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Fluorescence Studies of the Conformational Changes of Poly(methacrylic acid) with pH

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ABSTRACT: Steady-state and pulse laser studies of the fluorescence of pyrene hosted by poly(methacrylic acid) (PMA) in aqueous solution are described. Studies on the effect of pH on the fluorescence lifetime and the quenching of the fluorescence by O_2, Tl^+, and CH_3NO_2 are used to describe the conformational changes induced in the polymer by pH. At least two hydrophobic guest sites are suggested in PMA at pH around 5 for noncharged molecules such as pyrene. The data are actually interpreted in terms of two sites. The photophysical studies suggest the following concepts to describe the pH-induced conformational transition of PMA. The pH-induced change is not a homogeneous ionization of PMA with increasing pH, as only one site would be observed. Increasing the pH ionizes a number of COOH groups on PMA which leads to a hydrophobic core of PMA surrounded by a more hydrophilic mantle or ionized section of the polymer. Both sites act as hosts for pyrene, and the ionized site also binds cationic quenchers such as Tl^+ which increase the rate of decay of excited pyrene at this location. Further increase in pH leads to a decrease in the ratio of hydrophobic PMA core to ionized PMA "mantle". Eventually at high enough pH the polymer is extensively ionized, uncoils, and does not act as a host for pyrene.

Introduction

For many years, much effort has been dedicated to the study of macromolecules carrying ionized, or ionizable, groups in the side chain. These synthetic polyelectrolytes are important in many industrial applications and also as simplified models of natural polyelectrolytes. Thermodynamic and kinetic studies of synthetic polyelectrolytes can be used to gain relevant information of the physicochemical properties of biomolecules such as nucleic acids, polysaccharides, etc. Poly(methacrylic acid) (PMA) shows a marked pH-induced conformational transition. This process has been studied by different techniques: potentiometric titration,[1-3] viscometry titration,[4-6] calorimetry,[7-9] Raman spectrometry,[10] pH jump,[11,12] fluorescent probing,[13-16] etc. The data suggest that at low pH the macromolecule adopts a hypercoiled form in order to minimize the hydrophobic interactions. At a high degree of ionization (higher pH) and in the absence of electrolytes, the PMA chain stretches to a rodlike form. The conformational transition between the two states takes place at pH 4–6. However, the nature of this transition is still open to controversy. Some authors suggest that the transition is highly cooperative and occurs in one step,[5] while data from Raman spectroscopy indicate a multiplicity of structures.[10]

Some light may be thrown on this problem by use of fluorescent probes incorporated into the hydrophobic microdomain of PMA. The probes should exhibit photophysical properties that are strongly dependent on the medium. This approach has been employed previously,[12-15] but the authors have always monitored a variable that is a result of an average over the whole system. With pyrene, for example, spectral characteristics such as fluorescence intensity, ratio III/I, ratio monomer/excimer, etc. contain contributions from all Py* independent of its location. Thus, if there is more than one structure in the transition region, it would be impossible to distinguish between them, and these kind of measurements as a function of pH would show abrupt changes. An alternative procedure is to employ a property that could be uniquely separated from the overall sum of all contributions. The natural choice is the rate of emission decay which becomes multiexponential when there are various species with different lifetimes.

In this paper we report a study of PMA solutions in the region of conformational transition using pyrene as a fluorescent probe, together with quenchers to enhance the fluorescent lifetime differences in the different structures.

Experimental Section

Two kinds of poly(methacrylic acids) were used: one purchased from Polysciences, I, and the other synthesized with AIBN as initiator, II. The viscosity-average molecular weights were 120 000 and 250 000 respectively. These values were estimated from the intrinsic viscosity in 0.002 M HCl solution, using the Mark-

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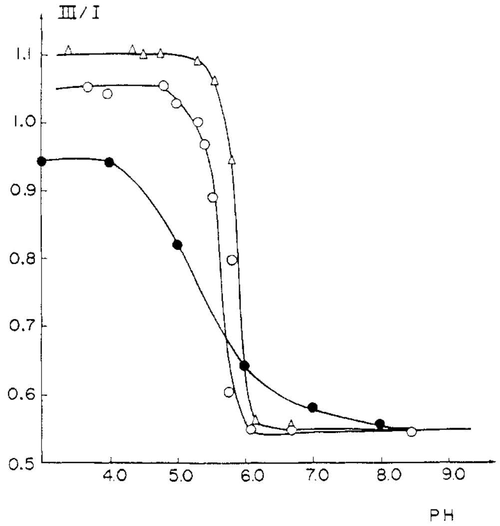

Figure 1. Fluorescence intensity ratio III/I of pyrene as function of pH. (△, a) in PMA(II) solution; (○, b) in PMA(I) solution; (●, c) from ref 14c, M - 10 000.

Houwink equation and the constants given in the literature.[17]

The degree of neutralization, α, was changed by adding 0.1 M NaOH. The relationship between α and pH is given by the equation

$$\text{pH} = \text{p}K - 2 \log ((1 - \alpha)/\alpha)$$

Pyrene (Aldrich) was recrystallized twice from ethanol; nitromethane, potassium chloride, potassium iodide, and thallium nitrate were used as received.

The fluorescence decay of singlet excited pyrene was monitored at 400 nm, following excitation with pulses from a LN1000 PRA nitrogen laser; a 7912 AD Tektronix digitizer captured the emission signals observed with a Hamamatsu 928 photomultiplier. A description of the time-resolved fluorescence system has been given previously.[18] Double-exponential decays were obtained by fitting time-dependent fluorescence data by an expression of the form

$$I(t)/I(0) = a \exp(-k_1 t) + (1 - a) \exp(-k_2 t)$$

where k_1 and k_2 are the rate constants for two different exponential decays of the excited species and a is the fraction that decays with the slower rate constant k_1; $I(t)$ and $I(0)$ are the fluorescence intensities at time t and $t = 0$, respectively. The fluorescence spectra were recorded with a Perkin-Elmer MPF-44B spectrophotometer. The ratio III/I corresponds to the ratio of intensities of peak 3 (λ = 384 nm to peak 1, λ = 373 nm). All the samples were prepared with deionized water. The concentrations used were 2 g/L and 5×10^{-6} M for the polymer and pyrene, respectively. Rate constants for quenching, k_q, of pyrene fluorescence by O_2, Tl^+, and CH_3NO_2 were obtained by the equation

$$k = k_0 + k_q[Q]$$

where k and k_0 are the measured rates of decay of excited pyrene with and without quencher, while [Q] is the quencher concentration.

Results and Discussion

Fluorescence of Pyrene in PMA. The transition of poly(methacrylic acid), from a hypercoiled to an expanded form, has been monitored by the change of the ratio III/I in the fluorescence spectrum of pyrene. The results are given in Figure 1 and have the same pattern found by other authors using different photophysical properties of a wide variety of probes. Curves a and b, determined in this work, are for PMA(I) and PMA(II). Curve c is from ref 14c for a PMA with molecular weight of 10 000.

As can be seen in Figure 1, the media sensed by pyrene at a pH lower than 6.0, as determined by the value of the ratio III/I, is quite dependent of the polyelectrolyte molecular weight. The limiting value, reached at a low pH that corresponds to the hypercoiled state, increases with increasing molecular weight. This fact indicates that the polymer adopts a more hydrophobic or more tightly coiled conformation at higher polymer molecular weight.

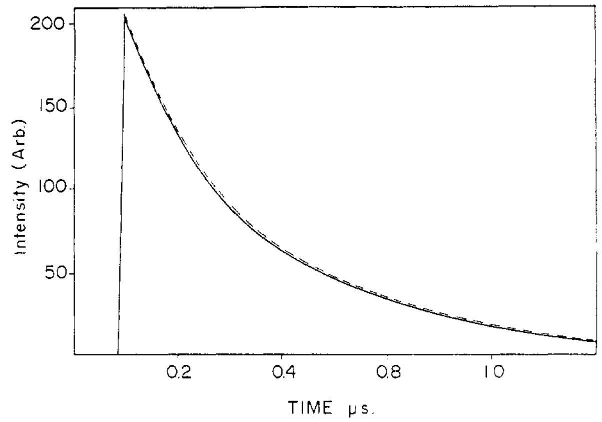

Figure 2. Exponential and double-exponential fit of the fluorescence decay of pyrene: (—) experimental; (- - -) fitted.

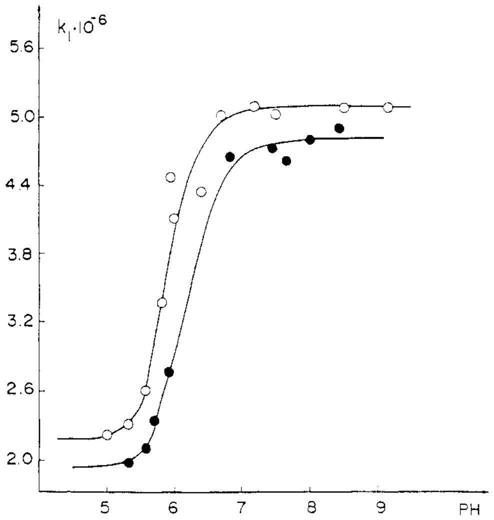

Figure 3. Plot of the slower rate constant from the double-exponential fit for the decay of pyrene versus pH: (○) in PMA(I) solution; (●) in PMA(II) solution.

The shape of the titration curves has been explained as follows:[4] Initial neutralization of the chain changes its conformation slightly, up to a value between pH 5 and 6 (0.2–0.3 dissociation degree), where the process is drastically accelerated. At this pH, the polyelectrolyte is stated to expand because of the electrostatic repulsion of the ionized COOH groups. As a consequence, the probe is expelled into the water phase.

However, data from Raman experiments suggest the existence of different structures during the transition process. This makes an interpretation of the transition more difficult via steady-state methods due to the possible existence of a distribution of probes, sensing the different environments.

To try to resolve the dilemma we have conducted time-resolved fluorescence experiments in the presence and absence of an excess of inert electrolyte.

Decay of Excited Pyrene. Figure 2 shows an experimental fluorescence decay of pyrene in PMA(II) at pH 5.7. The decay is multiexponential and the dashed curve is the fit to a double-exponential decay function. The biexponential decay is observed even at pH ranging from 3.5 to 5.0, but in these cases the difference between k_1 and k_2 is small and has little effect on the steady-state properties of the singlet excited state.

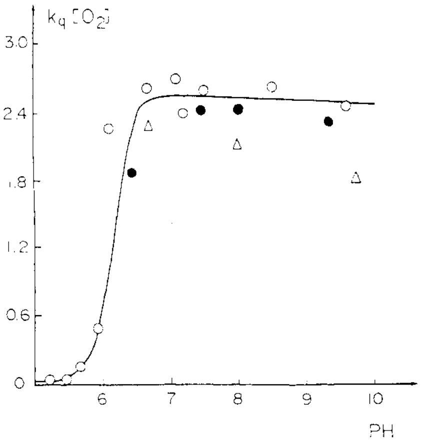

Figure 4. Dependence of the product $k_q[O_2]$ for the decay of pyrene with pH: (○) in PMA(I) solution; (●) in PMA(II) solution; (△) in water solution.

Table I
Rate Constants for Quenching of Pyrene by CH_3NO_2 in Water and PMA(I) Solution and as a Function of pH

PMA(I)		water	
pH	k_q, 10^8	pH	k_q, 10^8
5.30	1.0	6.90	64.0
5.50	8.3	7.50	60.0
5.70	15.0	8.20	55.0
6.00	49.0	9.70	47.0
6.40	62.0	10.40	30.0
7.10	60.0		
9.10	62.0		
9.60	43.0		
10.85			

Figure 3 shows a plot of k_1 as a function of pH, for pyrene in PMA. The curves have the same shape found in steady-state experiments, but now the position of the sharp changes in properties is shifted by approximately one pH unit. For the largest molecular weight, the curve is less abrupt and extends beyond a pH of 6.5. It is noteworthy that up to pH 6.0, k_1 and k_2 are smaller than the value for pyrene decay in water solution. At higher pH, the rate constant values are similar to that estimated in water under the same conditions of pH and pyrene concentration.

Quenching by O_2. The difference in the rate constants observed for the decay of fluorescence in the presence and absence of oxygen is given by the product $k_q(O_2)$. If we assume that the rate constant for the oxygen quenching, k_q, has the same value in the whole system, which is borne out as k_q is diffusion controlled in all systems studied to date, then $k_1(\text{air}) - k_1(N_2)$ is a measure of the accessibility of oxygen to the excited state and to this location. A plot of k_q versus pH is shown in Figure 4; values obtained in water solution are also included. The data indicate that pyrene is well protected from oxygen up to pH 5.5. From this point to pH 6.5–7.0, the opening of the coil permits a much easier entry of the quencher, eventually reaching the same efficiency of quenching as that obtained in water solution.

Quenching by CH_3NO_2. The rate constants for quenching of pyrene by nitromethane are collected in Table I and are depicted as a function of pH in Figure 5. The efficiency of quenching shows an increase at pH 5.5–6.5, a maximum at pH 7.0–9.0, and a decrease with further increase of pH. The increase in quenching rate constant is attributed to the unfolding of the polymer chain and consequently to an increased mobility of both pyrene and quencher. At pH 7.0 and up, the quenching process follows the same pattern as in homogeneous solution. Thus we can conclude that in this region the pyrene has been expelled to the water phase. The decrease in the rate constant, in basic media, is due to a reduction in the electron-transfer efficiency of nitromethane which is deprotonated by the hydroxide ion.[20] The same result was observed by Ghiggino and Tan,[16c] for the fluorescence quenching of dimethylanthracene attached as an end group in PMA. They ascribed this behavior to a recoiling of the polymer caused by an increase in the ionic strength of the solution. The additional ionic strength would come from the counterion of the base in the neutralization process. Our data comparing aqueous and polymer systems suggest that the prime cause of the OH^- effect is the ionization of CH_3NO_2.

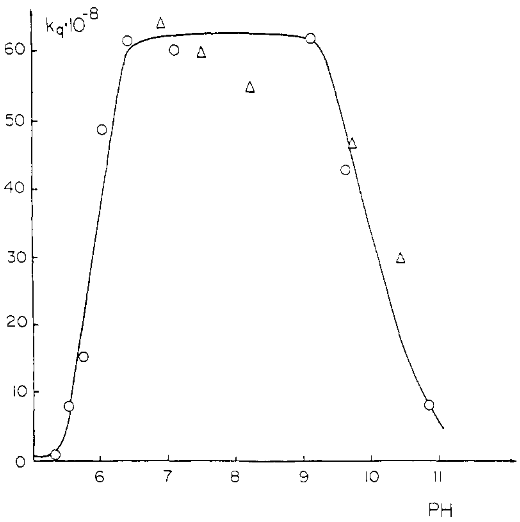

Figure 5. Plot of the quenching rate constant of pyrene by nitromethane versus pH: (○) in PMA(I) solution; (△) in water solution.

Table II
Decay Rate Constants from Double-Exponential Fit for Pyrene in PMA(II) Solution at pH 5.70

k_1	k_2	α	k_w	$[CH_3NO_2]$, mM
2.30	3.40	0.60	4.80	
2.40	6.20	0.68	16.0	1.54
2.50	7.00	0.68	26.0	3.08
3.10	13.0	0.67	48.00	6.16
3.30	20.00	0.66	69.00	9.24

Interestingly, in the region of pH 5.0–6.0, the addition of nitromethane increases the distinction between two kinds of fluorescence decay. The faster rate constant is initially two times larger than k_1 and increases rapidly with quencher concentration eventually becoming 5–6 times larger than k_1, Table II. The quenching rate constants obtained for these two different probe locations differ by 1 order of magnitude. Figure 6 shows k_1 and k_2 as a function of nitromethane concentration in a PMA(II) solution at pH 5.7. The curve for k_1 in homogeneous aqueous solution is included.

This result is interpreted as a consequence of different hydrophobic locations in the polymer structure. Even at this degree of neutralization (0.25) there is a microdomain where the pyrene is protected from a small quencher molecule such as nitromethane. At the same time there exists a less rigid environment where the quenching process occurs ten times faster. A similar observation has been made by Delaire et al. for CH_3NO_2 quenching of diphenylanthracene copolymerized with methacrylic acid.[21] This result argues in favor of a multiple structure during the conformation transition.

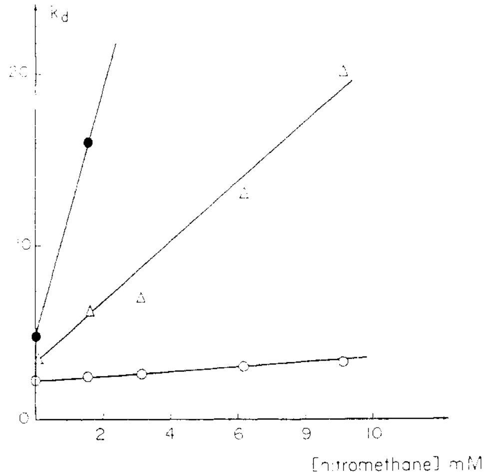

Figure 6. Decay rate constants for pyrene as a function of nitromethane concentration in PMA(II) solution at pH 5.7: (○) slower component, k_1; (▵) faster component, k_2; (●) slower component in water solution.

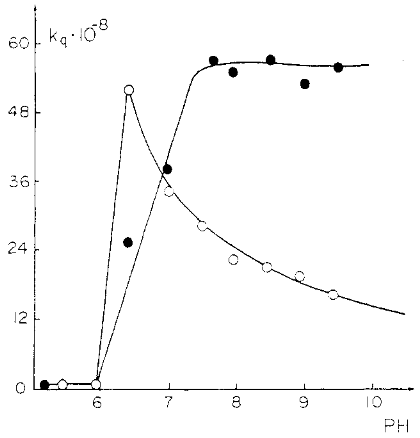

Figure 7. Plot of the quenching rate constants of pyrene by thallium ion in the presence of PMA(I) versus pH: (○) in the absence of KCl; (●) in the presence of 0.44 M KCl.

Table III
Thallium Quenching Rate Constant for Pyrene in PMA(I) as a Function of pH and Salt Concentration

[KCl] = 0.0 M		[KCl] = 0.44 M	
pH	k_q, 10^8	pH	k_q, 10^8
5.40	$<10^7$	5.10	$<10^7$
5.90	$<10^7$	5.90	0.2
6.40	52.0	6.40	25.0
7.00	35.0	7.00	38.0
7.50	28.0	7.70	57.0
7.90	22.0	7.90	55.0
8.40	21.0	8.50	57.0
8.90	19.4	9.00	50.0
9.40	16.0	9.50	53.0

Tl^+ Quenching. The quenching of pyrene by Tl^+ ions has some interesting features, the results are summarized in Table III and shown in Figure 7. At low pH the quenching is inefficient. At a pH of approximately 6.5 the quenching efficiency reaches a maximum and then begins to decrease with increasing degree of ionization. The decrease in the quenching rate constant is a consequence of the binding of the Tl^+ ions to the negatively charged atmosphere of the ionized polyelectrolyte. At higher pH pyrene is released to the bulk solution, and now the quenching involves the excited molecule in the aqueous phase and a quencher partner in the aqueous phase and partly on the polymer chain. It has been shown previously that in this kind of reaction the quenching rate decreases by a factor of 2–3.[19] This value agrees very well with that observed in the present work.

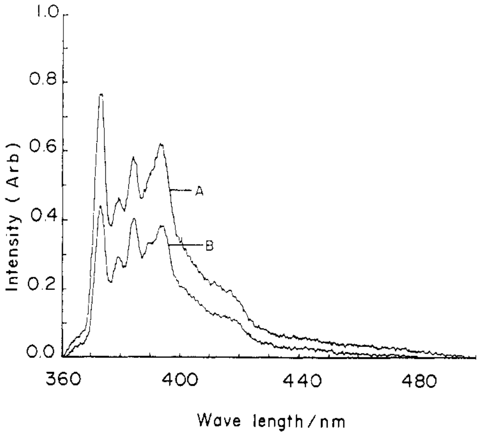

Figure 8. Fluorescence spectra of pyrene in PMA(I) solution at pH 5.8: (A) in the absence of quencher; (B) in the presence of 1.7 mM of Tl^+.

When an excess of inert salt is add to the system the curve for the quenching value versus pH is completely different. It begins to increase at pH 6.0 and reaches a plateau at pH 7.5. The maximum value for both curves is very similar to that measured for quenching in water. This effect probably arises from an exchange between the Tl^+ ions and the counterions bound to the polyelectrolyte, leading to a displacement of the equilibrium toward free Tl^+ ions.

Figure 8 compares the fluorescence spectra of pyrene dissolved in PMA(I) solution at pH 5.8 in the presence and absence of Tl^+ ions. There is a marked effect on the vibrational structure when the quencher is added. With no quencher the ratio III/I has a value of 0.76 and increases to 0.92 in the presence of 1.7 mM of Tl^+. The effect does not appear in water solution. These results may be interpreted as due to the existence of two kinds of excited states which are deactivated with different efficiencies by Tl^+ ions. As pointed out earlier, the steady-state parameters are an average over all the different distribution of probes present in the system. Thus, if the Tl^+ quenches more efficiently those probes located in the more polar environment, then the main contribution in the resulting spectra will come from the more protected excited molecules.

Conclusion

The data suggest that PMA at pH around 5–6 presents at least two hydrophobic guest sites for noncharged molecules such as pyrene. The data are interpreted in terms of two sites. The increased hydrophobicity exhibited by the pyrene site in PMA with increasing molecular weight and the slight shift to higher pH of the fluorescence or III/I ratio curves with increasing molecular weight suggest the following picture for the change in conformation of PMA with increasing pH. The change is not a homogeneous ionization of PMA with increasing pH, as only one site would be observed. Increasing pH ionizes a number of COOH groups on PMA, which leads to a hydrophobic core of PMA surrounded by a more hydrophilic mantle or ionized section of the polymer. Both act as hosts for pyrene, and the ionized site binds cationic quenchers such as Tl^+ to increase the rate of decay of excited pyrene at this location. Further increase in pH leads to a decrease in the ratio of hydrophobic PMA core to ionized PMA "mantle". Eventually at high enough pH the polymer is extensively ionized, uncoils, and does not act as a host for pyrene.

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Registry No. PMA, 25087-26-7; O_2, 7782-44-7; $TlNO_2$, 10102-45-1; CH_3NO_2, 75-52-5; pyrene, 129-00-0.

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Complex Formation in Polymer–Ion Solutions. 1. Polymer Concentration Effects

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ABSTRACT: We have studied the complexation of ions in polymer solutions and argue that when complexation leads to the formation of intramolecular cross-links (2:1 complexes) the usual law of mass action scheme adequate for small molecules must be revised. This limits the use of potentiometric methods in studying polymer–ion complexation. ^{11}B NMR spectroscopy on a suitably chosen borate–polyhydroxy compound (poly(glyceryl methacrylate)) system enables us to determine the concentration of free borate 1:1 and 2:1 complexes in a saline solution and to compare with a model system. The concentration of 1:1 complexes seems to be proportional to the free ligand concentrations, as for small molecule complexation. However, the formation of 2:1 complexes from 1:1 complexes (dicomplexation step) in dilute polymer solutions seems to be essentially independent of the global ligand concentration, contrary to the situation in model systems. Only when interchain 2:1 complexes are formed (in semidilute regime), a ligand concentration dependence appears. The number of intrachain complexes could be governed by the local polymer properties, e.g., chain stiffness.

I. Introduction

Metallic cations (Cu^{2+}, Cr^{3+}, ...) or basic anions ($B(OH)_4^-$, $Sb(OH)_6^-$) may be complexed by synthetic polymer (poly(vinyl alcohol), polyacrylamide, ...) or natural polymers (polysaccharides, proteins) bearing functional groups (i.e., ligands). Such water-soluble ion–polymer complexing systems are used in many applications including catalysis and petroleum or food industries.[1,2] The original properties[3-5] of these systems, such as gelation, demixing, or unusual rheological behavior, are governed by the complex formation. Various complexation equilibria have been studied for a long time mainly by potentiometric methods. Most of the time, the analysis of the polymer–ion complexation has been entirely inspired by analogy with reactions between ions and small model molecule.[6,7] In particular complexation is supposed to proceed by successive steps; each stage is controlled by the global ligand concentration in the solution and associated to a complexation constant k_i

$$M^- + L \overset{k_1}{\rightleftarrows} ML^- \qquad k_1 = |ML|^-/|M^-||L| \qquad (1)$$

$$ML^- + L \overset{k_2}{\rightleftarrows} ML_2^- \qquad k_2 = |ML_2^-|/|ML^-||L| \qquad (2)$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$ML_{n-1}^- + L \overset{k_n}{\rightleftarrows} ML_n^- \qquad k_n = |ML_n^-|/|ML_{n-1}^-||L| \qquad (3)$$

where M^- denotes the free ion, L is the free ligand site, and ML^-, ML_2^-, and ML_n^- are respectively the 1:1, 2:1, and *n*:1 coordinated complexes.

However, macromolecular systems exhibit some very particular features arising from the very fact that ligands are connected on the polymer chain, which greatly limits the analogy with classical complexation between small molecules. Two major problems come from polyelectrolyte effects and intrachain complex formation.

In order to realize the importance of the polymer nature of complexing species it is convenient to view the chains as random copolymers with some units bearing charges

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