenzophenone in the presence of K_2CO_3 (Scheme 1).[9] Polymerization of diiodide **2A** with 4,6-dimethoxy-1,3-phenylene diboric acid pinacol ester **3m** was attempted under typical reaction conditions (DMF, 6 h).[6] However, only the oligomer was obtained in 42% yield. On the other hand, when palladium nanocluster, prepared in situ from $Pd(OAc)_2$, PPh_3, and Bu_4NOAc, was employed, high-molecular-weight polyketone **4Am** was obtained in good yield. The color of the reaction mixture was changed from yellow to cloudy and brown within 5 min, and finally changed to black within 10 min, which strongly indicates the formation of palladium nanoclusters in situ the same as our previous reports.[8] Addition of Bu_4NOAc was requisite to smooth polymerization. Prolongation of reaction time from 1 to 2 h was ineffective in the increase of molecular weights. These results suggest that active nanocluster species are prepared just after addition and catalyze the Suzuki–Miyaura coupling polymerization, yielding high-molecular-weight aromatic polyketones.

As shown in Table 1, several regioisomeric polyketones were obtained in moderate yields.[9] When monomer **2B** was employed, the decrease of molecular weights was observed. The difference of reaction behaviors between monomers **2A** and **2B** probably results from steric effects in the transmetalation step. In fact, the reaction of 2,2′-bis[(2-iodobenzoyl)phenoxy]-1,1′-



Scheme 1. Synthesis of aromatic polyketones through Suzuki–Miyaura coupling polymerization.

Table 1. Synthesis of aromatic polyketones **4**[a]

2	3	4	Yield/%	M_n[b]	M_w[b]	$M_\mathrm{w}/M_\mathrm{n}$[b]
2A	**3m**	**4Am**	90	10100	16600	1.64
2A	**3p**	**4Ap**	91	5400	16700	3.09
2B	**3m**	**4Bm**	49	2100	7600	3.59
2B	**3p**	**4Bp**	63	3200	10500	3.27

[a]Reaction conditions: monomer **2** and **3** (0.2 mmol, respectively), palladium acetate (0.02 mmol), PPh_3 (0.04 mmol), potassium carbonate (2 mmol), Bu_4NOAc (2 mmol), MS4A (70 mg), dioxane (1 mL), reflux, 1 h. [b]Estimated by GPC (eluent; $CHCl_3$) based on polystyrene standards.

Table 2. Solubility and thermal properties of aromatic polyketones **4**[a]

4	MeOH	$CHCl_3$	THF	DMSO	DMF	T_g/°C[b]	T_d10/°C[c]
4Am	−	++	+−	+−	++	224	445
4Ap	−	++	+−	+	++	205	465
4Bm	−	++	++	++	++	188	480
4Bp	−	++	++	++	++	191	475

[a](++): soluble at rt; (+): soluble on heating; (+−): partially soluble; (−) insoluble. [b]Determined on the basis of DSC curves. Heating rate: 10 K min^{-1}. [c]Temperature where a 10% weight loss occurs. Heating rate: 10 K min^{-1}.

binaphthyl, which is more bulky, with **3m** afforded no polymerized products.

All of the polyketones thus obtained were excellently soluble in typical solvents as shown in Table 2. In particular, polyketones **4Bm** and **4Bp**, which are derived from the *m*-iodo-substituted monomer **2B**, shows excellent solubility. The excellent solubility is probably due to not only to the decrease of molecular weights but also the introduction of bent structures based on *m*-substitution.

Thermogravimetric analysis of the polyketones **4** disclosed excellent thermal stability. No loss of weight in the temperature which range up to ca. 450 °C under N_2 flow was observed. These thermal behaviors are similar to those of polyketones containing methoxy groups on aromatic rings, previously reported.[4] DSC measurement disclosed that all polyketones are amorphous. The glass-transition temperatures of polyketones **4** range from 188 to 224 °C, which are higher than those of most of the polyketones which we have synthesized thus far.[2–4] Specific three-dimensional structures around binaphthyl units by steric repulsion between two naphthalene rings not only suppress the free rotation of polymer chains but also bring about larger free volumes to polymers, which would give the suitable rigidity and the excellent solubility to polyketones **4**.

Figure 1 shows circular dichroism (CD) spectra of monomers **2** and polyketones **4**. Although larger Cotton effects in the spectra of **2B** and **4Bm** were observed than those of **2A** and **4Am**, there are almost no differences between monomer **2** and the corresponding polyketone **4**. These probably mean these polyketones **4** hold no specific regular secondary structures.

In conclusion, the Suzuki–Miyaura coupling polymerization catalyzed by palladium nanoclusters proceeded smoothly, giving 1,1′-binaphthyl-2,2′-dioxy-bearing optically active aromatic polyketones.

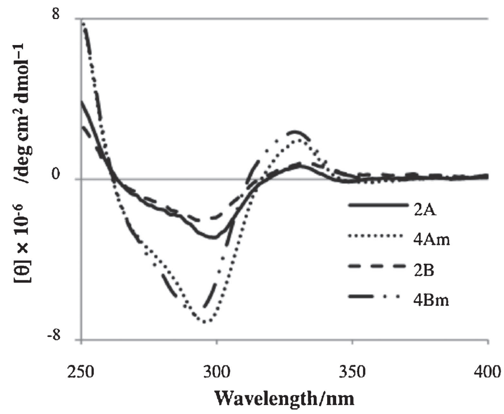


Figure 1. CD spectra of monomers **2** and aromatic polyketones **4**.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.