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Nickel-catalyzed Decarboxylative Polymerization of 6-Alkynylisatoic Anhydride

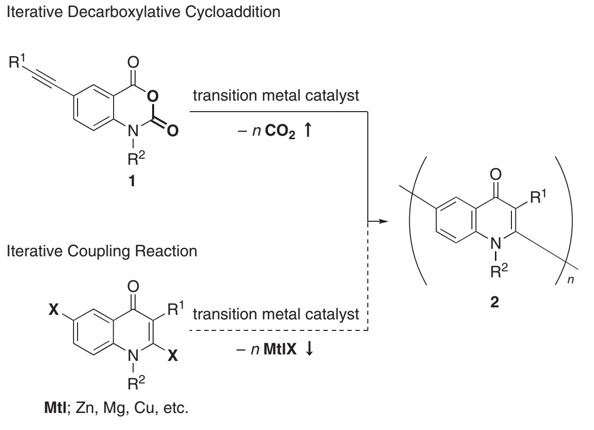
Kenichiro Nakai, Takahiro Shiba, Yasufumi Yoshino, Takuya Kurahashi,* and Seijiro Matsubara*
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510

(Received July 4, 2011; CL-110562; E-mail: tkuraha@orgrxn.mbox.media.kyoto-u.ac.jp)

A new methodology for preparation of polyquinolone was developed. Iterative nickel-catalyzed reaction of 6-alkynylisatoic anhydride monomer affords polyquinolone via decarboxylative cycloaddition without formation of residual by-product. It was demonstrated for the first time that decarboxylative cycloaddition can be an elementary process of chain growth polymerization for preparation of polyheterocycles with high regioregularity.

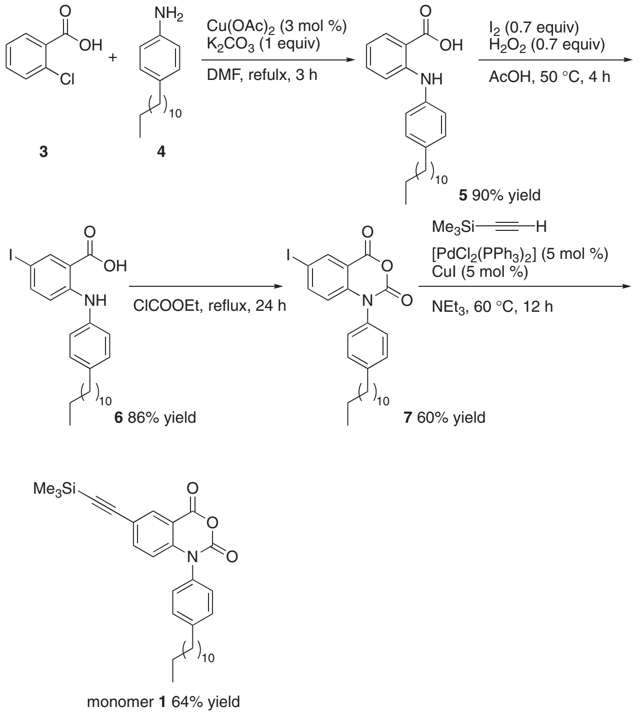
Since conjugated polymers are potentially important materials for applications such as semiconducting, conducting, and light-emitting materials, synthesis of polymers with a sp^2–sp^2 bond formation along the polymer chains has been an interesting research subject.[1] Although there are a large number of methods for synthesis of such polymers, the development of new methodologies, which would allow for unprecedented types of conjugated polymers, remains an important research topic. Recently, we demonstrated nickel-catalyzed decarboxylative cycloaddition of alkynes with isatoic anhydrides to give quinolone.[2–4] Our success in synthesis of a quinolone from the readily available isatoic anhydride and alkynes with decarboxylative cycloadditions prompted us to investigate new polymerization reactions, which would allow us to prepare an unprecedented type of polyheterocycle, polyquinolone **2**, from 6-alkynylisatoic anhydride **1** (Scheme 1). The process enables the straightforward synthesis of polyheterocycles without formation of residual by-product such as metal halides, which are usually produced when the polymer is synthesized with transition-metal-catalyzed polycondensation using dihalo-organic compounds and may contaminate the resulting polymer.[5] Herein, we report our results of nickel-catalyzed decarboxylative cycloaddition to provide polyquinolone **2** from 6-alkynylisatoic anhydride **1**.

Alkynylisatoic anhydride monomer **1** was prepared from 2-chlorobenzoic acid (**3**) according to the route shown in Scheme 2. The Cu-catalyzed reaction of **3** with 4-dodecylaniline (**4**) gave the coupling product **5** in 90% yield. Iodination of **5** with iodine and hydrogen peroxide afforded **6** in 86% yield, which was then reacted with ethyl chloroformate to give isatoic anhydride **7** in 60% yield. The palladium-catalyzed Sonogashira coupling reaction of **7** with trimethylsilylacetylene **8** furnished **1**, an alkynylisatoic anhydride monomer, in 64% yield. It is worth mentioning that the whole procedure to prepare monomer **1** from **3** did not require silica gel chromatography to purify the reaction products after each step. The purifications of the reaction products were done by recrystallization.

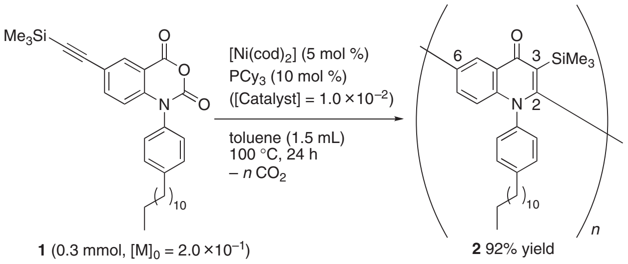


Scheme 1. Synthesis of polyquinolone **2**.

The decarboxylative polymerization of alkynylisatoic anhydride monomer **1** proceeded in toluene (80 °C, 12 h) and furnished polyquinolone **2** in 65% yield with $[\mathrm{Ni(cod)_2}]/\mathrm{PMe_3}$ catalyst. Among phosphine ligands examined, $\mathrm{PCy_3}$ gave the best yield of polyquinolone **2**. Thus, the polymerization of **1** with $[\mathrm{Ni(cod)_2}]/\mathrm{PCy_3}$ in toluene at elevated reaction temperature (100 °C) and prolonged reaction time (24 h) gave the desired polymer **3** in 92% yield (Scheme 3). In other reaction solvents, such as 1,4-dioxane and THF, yields were even lower. The reaction of **1** with palladium or rhodium catalyst (e.g., $[\mathrm{Pd(PPh_3)_4}]$ and $[\mathrm{RhCl(cod)}]_2$) did not afford any polymer or oligomer even with prolonged reaction time. MALDI-TOF MS was used to determine the structures of the polyquinolone **2**. It was observed that the spectrum has a peak repeat of



Scheme 2. Synthesis of alkynylisatoic anhydride **1**.



Scheme 3. Synthesis of polyquinolone **2** from monomer **1** with nickel-catalyzed decarboxylative cycloaddition.

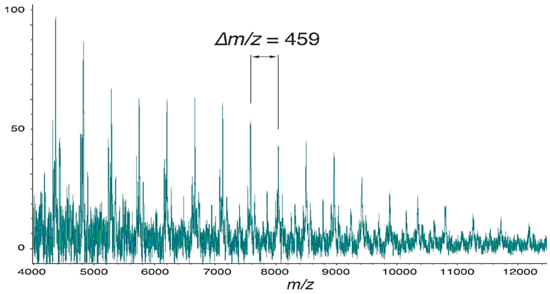


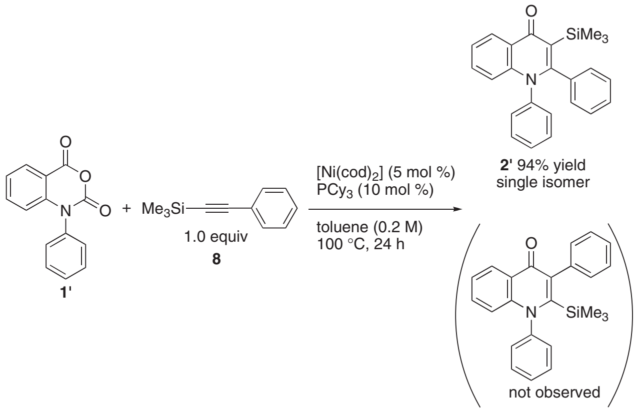
Figure 1. MALDI-TOF mass spectra of polyquinolone **2**.

$\Delta m/z = 459$, which corresponds to the molecular weight of the quinolone unit (Figure 1). This result clearly shows that the polymerization consisted of iterative decarboxylative cycloaddition of alkynylisatoic anhydride monomer **1**.

The molecular weight of the polymer **2** as well as the distribution of molecular weights was determined by gel permeation chromatography (GPC). The distribution of molecular weights was determined with polystyrene standards. It was found that the molecular weight (M_n) of polyquinolone **2** was 5.1×10^4 and the distribution of molecular weights (M_w/M_n) was calculated to be 4.92. Even though the molecular weight (M_n) and distribution of molecular weights (M_w/M_n) of polyquinolone **2** were not drastically affected by the reaction conditions of the polymerization (e.g., initial concentration of monomer and monomer/catalyst ratio), lower molecular weight ($M_n = 2.1 \times 10^4$) was observed when the polymerization was carried out in benzene in place of toluene presumably due to rapid precipitation of insoluble oligomer during the chain growth reaction.

Considering that the reaction of isatoic anhydride **1′** with phenyl(trimethylsilyl)acetylene (**8**) under the same reaction conditions afforded correspondingly substituted quinolone **2′** in 94% isolated yield with complete regioselectivity (Scheme 4),[3] we assumed that the polymerization of alkynylisatoic anhydride monomer **1** afforded polyquinolone **2**, which consisted of quinolone subunits connected with carbon–carbon bond between C-2 and C-6, regioselectively (Scheme 3). Indeed, only a single peak assigned to a trimethylsilyl group was observed by ^{1}H NMR measurement of polyquinolone **2**; the polymerization proceeded with high regioregularity.

In summary, a new methodology for preparation of polyquinolone was developed. We demonstrated for the first time that nickel-catalyzed decarboxylative cycloaddition can be an elementary process of chain growth polymerization for preparation of polyheterocycles with high regioregularity.[6]



Scheme 4. Regioselective reaction of **1′** with **8** (ref. 3).

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.