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(7) A (1→6)-α-pyranosyl residue refers to the structural unit in which the exocyclic acetal oxygen atom is axially oriented to the pyranose ring, whereas a (1→6)-β-pyranosyl residue refers to the structural unit in which the exocyclic acetal oxygen atom is equatorially oriented to the pyranose ring. The α- and β-pyranosyl residues are formed, respectively, by trans and cis opening of an anhydro ring.
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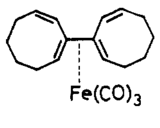
Novel Semiconducting Organometallic Polymers Containing $M(CO)_3$(1,3-diene) Groups (M = Fe, Ru)

The electrical properties of organometallic polymers containing mixed-valence transition metals have attracted much attention because of their unique conductivity behavior. (Bis(fulvalene)diiron)$^+$(TCNQ)$^{-\cdot}$ ($\sigma = 10^2$ S cm^{-1})[1] and the TCNQ salt of poly((3-vinylbis(fulvalene))diiron) ($\sigma = 10^{-3}$ S cm^{-1})[2] are among the best known examples. In our search for new semiconducting organometallic compounds, we have found that compressed disks of crystalline $Fe(CO)_3$[2-(1,7-cyclooctadienyl)-1,3-cyclooctadiene] (**1**)[3] prepared from $Fe_2(CO)_9$ and bis(2,4-cyclooctadienyl) show a fairly good conductivity ($\sigma_{dc} = 10^{-4}$ S cm^{-1}) at room temperature when doping was conducted with iodine. This finding prompted us to prepare novel conducting organometallic polymers containing a $M(CO)_3$(diene) group, which are readily cast into flexible films.



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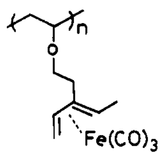

2(M=Fe), 3(M=Ru)

Table I
Direct-Current Conductivities for Undoped and Doped Organometallic Polymers

polymer	absorbed dopant/metal complex[a]	σ_{dc}, S cm^{-1}
polymer **2**	undoped	$<1.0 \times 10^{-10}$
polymer **2**	0.18 (I_2/Fe)	3.2×10^{-3}
polymer **2**	0.31 (SbF_6/Fe)	5.6×10^{-4}
polymer **3**	undoped	$<1.0 \times 10^{-10}$
polymer **3**	0.35 (I_2/Ru)	1.4×10^{-3}
polymer **6**	0.15 (I_2/Fe)	1.3×10^{-4}
copolymer(**6**/poly(MMA) = 1/1.2)	0.10 (I_2/Fe)	1.3×10^{-5}
copolymer(**6**/poly(MMA) = 1/5.8)	0.19 (I_2/Fe)	1.4×10^{-5}

[a] Molar ratio of absorbed dopant to metal complex.

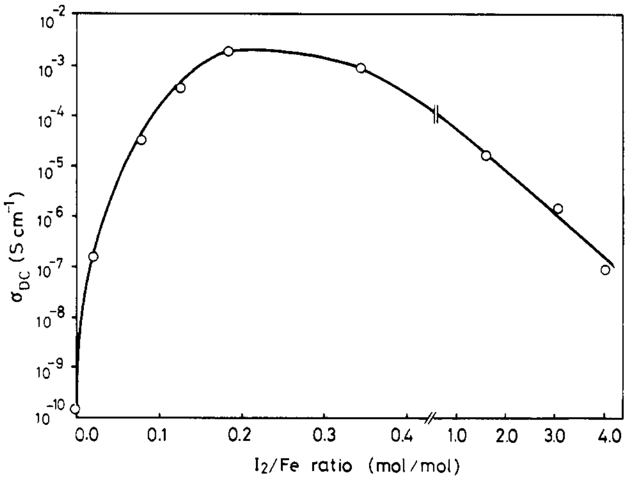

Figure 1. Dependence of dopant concentration (absorbed I_2) on the apparent conductivity of polymer **2**.

This paper describes the unique electrochemical properties of poly[$Fe(CO)_3$(3-((vinyloxy)ethyl)-η^4-1,3-pentadiene)] (**2**) and poly[$Ru(CO)_3$(3-((vinyloxy)ethyl)-η^4-1,3-pentadiene)] (**3**) after doping. Polymer **2** (M_n = 21 000) and polymer **3** (M_n = 15 000),[4,5] which are air-stable, can be cast into films by evaporation of their CH_2Cl_2 solutions and are insulators ($\sigma_{dc} < 10^{-10}$ S cm^{-1}). But doping with iodine increases the film conductivity by 6–7 orders of magnitude up to 3.2×10^{-3} S cm^{-1}, one of the highest values ever observed for organometallic polymers (Table I). When doping with iodine was conducted on films of **2** and **3** (thickness 0.1–0.15 mm) by sublimation, the direct-current conductivity increased rapidly in the range of I_2/Fe = 0.02–0.2 (mol/mol) to reach the level of $\sigma = 10^{-3}$ S cm^{-1} (Table I) before leveling off at I_2/Fe = 0.2 (Figure 1). The pale yellow film turned black on doping not only at the surface but also throughout the volume of the film. Addition of a large amount of dopant (I_2/Fe > 2.0) causes a decrease in conductivity. Doping with $(NO)SbF_6$ in nitromethane is also effective. Similar behavior has been observed in the doping of poly(vinylferrocene), poly(vinylferrocenylene), and poly(ethynylferrocene) with dichlorodicyanoquinone or iodine,[6] though their maximum conductivities (10^{-6}–10^{-9} S cm^{-1}) were 3–5 orders of magnitude lower than that of polymer **2**. Poly(ferrocenylmethyl methacrylate) (**4**) and poly(1-ferrocenylethyl methacrylate) (**5**), prepared by conventional methods,[7] also showed low conductivity (10^{-9} S cm^{-1}) after doping with iodine in the ratio I_2/Fe = 0.01–0.5. These results tell us that $[Cp_2Fe]^+I_3^-$ or its analogues[8] formed by doping do not construct semiconducting columns involving oriented $[Fe^{II}–Fe^{III}]^+$ species.

When polymer **2** doped with I_2 was held in a vacuum (10^{-2} torr for 1 day) or exposed to air (5 days), dedoping

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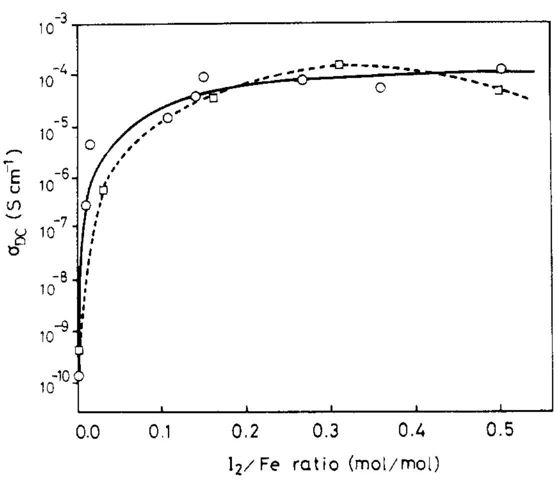
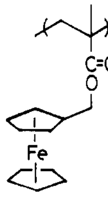


Figure 2. Direct-current conductivity of complex 7 (○) and complex 8 (□) as a function of dopant concentration.

proceeded and the initial polymer 2 could be recovered in >90% conversion as revealed by ^{13}C NMR analysis (67.5 MHz). A similar reversible reaction has been observed when polymer 2, oxidized with anhydrous HCl, was treated with $AgBF_4$ or $AgPF_6$.



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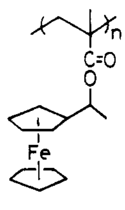

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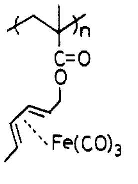

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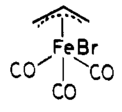
Poly[Fe(CO)$_3$((η^4-2,4-hexadienyl) methacrylate)] (6) prepared according to Pittman's procedure[9] also showed an enhanced conductivity in the semiconductor region ($\sigma = 10^{-4}$ S cm^{-1}) when sublimation of iodine was conducted on the film (thickness 0.15 mm) in a molar ratio of I_2/Fe = 0.03–0.2. Especially noteworthy is that 1:1.2 and 1:5.8 random copolymers of 2 with methyl methacrylate (polymerized with AIBN) still retain good conductivity ($\sigma = 10^{-5}$ S cm^{-1}, I_2/Fe = 0.4). This fact suggests the possibility that semiconducting materials may be obtained even by blending or mixing the M(CO)$_3$(η^4-diene) with conventional organic polymers. Actually, complex 1 (5–6 wt %) dispersed in polystyrene or poly(methyl methacrylate) showed a conductivity of 10^{-6} S cm^{-1} after doping (I_2/Fe = ca. 0.15). This procedure affords a facile method for preparation of novel conducting materials. Its practical utility is, however, limited because of difficulties involved in the homogeneous mixing of large quantities of the complexes (>5 mol %) with organic polymers. Phase separation and precipitation of the complex on the film as microcrystals occur very often. In this sense, homo- and copolymerization of organometallic monomers are superior to the above blending method.

To collect fundamental information on the electron conducting mechansim, chemical change during doping was investigated. The IR CO stretching vibration of 2 (2060, 1987, and 1970 cm^{-1}) shifted to higher wavenumbers (2110 and 2056 cm^{-1}) when 1 equiv of I_2 was added to 2 in CH_2Cl_2. This suggests that the Fe(CO)$_3$(1,3-pentadiene) group contained in 2 changed to [Fe^{II}(CO)$_3$(η^3-allyl)]$^+$X$^-$ (X = I_3, I_5, etc.) or Fe^{II}I(CO)$_3$(η^3-allyl) since the CO frequencies are very close to those of well-known [Fe(CO)$_4$(η^3-allyl)]$^+$X$^-$ (X = BF_4, PF_6)[10] or FeX(CO)$_3$(η^3-allyl) (X = Cl, Br) complexes.[11] The polymer containing the FeCl(CO)$_3$(η^3-allyl) species, which was prepared by reaction of 2 with dry HCl, also showed the CO absorption in nearly the same region (2080, 2035, and 2005 cm^{-1}). Thus, the doping of polymer 2 should give rise to the formation of [Fe^{II}]$^+$ or Fe^{II} species. However, these species themselves are insulators as evidencd by the low conductivities of FeBr(CO)$_3$(η^3-allyl) (7) ($\sigma_{dc} = 10^{-10}$ S cm^{-1}), of [FeCl(CO)$_3$]$_2$(1,3-η^3,8,10-η^3-1,9-octadiene-3,8-diyl) (8)[12] ($\sigma_{dc} = 10^{-9}$ S cm^{-1}), and of [Fe(CO)$_4$(η^3-allyl)]BF$_4$ ($\sigma_{dc} = 10^{-7}$ S cm^{-1}). Therefore, it seems most probable that electron conduction takes place through mixed-valence [Fe^{I}Fe^{II}]$^+$ and/or [Fe^{II}Fe^{III}]$^+$ species generated by the interaction between the [Fe^{II}]$^+$ species with Fe^I or Fe^{III} species. Complexes 7 and 8 also showed semiconductivity when the doping was performed with iodine on compressed disks (Figure 2). Both complexes behaved in a similar manner and no proximity effect was observed for 8. Electron conduction through the [Fe^{II}Fe^{III}]$^+$ species is most probable in these cases. Though measurements of EPR, magnetic susceptibility, and temperature dependency of the conductivity are required to ascertain the band gap of these semiconductors, the above findings raise the hope that doping pellets of conventional metal complexes will provide various semiconducting materials. Preliminary experiments have revealed that FeCl$_2$(PPh$_3$)$_2$, CoI$_2$(dppe), CoCl$_2$(*t*-BuNC)$_4$, and PdI$_2$(PPh$_3$)$_2$ have a conductivity of >10^{-6} S cm^{-1} after doping while Fe$_2$(CO)$_9$, Mo(CO)$_6$, W(CO)$_6$, and FeI(η^5-C$_5$H$_5$)(CO)$_2$ are insulators even when excess iodine is added. More precise experiments are in progress with single crystals of the Fe(CO)$_3$(η^4-diene) and related ML$_n$(polyene) complexes at various temperatures.



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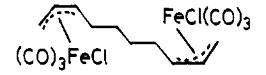

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Registry No. 2, 76171-61-4; 2 copolymer with methyl methacrylate, 92346-63-9; 3, 76171-63-6; 4, 35560-97-5; 5, 92346-61-7; 6, 92346-62-8; 7, 12192-46-0; 8, 92346-60-6; I_2, 7553-56-2; SbF$_6$, 17111-95-4.

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