Convenient Synthesis of Pyridine-Containing Polymers by the Cobalt(III)-Catalyzed Polymerization of Diynes with Nitriles

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Pyridine-containing polymers are useful materials as poly(Lewis base)s or as polymeric ligands that can support acids or transition-metal complexes. The electrical and optical properties of π-conjugated pyridine-containing polymers have been also paid much attention. These materials were prepared by the vinyl polymerization of vinylpyridine[1] or ethynylpyridine[2] and by the condensation polymerization of halogenated pyridines.[3] No example of the polymerization by means of the pyridine-forming reaction has been explored.

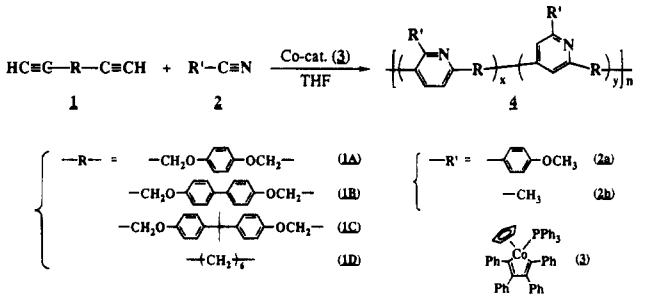
Recently, we have reported a novel synthetic method to obtain air-stable organocobalt polymers having cobaltacyclopentadiene moieties in the main chain.[4] By the polymer reactions of the organocobalt polymer, polymers containing various functional groups in the main chain were obtained.[5−8] Among them, the reaction with nitriles was found to produce pyridine-containing polymers in which the conversion of the organocobalt moieties into pyridine was dependent upon the substituents on both the organocobalt polymer and nitriles. In this case, molecular weights of the resulting pyridine-containing polymers increased in comparison with the starting organocobalt polymer as a result of the catalytic ring-forming reaction of nitrile with the end-acetylene moieties of the organocobalt polymer.[8]

Substituted pyridines are known to be produced by the ring-forming reaction of acetylenes with nitriles in the presence of transition-metal catalysts.[9] The reaction, however, accompanies the formation of a considerable amount of benzene derivatives as a result of cyclotrimerization of acetylenes.[9b] This might make it difficult to explore the polymerization based on this catalytic reaction for the production of linear polymers containing pyridine moieties in the main chain. Herein, we describe a direct synthesis of pyridine-containing polymers by the reaction of appropriate diynes with nitriles in the presence of a cobalt(III) catalyst by suppressing the benzene formation (Scheme 1).

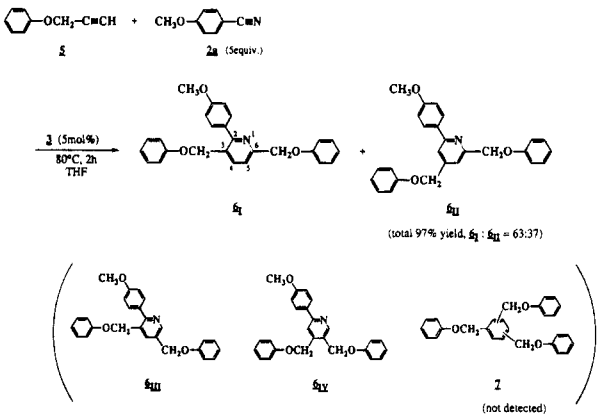
The reaction of 1,4-bis(propargyloxy)benzene (**1A**) with 4-methoxybenzonitrile (**2a**, 5 equiv relative to C≡C) was carried out at 80 °C in tetrahydrofuran (THF) in the presence of 5 mol % of **3** as a catalyst. The reaction was complete within 2 h to yield a polymer (**4Aa**) quantitatively.[10] **4Aa** is completely soluble in organic solvents such as chloroform, toluene, and THF. The number-average molecular weight (M_n) of the resulting polymer was estimated at 17 600 (GPC, based on polystyrene).

Under similar conditions, a model reaction was carried out by using phenyl propargyl ether (**5**) and **2a** in the presence of **3**. In this case, pyridine derivatives were obtained in 97% yield as a mixture of two isomers (i.e., $\mathbf{6_I}$, 3,6-bis(phenoxymethyl), and $\mathbf{6_{II}}$, 4,6-bis(phenoxymethyl) isomer, in the ratio of 63:37).[11] No other isomers ($\mathbf{6_{III}}$ and $\mathbf{6_{IV}}$)[12] or benzene derivatives (**7**), by the cyclotrimerization of **5**, were detected in the reaction products (Scheme 2).

Scheme 1



Scheme 2



The structure of **4Aa** was supported by ^{1}H-, and ^{13}C-NMR and IR analyses in comparison with those of model compounds ($\mathbf{6_I}$, $\mathbf{6_{II}}$, and **7**). In the ^{1}H-NMR spectrum of **4Aa** (Figure 1a), protons of the methoxy group, of the methylenes adjacent to pyridine rings, and of the aromatic rings were observed at 3.78, 4.66−5.34, and 6.31−8.08 ppm, respectively. The relative intensities of these peaks were in good agreement with the expected value based on the linear structure. In the ^{1}H-NMR spectrum of $\mathbf{6_I}$, protons of methylenes adjacent to the pyridine ring were observed at 5.08 (3-PhOCH$_2$−) and 5.26 ppm (6-PhOCH$_2$−), while the corresponding peaks in $\mathbf{6_{II}}$ were observed at 5.00 (4-PhOCH$_2$−) and 5.27 ppm (6-PhOCH$_2$−) (parts b and c of Figure 1, respectively). In the case of the polymer (**4Aa**), three peaks were observed at 4.90, 4.97, and 5.18 ppm. The former two peaks correspond to the methylenes at the 4- and 3-positions of pyridine rings. From the integral ratio of these two peaks, the isomeric units in the polymer were estimated as 3,6-(*para*):4,6-(*meta*) = ca. 60:40. This ratio is in good agreement with the result obtained in the model experiment. Small peaks at 2.49 and 4.57 ppm can be attributed to the end-propargyloxy moieties of the polymer.[13] By comparison of the intensities of these peaks with other ones, the molecular weight of the polymer could be estimated at 10 000 ± 2 000, assuming that **4Aa** contains acetylene moieties on both ends. In the ^{13}C-NMR spectrum of **7**,[14] carbons in the trisubstituted benzene rings appeared at 125.83, 127.51, 127.80, 129.07, 129.43, 134.75, 135.38, 137.28, and 137.83 ppm (Figure 2a). The corresponding peaks could not be detected in that of **4Aa** (Figure 2b), supporting little contribution of branched structures by means of benzene ring formation.

Polymerizations were carried out using various monomers (Table 1). Although internal diynes such as **1E**

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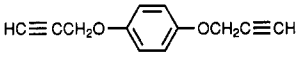
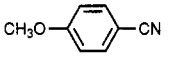
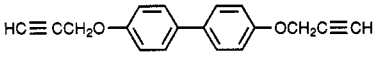
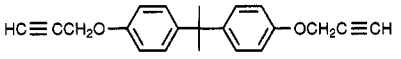
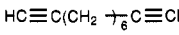
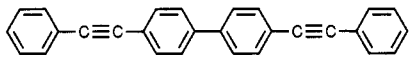
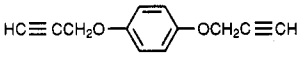
Table 1. Co(III)-Catalyzed Polymerization of Diynes with Nitriles[a]

run	diyne		nitrile		yield[b]	M_n (M_w/M_n)[c]
1		(**1A**)		(**2A**)	100	17600 (1.6)
2		(**1B**)		(**2a**)	94	6900 (1.3)
3		(**1C**)		(**2a**)	97	11700 (1.5)
4		(**1D**)		(**2a**)	95	5700 (1.1)
5		(**1E**)		(**2a**)	*d*	1100 (1.1)
6		(**1A**)	CH_3CN	(**2b**)	*e*	

[a] Polymerization was carried out in THF at 80 °C for 2 h in the presence of 3 (10 mol %) as a catalyst. [b] Isolated yield after fractionated by HPLC. [c] Estimated by GPC (THF, PSt, Std). [d] Trace yield. [e] Gelation took place.

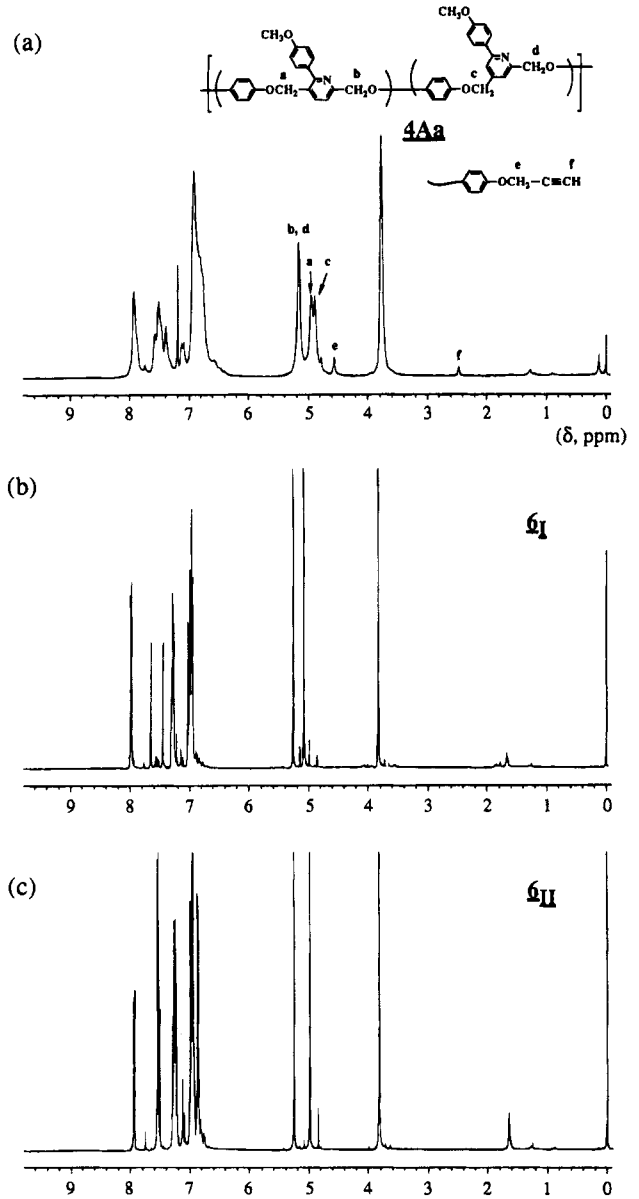


Figure 1. ^{1}H-NMR spectra (400 MHz, in $CDCl_3$) of **4Aa** (a), $\mathbf{6}_I$ (b), and $\mathbf{6}_{II}$ (c).

were less reactive for the catalytic polymerization with **2a**, polymers were obtained by using terminal diynes (**1A**–**D**) as monomers in almost quantitative yield. In the case of aliphatic nitriles such as **1b**, gelations were observed as a result of the considerable contribution of the cyclotrimerization of acetylene moieties.[15]

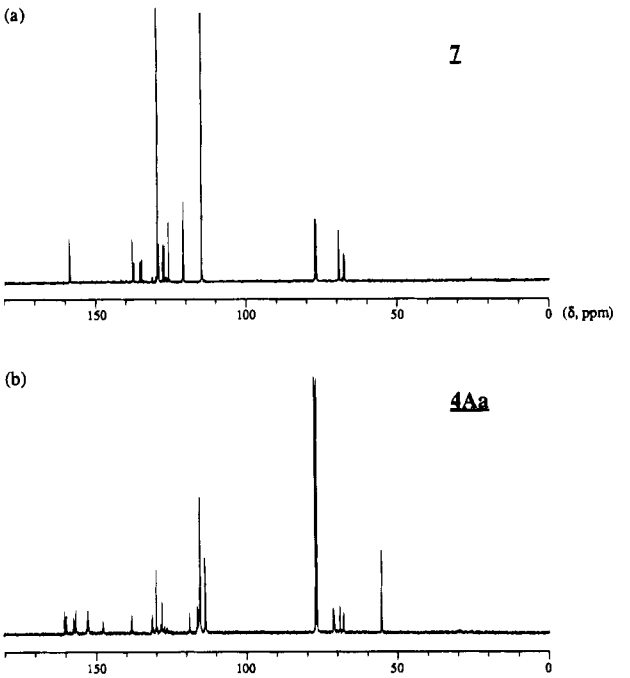


Figure 2. ^{13}C-NMR spectra (100 MHz, in $CDCl_3$) of **7** (a) and **4Aa** (b).

Although the present method was found to have some limitations on the structure of the monomers used, novel polymers containing pyridine moieties were obtained by the quite simple method. Further work on the polymerization and the application of the resulting polymers is now under investigation.

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References and Notes

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(10) The experimental procedure is shown as follows: A THF (10 mL) solution of **1A** (0.186 g, 1.00 mmol), **2a** (1.33g, 10.0 mmol), and **3** (0.074 g, 0.10 mmol) was heated at 80 °C for 2 h in a degassed sealed tube. After the reaction, **4Aa** was isolated by HPLC (Japan Analytical Industry LC 908 instrument, JAIGEL-1H, THF as eluent) in 100% (0.318 g). IR (KBr disk): 3044 (w), 3003 (w), 2930 (w), 2836 (w), 1609 (s), 1564 (m), 1505 (vs), 1456 (m), 1427 (m), 1402 (w), 1381 (w), 1296 (m), 1250 (s), 1202 (vs), 1175 (s), 1109 (m), 1030 (s), 829 (s), 752 (s), 702 (w) cm^{-1}. The polymer can be isolated by the precipitation with *n*-hexane. However, HPLC was used in this study to avoid the contamination of the lower molecular weight impurities (e.g., the cobalt catalyst) for the spectroscopic studies.
(11) The reaction of **5** (0.264 g, 2.00 mmol), **2a** (1.33 g, 10.0 mmol), and **3** (0.074 g, 0.10 mmol) was carried out in THF at 80 °C to yield the mixture of $\mathbf{6_I}$ and $\mathbf{6_{II}}$ in 97% yield (0.384 g, 0.97 mmol). Isomers ($\mathbf{6_I}$ and $\mathbf{6_{II}}$) were successfully separated by HPLC. $\mathbf{6_I}$. ^{13}C-NMR (100 MHz, in $CDCl_3$): δ 55.27, 68.51, 70.27, 114.09, 114.9, 116.39, 116.69, 121.06, 121.34, 128.32, 129.50, 131.63, 147.70, 156.96, 157.50, 158.24, 158.44, 160.56. IR (NaCl): 3063 (w), 3040 (w), 2934 (w), 2837 (w), 1599 (s), 1564 (m), 1516 (m), 1495 (s), 1456 (w), 1429 (m), 1385 (m), 1294 (m), 1248 (vs), 1177 (s), 1034 (s), 835 (s), 754 (s), 691 (m) cm^{-1}. $\mathbf{6_{II}}$. ^{13}C-NMR (100 MHz, in $CDCl_3$): δ 55.34, 67.23, 70.53, 113.93, 115.13, 119.39, 121.24, 129.52, 129.91, 130.36, 131.72, 138.38, 156.83, 157.58, 158.73, 160.00. IR (NaCl): 3061 (w), 3040 (w), 2934 (w), 2837 (w), 1597 (s), 1514 (m), 1495 (s), 1460 (m), 1402 (m), 1302 (m), 1248 (vs), 1175 (s), 1032 (s), 839 (m), 754 (s), 691 (m) cm^{-1}.
(12) The regioselective formation of the pyridine derivatives has been already reported in ref 9c.
(13) A small shoulder peak at 4.80 ppm might be attributed to protons in the cyclopentadienyl group on the cobalt moieties. That is, some catalyst remained in the main chain of the polymer as an intermediate for the pyridine rings.
(14) In the absence of **2a**, **7** was obtained as a mixture of regioisomers in lower yield (56% based on **5**, 0.148 g, 0.37 mmol) by the reaction of **5** (0.264 g, 2.00 mmol) with **3** (0.074 g, 0.10 mmol) at 80 °C for 24 h. **7**. ^{1}H-NMR (400 MHz, in $CDCl_3$): δ 5.00, 5.10 ($PhOCH_2$–, 6H), 6.64–7.82 (C_6H_3, C_6H_5, 18H). IR (NaCl): 3061 (w), 3038 (w), 2926 (w), 2872 (w), 1599 (s), 1494 (s), 1458 (w), 1377 (m), 1302 (m), 1238 (vs), 1173 (m), 1078 (w), 1032 (m), 1012 (m), 993 (w), 883 (w), 818 (w), 754 (s), 691 (s) cm^{-1}.
(15) By the model reaction of **2b** with **5** under the same conditions as ref 11, derivatives of benzene were obtained in 8% yield accompanied by the formation of substituted pyridines (66%). This result may support the cross-linking reaction by means of the cyclotrimerization of acetylene moieties.

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