# Synthesis of Thiophene- and Bithiophene-Based Alternating Copolymers via Pd-Catalyzed Direct C−H Arylation

Yohei Fujinami,[†] Junpei Kuwabara,[†] Wei Lu,[†] Hideki Hayashi,[‡] and Takaki Kanbara*,[†]

[†]Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan

[‡]Nagoya Municipal Industrial Research Institute, 3-4-41, Rokuban, Atsuta-ku, Nagoya 456-0058, Japan

S *Supporting Information*

ABSTRACT: Polycondensation via direct C−H arylation of thiophene derivatives gave thiophene- and bithiophene-based alternating copolymers in good yields. The optimization of the reaction conditions was investigated in terms of a catalytic system and reaction time. Under optimized conditions, the polycondensation reaction of 3,3′,4,4′-tetramethylbithiophene with 2,7-dibromo-9,9-dioctylfluorene gave poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5′-(3,3′,4,4′-tetramethyl-2,2′-bithiophene)] with a molecular weight of 31 800 in 91% yield. The polycondensation reaction proceeded with 2 mol % of Pd(OAc)$_2$ without the addition of a phosphine ligand in a short reaction time (3 h). Six kinds of π-conjugated polymers were synthesized by the polycondensation reaction without the use of bifunctional organometallic reagents as monomers.
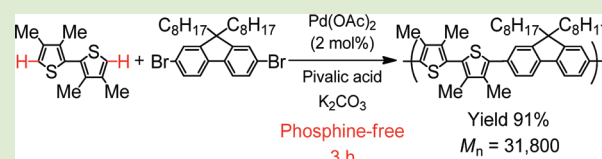
Because of their unique optical and electrical properties, π-conjugated polymers are considered to be promising materials, and they have been widely applied to optoelectronic devices such as organic thin-film solar cells, light emitting diodes, field effect transistors, and electrochromic devices.[1−5] Conventionally, many π-conjugated polymers are synthesized by polycondensation using transition metal catalyzed cross-coupling reactions such as the Suzuki−Miyaura coupling and the Migita−Kosugi−Stille coupling.[1−6] However, these methods require the prior preparation of bifunctional organometallic reagents as monomers, and the polycondensation reaction often produces a stoichiometric amount of toxic byproduct such as organostannyl compounds.

In recent years, catalytic dehydrohalogenative cross-coupling reactions of nonpreactivated arenes or heteroarenes with aryl halides, so-called direct arylation, have been actively investigated.[7,8] This protocol should be advantageous for the synthesis of π-conjugated polymers with respect to decreasing the number of reaction steps and reducing undesired waste from the organometallic reagents. We previously reported the polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene based on Pd-catalyzed direct arylation.[9] We thus envisioned the extension of this method to the synthesis of thiophene- and bithiophene-based alternating copolymers because thiophene and bithiophene are popular choices as monomer units for alternating π-conjugated copolymers, and these units provide various excellent semiconducting polymers for optoelectronic devices.[3−5] For example, poly(9,9-dioctylfluorene-*alt*-bithiophene), so-called F8T2, exhibits high performance when used for manufacturing organic field-effect transistors.[10,11] This current work is thus expected to bring significant benefits to the synthesis of materials for optoelectronic devices. Recently,

Ozawa and co-workers successfully synthesized poly(3-hexylthiophene) with high molecular weight and high regioregularity via direct arylation of 2-bromo-3-hexylthiophene.[12,13] However, polycondensation of thiophene derivatives with dihalogenated aromatic monomers has not been achieved. Herein, we report on a novel and efficient method for synthesis of thiophene- and bithiophene-based alternating copolymers via direct arylation.

Alternating copolymers containing bithiophene and fluorene units were selected as the first synthetic target of this methodology because polymers such as F8T2 are widely used as high-performance materials. Although C−H bonds at the α position in thiophene derivatives are most active for direct arylation reactions, some side reactions also occur at the β position.[7,8] To simplify the assessment of the possible usefulness of this methodology and determine optimized conditions, 3,3′,4,4′-tetramethylbithiophene was used as a monomer to avoid the side reactions at the β position in the bithiophene unit. The polycondensation reactions of 3,3′,4,4′-tetramethylbithiophene with 2,7-dibromo-9,9-dioctylfluorene were carried out at 100 °C in the presence of Pd(OAc)$_2$ (2 mol %), a phosphine ligand (4 mol %), pivalic acid (30 mol %), and K$_2$CO$_3$ (2.5 equiv) in dimethylacetamide (DMAc) (Scheme 1). Under the experimental conditions, poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5′-(3,3′,4,4′-tetramethyl-2,2′-bithiophene)] (polymer **1**) was obtained without the use of organometallic reagents as monomers.
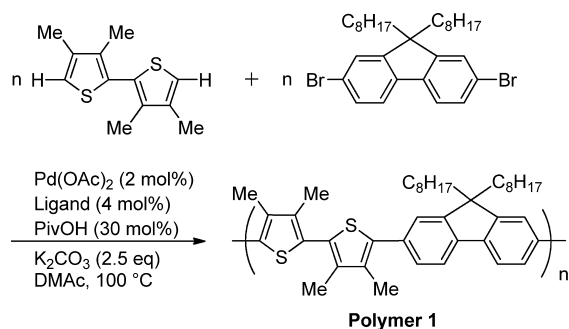
To determine the appropriate conditions, polycondensation reactions were carried out under various conditions. Table 1

Scheme 1. Polycondensation of 3,3′,4,4′-Tetramethyl-bithiophene and 2,7-Dibromo-9,9-dioctylfluorene

Table 1. Polycondensation of 3,3′,4,4′-Tetramethyl-bithiophene and 2,7-Dibromo-9,9-dioctylfluorene[a]

entry	ligand	time	M_n[b]	M_w/M_n[b]	DP[c]	yield (%)[d]
1	$PCy_3 \cdot HBF_4$	24 h	36100	2.76	59	82
2	$P^tBu_3 \cdot HBF_4$	24 h				0
3	$P^tBu_2Me \cdot HBF_4$	24 h				0
4	none	24 h	35400	5.30	58	87
5	$PCy_3 \cdot HBF_4$	3 h	16000	1.80	26	64
6	none	3 h	31800	2.46	52	91
7[e]	none	3 h	4000	2.12	6	72

[a]Reactions were carried out at 100 °C using $Pd(OAc)_2$ (2 mol %), ligand (4 mol %), pivalic acid (30 mol %), and K_2CO_3 (2.5 equiv) in DMAc (1.67 mL). [b]Estimated by gel permeation chromatography (GPC) calibrated on polystyrene standards. [c]The average degree of polymerization was calculated from GPC data and the molecular weight of the repeating unit. [d]The products were obtained by reprecipitation from $CHCl_3/MeOH$. [e]Without pivalic acid.

summarizes the results of the polycondensation reactions. Because $PCy_3 \cdot HBF_4$ was reported as an effective ligand for Pd-catalyzed direct arylation of thiophene derivatives,[14,15] the catalytic system of $Pd(OAc)_2$ with $PCy_3 \cdot HBF_4$ was examined first. The catalytic system using $PCy_3 \cdot HBF_4$ gave polymer **1** with high molecular weight in good yield (entry 1). In contrast, the catalytic system with $P^tBu_3 \cdot HBF_4$ or $P^tBu_2Me \cdot HBF_4$ did not promote the polycondensation reaction (entries 2 and 3), although $P^tBu_2Me \cdot HBF_4$ was the best ligand for the polycondensation of 1,2,4,5-tetrafluorobenzene with 2,7-dibromo-9,9-dioctylfluorene.[9] Because several phosphine-free catalytic systems promoted direct arylation reactions of thiophene derivatives,[16−18] the catalytic system without the addition of a phosphine ligand was examined in this polycondensation reaction. As expected, a high molecular weight polymer was obtained in high yield under the phosphine-free conditions (entry 4). To clarify the difference of catalytic activity, the polycondensation reactions with short reaction times were carried out in the presence or absence of $PCy_3 \cdot HBF_4$. The reaction using $PCy_3 \cdot HBF_4$ gave polymer **1** with a moderate molecular weight (16 000) and yield (64%, entry 5). Alternatively, the reaction without a phosphine ligand yielded better polycondensation results in terms of molecular weight (31 800) and yield (91%) of the polymer (entry 6). Because the polycondensation reaction in the absence of pivalic acid gave only oligomeric products (entry 7), the direct arylation reaction under phosphine-free conditions was likely to proceed via a metalation−deprotonation pathway.[19−21] These results demonstrated that the phosphine-free system in the presence of pivalic acid was more active than the catalytic

system with phosphine ligands. Hartwig and co-workers also reported a faster reaction of direct arylation under phosphine-free conditions than that with a phosphine ligand.[22] This phosphine-free system is valuable from the viewpoint that there is no need to remove phosphine compounds from the polymers. The removal of phosphine compounds was problematic because decomposed phosphine compounds are occasionally incorporated into the main chains of conjugated polymers during polycondensation.[23,24] Under the optimized conditions (entry 6), this polycondensation reaction gave a high molecular weight polymer within 3 h, which was superior to conventional polycondensation via cross-coupling reactions in terms of the reaction time. For example, syntheses of F8T2 by polycondensation via the Suzuki−Miyaura[25,26] and the Migita−Kosugi−Stille[27] cross-coupling reactions required long reaction times of more than 48 h.

The structure of polymer **1** was identified by NMR spectroscopy and elemental analysis. Figure 1 shows the [1]H
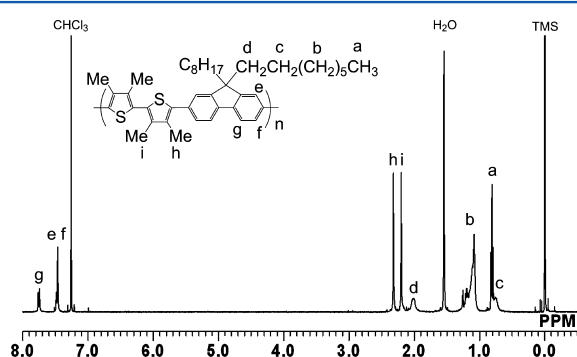
Figure 1. ^{1}H NMR spectrum of polymer **1** (400 MHz, in $CDCl_3$).

NMR spectrum of polymer **1**. All signals could be assigned to the protons in the repeating unit, and no signal of the terminal unit was observed in the spectrum. These results were consistent with the high molecular weight of the polymer. No signal of the branching structure was detected; this indicates that a negligible direct arylation reaction occurred at the aromatic C−H bonds in the fluorene units.
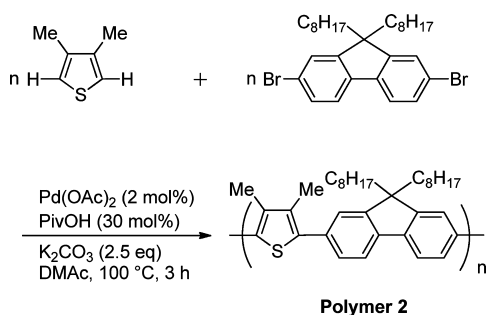
When 2,2′-bithiophene was used as a monomer in polycondensation with 2,7-dibromo-9,9-dioctylfluorene, insoluble products were obtained under the same conditions as in entry 6. The low solubility was presumably due to the cross-linked structure of the polymer. This result indicated that reactions of direct arylation occurred not only at the α position of bithiophene but also at the β position. To evaluate the undesired side reaction, a model reaction of 2,2′-bithiophene and 2 equiv of 1-bromo-4-methylbenzene was examined under the same conditions as the polycondensation reaction (Scheme 2). In addition to 5,5′-bis(4-methylphenyl)-2,2′-bithiophene, the formation of a trace amount of trisubstituted bithiophene as a mixture of regioisomers was confirmed by mass spectrometry (see the Supporting Information). Although the reaction at the β position was minor, the minor reaction probably induced the formation of the cross-linked structure.

3,4-Dimethylthiophene could be polymerized with 2,7-dibromo-9,9-dioctylfluorene under the optimized conditions (Scheme 3). In 3 h, the reaction gave poly[2,7-(9,9-dioctylfluorene)-alt-2,5-(3,4-dimethylthiophene)] (polymer **2**) with the molecular weight of 10 700 in 78% yield. In view of the molecular weight, the reactivity of 3,3′,4,4′-tetramethylbithio-

Scheme 2. Model Reaction of 2,2′-Bithiophene and 1-Bromo-4-methylbenzene

12 %

77 %

trace
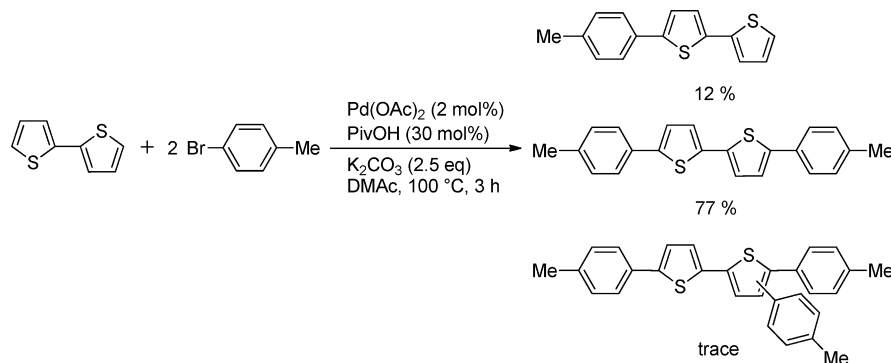
Scheme 3. Polycondensation of 3,4-Dimethylthiophene and 2,7-Dibromo-9,9-dioctylfluorene

Polymer 2

Table 2. Polycondensation Using Various Dibromo-Aromatic Compounds[a]

entry	polymer	$M_n{}^b$	$M_w/M_n{}^b$	DP[c]	yield (%)[d]
1	polymer 3	7300	2.13	11	81
2	polymer 4	32900	5.36	52	47
3	polymer 5	19200	2.90	29	88
4	polymer 6	13500	1.95	26	65

[a]Reactions were carried out for 3 h at 100 °C using Pd(OAc)$_2$ (2 mol %), pivalic acid (30 mol %), and K$_2$CO$_3$ (2.5 equiv) in DMAc (1.67 mL). [b]Estimated by GPC calibrated on polystyrene standards. [c]The average degree of polymerization were calculated from GPC data and molecular weight of the repeating unit. [d]The products were obtained by reprecipitation from CHCl$_3$/MeOH.

phene was higher than that of 3,4-dimethylthiophene. The higher reactivity of 3,3′,4,4′-tetramethylbithiophene is attributed to the fact that its π-conjugated system is larger than that of 3,4-dimethylthiophene.[28]

Various dibromo-aromatic compounds were examined as monomers of polycondensation with 3,3′,4,4′-tetramethylbithiophene owing to the high reactivity (Scheme 4). The results of the polymerizations are summarized in Table 2. The reaction of 3,6-dibromo-N-octadecylcarbazole as a monomer proceeded to give polymer 3 in 81% yield (entry 1). On the other hand, the reaction of 2,7-dibromo-N-octadecylcarbazole afforded polymer 4 in low yield (47%), even though the molecular weight was as high as 32 900 (entry 2). The low yield was due to the formation of insoluble products, indicating the presence of cross-linking structures. The large polydispersity ($M_w/M_n >$ 5) of the soluble part was consistent with the predicted cross-linking structures. Because high reactivity of the C−H bonds at the 3 and 6 positions in carbazole derivatives for direct arylation was reported,[29] the reactions at these C−H bonds were likely to form the cross-linking structures. The polycondensation

reaction of 2,8-dibromo-10,10-dioctyl-N-methylphenazasiline[30] gave the corresponding polymer (polymer 5) in moderate yield. Therefore, one can choose the compound as a monomer for the polycondensation reaction. Although 1,4-dibromo-2,5-dioctylbenzene possesses steric hindrance of the octyl groups at the ortho-position of the Br groups, the polycondensation reaction with 3,3′,4,4′-tetramethylbithiophene proceeded smoothly to yield the soluble polymer without a branching or cross-linking structure.

In summary, a novel and efficient method for the syntheses of thiophene- and bithiophene-based alternating copolymers via direct arylation was developed to successfully obtain six kinds of π-conjugated polymers. In addition to the benefit of reducing waste from organometallic reagents, the polycondensation reaction proceeded with a reduced amount of Pd catalysts (2 mol %) in a short reaction time (3 h) compared to conventional polycondensation based on cross-coupling reactions. The phosphine-free catalytic system can contribute to obtaining pure π-conjugated polymers because there are no

Scheme 4. Polycondensation of 3,3′,4,4′-Tetramethylbithiophene and Various Dibromo-Aromatic Compounds

Polymer 3   **Polymer 4**   **Polymer 5**   **Polymer 6**
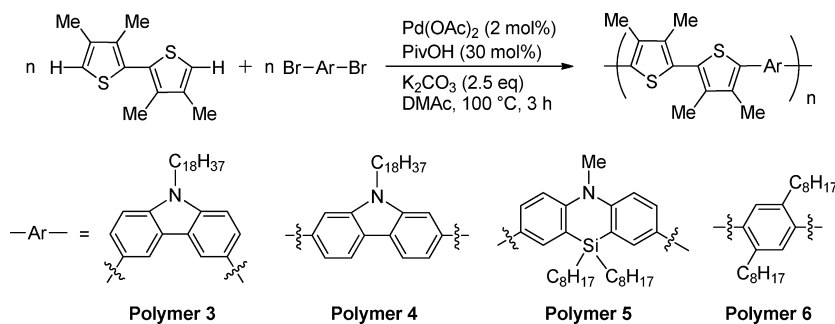
residual phosphine compounds. Further studies including the expansion of the application range of this synthetic method and improvement of the selectivity of reacting C−H bonds are in progress.

■ EXPERIMENTAL METHODS

A mixture of Pd(OAc)$_2$ (2.2 mg, 0.010 mmol), pivalic acid (0.017 mL, 0.15 mmol), K$_2$CO$_3$ (173 mg, 1.3 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.5 mmol), and 3,3′,4,4′-tetramethylbithiophene (111 mg, 0.5 mmol) was stirred in anhydrous dimethylacetamide (1.67 mL) for 3 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, MeOH, and hexane. The precipitate was dissolved in CHCl$_3$, and the solution was filtered through a plug of Celite to remove insoluble material. A reprecipitation from CHCl$_3$/MeOH gave polymer **1** as a pale yellow solid in 91% yield. M_n = 31 800, M_w/M_n = 2.46. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.75 (br, 4H), 0.81 (t, J = 7.6 Hz, 6H), 1.02−1.31 (br, 20H), 2.02 (br, 4H), 2.20 (s, 6H), 2.32 (s, 6H), 7.47 (m, 4H), 7.75 (d, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 151.3, 139.9, 138.8, 137.4, 133.6, 133.4, 128.3, 128.1, 123.7, 119.7, 55.2, 40.3, 31.8, 30.0, 29.2, 29.2, 23.9, 22.6, 14.5, 14.3, 14.1. Anal. Calcd. for H(C$_{41}$H$_{52}$S$_2$)$_{52}$Br: C, 80.66; H, 8.59. Found: C, 80.23; H, 8.39.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kanbara@ims.tsukuba.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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