Phosphorescence from a Bromonaphthalene Lumophore as a Photophysical Probe of Polymer Conformation and Interpolymer Interactions

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ABSTRACT: A bromonaphthalene-labeled poly(acrylic acid), BNPAA, was synthesized and found to be phosphorescent in solution at room temperature. The phosphorescence of the polymer was employed to investigate (1) the influence of pH on the conformations of the polymer in aqueous solutions, (2) the interactions of BNPAA with complementary polymers [poly(1-vinyl-2-pyrrolidinone) and poly(ethylene oxide)], and (3) conformations of the polymer adsorbed on a solid–liquid interface. The phosphorescence lifetimes of BNPAA provide a probe of changes in polymer conformations that result from inter- and intrapolymer interactions. The results suggest an unusual pH dependence for BNPAA conformations in dilute solutions; e.g., significant breaks in the lifetime/pH profile are found at pH 4 and pH 10. These unexpected results were confirmed by the observation of the same two breaks at pH 4 and pH 10 with the use of two independent photoluminescence probes, a pyrene-labeled poly(acrylic acid), PyPAA, and a ruthenium complex, $Ru(byp)_3^{2+}$. The two breaks in the conformation/pH profile are explained in terms of combination of hydrogen bonding and a hydrophobic substituent effect at low pH and charge screening at high pH. Phosphorescence lifetime measurements are also used to probe the interactions of the BNPAA with complementary macromolecules such as poly(1-vinyl-2-pyrrolidinone) and poly(ethylene oxide) and with a solid alumina surface. Finally, the interaction of BNPAA with a low molecular weight substance, the cationic surfactant dodecyltrimethylammonium bromide, was also investigated by employing the phosphorescent probe.

Introduction

Solutions of synthetic polyelectrolytes are important in many industrial applications and may serve as simple models of biological polyelectrolytes such as DNA and proteins.[1] For these reasons considerable effort has been devoted to the investigation of the structure and dynamics of solutions of synthetic macromolecules carrying ionized or ionizable groups in the side chains.[1,2]

Fluorescence has been useful in the investigation of such structures:[3-8] fluorescent probes, both covalently bound and noncovalently adsorbed on a polymer host, have been utilized[9-11] for the investigation of polymer conformation, especially in dilute solution where classical methods, such as viscosity measurements, are difficult or not applicable. In contrast to the wide use of fluorescence probes, phosphorescence of labeled polymers has not been extensively studied due to the very limited number of organic materials that give rise to readily measurable phosphorescence at room temperature in fluid solutions.

A poly(acrylic acid), BNPAA, covalently labeled with pendant phosphorescent bromonaphthalene groups was synthesized for the investigation of the conformational properties of BNPAA in aqueous and nonaqueous solutions at room temperature. It was found that the phosphorescence lifetime of the bromonaphthalene group depends on the local concentration of the chromophore so that the measured lifetime reflects the conformation of the backbone and the mobility of the side chain of the polymer.[12]

The phosphorescence probe methodology has been exploited to study several interesting and generally relevant aspects of polymer conformational behavior in dilute solution, such as the dependence of the conformation on pH and on polymer–polymer interactions. In addition, the effect of adsorption to a solid surface on polymer conformation was examined utilizing the phosphorescence properties of BNPAA.

The pH-induced conformational transitions of linear polyacids in aqueous solutions have been studied on many polymers by several techniques.[10-12] A wealth of data are consonant with the conclusion that at low pH linear polyacids adopt a hypercoiled, compact form as the result of hydrophobic interactions, whereas at high pH a high degree of ionization of the chain generates repulsions among the charged carboxylate groups and causes the linear chain to expand and stretch to a rodlike form. Since the nature of the transition is still open to debate, the results on the conformational behavior of BNPAA could be compared to independent investigations of pH-induced transitions for the same polymer backbone, employing covalently bound pyrene as an intrinsic fluorescence probe and a tris(2,2′-bipyridine) complex of ruthenium(II) as an extrinsic fluorescent probe. We shall show that the three probes give consistent results concerning the conformation of the polymer conformations as a function of pH variations.

The applicability of the phosphorescence probe methodology was also employed to investigate the solution interactions of BNPAA with two potentially complementary polymers, poly(1-vinyl-2-pyrrolidinone) (PVP) and poly(ethylene oxide) (PEO), with the goal of elucidating the usefulness of the photophysical properties of the bromonaphthalene label in studying the effect of various secondary forces in polymer association processes. Similarly, the phosphorescence probe method was employed to investigate the interaction of BNPAA with cationic surfactants in aqueous solution.

Finally, the phosphorescent probe method was utilized to determine the nature of the conformations adapted by BNPAA when it is adsorbed onto a solid alumina surface from aqueous solutions. The results reported herein demonstrate the utility of phosphorescent probes which, when applicable, possess at least two potential advantages over fluorescence probes, i.e., a higher sensitivity to

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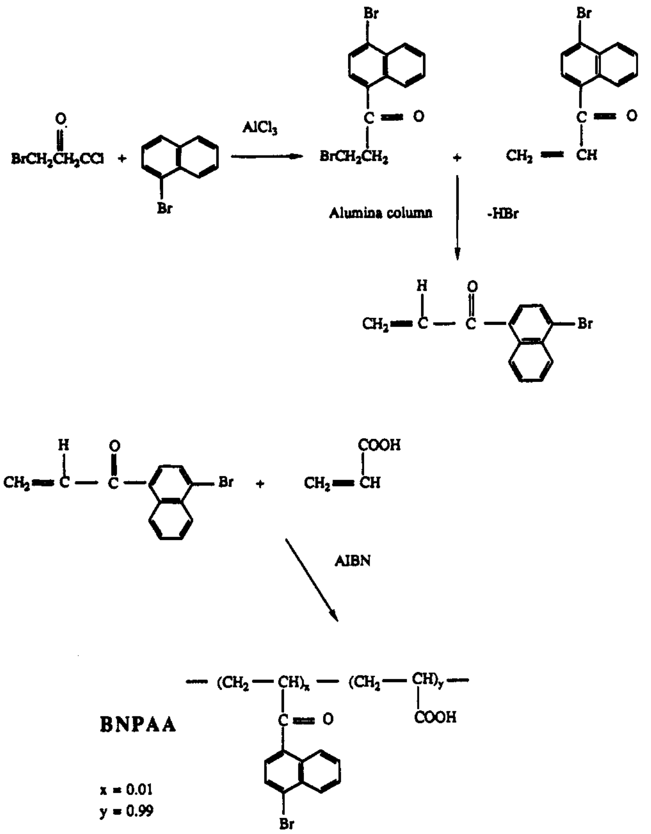

Figure 1. Synthetic scheme for the synthesis of BNPAA.

quenching and a longer time scale to probe dynamic interactions.

Experimental Section

Materials. The synthesis and structure of the bromonaphthalene-labeled poly(acrylic acid) polymer, BNAPP, are shown in Figure 1. The structure of the repeat units for BNPAA and the related pyrene-labeled poly(acrylic acid) polymer,[8] PyPAA, are analogous. It should be noted that the label for both polymers is very dilutely (one label per 100 acrylic acid monomers) concentrated along the linear polymer chain. Since the preparation and characterization of PyPAA were reported earlier,[8a] only the preparation of BNPAA is described below. The molecular weights of BNPAA and PyPAA were found from viscosity measurements to be 1.3 × 10^5 and 7.8 × 10^4, respectively.

Spectral grade solvents (Aldrich or Fisher) and deionized water were used in all measurements. Dodecyltrimethylammonium bromide (DTABr, 99.9%, Aldrich), was used as received. Sodium chloride, $NaNO_2$, bromonaphthoyl decyl sulfate,[8b] and (bromonaphthoylmethyl)trimethylammonium bromide[8c] were employed in the quenching experiments. The syntheses and purifications of the latter compounds are described elsewhere.[14,16] Sodium chloride (99.99%), poly(1-vinyl-2-pyrrolidinone) (PVP), and poly(ethylene oxide) (PEO) samples used in this study were purchased from Aldrich and used without further purification. Alumina samples were Linde A grade, supplied by Union Carbide Corp. (0.3-mm particle size, 15 m^2/g surface area).

The concentrations of the polymers reported in this work are expressed as concentrations of repeat units and refer to equivalents of repeat units per liter (reported as M). The stock solutions of the polyelectrolytes (concentration 10^{-2} M) were made immediately in advance of the measurements and were used for preparing solutions for phosphorescence or fluorescence measurements. The required amounts of stock solutions were mixed with water to obtain a 10-mL solution containing the required concentrations of polyelectrolytes. The pH of the polyacid solutions was adjusted by addition of 0.1 M HCl or NaOH. The samples for the investigations at the alumina-water interface were prepared adding 0.3 g of alumina to 10 mL of polymer solution after pH adjustment. The procedure for the preparation of the alumina suspension is reported in a previous paper.[17]

Methods. The phosphorescence emission lifetimes were determined with both a single-photon-counting (SPC) apparatus from Photochemical Research Associates (London, ON, Canada) and a Perkin-Elmer LS5 spectrophotometer using a phosphorescence decay program. Both series of measurements gave good first-order decays and yielded the same lifetimes within experimental error (±0.05 ms). Nitrogen was bubbled through the samples for at least 30 min prior to emission and lifetime measurements. Steady-state fluorescence measurements were performed on a SPEX Fluorolog-2 1680 double spectrophotometer. All measurements were done at 25 °C. Pyrene fluorescence emission spectra were recorded on a Perkin-Elmer LS5 spectrophotometer at 25 °C. All emission lifetime measurements were performed in duplicate with freshly prepared solutions, and the mean value of the measurements is reported. The spectra of the alumina slurries were recorded using a front-face setup of the spectrofluorimeter in order to reduce the noise, and at least 15 scans were averaged for each measurement.

All emission lifetime measurements were performed in duplicate with freshly prepared solutions, and the mean value of the measurements is reported. Measurements of pH were performed with a Beckman Model 21 pH meter at room temperature. The pH measurements were repeated on the samples after lifetime measurements to check constancy of pH values.

^1H NMR spectra were obtained on a Varian Model XL-200 (200 MHz) FT-NMR spectrometer. Spectroscopic parameters are reported as follows: (solvent), chemical shift (δ, ppm), multiplicity, coupling constant, integration, and assignment. Dilute-solution viscosity measurements were performed in a constant-temperature bath using a semimicro dilution Cannon-Ubbelohde viscosimeter.

The UV-vis absorption spectra were recorded on a Perkin-Elmer Model 559A UV-vis spectrophotometer. The absorption maxima (303, 295, 212, and 250 nm) were used to calculate the effective bromonaphthoyl concentration and extinction coefficients of the model monomer compound.

Preparation of Poly(acrylic acid-4-bromonaphthyl vinyl ketone) (BNPAA). The procedure employed for the synthesis of BNPAA is outlined in Figure 1. The details of the synthesis are described below.

4-Bromo-1-naphthyl Vinyl Ketone. 3-Bromopropionyl chloride (13.7 g, 0.08 mol) (Aldrich) was added to 10 mL of CH_2Cl_2. The solution was cooled to 0 °C and 10.7 g (0.08 mol) of $AlCl_3$ was added. A solution of 15 mL of CH_2Cl_2 and 11.1 mL (0.08 mol) of 1-bromonaphthalene (Aldrich) was then added dropwise. The solution was warmed to 20 °C and stirred for 1 h. The reaction mixture was poured in several portions (100 g) of cracked ice to which was added 10 mL of concentrated hydrochloric acid and then combined with ether. The ether layer was dried with $MgSO_4$ and filtered. The reaction produces a mixture of 1-(4-bromo-1-naphthoyl)-2-bromoethane and the dehydrohalogenated product, 4-bromo-1-naphthoyl ketone. The resulting mixture was passed through a neutral alumina column, and dehydrohalogenation was completed with some oligomer formation. After purification by silica gel chromatography using a mixture of hexanes and ether as an eluent, 0.95 g (4.5% yield) of 4-bromo-1-naphthyl vinyl ketone was isolated as a yellow oil. Most of the byproducts are oligomers and low molecular weight polymers. ^1H NMR: ($CDCl_3$), 6.08 ppm, doublet of doublets, J_{BX} = 11 Hz, J_{AB} = 1.2 Hz, 1 H; 6.25 ppm, doublet of doublets, J_{AX} = 17 Hz, J_{AB} = 1.2 Hz, 1 H, H_A; 6.91 ppm, doublet of doublets, J_{AX} = 17 Hz, J_{BX} = 11 Hz, 1 H, H_X; 7.53 ppm, doublet, $J_{2,3}$ = 7.7 Hz, 1 H, 3-position aromatic proton; 7.64 ppm, multiplet, 2 H, 6- and 7-position aromatic protons; 7.84 ppm, doublet, $J_{2,3}$ = 7.7 Hz, 1 H, 2-position aromatic proton.

Preparation and Characteriztaion of BNPAA. Bromonaphthoyl-labeled poly(acrylic acid), BNPAA, was prepared by copolymerization of acrylic acid and (4-bromo-1-naphthoyl)ethylene (vide supra and Figure 1). The copolymerization was conducted as follows. 4.27 g (59 mM) of freshly distilled acrylic acid, 0.156 g (0.598 mM) of purified 4-bromo-1-naphthyl vinyl ketone, 49.1 mg (0.299 mM) of AIBN, and 20 mL of freshly distilled DMF were introduced into a flask. The polymerized mixture was subjected to four freeze-pump-thaw cycles and then placed in an oil bath at 65 °C for 16 h with stirring. The viscous solution obtained was poured into excess ethyl acetate, and the solid obtained was filtered and dried. The dried product was dissolved in 100 mL of 1,4-dioxane, filtered, and precipitated in 1.5 L of ethyl acetate. The precipitated product was filtered and dried to give 4.08 g (92%) of a copolymer whose spectral properties are fully consistent with the structure for BNPAA shown in Figure 1.

^{1}H NMR: (DMSO-d_6), 1.52, 1.76, and 2.21 ppm, broad, acrylic acid carboxyl proton; 7.77, 8.00, and 8.24 ppm, broad, bromonaphthalene aromatic protons.

The intrinsic viscosity of the copolymer BNPAA was determined in 1,4-dioxane to be 0.27 dL g^{-1} at 30 °C. The viscosity-average molecular weight calculated by the Mark–Houwink–Sakurada (MHS) equation using K and a values for poly(acrylic acid) of 76 × 10^{-3} (mL/g) and 0.5, respectively,[19] was 1.3 × 10^5 (degree of polymerization = 1768).

Results and Discussion

Relationship between Phosphorescence Lifetimes of BNPAA and Polymer Conformation in Aqueous Solution. Self-quenching of aromatic triplets is one of the most important mechanisms for the commonly observed concentration dependence of phosphorescence.[20] Thus, the *phosphorescence lifetimes* and the interactions of bromonaphthoyl groups in aqueous solutions of BNPAA are expected to be sensitive to the *effective local concentrations* of the bromonaphthoyl groups, which in turn are determined by the *global polymer conformation.* According to our model, if the *polymer conformation is globular and compact,* the local concentrations of the bromonaphthoyl groups will be relatively high and significant self-quenching will occur, resulting in a *relatively short phosphorescent lifetime.* If, on the other hand, the *polymer conformation is rodlike and extended,* the local concentration of the bromonaphthoyl groups will be low, the phosphorescence will be protected from self-quenching, and the experimental manifestation of the rodlike, expanded conformation will be a *relatively long phosphorescence lifetime.* The phosphorescence lifetime is thus the measured parameter that reports polymer conformation. These simple ideas are exactly analogous to those employed for the use of pyrene as an excimer-forming fluorescence probe of PyPAA.[8] In the latter case globular, compact conformations favored excimer formation, and rodlike, extended conformations inhibited excimer relative to monomer emission. In this case, the ratio of intensity of the pyrene monomer fluorescence to pyrene excimer fluorescence reports on the polymer conformation. In summary, the basic idea of the bromonaphthoyl group as a phosphorescence probe of polymer conformation is that the phosphorescence lifetime of BNPAA is correlated to changes in conformation of BNPAA, with the efficiency of intrachain interaction between the bromonaphthoyl groups being expected to decrease as their local concentration decreases and thus with the expansion of the polymer chain. Simply put: compact conformation, short phosphorescence lifetime; extended conformation, long phosphorescence lifetime.

Conformational Changes of BNPAA as a Function of pH. To study the relationship between the phosphorescence properties of the covalently bound probe and polymer conformation, we measured phosphorescence lifetimes of the acid form of BNPAA as a function of pH at two dilute concentrations (5 × 10^{-3} and 5 × 10^{-4}) of polymer. The results are reported in Figure 2. Interpolymer interactions are expected to be negligible in sufficiently dilute solution, and we find the limiting concentration operationally describing "dilute" to be ca. 5 × 10^{-3} M. From previous results,[12] the measurements of phosphorescence lifetimes in solutions of BNPAA at different pHs were expected to provide information about conformation, chain mobility, and the environment and the interactions of bromonaphthalene groups.

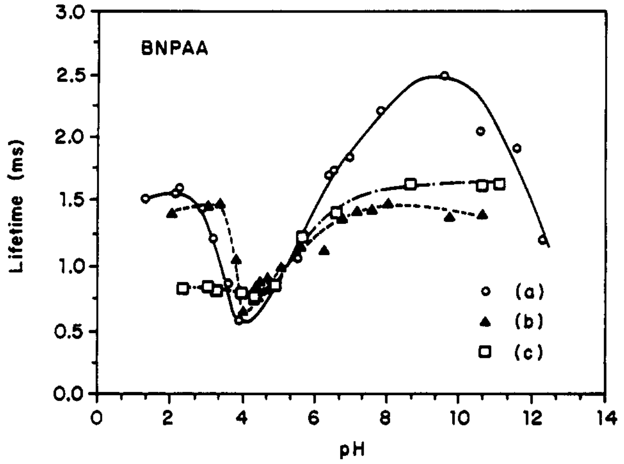

Figure 2. Effect of pH on phosphorescence lifetime of BNPAA: (a) [BNPAA] = 5 × 10^{-4} M in water; (b) [BNPAA] = 5 × 10^{-4} M in water with 5 × 10^{-2} M NaCl; (c) [BNPAA] = 5 × 10^{-3} M in water.

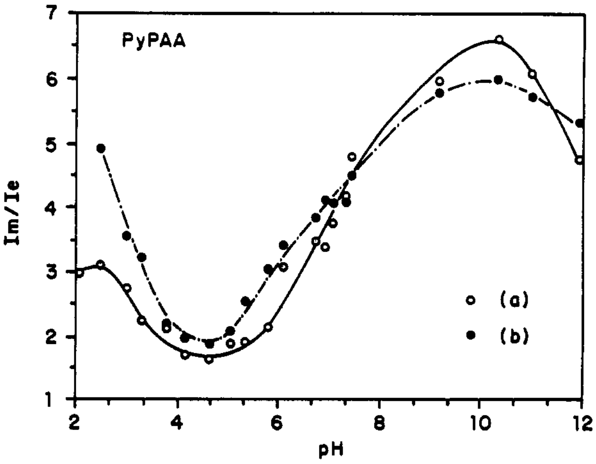

Figure 3. Effect of pH on I_m/I_e value of PyPAA: (a) [PyPAA] = 5 × 10^{-4} M in water; (b) aged sample (6 days).

For the most dilute sample (curve a in Figure 2 for which [BNPAA] = 5 × 10^{-4} M), the lifetime versus pH plot can be divided into three distinct regions: a decrease in lifetime is observed in the pH 2–4 range (region I), a sharp increase is seen in lifetime in the pH 4–10 region (region II), and finally above pH 10, the lifetimes decrease again (region III). In the presence of a strong electrolyte (Figure 2b) and at higher concentrations of BNPAA (Figure 2c) region III is not pronounced. Since the results imply an unexpected variation of conformation as a function of pH (first a contraction in region I, followed by an expansion in region II, and finally a contraction in region III), PyPAA, a previously investigated poly(acrylic acid) containing a covalently bound fluorescence pyrene label,[8a] was also examined to determine independently the relationship between the polymer conformation and pH. From previous studies,[8a] it was shown that I_m/I_e ratios (ratio of the intensity of pyrene monomer emission to the intensity of pyrene excimer emission) are a function of local effective concentration of pyrene groups and reflect polymer conformation and chain mobility. Thus, I_m/I_e is a probe parameter for PyPAA analogous to the phosphorescence lifetime of BNPAA: the greater the value of this parameter, the more extended the polymer. Plots of I_m/I_e as a function of pH are reported in Figure 3, and it is clear that the analogous three distinct pH regimes are reported by the probe (compare Figures 2a and 3a). These results both confirm the validity of the three conformational region phenomena and rule out specific probe interaction as the cause of the phenomena.

A further confirmation of this three-region peculiar behavior of Figures 2 and 3 was also found by employing the complex Ru(bpy)$_3$$^{2+}$ as an *extrinsic* photoluminescence probe for *unlabeled* poly(acrylic acid). Indeed, it was found that the steady-state luminescence of Ru(bpy)$_3$$^{2+}$ in the presence of unlabeled poly(acrylic acid) followed the same pH profile as found for BNPAA and PyPAA; i.e., at different pHs a pattern similar to that observed in Figures 2 and 3 is observed. The sample of unlabeled poly(acrylic acid) used in these experiments is of comparable molecular weight and concentrations with respect to the labeled polymer as the cases reported in Figures 2 and 3. Thus, in the pH 2–4 region (region I) the intensity of Ru(bpy)$_3$$^{2+}$ increases, in region II (pH 4–10) the emission decreases, and in region III, between pH 10 and pH 12, the intensities rise again.

Substituted poly(acrylic acids) have been found to undergo pH-induced conformational transitions in many studies.[10–12] Previous work on PyPAA in this laboratory[8a] has revealed a change from a compact form to an expanded one upon ionization of carboxylic groups along the chain, but no minimum was observed and a maximum at high pH was not as obvious as that found in Figures 2 and 3.

The behavior observed in Figures 2 and 3 can be accounted for by our model correlating polymer conformation with probe parameters as follows. In region I the pH was adjusted by adding hydrochloric acid; the strong acid suppresses the dissociation of the carboxylic acid side chains. This results in an increase in hydrogen bonding between carboxylic acid groups along the polymer chains, which leads to both a more compact conformation and a lower chain mobility. The previous effect is probably larger for the labeled polymers than for the native polymer because of the presence of hydrophobic substituent groups along the labeled polymer backbone. Hydrophobic interactions between bromonaphthalene groups for BNPAA (or pyrene groups in the case of PyPAA) on the same chain promote formation of loops and result in more coiled structures. Attractive interactions of hydrophobic groups attached to the polymer apparently provide a powerful resistance to chain expansion. The same mechanism to explain the behavior in region I is available for the Ru(bpy)$_3$$^{2+}$ probe. In this case, hydrophobic interactions between the ligands of the complex create hydrophobic environments around the complex and cause the collapse of the polymer chains about the complex. The effect of hydrophobic substituents on pH dependence has already been pointed out for different polymers.[10,11]

That the abrupt transition to more expanded structures within a narrow critical range centered around pH 4 suggests the operation of a cooperative process. The breakdown of coiled structures is well-known to occur when the acid is completely ionized. The behavior characteristic of region I was not observed in previous work[8] mainly because of the lower molecular weight used (7 × 10^3). Polymer coiling is strongly dependent on the molecular weight,[1] and increasing polymer concentration also induces a flattening of region I (curve c of Figure 2) and lowers lifetime values over the whole pH range. Evidently, in this case interpolymer interactions contribute to the global effect sense by quenching the probe; quenching interactions are taking place not only between groups on the same chain but also between segments belonging to distinct macromolecules.

In region II (pH 4–10) there is a continuous increase in chain expansion because of increasing ionization of the carboxylic groups on the polymer chain, and this expansion is clearly reported by the phosphorescence probe as an increase in lifetime and by the fluorescence probe as an increase in the parameter I_m/I_e. Repulsive interactions between negatively charged groups are the obvious factor responsible for the uncoiling of the polymer region II, but they cannot account for the decrease in lifetimes or in the decrease in the I_m/I_e ratio when pH is increased beyond 10 in region III.

We propose that in region III, since the pH is increased by adding NaOH, beyond pH 10 the concentration of sodium ions cannot be neglected; i.e., the change in the ionic strength produced by the formation of a strong electrolyte, NaCl, becomes a factor in determining the polymer conformation. The interactions of the Na counterions with the fixed charges on the polymer backbone produce a shielding effect. This modification of the balance of electrostatic forces will induce a change in the shape of the macromolecules toward more entangled conformations by screening the electrostatic repulsion of the charged carboxylate ions.

As further tests of the ionic strength interpretation, the same experiments were repeated in a 5 × 10^{-2} M solution of NaCl (Figure 2b); no maximum was detected around pH 10, confirming the leading role of electrostatic screening in this region. Due to the presence of an excess of Na$^+$ ions, the polymer does not reach the highly expanded conformations that exist without salt, a result consistent with the overall lower values of lifetimes in the high-pH regime in the presence of strong electrolyte.

The presence of electrolytes does not play a major role in controlling conformations in the first two regions of the plots of Figures 2 and 3, a result consistent with the explanation given above. The major determining factors in these pH domains are hydrogen-bonding interactions and hydrophobic attractions, both of which are only weakly influenced by electrostatic factors induced by changes in the ionic strength.

We propose that the variation in the emission intensity of Ru(bpy)$_3$$^{2+}$ as a function of pH in the presence of poly(acrylic acid) reflects the extent of protection of the complex from oxygen and from solvent quenching. When the ligands of Ru(bpy)$_3$$^{2+}$ as a function of pH in the presence of poly(acrylic acid) reflects the extent of protection of the complex from oxygen and from solvent quenching. When the ligands of Ru(bpy)$_3$$^{2+}$ interact with the polymer segments, the complex will be protected in closed hydrophobic loops (region I) which will tend to bury the complex in the interior of the loop. On the other hand, extended conformations of the ionized polymer (region III) will interact strongly with the complex via electrostatic attraction but will expose the complex toward the solution and expose the excited complex to quenching. The consequences of the variation of these interactions will produce a shape of the observed intensity versus pH profile that is analogous to that observed in Figures 2 and 3.

BNPAA Interactions with Nonionic Polymers. It is known from the literature[8,13] that at slightly acidic pH, poly(acrylic acid) (PAA) associates with poly(1-vinyl-2-pyrrolidinone) (PVP) and poly(ethylene oxide) (PEO) through formation of hydrogen bonds between carboxylic groups of PAA and the electronegative oxygens in PEO and PVP. The stronger association of PAA with PVP relative to PAA with PEO is attributed to the contribution of hydrophobic and Coulombic interactions in the former case.[14,15]

Table I
Effect of Poly(1-vinyl-2-pyrrolidinone) (PVP) on the Phosphorescence Lifetime of Bromonaphthalane in BNPAA

PVP/BNPAA	lifetime, ms	PVP/BNPAA	lifetime, ms
0.0	1.09	1.0	1.51
0.1	1.24	10.0	1.39

Dilute solutions of polymers are required in the study of interpolymer interaction of BNPAA and complementary water-soluble polymers in order to avoid the precipitation of interpolymer complexes. The concentration of BNPAA chosen for this study of interpolymer interactions was 5×10^{-4} M (pH 6), conditions for which the polymer chain is almost totally extended.[12] Lifetimes were measured at various BNPAA/PVP molar ratios in aqueous solution; the results are reported in Table I.

The phosphorescence lifetime of BNPAA increases with increasing PVP concentration up to an equimolecular ratio of the two polymers and then decreases as the amount of PVP becomes an excess. These results suggest that these BNPAA and PVP form 1:1 complexes and that the conformation of BNPAA in the complex is more extended when compared to that of uncomplexed BNPAA. Moreover, chain mobility decreases upon complexation and the probability for the bromonaphthalene chromophores to collide with each other will be decreased. At higher concentrations of BNPAA several factors probably contribute to the lowering of the lifetime. The labeled polymer contracts because of interchain interactions, changes occur in conformation of the interpolymer complex, and association occurs between interpolymer complexes and excess complementary polymer. Similar arguments and interpretations apply to the PyPAA system.

The interactions between polymers are also expected to be highly affected by the degree of ionization of BNPAA. For this reason the effect of pH on phosphorescence lifetime of BNPAA in the presence of complementary polymers was studied. The results are shown in Figure 4 for an equimolar solution of the two polymers. In the presence of PVP (Figure 4a) phosphorescence lifetimes are in general higher than for BNPAA alone (Figure 4c): an interpolymer complex is formed and its conformation is such to prevent bromonaphthalene group interactions. Lifetimes reach a minimum at pH 6 after which a slight increase follows (pH 6–10). The decrease in lifetimes can be explained in terms of reduction in hydrogen bonding upon ionization of the polymer. Lifetime values at high pH are similar to those obtained with BNPAA alone; since previous studies[8] exclude complex breakup even at high pH, we can postulate that coiling of the interpolymer complex will produce moieties with high bromonaphthoyl local concentrations.

The small change in luminescent properties for the potential complex between BNPAA and PEO (Figure 4b) indicates the weak nature in the secondary forces involved in the association of these polymers, namely, hydrogen bonding and Coulombic forces.

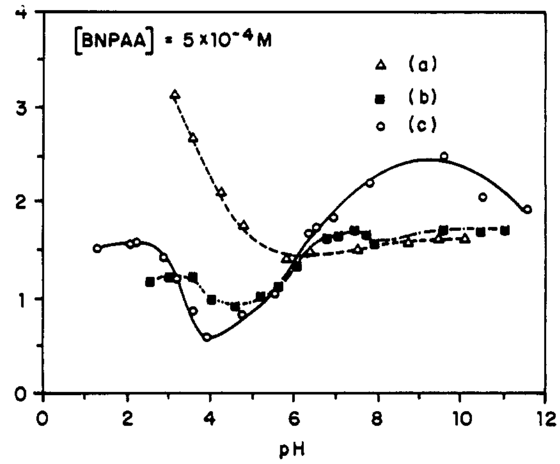

Figure 4. Effect of pH on lifetime of BNPAA in the presence of PVP (a), in the presence of PEO (b), and alone (c). [BNPAA] = 5×10^{-4} M. A 1:1 molar ratio of polymers was used.

Table II
Effect of Cationic Surfactant and Quencher Molecules on Phosphorescence Lifetimes of BNPAA

	lifetime, ms	
	water	water + $NaNO_2$[d]
BNPAA (acid)[a]	0.95	0.11
BNPAA (Na salt)[b]	1.62	0.81
BNPAA (Na salt)[b] + DTAB[c]	0.74	0.35

[a] [BNPAA] = 5×10^{-3} M. [b] [BNPAA] = 5×10^{-3} M. [c] [DTAB] = 4×10^{-3} M. [d] [$NaNO_2$] = 1×10^{-4} M.

Interactions of BNPAA with Charged Surfactants. Phosphorescence lifetimes of the chromophore of BNPAA have also been used to study the effect of cationic surfactants on the conformations of the polymer. Lifetimes were measured for a 5×10^{-3} M solution of both the acid form and salt form of the polymer in water, with and without the cationic surfactant dodecyltrimethylammonium bromide (DTABr). Since the concentration of the surfactant is 4×10^{-3} M, which is well below the DTABr critical micelle concentration of 16×10^{-3} M, in the absence of polymer, the surfactant is present in solution as individual monomer molecules and not as micelles. The results are reported in Table II together with the lifetime obtained when $NaNO_2$ was added to the previous system. $NaNO_2$ is an anionic quencher (NO_2^-), known to quench phosphorescence emission of bromonaphthalene, but the efficiency of quenching by NO_2^- depends on the conformation of the polymer and on the mode of surfactant association.

The important result from Table II is the observation that the addition of DTABr reduces the phosphorescence lifetime to a value lower than those obtained for the acid form. The lifetime of monomeric bromonaphthalene has been reported to *increase* in the presence of surfactant micelles.[16,17] The monomeric bromonaphthalene probe is in this case secluded and protected from quenching by the micellar microenvironment. Since, on the contrary, introduction of surfactant molecules causes a quenching of the bromonaphthalene probe of BNPAA, we conclude that the surfactant induces a coiling of the linear polymer, resulting in hydrophobic interactions with the aliphatic chain of the surfactant. The coiling enhances the probability of intrachain bromonaphthalene interactions and the lifetime decreases. The presence of Br^- ions might also be important in quenching in this case, but this possibility is considered unlikely since the lifetime of the *monomeric* bromonaphthalene probe is actually enhanced by inclusion in cationic micelles HDTBr which possess a high local concentration of Br^- gegenions.

When a molecule such as $NaNO_2$ is added to the system the quenching of the labled polymer is found to be lower in the case of the salt form than in the case of the acid form in water solution. This is easily explained considering the electrostatic repulsions between the anionic quencher and the carboxylate groups of the salt form. Quenching efficiency is improved when the surfactant is present in the system. Not only does the amphiphilic molecule provide a more hydrophobic environment with higher local

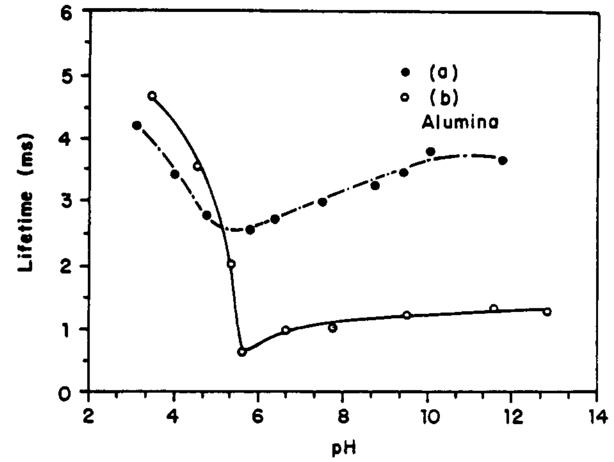

Figure 5. Effect of pH on lifetime for aqueous solution of BNPAA (a) and an equimolecular mixture of BNPAA and PVP adsorbed on alumina (b).

concentration of the naphthalene group, but it also neutralizes to some extent the negative charges on the polymer that would otherwise hinder the close approach of the quencher with the quenchee.

These experiments reveal how the use of phosphorescent probes covalently attached to a polymer can provide information on the process of association of polymers and monomer surfactant molecules and small charged species, processes that are extremely important in both industrial and biological fields.

Interactions of BNPAA with Solid Surfaces. The photophysical properties of BNPAA can readily be used to study the conformation of the labeled polymer at a water–solid interface. Previous research[17,18] has shown that poly(acrylic acid) and pyrene-labeled poly(acrylic acid) (PyPAA) are adsorbed on alumina particles from an aqueous solution and that the conformation of the adsorbed molecule depends on the pH of the solution from which adsorption occurs.

Figure 5a tracks the phosphorescence lifetime of the probe of BNPAA adsorbed on an alumina surface as a function of pH, and Figure 5b tracks the phosphorescence lifetime of an equimolar mixture of BNPAA and PVP adsorbed on alumina as a function of pH. Comparison of the solution results (Figure 2a) with the results on the solid surface (Figures 5a) shows that the lifetime of adsorbed BNPAA is much longer (ca. 2.5–3.5 ms) on the surface than in solution (ca. 0.5–1.5 ms) for region I (pH 2–4). The next salient difference is the absence of region III at high pH for the adsorbed polymer. The results suggest that the conformation of BNPAA after adsorption on the solid positive surface is highly extended or immobilized (long lifetimes) at low pH. Interaction of the elongated macromolecule with the surface of the alumina prevents interactions between the bromonaphthalene units almost completely. Increasing ionization of the polymer results in a minimum for the lifetime values at pH ca. 6, after which only a slight increase is recorded. Lifetime values at high pH are lower for the molecule in the adsorbed state than for the molecule in solution. From our model, we conclude that in contrast to the situation that occurs in solution, increasing the number of negative charges on the polymer actually induces additional coiling of the linear structure in order to optimize the balance between maximum contact between opposite charged groups and to minimize exposure of the hydrophobic part of the macromolecule to water and to the hydrophilic solid surface of the alumina.

When the PVP/BNPAA interpolymer complex is adsorbed onto the solid, no great variations are observed in lifetime values compared to the solution values. The results suggest that interpolymer attractions are prevailing; i.e., the complex is thus adsorbed on alumina without substantially losing its original solution conformation. At high pH the structure undergoes a small change, and the higher lifetime in this region can be explained by preferential adsorption on the solid due to electrostatic interactions between charges.

Conclusions

The photophysical properties of a bromonaphthalene moiety covalently bound to a linear polyacid can be used to study the pH-induced transitions in polymer conformation. The pH interval (2–12) screened in this study can be divided into three distinct regions of polymer conformation. At pH 4 a minimum in phosphorescence lifetime is observed corresponding to maximum coiling of the chain. Hydrogen bonding and hydrophobic substituent effects contribute to the creation of this minimum. Increasing pH leads to ionization and consequent elongation of the chain which overcomes the hydrogen bonding and hydrophobic effects and is revealed by the rise in the BNPAA lifetimes. The trend toward expansion is sharply inverted at pH 10, where charge screening by the Na ion involved in adjusting the pH induces further coiling. These results were supported by similar findings using pyrene as a label and ruthenium complexes as probes of the macromolecular structure in the same pH range and at the same BNPAA concentration.

Changes in phosphorescence lifetimes of BNPAA were also shown to provide information on the interactions of the labeled polyacid with complementary polymers, both in solution and adsorbed on alumina, as a function of pH. At low pH BNPAA exhibits more stretched and rigid conformations when it is adsorbed at an alumina–water interface than in solution. However, for an equimolecular mixture of BNPPA and PVP, no great difference was found between the solution or for the adsorbed system.

The interactions of BNPAA with cationic surfactant molecules and an anionic quencher were also monitored employing the photophysical properties of the label. The cationic surfactant was found to induce a lowering of the phosphorescent lifetime. This can be explained by the coiling of the polymer hydrophobic segment around the aliphatic chain of the amphiphilic molecule which strongly interacts with the polymer due to electrostatic forces. The surfactant molecules also enhanced the quenching efficiency of the anionic quencher by neutralizing the anionic charge on the polymer surface.

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