Macromolecules **1996,** *29,* 1600−1608

Photoinduced Electron Transfer in Porphyrin−Quinone End-Capped Poly(methacrylic acid). 1. Photophysical Studies

Maria Nowakowska,[†] Fumio Kataoka,[‡] and James E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received August 12, 1994; Revised Manuscript Received November 3, 1995[⊗]

ABSTRACT: Photoinduced electron transfer from porphyrin (P) to benzoquinone (Q) moieties covalently attached to poly(methacrylic acid) (PMAA) chain ends was studied. The effect of polymer chain length, pH, and ionic strength of the aqueous polymer solution on the rate constant of charge separation was determined.

Introduction

It is now generally recognized that the primary photochemical step in photosynthesis involves a one-electron transfer from the excited singlet state of a chlorophyll species to an electron acceptor.[1−3] The process takes place within the reaction center. In well-characterized bacterial reaction centers, molecules of ubiquinone or menaquinone act as the electron acceptors.[4] The photosystem II of green plants includes also a quinone moiety, plastoquinone, as an electron acceptor.[5] The main feature of the primary event is that electron transfer leads to separation of the charged species $Chl^{\bullet +}$ and $Q^{\bullet -}$, which undergo further reactions in the photosynthetic sequence.

During the past few years considerable progress has been made in the understanding of photoinduced electron transfer in relation to the primary step in photosynthesis. Studies have involved the electron transfer from chlorophylls or synthetic porphyrins to quinones. Elegant model systems containing covalently linked porphyrin−quinone molecules have been synthesized and used to determine how variables such as distance, orientation, type of solvent, and exothermicity influence the rates of charge separation and charge recombination, a back-reaction.[6]

This paper reports experiments which suggest an alternative approach to the construction of a model photosynthetic reaction center. The concept is based on the observation that photosynthesis actually occurs in an aqueous environment; the reaction center is usually surrounded by a hydrophobic protein pool which, as a whole, is suspended in aqueous medium.

In a previous paper from these laboratories, we have shown that relatively efficient intramolecular photoelectron transfer can occur in water solution between porphyrin and quinone moieties attached at random in a polyelectrolyte chain[7] and, furthermore, that the efficiency of this process can be adjusted by changing both the pH and the ionic strength of the solution. Experimental studies by Liu et al.[8] have shown that the end-to-end distance in polyelectrolyte chains in aqueous solution can be adjusted from very short (i.e., ∼10 Å) to very long distances (>100 Å) by changing the pH of the solution. For example, in poly(methacrylic acid) polymers (PMAA) end-capped with naphthalene and anthracene groups, the end-to-end distance, R_n, is a sharp function of pH as shown in Figure 1 (curve a). At low pH the carboxylic acid groups of PMAA are not ionized (Figure 1, curve b) and the polymer chain adopts a dense, coiled structure in solution. At high pH (∼9−11) the carboxyls are almost completely ionized and the chain is expanded due to the mutual repulsion of the charged species along the chain, so that R_n, the root-mean-square end-to-end distance, approaches that of a fully extended linear chain.

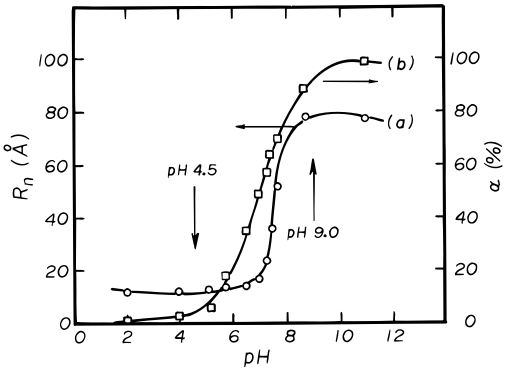


Figure 1. Dependence of end-to-end distance (R_n) (a) and degree of dissociation (α) (b) for PMAA (number of repeat units $\bar{n} = 78$) on pH of aqueous solution (data taken from ref 8).

Further studies of the end-capped polyelectrolyte poly(*N*-*tert*-butylaziridine hydrogen chloride) (PTBA) chains by Liu et al.[9] demonstrated that the end-to-end distance of fully ionized polyelectrolytes could be reduced substantially by increasing the ionic strength of the solution. This effect is well known in aqueous solutions of polyelectrolytes and is attributed to the screening effect of the additional ions which reduce the repulsive interactions between the charged groups on the polyelectrolyte backbone. In PTBA the R_n was reduced to one-half the original value on increasing the ionic strength to 0.5 M by addition of sodium chloride to the solution. Because of the pendant *tert*-butyl group, PTBA is a relatively stiff chain compared to PMAA, so even larger effects would be expected in the latter polymer.

Based on this previous research, it would appear that PMAA molecules containing porphyrin (P) and quinone (Q) groups at opposite ends should provide models of photoelectron transfer processes relevant to natural photosynthesis in aqueous media, wherein the distance

---

[†] Permanent address: Faculty of Chemistry, Jagiellonian University, Krakow, Poland.

[‡] Permanent address: Production Engineering Research Laboratory, Hitachi Ltd., 292 Yoshida-cho, Toksuka-ku, Yokohama 244, Japan.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

0024-9297/96/2229-1600$12.00/0

between the two chromophores and hence the efficiency of photoelectron transfer can be adjusted continuously via changes in the pH and ionic strength of the aqueous medium. This should provide a tunability of the electron transfer rates which is not available in porphyrin–quinone systems attached by rigid linkages with fixed dimensions.

Experimental Section

Ultraviolet–Visible Spectra Measurements. UV–vis absorption spectra of the samples were measured using a Hewlett-Packard 8451A diode-array spectrophotometer.

IR Spectra Measurements. IR spectra were recorded on a Nicolet 5DX spectrometer.

NMR Spectra Measurements. ^{1}H NMR spectra were obtained using a Varian XL400 spectrometer or a Gemini 200 spectrometer. The XL400 spectrometer was used for characterization of polymers. Chemical shifts are given in parts per million from tetramethylsilane.

Fluorescence Spectra Measurements. Steady-state fluorescence spectra of the samples were recorded at room temperature on an SLM fluorescence spectrometer.

Transient Measurements of Fluorescence Decay. Fluorescence decay curves were measured using a single-photon-counting apparatus. The solutions were deaerated by bubbling with argon gas for 30 min. The samples were excited at 420 nm and emission was measured at 650 nm. The nonlinear iterative deconvolution technique was used to fit the decay curves.

pH Measurements. The pH value for each sample was monitored by using a digital pH meter (Corning pH/ion meter Model 150). For pH adjustment, 0.1 N NaOH and 0.1 N HCl solutions were used.

GC Analysis. GC analysis was performed using a Varian Aerograph Series 2700 gas chromatograph.

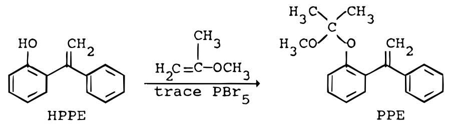
GPC Analysis. GPC work was performed on a Waters liquid chromatography system using a DuPont bimodal column pair and tetrahydrofuran (THF) as an eluent (1 mL/min). Both spectrofluorometer (Bio-Systems, Model 900) and refractometer (Waters, Model R410) were used as detectors. Four near-monodisperse poly(methyl methacrylate) standards (MW = 4100–60000 were used for calibration.

Elemental Analysis. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Polymerization. (1) General Procedure. The polymers used in this work were prepared by anionic polymerization. In order to incorporate methacrylic acid into the polymer chain in anionic polymerization, the carboxylic groups had to be protected. This was accomplished by preparing the trimethylsilyl derivative of methacrylic acid. Trimethylsilyl methacrylate (TMSM) was prepared by the reaction of methacrylic acid with hexamethyldisilazane according to the method of Chapman and Jenkins.[10] TMSM (bp 49 °C/20 Torr, lit.[10] bp 50 °C/20 Torr) was stored in an argon atmosphere in a freezer. Purity of the monomer was found to be >99% by GC analysis (column: OV-17 (3%); column temperature: 55 °C).

Polymerization was initiated by the anion formed by reaction of 1-phenyl-1-[*o*-(2′-methoxyprop-2′-oxy)phenyl]ethene (PPE) with butyllithium.

PPE was prepared as follows. A trace amount of phosphorus oxybromide in a capillary was added to a mixture of 0.8 g (4.1 mmol) of 1-(2′-hydroxyphenyl)-1-phenylethene (HPPE) and 2.5 g (35 mmol) of 2-methoxypropene. The reaction mixture was allowed to stand at room temperature for 5 days. The reaction was followed by thin-layer chromatography (TLC) (Merck Kiselgel 60 F_{254}; eluting solvent: hexanes–ethyl acetate (8:2 v/v)). After disappearance of a spot of a starting olefin, the reaction was quenched by adding a few drops of triethylamine. The reaction mixture was concentrated under high vacuum to give a quantitative amount of PPE in the form of a colorless liquid. Attempted distillation under high vacuum (10^{-4} Torr, bath temperature 120 °C) resulted in a reversion to the starting olefin. However, ^{1}H NMR and TLC analysis showed that the above product was practically pure, and it was used without further purification. IR (liq. film) 3085, 3060, 2995, 2945, 2835, 1615, 1595, 1485, 1385, 1370, 1240, 1060, 955, 885, 800, 765, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6H, methyl), 3.43 (s, 3H, methoxy), 5.50 (d, $J = 1.5$ Hz, 1H, vinyl), 5.77 (d, $J = 1.5$ Hz, 1H, vinyl), 7.25 (d of t, $J = 1.4$ and 7.5 Hz, 1H, aromatic), 7.4–7.6 (m, 8H, aromatic). UV (methanol) λ_{max} (ϵ) 242 nm (5900 dm^3 mol^{-1} cm^{-1}).



(1)

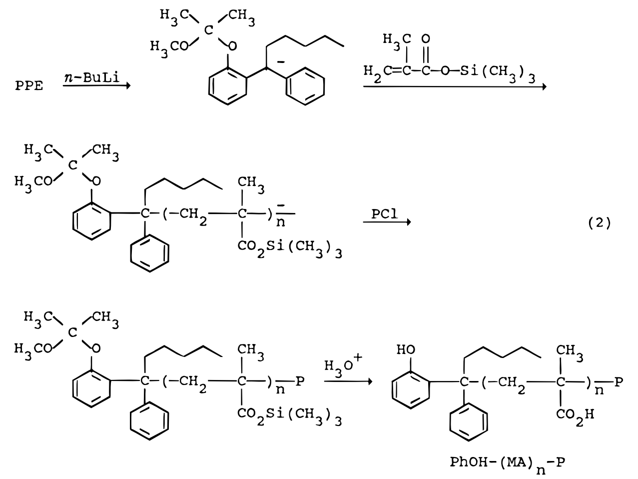
The substrate of this reaction, HPPE, was prepared by the Grignard reaction using 2-hydroxybenzophenone and methylmagnesium chloride as reactants. All spectral characteristics were identical with those reported in the literature.[11,12]

The polymerization was terminated with 5-(4′-(chlorocarbonyl)phenyl)-10,15,20-tri(*p*-tolyl)porphine (PCl). PCl was prepared using the procedure described by Kong et al.[13] A mixture of 180 mL of dry benzene and 18 mL of distilled thionyl chloride was added to 350 mg of 5-(4′-carboxyphenyl)-10,15,20-tri(*p*-tolyl)porphine, and the mixture was brought to reflux. After refluxing for 3 h, the solvent and the excess thionyl chloride were removed by distillation under a stream of dry Ar, and then the residue was dried under high vacuum (10^{-4} Torr). Dry benzene (60 mL) was added to the resulting residue, and the solvent was removed once again by distillation and vacuum to dryness. This operation was repeated three times, and the resulting green solid, PCl, was dried under high vacuum for 10 h to remove the trace amount of thionyl chloride. In the anionic polymerizations described in this work, freshly prepared PCl was used with precautions to avoid any trace of water.

(2) Synthesis of Phenol and Porphyrin-Capped Poly(methacrylic acids) (PhOH–(MA)$_n$–P). All reaction vessels used in this experiment were carefully dried under high vacuum (10^{-1} Torr). Polymerization was performed in THF. THF was dried with sodium using benzophenone as an indicator and distilled into the reaction vessels under high vacuum by a bulb-to-bulb distillation. TMSM was dried with finely pulverized calcium hydride for 2 days and distilled over it at room temperature just before polymerization.

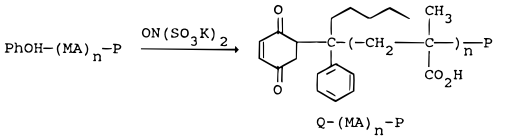
A synthesis of PhOH–(MA)$_{277}$–P is given as a typical synthetic example. Under vacuum, 0.20 mL (0.32 mmol) of 1.6 M *n*-butyllithium in hexanes was added by a syringe to a solution of 86 mg (0.32 mmol) of PPE in 30 mL of THF and reacted at room temperature for 30 min. After cooling to −78 °C, a solution of 10.5 g (67 mmol) of TMSM in 20 mL of THF was added dropwise to the reaction mixture and reacted for 2 h. The atmosphere in the reaction flask was replaced with dry Ar, and then a suspension of 350 mg (0.49 mmol) of 5-(4′-(chlorocarbonyl)phenyl)-10,15,20-tri(*p*-tolyl)porphine in 150 mL of THF was added to the reaction mixture from a second flask. The atmosphere of the second flask was pressurized by Ar to a level slightly higher than that of the reaction flask at such a rate that the reaction temperature was maintained at −78 °C. (A thin stainless steel tube was used to introduce the Ar to the second flask.) The reaction was carried out for 3 h and then the mixture was allowed to warm to room temperature. The reaction mixture was treated with 3 mL of 1 N HCl for 3 h and then poured into 700 mL of ether to precipitate the product. The resulting polymer was dissolved in 50 mL of methanol, and then the solution was poured into 700 mL of ether to reprecipitate. The reprecipitation was repeated three times from ether and benzene, respectively. The resulting polymer was dissolved in water and freeze-dried. This procedure gave 4.91 g of PhOH–(MA)$_{277}$–P (88% yield).

(3) Synthesis of Benzoquinone and Porphyrin-Capped Poly(methacrylic acid) Polymers (Q–(MA)$_n$–P). The

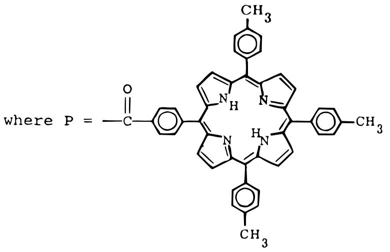


(2)

benzoquinone chromophores were introduced to the polymer chain by oxidizing the phenol moieties in PhOH−(MA)$_n$−P polymers with Fremy's radical. Four to six times excess amounts of the oxidant were used in this reaction. The synthesis of Q−(MA)$_{277}$−P is given as a typical example. To a solution of 1 g (11.6 mmol based on carboxyl groups) of PhOH−(MA)$_{277}$−P and 61.5 mg (5.8 mmol) of sodium carbonate in 20 mL of distilled water was added 150 mg (0.56 mmol) of potassium nitrosodisulfonate all at once. The resulting reaction mixture was stirred at room temperature for 2 h. After quenching the reaction by the addition of 9.28 mL of 1.25 N HCl, the water was removed by freeze-drying. The residue was extracted with methanol, and the insoluble inorganic materials were filtered off by suction filtration. The filtrate was concentrated and a small amount of THF was added to precipitate the inorganic material. This operation was repeated until no precipitate was obtained. The product was isolated by pouring the filtrate into 400 mL of ether. Reprecipitation from ether, followed by freeze-drying from water, gave 903 mg of Q−(PMA)$_3$−P (90% yield).

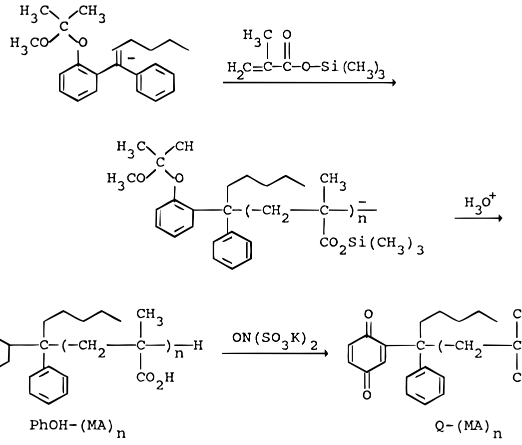


(3)



(4) Synthesis of Phenol-Capped Poly(methacrylic acid) (PhOH−(MA)$_n$) and Quinone-Capped Poly(methacrylic acid) (Q−(MA)$_n$) Polymers. The presence of the phenol and porphyrin chromophores in PhOH−(MA)$_n$−P polymers or quinone and porphyrin chromophores in Q−(MA)$_n$−P polymers has been confirmed by the measurements of their NMR and absorption spectra in the UV−vis spectral region. In order to precisely determine the content of phenol groups and the efficiency of their oxidation to the quinone, the spectroscopic data for these polymers were compared with the respective spectra of the PMAA labeled only with phenol (PhOH−(MA)$_n$) or with quinone (Q−(PNA)$_n$).

Synthetic routes used to obtain phenol- or quinone-capped PMAA were similar to those described above, with a difference only in application of diluted hydrochloric acid instead of chloride of porphine (PCl) for quenching the living polymerization (see below). The hydrochloric acid also induced hydrolysis of the trimethylsilyl ester and ether moiety in the polymeric anion.



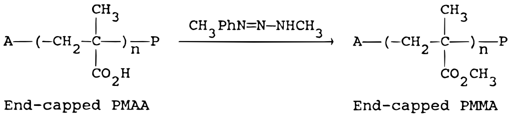
(4)

^{1}H NMR spectra for PhOH−(MA)$_n$ in CD_3OD solution show two peaks of methyl protons of the polymer backbone at 1.07 and 1.17 ppm as well as peaks for methylene protons at 1.87 and 1.99 ppm. The most prominent peaks at 1.07 ppm for methyl and 1.87 ppm for methylene are attributed to the polymer with syndiotactic configuration. Signals of aromatic protons corresponding to the phenyl group and the phenol moiety of the terminal group appeared at 6.50−6.62 (H_a), 6.78−6.88 (H_γ), 6.96−7.1 (Ph), 7.1−7.18 (Ph and H_b), and 7.30−7.42 (H_δ) ppm. Using the peaks of the aromatic protons as a standard and the integrated values for methyl and methylene protons, the degree of polymerization of PhOH−(MA)$_n$ was calculated.

The oxidation of PhOH−(MA)$_n$ with Fremy's radical resulted in formation of Q−(MA)$_n$ polymer. ^{1}H NMR spectra show that the peaks responsible for the presence of the benzoquinone structure appear at 6.48−6.64 and 6.66−6.86 ppm along with phenyl protons at 7.0−7.18 and 7.18−7.30 ppm. The yield of the oxidation was determined using the peaks of the methyl proton of the polymer as a standard. It was assumed that the methyl group is inert during the oxidation under the reaction conditions.

Measurements of the UV absorption spectra have shown that the peak at 278 nm, characteristic for the phenol group, disappeared after oxidation of the PhOH−(MA)$_n$ and a new peak corresponding to benzoquinone at 250 nm appeared.

(5) Methylation of the End-Capped PMAAs. In order to perform GPC characterization of the polymers obtained, some samples were prepared in which the acid groups on the backbone of the PMAA were esterified. This was performed as follows. To a suspension of 0.2 g of end-capped PMAA in 5 mL of benzene was added 0.35 g (2.3 mmol) of 3-methyl-1-*p*-tolyltriazene. The resulting mixture was stirred at 45−50 °C for 24 h. The stirring was continued for an additional 4 days and eight 0.2-g portions of the methylating reagent were added (i.e., one portion every 12 h). The product was isolated by precipitating from 300 mL of methanol−water (80/20 v/v) and purified by repeated reprecipitations from methanol. The polymers obtained were freeze-dried using benzene as a solvent to give the end-capped PMMAs (yield: 10−51%). Using ^{1}H NMR, it was found that 100% of the acid groups were methylated: ^{1}H NMR (acetone-d_6) δ 0.85 (s, 2.1H, methyl), 1.05 (s, 0.9H, methyl), 1.86 (s, 1.4H, methylene), 1.94 (s, 0.6H, methylene), 3.82 (s, 3H, methoxy).



(5)

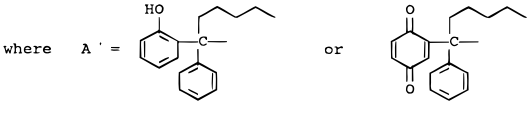


Table 1. Polymer Characteristics

desig	polymer	$\bar{M}_n$[a]	n_{MA}[b]	m_{PhOH}[c]	m_Q[c]	m_P[c]
	$PhOH-(MA)_{47}-P$	4 400	47	100	0	8.4
P1	$Q-(MA)_{47}-P$	4 400	47	0	100	8.4
	$PhOH-(MA)_{94}-P$	8 400	94	100	0	7.6
P2	$Q-(MA)_{94}-P$	8 400	94	0	100	7.6
	$PhOH-(MA)_{277}-P$	24 100	277	100	0	6.3
P3	$Q-(MA)_{277}-P$	24 100	277	0	100	6.3

[a] Determined by NMR. [b] n_{MA} = number of repeating methacrylic acid units in a polymer chain. [c] m_{PhOH}, m_Q, and m_P = average number of the phenol, quinone, and porphyrin end groups, respectively, per 100 polymer chains. Values were determined from UV−visible absorption spectra and NMR analysis.

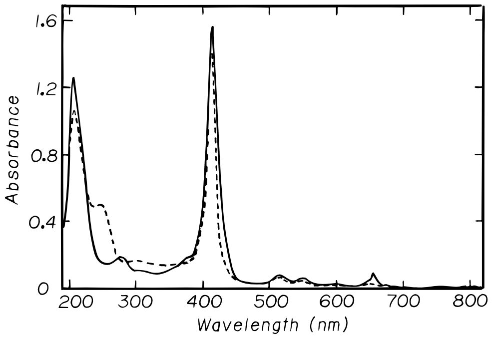


Figure 2. Electronic absorption spectra of $PhOH-(MA)_{47}-P$ and $Q-(MA)_{47}-P$ in methanol solution ($c_{pol} = 4.5 \times 10^{-5}$ M, cell thickness $l = 1$ cm): (—) PhOH; (- - -) Q.

Results

Polymer Characterization. These studies involved three PMAA polymers of different molecular weights, capped with 5-(4′-carbonylphenyl)-10,15,20-tri(*p*-tolyl)-porphine (P) at one chain end and with 2-(1′-phenylhexyl)-*p*-benzoquinone (Q) on the other ($Q-(MA)_n-P$). The corresponding polymers with the same content of P and 2-(1′-phenylhexyl)phenol (PhOH) at the chain ends served as the reference compounds. The molecular weight and composition of the polymers are summarized in Table 1. GPC analysis shows that the polydispersity of the polymers measured by the ratio $\bar{M}_w/\bar{M}_n$ was about 1.2. The polymers differ essentially in the length of the chains. In the case of the phenol-capped polymers, each chain contains a phenol group; in the case of the quinone-capped polymers, each chain contains a quinone group. The porphyrin was successfully attached to 8% of the polymer chains. This relatively low content of P does not influence the results of the studies presented in this paper because only those chains containing P absorbed at the wavelengths used in the experiments.

Photophysical Properties of Polymers. (1) Studies in Organic Solvent. The electronic absorption spectra of all of the polymers in methanol solution are qualitatively the same. Differences in the intensities of the respective absorption maxima can be correlated with the polymer compositions. Figure 2 shows, for example, the absorption spectra for the polymer $(MA)_{47}$ capped with phenol ($PhOH-(MA)_{47}-P$) or with quinone ($Q-(MA)_{47}-P$) on one chain end and porphyrin on the other. The comparison of the spectra with those obtained for model compounds (*o*-ethylphenol, *p*-tolylquinone,[14] 2-(1′-phenylhexyl)-*p*-benzoquinone, and 5,10,15,-20-tetratolylporphine) (TTP) demonstrates that attachment to the polymeric chain does not appreciably perturb their electronic structures. There is no broadening or shifts which would indicate the existence of specific ground-state interactions between chromophores. The fluorescence spectra of all polymers in methanol solution ($c_{pol} \approx 5 \times 10^{-5}$ M) are very similar to the emission of tetraphenylporphyrin (TPP) in the same solvent. All display one broad structureless emission band between 625 and 685 nm, with the maximum at 649 nm. The relative intensities of fluorescence in both phenol- and quinone-capped polymers in solution in the organic solvent are the same within experimental error. The fluorescence quantum yields for polymers were determined to be 0.14 ± 0.02, using TPP as a standard ($\phi_f = 0.11$ in benzene).[15] ϕ_f for the porphyrin polymer solutions agrees well with the literature value of the fluorescence quantum yield for the low-molecular-weight model 5-(4-carboxyphenyl)-10,15,20-tritolylporphine (TCP) ($\phi_f = 0.13 \pm 0.01$ in CH_2Cl_2 solution).[16]

These observations suggest that in methanol solution, there is practically no interaction between the polymer chain ends, as would be expected if the polymers adopt a random coil conformation.

Photophysical studies were performed on a solution containing TTP and Q (2-(1′-phenylhexyl)-*p*-benzoquinone) in methanol. Based on the absorption and excitation spectra, it was also concluded that there are no specific ground-state interactions between these two molecules. TPP fluorescence was efficiently quenched by Q ($c_{porph} \approx 1 \times 10^{-6}$ M, $0 \le c_Q \le 5 \times 10^{-3}$ M). The process can be described by the Stern−Volmer equation. The rate constant for the process was determined to be $(1.6 \pm 0.2) \times 10^{10}$ M^{-1} s^{-1}.

On the basis of the above observations, one can conclude that in methanol solution at polymer concentrations up to 5×10^{-5} M (concentrations of porphyrin up to 4×10^{-6} M), there are no inter- or intramolecular interactions between the polymer chain ends which would result in quenching of porphyrin fluorescence. All further photophysical studies were thus performed at polymer concentrations below 5×10^{-5} M.

(2) Studies in Aqueous Solutions. Both the absorption and emission spectra of the $Q-(MA)_n-P$ and $PhOH-(MA)_n-P$ polymers in aqueous solutions are strongly pH dependent. There are two main reasons for such behavior: pH-induced changes in the degree of ionization of methacrylic acid (MA) in the polymer backbone, and the shift in the equilibrium of the protonation of the porphyrin free base (diprotonation of porphyrin at low pH). Changes in the degree of ionization of MA units result in differences in polymer chain conformation, thus changing the distance between the chromophores at the chain ends.

The absorption spectra in the UV−visible region for all $Q-(MA)_n-P$ polymers are affected by the change in pH in the same way (Figure 3a,b). The spectra obtained for a given polymer at different pH values display major differences in absorption in the Soret band (see Figure 3c). The same differences are observed for the phenol-capped polymers, which indicates that they reflect the changes in porphyrin chromophore induced by changes in the hydrogen ion concentration in solution, rather than by interactions with a quinone group.

The emission spectra of the polymers obtained during excitation in the Soret region show two distinct bands with maxima around 654 and 603 nm. The relative intensities of the bands are strongly dependent on pH (Figure 4). At a given pH, the fluorescence spectra of the quinone- and phenol-capped polymers are qualitatively the same. It was noted, however, that in acidic and neutral solutions, the fluorescence intensities for the all quinone-containing polymers are lower than the intensities for the respective polymers with phenol chain ends. This suggests the existence of interactions between P and Q resulting in quenching of the porphyrin fluorescence. As the chromophores are located at the

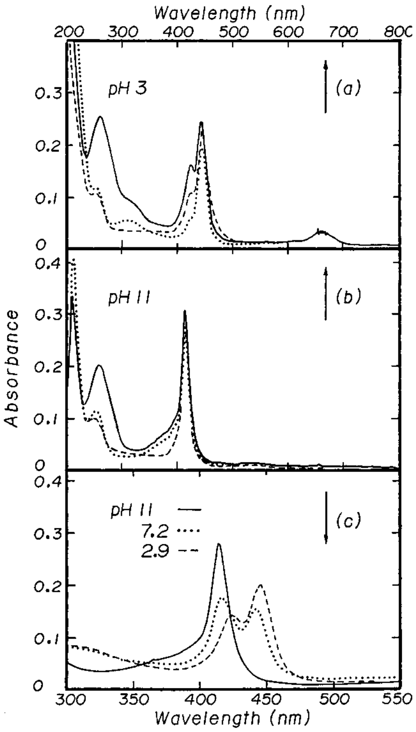


Figure 3. Electronic absorption spectra for aqueous solutions of Q−(MA)$_n$−P polymers (c_{pol} = 1 × 10^{-5} M): (a) pH 3, (—) Q−(MA)$_{47}$−P, (- - -) Q−(MA)$_{94}$−P, (···) Q−(MA)$_{277}$−P; (b) pH 11, (—) Q−(MA)$_{47}$−P, (- - -) Q−(MA)$_{94}$−P, (···) Q−(MA)$_{277}$−P. (c) Absorption characteristics in the Soret band at pH 2.9, 7.2, and 11.

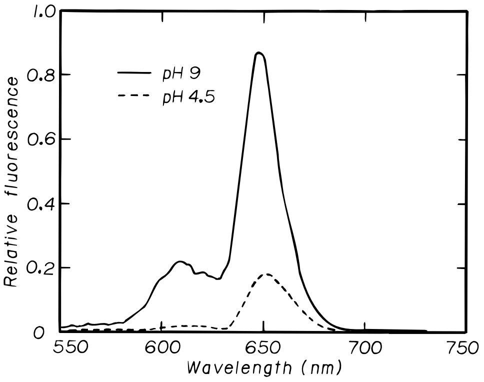


Figure 4. Fluorescence spectra of Q−(MA)$_{47}$−P in aqueous solution at pH = 4.5 and 9 (c_{pol} = 2.5 × 10^{-5} M, λ_{exc} = 420 nm).

polymer chain ends, the interactions can only be effective assuming that the polymers adopt a more compact conformation.

Data on the quantum yields of fluorescence for the six polymers in water solution at pH 4.5 and 9.0 are shown in Table 2. Also included are the values of $\bar{R}_n$, the root-mean-square end-to-end distance of the polymer chains, and $\bar{R}_H$, the hydrodynamic radius for the polymer coil calculated from the classical relations

$$\bar{R}_n = (2n\beta^2)^{1/2} \tag{6}$$

and

$$\bar{R}_{\mathrm{H}} = (0.875/6^{1/2})(2n\beta^2)^{1/2} \tag{7}$$

where n is the number of repeating units in the PMAA chain and β is the statistical bond length of the PMAA backbone. Liu et al.[8] determined the values of β directly from energy transfer studies between PMAA end-capped with naphthalene and anthracene. The values for β were 0.96 Å at pH 5.1 and 6.2 Å at pH 9. Also included is the value of $\bar{R}_{\mathrm{ex}}$, the theoretical length of the fully extended chain (2.53n).

Based on extensive studies of transfer between P and Q in model compounds, it is known that efficient transfer occurs only at separation distances less than about 20 Å, so one might expect to find this to occur in our polymeric systems only when $\bar{R}_n$ is equal to or less than about 20 Å, and this seems to be borne out by our experimental results.

In alkaline solutions the fluorescence intensities are the same within experimental error for polymers with or without P groups. This can be explained considering that methacrylic acid units on the polymer backbone are ionized in alkaline solution, and the polymer chain adopts an extended conformation with $\bar{R}_n$ values of ca. 60, 88, and 146 Å, respectively, despite the hydrophobic interactions between the P and Q end groups. It appears that the so-called "hydrophobic bonding" attractions must be small compared to the electrostatic repulsions between polyion segments. The fluorescence quantum yields at pH 9 are much higher than at pH 4.5 for all polymers as shown in Figure 4.

In acidic solutions, the intensities of the fluorescence of porphyrin in both types of polymers depend on the length of the polymer chain, reaching the highest values for the polymer of the highest molecular weight. The differences in fluorescence quantum yield for phenol-capped polymers are probably due to differences in micropolarity of the environment which the porphyrin experiences. The relative fluorescence intensity, calculated as a ratio of fluorescence quantum yield in quinone-capped polymer to the value found for the respective phenol-capped polymer, shows the same trend. As one does not expect quenching of porphyrin moieties by phenol at pH 4.4 (phenol is characterized by high energy levels, high redox potential, and K_{a} = 1.1 × 10^{-10}),[17] these data can be used to demonstrate the efficiency of porphyrin quenching by quinone. At pH 4.5, 44, 38, and 13% of the porphyrin chromophores are quenched by quinone moieties in Q−(MA)$_{47}$−P, Q−(MA)$_{94}$−P, and Q−(MA)$_{277}$−P, respectively. It is obvious that the polymer chain ends have to be close enough to ensure efficient quenching. One can expect that it is relatively easy to accomplish this in a case of the polymer with a short chain, like polymer (MA)$_{47}$ ($\bar{R}_n$ = 9.3 Å), and much more difficult in a case of the polymer with the very long chains, like polymer (MA)$_{277}$ ($\bar{R}_n$ = 22.6 Å).

Effect of Ionic Strength. The effect of ionic strength on the quantum yield of the porphyrin fluorescence in Q−(MA)$_n$−P polymers was also studied. Experimental data for all Q−(MA)$_n$−P polymers in acidic solution (pH 4.5) and in alkaline medium (pH 9) are displayed in Figure 5. Generally, an increase in the ionic strength of the aqueous solution results in reduction of porphyrin fluorescence. The extent of this process is, however, dependent on the length of the polymer backbone and, for a given polymer, on the pH of the solution used. The changes are much more pronounced in the basic than in the acidic solutions. This can be explained assuming that the introduction of the salt changes the conformation of the polymer chain due to "screening" of the charged carboxyl groups on the polymer chain by sodium and chloride ions. Thus at low pH, where the polymers are only partly ionized and the chains are already compact, the increase in the concentration of the counterions has a limited effect, especially for the polymers with longer chains (Figure 5a). On the other

Table 2. Fluorescence Quantum Yields (ϕ_f)[a] for the PhOH−(MA)$_n$−P and Q−(MA)$_n$−P Polymers in Aqueous Solutions[b]

		pH 4.5			pH 9			
desig	polymer	$\bar{R}_n$ (Å)	$\phi_f \times 10^2$	χ (%)[c]	$\bar{R}_n$ (Å)	$\phi_f \times 10^2$	$\bar{R}_\Theta$	$\bar{R}_{ex}$
	PhOH−(MA)$_{47}$−P	9.3	5.9 ± 0.3		60	15.9 ± 0.2	39	119
P1	Q−(MA)$_{47}$−P	9.3	3.3 ± 0.2	44	60	15.8 ± 0.2	39	119
	PhOH−(MA)$_{94}$−P	13.1	6.0 ± 0.3		88	14.7 ± 0.2	55	238
P2	Q−(MA)$_{94}$−P	13.1	3.7 ± 0.2	38	88	14.1 ± 0.2	55	238
	PhOH−(MA)$_{277}$−P	22.6	9.3 ± 0.3		146	14.0 ± 0.2	95	700
P3	Q−(MA)$_{277}$−P	22.6	8.1 ± 0.3	13	146	14.0 ± 0.2	95	700

[a] Determined from the integrated intensities relative to TPP, assumed to have a $\phi_f = 0.11$ in aerated benzene (see ref 15). [b] $\lambda_{ex} = 420$ nm, A_{420} nm = 0.24. [c] $\chi = (1 - \phi^{Q}/\phi^{PhOH}) \times 100$.

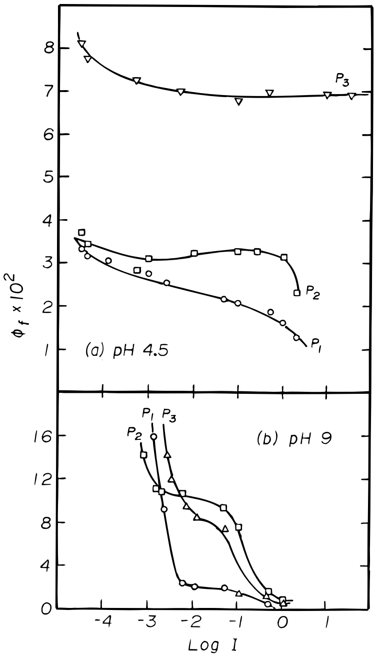


Figure 5. Dependence of the fluorescence quantum yield of porphyrin in Q−(MA)$_n$−P polymers on ionic strength of the solutions: (a) in acidic aqueous solutions (pH 4.5) and (b) in alkaline aqueous solution (pH 9).

hand, in basic solutions, where the majority of the carboxyl groups are ionized and the polymer chains are stretched, the change in ionic strength has a dramatic effect (Figure 5b). The partial neutralization of the charges on the polyions allows the polymer chain to adopt a more compact conformation in which the distances between polymer chain ends are shorter. This obviously favors the quenching process. The above observations indicate that the efficiency of porphyrin quenching by the quinone in the systems studied can be controlled in both acidic and basic conditions by changing the ionic strength of the aqueous solution.

Calculation of Electron Transfer Rates. The results of fluorescence quenching experiments can be interpreted in terms of electron transfer from P to Q followed by charge separation to prevent back-transfer.

Our experimental results can be interpreted assuming that the fluorescence quenching occurs by intramolecular electron transfer from the lowest excited singlet state of the porphyrin to the quinone. This is similar to the low-molecular-weight porphyrin−quinone bichromophoric systems[6,15,17−20] which have been studied extensively.

The energy barrier ΔG to electron transfer is given by the Marcus equation:[21]

$$\Delta G = (\Delta G° + \lambda)^2/4\lambda \qquad (8)$$

where λ is the total reorganization energy for charge separation. The driving force ($\Delta G°$) for photoinduced electron transfer in a polar solvent and at a relatively large donor−acceptor separation can be calculated from the equation given by Weller:[22]

$$\Delta G° = -E_{00} + e(E_D^{\,ox} - E_A^{\,red}) \qquad (9)$$

where E_D^{ox} and E_A^{red} are the ground-state one-electron oxidation potential of the donor and the reduction potential of the acceptor and E_{00} is the energy of the excited singlet state of the species excited. Taking the literature values for the oxidation potential of TTP ($E_D^{ox} = 1$ eV),[23] the reduction potential for *p*-benzoquinone ($E_A^{red} = -0.4$ eV),[23] and the energy of the excited singlet state of the porphyrin attached to the PMA chain in aqueous solution ($E_S = 1.90$ eV), the change in Gibbs free energy accompanying photoinduced electron transfer from porphyrin to quinone in a polar solvent was estimated to be −0.5 eV. Using the literature value of ca. 1 eV[24,25] for the solvent reorganization energy (λ) for the charge separation in porphyrin−quinone systems in polar solvents, the value of the barrier to electron transfer calculated from eq 8 was found to be very low, $\Delta G = 0.06$ eV.

The rate constant for photoinduced electron transfer and charge separation in porphyrin−quinone systems is related to the measured fluorescence quantum yield of the porphyrin in the bichromophoric system (ϕ) and that of the respective reference system (ϕ_{ref}) and the lifetime of the reference system (τ_{ref}):[26]

$$k_{cs} = [(\phi_{ref}/\phi) - 1]/\tau_{ref} \qquad (10)$$

For determination of k_{cs} in acidic medium, the phenol-capped polymers PhOH−(MA)$_n$−P in aqueous solutions were used as the reference compounds for the respective quinone-capped polymers. The lifetimes of porphyrin in these systems were determined by the single-photon-counting technique. The fluorescence decay profiles could not be described by a single-exponential function. Such behavior is often observed in fluorophores trapped in polymeric matrices. A double-exponential fit with the lifetimes of 3.8−5.3 and 8.9−11.8 ns, respectively, gave satisfactory deconvolution (see Table 3). It might be assumed that the two lifetimes represent average values for porphyrin chromophores which experience different microenvironments. The mean values of the fluorescence lifetimes were calculated (see Table 3) and used as the τ_{ref} in eq 10.

For the calculation of k_{cs} in alkaline solutions, the literature value of the lifetime for the model compound, TCP, was used.[16]

Tables 4 and 5 summarize the rate constants of charge separation calculated for the Q−(MA)$_n$−P polymers studied at two different pH values and at different ionic strengths of the aqueous solution. As expected, the rate constants are dependent on the length of the polymer chain, increasing as the chain is shortened. They are also strongly dependent on the ionic strength of the solution. Electron transfer occurs in acidic solutions, even without addition of NaCl. Only for

Table 3. Analyses of the Fluorescence Decay Profiles for PhOH−(MA)$_n$−P in Aqueous Solutions[a]

polymer	$A_1 \times 10^2$	$A_2 \times 10^2$	τ_1 (ns)	τ_2 (ns)	χ^2	$\langle\tau\rangle$ (ns)
PhOH−(MA)$_{47}$−P	5.4	2.3	3.8	8.9	1.28	6.4
PhOH−(MA)$_{94}$−P	5.8	2.0	3.9	10.0	1.29	6.8
PhOH−(MA)$_{277}$−P	1.5	3.2	5.3	11.8	1.16	10.7

[a] $\lambda_{ex} = 420$ nm, $\lambda_{em} = 650$ nm, $T = 298$ K, pH 4.5. [b] $\langle\tau\rangle = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Table 4. Rates of Photoinduced Charge Separation in Acidic Aqueous Solutions of Q−(MA)$_n$−P Polymers at Different Ionic Strengths[a]

	$k_{cs} \times 10^{-7}$ (s^{-1})[b]		
$I \times 10^3$	Q−(MA)$_{47}$−P	Q−(MA)$_{94}$−P	Q−(MA)$_{277}$−P
0.03	12.3	9.1	1.4
0.13	14.6	11.2	3.4
1.03	18.0	13.9	2.9
10.03	20.1	12.9	1.0
80.03	22.4	10.9	1.9
100.03	29.3	12.1	3.3
500.03	34.8	11.2	2.4
1000.03	41.9	13.5	3.2
2000.03	56.3	24.2	3.4

[a] pH 4.5, $T = 298$ K. [b] The maximum uncertainty in any given rate constant (k_{cs}) is ±10%.

Table 5. Rates of Photoinduced Charge Separation in Alkaline Aqueous Solutions of Q−(MA)$_n$−P Polymers at Different Ionic Strengths[a]

Q−(MA)$_{47}$−P		Q−(MA)$_{94}$−P		Q−(MA)$_{277}$−P	
$I \times 10^3$ (M)	$k_{cs} \times 10^{-7}$ [b,c] (s^{-1})	$I \times 10^3$ (M)	$k_{cs} \times 10^{-7}$ [b,c] (s^{-1})	$I \times 10^3$ (M)	$k_{cs} \times 10^{-7}$ [b,c] (s^{-1})
		1.0	0		
1.3	0	1.5	4.0		
2.3	8.2	2.0	4.1	2.8	0
				3.8	2.0
6.3	62.4	6.0	4.3	7.8	5.4
11.3	76.1	11.0	4.5	13.0	7.3
51.3	80.7	51.0	6.7	52.8	10.4
101.3	150.1	101.0	11.2	102.8	97.4
501.3	384.1	501.0	95.7	502.8	98.6
1001.3	859.2	1001.0	336.0	1002.8	288.1

[a] pH 9.0, $T = 298$ K. [b] The maximum uncertainty in any given rate constant (k_{cs}) is ±10%. [c] $\tau_{ref} = 9.2$ ns (see ref 16).

Q−(MA)$_{47}$−P (the shortest chain) does the rate constant steadily increase with an increase in ionic strength of the solution. For the other two quinone-capped polymers, the dependence of k_{cs} on ionic strength is weak, and k_{cs} reached much higher values only at relatively high ionic strength. In general, k_{cs} was at least an order of magnitude lower at pH 4.5 than at pH 9.0 and there was a strong dependence of k_{cs} on ionic strength (especially for higher ionic strength). Furthermore, in this case, electron transfer does not occur at all without addition of NaCl. The increase in ionic strength dramatically increases the rate constant of charge separation; the highest value (ca. 9 × 10^9 s^{-1}) was found for Q−(MA)$_{47}$−P, the shortest chain polymer, in the presence of 1 M of sodium chloride. The k_{cs} values for all polymers are higher in solutions of higher pH.

Although the values of k_{cs} found in this work are high (ca. 10^{10}), they are a factor of 10 lower than the values observed for the primary charge separation in natural photosynthesis ($k_{cs} \approx 10^{11}$ s^{-1}).[24]

Discussion and Conclusions

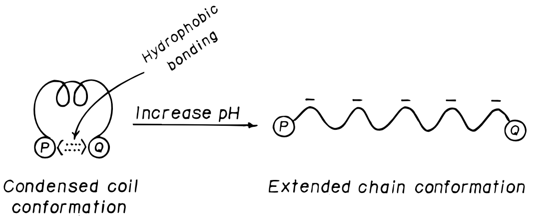
Conceptually, this work was designed to develop a bichromophoric P−Q model for the active center in photosynthesis which, unlike most such models, is water soluble and which also can be "tuned" to any desired rate of photoelectron transfer by adjustment of the interchromophoric distance. The feasibility of such a molecular device was demonstrated in an earlier publication[7] in which it was shown that a random copolymer of acrylic acid with small amounts of monomers containing P and Q showed photoinduced electron transfer whose efficiency depended on the pH of the aqueous solution. Later work[8] on PMAA end-capped with naphthalene and anthracene groups quantified the end-to-end distances R_n expected for this polymer in aqueous solution as a function of pH and ionic strength (see Figure 1).

The tunability of our system is due to the well-known changes in conformation of polyelectrolyte chains with changes in pH or ionic strength. However, PMAA shows an additional conformational change at low pH which is not shown by the analog poly(acrylic acid). This effect has been studied extensively because it resembles the well-known helix−coil transition in biopolymers. Below pH 6, PMAA seems to adopt a very compact "hypercoiled" structure which appears to be of nearly the same density as the polymer itself. In high-molecular-weight polymers ($\bar{M}_v > 20\,000$), these clusters appear to reach a maximum size of about 100 MAA units, and a large polymer may contain many such clusters separated by a sufficient section of the chain to permit isotropic rotation.[27] However, polymers with lower molecular weight appear to form only single domains. For example, Treloar[28] reported that PMAA with $\bar{M}_v = 9700$ containing solubilized perylene behaved as a "compact spherical particle" based on measurements of fluorescence depolarization of the aromatic chromophore. He also reported that the polarity of the interior of the compact form was similar to that of ethanol but becomes more polar due to the entry of water as the structure expands due to ionization of the carboxyl groups. More recently, Wang and Morawetz[29] and Bednar et al.[30] carried out fluorescence studies with absorbed Auramine O and bound dansyl groups on PMAA chains. The former authors showed evidence that Auramine O, which is an ionizable dye, can effect the transition of PMAA and that the conformational change had a low rate constant of 0.1 s^{-1}. Bednar et al. also noted an increase in the polarity of the microenvironment of the dansyl label with increasing pH, but in their studies they noted that the number of attached labels did not influence the conformational transitions of PMAA.

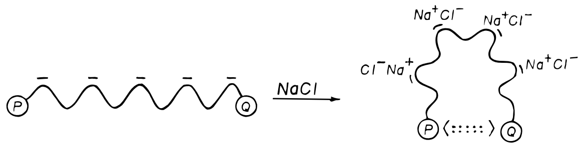
In all of the previous work, the PMAA samples were polydisperse and, except for Treloar's study, of significantly higher molecular weight than ours. Our samples were relatively monodisperse and contained hydrophobic groups whose fluorescence properties were nearly independent of the pH or ionic strength of the aqueous solutions. Thus we believe that in this work the polymers formed single clusters in their compact conformation which became less dense and possibly smaller as the pH was increased. The data on $\bar{R}_n$ and $\bar{R}_\Theta$ given in Table 2 confirm that $\bar{R}_n$ in the compact state is about one-quarter the value of the end-to-end distance in a random coil under Θ conditions. It is also noteworthy that in the extended form at pH 9, $\bar{R}_n$ is significantly smaller than $\bar{R}_{ex}$, the value expected for a fully extended chain.

Scheme 1 shows the expected change in polymer conformation as the pH is increased, and the PMAA undergoes a transition from a compact coil to an extended chain where $\bar{R}_n$ is proportional to n. The values of $\bar{R}_n$ for the three polymers used in this work,

Scheme 1



Scheme 2



calculated as mentioned above, are about 9.3, 13.1, and 22.6 Å, and 119, 238, and 700 Å when polymer chains adopt their extended chain conformation. Under the latter conditions, the average end-to-end distance is too great to expect efficient electron transfer, and its occurrence should be considered evidence for specific chromophore–chromophore interactions often referred to in biological systems as hydrophobic bonding. In the present case involving two relatively large, hydrophobic end groups in a water-soluble polymer, such interactions might well be expected.

Our experimental results are quite informative in that the values of k_{cs} are 1–2 orders of magnitude lower in acidic solution than at alkaline pH where the ionogenic carboxyl groups should be completely ionized. We can only assume that this is due to the high degree of protonation of the porphyrin units at low pH.

In basic medium (pH 9) where the PMAA is fully ionized, the system seems to work perfectly (Table 5 and Scheme 2). At low ionic strength, no photoelectron transfer is observed, even with the shortest polymer, whose end-to-end distance should be about 60 Å. However, as the ionic strength increases, k_{cs} increases continuously over 3 orders of magnitude to a value of 8.6×10^9 s^{-1}, a factor of only 10 less than that estimated for the photosynthetic unit in green plants. Even the highest molecular weight polymer ($n = 277$) shows a rate of 2.9×10^9 s^{-1}, which may be evidence for some hydrophobic bonding between the chromophores leading to a closer average distance than might be expected from molecular weight considerations alone.

This effect is almost certainly due to the partial neutralization of the negative charges on the polyelectrolyte (screening) by sodium ions which allows the coil to contract, as shown in Scheme 2. The coil dimensions must reach some sort of equilibrium, where the attractive hydrophobic bonding forces between P and Q are balanced by the repulsive forces between the carboxylate ions on the PMAA backbone.

The tunability of the electron transfer rate constants k_{cs} is demonstrated in Figure 6, where log k_{cs} is shown as a function of log I, the ionic strength of the aqueous solution. As expected, the polymer with the shortest chain ($n = 47$) shows the most sensitivity to small changes in ionic strength. It also reaches the highest value of k_{cs} at high ionic strength. However, the curve is nonlinear. On the other hand, the highest molecular weight polymer ($n = 277$) shows a continuous variation in the relationship between log k_{cs} and log I over a 1000-fold range in NaCl concentration. It seems likely that the smaller chains are not long enough to achieve anything like a random coil conformation, even with the maximum degree of ionic screening, leading to more complex behavior with changes in ionic strength than is observed with the longer chains.

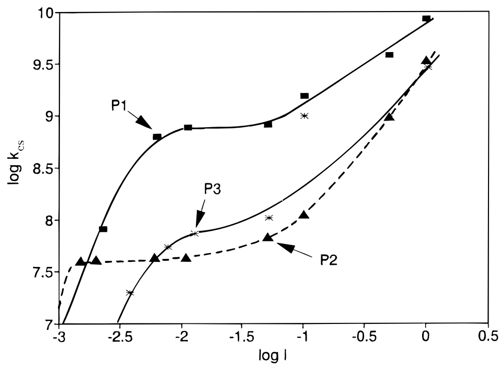


Figure 6. Dependence of log k_{cs} on log I for the Q–(MA)$_n$–P polymers at pH 9.

We conclude that polymers of the general type described in this paper provide useful water-soluble models for the active site in natural photosynthesis. The rates of photoelectron transfer in basic aqueous solution can be varied from zero to 10^{10} s^{-1} by adjusting the ionic strength by addition of up to 1 M sodium chloride.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research is gratefully acknowledged. M.N. thanks the Polish State Committee for Scientific Research for support in the form of a research grant. F.K. thanks Hitachi Ltd., Japan, for financial support during his stay in Canada.

References and Notes

(1) Porter, G.; Archer, M. *Interdiscip. Sci. Rev.* **1976**, *1*, 119.
(2) Katz, J. J.; Norris, J. R.; Shipman, L. L.; Thurnauer, M. C.; Wasielewski, M. R. *Annu. Rev. Biophys. Bioeng.* **1978**, *7*, 393.
(3) Wasielewski, M. R.; Norris, J. R.; Shipman, L. L.; Lin, C.-P.; Svec, W. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2957.
(4) Feher, G.; Okamura, M. Y. In *The Photosynthetic Bacteria*; Clayton, R. K., Sistrom, W. R., Eds.; Plenum Press: New York, 1978.
(5) Vermaas, W. F. J.; Govindjee *Photochem. Photobiol.* **1981**, *34*, 775.
(6) See reviews and citations therein: (a) Kong, J. L. Y.; Loach, P. A. In *Frontiers of Biological Energies—Electrons to Tissues*; Dutton, P. L., Leigh, J. S., Scarpa, A., Eds.; Academic Press: New York, 1978; Vol. 1, p 73. (b) Fox, M. A. *Adv. Photochem.* **1986**, *13*, 237. (c) Fox, M. A. *Photochem. Photobiol.* **1990**, *52*, 617. (d) Gust, D.; Moore, T. A. *Adv. Photochem.* **1991**, *16*, 1. (e) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 463. (f) Weaver, M. J. *Chem. Rev.* **1992**, *92*, 463.
(7) Guillet, J. E.; Takahashi, Y.; McIntosh, A. R.; Bolton, J. R. *Macromolecules* **1985**, *18*, 1788.
(8) Liu, G.; Guillet, J. E.; Al-Takrity, E. T. B.; Jenkins, A. D.; Walton, D. R. M. *Macromolecules* **1991**, *24*, 68.
(9) Liu, G.; Guillet, J. E.; Vlegels, M.; Goethals, E. J. *Macromolecules* **1991**, *24*, 4094.
(10) Chapman, A.; Jenkins, A. D. *J. Polym. Sci.* **1977**, *15*, 3075.
(11) Csiraghi, G.; Casnati, G.; Sartoni, G.; Balzani, L. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2027.
(12) Oude-Alink, B. A. M.; Chan, A. W. K.; Gutsche, C. D. *J. Org. Chem.* **1973**, *38*, 1993.
(13) Kong, J. L. Y.; Loach, P. A. *J. Heterocycl. Chem.* **1980**, *17*, 737.
(14) *Absorption Spectra in the Ultraviolet and Visible Region*; Lang, L., Ed.; Akad. Kiadó: Budapest, 1970.
(15) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1.
(16) Siemiarczuk, A.; McIntosh, A. R.; Ho, T.-H.; Stillman, M. J.; Roach, K. J.; Weedon, A. C.; Bolton, J. R.; Connolly, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 7224.
(17) Morrison, R. T.; Boyd, B. N. *Organic Chemistry*; Allyn and Bacon: Boston, 1974.
(18) Moan, M.; Wolf, C.; Ober, R. *Polymer* **1975**, *16*, 781.

(19) Ho, T.-F.; McIntosh, A. R.; Bolton, J. R. *Nature* **1980**, *286*, 254.

(20) Wasielewski, M. R.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1990**, *112*, 4559.

(21) Marcus, R. A. *J. Phys. Chem.* **1965**, *43*, 679.

(22) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *133*, 93.

(23) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043.

(24) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080.

(25) Joran, A. R.; Leland, B. A.; Felker, P. M.; Zewail, A. H.; Hopfield, J. J.; Dervan, P. B. *Nature* **1987**, *327*, 508.

(26) Antolovich, M.; Keyte, P. J.; Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. *J. Phys. Chem.* **1991**, *95*, 1934.

(27) See review and citations therein: Ghiggino, K. P.; Tan, K. L. In *Polymer Photophysics*; Phillips, D., Ed.; Chapman and Hall: London, 1985; Chapter 7.

(28) Treloar, F. E. *Chem. Scr.* **1976**, *10*, 219.

(29) Wang, Y.; Morawetz, H. *Macromolecules* **1986**, *19*, 1925.

(30) Bednář, B.; Trněná, J.; Svoboda, P.; Vajda, Š.; Fidler, K.; Procházka, K. *Macromolecules* **1991**, *24*, 2054.

MA946429Q