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Synthesis of a Novel π-Conjugated Organometallic Polymer, Poly(4,4'-biphenylene 2,5-cobaltacylopenta-2,4-dienylene), by Metallacycling Polymerization (MCP)

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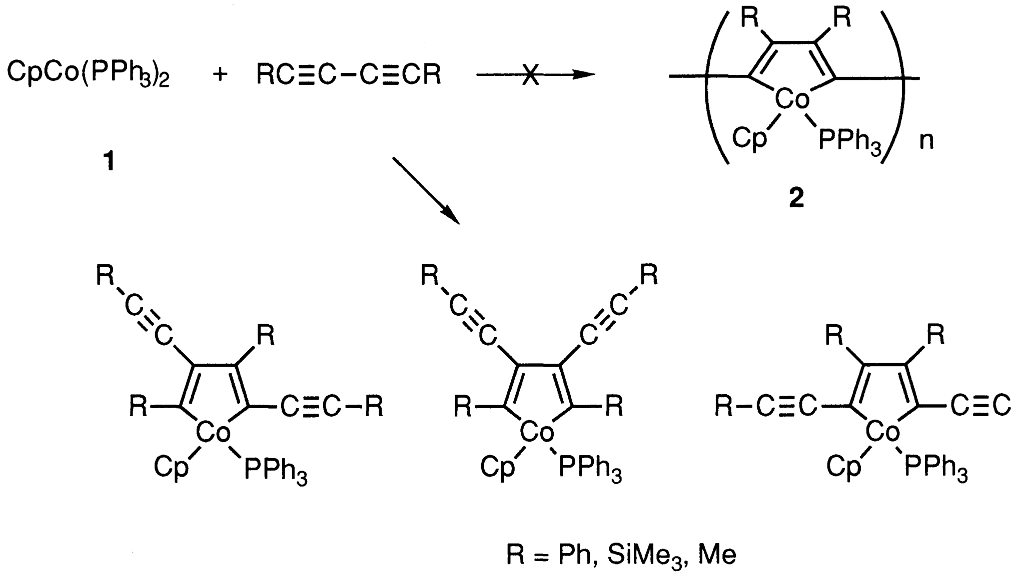
A new π-conjugated organometallic polymer of which framework is in part composed of cobaltacyclopentadienes has been synthesized by a metallacycle formation reaction of $CpCo(PPh_3)_2$ with 4,4'-diethynylbiphenyl. The polymer, poly(4,4'-biphenylene 2,5-cobaltacyclopenta-2,4-dienylene) has a strong absorption band around 500 nm, and is oxidized at + 0.306 V *vs.* Ag/Ag^+ in dichloromethane and reduced at -1.8 V in acetonitrile.

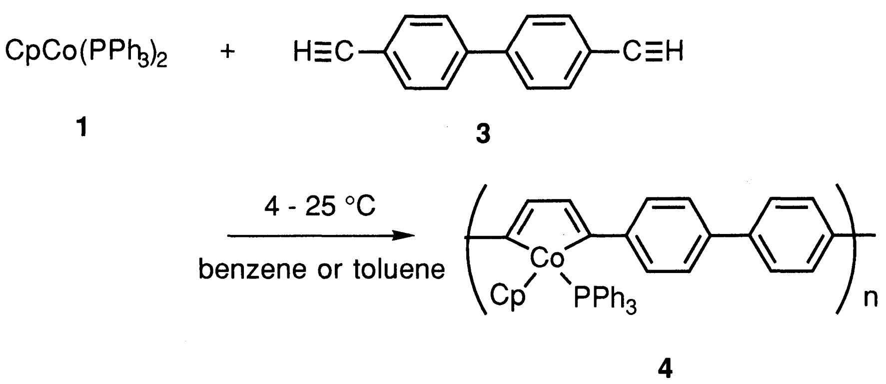
π-Conjugated organic polymers have been of recent interest because of their unique electrical, electrochemical and optical properties utilizable to various applications.1) Metallacyclopentadiene is structurally analogous to five-membered aromatic heterocycles (*e.g.*, thiophene or pyrrole), which are familiar fundamental units of such π-conjugated polymers showing high conductivity in the doped state.1) It is thus deduced that metallacyclopentadiene-based polymers can constitute a new class of organometallic conducting materials,2) but to our knowledge a method for their polymerization has not been developed.3) We present here a new method of polymerization based on metallacyclization reactions (this polymerization is abbreviated as MCP) and its utilization for the synthesis of a π-conjugated organometallic polymer wherein the framework is in part composed of cobaltacyclopentadienes. Preliminary spectroscopic and electrochemical characteristics of the polymer are also reported.

Reaction of $CpCo(PPh_3)_2$ (**1**) with two molecules of an acetylene derivative has been established as a synthetic method for thermally stable cobaltacyclopentadienes.4) This reaction suggests that α,β-diynes, $RC\equiv C\text{-}C\equiv CR$, would give organometallic π-conjugated polymers (**2**) if its successive and regioselective addition to **1** were to take place. Our attempts to effect this polymerization reaction using α,β–diynes with R = Ph, $SiMe_3$ and Me have resulted in isolation of only monomeric cobaltacyclopentadiene complexes having two alkynyl units.5) This resistance to polymerization is likely to be result of the seriously strained structure **2** due to bulky ligands such as Cp or PPh_3.6) The geometry of the formed complexes follows the regioselectivity rule of the cyclization process that the acetylenic carbon bearing a bulky substituent becomes the α-carbon of the metallacycle,5) which has been demonstrated experimentally and theoretically by Wakatsuki et al.7)

Our next approach to the synthesis of π-conjugated organometallic polymers by MCP was to use 4,4'-diethynylbiphenyl (**3**), in which the π-conjugated biphenylene moiety has been inserted between the two C-C triple bonds to eliminate the steric crowdedness which inhibits the successive metallacyclization reaction. The small terminal group, H, is effective for the regioselective metallacyclization at 2,5-positions. Reaction of **3** with **1** afforded a new π-conjugated organometallic polymer, **4**, by MCP under mild conditions.



(1)



(2)

In a typical reaction, 191 mg of **1** and 74 mg of **3** was mixed in 6.3 cm^3 of toluene and stirred at 4 °C for 72 h under Ar. Dark-brown precipitates formed and were collected, washed with toluene until the filtrate became colorless, and dried under vacuum for 1 day. Yield: 118 mg (61% assuming the structure **4**).8) The yield of the insoluble product is maximal when the mole ratio of **1** to **3**, is around one, as would be expected from the stoichiometry of the polymerization reaction (2).9) The UV-VIS diffuse-reflection spectrum of the polymer shows a strong 480 nm peak which is not seen in a monomeric cobaltacyclopentadiene complex (see Fig. 1). This band implies the highly conjugated structure1) that is possible only for the 2,5-substituted structure as **4**. It should be noted that a decrease in the mole ratio of **1** to **3** and/or lower reaction temperature lead to darkening in color, and an increase in λ_{max} (see Fig. 1), probably due to an the increase in the number of π-conjugated units.11) When the mole ratio of **1** to **3** is large (2.0), the product shows a weak $\nu(C_{acetylene}\text{-}H)$ band at 3300 cm^{-1}, but no $\nu(C_{acetylene}\text{-}H)$ bands are detectable in the IR spectra of the products when the mole ratio of **1** to **3** is less than 1.5. This indicates that the average molecular weight of the polymer increases with decreasing the mole ratio of **1** to **3**. The degree of polymerization roughly estimated from the ratio in absorbance of the $\nu(C_{acetylene}\text{-}H)$ band to the ν(C-C) band of biphenyl moiety at 1003 cm^{-1} based on the data of **3** ($\nu(C_{acetylene}\text{-}H)$ 3274; ν(C-C) 1004 cm^{-1}) is 20 (accordingly m.w. = *ca.* 11000) when the mole ratio of **1** to **3** is 2.0.

Cyclic voltammograms of films of **4** coated on indium-tin oxide (ITO)-coated glass electrodes are displayed

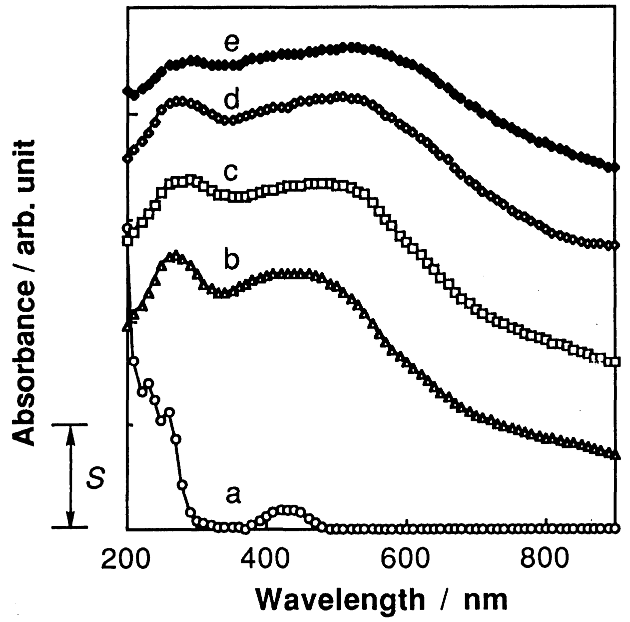


Fig. 1. Absorption spectrum of $Cp(PPh_3)[\overline{CoC(C{\equiv}CMe){=}CMe{-}CMe{=}C}(C{\equiv}CMe)]$ (1.4 μmol dm^{-3} in MeCN, S = 0.02) (a) and diffuse-reflection spectra of **4** prepared in benzene at room temperature when the mole ratio of **1** to **3** was 2.0 (b), 1.2 (c) and 0.8 (d) and in toluene at 4 °C with the ratio 0.8 (e). For (b) - (e), S = 0.5 and horizontal lines are shifted upwards by 0.4 absorbance units.

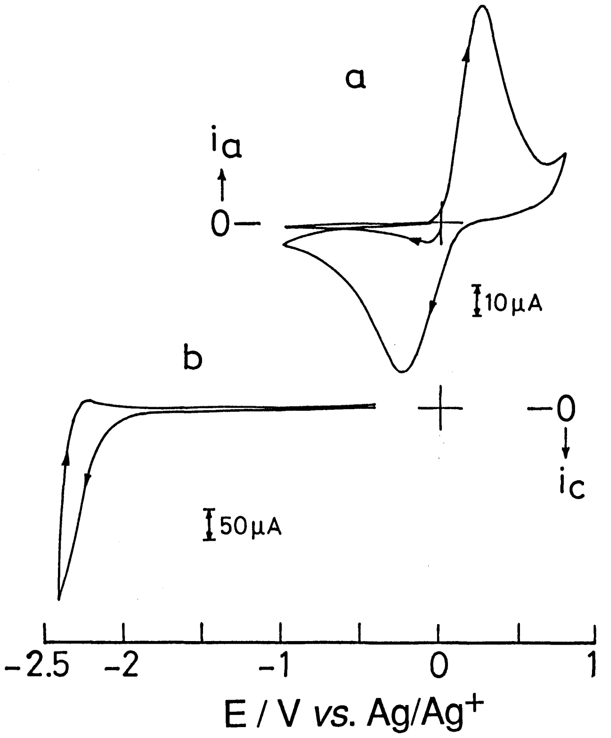


Fig. 2. Cyclic voltammograms of **4** coated on ITO at 20 mV s^{-1}: (a) in n-Bu_4NClO_4-CH_2Cl_2 at -63 °C, (b) in n-Bu_4NClO_4-MeCN at -24 °C.

in Fig. 2.[12] The oxidation reaction of **4** occurs at $E_{p,a}$ = +0.306 V *vs.* Ag/Ag$^+$ (10 mmol dm^{-3} $AgClO_4$ in 0.1 mol dm^{-3} n-Bu_4NClO_4-MeCN) and rereduction at $E_{p,c}$ = -0.236 V at a scan rate of 20 mV s^{-1} in 0.1 mol dm^{-3} n-Bu_4NClO_4-CH_2Cl_2 at -63 °C. This reversibility of the oxidation reaction decreases with increasing the temperature and only the oxidation wave is seen at room temperature even at 1 V s^{-1}. The oxidation potential is similar to that of analogous monomeric cobaltacyclopentadiene complexes.[5,10,13] Reduction of **4** occurs at *ca.* -1.8 V *vs.* Ag/Ag$^+$ (no peak appears) and a small reoxidation peak is observed at -2.25 V in 0.1 mol dm^{-3} n-Bu_4NClO_4-MeCN at -24 °C. This reduction potential is also similar to that of monomeric cobaltacyclopentadienes.[13,14] The brownish yellow film in the neutral form changes to black upon oxidation and dark brown upon reduction. A detail study of the electrical and thermal properties of the material and the synthesis of analogous new π-conjugated organometallic polymers using MCP are in progress.

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9) When the reaction was carried out in benzene at room temperature for 24 h, the yields were 5, 73, 80, 92, 70, and 63% when the mole ratio of **1** to **3** was 0.5, 0.8, 1.0, 1.2, 1.5, and 2.0, respectively.

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