Macromol. Symp. ***196***, *27–38 (2003)*

Organometallic Conducting Polymers Synthesized by Metallacycling Polymerization

Hiroshi Nishihara, Masashi Kurashina, Masaki Murata*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-0033, Japan

Summary: The study on the synthesis of π-conjugated polymers using cobaltacyclopentadiene formation reaction of $CpCo(PPh_3)_2$ and conjugated diacetylene and the structure and physical properties of the polymers is overviewed. The substituents on the diacetylene affect crucially the solubility, the degree of polymerization, redox properties, and electronic structures and so on. Recent synthesis of a ruthenacyclopentatriene polymers by metallacyling polymerization is also described.

Keywords: cobalt; conducting polymers; metallacycle; organometallic polymers; redox properties; ruthenium

Introduction

Discovery of so-called "conducting polymers" comprising organic π-conjugated polymer chains such as polyacetylene is one of the epoch-making scientific events in the last century.[1] This is because they exhibit various curious physical and chemical characteristics that exploded the concept of "durable" plastics. Main characteristics such as facile oxidation and reduction leading to charge storage, high electronic conductivity in the doped states, electrochromism, photo- and electro-luminescence are derived from π-electrons which can be delocalized along the π-conjugated chain.[2] One of the extended studies of such organic conducting polymers is to incorporate other functional molecular units into the polymer chain. For example, synthesis of ferromagnetic materials by attaching organic radicals as pendant groups of the π-conjugated main chain has been investigated extensively in recent years.[2] Another effective way to functionalize conducting polymers is to combine them with functional metal complex units, which gives a category of "organometallic conducting polymers".[3] Examples include polymetallocenylene,[4,5] poly(metalyne),[6-10] poly(metallo-phthalocyanine),[11,12] polydecker sandwich compounds,[13]

CCC 1022-1360/00/$ 17,50+.50/0

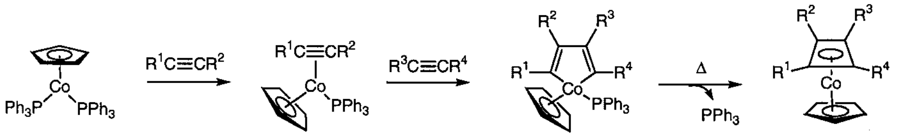
thiolate complex polymers,[14-16] cyclobutadienecobalt complex polymers,[17] and others.[18] A decade ago, we have developed a new class of organometallic conducting polymers wherein the framework of the polymer is π-conjugated and in part composed of cobaltacyclopentadienes.[19] In these polymers, the cobaltacyclopentadiene ring with its *d*-block heteroatom is structurally analogous to the rings found in other representative π-conjugated polymers, such as poly(pyrrole) and poly(thiophene), which contain *p*-block heteroatoms. Synthesis of the cobaltacyclopentadiene polymers has been accomplished by a new type of polymerization scheme, MetallaCycling Polymerization (MCP), that is based on successive metallacyclization. As for the similar kinds of metallacycle polymers, Endo *et al.* have reported the MCP reactions for cobalt complex polymers, independently,[20] and Tilley *et al.* have reported the MCP reactions for zirconacyclopentadiene polymers.[21] In these metallacyclopentadiene polymers, it is interesting to probe the effect that a *d*-transition metal heteroatom has on the π-system and electronic properties of a conducting polymer.

In the present article, we review the history of our study on the cobaltacyclopentadiene-based organometallic polymers and recent results on the ruthenacyclopentatriene-based organometallic polymers.

Synthesis of Cobaltacyclopentadiene Polymers

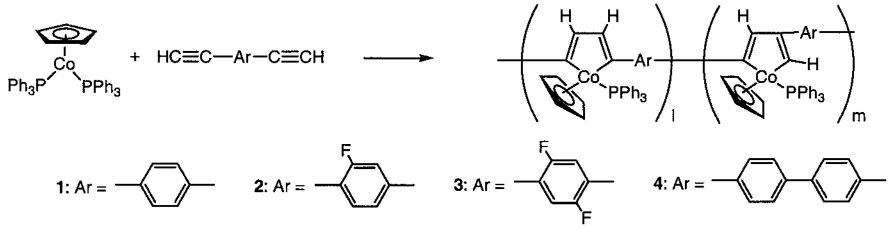
1. Polymers obtained from HC≡C-Ar-C≡CH

It is well established that the addition of two acetylenes to the metal center affords mtallacyclopentadiene, which is the precursor of the formation of six-membered aromatic rings.[22-25] This reaction accompanies the C-C bond formation, indicating that it can be used for MCP when diacetylene, which cannot cause intramolecular C-C coupling reaction, is employed. In the case of cobaltacyclopentadiene, the most common starting compound is $[\mathrm{CpCo(PPh_3)_2}]$ (Cp = η^5-$\mathrm{C_5H_5}$), which reacts with two acetylenes, $\mathrm{CR^1{\equiv}CR^2}$ and $\mathrm{CR^3{\equiv}CR^4}$ stepwise, affording $[\mathrm{CpCo(CR^1{\equiv}CR^2)(PPh_3)}]$ and then $[\mathrm{CpCo(CR^1{=}CR^2\text{-}CR^3{=}CR^4)(PPh_3)}]$ (Eq (1)). A further addition reaction with unsaturated compounds such as acetylene and nitrile gives aromatic six-membered rings. It is also known that the thermal reaction of cobaltacyclopentadiene $[\mathrm{CpCo(CR^1{=}CR^2\text{-}CR^3{=}CR^4)(PPh_3)}]$ affords cyclobutadiene complex, $[\mathrm{CpCo(\eta^4\text{-}C_4R^1R^2R^3R^4)}]$ (Eq (1)).[26] This kind of unique chemical reactivity of metallacyclopentadiene units can be utilized to obtain interesting polymeric substances from metallaycyclopentadiene polymers.



(1)

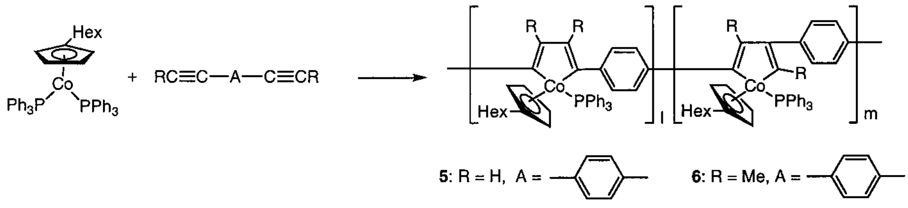
Application of the metallacyclization to the polymer synthesis has been successfully made using conjugated diacetylene with the formula, HC≡C-Ar-C≡CH (Ar = 1,4-phenylene, 2-fluoro-1,4-phenylene, 2,5-difluoro-1,4-phenylene, and 4,4'-biphenylene), and the polymers, **1** – **4**, respectively, were obtained as insoluble powders.[27] The insertion of the arylene moieties in the diacetylene is because the diacetylene without a spacer, RC≡C-C≡CR, could not yield polymers because of the high steric hindrance due to Cp and PPh_3 groups around the cobalt center.[28,29]

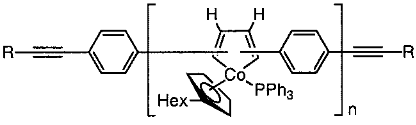


The regioselectivity of the metallacyclization is important to obtain highly π-conjugated polymers by MCP. When the cobaltacyclopentadiene unit is formed from two CR≡CR' molecules, there are three possible isomers, 2,4-R_2-3,5-R'_2, 2,5-R_2-3,4-R'_2 and 3,4-R_2-2,5-R'_2 forms. Wakatsuki *et al.* have shown the rule that the acetylenic carbon bearing a bulky group becomes the α-carbon of the metallacyclopentadiene.[30] The diacetylenes HC≡C-Ar-C≡CH of the first attempt have been chosen because they would give 2,5-Ar_2 structures according to the rule above. The polymers obtained are insoluble and could give films when the glass plates are immersed in the solution of the MCP synthesis. Electronic spectra of the polymers show the red shift of the absorption edge compared with the monomeric complex, indicating the extension of π-conjugation by the involvement of 2,5-Ar_2 structures in the polymers. However, the results on the soluble polymers suggest incomplete π-conjugation by the involvement of 2,4-Ar_2 units (*vide infra*).

2. Soluble polymers

The insolubility of the polymers often prevents their characterization and processability. An improvement of the solubility has carried out using hexylcyclopentadienyl (HexCp) ligand instead of Cp in the starting cobalt complex[31, 32] and/or using alkyl-terminated diacetylenes, RC≡C-Ar-C≡CR (R = Me, Bu).[33, 34] The purpose of the attempt to synthesize soluble cobaltacyclopentadiene polymers using $(HexCp)Co(PPh_3)_2$ was not only to increase the polymerization degree but also to characterize the polymers in detail including the regioselectivity in MCP reactions. An MCP reaction between $(HexCp)Co(PPh_3)_2$ and *p*-diethynylbenzene at 4 °C for 4 days gave no insoluble product, and the GPC spectrum of the reaction product indicated several oligomeric and polymeric components, **5**, the highest molecular weight of which is more than 7×10^4 based on the polystyrene standard.[32] The oligomeric components $HC{\equiv}C\text{-}C_6H_4[C_4H_2\{Co(HexCp)(PPh_3)\}\text{-}C_6H_4]_nC{\equiv}CH$ were separated up to nonamer, $\mathbf{5_2}$-$\mathbf{5_9}$. The ^1H NMR analysis indicated that the products were mixtures of these two isomeric structures, 2,5- *vs.* 2,4-substituted cobaltacyclopentadienes with the ratio of 4 : 6. As mentioned above, the regioselectivity is principally dominated by the steric effect of the substituents on the acetylenic carbon. However, this result indicates another factor, probably the dipole-dipole interaction of two acetylenes ligated to cobalt, is concerted in determining the conformation at the intermediate state. Reinvestigation of the stereochemistry of the metallacyclization for monomeric complexes actually support this consideration; a reaction of $(HexCp)Co(PPh)_2$ with ethynylbenzene afforded 2,5- and 2,4-diphenylcobaltacyclopentadienes with the ratio of 4 : 6.

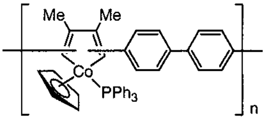




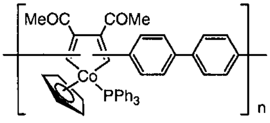
$\mathbf{5_2}$ - $\mathbf{5_9}$: n = 2 - 9

Our next attempt to increase the yield of 2,5-diarylcobaltacyclopentadiene using 1-propynylbenzene instead of ethynylbenzene, expecting the large steric repulsion between phenyl and methyl groups in the 2,4-diphenyl-3,5-dimethylcobaltacycllpentadiene, resulted in the yield of 80% of the desirable isomer.[32] This was applied to the polymer synthesis; MCP reactions between $(HexCp)Co(PPh_3)_2$ and *p*-di-1-propynylbenzene performed at room temperature and 40 °C affords a soluble product, **6**, of which GPC spectra shows a drastic enhancement of polymerization by the temperature increase.

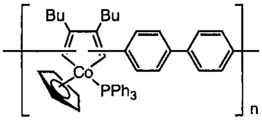
In the course of the study using RC≡C-Ar-C≡CR, we recognized the increase in solubility in organic solvents compared with the polymers of HC≡C-Ar-C≡CH, even if $CpCo(PPh_3)_2$ was used as the starting material. The reaction of $CpCo(PPh_3)_2$ with MeC≡C-*p*-C_6H_4-C_6H_4-*p*-C≡CMe,[33] with MeOCC≡C-*p*-C_6H_4-C_6H_4-*p*-C≡CCOMe,[33] with $BuC{\equiv}CC_6H_4C_6H_4C{\equiv}CBu$,[34] with MeC≡C-*p*-$C_6H_4$-C≡CMe,[35] and with MeC≡C-2,5-C_4H_2S-C≡CMe[35] afforded soluble polymers, **7** with $M_w/M_n = 4.0 \times 10^5$ ($M_w/M_n = 4.5$), **8** with 3.0×10^4 ($M_w/M_n = 3.7$), **9** with $M_n = 2.7 \times 10^5$ ($M_w/M_n = 5.2$), **10** with $M_n = 3.8 \times 10^5$ ($M_w/M_n = 4.5$), and **11** with $M_n = 4.4 \times 10^3$ ($M_w/M_n = 1.3$), respectively.



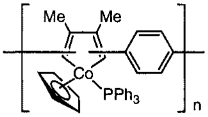
7



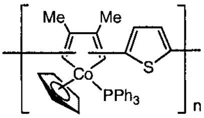
8



9



10

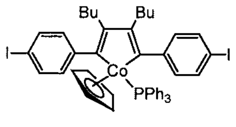


11

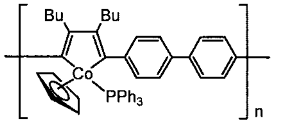
3. Perfectly conjugated polymers synthesized by polycondensation of a dihalogenated cobaltacyclopentadiene complex

As the regioselective polymerization had not been achieved by the metallacycling polymerization, another method utilizing a polycondensation of a dihalogenated cobaltacyclopentadiene complex, $Cp(PPh_3)[Co\text{-}C(4\text{-}C_6H_4I){=}CBu\text{-}CBu{=}C(4\text{-}C_6H_4I)]$ (**12**) , with $[Ni(cod)_2]$ (cod = cycloocta-1,5-

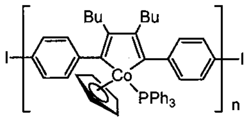
diene), was applied for the synthesis of perfectly π-conjugated polymer, **13**.[34] When the reaction of **12** was carried out with an excess amount of $Ni(cod)_2$ (2.0 eq) at 50 °C, the molecular weight, M_n, reached to 2.0×10^5 ($M_w/M_n = 2.8$) after 12 h. When the reaction of **12** was carried out with an equimolar of $Ni(cod)_2$ at a room temperature, the oligomers up to a hexamer were obtained. The polymer and oligomer could be purified with a recycling preparative GPC method. Especially, a dimer $\mathbf{13_2}$ and a trimer $\mathbf{13_3}$ were isolated and used as samples for investigating physical properties in detail.



12



13



$\mathbf{13_2}$: n = 2, $\mathbf{13_3}$: n = 3

Physical Properties of Cobaltacyclopentadiene Polymers

1. Electronic spectra

The color of all the cobaltacyclopentadiene polymers noted above is dark brown and the UV-Vis absorption spectra of the films of **1-4** coated on quartz glass show strong bands that have an edge at 500 to 600 nm.[32] As for the soluble polymer, the band edge shifts to the higher wavelength according to an increase in polymerization degree for **9** in CH_2Cl_2 solutions, indicating the formation of π-conjugated structure.[32] The perfectly π-conjugated polymer **13** prepared by polycondensation on dihalogenated complex exhibit a shift of the peak edge to the longer wavelength compared with the corresponding polymer, **9** prepared by metallacycling polymerization.[34]

Band gap energies, E_g, for the cobaltacyclopentadiene polymers were evaluated from the absorption edge based on the semiconductor theory.[36] The E_g values thus evaluated were 2.1 to 2.3 eV,[32] which correspond roughly to the value observed in poly(thiophene) (2.0 eV) and are relatively small when compared to the band gaps among previously known π-conjugated organic polymers.[2]

2. Redox properties

Cobaltacylopentadiene complexes undergo one-electron oxidation and their potential and chemical reversibility depend strongly on the substituents on the metallacycle.[37-40] This directly reflects the redox properties of the cobaltacylopentadiene polymers. The oxidation potential of the polymers becomes more positive when the electron-withdrawing substituents such as –COMe was bound to the metallacycle,[33] and the chemical reversibility increases in the order of the substituents, -COMe < -H < alkyl (-Me, Bu).[33] The polymers with alkyl groups as substituents show cyclic voltammograms indicating high chemical reversibility at a scan rate of 0.1 Vs^{-1} in NBu_4ClO_4-CH_2Cl_2. These results support our consideration that the HOMO based on *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 the oxidation occurs at metal sites.

In the cyclic voltammograms of a dimer $\mathbf{13}_2$ and a trimer $\mathbf{13}_3$, the waves are broader compared with that of the monomer, although only a single oxidation peak is observed for the dimer and the trimer.[34] This discrepancy suggests that Co(III) and Co(IV) sites are weakly interacted and the 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 $E^{0'}_1$ = -0.285 V and $E^{0'}_2$ = -0.212 V *vs.* ferrocenium/ferrocene (Fc^+/Fc) for the dimer, and $E^{0'}_1$ = -0.291 V, $E^{0'}_2$ = -0.248 V, and $E^{0'}_3$ = -0.189 V *vs.* Fc^+/Fc for the trimer.

Aoki and Chen have reported a theoretical insight on the redox properties of a linearly combined multi-redox system based on the electronic interaction energy between the neighbouring redox sites.[41] The parameters for evaluating the stability of the mixed-valence states, u_1 and u_2 can be evaluated from the redox potentials. When $u_1 = (u_{RR} + u_{OO})/2 - u_{OR}$ and $u_2 = (u_{OO} - u_{RR})/2$, the difference in redox potentials $E^{0'}_2 - E^{0'}_1$ for dimer corresponds to $2u_1$, and the differences $E^{0'}_2 - E^{0'}_1$ and $E^{0'}_3 - E^{0'}_2$ for trimer correspond to $2u_1 - 2u_2$ and $2u_1 + 2u_2$, respectively. From the experimental results for the dimer, u_1 is calculated to be 3.5 kJ mol^{-1}.[34] Similarly for the trimer, u_1 and u_2 are estimated at 3.0 and 0.96 kJ mol^{-1}, respectively. These 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-fifths compared with that for oligo(1,1'-dihexylferrocenylene)s.[42,43]

The oxidation wave in the cyclic voltammograms of thenylene-bridged cobaltacyclopentadiene polymer is fairly broader than that of the phenylene-bridged one.[35] This is because the energy level for the highest occupied π-orbital of thiophene is closer than that of phenylene to *d*-orbital level of the cobalt site, so that the internuclear electronic interaction through the thiophene ring is considered to be stronger. In the oxidation process, therefore, more than one oxidation waves due to the formation of mixed-valence states overlap, resulting in a broad wave in the cyclic voltammogram.

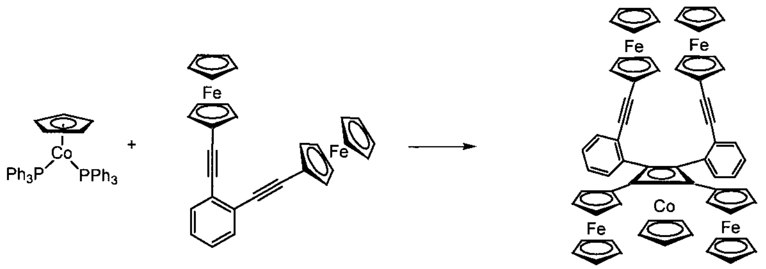
3. Electrical conductivity and photoconductivity

The cobaltacyclopentadiene polymers **4** and **7** show an electrical conductivity of 10^{-12} - 10^{-6} $\mathrm{Scm^{-1}}$ in the neutral form at room temperature.[33,44] When **7** was treated with I_2, the conductivity increased up to 10^{-4} $\mathrm{Scm^{-1}}$.[33] This result could be interpreted by the consideration that 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 electrochemical properties; and consequently, Co(III) and Co(IV) sites are interacted through a p-conjugated chain, causing the mixed-valence conductivity.

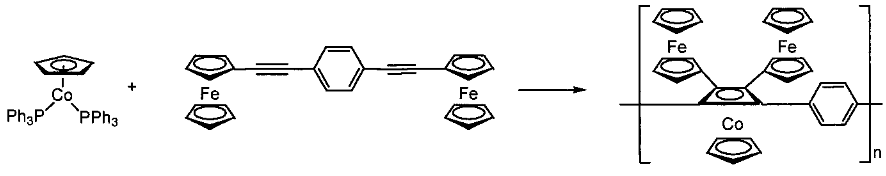
The intrinsic photoconductive property was found for a cobaltacyclopentadine polymer **6**.[32] Photo-response of i-V characteristics for ITO/**6**/ITO indicates that the polymer has a low conductivity in dark, and photocurrent is four times larger than the dark current. This kind of remarkable photoconductivity does not appear for common π-conjugated organic polymers in the undoped state but is caused by forming charge-transfer complexes with donor or acceptor molecules such as fullerene.[45,46] We propose that the metal d-character orbitals localized at cobalt sites and their energy level lying between valence and conduction bands act as the trapping sites of holes generated by photo-activation of electrons from the valence band to the conduction band.

Cyclobutadienecobalt Polymer Containing Ferrocenyl Groups

The reaction of $\mathrm{CpCo(PPh_3)_2}$ with a π-conjugated diacetylene, FcC≡C-*o*-$\mathrm{C_6H_4}$-C≡CFc, in which Fc = ferrocenyl, was found to give a cyclobutadienecobalt mononuclear complex, $\{\eta^4\text{-}\mathrm{C_4Fc_2}(o\text{-}\mathrm{FcC{\equiv}CC_6H_4})_2\}\mathrm{CoCp}$ (**14**), the crystal structure of which was determined by X-ray crystallography.[47] The complex **14** shows reversible $1e^-$ and $3e^-$ redox waves at $E^{0'}$ = 0.067 and 0.000 V *vs.* $\mathrm{Fc^+/Fc}$ according to the strong electronic interaction between ferrocenyl groups on the cyclobutadiene ring. In contrast, the reaction of $\mathrm{CpCo(PPh_3)_2}$ with FcC≡C-*p*-$\mathrm{C_6H_4}$-C≡CFc affords a polymer.[47] The reaction at 50 °C for 22 h, followed by reprecipitation from toluene-hexane afforded an orange powdery solid. Its ^{1}H NMR spectrum showed a signal of Cp coordinated to Co at δ5.00 and no signals due to PPh_3. This result and the broadness of the signals suggest the formation of a cyclobutadiene complex polymer, $[p\text{-}C_6H_4\{(\eta^4\text{-}C_4Fc_2)CoCp\}]_n$ (**15**). GPC analysis of **15** showed that M_n = 5500 and M_w = 9600, based on the polystyrene standard. The molecular weight of 5500 indicates that the degree of polymerization is ca. 9. There are two possibilities for the geometric structure of the cyclobutadiene unit, either a 1,2-diferrocenyl or 1,3-diferrocenyl conformation. The ratio of these two structures has not been determined because of the broadness of the ^{1}H NMR signals. However, the redox properties of **15** showing two chemically reversible redox waves at $E^{0'}$ = 0.149 and 0.210 V *vs.* Fc$^+$/Fc, indicating a strong electronic interaction between ferrocenyl groups suggest that 1,2-diferrocenylcyclobutadiene is the primary structure in the polymer.



14

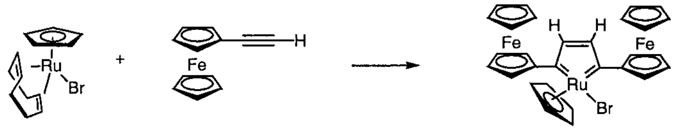


15

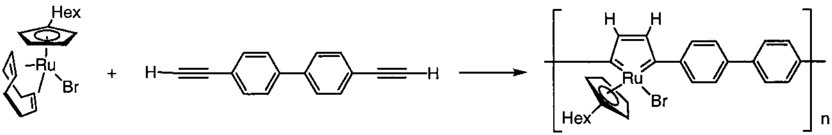
Ruthenacyclopentatriene Polymer

Ruthenacyclopentatriene is formed by the metallacycling reaction of two RC≡CH molecules with CpRuBr(cod) or $(\eta^5\text{-}C_5Me_5)RuCl(cod)$.[48,49] The difference in the cyclization reaction compared with the cobalt system described above is the regioselectivity of this reaction. It was reported that only 2,5-R_2 isomer is formed in the case R = Ph. Our study for the reaction using ethynylferrocene also afford one isomer, 2,5-bis(ferrocenyl)ruthenacyclopentatriene, **16**.[50] Cyclic voltammetry of this complex showed a reversible one-electron reduction due to the ruthenacycle and a two-step one-electron oxidation of the ferrocenyl moieties. Separation of the redox potentials of the ferrocenyl moieties was 0.24 V, and the electronic spectrum of one-electron oxidized species exhibited an intervalence-transfer band at 1180 nm. These results indicate the existence of significant electronic interactions between two ferrocenyl moieties through the ruthenacyclopentatriene ring.

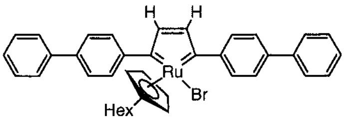
Utilization of the ruthenacycle formation reaction for the polymer synthesis has been recently achieved by the reaction of (HexCp)RuBr(cod) with $HC{\equiv}C\text{-}p\text{-}C_6H_4\text{-}C_6H_4\text{-}p\text{-}C{\equiv}CH$.[51] The reaction carried out at 0 °C for 90 h gave a polymer **17** with $M_n = 3400$ ($M_w/M_n = 1.7$). UV-vis spectra of the polymer shows a shift of the π–π^* band to a longer wavelength due to the enlargement of the π-conjugation. The polymer undergoes reversible reduction due to the ruthenacylcle moiety at −1.01 V vs. Fc^+/Fc, which is similar to that of the corresponding monomer, **18**.



16



17



18

Conclusion

The cobaltacyclopentadiene formation reaction using conjugated dieacetylnes affords a π-conjugated conducting organometallic polymers. Regioselectivity of the metallacyclization is important for the π-conjugation, and up to present, 80% of the regioselectivity has been achieved for the cobaltacylopentadiene polymers. Perfectly π-conjugated cobaltacyclopentadinene polymer was synthesized by a polycondensation of a dihalogenated cobaltacyclopentadiene complex. The oxidation of the cobalt center occurs facilely and the location of the Co *d*-orbital between the conduction and valence bands brings intrinsic photoconductivity. Ferrocenyl A π-conjugated ruthenacylcopentatriene polymer was also synthesized by the metallacyling polymerization.

Acknowledgments

This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 14044021 (area 412) ,14204066) from the Ministry of Culture, Education, Science, Sports, and Technology, Japan, and by The 21st Century COE Program for Frontiers in Fundamental Chemistry.

[1] H. Shirakawa, *Angew. Chem. Int. Ed. Engl.* **2001,** 40, 2575, and the references therein.
[2] H. S. Nalwa (Ed.), "Handbook of Organic Conductive Molecules and Polymers", Wiley-VCH, Weinheim 1997.
[3] H. Nishihara, in "Handbook of Organic Conductive Molecules and Polymers", H. S. Nalwa, Ed., Wiley, Weinheim 1997, Vol. 2, Chapter 19, pp. 799-832.
[4] E. W. Neuse, *J. Macromol. Sci.-Chem.* **1981,** *A16*, 3.
[5] T. Yamamoto, K. Sanechika, A. Yamamoto, *Inorg. Chim. Acta* **1983**, *73*, 75.
[6] Y. Okamoto, M. C. Wang, *J. Polym. Sci., Polym. Let. Ed.* **1980**, *18*, 249.
[7] K. Krikor, M. Rotti, P. Nagles, *Synth. Met.* **1987**, *21*, 353.
[8] H. Matsuda, H. Nakanishi, M. Kato, *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 107.
[9] N. Hagihara, K. Sonogashira, S. Takahashi, *Adv. Polym. Sci.* **1980**, *41*, 159.
[10] M. S. Khan, S. J. Davies, A. K. Kakkar, D. Schwartz, B. Lin, B. F. D. Johnson, J. Lewis, *J. Organomet. Chem.* **1992**, *87*, 424.
[11] J. W. P. Lin, L. P. Dudek, *J. Polym. Sci., Polym. Chem. Ed.* **1985,** *23*, 1579.
[12] S. Venkatachalam, K. V. C. Rao, P. T. Manoharan, *Synth. Met.* **1988**, *26*, 237.
[13] T. Kuhlmann, S. Roth, J. Rozière, W. Siebert, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 105.
[14] R. A. Clark, K. S. Varma, A. E. Underhil, J. Becher, H. Toftlund, *Synth. Met.* **1988**, *25*, 227.
[15] J. R. Reynolds, F. E. Karasz, C. P. Lillya, J. C. W. Chien, *J. Chem. Soc., Chem. Commun.* **1985**, 268.
[16] R. Vincete, J. Ribas, P. Cassoux, L. Valade, *Synth. Met.* **1986**, *13*, 265.
[17] M. Altmann, U. H. F. Bunz, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 569.
[18] H. S. Nalwa, *Appl. Organometal. Chem.* **1990**, *4*, 91.
[19] A. Ohkubo, K. Aramaki, H. Nishihara, *Chem. Lett.* **1993**, 271.
[20] I. Tomita, A. Nishio, T. Igarashi, T. Endo, *Polym. Bull.* **1993**, *30*, 179.
[21] J. R. Nitschke, S. Zurcher S, T. D. Tilley, *J. Am. Chem. Soc.*, **2000,** *122*, 10345.
[22] H. Yamazaki, N. Hagihara, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2260.

[23] Y. Wakatsuki, H.Yamazaki, *J. Chem. Soc., Chem. Commun.* **1973**, 280.

[24] Y. Wakatsuki, T. Kuramitsu, H. Yamazaki, *Tetrahedron Lett.* **1974**, 4549.

[25] H. Bönnenman, *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248.

[26] K. M. Nicholas, M. O. Nestle, D. Seyferth, in "Transition Metal Organometallics in Organic Synthess", H. Alper Ed., Academic Press, New York, 1978, Vol. 2.

[27] H. Nishihara, T. Shimura, A. Ohkubo, N. Matsuda, K. Aramaki, *Adv. Mater.* **1993**, *5*, 752.

[28] T. Shimura, A. Ohkubo, K. Aramaki, H. Uekusa, T. Fujita, S. Ohba, H. Nishihara, *Inorg. Chim. Acta* **1995**, *230*, 215.

[29] T. Fujita, H. Uekusa, A. Ohkubo, T. Shimura, K. Aramaki, H. Nishihara, S. Ohba, *Acta Cryst.* **1995**, *C51*, 2265.

[30] Y. Wakatsuki, O. Nomura, K. Kitaura, K. Morokuma, H. Yamazaki, *J. Am. Chem. Soc.* **1983**, *105*, 1907.

[31] N. Matsuda, T. Shimura, K. Aramaki, H. Nishihara, *Synth. Metals* **1995**, *69*, 559.

[32] T. Shimura, A. Ohkubo, N. Matsuda, I. Matsuoka, K. Aramaki, H. Nishihara, *Chem. Mater.* **1996**, *8*, 1307.

[33] I. Matsuoka, K. Aramaki, H. Nishihara, *Mol. Cryst. Liq. Cryst.*, **1996**, *285*, 199.

[34] I. Matsuoka, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.*, **1998**, 147.

[35] I. Matsuoka, H. Yoshikawa, M. Kurihara, H. Nishihara, *Synth. Metals* 1999, **102**, 1519.

[36] I. Kudmar, T. Seidel, *J. Appl. Phys.* **1962**, *33*, 771.

[37] R. S. Kelly, W. E. Geiger, *Organometallics* **1987**, *6*, 1432.

[38] B. T. Donovan, W. E. Geiger, *J. Am. Chem. Soc.* **1988**, *110*, 2335.

[39] B. T. Donovan, W. E. Geiger, *Organometallics* **1990**, *9*, 865.

[40] A. Ohkubo, T. Fujita, S. Ohba, K. Aramaki, H. Nishihara, *J. Chem. Soc., Chem. Commun.* **1992**, 1553.

[41] K. Aoki, J. Chen, *J. Electroanal. Chem.*, 1995, **380**, 35.

[42] T. Hirao, M. Kurashina, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.*, **1996**, 2929.

[43] H. Nishihara, T. Hirao, K. Aramaki, K. Aoki, *Synth. Metals*, **1997**, *84*, 935.

[44] H. Nishihara, A. Ohkubo, K. Aramaki, *Synth. Metals*, **1993**, *55*, 821.

[45] K. Yoshino, S. Morita, T. Kawai, H. Araki, X. H. Yin, A. A. Zakhidov, *Synth. Met.* **1993**, *56*, 2991.

[46] N. S. Sariciftci, L. Smilowitz, D. Braun, G. Srdaniov, V. Srdanov, F. Wudl, A. J. Heeger, *Synth. Met.* **1993**, *56*, 3125.

[47] M. Murata, T. Hoshi, I. Matsuoka, T. Nankawa, M. Kurihara, H. Nishihara, *J. Inorg. Organomet. Polym.* **2000**, *10*, 209.

[48] M. O. Albers, D. J. A. deWaal, D. C. Lies, D. J. Robinson, E. Singleton, M. B. Wiege, *J. Chem. Soc., Chem. Commun.* **1986**, 1681.

[49] C. Ernst, O. Walter, E. Dinjus, S. Arzberger, H. Görls, *J. Pract. Chem.* **1999**, *8*, 341.

[50] Y. Yamada, J. Mizutani, M. Kurihara, H. Nishihara, *J. Organomet. Chem.* **2001**, *80-83*, 637.

[51] M. Kurashina, MS thesis, The Univesisty of Tokyo, 2002.