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Synthesis of 4,4'-Dinonyl-2,2'-bithiazole-based Copolymers via Pd-Catalyzed Direct C–H Arylation

Wei Lu,^a Junpei Kuwabara^a and Takaki Kanbara^{*a}

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

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Direct arylation polycondensation of a bithiazole derivative with dibromoarylenes gave the corresponding bithiazole-based copolymers under the phosphine-free catalytic system in a short reaction time.

In recent years, polycondensation via direct arylation has become widely recognized as an atom-economic and environmentally friendly method for synthesis of π -conjugated polymers^{1–9} in comparison to polycondensation via traditional cross-coupling reactions.¹⁰ Ozawa and co-workers successfully developed polycondensation of 2-bromo-3-alkylthiophenes via direct arylation to give poly(3-alkylthiophene)s with high molecular weight and high regioregularity.³ Alternatively, we reported direct arylation polycondensation for the synthesis of 1,2,4,5-tetrafluorobenzene-based polymers, and demonstrated a hole-blocking function of the obtained polymer in organic light emitting diodes (OLEDs).⁵ Furthermore, direct arylation polycondensation of 3,3',4,4'-tetramethylbithiophene with dibromoarylenes proceeded with 2 mol% of Pd(OAc)₂ without addition of a phosphine ligand in a short reaction time.⁶ Most recently, the synthetic method via direct arylation also gave the π -conjugated polymers that can serve as efficient materials for polymer solar cells (PSCs).^{7–9} However, the majority of research was focused on polycondensation via direct arylation of thiophene derivatives. To develop direct arylation polycondensation as a general and reliable method, we expanded this methodology to include the polycondensation reaction of a thiazole derivative. Since π -conjugated polymers with thiazole units were reported to possess high potential as materials of OLEDs as well as PSCs,¹¹ synthesis of the polymers via direct arylation should be attractive for development of semiconducting polymers. Herein, we report the development of polycondensation via direct arylation of 4,4'-dinonyl-2,2'-bithiazole with dibromoarylenes.

The investigation began with the polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 2,7-dibromo-9,9-dioctylfluorene; since, 2,7-dibromo-9,9-dioctylfluorene possesses good reactivity towards polycondensation and high selectivity against side reactions.^{5,6} The reaction was conducted in the presence of Pd(OAc)₂ (5 mol%), PCy₃ (10 mol%), pivalic acid (30 mol%), and K₂CO₃ (2.5 equiv) in dimethylacetamide (DMAc) for 12 h at 100 °C,¹² giving poly[(4,4'-dinonyl-2,2'-bithiazole-5,5'-diyl)-(9,9-

dioctylfluorene-2,7-diyl)] (**Polymer 1**) with a molecular weight of 40000 in 84% yield (Scheme 1, entry 1 in Table. 1). In addition, the polycondensation reaction for 3 h produced **Polymer 1** in high molecular weight (35000) and yield (83%), suggesting that this time is sufficient for the polycondensation reaction (entry 2). Since the addition of pivalic acid induced direct arylation polycondensation of 3,3',4,4'-tetramethylbithiophene without use of a phosphine ligand,⁶ the polycondensation reaction of 4,4'-dinonyl-2,2'-bithiazole was examined under the phosphine-free system. Polycondensation in the absence of PCy₃ for 3 h gave a molecular weight of 30700 in 93% yield (entry 3). In addition, the high activity of the phosphine-free system enabled reduction of the Pd precursor to 2 mol%; the polycondensation with 2 mol% of Pd(OAc)₂ for 3 h gave **Polymer 1** with the maximum molecular weight of 45900 (entry 4). Under the optimized conditions, the polycondensation is more efficient than traditional cross-coupling reactions in terms of the molecular weight of the polymer and reaction time. For example, a similar polymer, poly[(4,4'-dihexyl-2,2'-bithiazole-5,5'-diyl)-(9,9-dioctylfluorene-2,7-diyl)] was synthesized for 2 days, with a molecular weight of 18400 in 69% yield by the polycondensation reaction via the Suzuki–Miyaura coupling reaction.^{11a}

Scheme 1. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 2,7-dibromo-9,9-dioctylfluorene

Table 1. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 2,7-dibromo-9,9-dioctylfluorene^a

Entry	Time	Additive	Quantity of Pd(OAc) ₂	M _n ^b	M _w /M _n ^b	DP ^c	Yield ^d
1	12 h	PCy ₃ :HBF ₄	5 mol%	40000	1.74	50	84%
2	3 h	PCy ₃ :HBF ₄	5 mol%	35000	1.79	43	83%
3	3 h	none	5 mol%	30700	3.07	38	93%
4	3 h	none	2 mol%	45900	2.32	57	90%

^a Reactions were carried out at 100 °C using Pd(OAc)₂, additive (10 mol %), pivalic acid (30 mol %), and K₂CO₃ (2.5 equiv) in DMAc (1.67 mL). ^b Estimated by GPC calibrated on polystyrene standards. ^c The average degree of polymerization was calculated from GPC data and molecular weight of the repeating unit. ^d The products were obtained by reprecipitation from CHCl₃/MeOH.

The chemical structure of the repeating unit of **Polymer 1** was identified by ¹H and ¹³C{¹H} NMR spectroscopy.^{11a} Figure 1 shows the ¹H NMR spectrum of **Polymer 1**. In the ¹H and ¹³C{¹H} NMR spectra (see Figure S-1 in Supporting Information), all signals could be assigned to the protons and carbons in the repeating unit, and no signal of the terminal units was observed. These results are consistent with the high molecular weight of the polymer. The MALDI-TOF-MASS spectrum also supported the repeating structure of **Polymer 1** (Figure S-12). The main peak corresponds to the alternating structure of the polymer with two 4,4'-dinonyl-5H-2,2'-bithiazole terminal units. Although the structures with other terminal units, such as a fluorene, were observed in the spectrum, no peak corresponding to branching structures was observed. These results demonstrate that the polymer has well-defined linkages between the recurring unit, and formation of branching structures scarcely occurs. In addition, the UV-vis absorption and photoluminescence spectra of **Polymer 1** were almost identical to those of a similar polymer synthesized by the Suzuki-Miyaura cross-coupling reaction (Figure S-17).^{11a} These photophysical data also support the linear structure of **Polymer 1**.

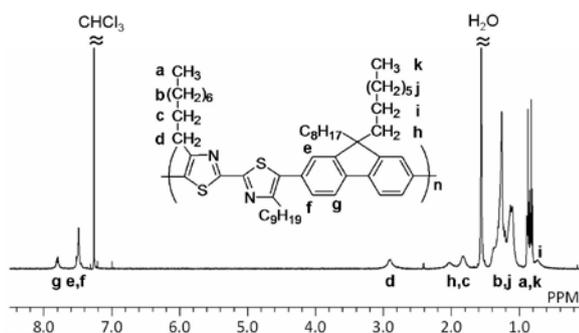


Figure 1. ¹H NMR spectrum of **Polymer 1** (400 MHz, in CDCl₃, 293 K).

To expand the application range of the protocol, four kinds of dibromoarylenes were examined as a monomer of polycondensation with 4,4'-dinonyl-2,2'-bithiazole (Scheme 2). Table 2 summarizes the results of the polycondensation reactions. The structures of the obtained polymers were identified by NMR and MALDI-TOF-MASS spectroscopies (see Supporting Information). In all reactions, the monomers had disappeared after 3 h and the corresponding polymeric products were obtained.

These observations suggest that C–C bond formations rapidly proceeded under the conditions. However, in contrast to **Polymer 1**, the reactions in Scheme 2 resulted in the polymers containing insoluble fractions in CHCl₃ under the same conditions (see entries 1, 3, and 5 in Table 2). The presence of insoluble products indicated formation of cross-linking structures that were caused by side reactions at the C–H bonds of each arylene moiety.^{5-7,9} Alternatively, the reaction for 10 min produced **Polymer 2** with a molecular weight of 10000 in 87% yield without formation of insoluble products (entry 2). This result exhibited that a certain amount of the C–C bond formation occurred in 10 min and the reaction at the C–H bond in the thiazole unit preferentially proceeded in comparison to the C–H bond in the diphenylene unit. In contrast to the results in 4,4'-dibromobiphenyl, the polycondensation reaction of 1,4-dibromobenzene produced a large quantity of insoluble product even in the 10 min reactions (entries 3 and 4). The reaction of the alkylated dibromobenzene derivative, 1,4-dibromo-2,5-dioctylbenzene, yielded **Polymer 4** (M_n = 15300) in a high yield (93%) without formation of the insoluble product in 0.5 h (entry 6). In the case of 1,4-dibromo-2,5-difluorobenzene as a monomer, soluble **Polymer 5** was obtained from the reaction for 3 h (entry 7). The suppression of side reactions in the polycondensations of 1,4-dibromo-2,5-disubstituted-benzenes is probably due to the steric hindrance of the substituents at the *ortho*-positions and reduction in the number of aromatic C–H bonds in the repeating unit of the polymer. The results in Table 2 indicated that the side reactions most frequently occurred in a simple 1,4-phenylene unit among the examined examples. Since non-substituted benzene possesses low reactivity for direct arylation,¹³ substitution of a bithiazolyl unit probably changes an electronic state of the 1,4-phenylene unit and increases the reactivity of the C–H bonds. This tentative proposal is consistent with the low cross-linking structure of **Polymer 2** in comparison with **Polymer 3**; the C–H bonds in the diphenylene unit were less affected by the bithiazolyl unit than those in the phenylene unit in **Polymer 3** because **Polymer 2** has only one bithiazolyl unit per one phenylene unit. These results provide new insights that the reactivity of C–H bonds in aromatic units could be regulated during the polycondensation reaction.

Scheme 2. Polycondensation of 4,4'-dinonyl-2,2'-bithiazole with dibromoarylene

Table 2. Polycondensation of dibromobenzene derivatives with 4,4'-dinonyl-2,2'-bithiazole ^a

Entry	Polymer	Time	M_n^b	M_w/M_n^b	Yield ^{c,d}
1	Polymer 2	3 h	14700	1.66	70% (16%)
2		10 min	10000	1.25	87%
3	Polymer 3	3 h	5300	1.29	10% (87%)
4		10 min	4300	1.16	16% (61%)
5	Polymer 4	3 h	35900	2.89	46% (42%)
6		0.5 h	15300	1.63	93%
7	Polymer 5	3 h	13000	4.45	93%

^a Reactions were carried out at 100 °C using Pd(OAc)₂, pivalic acid (30 mol %), and K₂CO₃ (2.5 equiv) in DMAc (1.67 mL). ^b Estimated by GPC calibrated on polystyrene standards. ^c The products were obtained by reprecipitation from CHCl₃/MeOH. ^d Yield of insoluble product in CHCl₃ is noted in brackets.

In summary, direct arylation polycondensation using the phosphine-free catalytic system can be adapted to the synthesis of bithiazole-based alternating copolymers. In comparison with conventional polycondensation via cross-coupling reactions, the polycondensation proceeded with a reduced amount of Pd catalyst (2 mol%) in a short reaction time (10 min to 3 h). Owing to the difference in reactivity of the C–H bond, controlling the reaction time was effective for suppressing the side reaction at the unexpected C–H bond and produced CHCl₃ soluble polymers in good yields. Since a thiazole unit provides different properties from a thiophene unit, the expansion of targeted monomers for direct arylation polycondensation leads to efficient synthetic methodology for design of semiconducting polymers.

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Experimental Part

Typical polycondensation of 4,4'-dinonyl-2,2'-bithiazole with 2,7-dibromo-9,9-dioctylfluorene under the optimized conditions (Table 1, Entry 4).

A mixture of Pd(OAc)₂ (2.2 mg, 0.010 mmol), pivalic acid (0.017 mL, 0.15 mmol), K₂CO₃ (173 mg, 1.3 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol), 4,4'-dinonyl-2,2'-bithiazole (210 mg, 0.50 mmol) were 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 aqueous solution of ethylenediaminetetraacetic acid tetrasodium salt (pH = 8). The suspension was stirred for 1 h at room temperature. The precipitates were separated by filtration and washed with 1 M HCl solution, distilled water, MeOH, and hexane. The gray solid was dissolved in CHCl₃ and the solution was filtered through a plug of Celite to remove insoluble materials. A reprecipitation from CHCl₃/MeOH gave yellow-green solid of poly[(4,4'-dinonyl-2,2'-bithiazole-5,5'-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (**Polymer 1**) in 90% yield. M_n = 45900, M_w/M_n = 2.32. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 7.80 (2H,

J = 7.6 Hz, H^a), 7.48 (4H, br, H^c, H^f), 2.90 (4H, br, H^d), 1.92 (8H, br, H^h, H^c), 1.22 (44H, br, H^b, Hⁱ), 0.88 (6H, t, J = 6.8 Hz, H^g), 0.83 (6H, t, J = 7.0 Hz, H^k), 0.74 (4H, br, H^j). ¹³C{¹H} NMR (100 MHz, CDCl₃, 293 K): δ 158.6, 154.1, 151.6, 140.5, 134.7, 130.9, 128.4 (CH), 123.8 (CH), 120.3 (CH), 55.4, 40.4 (CH₂), 31.9 (CH₂), 31.8 (CH₂), 30.5-29.0 (9×CH₂), 24.0 (CH₂), 22.7 (CH₂), 22.6 (CH₂), 14.1 (2×CH₃).

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