Synthesis of Organometallic Polymers Containing Cobaltacyclopentadiene Moieties in the Main Chain. Synthesis of Organocobalt Polymers from Various Diynes

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ABSTRACT: A series of diynes bearing flexible aliphatic, electron-donating, or electron-withdrawing groups between the acetylenes moieties or as lateral groups was prepared and subjected to the polymerization with (η^5-cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**). As a result, organocobalt polymers bearing various substituents in the side or the main chain were obtained in high yields. From the detailed structural elucidation of polymers or from the model experiments, some of the organocobalt polymers were found to be contaminated with (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt units. The regiochemistry of the main chain of the obtained polymers was also studied from the model experiments, from which 2,5-linkage of the main chain was found to be predominant in the case of diynes bearing less sterically hindered lateral substituents. The polymer obtained from **1** and a diyne having electron-withdrawing groups between the acetylenes and lateral aliphatic moieties (i.e., 1,4-bis(1-oxo-2-undecynyl)-benzene, **2I**) was found to have 100% of the cobaltacyclopentadiene moieties in the repeating units and the 2,5-selective (ca. 90%) main chain linkage.

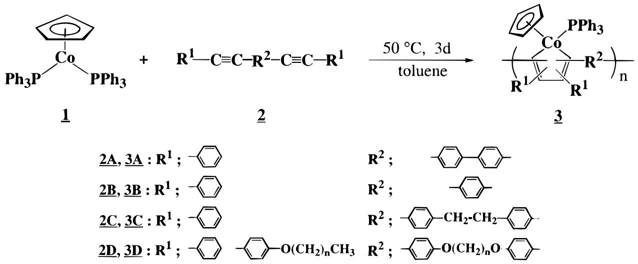
Introduction

During the past decades, metallacyclic compounds have become of interest owing to their potential physical properties and reactivities based on the carbon-metal bonds. Although most metallacyclic compounds are usually unstable in air, some, such as cobaltacyclopentadienes, are known to be stable in air.[1] Furthermore, they can be converted to derivatives of benzene, pyridine, thiophene, and other heterocycles by reaction with acetylenes, nitriles, sulfur, and other molecules having π- or lone-pair electrons, respectively.[2] Because cobaltacyclopentadienes can be regarded as precursors for various cyclic organic systems, it may be possible to construct novel reactive polymers by incorporating the metallacycle units into the polymer chain. From this point of view, we have recently reported the synthesis of the organometallic polymers **3** containing cobaltacyclopentadiene moieties in the main chain by the reaction of $CpCo(PPh_3)_2$ (**1**) with bifunctional diyne monomers **2** (Scheme 1).[3,4]

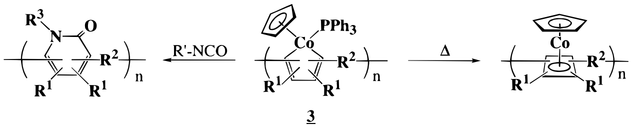
The obtained organocobalt polymers are air-stable, and they have unique reactivities. For instance, thermally stable polymers containing (η^5-cyclopentadienyl)-(η^4-cyclobutadiene)cobalt (CpCbCo) moieties were obtained by the thermal rearrangement of the main chain.[3b,5] 2-Pyridone-containing polymers were successfully obtained by the reaction with isocyanates (Scheme 2).[6]

Although the former rearrangement proceeded quantitatively, the latter reaction with isocyanates produced polymers contaminated with CpCbCo units (ca. 30%). The CpCbCo unit must be produced (at least partially) by the unimolecular thermal rearrangement of (η^5-cyclopentadienyl)(triphenylphosphine)cobaltacyclopentadiene units during the reaction with isocyanates, because the same side reaction could be observed in the model experiment using (η^5-cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene with *n*-butyl isocyanate. However, we could not exclude structural defects in the starting organocobalt polymers **3**, because a part of the CpCbCo unit in the 2-pyridone-containing polymers might be already present in the starting **3**. Furthermore, in our previous work,[3b] the organocobalt polymers **3D** could be found to contain the CpCbCo unit (ca. 10%, estimated by ^{1}H-NMR) as a byproduct due to the thermal rearrangement of the cobaltacyclopentadiene unit during the polymerization.

Scheme 1



Scheme 2



The regiochemistry of cobaltacyclopentadiene moieties in the polymer backbone is also an important point to be controlled because the regiochemistry of the polymers produced by derivatizations is directly related to that of the starting organocobalt polymers. It is also desirable to prepare organocobalt polymers having various flexible substituents, because polymers produced after derivatization might become less soluble in organic solvents.[5,6]

In order to overcome the above mentioned problems, we reinvestigated the structure of the organocobalt polymer **3A** and synthesized new organocobalt polymers **3E**−**3I** having various substituents in the side or the main chain from the designed diyne monomers.

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Experimental Section

Materials and Instruments. (η^5-Cyclopentadienyl)bis(triphenylphosphine)cobalt (**1**) was prepared according to the literature procedure.[1] Toluene was dried over sodium and distilled under nitrogen. Diphenylacetylene (**4A**) and 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 tetrahydrofuran (THF) as eluent (JAIGEL-1H and JAIGEL-2H). ^{1}H- and ^{13}C-NMR spectra were recorded on a JNM-EX400 spectrometer (400 and 100 MHz, respectively) 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 4,4′-Bis(propynyl)biphenyl (2Ea). (Trimethylsilyl)acetylene (4 mL, 30 mmol) was added to a diethylamine solution (100 mL) of diiodobiphenyl (4.2 g, 10 mmol), CuI (0.038 g, 0.2 mmol), $PdCl_2$ (0.018 g, 0.1 mmol), and PPh_3 (0.053 g, 0.2 mmol), and was stirred at 50−55 °C for 1 day. By column chromatography (Al_2O_3, benzene:*n*-hexane = 2:1), 4,4′-bis[(trimethylsilyl)ethynyl]biphenyl was obtained in 65% yield (2.3 g, 6.8 mmol).

The desilylation of the obtained diyne was carried out by stirring the diyne (2.3 g, 6.8 mmol) and KOH (1.12 g, 20 mmol) in methanol (200 mL) at room temperature for 6 h. After the removal of the solvent, diethyl ether was added. The ether-soluble part was washed with water and dried over $MgSO_4$. By the recrystallization from ethanol, bis(ethynyl)biphenyl was obtained in 65% yield (0.90 g, 4.4 mmol).

n-BuLi/*n*-hexane (1.6 N, 7 mL) was added to a THF (10 mL) solution of bis(ethynyl)biphenyl (0.90 g, 4.4 mmol) at −78 °C, and then the temperature was allowed to rise to room temperature. Methyl iodide (1.5 g, 11 mmol) was added dropwise to the mixture and then the mixture was kept stirring for 1 h. By the recrystallization from methanol, **2Ea** was obtained as white crystals in 53% yield (0.54 g, 2.3 mmol).

2Ea: mp, 173−175 °C; ^{1}H-NMR (δ, ppm) 1.94 ($-CH_3$, s, 6H), 7.1−7.6 ($-C_6H_4-$, 8H); ^{13}C-NMR (δ, ppm) 30.1, 80.0, 85.9, 124.3, 127.5, 128.3, 131.6; IR (KBr, cm^{-1}) 2962, 2910, 2847, 2253, 2216, 1491, 1394, 1109, 1003, 823. Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.74; H, 6.08.

Synthesis of 2Eb, 2F, and 2I. *n*-BuLi/*n*-hexane (1.65 N, 10 mL) was added to a THF (10 mL) solution of 1-decyne (2.07 g, 15 mmol) at −78 °C, which was kept stirring for 30 min at that temperature, and then the temperature was allowed to rise to room temperature. To the resulting 1-decynyllithium was added a THF (10 mL) solution of zinc bromide (3.52 g, 16 mmol) at 0 °C, the mixture was stirred for 1 h, and then the temperature was allowed to rise to room temperature. A THF (20 mL) solution of 4,4′-diiodobiphenyl (2.44 g, 6 mmol) and $Pd(PPh_3)_4$ (0.35 g, 0.3 mmol) was added to the mixture and was kept stirring for 12 h at room temperature. After the evaporation of the solvents, the crude product was extracted with $CHCl_3$ and washed with aqueous HCl (1 N, 30 mL) and then with water. After drying over $MgSO_4$, **2Eb** was obtained as a white solid (1.79 g, 4.2 mmol) by column chromatography (SiO_2, *n*-hexane). **2F** and **2I** were obtained by similar procedures.

2Eb: yield, 70%; mp, 71.0−72.0 °C; ^{1}H-NMR (δ, ppm) 0.89 ($-CH_3$, t, 6H, J = 6.8 Hz), 1.1−1.5 ($-CH_2-$, 20H), 1.60 ($-CH_2-$, m, 4H), 2.40 ($-CH_2-$, t, 4H, J = 7.0 Hz), 7.41, 7.44, 7.46, 7.48 ($-C_6H_4-$, 8H); ^{13}C-NMR (δ, ppm) 14.07, 19.48, 22.67, 28.78, 28.96, 29.14, 29.21, 31.85, 80.38, 91.03, 123.27, 126.56, 131.94, 139.34; IR (KBr, cm^{-1}) 2957, 2926, 2855, 1493, 1466, 824. Anal. Calcd for $C_{32}H_{42}$: C, 90.08; H, 9.92. Found: C, 90.09; H, 9.89.

2F: prepared by the reaction of 2 equiv of iodobenzene with 1,9-decadiyne; yield, 61%; white crystals; mp, <30 °C; ^{1}H-NMR (δ, ppm) 1.38−1.62 ($-CH_2-$, 8H), 2.36 ($-CH_2-$, t, 4H, J = 7.0 Hz), 7.20 ($-C_6H_5$, m, 6H), 7.39 ($-C_6H_5$, m, 4H); ^{13}C-NMR (δ, ppm) 19.21, 28.26, 28.48, 80.66, 90.11, 124.00, 127.29, 128.01, 131.37; IR (KBr, cm^{-1}) 3056, 2934, 2859, 2232, 1599, 1489, 1441, 1331, 1071, 1028, 912, 756, 691. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.24; H, 7.76.

2I: prepared by the reaction of 2 equiv of 1-decyne with terephthaloyl chloride; yield, 79%; white powder; mp, 36.5−37.0 °C; ^{1}H-NMR (δ, ppm) 0.89 ($-CH_3$, t, 6H, J = 6.8 Hz), 1.2−1.6 ($-CH_2-$, 20H), 1.69 ($-CH_2-$, m, 4H), 2.53 ($-CO-C{\equiv}CCH_2-$, t, 4H, J = 7.4 Hz), 8.22 ($-C_6H_4-$, s, 4H); ^{13}C-NMR (δ, ppm) 13.98, 19.19, 22.54, 27.68, 28.90, 29.03, 31.70, 79.63, 98.21, 129.40, 140.35, 177.16; IR (KBr, cm^{-1}) 2924, 2851, 2238, 2201, 1640, 1466, 1263, 1240, 1111. Anal. Calcd for $C_{28}H_{38}O_2$: C, 82.71; H, 9.42. Found: C, 82.94; H, 9.42.

Synthesis of 2G and 2H. A DMF (70 mL) suspension containing 4-iodophenol (6.6 g, 30 mmol), 1-bromododecane (7 mL, 29 mmol), and K_2CO_3 (12 g) was stirred at 110−120 °C for 1.5 h. The reaction mixture was poured into a beaker containing aqueous NaOH. (1 N, 1.2 L) and was intensely stirred for 30 min. The product was extracted by *n*-hexane and purified by column chromatography (SiO_2, *n*-hexane: diethyl ether = 5:1) to yield 1-iodo-4-(dodecyloxy)benzene in 94% yield (10.6 g, 27.3 mmol) as white crystals (mp, 33.0−35.0 °C).

(Trimethylsilyl)acetylene (5 mL, 35 mmol) was added to a diethylamine solution (60 mL) of the obtained 1-iodo-4-(dodecyloxy)benzene (7.8 g, 20 mmol), CuI (0.038 g, 0.2 mmol), $PdCl_2$ (0.018 g, 0.1 mmol), and PPh_3 (0.053 g, 0.2 mmol), and the mixture was reacted at 50−55 °C for 1 day. After removal of the solvent under reduced pressure, diethyl ether was added to the residue. The organic phase was washed with water and was passed through a short aluminum oxide column to remove the catalyst. After evaporation of the solvent, 1-(dodecyloxy)-4-[(trimethylsilyl)ethynyl]benzene was obtained in 87% yield (6.5 g, 17.3 mmol) as a pale orange oil. The desilylation of the obtained acetylene was carried out by stirring the acetylene (5.4 g, 15 mmol) and KOH (1.12 g, 20 mmol) in a mixture of methanol (60 mL) and THF (20 mL) at room temperature for 1 h. After removal of the solvents, *n*-hexane was added to the residue. The *n*-hexane-soluble part was washed with water and was purified by column chromatography (SiO_2, *n*-hexane: diethyl ether = 5:1). 1-(Dodecyloxy)-4-ethynylbenzene was obtained in 91% yield (4.1 g, 13.6 mmol) as pale yellow crystals (mp, <30 °C).

1-(Dodecyloxy)-4-ethynylbenzene (4.0 g, 14 mmol) was added to a diethylamine solution (60 mL) of 4,4′-diiodobiphenyl (2.8 g, 7 mmol), CuI (0.038 g, 0.2 mmol), $PdCl_2$ (0.018 g, 0.1 mmol), and PPh_3 (0.053 g, 0.2 mmol), and the mixture was stirred at 50−55 °C for 1 day. After removal of diethylamine under reduced pressure, $CHCl_3$ was added to the residue. The organic phase was washed with water, passed through a short aluminum oxide column to remove the catalyst, and dried over $MgSO_4$. By the recrystallization from $CHCl_3$, **2G** was obtained in 70% yield (3.6 g, 4.9 mmol) as hardly soluble white crystals. **2H** was obtained by the similar procedure.

2G: overall yield, 52%; mp, 280.0−283.0 °C; IR (KBr, cm^{-1}) 2955, 2919, 2874, 2849, 1609, 1599, 1512, 1474, 1285, 1250, 1022. Anal. Calcd for $C_{52}H_{66}O_2$: C, 86.37; H, 9.20. Found: C, 86.22; H, 9.11.

2H: prepared by the reaction of 2 equiv of 1-(dodecyloxy)-carbonyl-4-ethynylbenzene (1.6 g, 5 mmol) with 4,4′-diiodobiphenyl (1.0 g, 2.5 mmol); overall yield, 50%; white crystals; mp, 254.5−255.5 °C; ^{1}H-NMR (δ, ppm) 0.88 ($-CH_3$, t, 6H, J = 6.8 Hz), 1.1−1.5 ($-CH_2-$, 36H), 1.78 ($-CH_2-$, m, 4H), 4.33 ($-CO_2CH_2-$, t, 4H, J = 7.0 Hz), 7.60, 7.62, 7.63, 8.03, 8.05 ($-C_6H_4-$, 16H); ^{13}C-NMR (δ, ppm) 14.11, 22.69, 26.05, 28.72, 29.29, 29.63, 31.92, 65.37, 126.98, 129.51, 131.48, 132.29; IR (KBr, cm^{-1}) 2917, 2849, 1711, 1470, 1406, 1281, 1175, 1113. Anal. Calcd for $C_{54}H_{66}O_4$: C, 83.25; H, 8.54. Found: C, 83.25; H, 8.54.

Monoynes used for model experiments were prepared by procedures similar to the corresponding diynes.

1-Decynylbenzene (4E): yield, 83%; colorless oil; ^{1}H-NMR (δ, ppm) 0.89 ($-CH_3$, t, 3H, J = 6.8 Hz), 1.2−1.5 ($-CH_2-$, br, 10H), 1.58 ($-CH_2-$, m, 2H), 2.37 ($-C{\equiv}CCH_2-$, t, 2H, $J = 7.0$ Hz), 7.23 ($-C_6H_5$, m, 3H), 7.37 ($-C_6H_5$, m, 2H); ^{13}C-NMR (δ, ppm) 14.03, 19.36, 22.65, 28.76, 28.90, 29.12, 29.20, 31.83, 80.57, 90.28, 124.15, 127.31, 128.04, 131.46; IR (neat, cm^{-1}) 2928, 2857, 1599, 1572, 1491, 1468, 1441, 1069, 1015, 997, 912, 756, 731, 691. Anal. Calcd for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.50; H, 10.49.

1-[(4-Dodecyloxy)phenyl]-2-phenylacetylene (4G): yield, 79%; white solid; mp, 61.0−62.0 °C; ^{1}H-NMR (δ, ppm) 0.88 ($-CH_3$, t, 3H, $J = 6.8$ Hz), 1.2−1.5 ($-CH_2-$, 18H), 1.76 ($-CH_2-$, m, 2H), 3.93 ($-OCH_2-$, t, 2H, $J = 6.6$ Hz), 6.83−7.51 ($-C_6H_5$, $-C_6H_4-$, 9H); ^{13}C-NMR (δ, ppm) 14.11, 22.69, 26.01, 29.20, 29.38, 29.60, 29.65, 31.92, 68.04, 87.96, 89.51, 114.51, 115.09, 123.67, 127.82, 128.26, 131.41, 133.00, 159.22; IR (KBr, cm^{-1}) 3050, 2919, 2874, 2851, 1607, 1595, 1512, 1474, 1285. Anal. Calcd for $C_{26}H_{34}O$: C, 86.13; H, 9.45. Found: C, 85.74; H, 9.09.

1-[4-((Dodecyloxy)carbonyl)phenyl]-2-phenylacetylene (4H): yield, 78%; white powder; mp, 65.0−66.0 °C; ^{1}H-NMR (δ, ppm) 0.88 ($-CH_3$, t, 3H, $J = 6.8$ Hz), 1.2−1.5 ($-CH_2-$, 18H), 1.76 ($-CH_2-$, m, 2H), 4.31 ($-CO_2CH_2-$, t, 2H, $J = 6.6$ Hz), 8.01, 7.54, 7.34 ($-C_6H_5$, $-C_6H_4-$, 9H); ^{13}C-NMR (δ, ppm) 14.07, 22.65, 26.00, 28.67, 29.25, 29.32, 29.51, 29.56, 29.62, 31.88, 65.26, 88.65, 92.22, 122.70, 127.82, 128.35, 128.65, 129.41, 129.82, 131.41, 131.68, 166.03; IR (KBr, cm^{-1}) 2917, 2849, 1713, 1605, 1466, 1406, 1273, 1175, 1107, 1019. Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 82.76; H, 9.03.

1-Phenyl-1-oxo-2-undecyne (4I): yield, 79%; white powder; mp, 36.5−37.0 °C; ^{1}H-NMR (δ, ppm) 0.89 ($-CH_3$, t, 3H, $J = 7.2$ Hz), 1.0−1.8 ($-CH_2-$, 12H), 2.45 ($-C{\equiv}CCH_2-$, t, 2H, $J = 8.6$ Hz), 7.42, 7.55, 8.12 ($-C_6H_5$, 5H); IR (KBr, cm^{-1}) 2924, 2851, 2238, 2201, 1640, 1466, 1263, 1240, 1111. Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.09; H, 8.97.

Synthesis of (η^5-Cyclopentadienyl)bis(triphenylphosphine)cobaltacyclopentadiene-Containing Polymers (3E−3I). Typical Procedure for 3Eb. To a test tube were added **1** (0.380 g, 0.55 mmol), **2Eb** (0.235 g, 0.55 mmol) and 10 mL of toluene under N_2, and the mixture was kept stirring for 3 days at room temperature. After filteration and concentration, the condensed solution was precipitated with methanol. The resulting reddish brown powder was collected by filteration, washed with methanol, and then dried *in vacuo* to give 0.363 g of **3Eb**. Polymers **3F-3I** were prepared under the same conditions except for the reaction temperature.

3Ea (reaction carried out at room temperature): yield, quantitative (composed of 61% insoluble and 39% soluble parts); reddish brown solid; ^{1}H-NMR (soluble fractions, δ, ppm) 1.4−2.4 ($-CH_3$, 6H), 4.4−4.9 ($-C_5H_5$, 5H), 6.5−8.0 ($-C_6H_4-$, $-P(C_6H_5)_3$, 23H); IR (KBr, cm^{-1}) 3053, 3020, 2903, 2847, 1481, 1433, 1089, 1003, 808, 744, 696, 528. Anal. Calcd for $C_{41}H_{34}PCo$: C, 79.86; H, 5.56. Found: C, 79.61; H, 5.81.

3Eb: yield, 82%; reddish brown powder; ^{1}H-NMR (δ, ppm) 0.7−1.7 ($-CH_2-$, $-CH_3$, 30H), 1.9−2.5 ($-CH_2-$, 4H), 4.62, 4.68, 4.79 ($-C_5H_5$, 5H), 6.5−7.7 ($-C_6H_4-$, $-P(C_6H_5)_3$, 23H); ^{13}C-NMR (δ, ppm) 14.16, 22.70, 29.29, 30.00, 31.43, 31.90, 65.48, 81.39, 88.74, 89.22, 125.17, 125.94, 126.36, 126.80, 127.79, 128.26, 128.41, 129.18, 129.56, 129.74, 131.81, 132.14, 133.53, 133.68, 136.18, 136.73; IR (KBr, cm^{-1}) 2920, 2851, 1481, 1433, 1262, 1090, 804, 694, 527. Anal. Calcd for 0.79 ($C_{55}H_{62}PCo$) + 0.21 ($C_{37}H_{47}Co$): C, 81.14; H, 7.88. Found: C, 81.30; H, 8.35.

3F (reaction carried out at room temperature): yield, 89%; orange brown powder; ^{1}H-NMR (δ, ppm) 0.4−2.4 ($-CH_2-$, 12H), 4.4−4.9 ($-C_5H_5$, 5H), 6.4−7.4 ($-C_6H_5$, $-P(C_6H_5)_3$, 25H); ^{13}C-NMR (δ, ppm) 30.09, 31.59, 88.72, 89.09, 123.05, 126.95, 127.71, 127.95, 128.50, 128.68, 129.01, 129.47, 133.31, 133.62, 134.13, 153.33; IR (KBr, cm^{-1}) 3054, 2924, 2851, 1589, 1480, 1433, 1262, 1090, 806, 745, 696, 529. Anal. Calcd for $C_{45}H_{42}PCo$: C, 80.34; H, 6.29. Found: C, 80.63; H, 6.57.

3G (reaction carried out at 40 °C): yield, 98%; reddish brown powder; ^{1}H-NMR (δ, ppm) 0.88 ($-CH_3$, br, 6H), 1.1−1.5 ($-CH_2-$, 36H), 1.5−1.9 ($-CH_2-$, 4H), 3.6−4.0 ($-OCH_2-$, 4H), 4.5−4.8 ($-C_5H_5$, 5H), 6.2−7.6 ($-C_6H_4-$, $-P(C_6H_5)_3$, 31H); ^{13}C-NMR (δ, ppm) 14.13, 22.69, 26.12, 29.34, 29.45, 29.63, 31.90, 53.39, 67.55, 67.93, 83.00, 89.64, 112.22, 112.84, 113.98, 114.47, 124.68, 128.06, 129.78, 130.73, 131.41, 133.64, 155.40; IR (KBr, cm^{-1}) 3057, 2922, 2853, 1601, 1481, 1433, 1238, 1173, 1088, 1011, 808, 745, 694, 527. Anal. Calcd for 0.82 ($C_{75}H_{86}O_2PCo$) + 0.18 ($C_{57}H_{71}O_2Co$): C, 81.13; H, 7.93. Found: C, 81.04; H, 7.93.

3H (reaction carried out at 60 °C): yield, 85%; brown powder; ^{1}H-NMR (δ, ppm) 0.87 ($-CH_3$, br, 6H), 1.0−1.5 ($-CH_2-$, 36H), 1.6−1.8 ($-CH_2-$, br, 4H), 4.1−4.4 ($-CO_2CH_2-$, br, 4H), 4.5−4.9 ($-C_5H_5$, 5H), 6.3−8.1 ($-C_6H_4-$, $-P(C_6H_5)_3$, br, 31H); ^{13}C-NMR (δ, ppm) 14.09, 22.65, 26.01, 28.72, 29.31, 29.58, 31.88, 64.75, 89.77, 124.79, 125.68, 125.96, 126.36, 128.41, 128.66, 130.11, 131.17, 132.03, 133.11, 133.58, 167.12; IR (KBr, cm^{-1}) 3059, 2924, 2853, 1715, 1601, 1269, 1175, 1103, 1017, 814, 747, 696, 527. Anal. Calcd for 0.82 ($C_{77}H_{86}O_4PCo$) + 0.18 ($C_{59}H_{71}O_4Co$): C, 79.20; H, 7.53. Found: C, 78.81; H, 7.56.

3I (reaction carried out at 40 °C): yield, 81%; dark brown powder; ^{1}H-NMR (δ, ppm) 0.4−2.6 ($-CH_2-$, $-CH_3$, 34H), 4.4−5.2 ($-C_5H_5$, 5H), 7.0−8.4 ($-C_6H_4-$, $-P(C_6H_5)_3$, 19H); ^{13}C-NMR (δ, ppm) 14.09, 22.61, 29.10, 30.31, 31.74, 88.32, 128.08, 129.94, 133.66; IR (KBr, cm^{-1}) 3059, 2924, 2853, 1622, 1435, 1213, 1119, 1090, 816, 747. Anal. Calcd for $C_{51}H_{58}O_2PCo$: C, 77.25; H, 7.37. Found: C, 77.01; H, 7.61.

Synthesis of (η^5-Cyclopentadienyl)(η^4-cyclobutadiene)-cobalt-Containing Polymer. Thermal Rearrangement of 3Eb. A toluene (10 mL) solution of **3Eb** (0.163 g, 0.2 mmol/repeating unit) was stirred at 120 °C under N_2 for 1 day. After filteration and concentration, the solution was precipitated with methanol. The resulting yellow powder was filtered off, washed with methanol, and then dried *in vacuo* to give 0.091 g of the polymer: yield, 83%; ^{1}H-NMR (δ, ppm) 0.4−1.8 ($-CH_2-$, $-CH_3$, 30H), 2.0−2.8 ($-CH_2-$, 4H), 4.61 ($-C_5H_5$, 5H), 6.8−8.0 ($-C_6H_4-$, 8H); ^{13}C-NMR (δ, ppm) 14.13, 22.70, 27.40, 29.31, 30.06, 30.59, 31.88, 81.41, 126.10, 128.06, 137.53; IR (KBr, cm^{-1}) 2924, 2853, 1655, 1545, 1510, 1460, 1262, 1107, 804. Anal. Calcd for $C_{37}H_{47}Co$: C, 80.70; H, 8.60. Found: C, 80.30; H, 9.02.

Reaction of Diphenylacetylene (4A) with 1. Under conditions similar to the polymerization of **2A** with **1**, the reaction was carried out in toluene at 50 °C for 3 days. The products were isolated by HPLC. (η^5-Cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene (**5A**):[1] yield, 78%; dark brown solid; mp, 193−194 °C (lit.:[1] mp, 193−194 °C).

As a minor fraction, (η^5-cyclopentadienyl)(η^4-1,2,3,4-tetraphenylcyclobutadiene)cobalt (**6A**) was obtained in 5% yield as a yellow solid. mp, 269 °C (lit.:[7] mp 262−264 °C); ^{1}H-NMR (δ, ppm) 4.62 ($-C_5H_5$, s, 5H), 7.20 ($-C_6H_5$, m, 12H), 7.44 ($-C_6H_5$, m, 8H); ^{13}C-NMR (δ, ppm) 74.82, 83.16, 126.12, 127.88, 128.83, 136.42; IR (KBr, cm^{-1}) 3056, 1595, 1497, 1439, 1190, 1119, 812, 747. Anal. Calcd for $C_{33}H_{25}Co$: C, 82.49; H, 5.24. Found: C, 82.80; H, 5.55.

Reaction of 1-Decynylbenzene (4E) with 1. The reaction was carried out in toluene at room temperature for 3 days. (η^5-Cyclopentadienyl)(triphenylphosphine)diphenyldi-*n*-octylcobaltacyclopentadiene (**5E**) was isolated by HPLC in 88% yield as a reddish brown glassy solid: ^{1}H-NMR (δ, ppm) 0.6−2.6 ($-CH_2-$, $-CH_3$, 34H), 4.5−4.8 ($-C_5H_5$, 5H), 6.4−7.7 ($-C_6H_5$, $-P(C_6H_5)_3$, 25H); ^{13}C-NMR (δ, ppm) 14.05, 22.63, 29.18, 29.84, 31.74, 89.03, 123.03, 124.64, 126.91, 127.77, 129.19, 131.90, 133.31, 136.38, 153.28, 155.46, 160.72, 161.24; IR (KBr, cm^{-1}) 2963, 2924, 2853, 2361, 2199, 1720, 1603, 1433, 1262, 1100, 1024, 802. Anal. Calcd for $C_{55}H_{64}PCo$: C, 81.05; H, 7.92. Found: C, 80.81; H, 8.17. In this case, (η^5-cyclopentadienyl)(η^4-diphenyldi-*n*-octylcyclobutadiene)cobalt (**6E**) was not detected.

Reaction of 1-[(4-Dodecyloxy)phenyl]-2-phenylacetylene (4G) with 1. The reaction was carried out in toluene at 40 °C for 3 days. The products could not be separated by HPLC. Thus, the mixture of (η^5-cyclopentadienyl)(triphenylphosphine)bis[4-(dodecyloxy)phenyl]diphenylcobaltacyclopentadiene (**5G**) and (η^5-cyclopentadienyl)[η^4-bis(4-(dodecyloxy)phenyl)diphenylcyclobutadiene]cobalt **(6G)** (obtained as a reddish brown glassy solid in 89% total yield) was analyzed directly: ^{1}H-NMR (δ, ppm) 0.87 ($-CH_3$, br, 6H), 1.2−1.5 ($-CH_2-$, br, 36H), 1.5−1.8 ($-CH_2-$, br, 4H), 3.6−3.9 ($-OCH_2-$, 4H), 4.57 ($-C_5H_5$, s, 0.3H), 4.73 ($-C_5H_5$, s, 4.7H), 6.2$-$7.4 ($-C_6H_4-$, $-C_6H_5$, $-P(C_6H_5)_3$, 32.1H) (**5G**:**6G** = 94:6); ^{13}C-NMR (δ, ppm) 14.09, 22.65, 26.05, 29.31, 29.58, 31.87, 67.42, 67.71, 89.51, 112.15, 112.77, 122.83, 123.29, 126.10, 126.63, 127.97, 128.94, 129.47, 129.72, 130.42, 131.21, 133.55, 134.72, 134.79, 136.29, 136.71, 142.12, 146.18, 153.70, 155.18, 155.35, 156.72, 157.03, 157.58; IR (KBr, cm^{-1}) 3054, 2924, 2853, 2361, 1599, 1497, 1470, 1433, 1273, 1238, 1173, 1088, 1026, 808, 747, 696, 527.

Reaction of 1-[4-((Dodecyloxy)carbonyl)phenyl]-2-phenylacetylene (4H) with 1. The reaction was carried out in toluene at 60 °C for 3 days. The products were isolated by HPLC. (η^5-Cyclopentadienyl)(triphenylphosphine)bis[4-((dodecyloxy)carbonyl)phenyl]diphenylcobaltacyclopentadiene (**5H**): yield, 81%; reddish brown glassy solid; ^{1}H-NMR (δ, ppm) 0.88 ($-CH_3$, br, 6H), 1.2$-$1.4 ($-CH_2-$, br, 36H), 1.6$-$1.8 ($-CH_2-$, br, 4H), 4.1$-$4.3 ($-CO_2CH_2-$, 4H), 4.77 ($-C_5H_5$, br, 5H), 6.3$-$7.5 ($-C_6H_4-$, $-C_6H_5$, $-P(C_6H_5)_3$, 33H); ^{13}C-NMR (δ, ppm) 14.09, 22.63, 26.05, 28.65, 28.74, 29.29, 29.45, 29.56, 31.87, 64.64, 89.47, 89.60, 89.71, 123.67, 124.06, 124.15, 124.77, 124.86, 125.45, 126.34, 126.52, 126.91, 127.62, 127.79, 128.16, 128.57, 128.66, 130.05, 130.16, 130.26, 133.40, 141.23, 141.41, 153.01, 156.75, 157.82, 158.38, 158.84, 167.16; IR (KBr, cm^{-1}) 3056, 2924, 2853, 1713, 1597, 1433, 1269, 1171, 1101, 1015, 812, 737, 698. Anal. Calcd for $C_{77}H_{88}O_4PCo$: C, 79.22; H, 7.60. Found: C, 79.00; H, 7.63. (η^5-Cyclopentadienyl)[η^4-bis(4-((dodecyloxy)carbonyl)phenyl)diphenylcyclobutadiene]cobalt (**6H**): yield, 5%; orange red glassy solid; ^{1}H-NMR (δ, ppm) 0.87 ($-CH_3$, t, 6H, J = 6.6 Hz), 1.2$-$1.5 ($-CH_2-$, br, 36H), 1.7$-$1.9 ($-CH_2-$, br, 4H), 4.32 ($-CO_2CH_2-$, m, 4H), 4.63 ($-C_5H_5$, s, 5H), 7.24, 7.46, 7.87 ($-C_6H_4-$, $-C_6H_5$, m, 18H); ^{13}C-NMR (δ, ppm) 14.05, 22.63, 25.56, 26.03, 28.74, 29.29, 29.49, 29.56, 31.85, 65.02, 67.87, 73.29, 73.58, 76.14, 76.38, 83.38, 126.60, 126.74, 127.95, 128.04, 128.10, 128.37, 128.85, 129.19, 135.28, 135.39, 142.05, 142.18, 166.50; IR (KBr, cm^{-1}) 3059, 2926, 2855, 1719, 1605, 1466, 1271, 1177, 1113, 1017, 698. Anal. Calcd for $C_{59}H_{73}O_4Co$: C, 78.29; H, 8.13. Found: C, 78.19; H, 8.39.

Reaction of 1-Phenyl-1-oxo-2-undecyne (4I) with 1. The reaction was carried out in toluene at 40 °C for 3 days. (η^5-Cyclopentadienyl)(triphenylphosphine)dibenzoyldi-*n*-octylcobaltacyclopentadiene (**5I**) was isolated as a dark brown glassy solid in 69% yield: ^{1}H-NMR (δ, ppm) 0.4$-$2.5 ($-CH_2-$, $-CH_3$, m, 34H), 4.46 ($-C_5H_5$, s, 0.26H), 4.55 ($-C_5H_5$, s, 0.36H), 4.88 ($-C_5H_5$, s, 4.38H), 7.17$-$7.95 ($-C_6H_5$, $-P(C_6H_5)_3$, 25H); ^{13}C-NMR (δ, ppm) 13.96, 22.37, 22.41, 25.14, 28.52, 28.65, 28.72, 28.88, 29.05, 29.25, 29.45, 29.85, 30.15, 30.37, 30.64, 31.52, 31.57, 31.65, 34.43, 43.97, 84.22, 87.48, 87.88, 127.48, 127.73, 127.82, 127.95, 128.04, 128.30, 128.55, 129.12, 129.19, 129.62, 130.77, 131.02, 131.94, 133.64, 133.73, 133.88, 133.97, 139.00, 139.69, 155.25, 155.53, 157.36, 158.11, 159.35, 188.80, 189.11, 196.52; IR (KBr, cm^{-1}) 3059, 2924, 2853, 1616, 1595, 1576, 1435, 1229, 1171, 1119, 1024, 816, 694. Anal. Calcd for $C_{57}H_{64}O_2PCo$: C, 78.60; H, 7.41. Found: C, 78.99; H, 7.74. (η^5-Cyclopentadienyl)(η^4-dibenzoyldi-*n*-octylcyclobutadiene)cobalt (**6I**) was not detected.

Results and Discussion

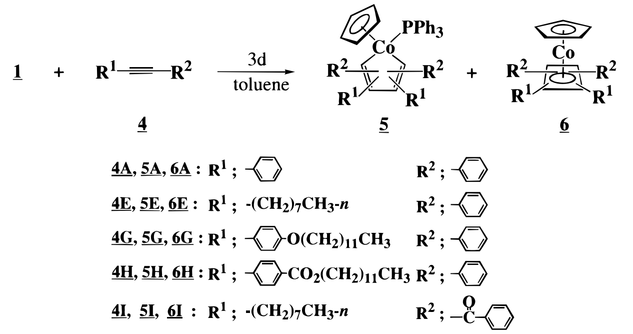
Model Experiments. Since the polymerization of diynes with the cobalt(I) complex **1** takes place via the formation of the cobaltacyclopentadiene rings (i.e., the intermolecular oxidative ring formation of **1** with two acetylene moieties), the structures of the resulting polymers should be governed by the cobaltacyclopentadiene formation step. Therefore, the detailed analysis of the products of model reactions of **1** with monoynes is probably relevant to the polymer structures. The results of the reactions of **1** with several kinds of acetylenes are summarized in Table 1.

Table 1. Reactions of 4 with 1[a]

			yield (%)[b]		
run	acetylene	temp (°C)	5	6	ratio of **5**:**6**
1	**4A**	50	78	5	94:6
2	**4E**	rt	88	0	100:0
3	**4G**	40	89[c]		94:6[d]
4	**4H**	60	81	5	94:6
5	**4I**	40	69[e]	0	100:0

[a] The reaction was carried out in toluene for 3 days under N_2. [b] Isolated yields by HPLC. [c] Total yield of **5** and **6**. [d] Estimated by the ^{1}H-NMR spectrum of the product mixture. [e] The product was composed of the isomers 2,5-, 2,4-, and 3,4-diphenyl-substituted cobaltacyclopentadienes and their ratio was 88:7:5 estimated by the ^{1}H-NMR spectrum.

Scheme 3



As a model of **3A**,[3a] the reaction of diphenylacetylene (**4A**) with **1** was carried out under the same conditions (i.e., at 50 °C for 3 days). (η^5-Cyclopentadienyl)(triphenylphosphine)-2,3,4,5-tetraphenylcobaltacyclopentadiene (**5A**), the desired structure in the polymer repeating unit, was isolated as a major product in 78% yield. Although no other product was isolated by the column chromatography technique, HPLC made it possible to detect a minor fraction (5% yield) from the crude reaction mixture, which proved to be (η^5-cyclopentadienyl)(η^4-1,2,3,4-tetraphenylcyclobutadiene)cobalt (**6A**) from the spectroscopic analyses. In the cases of 1-[4-(dodecyloxy)phenyl]-2-phenylacetylene (**4G**) and 1-[4-((dodecyloxy)carbonyl)phenyl]-2-phenylacetylene (**4H**), similar results were obtained where both the cobaltacyclopentadiene and the CpCbCo were detected in the reaction products. Thus, the electronic effects of the substituents on the aromatic moieties on the product distributions were not apparent.

In contrast to the results for **4A**, **4G**, and **4H**, 1-decynylbenzene (**4E**) and 1-phenyl-1-oxo-2-undecyne (**4I**), which bear aliphatic substituents on either side, yielded the cobaltacyclopentadiene as a single product. In fact, no peak for the cyclopentadienyl (Cp) moieties on the CpCbCo unit was observed in the ^{13}C-NMR spectrum of the crude reaction mixture (Figure 1a). In the ^{1}H-NMR spectrum, however, three peaks at 4.46, 4.55, and 4.88 ppm attributable to the Cp moieties were observed (Figure 1b). From the reported chemical shifts for the Cp groups on the cobaltacyclopentadiene moieties bearing various substituents,[1] the three peaks can be attributed to those of 2,5-, 2,4-, and 3,4-dibenzoyl-substituted isomers, respectively. The ratios of the regioisomers were determined to be 2,5-:2,4-:3,4- = 88:7:5 from the integral ratio of these peaks. The result is consistent with the reported fact that the larger (and probably also the electron-withdrawing) substituent on the starting acetylene tends to be located at the 2,5-position of the cobaltacyclopentadiene moieties preferentially in the metallacycle formation step.[8] The regioisomers were also observed in the case of (η^5-cyclopentadienyl)(triphenylphosphine)diphenyldi-*n*-octylcobaltacyclopentadiene (**5E**) in the ratio of 2,5-:2,4-:3,4-diphenyl-substituted isomer = 63:37:0.

Structural Investigation of 3A. Although the ^{1}H-NMR spectrum of the organocobalt polymer **3A** did not

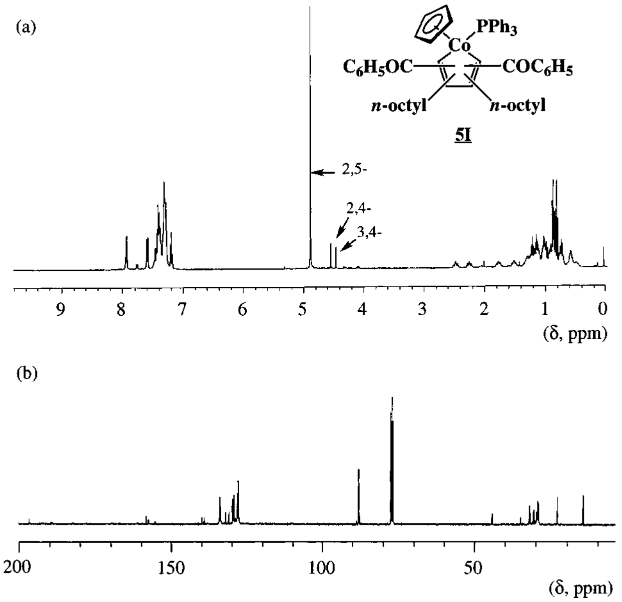


Figure 1. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of **5I**.

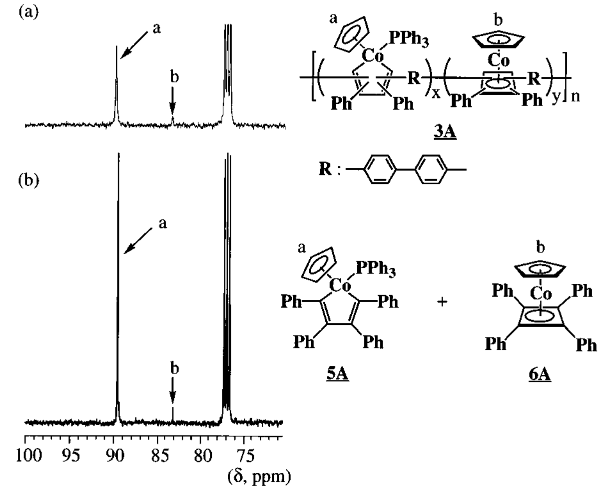


Figure 2. ^{13}C-NMR spectra of **3A** (a) and the crude products obtained by the model experiment (b).

give any information on the contamination of the polymer by the CpCbCo unit because of the poor resolution of the peak at 4.76 ppm,[3a] the model experiment indicated the existence of the CpCbCo unit (i.e., Table 1, run 1). To estimate the content of the unit, the ^{13}C-NMR spectrum of **3A** was re-examined and a small peak at 83.2 ppm was, in fact, observed.

In the ^{13}C-NMR spectrum of the products from the model experiment before the separation by HPLC, two peaks at 89.6 and 83.2 ppm attributable to Cp moieties of **5A** and **6A**, respectively, were observed (Figure 2b).[9] Although the ^{13}C-NMR technique may not be suitable for the quantitative analysis, the observed ratio (96:4) is close to the isolated ratio of **5A**:**6A** (94:6). In the case of the polymer **3A**, the corresponding two peaks were observed (Figure 2a), whose peak intensity ratio for the cobaltacyclopentadiene to the CpCbCo unit was proposed to be 84:16.

Attempts to prevent the formation of the CpCbCo moieties by lowering the polymerization temperature or by the addition of triphenylphosphine ligand to the polymerization system failed to result in the formation of oligomers having lower molecular weights.

Although the spectroscopic analyses gave no information on the regiochemistry of the main chain linkage at the cobaltacyclopentadiene moieties, 2,5-, 2,4-, and 3,4-linkages most probably exist statistically in the case of **3A**, because the regioselectivity for the formation of the cobaltacyclopentadiene moieties is reported to be governed by the steric bulkiness of the substituents on the starting acetylenes and 4,4′-bis(ethynylphenyl)biphenyl (**2A**) used for the synthesis of **3A** has sterically similar benzene rings on both ends of the acetylene moieties.

Scheme 4

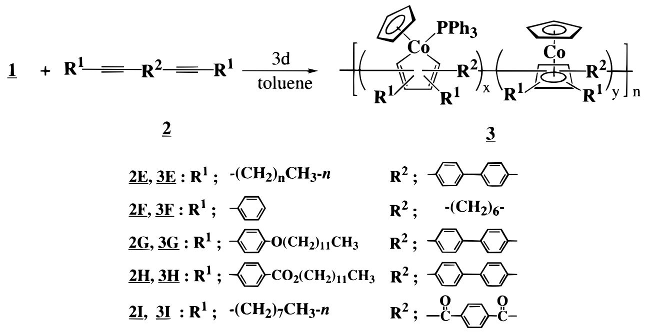


Table 2. Synthesis of Organocobalt Polymers Bearing Various Substituents[a]

run	polymer	temp (°C)	yield (%)[b]	ratio of x:y[c]	$M_n(M_w/M_n)$[d]
1	**3Eb**	rt	82	79:21	6800 (1.5)
2	**3F**	rt	89	100:0	2500 (2.3)
3	**3G**	40	98	82:18	22900 (1.6)
4	**3H**	60	85	82:18	9100 (1.3)
5	**3I**	40	81	100:0	8400 (2.0)

[a] Polymerization was carried out in toluene for 3 days under N_2. [b] Isolated yields by the precipitation with MeOH. [c] Estimated by ^{1}H-NMR and ^{13}C-NMR spectra. [d] Estimated by GPC (THF, PSt standard).

Synthesis of Various Organocobalt Polymers. In order to prevent the thermal rearrangement of cobaltacyclopentadiene moieties during the polymerization and to control the regioselectivity of repeating units, various diyne monomers **2E**−**2I** were designed and the polymerizations with **1** were carried out in toluene for 3 days under nitrogen (Scheme 4). The reaction conditions, yields, the ratios of the cobaltacyclopentadiene to the CpCbCo unit, and the molecular weights of the obtained plymers are summarized in Table 2.

According to the literature,[8] the sterically hindered substituent of acetylene tends to locate in the 2,5-position of cobaltacyclopentadine moieties. Actually, the reaction of 1-propynylbenzene with **1** brought about the formation of (η^5-cyclopentadienyl)(triphenylphosphine)-2,5-diphenyl-3,4-dimethylcobaltacyclopentadiene as a single isomeric product. Thus, the polymerization of 4,4′-bis(1-propynyl)biphenyl (**2Ea**) with **1** was carried out to obtain a polymer **3Ea** having high regioselectivity. However, the majority of the resulting polymer was insoluble in organic solvents.[10]

To improve the solubility of the polymers, 4,4′-bis(1-decynyl)biphenyl (**2Eb**) was used for the polymerization. While the polymeriation of diynes having aromatic substituents on both sides of the acetylene moieties **2A**−**2C** required a reaction temperature of 50 °C, the polymeriation of **2Eb** was found to take place at room temperature to give an organocobalt polymer **3Eb** in good yield (Table 2, run 1). 1,10-Diphenyl-1,9-decadiyne (**2F**) having an aliphatic substituent between the acetylene moieties also underwent the polymeriation at room temperature (run 2). The ^{13}C-NMR spectra of **3Eb**, **3F**, and the crude product obtained from the model experiment using **4E** are shown in Figure 3. In the cases of

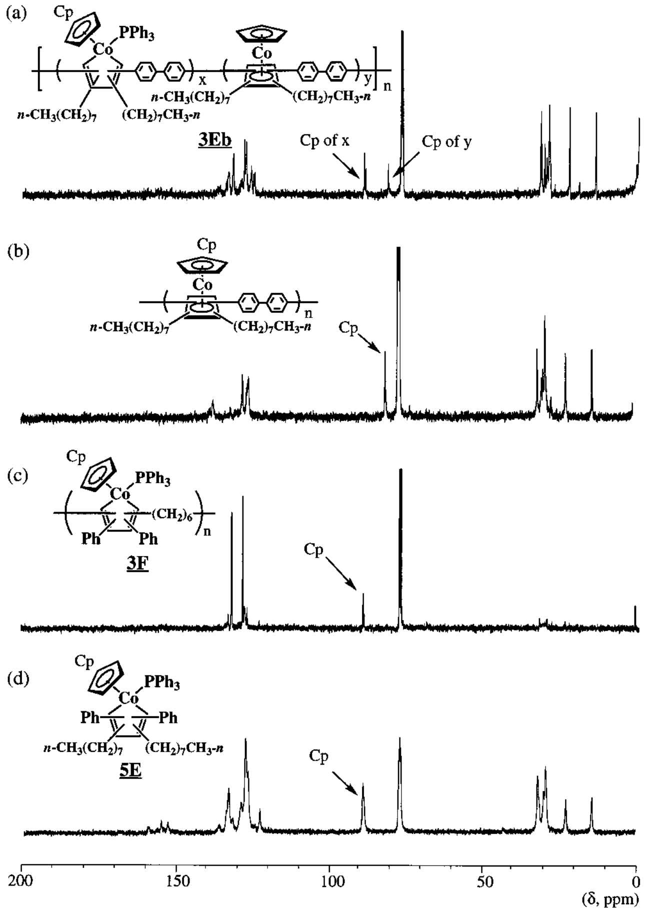


Figure 3. ^{13}C-NMR spectra of **3Eb** (a), a polymer obtained by the thermal rearrangement of **3Eb** (b), **3F** (c), and **5E** (d).

the products obtained by the model experiment and the polymer **3F**, peaks were observed at 89 ppm attributable to Cp of the cabaltacyclopentadiene moieties, indicating that the polymer **3F** has solely the cobaltacyclopentadiene unit. However, in the case of **3Eb**, a small peak was observed at 81.4 ppm besides the main peaks at 89 ppm for Cp of the cobaltacyclopentadiene moieties. The small peak is attributable to the Cp in the CpCbCo unit, judging from the chemical shift of Cp of the polymer produced by the thermal rearrangement of **3Eb** (Figure 3b). Although the result of the model experiment is in good agreement with that of the polymerization using **2F**, which yielded the polymer possessing the desired cobaltacyclopentadiene unit selectively, that using **2Eb** gave a polymer partially containing the CpCbCo unit. The reason for the CpCbCo formation in the case of **2Eb** is not clear; however, it might be due to the formation of the conjugated main chain system through the biphenyl moieties, which reduces the energy for the CpCbCo formation. This explanation might also be applicable to the fact that **3A** contained the CpCbCo unit (ca. 16%) more than expected from the model experiment (6%).

Two peaks were observed at 89 ppm in the ^{13}C-NMR spectra of both **3Eb** and **3F**, probably due to the geometric isomers of cobaltacyclopentadiene moieties (i.e., 2,5-diphenyl-3,4-di-*n*-octylcobaltacyclopentadiene and 2,4-diphenyl-3,5-di-*n*-octylcobaltacyclopentadiene).[8,11] The ^{1}H-NMR spectrum of **3Eb** is shown in Figure 4, where three peaks for Cp moieties were observed. A peak at 4.62 ppm can be assigned to the CpCbCo unit, because the polymer independently prepared by the thermal rearrangement showed a peak at the same chemical shift. Two other peaks at 4.79 and 4.68 ppm can be attributed to 2,4-diphenyl-3,5-di-*n*-octylcobaltacyclopentadiene and 2,5-diphenyl-3,4-di-*n*-octylcobaltacyclopentadiene moieties, respectively.[8] From their integral ratio, **3Eb** was estimated to have the cobaltacyclopentadiene (79 mol %) and the CpCbCo (21 mol %) units, and the ratio of 2,5- and 2,4-diphenyl-substituted isomers of the cobaltacyclopentadiene units was also estimated as 60:40. Similarly, **3F** was estimated to have 100% cobaltacyclopentadiene unit and the 2,5- to 2,4-isomeric ratio was also estimated as 63:37 by the ^{1}H-NMR spectrum.

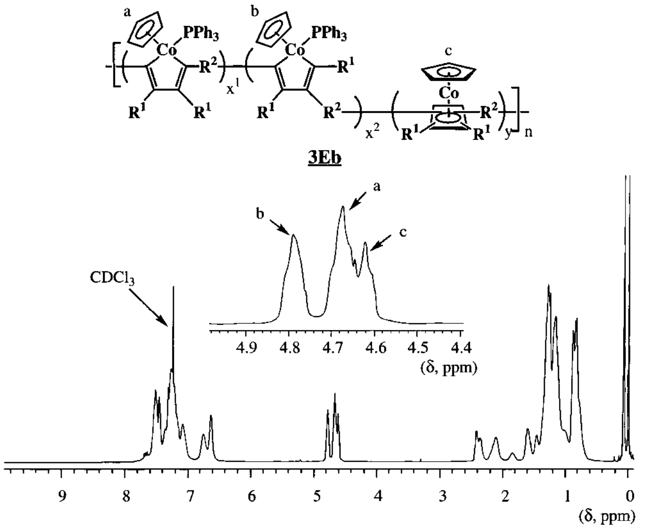
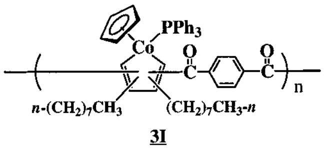


Figure 4. ^{1}H-NMR spectrum of **3Eb**.

In order to study the effects of the electronic character of the substituents on the acetylene moieties, 4,4′-bis[(4-(dodecyloxy)phenyl)ethynyl]biphenyl (**2G**) bearing elecron-donating groups in the side chain and 4,4′-bis[(4-((dodecyloxy)carbonyl)phenyl)ethynyl]biphenyl (**2H**) carrying elecron-withdrawing groups in the side chain were subjected to the polymerization with **1** to give the corresponding polymers (**3G** and **3H**, respectively). Although cobaltacyclopentadienes having electron-withdrawing substituents seem to be insensitive to the conversion to the CpCbCo moieties according to the literature,[12] no significant difference was observed in the ratios of the cobaltacyclopentadiene unit in **3G**, **3H**, and **3A**, which is also consistent with the results of the model experiments (i.e., the (cyclobutadiene)cobalt derivatives were obtained in ca. 6% yields irrespective of the substituents, see Table 1, runs 1, 2, and 4). The regioisomeric ratios in **3G** and **3H** may be statistical, same as for the case of **3A**, although their ^{1}H- and ^{13}C-NMR spectra did not give any information. Compared with the results of the previous work,[3b] **3G** was found to possess more CpCbCo units than the polymer having electron-donating substituents in the main chain by ca. 8%. It can be explained by the same reason mentioned in the cases of **3E** and **3F**.

A bis(ynone) bearing aliphatic lateral groups **2I** was also subjected to the polymerization with **1** for the purpose of obtaining an organocobalt polymer having 2,5-selective main chain linkage. As a result, polymer **3I** was obtained in 81% yield and was soluble in organic solvents. In good agreement with the result of the model experiment, polymer **3I** was found to have the sought after cobaltacyclopentadiene unit, selectively. That is, no peak assignable to the Cp of the CpCbCo moiety was detected in the range 80−85 ppm in the ^{13}C-NMR spectrum (Figure 5a), indicating that **3I** did not



3I

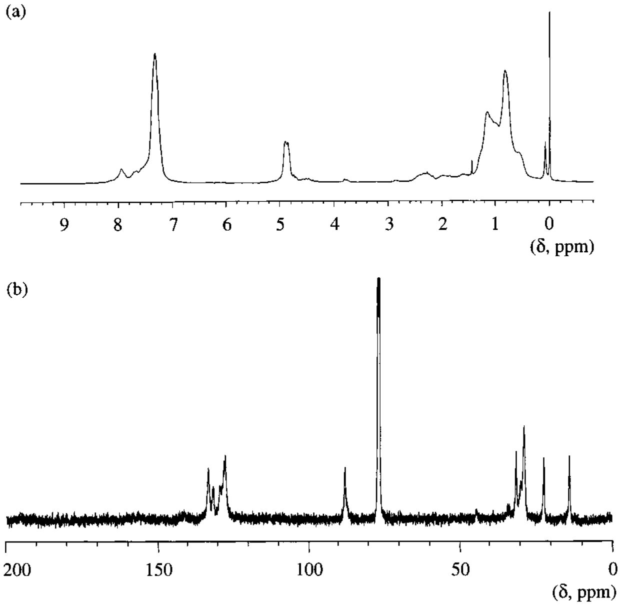


Figure 5. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of **3I**.

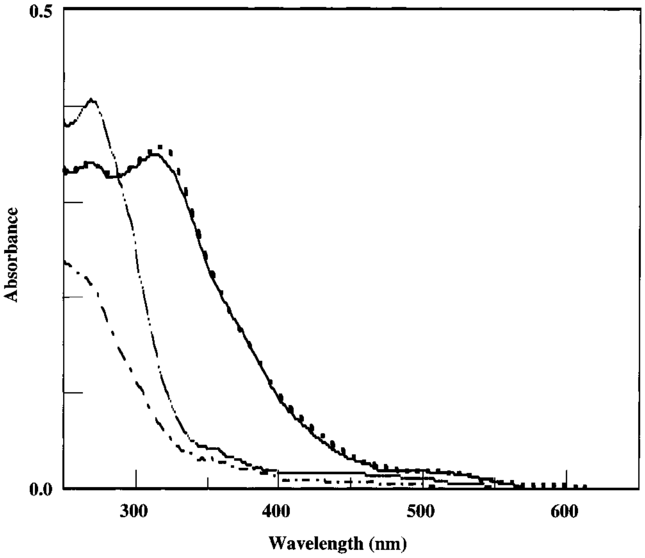


Figure 6. UV–vis spectra of **3A** (—), **3F** (– • –), **3G** (•••), and **5A** (– ••• –) (CHCl$_3$, c = 10^{-5} mol/L, recalculated per repeating unit).

contain the CpCbCo unit (at least in the ^{13}C-NMR sensitivity range). In the ^{1}H-NMR spectrum, peaks for the Cp moieties were observed, although they were too broad to be fully separated from each other. Polymer **3I** was found to have high regioselectivity of the main chain (2,5-,~90%) from the integral ratio of these peaks.

UV–Vis Spectra. UV–vis spectra of the obtained polymers **3A**, **3F**, **3G**, and the model compound **5A** are shown in Figure 6. The UV–vis spectrum of **5A** exhibits the lowest energy π–π* absorption peak at 269 nm. On the other hand, **3A** and **3G** had the corresponding absorption peaks at 312 and 316 nm, respectively, probably indicating the conjugation of repeating units along the polymer backbone. **3H** showed a similar absorption spectrum having a λ_{max} at 329 nm. No significant difference was observed in the absorption spectra of **3A**, **3G**, and **3H**, suggesting that the electronic effects of substituents on the phenyl are not important. Compared with the polymers having an aromatic main chain, **3F** and **3I** did not have λ_{max} at this range, indicating the breaking off of conjugation as a result of the insertion of the hexamethylene spacer and of the carbonyl group, respectively, in the main chain.

Table 3. Thermal Properties of Organocobalt Polymers[a]

	decomposition temp (°C)			
polymer	T_d	T_{d10}	T_{dp30}[c]	weight %[b]
3A	201	241	245	66
3Eb	198	231	225	43
3F	204	237	244	20
3G	202	228	218	43
3H	200	294	264	46
3I	199	226	225	41

[a] Thermogravimetric analyses (TG) were carried out at a heating rate of 10 °C/min. under N$_2$. [b] Weight residue after heating to 500 °C. [c] Temperature for the weight loss corresponding to 30% triphenylphosphine.

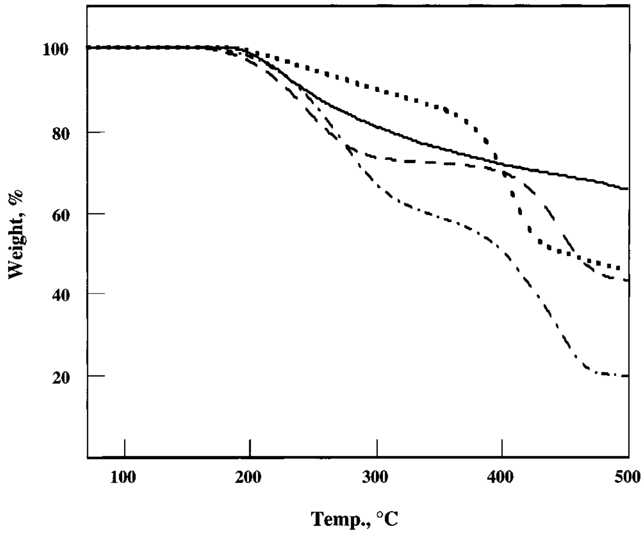


Figure 7. TG traces of **3A** (—), **3F** (– • –), **3G** (- - -), and **3H** (•••) under N$_2$ (10 °C/min.).

Thermal Properties. The thermal stability of the organocobalt polymers was examined by the TG method, and the results are given in Table 3 and Figure 7. Organocobalt polymers **3** except for **3A** showed two-step decompositons on TG below 500 °C. The first decomposition was ascribed to the rearrangement of the cobaltacyclopentadiene unit to the CpCbCo unit, by which the elimination of triphenylphosphine occurred. Although **3A** only showed the decomposition attributable to the elimination of triphenylphosphine, other polymers with aliphatic groups showed the second TG step at about 400 °C assigned to the degradation of polymeric chains (weight losses were approximately equal to the content of aliphatic groups). Especially, **3F** bearing a flexible aliphatic main chain was degraded to leave 20 wt % of the residue.

Although we could not find a remarkable difference in T_d (or T_{d10}), some trends were observed in T_{dp30}, which is the weight loss temperature of 30% of triphenylphosphine. That is, T_{dp30} was observed in the order of **3H** > **3A** > **3Eb** > **3G**, which is in agreement with the increasing order of electron-withdrawing character of the lateral groups. Namely, the higher electron-withdrawing ability of the substituent suppressed the rearrangement, which releases the triphenylphosphine ligand.

Summary

A series of polymers **3** having (η^5-cyclopentadienyl)cobaltacyclopentadiene moieties in the main chain and flexible aliphatic, electron-donating, or electron-withdrawing groups in the main chain or/and in the side chain has been synthesized, and their structures and properties were studied. Although some of the organocobalt polymers including **3A** were found to be contaminated with CpCbCo units, the polymers having an unconjugated main chain were found not to contain the unit. Especially, **3I** having electron-withdrawing groups between the acetylenes and lateral aliphatic groups was found to have predominant 2,5-selective main chain linkage (ca. 90%). The repeating units of the polymers with an aromatic main chain were found to be conjugated along the main chain in the UV−vis spectra. In TG analyses, polymers with higher aromatic contents and the substituent with higher electron-withdrawing character revealed higher thermal stabilities.

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(9) Although the peaks for the cyclopentadienyl moieties of **5A** and **6A** can be resolved well also in the ^{1}H-NMR spectrum (4.62 and 4.78 ppm for **5A** and **6A**, respectively), the corresponding peak could not be separated enough in the case of the polymer when the content of either component is predominant. Thus, the ^{13}C-NMR technique was used for the estimation.

(10) The number average molecular weight (M_n) of the soluble part is 8400. The polymerization of **2Ea** might proceed quantitatively because no diyne monomer remained in the reaction mixture. The lower solubility of the obtained polymer **3Ea** might be due to the higher regioregularity of the polymer, and the fraction with higher molecular weight might be less soluble than the fraction with lower molecular weight.

(11) The formation of 2,5-di-*n*-octyl-3,4-diphenylcobaltacyclopentadiene unit can be denied because the product bearing sterically more hindered phenyl substituents at both the 3- and 4-positions is the isomer most dificult to produce. This is also supported by the result on the model experiment.

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