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Photo-Redox Catalytic Behavior of Water-Soluble Copolymers of the 5,10,15,20-Tetra-*p*-tolylporphyrins Bearing a Vinyl Group in a Substituent at the Pyrrole Moiety and Their Zn-Complexes

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Synopsis. Water-soluble copolymers of the 5,10,15,20-tetra-*p*-tolylporphyrins bearing a *N*-(*p*-vinylphenyl)carbamoyl group in a substituent at the pyrrole moiety or their Zn complexes with *N*-vinyl-2-pyrrolidone have been effective as photo-redox catalysts for the FRA–L-ascorbic acid and the viologen–triethanolamine in aqueous solutions or in the copolymer films.

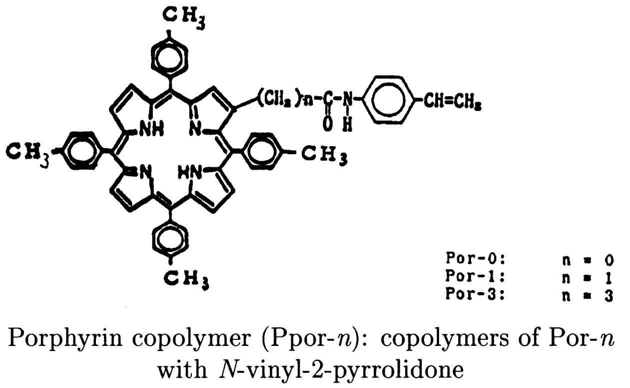
It has been long known that polymers bearing porphyrin or metalloporphyrin units catalyze some dark redox reactions related to biological processes.[1,2] Porphyrin polymers and their metal complexes catalyzing photo-redox reaction systems have been reported, using water-soluble copolymers of the semi-synthetic[1,3—5] or totally synthetic[6,7] porphyrins or metalloporphyrins bearing a vinylbenzyloxycarbonyl group with *N*-vinyl-2-pyrrolidone (VP). In the present note, we wish to report another water-soluble copolymers of porphyrin or Zn–porphyrin with VP which catalyze at least two redox systems with irradiation by visible light. The copolymers to be described here can be distinguished from those in previous studies.[1—7] The present porphyrin or Zn–porphyrin monomers, synthesized starting with pyrrole,[8,9] bear a *N*-(*p*-vinylphenyl)carbamoyl group in a substituent at the pyrrole moiety. The structural formula of the porphyrin monomers is shown as Por-*n* (Chart 1).

where *n* is selected from 0, 1, and 3.

Redox systems adopted were

1. Fast Red A (FRA)–L-Ascorbic Acid (AA) in aqueous solutions together with the copolymers, as shown in Chart 2.
2. 1,1′-Dibenzyl-4,4′-bipyridinium Dichloride (Viologen)–Triethanolamine (TEOA), either in aqueous solutions with the copolymers or embedded in the copolymer films.

Porphrin monomer:



Porphyrin copolymer (Ppor-*n*): copolymers of Por-*n* with *N*-vinyl-2-pyrrolidone
Chart 1.

Experimental

5, 10, 15, 20- Tetra- *p*- tolyl- 2- [ω- (*p*- vinylphenyl)- carbamoly]alkylporphyrin (Por- *n*; *n*=0, 1, 3). Preparative procedures were the same as those described in previous papers.[8,9]

Introduction of a Zn-Atom into Por-*n*. The same procedure as in a previous paper[9] was applied to afford Zn–porphyrin (ZnPor-*n*).

Preparation of Copolymer of Por-*n* or ZnPor-*n* with 1-Vinyl-2-pyrrolidone (VP). The same procedure as in the previous paper[9] was also employed to prepare copolymers for the present study. Table 1 gives various properties of the copolymers, which were all water-soluble.

Photo-Redox Procedure. (1) An aqueous solution of a porphyrin or Zn–porphyrin copolymer (Ppor-*n* or PZnpor-*n*; 2×10^{-4} mol dm^{-3} as Por-*n* or ZnPor-*n*), Fast Red A [FRA; 0.01 g (3×10^{-5} mol) dm^{-3}], and L-ascorbic acid [AA; 1.00 g (6×10^{-3} mol) dm^{-3}] was put into a 10 mm quartz cell. The cell open to air, or purged with nitrogen then sealed, was irradiated with a light at a distance of 10 cm from a 150 W xenon lamp provided with a filter that passes wavelengths greater than 390 nm and the resulting changes of visible absorption spectrum were recorded.

(2-1) An aqueous solution of Ppor-*n* or PZnpor-*n* (2.0×10^{-4} mol dm^{-3} as Por-*n* or ZnPor-*n*), TEOA [10.0 g (6.7×10^{-2} mol) dm^{-3}], and Viologen (1.2×10^{-3} mol dm^{-3}) was put into a 10 mm quartz cell. The cell was purged with nitrogen for 30 min then sealed. The solution was irradiated for 10 min with a light at a distance of 2.5 cm from the lamp and the resulting changes of visible absorption spectrum were recorded.

(2-2) Films of approximately 0.01 mm thickness, tightly sandwiched between two glass plates, were prepared in the same manner as in previous studies.[10,11] A solution of Ppor-*n* or PZnpor-*n* (2.0×10^{-3} mmol as Por-*n* or ZnPor-*n*), TEOA [1 mg (6.7×10^{-2} mmol)], and Viologen (1.2×10^{-2} mmol) in H_2O (5.0 ml) was used. Irradiation by visible light was carried out in the same manner as in (2-1).

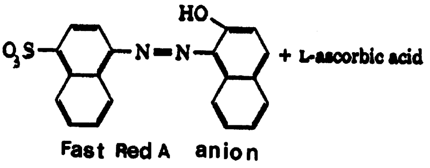


Chart 2.

Table 1. Copolymers Employed for the Photo-Redox Study

Copolymer[a]	Content of[b] (Zn)Por-*n* wt%	IR[c] $\mathrm{cm^{-1}}$	$\lambda_{\mathrm{max(absoptivity)}}$[d]	$[\eta]$[e]
Ppor-0	12.0	2950, 2870, 1650 (C=O), 1420, 1280	420.0 (18.88), 517.0 (0.85), 552.0 (0.55), 591.5 (0.38), 640.8 (0.40)	0.25
Ppor-1	6.0	2950, 2870, 1650 (C=O), 1420, 1280	420.5 (11.55), 516.0 (0.45)	0.28
Ppor-3	9.9	2960, 2880, 1660, (C=0), 1420, 1280	420.0, (13.10), 515.0 (0.40), 652.0 (0.57)	0.22
PZnpor-0	16.0	2960, 2870, 1650 (C=O), 1420, 1280,	420.0 (50.36), 517.5 (2.00), 550.0 (1.29), 648.0 (0.93)	0.30
PZnpor-1	26.9	2960, 2870, 1660 (C=O), 1420, 1290	421.0 (52.28)	0.32
PZnpor-3	35.9	2950, 2860, 1660 (C=O), 1420, 1280	420.0 (47.06), 518.0 (1.84), 553.5 (1.23), 593.0 (0.81), 650.0 (0.90)	0.28

a) Figures indicate n in the Por-*n* or ZnPor-*n* unit. b) Determined spectrophotometrically employing the Soret band. c) KBr-disc. d) λ_{max} (nm) with the absorptivity ($\mathrm{g^{-1}\,dm^3\,cm^{-1}}$) in parenthesis, the solvent being $\mathrm{CHCl_3}$. e) Intrinsic viscosity ($\mathrm{dl\,g^{-1}}$) in DMF at 25 °C.

Results and Discussion

Copolymers Ppor-*n* and PZnpor-*n* employed in the present study posed no serious problems (Table 1). The effect of the polymer in photo-redox system 1 is exemplified in Fig. 1 and summarized in Table 2.

Thus, the absorptions attributable to FRA with λ_{max} at 520 nm rapidly decreased during irradiation as a result of the photoreduction of FRA.[1] The FRA absorption became very small after only 5 min (Fig. 1). Differences in the initial FRA reduction rate among the copolymers were small, presumably because of high reduction rates. These rates were particularly high under $\mathrm{N_2}$ (Table 2). In system 2(-1,2), absorptions with λ_{max}s around 600 and 400 nm appeared, which were attributable to cation radicals[12] derived from Viologen by the one-electron reduction. The results are exemplified in Fig. 2 and summarized in Table 3.

In 2-1, the absorptions developed by the visible irradiation almost disappeared upon a 20-min standing in the dark even when the cell had been purged with $\mathrm{N_2}$, presumably by prompt recombination of the cation and anion radicals in aqueous solutions.[13] In contrast, the glass-sandwiched films (2-2) remained almost unchanged. This fact may indicate that, in the latter, the

Table 2. Effect of the Polymer Addition on the Initial FRA-Reduction Rate upon Irradiation of the Visible Light

Polymer added	Initial FRA-Reduction Rate[a] /% $\mathrm{min^{-1}}$ Open to air	Purged with $\mathrm{N_2}$
None	0.0	0.3
Ppor-0	22.3	25.0
Ppor-1	18.9	23.3
Ppor-3	15.0	26.4
PZnpor-0	16.7	27.1
PZnpor-1	14.0	25.0
PZnpor-3	21.1	23.3

a) Determined using initial tangents for the absorbance decreasing curves at 520 nm with the irradiation.

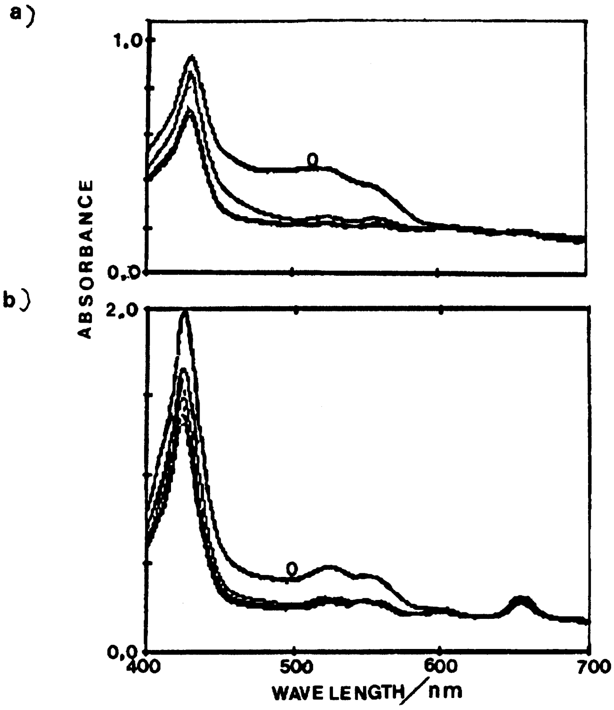


Fig. 1. Typical light-induced changes of the visible absorption spectrum for the FRA–AA system with the polymer addition under $\mathrm{N_2}$. Spectra 0 indicate those before irradiation. a) Ppor-0 added. b) PZnpor-3 added. Absorption decreases with the visible irradiation were shown in 5 min intervals.

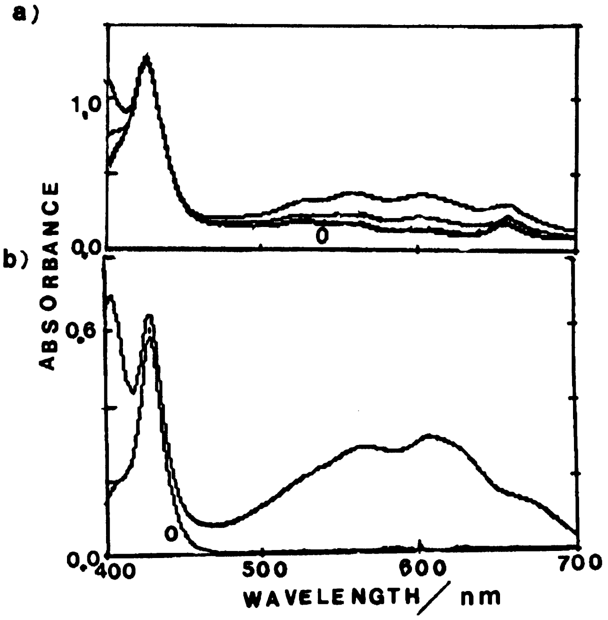


Fig. 2. Typical visible absorption spectra developed as a result of the visible irradiation against the Viologen–TEOA system with exclusion of air. Spectra 0 indicate the same as in Fig. 1. a) Ppor-0 added (aqueous solution under N_2). b) PZnpor-1 as matrix (glass-sandwiched film). Bleachings of the absorptions developed with the irradiation were shown in 10 min standing intervals in the dark.

Table 3. Effect of the Polymer Addition on the Color Development of the Viologen–TEOA System with Irradiation of the Visible Light[a)]

Polymer added	Absorbance increase at 600 nm induced by light[b)]			
	Solution/$\times 10^2$ mol^{-1} dm^3 cm^{-1}			Film
	Upon irrad.	10 min[c)]	20 min[c)]	Upon irrad.
None	0.00	0.00	0.00	0.001[d)]
Ppor-0	1.92	0.73	0.17	0.117
Ppor-1	2.49	0.15	0.00	0.024
Ppor-3	2.39	0.00	0.00	0.153
PZnpor-0	1.54	0.00	0.00	0.158
PZnpor-1	0.84	0.00	0.00	0.343
PZnpor-3	1.39	0.43	0.00	0.098

a) Under N_2. b) Values of molar absorptivity for solutions; values converted into 0.01 mm thickness for films. The values for films remained almost unchanged upon standing in dark. c) Standing time in dark after the irradiation. d) Embedded in VP-homopolymer.

radical cation produced is tightly bound to the VP portion of the solid-state copolymer and stabilized, so that the recombination may be prevented.[10,11,14,15)] In the solution state (2-1), the effect of the central Zn atom in the porphyrin portion of the copolymer as well as that of *n* on the reaction rate is not clear.

Por-*n* provide rather larger values of the rate than PZnpor-*n* do. In this case, however, poor stabilities of the cation radicals produced, as described above, appear to affect the values, so that exact evaluations could not be made.

As for the case of the glass-sandwiched film in which the cation radicals are stabilized due to binding to the VP portions of copolymers, on the other hand, the results obtained differ from those obtained in the solution. The introduction of the Zn atom into the porphyrin ring tends to improve the reaction rate significantly, particularly in the case of Ppor-1. This result is not clearly understood at present.

A probable mechanism of the photoredox reaction in system 1 was described eleswhere.[7)] In system 2(-1,2), photoactivation of the Por or ZnPor portion would also lead to activation of Viologen. The VP portion is considered to facilitate photogeneration of the highly-colored Viologen cation radical as well as to stabilize the latter.[16)]

In conclusion, it can be said that water-soluble porphyrin or Zn–porphyrin copolymers of the present study efficiently catalyze at least a couple of redox reactions in the solution and/or film states under illumination of visible light.

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