Phosphorescence Investigation of the Conformation of a Bromonaphthalene-Labeled Poly(acrylic acid)

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ABSTRACT: A copolymer of 4-bromo-1-naphthyl vinyl ketone and acrylic acid (BNPAA) has been prepared by free radical polymerization. The pendant bromonaphthalene (BN) groups endow the polymer with the unusual property of readily observable phosphorescence in solution at room temperature. The phosphorescence of BNPAA was investigated systematically in solution at room temperature as a function of polymer concentration, salt concentration, solvent structure, and other variables and shows that phosphorescence can serve as a probe of polymer conformation. By assuming that self-quenching of a triplet BN moiety by a pendant ground-state BN moiety on the same polymer chain determines the triplet lifetime, the phosphorescence lifetime of the labeled polymer at room temperature can be correlated to the chain conformation of the polymer BNPAA in dilute solution in the following manner: collapsed, globular conformations of the polymer correlate with significant self-quenching and relatively short phosphorescence lifetimes, and extended conformations of the polymer correlate with inhibition of self-quenching and relatively long phosphorescence lifetimes. Employing the phosphorescence lifetime criterion as a probe, the conformation of BNPAA was studied under a variety of conditions. The effect of different solvents on the polymer conformation was investigated and the strength of solvent–polymer interactions was found to decrease in the order water > methanol > dioxane. These results are consistent with those involving a pyrene-labeled poly(acrylic acid), PyPAA, for which the value of the monomer to excimer fluorescence emission ratio is correlated with the same solvent-dependence of polymer conformation. The influence of salt concentration was investigated, and the study of phosphorescence lifetimes as a function of added electrolytes allowed for the determination of the radius of gyration of the polymer in salt solution. The influence of solvent viscosity on polymer mobility and conformation was also studied by the phosphorescence probe technique. Quenching of phosphorescence with an aqueous phase quencher, $NaNO_2$, elucidated the role of polymer conformation on the quenching process.

Introduction

Molecular interactions in aqueous environments play a central role in the structure and functions of biological macromolecules. Water-soluble synthetic polymers have been widely used as simple models for complex biological structures to understand conformation–property relationships.[1] Polyelectrolytes, in particular, are an important class of water-soluble polymers which have been widely studied in their solution behavior.[1,2] A knowledge of the connections between conformation and properties of polymers and the interactions of polymers with other small molecules and other polymers is also essential for the synthesis of polymers whose structures are tailored for specific applications. Fluorescence spectroscopy has been found to be a powerful and versatile technique for the investigations of macromolecular structure and properties.[3-6] Fluorescence probes for polyelectrolytes have been frequently reported in past years; i.e., pyrene[7-13] and dansyl groups[14] covalently bound to polymers have been used as fluorescence labels.

Labeled polymers capable of phosphorescence have not been studied as extensively because only a few organic materials show significant phosphorescence in solution at room temperature.[15] A phosphorescence probe would have some particular advantages over a fluorescence probe due to the long lifetime of phosphorescence relative to fluorescence, allowing dynamic polymer processes which develop on longer time scales to be studied. Longer lifetimes also make phosphorescence extremely sensitive to small amounts of quenchers; this can also be used to advantage since quenching of fluorescence requires relatively large concentrations of quenchers, which may change the polarity, viscosity, and the ionic strength of the system under study. Bromonaphthalenes form one of the few classes of organic compounds showing significant phosphorescence at room temperature,[16-18] making them excellent candidates as phosphorescent labels attached to a polymer backbone.

The main purpose of the present investigation is to demonstrate whether phosphorescence properties, in particular phosphorescence lifetimes, of bromonaphthoyl groups covalently bound to a water-soluble polymer can be profitably employed to investigate the conformational transitions that a linear polymer undergoes in different solvents and at different concentrations. We also report here that the phosphorescence probe method allows investigation of the effect of electrolytes on the polymer conformation and offers a novel method for the determination of the radius of gyration of the polymer in solution. Finally, quenching experiments were also carried out in aqueous solution, and it was shown that different polymer conformations affect quenching to various degrees. The validity of the phosphorescence results are conveniently tested using pyrene (a well-established fluorescence probe of polymer conformation), covalently bound to a structurally identical polymer backbone (PAA).

Experimental Section

Materials. Commercially available chemicals were used in the preparation of the monomer containing the BN label. The polymers were purified, as required, using literature methods.[7] Spectrophotometric grade solvents (Aldrich or Fisher) and deionized water were used in all measurements.

The preparation and characterization of the sample of pyrene-labeled poly(acrylic acid) (PyPAA) used in this investigation were reported earlier.[7a] The content of chromophore in the polyelectrolyte was ca. 1% for PyPAA as well as for BNPAA. The

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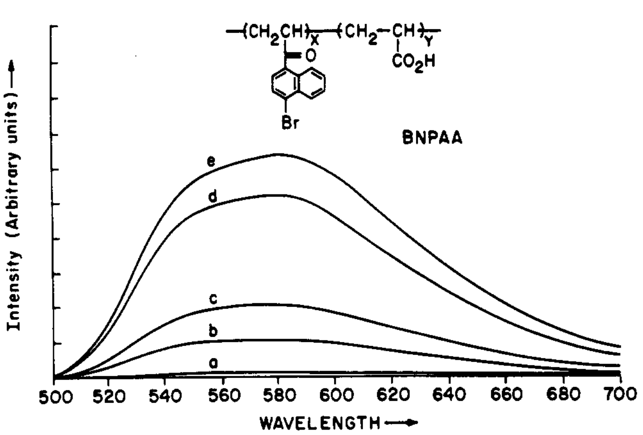

Figure 1. Phosphorescence emission spectra of aqueous solutions of BNPAA at 25 °C: (a) 10^{-4}, (b) 5×10^{-4}, (c) 10^{-3}, (d) 5×10^{-3}, and (e) 10^{-2} M.

preparation of the bromonaphthalene-labeled polymer, BNPAA, is reported elsewhere.[7b] Intrinsic viscosity measurements at 30 °C in 1,4-dioxane gave a molecular weight of 1.3×10^5 (degree of polymerization = 1768).

$NaNO_2$, bromonaphthoyl decyl sulfate, and (bromonaphthoylmethyl)trimethylammonium bromide were employed in a quenching experiments. The syntheses and purifications of the latter compounds are described elsewhere.[16,18]

Methods. ^1H NMR spectra were obtained using a Varian Model XL-200 (200 MHz) FT-NMR spectrometer and are reported below 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 Ubbelhode 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) of BNPAA were used to calculate the effective bromonaphthoyl concentration, using extinction coefficients of the monomer moiety as a model.

The phosphorescence emission spectra were recorded on a SPEX Fluorolog-2 1680 spectrofluorometer at 25 °C. The phosphorescence emission lifetimes were determined using a single-photon counting (SPC) apparatus (Photochemical Research Associates, London, Canada) and on an LS5 Perkin-Elmer spectrofluorometer possessing a rotating can attachment for phosphorescence lifetimes. Both methods gave identical results within the experimental error (±0.05 ms). Argon was bubbled through the samples for at least 30 min prior to emission and lifetime measurements. Pyrene fluorescence emission spectra were recorded on an LS5 Perkin-Elmer 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 concentrations of polymers reported in this work refer to equivalents of repeat units per liter (reported as M).

Results and Discussion

Photophysical Properties of BNPAA in Dilute Solution. From the polymerization method employed for its preparation, a dilute and random distribution of bromonaphthoyl groups is assumed for the primary microstructure of BNPAA. Since the interpolymer interactions in sufficiently dilute solutions of polymers could be assumed to be negligible, the photophysical properties of dilute solutions of BNPAA were expected to be determined by the intramolecular (conformational) interactions of the bromonaphthoyl groups in BNPAA.

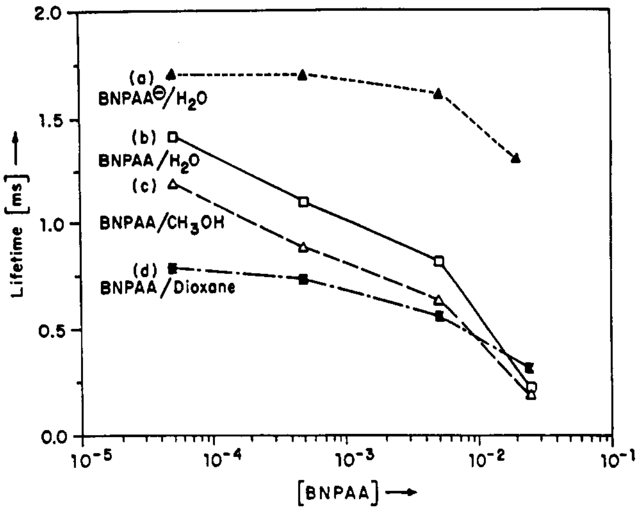

Figure 2. Phosphorescence lifetimes for BNPAA in various solvents as a function of polymer concentration: (a) salt form in water; (b) acid form in water; (c) acid form in methanol; (d) acid form in dioxane.

Figure 1 shows the emission spectra of BNPAA in aqueous solution at several concentrations of repeat units (between 10^{-2} and $<10^{-4}$ M). The emission at 575 nm corresponds to the readily monitored phosphorescence of the 1-bromonaphthalene lumophore,[14] and no significant fluorescence (expected at ca. 340 nm) is observed.

The phosphorescence lifetimes of BNPAA were obtained by two independent methods: one employing time-correlated single photon counting and the second employing a phosphorimeter attachment (rotating can) to an LS5 emission spectrofluorometer. The phosphorescence decay was found to be strictly monoexponential by both methods, and the quantitative lifetimes extracted from the phosphorescence decays determined by both methods were identical within the experimental uncertainty (error ±0.05 ms). For example, in a thoroughly argon purged aqueous solution, the phosphorescence decay is monoexponential with a lifetime of 1.62 ms by single photon counting, and an experimentally indistinguishable value of 1.59 ms was found for the same sample using an LS5 apparatus. For comparison, the maximum phosphorescence lifetime for a saturated aqueous solution of 1-bromonaphthalene is reported to be 5.5 ms in deoxygenated samples at room temperature.[21]

Phosphorescence lifetimes of BNPAA were measured at different concentrations of polymers in various solvent systems, and the results are reported in Figure 2. Lifetimes were found to decrease in the order (a) salt form in water > (b) acid form in water > (c) acid form in methanol > (d) acid form in dioxane. Since water and methanol are good solvents for PAA, whereas dioxane is a poor solvent for PAA, it is expected that the hydrodynamic volume of the polymer will decrease in the order water > methanol > dioxane. This trend is reflected in the lifetime values: higher concentrations of bromonaphthoyl groups give shorter lifetimes. We now show how these observed lifetime changes correlate with changes in the polymer conformation.

Although triplet excimer (phosphorescence) emission is an extremely rare observation in fluid solution, self-quenching of aromatic triplets is one of the most commonly observed mechanisms for the concentration dependence of phosphorescence[22,23] and may commonly proceed through triplet excimer formation. As a result, ideas that have been employed to exploit the measurement of excimer formation to study polymer conformation can be considered in terms of analogous self-quenching. From this line of thinking, the phosphorescence lifetimes and the interactions of bromonaphthoyl groups in the solutions of BNPAA are expected to be determined by the local effective concentration of bromonaphthoyl groups, which in turn are determined by the global polymer conformation. According to this 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. The experimental manifestation of such globular, compact conformation will be a relatively short phosphorescence lifetime resulting from significant self-quenching. If, on the other hand, the polymer conformation is extended, the local concentration of the bromonaphthoyl groups will be low and the BN triplet will be protected from self-quenching. The experimental manifestation of such extended conformation will be a relatively long phosphorescence lifetime. These simple ideas are exactly analogous to those employed for the use of pyrene as an excimer-forming fluorescence probe of PAA.[7] In the latter case globular, compact conformations favored excimer formation and extended conformations inhibited excimer emission relative to monomer emission.

With this simple model in mind, we now interpret the data in Figure 2. Curve 2a and curve 2d show only a weak dependence on polyelectrolyte concentration. At low BNPAA concentrations (<5 mM), the lifetime of the probe is both relatively high and relatively insensitive to concentration for the sodium salt form in water (Figure 2a). Thus, at sufficiently low concentrations for the salt form, the polymer maintains its extended conformation (long lifetime) due to electrostatic repulsion between charged carboxylic groups, even at a concentration up to 5 mM. Above this value significant interpolymer interactions are indicated by a decrease in lifetimes. On the other hand, dioxane is known to be a Θ solvent for PAA and is incapable of establishing preferential interactions with the polymer segments. In this case the polymer is already coiled at low concentrations and its conformation is insensitive to concentration effects. The probe lifetime (Figure 2d) is consequently relatively short and relatively insensitive to concentrations up to a certain point (ca. 5 mM). At higher concentrations (>5 mM), the phosphorescence lifetime decreases because *interpolymer* interactions are taking place in both solvents. For the acid form of BNPAA in water (Figure 2b) and methanol (Figure 2c), the lifetime decreases significantly as concentration increases, even in the low-concentration regime. We propose that an increase in the ionization of BNPAA with dilution causes elongation of the polymer chain and is responsible for the rise in the lifetime. The validity of this interpretation can be tested in a parallel experiment using pyrene fluorescence[7] as a photophysical probe of the same poly(acrylic acid) system.

Pyrene (Py), as a fluorescence probe, has been used extensively to report changes in conformation in polymers covalently bound to the molecule or as a host in the system.[7,12,13,25,26] The ratio of the intensities of monomer and excimer emission, I_e/I_m, was found to be correlated to the conformational structure of the polymer in aqueous solution and to the relative mobility of the chromophore. In this case the basic idea was that compact conformations lead to local concentrations of pyrene which favor excimer formation and enhance the intensity of excimer fluorescence emission. On the other hand, extended conformations lead to dilution of local concentrations and favor monomer fluorescence emission. Thus, the expected correlation results: high value of I_e/I_m, compact conformation; low value of I_e/I_m, extended conformation. Figure 3 shows the emission spectra of the acid form of PyPAA in (a) methanol, (b) water, and (c) dioxane and (d) the sodium salt form in water. The magnitude of the relative degree of excimer formation at 480 nm decreases in the order methanol, water, dioxane. The salt form in water shows the smallest relative amount of excimer contribution. From these data we reach the qualitative conclusions that compact conformations of the acid form of PAA are favored most by methanol, then by water, and least by dioxane. This is the same general pattern of conformational dependence on solvent deduced from the BNPAA probe (Figure 2) except for dioxane.

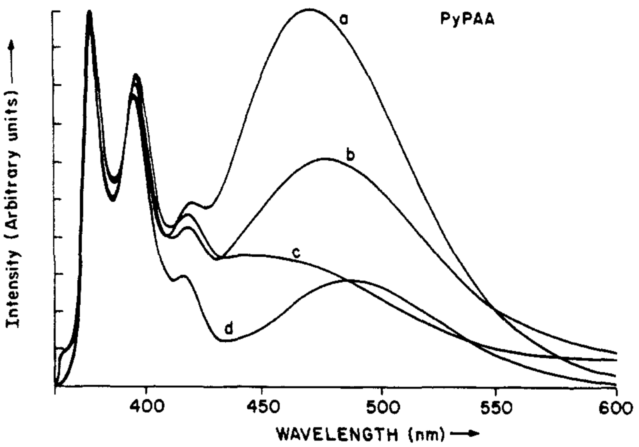

Figure 3. Fluorescence emission spectra of PyPAA in various solvents ([PyPAA] = 5×10^{-4} M): (a) acid form in methanol; (b) acid form in water; (c) acid form in dioxane; (d) salt form in water.

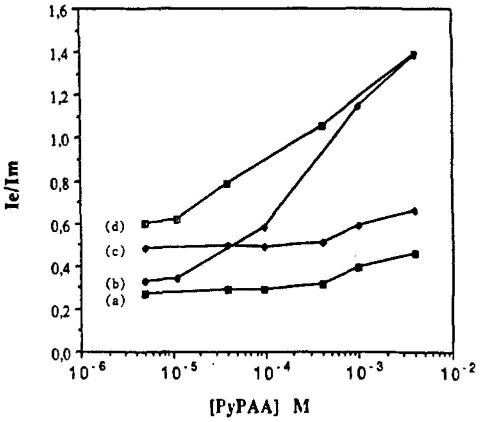

Figure 4. Excimer to monomer intensity ratio vs [PyPAA] in various solvents as a function of polymer concentration: (a) salt form in water; (b) acid form in water; (c) acid form in dioxane; (d) acid form in methanol.

It is always possible that a label may cause a modification of the polymer conformation due to specific interactions, e.g., hydrophobic interactions. To obtain information concerning such interactions of the Py and BN probes, the emission spectrum of PyPAA was recorded at different concentrations of PyPAA to determine the contribution of interchain interactions to the excimer emission. The I_e/I_m values for these spectra are given in Figure 4. As in the case of the BNPAA probe (Figure 2), the photoluminescence parameter shows the same trends: the I_e/I_m values were greatly dependent on concentration for water and methanol, with the probe indicating an increase in the compact form with increasing polymer concentration. As before, we conclude that the extent of excimer formation increases with increasing polymer concentration due to an increase in the local concentration of compact conformations due to interpolymer interactions. Again for dioxane and the salt form in water, the probe parameter, I_e/I_m, is lower and almost insensitive to concentration until interpolymer interactions start to occur (ca. 5 mM), which is consistent with the results of the BNPAA system.

Table I
Excitation Maxima for PyPAA (5×10^{-4} M) in Different Solvents

		wavelength (nm)		
water	monomer	273.0	324.5	340.0
	excimer	274.5	328.5	342.5
methanol	monomer	272.5	323.5	339.0
	excimer	273.0	324.5	339.5
dioxane	monomer	275.0	327.0	342.5
	excimer	275.0	327.0	342.5
Na salt in water	monomer	273.0	324.0	339.5
	excimer	273.5	326.5	340.0

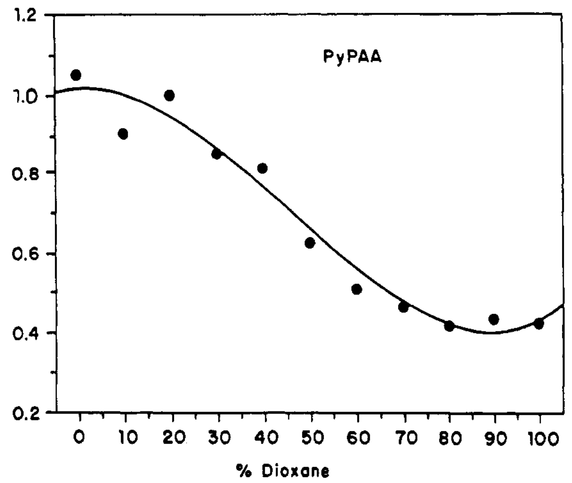

Figure 5. Excimer to monomer intensity ratio for PyPAA in water/dioxane solutions at different dioxane content.

Further tests for specific pendant probe interactions in the case of a dilute solution of the PyPAA polymer can be obtained from the excitation spectra for the pyrene monomer and the excimer for the four solvents of Figure 4. In Table I the wavelengths corresponding to the monomer and the excimer excitation spectra are reported for these conditions. In methanol and dioxane almost identical excitation spectra were obtained for the monomer and the excimer excitation. This indicates that the pyrene groups are predominantly unassociated but form excimers by a dynamic mechanism after photoexcitation. However, the acid form and the salt form in water show different excitation peaks for the monomer and the excimer. The general features of the spectra are similar, but the excimer is slightly shifted, an indication of weak or modest ground-state interactions between the pyrene groups.

The PyPAA (5×10^{-4} M) conformation dependency on the solvent was further investigated in some detail for the water/dioxane system (Figure 5). The addition of dioxane to an initially aqueous solution resulted in a decrease of the I_e/I_m value. The ratio decreases sharply in the region 0–60% dioxane and then remains almost constant in the region 60–100% dioxane. We interpret these results to mean that an increasing concentration of dioxane causes the breakup of pyrene dimer sites, leading to an increase in I_m and a corresponding decrease in the excimer contribution.

The same conclusion was reached by investigation of the ^{1}H FT-NMR spectra of PyPAA in different deuterated solvents (5×10^{-4} M). In dioxane and methanol relatively sharp resonances of aromatic protons of pyrene groups were obtained, whereas the ^{1}H resonances of pyrene in the labeled polymer in deuterated water and water/NaOD were broad. This broadening is attributed to increased dipolar interactions resulting from the same hydrophobic interactions of pyrene groups responsible for the shifts in the excitation spectra reported in Table I.

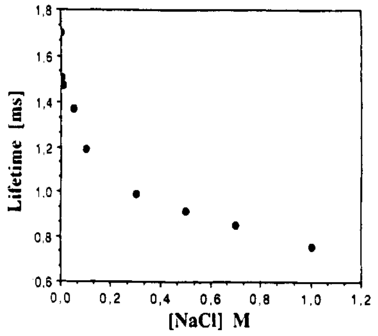

Figure 6. Effect of electrolyte concentration on phosphorescence lifetime of BNPAA and on calculated local concentration of chromophores.

The different behavior of BNPPA and PyPAA in dioxane may depend on the existence of interactions between the chromophores: ground-state association is expected to be much higher for the larger and more hydrophobic pyrene than for the smaller and more polar bromonaphthalene group.

Effect of Salt Concentration on Conformation. Evaluation of the Local Size of Conformational Pockets along the Polymer. It is already well established[1] that the presence of salt weakens the electrostatic repulsion between carboxylate anions along a polymer chain inducing the polymer to shrink and transform from an extended to a globular shape. Thus, an increase in the ionic strength of an aqueous solution containing a polyelectrolyte such as PAA will cause the hydrodynamic volume of the polymer to decrease and consequently increase the local concentrations of bromonaphthalene groups with increasing electrolyte concentration. To test whether the phosphorescence probe method could report on such variations in polymer conformation as a function of added strong electrolyte, the phosphorescence lifetimes of BNPAA were measured at constant concentration (5×10^{-4} M of the *salt* form) at different concentrations of sodium chloride.

The results reported in Figure 6 show that the phosphorescence lifetimes steadily decrease with increasing salt concentration. This can be explained assuming a decrease in the hydrodynamic volume of the polymer due to increasing contributions of compact conformations and a consequent increase in the extent of self-quenching of bromonaphthalene phosphorescence as a function of increasing salt concentration.

We now address briefly the possibility of relating the data for self-quenching in some quantitative manner to the size of the polymer coils. Wijmenga et al.[26] have proposed a model which allows the derivation of quantitative relationships between the phosphorescence lifetimes as a function of the effective local concentration of the chromophore groups, $C_{\mathrm{local,chrom}}$. This latter quantity is given by

$$C_{\mathrm{local,chrom}} = 0.01\sigma(1.5\pi\langle S^2\rangle)^{3/2} \qquad (1)$$

where σ is the local number of segments per molecule,[35] S is the radius of gyration of the macromolecule, and the factor 0.01 takes into account that only 1% of the monomer units contain the bromonaphthalene group. The radius of gyration has been calculated considering the wormlike chain approach for polyelectrolytes in the presence of salt developed by Odijk[27] and Fixman and Skolnick.[28] We have used a value for the monomer length of 0.25 nm and an intrinsic persistence length[29,30] $L_p = 1$ nm, taking into account the excluded volume parameter proposed in the literature.[31-34] The root-mean-square radius of gyration

Table II
Radii of Gyration of BNPAA in NaCl Solutions

[NaCl] (M)	R_g (Å)	[NaCl] (M)	R_g (Å)
0	1212	3×10^{-1}	207
5×10^{-3}	508	5×10^{-1}	192
1 × 10-12	418	7×10^{-1}	184
5×10^{-2}	283	1	175
1×10^{-1}	247		

[a] Root-mean-square radius of gyration. Computed from the theory of ref 27. See text for discussion.

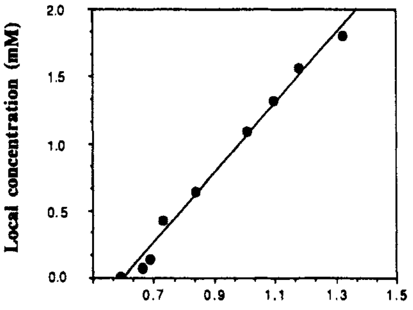

Figure 7. Relationship between reciprocal lifetimes of BNPAA and calculated local concentration of chromophore.

$\langle S^2\rangle^{3/2}$ calculated in this way is reported in Table II as a function of salt concentration.

We now test the hypothesis of a quantitative relationship between the salt effect on phosphorescence lifetimes and the polymer hydrodynamic volume. As mentioned above,[1] the presence of salt weakens the electrostatic repulsion between carboxylate anions of the polymer chains, and the polymer shrinks. This means that the hydrodynamic volume of the polymer decreases and the local concentration of bromonaphthalene groups increases with increasing sodium chloride concentration. Therefore, the decrease of lifetimes can be explained if we assume that self-quenching is operating to determine the lifetimes in the system.

Figure 7 shows the results of the test of the hypothesis, and it is seen that the reciprocal lifetimes of phosphorescence possess a *linear* relationship with the chromophore concentration, which is related to $\langle S^2\rangle^{-3/2}$ by eq 1. These results support the conclusion that ground-state bromonaphthoyl groups are acting as self-quenchers. We propose that self-quenching is a plausible mechanism for the observed lifetime decrease, since the rate of quenching (inverse of lifetime) shows a linear correlation with the extent of polymer coiling (Figure 7). Since the radius of gyration, according to eq 1, is proportional to the local effective concentration, it is reasonable from this model that the lifetimes are directly correlated to the radius of gyration of the polymer in solution. Thus, the results demonstrate that lifetime measurements can be employed to calculate the radius of gyration by measuring phosphorescence lifetimes (see Table II).

Effect of Solvent Viscosity on Polymer Conformation. The phosphorescence of a bromonaphthalene group covalently bound to the polymer can also report on the effect of the viscosity on the intrachain diffusional motion of the polymer, since this motion is expected to be rate limiting for the self-quenching processes. The macroscopic viscosity was varied by adding different amounts of glycerol to an initially aqueous solution of BNPAA (salt form). The phosphorescence lifetimes decreased slightly in the first stage and then increased linearly with the increasing percent of glycerol (Figure 8). The initial drop of lifetime might be due to a weaker solvating effect of glycerol compared to water. To elucidate this point the effect of viscosity was studied for the sodium salt of BNPAA. As shown in Figure 8, again the lifetime is more or less constant at low glycerol concentration and then increases upon further addition of glycerol.

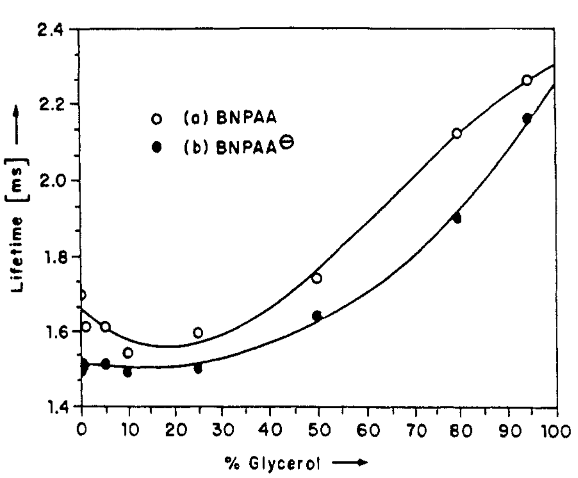

Figure 8. Viscosity (percent glycerol) effect on phosphorescence lifetimes of BNPAA: (a) acid form; (b) salt form.

Since at low viscosities, i.e., low glycerol concentrations, phosphorescence lifetimes are almost constant, we conclude that the interactions between BNPAA and glycerol are weak and that chain mobility still determines the extent of self-quenching and therefore the lifetime. However, the extent of intrapolymer interactions becomes progressively restricted with increasing viscosity as a result of inhibition of both intra- and intermolecular mobility; thus an increase in the lifetime is observed as the macroscopic viscosity increases.

Influence of Polymer Conformation on External (Aqueous Phase) Quenching. The conformation of the polymer and conformer dynamics are expected to affect directly the efficiency of quenching of the triplet bromonaphthalene label by "external" quenchers which exist exclusively in the aqueous phase. Expansion of the polymer main chain leads to exposure of naphthalene moieties to the aqueous phase and to quenchers which may exist in the aqueous phase, so that a higher quenching efficiency is expected to correlate with expanded chain conformations. Since charge repulsion opposes quenching by substances of the same charge, sodium nitrite was used as an anionic, "same charge" quencher. The efficiency of quenching in solution of BNPAA (5×10^{-4} M) was measured in terms of Stern–Volmer constants obtained from the slope of the reciprocal lifetime against quencher concentration.

The Stern–Volmer plots for the acid and the salt forms of the polymer are reported in Figure 9. The corresponding quenching constants were calculated to be 8×10^7 and 9×10^6 M^{-1} s^{-1}, respectively. The difference is attributed to the electrostatic repulsion between the quencher anions and the carboxylate groups of the polymer, which causes the quenching to be lower for the salt form.

To determine whether the self-quenching rate constants were reasonable, we performed analogous quenching experiments with low molecular weight model compounds: both negatively and positively charged. Phosphorescence lifetimes of the low molecular weight compounds, bromonaphthoyl decyl sulfate and (bromonaphthoylmethyl)trimethylammonium bromide, were measured at different concentrations. The quenching rate constants obtained from the Stern–Volmer plots for the anionic and cationic models were 5×10^6 and 6×10^6 M^{-1}

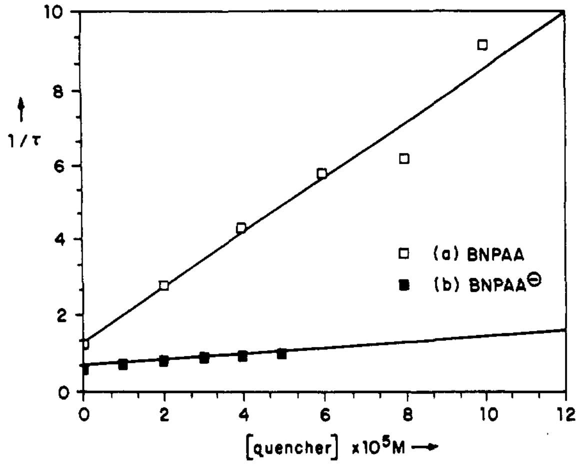

Figure 9. Stern–Volmer plots for the quenching of the acid (a) and salt form (b) of BNPAA with sodium nitrite.

s^{-1}, typical for self-quenching rate constants of aromatic molecules.[21] The self-quenching constant of the salt form of BNPAA, based on the local effective concentration of the bromonaphthalene groups, is found to be 4×10^5 M^{-1} s^{-1}. This value is one order of magnitude lower than the value found for the low molecular weight compounds as expected for an additional energy barrier for rotation of the polymer chains.

Conclusions

The study reported here demonstrates that phosphorescence labeling[7c] of polymers provides a useful tool to study the conformation of macromolecules and their interactions with solvents as well as with quencher molecules.

The results are consistent with the hypothesis that compact conformations of the BNPAA polymer labeled with a phosphorescence probe favor self-quenching of the pendant bromonaphthalene groups and cause a reduction in the phosphorescence lifetimes. The interpretations of the results for BNPAA are confirmed by the results obtained using the same polymer labeled with the fluorescence probe pyrene and by quenching experiments with low molecular weight compounds containing bromonaphthalene groups. Although another possible interpretation of the results is that the conformational changes that occur cause an unspecified "chain" quenching to occur, we prefer the self-quenching interpretation because of its clear physical sense, because this interpretation is consistent with the self-quenching of model compounds possessing the same lumophore and because of the similar behavior exhibited by the analogue of excimer formation with a pyrene-labeled polymer, PyPAA.

The phosphorescence lifetimes of the acid form of BNPAA have been found to depend on the solvent used: water > methanol > dioxane; more compact structures are developed in this order, in agreement with the expected solvation efficiency of the solvents for a hydrophilic polymer.

Phosphorescence studies are also suitable for investigating the dependence of polymer conformation on polymer concentration. For dioxane and for the salt form in water, concentration has little effect on polymer conformation and only induces interpolymer interaction above a critical concentration. For the polar solvents, water and methanol, the results suggest a coiling of the chain with increasing concentration even in dilute solutions. These interpretations were confirmed by analogous experiments with pyrene-labeled poly(acrylic acid). In this case, the monomer to excimer ratio was used to monitor conformational transitions.

The dependence of polymer conformation on the salt content of the solution has also been investigated, and a theoretical interpretation of the experimental data allows the radius of gyration of the polymer in solution to be determined by measuring phosphorescence lifetimes.

Finally, BNPAA has also been shown to be a suitable polymer for quenching studies; the long lifetime of phosphorescence is especially useful for the quenching experiments because phosphorescence is several orders of magnitude more sensitive than fluorescence and report on phenomena evolving on a much longer time scale.

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