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Regioselective synthesis and electrochemical properties of π-conjugated cobaltacyclopentadiene oligomer and polymer complexes

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Perfectly π-conjugated cobaltacyclopentadiene oligomer and polymer complexes were synthesized by polycondensation of a dihalogenated cobaltacyclopentadiene complex, $[\overline{\mathrm{Co}\{\mathrm{C}(\mathrm{C_6H_4I\text{-}4})\!=\!\mathrm{CBu^nCBu^n}\!=\!\mathrm{C}}(\mathrm{C_6H_4I\text{-}4})\}\text{-}(\mathrm{cp})(\mathrm{PPh_3})]$ (cp = η^5-C_5H_5), with $[\mathrm{Ni(cod)_2}]$ (cod = cycloocta-1,5-diene). Their internuclear electronic interaction energy in the mixed-valence state, u_{OR}, was estimated to be *ca.* -2 kJ $\mathrm{mol^{-1}}$ by electrochemical analysis.

Organometallic π-conjugated polymers involving transition metals, so called 'conducting polymer complexes', show unique properties due to electronic and magnetic interactions between the metal sites through the π-conjugated chain.[1] We have previously reported a metallacycling polymerization (MCP), which involves a successive addition of diacetylenes to $[\mathrm{Co(cp)(PPh_3)_2}]$ **1** (cp = η^5-C_5H_5), providing a new class of organometallic polymers consisting of cobaltacyclopentadiene units [Scheme 1, equation (1)].[2] Endo *et al.*[3] have reported similar MCP reactions independently. The complex polymers are structurally analogous to organic conducting polymers such as polypyrrole and polythiophene[4] which have five-membered aromatic heterocycles in the main chain. We have recently found that the oxidized forms of the polymer complexes are stable even at room temperature and thus reversible redox doping is possible when methyl groups are substituents on the cobaltacyclopentadiene rings.[5] In these polymers internuclear electronic interaction between the cobalt atoms through the π-conjugated chain should be possible. Unfortunately, however, the complex polymers did not comprise sufficiently long and linear π-conjugated chains, notwithstanding the high molecular weight ($M_n > 10^5$), because satisfactory regioselective polymerization does not take place in the MCP method, forming three binding modes in the polymers [equation (1)].

In this study we have succeeded in synthesizing perfectly linear π-conjugated cobaltacyclopentadiene oligomer and polymer complexes by the polycondensation of a dihalogenated cobaltacyclopentadiene complex, $[\overline{\mathrm{Co}\{\mathrm{C}(\mathrm{C_6H_4I\text{-}4})\!=\!\mathrm{CBu^nCBu^n}\!=\!\mathrm{C}}(\mathrm{C_6H_4I\text{-}4})\}(\mathrm{cp})(\mathrm{PPh_3})]$ with $[\mathrm{Ni(cod)_2}]$. This polymerization method involving polycondensation of dihalogenated compounds with zerovalent nickel complexes has been established by Yamamoto *et al.*[6] for the synthesis of fully π-conjugated polymers such as polythiophene and poly(*p*-phenylene). The internuclear electronic interaction between the cobalt atoms is discussed based on the electrochemical properties of the oligomers thus obtained.

Experimental

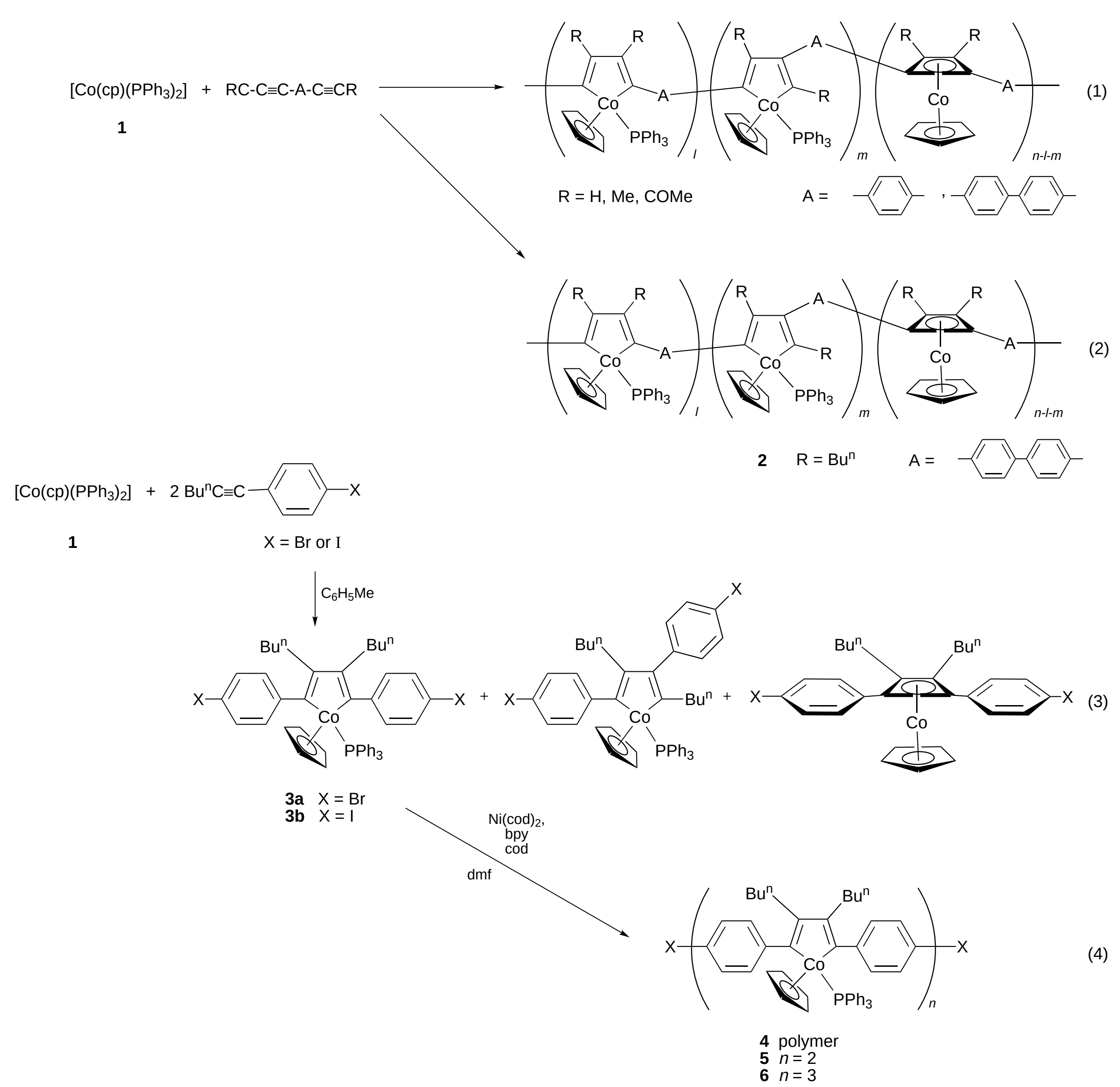
All the reactions were carried out under a nitrogen atmosphere. The complex $[\mathrm{Co(cp)(PPh_3)_2}]\cdot 0.5\mathrm{C_6H_{14}}$ **1** was prepared according to the literature method[7] and recrystallized from toluene–hexane before use. Acetylenic compounds, 4,4′-di(hex-1-ynyl)biphenyl, 1-bromo-4-hexynylbenzene and 1-(hex-1-ynyl)-4-iodobenzene were prepared by the coupling of hex-1-yne with 4,4′-diiodobiphenyl, 1-bromo-4-iodobenzene and 1,4-diiodobenzene, respectively, as described in the literature.[8] The complex $[\mathrm{Ni(cod)_2}]$ and anhydrous solvents were obtained from Kanto Chemicals. Tetra-*n*-butylammonium perchlorate was obtained from Tomiyama Chemicals as lithium battery grade. Dichloromethane used for electrochemical measurements was a HPLC grade chemical from Kanto Chemicals. The NMR and UV/VIS spectra were recorded with JEOL GX400 and JASCO V-570 spectrometers, respectively. Gel permeation chromatography (GPC) analysis of polymerization processes was carried out with a Shimadzu LC-4A HPLC apparatus (column, Tosoh TSKgel 45000HGX; detector, Shimadzu SPD2A UV spectrometer monitoring 254 nm). Separation and purification of polymers and oligomers were carried out with a JAI LC-908 recycling preparative HPLC apparatus with JAIGEL 2H and 3H columns.

Synthesis of cobaltacyclopentadiene polymer 2 [Scheme 1, equation (2)]

To a stirred solution of complex **1** (211 mg, 0.305 mmol) in toluene (5 $\mathrm{cm^3}$) was slowly added a solution of 4,4′-di(but-1-ynyl)biphenyl (95.9 mg, 0.305 mmol) in toluene (2 $\mathrm{cm^3}$). After stirring for 24 h at room temperature the reaction mixture was chromatographed with a recycling preparative GPC apparatus. The solution was concentrated to *ca.* 1 $\mathrm{cm^3}$, to which hexane (15 $\mathrm{cm^3}$) was added. Orange powdery precipitates thus formed were collected by filtration, washed thoroughly with hexane and dried under vacuum. Yield 164 mg, 77% [Found: C, 79.72; H, 7.00. $\mathrm{C_{44.30}H_{43.75}CoP_{0.85}}$ (see Table 1) requires C, 80.43; H, 6.67%]. ^{1}H NMR (C_6D_6): δ 0.8–1.1 (6 H, m, $\mathrm{CH_3}$), 1.2–1.5 (4 H, m, $\mathrm{CH_3C\mathit{H}_2CH_2CH_2}$), 1.6–1.9 (4 H, m, $\mathrm{CH_3CH_2C\mathit{H}_2CH_2}$), 2.4–2.7 (4 H, m, $\mathrm{CH_3CH_2CH_2C\mathit{H}_2}$), 4.6–4.9 (5 H, m, C_5H_5) and 6.8–7.8 (33 H, m, aryl). ^{13}C NMR (C_6D_6): δ 13.94, 14.35, 19.66, 21.60, 23.11, 23.66, 31.81, 32.41, 33.46, 38.96, 81.76, 89.91, 91.52, 123.35, 126.28, 126.73, 126.93, 126.99, 127.26, 128.67, 128.72, 129.02, 129.16, 129.72, 132.52, 132.63, 141.23, 153.73, 156.21, 160.76 and 161.00. ^{31}P NMR (C_6D_6): δ 52.42 (s, $\mathrm{PPh_3}$) and 56.17 (s, $\mathrm{PPh_3}$).

Synthesis of dihalogenated cobaltacyclopentadiene monomers [Scheme 1, equation (3)]

$[\overline{\mathrm{Co}\{\mathrm{C}(\mathrm{C_6H_4Br\text{-}4})\!=\!\mathrm{CBu^nCBu^n}\!=\!\mathrm{C}}(\mathrm{C_6H_4Br\text{-}4})\}(\mathrm{cp})(\mathrm{PPh_3})]$ 3a. Complex **1** (1.08 g, 1.56 mmol) and $\mathrm{Bu^nC{\equiv}CC_6H_4Br\text{-}4}$ (0.74 g, 3.12 mmol) were dissolved in dry toluene (30 $\mathrm{cm^3}$) and the solution was stirred at room temperature for 8 h. The solvent was removed under reduced pressure, and the residue recrystal-



Scheme 1 cp = η^5-C_5H_5, cod = cycloocta-1,5-diene, bpy = 2,2′-bipyridine, dmf = dimethylformamide

lized from benzene–hexane twice to afford **3a** as brown needles. Yield 187 mg, 14%. ^{1}H NMR ($CDCl_3$): δ 0.74 (6 H, t, CH_3, J = 6.93 Hz), 1.10–1.40 (8 H, m, $CH_3CH_2CH_2CH_2$), 2.01 (4 H, m, $CH_3CH_2CH_2CH_2$), 4.57 (5 H, s, C_5H_5), 6.40 (4 H, m, aryl), 6.68 (4 H, m, aryl) and 7.03–7.50 (15 H, m, PPh_3).

[$\overline{Co\{C(C_6H_4I\text{-}4)=CBu^nCBu^n=C}(C_6H_4I\text{-}4)\}(cp)(PPh_3)$] 3b. A mixture of complex **1** (557 mg, 1.56 mmol) and $Bu^nC\equiv CC_6H_4I$-4 (457 mg, 3.12 mmol) dissolved in dry toluene (16 cm^3) was stirred at room temperature for 12 h. The solution was concentrated to *ca.* 1 cm^3 under reduced pressure and hexanes (5 cm^3) was added slowly. The brown precipitates formed were collected and then recrystallized from benzene–MeOH to afford **3b** as brown needles. Yield 244 mg, 32% (Found: C, 59.02; H, 4.99. $C_{47}H_{46}CoI_2P$ requires C, 59.11; H, 4.86%). ^{1}H NMR (C_6D_6): δ 0.84 (6 H, t, J = 6.52 Hz, CH_3), 1.24–1.50 (8 H, m, $CH_3CH_2CH_2CH_2$), 2.37 (4 H, m, $CH_3CH_2CH_2CH_2$), 4.54 (5 H, s, C_5H_5), 6.35 (4 H, m, aryl) and 6.79–7.63 (19 H, m, aryl). ^{13}C NMR (C_6D_6): δ 14.33, 23.37, 31.90, 34.25, 89.49, 128.44, 128.53, 128.79, 128.90, 129.76, 129.89, 130.35, 130.45, 131.11, 133.31, 133.41, 133.47, 133.57, 134.44, 134.53, 136.58, 153.25, 156.08, 156.11, 159.51 and 159.79. ^{31}P NMR (C_6D_6): δ 51.76 (s, PPh_3).

Polymerization of monomers with [Ni(cod)$_2$]

The reaction giving polymer **4** was carried out according to Scheme 1, equation (4). To a stirred solution of complex **3b** (99 mg, 0.10 mmol) in dry dmf (4 cm^3), 2,2′-bipyridine (31 mg, 0.20 mmol), cycloocta-1,5-diene (22 mg, 0.20 mmol) and [Ni(cod)$_2$] (55 mg, 0.20 mmol) were added. The mixture was stirred at 50 °C. The progress of the polymerization was monitored by GPC analysis. The change in GPC chromatogram became negligible after 12 h of reaction. The solvent was removed under reduced pressure and the brown residue chromatographed with a recycling preparative GPC apparatus using toluene as eluent. The solution was concentrated to *ca.* 1 cm^3 and hexane (10 cm^3) slowly added. The brown precipitates thus formed were collected with a glass filter, washed well with hexane and dried in vacuum. Yield 40 mg, 55% [Found: C, 77.62; H, 6.82. $(C_{47}H_{46}CoP)_n$ requires C, 80.54; H, 6.62%]. ^{1}H NMR (C_6D_6): δ 0.8–1.0 (6 H, m, CH_3), 1.1–1.8 (8 H, m, $CH_3CH_2CH_2CH_2$), 2.3–2.7 (4 H, m, $CH_3CH_2CH_2CH_2$) 4.7–4.9 (5 H, m, C_5H_5) and 6.9–7.8 (23 H, m, aryl). ^{13}C NMR (C_6D_6): δ 14.38, 23.55, 32.23, 34.55, 89.75, 125.80, 126.69, 127.77, 128.25, 128.46, 128.54, 128.90, 129.58, 131.60, 132.44, 133.77, 134.71, 136.94, 152.74 and 155.98. ^{31}P NMR (C_6D_6): δ 52.66 (s, PPh_3).

When the reaction was carried out under milder conditions, oligomers with n_{max} = 6 were obtained, where n_{max} refers the highest polymerization degree. The procedure to isolate dimer **5** and trimer **6** is given below.

The complex [Ni(cod)$_2$] (27 mg, 0.10 mmol), bpy (15 mg, 0.10 mmol) and cod (11 mg, 0.10 mmol) were dissolved in dry dmf

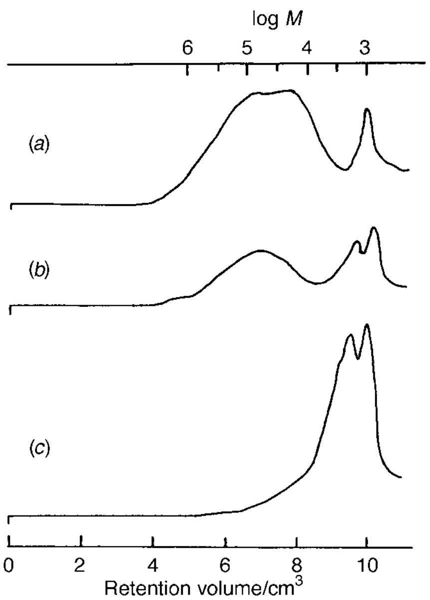


Fig. 1 The GPC spectra for the MCP reaction between $[Co(cp)(PPh_3)_2]$ and $BuC\equiv CC_6H_4C_6H_4C\equiv CBu$ (*a*), and polycondensation of complex **3b** and $[Ni(cod)_2]$ at 50 °C (*b*) and at room temperature (*c*)

(2 cm³). The mixture was stirred for 0.5 h at room temperature to afford a purple solution of [Ni(bpy)(cod)] which was added to a solution of $Bu^nC\equiv CC_6H_4I$-4 (80 mg, 0.084 mmol) in dmf (2 cm³). The mixture was stirred for 48 h at room temperature. The solution was condensed under reduced pressure and the residue chromatographed with a recycling preparative GPC apparatus, resulting in the isolation of dimer **5** and the trimer **6**.

Complex **5**: yield 6.1 mg, 7.6% (Found: C, 68.50; H, 5.78. $C_{94}H_{92}Co_2I_2P_2$ requires C, 68.20; H, 5.60%); ^1H NMR (C_6D_6): δ 0.87 (12 H, t, $J = 7.22$ Hz, CH_3), 1.31–1.62 (16 H, m, $CH_3CH_2CH_2CH_2$), 2.45 (8 H, m, $CH_3CH_2CH_2CH_2$), 4.69 (10 H, s, C_5H_5) and 6.4–7.4 (46 H, m, aryl); ^{13}C NMR (C_6D_6): δ 14.28, 21.89, 32.02, 34.38, 89.64, 122.59, 125.66, 125.83, 127.81, 128.19, 128.29, 128.40, 136.59 and 149.13; ^{31}P NMR (C_6D_6): δ 52.19 (s, PPh_3).

Complex **6**: yield 5.8 mg, 7.2% (Found: C, 71.73; H, 6.20. $C_{141}H_{138}Co_3I_2P_3$ requires C, 71.86; H, 5.91%); ^1H NMR (C_6D_6): δ 0.88 (18 H, t, CH_3), 1.33–1.63 (24 H, m, $CH_3CH_2CH_2CH_2$), 2.45 (12 H, m, $CH_3CH_2CH_2CH_2$), 4.70 (10 H, s, C_5H_5 of end Co atoms), 4.83 (5 H, s, C_5H_5 of center Co atoms) and 6.46–7.43 (69 H, m); ^{13}C NMR (C_6D_6): δ 14.33, 23.37, 31.90, 34.25, 89.49, 128.44, 128.53, 128.79, 128.90, 129.76, 129.89, 130.35, 130.45, 131.11, 133.31, 133.41, 133.47, 133.57, 134.44, 134.53, 136.58, 153.25, 156.08, 156.11, 159.51 and 159.79; ^{31}P NMR (C_6D_6): δ 52.31 (2 P, s, PPh_3 of end Co atoms) and 52.86 (1 P, s, PPh_3 of center Co atoms).

Electrochemical measurements

A glassy carbon rod (outside diameter 5 mm, Tokai Carbon GC-20) was embedded in Pyrex glass and the cross-section used as a working electrode. Cyclic voltammetry was carried out in a standard one-compartment cell under an argon atmosphere equipped with a platinum-wire counter electrode and a $Ag–Ag^+$ reference electrode (10 mmol dm^{-3} $AgClO_4$ in 0.1 mol dm^{-3} NBu_4ClO_4–MeCN) with a BAS CV-50W voltammetric analyzer. The computer software DIGISIM 2 (BAS) of Rudolph *et al.*[9] was used for simulation of cyclic voltammograms.

Results and Discussion

Regioselective synthesis of cobaltacyclopentadiene oligomer and polymer

Table 1 Regioselectivity in the MCP reactions*

R	*l*/*n*	*m*/*n*
Me	0.70	0.15
Bu^n	0.57	0.28

* The values of *l* and *m* are the numbers of cobaltacyclopentadiene units binding at the 2,5 and 2,4 positions, respectively, as shown in Scheme 1, equation (1); *n* is the degree of polymerization.

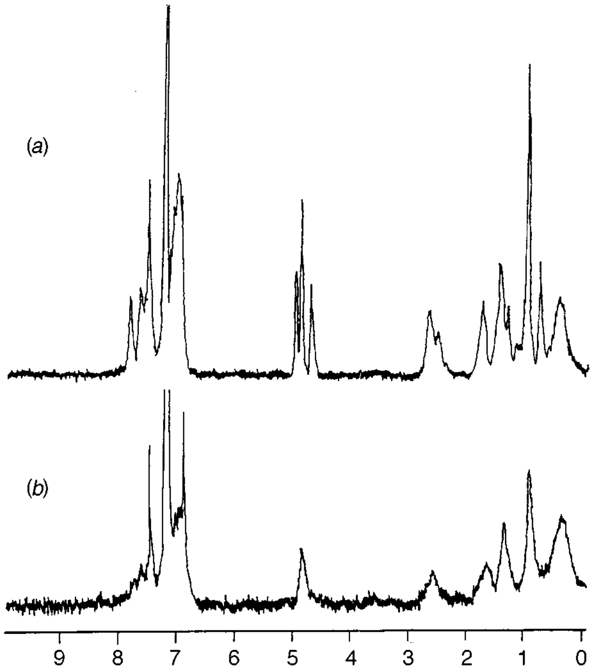


Fig. 2 Proton NMR spectra of compounds **2** (*a*) and **4** (*b*) in C_6D_6

An MCP reaction between $[Co(cp)(PPh_3)_2]$ **1** and the diacetylene $BuC\equiv CC_6H_4C_6H_4C\equiv CBu$ was carried out in order to obtain more information on the regioselectivity [Scheme 1, equation (2)]. The synthetic procedure was similar to that we have previously reported.[5] The polymer obtained was more soluble than the corresponding methyl-substituted polymer and could be purified readily with a GPC apparatus. The GPC spectrum of compound **2** is shown in Fig. 1(*a*). Its number-average molecular weight, M_n, was 2.7×10^5 ($M_w/M_n = 5.2$).

In the ^1H NMR spectrum three singlet signals for cyclopentadienyl groups were observed clearly at δ 4.9, 4.8 and 4.6 [Fig. 2(*a*)]. The ^{13}C NMR spectrum also showed three signals for cyclopentadienyl groups at δ 91.52, 89.91 and 81.76. By comparison with related monomeric complexes, they are attributed to 2,4-diaryl-3,5-di-*n*-butylcobaltacyclopentadiene, 2,5-diaryl-3,4-di-*n*-butylcobaltacyclopentadiene and (η^4-cyclobutadiene)cobalt complexes, respectively. The ^{31}P NMR spectrum showed two signals at δ 52.42 and 56.17 for triphenylphosphine ligands due to the presence of two geometric isomers of cobaltacyclopentadiene. The ratio of the three units was calculated by integration of the values for the cyclopentadienyl rings and the results are in Table 1. As for the regioselectivity of metallacyclization, Wakatsuki *et al.*[10] have shown that the acetylenic carbon bearing a bulky group becomes the α-carbon of the metallacyclopentadiene. In the MCP reaction the regioselectivity with *n*-butyl groups is thus lower than that with methyl groups.

We next attempted to synthesize a cobaltacyclopentadiene polymer comprising a single unit structure using a dihalogenated monomer. For this purpose compounds **3a** and **3b** were newly synthesized by double addition of acetylene $Bu^nC\equiv CC_6H_4X$-4 (X = Br or I) to $[Co(cp)(PPh_3)_2]$ **1**. At the end of the reaction the presence of geometric isomers of **3a** or **3b** was

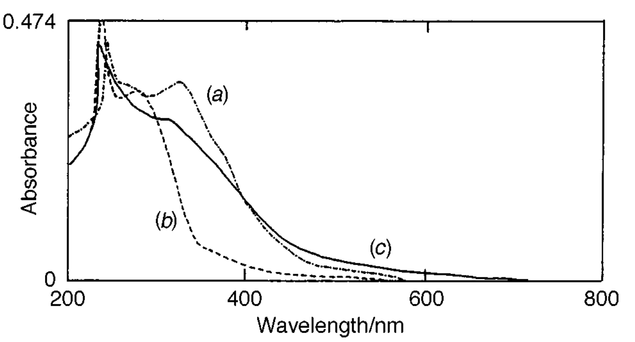


Fig. 3 The UV/VIS spectra of compounds **2** (*a*), **3b** (*b*) and **4** (*c*) in CH_2Cl_2

found by NMR measurements, but they could be removed by recrystallization. The method of polymerization was similar to that for linear π-conjugated polymers reported by Yamamoto *et al.*[6] using $[Ni(cod)_2]$ as a C–C coupling reagent and dmf as solvent. The dibromo-derivative caused no reaction even at 50 °C for 2 d. On the contrary, the diiodo-derivative, **3b**, reacted readily and the progress of the polymerization was monitored by GPC analysis. When the reaction of **3b** was carried out with an excess amount of $[Ni(cod)_2]$ (2.0 equivalents) at 50 °C, the molecular weight, M_n, reached 2.0×10^5 ($M_w/M_n = 2.8$) after 12 h [Fig. 1(*b*)]. When the reaction was carried out with an equimolar amount of $[Ni(cod)_2]$ at room temperature oligomers up to a hexamer were obtained. The polymer and oligomer could be purified with a recycling preparative GPC method. A dimer **5** and a trimer **6** were isolated and used as samples for investigating physical properties in detail. They are soluble in common organic solvents such as toluene, dichloromethane and tetrahydrofuran.

In the ^1H and ^{13}C NMR spectra of compound **4** only a signal for the cyclopentadienyl group appeared at δ 4.8 [Fig. 2(*b*)] and 89.75, respectively. Its ^{31}P NMR spectrum also showed one singlet at δ 52.66 for PPh_3. These results indicated that the cobaltacyclopentadiene polymer consists of only one unit structure.

The UV/VIS absorption spectra of compounds **2**, **3b** and **4** are displayed in Fig. 3. The peak edge in the visible region for polymers **2** and **4** is shifted to longer wavelength than that of the monomer, **3b**. This indicates the formation of a highly π-conjugated structure in the polymer complexes. The peak edge for **4** was further shifted to longer wavelength compared with **2**, because the latter contains structures with unit-to-unit binding at the 2,4 positions of the cobaltacyclopentadiene, unfavorable for π conjugation.

Electrochemistry of cobaltacyclopentadiene complexes

Cyclic voltammograms of the cobaltacyclopentadiene monomer **3b** and polymers **2** and **4** at a glassy carbon electrode in 0.1 mol dm^{-3} NBu_4ClO_4–CH_2Cl_2 are shown in Fig. 4. The monomer undergoes a reversible oxidation at *ca.* −0.02 V and an irreversible oxidation at *ca.* +0.9 V *vs.* Ag–Ag^+ at room temperature [Fig. 4(*a*)]. These results are similar to those for previously reported cobaltacyclopentadiene complexes with no halide groups.[2,4,11,12] The $E^{\circ\prime}$ value and the reversibility of the oxidation reaction of the polymer were almost consistent with those of oligomers [Fig. 4(*b*), (*c*)]. These results support our previous conclusions[12] that the highest occupied molecular orbital (HOMO) based on the d orbital of the metal atoms in the polymer exists between the valence band (VB) and the conduction band (CB) derived from π conjugation, and that oxidation occurs at metal sites. For the polymer, **2** synthesized by the MCP reaction, a small irreversible oxidation wave was found at $E_{p,a} = +0.5$ V *vs.* Ag–Ag^+, similar to the oxidation of $[Co(cp)(\eta^4\text{-}C_4(SiMe_3)_2(C_6H_4C_6H_4C{\equiv}CSiMe_3)_2)]$,[13] indicating that **2** contains (η^4-cyclobutadiene)cobalt complex moieties as noted above.

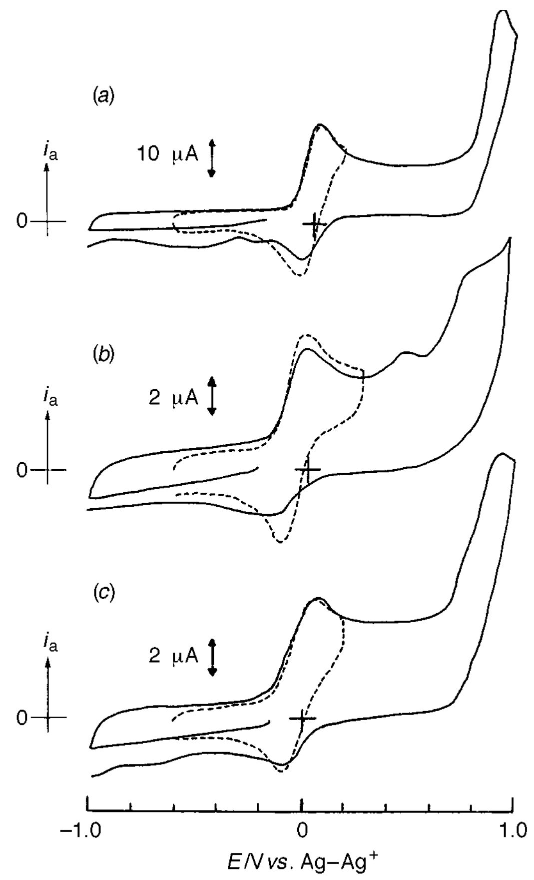


Fig. 4 Cyclic voltammograms of compounds **3b** (*a*), **2** (*b*) and **4** (*c*) at a glassy carbon electrode in 0.1 mol dm^{-3} NBu_4ClO_4–CH_2Cl_2 at a scan rate of 0.1 V s^{-1}

$$\underset{\mathbf{5}}{[\mathrm{Co^{III}}_2]} \overset{E^{\circ\prime}_1}{\rightleftharpoons} [\mathrm{Co^{III}Co^{IV}}] \overset{E^{\circ\prime}_2}{\rightleftharpoons} [\mathrm{Co^{IV}}_2] \qquad (5)$$

$$\underset{\mathbf{6}}{[\mathrm{Co^{III}}_3]} \overset{E^{\circ\prime}_1}{\rightleftharpoons} [\mathrm{Co^{III}Co^{IV}Co^{III}}] \overset{E^{\circ\prime}_2}{\rightleftharpoons} [\mathrm{Co^{IV}Co^{III}Co^{IV}}] \overset{E^{\circ\prime}_3}{\rightleftharpoons} [\mathrm{Co^{IV}}_3] \qquad (6)$$

Scheme 2

The oxidation processes of the dimer and the trimer are shown in Scheme 2, where Co^{III} and Co^{IV} are in neutral and oxidized cobaltacyclopentadiene units, respectively. Although only a single oxidation peak is observed for the dimer and the trimer [see full lines in Fig. 5(*a*), (*b*)], the waves are broader compared with that of the monomer. This discrepancy suggests that the cobalt-(III) and -(IV) sites are weakly interacting and mixed-valence states $Co^{III}Co^{IV}$, $Co^{III}Co^{IV}Co^{III}$ and $Co^{IV}Co^{III}Co^{IV}$ are generated within a narrow potential range. On the basis of computer simulation, the oxidation potentials are calculated to be $E^{\circ\prime}_1 = -75$ and $E^{\circ\prime}_2 = -2$ mV *vs.* Ag–Ag^+ for the dimer, and $E^{\circ\prime}_1 = -81$, $E^{\circ\prime}_2 = -38$ and $E^{\circ\prime}_3 = 21$ mV *vs.* Ag–Ag^+ for the trimer.

Aoki and Chen[14] have reported a theoretical insight on the redox properties of a linearly combined multiredox system based on the electronic interaction energy between neighbouring redox sites. The parameters for evaluating the stability of the mixed-valence states, u_1 and u_2, can be evaluated from the redox potentials. When $u_1 = \frac{1}{2}(u_{RR} + u_{OO}) - u_{OR}$ and $u_2 = \frac{1}{2}(u_{OO} - u_{RR})$, where R and O refer to reduced and oxidized sites respectively the difference in redox potentials $E^{\circ\prime}_3 - E^{\circ\prime}_1$ for a dimer corresponds to $2u_1$, and the differences $E^{\circ\prime}_2 - E^{\circ\prime}_1$ and $E^{\circ\prime}_3 - E^{\circ\prime}_2$ for a trimer correspond to $2u_1 - 2u_2$ and $2u_1 + 2u_2$, respectively. From our experimental results for the dimer, u_1 is calculated to be 3.5 kJ mol^{-1}. Similarly for the trimer, u_1 and u_2 are estimated at 3.0 and 0.96 kJ mol^{-1}, respectively. These

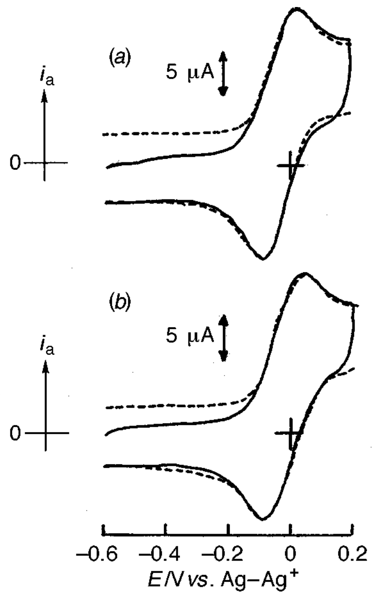


Fig. 5 Cyclic voltammograms of compounds **5** (*a*) and **6** (*b*) at a glassy carbon electrode in 0.1 mol dm^{-3} NBu_4ClO_4–CH_2Cl_2 at a scan rate of 0.1 V s^{-1} (full lines) and their simulation based on the open-boundary finite-diffusion model (broken lines)

values are reasonable because the difference in u_1 between the dimer and the trimer is small. If the value of u_{RR} is assumed to be zero since R is a neutral form and the interaction between neutral forms should be weak, u_{OR} is estimated to be −2 kJ mol^{-1} and is about one-fifth that for poly(1,1′-dihexylferrocenylenes).[15]

A possible rationale of the weak interaction noted above could be the significant difference in energy levels between the occupied π orbital of the phenylene moieties and the HOMO localized on cobalt sites. The energy level of this occupied π orbital should be much lower than that of the HOMO and thus the electronic interaction between the cobalt atoms through the phenylene groups is weak. The lack of coplanarity for the benzene and cobaltacyclopentadiene rings may also contribute to the weak internuclear interaction. This is supported by X-ray crystallographic analysis data that we have reported previously for a 2,4-diphenylcobaltacyclopentadiene complex,[16] indicating that the dihedral angle between the benzene ring at the 2 position and the cobaltacyclopentadiene ring is 58°, larger than the dihedral angle of benzene rings in poly(*p*-phenylene).[17]

Conclusion

The polycondensation method involving a dihalogenated cobaltacyclopentadiene complex and $[Ni(cod)_2]$ has solved the problems of preparing fully π-conjugated cobaltacyclopentadiene polymers which had not been obtained by the MCP method. It is found that the interaction between the cobalt sites in poly(biphenylene cobaltacyclopentadienylene) is rather weak (u_{OR} = *ca.* −2 kJ mol^{-1}).

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