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Syntheses and Reactions of Ferrocene-Containing Polymers. VI. Polarography and Electron Transfer Equilibria of Some Ferrocene-Containing Polymers[1)]

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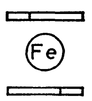
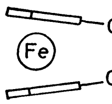
Polarography and electron transfer equilibria of some ferrocene-containing polymers were studied in comparison with small-molecule analogs. The oxidation half-wave potentials of polyvinylferrocene and polydivinylferrocene (almost completely cyclized) in CH_2Cl_2 were close to those of ferrocene and [3]ferrocenophane, respectively. This is in line with structural similarity. Only one oxidation step was observed in the polarogram of triferrocenylbenzene and polyethynylferrocene, suggesting that the electronic interactions between ferrocene units are small in these compounds. Electron transfer equilibrium was observed between ferrocene units in polymer and iodine. Equilibrium constants of the [3]ferrocenophane unit were greater than those of the unbridged ferrocene unit. The ferrocene unit in polymer showed greater equilibrium constants than those of their small-molecule analogs.

Ferrocene-containing polymers are expected to show interesting physical properties,[2)] and the electrical property of the polymers prepared by polycondensation and polyrecombination has been studied.[3)] However, detailed structural studies were often difficult, since many of these polymers were infusible and insoluble, and it was not possible to clarify the correlation between structure and property.

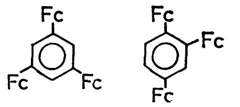
We have synthesized some ferrocene-containing polymers through addition polymerization of vinylferrocene, 1,1′-divinylferrocene and ethynylferrocene, and determined their structures by spectroscopic and other means.[4–7)] Since the structures are rather simple, it was thought that the structure-property relationship would be comparatively straightforward. In this paper we describe the results of polarographic study and electron-transfer equilibria of these polymers in solutions.



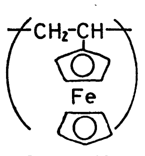
Ferrocene



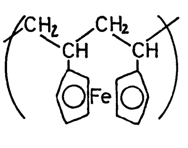
[3] Ferrocenophane



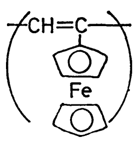
1,3,5- and 1,2,4-Triferrocenylbenzene



Poly(vinylferrocene)



Cyclized poly(divinylferrocene)



Poly(ethynylferrocene)

Fc: Ferrocenyl group

Experimental

Materials. Polymerizations of vinylferrocene, 1,1′-divinylferrocene and ethynylferrocene have been described.[4–7)] The polymerization conditions are given in each case. Triferrocenylbenzene (mixture of 1,3,5- and 1,2,4-isomers) was prepared by the trimerization of ethynylferrocene.[7)] [3]-Ferrocenophane(1,1′-trimethyleneferrocene) was prepared from formylferrocene according to the method of Rinehart *et al.*,[8)] mp 97.3—99.0°C (lit, mp 107.5—108°C). The NMR spectrum showed sharp singlets in line with that in literature. Minor impurity ($<4\%$) peaks observed might be ascribed to *n*-propylferrocene and/or to 1,2-trimethyleneferrocene. Found: C, 69.05; H, 6.08%. Calcd for $C_{13}H_{14}Fe$: C, 69.05; H, 6.25%.

Methyltriethylammonium triiodide was prepared from triethylamine, methyl iodide, and iodine, according to the method of Buckles *et al.*,[9)] mp 65.0—65.6°C; λ_{max} ($CHCl_3$) 365 nm ($\varepsilon=2.4\times10^4$) (lit,[9)] $(CH_3)_4NI_3$ λ_{max} ($ClCH_2CH_2Cl$) 365 nm ($\varepsilon=2.53\times10^4$)).

Instruments. Polarographic study was carried out with a Yanagimoto Polarograph PA 102 using rotating platinum electrode as a cathode and mercury pool as an anode. Electronic spectra were obtained with a Shimadzu UV 200 spectrophotometer.

Results and Discussion

Polarography. It is well-known that ferrocene compounds undergo one-electron oxidation to ferricenium ions electrolytically, photolytically, and by organic and inorganic oxidants. Thus polarographic studies have been made for many ferrocene derivatives

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[1)] Contribution No. 267 from this department.

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Table 1. Oxidation half-wave potential of polymers and related compounds

Rotating platinum electrode *vs.* mercury pool.
Solvent: methylene chloride.
Supporting electrolyte: n-Bu_4NBF_4, 0.1M.

Sample (concn. of ferrocene unit)	(mM)	Half-wave potential ($E_{1/2}$) (V)
Ferrocene	(0.1)	0.55±0.01
	(1)	0.50±0.01
[3] Ferrocenophane	(0.1)	0.47±0.01
	(1)	0.44±0.01
Triferrocenylbenzene[a]	(0.1)	0.57±0.02
	(1)	0.60±0.03
Poly(vinylferrocene)[b]	(1)	0.54±0.01
Cyclized poly(divinylferrocene)[c]	(1)	0.43±0.02
Poly (ethynylferrocene)[d]	(1)	0.60±0.01
Poly (ethynylferrocene)[e]	(1)	0.58±0.01

a) Approximately 1: 1 mixture of the 1,3,5- and 1,2,4-isomers.
b) Polymerization condition: Et_2AlCl/t-BuCl (1/1), CH_2Cl_2, 0°C (Ref. 4).
c) Polymerization condition: AIBN, benzene, 60°C (Ref. 5).
d) Polymerization condition: Al(i-Bu)$_3$/Ti(OBu)$_4$(5/1), toluene, 80°C (Ref. 7).
e) Polymerization condition: Al(i-Bu)$_3$/Ti(OBu)$_4$(10/1), toluene, 80°C (Ref. 7).

(small molecules).[10-13] On the other hand, ferrocene-containing polymers have seldom been investigated polarographically, because of the limited solubility in solvents used for the polarographic study.[14,15]

Polarographic measurements were made in CH_2Cl_2 solution with tetra-n-butylammonium fluoroborate (n-Bu_4NBF_4) as supporting electrolyte. The system was selected beacuse of better solubility and conductivity than the following combinations: $LiClO_4$/tetrahydrofuran, $LiClO_4$/benzene–dioxane, and n-Bu_4NBF_4/benzene–dioxane. The oxidation half-wave potentials ($E_{1/2}$) of the ferrocene-containing polymers and their low-molecular-weight analogs are given in Table 1. The potentials are given relative to that of the mercury pool. Sample concentrations were 0.1 and 1 mM. Reproducibility of $E_{1/2}$ was good, being almost independent of concentration. However, lower concentrations seem to be favorable for removing the maxima on the polarogram which seem to be due to the adsorption of the product on the electrode. The $E_{1/2}$ values of polyvinylferrocene and cyclized polydivinylferrocene were close to those of ferrocene and [3]ferrocenophane, respectively. This supports the fact that the repeat unit of cyclized polydivinylferrocene is a [3]ferrocenophane derivative.[5] The polymer main chain does not seem to exert a great influence upon the oxidation potential of the pendent ferrocene ring.

It is established that two cyclopentadienyl rings of ferrocene are parallel with each other with 3.3 Å separation.[16] However, the two rings cannot be parallel in some heteroannularly-bridged ferrocenes such as [*m*]ferrocenophane with $m \leq 3$, owing to geometrical limitation.[17,18] Ferrocene derivatives of this type (hot-dog structure) are known to possess unique electronic properties.[19-21]

A polarographic study of bridged ferrocenes has been reported by Gorton *et al.*[13] They found that the half-wave potential of [2]ferrocenophane was appreciably lower than that of its unbridged counterpart, but the half-wave potential of [3]ferrocenophane was close to that of 1,1′-diethylferrocene. The difference in $E_{1/2}$ we observed between ferrocene and [3]ferrocenophane ($\Delta E_{1/2} = -0.07$ V) coincides with their data. Thus, the influence of bridging on the electronic property does not seem to be great in [3]ferrocenophane compared with that in [2]ferrocenophane. On the other hand, the difference in $E_{1/2}$ between polyvinylferrocene and cyclized polydivinylferrocene ($\Delta E_{1/2} = -0.11$ V) is greater than that found between 1-alkyl and 1,1′-dialkylferrocenes (small molecule).[11] Thus bridging seems to lower the oxidation potential.

Only one-step oxidation was observed in the polarogram of triferrocenylbenzene. It is known that two-step oxidation is involved with some binuclear ferrocene derivatives such as [1.1]ferrocenophane[13] and biferrocenyl.[22] This is interpreted as follows. A ferricenium group formed in the initial oxidation enhances the oxidation potential of the second ferrocene nucleus by interactions operating through the carbon skeleton of the ligands or directly between the iron atoms. The one-step oxidation polarogram indicates that there is no appreciable interaction among ferrocene nuclei in triferrocenylbenzene.

The electronic spectral data similarly indicate that there is no strong interaction between the ferrocene nuclei. The absorption coefficient of triferrocenylbenzene at 450 nm region (d-d^* transition of ferrocene nucleus) was approximately three times as large as that of phenylferrocene.[23]

The $E_{1/2}$ value of polyethynylferrocene agreed with that of triferrocenylbenzene within experimental error (0.59 and 0.58 V, respectively), which also shows that there is not much interaction between ferrocene nuclei directly or through the polyene chain.

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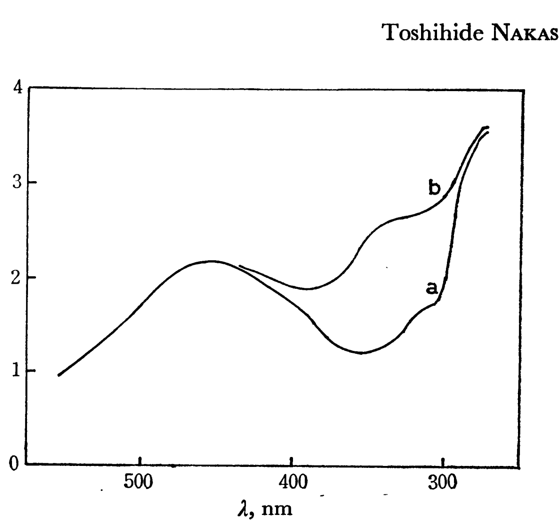
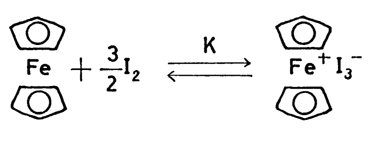


Fig. 1. Electronic spectra of poly(vinylferrocene). Solvent a: cyclohexane, b: CCl_4.

Electron Transfer Equilibria. Although ferrocene-containing polymers have been shown to react with appropriate acceptors to give corresponding ferricenium ions,[24] no quantitative studies have been made on electron transfer.

The electronic spectrum of ferrocene shows a peculiar solvent effect at around 300 nm in some halogenated hydrocarbon solvents. This was attributed to the dissociative charge transfer between ferrocene and a solvent molecule.[25] A similar solvent effect was observed in polyvinylferrocene as shown in Fig. 1. The extinction coefficient in the 300—400 nm region is greater in CCl_4 than in cyclohexane.

It has been reported that electron transfer equilibria hold between ferrocene and iodine in appropriate solvents.[25,26]



(1)

The equilibrium was studied in chloroform with ferrocene-containing polymers. The equilibrium constant K was determined from the absorption of the triiodide anion at 365 nm.

$$K = \frac{[Fc^+I_3^-]}{[Fc][I_2]^{3/2}} = \frac{[Fc^+I_3^-]}{([Fc]_0-[Fc^+I_3^-])([I_2]_0-3/2[Fc^+I_3^-])^{3/2}} \quad (2)$$

Fc: ferrocene unit

It was confirmed by using $CH_3(C_2H_5)_3N^+I_3^-$ that Beer's law holds. Formation of the triiodide anion by dissociation of iodine was negligible under the experimental conditions. The absorption at 365 nm was measured by the continuous variation method. The variation of absorption intensity with composition is given in Fig. 2.

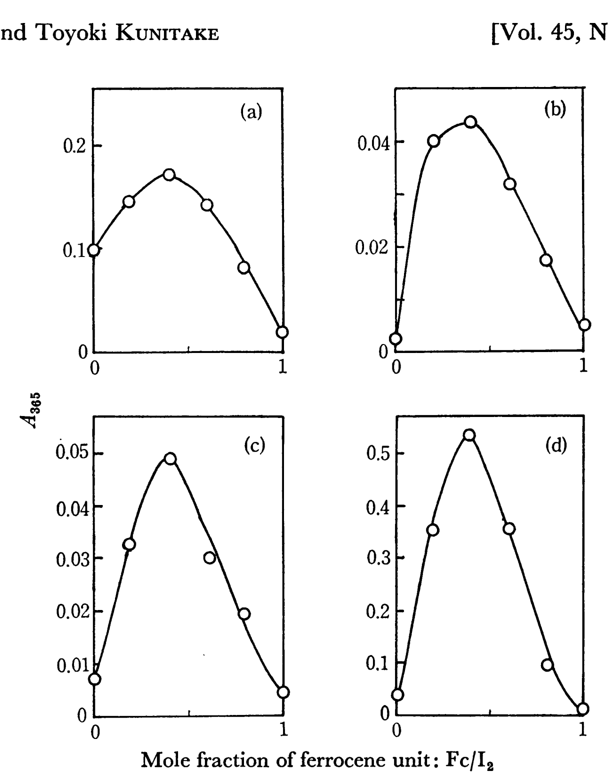


Fig. 2. Determination of the equilbrium constant of electron transfer by the continuous variation method. Solvent: chloroform. 1 cm silica cell. A_{365}: absorption intensity of I_3^- at 365 nm.
a: Ferrocene/I_2 (total concentration, 10^{-3} M), b: [3]Ferrocenophane/I_2 (total concentration, 10^{-4} M), c: Poly(vinylferrocene)/I_2 (total concentration, 10^{-4} M), d: Poly(divinylferrocene)/I_2, (total concentration, 10^{-4} M)

The maximum of A_{365} (absorption intensity at 365 nm) observed for ferrocene–iodine, mole fraction of ferrocene *ca.* 0.4, was in line with the stoichiometry of Eq. (1). Similar results were obtained for [3]ferrocenophane and ferrocene-containing polymers. The total concentration was set at 10^{-4}M in the case of ferrocene-containing polymers in order to avoid precipitation of oxidized polymers. Since polyethynylferrocene possesses a broad absorption in this region, determination of the equilibrium constant was impossible.

Table 2. Equilibrium constant of the electron transfer reaction from polymers and related compounds to iodine
28±2°C, Total concentration 10^{-4}M.

Sample	log K				
	Mole fraction of ferrocene unit				Average
	0.2	0.4	0.6	0.8	
Ferrocene[a]	3.0	3.0	3.1	3.2	3.1
[3]Ferrocenophane	5.4	5.3	5.3	5.5	5.4
Poly(vinylferrocene)	5.4	5.3	5.4	5.6	5.4
Poly(vinylferrocene)	5.4	5.3	5.3	5.5	5.4
Cyclized poly(divinylferrocene)	7.2	7.1	7.0		7.1
Cyclized poly(divinylferrocene)	6.5	6.5	6.2	7.2	6.6

a) Total concentration 10^{-3}M.

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The equilibrium constants were calculated for each run (Table 2). It is of interest that the bridged ferrocene units show greater *K* values than the unbridged units ([3]ferrocenophane *vs.* ferrocene, and cyclized polydivinylferrocene *vs.* polyvinylferrocene). Thus, electron transfer occurs more readily with the ferrocenophane structure, in line with the polarographic data. On the other hand, the polymers possess greater equilibrium constants than the low-molecular-weight analogs, in contrast with the polarographic results. Accumulation of the ferrocene unit along the polymer chain may make electron transfer favorable, probably through interactions of neighboring cyclopentadienyl rings with iodine molecule and/or through the change of polymer conformation associated with the reaction with iodine.

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