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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis, Redox Behavior, Sensitizer Activity, and Oxygen Transfer of Covalently Bound Polymeric Porphyrins

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To cite this Article Wohrle, Dieter , Gitzel, Jörg , Krawczyk, Gerhard , Tsuchida, Eishun , Ohno, Hiroyoki , Okura, Ichiro and Nishisaka, Tsuyoshi(1988) 'Synthesis, Redox Behavior, Sensitizer Activity, and Oxygen Transfer of Covalently Bound Polymeric Porphyrins', Journal of Macromolecular Science, Part A, 25: 10, 1227 – 1254

To link to this Article: DOI: 10.1080/00222338808053418

URL: <http://dx.doi.org/10.1080/00222338808053418>

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SYNTHESIS, REDOX BEHAVIOR, SENSITIZER ACTIVITY, AND OXYGEN TRANSFER OF COVALENTLY BOUND POLYMERIC PORPHYRINS*

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*Part 8 of the series "Polymeric Bound Porphyrins and Their Precursors."
For Part 7, see Ref. 1.

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ABSTRACT

Metal complexes of covalently bound porphyrins are used as sensitive probes for several investigations. Substituted derivatives of tetraphenylporphyrin, phthalocyanine, and naphthalocyanine are synthesized at positively and negatively charged as well as uncharged polymers. The photo-redox activities were studied under irradiation with visible light in the presence of a donor and an acceptor. The triplet life times of covalently bound porphyrin moieties are strongly enhanced compared with the analogous monomeric porphyrins. In addition, the polymer binding results in higher photocatalytic activity. The electron-transfer reactions of Mn(III)-containing porphyrins using the reducing agent dithionite are strongly influenced by the polymer environment. In contrast to monomeric Mn(III)-porphyrins, the porphyrins containing polymers exhibit a two-step reduction which may be due to the change of the conformation of the polymer coil. The catalytic epoxidation of 2,5-dihydrofuran with hypochlorite with formation of 3,4-epoxytetrahydrofuran occurs with water-soluble porphyrins in water. No influence of the polymer environment exists. The different reactions require reaction times from milliseconds up to hours.

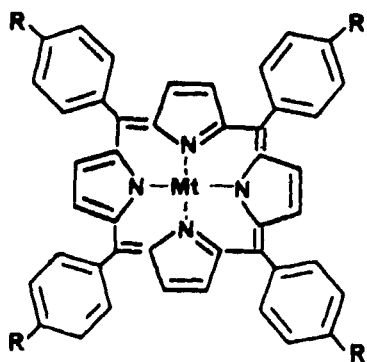
INTRODUCTION

Metal complexes incorporated into polymers can act as sensitive probes to study the influence of the polymer environment on the behavior of the metal complex. In addition, the combination of a polymer and a metal complex may strongly improve the development of new materials with unconventional properties. The present paper selects derivatives of porphyrins like 5,10,15,20-tetraphenylporphyrin (*1a*), phthalocyanine (*2a*), and tetranaphtho (2,3-b:2',3'-g:2'',3''-1:2''',3'''-q-porphyrazine (*3a*, naphthalocyanine)) as metal complexes. Poly(styrene-*co*-chloromethylstyrene), poly(vinylbenzyltriethylammonium chloride), poly(methacrylic acid), and poly(*N*-vinylpyrrolidone-*co*-methacrylic acid) were used as polymers in combination with the porphyrins *1-3*, providing very different environments for the metal complexes. The results given here concentrate on investigations in solution. In order to exclude migration of the metal complexes from the polymer coil to the solvent, covalently bound polymeric porphyrins were synthesized.

Monomeric porphyrins exhibit a great variety of interesting properties in solution: multielectron reduction or oxidation (at the ligand and in some

cases also at the metal ion) [2-4], activity as sensitizer in the conversion of visible light into chemical energy (e.g., hydrogen evolution from water) [2, 4-6], and oxygen transfer for the oxygenation of organic compounds like alkenes [7-9]. These reactions are similar to some occurring in natural systems (electron mediation, photosynthesis, cytochrome P450).

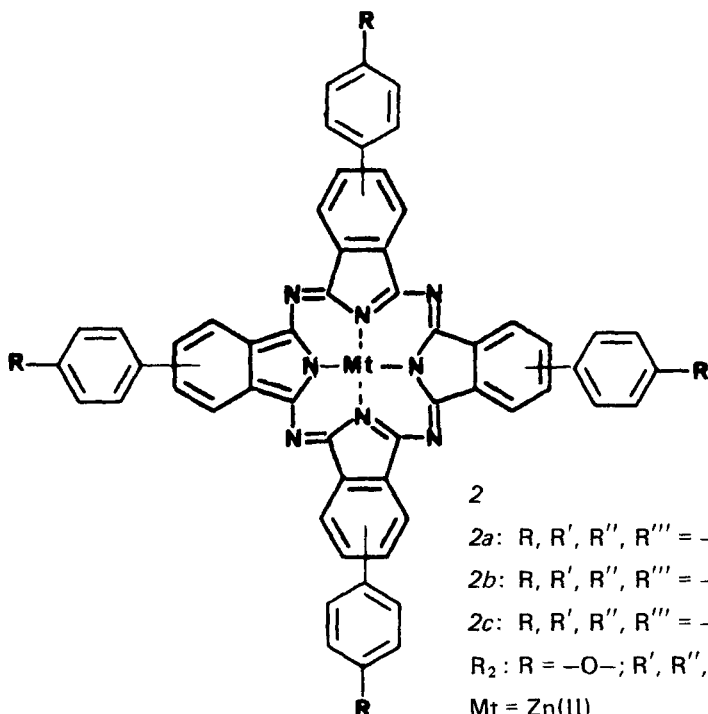
Polymers containing covalently bound porphyrin moieties enable us to study this combination in the direction of enhanced activities.



1

1a: $R, R', R'', R''' = -H$ 1b: $R, R', R'', R''' = -NH_2$ $R_1: R = -NH-; R', R'', R''' = -NH_2$

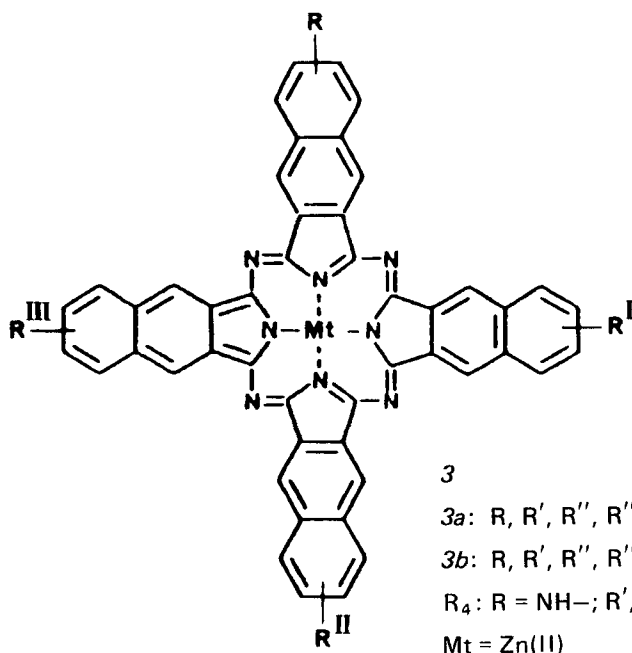
Mt = Zn(II), Mn(III)-OH



2

2a: $R, R', R'', R''' = -H$ 2b: $R, R', R'', R''' = -OH$ 2c: $R, R', R'', R''' = -NH_2$ $R_2: R = -O-; R', R'', R''' = -NH-$

Mt = Zn(II)



EXPERIMENTAL

Synthesis of Materials

The syntheses of the monomeric porphyrins *1b*, *2b*, *2c*, and *3b* are described elsewhere [1, 10-13]. Preparation, purification, and determination of the composition of the various Polymers 4-7 are included in detail in our other papers [1, 10-13].

Spectra

UV/VIS spectra were recorded with a Hitachi U 3200 and fluorescence spectra with a Hitachi 850.

Electron Transfer Reactions

The reduction of the Mn(III) chelates of *5* (with R_1), *6* (with R_1), *8*, and *9* with sodium dithionite was carried out in an argon atmosphere between 15

and 30°C at pH 7 (buffer solution of trihydroxymethylaminomethane and sodium hydroxide) and an ionic strength of 0.25 (KCl). The concentration of the polymer-bound manganese(III)-porphine was 10^{-4} - 10^{-6} mol/L, that of sodium dithionite was 10^{-2} - 10^{-3} mol/L as determined by titration with methylene blue. Titration of sodium dithionite was carried out before and after the measurements, and the results never differed by more than 5%, which showed that sodium dithionite is stable under the reaction conditions. The stopped-flow measurements were conducted with a Aminco-Morrow apparatus. The measurements were carried out by adding a solution of sodium dithionite to a solution of the porphyrin containing the buffer and KCl. The reaction was followed by recording the disappearance of the absorption at ~ 470 nm [Mn(III)-porphyrin] or increase of the absorption at ~ 440 nm [Mn(II)-porphyrin].

Lifetime Measurements

Laser flash photolysis was carried out at room temperature in DMF/H₂O (2/1 v/v) by using a Nd-VAG laser (Model Quanta Ray DC R-2A 10). The wavelength of the laser pulse (10 ns) was 532 nm (~ 350 mJ/pulse). Sample solutions were deaerated by bubbling oxygen-free nitrogen through the solution for some minutes. The light beam of a polychromatic lamp (Nikon, 12 V, 50 W) was passed through a quartz sample cell and came into the entrance slit cell of a monochromator (Model B2B Spectronic BM 50/50). The output from a Hamamatsu photomultiplier (R 446) attached to the exit of the monochromator was displayed on a Hitachi oscilloscope (U 1050 E, 100 MHz).

Photoredox Measurements

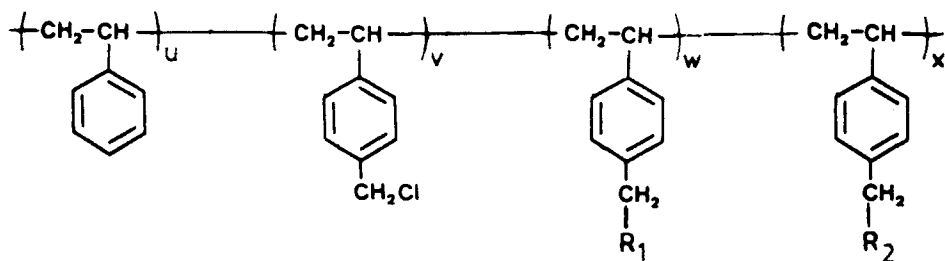
The measurements were carried out in a Pyrex cell (volume 10 mL) with a magnetic stirrer. Typically, a solution (6.6 mL) containing sensitizer (around 10^{-6} mol/L), mercaptoethanol (0.54 mol/L), and methylviologen (MV²⁺; 0.75 mmol/L) in buffer solution (trihydroxymethylaminomethane/HCl) at pH 7.8 was used in DMF/water (2/1 v/v). After bubbling with nitrogen for some minutes in the dark, the cell was placed at 303 K in the light beam path of a 200-W tungsten lamp. Light of wavelength less than 390 nm was cut off with a Toshiba filter (L-39). The reaction vessel was 7.0 cm from the light source. The experiments were carried out under continuous irradiation, and the formation of MV^{•+} was determined with a commercial UV/VIS spectrometer. The concentration of MV^{•+} was calculated from the increased absorbance at 610 nm with $\epsilon = 13\,700 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$.

Oxygenation of 2,5-Dihydrofurane

Mn(III)-porphyrin (6.25 μmol) (or polymer containing the same amount of Mn(III)-porphyrin), 10 μL (0.13 mmol) pyridine, and 70 μL (10 mmol) 2,5-dihydrofuran were dissolved in 2.5 mL water. 7.5 mL of an aqueous solution of 0.24 mol/L sodium hypochlorite (1.8 mmol) was added. The mixture was stirred and analyzed after 4 h by gas chromatography.

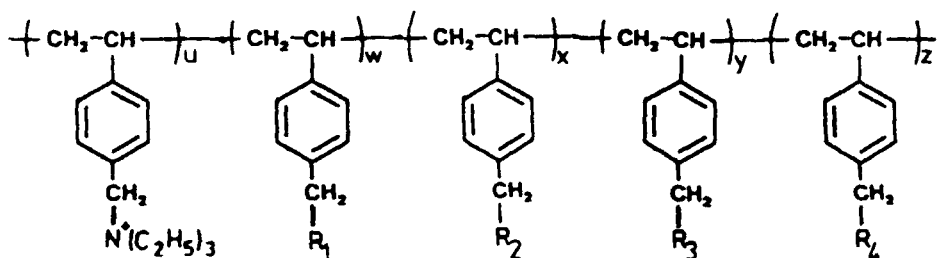
SYNTHESIS OF COVALENTLY BOUND POLYMERIC PORPHYRINS

The selected substituted porphyrins *1b*, *2b*, *2c*, and *3b* contain nucleophilic groups of similar reactivities. Therefore, an identical synthetic procedure can be applied to achieve covalent binding to a polymer. Besides binding of one porphyrin [1, 10-13], addition of different porphyrins to the reaction mixture allows the binding of two or three porphyrins to one polymer system in a one-step procedure [1, 12, 13]. Generally, a method was selected in which a dilute solution of the polymer was dropped into a dilute solution of the porphyrins. The reaction of poly(styrene-*co*-chloromethylstyrene) in the presence of a small amount of triethylamine in DMF results in the formation of the Polymers **4**, which are soluble only in organic solvents such as DMF and toluene [10, 12].



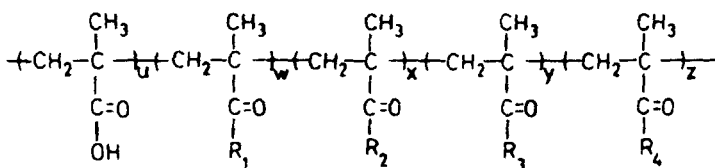
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If the reaction of poly(chloromethylstyrene) is run in the presence of an excess of triethylamine, the covalent binding of the porphyrin and quaternization occur simultaneously. Positively charged Polymers **5**, soluble in water, were obtained [1].



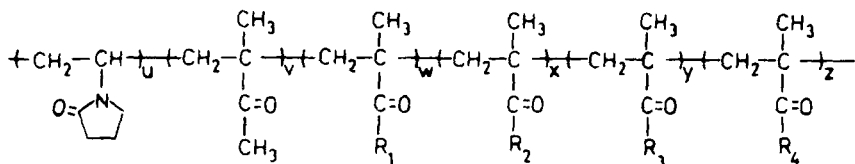
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Negatively charged Polymers 6, containing porphyrin moieties, are easily synthesized by the reaction of poly(methacrylic acid) (activation of the carboxylic acid group by carbodiimides or triphenylphosphine/ CCl_4) with the porphyrins [11, 13].



6

Uncharged water-soluble Polymers 7 containing the porphyrin moieties are obtained by the reaction of poly(*N*-vinylpyrrolidone-co-methacrylic acid) with the monomeric substituted porphyrins in the presence of the same activating agents for the carboxylic acid groups.



7

Residual carboxylic acid groups were converted to methyl ester [13]. For purification the polymers were dissolved in water, filtered from unreacted porphyrins, and then dialyzed. The pure materials were isolated by freeze-drying.

TABLE 1. Composition of the Covalently Bound Polymeric Porphyrins

Sample	Inserted porphyrine	Composition ^a								λ in nm (DMF) ^b
		u	v	w	x	y	z			
4 with R ₁ ; Mt = Zn	<i>Ib</i>	16	0.55	0.45 (46; 3.7)						438
4 with R ₂ ; Mt = Zn	<i>2b</i>	16	0.58	—	0.42 (31; 3.6)					678
4 with R ₁ , R ₂ ; Mt = Zn	<i>Ib + 2b</i>	16	0.30	0.28 (47; 3.8)	0.42 (47; 2.1)	—				678, 439
5 with R ₁ ; Mt = Zn	<i>Ib</i>	122	—	1 (53.2; 24)	—					443
5 with R ₁ ; Mt = Mn(OH)	<i>Ib</i>	49	—	1 (76.3; 5.8)	—					481
5 with R ₂ ; Mt = Zn	<i>2b</i>	675	—	—	1 (9.7; 0.98)	—				683
5 with R ₁ , R ₂ ; Mt = Zn	<i>Ib + 2b</i>	1635	—	3.1 (4.0; 0.41)	1 (12.2; 0.9)					685, 445
5 with R ₁ , R ₃ , R ₄ ; Mt = Zn	<i>Ib + 2c + 3b</i>	675	—	1.1 (11.2; 0.83)		3.1 (31; 3.1)	1 (9.9; 0.83)			774, 682, 438
6 with R ₁ ; Mt = Zn	<i>Ib</i>	700	—	1 (16.6; 1.2)						434
6 with R ₁ ; Mt = Mn(OH)	<i>Ib</i>	49	—	1 (184; 13.7)						474
6 with R ₂ ; Mt = Zn	<i>2b</i>	447	—	—	1 (26.0; 2.6)					680
6 with R ₁ , R ₂ ; Mt = Zn	<i>Ib + 2b</i>	1056	—	1.8 (11.0; 1.1)	1 (20.0; 1.5)					679, 434
7 with R ₁ ; Mt = Zn	<i>Ib</i>	927	102	1 (8.7; 0.56)						436
7 with R ₁ ; Mt = Mn(OH)	<i>Ib</i>	45	4	1 (110; 8.2)						479
7 with R ₂ ; Mt = Zn	<i>2b</i>	1963	217	—	1 (4.2; 0.42)					682
7 with R ₁ , R ₂ ; Mt = Zn	<i>Ib + 2b</i>	1028	112	1 (9; 0.99)	1.1 (8; 0.59)					683, 436
7 with R ₁ , R ₃ , R ₄ ; Mt = Zn	<i>Ib + 2c + 3b</i>	658	68	1.3 (16.5; 1.2)	—	2.4 (30.6; 3.1)	1 (12.5; 1.0)			768, 682, 432

^aIn parentheses: content of bound porphyrin in $\mu\text{mol/g}$, wt%.^bOnly Q band of bound moieties of *2b*, *2c*, *3b*, and Soret band of *Ib*.

The purification could be easily controlled by TLC because unreacted monomeric porphyrins were identified by R_f values above zero whereas the polymers have R_f equal to zero. The porphyrin contents of the polymers were determined by quantitative VIS spectra and determination of metal content.

Some results for linear Copolymers 4-7 with covalently bound moieties of porphyrins with the residue R_1 - R_4 are included in Table 1. The prepared polymers contain porphyrin moieties up to 6.2 wt%. The porphyrins 1*b*, 2*b*, 2*c*, and 3*b* contain four reactive functional groups. Therefore, inter- and intramolecular crosslinking may occur in the reaction with the polymers. Intermolecular crosslinking could be avoided up to a concentration of 0.02 mol of porphyrin per monomer unit in the polymers. Higher amounts of porphyrins under our reaction conditions resulted in the formation of gels due to intermolecular crosslinking. Viscosity measurements may indicate intramolecular crosslinking (microgel formation). The changes of the intrinsic viscosity at 293 K in methanol were as follows: poly(vinylbenzyltriethylammonium chloride) 549 mL/g, Polymers 5 ~30 mL/g; poly(methacrylic acid) 48 mL/g, Polymers 6 ~48 mL/g; poly(*N*-vinylpyrrolidone-*co*-methacrylic acid) 15 mL/g, Polymers 7 ~21 mL/g. Therefore, it is assumed that microgel formation is evident only in the case of the cationic charged polymers.

Table 2 contains the main absorption bands of the porphyrins in the visible region (R_1 Soret band; R_2 , R_3 , R_4 Q-band). Figure 1 gives one example of a Polymer 5 with combined moieties of all porphyrins 1-3. It is known that water-soluble phthalocyanines aggregate strongly in aqueous solutions [14]. This can be seen by a shift of the Q band to shorter wavelength. The cationically charged polymers, 5, show no aggregation (Fig. 1) whereas the other polymers, 6 and 7, slightly aggregate in water. In DMF/water mixtures (e.g., 2/1 v/v) aggregation was never observed. Therefore, the polymer backbone

TABLE 2. Absorption (Soret) and Fluorescence Band of some Porphyrins (Mt = Zn) in DMF/H₂O (2/1 v/v)

Compound	Absorption, λ in nm	Fluorescence, λ in nm
1 <i>b</i>	436.3	636.5
4 with R_1	436.2	632.1
5 with R_1	447.3	645.7
6 with R_1	432.3	621.4/667
7 with R_1	435.1	628.1

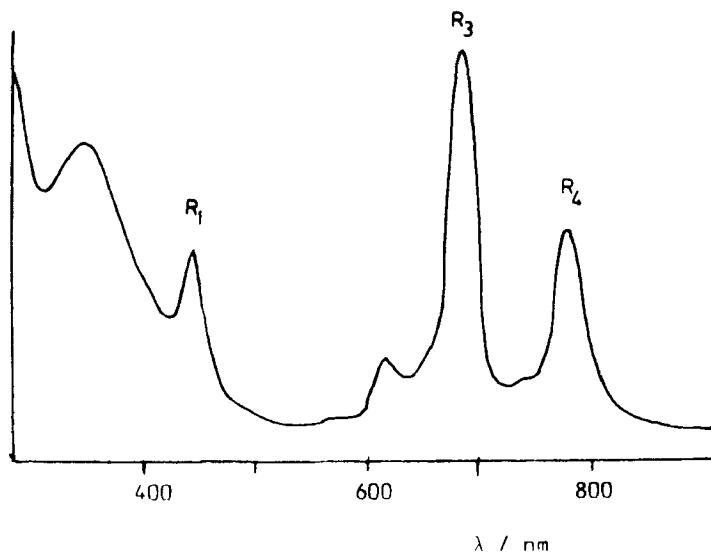


FIG. 1. UV/VIS spectra of 5 (with R_1 , R_3 , R_4 ; Mt = Zn) in water.

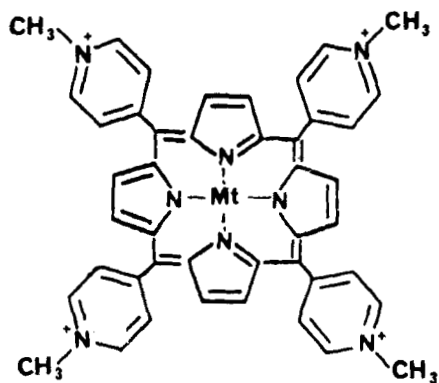
may inhibit strong intermolecular porphyrin/porphyrin interaction. The position of the Soret and fluorescence band of Polymers 4-7 containing R_1 also gives a hint of the influence of the polymer environment on the porphyrins (Table 2). The strongest long wavelength shift exists in the positively charged polymers, 5, and the shortest wavelength shift in the negatively charged ones, 6. For the other polymers, including the monomeric porphyrin 1b, no great influence can be found. The positive charges of the polymer backbone interact strongly with the electron-rich metal chelates, which prevent the porphyrin/porphyrin interaction, as mentioned before.

ELECTRON-TRANSFER REACTIONS

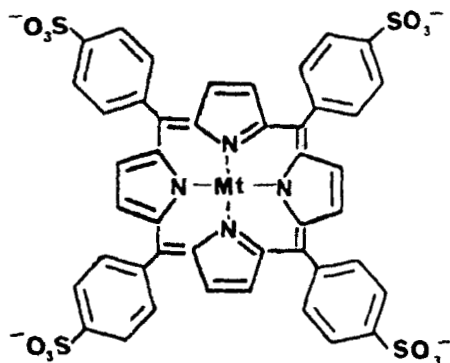
The interest in electron-transfer reactions of synthetic metalloporphyrins originates from comparison with the redox reactions of metalloporphyrin-protein complexes *in vivo*, e.g., metalloenzymes like cytochromes [7-9, 15-18]. Since metalloporphyrins in enzymatic systems are embedded in a polymer environment, synthetic metalloporphyrins with a modified environment, especially polymer-bound porphyrins, should be better model systems than the simple low molecular weight porphyrins. However, only a few papers on

this subject have appeared [10, 11, 19, 21]. No report compares the influence of different polymer environments on electron transfer reactions of porphyrins.

The prepared water-soluble polymer-bound porphyrins 5 (with R_1), 6 (with R_1), and 7 (with R_1) containing Mn(III)OH were employed to study electron transfer from sodium dithionite as reducing agent. Some papers describing the reduction of low molecular weight Mn(III), Fe(III), or Cr(III) porphyrins with dithionite are known [22-24]. Due to the position of the redox potentials of monomeric Mn(III)/Mn(II)-tetraphenylporphyrins, like the positively charged 8 (+0.24 V vs NHE) or the negatively charged 9 (+0.01 V vs NHE) and the redox potential of the $E(S_2O_4^{2-}/SO_3^{2-})$ (-1.12 V vs NHE), the reduction of Mn(III)-porphyrins occurs easily [25, 26].

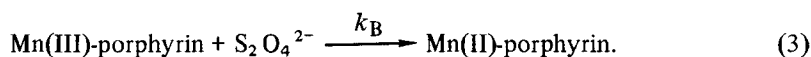
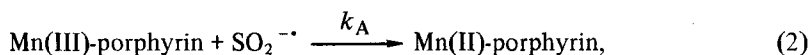
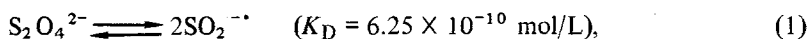


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9

The reduction of a Mn(III)-porphyrin can be followed by electronic spectra: the charge-transfer band of Mn(III)-tetraphenylporphines at ~ 470 nm, the Soret band of Mn(II)-tetraphenylporphines at ~ 440 nm. The reducing agent is mainly the sulfoxylate radical anion [22]. The reactions (Eqs. 1-3) occur with formation of isobestic points in the millisecond to second time range and, therefore, must be measured by the stopped-flow technique [10, 11].



Beside the polymer-bound porphyrins 5 (with R_1), 6 (with R_1), and 7 (with R_1), the positively charged tetrakis(4-*N*-methylpyridyl)porphine (8) and the negatively charged tetrakis(*p*-sulfonatophenyl)porphine (9) (all porphyrins contain Mn(III)OH) were used, too. The reactions were carried out by rapid mixing of two aqueous solutions containing an excess of sodium dithionite and the porphyrin (concentration from 10^{-5} to 10^{-6} mol $^{-1}$). The solutions were adjusted to pH 7 and an ionic strength of 0.25 mol/L.

The pseudo-first-order plots (excess of dithionite) were linear only in the case of the monomeric porphyrins 8 and 9, whereas the polymer-bound ones exhibit curved first-order plots (Fig. 2). Equations (4) and (5) were used to determine k_{obs} and k for the reduction of the monomeric porphyrins [27].

$$-\frac{dc_{\text{Mn(III)}}}{dt} = k \cdot c_{\text{Mn(III)}} \cdot C_{\text{dithionite}} \quad (4)$$

$$\approx k_{\text{obs}} \cdot C_{\text{Mn(III)}}, \quad C_{\text{Mn(III)}}^{\circ} \ll C_{\text{dithionite}}^{\circ}$$

$$k = \frac{k_{\text{obs}}}{(K_{\text{Dn}} \cdot C_{\text{dithionite}})^{1/2}} \quad (\text{for } k_A \gg k_B). \quad (5)$$

For the polymers with porphyrin moieties, the deviation from first order kinetics is due to the influence of the polymer chains. The kinetics were treated in the following way. Reversible, serial, and parallel reactions to different products can be excluded. The total reaction could be separated into two parallel first-order reactions of the species A_1 and A_2 to the product P (Eq. 6) [28-31]. By this method it can be seen that the kinetics of the reduction of polymer-bound Mn(III) porphyrins can be described by

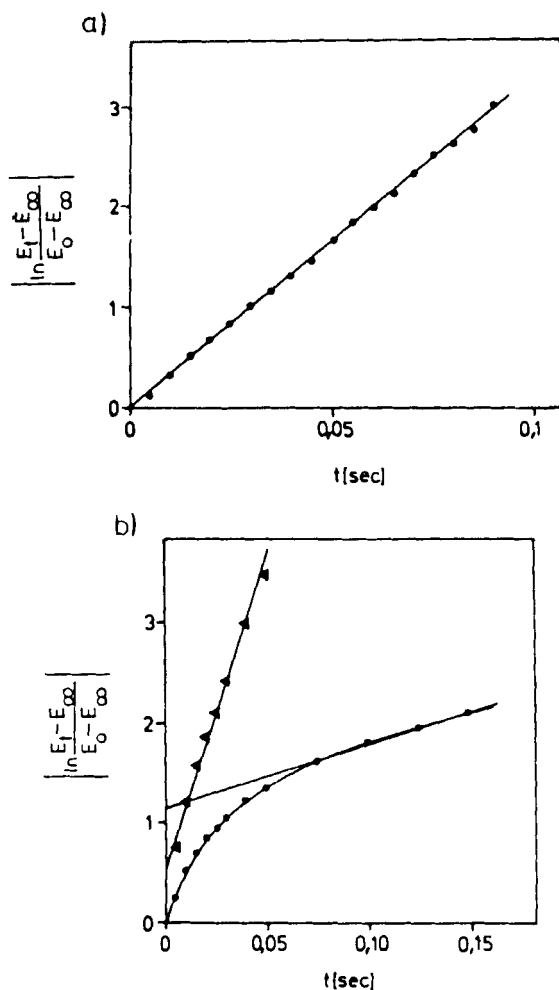


FIG. 2. First-order plots for the reduction of porphyrins with dithionite (10^{-2} mol/L) in water at pH 7 and 15°C , ionic strength 0.25. a) Monomeric 8 (Mt = Mn(OH) $3.1 \mu\text{mol/L}$). b) Polymer 5 (with R_1 , Mt = Mn(OH), concentration of porphyrin $19 \mu\text{mol/L}$). (●) Plots of Eq. (2). (▲) Calculation for k_1 according to $c_{A1} = c_{A1} - c_p - c_{A2}$ (see Eq. 3). (—) Linear curve for k_2 .

TABLE 3. Specific Reaction Rate Constants and Activation Parameters for strength 0.25)

Sample (concentration in mol/L)	Dithionite, mmol/L	T , °C	k_{obs} or $k_{\text{obs}1}$ ($k_{\text{obs}2}$), s^{-1}
8 (3.1×10^{-6})	2.54	15.2	33.2
		22.0	72.6
		26.0	102.7
		30.1	164.5
9 (4×10^{-6})	2.77	14.8	0.84
		21.0	1.77
		25.2	2.81
		30.6	5.62
5 with R_1 (1.9×10^{-5})	8.32	15.6	61.2 (6.49)
		21.0	60.8 (7.39)
		25.2	47.5 (9.11)
		30.4	61.2 (7.31)
6 with R_1 (5.8×10^{-5})	3.05	15.2	0.62 (0.10)
		21.2	1.09 (0.21)
		25.8	2.93 (0.38)
		31.4	4.49 (0.59)
7 with R_1 (1.9×10^{-5})	10.9	14.9	7.70 (0.59)
		21.5	11.66 (1.01)
		25.9	13.49 (1.38)
		30.5	21.40 (1.88)

the Reduction of Mn(III) Porphyrins in Aqueous Solution (ph 7.0, ionic

k or $k_1 \times 10^{-5}$ ($k_2 \times 10^{-6}$), $\text{L}\cdot\text{mol}^{-1}\text{ s}^{-1}$	E_a or E_{a1} (E_{a2}), $\text{kJ}\cdot\text{mol}^{-1}$	H^\ddagger or ΔH_1^\ddagger (ΔH_2^\ddagger), $\text{kJ}\cdot\text{mol}^{-1}$	ΔG^\ddagger or ΔG_1^\ddagger (ΔG_2^\ddagger), $\text{kJ}\cdot\text{mol}^{-1}$	ΔS^\ddagger or ΔS_1^\ddagger (ΔS_2^\ddagger), $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
26.4	77.0	74.6	28.8	156.1
54.6				
81.5				
130.5				
0.64	86.7	84.3	3.7	159.0
1.35				
2.14				
4.27				
26.8 (28.5)	6.5 (8.4)	4.0 (5.9)	29.9 (35.3)	-88.1 (-100.0)
26.7 (32.4)				
42.7 (39.9)				
26.8 (32.1)				
4.49 (0.78)	94.5 (77.9)	92.0 (75.5)	38.6 (42.9)	182.2 (111.0)
7.90 (1.58)				
21.1 (2.76)				
32.6 (4.31)				
2.95 (0.23)	45.3 (54.1)	42.8 (51.6)	34.7 (40.7)	27.8 (37.3)
4.47 (0.39)				
5.17 (0.53)				
8.20 (0.72)				

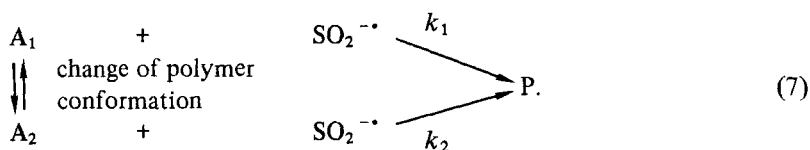
a fast reaction followed by a slower reaction (Fig. 2). The values of $k_{\text{obs}1}$, $k_{\text{obs}2}$, k_1 , and k_2 were then calculated according to Eqs. (4) and (5) (Table 3). As expected, the positive charges of the porphyrin 8 or the Polymer 5 (with R_1) enhance the rate of the reactions with the anionic dithionite in comparison to the negatively charged porphyrin 9 or the Polymer 6 (with R_1) by a factor of around 50 (k_1 of the polymer considered). The uncharged Polymer 7 (with R_1) exhibits an intermediate reaction rate.



Great differences of the activation parameter [32] exist between the monomeric porphyrins and the polymers with porphyrin moieties (Table 3). Whereas the parameters of the monomeric porphyrins 8 and 9 exhibit only small differences in the charge dependence, great difference can be seen with Polymers 5, 6, and 7. Reduction of the positively charged Polymer 5 (with R_1) with dithionite results in a very low activation energy E_a . These values increase from the uncharged Polymer 7 (with R_1) to the negatively charged Polymer 6 (with R_1). Surprising is the very low activation entropy of 5, which indicates a highly ordered transition state. Therefore, it can be concluded that the association of the polymeric ion with the reducing agent and its effective local concentration in the polymer domain have the principal influence on the electron transfer [33-35]. Polyelectrolytes are more efficient in the acceleration and in the retardation of reactions in comparison to monomeric electrolytes. This is due to the higher local concentration of ionic groups in the polymer coil with respect to the ionic strength. The simple Debye-Hückel theory cannot be used to explain the reaction in a polymer coil with respect to the ionic strength.

As mentioned before, all polymers contain covalently bound moieties of porphyrins with two different active reaction species. Also, the reduction of metals in porphyrinic prosthetic groups of cytochrome C and myoglobin occurs at different rates [36, 37]. It was assumed that this effect may be due to a change of the conformation of the surrounding polymer. Due to the presence of inorganic salts in solutions, the investigated Polymers 5-7 exist in a swollen random coil. Porphyrins located in the outer sphere of the coil are reduced more easily and are responsible for the calculated $k_{\text{obs}1}$, k_1 , E_{a1} , ΔH_1^\ddagger , ΔG_1^\ddagger , and ΔS_1^\ddagger values. The change of the conformation of the coils with time results in transport of inner sphere porphyrins to the outer sphere area. Therefore the values of $k_{\text{obs}2}$, k_2 , E_{a2} , ΔH_2^\ddagger , ΔG_2^\ddagger , and ΔS_2^\ddagger consist

of terms including the change of the conformation of the polymer and the electron transfer of porphyrins. All porphyrins exhibit the same reactivity, but the reactive centers are accessible in a different manner and/or time. In some experiments the reducing agent dithionite was added in a molar amount lower than the polymer-bound porphyrin. The stopped-flow measurements with an excess of dithionite results in the same situation, as described in Table 3. Therefore, the whole situation can be explained as shown in Eq. (7) (A_1 , reactions with porphyrins more at the outer sphere the polymer coil; A_2 , reactions with porphyrins more at the inner sphere of the polymer coil).

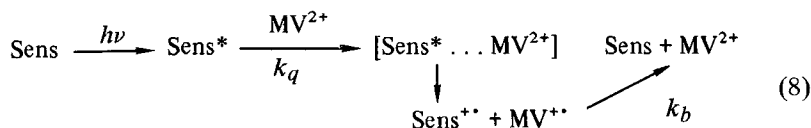


In analogy to the mechanism of the reduction of monomeric Mn(III)-porphyrins in aqueous solution [22-24] and the reduction of the metal in cytochrome C [38, 39], a peripheral outer-sphere electron-transfer mechanism is assumed. An axial mechanism is probably not due to the fact that inorganic ions usually do not coordinate to the Mn(III)-porphyrins [22], and no pH dependence (pH 7-11) of the velocity of the reduction is observed. A peripheral inner-sphere mechanism does not seem likely since the velocity of the reduction shows no great dependence on the ionic strength and pH of the solution. These results will be published later.

PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES

The porphyrins *1a* and *2a* are known to work as sensitizers in the presence of a donor and acceptor for the conversion of visible light into chemical energy of an oxidized donor and reduced acceptor [4-6]. With water-soluble derivatives of *1a*, water photolysis with hydrogen evolution is an example for a light-induced process. In order to convert more light into chemical energy, the simultaneous use of various sensitizers absorbing at different wavelengths in the visible region of light, like *1-3* (see, e.g., Fig. 1), would be very important. Surprisingly, a mixture of the monomeric porphyrins *1b* and *2b* leads to a decrease in photocatalytic activity [12]. This may be due to intermolecular porphyrin/porphyrin interaction. Therefore, the employment of the porphyrins *1-3* covalently bound moieties to polymers is interesting in order to prevent this intermolecular interaction.

The monomeric porphyrins (Mt = Zn) possess good basic requirements to achieve highly active photosensitization: efficient photoabsorption over a wide range of wavelength (e.g., in DMF: *1b* λ 436 nm, ϵ 125 000 L·mol⁻¹·cm⁻¹; *2b* λ 678 nm, ϵ 103 000 L·mol⁻¹·cm⁻¹; *3b* λ 768 nm, ϵ 170 000 L·mol⁻¹·cm⁻¹); efficient quenching (oxidative in the presence of methylviologen) [3-5, 43]. A general scheme using methylviologen (MV²⁺) as acceptor is shown in Eq. (8). In order to study the photosensitization, investigation of the activity of the photoredox process (in the presence of donor and acceptor), the triplet lifetime, the quenching rate constant k_q , and the rate constant k_b for the back reaction are necessary. Some results of the measurements with the porphyrins containing Zn are described below.



The photoredox behavior upon irradiation with visible light was investigated in DMF/H₂O (2/1 v/v) in the presence of excess of mercaptoethanol (0.5 mol/L) as donor and MV²⁺ (0.75 mmol/L) as acceptor in pH 7.8 buffer solution. The concentration of the sensitizers are of the order of $\mu\text{mol/L}$. The activity was determined by measurement of the concentration of MV^{+\cdot}. The concentrations of this cation radical (in $\mu\text{mol/L}$) in dependence on the irradiation time with some monomeric sensitizers are as follows: *1b* (3.3 $\mu\text{mol/L}$): 3 min 44, 15 min 72, 30 min 96; *2b* (3.9 $\mu\text{mol/L}$): 3 min 41, 15 min 71, 30 min 126; *3b* (3.6 $\mu\text{mol/L}$): 3 min 42, 15 min 74, 30 min 93.

Table 4 contains the relative activities of the various sensitizers for the formation of MV^{+\cdot}. These values are obtained as follows. For single monomeric sensitizers and also single polymer-bound ones, calibration curves containing the dependence of MV^{+\cdot} formation on the concentration of the sensitizers after 30 min irradiation (constant concentration of mercaptoethanol and MV²⁺) were drawn. Taking into account the extinction values of the various polymer-bound sensitizers and of mixtures of sensitizers, the concentrations of these sensitizers in solution and then their theoretical activity (relative to *1b*, *2b*, *2c*, or *3b* to get the activity in relationship to monomeric porphyrins, and to the various single-bound polymer porphyrins to get the same in relationship to these polymer-bound ones) could be calculated. The relative activities could be obtained using the relationship of found and theoretical concentrations of MV²⁺.

It can be seen from Measurements 3 and 4 (Table 4) that a mixture of monomeric sensitizers does not enhance the activity (55% relative activity).

The determination of the triplet lifetimes (Table 4) shows a decrease of the lifetime of *Ib* in the mixture which may be due to intermolecular porphyrin/porphyrin interaction. In general, all covalently bound porphyrins exhibit an enhanced lifetime in comparison with the monomeric sensitizers. Generally, positively charged Polymers 5 with porphyrin moieties are superior by a very long lifetime of the excited state. It was mentioned before that Polymers 5 exhibit the strongest wavelength shifts of the main absorption in the visible region. Therefore, the positive charges of the polymer near the electron-rich porphyrins shield them, with the result of decreased quenching by, e.g., solvent molecules. Also, the polymers containing combined moieties of porphyrins are characterized by longer lifetimes of the excited state in comparison with a mixture of the monomeric porphyrins (Measurements 3 and 4). In addition, a mixture of a low molecular weight and a polymeric porphyrin (measurements 8 and 14) or, even more pronounced, a mixture of two polymeric porphyrins (Measurement 15) leads to an enhanced lifetime. It can therefore be estimated that the polymeric environment stabilizes the lifetime of the excited state and reduces the intermolecular porphyrin/porphyrin interaction. These results are unexpected because polymer-bound positively charged tris(2,2'-bipyridine)ruthenium(II) complexes exhibit reduced or only slightly enhanced triplet lifetimes [44-46].

Looking again at the photoredox reaction, the activities with covalently bound sensitizers (either single, combined bound moieties, or mixtures of single bound moieties) are in most cases higher than the monomeric sensitizers (Table 4). In general, the following order of activity with two sensitizers can be seen: two low molecular < one low molecular + one polymer-bound < two combined polymer-bound \approx one polymer-bound + one polymer-bound. Surprisingly, the dependence on the charge of the polymer shows no general trend.

The quenching rate constants determined from the dependence of the lifetime on the concentration of MV^{2+} (Stern-Volmer plot) are, surprisingly, very similar for all polymers but lower than the monomeric *Ib* (Table 4). First measurements on the reverse electron transfer constant k_b clearly show that in the reaction of the monomeric porphyrins it is twice as high as for polymer-bound porphyrins.

In summary, the overall electron transfer efficiency becomes higher with the polymers. This is due to the higher lifetimes of the excited state and the lower reverse electron transfer and not to the quenching rate. The polymer coils slightly reduce the diffusion of the reactants. The fact that the positively charged Polymer 5, with the highest lifetime, does not exhibit the highest activity may point out the influence of the polymer environment. In the

TABLE 4. Photochemical^a and Photochemical^b and Photophysical Properties of Some Monomeric and Covalently Bound Sensitizers (Mt = Zn) in DMF/H₂O (2/1 v/v)

Measurement	Sample (Mt = Zn)	Relative activity (in %) in the photoreduction of MV ²⁺ in comparison to the analogous		Triplet life time, μ s	Quenching rate constant, $M^{-1}s^{-1}$
		Monomeric porphyrins	Polymer-bound porphyrins		
1	<i>1b</i>	--	--	80	4×10^9
2	<i>2b</i>	--	--	40	
3	<i>1b + 2b</i>	55	--	55	
4	<i>1b + 2c + 3b</i>	50	--		
5	4 with R ₁	120	--	300	1×10^8
6	4 with R ₂	232	--	160	
7	4 with R ₁ , R ₂	91	88	160	
8	2 <i>b</i> + 4 with R ₁	83	60	80	
9	4 with R ₁ + 4 with R ₂	72	67		

10	5 with R_1	180	—	1900	1×10^8
11	5 with R_2	62	—	710	
12	5 with R_1, R_2	140	160	1000	
13	5 with R_1, R_3, R_4	60	43	2400	
14	2b + 5 with R_1			500	
15	4 with R_2 + 5 with R_1			1950	
16	6 with R_1	174		455	2×10^8
17	6 with R_2	178		200	
18	6 with R_1, R_2	170	107	400	
19	7 with R_1	184		110	4×10^8
20	7 with R_2	126		80	
21	7 with R_1, R_2	84	82	155	2×10^8
22	7 with R_1, R_3, R_4	35	31	170	

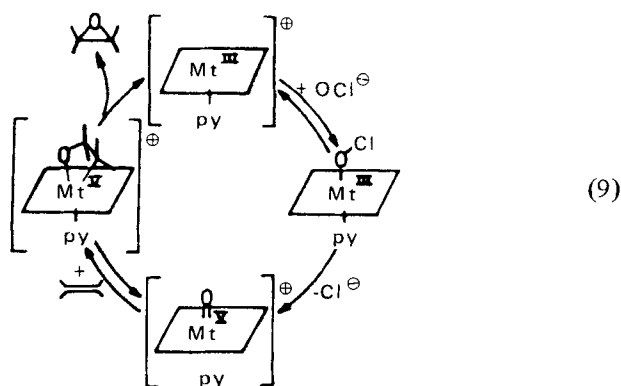
^aIn the presence of mercaptoethanol as donor.

^bFor explanation, see text.

case of Polymers 5, the diffusion of MV^{2+} is retarded whereas the influence of Polymers 4, 6, and 7 results in a reduced lifetime and slower diffusion of the products of the photoredox reaction. It should be mentioned that the positively charged covalently bound polymeric tris(2,2'-bipyridine)ruthenium(II) complexes, in most cases, did not affect the reaction in the direction of enhanced activity [44-46]. Therefore, the photocatalytic activities of the uncharged porphyrin moieties in the polymers are not influenced to as great an extent as the charged sensitizers.

OXYGEN-TRANSFER REACTIONS

Synthetic porphyrins containing Fe(III), Mn(III), or Co(III) are considered as model compounds for cytochrome P-450 [7-9]. Peroxides, hypochlorite, or iodosobenzene are used as oxygen sources for the catalytic oxygenation of alkenes. With hypochlorite, the reactions were carried out in a three-phase system (organic solvent like dichloromethane, water, and a phase-transfer catalyst). Polymer-bound porphyrins, dissolved in the organic phase, increase the rate of oxygenation because the formation μ -oxo dimers is partly inhibited [19-21]. The mechanism of the epoxidation of alkenes is shown in Eq. (9). The rate-determining step is the formation of the intermediate complex between the metal-oxo compound and the alkene [40, 41].



The resulting water-soluble polymer-bound porphyrins 5 (with R_1), 6 (with R_1), and 7 (with R_1), containing Mn(III), offer the possibility to study the oxygen transfer to water-soluble alkenes in water. The monomeric charged Mn(III) complexes 8 and 9 were used as model compounds. The epoxidation of 2,5-dihydrofuran with sodium hypochlorite was studied.

TABLE 5. Catalytic Epoxidation of 2,5-Dihydrofuran with Water-Soluble Porphyrins in Water with Sodium Hypochlorite as the Oxygen Source^a

Sample	Conversion of 2,5-dihydrofuran, %	Yield of 3,4-epoxytetrahydrofuran, %
5 (with R ₁ , Mt = MnOH)	95.3	52.5
6 (with R ₁ , Mt = MnOH)	98.4	1.5
7 (with R ₁ , Mt = MnOH)	78.1	48.8
8	93.5	70.3
9	97.6	59.7

^aReaction temperature 20°C, reaction time 4 h.

Apart from one paper describing the use of Mn(III)-porphyrins in polymeric vesicles [42], no results are known about mono-oxygen transfer in aqueous solution.

The results of the oxidation of 2,5-dihydrofuran show that, independent of the kind of porphyrin employed (monomeric or polymer bound), nearly quantitative conversion of the substrate occurs (Table 5). Also, the use of different charged polymers has no influence on the conversion. The yield of 3,4-epoxytetrahydrofuran is (with one exception) of the order of 50-70%. As mentioned before, the rate-determining step is the formation of an intermediate between the metal-oxo compound and the alkene. Therefore, the long reaction time of 4 h eliminates the influence of the environment of the porphyrins (charge, polymer).

CONCLUSIONS

Methods were developed to synthesize covalently bound polymeric porphyrins in different environments. The polymers include uncharged and positively or negatively charged ones soluble either in water or some organic solvents. The polymer binding involves different porphyrins. The methods selected allow binding of one, two, or three porphyrins to one polymer. The procedures consist mainly of simple one-step reactions.

The porphyrin moieties in the polymers can act as probes for reactions

in a variable time scale: nanosecond to microsecond range, singlet lifetime; microsecond to millisecond range, triplet lifetime; millisecond to second range, electron transfer; minute range, photoelectron transfer; and hour range, oxygen transfer.

By studying these reactions, information concerning the polymer environment can be obtained. Due to the very complicated nature of the processes, only some general statements can be given at this time. Reaction conditions were selected where random coil conformation of the polymers is evident. It should be emphasized that long-chain molecules are dynamic systems with a broad range of motions in time, so that measurements of the conformations and chain dimensions of polymers will depend on the sampling time and experimental conditions. Measurements like singlet lifetime, which can lead to information about side-chain motions or segmental motions relative to a few monomer units of the undistorted macromolecule [47, 48], have not yet been carried out with the described polymers.

The determination of the triplet lifetime in the microsecond to millisecond range results in the fundamental finding that all polymer-bound porphyrins exhibit a higher lifetime than monomeric porphyrins. In general, the lifetimes increase in the order: monomeric porphyrins < porphyrins on uncharged polymers < porphyrins on negatively charged polymers << porphyrins on positively charged polymers.

Therefore, the polymer environment results in a strong to very strong shielding effect. There is no evidence for triplet energy migration via a cross-coil segmental diffusion or intracoil energy transfer as reported for other luminescence active molecules in polymers [47, 48]. But a so-called "polymer effect" may induce a lower energy of the triplet state than in the monomeric model compound. The results of triplet measurements also indicate that the coil behaves as if it had a constant effective hydrodynamic volume.

The electron-transfer reactions studied in the second to millisecond range show a strong dependence on the kind of charge of the polymer. The experiments were performed by mixing the reducing agent and the polymer and then directly measuring the electron transfer. In accordance with the literature, the change in the conformation of large segments of the polymer is responsible for the slower reaction of the electron transfer. But the hydrodynamic volume of the coils will not change on addition of reducing agent due to the ionic strength of the polymer solutions. Rapid electron transfer may occur efficiently by changing the polymer conformation. In comparison with monomeric salts, polyelectrolytes can accelerate or retard an electron transfer much more efficiently.

The photoelectron-transfer reactions were carried out in a different manner. The irradiation which induces the electron transfer was started around 10 min after mixing the reagents. Therefore, formation of random coils with partly included donor and acceptor molecules exist in solution. For poly(methacrylic acid), incorporation of several water-soluble organic molecules was shown [48]. These molecules may be bound to the polyelectrolyte by both electrostatic and nonelectrostatic forces. Surprisingly, the photoelectron transfer occurring in the minute time range is relatively independent of the charge of the polymer. No general trend can be seen. In addition, the covalently bound porphyrins are more efficient sensitizers than the monomeric ones, partly due to the higher triplet lifetime of the polymer-incorporated moieties. Therefore, the polymer coil, partly changing its conformation in the minute time scale, does not strongly attenuate the diffusion of the monomeric reagents. The detailed mechanism includes several single steps, like lifetime, quenching, back reaction, and others. Further investigations are necessary to get a more clear picture of the dependence of these reactions on the influence of the charge of the polymer.

The last investigated reaction, which occurs in an hour scale, was the oxygen transfer. In this case the polymer environment does not play a significant role because the kinetics of the reaction are not influenced by the polymer coil or its charge but by another reaction which includes oxygen transfer. The polymer is only important to provide solubility in a special solvent. The employment of Mn(III)-porphyrins bound in insoluble polymers would offer the possibility of easy separation of the reaction products from the reaction mixture.

Summarizing, it was shown that covalently bound porphyrins, as one example of macromolecular complexes, play an important role in many reactions. In all mentioned reactions, the incorporation of the metal complexes in a polymer results in a strong positive effect on the properties of the materials. The results may encourage study of the mentioned reactions in more detail and enlarge the field in the direction of new materials with unconventional properties.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support by Deutsche Forschungsgemeinschaft (for G.K. and J.G.), Ministry of Education and Science of Japan (for J.G.), and DAAD (for G. K.).

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Received January 21, 1988