# Nickel(0)-Catalyzed Cycloaddition Copolymerization of Diynes with Isocyanates to Poly(2-pyridones)

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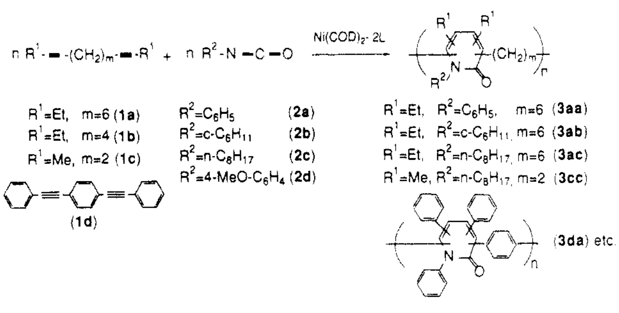
Recently we have reported the nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes with $CO_2$ to poly(2-pyrones).[1] If various cycloaddition components can be used instead of $CO_2$, this transition metal-catalyzed cycloaddition copolymerization of diynes will be of wide application as an efficient synthetic method of novel polymers. We report here nickel(0)-catalyzed 1:1 cycloaddition copolymerization of diynes (**1**) with isocyanates (**2**) to unprecedented poly(2-pyridones) (**3**;[2] eq 1), which has various different features from that of diynes with $CO_2$ and also opens a new aspect of the transition metal-catalyzed cycloaddition reaction.[3]



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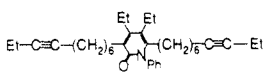

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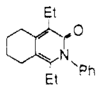

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The results of copolymerization of 3,11-tetradecadiyne (**1a**) with phenyl isocyanate (**2a**) are summarized in Table I. The copolymerization proceeded well in a THF solvent at 40–60 °C using a tri-*sec*-alkylphosphine ligand such as tricyclohexyl- or tri-*sec*-butylphosphine to afford poly(2-pyridone) **3aa** with molecular weights of 10 000–25 000 in good yields. Use of an excess of **2a** to **1a** afforded **3aa** with the higher molecular weight. The $PCy_3$/Ni ratio of 2 gave **3aa** with the higher molecular weight than that of 3, but catalyst decomposition was observed at 90 °C in the reaction using $PCy_3/Ni = 2$. Increase of the diyne concentration raised the copolymer yield and molecular weight. An acetonitrile cosolvent retarded the copolymerization. The poly(2-pyridone) **3aa** was soluble in benzene, methylene chloride, chloroform, THF, and methanol but was insoluble in hexane and ether.

The diyne–isocyanate copolymerization exhibited different ligand and solvent effects from those of the diyne–$CO_2$ copolymerization:[1] in the latter, tricyclohexylphosphine is ineffective and acetonitrile is a unique cosolvent. Unlike the diyne–$CO_2$ copolymerization, the catalyst amount could be reduced to 2 mol % in the diyne–isocyanate copolymerization.

Formation of copolymer **3aa** was demonstrated by the following spectroscopic data of the copolymer. IR $\nu$(C=O) absorption appeared at 1644 $cm^{-1}$. Its $^{13}C$ NMR spectrum exhibited five groups of absorptions (Figure 1a) at $\delta$ 116.3–118.4 (m), 128.7–130.7 (m), 143.3–145.0 (m), 150.3–152.3 (m), and 163.0–163.4 (m), which are characteristic of a 2-pyridone ring,[4] along with four phenyl absorptions at $\delta$ 128.4–128.7 (m), 129.2–129.5 (m), 129.5–129.8 (m), and 140.6–141.0 (m) but did not show C=C absorptions ($\delta$ 137.0–137.4 (m) and 138.4–138.7 (m)) of the homopolymer of **1a**. $^1H$ NMR peaks were observed at $\delta$ 0.85–1.27 ($CH_3$ and $CH_2$, 14 H), 2.10–2.75 ($CH_2C{=}C$, 8 H), and 7.10–7.60 ($C_6H_5$, 5 H) with satisfactory relative peak areas.

To confirm further the copolymer structure, four regioisomeric 2-pyridone co-oligomers consisting of two diyne molecules and one isocyanate molecule were prepared by shortening the reaction time and using an excess of **1a** to **2a**. Among them, which were obtained in ca. 80% yield, one pure regioisomer **4** was isolated in 17% yield. Co-oligomer **4** exhibited $^{13}C$ NMR C=C and C=O absorptions of its 2-pyridone ring at $\delta$ 117.8, 128.63, 143.0, 151.6, and 163.0 along with C≡C absorptions at $\delta$ 79.2, 79.6, 81.5, and 81.7 and phenyl absorptions at $\delta$ 128.1, 128.57, 129.2, and 139.8 (Figure 1b). Excellent corre-

**Table I**
**Nickel(0)-Catalyzed 1:1 Cycloaddition Copolymerization of 3,11-Tetradecadiyne (1a) with Phenyl Isocyanate (2a) to Poly(2-pyridone) 3aa**[a]

| Ni/1a | ligand (L) | solvent | temp, °C | 3aa<br>yield,[b] % | <br>$M_n$[c] | <br>$M_w/M_n$[c] |
|---|---|---|---|---|---|---|
| 0.1 | $PCy_3$ | THF | 90 | 84 | 11 200 | 2.8 |
| | | | | 86[e] | 11 200 | 2.8 |
| | | | 60 | 72 | 13 500 | 3.6 |
| | | | | 76[e] | 9 700 | 3.0 |
| | | | | 91[g] | 25 600 | 2.1 |
| | | | 40 | 71 | 16 600 (12 300)[d] | 2.2 |
| | | | | 84[e] | 8 700 | 2.4 |
| | | | room temp | 64 | 8 400 | 1.9 |
| | | | 60 | 92[h] | 22 900 | 2.3 |
| 0.05 | | | | 79 | 14 200 | 2.9 |
| 0.02 | | | | 63 | 14 900 (9 000)[d] | 2.1 |
| 0.1 | | toluene | | 75 | 12 400 | 3.2 |
| | | THF–MeCN | | 52[f] | 4 000 | 2.3 |
| | P(*sec*-Bu)$_3$ | THF | | 84 | 12 600 | 3.4 |
| | $PEt_3$ | | | 42 | 3 700 | 1.7 |
| | P(*n*-$C_8H_{17}$)$_3$ | | | 40 | 5 500 | 1.3 |
| | dppb | | | 0 | | |

[a] **1a**, 1 mmol; **1a**/**2a** = 1; L/Ni = 2; solvent, 5 mL; time, 20 h. [b] Based on the formation of a 1:1 copolymer. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform. [e] L/Ni = 3. [f] Solvent, 5 mL; THF/MeCN = 1 (v/v). [g] **2a**/**1a** = 3. [h] Solvent, 2.5 mL.

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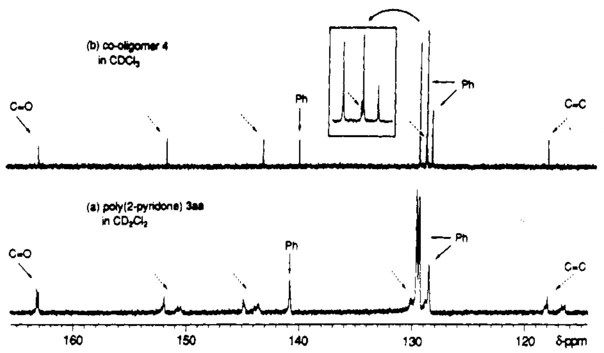

**Figure 1.** $^{13}$C NMR C=C and C=O absorptions of poly(2-pyridone) **3aa** (a) and co-oligomer **4** (b).

**Table II**
**Nickel(0)-Catalyzed 1:1 Cycloaddition Copolymerization of Diynes 1 with Isocyanates 2 to Poly(2-pyridones) 3**[a]

| 1 | 2 | 3 | | | |
|---|---|---|---|---|---|
| | | | yield,[b] % | $M_n$[c] | $M_w/M_n$[c] |
| **a** | **b** | **ab** | 96 | 38000 | 1.6 |
| **a** | **c** | **ac** | 68 | 19100 | 2.2 |
| **a** | **d** | **ad** | 81 | 12900 | 3.1 |
| **b** | **a** | **ba** | 34[e,g] | 4100 | 2.0 |
| **b** | **a** | **ba** | 57 | 6700 | 2.2 |
| **b** | **a** | **ba** | 68[f] | 8900<br>(6000)[d] | 2.0 |
| **c** | **c** | **cc** | 76 | 11700 | 1.4 |
| **d** | **a** | **da** | ~100 | 10700<br>(4200)[d] | 3.1 |
| **d** | **d** | **dd** | 73 | 8000 | 2.6 |

[a] Diyne, 1 mmol; 1/2 = 1; $PCy_3/Ni(COD)_2$ = 2; solvent, THF, 5 mL; temp, 60 °C; time, 20 h. [b] Based on the formation of a 1:1 copolymer. [c] Determined by GPC with polystyrene standards in chloroform. [d] Determined by VPO in chloroform. [e] Solvent, 10 mL. [f] Solvent, 2.5 mL. [g] Bicyclic 2-pyridone **5** was obtained in 12% yield as a minor product.

spondence (Figure 1) of the $^{13}$C NMR spectrum related to the 2-pyridone ring of **3aa** with that of **4** indicates that efficient 1:1 cycloaddition copolymerization of **1a** with **2a** occurs to produce poly(2-pyridone) **3aa**.

Various isocyanates and diynes could be used for the copolymerization (Table II). Cyclohexyl (**2b**), *n*-octyl (**2c**), and 4-methoxyphenyl (**2d**)[5] isocyanates were copolymerized with **1a**. 2,6-Octadiyne (**1c**), owing to its short methylene chain, gave insoluble copolymer **3ca** with **2a**, but use of **2c** afforded soluble copolymer **3cc**. 3,9-Dodecadiyne (**1b**) reacted with **2a** to give poly(2-pyridone) **3ba**. This finding is in marked contrast to the **1b**–$CO_2$ reaction,[1] where the bicyclic 2-pyrone,[6] an intramolecular cyclization product, is a main product. Bicyclic 2-pyridone **5** was formed only as a minor product in the **1b**–**2a** copolymerization (Table II).

Interestingly, 1,4-bis(phenylethynyl)benzene (**1d**), the diyne with a bulky phenyl substituent, which does not copolymerize with $CO_2$, gave copolymers with isocyanates. Nickel(0)-catalyzed homopolymerization of **1d** produced an insoluble polymer, but copolymerization of **1d** with **2a** afforded structurally interesting poly(2-pyridone) **3da**, which was soluble in benzene, methylene chloride, and THF.

Thus, the nickel(0)-catalyzed cycloaddition copolymerization of diynes with isocyanates to a new class of polymer of poly(2-pyridones) demonstrates a different reactivity between isocyanates and $CO_2$ as the cycloaddition component and also has a significant advantage over that of diynes with $CO_2$, that is, synthesis of a variety of poly(2-pyridones) by the use of various diynes and isocyanates. Because of a variety of chemical reactions[7] of the 2-pyridone ring such as the Diels–Alder reaction,[7a] photochemical reaction,[7b] and molecular aggregation[7c] besides its biological activity,[4b] poly(2-pyridones) may be expected to have many uses.

The present synthesis of poly(2-pyridones) strongly suggests that the transition metal-catalyzed cycloaddition copolymerization of diynes can utilize various cycloaddition components[3] including heterocumulenes, nitriles, carbon monoxide, etc., and is of wide application as an efficient synthetic method of novel polymers, providing a new aspect of the transition metal-catalyzed cycloaddition reaction.

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**Supplementary Material Available:** Experimental section including characterization data of copolymers and co-oligomers (7 pages). Ordering information is given on any current masthead page.

## References and Notes

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(2) 2-Pyridone synthesis from monoynes and isocyanates catalyzed by an equimolar mixture of $Ni(COD)_2$ and a $PCy_3$ or $PEt_3$ ligand in toluene at −20 to +20 °C has been known, where the monoyne is added very slowly over 1 h into the reaction mixture. See: Hoberg, H.; Oster, B. W. *Synthesis* **1982**, 324. In the present copolymerization, all reaction components were successively added at a time at ambient temperature and the resulting reaction mixture was heated at the prescribed temperature.

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