expressed as a function of p':

$$\alpha' = 2(1 - p' - 1/\bar{x}_n') \quad \text{(A1)}$$

which, together with eq 15, is then substituted into eq 13 to yield a quadratic equation in p'. Only the larger root is physically meaningful, and this takes the form

$$[-B + (B^2 - 4AC)^{1/2}]/2A \quad \text{(A2)}$$

where

$$-B = 5\bar{x}_w' + 1 - 4r' - 2/\bar{x}_n'$$

$$A = 4\bar{x}_w' + 2$$

$$C = \bar{x}_w' - 3 + 2/\bar{x}_n'$$

$$r' = \bar{x}_w'/\bar{x}_n'$$

Values of p' thus obtained are listed in the fourth column of Table II. From eq A1 and 15, α' and $\bar{y}_w'$ can be obtained.

Likewise, α can be eliminated from eq 10 and 11, and the result is a quadratic equation in u with the solution again in the form of (A2). The coefficients are

$$-B = s(1 - \alpha')$$

$$A = 1$$

$$C = s\alpha'$$

Since s is a measured quantity and α' calculated from (A2), the values of u can be calculated. α and α'' are then calculated by using eq 10 and 9, and these are listed in Table III.

Registry No. Lignin, 9005-53-2; dioxane lignin, 8068-03-9.

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Photophysical Studies of a Water-Soluble Copolymer of Methacrylic Acid and 1-Pyreneacrylic Acid

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ABSTRACT: The chromophore pyrene was located in poly(methacrylic acid) in three different ways: (a) as a guest molecule by simple solubilization, (b) covalently attached to the polymer ends, and (c) randomly bound to the chain. The photophysical properties of pyrene, fluorescence, and triplet–triplet absorption were then used to investigate the nature of the chromophore environment on the polymer and the restriction placed by the polymer on movement of reactive molecules to pyrene. pH, which markedly affects the architecture of the polymer (closed coil at low pH (<4), randomly open coil at higher pH (~6)), had a marked influence on the observed kinetics. The effect of pH was interpreted for each probe situation (a, b, and c) as related to the position of the chromophore with respect to the water interface, or the degree of penetration of water into the polymer coil, and the ease of exit of nonbound pyrene (situation a). Some studies on poly(acrylic acid) are also reported and compared to those for poly(methacrylic acid). It is concluded that photophysical methods are powerful techniques for the study of dynamics of polyelectrolytes.

Introduction

The past decade has seen an increasing interest in the effects of organized assemblies on photochemical reactions.[2–4] For the most part micelles and microemulsion systems have been studied where the photosystem of interest is solubilized either partly or completely by the organized assembly. On excitation the micelle or its surface participates in the reaction and directs certain reaction features of interest. Such studies have many applications in model systems for the storage of energy and also as models for the solubilization of organic molecules by biosystems. One of particular interest is the solubilization of carcinogenic materials by DNA.[5] Several other systems serve to solubilize insoluble organic molecules in aqueous systems by providing a vehicle for the molecule of interest; e.g., clay systems or colloidal clays solubilize organic materials in many river systems, while caffeine can effectively solubilize molecules such as pyrene in water.[6] Of immediate interest is the possibility of using polymers for such studies. For example, there are reports of the solubilization

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of organic molecules by poly(methacrylic acid) in its closed compact form.[7,8] These studies show that pyrene and other aromatic molecules were solubilized only in the compact form of an aqueous solution of poly(methacrylic acid) (PMA) below a degree of ionization 0.2. The extended form, which occurs at higher degrees of dissociation of the acid, does not lead to solubilization. Spectroscopic studies showed that pyrene when solubilized in such a system experienced a more hydrophobic and more rigid environment than it would experience in comparable micelle systems.[8] Other studies show similar photophysical effects for dyes solubilized by PMA and other polyelectrolytes[9] and for dansylated copolymers of maleic anhydride and alkyl vinyl ethers.[10] In order to extend these studies further, a copolymer of methacrylic acid with 1-pyreneacrylic acid with not more than one pyrene unit included per polymer chain was constructed. The pyrene chromophore was bound randomly in the PMA chain and also at the polymer ends. Studies with these polymers were compared to earlier studies where pyrene was solubilized (not bound) in poly(methacrylic acid) at random. The interests in such a system lie in the fact that nonbound pyrene is solubilized only in compact PMA systems, at pH <4, while if the polymer is extensively extended, pH >5, the pyrene is not solubilized by the polymer and residues in the aqueous phase. With pyrene covalently bonded to PMA it is possible to carry out studies of the environment of the polymer under all pH conditions and also to ascertain the effect of such conditions on the approach of other molecules to the polymer, molecules that quench with excited pyrene.

Experimental Section

1-Pyreneacrylic acid was made according to the standard procedure (Elsevier's "Encyclopedia of Organic Chemistry", Vol 14, p 442S).

Preparation of Polymer. Copolymers of 1-pyreneacrylic acid with both methacrylic acid and acrylic acid were made by polymerization of the appropriate materials in dimethylformamide with AIBN as initiator. A typical sample was 4.0 g of methacrylic acid monomer, 0.1 g of 1-pyreneacrylic acid, and 0.02 g of initiator in 25 mL of solvent, dimethylformamide. The monomer methacrylic acid (Aldrich) was purified by vacuum distillation. 1-Pyreneacrylic acid was purified by recrystallization from methanol. Polymerization proceeded in the above mixtures under a nitrogen atmosphere at 70 °C for 20 h. The copolymer was precipitated and washed with diethyl ether four or five times, reprecipitated from dimethylformamide (DMF), and finally vacuum-dried. These samples contained pyrene randomly bound to the polymer chain. A copolymer of PMA with pyrene as a end group was prepared by polymerizing methacrylic acid and bromopyrene, where the latter molecule acts as an inefficient chain-transfer agent. The molecular weight of the polymer was measured by standard viscosity techniques. The ratios of 1-pyreneacrylic acid and methacrylic acid in the polymer were determined on a Perkin-Elmer 552 UV spectrophotometer, using the characteristic absorption spectrum for a substituted pyrene and established extinction coefficients in the 3300-Å region. For example, the following numbers were obtained: the mole ratio of pyrene to monomer in the polymer for poly(methacrylic acid) was 1 to 1390 and the molecular weight of this polymer was 1.2×10^5, while for poly(acrylic acid), a ratio of 1 pyrene for 1150 acrylic acid units was obtained, the molecular weight of this polymer being 8.3×10^4. Repeated solution of the copolymers in water followed by freeze-drying did not change the fluorescence content of the material. Spectroscopic and quenching data confirm that all pyrene was bound to PMA.

Pyrene fluorescence spectra were measured on a Perkin-Elmer MPF 44 spectrofluorometer. The lifetime of pyrene fluorescence was measured by a standard pulsed technique following excitation of the pyrene with a Lambda Physik EMG 100 nitrogen laser with a 6-ns pulse.[11] The quenching rate constant of excited pyrene by added quenchers were measured either directly by the rate of increase of decay of the excited state on addition of quencher molecules or from the Stern–Volmer[11] type behavior of fluorescence quenching measured on the spectrofluorometer. In this latter technique the intensity I_0 of the emission in the absence of quencher to that in the presence of the quencher, I, is related to the quenching rate constant (k_q), the natural pyrene fluorescence lifetime (τ_f), and the quencher concentration ([Q]) by the relationship

$$I_0/I = 1 + k_q\tau_f[Q]$$

All solutions were prepared with deionized water, and all quenchers were purified by recrystallization from a suitable solvent.

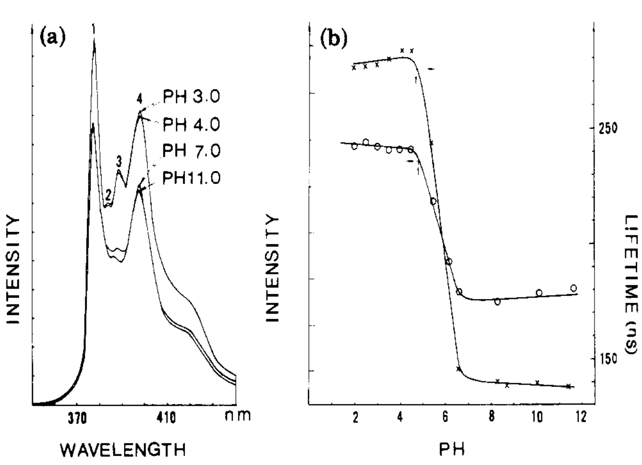

Figure 1. Fluorescence characteristics of a 10^{-2} M methacrylic acid–1-pyreneacrylic acid copolymer in aqueous solution: (a) emission spectra of deaerated copolymer at various pHs; (b) relative intensity and lifetime of bound pyrene in copolymer as a function of pH in aerated solutions.

Experimental Data and Discussion

Several studies[12-15] have shown that the degree of ionization of poly(methacrylic acid) is increased by addition of alkali and that the polymer chain tends to open or uncoil in the pH range 3–4, where the degree of ionization of the acid, α, is about 0.2.

Spectroscopic Data. Previous fluoroescence studies using pyrene solubilized in poly(methacrylic acid)[8] have shown that a sharp charge in photophysical properties occurs as the polymer opens (pH >3–4) and ejects pyrene into the aqueous phase, where it exhibits a decreased fluorescence quantum yield and lifetime. The data given in Figure 1a show the effect of pH on a copolymer of 1-pyreneacrylic acid and methacrylic acid. It can be seen that in the compact or closed coil, at pH ~3, the pyrene fluorescence spectrum consists of four peaks, marked 1–4. The observed fluorescence spectra are typical of a substituted pyrene in a nonpolar environment. however, a distinct change in the fluorescence spectrum is observed as the pH increases and the polymer opens such that pyrene, although still bound to the polymer, comes into contact with the aqueous phase. Figure 1 shows that increasing pH leads to a sharp decrease in the ratio of peak 3 with respect to peak 1. Similar effects are observed for unbound pyrene[8] and for end-bound and randomly bound pyrene. Figure 1b shows that fluorescence intensity and the lifetime of pyrene fluorescence as a function of pH. It can be seen that at pH ≥4 a sharp decrease in fluorescence yield and a sharp decrease in the fluorescence lifetime occur as the pyrene probe experiences more polar environments at higher pH. The effect apparently reaches a limit at pH ~7. It should be noted that the midpoint of this transition is at pH 5.7. The pH–fluorescence yield or pH–lifetime plots exhibit a transition point that is at

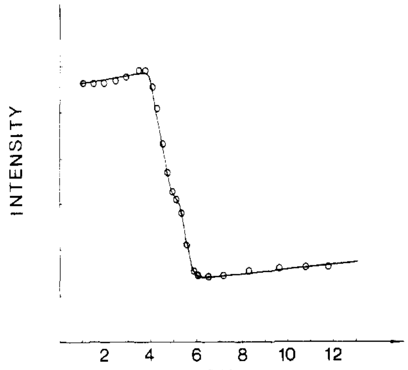

Figure 2. Relative fluorescence intensity vs. pH in aerated 10^{-2} M copolymer solution containing 10^{-5} M pyrene.

higher pH values for bound pyrene than observed earlier for the nonbound pyrene contained as a guest molecule in a simple poly(methacrylic acid) system.[8]

However, if pyrene is added to this particular system, so that the system consists of pyrene bound to the polymer as well as pyrene solubilized by the polymer, then the fluorescence vs. pH data observed are as shown in Figure 2. It is quite clear that there is initially a transition starting around pH 3.5 which is completely at pH ~5, followed by a shoulder or second transition at pH 5.5. The first transition is associated with an initial opening of the polymer chain, which leads to ejection of unbound pyrene into the aqueous phase and leads to a decrease in the fluorescence of the bound pyrene. The further decrease at pH 5–6 is consistent with a further opening of the polymer and with greater water contact with bound pyrene, which also leads to a decreased fluorescence. These data indicate that the two methods of probing the polymer coil reveal successive stages for opening of the PMA system. The data also indicate that even though the polymer is coiled at pH ~5 and not completely opened into a random form, nevertheless unbound pyrene is no longer solubilized by this system. However, bound pyrene is still maintained by the polymer and can be useful as an indicator of further changes in the polymer coil at higher pH and further degrees of uncoiling.

Quenching Reactions. The change in the environment of bound pyrene on neutralization and uncoiling of the polymer can also be demonstrated by the restrictive effects that the polymer imposes on the approach of quencher molecules such as thallium or iodide ions to pyrene solubilized in or bound to the polymer. Earlier studies[8] showed that it was indeed very difficult for ionic quenchers to traverse the polymer and react with pyrene located in the polymer coil. Similar behavior is found for bound pyrene, and Figure 3 shows the decrease in the fluorescence of pyrene bound to poly(methacrylic acid) vs. pH in the presence of Tl^+ ions. Again, it is seen that as the polymer coil starts to open, the effectiveness of the quencher Tl^+ in quenching bound pyrene increases and leads to a decrease in the intensity of pyrene fluorescence. These data show a more marked decrease in fluorescence yield than the data in the absence of Tl^+ (Figure 1). The same kinetic picture, that the hydrophobic environment of the polymer chain denies entry of H_2O, thallium, or iodide to the pyrene bound to the polymer, may be used for both systems. However, as the chain is expanded the pyrene environment becomes progressively more polar as water penetrates to the probe, a situation that also allows the ionic quenchers to more readily approach pyrene. In the case of thallium, the negative charge of the polymer increases the local concentration of these cations around the polymer, which leads to a dramatic increase in quenching with increasing pH and increasing negative charge of PMA. In the case of iodide the effect is not as remarkable as the thallium, even in the uncoiled case, tends to be repelled by the negative charge.

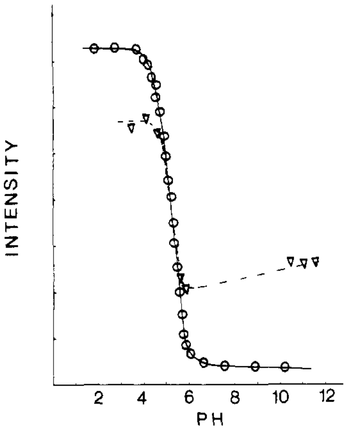

Figure 3. Effect of Tl^+ and I^- on the relative fluroescence intensity of aerated copolymer solution. (○) 4×10^{-4} M $TlNO_3$ in 10^{-2} M copolymer; (▽) 5×10^{-2} M NaI in 10^{-2} M copolymer.

Table I
Quenching of Bound Pyrene in Methacrylic Acid–1-Pyreneacrylic Acid Copolymer for Various Quenchers

quencher	pH	k_q, M^{-1} s^{-1}	A^b
$TlNO_3$	2.5	4.3×10^7	5×10^2
	11.8	2.4×10^{10}	
$CuSO_4$	2.2	1.1×10^8	1×10^2
	7.2	1.2×10^{10}	
O_2	2.5	5.4×10^8	6.3
	11.8	3.4×10^9	
NaI	2.5	7.2×10^6	6.8
	11.8	5.2×10^7	
CH_3NO_2	4.0	5.4×10^8	13
	7.0	7.0×10^9	
CPC[a]	2.2	1.6×10^{10}	1.2
	7.2	1.9×10^{10}	

[a] Cetylpyridinium chloride. [b] $= k_q(\text{uncoiling})/k_q(\text{coiling})$.

Table I lists data on the quenching of bound pyrene in methacrylic acid–1-pyreneacrylic acid copolymer for various quenchers at pH 2.5 and around pH 11.8, i.e., where the polymer coil is completely closed and where it is completely open. The quenching values tend to increase as the polymer chain opens. For the neutral quencher oxygen, there is a slight increase, a factor of 6, on opening of the polymer to expose pyrene to the aqueous phase. The effect is larger in the case of the other neutral quencher, nitromethane, where an increase of about 13 is observed, which again shows greater access of the quencher to pyrene when there is an aqueous phase surrounding it. These data show that O_2 tends to penetrate the polymer coil to a much greater extent than CH_3NO_2. However, some quenchers such as cetylpyridinium chloride (CPC) show no particular effect on opening or closing of the polymer. This is associated with a binding of this cationic surfactant to both the closed- and open-chain polymer, a situation where its relative effectiveness in quenching would be similar in both cases. The quenching with CPC is not a dynamic quenching, as observed with Tl^+, O_2, and CH_3NO_2, but static. The data for CPC quenching do not exhibit a change in fluorescence lifetime with incresing quenching concentration, but merely a decrease in fluorescence intensity. The quencher CPC binds close to the pyrene at all polymer configurations and quenching is extremely rapid compared to the fluorescence lifetime. Other pos-

Table II
Quenching of Bound Pyrene in Acrylic Acid–1-Pyreneacrylic Acid Copolymer for Various Quenchers

quencher	pH	k_q, M^{-1} s^{-1}	A^a
$TlNO_3$	2.0	2.2×10^{10}	50
	7.2	1.0×10^{11}	
$CuSO_4$	2.1	2.1×10^{9}	21
	7.6	4.5×10^{10}	
O_2	2.0	3.7×10^{9}	1.0
	7.5	3.6×10^{9}	
NaI	2.0	1.0×10^{8}	1.0
	8.0	1.0×10^{8}	
CH_3NO_2	2.2	3.5×10^{9}	1.1
	7.2	3.9×10^{9}	
CPC	2.0	1.4×10^{11}	0.2
	6.7	2.1×10^{10}	

[a] $=k_q(\text{uncoiling})/k_q(\text{coiling})$.

itively charged quenchers such as thallium and cupric ion show a much larger quenching efficiency when the polymer is neutralized and the coil is open. This is due to greater access of these ionic quenchers to the pyrene in the open coil state and also to the fact that these cations are more strongly bound to the unwound polymer, which has a larger negative charge.

Table II shows quenching data for the acrylic acid–1-pyreneacrylic acid copolymer. The data are similar to those for the copolymer with PMA (Table I), apart from the fact that the effects are much smaller. This indicates that poly(acrylic acid) is more loosely coiled than poly(methacrylic acid) in the closed compact form, allowing greater access of the quenchers to the bound pyrene, as observed. Similar effects of alkyl side chains have been observed for other polymers in aqueous solution.[10]

Further evidence to support binding of cations to the neutralized anionic polymer is provided by the effect of thallium ion quenching on 1-pyrenesulfonic acid in water. This derivative of pyrene is not solubilized by the polymer either in the compact form or at a pH of 7 when the polymer is fully stretched. 1-Pyrenesulfonic acid is quenched efficiently by thallium ions; the rate constant for this reaction in aqueous solution is 2.1×10^{10} L mol^{-1} s^{-1}. However, when 2×10^{-2} mol of poly(methacrylic acid) is added to this system at pH 7, the rate constant drops to 0.9×10^{10} L mol^{-1} s^{-1} and thallium ions, about 50%, are bound to the anionic polymer and are no longer available for quenching of pyrenesulfonic acid in the aqueous bulk. The effect if not quite as large with poly(acrylic acid); the rate constant drops to 1.1×10^{10} L mol^{-1} s^{-1}. These data confirm the mechanism of cation quenching shown in Tables I and II, namely, that cations bind to the neutralized polymer or extended polymer.

It was indicated earlier that the degree to which pyrene fluorescence is decreased with increasing pH depends on whether the pyrene is bound to the internal part of the polymer chain or whether it is loosely held or solubilized by the polymer. Different arrangements of pyrene and PMA can be achieved, and the data are shown in Figure 4. This figure shows the effect of pH in decreasing the fluorescence intensity of pyrene bound randomly to a PMA polymer as indicated previously, solubilized in the polymer, and bound to the end of the polymer. In all cases the same concentration of polymer was used and the pyrene content was 10^{-5} mol/L; the experiments were carried out in air to maximize the fluorescence intensity change with pH, as oxygen produces a much larger quenching of the opened polymer. As indicated before, pyrene merely solubilized in PMA polymer shows a decrease in fluorescence at a lower pH than that observed for pyrene randomly bound to PMA. However, pyrene bound to the end of the polymer also shows an earlier transition point. This is indicative of the fact that pyrene bound at the end of the polymer might be solubilized closer to the PMA–water interface. Unwinding of the polymer with increasing pH releases the polymer ends more effectively than the polymer core. Pyrene attached to the ends thus experiences an aqueous environment at an earlier stage than randomly bound pyrene.

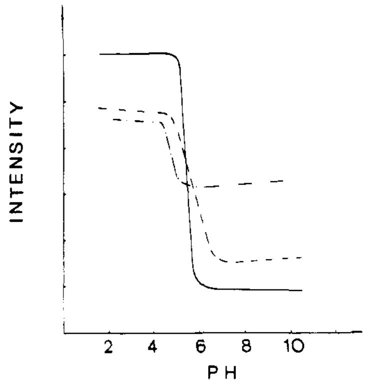

Figure 4. Effect of arrangement of pyrene ([pyrene] = 10^{-5} M) on the transition point with pH: (—) pyrene bound to the end of the copolymer; (- - -) pyrene bound randomly in the copolymer; (-·-) free pyrene in poly(methacrylic acid).

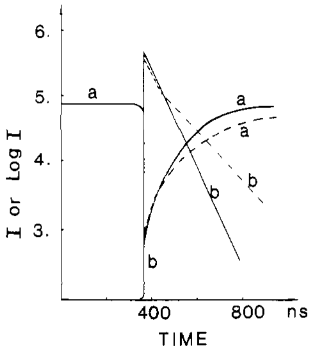

Figure 5. Fluorescence decay for bound pyrene in the aerated copolymer at pH 3 (- - -) and at pH 10 (—). *I* refers to fluorescence intensity; (a) refers to *I* vs. time and (b) refers to log *I* vs. time.

The above experiments tend to indicate that a polymer which contains randomly bound pyrene might provide a heterogeneous environment for the pyrene; in other words, it is possible that the coiling of such a polymer might lead to a condition where some pyrene is located close to the surface of the coiled polymer, whereas some pyrene is in the interior. In fact, evidence for such an effect can be obtained from both fluorescence quenching and fluorescence lifetimes of pyrene in a pyrene–PMA copolymer with pyrene bound randomly to the chain. For example, Figure 5 shows the fluorescence decay vs. time of bound pyrene in the aerated copolymer of methacrylic acid with 1-pyreneacrylic acid at pH 3 and at pH 10, i.e., where the polymer is closed and opened, respectively. At pH 10, conventional fluorescence decay behavior is obtained, and a single-exponential decay for the pyrene is observed, indicating that it has a unique environment, i.e., that of being bound to the polymer while also in an aqueous environment. The fluorescence lifetime under these conditions is 140 ns. However, in the bound condition in an aerated solution at pH 3, two distinct exponential decays are observed, 65% of which decays with a lifetime of 160 ns and 35% of which decays with a lifetime of 276 ns, while in deaerated solutions the lifetimes are 180 and 294 ns, re-

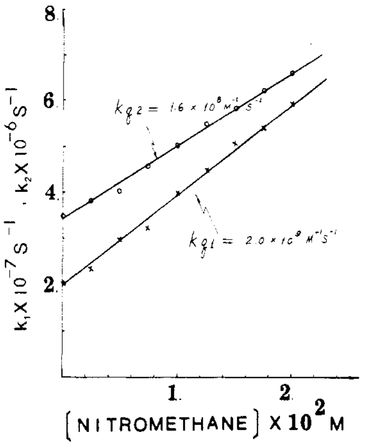

Figure 6. Plot of rate constants for decay of bound pyrene fluorescence in 10^{-2} M copolymer, pH 2.8, with increasing concentration of nitromethane.

spectively. The two lifetimes are obtained by fitting the data, such as those shown in Figure 5, by a double-exponential expression of the form

$$I_t = I(0)[\alpha e^{-k_1 t} + (1-\alpha)e^{-k_2 t}] \qquad (1)$$

where k_1 and k_2 are the rate constants for two different exponential decays of the excited species and α indicates the fraction that decays with a rate constant k_1. I_t and $I(0)$ are the fluorescence intensities at time t and $t = 0$, respectively. The faster lifetimes approach that obtained in the open system and are indicative of pyrene that is located close to the surface, while the longer one of 276 ns (air) or 294 (N_2) is indicative of pyrene that is located away from the water and in the hydrocarbon coil.

Addition of nitromethane to the systems leads to an increased rate of fluorescence decay for both pyrene sites. Figure 6 shows the increase in both rate constants k_1 and k_2 extracted from the previous expression, keeping α constant at 0.65, with nitromethane concentration. Rate constants for quenching, k_{q_1} (2.0×10^9 M^{-1} s^{-1}) and k_{q_2} (1.6×10^8 M^{-1} s^{-1}), are then obtained from the slopes of the lines according to the equation $k = k^0 + k_q[Q]$.

The steady-state data also agree with this kinetic analysis via the following equation, which describes the fluorescence intensity I at a specific quencher concentration where the rate constants are k_1 and k_2 (the superscript zero refers to zero [quencher]):[11]

$$I_0/I = \left(\frac{\alpha}{k_1^0} + \frac{1-\alpha}{k_2^0}\right) \Bigg/ \left(\frac{\alpha}{k_1} + \frac{1-\alpha}{k_2}\right)$$

Table III shows a comparison of calculated and observed I_0/I. The calculated I_0/I are derived from the above equation with $\alpha = 0.65$ and k_1^0, k_2^0, k_1, and k_2 measured from the pulsed experiments. The agreement of the data shows that all quenching is dynamic in character.

It is suggested that pyrene, with the shorter fluorescence lifetime and exhibiting the more rapid quenching by CH_3NO_2, resides at the outer region of the polymer coil and close to the aqueous phase.

Quenching of the Pyrene Triplet State. It is also possible to observe the pyrene triplet state in polymer–pyrene systems by observing the pyrene triplet by its characteristic absorption at 4150 Å by flash photolysis studies.[15] Figure 7 shows typical data for the quenching of the pyrene triplet state by oxygen at pH 7 and at pH 3. At pH 7, a single decay curve is observed, indicating one site for pyrene, in agreement with earlier fluorescence quenching data. The O_2–pyrene triplet quenching rate constant is 1.0×10^9 M^{-1} s^{-1}, which is some 10 times smaller than that measured for this reaction in homogeneous solution. This again indicates the restriction that PMA places on oxygen movement to the pyrene triplet. However, at pH 3, where the polymer is coiled, two distinct quenching regions are observed. The initial fast O_2 quenching of pyrene triplet occurs at a rate constat k_q of 2.13×10^8 M^{-1} s^{-1} followed by a much slower rate, a k_q of 0.41×10^8 M^{-1} s^{-1}. These data indicate a region of pyrene that is close to the surface where O_2 accessibility to pyrene is high and a region that is further into the polymer coils where O_2 accessibility is lower and where triplet quenching occurs more slowly. Both of these quenching rate constant are significantly smaller than observed in homogeneous solution, indicating the protective nature of the polymer chain on pyrene attached to it.

Table III
Comparison of the Experimental and Calculated Values of Quenching of Bound Pyrene in Methacrylic Acid-1-Pyreneacrylic Acid Copolymer at pH 2.8 (N_2 Degassed) by Nitromethane[a]

[Q] × 10^2, M	I_0/I obsd	I_0/I calcd
0.25	1.16	1.14
0.50	1.32	1.29
0.75	1.51	1.43
1.0	1.59	1.57
1.25	1.74	1.70
1.50	1.81	1.85
2.00	1.95	2.11

[a] $\alpha = 0.65$; $I_0/I = [\alpha/k_1^0 + (1-\alpha)/k_2^0]/[\alpha/k_1 + (1-\alpha)/k_2]$. This follows from the integration $I = k_r\int_0^\infty I_t\,dt$ and eq 1. The same radiative rate constant is taken for both regions, which is confirmed by the good agreement of both calculated and experimental data.

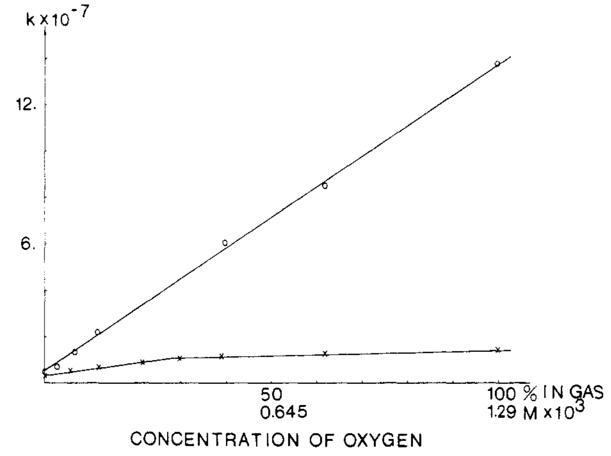

Figure 7. Quenching constant of excited triplet of bound pyrene in copolymer by oxygen: (O) at pH 7 ($k_q = 1.0 \times 10^9$ M^{-1} s^{-1}); (X) at pH 3 ($k_{q_1} = 2.13 \times 10^8$ M^{-1} s^{-1}; $k_{q_2} = 0.4 \times 10^8$ M^{-1} s^{-1}).

Effect of Surfactants on Pyrene Bound to Poly(methacrylic acid). The surfactant CPC efficiently quenches pyrene bound to PMA, and analysis of the data suggest that CPC binds to both the compact and stretched forms of PMA. At high CPC or other cationic detergent (e.g., cetyltrimethylammonium bromide (CTAB)) concentration, the PMA precipitates out of solution. Anionic, cationic, and neutral surfactants have little effect on the photophysical properties of pyrene in PMA, unless the surfactant contains a quenching group as with CPC. This indicates little change in aqueous solutions of PMA on

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interaction with surfactants.

Conclusion

The present work shows that copolymers of 1-pyreneacrylic acid with methacrylic acid and acrylic acid show significant structural changes with pH, structural changes that affect the pyrene environment. The changes may be interpreted in terms of what is already known from NMR, light scattering, and other physical measurements with regard to PMA unwinding with increasing pH. This lends support to the present studies on insights that can be gained from photophysical studies of probes, either solubilized or bound to polymer systems. In particular, the location of the probe molecule, either at the chain end, randomly bound to the chain, or simply solubilized in compact PMA, indicates different stages of opening of the polymer as its degree of dissociation increases. In each case a discrete pH region is indicated. However, the uncoiling of PMA appears to be a continuous process over several pH units. The present studies show that the fluorescent probe pyrene is a sensitive indicator of the conformational behavior of PMA. Water-soluble polymers are often used as solubilizing or stabilizing agents for many colloidal systems such as clays, where the polymer may bind to the clay edge and prevent flocculation. Little is known about the nature of this binding, but copolymers containing fluorescent probes could give useful information on the nature of the polymer colloid binding, e.g., on the environment of colloidal clay edges.

Registry No. $TlNO_3$, 10102-45-1; $CuSO_4$, 7758-98-7; O_2, 7782-44-7; NaI, 7681-82-5; CPC, 123-03-5; (1-pyreneacrylic acid)·(methacrylic acid) (copolymer), 91816-90-9; (1-pyreneacrylic acid)·(acrylic acid) (copolymer), 91816-91-0; pyrene, 129-00-0; poly(methacrylic acid), 25087-26-7; nitromethane, 75-52-5.

References and Notes

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Monte Carlo Calculations of Particle Scattering Functions of Polymer Chains

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ABSTRACT: Relationships between particle scattering functions and chain structure are investigated through calculations of $P(Q)$ for unperturbed polymethylene (PM), poly(oxyethylene) (POE), and poly(dimethylsiloxane) (PDMS) chains of up to 150 skeletal bonds. The calculations employ a Monte Carlo technique with Metropolis sampling and realistic rotational isomeric state models (RISM) using established molecular parameters. $P(Q)$ is calculated for each accepted configuration of a Metropolis sample using the exact Debye expression for a collection of point scatterers. For PM and POE, scattering centers are assumed to be located in the chain backbone, and for PDMS the effect of offsetting the scattering centers to account for the methyl side groups is investigated. Differences in contrast factors between chain segments and background medium, which are important for comparisons with experimental data, are also taken into account and are shown to affect the form of $P(Q)$ in the intermediate-Q and high-Q regimes. A moment expansion method used previously in the literature is investigated for PM and shown, except for $Q < 0.1$ Å^{-1}, to give values of $P(Q)$ in poor agreement with those from the full, Monte Carlo procedure. The effects of chain length, chain structure, and flexibility (temperature) on the form of $P(Q)$ are illustrated and discussed.

Introduction

Small-angle neutron scattering (SANS)[1-4] allows measurements of the scattered intensity from polymeric systems to be made over a much wider range of scattering vector Q $(=(4\pi/\lambda) \sin (\theta/2))$ than is accessible using classical light scattering.[5] Experimentally

$$I(Q)/I(0) = P(Q)S(Q) \qquad (1)$$

when $I(Q)$ and $I(0)$ denote the scattered intensity at Q =

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