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# Electrostatic Potential and Polarity at the Molecular Surface of Polyelectrolytes As Probed by pH-Sensitive Chromophores Covalently Attached to the Main Chain

**Yotaro Morishima,* Takaomi Kobayashi, and Shun-ichi Nozakura**

*Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.* *Received February 10, 1987; Revised Manuscript Received July 27, 1987*

ABSTRACT: The electrostatic potential ($\psi$) at the "molecular surface" of poly(sodium 2-acrylamido-2-methylpropanesulfonate) (PAMPS) and poly[[3-(methacryloylamino)propyl]trimethylammonium chloride] (PMAPTAC) was determined by the p$K$ shifts of pH-sensitive merocyanine dye residues (Mc) covalently attached to the main chain of these polyelectrolytes. The microenvironmental dielectric constant ($\epsilon_m$) was estimated by the solvatochromic behavior of Mc to be 64 and 61 for the polyanion and polycation, respectively. As a neutral reference polymer poly(acrylamide) was also tagged with Mc. The $\epsilon_m$ value for this polymer was found to be similar ($\epsilon_m = 69$) to those for the above polyions. Therefore, the p$K$ value observed for this neutral polymer could be used as a reference p$K$ value for the "intrinsic" neutral surface (p$K^i$) to calculate $\psi$ from $pK^c - pK^i = -F\psi/2.3RT$, where p$K^c$ is the apparent p$K$ observed for the polyions. Thus, $\psi = -131$ and $+146$ mV were obtained for the polyanion and polycation, respectively. The p$K^i$ value could also be indirectly estimated according to the method of Fernândez and Fromherz by taking into consideration the dielectric contribution to p$K$ and the primary medium effect of the proton. To estimate the effect of $\epsilon_m$ on the dissociation constant of acid–base equilibria, the p$K$ values for the molecular merocyanine dye were measured in dioxane/water mixtures of known dielectric constants. The $\psi$ values thus calculated were essentially identical with those determined by using the neutral reference polymer.

## Introduction

Electrostatic effects of polyions on the rates of a variety of chemical reactions involving charged reacting species have been well documented in the literature.[1,2] These effects are particularly marked in reactions between a functional group covalently attached to a polyion and a charged low molecular weight reaction partner.[1]

We have demonstrated that polyions with photoactive redox groups covalently attached to their main chains would critically modify the reactivity toward photoinduced electron transfer to or from low molecular weight donors or acceptors in aqueous solutions.[3] Thus, this type of polyion with photochemical functionality may serve as a promising photoredox system in which an efficient charge separation can be achieved.[3e,f,h,i]

The extent of the rate modification is strongly related to the magnitude of the electrostatic potential at the boundary area of a polymer skeleton and the water phase (molecular surface) where the reactions take place. Therefore, the estimation of the surface potential of polyions is important for a quantitative understanding of the reactivity of the functional groups attached to the polyion surface.

The local charge effect of polyanions has been known to be reflected in the titration curves of weak polyacids such as poly(acrylic acid) and poly(methacrylic acid).[4] The apparent dissociation constant of a weak polyacid changes with the dissociation degree of the polyelectrolyte because the work to remove a proton from the acid site into an aqueous bulk phase is dependent on the electrostatic potential at the polyelectrolyte backbone. For a quantitative interpretation of this local charge effect theoretical calculations of the surface potential of polyelectrolytes have been reported.[5] The Poisson–Boltzmann equation is commonly used for these calculations by assuming a polyelectrolyte molecule to be a cylindrical rod with a uniform surface charge distribution.[5,6]

Another promising approach to the determination of the surface potential is an incorporation of moieties of optical probes into polyelectrolytes through covalent bonding. The 1-(dimethylamino)naphthalene-5-sulfonyl group (DNS) is a commonly used optical probe for the microenvironmental properties of synthetic polypeptides[7] and proteins.[8] The attachment of DNS onto maleic anhydride copolymers of methyl and butyl vinyl ethers has been reported.[9]

The measurements of the surface potential of organized molecular assemblies such as micelles and vesicles by using optical probe molecules are rather common.[10-20] The potential values obtained with the probe molecules are crucially dependent on the position they occupy in the molecular assemblies. Amphiphilic probes with a long alkyl chain are used to ensure their incorporation into the assemblies so that they exclusively sense the interfacial potential.[17-20] Application of this relatively well-established technique to polyelectrolyte systems as such has a limitation, i.e., the probe molecules with a charge opposite to that of polyions may be distributed between the polyelectrolyte surface and the bulk aqueous phase because the binding between a polyion and a probe is not necessarily a strong site binding. Therefore, for a quantitative measurement of the surface potential it is necessary for the moieties of the probe molecules to be covalently linked to the polyelectrolyte molecular surface.

The purpose of the present paper is to report on the quantitative estimation of the electrostatic potential as well as the local polarity at the molecular surface of polyelectrolytes with pH-sensitive chromophores covalently incorporated into the polymer main chain. In a preceding paper we have reported on the synthesis of a methacrylate-type monomer containing a merocyanine dye moiety and its copolymerization with 2-acrylamido-2-methylpropanesulfonic acid (AMPS).[21] Preliminary results on the spectroscopic behavior of the copolymer in aqueous solutions suggested that the merocyanine dye residues incorporated in the polyion would serve as a useful potential probe.[21] In the present article we describe in detail the spectroscopic investigation on anionic, cationic, and nonionic water-soluble polymers tagged with a small fraction of the merocyanine optical probes. We demonstrate the usefulness of this chemical modification of polyions for a quantitative estimation of the surface potential and polarity.

## Experimental Section

**Materials.** Synthesis of 1-[2-(methacryloyloxy)ethyl]-4-[2-(4-hydroxyphenyl)ethenyl]quinolinium bromide (MA-Mc) was

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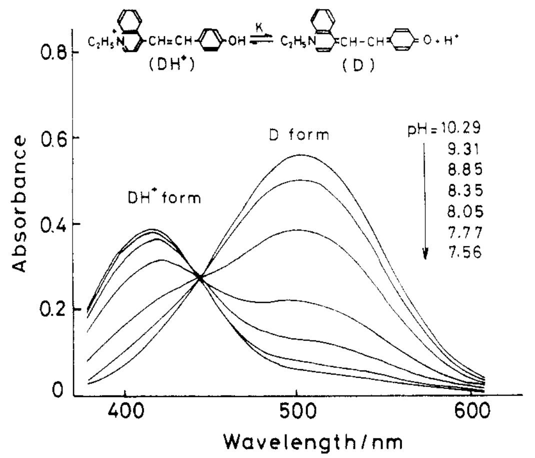


**Figure 1.** Absorption spectra of Et-Mc in aqueous solutions at various pHs; [Et-Mc] = $1.8 \times 10^{-5}$ mol/L.

reported previously.[21] 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) and [3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC) were provided in a pure form through the courtesy of Nitto Chemical Industry Co. and used as received. Acrylamide (Waco Chemical Co.) was purified by recrystallization from ethanol. A merocyanine dye, 1-ethyl-4-(2-(4-hydroxyphenyl)ethenyl)quinolinium bromide (Et-Mc), was purchased from the Japan Research Institute for Photosensitizing Dye Co. and used without further purification. Water was doubly distilled and deionized by passing through an ion-exchange column.

**Copolymerizations.** The copolymerization of MA-Mc and AMPS was carried out as reported previously[21] by using 0.032 g (0.07 mmol) of MA-Mc and 2.07 g (10 mmol) of AMPS in 15 mL of *N*,*N*-dimethylformamide (DMF) in the presence of 0.5 mol % (on the basis of the total monomers) of 2,2′-azobis(2-methylpropionitrile) (AIBN) at 60 °C for 24 h: yield 0.21 g (10% conversion). The copolymer was purified as previously described.[21] The copolymerization of MA-Mc and MAPTAC was performed under the same conditions as above, using methanol as a solvent in place of DMF. The resulting copolymers were purified by reprecipitating twice from methanol into a large excess of ether. The polymers were then dissolved in water, dialyzed against pure water for 5 days, and recovered by lyophilization: yield 0.59 g (25.4% conversion).

A copolymer of MA-Mc with acrylamide was prepared and purified analogously. DMF was used for the polymerization solvent: yield 0.20 g (23.8% conversion).

The mole fractions of the MA-Mc units in the copolymers were determined by the C/N ratio of microanalysis and confirmed by the absorption spectra of methanol solutions of the copolymers.

**Measurements.** The dissociation constants of the merocyanine dye residues were determined by spectroscopic titration of the aqueous solutions by using the absorbance of the benzenoid ($DH^+$) and quinoid (D) forms of the merocyanine dye residues (see text). The pH of the solutions was adjusted with aqueous sodium hydroxide and hydrochloric acid. The pH readings were obtained on a Horiba H-7 LD pH metar equipped with a Horiba combination electrode no. 6326.

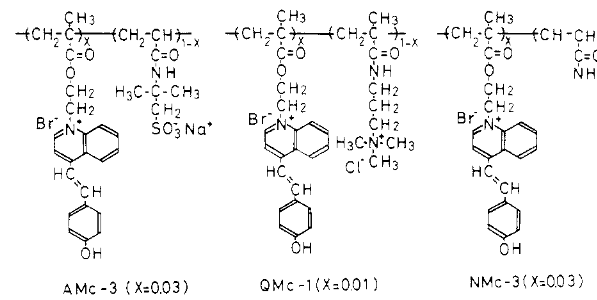
Titrations of Et-Mc were carried out in dioxane/water mixtures with various ratios. The pH readings were corrected according to the literature.[22]

Absorbances were measured at room temperature (20 °C) by using a Hitachi 142 spectrophotometer.

## Results

The merocyanine dye, 4-[2-(1-ethyl-1,4-dihydroquinolinylidene)ethylidene]cyclohexa-2,5-dienone (Et-Mc), exhibits a sufficiently large spectral change according to the acid–base equilibrium, and therefore it serves as a sensitive pH indicator.[23] Figure 1 shows absorption spectra of Et-Mc measured in aqueous solutions at various pHs. The merocyanine dye changes its color from yellow to red upon increasing pH from an acidic to a basic region: the 415 and 502 nm bands are due to the benzenoid ($DH^+$) and quinoid (D) forms, respectively. The spectra possess an isosbestic point at 443 nm and therefore can be resolved quantitatively into the two components due to the $DH^+$ and D forms. From these spectral data the p*K* value (the negative logarithm of the dissociation constant) for Et-Mc was determined to be 8.61.

**Chart I**



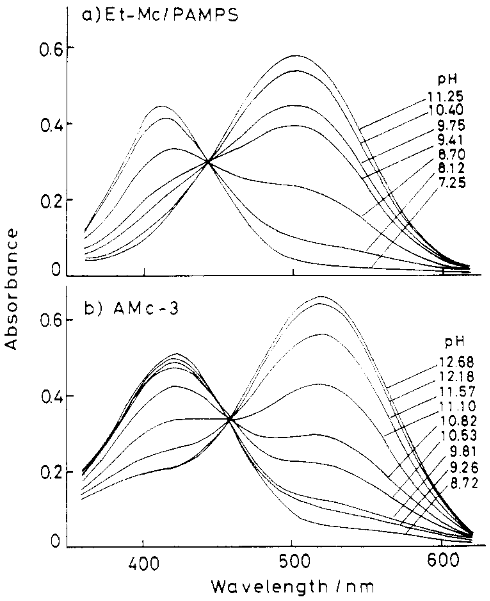


**Figure 2.** Absorption spectra of (a) Et-Mc in the presence of PAMPS and (b) AMc-3 at various pHs; [Et-Mc] = $2.0 \times 10^{-5}$ mol/L, [PAMPS] = $2.5 \times 10^{-2}$ unit mol/L, and [AMc-3] = $6.5 \times 10^{-4}$ unit mol/L.

The polyanion and polycation tagged with the merocyanine dye residues (Mc) in the present work are illustrated in Chart I (abbreviated as AMc-3 and QMc-1, respectively). As a neutral reference polymer for these polyions, poly(acrylamide) was also tagged with Mc (NMc-3). The loading amount of Mc on these polymers was limited to a low level (1–3 merocyanine residues per 100 repeating units of the polymers) to minimize possible disturbance of the properties of these polymers by the probe.

The electric charges on the polyions have a strong influence on the ionization equilibrium of Mc. In Figure 2 the spectral dependence of Mc in AMc-3 on pH was compared with that of Et-Mc physically mixed with the AMPS homopolymer (PAMPS). Figure 3 shows the same comparison of QMc-1 with the mixture of Et-Mc and the MAPTAC homopolymer (PMAPTAC). It is obvious from these spectral data that the copolymer systems have a distinctly larger effect on the acid–base equilibrium of Mc than do simple physical mixture systems.

The degrees of dissociation of Mc determined from the spectroscopic titration were plotted as a function of bulk pH in Figure 4. The apparent p*K* values ($pK_{obsd}$) estimated from the pH values at 50–% dissociation are summarized in Table I. The neutral systems, both NMc-3 and

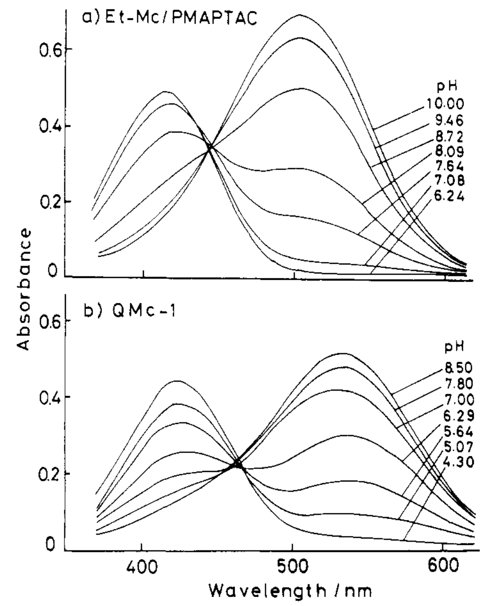


**Figure 3.** Absorption spectra of (a) Et-Mc in the presence of PMAPTAC and (b) QMc-1 at various pHs; [Et-Mc] = $2.0 \times 10^{-5}$ mol/L, [PMAPTAC] = $2.5 \times 10^{-2}$ unit mol/L, and [QMc-1] = $1.9 \times 10^{-3}$ unit mol/L.

**Table I**
**Microenvironmental Effective Dielectric Constants and Electrostatic Potentials Calculated from Equation 2**

| sample | $\lambda_{DH^+}$/nm[a] | $\epsilon_m$[b] | p$K_{obsd}$[c] | p$K^c$ − p$K^i$ | $\psi$/mV[d] |
|---|---|---|---|---|---|
| NMc-3 | 418 | 69 | 8.68 (p$K^i$) | | |
| AMc-3 | 420 | 64 | 10.92 (p$K^c$) | +2.24 | −130 |
| QMc-1 | 421 | 61 | 6.18 (p$K^c$) | −2.50 | +145 |
| Et-Mc/PAAm[e] | 415 | 78 | 8.55 (p$K^i$) | | |
| Et-Mc/PAMPS[e] | 415 | 78 | 9.19 (p$K^c$) | +0.64 | −32 |
| Et-Mc/PMAPTAC[e] | 415 | 78 | 8.36 (p$K^c$) | −0.15 | +9 |

[a] Absorption maxima due to the DH$^+$ form of Mc. [b] Dielectric constants estimated by $\lambda_{DH^+}$ and the relation presented in Figure 5. [c] Observed p$K$ values. [d] Electrostatic potentials calculated from eq 2. [e] Aqueous solutions of Et-Mc in the presence of respective homopolymers.

the mixture of Et-Mc and poly(acrylamide) (PAAm), gave apparent p$K$ values of 8.68 and 8.55, respectively. These values are similar to the p$K$ value of Et-Mc in pure water (p$K^w$ = 8.61). In the case of Et-Mc mixed with PAMPS the p$K_{obsd}$ value showed a shift of 0.64 pH unit from the p$K$ value of Et-Mc mixed with PAAm.

According to Manning's theory[24] a polyion is characterized by a dimensionless charge density parameter $\xi$,

$$\xi = e^2/DkTb \qquad (1)$$

where $e$ is the proton charge, $D$ is the dielectric constant of water, $b$ is the axial average spacing between charged groups on the linear polyelectrolyte chain, and the other symbols have their usual meaning. When $\xi > 1$, in the presence of monovalent counterions, counterions condense onto the polyion until the fraction $(1 - \xi^{-1})$ of the line charge is neutralized. If we assume $b$ = 2.55 Å for PAMPS, the common value for fully extended vinylic polyions, the corresponding value of $\xi$ is 2.8. In this case a fraction, 0.64, of the sulfonate groups on PAMPS are compensated by condensed monovalent counterions. Given that in Manning's theory the counterion condensation does depend on the counterion valence and not on the type of the counterion, the DH$^+$ form of Et-Mc will condense onto PAMPS competing with Na$^+$ ions. A simple calculation shows that at 50-% dissociation approximately 32% of Et-Mc may be condensed on PAMPS and the rest of the dye molecules in the DH$^+$ form may be distributed in the bulk aqueous phase experiencing the Debye–Hückel ionic atmosphere. This may be the reason for the p$K$ shift observed for Et-Mc in the presence of PAMPS.

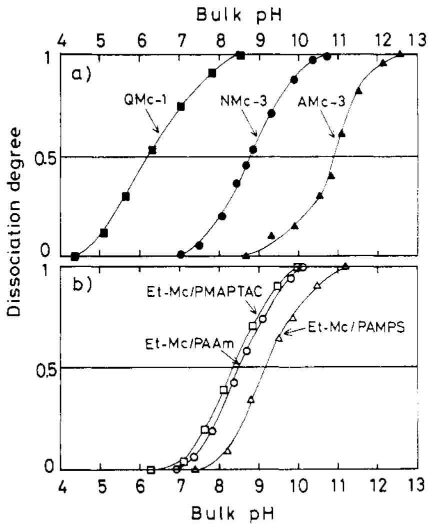


**Figure 4.** Titration curves of AMc-3, QMc-1, NMc-3, and Et-Mc in the presence of PAMPS, PMAPTAC, and PAAm.

It is noteworthy that the p$K$ shift observed for AMc-3 was strikingly larger than that of the corresponding physical mixture system. This is obviously due to the fact that all the dye moieties are confined to the polyion surface. A p$K_{obsd}$ value of 10.92 for AMc-3 is higher than that for NMc-3, a neutral reference, by 2.24 pH units (Table I). This large p$K$ shift toward a higher bulk pH signifies a considerably higher proton activity at the negatively charged macromolecular surface than at the neutral polymer surface.

In the case of Et-Mc mixed with PMAPTAC the titration curve was quite similar to that of the mixture of Et-Mc and PAAm. This is a reasonable consequence because the DH$^+$ form of Et-Mc is electrostatically rejected by the polycation and is partitioned in the bulk aqueous phase without experiencing the polymer microenvironments. By contrast, QMc-1 exhibited a remarkable p$K$ shift due to the fact that the covalently bonded dye moieties are forced to experience the polycation microenvironments. A p$K_{obsd}$ value of 6.18 observed for QMc-1 is lower than that for NMc-3 by 2.50 pH units, reflecting a considerably lower proton activity at the positively charged polymer surface.

Fixed charges along a polyion chain create a strong electrostatic potential at the boundary of the polymer skeleton and water with the protons distributed from the polymer surface toward the aqueous bulk phase according to Boltzmann's law.[10–20] The acid–base equilibrium of Mc bound to the charged polymer surface is affected not only by the local proton activity but also by nonelectrostatic local parameters such as a local polarity.[17,23] It is well-established that an electrostatic potential can simply be related to a difference in the apparent p$K$ at the charged surface (p$K^c$) and that at the "intrinsic" neutral surface (p$K^i$) according to

$$pK^c - pK^i = -F\psi/2.3RT \qquad (2)$$

where $\psi$ is the electrostatic potential, $F$ the Faraday constant, and $R$ the universal gas constant.[10,11] It should be noted that the p$K^i$ value is unknown, i.e., it is not directly measurable. However, if the neutral reference with the same nonelectrostatic surface properties as that of the

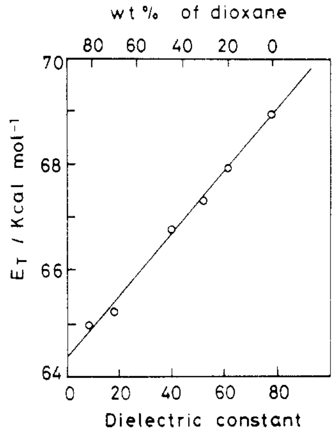


**Figure 5.** Plot of the calculated transition energy $E_T$ of the absorption band due to the $DH^+$ form for Et-Mc against the dielectric constant of the mixed solvent of dioxane and water.

**Table II**
**Absorption Maxima Due to the $DH^+$ Form of Et-Mc and the p$K$ Values in Dioxane/Water Mixtures of Various Ratios**

| dioxane/ water (w/w) | dielectric const[a] | $\lambda_{DH^+}$/nm[b] | p$K_{obsd}$ | $\Delta$p$K^m$ [c] |
|---|---|---|---|---|
| 0/100 | 78.3 | 415 | 8.61 | |
| 20/80 | 60.8 | 421 | 8.68 | 0.07 |
| 30/70 | 51.9 | 425 | 8.72 | 0.11 |
| 45/55 | 38.5 | 428 | 8.78 | 0.17 |
| 70/30 | 17.7 | 438 | 8.90 | 0.29 |
| 82/18 | 9.5 | 440 | 9.03 | 0.42 |

[a] Cited from ref 25. [b] Absorption maxima due to the $DH^+$ form of Et-Mc. [c] $\Delta$p$K^m$ = p$K_{obsd}$ − p$K^w$, where p$K^w$ = 8.61 (see text).

charged surface in question is available, the apparent p$K$ values obtained for the reference system can be used as the p$K^i$ value, thus allowing the calculation of the potential by use of eq 2.[15,16] It has been shown that in a number of studies using pH-indicator probes in surfactant micellar systems neutral micelles often provide useful references for the calculation of the surface potentials of charged micelles.[15–17,20] The most crucial criteria for the reference involve the fact that the effective local dielectric constant is the same as that of the charged system in question.

The merocyanine dye used in the present study is known to show solvatochromism;[23] i.e., the absorption maximum due to the $DH^+$ form ($\lambda_{DH^+}$) is sensitive to the solvent polarity. In Figure 5 the transition energy ($E_T$) of Et-Mc at the 400-nm band was plotted against the dielectric constant of the mixture of dioxane and water[25] (the data are also listed in Table II). Using this relationship, we were able to calibrate the effective local dielectric constants, and the results thus obtained are listed in Table I. It is worth noting that the microenvironmental dielectric constants at the location of the covalently linked Mc in AMc-3, QMc-1, and NMc-3 are very similar, implying that NMc-3 can serve as an appropriate neutral reference system for AMc-3 and QMc-1. Accordingly, use of eq 2 and the apparent p$K$ value of NMc-3 allows the determination of the $\psi$ values for AMc-3 and QMc-1. The results are given in Table I. In the case of Et-Mc mixed with PAAm, PAMPS, or PMAPTAC in an aqueous solution the dye molecules are experiencing the dielectric constant of water itself. This implies that the dye molecules are not closely associated with the polymer surface even in the case with PAMPS onto which the condensation of the $DH^+$ form of Et-Mc is expected to occur to some extent. In fact, the values calculated for the mixture systems are much lower than those determined for the covalently linked systems.

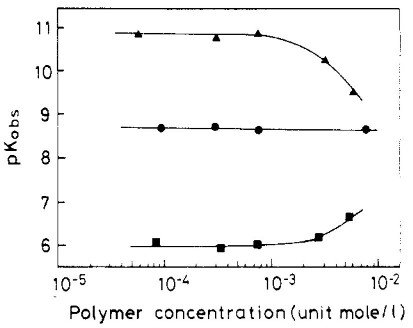
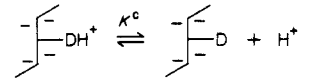


**Figure 6.** Effect of the polymer concentration on the observed p$K$ values for AMc-3, QMc-1, and NMc-3.

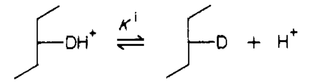
Figure 6 shows a plot of p$K_{obsd}$ for the covalently linked systems against polymer concentrations. The p$K_{obsd}$ values for AMc-3 decreased with increasing the polymer concentration while those of QMc-1 exhibited a reverse change. However, in the concentration region lower than about 0.2 mM of the polymer repeating units the p$K_{obsd}$ values were essentially independent of the polymer concentration. In contrast, the p$K_{obsd}$ values for NMc-3 were constant regardless of the large concentration changes. These observations may be rationalized by the fact that polyelectrolyte chains tend to retain a compact conformation at a higher concentration as a result of an electrostatic shielding of the mutual repulsion of the charged segments. Accordingly, it is reasonable to consider that the p$K_{obsd}$ values at lower concentrations (<0.2 mM) of the polyions reflect the potentials at the surface of an extended-chain conformation.

## Discussion

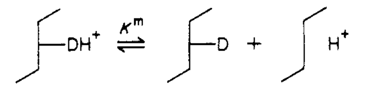
The p$K^i$ value may indirectly be estimated from the following consideration in accordance with Fernàndez and Fromherz.[17] The following types of acid–base equilibra for Mc incorporated into polymers may be considered:



(3)



(4)



(5)

Equation 3 represents the dissociation of a polyion-bound $DH^+$ form of Mc into a polyion-bound D form and a proton in the bulk aqueous phase (a bulk proton) with the equilibrium constant of $K^c$ (eq 3 represents the polyanion case by example). Equations 4 and 5 represent hypothetical equilibria of the $DH^+$ form attached to a neutral polymer surface having nonelectrostatic surface properties identical with those of the charged surface in question. These dissociations create polymer-bound D forms and a bulk proton according to eq 4 or a "hypothetical" polymer-bound proton according to eq 5. The latter proton is experiencing the same microenvironment as are the polymer-bound $DH^+$ and D forms. The dissociation constants for eq 4 and 5 are denoted as $K^i$ and $K^m$, respectively. Note that the values of p$K^i$ and p$K^m$ cannot be directly measured for the polymer-bound system. The difference between p$K^i$ and p$K^m$ involves "the primary medium effect of proton", i.e., the work required to transfer the proton from the bulk aqueous phase to the polymer surface, thus leading to

$$\Delta pK^i - \Delta pK^m = -(\mu^{0m}{}_{H^+} - \mu^{0w}{}_{H^+})/2.3RT \qquad (6)$$

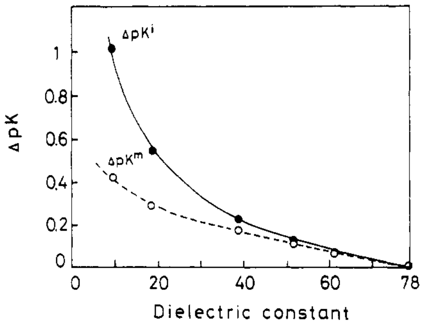


**Figure 7.** Plot of the shifts of p$K$ against the dielectric constant of the mixed solvent of dioxane and water: $\Delta pK^m = pK^m - pK^w$ and $\Delta pK^i = pK^i - pK^w$. The difference between $pK^i$ and $pK^m$ corresponds to the primary medium effect of the proton (see text).

where $\Delta pK^i$ and $\Delta pK^m$ are the shifts of p$K$ from that in pure water ($pK^w$), i.e., $\Delta pK^i = pK^i - pK^w$ and $\Delta pK^m = pK^m - pK^w$ and $\mu^{0m}{}_{H^+}$ and $\mu^{0w}{}_{H^+}$ denote the standard chemical potentials of protons in the neutral polymer microenvironment and in the bulk aqueous phase, respectively.[17] The difference of $\Delta pK^c$ ($=pK^c - pK^w$) and $\Delta pK^i$ can be related to only an electrstatic potential according to

$$\Delta pK^c - \Delta pK^i = -F\psi/2.3RT \qquad (7)$$

If a neutral reference system having the same microenvironmental polarity as that of the charged polymer surface is actually available, then the apparent p$K$ value observed for the reference system can be taken as $pK^i$ for the charged polymer surface. This is the case of NMc-3 in the present study. Fernândez and Fromherz[17] have demonstrated that $\Delta pK^i$ can be estimated from eq 6 even though such a neutral reference is unavailable. They have titrated pH indicators in a series of dioxane/water mixtures with known dielectric constants to estimate $\Delta pK^m$ indirectly,[17] and they have estimated the primary medium effect of the proton by approximating it with the mean degenerate activity coefficient of HCl ($f_{HCl}{}^0$) for the dioxane/water mixtures of known ratios according to

$$\mu^{0m}{}_{H^+} - \mu^{0w}{}_{H^+} \simeq 2.3RT \log f_{HCl}{}^0 \qquad (8)$$

Application of this method to the present system enables us to estimate the $\Delta pK^i$ value. Table II lists the $\Delta pK^m$ values, the difference of the apparent p$K$ values for Et-Mc observed in a series of dioxane/water mixtures and $pK^w$. In Figure 7 the $\Delta pK^m$ values were plotted against the dielectric constant of the medium. The $\Delta pK^m$ values showed a gradual increase with decreasing dielectric constant of the medium; i.e., the dissociation of the DH$^+$ form of Et-Mc into the D form and a proton becomes less favorable in media with lower dielectric constants.

Fernândez and Fromherz[17] compared the behavior of two conjugate pH indicators of type I and II.

$$A \rightleftharpoons B^- + H^+ \qquad (I)$$

$$A^+ \rightleftharpoons B + H^+ \qquad (II)$$

Type I is the dissociation of a molecular acid A to give an anionic base B$^-$ and a proton and type II the dissociation of a cationic acid A$^+$ to give a neutral base B and a proton. They pointed out that with lowering the dielectric constant the p$K$ values for type I exhibited a large increase while those for type II showed a slight decrease.[17] These facts were rationalized by taking into account a change in the electric charge before and after the dissociation, i.e., upon dissociation type I creates two ions whereas the number of ions remains the same for type II. In view of the change in the net charge, Et-Mc may seem to be a type II dye (see the insert in Figure 1). However, the behavior exhibited in Figure 7 seems more like that of the type I because the $\Delta pK^m$ value increases with decreasing the dielectric constant. Since the D form of Et-Mc is a highly polar molecule although the net charge is zero, it would be less stabilized in less polar media. Therefore it may be reasonable that Et-Mc behaves as though it were a type I dye. From eq 6 and 8, using the $f_{HCl}{}^0$ values for dioxane/water mixtures, the $\Delta pK^i$ values were calculated and were plotted against the dielectric constant of the media in Figure 7.

**Table III**
**Electrostatic Potentials Calculated from Equation 7**

| sample | $\epsilon_m$[a] | $pK_{obsd}$[b] ($\equiv pK^c$) | $\Delta pK^c$[c] | $\Delta pK^i$[d] | $\Delta pK^c - \Delta pK^i$ | $\psi$/mV[e] |
|---|---|---|---|---|---|---|
| AMc-3 | 64 | 10.92 | +2.31 | 0.06 | +2.25 | −131 |
| QMc-1 | 61 | 6.18 | −2.43 | 0.08 | −2.51 | +146 |
| Et-Mc/ PAMPS | 78 | 9.19 | +0.58 | 0.04 | +0.54 | −31 |
| Et-Mc/ PMAP-TAC | 78 | 8.36 | −0.25 | 0 | −0.25 | +15 |

[a] Microenvironmental dielectric constants estimated from Figure 5 by using the $\lambda_{DH^+}$ values. [b] Observed pK values. [c] $\Delta pK^c = pK^c - pK^w$, where $pK^w = 8.61$ (see text). [d] Estimated from Figure 7 by using the $\epsilon_m$ values. [e] Calculated from eq 7.

Knowing the effective microenvironmental dielectric constants of AMc-3 and QMc-1, one can readily obtain the $pK^i$ values from Figure 7. Thus, the electrostatic potentials can be calculated from eq 7 (Table III). The electrostatic potential values thus estimated for AMc-3 and QMc-1 are essentially identical with those calculated from eq 2 by using the apparent p$K$ value of NMc-1 as the $pK^i$ value (Table I). Although the method of Fernândez and Fromherz[17] to evaluate the $\Delta pK^i$ values may seem to be an overly simplified method, the validity of their method for the evaluation of surface potentials may be supported by the present results. In view of the fact that the use of an appropriate neutral reference system is practically very limited, the results of Fernândez and Fromherz have opened wide application of the pH-indicator method for the quantitative estimation of surface potentials.

The length of the pendant merocyanine dye moieties from the main chain of the polyions is approximaely 16 Å when they are stretched out from the main chain. It is reasonable to consider that the electrostatic repulsion among the fixed charges on a polyion would force a flexible vinylic main chain to be fairly straight and to behave as a rigid cylinder.[6] In the present study the radius of the cylinder may be roughly estimated to be 8 Å for PAMPS and PMAPTAC by assuming that the pendant charged groups are projected from the main chain. From these assumptions we may expect the Mc probe to "report" microenvironmental information on the region within a distance of roughly 8 Å from the cylinder surface.

According to condensation theory, when $\xi > 1$, the volume of the region within which the condensation occurs is given by[24c]

$$V_p = 8\pi e N_A(\xi - 1)b^3 \qquad (9)$$

in the low-concentration limit of a 1:1 salt, where $e$ is the base of natural logarithms and $N_A$ is Avogadro's number. $V_p$ has the units centimeters cubed per unit mole of polyions when $b$ is expressed in angstroms. By use of eq 9 the thickness ($\Delta x$) of a cylindrical shell of the condensation volume ($V_p$) about the polyions in the present study is calculated to be $\Delta x = 7$ Å in the low-concentration limit. Therefore, the Mc probe may be sensing mostly the microenvironments within the condensation layer.

Table IV
Effective Dielectric Constants and Electrostatic Potentials

| polymer[a] | [NaCl]/mM | $\lambda_{DH^+}$/nm | $\epsilon_m$[b] | p$K_{obsd}$ | $\psi$/mV[c] |
|---|---|---|---|---|---|
| NMc-3 | 2 | 419 | 68 | 8.68 | |
| NMc-3 | 20 | 419 | 68 | 8.70 | |
| NMc-3 | 200 | 419 | 68 | 8.68 | |
| AMc-3 | 2 | 421 | 61 | 10.72 | -120 |
| AMc-3 | 20 | 424 | 54 | 10.28 | -90 |
| AMc-3 | 200 | 426 | 47 | 9.55 | -21 |
| QMc-1 | 2 | 421 | 61 | 6.40 | +126 |
| QMc-1 | 20 | 422 | 58 | 6.75 | +93 |
| QMc-1 | 200 | 423 | 56 | 7.70 | +48 |

[a] Concentration, $6.5 \times 10^{-4}$ unit mol/L. [b] Effective dielectric constants. [c] Electrostatic potentials calculated from eq 7.

Although Manning's theory has been receiving considerable attention for quantitative understandings of transport and thermodynamic properties of polyelectrolyte solutions, there is still some ambiguity about the theoretical foundation. Recently, Le Bret and Zimm[26] have shown that the Manning's theory has a mathematical foundation in the Poisson–Boltzmann equation. They have demonstrated on the basis of an analytical solution of the Poisson–Boltzmann equation that the counterion condensation is a necessary consequence for a cylindrical polyion surrounded only by its own counterions and that a radius $R_M$ within which the Manning fraction $(1 - \xi^{-1})$ of counterions resides can be rather large to form a diffuse cloud and is enlarged to infinity upon infinite dilution. They have mathematically shown the unique behavior of counterions that a smaller fraction ($F$) of the counterions stays within a finite radius $a \exp[F/(\xi - 1)(F_0 - F)]$ upon infinite dilution, where $a$ is the radius of the polyion cylinder and $F_0 = 1 - \xi^{-1}$. Applying this equation to the present study, a fraction of 0.36 (56% Manning fraction) of the counterions resides within the distance of 8 Å from the cylinder surface. The electrostatic potential that the probe dye moieties are experiencing depends on the extent of the neutralization of polyion surface charges by the condensed counterions within the distance at which the probes are fixed. In this context the use of a series of probe dyes with different spacings from the main chain may provide useful experimental information on the spatial distribution of counterions to compare with theories. We are now exploring the feasibility of such an approach from a synthetic point of view.

According to Manning's theory, the condensation fraction and $V_p$ are insensitive to salt concentration.[24c] Guéron and Weisbuch[27] have shown, based on numerical solutions of the Poisson–Boltzmann equation, that the counterion distribution is essentially salt independent in the vicinity of the cylinder surface, although $V_p$ enlarges infinitely in the limit of infinite dilution. Table IV shows the surface potentials in the presence of salt. It is important to note that the potential values are little affected up to 2 mM salt concentration. This seems to be consistent with the theories discussed above. The effective dielectric constant of AMc-3 and QMc-1 decreased with an increase of the salt concentration while that of NMc-1 remained constant (Table IV). These facts suggest that the conformation of the polyions changes from an extended to compact form with increasing ionic strength, while that of the neutral polymer remains intact. In this situation Mc would be encaged within the compact coils of the polyions, thus experiencing a lower polarity than at the surface of an extended polyion chain. For the calculation of electrostatic potentials in solutions with a high concentration of NaCl, NMc-3 can no longer be used as a neutral reference because the effective dielectric constants of AMc-3 and QMc-1 differ from that of NMc-3 under these conditions. Therefore, the potentials can only be calculated from eq 7 by using the $\Delta pK^i$ values estimated from Figure 7. The electrostatic potentials are considerably lowered in both the polyanion and polycation cases at a salt concentration of 200 mM (Table IV), implying that the polyions retain highly coiled conformations.

## Conclusion

A polyanion (PAMPS) and polycation (MAPTAC) were tagged with pH-sensitive merocyanine dye residues (Mc) by means of covalent bonding. The apparent p$K$ values for Mc in the polyanion (AMc-3) (p$K^c$) showed an increase of 2.31 pH units from the p$K$ value of the merocyanine dye molecule (Et-Mc) in pure water (p$K^w$), while the p$K^c$ value for Mc in the polycation (QMc-1) showed a decrease of 2.43 pH units from the p$K^w$ value. The shifts of the p$K$ values for the aqueous solutions of Et-Mc in the presence of the corresponding homopolyelectrolytes (PAMPS and PMAPTAC, respectively) were much lower than those of AMc-3 and QMc-1; an increase of 0.21 pH unit and a decrease of 0.25 pH unit were observed in the presence of PAMPS and PMAPTAC, respectively. These facts indicate that in the physical mixture the probe dye is not experiencing microenvironments at the molecular surface of the polyelectrolyte skeleton.

The effective dielectric constants ($\epsilon_m$) at the locations of Mc were estimated from the absorption spectra of Mc to be 64 and 61 for AMc-3 and QMc-1, respectively. Poly(acrylamide) was also tagged with Mc (NMc-3). The value of the effective dielectric constant was found to be similar ($\epsilon_m = 69$) to those of AMc-3 and QMc-1. The p$K$ value for NMc-3 showed a slight increase (0.07 pH unit) from the p$K^w$ value, which is attributed to a nonelectrostatic (dielectric) contribution to the acid–base equilibrium of Mc. The electrostatic potentials for the polyions were calculated by using NMc-3 as a neutral reference to be -131 and +146 mV for AMc-3 and QMc-1, respectively.

The p$K$ values for Et-Mc were measured in a series of dioxane/water mixtures of known dielectric constants. Taking into account the primary medium effect of protons, which was approximated by the mean degenerate activity coefficient of HCl in the medium, the "intrinsic" microenvironmental contribution (p$K^i$) to p$K^c$ was estimated as a function of the effective dielectric constant. The electrostatic potentials calculated by using the p$K^i$ values thus estimated were identical with those obtained by use of NMc-3 as a neutral reference.

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**Registry No.** (MA-MC)(AMPS) (copolymer), 111026-41-6; (MA-MC)(MAPTAC) (copolymer), 111026-42-7; (MA-MC)(AA) (copolymer), 111026-43-8; Et-MC, 111026-44-9; PAMPS, 35641-59-9; PMAPTAC, 68039-13-4; PAA, 9003-05-8.

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# Kinetics of Ion-Pair Interchange in Ionomer Solution

**Herbert Morawetz* and Yongcai Wang**

*Department of Chemistry, Polytechnic University, Brooklyn, New York 11201.*

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ABSTRACT: Solutions of polystyrene in which 3.4 and 6.9 mol % of the monomer residues were sulfonated were partially neutralized with 2-(aminomethyl)naphthalene and 9-(aminomethyl)anthracene, respectively. The solutions were mixed in a stopped-flow apparatus and the interchange of the two counterions was followed by the increase in the anthracene emission intensity, when the solution was irradiated in the naphthalene absorption band, due to an increasing efficiency of nonradiative energy transfer. The kinetics of the process were studied as a function of the polymer concentration in dioxane and a 1:1 mixture of dioxane and cyclohexane, as a function of the excess of unneutralized sulfonic acid groups, and as a function of temperature.

## Introduction

Although factors affecting the equilibrium of ion-pair formation in media of low dielectric constant have been explored in great detail,[1] no studies of the kinetics of such processes seem to have been reported. Rate constants for the complexation of monovalent cations with crown ethers have been determined with the use of NMR[2] and ultrasonic relaxation techniques,[3] and corresponding rates for the $Na^+$ complexation with the cyclic polypeptide Gramicidin A have also been measured.[4] As would be expected, the exchange of alkali cations with their cryptates[5] is much slower than with the less stable crown ether complexes. All these complexes involve several ligand groups so that the kinetics of their formation and dissociation involves different considerations than the formation of an ion pair, depending only on the interaction of a cation and an anion.

The kinetics of ion-pair interchange in organic solvents is not only of general physicochemical interest but concerns the polymer chemist for two specific reasons: (a) In the anionic polymerization of vinyl compounds, the rate constant for chain propagation is different for chains terminated by "contact ion pairs" and "solvent-separated ion pairs", leading to a bimodal molecular weight distribution if ion-pair interchange is slow.[6] (b) The interaction between ion pairs in ionomers leads to a sharp increase in viscosity both in bulk and in solution.[7,8] It has been suggested[9] that such effects on the rheology of the system should be sensitive to the rate of ion-pair interchange.

The present investigation is based on the following idea: In a dilute ionomer solution in which half of the anionic chains carry donor and half carry acceptor fluorophores, the donor–acceptor distances are too large for a significant nonradiative energy transfer ("Förster transfer"[10]). However, as the counterions are interchanged, so that donor and acceptor fluorophores come to be associated with the same polymer chain, their spacing becomes sufficiently short so that the efficiency of energy transfer from the donor to the acceptor fluorophore is substantially increased. The emission intensity of the acceptor, when the solution is irradiated in the donor absorption band, is then a measure of the extent of counterion exchange. This paper reports initial results in which this principle is used by mixing solutions of slightly sulfonated polystyrene with fluorescent counterions in a stopped-flow apparatus.

## Experimental Section

**Materials.** Polystyrene (number-average molecular weight 105 000) with 3.4% and 6.9% of the monomer residues converted to the sulfonic acid was donated to us by Dr. R. D. Lundberg of the Exxon Chemical Co., Linden, NJ. 9-(Hydroxymethyl)-anthracene (Aldrich) was converted to 9-(chloromethyl)anthracene and the method of Hezowski et al.[11] was used for the preparation of 9-(anthrylmethyl)phthalimide and its hydrazenolysis to 9-(aminomethyl)anthracene (AMA) (mp 105–110 °C). The same procedure was used to convert 2-(chloromethyl)naphthalene (Aldrich to 2-(aminomethyl)naphthalene (AMN) (bp 114–118 °C at 0.1 Torr).

**Kinetics.** Solutions of partially sulfonated polystyrene containing AMA or AMN counterions were mixed in the stopped-flow apparatus with fluorescence detection previously described.[12] The solutions were irradiated at 282 nm, the absorption maximum for AMN. At this wavelength the molar extinction coefficients

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