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

Tetsuo Tsuda* and Akihiko Tobisawa[†]

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan

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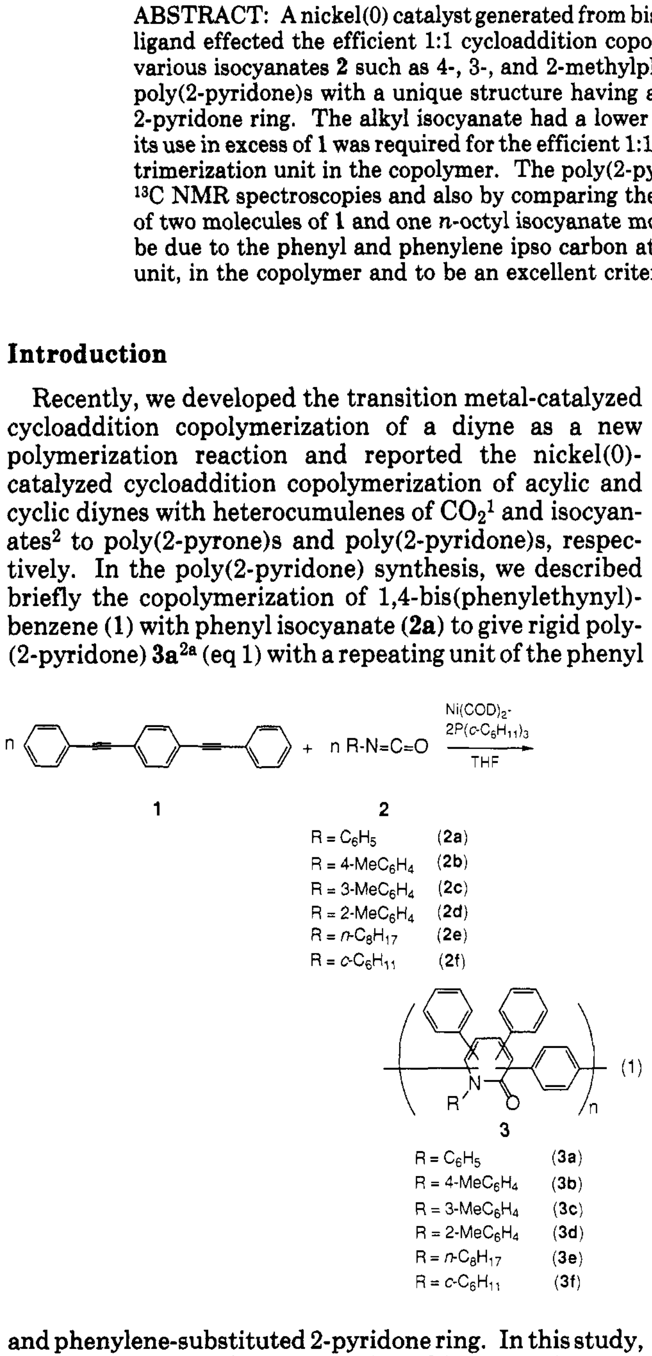
ABSTRACT: A nickel(0) catalyst generated from bis(1,5-cyclooctadiene)nickel and a tricyclohexylphosphine ligand effected the efficient 1:1 cycloaddition copolymerization of 1,4-bis(phenylethynyl)benzene (1) with various isocyanates 2 such as 4-, 3-, and 2-methylphenyl isocyanates and *n*-octyl isocyanate to afford rigid poly(2-pyridone)s with a unique structure having a repeating unit of a phenyl and phenylene-substituted 2-pyridone ring. The alkyl isocyanate had a lower copolymerizability with 1 than the aryl isocyanate and its use in excess of 1 was required for the efficient 1:1 copolymerization to suppress the formation of the diyne trimerization unit in the copolymer. The poly(2-pyridone)s obtained were identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies and also by comparing their spectral data with those of the cooligomer consisting of two molecules of 1 and one *n*-octyl isocyanate molecule. The ^{13}C NMR absorption at δ 141 was found to be due to the phenyl and phenylene ipso carbon atoms of the benzenoid unit, i.e., the diyne trimerization unit, in the copolymer and to be an excellent criterion for the 1:1 copolymerizability of 1 with 2.

Introduction

Recently, we developed the transition metal-catalyzed cycloaddition copolymerization of a diyne as a new polymerization reaction and reported the nickel(0)-catalyzed cycloaddition copolymerization of acylic and cyclic diynes with heterocumulenes of CO_2[1] and isocyanates[2] to poly(2-pyrone)s and poly(2-pyridone)s, respectively. In the poly(2-pyridone) synthesis, we described briefly the copolymerization of 1,4-bis(phenylethynyl)benzene (1) with phenyl isocyanate (**2a**) to give rigid poly(2-pyridone) **3a**[2a] (eq 1) with a repeating unit of the phenyl and phenylene-substituted 2-pyridone ring. In this study, we have investigated the synthesis of this interesting type of poly(2-pyridone) 3 in detail by using other aryl isocyanates in addition to **2a**, namely, 4-, 3-, and 2-methylphenyl isocyanates **2b–d**, along with alkyl isocyanates, namely, *n*-octyl (**2e**) and cyclohexyl (**2f**) isocyanates (eq 1).



Experimental Section

Instrumentation and general procedures are described in the previous reports[1b–d] 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 unless otherwise stated. 1,4-Bis(phenylethynyl)benzene (1) was prepared by the literature procedure.[3] Phenyl isocyanate (**2a**), 4-methylphenyl isocyanate (**2b**), 3-methylphenyl isocyanate (**2c**), 2-methylphenyl isocyanate (**2d**), *n*-octyl isocyanate (**2e**), and cyclohexyl isocyanate (**2f**) were commercial reagents and were distilled under nitrogen.

Copolymerization of 1,4-Bis(phenylethynyl)benzene (1) with 4-Methylphenyl Isocyanate (2b). The reaction was carried out under nitrogen. Bis(1,5-cyclooctadiene)nickel (Ni(COD)$_2$; 0.0275 g, 0.100 mmol) in a THF solution (3.00 mL), $P(c\text{-}C_6H_{11})_3$ (0.0561 g, 0.200 mmol) in a toluene solution (0.250 mL), **2b** (0.640 mL, 5.00 mmol), and 1 (0.278 g, 1.00 mmol) in a THF solution (10 mL) were placed in this order in a 50 mL stainless steel autoclave under magnetic stirring at ambient temperature. The reaction mixture was heated at 60 °C for 20 h under magnetic stirring. Evaporation of volatile matters under vacuum and addition of ether (20 mL) precipitated copolymer **3b**, which was purified twice by dissolving in CH_2Cl_2 (3.0 mL) and adding a mixture of methanol (15 mL) and ether (15 mL) to the CH_2Cl_2 solution. Precipitated **3b** was isolated by centrifugation and dried under vacuum to give **3b** (0.28 g, 67%). **3b**: IR (KBr, cm^{-1}) 3060, 1638, 1606, 1581, 1508, 1108, 1020, 849, 799, 752, 699; ^{1}H NMR 1.95–2.55 (m, 3 H), 6.55–7.45 (m, 18 H); ^{13}C NMR 20.6–21.8 (m), 119.0–121.9 (m), 124.7–139.0 (m), 144.9–147.2 (m), 149.7–151.9 (m), 161.7–162.8 (m). The result of the elemental analysis of **3b** was not satisfactory. Anal. Calcd for $(C_{30}H_{21}NO)_n$: C, 87.56; H, 5.14; N, 3.40. Found: C, 85.23; H, 5.24; N, 3.26. It was found that ashes were formed after combustion analysis. This finding indicates that nickel salts contaminate **3b**. Poly(2-pyridone)s **3a** and **3c,d** were similarly prepared. **3a**: IR (KBr, cm^{-1}) 3058, 1644, 1601, 1580, 1570, 1507, 1489, 1104, 1024, 846, 734, 695; ^{1}H NMR 6.00–7.50 (m); ^{13}C NMR 118.6–122.0 (m), 125.4–140.0 (m), 144.1–146.9 (m), 149.0–151.8 (m), 161.2–162.5 (m). **3c**: IR (KBr, cm^{-1}) 3056, 1648, 1607, 1574, 1525, 1482, 1086, 1016, 849, 778, 749, 694; ^{1}H NMR 1.90–2.45 (m, 3 H), 5.90–7.50 (m, 18 H); ^{13}C NMR 20.4–22.1 (m), 120.4–121.8 (m), 125.0–140.3 (m), 145.0–147.1 (m), 149.3–152.1 (m), 161.4–162.7 (m). **3d**: IR (KBr, cm^{-1}) 3059, 1647, 1600, 1581, 1490, 1022, 851, 734, 696; ^{1}H NMR ($CDCl_3$) 1.90–2.50 (m), 6.00–7.50 (m); ^{13}C NMR 17.5–19.0 (m), 119.4–122.1 (m), 125.6–140.0 (m), 144.6–147.0 (m), 149.8–152.2 (m), 160.8–162.1 (m).

[†] Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan.

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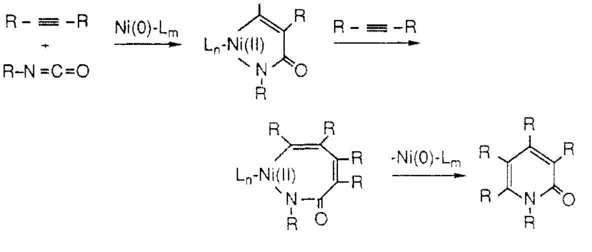
Copolymerization of 1,4-Bis(phenylethynyl)benzene (1) with *n*-Octyl Isocyanate (2e). The reaction was carried out under nitrogen. $Ni(COD)_2$ (0.0275 g, 0.100 mmol) in a THF solution (3.00 mL), $P(c\text{-}C_6H_{11})_3$ (0.0561 g, 0.200 mmol) in a toluene solution (0.250 mL), **2e** (0.882 mL, 5.00 mmol), and 1 (0.278 g, 1.00 mmol) in a THF solution (10 mL) were placed in this order in a 50-mL stainless steel autoclave under magnetic stirring at ambient temperature. The reaction mixture was heated at 60 °C for 20 h under magnetic stirring. Evaporating volatile matters under vacuum, dissolving a resulting residue by addition of CH_2Cl_2 (4 mL), and adding methanol (40 mL) to the CH_2Cl_2 solution precipitated poly(2-pyridone) **3e**, which was purified by dissolving in CH_2Cl_2 (4.0 mL) and by adding methanol (40 mL). Precipitated **3e** was isolated by centrifugation and dried under vacuum to give **3e** (0.22 g, 51%). **3e**: IR (KBr, cm^{-1}) 3057, 1638, 1603, 1585, 1522, 1490, 1071, 1020, 843, 753, 696; ^1H NMR 0.75–0.96 (m, 3 H), 0.96–1.80 (m, 12 H), 3.20–4.00 (m, 2 H), 6.00–7.55 (m, 14 H); ^{13}C NMR 14.1–32.5 (m), 46.2–48.0 (m), 119.5–121.5 (m), 124.6–139.2 (m), 145.6–147.5 (m), 148.7–152.1 (m), 160.9–162.0 (m). Poly(2-pyridone) **3f** was similarly prepared. **3f**: IR (KBr, cm^{-1}) 3056, 1645, 1601, 1576, 1507, 1489, 1059, 1020, 841, 746, 699; ^1H NMR 0.90–2.00 (m), 3.20–3.80 (m), 5.70–7.60 (m); ^{13}C NMR 14.0–34.0 (m), 63.1–64.5 (m), 120.1–122.6 (m), 125.3–135.8 (m), 135.8–137.4 (m), 137.4–140.1 (m), 146.5–149.0 (m), 149.0–151.6 (m), 162.5–163.0 (m).

Preparation of Cooligomer 4 from 1,4-Bis(phenylethynyl)benzene (1) with *n*-Octyl Isocyanate (2e). The reaction was carried out under nitrogen. $Ni(COD)_2$ (0.0275 g, 0.100 mmol) in a THF (3.00 mL) solution, tricyclohexylphosphine (0.0561 g, 0.200 mmol) in a toluene solution (0.250 mL), **2e** (0.882 mL, 5.00 mmol), and 1 (0.0278 g, 1.00 mmol) in a THF solution (10 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 4 min under magnetic stirring. After the reaction mixture was cooled by ice water, it was subjected to PLC (AcOEt/hexane = 1/1 (v/v)) followed again by PLC (AcOEt/hexane = 3/1 (v/v)) to give cooligomer 4 involving two from its four possible regioisomers (eq 4) (0.035 g, 10%). Cooligomer 4: mp 177–180 °C; IR (KBr, cm^{-1}) 3057, 1635, 1594, 1513, 1068, 1018, 838, 754, 689; ^1H NMR 0.857 (t, J = 7.1, 1.5 H), 0.861 (t, J = 7.1, 1.5 H), 1.05–1.40 (m, 10 H), 1.60–1.72 (m, 2 H), 3.80–3.90 (m, 2 H), 6.75–7.60 (m, 28 H); ^{13}C NMR 14.2, 14.3, 22.97, 23.01, 27.2, 28.85, 28.88, 29.17, 29.22, 29.40, 29.43, 32.09, 32.14, 47.6, 88.8, 89.26, 89.31, 89.7, 89.8, 89.9, 90.8, 120.4, 120.9, 121.2, 121.4, 121.6, 123.2, 123.4, 123.7, 126.4–132.3 (m), 134.9, 135.0, 137.05, 137.10, 137.6, 138.3, 138.8, 139.0, 146.1, 147.0, 149.5, 149.8, 161.7; MS *m/e* (relative intensity) 598 (73), 599 (100), 600 (57), 612 (54), 694 (35), 711 (54), 712 (M^+, 51). Repeated purification of 4 by PLC did not give a satisfactory result for the elemental analysis. The purity of 4 was estimated to be ca. 93% on the basis of the phenyl and phenylene proton peak of its ^1H NMR spectrum.

Results and Discussion

The results of the nickel(0)-catalyzed cycloaddition copolymerization of 1 with aryl isocyanates **2a–d** (eq 1)[4] are summarized in Table 1. The 2-pyridone ring formation in the nickel(0)-catalyzed reaction of the monoyne with the isocyanate has been proposed to proceed according to eq 2.[5] A competing side reaction of the formation of 3, which reduces a 1:1 copolymerizability of 1 with 2, may be the diyne trimerization to produce benzenoid repeating units in the copolymer (eq 3) because it is known that the nickel(0) catalyst effects the trimerization of diphenylacetylene to produce hexaphenylbenzene.[6] The molar ratio of the 1 component to the **2b** or **2c** one in the copolymer, which measures the 1:1 copolymerizability, was determined by the ^1H NMR relative peak area of the methyl protons to the phenyl and phenylene protons of the copolymer. The results indicate that **3b** and **3c** with an excellent 1:1 copolymerizability were formed from an equimolar monomer feed. Similarly, formation of the 1:1 copolymer **3a** by the equimolar **1**/**2a** copolymerization was confirmed by ^{13}C NMR analysis (vide post). The composition of **3d** was approximate because methyl absorptions centered at δ 2.1 and unidentified broad absorptions around δ 1.7 overlapped each other in the ^1H NMR spectrum of **3d**. ^{13}C NMR spectroscopic analysis indicates a lower 1:1 copolymerizability of **2d** than those of **2a–c** (vide post). Therefore an excess of **2d** was required for the 1:1 copolymerization. Poly(2-pyridone)s **3a–d** were dark yellow powders, which were soluble in DMF, acetic acid, THF, $CHCl_3$, CH_2Cl_2, and benzene but insoluble in ethyl acetate, acetone, ether, and methanol.

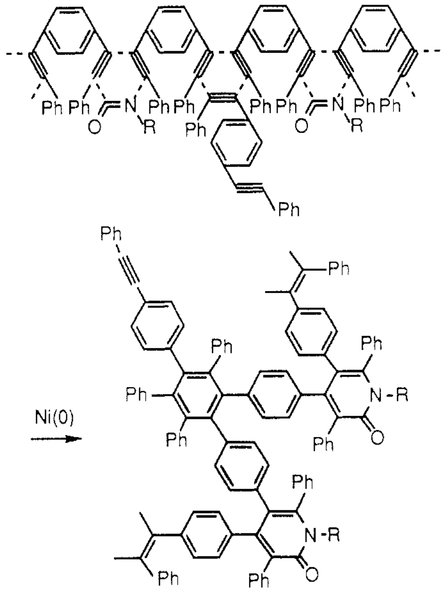


(2)

Table 1. Nickel(0)-Catalyzed Cycloaddition Copolymerization of 1,4-Bis(phenylethynyl)benzene (1) with Aryl Isocyanates (2) to Poly(2-pyridone)s (3) (Eq 1)[a]

				3				
2	2/1[b]	amt of solvent, mL	temp, °C		yield, %[c]	M_n[d]	M_w/M_n[d]	[2]/[1][e]
a	1	13	60	**a**	68	19 700	1.9	
	2				68	16 800 (6 800)[g]	1.6	
	5		90		50	19 600	1.8	
b	1		60	**b**	74	26 200	2.6	1.0
	2				68	21 500	1.9	n.d.[h]
	5				67	29 500	1.8	
			90		81[f]	28 500	3.6	
	1	6			86	32 200	7.4	
c		13	60	**c**	53	38 000	3.7	0.96
	2				40	40 200	3.2	n.d.[h]
	5				45	40 800	2.0	
	1		90		70[f]	32 100	4.8	
d			60	**d**	53	45 800	4.0	
	5				50	23 900	1.9	ca. 1

[a] 1, 1 mmol; $Ni(COD)_2/1 = 0.1$; $P(c\text{-}C_6H_{11})_3/Ni = 2$; solvent, THF; time, 20 h. [b] The molar ratio. [c] Based on the quantitative formation of the 1:1 copolymer. [d] Determined by GPC with polystyrene standards in chloroform. [e] The molar ratio of **2** and **1** components in the copolymer determined by the ^1H NMR relative peak area of methyl to phenyl and phenylene absorptions. [f] $P(c\text{-}C_6H_{11})_3/Ni = 3$. [g] Determined by VPO in chloroform. [h] Not determined.



(3)

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

				3				
2	2/1[b]	amt of solvent, mL	temp, °C		yield, %[c]	M_n[d]	M_w/M_n[d]	[2]/[1][e]
e	1	13	60	e	52	26 200	2.8	0.51
	2				44	23 500	3.0	0.85
	5				51	12 300 (6 200)[h]	1.5	0.97
		6			62	13 800	1.8	n.d.[i]
		13	90		31	22 300	1.9	
					88[f]	14 200	1.6	
f	1		60	f	100[g]			
	2				79	26 200	10	0.48
	5				66	18 800	4.4	0.79

[a] 1, 1 mmol; $Ni(COD)_2/1 = 0.1$; $P(c\text{-}C_6H_{11})_3/Ni = 2$; solvent, THF; time, 20 h. [b] The molar ratio. [c] Based on the quantitative formation of the 1:1 copolymer. [d] Determined by GPC with polystyrene standards in chloroform. [e] The molar ratio of 2 and 1 components in the copolymer determined by the ^1H NMR relative peak area of alkyl to phenyl and phenylene absorptions. [f] $P(c\text{-}C_6H_{11})_3/Ni = 3$. [g] The insoluble copolymer. [h] Determined by VPO in chloroform. [i] Not determined.

The results of the copolymerization of **1** with alkyl isocyanates **2e** and **2f** are shown in Table 2, which indicates a lower copolymerizability of **2e** and **2f** than aryl isocyanates **2a–d**. The equimolar **1**/**2e** copolymerization produced a copolymer containing a considerable amount of the diyne trimerization unit.[7] The use of a 5-fold molar excess of **2e** to **1** was necessary for the formation of the 1:1 copolymer. Poly(2-pyridone) **3e** was a white powder and showed solubility similar to that of **3a–d** except in ethyl acetate where **3e** was soluble. The copolymerizability of **2f** was much lower than that of **2e**. The equimolar **1**/**2f** copolymerization produced an insoluble copolymer and even the copolymerization using a 5-fold molar excess of **2f** to **1** gave a copolymer containing a considerable amount of the diyne trimerization unit. Branching and/or crosslinking of the copolymer originating from the $C\equiv C$ bond of the diyne trimerization unit (eq 3) may be a cause for the formation of the insoluble copolymer and may explain the unusually high M_w/M_n value of 10 for the copolymer obtained from the monomer feed of **1**/**2f** = 1/2. Previously, we reported the nickel(0)-catalyzed cycloaddition copolymerization of **2e** or **2f** with aliphatic diynes, where the 1:1 copolymers are obtained efficiently from an equimolar monomer mixture.[2a] Therefore **1** has a lower copolymerizability with the isocyanate than the aliphatic diyne.

The relationship between the molecular weight of **3a** or **3e** and the reaction time was examined by periodic GPC analysis of the reaction mixture. The result is shown in Figure 1. The equimolar **1**/**2a** copolymerization was almost finished by 2 h. In another experiment, a mixture of 3,11-tetradecadiyne, $EtC\equiv C(CH_2)_6C\equiv CEt$, and **2a** (1 mmol each) was added to the reaction mixture after 6 h. The powdery copolymer produced was considered not to contain the 3,11-tetradecadiyne/**2a** copolymer because **3a** was a powder and the poly(2-pyridone)[2a] from 3,11-tetradecadiyne and **2a** was a resinlike solid. Formation of the 3,11-tetradecadiyne/**2a** copolymer was also not indicated by IR and ^{13}C NMR spectroscopies. These results suggest that deactivation of the nickel(0) catalyst took place after several hours under the reaction conditions of Table 1 although its mechanism is not clear at the present time. A second addition of the new nickel(0) catalyst (10 mol %) to the reaction mixture after 6 h (Figure 1) did not cause further efficient growth of the copolymer. This may be due to the decreased concentration and reactivity of the terminal propagating $C\equiv C$ bond of the copolymer along with catalyst deactivation.

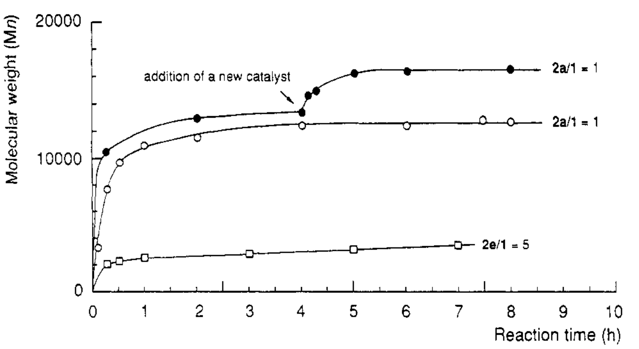


Figure 1. Relationship between the molecular weight of copolymer **3a** or **3e** and the reaction time in the copolymerization of 1,4-bis(phenylethynyl)benzene (**1**) with phenyl isocyanate (**2a**) or *n*-octyl isocyanate (**2e**) at 60 °C.

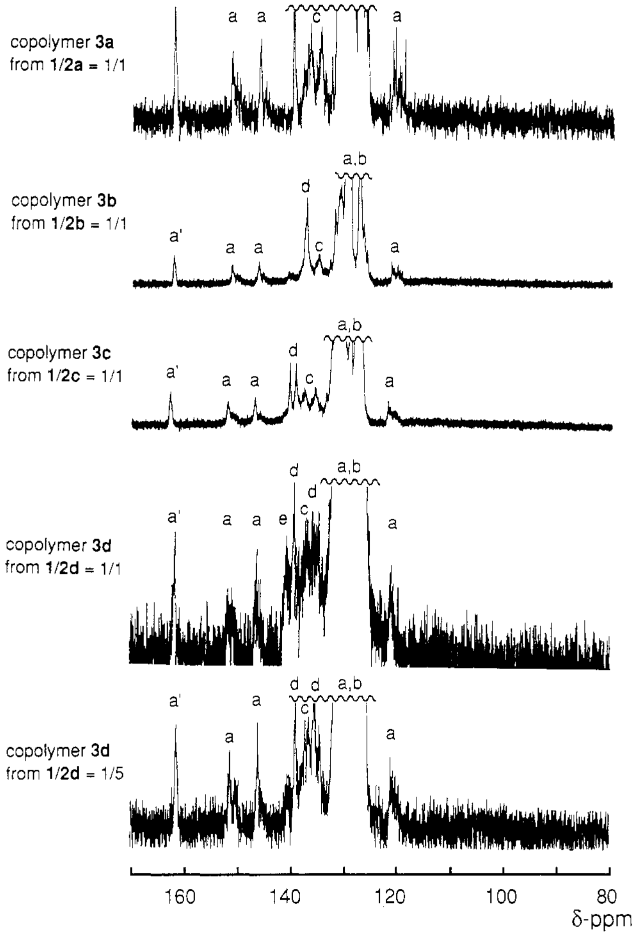


Figure 2. ^{13}C NMR C=O and C=C absorptions of copolymers **3a–d**.

The copolymer growth in the **1**/**2e** copolymerization (**1**/**2e** = 1/5) proceeded quite slowly (Figure 1). Addition of a mixture of 3,11-tetradecadiyne and **2e** (1 mmol each) to the reaction mixture after 6 h produced a resinlike copolymer while **3e** was a powder. The copolymer obtained exhibited a small, but distinct, ^{13}C NMR C=O absorption of the 3,11-tetradecadiyne/**2e** copolymer at δ 162.0–162.7 in addition to the C=O absorption of **3e** at δ 161.0–162.0. This result indicates that the nickel(0) catalyst activity was maintained during the slow copolymerization of **1** with **2e**. Thus, the different behavior of the nickel(0) catalyst in the **1**/**2a** copolymerization from that in the **1**/**2e** copolymerization is noteworthy. The molecular weight vs reaction time curve of the **1**/**2a** or the **1**/**2e** copoly-

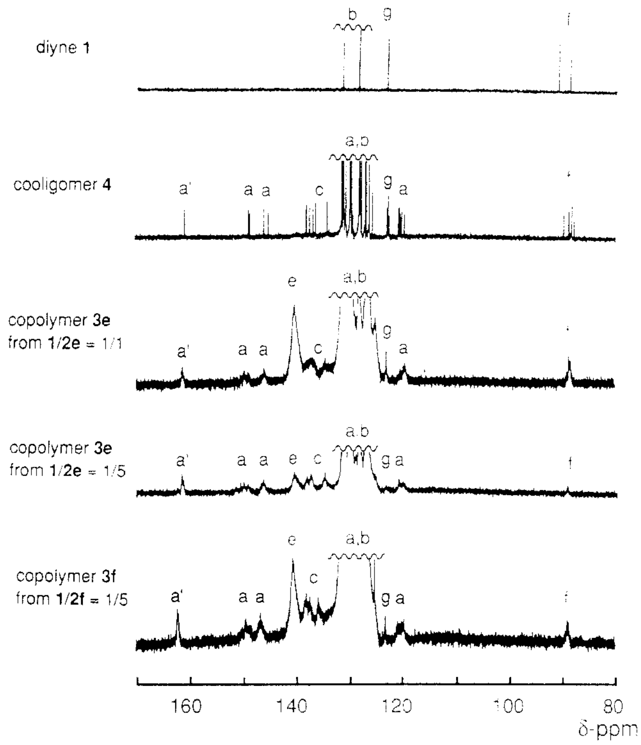
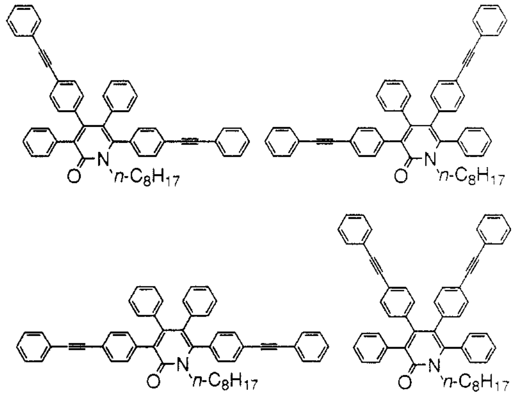


Figure 3. ^{13}C NMR C=O, C=C, and C≡C absorptions of copolymers **3e** and **3f** along with related compounds.

merization differs from that of the aliphatic cyclic diyne/**2f** copolymerization, where the molecular weight of the ladder poly(2-pyridone) increases with the reaction time at least up to 20 h.[2b]

Poly(2-pyridone)s **3a–f** were identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies, as described in the Experimental Section. ^{13}C NMR spectroscopy was the most useful. Poly(2-pyridone)s **3a–f** exhibited four groups of ^{13}C NMR peaks assignable to the C=O and C=C absorptions of their 2-pyridone rings (carbons a′ and a of **5**, which represents the 2-pyridone unit followed by the diyne trimerization unit in the copolymer) (Figures 2 and 3). The one remaining group of the C=C absorptions of the 2-pyridone ring (carbons a of **5**) is considered to overlap the δ 125–133 absorptions (carbons b of **5**) (vide post). This is based on the finding that the poly(2-pyridone) obtained from 3,11-tetradecadiyne and **2e** showed this absorption around δ 130.[2a]

To further confirm the poly(2-pyridone) structure, cooligomer **4** was prepared by shortening the reaction time. Its ^{13}C NMR C=O and C=C absorptions are shown in Figure 3. Two sets of the C=C absorptions of the 2-pyridone ring were observed at δ 145–150. This result indicates that two regioisomers of **4**, among four possible ones, were selectively formed although their structures were not determined at the present time. The four groups of C=O and C=C absorptions of **3a–f** (carbons a′ and a of **5**) corresponded to those of **4** (Figures 2 and 3). Thus the presence of the 2-pyridone repeating unit in the copolymer was confirmed.



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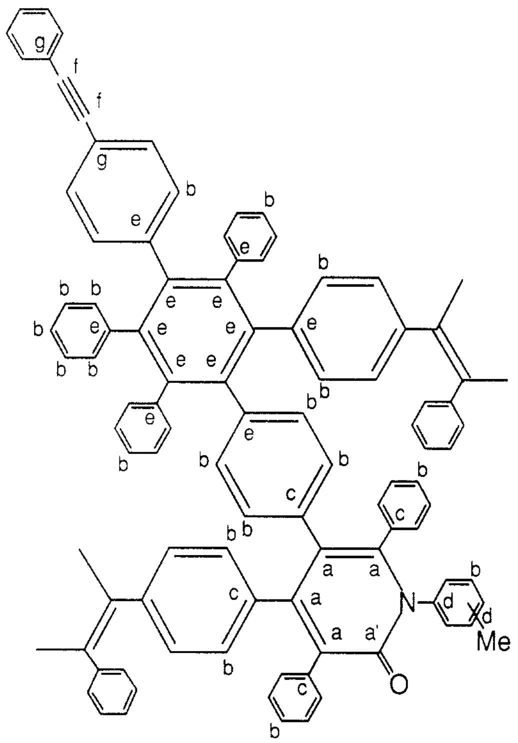

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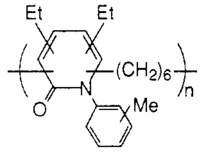
The assignment of the ^{13}C NMR absorptions of the phenyl and phenylene carbon atoms was also possible. The weak absorptions of **3a–f** between δ 133 and 139 may be attributed to carbons c of **5** on the basis of the findings that these absorptions were not observed in the spectra of **6b–d**[8] (Figure 4), which were prepared by the nickel(0)-catalyzed cycloaddition copolymerization of 3,11-tetradecadiyne with **2b–d**, and were observed in the spectrum of **4**. The absorption of the corresponding phenyl carbon atom of 3-ethyl-6-phenyl-2-pyridone is known to appear at δ 137.2.[9] The absorptions between δ 125 and 133 are due to carbons b of **5**. The corresponding absorptions of 3-ethyl-6-phenyl-2-pyridone appear at δ 126.5, 129.1, and 129.6.[9] The absorptions at δ 135–140 of **3a–d** may be assigned to the aryl carbons bound to the nitrogen atom and the methyl group in their aryl isocyanate component (carbons d of **5**) because **6b–d** clearly showed these absorptions (Figure 4).



6b: 4-Me, **6c**: 3-Me, **6d**: 2-Me

A noteworthy absorption is the one around δ 141 clearly observed in the spectra of **3e** and **3f** prepared from the monomer feed of **1**/**2e** = 1/1 and **1**/**2f** = 1/5, respectively (Figure 3). This absorption was found to be the spectral demonstration of the trimerization unit of **1** in **3** (eq 3) and, accordingly, to be an excellent criterion for the 1:1 copolymerizability of **1** with **2**. Considering the result of Table 2 that the diyne trimerization was noticeable in the

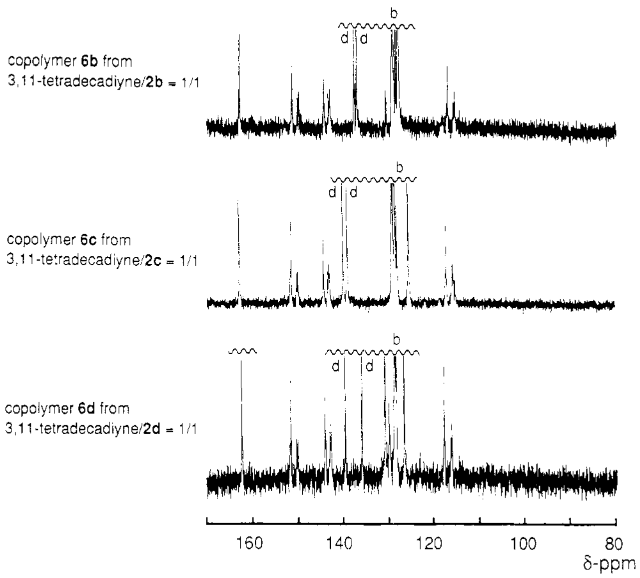


Figure 4. ^{13}C NMR C=O and C=C absorptions of copolymers **6b–d**.

1/**2e** = 1/1 and **1**/**2f** = 1/5 copolymerization, the δ 141 absorption may be assigned to carbon atoms (carbons e of **5**) of the benzene ring of the diyne trimerization unit and its ipso phenyl and phenylene carbons (carbons e of **5**). This assignment is supported by the fact that hexaphenylbenzene[10] exhibits the ipso carbon absorptions at δ 140.7 and 141.1 together with absorptions due to para, ortho, and meta carbon atoms of the phenyl group at δ 124.8, 126.1, and 130.6, respectively.

Poly(2-pyridone)s **3a–c** obtained from an equimolar monomer feed showed no or a quite small δ 141 absorption. On the other hand, **3d** exhibited the distinct δ 141 absorption while the use of excess **2d** decreased its intensity. These findings indicate (1) an excellent 1:1 copolymerizability of **2a–c**, (2) a little lower 1:1 copolymerizability of **2d** than that of **2a–c**, and (3) a higher 1:1 copolymerizability of the aryl isocyanate than the alkyl isocyanate. Poly(2-pyridone) **3f** from the monomer feed (**1**/**2f** = 1/5) showed the noticeable δ 141 absorption while the corresponding **3e** showed only the small one, which indicates a lower 1:1 copolymerizability of **2f** than **2e**. Thus the ^{13}C NMR analysis of **3a–f** using the δ 141 absorption supports decisively the discussion on the results of Tables 1 and 2 using the ^{1}H NMR method (vide ante).

The C≡C absorption around δ 90 appeared in the spectra of **3e** and **3f**. There are two possibilities for the origin of this absorption, that is, the C≡C bond (carbons f of **5**) of the diyne trimerization unit and the terminal C≡C moiety of the copolymer. Three experimental results that (1) the difference of the molecular weights of poly(2-pyridone)s **3a** and **3e** or **3f** was not so remarkable, (2) the intensity of the C≡C absorption seems to be proportional to that of the absorption around δ 141, and (3) the alkyl isocyanate had a lower 1:1 copolymerizability than the aryl isocyanate suggest the former possibility. The absorptions around δ 123 may be assigned to carbons g of **5** on the basis of the corresponding absorptions of **1** and **4**. Thus the ^{13}C NMR absorptions of poly(2-pyridone)s **3a–f** in the C=O, C=C, and C≡C region are reasonably elucidated.

The intensity of the δ 141 absorption of **3b** with M_w/M_n = 7.4 was similar to that of **3b** with M_w/M_n = 2.6 (Table 1). This finding suggests that the broader molecular weight distribution of the former corresponds to the longer poly(2-pyridone) branch rather than larger numbers of the branches. Thus the M_w/M_n value of the copolymer obtained by the nickel(0)-catalyzed cycloaddition copolymerization of the diyne may be a criterion for the branching of the copolymer.[11]

Examination of physical properties and chemical reactions of unique poly(2-pyridone) **3** prepared in this study is a further interesting research subject. Thermogravimetric analysis (TGA) indicated that **3a** had a high thermal stability and showed a rapid weight loss around 500 °C in air while **3e** decomposed around 400 °C.

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References and Notes

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