Oxygenation of Polymer–Covalently Bonded Metalloporphyrins

Eishun Tsuchida,*[1] Etsuo Hasegawa, and Tatsuya Kanayama

Department of Polymer Chemistry, Waseda University, Tokyo 160, Japan.

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ABSTRACT: Polymer–covalently bonded cobalt(II) and iron(II) porphyrin complexes were prepared by the copolymerization of styrene with the porphyrin vinyl monomers, protoporphyrin IX styrylamide (PPStA), 5-mono(*p*-acrylamidophenyl)-10,15,20-triphenylporphine (ATPP), and 5,10,15,20-tetra($\alpha,\alpha,\alpha,\alpha$-*o*-methacrylamidophenyl)porphine (TmPP). The reactions of these polymer–metalloporphyrins with molecular oxygen were studied in dry aprotic solvents by measuring electron spin resonance and visible absorption spectra. The oxygen-binding affinity of the cobaltous porphyrin was increased by binding to a polymer chain. Especially, covalent attachment increased it most effectively due to the desolvation of the cobalt porphyrins by steric restriction of the polymer chain. The oxygen-binding affinity of the cobaltous porphyrin also increased by constructing tetraamide groups on one side of the porphyrin ring. The covalent attachment dispersing on a large polymer chain prevents metalloporphyrin residues from dimerization and a dimeric oxidation process can be prohibited under the condition where the molar ratio of a comonomer (comonomers) to the porphyrin residue of the copolymer is larger than 1000. Thus relatively stable monomeric oxygen complexes could be formed. However, a slow monomolecular oxidation occurred at room temperature. The shape of the polymer chain in solution scarcely affected the stability of the oxygen complexes. The most stable oxygen adduct was formed in the copoly(styrene–TmPP metal(II)) complex, indicating that the tetraamide groups fixed on the porphyrin ring were responsible for preventing a monomeric oxidation.

Since Tsumaki found in 1938 the reversible binding of the oxygen molecule by the *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) complex,[2] many studies have been made on synthetic oxygen carriers such as Co(II),[3,4] Ir(II),[5] and Rh(I)[6] complexes. Apart from the studies that the iron(II) porphyrin imbedded in a polystyrene matrix absorbs molecular oxygen reversibly[7-9] as well as the phthalocyanine iron(II) complex does in the solid state,[10] few systematic studies have been made on the iron(II) porphyrin complexes. Recently, Traylor[11] and Collman[12] have considered the behavior of modified porphyrin complexes and reported kinetic analyses on their ligation.

Prior to work by Collman et al.,[13] the following factors were believed to be important for the formation and stabilization of an oxygen complex of a iron(II) porphyrin on the basis of information from hemoglobin and myoglobin studies.

(1) The hydrophobic pocket constructed by the hydrophobic amino acid residues of the globin chain prevents an electron transfer from a ferrous iron to a bound oxygen molecule, so that a monomolecular oxidation as shown in eq 1 may be restricted.[9-11] (2) The sixth coordination site of a hemeiron is vacant or is occupied by a weak ligand. (3) The distal histidine prevents an irreversible oxidation by hydrogen bonding to a bound oxygen molecule.[14,15] (4) The proximal base increases the oxygen-binding affinity of the ferrous ion.

$$\overset{|}{\underset{|}{\mathrm{Fe}}} + \mathrm{O_2} \rightleftharpoons \overset{|}{\underset{|}{\mathrm{Fe}}}\text{-}\mathrm{O_2} \rightleftharpoons \overset{|}{\underset{|}{\mathrm{Fe}}}{}^{\mathrm{III}} + \mathrm{O_2}^{-} \qquad (1)$$

The fact that anomalous hemoglobins containing no distal bases[16] and erythro-cruorins without any distal one[17-19] can bind oxygen reversibly indicates some uncertainty in the role of the distal histidine on the stabilization of oxygen complexes.

Cohen and Caughey virtually postulated that the principle route of oxidation in $\mathrm{Fe^{II}O_2}$ porphyrin complexes should be a dimeric process [eq 4].[20]

Meanwhile, Hammond and Wu[21] studied the autoxidation of $\mathrm{Fe^{II}Cl_2}$ with molecular oxygen in aqueous media and reported that the rate of autoxidation was proportional to $k[\mathrm{Fe^{II}}]^2[\mathrm{O_2}]$. Thus both researches demonstrated that a stable oxygen complex should be prepared when the dimerization was restricted, supposing the following oxygenation and oxidation process.[12,13,22]

oxygenation

$$\mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}} + \mathrm{O_2} \rightleftharpoons \mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{O_2} \qquad (2)$$

$$\mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{B} + \mathrm{O_2} \rightleftharpoons \mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{O_2} + \mathrm{B} \qquad (3)$$

oxidation

$$\mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{O_2} + \overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{B} \rightarrow \overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{OO}\overset{|}{\underset{|}{\mathrm{Fe}}} \rightarrow \overset{|}{\underset{|}{\mathrm{Fe}}}{}^{\mathrm{IV}}\mathrm{O} \xrightarrow{\mathrm{FeP}} \overset{|}{\underset{|}{\mathrm{Fe}}}{}^{\mathrm{III}}\,\mathrm{O^{2-}}\,\overset{|}{\underset{|}{\mathrm{Fe}}}{}^{\mathrm{III}} \qquad (4)$$

$$\mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}}\mathrm{O_2} + \mathrm{H^+} \rightarrow \mathrm{B}\overset{|}{\underset{|}{\mathrm{Fe}}}{}^{\mathrm{III}} + \cdot\mathrm{O_2H} \qquad (5)$$

In order to prevent the bimolecular oxidation process, several groups have synthesized hindered porphyrins, for example the picket fence cobalt(II) and iron(II) porphyrin complexes,[13,22] the capped porphyrin iron(II) complex,[23] the cyclophane porphyrin iron(II) complex,[24] the strapped porphyrin iron(II) complex,[25] and the crowned porphyrin iron(II) complex.[26] The picket fence porphyrin iron(II) forms the most stable oxygen complex at 25 °C in homogeneous solution and has been well characterized.[22]

Another approach has been made by Chang and Traylor,[5,27] who paid attention to the proximal base. Iron(II)[5,27,28] and cobalt(II) porphyrins[29] having a proximal base have been prepared. Very marked and rather obvious effects on kinetics of ligation of iron(II) porphyrins have been documented,[30] even though the affinities of cobalt(II) porphyrins for molecular oxygen were not greatly affected.[29]

Metalloporphyrins fixed on the polymeric supports have been studied in solid states.[7,12,31] In these complexes, the metalloporphyrins themselves cannot move at all, while in homogeneous solutions they do. The complexes formed between artificial polymers and metalloporphyrins are interesting as hemoprotein models. Their structures,[32] functions,[33] and redox reactivities with nicotinamide derivatives[34,35] have been clarified. The polymer–covalently bonded metalloporphyrin complexes have been

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Table I
Results of Copolymerizations of the Porphyrin Vinyl Monomers[a]

no.	porphyrin, g (mol)	comonomers,[b] g (mol)	[total monomer]/[I]	solvent[c] (mL)	reaction time, h	yield, g	copolymer composition[d]	$[\eta]^{30}$, dL/g
1	TmPP, 0.0084 (8.8×10^{-6})	St, 5.0	200	Bz (3)	3	1.63	$St_{4400}TmPP_1$	
2	TmPP, 0.0307 (3.2×10^{-5})	St, 2.5	220	Bz (2)	3	0.81	$St_{1000}TmPP_1$	0.40 (Bz)
3	PPStA, 0.040	St, 20.0	500	DMF (10)	4	6.75	$St_{2200}PPStA_1$	0.35 ($CHCl_3$)
4	ATPP, 0.0298 (4.3×10^{-5})	St, 20.0	400		2	6.15	$St_{1700}ATPP_1$	0.33 ($CHCl_3$)
5	$ATPPFe^{III}$ 0.0100 (1.3×10^{-5})	St, 3.76, NVIm, 0.645	300	DMF (3)	2	1.21	$St_{6040}NVIm_{210}$ $ATPPFe_1$	0.28 ($CHCl_3$)

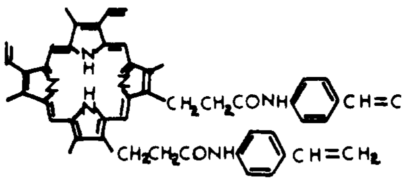
[a] Polymerization temperature; 80 °C. Initiator (I); azobis(isobutyronitrile). [b] St, styrene; NVIm, *N*-vinylimidazole. [c] Bz, benzene; DMF, *N*,*N*-dimethylformamide. [d] Determined spectrophotometrically using the assumption that the molar extinction coefficient of a porphyrin residue of a copolymer is the same as that of its monomeric model porphyrin.

synthesized from the standpoint that a dimeric oxidation might be prevented by dispersing each metalloporphyrin on a large polymer chain by covalent bond.[36-38] The same idea has been employed by Bayer and Holzbach[39] who found that the polyethylene oxide bonded ferrous porphyrin complex can absorb molecular oxygen reversibly at 25 °C in solution.

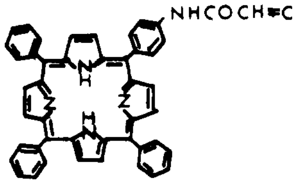
In this paper, we report on the syntheses of new polymer–covalently bonded metalloporphyrins and discuss the role of a polymer chain in the reaction of these polymer–covalently bonded Fe(II) and Co(II) complexes with molecular oxygen in homogeneous solutions.

Results and Discussion

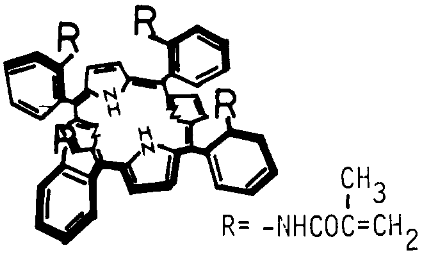
Syntheses of Polymer–Covalently Bonded Metalloporphyrins. The polymer–covalently bonded metalloporphyrins were prepared by the incorporation of metal ions into the preformed copolymers of styrene and the porphyrin vinyl monomers, which were prepared by the radical copolymerization of styrene and the corresponding porphyrin vinyl monomers. The method which includes the copolymerization of styrene and metalloporphyrins was not used because it has been reported that a metal ion like the ferric iron of hemin reacts with radicals to retard the radical copolymerization.[40] The porphyrin vinyl monomers prepared in this paper (as shown in Figure 1) are *N*,*N*′-bis(*p*-vinylphenyl)-7,12-divinyl-3,8,13,17-tetramethylporphyrin-2,18-dipropylamide (protoporphyrin IX styrylamide, PPStA), 5-mono(*p*-acrylamidophenyl)-10,15,20-triphenylporphine (ATPP), and 5,10,15,20-tetra(*α*,*α*,*α*,*α*-*o*-methacrylamidophenyl)porphine (TmPP). PPStA was synthesized by the reaction of protoporphyrin IX di(acid chloride) with *p*-aminostyrene. ATPP was synthesized by the reaction of 5-mono(*p*-aminophenyl)-10,15,20-triphenylporphine ($M_{NH_2}TPP$) with acrylic acid chloride. $M_{NH_2}TPP$ was prepared by the reduction of the corresponding mononitro derivative which had been separated from the reaction products of pyrrole, *p*-nitrobenzaldehyde, and benzaldehyde by the use of column chromatography on silica gel. TmPP was prepared by the reaction of 5,10,15,20-tetra(*α*,*α*,*α*,*α*-*o*-aminophenyl)porphine ($T_{NH_2}PP$) with methacrylic acid chloride. $T_{NH_2}PP$ was prepared according to the method of Collman et al.[22]



A. Protoporphyrin IX Styrylamide (PPStA)



B. 5-Mono-(p-acrylamidophenyl)-10,15,20-triphenylporphine (ATPP)



C. 5,10,15,20-Tetra(α,α,α,α-o-methacrylamidophenyl)-porphine (TmPP)

Figure 1. Schematic representations of the structures of porphyrin vinyl monomers.

The results of the copolymerization are summarized in Table I. The high molecular weight porphyrin copolymer was separated from the unreacted porphyrin vinyl monomer and low molecular weight copolymer (<14 000) by reprecipitation and gel permeation chromatography on Bio Beads S-X1. The results of the GPC are presented in Figure 2. The first eluents containing high molecular weight porphyrin copolymer were collected. The second eluents contained low molecular weight copolymer. The visible absorption maxima of these porphyrin vinyl monomers and their copolymers with styrene are summarized in Table II.

The central metal ions were incorporated into the thus prepared metal-free porphyrin polymers by the method

Table II
Visible Absorption Maxima of Various Porphyrins in Toluene

porphyrins	abs max (nm)	ref
TmPP	424, 516, 548, 591, 647	
copoly(St-TmPP)	424, 518, 548, 599, 661	
copoly(St-TmPPCo^{II})	417, 529, 623	
copoly(St-TmPPCo^{II}-NEtIm)	417, 530, 625	
copoly(St-TmPPCo-NEtIm-O_2)	439, 550, 630	
oxidation product	444, 555, 631	
copoly(St-TmPPFe^{III}Cl)	426, 516, 606, 662	
copoly(St-TmPPFe^{II}-NEtIm)$_2$)	434, 537, 564, 608	
copoly(St-TmPPFe-NEtIm-O_2)	432, 540, 628	
oxidation product	428, 516, 606 (sh), 660 (sh)	
TPPFe^{III}Cl	380, 417, 511, 577, 658, 690 $CHCl_3$	53
μ-oxo-dimer of FeTPP	409, 570, 612 $CHCl_3$	53
μ-oxo-dimer of FeTpivPP	408, 575, 615 $CHCl_3$	22
copoly(St-ATPPFe^{III}-NVIm)	423, 510, 570, 601, 660	
copoly(St-ATPPFe^{II}-NVIm)	430, 536, 570	
copoly(St-ATPPFe-NVIm-O_2)	428, 539	
oxidation product	424, 510, 572, 602, 660	
PPME	408, 506, 541, 577, 632 pyridine	
PPStA	408, 506, 541, 577, 632 pyridine	
copoly(St-PPStA)	408, 506, 540, 576, 630 DMF	
copoly(St-PPStACo^{II})	402, 526, 556 DMF	
copoly(St-PPStAFe^{III}Cl)	375, 400, 510, 560, 635 $CHCl_3$	
TpivPPFe^{III}Br	420, 512, 544, 587, 641 toluene	22
TpivPPFe^{II}(NMIm)$_2$	432, 537, 562 benzene	22
TpivPPFe-NMIm-O_2	429, 548 benzene	22
pyridylTPPCo^{II}*[a]	533 CH_2Cl_2	29
pyridylTPPCo-O_2	546 CH_2Cl_2	29

[a] 5-(2-(4-(3-pyridylcarbamide)-*n*-butoxy)phenyl)-10,15,20-tritolylporphine-Co^{II}.

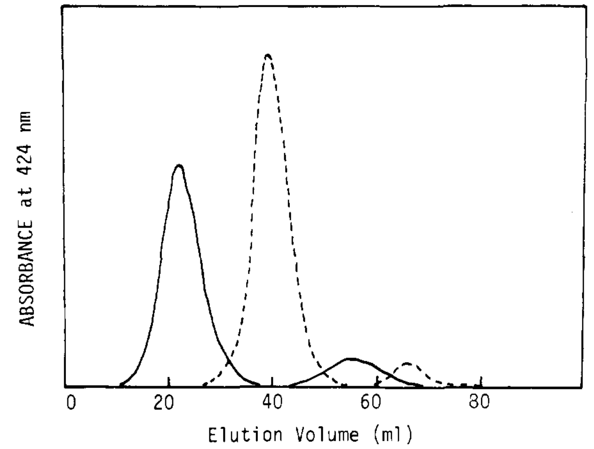


Figure 2. Results of GPC of the porphyrin copolymers with styrene: copoly(styrene–ATPP) (—) and copoly(styrene–TmPP) (- - -). GPC on Bio Beads S-X1 using benzene. Column: 1.2 × 90 cm (- - -), 1.2 × 60 cm (—).

of Adler et al.[41] using Co^{II}Cl$_2$ and Fe^{II}Cl$_2$ in *N*,*N*-dimethylformamide (DMF). This method causes no side reactions during the metal incorporation into a porphyrin.[41] The incorporation of Co(II) ion into the porphyrin copolymers was completed within 15 min under the experimental condition used in this paper, as determined by measuring visible absorption spectra. The absorption maxima in the visible region are summarized in Table II. The absorptions of the polymer–covalently bonded cobalt(II) porphyrins thus prepared are in agreement with those of the corresponding monomeric porphyrin cobalt(II) complexes. The metal incorporation was also supported by the electron spin resonance (ESR) measurement. Figure 3 shows the typical ESR signals due to a cobalt(II) porphyrin. In toluene containing *N*-ethylimidazole, the three lines of superhyperfine structure due to the interaction of a Co(II) with one nitrogen atom of *N*-ethylimidazole indicated the formation of the pentacoordinated cobalt(II) porphyrin complex.[42,43] The metalloporphyrin content of the copolymer, which was determined spectrophotometrically under the assumption that the molecular extinction coefficient of the porphyrin residue of the copolymer is the same as that of the corresponding monomeric porphyrin (complex), was in agreement with the value for the metal-free porphyrin copolymer within experimental error. This also supported the complete incorporation of the central metal ions.

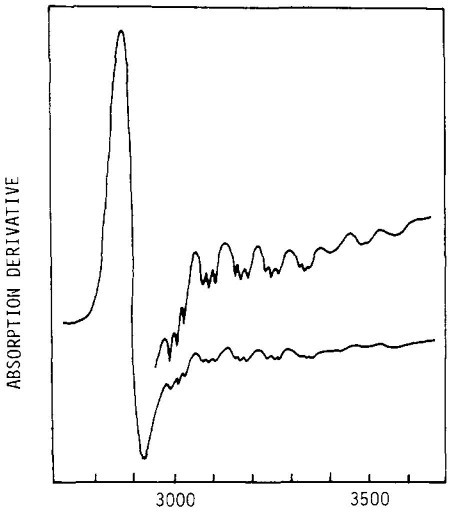


Figure 3. Superhyperfine splitting structure due to the pentacoordinated deoxy complex of the copoly(styrene–PPStACo^{II}) with *N*-ethylimidazole in toluene at −120 °C. [Cobalt(II) porphyrin residue]$_0$ = 1×10^{-4} unit mol/l, [*N*-ethylimidazole]$_0$ = 2×10^{-4} mol/L.

The incorporation of an iron ion into the copolymers was carried out according to the method described above. The incorporation of a ferric iron into the copolymer of styrene with ATPP was complete within 15 min, but that of the copolymer of styrene with TmPP was complete after 2 h. The complete incorporation of an iron into the copolymer of styrene and TmPP was confirmed by adding concen-

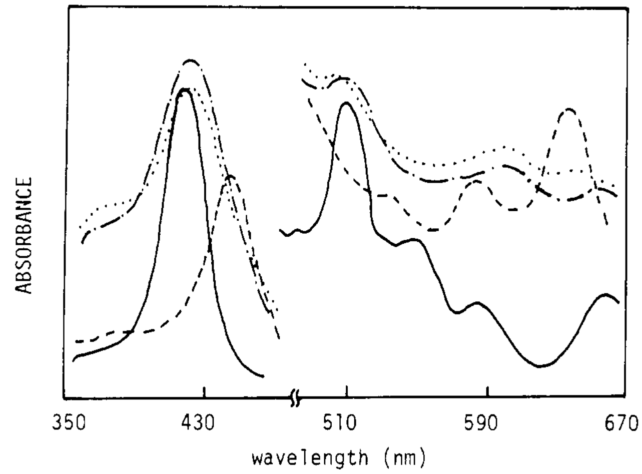


Figure 4. Visible absorption spectra of the copoly(styrene–TmPP) in the absence (—) and in the presence (- - -) of hydrochloric acid and of the copoly(styrene–TmPPFe^{II}Cl) in the absence (---) and in the presence (···) of hydrochloric acid. Solvent: a benzene/tetrahydrofuran (1/1 (vol/vol)) mixture at room temperature.

trated HCl to the polymer solution then measuring the visible absorption spectra as shown in Figure 4. The addition of HCl causes shifts in the absorption maxima of the metal-free copolymer. However, no significant changes were observed when HCl was added to the metalloporphyrin copolymer after the indicated times. The absorption maxima in the visible region are also summarized in Table II. The fact that no emission bands were observed in the fluorescence measurements of the thus prepared iron porphyrin copolymers supported the complete metal incorporation. Any free metal ions were completely excluded by the column chromatography on silica gel as confirmed by ESR measurements. It should be noted that the treatment with silica gel produced no μ-oxo-dimers in the case of the copolymer of styrene and PPStAFe^{III}, although it is well known that this treatment forms μ-oxo-dimers of protoporphyrin IX dimethyl ester iron(III).[44] This indicated that the porphyrin residues of the copolymer are effectively prevented from dimerization by the steric hindrance of the large polymer chain.

Terpolymers having *N*-vinylimidazole as one of the comonomers were synthesized by the copolymerization of styrene, *N*-vinylimidazole, and the porphyrin iron(III) vinyl monomers. Metal-free porphyrin monomers were not used in the terpolymerization because it was very difficult to purify the terpolymer by column chromatography on silica gel after the metal incorporation.

Reaction of Polymer–Covalently Bonded Cobalt(II) Porphyrins with Molecular Oxygen. The reactions of the polymer–covalently bonded cobalt(II) porphyrins with molecular oxygen in toluene were examined initially because (1) the Co(II) complexes can be prepared without any reduction procedures and (2) the Co(II) complexes are sensitive for the ESR measurement, so that the electronic state of the adduct is easily studied.

Figure 5 shows the ESR spectra of the copoly(styrene–TmPPCo^{II}) (B) and the copoly(styrene–ATPPCo^{II}) (A) in toluene containing *N*-ethylimidazole under oxygen at −196 °C. The superhyperfine splitting can be attributed to the monomeric oxygen adduct showing anisotropic property.[42] Figure 6 shows the temperature dependence of the ESR signals of the copoly(styrene–PPStACo^{II}–*N*-ethylimidazole), the copoly(styrene–*N*-vinylimidazole)–Co^{II}PPME and the *N*-ethylimidazole–Co^{II}PPME under oxygen in toluene containing imidazole derivatives. The signals at $g = 2.02$ observed under oxygen were not observed under vacuum and reversibly changed their absorption intensities dependent on the oxygen pressure. The g values and the eight-line superhyperfine (shf) splitting structure can be attributed to the isotropic spectra of the monomeric oxygen adducts. The results of Walker[42] and Hoffman and Petering[43] support our conclusion.

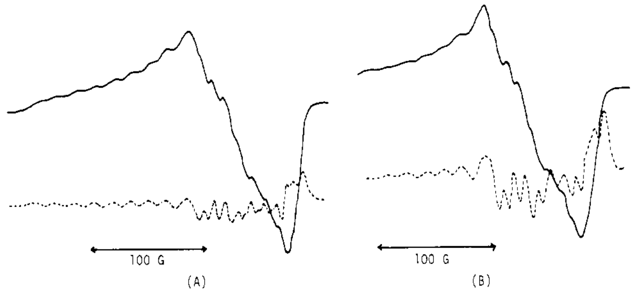


Figure 5. Hyperfine splitting structures of the monomeric oxygen adducts of the copoly(styrene–ATPPCo^{II}–*N*-ethylimidazole) (A) and the copoly(styrene–TmPPCo^{II}–*N*-ethylimidazole) (B) in toluene at −196 °C. P_{O_2} = 760 mmgH. The first derivatives (—) and the second derivatives (- - -). [*N*-Ethylimidazole]$_0$ = 5%, [cobalt(II) porphyrin residue]$_0$ = 1 × 10^{-4} unit mol/L.

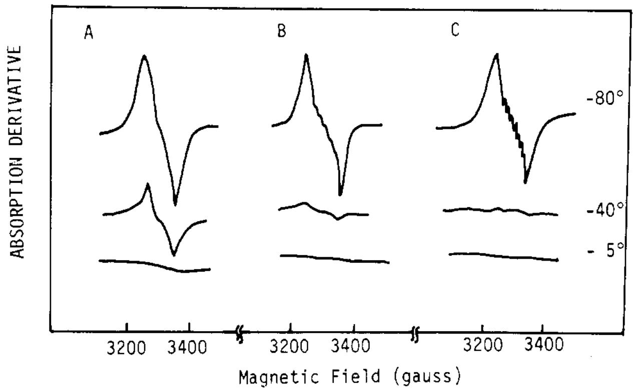


Figure 6. Temperature dependence of the ESR spectra of three types of cobalt(II) porphyrin complexes in toluene under oxygen (760 mmHg): (A) copoly(styrene–PPStACo^{II}–*N*-ethylimidazole); (B) copoly(styrene-*N*-vinylimidazole)–PPMECo^{II} complex; (C) PPMECo^{II}–*N*-ethylimidazole complex; [ligand]$_0$/[cobalt(II) porphyrin]$_0$ = 2.

From Figure 6, it is also obvious that the oxygen-binding affinity of the polymer–covalently bonded cobalt^{II} porphyrin–*N*-ethylimidazole complex is much larger than those of the Co^{II}PPME complexes with copoly(styrene–*N*-vinylimidazole) or *N*-ethylimidazole as ligand under the same conditions. For example, at −40 °C, the polymer–covalently bonded cobalt(II) porphyrin formed a large amount of an oxygen adduct while the Co^{II}PPME–*N*-ethylimidazole complex showed much less complex formation. Table III summarizes the ESR parameters of the monomeric oxygen adducts of various cobalt(II) porphyrin derivatives.

Table IV summarizes the effect of temperature on the change of the ESR signals due to the monomeric oxygen adducts from isotropy to anisotropy and the resolution of the spectra. For example, the simple Co(II) complex, Co^{II}(acacen) (*N*,*N*′-ethylenebis(acetylacetoneiminato)cobalt(II)), showed an isotropic spectra with no shf at −39 °C and with shf splitting at −58 °C and an anisotropic spectra with shf at liquid nitrogen temperature.[45] Figure 7 shows the hyperfine splitting structures of the oxygen adducts of the three types of cobalt(II) porphyrins. The oxygen adducts of the Co^{II}PPME with *N*-ethylimidazole or copoly(styrene–*N*-vinylimidazole) showed the shf structure at −40 and −60 °C, respectively, although the resolution was clearer in the former than in the latter. The

Table III
ESR Parameters of the Monomeric Oxygen Adducts of Various Cobalt(II) Porphyrins

complex[a]	g_{iso}	$g_{\perp}$	$g_{\parallel}$	solvent[b]	temp, °C
CoPPME-DMF-O_2[45]	2.0197			DMF	-44
CoPPME-Py-O_2	2.0207			CH_3CN	-43
CoPPME-Py-O_2[42]	2.02			DMF	+20
copoly(St_{2200}-PPStACo-NEtIm-O_2)	2.019			toluene	-120
copoly($St_{0.975}$NVIm$_{0.025}$)-CoPPME-O_2	2.022			toluene	-80
(*o*-OCH_3)TPPCo-Py-O_2[41]		2.002	2.077	toluene	-196
copoly(St_{1000}-TmPPCo-NEtIm-O_2)	2.00[c]	2.003	2.033	toluene	-196
copoly(St_{1700}-ATPPCo-NEtIm-O_2)	2.017[d]	2.004	2.071	toluene	-196

[a] CoPPME, protoporphyrin IX cobalt(II); DMF, *N*,*N*-dimethylformamide; Py, pyridine; St, styrene; NVIm, *N*-vinylimidazole; (*o*-OCH_3)TPP, tetra(*o*-methoxyphenyl)porphine. [b] DMF, *N*,*N*-dimethylformamide; CH_3CN, acetonitrile. [c] At +20 °C. [d] At -80 °C.

Table IV
Changes of ESR Spectra Dependent on Temperature

complex	spectra	temp, °C
Co(acacen)-Py-O_2[44]	isotropic (no shf splitting)	-39
	isotropic (8 lines shf)	-58
	anisotropic	-196
copoly(St_{2200}-PPStACo-NEtIm-O_2)	isotropic (no shf splitting)	-20 to -80
	isotropic (poor resolved 8 lines)	-120
	anisotropic	-196
copoly($St_{0.975}$-NVIm$_{0.025}$)-CoPPME-O_2	isotropic (poor resolved 8 lines)	-20 to -120
	anisotropic	-196

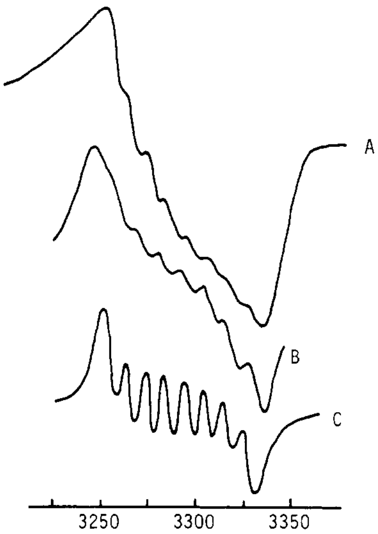


Figure 7. Superhyperfine splitting structure due to the monomeric oxygen adducts of three types of cobalt(II) porphyrin complexes. Experimental conditions were the same as in Figure 6. Temperature: A, -120 °C; B, -80 °C; C, -80 °C.

copoly(styrene-PPStACo^{II}-*N*-ethylimidazole)oxygen complex showed no shf at -80 °C and only isotropic behavior even at -120 °C in solid toluene with eight lines shf. In general, with lower temperature, an increase in the solvent viscosity results in the restriction of the rotation of the complex which is observed by the change of the ESR signals from isotropic to anisotropic. But the results mentioned above on the polymer-metalloporphyrins indicated no effect of the increase of the microsolvent viscosity even at low temperature. This indicated that desolvation of the porphyrin residues had taken place in the domain constructed by the large polymer chain. This consideration is also supported by the fact that the oxygen-binding affinity of the cobaltous porphyrin increased by attaching it to the polymer chain, especially by covalent bonding. This desolvation effect increasing an oxygen-binding affinity was suggested by Collman[19] who observed the large oxygen-binding affinity of the picket fence porphyrin cobalt(II) in the solid state.

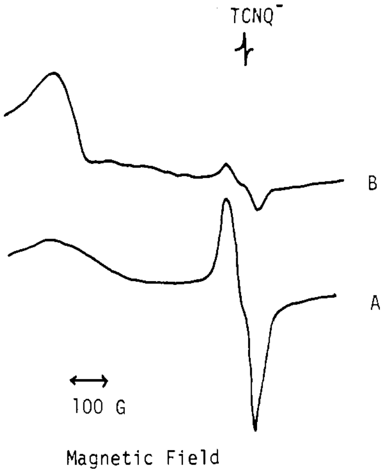


Figure 8. ESR spectra of the copoly(styrene-TmPPCo^{II}) (A) and the copoly(styrene-ATPPCo^{II}) (B) in toluene containing *N*-ethylimidazole under oxygen (760 mmHg) at 20 °C. [Cobalt(II) porphyrin residue]$_0$ = 1×10^{-4} unit mol/L, [*N*-ethylimidazole]$_0$ = 5%.

The ESR spectra of the copoly(styrene-ATPPCo^{II}) and the copoly(styrene-TmPPCo^{II}) in toluene containing *N*-ethylimidazole at 20 °C under oxygen (760 mmHg) are shown in Figure 8. The large signal at $g = 2.0$ due to the monomeric oxygen adduct was observed in the copoly(styrene-TmPPCo^{II}-*N*-ethylimidazole) complex even at 20 °C with the small signal due to the deoxy pentacoordinated complex at $g = 2.3$. It is well known that the oxygen-binding affinity of the Co^{II}PPME-*N*-methylimidazole complex is so small that less than 3% of the cobalt(II) porphyrin can add molecular oxygen in toluene at 23 °C.[46,47] The fact that the copoly(styrene-ATPPCo^{II}-*N*-ethylimidazole) complex, in which a porphyrin ring has no substituents except one acrylamide residue, formed only a slight amount of an oxygen adduct under the same experimental conditions as in the copoly(styrene-TmPPCo^{II}-*N*-ethylimidazole) complex suggests that the increase of the oxygen binding affinity of the cobalt(II) porphyrin in the copoly(styrene-TmPPCo^{II}) is explained

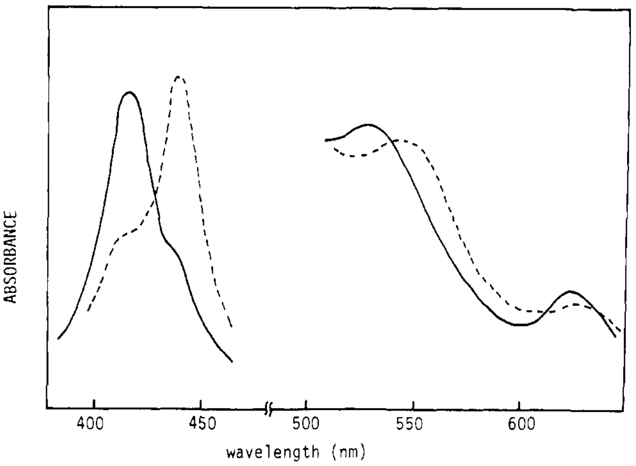


Figure 9. Change of the visible absorption spectra of the copoly(styrene–TmPPCo^{II}) in toluene containing 5% *N*-ethyimidazole at 20 °C under vacuum (—) and under oxygen (---). [Cobalt(II) porphyrin residue]$_0$ = 2.4 × 10^{-4} unit mol/L.

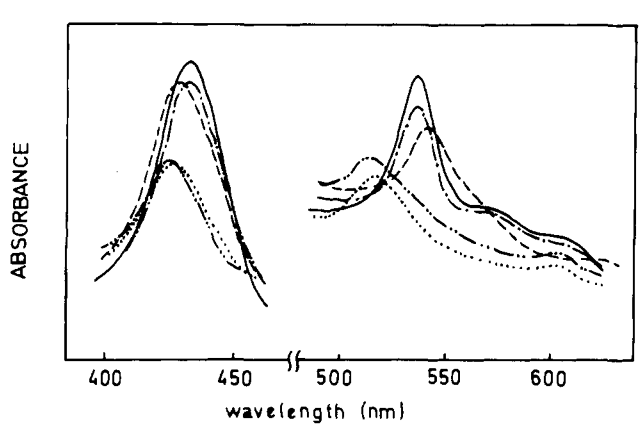


Figure 10. Absorption spectra of copoly(styrene–TmPPFe^{II}) containing *N*-ethylimidazole as axial ligand. [Iron porphyrin]$_0$ = 1.8 × 10^{-5} unit mol/L, [*N*-ethylimidazole]$_0$ = 1.29 × 10^{-3} mol/L, at 20 °C. Before reduction (Fe(III)) (-···-), reduced (Fe(II)) (—), immediately after contact with oxygen (760 mmHg) (---), evacuated after contact with oxygen (760 mmHg) for 15 min (-·-), and oxidized (···).

by the intrasolvation around the sixth ligand due to four amide groups, the desolvation by picket fence, and the desolvation of the porphyrin residues by polymer chain. It has been reported by Collman et al.[48] that the cobalt(II) porphyrin containing tetrapivalamide groups on one side of the tetraphenylporphine ring (T$_{piv}$PPCo^{II}–*N*-methylimidazole complex) can absorb molecular oxygen reversibly at room temperature in toluene. More than 30% of this cobalt(II) porphyrin complex can add oxygen under oxygen pressure of 760 mmHg at 25 °C. This indicated that the affinity of the central cobaltous ion for molecular oxygen is increased by constructing bulky tetraamide groups on the porphyrin ring, on the side which an oxygen is fixed by a coordination bond.[22] A holding effect of these tetraamide groups has been suggested by Traylar et al.[49] This proposal was based on the effect of aprotic polar solvents which increased the oxygen-binding affinity of a cobalt(II) porphyrin remarkably and stabilized an oxygen adduct even at room temperature.[49-52] This solvent effect can be explained such that the polar solvent molecules stabilize the dative bond structure of the oxygen adduct (Co^{III}–O$_2^-$) resulting in an increase in the bond order of the Co–O bond, so that the oxygen affinity of the Co(II) ion increase. Collman[12] insisted that the desolvation is the most important effect, but the question still remains unresolved. Our results on the polymer–covalently bonded Co(II) complexes indicated that intrasolvation of the bound oxygen by the four amide groups may be the main cause in increasing the oxygen-binding affinity in toluene.

From the spectral measurement in the visible region as shown in Figure 9, in which the absorption maxima of the deoxy complex are found at 417 and 530 nm under vacuum and those of the oxy complex are found at 439 and 550 nm under oxygen (760 mmHg), about 70% of the cobalt(II) porphyrin adds molecular oxygen at 20 °C. This spectral change upon oxygenation is consistent with those of the proximal base porphyrin cobalt(II) complexes in toluene at low temperature.[29] The half-life of the oxygen complex was more than 1 day at room temperature under oxygen (760 mmHg). In the case of unpurified copolymers containing a small amount of free cobaltous ions, an irreversible oxidation occurred. Within 20 h, the copolymer was completely oxidized and the absorption maxima of the oxidized product were 444, 555, and 631 nm.

Reaction of Polymer–Covalently Bonded Iron(II) Porphyrins with Molecular Oxygen. The reaction of the polymer-bound ferrous porphyrin complexes with molecular oxygen was studied. The reduction of the ferric complex to the ferrous one was carried out by using Cr^{II}(acac)$_2$ in a dry vacuum box according to the method of Collman et al.[20] The absorption maxima of the ferrous complexes are also summarized in Table II. Figure 10 shows the spectral changes in the visible region upon oxygenation. The absorption maxima due to the deoxy complex of the copoly(styrene–TmPPFe) at 434, 537, 564, and 608 nm under vacuum shifted to the blue in the Soret region and to the red in the Q-band region upon contact with oxygen. The spectrum changed reversibly to that of the deoxy ferrous complex by evacuation using a vacuum line. The half-life time of the monomeric oxygen adduct was about 40 min under 760 mmHg, as determined by measuring the change of the absorbance at 432 nm at 20 °C. The oxidation product, the absorption maxima of which were found at 428, 516, 606 (shoulder), and 660 nm (shoulder), was not the μ-oxo-dimer, but resembled the monomeric iron(III) porphyrin. This indicated that a dimeric oxidation was prohibited in this polymer–covalently bonded iron porphyrin complex.

In the reaction of the copoly(styrene–ATPPFe^{II}) complex with *N*-ethylimidazole, the absorption maximum due to the deoxy ferrous complex changed rapidly upon contact with oxygen resulting in the new band at 428 nm. After contact with oxygen for 5 min at 20 °C, the bubbling of carbon monoxide gas changed the absorption maximum from 428 to 426 nm, which can be attributed to the copoly(styrene–ATPPFe^{II}–*N*-ethylimidazole–CO). However, in this case, about 60–70% of the iron porphyrin residues remained unoxidized. That is, an irreversible oxidation occurred with a half-life time for the oxygenated complex at 20 °C of about 5–7 min in toluene under 760 mmHg of oxygen. This half-life time is much larger than that of the oxygen adduct of tetraphenylporphine iron(II) in toluene containing *N*-methylimidazole, which is oxidized completely within 30 s.[26] Significantly, as shown in Table II, the oxidation product was not a μ-oxo-dimer because the absorption maxima of the oxidation product are quite different from those of the oxo-dimer.[20,53] Here, it should be noted that the added ligand (*N*-ethylimidazole) does not affect the absorption spectra of a μ-oxo-dimer of an iron porphyrin because the iron is out-of-plane by 0.5 Å toward the bridging oxygen atom[54,55] and the formation constant of the complex between the copoly(styrene–ATPPFeIII) and *N*-ethylimidazole was seen to be small. As the unit molar ratio of [metalloporphyrin unit]/[St] was more than 1000, the steric hindrance of macromolecular

Table V
Oxygenation Behavior and Stability of Oxygen Adducts of Various Porphyrin Complexes in Homogeneous Solution

metal ion	porphyrin[a]	oxygenation[b] at 25 °C	$t_{1/2}$	oxidation product	solvent
Co(II)	tetraphenylporphine	no		μ-dioxo-dimer	toluene
	$St_{2200}PPStA_1$	no		(not dimer)[d]	toluene
	$St_{1000}TmPP_1$	yes	>1 day	(not dimer)	toluene
Fe(II)	tetraphenylporphine	yes	<<30 s[c]	μ-oxo-dimer	toluene
	$St_{1700}ATPP_1$	yes	5-7 min	not dimer	toluene
		yes	5-7 min	not dimer	cyclohexane
	$St_{6040}ATPP_1NVIm_{210}$	yes	5-7 min	not dimer	toluene
		yes	15 min	not dimer	DMF
	$St_{1000}TmPP_1$	yes	40 min	not dimer	toluene

[a] St, styrene; NVIm, *N*-vinylimidazole. [b] Under 760 mmHg of oxygen. [c] $Fe^{II}TPP$ is completely oxidized to the μ-oxo-dimer within 30 s in toluene. [d] Unknown product.

chain might affect the ligation of metalloporphyrin residues. Indeed, the *N*-ethylimidazole ligand does not change the absorption spectra of the iron porphyrins in either oxidation compounds.

Sodium dithionite was also used to generate reduced ferrous porphyrin. A methylene dichloride solution of the copoly(styrene–ATPPFe^{III}) was shaken vigorously for 0.5 h with an aqueous solution of dithionite under carbon monoxide atmosphere and the organic layer was collected and then evaporated to dryness yielding powder containing the Fe^{II}–*N*-ethylimidazole–CO complex.[9] Almost the same results were obtained in the reaction with molecular oxygen in toluene as with the Fe(II) complex prepared by the reduction with $Cr^{II}(acac)_2$.

The results indicated that the dimeric oxidation reaction can be prevented by covalent attachment of metalloporphyrins to the polymer chain with highly diluted concentration, allowing relatively stable monomeric oxygen adducts to be formed in these polymer–iron(II) porphyrins. However, a monomolecular oxidation, in which H^+ ions are not involved, occurs irreversibly. The result that the iron(II) porphyrin imbedded into solid polystyrene film can form a stable oxygen complex may suggest that the restriction of the thermal movement of the metalloporphyrin itself may supress a monomolecular oxidation.

Solvent effects were studied to answer two questions: (1) Does the shape of the polymer chain affect the stability of the oxygen adducts? (2) Do polar aprotic solvents stabilize an oxygen complex or not? For these purposes, two solvents, cyclohexane and *N*,*N*-dimethylformamide, were used and the oxygenation behavior was compared with that in toluene. Both solvents are poorer solvents than toluene, so that the polystyrene chain shrinks in the former solvents. Dielectric constants of cyclohexane, toluene, and *N*,*N*-dimethylformamide are 2.0, 2.4, and 36.1, respectively.

In cyclohexane no detectable difference in the reaction behavior of the copoly(styrene–ATPPFe^{II}) with oxygen was found in comparison with that in toluene. The stability of the oxygen adduct was as good as that in toluene. The stabilities of the monomeric oxygen adducts of various metalloporphyrins are summarized in Table V.

In *N*,*N*-dimethylformamide, a relatively stable oxygen complex, was formed as summarized in Table V. Figure 11 shows the spectral changes in the visible region of the copoly(styrene–ATPPFe^{II}–*N*-vinylimidazole). After contact with molecular oxygen (760 mmHg) for 15 min, the evacuation showed the partial reversible change from the absorption maxima at 428 and 539 to those at 430 and 536 nm due to the deoxy Fe(II) complex. The greater stability of the oxygenated complex in DMF (half-life of 15 min) over that in toluene (half-life of 5–7 min) can be explained in that polar aprotic solvent molecules stabilize the oxygen adduct.[51,52] These oxygenation stabilities suggest that the rate of oxidation is not dependent on the shape of the polymer chain in different solvents. Thus, the oxidation reaction was not a dimeric process in these aprotic solvents when metalloporphyrins are dispersed on the large polymer chain by covalent bonding.

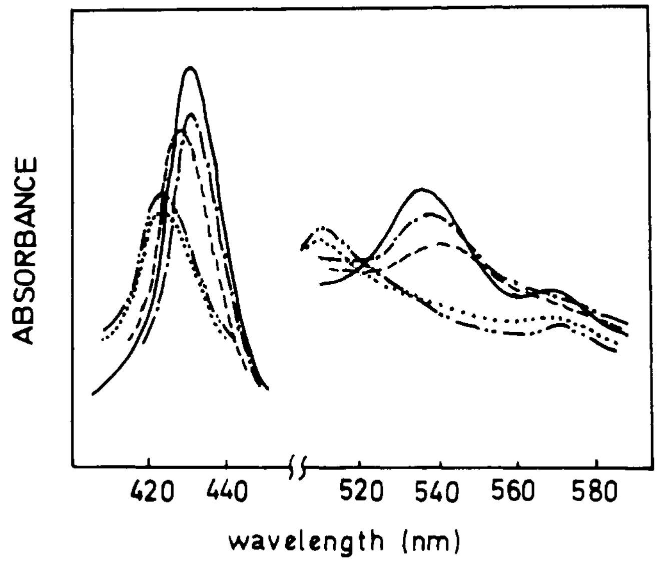


Figure 11. Absorption spectra of copoly(styrene–ATPPFe^{II}–*N*-ethylimidazole) at 25 °C. [Iron porphyrin residue]$_0$ = 1×10^{-5} unit mol/L, [*N*-ethylimidazole]$_0$ = 7.5×10^{-4} mol/L. Fe(III) (-···-) in toluene. Fe(II) (—), immediately after contact with oxygen (- - -), evacuated after contact with oxygen (760 mmHg) for 15 min (-··-) in *N*,*N*-dimethylformamide, oxidized in toluene (- - -).

From the results obtained in this paper on the polymer–covalently bonded cobaltous and ferrous porphyrins in aprotic solvents, it can be concluded that an irreversible dimeric oxidation is prevented by dispersing metalloporphyrin residues on the large polystyrene chain by covalent bond with high dilution. The stability of the polymeric porphyrin complex was 10 to 80 times as long as that of a simple porphyrin complex. Nevertheless, even in aprotic solvents, an irreversible oxidation through a monomolecular process occurred. Such monomolecular oxidation may well be circumvented by incorporating tetraamide groups on one side of a porphyrin ring.

Experimental Section

Reagents. Commercial grade pyrrole was dried over potassium hydroxide pellets and then distilled under reduced pressure. *o*-Nitrobenzaldehyde and benzaldehyde were used without purification. Methacrylic acid chloride and acrylic acid chloride purchased from Osaka Yuhki Co. were distilled. Reagent grade acetic acid and $SnCl_2 \cdot 6H_2O$ were used. *N*-Ethylimidazole was dried over potassium hydroxide pellets and then distilled under reduced pressure. It was redistilled after dehydration with metallic sodium immediately before use. Commercial grade toluene was refluxed over metallic sodium for 3–5 h and then distilled immediately before use. It was used within 4 h after distillation. Commercial grade *N*,*N*-dimethylformamide was distilled under reduced pressure after treating with molecular sieves 4Å. Commercial grade styrene was distilled in vacuo. *N*-Vinylimidazole was distilled in vacuo after the dehydration with potassium hydroxide pellets. $Cr^{II}(acac)_2$ was prepared according to the literature.[55] Commercial grade sodium dithionite was used. Protoporphyrin IX dimethyl ester (PPME) was purchased from Sato Yakugaku Co. (Tokyo) and purified by column chromatography on silica gel. *p*-Aminostyrene was prepared according to the literature by the dehydration of *p*-hydroxyethylaniline.[56] Cyclohexane was distilled after refluxing with metallic sodium.

Synthesis of 5,10,15,20-Tetra(*o*-nitrophenyl)porphine ($T_{NO_2}PP$). To a 1000 mL four-necked flask was added 24.2 g of *o*-nitrobenzaldehyde and 500 mL of acetic acid and the solution was warmed to reflux in an oil bath. To this was added 11.1 mL of pyrrole dropwisely for 0.5 h and then the mixture was refluxed for 25 min. The reaction mixture was then cooled to 35 °C and the precipitate was collected on a glass filter, washed with chloroform and then methanol, and dried in vacuo. The yield was 4.06 g (12.8 wt %). Elemental analyses gave C, 66.16 (66.50); N, 14.25 (14.10); H, 3.26 (3.30) (values in parentheses mean calculated ones for $C_{44}H_{26}N_8O_8$).

Synthesis of 5,10,15,20-Tetra($\alpha,\alpha,\alpha,\alpha$-*o*-aminophenyl)porphine ($T_{NH_2}PP$). To a flask containing 3.0 g of $T_{NO_2}PP$ was added 100 mL of concentrated HCl. It was kept at 65–70 °C on a water bath and then 10 g of $SnCl_2 \cdot 6H_2O$ was added. The mixture was reacted for 25 min with agitation, neutralized by adding 110 mL of concentrated NH_4OH, and then extracted with chloroform. The chloroform layer was washed with dilute NH_4OH and then with water. It was concentrated to 100 mL and then 40 mL of heptane and 25 mL of ethanol were added. Next it was concentrated by evaporation and the precipitates were collected, washed with methanol, and dried in vacuo. The yield was 2.28 g (89.5 wt %). The $\alpha,\alpha,\alpha,\alpha$ isomer was separated from other $\alpha,\beta,\alpha,\beta$; $\alpha,\alpha,\beta,\beta$; and $\alpha,\alpha,\alpha,\beta$ isomers according to the method of Collman et al.[18] The last three isomers were eluted by a benzene/diethyl ether (1/1 (v/v)) mixture and then the $\alpha,\alpha,\alpha,\alpha$ component was eluted by an acetone/diethyl ether (1/1 (v/v)) mixture. The solution was used immediately for the next reaction.

Synthesis of 5,10,15,20-Tetra($\alpha,\alpha,\alpha,\alpha$,-*o*-methacrylamidophenyl)porphine (TmPP). To 100 mL of an acetone/diethyl ether mixture containing 0.076 g (1.1×10^{-3} mol) of $T_{NH_2}PP$ in a 300-mL flask was added 1 mL of pyridine and the solution was kept at 0–5 °C in an ice–water bath. To this solution was added 1.0 mL (0.01 mol) of methacrylic acid chloride. The mixture was reacted at room temperature for 1 h with agitation, evaporated to dryness at 20 °C, dissolved in chloroform, neutralized with dilute NH_4OH, and washed with water. After concentrating the chloroform layer by evaporation at 20 °C, it was purified by chromatography on silica gel. The yield was 0.0402 g (38 wt %). Elemental analyses gave C, 74.49 (76.09); N, 11.69 (11.83); H, 5.46 (5.32) (values in parentheses mean calculated ones for $C_{60}H_{50}N_8O_4$). Infrared absorption maxima on KBr pellet (cm^{-1}): 1680 $\nu_{C=O(amide)}$, 1510 $\delta_{NH(amide)}$, 1630 $\nu_{C=C(vinyl)}$, 925 $\delta_{CH(vinyl)}$; mass spectrum, *m*/*e* 947 (100), 948 (45), 947 (17) (values in parentheses mean ratios of peak intensity); NMR δ −2.7 (s, 2 H, pyrrole NH), 1.14 (s, 12 H, methyl), 4.42 (d, 8 H, = CH_2), 7.4–8.1 (m, 16 H, ortho-substituted phenyl), 8.81 (s, 4 H, amide NH), 8.98 (s, 8 H, pyrrole β-CH) (solvent; $CDCl_3$; internal reference, Me_4Si); visible absorption maxima (nm in $CHCl_3$) 424, 516, 548, 591, 647.

Synthesis of *N*,*N*′-Bis(*p*-vinylphenyl)-7,12-divinyl-3,8,13,17-tetramethylporphyrin-2,18-dipropylamide (PPStA). The PPStA was synthesized according to the previous paper.[36] Protoporphyrin IX dimethyl ester (PPME) was hydrolyzed by treating with 10 mL of 25% HCl with stirring for 5 h at room temperature in the dark. The precipitate was collected and dried in vacuo over potassium hydroxide pellets, reacted with 2 mL of thionyl chloride under nitrogen atmosphere at room temperature for 3 h, and evaporated to dryness.[27] It was used without further purification. To the acid chloride was added tetrahydrofuran and then excess *p*-aminostyrene (0.4 mL). After reacting under N_2 for 10 h with stirring, the solution was washed with aqueous NH_3 and then with water. The organic solvent was removed by a vacuum pump. The PPStA was purified by chomatography on silica gel eluting with the use of a chloroform/methanol mixture and was dried in vacuo. The yield was 45 wt %. The structure was confirmed by elemental analyses and infrared, NMR, and visible absorption spectral measurements.[36] Elemental analyses gave C, 70.73 (71.67); N, 10.02 (10.02); H, 6.66 (6.02) (values in parentheses mean calculated ones for $C_{50}H_{50}O_2N_6Cl_2$ as dichloric acid salt).

Synthesis of 5-Mono(*p*-nitrophenyl)-10,15,20-triphenylporphine ($M_{NO_2}TPP$). A 1000-mL four-necked flask containing 800 mL of propionic acid was warmed to refluxing. To it was added 0.24 mol of benzaldehyde and 0.08 mol of *p*-nitrobenzaldehyde and then 0.32 mol of pyrrole were added dropwisely. The mixture was refluxed for 20 min. After cooling, tarry precipitates were washed with an acetone/diethyl ether mixture (1/10 (v/v)) and insoluble parts were collected on a glass filter, and the solution was washed with methanol. The precipitate was extracted with an acetone/diethyl ether mixture (1/1 (v/v)). The soluble part was evaporated to dryness and washed with methanol and then with hot water. It was dried in vacuo. The yield was 12.45 g. The residue was purified and separated by column chromatography on silica gel using benzene/*n*-hexane mixtures. After the first and second elutes by a benzene/*n*-hexane (1/1 (v/v)) mixture, the elute by a benzene/*n*-hexane (2/1 (v/v)) mixture was collected and evaporated to dryness. This last component was further purified on silica gel. The yield was 1.59 g (2.7 wt %). Elmental analyses gave C, 80.45 (80.09); N, 11.00 (10.62); H, 4.17 (4.04) (values in parentheses mean calculated ones for $C_{44}H_{29}N_5O_2$). IR on KBr pellet (cm^{-1}) $\nu_{as(NO)}$ 1518, $\nu_{s(NO)}$ 1350, $\nu_{C=C(phenyl)}$ 1596, $\delta_{CH(monosub\ phenyl)}$ 1188, 1176, 1155, $\delta_{CH(p\text{-}sub\ phenyl,\ out\ of\ plane)}$ 795; R_f value on silica gel plate in chloroform 0.53; NMR δ 7.72 (multiplet, 9 H, m, *p*-H of monosubstituted phenyl), 8.15 (multiplet, 6 H, *o*-H of monosubstituted phenyl), 8.46 (quartet, 4 H, para-substituted phenyl), 8.66 (doublet, 2 H, 3,7-CH of pyrrole), 8.83 (doublet, 2 H, 2,8-CH of pyrrole), 8.79 (singlet, 4 H, 12,13,17,18-CH of pyrrole); visible absorption maxima (nm, in *N*,*N*-dimethylformamide) 417.6, 514.0, 549.6, 591.2, 641.2.

Synthesis of 5-Mono(*p*-aminophenyl)-10,15,20-triphenylporphine ($M_{NH_2}TPP$). To 0.60 g of $M_{NO_2}TPP$ was added 25 mL of HCl. After adding 3.0 g of $SnCl_2 \cdot 2H_2O$, the solution was kept at 65 °C for 25 min, neutralized with concentrated NH_4OH, and extracted with chloroform. The chloroform layer was filtered, concentrated, and further washed with dilute NH_4OH, washed with 200 mL of water twice, and evaporated to dryness. The residue was separated on silica gel using a chloroform/benzene (1/9 (v/v)) mixture as a solvent and the main component was collected and evaporated to dryness and further purified by column chromatography on silica gel: yield 0.47 g (82 wt %); IR on a KBr pellet (cm^{-1}) ν_{NH} 3380, 3450; δ_{NH} 1615; R_f value on silica gel plate (chloroform) 0.47; visible absorption maxima (nm, in *N*,*N*-dimethylformamide) 420.8, 520.0, 560.4, 596.0, 656.0. Elemental analyses gave C, 83.90 (83.91); N, 11.28 (11.12); H, 4.93 (4.97) (values in parentheses mean calculated ones for $C_{44}H_{31}N_5$).

Synthesis of 5-Mono(*p*-acrylamidophenyl)-10,15,20-triphenylporphine (ATPP). A mixture of 20 mL of tetrahydrofuran, 4 mL of pyridine, and 0.5 g of $M_{NH_2}TPP$ was kept at 0–5 °C and 1 mL of acrylic acid chloride was added dropwisely. The mixture was kept at room temperature for 2 h with stirring and then it was evaporated to dryness. This mixture was dissolved in 200 mL of chloroform and 100 mL of dilute NH_4OH. After agitating vigorously, the chloroform layer was collected, concentrated by evaporation, and purified by column chromatography on silica gel twice using chloroform as a solvent: yield 0.495 g (91 wt %); IR on a KBr pellet (cm^{-1}) $\nu_{C=O(amide)}$ 1680; $\nu_{C=C(vinyl)}$ 1640; R_f value (silica gel plate, chloroform) 0.14; soluble in *N*,-*N*-dimethylformamide, chloroform, acetone, ethyl acetate, tetrahydrofuran; insoluble in petroleum ether, *n*-hexane; mass specra (*m*/*e*) 683 (100), 684 (51), 685 (16) (molecular weight of ATPP 683) (values in parentheses mean ratios of peak intensity); visible absorption maxima (nm, in *N*,*N*-dimethylformamide) 421.2, 517.6, 553.2, 594.8, 650.4. Elemental analyses gave C, 82.98 (82.54); N, 10.21 (10.24); H, 4.87 (4.87) (values in parentheses mean calculated ones for $C_{47}H_{33}N_5O_1$).

Copolymerization of Porphyrin Vinyl Monomers. The copolymerization was carried out according to the previous paper.[36]

To a Pyrex polymerization tube was added the prescribed amount of a porphyrin vinyl monomer, styrene, azobisisobutyronitrile, and solvent. This was evacuated by the freeze–thaw method and then sealed. The mixture was reacted at constant temperature with stirring. After the polymerization was over, the reaction mixture was poured into a large amount of methanol or isopropyl alcohol, collected, and dried in vacuo. It was purified further by several reprecipitations and then purified by GPC on Bio Beads S-X1 in benzene.

Incorporation of Metal Ions into the Metal-Free Porphyrin Copolymers. The incorporation of cobaltous and ferric ions was carried out according to the method of Adler et al.[40] using $Co^{II}Cl_2$ and $Fe^{II}Cl_2$ in *N,N*-dimethylformamide. The Co(II) complex was purified by chromatography on silica gel under nitrogen and the elute was evaporated to dryness and dried at 150 °C for 5 h in vacuo. The Fe(III) complexes were also purified by chromatography on silica gel after treating with dilute HCl and then with water. The metalloporphyrin copolymers were freeze–dried from dry benzene immediately before use.

Electron Spin Resonance Measurements. ESR measurements were carried out using a JEOL JES-FE3X ESR spectrometer as described in the previous papers.[36,37] Unoxygenated samples were prepared by a vacuum line. Oxygenated samples were prepared by mixing directly any required ligand solution and the copolymer solution. The quartz tube with a diameter of 4 mm was used. The g values were determined using 7,7,8,8-tetracyanoquinodimethane anion radical ($g = 2.0026$).

Measurement of Visible Absorption Spectra. The spectra were measured by a Union Giken SM-401 spectrophotometer. The spectra were measured using a quartz vacuum cell with a path length of 10 mm. Degassing was done by the freeze–thaw method using a vacuum line.

Purification of Nitrogen and Oxygen Gas. Nitrogen gas was deoxygenated and dried by passing it through a reduced CuO column (8 × 100 cm) at 160 °C followed by concentrated H_2SO_4, potassium hydroxide pellets, granular calcium chloride, and then molecular sieves 4Å. Oxygen was dehydrated by concentrated H_2SO_4, potassium hydroxide pellets, and molecular sieves 4Å.

Reduction of Fe(III) to Fe(II). The same method was used for the reduction by $Cr^{II}(acac)_2$ as reported by Collman et al.[18] The treatments were carried out in a drybox under argon atmosphere. The reduction using $Na_2S_2O_4$ was carried out in a heterogeneous methylene dichloride/water system under carbon monoxide according to the method of Wang.[7] The $Fe^{II}CO$ adducts were separated as solids. Carbon monoxide was removed by a high vacuum pump at 60–70 °C.

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