Macromolecules **1996,** *29,* 4544−4548

Cobaltocene-Catalyzed Cycloaddition Copolymerization of Diyne with Nitriles to Poly(pyridine)s

Tetsuo Tsuda* and Hiroaki Maehara[†]

Department of Polymer Chemistry, Graduate School of Engineering, and Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan

Received July 14, 1995; Revised Manuscript Received April 1, 1996[⊗]

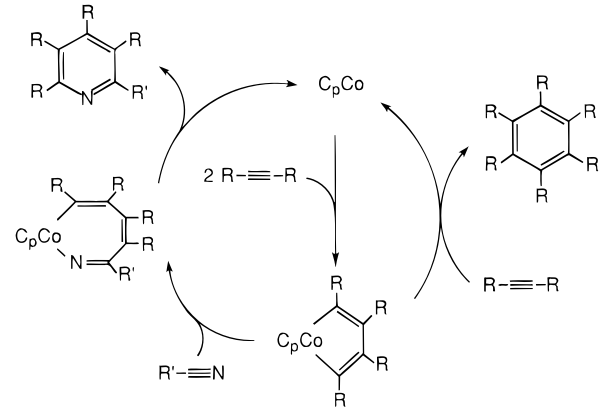
ABSTRACT: A cobaltocene catalyst effected a cycloaddition copolymerization of 1,11-dodecadiyne (**1a**) with acetonitrile (**2a**) in toluene at 150 °C to afford a poly(pyridine) with a molecular weight up to 18 000. An excess of **2a** to **1a** was necessary for the preparation of a soluble poly(pyridine) without diyne trimerization units. The structure of the nitrile influenced remarkably its copolymerizability with **1a**: the copolymerizability order was *p*-tolunitrile > acetonitrile > *n*-octyl cyanide. The length (m) of a methylene chain tethering two C≡C bonds of a diyne $HC{\equiv}C(CH_2)_mC{\equiv}CH$ controlled the diyne/nitrile copolymerization: 1,9-decadiyne with $m = 6$ or 1,7-octadiyne with $m = 4$ did not copolymerize with **2a** effectively to give a diyne trimer or a bicyclic pyridine as a main low-molecular weight product, respectively. The poly(pyridine) formation is the first example of an efficient cycloaddition copolymerization of a terminal diyne.

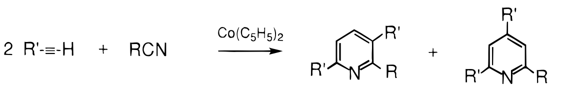
Introduction

We developed recently the new polymerization reaction of a transition metal-catalyzed cycloaddition copolymerization of a diyne.[1] A variety of diynes and cycloaddition components could be used for the copolymerization to afford various new polymers containing hetero- or carbocycle moieties in their repeat units: poly(2-pyrone)s,[2] poly(2-pyridone)s,[3] and poly(bicyclo[2.2.2]oct-7-ene)s[4] were obtained by the nickel(0)−catalyzed cycloaddition copolymerization of diynes with carbon dioxide, isocyanates, and N-substituted maleimides, respectively. As for a carbene-type cycloaddition component, we found a poly(enone)[5a] and poly(thiophene)[5b] syntheses by a cobalt-catalyzed cycloaddition terpolymerization of a diyne, a diene, and carbon monoxide, and a palladium-catalyzed cycloaddition copolymerization of a diyne with elemental sulfur S_8, respectively. Recently, transition metal-containing polymers were prepared from diynes and low-valent transition metal complexes by using the diyne cycloaddition copolymerization technique.[6] It is important to expand further a scope of the diyne cycloaddition copolymerization reaction.

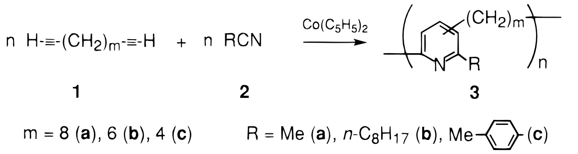
A variety of cobalt catalysts are known to effect a cycloaddition of two molecules of a terminal alkyne and one molecule of a nitrile to produce pyridine derivatives.[7] Commercially available cobaltocene catalyzes also the reaction of an aliphatic terminal alkyne with a nitrile to afford two regioisomeric pyridine derivatives (eq 1).[8] A proposed mechanism of the cobaltocene-catalyzed pyridine formation is shown in Scheme 1.[7c,8] In this study, we have explored a cobaltocene-catalyzed cycloaddition copolymerization of terminal diynes with nitriles to poly(pyridine)s (eq 2). Previously there was no example of an efficient cycloaddition copolymerization of a terminal diyne.[3d]

Scheme 1





(1)



(2)

1 2 3

m = 8 (**a**), 6 (**b**), 4 (**c**) R = Me (**a**), *n*-C8H17 (**b**), Me- -(**c**)

Experimental Section

General Procedures. IR spectra were recorded on a Perkin-Elmer 1600 spectrophotometer. ^1H NMR (270 MHz) and ^{13}C NMR (67.5 MHz) spectra were taken in CD_2Cl_2 on a JEOL JNM-EX-270 instrument unless otherwise stated. Chemical shifts are reported in ppm on the δ scale relative to CH_2Cl_2 as 5.32 ppm. Mass spectra were obtained on a JEOL JMS-SX-102A (FAB) and a JEOL JMS-DX-300 (EI). Preparative layer chromatography (PLC) was carried out by using a 20 × 20 × 0.2 cm plate prepared with Merck silica gel 60 PF-254. GPC was performed in tetrahydrofuran using TOSOH TSK_{gel} $G3000H_{XL}$ or $G4000H_{XL}$ columns with polystyrene standards. 1,11-Dodecadiyne, 1,9-decadiyne, 1,7-octadiyne, acetonitrile, *p*-tolunitrile, and *n*-octyl cyanide were commercial reagents and were distilled under nitrogen. Cobaltocene was purchased from Aldrich Chemical Co., Inc. and was purified by sublimation. Toluene was distilled over CaH_2 under nitrogen. Tetrahydrofuran (THF) was distilled over $LiAlH_4$ under nitrogen.

Copolymerization of 1,11-Dodecadiyne (1a) with Acetonitrile (2a). The reaction was carried out under nitrogen. In a 50 mL stainless steel autoclave, toluene (4.4 mL), a toluene solution (0.58 mL) of cobaltocene (0.10 mmol), **2a** (0.52

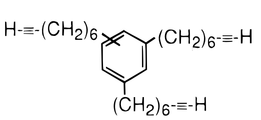
[†] Department of Synthetic Chemistry.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

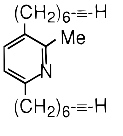
S0024-9297(95)01017-5 CCC: $12.00

mL, 10 mmol), and **1a** (0.200 mL, 1.00 mmol) were placed in this order under magnetic stirring at ambient temperature. The reaction mixture was heated at 150 °C for 20 h under magnetic stirring. After the reaction mixture was cooled by ice water, it was concentrated under vacuum. Addition of hexane (20 mL) to a resulting residue precipitated copolymer **3aa**, which was further purified by dissolution in toluene (2 mL) and precipitation by the addition of hexane (20 mL). Drying in vacuo at room temperature gave **3aa** as a brown semisolid (0.11 g, 52% based on the formation of poly(pyridine) **3aa**). **3aa**: IR (film, cm^{-1}) 1719, 1606, 1567, 1464, 1436, 1065, 723; ^1H NMR 1.10−1.77 (m, 12 H), 2.33−2.75 (m, 7 H), 6.70−7.36 (m, 2 H); ^{13}C NMR (THF-d_8) 23.6−40.2 (m), 121.4, 121.6, 122.0, 134.3, 138.1, 153.5, 157.4, 159.4, 160.7, 163.4. The copolymerizations of **1a** with *n*-octyl cyanide (**2b**) and *p*-tolunitrile (**2c**) were carried out similarly to the **1a**/**2a** copolymerization. Copolymers **3ab** and **3ac** were purified by toluene/methanol and toluene/hexane, respectively. **3ab**: IR (film, cm^{-1}) 1718, 1604, 1565, 1464, 722; ^1H NMR ($CDCl_3$) 0.70−1.00 (br s, 3 H), 1.00−1.91 (m, 24 H), 2.34−2.84 (m, 6 H), 6.63−7.34 (m, 2 H); ^{13}C NMR (THF-d_8) 14.5−39.0 (m), 120.2, 120.4, 125.9, 132.7, 137.3, 152.3, 159.5, 159.8, 162.2. In the ^{13}C NMR spectrum, small peaks were observed at δ 129.0 and 138.3. **3ac**: IR (film, cm^{-1}) 1602, 1560, 1515, 1458, 1423, 868, 720; ^1H NMR ($CDCl_3$) 1.00−2.00 (m, 12 H), 2.20−2.44 (br s, 3 H), 2.44−2.66 (m, 2 H), 2.66−2.90 (m, 2 H), 6.70−8.00 (m, 6 H); ^{13}C NMR ($CDCl_3$) 20.4−39.4 (m), 117.6 (br s), 120.8 (m), 126.7 (br s), 128.6 (m), 129.1 (m), 132.3 (m), 137.2 (br s), 137.6 (m), 152.2 (br s), 156.5 (br s), 157.8 (br s), 159.1 (m), 162.0 (br s). Elemental analysis of **3ac** obtained from the copolymerization with **2c**/**1a** = 10 in 5 mL of toluene was not satisfactory. Anal. Calcd for $(C_{20}H_{25}N)_n$: C, 85.97; H, 9.02; N, 5.01. Found: C, 84.28; H, 8.68; N, 4.39. The value of each element was lower than the calculated one. This result may be partly ascribed to contamination of **3ac** with the cobalt atom of the cobaltocene catalyst, which was confirmed by X-ray fluorescence analysis. Its removal by an EDTA complex formation as well as by acid and base treatments was unsuccessful.

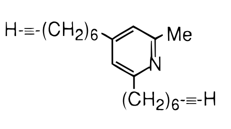
Reaction of 1,9-Decadiyne (1b) with Acetonitrile (2a). The reaction was carried out under nitrogen. In a 50 mL stainless steel autoclave, toluene (12.1 mL), a toluene solution (2.9 mL) of cobaltocene (0.50 mmol), **2a** (2.6 mL, 50 mmol), and **1b** (0.82 mL, 5.0 mmol) were placed in this order under magnetic stirring at ambient temperature. The reaction mixture was heated at 150 °C for 20 h under magnetic stirring. After the reaction mixture was cooled by ice water, it was concentrated under vacuum to give a residue (0.27 g) with M_n (GPC, THF) = 400 and M_w/M_n = 26. The residue was subjected to repeated PLC (ether/hexane = 1/2 (v/v)) to afford **5b** (0.096 g, 14%), **6ba** (0.027 g, 3.5%), and **7ba** (0.033 g, 4.3%).



5b



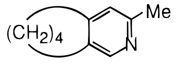
6ba



7ba

5b: IR (film, cm^{-1}) 2117, 1602, 1499, 1458, 1261, 1074, 801; ^1H NMR 1.20−1.68 (m, 24 H), 1.89−2.00 (m, 3 H), 2.08−2.24 (m, 6 H), 2.44−2.63 (m, 6 H), 6.74−7.07 (m, 3 H); ^{13}C NMR 18.7−31.9 (m), 68.2, 85.0, 126.07, 126.19, 129.32, 129.59, 138.0, 140.46, 140.62, 143.0; MS (EI) *m/z* (relative intensity) 57 (96), 69 (100), 81 (54), 97 (34), 111 (18), 129 (31), 149 (64), 167 (15), 185 (14), 256 (19), 402 (M^+, 5). **6ba**: IR (film, cm^{-1}) 2117, 1593, 1571, 1465, 1400, 626; ^1H NMR 1.24−1.76 (m, 16 H), 1.93−2.00 (m, 2 H), 2.11−2.25 (m, 4 H), 2.46 (s, 3 H), 2.56 (t, J = 7.6, 2 H), 2.67 (t, J = 7.9, 2 H), 6.89 (d, J = 7.9, 1 H), 7.30 (d, J = 7.9, 1 H); ^{13}C NMR 18.6, 22.3, 28.8, 28.95, 28.99, 29.25, 29.33, 30.17, 30.23, 32.6, 38.2, 68.21, 68.28, 85.0, 120.1, 133.0, 136.8, 156.0, 159.2; FAB MS *m/z* 310 (MH^+). **7ba**: IR (film, cm^{-1}) 2117, 1707, 1606, 1566, 1463, 1433, 630; ^1H NMR 1.23−1.75 (m, 16 H), 1.93−1.98 (m, 2 H), 2.10−2.23 (m, 4 H), 2.42 (s, 3 H), 2.52 (t, J = 7.8, 2 H), 2.66 (t, J = 7.9, 2 H), 6.77 (d, J = 5.3, 2 H); ^{13}C NMR 18.6, 24.5, 28.81, 28.88, 29.00, 29.06, 29.3, 30.2, 30.7, 35.4, 38.6, 68.25, 68.30, 84.96, 85.07, 120.0, 120.8, 152.3, 157.8, 161.9; FAB MS *m/z* 310 (MH^+).

Reaction of 1,7-Octadiyne (1c) with Acetonitrile (2a). The reaction was carried out under nitrogen. In a 50 mL stainless steel autoclave, toluene (4.4 mL), a toluene solution (0.58 mL) of cobaltocene (0.10 mmol), **2a** (0.52 mL, 10 mmol), and **1c** (0.130 mL, 1.00 mmol) were placed in this order under magnetic stirring at ambient temperature. The reaction mixture was heated at 150 °C for 20 h under magnetic stirring. After the reaction mixture was cooled by ice water, it was concentrated under vacuum to give a residue (0.090 g) with M_n (GPC, THF) = 300 and M_w/M_n = 9.8. The residue was subjected to PLC (ether/hexane = 4/1 (v/v)) to afford cooligomer **4ca** (0.052 g, 35%). **4ca**: IR (film, cm^{-1}) 1727, 1605, 1560, 1458, 1261, 1071, 804, 666; ^1H NMR 1.69 (m, 4 H), 2.32 (s, 3 H), 2.60 (m, 4 H), 6.74 (s, 1 H), 8.04 (s, 1 H); ^{13}C NMR 22.9, 23.2, 23.8, 26.2, 28.9, 123.3, 130.2, 146.5, 149.9, 155.0; MS (EI) *m/z* (relative intensity) 147 (M^+, 100), 146 (96), 132 (37), 119 (56), 91 (20), 77 (21), 51 (22), 39 (38). HRMS (EI) calcd for $C_{10}H_{13}N$: 147.1048. Found: 147.1005.



4ca

Results and Discussion

The cobaltocene catalyst was found to effect the cycloaddition copolymerization of 1,11-dodecadiyne (**1a**) with acetonitrile (**2a**) to afford poly(pyridine) **3aa** (eq 2). The copolymerization results are summarized in Table 1. Several copolymerization factors such as reaction temperature, a nitrile/diyne monomer feed ratio, solvent, solvent amount, and catalyst amount were examined. The reaction temperature of 150 °C was necessary for an effective copolymerization. Use of at least a 5-fold excess of **2a** to **1a** was necessary for the formation of a soluble poly(pyridine) under the reaction conditions using 1 mmol of **1a** and 5 mL of a toluene solvent, while the copolymerization with **2a**/**1a** = 3 produced partly a THF-insoluble copolymer. A side reaction in the cobalt-catalyzed pyridine formation from an alkyne and a nitrile is an alkyne trimerization to produce regioisomeric 1,3,5- and 1,2,4-trisubstituted benzene derivatives (Scheme 1).[8] The observed copolymer insolubility therefore may be due to copolymer branching and/or cross-linking originating from a pendent C≡C bond of the diyne trimerization unit in a copolymer. Thus the excess use of **2a** to **1a** may suppress the diyne trimerization to afford a soluble poly(pyridine). Decrease of a solvent amount, i.e., increase of a diyne concentration, also promoted the diyne trimerization and gave a poorly soluble or insoluble copolymer. THF could be used as a solvent instead of toluene to produce **3aa** in high yield. Poly(pyridine) **3aa** was a brown semisolid. It was soluble in toluene, THF, CH_2Cl_2, and $CHCl_3$ but was sparingly soluble in ether and ethyl acetate and insoluble in hexane and methanol.

In relation to the formation of the diyne trimerization unit in a copolymer, a cobaltocene-catalyzed homopolymerization of **1a** under conditions similar to those of the **1a**/**2a** copolymerization was carried out. The homopolymerization for 20 h gave an insoluble polymer while the one after the short reaction time of 5 h afforded a toluene-soluble, but methanol-insoluble, homopolymer. Its ^{13}C NMR C=C absorptions are observed

Table 1. Cobaltocene-Catalyzed Cycloaddition Copolymerization of 1,11-Dodecadiyne (1a) with Acetonitrile (2a) to Poly(pyridine) 3aa (Eq 2)[a]

2a/**1a**[b]	solvent, mL	**3aa** yield, %[c]	**3aa** M_n[d]	**3aa** M_w/M_n[d]	remarks
13	7	27	8 000	1.3	
3	5	55	18 800	1.6	A THF-insoluble copolymer was partly formed.
5	5	34	18 300	1.3	
7	5	36	17 000	1.3	
10	5	52	15 900	1.3	
10	5	52[e]	14 200	1.5	
10	5	22[f]	13 700	1.5	
10	5	18[g]	9 800	1.4	
10	5	91[h]	10 100	2.1	
13	5	42	17 100	1.3	
13	3.5	64	12 900	1.5	
10	3.5	85[h]	10 700	2.3	
7	2.5				A toluene-insoluble copolymer was formed.
10	2.5	76	18 700	1.7	A toluene-insoluble copolymer was partly formed.
13	2.5	90	26 900	1.3	The copolymer became THF-insoluble during purification.

[a] **1a** = 1 mmol; $Co(C_5H_5)_2$/**1a** = 0.1; solvent, toluene; temperature, 150 °C; time, 20 h. [b] A molar ratio. [c] Based on the quantitative formation of **3aa**. [d] Determined by GPC with polystyrene standards in THF. [e] $Co(C_5H_5)_2$/**1a** = 0.05. [f] $Co(C_5H_5)_2$/**1a** = 0.02. [g] Temperature, 130 °C. [h] Solvent, THF.

at δ 125.7-126.1 (m), 128.8−129.4 (m), 140.0−140.2 (m), and 142.6, which are assignable to benzene derivative components in the homopolymer (vide post), along with absorptions at δ 98.3−108.0 (m) and 160.7−161.3 (m). Its ^{1}H NMR spectrum exhibited absorptions at δ 4.40−6.00 along with absorptions at δ 0.96−1.72, 1.76−1.88, 2.05−2.23, 2.30−2.72, and 6.66−7.12, which are assignable to benzene derivative components in the homopolymer.

Poly(pyridine) **3aa** was identified by IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. **3aa** showed four IR ν(C=N) and (C=C) absorptions of a pyridine ring at 1600−1430 cm^{-1}. Its ^{1}H NMR spectrum exhibited pyridine C-3, C-4, and C-5 proton absorptions around δ 7.00 without pyridine C-2 and C-6 proton absorptions around δ 8.50. Thus the poly(pyridine) formation from **1a** and **2a** proceeded according to the regiochemistry of the monoyne/nitrile reaction shown in eq 1. The ^{13}C NMR spectrum of **3aa** obtained from the monomer feed ratios of **2a**/**1a** = 10 and 13 exhibited ten C=N and C=C absorptions corresponding to two regioisomeric pyridine rings.

Trialkyl-substituted benzenes **5b** were obtained as a model compound of the diyne trimerization unit in a copolymer (vide post). Their ^{13}C NMR C=C absorptions are shown in Figure 1 and are observed in the ^{13}C NMR spectrum of the homopolymer of **1a** (vide ante). **3aa** prepared from the copolymerization with **2a**/**1a** = 10 and 13 showed weak or negligible C=C absorptions of the diyne trimerization unit in the copolymer, respectively (Figure 1). This finding indicates that an efficient 1:1 cycloaddition copolymerization of **1a** with **2a** occurs to afford **3aa**. On the other hand, the copolymer obtained from **2a**/**1a** = 5 clearly exhibited the absorptions of the diyne trimerization unit (Figure 1). This result is experimental evidence showing the formation of the diyne trimerization unit in a copolymer. Thus the ^{13}C NMR C=C signals are an excellent criterion for the efficient 1:1 cycloaddition copolymerization of the diyne with the nitrile. For example, the ^{13}C NMR spectrum of **3aa** obtained in THF indicates that the 1:1 copolymerization takes place less effectively in THF than in toluene.

Comparison of the ^{13}C NMR pyridine C=N and C=C absorptions of **3aa** with those of substituted pyridines **6ba** and **7ba** (vide post) confirmed the formation of **3aa** further. The ^{13}C NMR pyridine C=N and C=C absorptions of **3aa** were a superposition of those of two regioisomeric pyridine derivatives **6ba** and **7ba** (Figure 1). This finding demonstrates that **3aa** has two kinds of repeat units containing two regioisomeric pyridine rings of **6ba** and **7ba**.

Table 2. Cobaltocene-Catalyzed Cycloaddition Copolymerization of 1,11-Dodecadiyne (1a) with Nitriles (2) to Poly(pyridine)s 3 (Eq 2)[a]

2	**2**/**1a**[b]	solvent, mL	**3**	**3** yield, %[c]	**3** M_n[d]	**3** M_w/M_n[d]
b	10	5	**ab**	32	8500	1.4
	30			44	3700	1.4
c	1	5	**ac**	70	9900	1.9
	2	5		72	9500	1.7
	5	5		65	9300	1.8
	10	5		54	8300	1.3
	10	3.5		58	11800	1.7

[a] **1a** = 1 mmol; $Co(C_5H_5)_2$/**1a** = 0.1; solvent, toluene; temperature, 150 °C; time, 20 h. [b] A molar ratio. [c] Based on the quantitative formation of **3**. [d] Determined by GPC with polystyrene standards in THF.

A structure of the nitrile influenced remarkably its copolymerizability with the diyne. *n*-Octyl cyanide (**2b**) showed a reduced copolymerizability in comparison with **2a**. Thus the copolymer obtained from a monomer feed of **2b**/**1a** = 10 exhibited distinct ^{13}C NMR C=C absorptions (δ 128.4−129.9, 139.6−140.6, and 142.1−143.1) of the diyne trimerization unit in comparison with those of **3aa** obtained from **2a**/**1a** = 10. The copolymerization in **2b** as a solvent (**2b**/**1a** = 30) effected an almost 1:1 copolymerization (Table 2): poly(pyridine) **3ab** obtained did not show the ^{13}C NMR C=C absorptions of the diyne trimerization unit although small unidentified peaks appeared at δ 129.0 and 138.3 (Figure 1). *p*-Tolunitrile (**2c**) showed a higher copolymerizability than **2a** and afforded poly(pyridine) **3ac** without the diyne trimerization unit in the copolymerization with **2c**/**1a** = 5 (Table 2 and Figure 1). Further, copolymer **3ac** prepared from **2c**/**1a** (1 mmol) = 2 in toluene (5 mL) or from **2c**/**1a** (1 mmol) = 10 in toluene (3.5 mL) exhibited negligible (Figure 1) or no absorptions of the diyne trimerization unit, respectively, and was soluble in toluene, THF, and $CHCl_3$. Thus a copolymerizability order of *p*-tolunitrile > acetonitrile > *n*-octyl cyanide was obtained from the ^{13}C NMR spectral data of **3aa**−**3ac**. The absence of the pyridine C-2 and C-6 proton absorptions around δ 8.50 in the ^{1}H NMR spectra of **3ab**

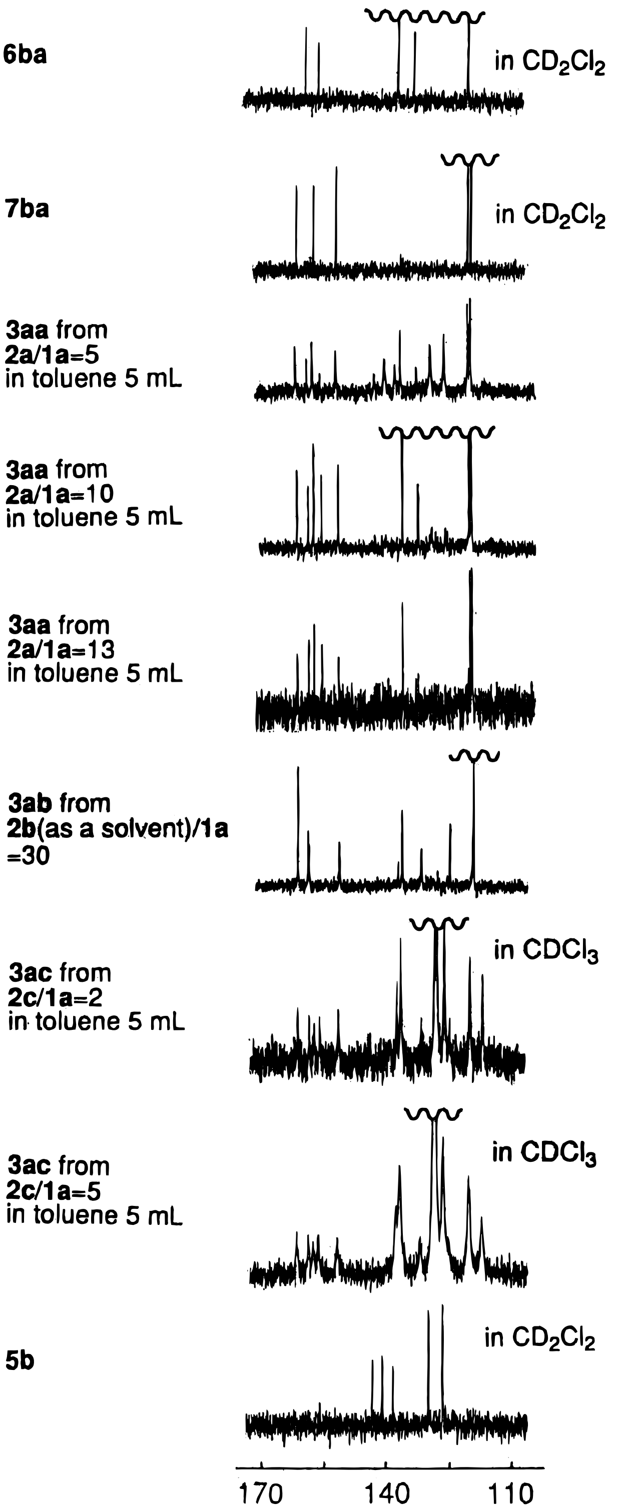


Figure 1. ^{13}C NMR C=C and C=N absorptions of poly(pyridine)s **3aa**−**3ac** and related compounds (THF-d_8, δ ppm).

or **3ac** indicates that the **1a**/**2b** or **1a**/**2c** copolymerization proceeded according to the regiochemistry similar to that of the **1a**/**2a** copolymerization.

The transition metal-catalyzed cycloaddition copolymerization of a diyne with a cycloaddition component is controlled by the relative rate of an intermolecular cyclization of the diyne including the cycloaddition component to its intramolecular one.[1a,2a] Aromatic diynes such as 1,4-diethynylbenzene[3d] and 1,4-bis(phenylethynyl)benzene[3c] and cyclic diynes such as 1,7-cyclotridecadiyne[2a,f] do not undergo easily the intramolecular cyclization, due to steric reasons, to afford the corresponding cycloaddition copolymers. On the other hand, for example, the cycloaddition copolymerization of an aliphatic diyne $EtC\equiv C(CH_2)_mC\equiv CEt$ with CO_2 depended upon the length (m) of a methylene chain: the diyne with $m = 6$ underwent the cycloaddition copolymerization smoothly,[2a] while the diyne with $m = 4$ underwent predominantly the intramolecular cycloaddition involving CO_2 to give a bicyclic 2-pyrone.[1a,9]

The length (m) of a methylene chain of the terminal diyne $HC\equiv C(CH_2)_mC\equiv CH$ was found to influence remarkably the diyne/nitrile copolymerization. The reaction of 1,7-octadiyne (**1c**) with **2a** under conditions similar to those of the **1a**/**2a** copolymerization produced only low-molecular weight products with M_n (GPC, THF) = 300 and $M_w/M_n = 9.8$ after evaporating the resulting reaction mixture under vacuum. From these products, cooligomer **4ca** was isolated by PLC as a major one in 35% yield. This type of bicyclic pyridine formation by a cobalt-catalyzed diyne/nitrile reaction is known: Vollhardt and Naiman[10] reported the bicyclic pyridine formation by a $CpCo(CO)_2$-catalyzed cycloaddition of $HC\equiv C(CH_2)_mC\equiv CH$ ($m = 3-5$) with various nitriles under extremely high dilution conditions, and Vitulli et al.[11] also found that bicyclic pyridines are formed by an arene-solvated cobalt atom-catalyzed reaction of **1c** and 1,8-nonadiyne with **2a**. Thus it may be concluded that the intramolecular cyclization of **1c** involving **2a** predominates to suppress its intermoleclar cyclization to poly(pyridine) **3ca**.

In contrast to our expectation, 1,9-decadiyne (**1b**) neither copolymerized with **2a** nor underwent effectively the intramolecular cyclization involving **2a** to form the cycloadduct such as **4ca**. Evaporating the resulting **1b**/**2a** reaction mixture under vacuum gave low-molecular weight products with a wide-molecular weight distribution (M_n(GPC, THF) = 400 and $M_w/M_n = 26$). From these products, diyne trimerization product **5b** and two regioisomeric pyridines **6ba** and **7ba** were isolated by PLC in 14, 3.5, and 4.3% yields, respectively. This result makes a sharp contrast with the previous finding that the diyne $EtC\equiv C(CH_2)_6C\equiv CEt$ copolymerized efficiently with CO_2 to a poly(2-pyrone) (vide ante).[2a] The fact that both diyne trimer **5b** and diyne/nitrile cooligomers **6ba** and **7ba** contain an unreacted C≡C bond is noteworthy and indicates a reduced cycloaddition reactivity of the C≡C bond of **1b** with **2a** and, accordingly, a low copolymerizability of **1b** with **2a**. Explanation of these observations, however, is not clear at the present time. The alkyl-substituted pyridines like **6ba** and **7ba** are also known to be formed along with diyne trimerization products[12] such as **5b** in the arene-solvated cobalt atom-catalyzed reaction of **1c** and 1,8-nonadiyne with **2a** (nitrile/diyne = 5),[11] which agrees with our experimental results. As for the copolymerization of an internal diyne, $MeC\equiv C(CH_2)_2O(CH_2)_4O(CH_2)_2C\equiv CMe$[2g] or 1,7-cyclotridecadiyne[2a,f] did not copolymerize with **2a**.

Thus it has been found in this study that the diyne with a long alkylene chain tethering two C≡C bonds undergoes the cobaltocene-catalyzed cycloaddition copolymerization with the nitrile to afford the poly(pyridine). Poly(vinylpyridine)s with pendent pyridine groups are well-known, but to our knowledge, there is no report on the catalytic synthesis of the poly(pyridine) having pyridine rings in a polymer main chain although π-conjugated poly(pyridine)s and related polymers containing pyridine rings[13a,b] were prepared by a dehalogenation polycondensation using a stoichiometric amount of a nickel(0) complex and a ladder polymer containing pyridine rings was synthesized by a cyclization reaction in the repeat unit of a linear precursor polymer.[13c] The diyne/nitrile copolymerizaion is a new entry in the transition metal-catalyzed diyne cycloaddition copolymerization[1] and has now expanded its scope. The present poly(pyridine) synthesis is the first example of an efficient cycloaddition copolymerization of a terminal diyne.

References and Notes

(1) (a) Tsuda, T. *Gazz. Chim. Ital.* **1995**, *125*, 101. (b) Tsuda, T. In *The Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL (in press).

(2) (a) Tsuda, T.; Maruta, K.; Kitaike, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1498. (b) Tsuda, T.; Maruta, K. *Macromolecules* **1992**, *25*, 6102. (c) Tsuda, T.; Ooi, O.; Maruta, K. *Macromolecules* **1993**, *26*, 4840. (d) Tsuda, T.; Kitaike, Y.; Ooi, O. *Macromolecules* **1993**, *26*, 4956. (e) Tsuda, T.; Hokazono, H. *Macromolecules* **1994**, *27*, 1289. (f) Tsuda, T.; Yasukawa, H.; Hokazono, H.; Kitaike, Y. *Macromolecules* **1995**, *28*, 1312. (g) Tsuda, T.; Yasukawa, H.; Komori, K. *Macromolecules* **1995**, *28*, 1356. For a spontaneous diyne/CO_2 copolymerization to form a poly(4-pyrone), see: (h) Tsuda, T.; Hokazono, H.; Toyota, K. *J. Chem. Soc., Chem. Commun.* **1995**, 2417.

(3) (a) Tsuda, T.; Hokazono, H. *Macromolecules* **1993**, *26*, 1796. (b) Tsuda, T.; Hokazono, H. *Macromolecules* **1993**, *26*, 5528. (c) Tsuda, T.; Tobisawa, A. *Macromolecules* **1994**, *27*, 5943. (d) Tsuda, T.; Tobisawa, A. *Macromolecules* **1995**, *28*, 1360.

(4) Tsuda, T.; Mizuno, H. The 69th Annual Meeting of The Chemical Society of Japan, Kyoto, 1995; 2H435.

(5) (a) Tsuda, T.; Tsugawa, F. *J. Chem. Soc., Chem. Commun.*, in press. (b) Tsuda, T.; Takeda, A. *J. Chem. Soc., Chem. Commun.*, in press.

(6) For example: (a) Nishihara, H.; Shimura, T.; Ohkubo, A.; Matsuda, N.; Aramaki, K. *Adv. Mater.* **1993**, *5*, 752. (b) Tomita, I.; Nishio, A.; Endo, T. *Macromolecules* **1994**, *27*, 7009. (c) Mao, S. S. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 7031.

(7) For example: (a) Wakatsuki, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2715. (b) Bönnemann, H.; Brijoux, W. *New J. Chem.* **1987**, *11*, 549. (c) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1278.

(8) Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26.

(9) (a) Tsuda, T.; Sumiya, R.; Saegusa, T. *Synth. Commun.* **1987**, *17*, 147. (b) Tsuda, T.; Morikawa, S.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 3140. (c) Tsuda, T.; Morikawa, S.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1990**, 9. (d) Tsuda, T.; Morikawa, S.; Hasegawa, N.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2978.

(10) Naiman, A.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 708.

(11) Vitulli, G.; Bertozzi, S.; Vignali, M.; Lazzaroni, R.; Salvadori, P. *J. Organomet. Chem.* **1987**, *326*, C33.

(12) Vitulli, G.; Bertozzi, S.; Lazzaroni, R.; Salvadori, P. *J. Mol. Catal.* **1988**, *45*, 155.

(13) (a) Saito, N.; Kanbara, T.; Nakamura, Y.; Yamamoto, T. *Macromolecules* **1994**, *27*, 756. (b) Yamamoto, T.; Maruyama, T.; Zhou, Z-h.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (c) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723.

MA951017I