Electron transfer reaction between metallo-porphyrins covalently bound to polystyrene in *N,N*-dimethylformamide

Joerg Gitzel, Hiroyuki Ohno and Eishun Tsuchida*
Department of Polymer Chemistry, Waseda University, Tokyo 160, Japan

and Dieter Woehrle
Bremen University, Fachbereich 2/NW 2, 2800 Bremen 33, FRG
(Received 24 January 1986; revised 6 May 1986)

Iron(III) chloro- and manganese(III) chloro-complexes of 5,10,15,20-tetrakis-(4-aminophenyl)-21*H*,23*H*-porphin were covalently bound to a polymer of ethenylbenzene with (4-chloromethyl)ethenylbenzene. Electron transfer from the polymer-bound manganese(II) complex to the polymer-bound iron(III) complex was investigated by stopped-flow visible spectrometry under pseudo-first-order conditions in *N*,*N*-dimethylformamide. The observed data for the electron transfer were compared with those for electron transfer between the corresponding low molecular weight metallo-porphyrins. It was found that the pseudo-first-order rate constants for the reaction between the low molecular weight metallo-porphyrins were higher than those for the same process between the polymer complexes. On the other hand, the activation energy for electron transfer between the polymer-bound metallo-porphyrins (9.2 kJ mol^{-1}) was considerably lower than that corresponding to the reaction between the low molecular weight metallo-porphyrins (16.8 kJ mol^{-1}). These effects are discussed with reference to the role of polymer chains.

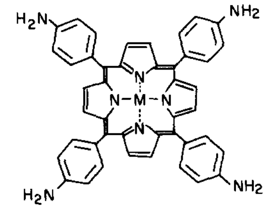
(Keywords: metallo-porphyrin; electron transfer; polymeric domain; polymer–polymer interaction; stopped-flow spectrometry)

INTRODUCTION

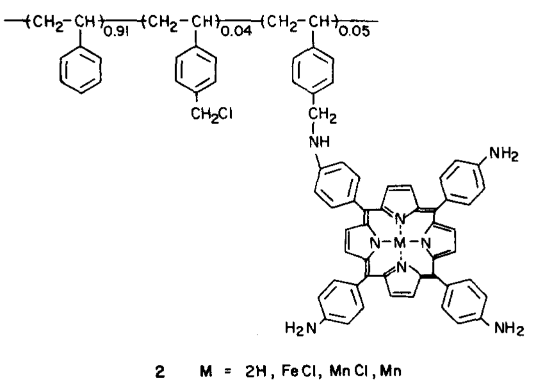
The influence of polymeric environment on the reactivity of polymer–metal complexes[1-4] and the formation of interpolymer complexes[5-7] have been studied by us over a decade. Polymer-bound porphyrins have mainly been investigated to develop their catalytic activities or ability to bind molecular oxygen[8-12]. Recently, the investigation of electron transfer reactions of low molecular weight porphyrins was carried out with metallo-porphyrins bound to carbon electrodes[13-15]. Electron transfer reactions concerning low molecular weight porphyrins have been studied intensively with a great variety of reagents[16-24] and also light-driven electron transfer reactions of metallo-porphyrins or metallo-phthalocyanines[25-27] have been investigated to a very large extent. Although a little work has been done on electron self-exchange reactions among cobalt porphyrins[28,29] and electron transfer from cobalt porphyrins to metallo-porphyrin cation radicals[30,31], to our knowledge no investigations have been made so far concerning the influence of polymeric environment on the electron transfer properties of polymer-bound metallo-porphyrins or metallo-phthalocyanines.

Polymer-bound porphyrins are available by polymerization of vinyl-group-containing porphyrins or by immobilization of suitable porphyrins on reactive polymers[8-12]. The latter method has the advantage that the probably complicated preparation of suitable vinyl monomers can be avoided. More easily accessible starting compounds are substituted tetraphenylporphyrins. Therefore, the immobilization of a substituted tetraphenylporphyrin on a well defined polymer of ethenylbenzene with (4-chloromethyl)ethenylbenzene will be carried out with 5,10,15,20-tetrakis-(4-aminophenyl)-21*H*,23*H*-porphin (**1**) (M = 2H).

The present work deals with the study of electron transfer reaction between a polymer-bound iron(III) porphyrin, (**2**) (M = FeCl), and a polymer-bound manganese(II) porphyrin, (**2**) (M = Mn), in order to investigate the influence of polymeric environment on electron transfer properties.



1 M = 2H, FeCl, MnCl, Mn



2 M = 2H, FeCl, MnCl, Mn

---

* To whom correspondence should be addressed

0032-3861/86/111781$03.00

EXPERIMENTAL

Materials

All materials were of the highest available purity and were used as purchased unless otherwise stated.

5,10,15,20-Tetrakis-(4-aminophenyl)-21H,23H-porphin (**1**) *(M = 2H)*

Compound (**1**) (M = 2H) was synthesized according to Semeikin *et al.*[32] by reduction of 5,10,15,20-tetrakis-(4-nitrophenyl)-21*J*,23*H*-porphin. The crude 5,10,15,20-tetrakis-(4-nitrophenyl)-21*H*,23*H*-porphin was recrystallized twice from pyridine to give a yield of 11.9% of fairly pure product which was then used for the reduction.

Visible spectrum (DMF), λ (nm): 421, 513, 548, 588, 643.

5,10,15,20-Tetrakis-(4-nitrophenyl)-21*H*,23*H*-porphin was reduced with stannous chloride dihydrate/concentrated hydrochloric acid and the crude product was purified by chromatography on basic aluminium oxide with tetrahydrofuran to give a yield of 88.1% after evaporating the solvent and drying in vacuum at 60°C.

Visible spectrum (DMF), λ (nm) (ε in $1\ \mathrm{mol^{-1}\ cm^{-1}}$): 434 (152000), 526 (8600), 573 (14700), 664 (8000).

^{1}H n.m.r. spectrum (DMSO-d_6, TMS as internal standard), δ (ppm): 5.47 (singlet, $-NH_2$), 6.82–7.96 (multiplet, phenyl H), 8.80 (singlet, pyrrole H).

Infra-red spectrum (KBr) ($\mathrm{cm^{-1}}$): 3350 (NH valence), 1600 (NH bending), no evidence of remaining nitro groups.

Metal introduction into (**1**) *(M = 2H)*

Iron or manganese ions were introduced into (**1**) (M = 2H) in refluxing *N*,*N*-dimethylformamide (DMF) according to Adler *et al.*[33,34]

(**1**) *(M = MnCl)*. 100 mg (0.15 mmol) (**1**) (M = 2H) were dissolved in 10 ml of refluxing DMF and a five-fold molar excess of manganese(III) chloride tetrahydrate was successively added over a period of 5 h. The solution was cooled in an ice bath, the metallo-porphyrin precipitated with an ice-cold saturated solution of potassium chloride in water, collected on a glass funnel, washed with water and dried in vacuum at 60°C. The dried product was recrystallized from pyridine/n-hexane and the green crystals were dried in vacuum at 60°C. The product was easily soluble in methanol and soluble in tetrahydrofuran and chloroform.

Yield: 42 mg (34%).

Visible spectrum (DMF), λ (nm) (ε in $1\ \mathrm{mol^{-1}\ cm^{-1}}$): 349 (27200), 386 (35000), 438 (40500), 480 (70800), 592 (9200) shoulder, 638 (15100).

Infra-red spectrum (KBr) ($\mathrm{cm^{-1}}$): 1005 (metal frame vibration).

Cyclic voltammetry (DMSO): $E_{1/2}$(Mn(II)/Mn(III)) = −0.36 V vs. SCE.

(**1**) *(M = FeCl)*. The introduction of iron was done analogously using water-free iron(III) chloride.

Yield: 65 mg (51.4%).

Visible spectrum (DMF), λ (nm) (ε in $1\ \mathrm{mol^{-1}\ cm^{-1}}$): 340 (26300) shoulder, 376 (32200) shoulder, 427 (55500) broad, 558 (7500) shoulder, 638 (4200).

Infra-red spectrum (KBr) ($\mathrm{cm^{-1}}$): 995 (metal frame vibration).

Cyclic voltammetry (DMSO): $E_{1/2}$(Fe(II)/Fe(III)) = +0.13 V vs. SCE.

Polymer of ethenylbenzene with (4-chloromethyl)ethenylbenzene

20.37 g (0.196 mol) freshly distilled ethenylbenzene and 2.19 g (0.014 mol) freshly distilled (4-chloromethyl)ethenylbenzene were dissolved in 45.6 ml purified benzene to give a 3 M solution. This solution was heated with 2 mol% 2,2′-azobis-(2-methylpropanoic acid nitrile) (recrystallized from ethanol) in a sealed reaction tube for 3.5 h at 60°C. The copolymer was precipitated in methanol, reprecipitated from benzene/methanol and dried in vacuum at 60°C.

Yield: 5.44 g.

The composition of the copolymer was determined by Volhard titration of the chloromethyl groups. The copolymer composition was found to be 10:1 (molar ratio of ethenylbenzene units to (4-chloromethyl)ethenylbenzene units). The intrinsic viscosity $[\eta]$ in methanol at 34°C was determined as $12.8\ \mathrm{ml\ g^{-1}}$, which corresponds to a molecular weight $\bar{M}_n$ of about 17000. $\bar{M}_w$ was found to be 14000 by vapour pressure osmometry in benzene.

Polymer-bound 5,10,15,20-tetrakis-(4-aminophenyl)-21H,23H-porphin (**2**) *(M = 2H)*

500 mg (equals 0.412 mmol of chloromethyl groups) polymer of ethenylbenzene with (4-chloromethyl)-ethenylbenzene, 418 mg (0.619 mmol = 1.5-fold molar excess) (**1**) (M = 2H) and 0.6 ml triethylamine (4.12 mmol) were dissolved in 25 ml DMF and heated to 150°C for 72 h in the dark under N_2 atmosphere. New portions of triethylamine were added every 18 h. The DMF was expelled by evaporation under reduced pressure at 75°C, then methanol was added to the residue to wash out the unreacted components. The product was collected on a glass filter and dried. For purification of remaining free porphyrin, the product was reprecipitated from benzene/methanol and afterwards treated with methanol in a Soxhlet extractor until the extract was colourless. The purified polymer was finally dried in vacuum at 60°C. The absence of free porphyrin was confirmed by using either thin-layer chromatography (silica gel/methanol) or by gel permeation chromatography (Sephadex LH 20/dichloromethane). In both cases no free porphyrin was found. Degree of substitution of the chloromethyl groups was determined by the visible spectrum using the extinction coefficient of the free porphyrin ($\varepsilon_{434} = 225.5\ \mathrm{l\ g^{-1}\ cm^{-1}}$ in DMF) and was found to be 53%. The visible spectrum was the same as that of the free porphyrin. The infra-red spectrum showed typical absorptions for the copolymer and the porphyrin.

Yield: 540 mg.

Metal introduction into (**2**) *(M = 2H)*

Manganese or iron ions were incorporated into the polymer-bound porphyrin (**2**) (M = 2H) in the same way as for the free porphyrin except that recrystallization was from pyridine/n-hexane.

Preparation of zinc amalgam

Zinc amalgam was prepared according to Fleischer *et al.*[17] The amalgam was rinsed with acetone after washing with water and blown dry with air. Since the amalgam is sensitive to moisture and air and is deactivated after about 12 h, only freshly prepared amalgam should be used.

Reduction of (1)(*M* = *MnCl*) *and* (2)(*M* = *MnCl*) *with zinc amalgam*

About 10 ml portions of 10^{-4} M to 10^{-5} M solutions of (1)(M = MnCl) or (2)(M = MnCl) in purified DMF were flushed with argon for about 10 min; then 4 g of freshly prepared zinc amalgam were added and the solutions were reduced for 20 min while purging with argon. The colour of the solutions changed from dark green to light green upon reduction and the Soret band shifted from 480 nm to 445 nm. The charge transfer bands at wavelengths below 450 nm disappeared totally. The reduced solutions containing (1)(M = Mn) or (2)(M = Mn) are extremely sensitive to oxygen and they must therefore be kept over amalgam in a sealed bottle.

MEASUREMENTS

Infra-red spectra were measured with a Shimadzu IR 400, visible spectra with Shimadzu UV-240, ^{1}H n.m.r. spectra on a Varian MAT EM-360. Vapour pressure osmometry was carried out with a Hitachi Model 117 vapour pressure osmometer.

Cyclic voltammetry

Cyclic voltammetry measurements of (1)(M = MnCl) and (1)(M = FeCl) were carried out with 1.0 mM solutions in dimethylsulphoxide and tetrabutylammonium perchlorate as supporting electrolyte (0.1 M). Measurements were done with a normal three-electrode arrangement using a Nikko Keisoku Function Generator NFG-3, Dual Potentiogalvanostate DPSG-3, Rotating-Ring-Disc-Electrode RRDE-1 and a Watanabe WX 4403 *XY* recorder. A platinum disc (4 mm in diameter) was used as working electrode.

Stopped-flow visible spectroscopy

Stopped-flow measurements were carried out with a RA-401 stopped-flow spectrometer, a UE-010 RA control unit and a RA-451 computer by Union Giken, Japan. The data were printed out on a National VP-6414 A *XY* Plotter. Since the reduced manganese complexes are extremely sensitive to oxygen, all the handling was done in an argon atmosphere with syringes.

RESULTS

5,10,15,20-Tetrakis-(4-aminophenyl)-21*H*,23*H*-porphin (1)(M = 2H) could be bound covalently to a polymer of ethenylbenzene with (4-chloromethyl)ethenylbenzene with formation of the polymer (2)(M = 2H). This polymer contained about 5 mol % of covalently bound porphyrin. Owing to the diluted reaction conditions, crosslinking reaction of the tetrasubstituted porphyrin was not observed. Manganese and iron were inserted into (1)(M = 2H) and (2)(M = 2H) in refluxing DMF with formation of (1)(M = MnCl, FeCl) and (2)(M = MnCl, FeCl).

Figures 1a–e show the infra-red spectra of the low molecular weight porphyrins and the polymer-bound complexes. *Figures 1a* and *1b* depict typical spectra for a tetraphenylporphin and a metallo-tetraphenylporphin[35,36], respectively. Upon insertion of manganese into (1)(M = 2H), the metal-sensitive band at 965 cm^{-1} shifts to 1005 cm^{-1}. The spectrum of the copolymer (*Figure 1c*) shows the absorption typical of the chloromethyl group at 1260 cm^{-1}. After binding of the porphyrin to the copolymer, absorptions for the porphyrin and the copolymer can be seen in the spectra (*Figures 1d* and *1e*).

Electron transfer reaction between model compounds

First of all, we studied the electron transfer reaction between model compounds of the corresponding polymer-bound metallo-porphyrins, i.e. between (1) (M = Mn) and (1) (M = FeCl).

The difference between the half-wave potentials for reduction and oxidation of the central metal atom of (1) (M = FeCl) and (1) (M = MnCl) is about 0.5 V as shown in *Figure 2*. Therefore, this should be a suitable system for investigation of the electron transfer reaction between different metallo-porphyrins.

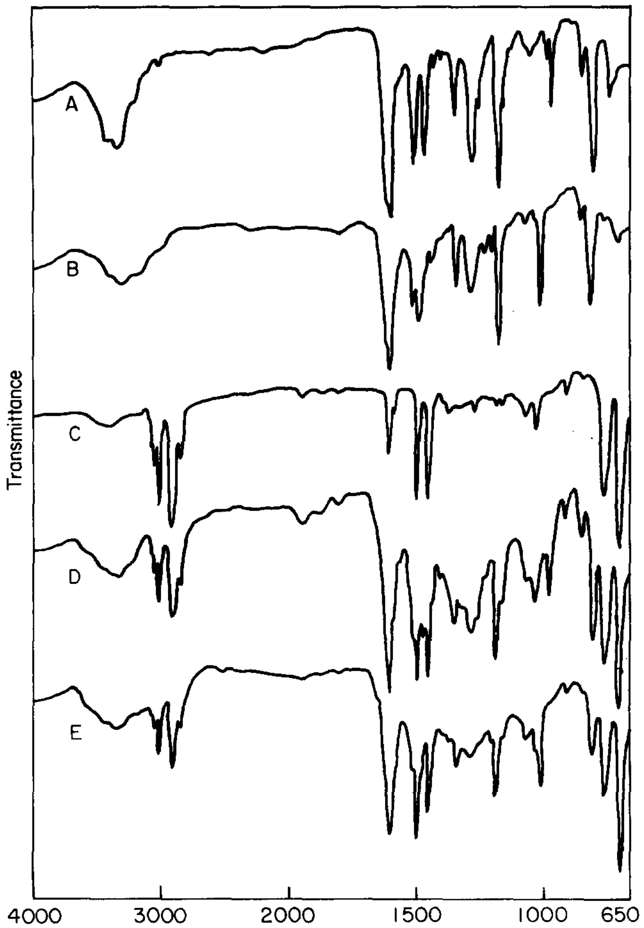


Figure 1 Infra-red spectra of porphyrins, metallo-porphyrins and polymers: (A) (1)(M = 2H); (B) (1)(M = MnCl); (C) polymer of ethenylbenzene with (4-chloromethyl)ethenylbenzene; (D) (2)(M = 2H); (E) (2)(M = MnCl)

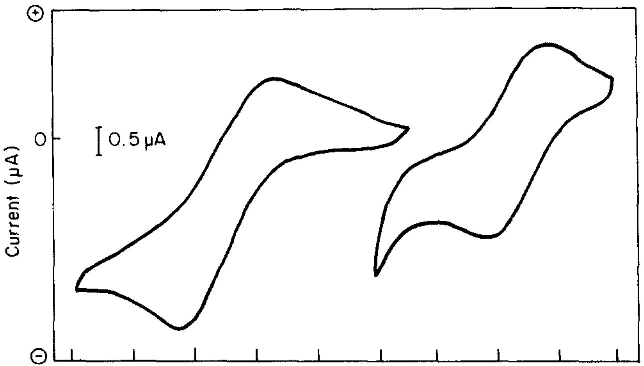


Figure 2 Cyclic voltammograms of (1)(M = MnCl) (*left*) and (1) (M = FeCl) (*right*) in dimethylsulphoxide

Solutions of **(1)** (M = Mn) and **(1)** M = FeCl) in DMF were mixed by a stopped-flow apparatus and the formation of **(1)** (M = MnCl) was observed at 480 nm as shown in *Figure 3*. The same experiment was investigated at different temperatures.

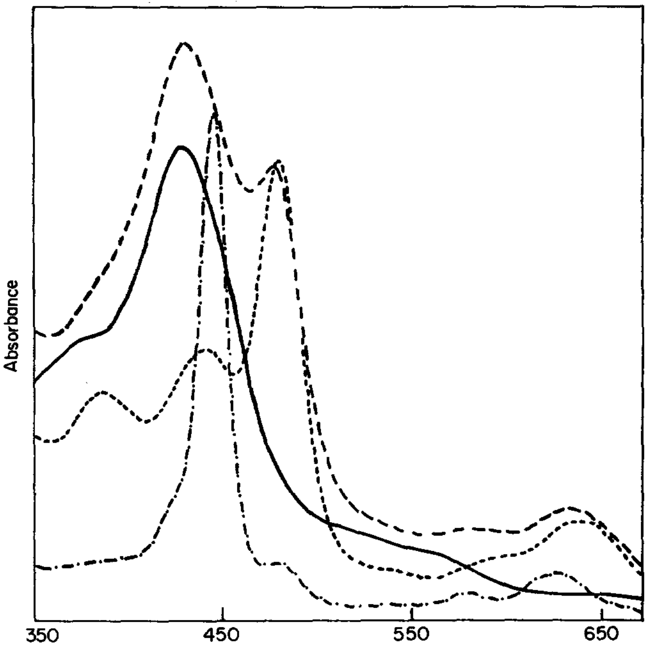


Figure 3 Visible spectra in *N,N*-dimethylformamide of metallo-porphyrins: ——— (1)(M = FeCl); ---·-- (1)(M = MnCl); -·-·- (1)(M = Mn); --- reaction of (1)(M = FeCl) with (1)(M = Mn)

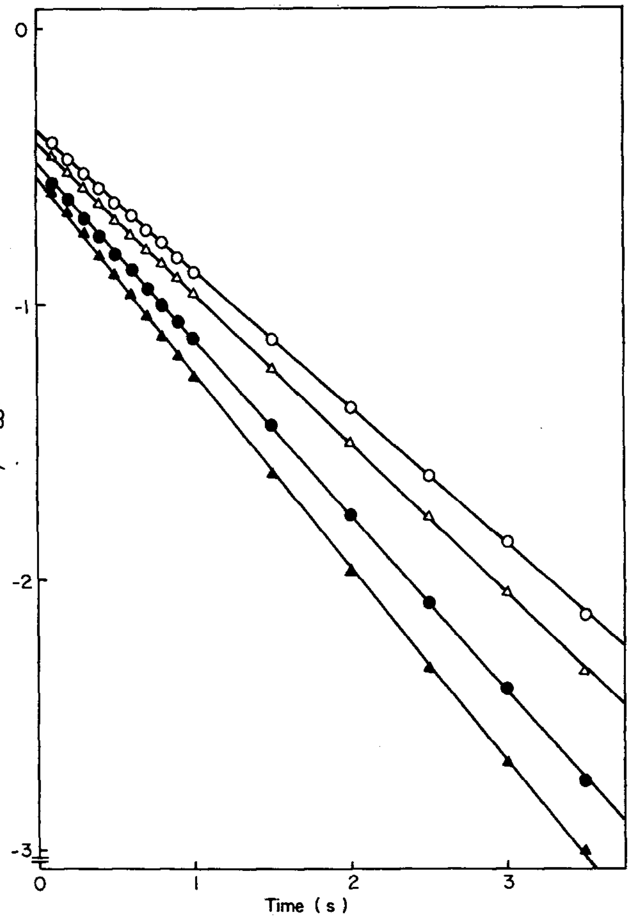


Figure 4 $\mathrm{Ln}|A_t - A_\infty|$ vs. time plot of the reaction of (1)(M = FeCl) with (1)(M = Mn): (○), 14.5; (△), 19.9; (●), 24.6; (▲), 29.6°C

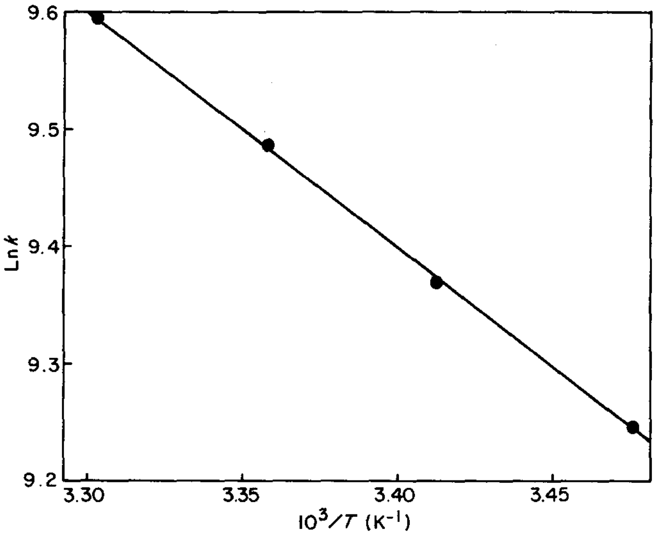


Figure 5 Arrhenius plot of the reaction of (1)(M = FeCl) with (1)(M = Mn)

Table 1 Kinetic data for oxidation of (1)(M = Mn) with (1)(M = FeCl) in DMF

T (°C)	$k \times 10^{-3}$ (s^{-1})
14.5	10.4 ± 0.06
19.9	11.7 ± 0.06
24.6	13.2 ± 0.08
29.6	14.7 ± 0.06

Initial concentrations:
(1)(M = Mn) = 1.25×10^{-5} M
(1)(M = FeCl) = 5.00×10^{-5} M

(1) (M = FeCl) could not be used in a higher concentration than a four-fold molar excess to **(1)** (M = Mn) since then the absorption of the forming manganese(III) complex, **(1)**(M = MnCl), would be totally obscured by the broad absorption of the iron complex. Although **(1)** (M = FeCl) was used only in a four-fold molar excess, $\ln|A_t - A_\infty|$ decreased linearly with time and the pseudo-first-order rate constant was determined from the slope of the individual plot (*Figure 4*).

The activation energy E_A was calculated from the slope of the relation between the logarithms of the obtained rate constants and the inverse absolute temperature (Arrhenius plot) as shown in *Figure 5*.

$\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from

$$\Delta G^{\ddagger} = RT\ln(RT/Nh) - RT\ln k \qquad (1)$$

$$\Delta H^{\ddagger} = E_A - RT \qquad (2)$$

$$\Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta G^{\ddagger})/T \qquad (3)$$

where *R*, *N* and *h* are the gas constant, Avogadro's constant and Planck's constant.* Kinetic data and activation parameters for this system are summarized in *Table 1* and *Table 4*, respectively.

Electron transfer between (1) *(M = FeCl) and* (2) *(M = Mn) or* (2) *(M = Mn) and* (2) *M = FeCl)*

Electron transfer between the low molecular iron porphyrin, (1) (M = FeCl), and polymer-bound

---

* For these treatments, rate constants obtained as pseudo-first-order rate constants were divided by the concentration of metallo-porphyrin to obtain the second-order rate constants, because these transition state equations should be used for the elementary reactions

manganese porphyrin, (2) (M = Mn), and between the polymer-bound complexes, (2) (M = FeCl, Mn) were also investigated in the same way as for the model reaction mentioned above.

As can be seen from *Tables 2, 3* and *4* the activation energy E_A and the activation entropy $\Delta S^{\neq}$ decrease when applying polymer-bound complexes. It is therefore suggested that the polymeric domain has a positive effect on the activation energy but also has a negative influence on the activation entropy.

DISCUSSION

Electron transfer between the metal centres of metalloporphyrins occurs via an inner- or outer-sphere mechanism through axial electron transfer[28,37]. The present electron transfer reaction was analysed in DMF, which will replace the axial chloride anion at the iron(III). There was less possibility of inner-sphere electron transfer because of the absence of a ligand with bridging capability[28]. In the present case an outer-sphere mechanism is therefore assumed.

The reaction between low molecular weight porphyrins (*Figure 10a*) should obey pseudo-first-order kinetics in the presence of an excess of one reaction component. This result can actually be seen in *Figures 4* and *5*. By changing one or both components from the low molecular weight complex to the polymer-bound one, the reaction occurred through a different mechanism as shown in *Figures 6* and *8*. Electron transfer now proceeds in two steps with different rate constants and activation parameters (*Tables*

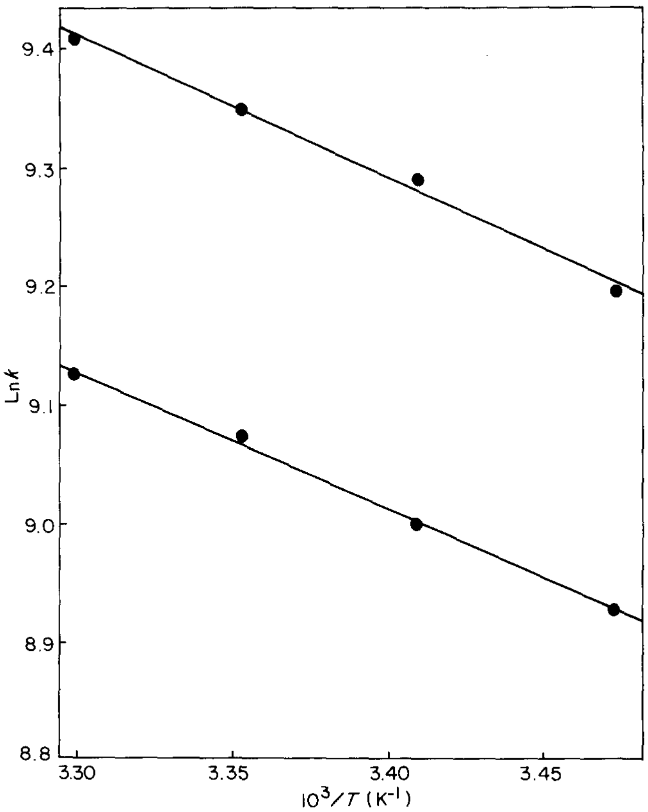


Figure 7 Arrhenius plot of the reaction of (1)(M = FeCl) with (2)(M = Mn). The upper curve corresponds to the fast reaction step, the lower one to the slower reaction step

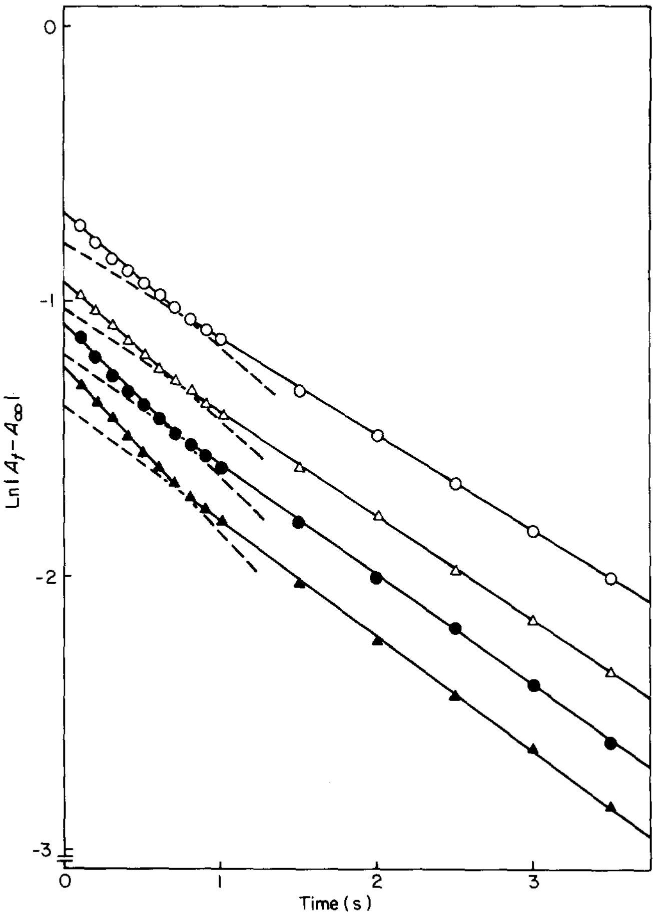


Figure 6 Ln|$A_t - A_\infty$| vs. time plot of the reaction of (1)(M = FeCl) with (2)(M = Mn): (○), 14.7; (△), 20.1; (●), 25.1; (▲), 29.9°C

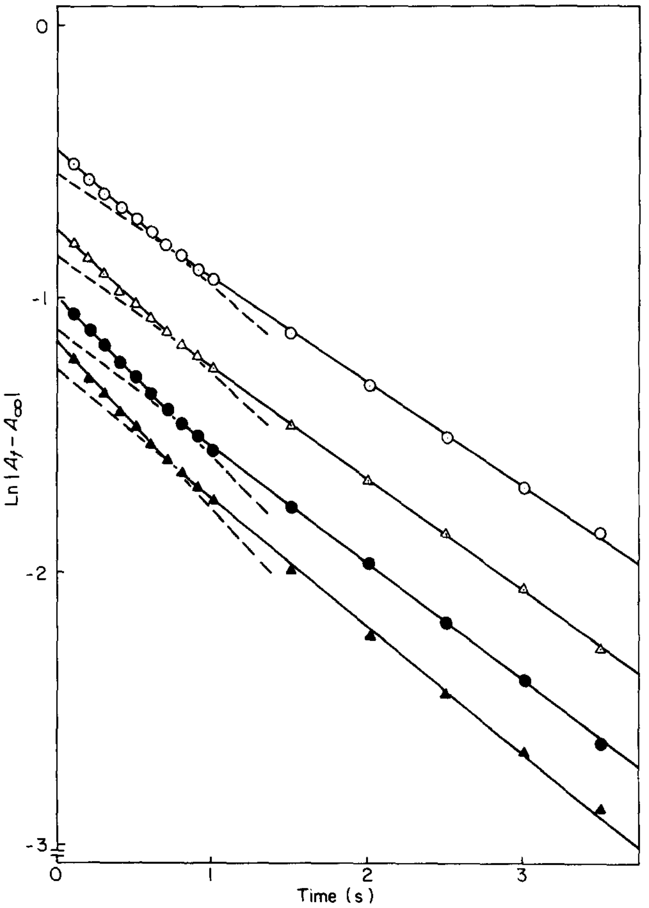


Figure 8 Ln|$A_t - A_\infty$| vs. time plot of the reaction of (2)(M = FeCl) with (2)(M = Mn): (○), 14.6; (△), 19.6; (●), 24.7; (▲), 29.5°C

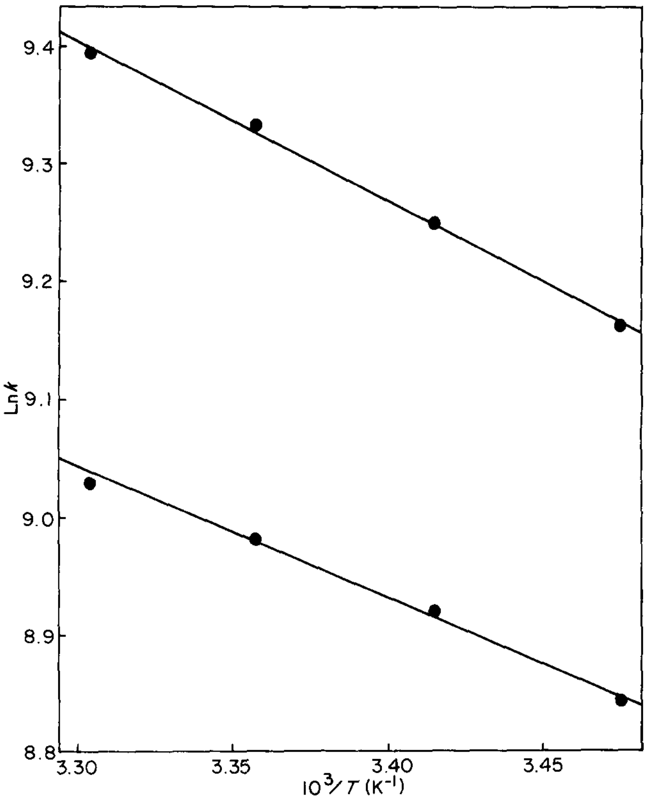


Figure 9 Arrhenius plot of the reaction of **(2)**(M = FeCl) with **(2)**(M = Mn). The upper curve corresponds to the fast reaction step, the lower one to the slower reaction step

2, 3 and *4*). The plots in *Figures 6* and *8* show fast and slow reaction steps. By comparing the data in *Table 4*, it is found that the pseudo-first-order rate constants k are all of the same order of magnitude but that there are considerable changes in the activation energy E_A and the activation energy $\Delta S^{\ddagger}$ caused by the polymeric environment. The rate constant k at 25°C varies between $13.2 \times 10^3\ s^{-1}$ and $11.3 \times 10^3\ s^{-1}$ within the first 0.7 s. In the low molecular weight–low molecular weight system there was no further change, whereas in the low molecular weight–polymer and polymer–polymer systems k values drop of $8.7 \times 10^3\ s^{-1}$ and $8.0 \times 10^3\ s^{-1}$, respectively. An even greater influence of polymeric domain is observed for the activation energy E_A and the activation entropy $\Delta S^{\ddagger}$. Within the first 0.7 s of the reaction E_A drops from 16.8 kJ mol^{-1} in the low molecular weight–low molecular weight system to 9.9 kJ mol^{-1} in the low molecular weight–polymer and to 11.4 kJ mol^{-1} in the polymer–polymer system and remains around 9.5 kJ mol^{-1} for the second slower reaction step in the systems with polymeric compounds involved.

According to a higher concentration of the reaction partners and a therefore higher efficiency in the polymeric domain, the activation entropy $\Delta S^{\ddagger}$ becomes considerably smaller, changing from -47.1 J K^{-1} mol^{-1} in the low molecular weight–low molecular weight system to around -70 J K^{-1} mol^{-1} in the other two systems.

In the case of the reaction between polymer-bound manganese porphyrin and low molecular weight iron porphyrin, the lower activation energy observed was suggested to be due to a local concentration effect caused by the polymer. After the low molecular weight iron complex has begun to interact with the polymer-bound complex, the reaction can proceed relatively easily since now there is a high concentration of the manganese complex around (*Figure 10b*). This is to say, the low molecular weight complex has been trapped in the polymeric domain. The two reaction steps with different rate constants can be explained as follows. The fast step might be due to reaction at the surface of the polymer coils and the second step to reaction of molecules that have penetrated into the polymeric domain; the latter would therefore be slower because of the sterically hindered diffusion into the polymer coils or the conformational changes required for the reaction.

In the polymer–polymer case (*Figure 10c*), the activation energy for the fast reaction step increases again but is still considerably lower than in the low molecular weight–low molecular weight system. This increase is attributed to the diminished mobility of the reaction components fixed at the polymer chain. The decrease compared to the reaction between the low molecular weight complexes can be explained by polymer–polymer

Table 2 Kinetic data for oxidation of **(2)** (M = Mn) with **(1)** (M = FeCl) in DMF

T (°C)	$k_1 \times 10^{-3}$ (s^{-1})	$k_2 \times 10^{-3}$ (s^{-1})
14.7	9.9 ± 0.16	7.5 ± 0.08
20.1	10.8 ± 0.26	8.1 ± 0.04
25.1	11.5 ± 0.08	8.7 ± 0.06
29.9	12.2 ± 0.16	9.2 ± 0.16

k_2 Pseudo-first-order rate constant calculated between 0.1 and 0.7 s
k_2 Pseudo-first-order rate constant calculated between 0.8 and 3.5 s
Initial concentrations:
(2) (M = Mn) = 1.25×10^{-5} M
(1) (M = FeCl) = 5.00×10^{-5} M

Table 3 Kinetic data for oxidation of **(2)** (M = Mn) with **(2)** (M = FeCl) in DMF

T (°C)	$k_1 \times 10^{-3}$ (s^{-1})	$k_2 \times 10^{-3}$ (s^{-1})
14.6	9.5 ± 0.28	6.9 ± 0.04
19.6	10.4 ± 0.26	7.5 ± 0.08
24.7	11.3 ± 0.38	8.0 ± 0.08
29.5	12.0 ± 0.26	8.3 ± 0.10

k_1 Pseudo-first-order rate constant calculated between 0.1 and 0.7 s
k_2 Pseudo-first-order rate constant calculated between 0.8 and 3.5 s
Initial concentrations:
(2) (M = Mn) = 1.25×10^{-5} M
(2) (M = FeCl) = 5.00×10^{-5} M

Table 4 Activation parameters for oxidation of **(1)** (M = Mn) or **(2)** (M = Mn) with **(1)** (M = FeCl) or **(2)** (M = FeCl) at 25°C in DMF

Activation parameter	**(1)** (M = Mn) + **(1)** (M = FeCl)	**(2)** (M = Mn) + **(1)** (M = FeCl)	**(2)** (M = Mn) + **(2)** (M = FeCl)
$E_{A,1}$ (kJ mol^{-1})	16.8 ± 0.3	9.9 ± 0.6	11.4 ± 0.4
$E_{A,2}$ (kJ mol^{-1})		9.6 ± 0.3	9.2 ± 0.6
$\Delta G_2^{\ddagger}$ (kJ mol^{-1})	28.3 ± 0.01	28.7 ± 0.02	28.7 ± 0.08
$\Delta G_2^{\ddagger}$ (kJ mol^{-1})		29.4 ± 0.02	29.6 ± 0.02
$\Delta H_1^{\ddagger}$ (kJ mol^{-1})	14.3 ± 0.3	7.4 ± 0.6	8.9 ± 0.4
$\Delta H_2^{\ddagger}$ (kJ mol^{-1})		7.1 ± 0.3	6.7 ± 0.6
$\Delta S_1^{\ddagger}$ (J K^{-1} mol^{-1})	47.1 ± 0.8	−71.5 ± 1.7	−66.6 ± 1.3
$\Delta S_2^{\ddagger}$ (J K^{-1} mol^{-1})		−74.8 ± 0.8	−76.8 ± 2.1

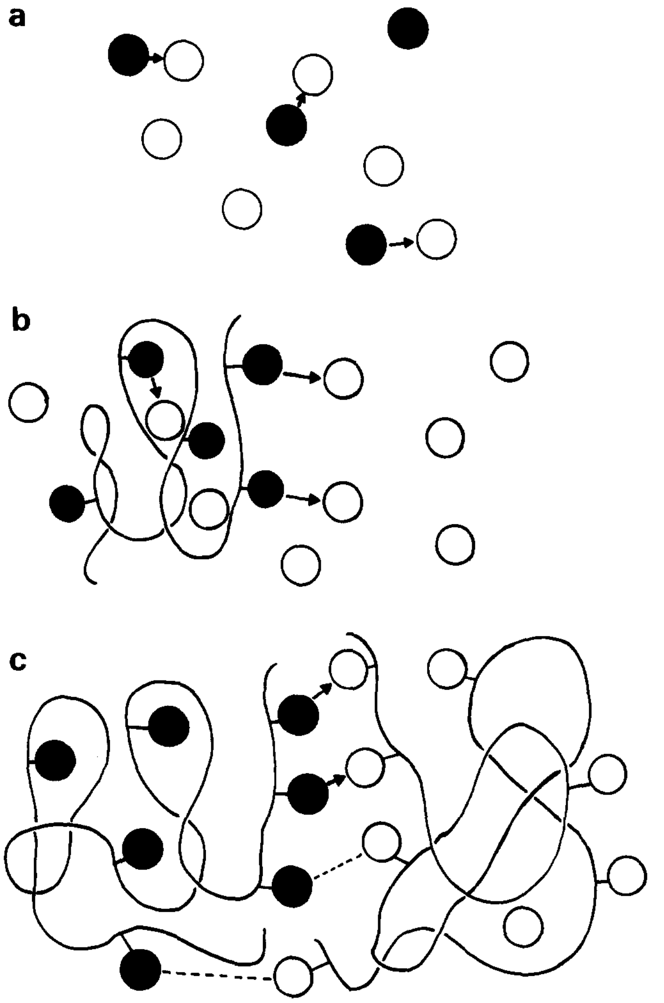


Figure 10 Scheme of the reaction between metallo-porphyrins in solution: (a) (**1**)(M=FeCl) (○) and (**1**)(M=Mn) (●); (b) (**1**)(M=FeCl) (○) and (**2**)(M=Mn) (●); (c) (**2**)(M=FeCl) (○) and (**2**)(M=Mn) (●)

interaction. Once the polymer chains are interacting with each other, the reaction proceeds easily, being enhanced by a local concentration effect as in the low molecular weight–polymer system and a so-called 'zipper effect' as shown in *Figure 10c* by the broken lines. The observed slower reaction step is the electron transfer accompanied by conformational changes of the polymer chains as mentioned above.

It has been found that polymer domain has a considerable influence on the electron transfer reactions between metallo-porphyrins, which was especially seen in the kinetics, activation energy and activation entropy. In the present work, the interaction force between the polymer chains is mainly van der Waals force. It should be interesting to investigate electron transfer between polymer-bound porphyrins at polymers bearing ionic or polar functions leading to electrostatic interaction or hydrogen bonds between the polymer chains which are much stronger than secondary binding forces. Such investigations will be summarized in the near future.

ACKNOWLEDGEMENT

This work was partially supported by a grant from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1 Tsuchida, E., Karino, Y., Nishide, H. and Kurimura, Y. *Makromol. Chem.* 1974, **175**, 161
2 Tsuchida, E., Karino, Y., Nishide, H. and Kurimura, Y. *Makromol. Chem.* 1974, **175**, 171
3 Tsuchida, E., Nishide, H., Okawa, T. and Kurimura, Y. *Nippon Kagaku Kaishi* 1974, 1768
4 Ohno, H., Hosoda, N. and Tsuchida, E. *Makromol. Chem.* 1983, **184**, 1061
5 Abe, K., Koide, M. and Tsuchida, E. *Macromolecules* 1977, **10**, 1259
6 Tsuchida, E., Osada, Y. and Ohno, H. *J. Macromol. Sci., Phys.* 1980, **B17**, 683
7 Ohno, H., Matsuda, H. and Tsuchida, E. *Makromol. Chem.* 1981, **182**, 2267
8 Hasegawa, E., Kanayama, T. and Tsuchida, E. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 3039
9 Hasegawa, E., Kanayama, T. and Tsuchida, E. *Biopolymers* 1978, **17**, 651
10 Tsuchida, E., Hasegawa, E. and Kanayama, T. *Macromolecules* 1978, **11**, 947
11 Woehrle, D. *Adv. Polym. Sci.* 1983, **50**, 45
12 Rollmann, L. D. *J. Am. Chem. Soc.* 1975, **97**, 2132
13 Lennox, J. C. and Murray, R. W. *J. Electronanal. Chem.* 1977, **78**, 395
14 Jester, C. P., Rocklin, R. D. and Murray, R. W. *J. Electroanal. Chem.* 1980, **127**, 1979
15 Kobayashi, N., Fujihira, M., Osa, T. and Dong, S. *Chem. Lett.* 1982, 575
16 Hambright, P. and Fleischer, E. B. *Inorg. Chem.* 1965, **4**, 912
17 Fleischer, E. B. and Cheung, S. K. *J. Am. Chem. Soc.* 1976, **98**, 8381
18 Hambright, P. and Chock, P. B. *Inorg. Chem.* 1974, **13**, 3029
19 Pasternack, R. F. *Inorg. Chem.* 1976, **15**, 643
20 Pasternack, R. F. and Spiro, G. *J. Am. Chem. Soc.* 1978, **100**, 968
21 Langley, R. and Hambright, P. *Inorg. Chem.* 1985, **24**, 1267
22 Cohen, I. A., Jung, C. and Governo, T. *J. Am. Chem. Soc.* 1972, **94**, 3003
23 Pasternack, R. F. and Sutin, N. *Inorg. Chem.* 1974, **13**, 1956
24 Balahura, R. J. and Trivedi, C. P. *Inorg. Chem.* 1978, **17**, 3130
25 Darwent, J. R., Douglas, P., Harriman, A., Porter, G. and Richoux, M.-C. *Coord. Chem. Rev.* 1982, **44**, 83
26 Tanno, T., Woehrle, D., Kaneko, M. and Yamada, A. *Ber. Bunsenges. Phys. Chem.* 1980, **84**, 1032
27 Woehrle, D., Gitzel, J., Okura, I. and Aono, S. *J. Chem. Soc., Perkin Trans. II* 1985, 1171
28 Chapman, R. D. and Fleischer, E. B. *J. Am. Chem. Soc.* 1982, **104**, 1575
29 Chapman, R. D. and Fleischer, E. B. *J. Am. Chem. Soc.* 1982, **104**, 1582
30 Neta, P., Gebel, V. and Levanon, H. *J. Phys. Chem.* 1981, **85**, 2117
31 Neta, P. *J. Phys. Chem.* 1981, **85**, 3678
32 Semeikin, A. S., Koifman, O. I. and Berezin, B. D. *Khim. Geterotsikl. Soed.* 1982, **10**, 1354
33 Adler, A. D., Longo, F. R., Kampas, F. and Kim, J. *J. Inorg. Nucl. Chem.* 1970, **32**, 2443
34 Adler, A. D., Longo, R. F. and Varadi, V. *Inorg. Synth.* 1976, **16**, 213
35 Thomas, D. W. and Martell, A. E. *J. Am. Chem. Soc.* 1959, **81**, 5111
36 Kincaid, J. and Nakamoto, K. *J. Inorg. Nucl. Chem.* 1975, **37**, 85
37 Castro, C. E. in 'The Porphyrins', (Ed. D. Dolphin), Academic Press, New York, 1978, Vol. 5, p. 1