

Polyelectrolyte Effects on the Quenching of Pyrene Fluorescence in Solutions of a Pyrene Substituted Poly(acrylic acid)

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Synopsis

The quenching of pyrene fluorescence by nitromethane, Tl^+ , Cu^{2+} , I^- , and 4-dimethylaminopyridine (DMAP) in aqueous solutions of a pyrene substituted poly(acrylic acid) (1) was influenced by the "polyelectrolyte effect" of 1. The efficiency of quenching in solutions of 1 was measured in terms of the Stern-Volmer constants for dynamic and static quenching which were obtained from comparison of the intensity and lifetime of pyrene fluorescence in solutions of 1 and a monomer model compound. The efficiency of quenching in solutions of 1 was always greater at high pH (9) in comparison to that at low pH (4). The ionization of carboxylic groups in 1 caused an expansion of the polymer mainchain and concomitant exposure of the pyrene molecules to the aqueous phase and quencher. The polyanion domain of 1 favored the condensation of cationic quenchers and could account for very efficient quenching in case of Cu^{2+} and Tl^+ . A very efficient quenching of pyrene fluorescence in solutions of 1 by DMAP at high pH was attributed to the hydrophobic interactions of DMAP and pyrene moiety. The iodide ions were less efficient quenchers of pyrene fluorescence due to electrostatic repulsion from the polyanion. The efficiency of quenching by nitromethane was not significantly affected by ionization of the carboxylic groups in 1.

INTRODUCTION

Photophysical properties of the pyrene chromophore covalently bound to poly(acrylic acid) (1, Fig. 1) have been used by us to investigate the interpolymer interactions in solutions of 1 and complementary polymers.^{1,2} In the course of these investigations we found that the photophysical properties of 1 were dependent on the conformation (coiled or expanded form) of 1 in solution. In particular, fluorescence lifetime, ratio of the intensity of pyrene and excimer fluorescence and the shape of absorption and excitation spectra of 1 were found to depend on the pH of solution. These effects could be attributed to the coiling of polymer chain at pH values less than 4.5 and an expansion of polymer chain due to increased charge density at pH values greater than 6. The intrachain interactions of pyrene groups in 1 were favored at low pH values and these interactions were reduced at high pH values thus affecting the photophysical properties of pyrene. Interchain interactions were not considered to be possible in solutions of 1 due to low concentrations of polymers ($< 1 \text{ mM}$) used in our experiments.

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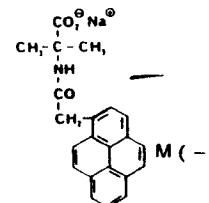
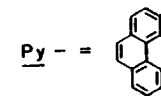
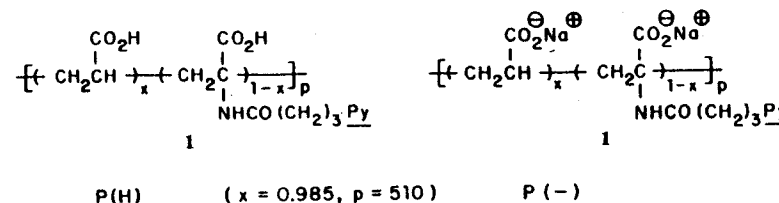


Fig. 1. Chemical structures of the pyrene containing compounds.

The quenching of pyrene fluorescence in solutions of 1 with different quenchers are reported here as part of our research program dealing with photophysical investigations of polymer interactions. Fluorescence can be quenched by a variety of processes.³ We are mainly concerned with dynamic and static quenching of pyrene in these investigations. The contact of fluorophore and quencher is required for dynamic as well as static quenching of fluorescence. Therefore, investigations of fluorescence quenching in solutions of 1 could be expected to provide information about the environment of pyrene groups in 1. Furthermore, photophysics of a variety of chromophores bound to water soluble polymers have been investigated in order to design synthetic polymers for use in solar energy retrieval and storage.^{4,5} We were interested in investigations of the "polymer effect" on the quenching of pyrene fluorescence in solutions of 1. Chu and Thomas⁶ have investigated the photophysical behavior of pyrene bound to poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA). However, the concentration of pyrene bound to PAA or PMA in the experiments of Chu and Thomas was low so that no intrachain interactions of pyrene groups were observed. The quenching of fluorescence from other aromatic hydrocarbons covalently bound to polyelectrolytes have also been investigated.^{5,7} The supercoiled structures of PAA under low pH conditions have also been used to modify chemical reactions performed in the presence of polymers.⁸ Transfer of electronic energy, a process for quenching of fluorescence, has also been used to study polymer interactions.⁹

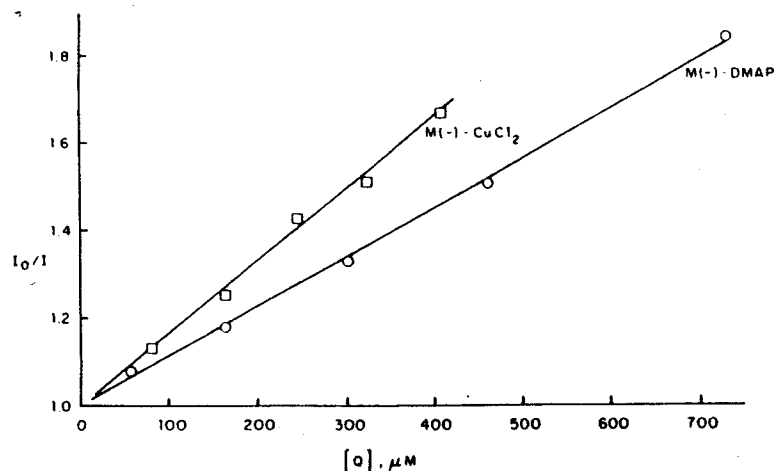


Fig. 3. Stern-Volmer plots for the quenching of pyrene fluorescence in solutions of M(-) by Cu^{2+} and DMAP.

of Stern-Volmer plots $[(K_{SV})_I]$ could be used to calculate the static component of quenching, K_S , according to eq. (7).

$$(K_{SV})_I = K_S + (K_{SV})_T \quad (7)$$

There were no changes in the excitation spectrum of M(-) in the presence of DMAP and CuCl_2 . The absorption spectrum of M(-) was perturbed by the presence of DMAP suggesting ground-state interactions of DMAP and pyrene moiety in M(-). These ground-state interactions probably resulted in static quenching of pyrene fluorescence. No changes were observed in the absorption spectrum of M(-) in the presence of CuCl_2 . Cupric ions produced in solutions of CuCl_2 could coordinate with the carboxylate groups in M(-) leading to static quenching. This coordination was not observed in the absorption spectrum of the pyrene moiety.

For the quenching of pyrene fluorescence by an uncharged quencher (nitromethane) linear plots of I_0/I and τ_0/τ against $[Q]$ were obtained for P(H) and P(-) (I_0/I plots are shown in Fig. 4). The values of $(K_{SV})_I$ and $(K_{SV})_T$ obtained from the slopes of these plots (Table I) were comparable in magnitude indicating dynamic nature of the quenching of pyrene in these solutions. However, the values of k_q were reduced in solutions of P(H) and P(-) in comparison to that of M(-). The value of k_q in collisional quenching is related to the diffusion coefficients and molecular radii of the fluorophore and quencher (Smoluchowski equation).³ The diffusion coefficient of polymers could be expected to be lower than that of M(-). Therefore, a lower value of k_q in P(H) and P(-) could be attributed to lower diffusion coefficient of polymers. The value of k_q was increased slightly in solutions of P(-) in comparison to that in P(H) which could arise from an expanded conformation of P(-). The differences in k_q value for P(H) and P(-) were not large which could be attributed to the amphiphilic nature of nitromethane.

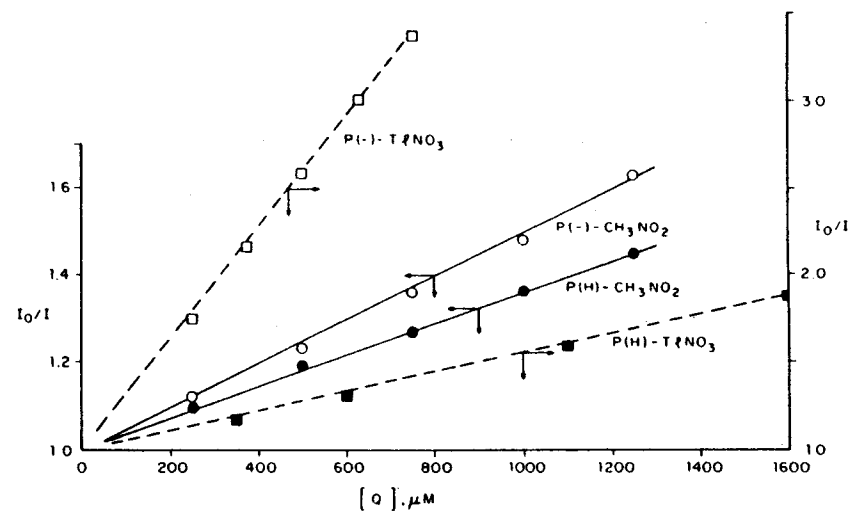


Fig. 4. Stern-Volmer plots for the quenching of pyrene fluorescence in solutions of P(H) and P(-) by nitromethane and TI^+ .

The plots of I_0/I against $[Q]$ for the quenching of pyrene fluorescence in solutions of P(-) with Cu^{2+} and of P(H) with DMAP and Cu^{2+} (Fig. 4) were found to show deviations from linearity. These data could be used to calculate the true dynamic and static components of the fluorescence quenching processes. The values of $(K_{SV})_I$ in these cases were obtained here from slopes of the early (linear) part of the plots. Linear Stern-Volmer plots were obtained in all other cases (Figs. 4-6) and $(K_{SV})_I$ values obtained from these plots are given in Table I.

Excimer fluorescence due to intrachain interactions of pyrene groups in solutions of P(H) and P(-) was observed.^{1,2} The quenching of monomer fluorescence could be described by a Stern-Volmer type equation in these cases¹⁴ if the rate of excimer dissociation was small. This was considered to be possible in solutions of 1 at low and high pH because the hydrophobic intrachain interactions of pyrene groups led to excimer formation. These interactions could be expected to be favored by coiled conformations of P(H). In solutions of P(-) excimer formation was possible from neighboring pyrene groups only.^{1,2}

The lifetime of pyrene fluorescence in solutions of P(H) or P(-) was reduced in the presence of TINO_3 , CuCl_2 , and DMAP. Thus, both static and dynamic quenching were possible in these solutions. The dynamic component for the quenching of pyrene fluorescence in solutions of P(H) or P(-) was calculated from the values of k_q for M(-) with the assumption that the change in k_q for polymers with other quenchers would be similar to that observed for nitromethane quencher. Eq. (8) was used to calculate $(K_{SV})_T$ values for P(H) and P(-)

$$(K_{SV})_T = k_q [k_q(P)/k_q(M)] \tau_0 \quad (8)$$

nerit was present with Cu^{2+} as quencher. A coiled conformation of P(H) prevented the association of P(H) with a weakly binding quencher (Ti^+) more effectively than that with a strongly binding quencher (Cu^{2+}).

The changes in quenching behavior of pyrene fluorescence with Cu^{2+} and Ti^+ in solutions of P(H) and P(-) were similar to those reported by Chu and Thomas⁶ in their investigation of a pyrene substituted poly(acrylic acid). However, Chu and Thomas have reported a more significant effect of coiling on the fluorescence quenching by Cu^{2+} and Ti^+ . The differences between the quenching of pyrene fluorescence in the two polymers could arise from differences in the molecular weight and the content of pyrene groups of the two polymers (the DP of polymer used by Chu and Thomas was about 1000 and the polymer contained < 0.1 mol % of pyrene groups).

The quenching behavior of DMAP could be attributed to the association of DMAP and the pyrene containing polymers through Coulombic and hydrophobic interactions. A significant amount of DMAP molecules could be protonated in solutions of P(H) at pH 4 due to reaction between P(H) (and added acid) and DMAP. The protonation of DMAP could be expected to affect the quenching behavior of DMAP. Furthermore, Coulombic interactions between the cationic quencher and the partially charged P(H) could be expected under these conditions. Only hydrophobic interactions could be expected in solutions of P(-) due to uncharged nature of DMAP under these conditions (pH 9). The values of K_S show that these hydrophobic interactions led to very efficient quenching of pyrene fluorescence in solutions of P(-). This effect was also noticed in the DMAP quenching of pyrene fluorescence in solution of M(-). The quenching was less efficient in solutions of P(H), in particular, at low concentrations of DMAP, even when Coulombic interactions were expected to aid the association of DMAP and P(H). This lower K_S value for P(H) could be attributed to coiled conformations of P(H) under these conditions and the presence of DMAP in a protonated form. There was a significant increase in the quenching efficiency of DMAP in solutions of P(H) at higher concentrations of DMAP (Fig. 5). This effect could be attributed to the ionization of 1 caused by an acid-base reaction of DMAP and 1.

The quenching of pyrene fluorescence by iodide ions was significantly reduced in solutions of 1 in comparison to that in M(-). The iodide ions could be prevented from contacts with the pyrene moiety in P(H) due to coiled conformation and Coulombic repulsion of polymer mainchain. The negative charge of P(-) could be expected to reduce the fluorescence quenching of pyrene by iodide ions.

CONCLUSIONS

These investigations have shown that the quenching of pyrene fluorescence in solutions of the pyrene substituted PAA (1) was dependent on the association of polymer and quencher and the conformation of 1. The Stern-Volmer constants, $(K_{SV})_1$ or K_S , for the polymers were increased several fold in case of Cu^{2+} and DMAP in comparison to those for a monomer model compound due to association of polymer and quencher. The quenching of pyrene fluorescence by iodide ions was, however, reduced by the electrostatic repulsion of the polymer mainchain and quencher molecules. In the case of nitromethane

no significant effect of the degree of ionization of 1 on the quenching rate of pyrene fluorescence was observed. The quenching of fluorescence was also dependent on the conformation of polymer in solution as the Stern-Volmer constants, $(K_{SV})_1$ and K_S , were always greater for P(-) in comparison to those for P(H). The coiled conformations of P(H) prevented contact of pyrene and quenchers.

EXPERIMENTAL

Preparation and properties of 1 have been reported earlier.^{1,2} The sample of 1 used in these investigations had a degree of polymerization of 510 (viscosimetry) and contained 1.5 mol % of pyrene groups. The sample of M(-) used was a gift of Professor C. G. Overberger (University of Michigan, Ann Arbor) and was prepared by the hydrolysis of its methyl ester¹⁵ [mp 259–260°C, dec. ¹H-NMR (WM360, DMSO-*d*₆) 1.38, s, 6H, (CH₃)₂; 4.24, s, 2H, CH₂CO; 8.00–8.55, m, 9H, pyrenyl ring protons; 12.16, br, 1H, CO₂H. Elemental analysis, calculated for C₂₂H₁₉NO₃: C, 76.50; H, 5.54; N, 4.06. Found C, 76.35; H, 5.69; N, 3.98].¹⁵ Spectroscopic grade nitromethane (Fisher) was used as received. CuCl₂ (Fisher), TiNO₃ (Aldrich), DMAP (Aldrich) and KI (Fisher) were analytical grade chemicals and used as received. Distilled deionized water was used in all measurements.

Solutions of 1 and M(-) were prepared by dilution of the stock solutions of these compounds to obtain concentrations of 0.5–1.0 μM repeat units and 10 μM respectively. The concentrations were monitored by measuring the absorbance at 322 nm (0.1–0.2) to obtain 5–10 μM concentration of the pyrene chromophore. Fluorescence intensities and spectra were obtained with a Perkin-Elmer Model LS-5 luminescence spectrophotometer at 20°C. The light of wavelength 313 nm was used for excitation and (0,0) peak in the fluorescence spectrum (378 ± 1 nm) was used to monitor the fluorescence intensity of pyrene in quenching experiments. Solutions were deaerated by bubbling argon or nitrogen for 5 min before each measurements. DMAP was found to have no significant absorption at 313 nm and was found to give no fluorescence at concentrations used in these experiments. Fluorescence lifetimes were determined with a single photon counting instrument and deconvolution program (PRA, Ontario, Canada).² The pH of polymer solutions was adjusted by addition of 0.1N HCl or NaOH and measured with a Beckman Model φ21 pH meter. Quenching experiments with CuCl₂, TiNO₃, and KI were performed in 0.1M NaCl in order to maintain constant ionic strengths. Experiments were performed in duplicate.

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