Journal of Fluorescence, Vol. 8, No. 4, 1998

Luminescence Characterization of a Novel, Hydrophobically Modified and Heavy Atom-Functionalized, Water-Soluble Polymer

Nicholas J. Flint,[1] Rachael Haywood,[1] Ian Soutar,[1,2] and Linda Swanson[1]

Received January 25, 1998; Accepted July 7, 1998

A hydrophobically modified water-soluble polymer, based upon acrylic acid and styryl derivatives, was synthesized. A proportion (ca. 75 mol%) of the styryl residues in the copolymer contain a bromine substituent as a "heavy-atom" functionality. It has been shown that room-temperature phosphorescence (RTP) can be induced in an acenaphthylene (ACE) label, covalently bound to the polymer chain, through intramacromolecular interactions in dilute solutions of the copolymer. This is the first instance in which RTP has been generated in either label or solubilized guest, in such a fashion. The conformational behavior of the functionalized copolymer, BrSTY/STY/AA, has been studied using RTP, fluorescence lifetime, and time-resolved anisotropy measurements and compared to that of both its unbrominated, styrene-modified analogue, STY/AA, and poly(acrylic acid) PAA itself. The conformation transition which accompanies conversion of each polyacid into the corresponding fully neutralized polysalt is much more dramatic in either hydrophobically modified species than in poly(acrylic acid). Intramacromolecular aggregation leading to the creation of hydrophobic domains within the coils of the macromolecules is enhanced at a low pH and severely impedes segmental motion in the two styrene-modified polyacids. The effect is greater in the bromine-containing polymer, which suggests that more densely packed domains are formed in this species than in STY/AA. In addition to altering the magnitude of the effect that neutralization has upon the molecular dynamics of the polyacid in aqueous media, hydrophobic modification raises the pH range over which the change in conformational behavior of the macromolecule is apparent.

KEY WORDS: Anisotropy; heavy atom; phosphorescence; water-soluble polymer.

INTRODUCTION

Photophysical techniques are both versatile and powerful as means of characterizing macromolecular systems. Their sensitivity allows polymer behavior to be scrutinized at the molecular level. Consequently, luminescence spectroscopy has found many applications in polymer science. (For reviews, please see Refs. 1–4 and references therein.)

[1] The Polymer Centre, School of Physics and Chemistry, Lancaster University, Lancaster LA1 4YA, UK.
[2] To whom correspondence should be addressed.

Environmental and other concerns have fostered much recent interest in the factors governing the performance of water-soluble and aqueous-dispersible polymers (see, for example, Refs. 5 and 6 and references therein). Fluorescence studies, involving both covalently bound labels and solubilized probes, have helped promote understanding of the complex behaviors exhibited by such systems, as has been discussed in recent overview articles [7,8]. In addition, the microenvironments created within dilute solutions of certain water-soluble polymers, and their hydrophobically modified forms, have proved conducive to both the promotion and the sustenance of enhanced populations of triplet excited

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states [9–13]. This, in turn, has introduced the possibility of using phosphorescence to study the conformational behavior of macromolecules in aqueous media [8,11,13].

In the current presentation, we describe the synthesis and characterization of two novel, hydrophobically modified polyelectrolytes based upon acrylic acid. Both species contain phenyl derivatives as hydrophobic modifiers. One is a (statistical) copolymer of styrene and acrylic acid. The other is a (statistical) terpolymer of 4-bromostyrene, styrene, and acrylic acid.

This preliminary investigation had several objectives:

(i) to examine the occurrence and extent of hydrophobic domain formation through intramolecular aggregations within the two polyacids and to compare the characters of the microdomains created in the two species;

(ii) to gauge the potential of heavy-atom quenchers which are integral components of the polymer structure, to enhance investigations of the conformational behavior of the macromolecule using fluorescence labeling techniques;

(iii) to investigate the ability of such heavy-atom species to promote room-temperature phosphorescence (RTP) in aromatic labels or guests, sequestered within the hydrophobic regions created in the coils of the polymer, in aqueous solution; and

(iv) to assess the potential of the RTP generated in chromophoric labels, in such a fashion, for application in future studies of the solution characteristics of hydrophobically modified water-soluble polymers.

This is the first instance in which a heavy-atom species, which is extrinsic to the luminescent label but an integral component of the macromolecular host, has been used (a) to characterize the dilute solution behavior of polymers in aqueous media and (b) to promote phosphorescence in a guest moiety (in this case, a covalently bound label).

EXPERIMENTAL

Materials

Styrene (STY), bromostyrene (BrSTY), and methyl methacrylate (MMA) (all Aldrich) were purified by washing with sodium hydroxide (10%, w/v), followed by distilled water until neutral to litmus. The monomers were subsequently dried over molecular sieves, prepolymerized with uv light to remove any residual inhibitor, and fractionally, vacuum distilled (ca. 10^{-4} Torr) immediately prior to use.

Acrylic acid (AA) was vacuum distilled. Acenaphthylene (85%; ACE) was purified by multiple recrystallisation (×3) from ethanol, followed by sublimation. Benzene and methanol (both spectroscopic grade) were used as received. Diethyl ether (May and Baker) was distilled prior to use.

Statistical, fluorescently labeled terpolymers of AA and ACE (0.5 mol% of total monomer feed) with BrSTY and/or STY were prepared by free radically initiated solution (benzene) polymerization at 70°C under high vacuum using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The polymers were purified by multiple reprecipitation from methanol into diethyl ether.

The feeds employed in copolymerization contained 20 mol% aromatic monomer (STY or STY + BrSTY) and 79.5 mol% AA, expressed as (molar) compositions of the total monomer content. The resultant copolymers contained ca. 35 mol% aromatic monomer and the STY: BrSTY molar ratio in the heavy-atom functionalized macromolecule was 1:3. These copolymer compositions were determined by both NMR and elemental analyses. The fluorescently labeled, hydrophobically modified copolymers are designated STY/AA and BrSTY/STY/AA, respectively.

A fluorescently labeled sample of poly(acrylic acid) PAA, containing 0.5 mol% ACE, was prepared using solution polymerization and purification procedures similar to those employed in copolymerization, as described above.

Solutions for spectroscopic analyses contained 10^{-2} wt% of polymer. For phosphorescence measurements, the samples were purged by nitrogen bubbling (ca. 20 minutes) and sealed in quartz cells. Doubly distilled water was used throughout.

Instrumentation

Steady-state fluorescence and phosphorescence spectra were recorded on a Perkin–Elmer LS50 luminescence spectrometer.

Fluorescence lifteimes were acquired on an IBH System 5000 spectrometer operating on the time-correlated single-photon counting (TSCPC) principle using a a thyratron-gated coaxial flashlamp for excitation.

Time-resolved phosphorescence measurements were made using a specially constructed spectrometer based upon an earlier design [14] which incorporates an Edinburgh Instruments optics and monochromation system using conventional MCA and NIM unit technology. The excitation source was a pulsed Xe arc lamp (Chelsea

Instruments W3101) triggered using a Lyons pulse generator (type PG71N) which sends a synchronized, delayed signal to initiate a multichannel scaling sweep in the MCA (Inotech 5300). An EMI 9863 (D307) red-sensitive photomultiplier tube was used as the detector.

Time-resolved anisotropy measurements (TRAMS) using vertically polarized excitation were performed using radiation from the Synchrotron Radiation Source (SRS; CLRC, Daresbury Laboratory, UK). Collection of the fluorescence intensities tramsitted by a polarizer, analyzing in planes parallel $\{I_{\parallel}(t)\}$ and perpendicular $\{I_{\perp}(t)\}$ to that of the polarized excitation, was achieved using a "toggling procedure": the analyzer was rotated sequentially through 90° while memory segments in the MCA (Inotech 5400) were simultaneously switched. Excitation wavelengths of 290 and 340 nm, respectively, were employed. Details of the TCSPC detection system employed at the SRS are described elsewhere [14].

Analysis of Time-Resolved Fluorescence Data

Time-resolved fluorescence data, collected using the TCSPC technique, were analyzed, through iterative reconvolution, using multiexponential functions to model the temporal dependence of the response of the fluorescence from the ACE label of the various polymers examined in this work, as described below (see Results and Discussion). The "goodness of fit" was assessed by a number of statistical criteria such as the reduced χ^2, distribution of residuals, and autocorrelation of residuals. These analytical approaches have been described elsewhere [15].

TRAMS data were analyzed using the impulse reconvolution [16] approach, as described previously described, in comparison with other methods of data retrieval from fluorescence anisotropy information [14,16,17].

RESULTS AND DISCUSSION

Fluorescence Lifetime Data

The lifetime of the excited singlet state of an ACE-labeled water-soluble polymer is sensitive to the conformation adopted by the macromolecule [18,19]. Since a fluorescent label will be incorporated into a variety of environments within the coils of a polymer dispersed in aqueous media, its time-resolved emission would not be expected, in general, to obey a simple first-order decay law. In the case of ACE-labeled poly(methacrylic acid), PMAA, for example, the fluorescence of the ACE label can be adequately described by a single-exponential decay function at high pH, where the polymer adopts a relatively open, randomly coiled conformation [8,18]. However, in acidic media, at pH values less than those at which neutralization of the polyacid is effected, the observed decay behavior is more complex [8,18]. Similar observations have been made by Chu and Thomas [20] in studies of the excited-state behavior of a pyrenyl-based label of PMAA.

In the current study, the fluorescence decay characteristics of the ACE-labeled AA copolymers, hydrophobically modified with STY and/or BrSTY, were found to be complex at all values of pH. Consequently, the transient fluorescence data, $i(t)$, were characterized using model functions consisting of sums of exponential terms of the form

$$i(t) = \sum_i A_i \exp(-t/\tau_i) + B \qquad (1)$$

where $i = 2$ or 3 (as required to achieve statistically adequate fitting), A_i represents the various preexponential terms, and B is a "background" parameter. Within this context, we have adopted an "average lifetime," $\langle\tau\rangle$, determined as

$$\langle\tau\rangle = \frac{\Sigma A_i \tau_i^2}{\Sigma A_i \tau_i} \qquad (2)$$

as a parameter characteristic of the persistence of the fluorescence from the ACE label. This approach reflects our belief that Eq. (1) serves merely to parameterize the temporal dependence of the intensity of fluorescence, $i(t)$, from the ACE label: we do not feel that the τ_i derived using Eq. (1) have physical significance in terms of representing *distinct* distributions of labels located, for example, in different domains within the individual macromolecules. We have adopted a similar approach, previously, in description of the time-dependent fluorescences of guests solubilized within a variety of hydrophobically modified AA copolymers [8]. This approach is vindicated, to some extent, by the fact that the resultant $\langle\tau\rangle$ data agree, within experimental error, with estimates of the "fluorescence lifetime" of the ACE label consequent upon single-exponential analyses (which are not statistically justified, according to the strict criteria described under Experimental).

Figure 1 shows the variation in "fluorescence lifetime," τ_f, of the ACE label (estimated either as $\langle\tau\rangle$ or from "forced" single-exponential fits to the time-resolved decay data, as described above) of the STY/AA copolymer as a function of pH. The data clearly reveal the conformational transition (with an onset at a pH of ca. 6.5) which accompanies neutralization of the acrylic

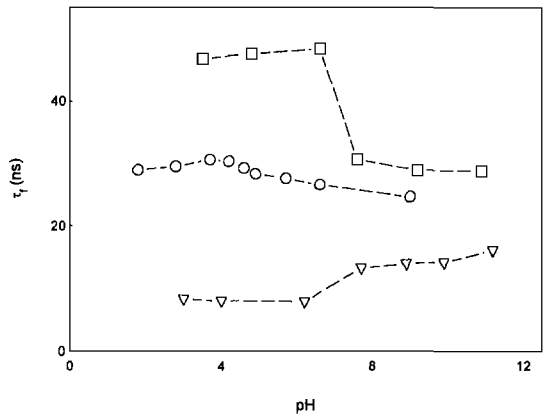

Fig. 1. Fluorescence lifetime, τ_f, as a function of pH for ACE-labeled PAA (○), STY/AA (□), and BrSTY/STY/AA (▽).

acid constituents of the copolymer. The effect of pH upon τ_f of the ACE label is *much* greater than that induced during neutralization of PAA itself (cf. Fig. 1).

Furthermore, hydrophobic modification of the polymer results in a shift in the pH range over which the effects of the conformational transition are apparent relative to that for ACE–PAA. Time-resolved anistropy measurements (TRAMS) upon various fluorescently labeled and hydrophobically modified, water-soluble polymers have confirmed that alteration of the hydrophobic–hydrophilic balance of water-soluble polyacids through copolymerization shifts the pH range over which the effects of ionization of the acidic components of the macromolecules are apparent [7,8,21].

In the case of the STY/AA copolymer, τ_f decreases from a value of ca. 48 to ca. 29 ns as the habitat of the ACE label changes from that created in the hydrophobic domains which characterize the acid form of the copolymer to the more polar interiors formed within its polysalt. The relative change in τ_f of the ACE label is similar to that exhibited for ACE-labeled PMAA, a polymer which fluorescence lifetime [18], quenching [8,18], and TRAMS [17] data indicate that the ACE labels are sequestered within relatively densely packed hydrophobic domains created through intramolecular aggregations within the acidic form of the polyelectrolyte. TRAMS data (discussed below) indicate that intramolecular domain formation is also prevalent in STY/AA at low pH.

Excited-state fluorescence lifetime data for ACE-labeled BrSTY/STY/AA, as shown in Fig. 1, also reveal the conformational transition of this hydrophobically modified AA-based polymer. However, in this instance, the conformational transition results in an increase in τ_f of the ACE label as neutralization of the polyacid is effected. The data provide further evidence of the formation of hydrophobic aggregates within the copolymer coil.

At low pH values, the ACE labels, incorporated into the hydrophobic domains formed by intramolecular aggregation of BrSTY and STY residues, are brought into close proximity to the heavy-atom Br substituents. Considerable quenching of the ACE fluorescence results, producing a τ_f of ca. 8 ns, compared to that of ca. 47 ns in the umbrominated analogue, STY/AA. (TRAMS data, discussed below, indicate that the hydrophobic domains created in the brominated copolymer may constitute more compact and restricted microenvironments than are evident in STY/AA. Consequently, the resultant degree of *effective* quenching of the ACE fluorescence might be considerably greater than suggested by this simple comparison of fluorescence lifetimes.) As neutralization of the brominated polyacid is brought about, the polymer coil expands, creating less crowded domains in which the ACE labels experience less quenching than at pH values below the conformational transition. It should be noted, however, that the labels are subject to *some* quenching in the polysalt of the brominated macromolecule: the fluorescence decay time of 14 ns is to be compared with that of ca. 29 ns in the polysalt of the analogous unbrominated copolymer. Such quenching could result either from dynamic encounters induced by the flexible coils which usually characterize polysalt forms of, for example, PMAA and PAA [7,8,22,23] or might be indicative that intramolecular aggregates exist even in the polysalt form of the brominated copolymer. TRAMS data, as discussed below, support the latter interpretation of the τ_f behavior, at least over some of the pH range examined above the conformational transition of this polymer.

Time-Resolved Anisotropy Measurements (TRAMS)

The intramolecular segmental relaxation behavior of the hydrophobically modified AA copolymers is complex. Attempts to model the true anisotropy, $r(t)$, using a function of the form

$$r(t) = r_0 \exp(-t/\tau_c) + r_\infty \quad (3)$$

resulted in fits which proved statistically adequate. However, the resultant fitting parameters gave cause for concern.

(i) The "background" term, r_∞, was consistently significantly greater than zero.

(ii) The value of the intrinsic anisotropy, r_0, recovered in IR analyses was, in each case, less than that of ca. 0.13, expected for an ACE label of

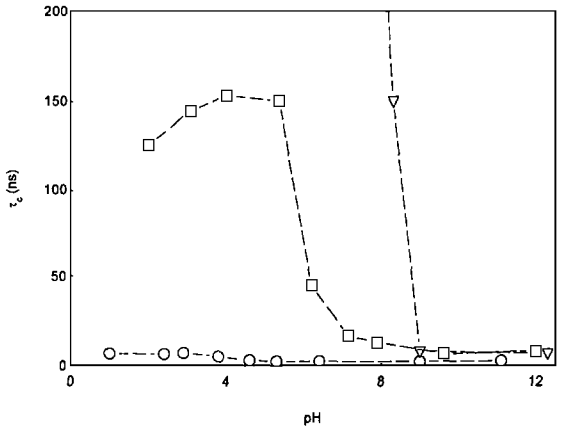

Fig. 2. Variation of segmental mobilities of PAA (○), STY/AA (□), and BrSTY/STY/AA (▽).

a polyelectrolyte, such as PMAA [17] in dilute aqueous solution.

We have observed similar complexities in TRAMS studies of other hydrophibocally modified polyacids [21,22]. As in previous investigations, we suggest that the complex TRAMS behavior reflects the broad range of heterogeneous environments experienced by the segments of these polyelectrolytes in aqueous media.

Since there is no reason to believe that the relaxation characteristics of the macromolecules currently under investigation should result in a residual anisotropy, r_∞, we have employed a single-exponential function, of the form of Eq. (3) in which r_∞ is constrained to zero, to describe the dynamic behavior of these polymers. This approach reflects our belief that adoption of more complex models for $r(t)$ would merely parameterize the TRAMS data and that some form of average correlation time would have to be adopted in characterization of the polymer behavior.

Figure 2 shows the variation in τ_c of PAA and of the STY/AA and BrSTY/STY/AA copolymers with pH. Two points are immediately apparent.

(i) Hydrophobic modification has a dramatic effect upon the conformational behavior of the resultant polyacid compared to that of PAA itself. In PAA, neutralization of the polyacid produces a relatively modest change in its segmental dynamics. In contrast, both hydrophobically modified copolymers exhibit marked inhibitions of their segmental mobilities in acid media. These restrictions upon polymer relaxation are the result of the formation of domains, within the polymer coils, through intramolecular aggregations between the hydrophobic constituents introduced by copolymerization.

(ii) The effects of the hydrophobic modifier, upon τ_c, are significantly different for BrSTY compared with STY. This is a surprizing observation: it was expected that the intramacromolecular hydrophobic domains created in the STY/AA and BrSTY/STY/AA copolymers would be of similar character. If anything, we anticipated that the more polar BrSTY residues would produce aggregates of a more open, water-permeated nature than those of the STY/AA copolymer. By analogy with observations of the effects of methyl methacrylate (MMA) as modifying comonomer [21], it was assumed that the BrSTY/STY/AA copolymer might exhibit greater degrees of segmental freedom than its STY/AA analogue. In contrast, the current data indicate that the domains formed in the BrSTY/STY/AA system are much more closely packed entities than those of STY/AA: the resultant restrictions upon segmental mobility of the polyacid are such as to render τ_c values for the relaxation of the brominated macromolecule beyond (reliable) resolution through TRAMS experiments involving ACE as a label at pH values less than ca. 8.5.

Either hydrophobic modifier shifts the conformational transition accompanying neutralization of the AA components of the polyelectrolyte to higher values of pH. This trend is consistent with earlier studies of STY- or MMA-modified polyacids [21,22]. The shift is more pronounced in the case of the brominated polymer as might be expected given the indications from segmental relaxation data that the presence of brominated hydrophobic constituents produces more compacted aggregates of the aromatic derivatives.

Room-Temperature Phosphorescence (RTP)

The principal aim of synthesizing polymers containing substituents bearing bromine as a heavy-atom species was to assess the capability of these derivatives to induce RTP in the ACE label. This synthetic strategy was successful, as illustrated in Fig. 3, which shows the spectrum of the phosphorescence of the ACE label in dilute aqueous solution of the BrSTY/STY/AA copolymer at a pH of 6.2.

RTP from the ACE label was observable at all values of pH studied (between 3 and 11.2). The fact that RTP of the label can be observed at pH values greater than 9 demonstrates that the existence of "protective"

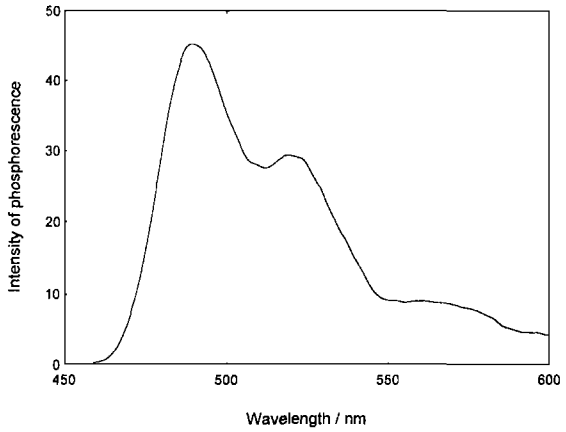

Fig. 3. Phosphorescence spectrum of ACE-labeled BrSTY/STY/AA in aqueous solution (10^{-2} wt% in polymer) at 298K. λ_{ex} = 290 nm.

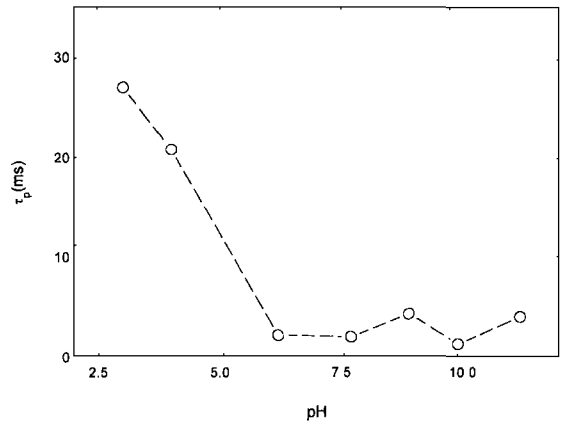

Fig. 4. Phosphorescence lifetime, τ_p, of ACE-labeled BrSTY/STY/AA as a function of pH.

hydrophobic domains is not a necessary prerequisite for observation of triplet state emission. In this context, the data reinforce earlier observations concerning the induction of RTP in a 1-vinylnaphthalene label of PMAA in dilute aqueous solution [9,18,24] using Tl^+ ions as an *extrinsic*, aqueous-borne, heavy-atom promoter. In the latter instance, RTP from the luminescent label was promoted at high pH by neutralization of the PMAA as a result of two effects. First, repulsions between the ionized substituents of the polysalt serve to expand the polymer coil, allowing greater ingress of the bulk aqueous medium (and, thence, solubilized Tl^+ ions). Second, the negative "charge cloud" of the neutralized PMAA attracts a high local concentration of positively charged ions (including Tl^+) in the vicinity of the naphthyl label. Neither process, in itself, can act to promote RTP in the current study.

In the Br STY/STY/AA labeled copolymer, several factors will influence the accessibility of the label to the heavy-atom promoter of phosphorescence *and* the stability of the ACE triplet states created through enhanced intersystem crossings induced by the bromine substituents. Hydrophobic domain formation, enhanced at low pH values and evident in the fluorescence lifetime and TRAMS studies described above, will bring the BrSTY residues into closer proximity with the ACE labels since both will be incorporated, preferentially, into the hydrocarbon-rich aggregates. This, coupled with the "protective nature" of the compact domain structures, will enhance RTP of the ACE label. On the other hand, the restricted motion of the polymer segments within these highly coiled structures will inhibit access of the heavy-atom promoter to the ACE labels. The latter effect is shown, to an extent, in Fig. 4, which shows the pH dependence of the lifetime, τ_p, of the RTP of the ACE label. As the pH increases and neutralization of the polyacid is effected, the polymer coils begin to expand. The hydrophobic domains will become less crowded and molecular mobility will increase. τ_p will decrease on two counts: ingress of water and a general increase in fluidity of the host domain will serve to deactivate the triplet-state population. In addition, increased mobility of the heavy-atom substituents within the hydrophobic cavities will serve to enhance the bromine-mediated deactivation of these excited states through their (heavy-atom) promotion of both radiative and nonradiative pathways to the ground state (S_o) of the ACE label.

Figure 4 illustrates how RTP can be used to characterize the conformational behavior of the BrSTY/STY/AA copolymer. The RTP data clearly are capable of complementing studies based upon fluorescence lifetime, anisotropy and other photophysical properties. However, reference to Fig. 4 indicates that the link between the information furnished by the singlet states and triplet states of luminescent labels has yet to be established: τ_p of the ACE label achieves a minimum value of ca. 2 ms at a pH of ca. 6, which is maintained, more or less, at higher values of pH. Fluorescence lifetime data, on the other hand, in both the presence and the absence of a heavy-atom promoter, suggest that this pH merely marks the *onset* of the conformational change of the two hydrophobically modified polyacids. TRAMS data, while elucidating differences between the two hydrophibically modified systems, clearly demonstrate (Fig. 2) that hydrophobic domains continue to exist within the

BrSTY/STY/AA copolymer even when the pH is increased to values of the order of 8–8.5.

The relationship between the information afforded by RTP and fluorescence studies of heavy-atom functionalized water-soluble polymers concerning the conformational behavior of such species warrants further investigation. Work in this area continues at Lancaster. In the meantime, it can be noted that the plateaux observed in τ_p and τ_f for the ACE label of BrSTY-containing polymers at higher pH values, are consistent with access of the heavy-atom quencher to the luminescent label in the polysalt forms of these hydrophobically modified macromolecules. Consideration of the TRAMS data would infer that these label-quencher interactions occur at high pH values, in the absence of aggregation between hydrophobic constituents of the copolymer and result from encounters promoted by the intrinsic flexibility of the hydrophobically modified polysalt.

CONCLUSIONS

1. The conformational behavior of a polyacid can be markedly affected by intramolecular hydrophobic interactions between relatively rigid, aromatic modifying substituents of the polymer backbone: the pH range over which the conformational transition is apparent is shifted to higher values of pH than that for the parent polyacid.

2. The lifetime of the fluorescence emitted by an ACE label is altered dramatically by the introduction of intramolecularly associative hydrophobic substituents, such as STY. For polyelectrolytes based upon acrylic acid, the conformational transition which characterizes neutralization of the polyacid, is marked by a much more dramatic change in τ_f of the ACE label of the modified polymer than is evident for the parent species, PAA/ACE.

3. Incorporation of bromine substituents causes a significant reduction in τ_f of an ACE label, especially at low pH values where the polyelectrolyte exists in its acidic form.

4. STY/AA/ACE and/or BrSTY/STY/AA/ACE copolymers of varying composition could form the basis of a series of fluorescence lifetime sensors of pH in which the range of pH over which the sensor is activated could be altered through synthetic design.

5. TRAMS have shown that intramolecular hydrophobic domain formation significantly reduces the segmental mobility of polyacids in aqueous media. It is apparent that the microdomains formed within the coils of STY-modified PAA and a polymer of similar aromatic content but incorporating BrSTY in addition to STY have different characters. The presence of BrSTY seems to cause greater degrees of inhibition of the segmental mobility of the polymer.

6. The presence of bromine as a heavy atom substituent of the BrSTY/STY/AA copolymer promotes phosphorescence from the ACE-labeled macromolecule. Since STY-modified AA copolymers are capable of solubilizing organic guest molecules in aqueous media [21], it is likely that copolymers incorporating BrSTY residues will be capable of producing RTP from suitable aromatic guest species occluded within the hydrophoboc domains which exist in dilute solutions of such copolymers. Studies of such systems continue at Lancaster.

ACKNOWLEDGMENTS

The authors wish to thank the Leverhulme Trust for funding a postdoctoral research fellowship (to N.J.F.) and the EPSRC for access to the SRS (Daresbury).

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