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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-alkylthiophenes) 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, the polycondensation reaction of 4,4′-dinonyl-2,2′-bithiazole was examined under the phosphine-free system. Polycondensation in the absence of PCy$_3$ 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 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, the polycondensation reaction of 4,4′-dinonyl-2,2′-bithiazole was examined under the phosphine-free system. Polycondensation in the absence of PCy$_3$ 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 reaction 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-diocetylfluorene-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.

Scheme 1. Polycondensation of 4,4′-dinonyl-2,2′-bithiazole with 2,7-dibromo-9,9-diocetylfluorene
The chemical structure of the repeating unit of Polymer 1 was identified by $^1$H and $^{13}$C{$_{1H}$} NMR spectroscopy.$^{11a}$ Figure 1 shows the $^1$H NMR spectrum of Polymer 1. In the $^1$H and $^{13}$C{$_{1H}$} 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 supports the repeating structure of Polymer 1 (Figure S-12). The main peak observed in the spectrum, no peak corresponding to branching structures with other terminal units, such as a fluorene, were 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. 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 CHCl$_3$ 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 thiazoyle 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 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.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time</th>
<th>Additive</th>
<th>Quantity of $M_n$ b</th>
<th>$M_n/M_n$ b</th>
<th>DP c</th>
<th>Yield d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12 h</td>
<td>PCy$_3$/HBF$_4$</td>
<td>5 mol%</td>
<td>400000</td>
<td>1.74</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>3 h</td>
<td>PCy$_3$/HBF$_4$</td>
<td>5 mol%</td>
<td>350000</td>
<td>1.79</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>3 h</td>
<td>none</td>
<td>5 mol%</td>
<td>307000</td>
<td>2.07</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>3 h</td>
<td>none</td>
<td>2 mol%</td>
<td>459000</td>
<td>2.32</td>
<td>57</td>
</tr>
</tbody>
</table>

a Reactions were carried out at 100 °C using Pd(OAc)$_2$, additive (10 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 was calculated from GPC data and molecular weight of the repeating unit. d The products were obtained by reprecipitation from CHCl$_3$/MeOH.

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.
Table 2. Polycondensation of dibromobenzene derivatives with 4,4′-dinonyl-2,2′-bithiazole

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Time</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polymer 2</td>
<td>3 h</td>
<td>14700</td>
<td>1.66</td>
<td>70%</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>10 min</td>
<td>10000</td>
<td>1.25</td>
<td>87%</td>
</tr>
<tr>
<td>3</td>
<td>Polymer 3</td>
<td>3 h</td>
<td>5300</td>
<td>1.29</td>
<td>10%</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>10 min</td>
<td>4300</td>
<td>1.16</td>
<td>16%</td>
</tr>
<tr>
<td>5</td>
<td>Polymer 4</td>
<td>3 h</td>
<td>35900</td>
<td>2.89</td>
<td>46%</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.5 h</td>
<td>15300</td>
<td>1.63</td>
<td>93%</td>
</tr>
<tr>
<td>7</td>
<td>Polymer 5</td>
<td>3 h</td>
<td>13000</td>
<td>4.45</td>
<td>93%</td>
</tr>
</tbody>
</table>

Reactions were carried out at 100 °C using Pd(OAc)$_2$, pivalic acid (30 mol %), and K$_2$CO$_3$ (2.5 equiv) in DMAc (1.67 mL). Estimated by GPC calibrated on polystyrene standards. The products were obtained by reprecipitation from CHCl$_3$/MeOH. Yield of insoluble product in CHCl$_3$ is noted in brackets.

Notes and references