Nickel(0)-Catalyzed Cycloaddition Copolymerization of 1,4-Diethynylbenzene with Isocyanates to Poly(2-pyridone)s

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ABSTRACT: The nickel(0)-catalyzed cycloaddition copolymerization of 1,4-diethynylbenzene (**1**) with 4-methylphenyl (**2a**) or *n*-octyl (**2b**) isocyanate to poly(2-pyridone) **3a** or **3b**, respectively, was studied. Equimolar copolymerization of **1** with **2a** or **2b** in THF at 60 °C produced an insoluble or poorly soluble copolymer. Use of an excess amount of **2a** or **2b** and the short reaction time of 5–10 min afforded soluble poly(2-pyridone) **3a** or **3b**, although its molecular weight was not high. Prolonging the copolymerization to 20 h gave insoluble **3a**, while it produced soluble branched poly(2-pyridone) **3b** with a broad molecular weight distribution, i.e., a high M_w/M_n value. The M_w/M_n value was found to be a useful criterion for the poly(2-pyridone) branch. Poly(2-pyridone)s **3a,b** were identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies and also by comparing their spectral data with those of a model 2-pyridone compound prepared from phenylacetylene and *n*-octyl isocyanate.

Introduction

We developed the new polymerization reaction of transition-metal-catalyzed cycloaddition copolymerization of a diyne and reported the nickel(0)-catalyzed cycloaddition copolymerization of acyclic and cyclic internal diynes with heterocumulenes of CO_2[1] and isocyanates[2] to unprecedented poly(2-pyrone)s and poly(2-pyridone)s, respectively. The nickel(0)-catalyzed cycloaddition copolymerization of a terminal diyne with CO_2, however, was unsuccessful on account of its high cyclotrimerization reactivity. In this study, we have investigated the cycloaddition copolymerization of 1,4-diethynylbenzene (**1**) with the isocyanate (eq 1)[3] as the first example of the nickel(0)-catalyzed cycloaddition copolymerization of a terminal diyne with the isocyanate. Very recently we reported the copolymerization of 1,4-bis(phenylethynyl)benzene (1,4-PhC≡CC$_6$H$_4$C≡CPh) with isocyanates to rigid poly(2-pyridone)s with a repeating unit of a phenyl- and phenylene-substituted 2-pyridone ring.[2c] Comparison of the copolymerization behavior of **1** with that of 1,4-bis(phenylethynyl)benzene is one important point of this study because terminal diyne **1** tends to form poly(2-pyridone) branches through cyclotrimerization. Synthesis of a soluble branched poly(2-pyridone) and its characterization are interesting problems in the transition-metal-catalyzed cycloaddition copolymerization of a diyne.

Experimental Section

Instrumentation and general procedures are described in the previous reports[1b–d,3] unless otherwise stated. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken in CD_2Cl_2 on a JEOL JNM-JX-400 or GSX-400 instrument. 1,4-Diethynylbenzene (**1**) was a commercial reagent and was purified by sublimation. 4-Methylphenyl isocyanate (**2a**) and *n*-octyl isocyanate (**2b**) were commercial reagents and were distilled under nitrogen.

Copolymerization of 1,4-Diethynylbenzene (1) with 4-Methylphenyl Isocyanate (2a). The reaction was carried out under nitrogen. THF (9.39 mL), Ni(COD)$_2$ (0.0275 g, 0.100 mmol) in a THF solution (2.16 mL), P(*c*-C$_6$H$_{11}$)$_3$ (0.0561 g, 0.200 mmol) in a toluene solution (0.250 mL), **2a** (0.640 mL, 5.00 mmol), and **1** (0.126 g, 1.00 mmol) in a THF solution (1.46 mL) were placed in this order in a 50-mL flask under magnetic stirring at ambient temperature. The reaction mixture was heated at 60 °C for 10 min under magnetic stirring. Evaporation of volatile matters under vacuum and addition of ether (20 mL) precipitated copolymer **3a**, which was purified twice by dissolving in CH_2Cl_2 (2.0 mL) and adding a mixture of methanol (10 mL) and ether (10 mL) to the CH_2Cl_2 solution. Precipitated **3a** was isolated by centrifugation and dried under vacuum to give **3a** as an ocherous solid (0.19 g, 73%). **3a**: IR (KBr, cm^{-1}) 3035, 1666, 1594, 1511, 817; ^{1}H NMR δ 2.00–2.50 (m, 3 H), 6.30–7.80 (m, 10 H); ^{13}C NMR δ 20.5–22.0 (m, methyl group), 118.5–120.4 (m), 120.4–122.5 (m), 151.0–154.5 (m), 160.5–162.5 (m, 2-pyridone ring), 125.0–132.5 (phenylene and 4-methylphenyl groups), 132.5–143.0 (2-pyridone ring together with phenylene and 4-methylphenyl groups).

Copolymerization of 1,4-Diethynylbenzene (1) with *n*-Octyl Isocyanate (2b). The reaction was carried out under nitrogen. THF (1.30 mL), Ni(COD)$_2$ (0.0275 g, 0.100 mmol) in a THF solution (2.24 mL), P(*c*-C$_6$H$_{11}$)$_3$ (0.0561 g, 0.200 mmol) in a toluene solution (0.25 mL), **2b** (1.23 mL, 7.00 mmol), and **1** (0.126 g, 1.00 mmol) in a THF solution (1.46 mL) were placed in this order in a 50-mL flask under magnetic stirring at ambient temperature. The reaction mixture was heated at 60 °C for 5 miin under magnetic stirring. Evaporation of volatile matters under vacuum and addition of hexane (30 mL) precipitated copolymer **3b**, which was washed with hexane (30 mL) and then with methanol (30 mL). The copolymer was purified twice by dissolving in CH_2Cl_2 (2.0 mL) and adding hexane (20 mL). Precipitated **3b** was isolated by centrifugation and dried under vacuum to give **3b** as a yellow solid (0.20 g, 72%). **3b**: IR (KBr, cm^{-1}) 3041, 1663, 1597, 1507, 1462, 1363, 838; ^{1}H NMR δ 0.80–0.95 (m, 3 H), 0.95–1.95 (m, 12 H), 3.70–4.15 (m, 2 H), 6.10–7.90 (m, 6 H); ^{13}C NMR δ 14.0–32.5 (m), 49.5–50.5 (m, *n*-octyl group), 119.0–120.5 (m), 120.5–121.5 (m), 137.6–138.8 (m), 151.0–153.0 (m), 161.0–162.5 (m, 2-pyridone ring), 126.0–133.0 (m), 135.5–144.0 (m, phenylene group). The result of the elemental analysis of **3b** was not satisfactory. Anal. Calcd for $(C_{19}H_{23}NO)_n$: C, 81.10; H, 8.24; N, 4.98. Found: C, 78.36; H, 8.12; N, 4.35.

Preparation of Model Compound 4 from Phenylacetylene and *n*-Octyl Isocyanate (2b). The reaction was carried out under nitrogen. Ni(COD)$_2$ (0.0275 g, 0.100 mmol) in a THF (3.00 mL) solution, P(*c*-C$_6$H$_{11}$)$_3$ (0.0561 g, 0.200 mmol) in a toluene solution (0.250 mL), **2b** (0.352 mL, 2.00 mmol), and phenylacetylene (0.22 mL, 2.00 mmol) were placed in this order in a 50-mL flask under magnetic stirring at ca. 0 °C. The reaction mixture was allowed to stand at ambient

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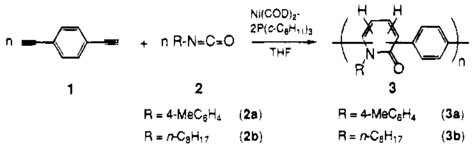
temperature for 24 h under magnetic stirring. Evaporation of volatile matters under vacuum gave a residue, which was purified by PLC (AcOEt/hexane = 2/1 (v/v)) followed by a repeated one (AcOEt/hexane = 3/1 (v/v)) to give *N*-*n*-octyl-4,5-diphenyl-2-pyridone **4** (0.057 g, 16%) as a semisolid. Further purification by PLC did not give a pure compound. The purity of **4** was estimated to be ca. 80% on the basis of its ^{1}H NMR spectrum. **4**: IR (film, cm^{-1}) 3058, 1660, 1611, 1592, 768, 700; ^{1}H NMR δ 0.89 (t, $J = 7.0$ Hz, 3 H), 1.20−1.50 (m, 10 H), 1.81 (quint, $J = 7.5$ Hz, 2H), 3.99 (t, $J = 7.5$ Hz, 2 H), 6.55 (s, 1 H), 7.01−7.05 (m, 2 H), 7.10−7.14 (m, 2 H), 7.19−7.28 (m, 6 H), 7.34 (s, 1 H); ^{13}C NMR δ 14.2, 23.0, 27.1, 29.55, 29.63, 29.8, 32.2, 49.9 (*n*-octyl group), 120.60, 120.64, 138.0, 152.7, 161.9 (2-pyridone ring), 127.1, 128.36, 128.44, 129.2, 129.8, 137.4, 138.6 (phenyl group); MS *m*/*e* (relative intensity) 105 (34), 247 (100), 248 (38), 261 (96), 263 (36), 342 (100), 358 (38), 359 (M$^+$, 67).

Results and Discussion

In the nickel(0)-catalyzed cycloaddition copolymerization of 1,4-bis(phenylethynyl)benzene with isocyanates, an aryl isocyanate exhibited a higher copolymerizability than an alkyl isocyanate; the 1:1 copolymerization of the aryl isocyanate was effected using an equimolar monomer feed, while the 1:1 copolymerization of the alkyl isocyanate required use of its excess amount to the diyne.[2c] 4-Methylphenyl (**2a**) and *n*-octyl (**2b**) isocyanates therefore were chosen as representative isocyanates in the present nickel(0)-catalyzed copolymerization of **1** with the isocyanate (eq 1).[3]

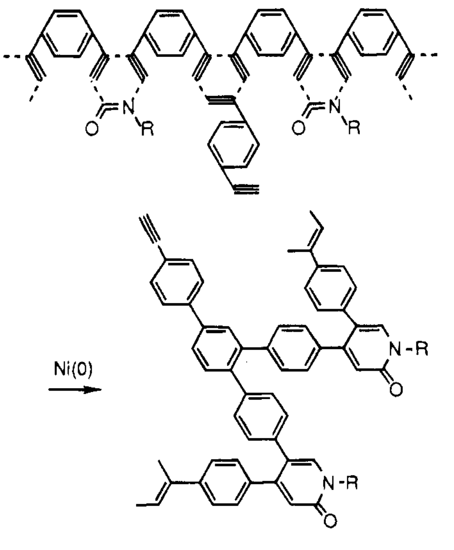


(1)

1 2 3

R = 4-MeC$_6$H$_4$ (**2a**) R = 4-MeC$_6$H$_4$ (**3a**)
R = *n*-C$_8$H$_{17}$ (**2b**) R = *n*-C$_8$H$_{17}$ (**3b**)

First, the equimolar copolymerization of **1** with **2a** was carried out at 60 °C in THF for 20 h using a Ni(COD)$_2$ (10 mol %)/2P(*c*-C$_6$H$_{11}$)$_3$ catalyst according to a standard copolymerization condition of 1,4-bis(phenylethynyl)benzene with **2a**.[2c] An insoluble copolymer having an IR ν(C=O) absorption of a 2-pyridone ring at 1659 cm^{-1} was formed. Use of an excess amount of **2a** to **1** up to the molar ratio of 10 or employment of other phosphorus ligands such as P(*sec*-Bu)$_3$, P(*n*-C$_8$H$_{17}$)$_3$, PPh$_3$, and Ph$_2$P(CH$_2$)$_4$PPh$_2$ instead of P(*c*-C$_6$H$_{11}$)$_3$ did not improve the result. Insolubility of the copolymer may be ascribed to a side reaction generating an alkyne trimerization unit in the copolymer (eq 2). Its remaining C≡C bond may induce formation of a branched and/or cross-linked insoluble copolymer in the progress of the copolymerization reaction.[2c] High homopolymerizability of **1** was confirmed; nickel(0)-catalyzed homopolymerization of **1** in THF under the reaction conditions of Table 1 produced an insoluble polymer in 2 min.



(2)

Table 1. Nickel(0)-Catalyzed Cycloaddition Copolymerization of 1,4-Diethynylbenzene (1) with Isocyanates 2 to Poly(2-pyridone)s 3 (eq 1)[a]

			3				
2	**2**/**1**[b]	time, min		yield,[c] %	M_n[d]	M_w/M_n[d]	[**2**]/[**1**][e]
a	1	5	**a**	0[g]			
	5			81[h]			
		10		4[f]			
				73[i]	3300	1.3	1.0
	10	1200		0[g]			
b	1	5	**b**	61[h]	7900	1.7	
	5			70	9000	1.4	0.82
	7			72	7900 (4100)[l]	2.3	1.0
		120		68	13200[j]	6.1	
		1200		76	16100[k]	18	1.0
	12			81	5400[k]	11	1.0

[a] **1**, 1 mmol; Ni(COD)$_2$/**1** = 0.1; P(*c*-C$_6$H$_{11}$)$_3$/Ni = 2; solvent, THF, 5 mL; temperature, 60 °C. [b] The molar ratio. [c] Based on the quantitative formation of the soluble 1:1 copolymer. [d] Determined by GPC with polystyrene standards in chloroform. [e] The molar ratio of **2** to **1** components in the copolymer determined by ^{1}H NMR. [f] Major products are insoluble copolymers. [g] Insoluble copolymers were formed. [h] Poorly soluble copolymers. [i] Solvent, THF, 13 mL. [j] Two GPC peaks were observed. [k] One broad GPC peak was observed. [l] Determined by VPO in chloroform.

The **1**/**2a** copolymerization reaction therefore was stopped at an early stage of the copolymerization to avoid the formation of an insoluble copolymer and to obtain a soluble copolymer. The results are summarized in Table 1. Formation of the soluble **1**/**2a** copolymer depended upon the **2a**/**1** molar ratio, the copolymerization time, and the substrate concentration. The copolymerization time of 10 min in the copolymerization using **2a**/**1** = 5 gave an insoluble copolymer, but shortening a copolymerization time to 5 min produced a soluble copolymer in high yield although its solubility was not high. Increase of a solvent amount afforded a soluble copolymer with a low molecular weight. The copolymerization with **2a**/**1** = 1 gave an insoluble copolymer after 5 min.

On the other hand, use of a large excess of **2b** to **1** produced a soluble 1:1 copolymer (Table 1). Thus the equimolar copolymerization produced a poorly soluble copolymer and the copolymerization with **2b**/**1** = 5 gave a copolymer containing the diyne trimerization unit, but the copolymerization with **2b**/**1** = 7 afforded a soluble 1:1 copolymer. It is noteworthy that prolonging the copolymerization with **2b**/**1** = 7 to 120 min or 20 h produced a soluble poly(2-pyridone) **3b**, but it had a high M_w/M_n value of 6.1 or 18, respectively. The relationship between the GPC profile and the reaction time of the copolymerization therefore was examined.

The GPC profile versus the reaction time in the copolymerization with **2b**/**1** = 7 under the copolymerization conditions of Table 1 disclosed one feature of the **1**/**2** copolymerization. A bimodal character of the GPC profile was observed (Figure 1); a copolymer with a lower molecular weight was first formed, and it was then transformed into a copolymer with a higher molecular weight. This transformation was accordingly accompanied by broadening of the molecular weight distribution of the copolymer, i.e., an increase of the M_w/M_n value of the copolymer, as shown in Table 2.

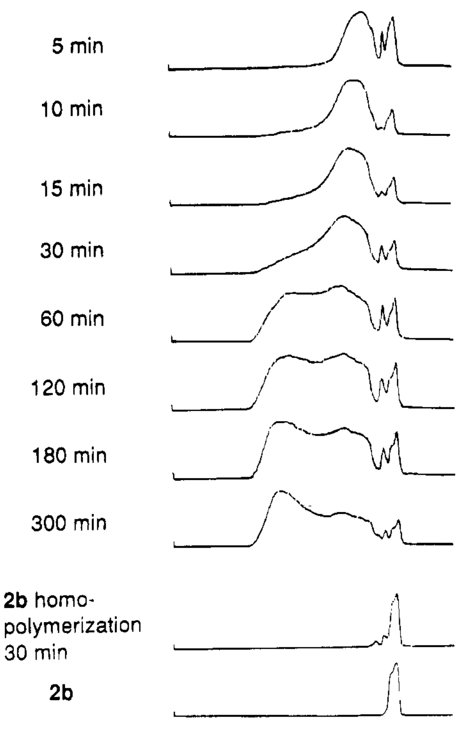


Figure 1. GPC profile versus the reaction time in the copolymerization of 1,4-diethynylbenzene (**1**) and *n*-octyl isocyanate (**2b**) (**2b/1** = 7) under the reaction conditions of Table 1.

Table 2. Relationship between the GPC Molecular Weight of Copolymer 3b and the Reaction Time in the Nickel(0)-Catalyzed Copolymerization of 1,4-Diethynylbenzene (1) with *n*-Octyl Isocyanate (2b)[a]

	copolymer 3b	
reaction time, min	M_n[b]	M_w/M_n[b]
5	5 400	1.5
10	8 400	4.4
15	9 700	5.1
20	11 400	7.3
30	14 100	8.3
45	17 700	10
60	23 500	13
120	23 200	15
180	25 200	17
300	29 700	16

[a] **1**, 1 mmol; **2b/1** = 7; $Ni(COD)_2$/**1** = 0.1; $P(c\text{-}C_6H_{11})_3/Ni$ = 2; solvent, THF, 5 mL; temperature, 60 °C. [b] Determined by GPC with polystyrene standards in chloroform.

A plausible explanation of the bimodal character and the time-dependent change of the GPC profile along with the broadening of the molecular weight distribution of the copolymer is as follows: a low molecular weight poly(2-pyridone) containing the diyne trimerization unit (eq 2) is first formed, and then a higher molecular weight poly(2-pyridone) with a longer poly(2-pyridone) branch is produced by growth of a poly(2-pyridone) branch originating from the C≡C bond of the diyne trimerization unit together with growth of a poly(2-pyridone) main chain. The number of branches per one poly(2-pyridone) main chain is few so far as excess **2b** is used because the molar ratio of **2b** to **1** components in **3b** determined by ^1H NMR spectroscopy was almost 1 (Table 1).

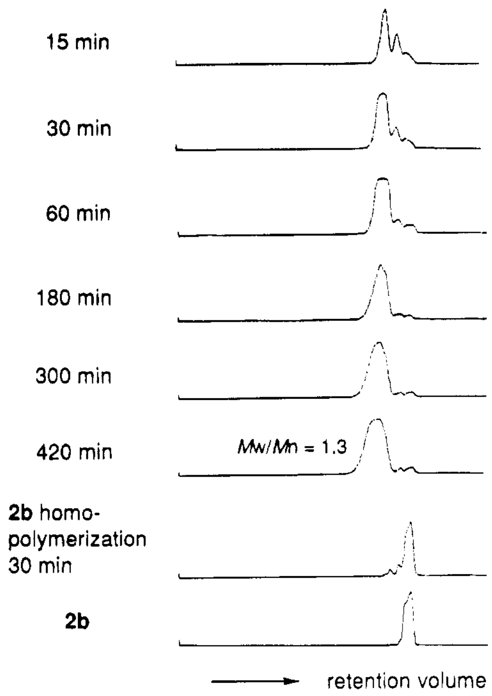


Figure 2. GPC profile versus the reaction time in the copolymerization of 1,4-bis(phenylethynyl)benzene and *n*-octyl isocyanate (**2b**) (**2b**/1,4-bis(phenylethynyl)benzene = 5) under the reaction conditions of footnote *i* of Table 1.

The GPC profile versus the reaction time in the copolymerization of 1,4-bis(phenylethynyl)benzene with excess **2b** is shown in Figure 2 in comparison with that of the **1/2b** copolymerization. The bimodal nature of the GPC profile was not observed. Considering this and previous findings that an equimolar monomer mixture of **1** and **2a** gives an insoluble branched and/or cross-linked copolymer while that of 1,4-bis(phenylethynyl)benzene and **2a** affords a soluble 1:1 copolymer,[2c] it may be concluded that terminal diyne **1** has a lower copolymerizability with the isocyanate than 1,4-bis(phenylethynyl)benzene, which is an internal diyne. The higher copolymerizability of 1,4-bis(phenylethynyl)benzene in comparison with **1** may be ascribed to the facile formation of metallacycle intermediates involving diyne and isocyanate components.[2c,4a,5]

In our recent report,[2c] the correlation between branching of the poly(2-pyridone) and its M_w/M_n value was suggested on the basis of ^1H and ^{13}C NMR spectroscopic analyses of a copolymer. In this study, reliable experimental evidence indicating the formation of a branched poly(2-pyridone) with a broad molecular weight distribution was presented by the GPC analysis of the copolymerization reaction. Thus, the M_w/M_n value of the copolymer may be a criterion for the formation of a branched copolymer in the nickel(0)-catalyzed cycloaddition copolymerization of a diyne. The formation of a branched copolymer is one extreme case of the nickel(0)-catalyzed cycloaddition copolymerization of a diyne but may be useful for understanding its characteristics.

Poly(2-pyridone)s **3a,b** were identified by IR, ^1H NMR, and ^{13}C NMR spectroscopies. They exhibited an IR ν(C═O) absorption of a 2-pyridone ring in the region of 1660 cm^{-1}. Soluble poly(2-pyridone) **3a** exhibited ^1H NMR methyl and phenylene absorptions at 2.00−2.50 and 6.30−7.80 ppm, respectively, with reasonable relative peak areas but showed also unidentified small and broad absorptions at 1.35−2.00 ppm. Soluble poly(2-pyridone) **3b** gave a reasonable ^1H NMR relative peak area of *n*-octyl to phenylene absorptions and showed a ^1H NMR NCH_2 absorption at 3.35−4.15 ppm.

^{13}C NMR spectroscopy is the most useful method for identifying a 2-pyridone ring. ^{13}C NMR C═O and C═C

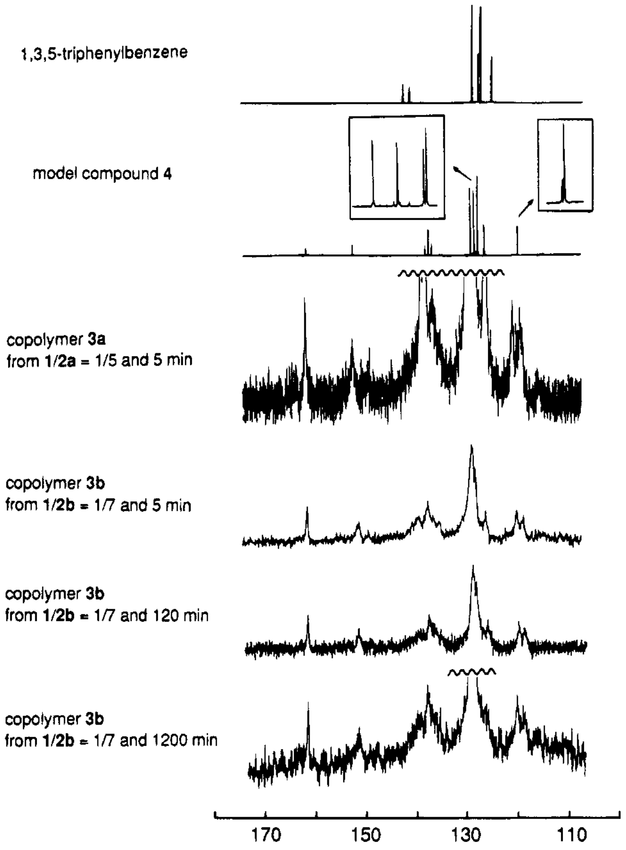
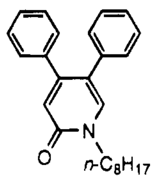


Figure 3. ^{13}C NMR C=O and C=C absorptions of copolymers **3a** and **3b** along with related compounds (δ, ppm).

absorptions of **3a,b** are shown in Figure 3. In the previous studies on the poly(2-pyridone) synthesis,[2] a cooligomer prepared from diyne and isocyanate compounds is utilized for the determination of a poly(2-pyridone) structure. Several attempts to prepare a cooligomer consisting of two molecules of **1** and one molecule of **2b**, however, were unsuccessful. *N*-*n*-Octyl-4,5-diphenyl-2-pyridone (**4**) as a model 2-pyridone compound for identifying a 2-pyridone ring of **3a,b** therefore was prepared from phenylacetylene and **2b** with reference to the literature.[4] Its regiochemistry was confirmed by the two sharp ^{1}H NMR (400 MHz) singlets of 2-pyridone protons at 6.55 and 7.34 ppm. Formation of *N*-phenyl-4,5-diphenyl-2-pyridone by the nickel(0)-catalyzed reaction of **1** with phenyl isocyanate has been reported.[4b] The C−H COSY measurement of **4** indicated that its ^{13}C NMR absorptions at 120.60 and 138.0 ppm (Figure 3) are due to the 2-pyridone carbons with a proton. ^{13}C NMR absorptions at 120.65, 152.7, and 161.9 ppm are reasonably assigned to 2-pyridone ring carbons based on the previous ^{13}C NMR analysis of the poly(2-pyridone) with a tetrasubstituted 2-pyridone ring.[2] Poly(2-pyridone)s **3a,b** exhibited ^{13}C NMR C=O and C=C absorptions quite similar to those of **4**. This result demonstrates the formation of poly(2-pyridone)s **3a,b**.



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The conclusion based on the ^{1}H NMR analysis of **3b** that the number of branches per one poly(2-pyridone) main chain is few was also supported by the ^{13}C NMR analysis of **3b**. Thus a ^{13}C NMR spectrum of **3b** did not exhibit distinct absorptions corresponding to ipso carbon absorptions (141.4 and 142.7 ppm) of 1,3,5-triphenylbenzene (Figure 3), which is a model compound for the alkyne trimerization unit in the copolymer (eq 2). No considerable change of the ^{13}C NMR spectrum of **3b** with reaction time was observed (Figure 3). This finding suggests that the formation of the alkyne trimerization unit in the copolymer takes place at an early stage of the copolymerization and growth of the poly(2-pyridone) branch occurs in the progress of the copolymerization.

The 2-pyridone ring is well-known to exhibit a variety of chemical reactivities. The poly(2-pyridone) having a 2-pyridone ring with two unsubstituted carbon atoms such as **3a** and **3b** may be expected to undergo a facile polymer reaction related to a 2-pyridone ring in comparison with the poly(2-pyridone)[2] with a tetrasubstituted 2-pyridone ring. The reaction of poly(2-pyridone)s **3a,b** such as the Diels−Alder reaction[6a] or a photochemical cycloaddition reaction[6b] is an interesting future research subject.

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References and Notes

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(3) The expression of a repeating unit of **3** in eq 1 is based on the undetermined regiochemistry of a 2-pyridone ring of **3**, although it is considered to have mainly the regiochemistry of model compound **4**.

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(5) Diyne **1** was found to have an alkyne trimerization reactivity (eq 2) similar to that of 1,4-bis(phenylethynyl)benzene. A trimerization reactivity order of **1**, 1,4-bis(phenylethynyl)benzene, and 3,11-tetradecadiyne ($EtC{\equiv}C(CH_2)_6C{\equiv}CEt$) was determined by GC analysis of unreacted diynes in the nickel(0)-catalyzed cooligomerization and/or copolymerization reaction of an equimolar mixture of these three diynes in the absence of the isocyanate. The order obtained was 1,4-bis(phenylethynyl)benzene = **1** ≫ 3,11-tetradecadiyne. Thus there was no relation between the copolymerization behavior of the two aromatic diynes and their homopolymerization behavior. A low homopolymerizability of the aliphatic diyne, however, is noteworthy and may be related to the facile formation of a variety of poly(2-pyridone)s from various aliphatic diynes and isocyanates.[2a,b]

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