Synthesis and basic chemical properties of polyindazoles

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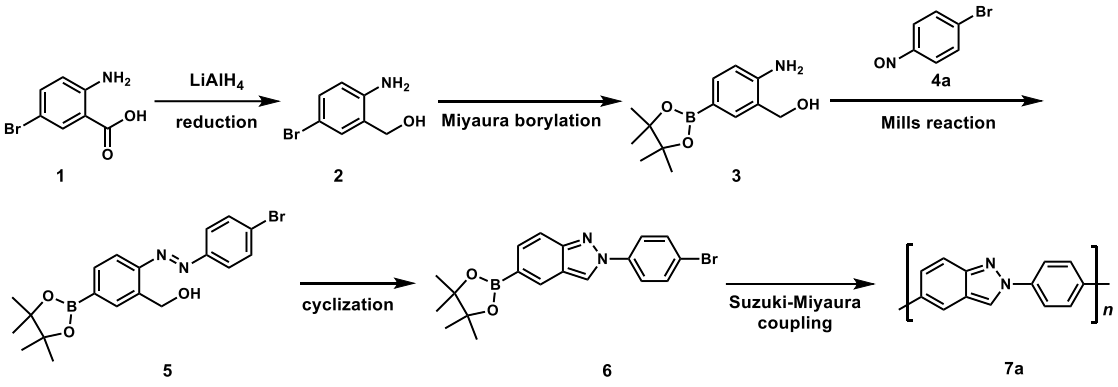
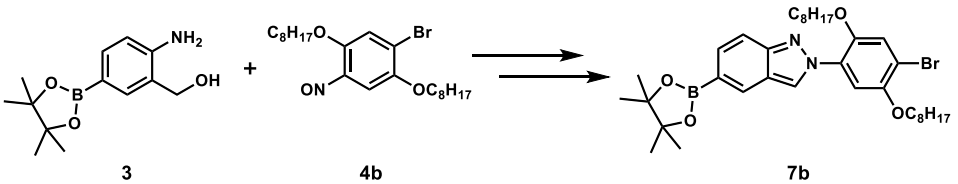
Keywords: *indazole, heat resistance, π-conjugation*

Polymers with aromatic heterocycles, which are used for heat-resistant materials and organic solar cells, are classified into benzenoid and quinonoid types. The quinonoid-type polymers have been less explored despite their unique luminescence and conductivity due to difficult synthesis of the corresponding quinonoid monomers. Polymers containing 2*H*-indazoles with a quinonoid structure in the mainchain have also never been reported. Here, we report a synthesis of polymerizable 2*H*-indazoles and polyindazoles by Suzuki-Miyaura coupling of the obtained monomer (Scheme 1). Compound **2** obtained by reduction of 2-amino-5-bromo benzoic acid **1** with lithium aluminum hydride reacted with bis(pinacolato)diboron to give **3**. Next, Mills reaction of **3** with 1-bromo-4-nitrosobenzene **4a** gave **5**. Intramolecular cyclization[1] of **5** afforded monomer **6**, which was polymerized by Suzuki-Miyaura coupling to give poryindazole **7a**.

The synthesized polymer was insoluble in organic solvents such as $CHCl_3$ and THF, being difficult to evaluate physical properties. Thus, its structure was determined by IR spectrum, comparable to that of the monomer **6**. Thermogravimetric analysis revealed that the 5% weight loss temperature was about 320 ºC. We are currently investigating the synthesis of polyindazole with long-chain alkyl groups to improve their solubility (Scheme 2), which will be reported in this presentation.



Scheme 1



Scheme 2

1) Kondo, M.; Takizawa, S.; Jiang, Y.; Sasai, H. *Chem. Eur. J.* **2019**, *25*, 9866-9869.