Fluorescence Studies of the Dynamic Behavior of Poly(dimethylacrylamide) and Its Complex with Poly(methacrylic acid) in Dilute Solution

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ABSTRACT: Fluorescence techniques, including quenching and anisotropy measurements, have been used to study the dynamic behavior of poly(*N*,*N*-dimethylacrylamide) (PDMAC) in both dilute methanolic and aqueous solution, respectively. These studies indicate that the polymer exists as a flexible and relatively open coil in aqueous media whose behavior is largely unaffected by changes in pH. Preliminary time-resolved anisotropy measurements reveal that complexation with poly(methacrylic acid) (PMAA) produces a relatively rigid species in which the segmental mobility of the PDMAC is dramatically reduced.

Introduction

Studies of water-soluble polymers have been much in evidence in recent years (see, for example, refs 1 and 2 and references therein). The sensitivity of the luminescence approach makes emission spectroscopy an extremely attractive means of studying the intramolecular processes which govern the physical behavior of polymers in truly dilute aqueous solutions. Luminescence investigations of the behavior of water-soluble macromolecules can employ either solubilized probes or covalently attached labels as the radiative reporting "guests" in the medium of interest. In the past, such studies have involved spectroscopic and excited-state lifetime estimates (see, for example, refs 3−12), excimer formation (see, for example, refs 9 and 13−17), energy transfer (see, for example, refs 18−20), and dynamic quenching (see, for example, refs 10, 12, and 21−24) in attempts to characterize the hydrophobic domains extant within the polymer coil. However, emission anisotropy measurements, in particular, *time-resolved* fluorescence anisotropy measurements (TRAMS) involving suitably labeled polymers, have the potential to interrogate, directly, the intramolecular relaxation characteristics of macromolecules in ultradilute solutions (see, for example, refs 25−27).

Poly(dimethylacrylamide) (PDMAC)-based resins have found increasing use in a variety of synthetic applications ranging from, for example, polymer supports[28,29] for synthesis of proteins to catalysts for two-phase reactions.[30] In addition, several reports have discussed the role of PDMAC in formation of interpolymer complexes,[31,32] interpenetrating networks,[33] and hydrogels.[34,35] The solution properties of the homopolymer have been studied through the use of light scattering,[36] viscosity[36] and calorimetry.[37] However, to date, there have been no reports of the use of fluorescence measurements in the study of the dynamic behavior of PDMAC. Polyacrylamide and its derivatives also find applications in technologies based upon adsorption phenomena. In view of its strong propensity for H-bonding,[38] we decided to investigate the interactions of PDMAC at a variety of solid/water interfaces[39] and regard studies of the dilute solution properties of PDMAC as a necessary prelude to the adsorption experiments.

In this paper, we report upon these preliminary investigations, using fluorescence techniques, [particularly time-resolved anisotropy measurements (TRAMS)], to study the dynamic behavior of PDMAC in dilute solution and its interpolymer complex with poly(methacrylic acid).

Experimental Section

Materials. Acenaphthylene (ACE; Aldrich) was triply recrystallized from ethanol and triply sublimed under high vacuum. Dimethylacrylamide (DMAC; Aldrich) and methacrylic acid (MAA; Aldrich) were prepolymerized (UV radiation) and fractionally, vacuum distilled immediately prior to use. Benzene (BDH) and diethyl ether (May and Baker) were purified by fractional distillation. Methanol (Aldrich; spectroscopic grade), carbon tetrachloride (Aldrich; 99.9%), thallium nitrate (Aldrich; 99.999%), and nitromethane (Aldrich; Gold Label) were used withour further purification. Water was doubly distilled.

Fluorescently labeled poly(dimethylacrylamide) (ACE/PDMAC) was prepared by copolymerizing DMAC with *ca.* 0.5 mol % ACE in benzene solution at 60 °C using AIBN as initiator. Unlabeled PDMAC was prepared in a manner similar to that employed in the synthesis of the fluorescently labeled sample. Unlabeled poly(methacrylic acid) (PMAA) was prepared via free-radical polymerization in benzene solution using AIBN as initiator at 60 °C.

Purification of all polymer samples was accomplished by multiple precipitations from methanol into ether.

All spectroscopic samples prepared in methanol contained 10^{-2} wt % of polymer. For aqueous samples (10^{-3} wt % of polymer), the pH was adjusted by addition of sodium hydroxide, sulfuric acid (May and Baker), or hydrochloric acid (Aldrich; Spectrosol) as required.

Characterization. Estimates of the molar masses (M_n and M_w, respectively) were obtained using size exclusion chromatography (SEC). The sample volume was 0.25% w/v with an injection volume of 100 μL. The eluent was DMF (Fisons; GPC grade) containing 0.1% w/v LiBr, using a flow rate of 1 mL/min. Aniline was used as a flow rate marker. Relative molar masses were estimated using poly(ethylene oxide) calibration standards. The SEC system incorporated a Knauer 64 pump, a Rheodyne injector, a Knauer oven at 70 °C, Polymer Laboratories mixed B gel (2 × 30 cm) columns, and a Hewlett-Packard 1047A RI detector at 50 °C.

The molar mass characteristics of ACE/PDMAC were determined as $M_n = 97$K and $M_w = 170$K, respectively.

Instrumentation. Steady-state fluorescence spectra and anisotropy data were recorded on a Perkin-Elmer MPF-3L spectrometer. Pure unlabeled PDMAC solutions were used as corrective "scatter blanks" in all anisotropy determinations.

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Estimates of fluorescence "lifetimes" were obtained from time-resolved data recorded on an Edinburgh Instruments 199 spectrometer operating on the time-correlated single-photon-counting (TCSPC) principle. A nanosecond, thyratron-gated flashlamp (with H_2 as the discharge medium) was used as the excitation source.

Time-resolved fluorescence anisotropy measurements, using vertically polarized excitation, were performed using radiation from the Synchrotron Radiation Source, SRS (EPSRC, Daresbury Laboratory, UK). Collection of the fluorescence intensities transmitted by a polarizer, analyzing in planes parallel [$I_{||}(t)$] and perpendicular [$I_{\perp}(t)$] to that of the polarized excitation, was achieved by means of a "toggling procedure": the analyzer was rotated sequentially through 90° while memory quarters in the MCA (Inotech 5400) were switched simultaneously. Excitation and emission wavelengths of 290 and 340 nm, respectively, were employed. A description of the SRS and associated TCSPC detection system can be found elsewhere.[40]

Results and Discussion

Dynamic Behavior of Poly(dimethylacrylamide) in Dilute Methanol Solution. The rate of rotational reorientation of a chromophore can be determined through examination of the intensities of luminescence emitted in planes parallel, $I_{||}$, and perpendicular, $I_{\perp}$, to that of vertically polarized excitation. In the photostationary state, the anisotropy, r, is a measure of the extent to which fluorescence polarization is retained within the excited-state lifetime and is constructed according to eq 1.

$$r = \frac{I_{||} - I_{\perp}}{I_{||} + 2I_{\perp}} = \frac{D}{S} \tag{1}$$

The correlation time, τ_c, characteristic of rotational motion may be derived from steady-state anisotropy information via the Perrin relationship

$$r^{-1} = r_0^{-1}(1 + \tau/\tau_c) \tag{2}$$

where τ is the lifetime of the fluorescent excited state and r_0 is the intrinsic anisotropy of the chromophore.

Estimation of τ_c from empirical r data can be achieved through independent measurement of τ and r_0. The value of τ may be determined directly by, for example, TCSPC. Determination of r_0, however, requires extrapolation of empirical r^{-1} data to zero τ/τ_c. Considerable limitations exist in attempts to perform extrapolations of r^{-1} data to the limit of $\tau_c = \infty$ in polymer science.[25,26] An alternative approach is to reduce τ through the addition of varying amounts of a dynamic quencher[41] and extrapolate the associated r^{-1} data to $\tau = 0$. However, this procedure can also be problematic, particularly in investigations of polyelectrolyte samples in aqueous media.[42] (Indeed, one of the aims of the current investigation is to assess the suitability of this method of extrapolation to r_0^{-1} for an *uncharged* polymer in dilute aqueous solution.)

The Stern−Volmer equation relates the fluorescence intensity in the absence of quencher ($I°$) to that (I) for a given concentration ([Q]) of quencher by the relationship

$$\frac{I°}{I} = \frac{\tau°}{\tau} = 1 + k_q\tau°[Q] \tag{3}$$

where k_q is the bimolecular rate constant governing the collisional deactivation of the excited state. Table 1 lists the resultant k_q values for quenching of ACE/PDMAC

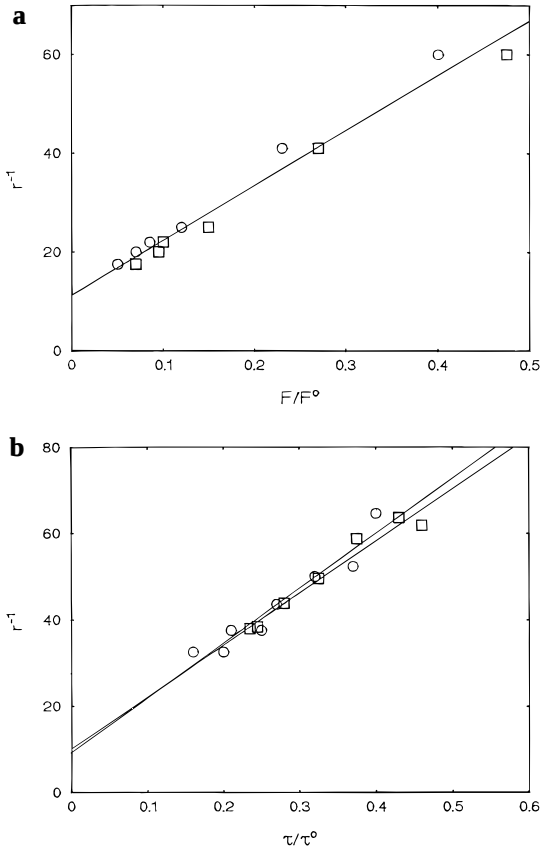

Figure 1. (a) "Perrin plot" for ACE/PDMAC (10^{-2} wt %) in methanol at 298 K. [F = fluorescence intensity (○) or lifetime (□); $F°$ = fluorescence parameter in absence of quencher (CCl_4)]. (b) "Perrin plot" derived from lifetime (τ) data for ACE/PDMAC (10^{-2} wt %) at pH 3.9 (○) and pH 1.2 (□) [$\tau°$ = lifetime in absence of quencher (Tl^+)].

Table 1. Bimolecular Quenching Constants Derived from Lifetime [$k_{q(\tau)}$] and Intensity [$k_{q(I)}$] data for ACE/PDMAC

Q	solvent	$k_{q(I)} \times 10^{-9}$ (dm^3 mol^{-1} s^{-1})	$k_{q(\tau)} \times 10^{-9}$ (dm^3 mol^{-1} s^{-1})
CH_3NO_2	water; pH 1.3	6.6	3.3
CH_3NO_2	water; pH 3.6	6.4	4.2
CH_3NO_2	water; pH 7.4	6.1	4.2
Tl^+	water; pH 1.0	4.8	3.1
Tl^+	water; pH 4.0	3.4	2.6
Tl^+	water; pH 10.7	3.4	2.7
CCl_4	methanol	3.7	3.0

by CCl_4 in methanol. Equivalent (within experimental error) intensity ($I°/I$) and lifetime ($\tau°/\tau$) quenching ratios were obtained at each quencher concentration (as required by eq 3). This infers that the quenching of the singlet excited state of the ACE label by CCl_4 occurs, in methanol, by a truly dynamic mechanism. The average value of k_q, of the order of 3.4×10^9 dm^3 mol^{-1} s^{-1}, is typical of that which would be expected for a freely diffusing quencher of fluorescence from a "tagged" polymer in dilute, low-viscosity solution.[43]

Figure 1a shows the variation of r^{-1} with $I/I°$ and $\tau/\tau°$ respectively for ACE/PDMAC in methanol using CCl_4 as the quencher. The resultant spectroscopic and relaxation parameters are listed in Table 2. Incorporation of the estimate of r_0^{-1} {10.7} into eq 2 with the value for the fluorescence lifetime appropriate to a given r^{-1} value results in an estimate of τ_c of 1.7 ns. Such a value would imply that ACE/PDMAC exists as a relatively flexible coil in dilute methanol solution at room temperature. However, although relaxation data resultant upon steady-state anisotropy analyses can, in

Table 2. Steady-State Fluorescence Anisotropy and Relaxation Data for ACE/PDMAC

solvent	r^{-1} [c]	r_0^{-1}	$\tau°$/ns (±0.2 ns)	τ_c/ns (±0.2 ns)
methanol[a]	114.0	10.7	18.1	1.7
water; pH 3.9[b]	136.4	8.4	36.1	2.3
water; pH 11.2[b]	130.0	10.0	35.7	3.0

[a] Using CCl_4 as quencher. [b] Using Tl^+ as quencher. [c] Estimates of r^{-1} (derived from "least-squares best fit" to "Perrin" plots) at $\tau/\tau° = 1$.

Table 3. Rotational Correlation Times Derived Using the Impulse Reconvolution (IR), Autoreconvolution (AR), and Direct Analysis (DA) Procedures of Data Analysis of TRAMS Data for ACE/PDMAC in Methanol at 298 K

τ_c(IR)/ns (±0.1 ns)	τ_c(DA)/ns (±0.1 ns)	τ_c(AR)/ns (±0.1 ns)
1.5	1.3	1.4

practice, compare well with those derived from time-resolved experiments,[44,45] problems can be encountered, particularly in investigations of certain water-soluble polymers.[42] Consequently, it would be reassuring to confirm the reliability of the steady-state approach in probing the segmental dynamics of the PDMAC/methanol system.

Time-resolved anisotropy measurements (TRAMS), where macromolecular dynamics can be measured *directly*, without need of addition of an external quenching species, can, in principle, overcome some of the limitations of a steady-state approach. For a pseudo-spherical rotor, characterized by a single correlation time τ_c, the time-dependent anisotropy function, $r(t)$, would adopt the form

$$r(t) = r_0 \exp(-t/\tau_c) + r(\infty) \qquad (4)$$

in which $r(\infty)$, the residual anisotropy, should be zero, under conditions of unrestricted rotation. However, the TRAMS approach has the additional advantage of allowing the anisotropy function to be analyzed in terms of more complex analytical forms than that of the single-exponential decay described by eq 4 (and assumed as the basis for the steady-state, extrapolative, approach), should this prove warranted.

In the current work, TRAMS were carried out on the ACE/PDMAC system, in methanol at 298 K, using radiation from the synchrotron (SRS, Daresbury) for excitation. The raw anisotropy data, $R(t)$, may be generated via eq 1, from the observed time-dependent intensity components, $I_{\parallel}(t)$ and $I_{\perp}(t)$ analyzed in planes parallel and perpendicular, respectively, to that of the vertically polarized pulse of excitation. Direct analysis (DA) of $R(t)$, using a single-exponential decay model of the form described by eq 4, yielded an estimate for τ_c of 1.3 ns under these conditions (*cf.* Table 3). Figure 2 shows a typical single-exponential fit to $R(t)$. On this evidence (as judged by the values of χ^2 and the randomly distributed residuals), application of a more complex mathematical model of the macromolecular dynamics could not be justified on statistical grounds. However, as we have reported earlier[40,46] (and will only briefly allude to here), there are distinct problems associated with this form of analysis, particularly (as in this case) when the rotational correlation time, τ_c, is comparable to the width of the observed excitation (instrumental response) profile. [The observed fluorescence responses, $I_{\parallel}(t)$ and $I_{\perp}(t)$, differ from the true response functions, $i_{\parallel}(t)$ and $i_{\perp}(t)$, at short times, due to the distorting influence of the excitation pulse. Hence, the combination function, $R(t)$, is also distorted compared to the true

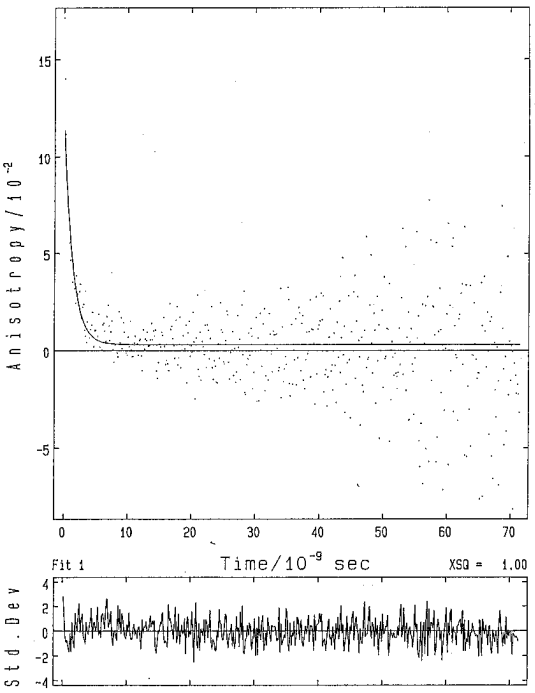

Figure 2. Direct analysis of anisotropy data for ACE/PDMAC (10^{-2} wt %) in methanol at 298 K.

anisotropy profile, $r(t)$, which we wish to model.] Furthermore, using this form of analysis, it is not possible to derive a value for the intrinsic anisotropy r_0. Consequently, there is considerable uncertainty in the "start channel" from which anisotropy decay analysis should be initiated. This creates further problems in that the anisotropy may be subject, at early sampling times, to distortions introduced by the presence of scattered radiation and timing instabilities, in addition to those induced by the finite width of the excitation pulse.

Some of these difficulties can be overcome in practice by using alternative forms of analysis. Impulse reconvolution (IR)[47,48] is the most reliable and sophisticated method developed to date for recovery of relaxational information from TRAMS data. The method recognizes the fact (by consideration of the definition of the anisotropy revealed in eq 1) that

$$\{Ir(t)\}\{Is(t)\} = \{Id(t)\} \qquad (5)$$

where $\{Ix(t)\}$ represents the impulse response function characteristic of the time dependence of $x(t)$, where $x = r$, s, or d. In the IR approach, the experimentally derived sum function is parameterized using a model function which achieves statistically adequate fitting to $S(t)$ in iterative reconvolution using the observed excitation prompt. The resultant $\{Is(t)\}$ is then combined with an assumed model for the true anisotropy decay, $r(t)$, in an iterative, least-squares reconvolution procedure to fit the observed difference data, $D(t)$. The resultant "best fit", $\{Ir(t)\}$, allows a judgement to be made regarding the complexity of the anisotropy decay kinetics and provides (within the limits of the adopted model) rate parameters characteristic of the relaxation process-(es) occurring in the system.

In autoreconvolution (AR)[40,46] (the most recently developed method for the recovery of rotational relaxation information from TRAMS) functional forms appropriate to modeling the decays of fluorescence, $s(t)$, and anisotropy are assumed. In the simplest case, when both the fluorescence and emission anisotropy obey a

first-order decay law, $i_{||}(t)$ and $i_{\perp}(t)$ (the "true" emission intensity profiles) are given by

$$i_{||}(t) = \exp(-t/\tau)[1 + 2r_0 \exp(-t/\tau_c)] \quad (6)$$

$$i_{\perp}(t) = \exp(-t/\tau)[1 - r_0 \exp(-t/\tau_c)] \quad (7)$$

Examination of eqs 6 and 7 reveals that $i_{||}(t)$ serves to augment $i_{\perp}(t)$ in a manner similar to that of an excitation "prompt" feeding a fluorescence decay. Consequently, the component of fluorescence observed in a plane parallel to that of the polarization of the excitation beam, $I_{||}(t)$, may subsequently be used to deconvolute $I_{\perp}(t)$ according to

$$I_{\perp}(t) = I_{||}(t) \otimes m(t) + aI_{||}(t) \quad (8)$$

where $m(t)$ is a single-exponential function when $i_{||}(t)$ and $I_{\perp}(t)$ are described by eqs 6 and 7, respectively, and

$$a = (1 - r_0)G/(1 + 2r_0) \quad (9)$$

(In the current synchrotron-generated TRAMS, a G factor of unity, within experimental error, was determined for all excitation/emission wavelengths accessed.

Both IR[47,48] and AR[40,46] analyses of the TRAMS data for ACE/PDMAC in methanol produced adequate fits when single-exponential functions of the form shown in eq 4 were used to model the time dependence of the anisotropy (*cf.* Table 3). Furthermore, the values of τ_c derived using all three forms of analysis (IR, AR, and DA) were, within experimental error, in agreement. [It is also gratifying to note that the τ_c derived from the steady-state approach (1.7 ns) agrees reasonably well with the relaxation data obtained using TRAMS.] The resultant estimate for τ_c of 1.4 ± 0.1 ns indicates that PDMAC, in methanol at 298 K, exhibits a segmental mobility which is similar to that of poly(acrylic acid) (PAA) under the same conditions[40] and of poly(methyl acrylate) in toluene at 298 K.[45] In this respect, the current data support the observations of Trossarelli and Meirone,[36] who concluded, on the basis of viscosity and light scattering measurements, that the dimethylamino group did not exert a major influence upon the configurational character of PDMAC when compared to other acrylic systems.

Dynamic Behavior of Poly(dimethylacrylamide) in Dilute Aqueous Solution. Examination of bimolecular quenching data can provide valuable information regarding the microenvironment experienced both by probes solubilized in[49] and labels covalently bound to[50−54] polyelectrolyte coils in aqueous media. In principle, information regarding polymer characteristics such as coil compactness and charge density may be accrued through comparison of the differing degrees of quenching induced in a variety of fluorescent labels by addition of certain small-molecule quenchers.

In studying ACE/PDMAC in aqueous solution at various values of pH, we have used two small-molecule quenchers of fluorescence: the thallous ion and nitromethane. It was thought that the use of the cationic quencher would furnish information regarding the efficiency of deactivation of the label's fluorescence over a wide pH range. The experiments would therefore report upon the polymer's conformational state under diverse conditions, in aqueous media. Furthermore, in conjunction with steady-state anisotropy data, the measurements would allow quantification of the polymer dynamics. In addition, this "heavy-atom" species might provide access to the triplet state of ACE: Tl^+ is known[54−56] to act as a promoter of room temperature stabilized phosphorescence (RTSP) in certain water-soluble polymers. If the PDMAC were to prove capable of sustaining RTSP in the ACE label, the phosphorescence might serve as a further spectroscopic route to interrogation of the polymer's behavior. Nitromethane (an example of a neutral quencher) has been widely used to quench fluorescence in the study of water-soluble polymers[51−54] and would therefore allow comparison between ACE/PDMAC and other aqueous systems (particularly polyelectrolytes).

Table 1 lists the resultant parameters characteristic of CH_3NO_2 quenching of the fluorescence of ACE/PDMAC at various values of pH. The data show clear evidence of a contribution from a static component to the quenching: the intensity ($I°/I$) and lifetime ($\tau°/\tau$) quenching ratios obtained at each quencher concentration are not equivalent. Indeed, static components appear to be a general feature of the quenching, by nitromethane, of the fluorescence of a variety of polymer−label combinations, even when dispersed in fluid *organic* solvents.[45] The dynamic quenching (represented by lifetime data) of the emission from ACE/PDMAC appears to be unaffected by pH. Values of k_q of the order of $(3-4) \times 10^9$ mol dm^{-3} s^{-1} were obtained. These are close to that expected for a diffusion-controlled interaction between a mobile quencher and a fluor bound to a polymer chain dissolved in water at 298 K. In this respect, the quenching behavior or ACE/PDMAC using nitromethane is similar in efficiency to that reported for poly(acrylic acid) at low pH[57] but much more efficient than that shown for the hypercoiled form of poly(methacrylic acid).[54] These observations are consistent with the view that PDMAC exists as a relatively open, hydrated, random coil regardless of pH.

Bimolecular quenching constants (derived from both lifetime and intensity data) for ACE/PDMAC using Tl^+ as quencher at three pHs are listed in Table 1. Consideration of these k_q values reveals that not only is the fluorescence quenching process largely dynamic (i.e., the intensity and lifetime ratios are equivalent at any given Tl^+ concentration) but that there is no real pH dependence on the efficiency of quenching of the ACE label by Tl^+. The value derived (*ca.* 3×10^9 mol dm^{-3} s^{-1}) is similar to that observed for CH_3NO_2 quenching of ACE/PDMAC in aqueous solution. Significantly, at high pH, the k_q value observed is a factor of 200 less than that reported[54] for Tl^+ quenching of a 1-vinylnaphthalene-labeled PMAA. Bimolecular quenching constants in excess of diffusion control have been observed[12,54] when quenching labeled polyacids with Tl^+ at high pH. Such effects have been attributed[12,54] to the presence of a high local concentration of Tl^+ ions in the vicinity of the fluor due to the attraction of the cations to the "negative charge cloud" of the polysalt. This high concentration of Tl^+, in turn, enhances[54] the observed intensity of *phosphorescence* from the chromophore as a consequence of the increased efficiency of quenching of S_1 (to populate T_1) and promotion of the radiative decay of T_1 (which also occurs via "contact" quenching). Subsequently, an appreciable level of RTSP can be observed[54] from oxygen-free solutions of the neutralized forms of labeled polyacids.

Following nitrogen purging of samples containing various concentrations of Tl^+, no appreciable level of phosphorescence was observed from ACE/PDMAC at *any* value of pH. This presumably reflects the fact that since PDMAC is uncharged, the high (local) concentrations of quencher, necessary for "superdiffusional"

Table 4. Relaxation Data Afforded by Impulse Reconvolution Analysis at 298 K

system	pH	τ_{c1}/ns	τ_{c2}/ns	$10^3 r(\infty)$	r_0	χ^2
ACE/PDMAC	1.8	3.4		2	0.10	1.1
	2.2	3.1		2	0.10	1.0
	3.3	3.3		2	0.10	1.1
	4.7	3.4		4	0.10	1.0
	6.3	3.4		1	0.11	1.1
	10.7	3.4		1	0.09	1.2
PDMAC:PMAA	0.5	24.0		70	0.11	0.9
(1:1 by weight)	5.5	3.3	30.4	20	0.11	1.2
	0.5	203.7		0	0.10	1.1[a]
	5.5	6.3	87.8	0	0.11	1.2[a]

[a] $r(\infty)$ fixed at 0.

quenching of S_1 and consequent promotion of RTSP, are not created in this system. These observations elucidate the role played by polymeric hosts in generation of RTSP from sequestered guests or labels using an external heavy-atom promoter: the principal function of the polymer is not to provide a "protective habitat" for the triplet states created but to generate a high local concentration of the heavy-atom quencher (through attraction, for example, of Tl^+ by the carboxylate anions in neutralized PAA and/or PMAA).

Since the thallous ion acts as a dynamic quencher across the pH range in this system, we have subsequently used it in order to reduce the excited-state lifetime of the ACE label and thence, using eq 2, extrapolate steady-state r^{-1} data to a value for r_0^{-1}. Figure 1b shows the variation of r^{-1} with $\tau/\tau°$ for ACE/PDMAC at low and high pH. The resultant anisotropy information for each pH, derived from the "Perrin plot", is listed in Table 2. Consideration of the values of τ_c estimated by this method reveals that the relaxation behavior of ACE/PDMAC is independent of pH. However, the τ_c values are somewhat larger than that of ACE/PDMAC in methanol. Since the opportunity for increased hydrogen-bonding interactions exist (e.g., intramolecular polymer−polymer and intermolecular polymer−solvent) for PDMAC in water relative to that in methanol, such a decrease in macromolecular mobility might be expected. However, given our reservations, expressed above, regarding the deficiencies of the steady-state anisotropy approach in characterizing the dynamic behavior of certain polymers in aqueous media, the authenticity of the relaxation information derived above should be verified. This can be done most conveniently using TRAMS.

Time-resolved anisotropy studies of the intramolecular segmental mobility of ACE/PDMAC were performed using radiation from the SRS. IR[47,48] analyses, using eq 4 as the model function, reveal that the relaxation behavior of the polymer is unaffected by pH and is characterized by a correlation time of 3.4 ± 0.4 ns (*cf.* Table 4). A typical fit is shown in Figure 3. At no pH was there any statistical justification in the use of a more complex function to model $r(t)$. In addition, both AR[40,46] and direct analyses of time-resolved anisotropy data for ACE/PDMAC provided similar estimates of τ_c to that of the IR[47,48] method at each pH studied.

Comparison of the relaxation data extracted from TRAMS (*ca.* 3.3 ns) with that estimated by the steady-state approach (*ca.* 2.7 ns) reveals a reasonable agreement between the two methods. Since steady-state estimates of τ_c are very sensitive to that of r_0, the lifetime range over which the extrapolation (to zero τ) is performed must be kept as short as possible. This, in turn, requires that a relatively large amount of

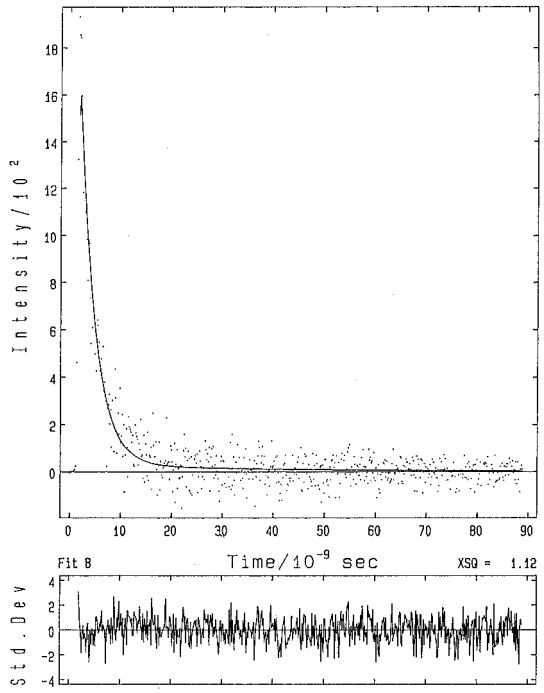

Figure 3. Difference function, $D(t)$, and impulse reconvolution fit for ACE/PDMAC (10^{-3} wt %) in aqueous solution at 298 K; pH = 3.3.

quencher be added to the system under study. One of the potential problems associated with this form of extrapolative procedure is that addition of such large amounts of quencher could perturb the solvent environment of the polymer and thence the motion that we wish to study. With the degree of hindsight afforded by the TRAMS experiments, it would appear that this is not the case with the current data. Indeed, given a relatively simple aqueous system where fluorescence quenching occurs largely by a dynamic process, it is clear that the steady-state approach can provide reasonable estimates of rotational correlation times of water-soluble polymers.

The TRAMS experiments indicate that PDMAC exists as a reasonably flexible species in aqueous solution: PDMAC exhibits a segmental relaxation rate which is intermediate between that of poly(methyl methacrylate) in toluene (*ca.* 2.1 ns[45]) and poly(methacrylic acid) in methanol (*ca.* 4 ns[40]) at 298 K. Comparison with other polymers in aqueous solution reveals that PDMAC has a flexibility comparable with that of the fully neutralized form of PAA[45] but is more mobile than the polyacid itself. In contrast, PDMAC enjoys a segmental relaxation rate which is much greater than that of PMAA[58] across the entire pH range. Pascal et al.[59] have reported a correlation time of 10 ns for an ACE-labeled polyacrylamide. All other things being equal, it would be expected (given our earlier observations upon the similarity between the inherent flexibilities of PDMAC, PAA, and PMA) that the segmental relaxation rates of PDMAC and polyacrylamide would be comparable. Presumably the 3-fold difference in rates of segmental motion between polyacrylamide and PDMAC must reflect differences in H-bonding interactions exhibited by the two polymers.

The complexation studies of Wang and Morawetz[31] have shown that the repeat units derived from acrylamide and DMAC, respectively, have different propensities for acting as acceptors in H-bonding interactions with PAA. Day and Robb[37] have observed that the

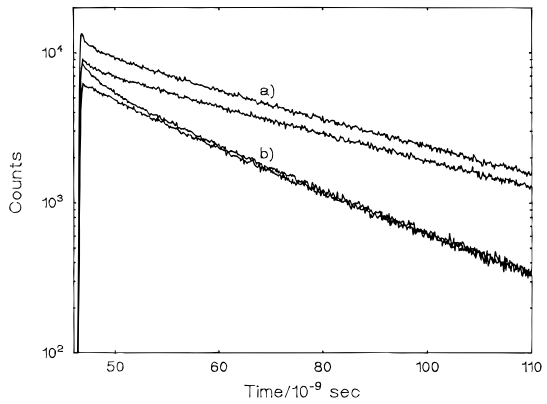

Figure 4. Parallel and perpendicular fluorescence components of the time-dependent anisotropy of ACE-labeled PDMAC (b) and PDMAC/PMAA complex (a) in highly acidic media (see text).

heats of dilution of polyacrylamide and PDMAC are of opposite thermicity in water: that of polyacrylamide is endothermic, while that of PDMAC is exothermic. However, these heats of dilution, reflecting the differences in enthalpies between two states of the system, do not, in themselves, give information regarding differences between the associative behaviors of the two polymers in dilute solution. However, even had such information been available, it would have been difficult to predict which of the polymers would appear to be the more flexible in aqueous solution: on the one hand, H-bonding to the solvent might serve to increase the bulk of the kinetic unit (polymer segment + solvent sheath), thereby reducing τ_c. Alternatively, increased polymer−solvent associations could also lead to a reduction in the number of intramolecular polymer−polymer interactions, promoting segmental mobility.

The TRAMS data confirm the inferences of the steady-state anisotropy experiments: PDMAC is a more flexible species in methanol than in water at 298 K. Trossarelli and Meirone[36] inferred, on the basis of unpertubed coil dimensions, that PDMAC would exhibit a greater flexibility in methanol than in water. Our observations agree with this conclusion but do not shed any light on the "abnormal behavior"[36] of the polymer in water.

Interpolymer Complex Formation with Poly(methacrylic acid). Polymers containing DMAC have the ability to form interpolymer complexes with polyacids. Wang and Morawetz[31] have shown, using fluorescence spectroscopy, that the complexation of copolymers of acrylamide and DMAC with PAA is critically dependent upon the DMAC content of the copolymer. PDMAC complexes with both PAA and PMAA.[39,45] In this paper, we present preliminary time-resolved anisotropy information on the effect of pH on a complex formed between PDMAC and PMAA. The dramatic effect that complexation between PDMAC and PMAA has upon the fluorescence characterstics of the ACE label of the PDMAC is exemplified in Figure 4. At a given pH, the fluorescence lifetime of the ACE label is considerably extended in the interpolymeric complex relative to that of the labeled, uncomplexed PDMAC. More importantly, it is to be noted that the fluorescence decays of the intensity components, $I_{\parallel}(t)$ and $I_{\perp}(t)$, characteristic of the complex, contain a markedly increased amount of anisotropy information compared to those of uncomplexed species.

At low pH (0.5), complexation appears to be complete: The anisotropy behavior, as revealed in impulse reconvolution, *appears* to be well described ($\chi^2 = 0.9$; residuals are randomly distributed) by a single-exponential model function of the form of eq 4. A value of τ_c of 24.0 ns evolves (*cf.* Table 4).

The "natural" pH of the complexing mixture (1:1 by weight; each polymer concentration being 10^{-3} wt %) of labeled PDMAC and PMAA is 5.5. At this pH, the anisotropy decay of the ACE label in the complexing system is afforded a reasonably statistically justified description ($\chi^2 = 1.4$) by a single-exponential function. An *apparent* value of τ_c of 16.7 ns results. However, examination of the distribution of the residuals and the associated autocorrelation function indicates that adoption of a more complex model function is justified. Dual exponential modeling of $r(t)$ of the form of eq 10

$$r(t) = r_1 \exp(-t/\tau_{c1}) + r_2 \exp(-t/\tau_{c2}) + r(\infty) \quad (10)$$

using IR analysis results in evolution of two anisotropy decay parameters, τ_{ci}, of 3.3 and 30.4 ns, respectively (*cf.* Table 4). Direct analysis of $r(t)$, which should be reliable for τ_c values of this magnitude considering the breadth of the instrument response function, yields values of 3.4 and 32.3 ns for τ_{c1} and τ_{c2}, respectively.

However, closer examination of the complexation data listed in Table 4 reveals that the analyses adopted produce high values for the residual anisotropy, $r(\infty)$. Similar problems have been encountered[39] in analyses of TRAMS data in other investigations of interpolymer interactions. These problems in analysis are a consequence of the very slow relaxation processes which characterize the solution behavior of the complex. In the presence of uncomplexed PDMAC (i.e., at either low molar base/acid ratios or pHs between 5 and 6), $r(t)$ will contain contributions from slower interpolymer relaxation processes and faster "free" PDMAC in solution. At lower values of pH and higher acid/base ratios, the anisotropy will be dominated by contributions from slower polymer relaxation processes: problems in attaining a unique mathematical solution are then experienced[39] since the fitting procedure has difficulties in distinguishing between a long-lived anisotropy and the "background". This results[39] in a strong cross-correlation between τ_c and $r(\infty)$ (eqs 4 and 10) when all the fitting parameters are allowed to vary freely. Since there is no reason to suppose that the relaxation of the PDMAC:PMAA complex should produce such a residual anisotropy in the fluorescence of its ACE label, we have analyzed the TRAMS data, imposing the restriction that $r(\infty) = 0$ to help the fitting procedure converge to a solution which produces a physically meaningful value of τ_c representative of the dynamic behavior of the complex. The resultant data are listed in Table 4.

The correlation time τ_{c1} produced in dual-exponential modeling of PDMAC:PMAA at pH 5.5 correlates reasonably well with that characteristic of intramolecular segmental relaxation of the ACE-labeled PDMAC in dilute aqueous solution (*cf.* Table 4). Its counterpart, τ_{c2} (*cf.* Table 4), is much less than that which results from single-exponential modeling of the anisotropy decay of the labeled PDMAC/PMAA complex at low pH (*cf.* Table 4). This would be consistent with a proposal that, at pH 5.5, interpolymer complexation is not complete. Furthermore, "deformities" exist in partially neutralized PMAA at pH 5.5 (in the form of carboxylate groups) which reduce the propensity for H-bonding with the PDMAC. Presumably the complex formed under these circumstances has a looser structure, involving less tightly bound segments, than that extant under

very acidic conditions. Consequently, at pH 5.5, it might be expected that the fluorescence anisotropy would contain contributions from both the complexed form of ACE/PDMAC and the uncomplexed form of the polymer, in dynamic equilibrium with its complexed counterpart. This interpretation seems to be in accord with observation. Clearly, further investigation using TRAMS of the effects of pH and variation of the base/acid ratio are warranted.

The relaxation behavior of the PDMAC/PMAA complex at low pH is characterized by correlation times greatly in excess of the excited-state lifetime of the ACE label. Such observations are consistent with the findings of previous TRAMS investigations of different polyacid/polybase combinations.[39,45,60] Since the duration of the excited state essentially establishes the time base for the TRAMS experiment, the ACE label in the current study might be considered "ill-matched" since $\tau_c \gg \tau$. Consequently, labeling with a longer-lived species such as vinylpyrene[39] might appear to be more appropriate and forms the basis of a continuing research program.

Conclusions

1. PDMAC behaves as a relatively flexible polymer in methanol. The correlation time of *ca*. 1.4 ns, characteristic of intramolecular segmental motion of the polymer, is comparable to that obtained, at 298 K, using TRAMS, for poly(acrylic acid)[40] in the same solvent.

2. Intramolecular segmental relaxation of PDMAC in aqueous media is slower (by a factor of *ca*. 2.4) than that observed in methanol: PDMAC exists as a flexible and relatively open coil whose behavior is largely unaffected by changes in pH.

3. PDMAC complexes with PMAA. The complexation behavior is pH-dependent. In highly acidic media, complexation between PDMAC and PMAA appears to be complete: rotational reorientation of the complex is characterized by a correlation time of *ca*. 200 ns. At higher pH values, TRAMS data reflect the existence of an equilibrium between complexed and uncomplexed macromolecules.

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Dedication

This paper is dedicated to the memory of the late Gordon Thorpe, a dear friend and colleague.

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