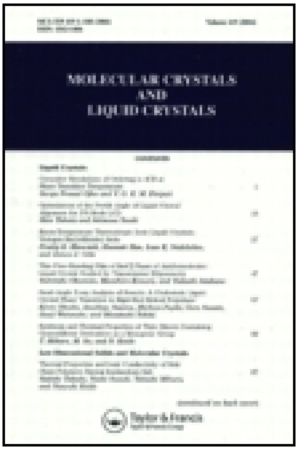

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Synthesis of Poly(Arylene Cobaltacyclopentadienylene)s and Their Oxidative Doping Behaviors

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SYNTHESIS OF POLY (ARYLENE COBALTACYCLOPENTADIENYLENE)S AND THEIR OXIDATIVE DOPING BEHAVIORS

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Abstract Two poly(arylene cobaltacyclopentadienylene)s, **3b** and **3c** were synthesized and their electrochemical properties investigated. The polymer with methyl groups at 3,4-positions of cobaltacyclopentadiene ring, **3b** undergoes reversible oxidation at room temperature and shows 10^{-4} Scm^{-1} of electrical conductivity when chemically doped with I_2.

INTRODUCTION

π-Conjugated organic polymers have attracted much interest because of their unique electrical, electrochemical and optical properties utilizable to various applications. We have previously reported that metallacycling polymerization (MCP), the successive addition of diacetylenes to $CpCo(PPh_3)_2$ (**1**), provides a new kind of organometallic π-conjugated polymer complexes, poly(arylene cobaltacyclopentadienylene)s.[1] They are structurally analogous to the organic conducting polymers such as polypyrrole and polythiophene which have five-membered aromatic heterocycles in the main chain, and expected to show electronic interaction between transition metal atoms through the π-conjugated chain. Therefore, their physical and chemical properties are of great interest.

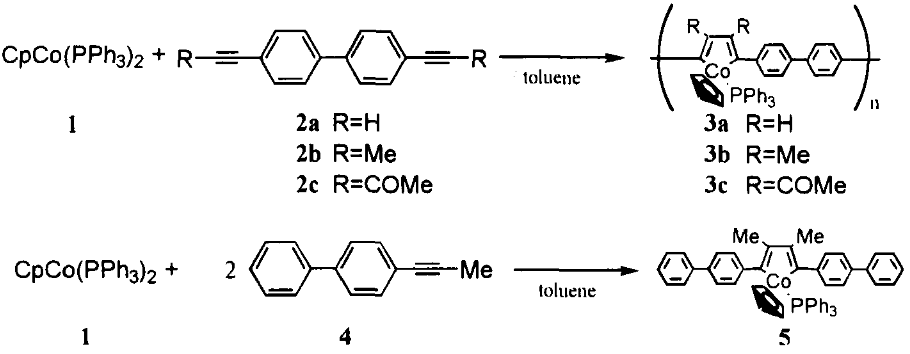
Our preceding study has shown that a polymer complex, **3a**, undergoes quasi-reversible oxidation at +0.04 V *vs.* Ag/Ag^+ at 210 K in Bu_4NClO_4-CH_2Cl_2 but the oxidation becomes irreversible at room temperature.[2] In this study, we have synthesized its derivatives, **3b** and **3c**, and investigated the effects of the substituents at cobaltacycle on the electrochemical properties and oxidative doping behaviors. In order to characterize the polymers in detail, a related monomeric cobaltacyclopentadiene complex, **5**, was also synthesized as a reference.

EXPERIMENTAL

1. Synthetic procedure

All the reactions were carried out under nitrogen or argon. $CpCo(PPh_3)_2$ (**1**) was synthesized according to the literature.[3] 4,4'-Di(1-propynyl)-biphenyl (**2b**) and 4-(1-propynyl)biphenyl (**4**) were synthesized by a coupling reaction of 1-propyne with 4,4'-diiodobiphenyl and 4-bromobiphenyl, respectively.[4] 4,4'-Bis(3-oxo-1-butynyl) biphenyl (**2c**) was synthesized by oxidation of 4,4'-bis(3-hydroxy-1-butynyl)biphenyl,[5] obtained by a coupling reaction of 1-butyn-3-ol with 4,4'-diiodobiphenyl.[4]

SCHEME



Poly(4,4'-biphenylene dimethylcobaltacyclopentadienylene) (**3b**)

To a stirred solution of **1** (127 mg, 0.184 mmol) in 5 cm^3 toluene was slowly added a solution of **2b** (42.3 mg, 0.184 mmol) in 2 cm^3 toluene. After stirring for 12 h at room temperature, the reaction mixture was chromatographed with a JAI LC-908 recycling preparative HPLC apparatus with JAIGEL-2H and JAIGEL-3H columns and toluene as an eluent. The solution was concentrated into ca. 2 cm^3, to which 10 cm^3 of hexane was slowly added to give an orange powdery precipitate, which was collected by filtration. Yield 60.0 mg, 53%. ^{1}H NMR (C_6D_6) δ 8.0-6.8 (m, 23H, aryl group), 4.9-4.4 (m, 5H, Cp), 2.4-1.8 (m, 6H, methyl group), IR (KBr) 3019, 2921, 2847, 1561, 1482, 1089, 1003, 745, 696, 529 cm^{-1}.

Poly(4,4'-biphenylene diacetylcobaltacyclopentadienylene) (**3c**)

To a stirred solution of **1** (181 mg, 0.262 mmol) in 5 cm^3 THF was slowly added a solution of **2c** (74.9 mg, 0.262 mmol) in THF (2 cm^3). After stirring for 72 h at room temperature, the solution was filtered and concentrated into ca. 2 cm^3, to which 10 cm^3 of hexane was slowly added to give an brown powdery precipitated. Yield 91.5 mg, 53%. IR (KBr) 3053, 2197, 1670, 1638, 1601, 1482, 1433, 1350, 1312, 1183, 1090, 1001, 837,747, 696, 527 cm^{-1}.

2,5-Dibiphenylyl-3,4-dimethylcobaltacyclopentadiene (**5**)

1 (295 mg, 0.426 mmol) and **4** (164 mg, 0.852 mmol) were dissolved in 5 cm^3 toluene and stirred at room temperature for 12 h to give a dark brown solution. The solution was concentrated into ca. 2 cm^3, to which 10 cm^3 of hexane was slowly added to give a brown precipitate, which was recrystallized from benzene-hexane to afford brown needles of **5**. Yield 180 mg, 55%. ^{1}H NMR (C_6D_6) δ 7.84-7.04 (m, 33H, aryl group), 4.87 (s, 5H, Cp), 2.09 (s, 6H, methyl group). IR (KBr) 3022, 2924, 2851, 1597, 1482, 1433, 1090, 1007, 760, 696, 531 cm^{-1}.

2. Measurements of Physical Properties

Cyclic voltammetry was carried out using a standard three-electrode cell equipped with an ITO-coated glass sheet (area, 2 cm^2) or a glassy-carbon (GC) disk (5 mm-o.d.) working electrode, platinum-wire counter electrode and an Ag/Ag$^+$ reference electrode. VIS spectra during the electrolysis were obtained using a JASCO V-570 UV/VIS/NIR spectrophotometer. Oxidative doping of polymeric complexes was carried out by exposing them under vapor of I_2 for several hours and drying under vacuum for 8 h. Electrical conductivity was measured by a two-contact method under vacuum.

RESULTS AND DISCUSSION

1. Molecular weight of the polymer complexes.

Molecular weight of the obtained polymer complexes were estimated by GPC analysis based on the polystyrene standard. The Mn and Mw values of **3b** were 4.0×10^5 and 1.8×10^6, and those of **3c** were 3.0×10^4 and 1.1×10^5, respectively. Lower molecular weight of **3c** than **3b** should be due to slow rate of addition of **2c** to **1** because electron density on the triple bond of **2c** is lower by electron withdrawing effect of acetyl group.

2. Electrochemistry

Cyclic voltammograms of polymeric and monomeric complex are shown in Figure 1. A polymer **3b** undergoes reversible oxidation at $E^{0'} = -0.03$ V *vs.* Ag/Ag$^+$ even at room temperature. The $E^{0'}$ value is similar to that of the monomeric complex, **5**, indicating slight effects of elongation of π-conjugated chain. This strongly suggests that the oxidation occurs at the Co site as has been reported previously.[1] On the other hand, oxidation of **3c** is irreversible even at 210 K at ca. 0.2 V *vs.* Ag/Ag$^+$, a potential more positive to that of **3b**. The lower $E^{0'}$ and higher reversibility of oxidation for **3b** than **3a** and **3c** might be explained by the stabilization of radical cation of **3b** because of the electron donating effect of the methyl group on the cobaltacyclopentadiene ring.

3. Spectroelectrochemistry

VIS spectra of **3b** and **5** in the neutral form are displayed in Figure 2A, in which the peak edge for **3b** is shifted to a longer wavelength compared with that for **5** due to the increase of π-conjugation length. Spectroelectrochemistry was carried out for a thin film of **3b** spin-coated on ITO and **5** dissolved in solution and the result is given in Figure 2B. When potential is held at +0.1 V, where both the complexes are partly oxidized, absorbance at $\lambda > 550$ nm increases, instead of decreasing absorbance at shorter wavelength. Especially for **3b**/ITO, absorbance around 800 nm increased significantly, which is not observed for **5**. This changes in VIS spectra should be the intervalence-transfer (IT) band due to the electronic interaction between Co(III) and Co(IV) through a π-conjugated chain as the mixed-valence state is formed when Co sites are partly oxidized.

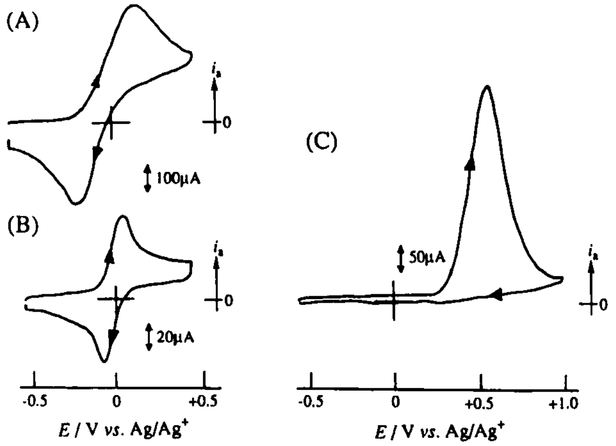


FIGURE 1 Cyclic voltammograms of **3b**/ITO in Bu_4NClO_4-MeCN at r.t. (A), **5** in Bu_4NClO_4-CH_2Cl_2 at r.t. (B), and **3c**/ITO in Bu_4NClO_4-MeCN at 210 K (C) at a scan rate of 0.1 Vs^{-1}.

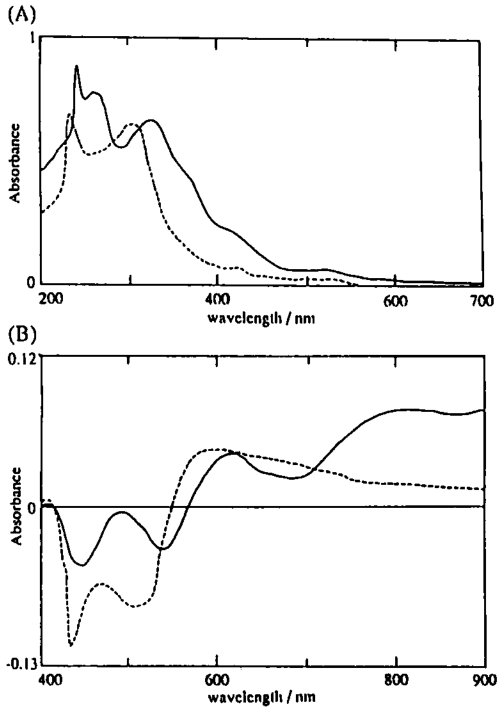


FIGURE 2 (A) UV-VIS spectra of **3b** (solid line) and **5** (broken line) in neutral forms. (B) Differences in VIS spectra of **3b** (solid line) and **5** (broken line) at -0.5 V from those at +0.1 V.

4. Electrical conductivity

Arrhenius plots of electrical conductivity for polymer complexes, **3a** and **3b**, are displayed in Figure 3. We have already reported that **3a** has 10^{-9} Scm^{-1} of conductivity in the undoped state at room temperature.[6] Conductivity of the methyl-substituted polymer, **3b**, was 10^{-6} Scm^{-1} at room temperature. When **3b** was chemically doped by I_2, conductivity increased up to 10^{-4} Scm^{-1}. This result could be interpreted as follows: I_2-doping generates Co(III) / Co(IV) mixed-valence states in the polymer chain; this state is stable to some extent as suggested by the measurements of cyclic voltammetry; and consequently, Co(III) and Co(IV) sites are interacted through a π-conjugated chain, causing the mixed-valent conductivity.

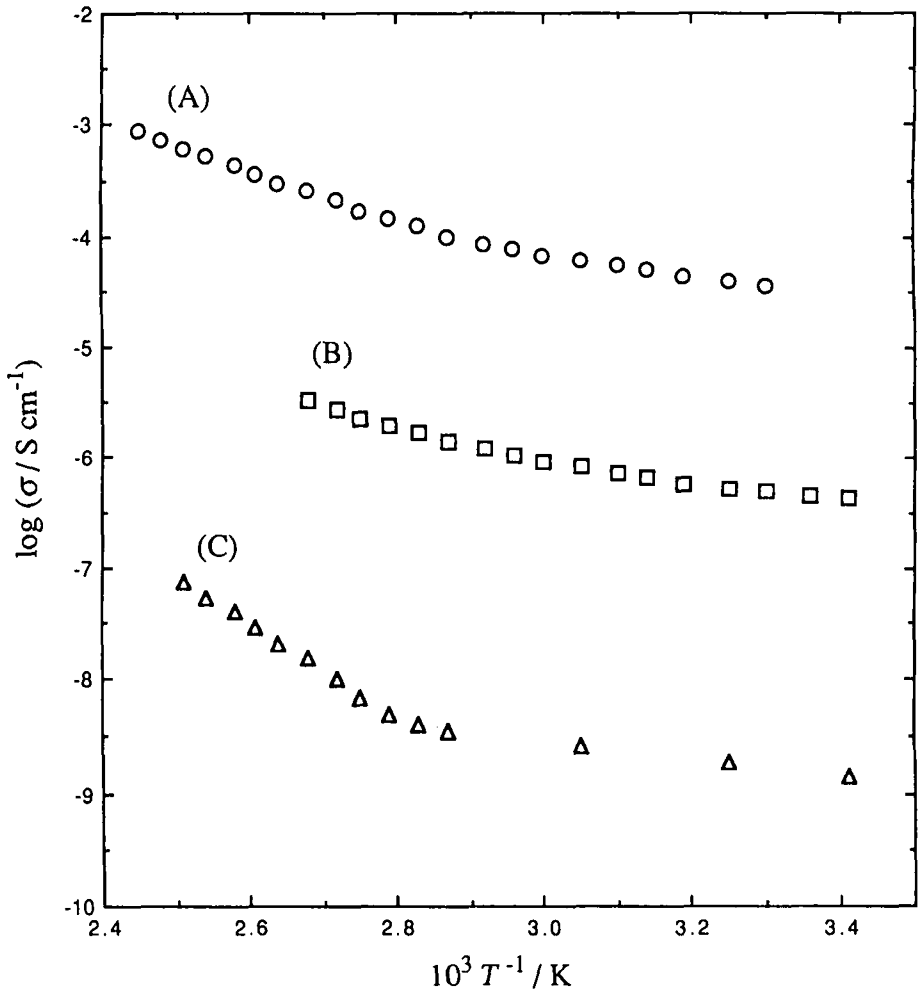


FIGURE 3 Arrhenius plots of electrical conductivity for the polymer complexes, I_2-doped **3b** (A), undoped **3b** (B), and undoped **3a** (C).

CONCLUSION

We have synthesized new poly(arylene cobaltacyclopentadienylene)s involving methyl group, **3b**, and acetyl group, **3c**. Reversible oxidation occurs for **3b** at room temperature, whereas the oxidation of **3c** is irreversible. Electronic interaction between Co sites in the mixed-valence state for **3b** was suggested by measurements of spectroelectrochemistry. Electrical conductivity increased up to 10^{-4} Scm^{-1} by oxidative doping with I_2.

ACKNOWLEDGMENTS

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REFERENCES

1. H. Nishihara, T. Shimura, A. Ohkubo, N. Matsuda and K. Aramaki, *Adv. Mater.*, 1993, **5**, 752.
2. A. Ohkubo, K. Aramaki and H. Nishihara, *Chem. Lett.*, **1993**, 271.
3. Y. Wakatsuki and H. Yamazaki, *Inorg. Synth.*, 1989, **26**, 191.
4. K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, **50**, 4467.
5. K. Bowden, I. M. Heilbron, E. E. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, **1946**, 39.
6. H. Nishihara, A. Ohkubo and K. Aramaki, *Synth. Met.*, 1993, **55**, 821.