

Nickel-catalyzed Decarbonylative Polymerization of 5-Alkynylphthalimides: A New Methodology for the Preparation of Polyheterocycles

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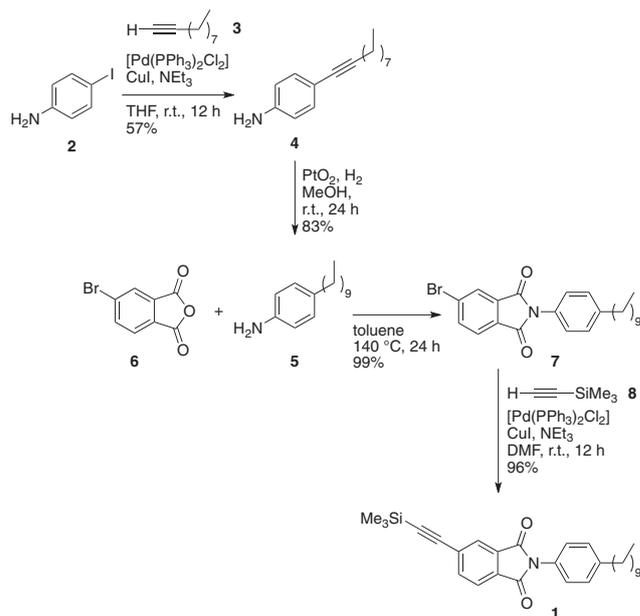
A nickel-catalyzed decarbonylative cycloaddition was developed, in which 5-alkynylphthalimides reacted to afford a new type of polyisoquinolone. It was demonstrated for the first time that decarbonylative cycloaddition can be an elementary process of polycondensation for the preparation of heterocyclic polymers.

Poly- and oligoheterocycles are important classes of organic functional materials for such as semiconductors, conductors, and light-emitting materials.¹ In this context, the development of new methods that would allow for unprecedented types of π -conjugated polymers remains an important research topic.² Recently, we demonstrated the nickel-catalyzed reaction of 6-alkynylisatoic anhydride to afford polyquinolone through decarboxylative cycloaddition (Scheme 1a).³ Our success in the synthesis of polyquinolone with iterative cycloadditions prompted us to investigate a new polymerization reaction, which would allow us to prepare polyisoquinolone from 5-alkynylphthalimides (Scheme 1b).⁴ Herein, we report our results on nickel-catalyzed iterative decarbonylative cycloaddition to give polyisoquinolone, which is a structural isomer of polyquinolone.

Our investigation began with the preparation of the alkynylphthalimide monomer **1** (Scheme 2). The palladium-catalyzed Sonogashira reaction of 4-iodoaniline (**2**) with 1-decyne (**3**) provided **4** in 57% yield. The hydrogenation of **4** in the presence of a platinum oxide catalyst furnished **5**, which was reacted with 5-bromophthalic anhydride (**6**) to give the phthalimide **7** in quantitative yield. The coupling reaction of **7** with trimethylsilylacetylene (**8**) gave the monomer **1**. We then examined the polymerization with the decarbonylative cycloaddition of monomer **1** in the presence of a nickel catalyst,

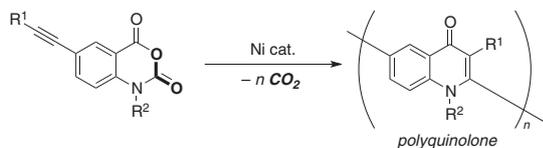
which was prepared in situ from $[\text{Ni}(\text{cod})_2]$ (10 mol %), and PMe_3 (20 mol %), in refluxing toluene for 24 h (Scheme 3). However, this provided polyisoquinolone as a polymer consisting of two different components **9** and **10**. The examination of other reaction conditions such as phosphine ligands, reaction medium, and temperature did not improve the situation.

To our delight, we found that the cycloaddition of the methoxy-substituted phthalimide **11** with **12** in the presence of the nickel catalyst furnished **13** as the sole product (Scheme 4).

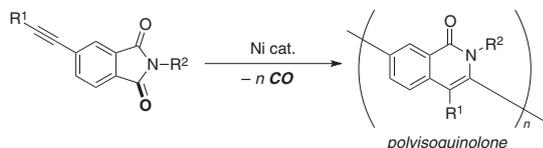


Scheme 2. Synthesis of 5-alkynylphthalimide.

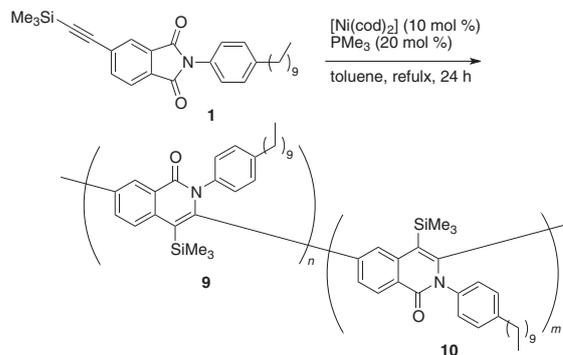
(a) **Previous Report:** Iterative Decarboxylative Cycloaddition



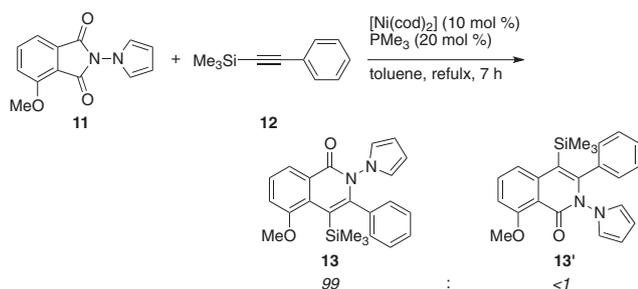
(b) **Present Work:** Iterative Decarbonylative Cycloaddition



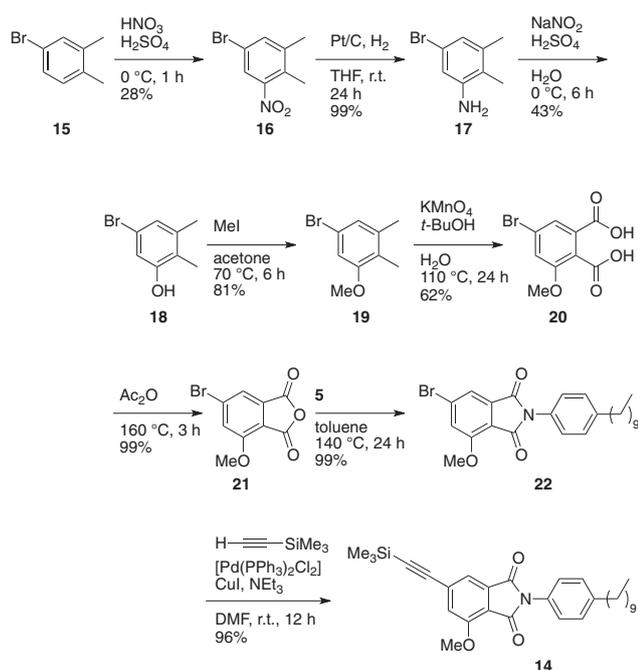
Scheme 1. Synthesis of polyquinolone and polyisoquinolone.



Scheme 3. Nickel-catalyzed decarbonylative cycloaddition of monomer **1** to form polyisoquinolone.



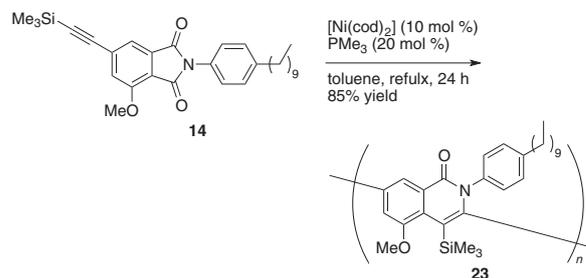
Scheme 4. Effects of methoxy substituent on the regioselectivity of nickel-catalyzed cycloaddition.



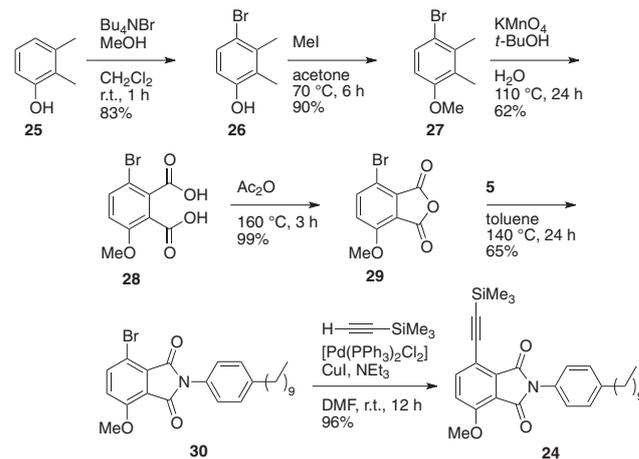
Scheme 5. Synthesis of 5-alkynyl-7-methoxyphthalimide.

The observed regioselectivity in the reaction is ascribed to the coordination of the nickel catalyst to the methoxy moiety of **11**, which promotes oxidative addition of the neighboring amide to Ni(0) selectively.^{4b} Thus, we envisioned that the use of a phthalimide monomer possessing a methoxy moiety at an appropriate position as a directing group would afford polyisoquinolone with regioregularity via selective oxidative addition to Ni(0). To test our hypothesis, we prepared the 5-alkynyl-7-methoxyphthalimide monomer **14** according to the route shown in Scheme 5.

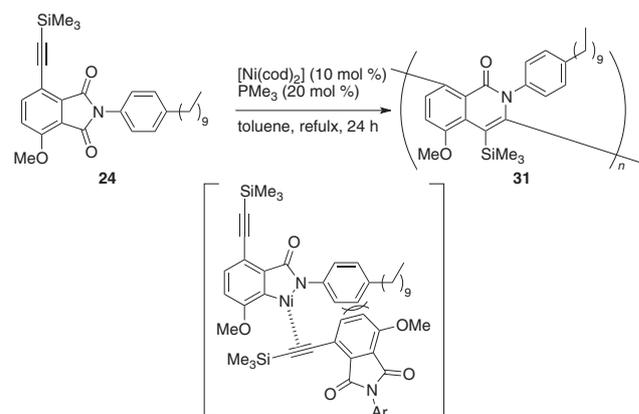
The nickel-catalyzed decarbonylative polymerization of the monomer **14** proceeded in toluene to furnish polyisoquinolone **23** (Scheme 6). MALDI-TOF mass spectrometry was used to determine the structure of the polyisoquinolone **23**. It was observed that the spectrum has a peak repeat of m/z 461, which corresponds to the molecular weight of the isoquinolone unit. This result clearly shows that the polymerization consisted of the iterative decarbonylative cycloaddition of the 5-alkynyl-7-methoxyphthalimide monomer **14**. The molecular weights of polymer **23** and the distribution of molecular weights were



Scheme 6. Nickel-catalyzed decarbonylative cycloaddition of monomer **14** to form polyisoquinolone **23**.



Scheme 7. Synthesis of 4-alkynyl-7-methoxyphthalimide.



Scheme 8. Nickel-catalyzed decarbonylative cycloaddition of monomer **24**.

determined by gel permeation chromatography. The distribution of molecular weights was determined by using polystyrene standards. The number-average molecular weight (M_n) of polyisoquinolone **23** was determined to be 1.3×10^4 , and the molecular weight distribution (polydispersity index, M_w/M_n) was found by gel permeation chromatography to be 2.08.

We also examined whether 4-alkynyl-7-methoxyphthalimide could participate in decarbonylative polymerization to furnish the correspondingly substituted polyisoquinolone. Thus, monomer **24** was synthesized according to the procedure

illustrated in Scheme 7. Then, we examined the polymerization with the decarbonylative cycloaddition of monomer **24** in the presence of the nickel catalyst, which was prepared in situ from $[\text{Ni}(\text{cod})_2]$ (10 mol %) and PMe_3 (20 mol %), in refluxing toluene for 24 h (Scheme 8). However, this did not provide polyisoquinolone **31**, and the monomer **24** was recovered unchanged, probably owing to the steric hindrances of monomer **24** retarding the coordination of an alkyne moiety to the azanickelacycle intermediate.

In summary, a new methodology for the preparation of polyisoquinolone has been developed.⁵ We have demonstrated for the first time that nickel-catalyzed decarbonylative cycloaddition can be an elementary process of polycondensation for the preparation of polyheterocycles.⁶

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- 5 For additional examples for attempted decarbonylative polymerization of different phthalimide monomers, see Supporting Information.⁶
- 6 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.