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Rearrangement of the main chain of the organocobalt polymers

2. Synthesis of novel poly(pyridine-diyl-*alt*-biphenyl-4,4′-diyl) by the reaction with nitriles (1)

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Summary

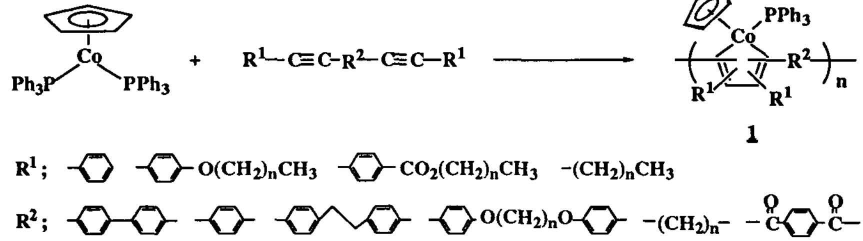
The polymers **3** having pyridine moieties in the main chain were synthesized by the reaction of the organocobalt polymers **1** having cobaltacyclopentadiene moieties in the main chain with various nitriles **2**. When brown colored **1** and excess **2** were heated in tetrahydrofuran at 80°C for 24 h and then at 150°C for 12 h in a sealed tube, the polymers **3** were obtained by the precipitation with methanol in good yields. From the spectroscopic measurements, the resulting polymers **3** were found to contain 35-90% of the pyridine moieties depending on the structures of **1**.

Introduction

Poly(vinylpyridine)s (2) and poly(ethynylpyridine)s (3) bearing pyridine moieties in the side chain have been synthesized by the chain polymerizations of vinyl monomers several decades ago, and recently poly(pyridine)s (4) having pyridine moieties in the main chain have been prepaered by the polycondensations of dihalopyridine derivatives with expectations as polymeric ligand, electron conducting polymers, photo active materials, and so on. We (5) and Tsuda et al. (6) have independently reported the novel synthetic methodology of poly(pyridine)s by the pyridine formation reaction of diynes with nitriles using organocobalt complexes as a catalyst. Nevertheless, the catalytic polymerization can be carried out only in cases of the terminal diynes and aromatic nitriles because of the insufficient activity towards the ring formation reaction or of the insufficient selectivity of the pyridine ring formation. In fact, the polymerization of internal diynes does not proceed smoothly and the gelation by the cyclotrimerization of the acetylene moieties takes place in the case of aliphatic nitriles. These limitations based on monomer structures may make it difficult to apply the catalytic polymerization.

Cobaltacyclopentadiene derivatives are known to be converted to pyridine, benzene, 2-pyridone, thiophene derivatives, and other heterocycles by the reactions with nitriles, acetylenes, isocyanates, sulfur, and other molecules having π- or lone-pair electrons, respectively (7). As the cobaltacyclopentadienes can be regarded as precursors for various cyclic organic systems, polymers having the corresponding metallacycle units in the main chain are expected to serve as novel reactive polymers. From the point of view, we have re-

Scheme 1



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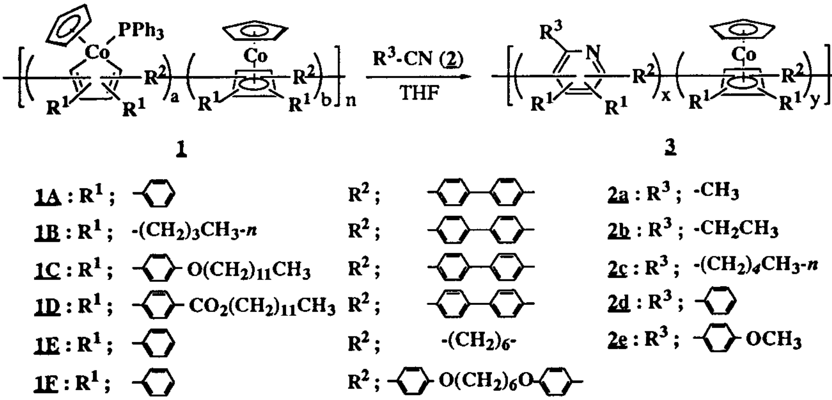
cently reported a novel synthetic methodology to obtain air-stable organocobalt polymers having cobaltacyclopentadiene moieties in the main chain by the oxidative coupling reaction (i.e, the oxidative ring formation reaction) of diynes with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt (8a). The organocobalt polymers bearing various substituents can be likewise obtained from the diynes bearing several kinds of substituents between the acetylene moieties and/or as lateral groups (Scheme 1) (8b). Although some of the organocobalt polymers were found to be contaminated with the (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt (9) units as a result of the thermal rearrangement of the cobaltacyclopentadiene moieties during the polymerization, the structures of the organocobalt polymers could be easily designed by the diyne structures. As expected, the obtained organocobalt polymers revealed unique reactivities. For instance, the thermally stable polymers containing (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt repeating units were obtained by the thermal rearrangement of the main chain (10). 2-Pyridone-containing polymers were successfully obtained by the reaction with isocyanates (1).

As to explore the reactivity of the organocobalt polymers, the reaction of the organocobalt polymers **1** with nitriles **2** was carried out to prepare polymers **3** containing the pyridine moieties in the polymer backbone (Scheme 2).

Scheme 2



Experimental

Materials and Instruments. The organocobalt polymers **1** (8b) and a cobaltacyclopentadiene derivative **4** (11) were obtained according to the literature procedure. Tetrahydrofuran (THF) was dried over sodium and distilled under nitrogen. Acetonitrile **2a**, propionitrile **2b**, hexanenitrile **2c**, and benzonitrile **2d** were distilled and stored under nitrogen. Other reagents were used as received.

The purification of products obtained by model reactions was carried out on a JAI LC-908 recycling preperative high-performance liquid chromatography (HPLC) using chloroform ($CHCl_3$) as eluent (JAIGEL- 1H and JAIGEL- 2H). ^1H-NMR spectra were recorded on a JNM-EX400 spectrometer or on a JEOL-EX90 spectrometer (400 or 90 MHz, respectively) in $CDCl_3$ (tetramethylsilane as internal standard). ^{13}C-NMR spectra were recorded on a JNM-EX400 spectrometer (100 MHz) in $CDCl_3$ (tetramethylsilane as internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. Gel permeation chromatographic (GPC) analyses were performed on a Tosoh HLC-8020 (TSK gel G2500HXL, G3000HXL, G4000HXL and G5000HXL, THF as eluent) on the basis of polystyrene standards. UV-vis spectra were recorded on a Shimadzu UV-2100 spectrometer in $CHCl_3$. Thermogravimetric analyses (TGA) were carried out on a Seiko TG/DTA 220 instrument at a heating rate of 10 °C/min under nitrogen.

Synthesis of Pyridine Derivatives 5a-5c (Typical Procedure for the Synthesis of 5a) (7b). To a test tube were added **4** (0.371g, 0.500mmol), **2a** (0.41g, 10mmol), and a 10ml of THF under nitrogen. The mixture was kept stirring at 80°C for 24 h and was further heated at 150°C for 12 h. After the filteration, the products were seperated by the HPLC method.

5a: yield 82% (0.162g, 0.410mmol); white solid; mp 166-168°C; ^{1}H-NMR (δ, ppm) 2.48(-CH$_3$, s, 3H), 6.6-7.4(-C$_6$H$_5$, 20H); ^{13}C-NMR (δ, ppm) 24.18, 125.99, 126.51, 126.80, 127.11, 127.22, 127.51, 127.73, 129.83, 129.94, 130.13, 131.26, 132.52, 134.63, 138.03, 138.30, 138.70, 140.84, 149.18, 155.22, 156.06; IR (KBr, cm^{-1}) 3059, 3029, 2922, 1601, 1578, 1537, 1491, 1441, 1399, 912, 799. (η^5-Cyclopentadienyl)(η^4-1,2,3,4-tetraphenylcyclobutadiene)cobalt **6** was obtained as a yellow solid in 14% yield (0.033g, 0.070mmol). mp 269°C (lit (9): mp 262-264°C).

5b (from **4** (0.371g, 0.500mmol) and **2b** (0.55g, 10mmol)): yield 85% (0.175g, 0.425mmol); white solid; mp 184-185°C; ^{1}H-NMR (δ, ppm) 1.25(-CH$_3$, t, 3H, *J*=7.5Hz), 2.77(-CH$_2$-, q, 2H, *J*=7.5Hz), 6.6-7.4(-C$_6$H$_5$, 20H); ^{13}C-NMR (δ, ppm) 13.96, 29.45, 125.94, 125.98, 126.49, 126.78, 127.11, 127.24, 127.48, 127.59, 129.98, 130.16, 131.30, 132.27, 134.13, 138.21, 138.47, 141.03, 149.35, 156.06, 159.77; IR (KBr, cm^{-1}) 3057, 3027, 2966, 2932, 1601, 1578, 1537, 1491, 1443, 1399, 912, 760. **6**: yield 10% (0.023g, 0.050mmol).

5c (from **4** (0.371g, 0.500mmol) and **2c** (0.55g, 10mmol)): yield 86% (0.190g, 0.430mmol); white solid; mp 106-109°C; ^{1}H-NMR (δ, ppm) 0.81(-CH$_3$, t, 3H, *J*=5.6Hz), 1.10-1.30(-CH$_2$-, br, 4H), 1.70-1.90(-CH$_2$-, br, 2H), 2.75(-CH$_2$-, t, 2H, *J*=7.8Hz), 6.6-7.4(-C$_6$H$_5$, 20H); ^{13}C-NMR (δ, ppm) 13.94, 22.34, 29.32, 31.76, 36.13, 125.94, 126.47, 126.78, 127.11, 127.24, 127.49, 127.53, 130.00, 130.18, 130.26, 131.32, 132.21, 134.37, 138.28, 138.48, 141.05, 149.31, 156.00, 158.99; IR (KBr, cm^{-1}) 3056, 3029, 2861, 1599, 1578, 1537, 1491, 1443, 1279. **6**: yield 14% (0.036g, 0.070mmol).

Synthesis of Pyridine-Containing Polymers 3Aa-3Ae and 3Ba-3Fa (Typical Procedure for the Synthesis of 3Aa). To a test tube were added **1A** ($\overline{M}_n$ = 3800, M_w / M_n = 1.5, 0.148g, 0.200mmol), **2a** (0.41g, 10mmol), and a 10ml of THF under nitrogen. The reaction was carried out at 80°C for 24 h and then at 150°C for 12 h. After filteration and concentration *in vacuo*, the resulting solution (ca. 2ml) was precipitated with *n*-hexane. The resulting yellowish green powder was collected by filteration, washed with *n*-hexane, and then dried *in vacuo* to give 0.066g of **3Aa** (80% yield). Polymers **3Ab-3Ae** and **3Ba-3Fa** were prepared under the similar conditions.

3Aa: yield 80%; yellowish green powder; ^{1}H-NMR (δ, ppm) 2.50(-CH$_3$, br, 3Hx0.80), 4.66(-C$_5$H$_5$, br, 5Hx0.20), 6.6-7.8(-C$_6$H$_4$-, -C$_6$H$_5$, 18H); ^{13}C-NMR (δ, ppm) 24.33, 83.24, 113.76, 126.18, 127.00, 127.44, 127.75, 127.95, 128.48, 128.98, 129.94, 130.24, 131.35, 131.90, 136.38, 136.86, 137.86, 149.15, 155.47; IR (KBr, cm^{-1}) 3029, 2922, 2853, 1676, 1601, 1577, 1537, 1497, 1443, 1395, 909, 826.

3Ab (from **1A** (0.148g, 0.200mmol) and **2b** (0.55g, 10mmol)): yield 87% (0.073g); yellowish green powder; ^{1}H-NMR (δ, ppm) 1.26(-CH$_3$, br, 3Hx0.80), 2.69(-CH$_2$-, br, 2Hx0.80), 4.64(-C$_5$H$_5$, br, 5Hx0.20), 6.6-7.8(-C$_6$H$_4$-, -C$_6$H$_5$, 18H); ^{13}C-NMR (δ, ppm) 14.01, 29.12, 83.14, 113.74, 126.19, 127.44, 127.73, 127.90, 128.47, 129.93, 130.20, 131.38, 131.90, 136.35, 136.80, 137.86, 140.56, 149.30, 155.45, 158.90; IR (KBr, cm^{-1}) 3029, 2930, 1674, 1599, 1578, 1535, 1495, 1443, 1393, 909, 816, 733.

3Ac (from **1A** (0.148g, 0.200mmol) and **2c** (0.97g, 10mmol)): yield 81% (0.074g); yellowish green powder; ^{1}H-NMR (δ, ppm) 0.7-1.8(-CH$_2$-, -CH$_3$, br, 9Hx0.75), 2.72(-CH$_2$-, br, 2Hx0.75), 4.64(-C$_5$H$_5$, br, 5Hx0.25), 6.6-7.7(-C$_6$H$_4$-, -C$_6$H$_5$, 18H); IR (KBr, cm^{-1}) 3030, 2926, 2857, 1672, 1599, 1576, 1539, 1499, 1443, 1397, 912, 824, 754.

3Ad (from **1A** (0.148g, 0.200mmol) and **2d** (1.03g, 10mmol)): yield 79% (0.073g); yellowish green powder; ^{1}H-NMR (δ, ppm) 4.64(-C$_5$H$_5$, br, 5Hx0.15), 6.6-7.7(-C$_6$H$_4$-, -C$_6$H$_5$, 18H+5Hx0.85); IR (KBr, cm^{-1}) 3029, 2953, 1674, 1601, 1576, 1497, 1443, 1391, 816, 756.

3Ae (from **1A** (0.148g, 0.200mmol) and **2e** (1.33g, 10mmol)): yield 95% (0.092g); yellowish green powder; ^{1}H-NMR (δ, ppm) 3.75(-OCH$_3$, br, 3Hx0.75), 4.65(-C$_5$H$_5$, br, 5Hx0.25), 6.7-7.5(-OC$_6$H$_4$-, -C$_6$H$_4$-, -C$_6$H$_5$, 18H+4Hx0.75); ^{13}C-NMR (δ, ppm) 55.16, 55.56, 68.00, 83.27, 104.02, 113.08, 114.76, 119.24, 125.53, 125.77, 126.13, 127.58, 127.98, 128.46, 128.58, 129.13, 130.25, 131.33, 131.58, 131.95, 132.08, 132.17, 133.83, 134.01, 162.86; IR (KBr, cm^{-1}) 3029, 2955, 1674, 1605, 1576, 1499, 1443, 1391, 831, 754.

3Ba (from **1B** (0.140g, 0.200mmol) and **2a** (0.41g, 10mmol)): yield 80% (0.061g); yellowish green powder; ^{1}H-NMR (δ, ppm) 0.4-1.7($-CH_2-$, $-CH_3$, 14H), 2.1-2.8($-CH_2-$, $-CH_3$, 4H+3Hx0.70), 4.4-4.7($-C_5H_5$, br, 5Hx(0.30), 7.2-7.9($-C_6H_4-$, 8H); ^{13}C-NMR (δ, ppm) 13.34, 13.67, 32.49, 81.12, 125.79, 126.21, 126.52, 127.73, 128.99, 129.51; IR (KBr, cm^{-1}) 3029, 2957, 2870, 1636, 1557, 1499, 1458, 1408, 804.

3Ca (from **1C** (0.222g, 0.200mmol) and **2a** (0.41g, 10mmol)): yield 80% (0.138g); yellow powder; ^{1}H-NMR (δ, ppm) 0.8-2.5($-CH_2-$, $-CH_3$, 46H+3Hx0.35), 3.7-4.1($-OCH_2-$, 4H), 4.64($-C_5H_5$, br, 5Hx0.65), 6.4-7.7($-C_6H_4-$, $-OC_6H_4-$, 16H); ^{13}C-NMR (δ, ppm) 13.80, 22.30, 25.79, 29.29, 31.57, 67.62, 82.69, 113.67, 125.65, 128.54, 129.94, 130.13, 157.38; IR (KBr, cm^{-1}) 3032, 2924, 2853, 2361, 2340, 1609, 1572, 1512, 1385, 804, 721.

3Da (**1D** (0.233g, 0.200mmol) and **2a** (0.41g, 10mmol) were reacted at 80°C for 3days and then at 150°C for 12h): yield 80% (0.14g); yellowish green powder; ^{1}H-NMR (δ, ppm) 0.8-2.6($-CH_2-$, $-CH_3$, 46H+3Hx0.70), 4.1-4.4($-CO_2CH_2-$, 4H), 4.66($-C_5H_5$, br, 5Hx0.30), 6.7-8.0($-C_6H_4-$, 16H); IR (KBr, cm^{-1}) 3032, 2924, 2853, 1605, 1578, 1499, 1389, 812, 770.

3Ea (from **1E** (0.131g, 0.200mmol) and **2a** (0.41g, 10mmol)): yield 84% (0.057g); orange green powder; ^{1}H-NMR (δ, ppm) 0.5-1.8($-CH_2-$, 8.0H), 2.0-2.6($-CH_2-$, $-CH_3$, 4H+3Hx0.90), 4.52($-C_5H_5$, br, 5Hx0.10), 7.0-7.5($-C_6H_5$, 10H); IR (KBr, cm^{-1}) 3057, 3027, 2928, 2857, 1601, 1575, 1545, 1493, 1443, 1408, 910, 702.

3Fa (from **1F** (0.171g, 0.200mmol) and **2a** (0.41g, 10mmol)): yield 85% (0.097g); orange green powder; ^{1}H-NMR (δ, ppm) 1.1-1.9($-CH_2-$, $-CH_3$, 8H+3Hx0.40), 3.94($-OCH_2-$, br, 4H), 4.59($-C_5H_5$, br, 5Hx0.60), 6.4-8.0($-OC_6H_4-$, $-C_6H_5$, 18H); IR (KBr, cm^{-1}) 3057, 2934, 2863, 1605, 1572, 1512, 1443, 1391, 806.

3Ee (from **1E** (0.131g, 0.200mmol) and **2e** (1.33g, 10mmol)): yield 76% (0.064g); orange green powder; ^{1}H-NMR (δ, ppm) 0.6-1.8($-CH_2-$, 8H), 2.0-2.6($-CH_2-$, 4H), 3.6-3.8($-OCH_3$, 3Hx0.90), 4.52($-C_5H_5$ br, 5Hx0.10), 6.6-7.6($-OC_6H_4-$, $-C_6H_5$, 10H+4Hx0.90); IR (KBr, cm^{-1}) 3057, 2928, 2855, 1608, 1578, 1510, 1458, 1400, 910, 702.

Results and discussion

Although the reaction of the cobaltacyclopentadienes with nitriles have been reported to give the substituted pyridines in 20-72% yields (7b), the information on the side products and the optimum yields in this reaction is not clear. By applying this reaction to the polymer **1**, all of the structures originated from the side reaction may be incorporated and the yields of the conversion reaction will influence on the produced polymer structures. To confirm the all of the detectable side products and to find out the better conditions for the conversion of the cobaltacyclopentadienes into the pyridine derivatives, the model reaction was carried out under several conditions by using (η^5-cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene **4** with **2** (Table 1). By the reaction of **4** with propionitrile **2b** (20equiv. relative to **4**) in tetrahydrofuran (THF) at 80°C for 24 h in a sealed tube, a derivative of pyridine **5** was isolated in 73% yield (by HPLC). Besides, (η^5-cyclopentadienyl)(η^4-cyclobutadine)cobalt (CpCbCo) **6** (9) was isolated as a minor fraction in 9% and the starting **4** was also recovered in 6% (Run 1). Although the starting **4** was converted completely by the reaction at 150°C, the yield of the objective **5** decreased to 49% (Run 2). Under the two step heating conditions (i.e., at 80°C for 24 h and then at 150°C for 12 h), the isolated yield of **5** increased up to 85% where **4** was converted completely without obvious increase of the formation of **6** (Run 3). The reaction of **4** with **2a** or with **2c** was also carried out under the same conditions to yield the corresponding pyridine derivatives over 80% yield (Table 1, Runs 4 and 5).

The reaction of an organocobalt polymer **1A** with **2b** (50equiv.) was carried out under the same conditions (i.e., at 80°C for 24 h and then at 150°C for 12 h). The reaction proceeded in a homogeneous system to give a yellowish green powdery polymer (i.e. poly(pyridine-diyl-*alt*-biphenyl-4,4'-diyl), **3Ab**) by the precipitation with methanol in 87% yield.

Scheme 3

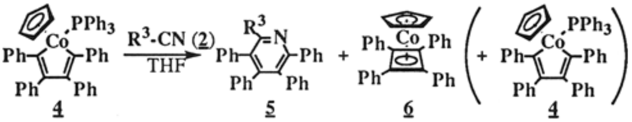


Table 1. Reactions of 4 with 2[a)]

Run	Nitrile	Temp.(°C) / Time (h)	Yield(%)[b)]		
			5	6	4
1	2b	80 / 24	73 (5b)	9	6
2	2b	150 / 12	49 (5b)	51	0
3	2b	80 /24 ⟶ 150 /12[c)]	85 (5b)	10	0
4	2a	80 / 24 ⟶ 150 /12[c)]	82 (5a)	14	0
5	2c	80 / 24 ⟶ 150 /12[c)]	85 (5c)	15	0

a) The reaction of (η^5-cyclopentadienyl)(triphenylphosphine)cobalta(2,3,4,5-tetraphenyl)-cyclopentadiene 4 with nitriles 2 (20 equiv.) was carried out in THF. b) Isolated yield by HPLC. c) The reaction was carried out at 80°C for 24 h and then at 150 °C for 12 h.

The structure of **3Ab** was confirmed by IR and ^{1}H-NMR spectra in comparison with those of the model compound **5b**. In the IR spectra of **3Ab** and **5b**, the peaks atrributable to the C=C and C=N stretching in the pyridine moieties were observed at 1600, 1575, and 1500 cm^{-1}. In the ^{1}H-NMR spectrum of **3Ab** (Figure 1b), peaks attributable to the ethyl group (1.26 and 2.69 ppm) and those of aromatic protons (6.6-7.8 ppm) were observed, similar to the case of **5b** (Figure 1a). A peak for the cyclopentadienyl group (Cp) was also observed at 4.64 ppm in the ^{1}H-NMR spectrum of **3Ab**, which is corresponded to the Cp in the CpCbCo moieties judging from the chemical shift of the corresponding peaks of the model compound **6** (4.62 ppm) (12). From the integral ratio of the Cp protons and those of the methylene adjacent to the pyridine rings, **3Ab** was found to be consisted of 80% of the pyridine and 20% of the CpCbCo moieties.

The present polymer reaction may be considered to proceed by the same mechanism proposed for the reaction of cobaltacyclopentadienes with nitries (7b), as shown in Scheme 5. That is, the triphenylphosphine ligated on the cobalt atom dissociates at the initial stage to produce the coordinatively unsaturated species, to which the nitriles may displace as a ligand. The re-

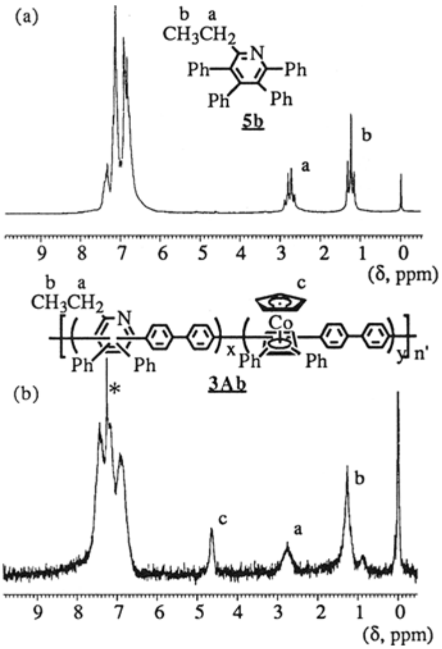
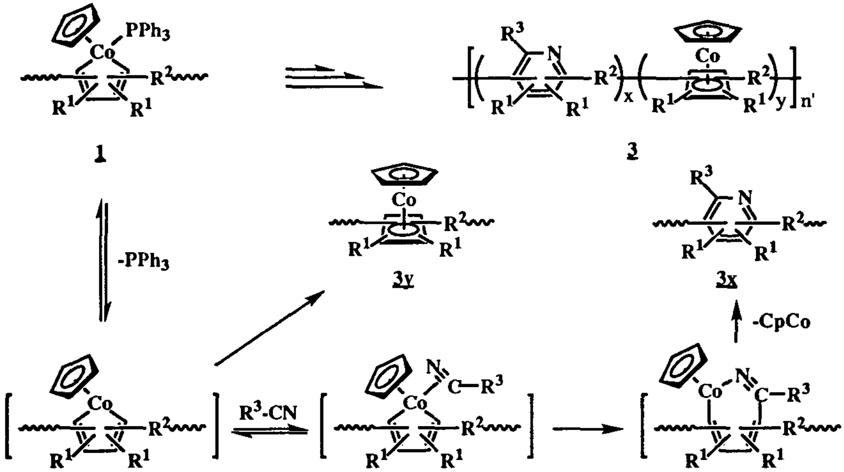


Figure 1. ^{1}H-NMR spectra of the model compound **5b** (a) and the polymer **3Ab** (b). * : $CDCl_3$

Scheme 4



sulting complex undertakes the insertion of C≡N moieties toward the carbon-cobalt bond followed by the reductive elimination of (cyclopentadienyl)cobalt (CpCo) species to produce pyridine moieties 3x. The coordinatively unsaturated cobaltacyclopentadiene may undergo a competitive unimolecular rearrangement to form CpCbCo moieties 3y which may be controlled by the reaction conditions.

From the above mentioned mechainsm, the ratio of pyridine and CpCbCo moieties in the produced polymer 3 is also proposed to be influenced by the coordination ability of the nitrile. Thus, the reactions of 1A with excess amount of various nitriles (2a-2e) were carried out under the similar conditions to yield poly(pyridine-diyl-alt-biphenyl-4,4'-diyl)s 3Aa-e containing more than 70% of the objective pyridine moieties (Table 2). However, the characters (i.e., both electronic and sterric effects) of nitriles did not influence significantly on the structures of the obtained polymers.

Obviously, the number average molecular weights (M_n) of the produced polymers 3A (M_n = 9000-12000) increased compared with the starting organocobalt polymer 1A (M_n= 3800). In the case of the thermal rearrangement of 1A (Run 6) or by using 1 A higher molecular weight (Run 7), the molecular weight did not increase significantly. Thus, the increase of the molecular weights in Runs 1-5 is not due to the GPC peculiarity. From our previous study, it was confirmed that the organocobalt polymers have the unreacted acetylene moieties as the end groups (8a, 10b). Judging from the fact that the cobaltacyclopentadiene

Table 2. Reactions of 1A with various nitriles 2[a]

Run	Nitrile	Product	Yield (%)[b]	x	: y[c]	M_n (M_w / M_n)[d]
1	2a	3Aa	80	80	20	10700 (3.5)
2	2b	3Ab	87	80	20	8900 (2.7)
3	2c	3Ac	81	75	25	9600 (2.0)
4	2d	3Ad	79	85	15	12100 (4.0)
5	2e	3Ae	95	75	25	10900 (2.0)
6	none[e]	-[f]	95	0	100	3900 (2.1)
7[g]	2a	3Aa	76	70	30	9300 (1.3)

a) The reaction of organocabalt polymer 1A (M_n=3800) was carried out in THF at 80°C for 24 h and then at 150°C for 12 h. b) Isolated yield by the precipitation with hexane. c) Determined by ^{1}H-NMR. d) Estimated by GPC (THF, PSt standard). e) Heating without nitrile. f) Thermally rearranged cyclobutadienecobalt polymer was obtained. g) 1A (M_n=11700) was used.

Table 3. Reaction of **1** with acetonitrile (**2a**)[a]

Run	**1**			**3**			
	Reactant	Ratio of a[b]	*Mn* (*Mw* / *Mn*)[c]	Product	Yield (%)[d]	Ratio of x[b]	*Mn* (*Mw* / *Mn*)[c]
1	**1A**	84	3800 (1.5)	**3Aa**	80	80	10700 (3.5)
2	**1B**	79	10700 (1.6)	**3Ba**	80	70	12400 (1.7)
3	**1C**	82	14600 (1.5)	**3Ca**	85	35	27400 (2.6)
4[e]	**1D**	82	9100 (1.3)	**3Da**	81	70	19600 (2.6)
5	**1E**	100	2500 (2.3)	**3Ea**	84	90	1600 (2.6)
6[f]	**1E**	100	2500 (2.3)	**3Ee**	76	90	7700 (1.4)
7	**1F**	90	2600 (2.5)	**3Fa**	85	40	4600 (3.0)

a) The reaction was carried out in THF at 80°C for 24 h, and then at 150°C for 12 h. b) Determined by ^{1}H-NMR. c) Estimated by GPC (THF, PSt standard). d) Isolated yield by the precipitation with MeOH. e) The reaction was carried out at 80°C for 3 d and then at 150°C for 12 h. f) The Reaction was carried out with anisonitrile (**2e**).

derivatives serve as a catalyst in the pyridine-formation reaction of acetylenes with nitriles (4), the end acetylene moieties in the polymers are probably converted to the cobaltacyclopentadiene moieties by the reaction with "CpCo" eliminated from the polymer chain during the reaction with nitrile. Consequently, the M_ns of the produced polymers might increase in conparison with the starting polymer.

The reaction of the organocobalt polymers **1B**-**1F** bearing various substituent in the side and/or the main chain with acetonitrile **2a** was carried out to prepare various pyridine-containing polymers (Table 3). In the case of **3Ca** and **3Fa** obtained from **1C** and **1F** bearing the electron-donating substituents in the side and in the main chain, respectively, the pyridine-contents were rather low (35 and 40%, Runs 3 and 7, respectively). As cobaltacyclopentadiene derivatives bearing electron-donating substituents have been reported to undergo the thermal rearrangement to CpCbCo derivatives more smoothly than those bearing electron-withdrawing substituents (13), the cobaltacyclopentadiene unit can facilitate to be converted to CpCbCo unit rather than pyridine unit. **1D** bearing the electron-withdrawing substituents in the side chain was found to require longer reaction period (at 80°C for 3 days and then at 150°C for 12 h) and was converted slowly into the polymer **3Da** having 70% of the pyridine moieties (Run 4). Within the examined systems, **1E** consisted of 100% of cobaltacyclopentadiene moieties gave **3Ea** and **3Ee** with highest pyridine-contents (90%) by the reaction both with acetonitrile **2a** and with anisonitrile **2e** in high yields. The increase in the molecular weights through the polymer reaction was observed in most cases by the same reason as mentioned above.

UV-vis spectra of the organocobalt polymer **1A**, and the obtained pyridine-containing polymers **3Aa** and **3Ae** are shown in Figure 2. The lowest energy π-π* absorption peaks of **1A**, **3Aa**, and **3Ae** are observed at 312, 315, and 328nm, respectively. Although **1A** shows stronger absorbance in the range of 350-550nm probably due to metal to ligand elect-

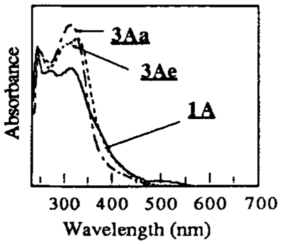


Figure 2. UV-vis spectra of 1A, 3Aa, and 3Ae in CHCl3.

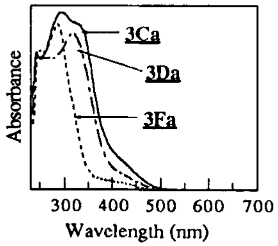


Figure 3. UV-vis spectra of 3Ca, 3Da, and 3Fa in CHCl3.

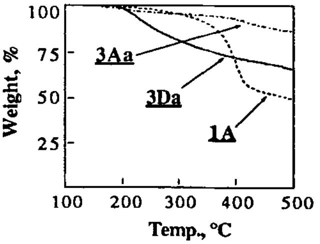


Figure 4. TG traces of 1A, 3Aa, and 3Da under nitrogen (10°C/min.).

ron transfer, no corresponding absorption was found in the UV-vis spectra of **3Aa** and **3Ae**. Compared with the UV-vis spectra of **3Ca**, **3Da**, and **3Fa**, absorption of **3Ca** and **3Da** shifted to longer wavelength than that of **3Fa** by ca. 40nm, which might indicate the conjugation of repeating units along the polymer backbone (Figure 3).

The thermal properties of the pyridine-containing polymers **3** were examined by thermogravimetric analyses (TGA) and the results are given in Figure 4. The 10% weight loss (Td_{10}) of **3Aa** was observed at 431°C, while the starting organocobalt polymer **1A** had Td_{10} at 241°C. As the CpCbCo units in **3Aa** are thermally stable up to 400°C (8a, 10a), the degradation of **3Aa** may be originated from the decomposition of pyridine moieties. In the case of **3Da** with aliphatic side groups, the intensive degradation was observed above 400°C that can be ascribed to the degradation of aliphatic side chains (the weight loss was approximately equal to the content of aliphatic groups). From the differential scanning calorimetry (DSC) analysis of **3Aa** and **3Da**, no peaks based on glass transition and melting were observed below the decomposition temperature.

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12. In the ^{13}C-NMR spectra of **3Ab** and **6**, the peaks for the Cp were appeared at the same chemical shift (83 ppm).
13. Concerning on the synthesis of the organocobalt polymers, the diynes bearing electron-donating substituents tends to increase the content of CpCbCo unit in the resulting polymers in comparison with those bearing electron-withdrawing substituents. Namely, the CpCbCo-content in the polymers bearing electron-donating substituents is higher than those bearing electron-withdrawing groups. See, ref (8b).