

Photophysical Investigations of Interpolymer Interactions in Solutions of a Pyrene Substituted Poly(acrylic acid), Poly(vinyl amine), Poly(1-aminoacrylic acid), and Poly(1-acetylaminacrylic acid)

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Synopsis

Photophysical properties of the pyrene chromophore covalently bound to poly(acrylic acid) were used to investigate the interactions of a pyrene substituted poly(acrylic acid) (1) with poly(vinyl amine hydrochloride) (PVAm), poly(1-aminoacrylic acid) (PDA), and poly(1-acetylaminacrylic acid) (PADA) in aqueous solutions. A number of photophysical parameters were obtained from fluorescence emission and excitation spectra, the deconvolution of decay curves for pyrene monomer, and excited state complex fluorescence and the quenching of pyrene monomer fluorescence by nitromethane in polymer solutions. These photophysical parameters were considered to reflect the inter- and intrapolymer interactions in solutions of 1, PVAm, PDA, and PADA. The formation of interpolymer complexes between 1 and PVAm was noticed at low (< 4) as well as high (> 8) values, whereas PDA and 1 formed interpolymer complexes at low pH only. No interpolymer complex formation was detected in solutions of 1 and PADA under low or high pH conditions. The structures of interpolymer complexes formed between 1 and PVAm under low and high pH conditions were found to be determined by the conformation of 1. There were significant differences in the interpolymer interactions of 1 and PDA in comparison to those of 1 and PVAm; in particular, the fluorescence from the excited state complex was enhanced in solutions of 1 and PVAm but quenched in solutions of 1 and PDA. The investigations of terpolymer solutions of 1, PVAm, and PADA indicated that the nature of interpolymer complexes formed in terpolymer solutions was determined by Coulombic interactions of the amino and carboxylic group containing polymers.

INTRODUCTION

Synthetic polyelectrolytes have been widely employed to serve as simple models for complex biological macromolecules and to elucidate the role of macromolecular structures (polymer effects) on the properties of charged molecules.¹ Inter- and intramolecular interactions play an important role in the properties and functions of polyelectrolytes. A variety of secondary forces, such as cooperative forces, hydrogen bonding, hydrophobic, Coulombic and dipolar interactions, can be responsible for these interactions; however, Coulombic interactions can be expected to be the dominant secondary force in the interactions of polyelectrolytes.² Polyelectrolyte complexes are known to form in solutions of complementary polyelectrolytes as a result of interpolymer interactions; the investigations of the formation and properties of poly-

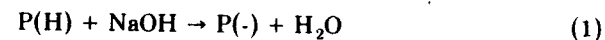
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electrolyte complexes are of fundamental interest as well as technological importance.³ We have reported the synthesis of a pyrene substituted poly(acrylic acid) (1) and have used the photophysical properties of the pyrene chromophore to investigate the interactions of 1 with complementary polymers, namely, poly(ethylene oxide) (PEO), poly(1-vinyl-2-pyrrolidinone) (PVP), and poly(vinyl amine, hydrochloride) (PVAm), in dilute solutions.⁴ The utilization of the photophysical properties of the pyrene group to study the interpolymer and terpolymer interactions in dilute solutions of 1 and poly(1-aminoacrylic acid) (polydehydroalanine, PDA), poly(1-acetylaminacrylic acid) [poly(*N*-acetyldehydroalanine), PADA], and PVAm is reported here. The interactions and formation of polyelectrolyte complexes of poly(acrylic acid) (PAA) with PVAm, PADA, or PDA have not been reported; the repeat units of 1, PVAm, PDA, and PADA contain only simple ionic groups, namely, the carboxylate and the amino groups.

RESULTS AND DISCUSSION

The emission and excitation spectra of the pyrene moiety in 1 provided four photophysical parameters which were found to be useful in determination of the intrapolymer (chain) interactions in dilute solutions of 1. The significances and definitions of these parameters in terms of the intrachain interactions of pyrene groups in 1 are given in Table I. The concentrations of 1 used in our experiments were selected to prevent significant interchain interactions.⁴ Chemical structures of repeat units of polymers are given in Figure 1. The formation of P(-) [eq. (1)] was accompanied by an increase in



I_M/I_E and P_M values, a bathochromic shift in λ_E and a decrease in P_E value. The photophysical parameters for P(H) and P(-) are given in Table II.

TABLE I
Definition and Significance of the Photophysical Parameters of Pyrene in the Pyrene Substituted Poly(acrylic acid) (1)*

Symbol	Definition	Significance
I_M/I_E	Ratio of intensities of monomer (0,0) and excimer (exciplex) emission (at λ_E)	[Py-Py]* (excimer), [Py-NH ₂]* (exciplex), and Py*·NH ₂ (fluorescence quenching) interactions were reflected in this parameter
λ_E	Wavelength corresponding to maximum in the excimer (exciplex) emission	The nature and orientation of the groups involved in excimer (exciplex) emission affected λ_E
P_M	Peak-to-valley ratio for the (0,0) transition in ¹ L _a band in the excitation spectrum viewed at 380 nm	The interactions of isolated pyrene groups were reflected in P_M values
P_E	Peak-to-valley ratio for the (0,0) transition in ¹ L _a band in the excitation spectrum viewed at 480 nm	The interactions of excimer forming pyrene groups were reflected in P_E values

*Py represents 1-pyrenyl group, and NH₂ represents amino groups in the polymers.

pyrene groups present in neighboring repeat units of 1 (Fig. 2; II and IV) could be expected to produce efficient intrachain interactions (low P_E and higher λ_E) compared to those of pyrene groups separated by large PAA blocks.

The ionization of P(H) also caused changes in the absorption spectrum of pyrene groups⁴ as well as shifts in the positions of (0,0) transitions in the excitation spectra of pyrene groups viewed at 380 and 480 nm. The changes in absorption spectrum, that is, a sharpening of peaks,⁴ were consistent with an expansion of polymer mainchain and reduced intrachain interactions of pyrene groups. The magnitude of changes in these parameters was small, and therefore these parameters were not considered suitable for investigating the intrachain interactions of pyrene groups.

Single photon counting was used to determine lifetimes of pyrene and excimer fluorescence in solutions of 1. Photophysical processes reflected in fluorescence decay behavior are related to the dynamics and environment of fluorophores.⁸ In the absence of excited state interactions, fluorescence from pyrene in aqueous solutions of pyrene containing molecules is expected to show monoexponential decay behavior with a lifetime of 120–140 ns.⁹ Intermolecular and intramolecular interactions of pyrene groups could be expected to influence the decay behavior and lifetimes of pyrene monomer and excimer fluorescence. The measurement of fluorescence lifetimes in solutions of 1 was expected to provide information about the environment and interactions of pyrene groups in 1. The measurement of fluorescence lifetimes of pyrene and

TABLE III
Fluorescence Lifetimes of Pyrene and Excited State Complex
in Solutions of Polyelectrolytes^a

Polymers in solution ^b	λ_{em}^c	τ_1^{ob} (ns)	τ_2^{ob} (ns)	χ^2
P(H)	378	41.5 ± 1.8	144.9 ± 1.4	1.40
	480	42.8 ± 3.3	85.8 ± 4.1	1.38
P(-)	378	40.3 ± 7.0	119.4 ± 3.0	1.30
	480	26.9 ± 0.4	63.1 ± 0.4	1.15
P(H): PVAm	378	50.2 ± 2.6	147.8 ± 0.2	1.45
	480 ^d	59.4 ± 2.5	143.1 ± 4.8	1.30
P(-): PVAm	378	33.8 ± 0.8	128.7 ± 0.1	1.12
	480 ^d	54.0 ± 0.7	144.5 ± 1.3	1.35
P(H): PDA	378	44.3 ± 2.6	154.2 ± 4.1	1.15
	480	19.6 ± 4.1	80.0 ± 2.8	1.26
P(-): PDA	378	51.7 ± 8.1	128.7 ± 3.3	1.35
	480	39.8 ± 4.4	81.3 ± 6.6	1.27
P(H): PADA	378	41.8 ± 4.7	142.5 ± 2.7	1.22
	480	39.7 ± 0.2	83.6 ± 0.7	1.65
P(-): PADA(-)	378	40.0 ± 0.6	117.5 ± 1.8	1.28
	480	30.4 ± 0.9	65.1 ± 1.2	1.30

^a[P(H)] or [P(-)] = 5×10^{-4} mol L⁻¹. All measurements were performed at 20°C using a single photon counting instrument. In the text monomer lifetimes are referred with a subscript M and excimer lifetimes are referred with a subscript E.

^bSee Figure 1 for chemical structures.

^cWavelength for emission (nm).

^dA third component (9 ± 2 ns) was also observed in these fluorescence decay curves.

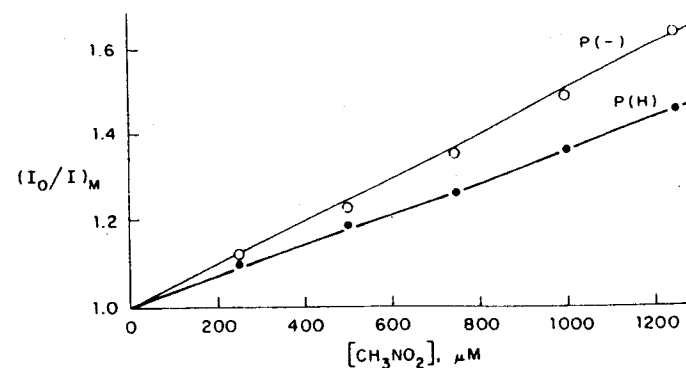


Fig. 3. Stern-Volmer plots for the quenching of pyrene monomer fluorescence by nitromethane in solutions of P(H) or P(-).

excimer in solutions of 1 provided support for structures of P(H) and P(-) proposed in Figure 2. The decay curves for excimer fluorescence from P(H) and P(-) did not show a growth term, implying a rapid formation of excimers under the conditions of these measurements. The decay curves for pyrene and excimer fluorescence could be fit to an equation containing two exponential terms each. The rate parameters (τ_1^{ob} and τ_2^{ob}) obtained from fluorescence decay curves are given in Table III.

The fluorescence from isolated pyrene groups in 1 (Fig. 2; I, V, and VI) could be expected to decay according to eq. (2) following excitation by a δ -function pulse.¹⁰ $I_M(t)$ is the intensity of pyrene fluorescence and is related to the concentration of excited pyrene groups at time t following excitation, and τ_M is the fluorescence lifetime of pyrene.

$$I_M(t) = A_1 \exp\left(-\frac{t}{\tau_M}\right) \quad (2)$$

The pyrene groups separated by large PAA blocks (Fig. 2; I, III) could form excimers if the coiling of the polymer chain allowed the interaction of an excited pyrene group and another pyrene group on the polymer chain. The kinetics of intramolecular excimer formation¹¹ could be used in this case. The intensity of pyrene fluorescence would be expected to decay as a sum of two exponential terms [(eq. (3)) and excimer fluorescence intensity [$I_E(t)$] as a difference of two exponential terms [(Eq. (4))].

$$I_M(t) = A_2 \exp\left(\frac{-t}{\tau_1}\right) + A_3 \exp\left(\frac{-t}{\tau_2}\right) \quad (3)$$

$$I_E(t) = A_4 \exp\left(\frac{-t}{\tau_1}\right) - A_5 \exp\left(\frac{-t}{\tau_2}\right) \quad (4)$$

The rate parameters τ_1 and τ_2 obtained from fluorescence decay measure-

and presence of quencher. The values of $(K_{SV})_M$ for P(H) and P(-) were determined to be 4.40×10^2 and $4.30 \times 10^2 \text{ M}^{-1}$ respectively. The dynamic nature of the quenching of pyrene fluorescence in solutions of 1 was indicated by comparable values of $(K_{SV})_M$ obtained by fluorescence intensity and lifetime measurements.¹⁸

The Stern-Volmer constant for excimer quenching could be obtained from measurement of fluorescence lifetimes $[(\tau_2^{ob})_E]$ for P(H) and P(-) in the presence of nitromethane [eq. (9)]. The rate constant for dynamic quenching of excimer was then determined by use of eq. (10). τ_0 and τ are fluorescence lifetimes for excimer [Table IV; $(\tau_2^{ob})_E$] in the absence and presence of quencher and $(\tau_2^{ob})_{E,0}$ is the fluorescence lifetime of excimer in the absence of quencher (table IV).

$$\frac{\tau_0}{\tau} = 1 + (K_{SV})_E [Q] \quad (9)$$

$$(K_{SV})_E = (k_q)_E (\tau_2^{ob})_{E,0} \quad (10)$$

The values of $(k_q)_E$ for P(H) and P(-) were found to be 2.27×10^9 and 2.15×10^9 respectively. As in the quenching of pyrene monomer fluorescence, there was no significant difference in the quenching of excimer fluorescence by nitromethane in solutions of P(H) and P(-) due to the amphiphilic nature of the quencher.

The above measurements of photophysical parameters, fluorescence lifetime, and quenching rate for monomer fluorescence of the pyrene substituted poly(acrylic acid) provided information about intra- and interchain interactions of pyrene groups which in turn were related to the polymer structure in solution. Similar measurements were performed in solutions of P(H) or P(-) and other polyelectrolytes, namely, PVAm, PDA and PADA, in order to elucidate the nature and extent of interpolymer interactions in the solutions of these polymers. Interpolymer complexes formed in solutions of complementary polymers are often insoluble in water³ and therefore can result in the formation of a precipitate or turbidity. This was not a problem in our experiments because very low concentrations of polymers were needed in order to investigate the interactions of polymers by fluorescence spectroscopy, and the interpolymer complexes formed under these conditions did not cause an immediate precipitation or turbidity. However, prolonged standing (overnight) of polyelectrolyte solutions produced turbidity in solutions of polyelectrolyte complexes.

The various types of interpolymer interactions expected in polymer solutions are schematically shown in Figure 4. In addition to cooperative and hydrophobic interactions, Coulombic and hydrogen-bonding interactions (Scheme C) could be expected to lead to interpolymer complex formation in solutions of polymer containing amino and carboxylate groups. The intrachain interactions of pyrene groups present in 1 could be expected to change as a result of interpolymer complex formation. In particular, the intrachain interactions of pyrene groups separated by large PAA blocks could be reduced by interpolymer complex formation as the intrapolymer interactions would be opposed by the interpolymer interactions (Fig. 4, Scheme D). As a result of

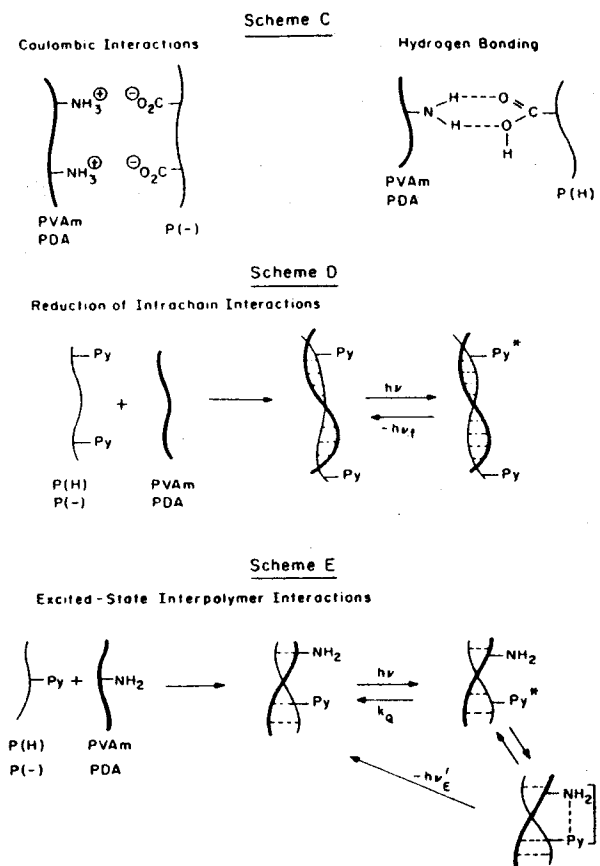


Fig. 4. A schematic representation of interpolymer interactions in solutions of polyelectrolytes. Py represents 1-pyrenyl groups. Interpolymer association of polymers is shown by broken lines in Schemes D and E. Amino and carboxylic groups are not shown on polymer mainchain in Schemes D and E for the sake of clarity.

the interpolymer complex formation excited state interactions between pyrene and amino groups could be expected. These interactions could cause quenching of pyrene fluorescence and/or lead to formation of an exciplex (Fig. 4, Scheme E).

A number of parameters could be expected to influence the interactions of pyrene substituted poly(acrylic acid) (1) with PVAm, PDA, and PADA. The pH of solutions could be expected to play an important role in the interactions of 1 as charge density and conformation of 1 depended on pH. The I_M/I_E value was used to study the effects of pH on inter- and intrapolymer interactions in solutions of P(H), P(H):PVAm, P(H):PDA and P(H):PADA as I_M/I_E value showed a large variation with changes in intrapolymer interactions; the results are shown in Figure 5. The curves for P(H) and P(H):PADA were identical, and the one for P(H) was not shown in Figure 5

neutral pH values and expanded conformations of PVAm are considered to be present under acidic and basic conditions.²² The I_M/I_E value of P(H):PVAm was not much different from that of P(H). The reduction in excimer emission expected due to reduced intrachain interactions of pyrene groups in P(H):PVAm (Fig. 4, Scheme D) was not observed in this case. The formation of a fluorescent exciplex between pyrene and amino groups in P(H):PVAm (Fig. 4, Scheme E) was thought to be responsible for comparable I_M/I_E values of P(H) and P(H):PVAm. Fluorescence of pyrene can be quenched by a variety of primary, secondary, and tertiary amines. The formation of a fluorescent exciplex has been reported to be possible in solutions of pyrene and a variety of tertiary amines.²³ The formation of fluorescent exciplex in solutions of P(H):PVAm was thought to arise from "polymer effects." A variety of polymers containing pyrene and amino moieties have been reported to show exciplex emission^{24,25} due to inter- and interpolymer interactions. Exciplex emission in solutions of these polymers has been attributed to the proximity of pyrene and amino moieties. The interactions of pyrene and amino groups in solutions of P(H) and PVAm could also be favored by interpolymer complex formation. The excited state interactions of pyrene and amino groups could occur via electron or proton transfer reactions between excited state pyrene and amino groups.²³

Evidence for exciplex formation in solutions of P(H):PVAm was also provided by decrease in P_M and P_E values of P(H):PVAm in comparison to those of P(H) (Table II). Furthermore, the absorption spectra of the pyrene chromophore in P(H):PVAm were significantly distorted. The λ_E for P(H):PVAm was blue-shifted in comparison to that of P(H), indicating change in the nature and environment of emitting species due to exciplex formation.

A coiled conformation and low degree of ionization could be expected for P(H) at pH 4, whereas the mainchain of PVAm would have an expanded conformation and a high degree of charge density under these conditions. Therefore the association of P(H) and PVAm could be expected to occur mainly via hydrogen bonding and hydrophobic interactions. If the mainchain of P(H) in P(H):PVAm could be considered to be in a coiled conformation, then more than an equivalent amount of P(H) could be complexed with PVAm due to an expanded conformation of PVAm. This conjecture was supported by a measurement of the photophysical parameters of 2P(H):PVAm which were similar in magnitude to those of P(H):PVAm (Table II).

The fluorescence lifetime of pyrene in P(H):PVAm [$(\tau_2^{ob})_M$] was somewhat higher than that of P(H). The fluorescence decay curve for the long wavelength (480 nm) emission from solutions of P(H):PVAm was found to be multiexponential and was deconvoluted to fit an equation containing three exponential terms. These rate parameters were higher than the corresponding parameters for P(H) (Table III). The interpretation of these rate parameters was not attempted because both excimer and exciplex emissions contributed to the fluorescence decay curves. The value of $(\tau_2^{ob})_E$ for P(H):PVAm was significantly increased in comparison to that for P(H) (Table III). Fluorescence lifetimes of intrapolymer excimer and interpolymer exciplex in some other pyrene group containing polymers have been reported to be 50 and 101 ns, respectively, in tetrahydrofuran.²⁵

The rate constant for quenching of pyrene in P(H):PVAm by nitromethane was reduced by a factor of $\frac{1}{7}$ compared to that for P(H) (Table IV). The formation of interpolymer complex, P(H):PVAm, could be expected to reduce the accessibility of pyrene groups to the quencher molecules and the value of $(k_q)_M$ could be expected to decrease.

At pH 8.5, the mainchain of P(-) and PVAm could be expected to have considerable charge density and expanded conformations. Under these conditions interpolymer complex formation could occur through Coulombic interactions. The photophysical parameters of P(-):PVAm (Table II) were considered to reflect strong interpolymer interactions. The I_M/I_E , P_M and P_E values for P(-):PVAm were significantly reduced in comparison to those for P(-) and P(H):PVAm. The reduction in I_M/I_E was caused by a contribution from exciplex emission due to strong interpolymer interactions in P(-):PVAm. The enhanced interactions of pyrene-pyrene and pyrene-amino groups caused reduction in P_M and P_E . The λ_E value for P(-):PVAm was blue-shifted in comparison to that for P(-).

The fluorescence lifetime of pyrene groups in P(-):PVAm (Table III) was increased compared to that in P(-), which could be attributed to the formation of interpolymer complexes and consequent changes in the photophysical behavior of pyrene groups. The interpretation of changes in the fluorescence decay behavior of the long wavelength emission in P(-):PVAm was not attempted due to contributions from excimer and exciplex emissions. However, the value of $(\tau_2^{ob})_E$ for P(-):PVAm was comparable to that for P(H):PVAm but higher than that for P(H) and P(-) (Table III). These photophysical properties of P(-):PVAm were consistent with the formation of interpolymer complexes between P(-) and PVAm and consequent reduction of the intrachain interactions of pyrene groups (Fig. 4; Scheme D) and the formation of a fluorescent exciplex due to interpolymer interactions of pyrene and amino moieties (Fig. 4, Scheme E). The value of $(k_q)_M$ for P(-):PVAm was higher than that for P(H):PVAm and comparable to those of P(H) and P(-) (Table IV). This could be attributed to an expanded conformation of P(-) in P(-):PVAm, and therefore the pyrene groups in P(-):PVAm were more accessible to quencher molecules. The intensity of long wavelength emission from solutions of P(-):PVAm was not affected by addition of nitromethane. This could be taken as evidence for exciplex formation in P(-):PVAm because excimer fluorescence in P(-) was quenched by nitromethane.

The association of P(H) and PVAm was also noticed in the titration of P(H) in the presence of PVAm (Fig. 6). The presence of a monomer model compound, namely, 1-ethylpropylamine, hydrochloride [M(+)], did not affect the titration of P(H) in a significant manner. The pK_a value of P(H) determined under these conditions was 6.43, whereas that in the presence of M(+) was 6.31. Therefore changes in the titration behavior of P(H) in the presence of PVAm could not be attributed to the salt effect. The presence of M(+) did not have a significant effect on the pH of a solution containing P(H) (Fig. 6), whereas the presence of PVAm reduced the pH of a solution containing P(H). The pH of solution containing P(H):PVAm could be reduced due to the complexation of P(H) and PVAm and release of HCl.² A transition was observed in the titration curve of P(H):PVAm near pH 4.5, which could be attributed to an expansion of I as a result of increased charge density of I.

another equivalent of PVAm to the above terpolymer solution gave PVAm:PADA(-):P(-):PVAm, and photophysical parameters in this terpolymer solution were found to be comparable to those of P(-):PVAm. These results implied that Coulombic interactions led to the formation of an interpolymer complex in solutions of PVAm and PADA(-) and therefore the addition of one equivalent of P(-) to the above solution did not lead to association of P(-) and PVAm. However, the addition of another equivalent of PVAm to the above terpolymer solution caused association of P(-) and PVAm. The resulting solution could be considered to contain interpolymer complexes PVAm:PADA(-) and P(-):PVAm. Photophysical parameters of a terpolymer solution [P(-):PADA(-):PVAm] obtained by addition of an equivalent amount of PVAm to a solution of P(-) and PADA(-) indicated that PVAm, as could be expected, complexed with both the carboxylic group containing polymers. The photophysical parameters of P(-):PADA(-):PVAm were different from those of P(-):PVAm and were indicative of reduced interactions of P(-) and PVAm. When another equivalent of PVAm was added to the above terpolymer solution, the photophysical parameters [P(-):PADA(-):2PVAm] were found to be comparable to those of P(-):PVAm. An excess of carboxylic groups in P(-):PADA(-):PVAm implied that only some of P(-) and PADA(-) could form interpolymer complex with PVAm, and the resulting solution was expected to contain free P(-) and PADA(-) in addition to inter- and terpolymer complexes of PVAm, PADA(-), and P(-). The addition of more PVAm led to its complexation with free P(-) and PADA(-) and the formation of inter- and terpolymer complexes. These results indicated that the formation of interpolymer complexes in these solutions was largely governed by stoichiometry of the carboxylic and amino groups.

CONCLUSIONS

The measurements of fluorescence emission and excitation spectra, decay of pyrene monomer and excited state complex fluorescence, and the quenching of pyrene monomer fluorescence in solutions of 1, PVAm, PADA, and PDA provided a number of photophysical parameters of the pyrene chromophore covalently bound to poly(acrylic acid) (1). The values of photophysical parameters were considered to reflect intra- and interpolymer interactions in the solutions of these polymers. The utilization of different photophysical techniques and a complementary nature of the information provided by the photophysical parameters enabled the investigations of interpolymer interactions in these complex systems.

Interpolymer interactions were investigated at low (< 4) and high (> 8) pH values because 1 was expected to be in a coiled form under low pH and to be in an expanded conformation at high pH. The formation of interpolymer complexes between 1 and PVAm was found to occur at low and high pH, whereas 1 and PDA showed the formation of interpolymer complex at low pH only. No interpolymer complex formation between 1 and PADA was possible at both low and high pH. Therefore, the formation of interpolymer complexes in solutions of these polyelectrolytes was determined by Coulombic interactions. The structure of interpolymer complex formed between 1 and PVAm depended on the conformation of 1. At low pH the mainchain of 1 was in a

coiled form, whereas at high pH an expanded form of 1 was present in the interpolymer complex formed between 1 and PVAm. There were significant differences in the excited state interactions of pyrene and amino groups in solutions of P(H) and PVAm or PDA.

Photophysical parameters obtained from fluorescence emission and excitation spectra were found to be useful indicators of inter- and intrapolymer interactions in polymer solutions. The conclusions drawn from consideration of the values of these parameters were supported by other photophysical measurements. Investigations of terpolymer solutions by use of these photophysical parameters indicated that the formation of interpolymer complexes was dependent on the Coulombic interactions of PVAm with P(-) and PADA(-) and PVAm formed interpolymer complexes with both the carboxylic group containing polymers.

EXPERIMENTAL SECTION

Commercially available chemicals used in the preparation of polymers were purified, if required, using appropriate methods.²⁶ Double distilled deionized water was used in all measurements. The preparation and characterization of the samples of P(H) and PVAm used in this investigation was reported earlier.⁴ The degree of polymerization (DP) of P(H) was found to be 510 by viscosimetry (*p*-dioxane solvent) and 1.5 mole% of pyrene groups were present in P(H). The DP of P(H) was previously reported to be 249 based on viscosimetric determination in 2 *M* sodium hydroxide. The differences in the two values of DP of P(H) measured in 2 *M* NaOH and *p*-dioxane might be due to errors in the determination of the Mark-Houwink-Sakurada parameters for PAA in 2 *M* NaOH.²⁷ PVAm was found to have a DP of 960 (viscosimetry).⁴ Dilute solution viscosity measurements were performed in a constant temperature bath using a Cannon-Ubbelohde semimicro dilution viscometer. Poly(1-acetylaminoacrylic acid) was prepared according to a literature procedure²⁸ and was determined to have an inherent viscosity of 1.23 dL/g ($c = 1.00$ g/dL) in DMF at 30°C. PDA was obtained by hydrolysis of PADA.²⁸ The molecular weights of PADA and PDA could not be determined by viscosimetry because Mark-Houwink-Sakurada parameters for these polymers have not been reported in the literature. The concentrations of polymers reported in this work refer to the concentrations of repeat units shown in Figure 1 and are given as equivalents of repeat units per liter (abbreviated mol L⁻¹).

The stock solutions of polyelectrolytes (concentration 10⁻² mol L⁻¹) were made in advance and used for preparing solutions for fluorescence measurements. The required amounts of stock solutions were mixed with water to obtain a 10 mL solution containing the required concentrations of polyelectrolytes. The pH of polyelectrolyte solutions were adjusted by addition of 0.1 *M* HCl or NaOH. Measurements of pH were performed with a Beckman model 021 pH meter at room temperature.

The fluorescence spectra were recorded on a Perkin-Elmer Model LS-5 luminescence spectrophotometer at 20°C. Emission and excitation spectra (uncorrected) were recorded after making the solutions at the desired pH. The polymers were designated by the acronyms shown in Figure 1. The concentra-