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

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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 in comparison to polycondensation via traditional cross-coupling reactions. 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. 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). 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, 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). 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 for OLEDs as well as PSCs, 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′-dihexyl-2,2′-bithiazole with dibromoarylenes.

The investigation began with the polycondensation of 4,4′-dibromo-9,9-dioctylfluorene; since, 2,7-dibromo-9,9-dioctylfluorene possesses good reactivity towards polycondensation and high selectivity against side reactions. 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, giving poly[(4,4′-dibromo-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 polycoupling reaction for 3 h produced Polymer with a molecular weight of 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, the polycondensation reaction of 4,4′-dibromo-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 was 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 polycoupling reaction via the Suzuki-Miyaura coupling reaction.

Scheme 1. Polycondensation of 4,4′-dibromo-9,9-dioctylfluorene with 2,7-dibromo-9,9-dioctylfluorene
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 polycoupling with 4,4’-dinitrolyl-2,2'-bithiazole (Scheme 2). Table 2 summarizes the results of the polycoupling reactions. The structures of the obtained polymers were identified by NMR and MALDI-TOF-MASS spectrosopies (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 insoluable products indicated formation of cross-linking structures that were caused by side reactions at the C–H bonds of each areylene moiety.⁸–⁹ 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 thiazolet unit preferentially proceeded in comparison to the C–H bond in the diphenylene unit. In contrast to the results in 4,4’-dibromobiphenyl, the polycoupling 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 (Mₙ = 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 polycouplings 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 polycoupling reaction.

Scheme 2. Polycoupling of 4,4’-dinitrolyl-2,2’-bithiazole with dibromoarylene.
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. $M_n = 45900$, $M_d/M_n = 2.32$. ¹H NMR (400 MHz, CDCl₃, 293 K): δ 7.80 (2H, d, $J = 7.6$ Hz, $H^6$), 7.48 (4H, br, $H^f$), 2.90 (4H, br, $H^d$), 1.92 (8H, br, $H^g$), 1.22 (44H, br, $H^a$), 0.88 (6H, t, $J = 6.8$ Hz, $H^k$), 0.83 (6H, t, $J = 7.0$ Hz, $H^j$), 0.74 (4H, br, $H^l$). ¹³C{¹H} NMR (100 MHz, CDCl₃, 293 K): δ 158.6, 154.1, 151.6, 140.5, 137.4, 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).

Notes and references