Pyrene as a photophysical probe for intermolecular interactions of water-soluble polymers in dilute solutions

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Poly(acrylic acid) containing 1.5 mole% pyrene groups in side chains [P(H)] was prepared by a free-radical initiated copolymerization of acrylic acid and 2-[4-(1-pyrene)]butanoylaminopropenoic acid. The u.v. absorption and fluorescence emission spectra of P(H) showed that interactions of pyrene groups took place in solutions of P(H). A random distribution of the pyrene groups, in isolated and neighbouring repeat units, was assumed in the microstructure of P(H). The ratio of the intensities of monomer and excimer emission (I_M/I_E) was found to be related to the structure of P(H) in aqueous solutions; an increase in I_M/I_E value was indicative of the expansion of polymer chain. The variation of I_M/I_E values were consistent with polymer chain expansion as a result of increasing charge density of P(H) main chain. The association of P(H) with complementary polymers, namely, poly(ethylene oxide), poly(1-vinyl-2-pyrrolidinone) and poly(vinylamine hydrochloride), was revealed in a characteristic manner by measurement of the I_M/I_E values. The I_M/I_E values in the emission spectra of P(H) in the presence of complementary polymers were used to study the extent of interpolymer association, specific association of P(H) and polymer displacement reactions for terpolymer systems in aqueous solutions. Emission lifetime measurements on solutions of P(H) alone and in the presence of complementary polymers were also performed.

(Keywords: photophysical probes; interpolymer complexes; polymer–polymer interactions; polyelectrolyte complexes; polymer displacement reactions)

INTRODUCTION

Molecular interactions play a central role in the functions and structures of biological macromolecules. Synthetic polymers have been widely used as simple models for biological macromolecules in order to understand the structure–property relationships of the complex natural macromolecules. A knowledge of the structure–property relationships of polymers and the interactions of polymers with other small and large molecules is also essential for the synthesis of polymers tailored for specific applications. Fluorescence spectroscopy has been found to be a versatile technique for the investigations of macromolecular structure and properties[1]. A luminescent molecule required for the studies of polymers by fluorescence techniques can be either inherent in the polymer or introduced extrinsically. For an intrinsic introduction of the fluorescent molecule, a covalent bonding of the fluorescent probe to the polymer is a preferred approach because this obviates ambiguities arising from the uncertainty in location of the fluorescent probe in the system under investigation. The photophysical probe containing polymers can be investigated by a variety of photophysical phenomena, such as quenching of fluorescence, emission anisotropy, medium sensitivity of emission, excimer formation and energy transfer[1,2].

Water-soluble polymers, in particular, are useful as analogs in understanding the behaviour of biological macromolecules. Polyelectrolytes are an important class of water-soluble polymers which have been widely studied for their solution behaviour[3]. Pyrene has been widely used as a photophysical probe for macromolecular interactions. The long fluorescence lifetime, a great propensity for excimer formation and the medium sensitivity of emission of the pyrene molecule[4] have contributed to the versatility of pyrene as a photophysical probe. Now, we report the use of pyrene as a photophysical probe for investigations of the interactions of water-soluble polymers.

Fluorescent probes of polyelectrolytes have been reported. Strauss and Vesnaver[5] used the luminescence characteristics of dansyl groups covalently bound to copolymers of maleic anhydride and alkyl vinyl ethers to investigate the microenvironment and conformational transitions of these polymers in aqueous solutions. Morawetz and coworkers[6] have also used the fluorescence properties of dansyl groups attached to poly(acrylic acid) (PAA) to investigate the association of PAA with poly(ethylene oxide) (PEO) and poly(1-vinyl-2-pyrrolidinone) (PVP). Klotz and coworkers[7] have used fluorescence properties of the pyrene group covalently bound to poly(ethylenimine) (PEI) derivatives to investigate the conformational behaviour of these polymers in aqueous solutions. Herkstroeter and coworkers[8] investigated some pyrene containing polyelectrolytes in aqueous solutions and showed that the absorption, emission and excitation spectra of the polymers provided useful information about the structures of these polymers in aqueous solutions. Non-radiative energy transfer between photophysical probes covalently bound to complementary polymers has been used to study the association of these polymers in aqueous

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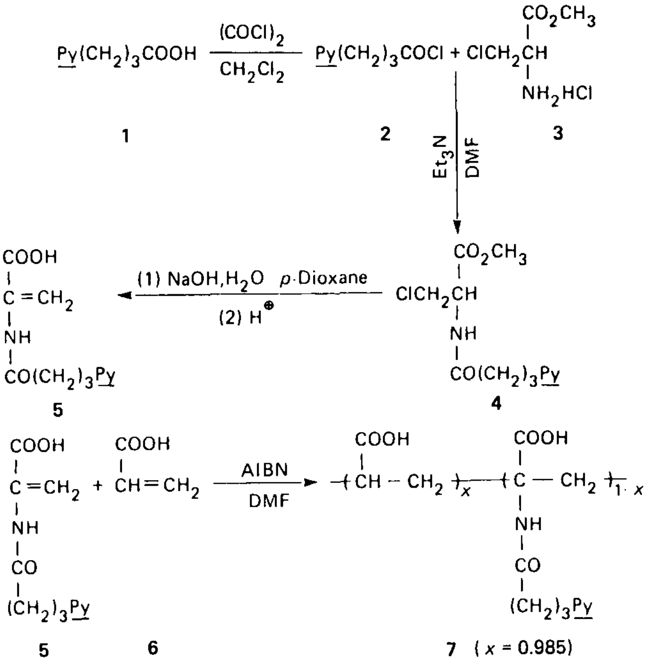
solutions[9]. Photophysical properties of copolymers of 1-pyreneacrylic acid and methacrylic acid or acrylic acid have been reported recently[10]. Webber and coworkers[11] have used fluorescence techniques to study the diphenylanthracene group containing poly(methacrylic acid).

The main purpose of our present investigations was to demonstrate that photophysical properties of pyrene group covalently bound to a water-soluble polymer could be used to investigate the intermolecular interactions of complementary polymers in dilute solutions. A frequent problem encountered in the studies of complementary polymers is the formation of an insoluble interpolymer complex which may be prevented by the use of dilute solutions of polymers and a careful selection of the reaction conditions. The formation of interpolymer complexes has been investigated by a variety of techniques but fluorescence spectroscopy has not been much used for this purpose[12]. Fluorescence techniques can be used with very dilute solutions of chromophores. Therefore, we thought that intermolecular interactions of complementary polymers could be investigated by fluorescence techniques without facing problems due to the precipitation of interpolymer complexes. Poly(acrylic acid) (PAA) was chosen as the pyrene group containing water-soluble polymer and interactions of the pyrene group containing PAA [P(H),7] with three different complementary polymers, namely, poly(ethylene oxide) (PEO), poly(1-vinyl-2-pyrrolidinone) (PVP) and poly(vinylamine, hydrochloride) (PVAm) were investigated. The selection of complementary polymers was based on the nature of secondary forces involved in the interactions of these polymers[12a]. In addition to the cooperative and hydrophobic interactions, PEO and PAA are thought to interact via hydrogen bonding, PAA and PVP are thought to interact mainly via hydrogen bonding with some contribution from Coulombic forces and PAA and PVAm are expected to interact mainly via Coulombic forces. The present work differs from other studies of photophysical properties of polyelectrolytes[5,6,11] because pyrene was used as a photophysical probe and the probe was covalently bound to PAA in such a way that the carboxylic groups were uniformly distributed along the main chain of the labelled PAA, that is, P(H). Thomas and coworkers[10] have also reported the photophysical properties of a copolymer of acrylic acid containing pyrene groups. The present work was carried out independent of that report and the content of pyrene groups in P(H) and concentrations of polymers used in spectroscopic measurements in this investigation were different from those used by Chu and Thomas[10a]. Both of these factors could be expected to lead to different inter- and intrapolymer interactions in solutions of P(H) compared to those in the studies of Chu and Thomas.

EXPERIMENTAL

Melting points were determined using a Thomas–Hoover capillary melting point apparatus and are reported uncorrected. The ^{1}H n.m.r. spectra were obtained using a Varian Model XL-200 (200 MHz) FT-NMR spectrometer and are reported as follows: (solvent): chemical shift (δ, ppm), multiplicity (br = broad, d = doublet, m = multiplet, q = quartet, s = singlet), coupling constant, integration and assignment. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee; the calculated values are shown in parentheses. Dilute solution viscosity measurements were performed in a constant temperature bath using a Cannon-Ubbelohde semi-micro dilution viscometer. The absorption spectra were recorded on a Perkin–Elmer Model 559A UV/VIS spectrophotometer. The fluorescence emission spectra were recorded on a Perkin–Elmer Model LS-5 fluorescence spectrophotometer at 20°C. The fluorescence emission lifetimes were determined using a single photon counting (SPC) apparatus from Photochemical Research Associates, London, Canada. The SPC apparatus was interfaced with a Hewlett–Packard 87XM computer for data analysis. The software used for SPC data analysis was written by Dr C. E. Doubleday, Jr of these laboratories; similar computer programs have been reported in the literature[13]. Nitrogen or argon gas was bubbled through the samples for at least ten minutes prior to emission lifetime measurements. All emission lifetime measurements were performed in duplicate with freshly prepared solutions and the mean values of the two measurements are reported; the errors given for lifetime values refer to twice the standard deviation of the mean value.



Scheme 1 Preparation of the pyrene group containing poly(acrylic acid) (Py- = 1-pyrenyl group)

Commerically available chemicals used in the preparation of monomer (**5**) (see *Scheme 1*) and polymers were purified, if required, using appropriate methods[14]. Spectrophotometric grade solvents (Aldrich or Burdick and Jackson) and deionized water were used in all measurements. Poly(1-vinyl-2-pyrrolidinone) (PVP) and poly(ethylene oxide) (PEO) samples used in this study were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. The degree of polymerization of PEO and PVP samples used in this study were calculated from the molecular weights of the samples provided by the manufacturer.

Measurements of pH were performed using a Beckman Model ϕ21 pH meter at room temperature. Titrations of the polymer samples were performed in a jacketed vessel to control the temperature. A solution containing *ca.* 10^{-3} mol per litre of P(H) was used for titration with 0.1 M sodium hydroxide solution. The pH values for the determination of I_M/I_E values were adjusted by addition of NaOH or HCl.

The concentration of polymers and monomers reported in this work refer to the concentrations of repeat units shown in *Figure 1* and refer to equivalents of repeat units per litre (reported as mol l^{-1}).

4-(1-Pyrene)butanoyl chloride (**2**)

A suspension of 2.01 g (7 mM) of 4-(1-pyrene)butanoic acid, 1.6 ml (18 mM) of oxalyl chloride and 40 ml of dichloromethane was refluxed for 4 h. The volatiles were removed under reduced pressure and the brown solid obtained was recrystallized from a mixture of hexanes and carbon tetrachloride to give 1.21 g (56%) of **2**, m.pt. 81°C–83°C (lit.[15] 74°C–75°C).

(R,S)-Methyl 2-amino-1-chloropropanoate hydrochloride (**3**)

The compound **3** used in the preparation of **5** was prepared from (D,L)-serine methyl ester, hydrochloride according to the procedure of Plattner and coworkers[16], m.pt. 133°C–134°C (lit.[16] 134°C–136°C).

2-[4-(1-Pyrene)butanoyl]aminopropenoic acid (**5**)

To a suspension of 1.09 g (4 mM) of **2** in 10 ml of dry DMF, 0.66 g (4 mM) of **3** was added and then a dropwise addition of a solution containing 1.0 ml (8 mM) of triethylamine and 10 ml of dry DMF was completed. The reaction mixture was stirred at room temperature for 14 h and then volatiles were removed under reduced pressure. The oily solid obtained was triturated with water, solid filtered and then washed with water, dil. HCl, again water and finally dried to give 1.07 g (76%) of **4**, m.pt. 127°C–130°C. ^{1}H n.m.r. ($CDCl_3$), 2.08–2.54, m, 4H, $-C\underline{H}_2C\underline{H}_2Py$; 3.40, t, 8 Hz, 2H, $-C\underline{H}_2CO-$; 3.82, s, 3H, $-C\underline{H}_3$; 3.92–4.00, m, 2H, $-C\underline{H}_2Cl$; 4.98–5.12, m, 1H, $-C\underline{H}-$; 6.40, br, 1H, $-N\underline{H}-$; 7.80–8.38, m, 9H, pyrenyl group protons.

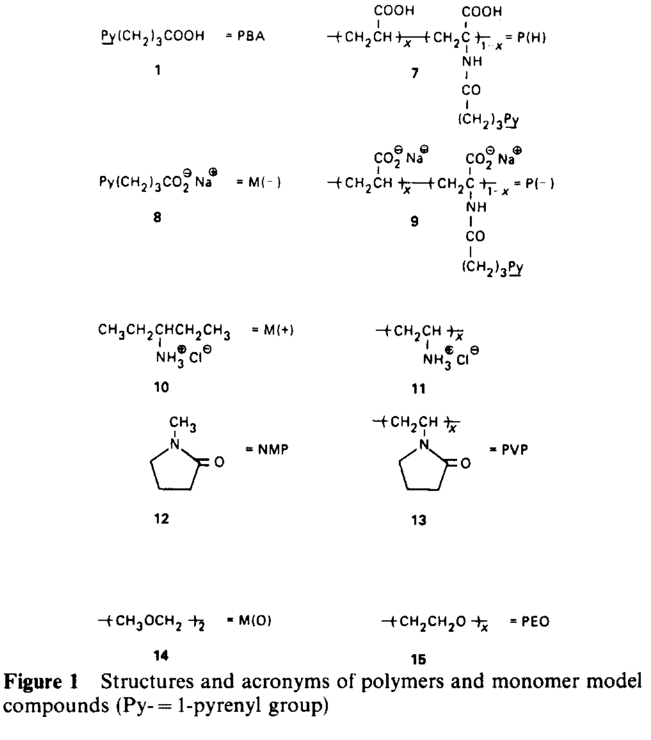


Figure 1 Structures and acronyms of polymers and monomer model compounds (Py- = 1-pyrenyl group)

To a suspension of 1.07 g (3 mM) of **4** in 50 ml of *p*-dioxane, 9.0 ml of 1M NaOH (9 mM) was added and the resulting mixture stirred for 1 h. To complete the reaction, 85 ml of water was added intermittently over a period of 3.5 h so that no precipitation took place. The resulting solution was stirred for 12 h and then evaporated under reduced pressure to half of the original volume. Addition of dilute HCl to the resulting solution gave a yellow precipitate which was filtered, washed with water and then dried. The dried material was recrystallized from a solvent mixture of ethanol and ethyl acetate to give 0.48 g (37% from **2**) of **5**, m.pt. 201°C–204°C, dec. A second crop weighing 0.10 g (total yield 45% from **2**), m.pt. 198°C–201°C, dec., was also obtained from the mother liquor. ^{1}H n.m.r. (DMSO-d_6), 2.52, t, 8 Hz, 2H, $-C\underline{H}_2Py$; 2.02, m, 8 Hz, 2H, $-C\underline{H}_2CH_2Py$; 3.34, t, 8 Hz, 2H, $-C\underline{H}_2CO-$; 5.72, s, 1H, vinylic proton (anti- or carboxylic group); 6.28, s, 1H, vinylic proton; 7.90–8.40, m, 9H, pyrenyl group protons; 9.20, s, 1H, $-N\underline{H}-$. $C_{23}H_{19}NO_3$: C 76.59 (77.29), H 5.71 (5.36), N 3.45 (3.92).

Poly[acrylic acid-co-2-(4-(1-pyrene)butanoyl)aminopropenoic acid] [**7**] *P(H)*

In a flask, fitted with a rubber septum and a magnetic stir-bar, 1.40 ml (20.4 mM) of freshly distilled acrylic acid, 0.096 g (0.3 mM) of **5**, 0.034 g (1 mole% based on total amount of monomers) of AIBN and 10 ml of dry DMF were introduced. The polymerization mixture was subjected to four freeze-pump thaw cycles and then placed in an oil-bath at 65 ± 3°C for 16 h with stirring. The viscous solution obtained was poured into excess ethyl acetate and the solid obtained was filtered and dried. The dried product was dissolved in 20 ml of methanol and then precipitated by a slow addition of 450 ml of ethyl acetate. The precipitated product was filtered and dried to give 1.01 g (65%) of **7**. ^{1}H n.m.r. (DMSO-d6), 1.48, 1.72, 2.18, br, acrylic acid protons; 3.05–3.60, 7.85–8.40, br, protons corresponding to **5**. Elemental analysis: C 49.94 (51.92), H 6.03 (5.58), N 0.31 (0.27).

The intrinsic viscosity of P(H) determined in 2M sodium hydroxide solution was 0.28 dl g^{-1} at 20°C. The viscosity average molecular weight calculated by Mark–Houwink–Sakurada (MHS) equation using K and a values for poly(acrylic acid)[17] was 19×10^3 (degree of polymerization = 249).

Poly(vinylamine, hydrochloride) [*PVAm*,**11**]

PVAm was prepared from acryloyl chloride according to the literature procedures[18]. The intrinsic viscosity of PVAm determined in 0.01M sodium hydroxide/0.1M sodium chloride solution was 1.23 dl g^{-1} at 21°C. The viscosity average molecular weight calculated by MHS equation using K and a values reported in the literature[18b] was 76.5×10^3 (degree of polymerization = 962).

RESULTS AND DISCUSSION

Preparation and characterization of the pyrene group containing poly(acrylic acid), P(H)

The pyrene group containing poly(acrylic acid) (P(H)) was prepared by copolymerization of acrylic acid and the pyrene substituted *N*-acylated dehydroalanine (**5**). The advantage of this method over a grafting reaction to prepare a pyrene group containing PAA is that the carboxylic groups are present in all repeat units of the resulting polymer. Furthermore, attachment of the pyrene group to the polymer main chain via an amide bond is desirable for studies of the resulting polymer over a wide pH range.

The desired monomer, **5**, was prepared from the available 4-(1-pyrene)-butanoic acid (**1**) and **3** according to a literature procedure for the preparation of a homologous monomer[19] (*Scheme 1*). The compound **4** prepared by the acid chloride method from **2** and **3** was treated without purification with excess sodium hydroxide in a solvent mixture of water and p-dioxane. After the work-up and recrystallization a 25% yield of **5**, from **1**, was obtained. The copolymerization of **5** with acrylic acid (**6**) to prepare P(H) was performed in DMF as solvent with AIBN as a free-radical initiator (*Scheme 1*). The amount of **5** in the monomer feed ratio for the copolymerization reaction was 1.5 mole% of **6** and was based on the following criteria. (1) The polymer, P(H), should be soluble in water. (2) The amount of pyrene in P(H) should be adequate for the investigations of P(H) in dilute solutions (polymer concentrations *ca.* 10^{-3}–10^{-4} mol l^{-1}). The first of these requirements was expected to be easily satisfied as Itoh and coworkers[20] have shown that a large amount of a hydrophobic monomer could be introduced in a copolymer of a hydrophilic monomer and a hydrophobic monomer without losing the water solubility of the resulting amphiphilic copolymer. A low amount of pyrene in P(H) was required so that intramolecular excimer formation, which is known to predominate at higher concentrations of pyrene[7a,20], does not become the main fate of excited pyrene molecules in P(H). The minimization of intramolecular excimer formation ideally requires a random distribution of pyrene groups interspersed with large blocks of PAA in P(H). However, the microstructure of a copolymer is largely controlled by the reactivity ratios and the feed ratio of monomers used in the copolymerization reaction[21]. The reactivity ratios of acrylic acid and *N*-acetyldehydroalanine (2-acetylamino-2-propenoic acid), an analogue of **5**, have been reported as 1.41 and 0.49 in a benzoyl peroxide initiated copolymerization reaction at 70°C[22]. The product of two reactivity ratios suggested that acrylic acid and *N*-acetyldehydroalanine could be expected to show ideal behaviour in free radical copolymerization[21]. If steric effects on the reactivity ratio of **5** due to the presence of pyrene group were neglected, ideal behaviour could also be expected in the copolymerization of **5** and **6**. Thus, a control over the amount of **5** in P(H) should be possible by appropriate choice of the monomer feed ratio. A small amount of **5** was used in the monomer feed ratio for the preparation of P(H) as under ideal copolymerization conditions the amount of comonomer incorporated in the copolymer should be directly proportional to the amount of comonomer in the feed. A 1.5 mole% of **5** was considered adequate because fluorescence measurements could be performed with pyrene concentration of *ca.* 10^{-6} mol l^{-1}.

The yield of P(H) obtained after purification of the copolymer was 65%. High resolution (200 MHz) ^{1}H n.m.r. spectrum of P(H) in deuterated water did not show significant aromatic region absorptions due to **5** in both aromatic and aliphatic regions. The absence of absorptions due to **5** in the spectrum of P(H) in deuterated water was due to a very small amount of **5** in P(H) and dipolar broadening of the resonances due to **5** because of the hydrophobic interactions of pyrene groups. The amount of **5** in P(H) could not be determined from the integration ratios of the ^{1}H n.m.r. spectrum of P(H) in d_6-DMSO due to the very small amount of **5** in P(H). The polymer P(H) was soluble in water, methanol, DMF, DMSO and *N*-methyl-2-pyrrolidinone (NMP).

The u.v. absorption spectrum of P(H) in water or methanol as solvent showed the presence of pyrene. The positions of (0,0) transitions of ^1L_a, ^1B_b and ^1B_a bands were 342, 275 and 242 nm in methanol and 345, 277 and 243 nm in water. The concentration of pyrene in P(H) was calculated from the absorbance due to (0,0) transition in ^1L_a band in the absorption spectrum of pyrene in P(H) and the extinction coefficient of the same transition in the absorption spectrum of 4-(1-pyrene)butanoic acid (PBA) in methanol. The concentration of **5** was calculated as 6.6% by weight whereas the amount of **5** in the monomer feed was 6.5%. Therefore, a 1.5 mole% of **5** was assumed in the structure of P(H) in all calculations. The elemental analysis (nitrogen content) of P(H) also showed that the amount of **5** in P(H) was the same as that used in monomer feed. A good agreement between amount of **5** in the monomer feed and that found in P(H) supported the assumption of ideal copolymerization behaviour of **5** and **6**.

The titration curves of P(H) obtained by titration of P(H) with sodium hydroxide in water and in 0.1 M sodium chloride solution are given in *Figure 2* as plots of pK_a and α, where α is the degree of ionization of P(H) and pK_a is given by equation (1)[23].

$$pK_a = pH + \log((1-\alpha)/\alpha) \qquad (1)$$

The pK_0 values for P(H) calculated by fitting the titration curves of *Figure 2* to a biexponential equation[23] were 5.5 (water) and 4.8 (0.1 M NaCl). These values were slightly greater than those reported for PAA, 4.8 (water) and 4.5 (0.1 M NaCl)[23]. Poly(*N*-acetyldehydroalanine) [poly(2-acetylamino-2-propenoic acid)], an analogue of homopolymer of **5**, has been reported to have a pK_0 value of 6.4 in water[24]. The higher pK_0 values of P(H) could be attributed to hydrophobic interactions of pyrene groups in this polymer analogous to the behaviour of polysoaps[25]. No transition was observed in the titration curve for P(H) unlike the behaviour of polysoaps which could be due to a small amount of pyrene groups in P(H).

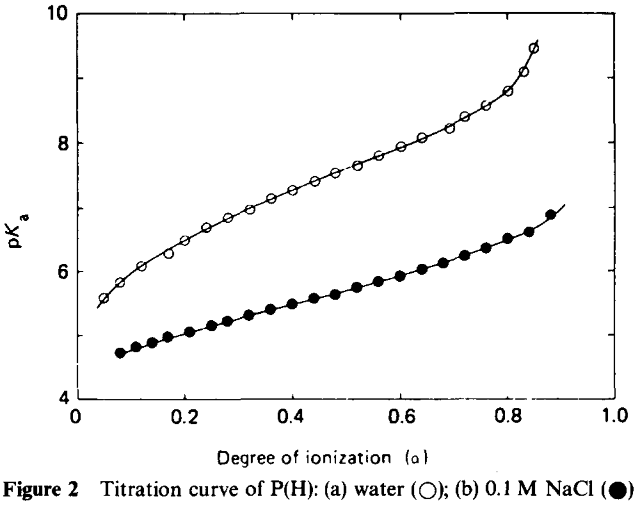


Figure 2 Titration curve of P(H): (a) water (○); (b) 0.1 M NaCl (●)

Fluorescence emission spectrum of P(H), polymer concentration *ca.* $10^{-4}\,\mathrm{mol\,l^{-1}}$, consisted of pyrene monomer emission and a long wavelength 'red' structureless emission due to pyrene excimer (see below) in water or methanol as solvent (*Figure 3*). The peaks for pyrene monomer emission in P(H) in methanol were observed at 377, 396 and 419 nm and at 378, 397 and 419 nm in water. The pyrene excimer emission in P(H) was observed to have a maximum at 476 nm in methanol and at 480 nm in water as solvent.

Photophysical properties of P(H) in dilute solutions

Emission and absorption spectroscopy. Interpolymer interactions could be assumed to be insignificant in sufficiently dilute solutions of polymers. The photophysical properties of P(H) in dilute solutions were expected and found (see below) to be determined by the intramolecular interactions of the pyrene groups in P(H). Due to the polymerization method used in the preparation of P(H), a random distribution of pyrene groups could be expected in the microstructure of P(H). The interactions of pyrene groups in the solutions of P(H) were expected to be determined by the conformation of P(H) and the length of PAA blocks separating neighbouring pyrene groups in P(H) as shown in *Figure 4*. If the number of acrylic acid units separating the neighbouring pyrene groups was small or zero then the neighbouring pyrene groups should be expected to interact in an expanded (II) as well as a compact form (IV) of P(H). If the length of PAA blocks separating the neighbouring pyrene groups was of an intermediate range, the interactions of pyrene groups should be possible in a compact form (III) but not in an expanded form (I) of P(H). As shown in (V), if the lengths of PAA blocks separating the neighbouring pyrene groups were very large or only one pyrene group was present in a molecule of P(H) no intramolecular interactions of pyrene groups should be possible in a compact (V) as well as an expanded form of P(H). The polymer, P(H), used in this study was expected to comprise the three different types of neighbouring pyrene groups depicted above. The efficiency of intrachain excimer formation between the pyrene groups could be expected to decrease with the expansion of polymer chain thus the ratio of intensities of monomer (0,0) emission and excimer emission (I_M/I_E value) of P(H) was expected to reflect the changes in conformation of P(H).

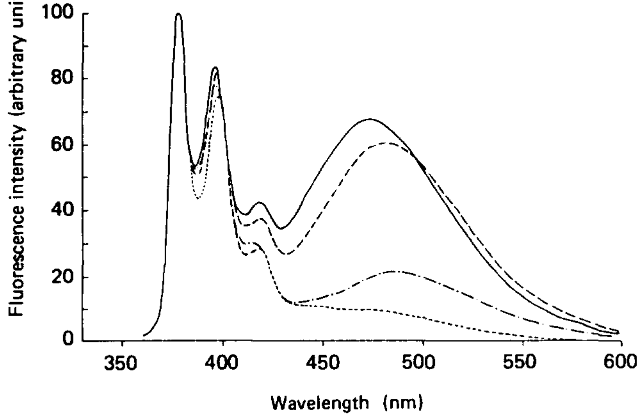


Figure 3 Emission spectra of P(H) in methanol (———), water (– – –), water/NaOH (–·–·–) and NMP (-----). [P(H)] = $10^{-4}\,\mathrm{mol\,l^{-1}}$

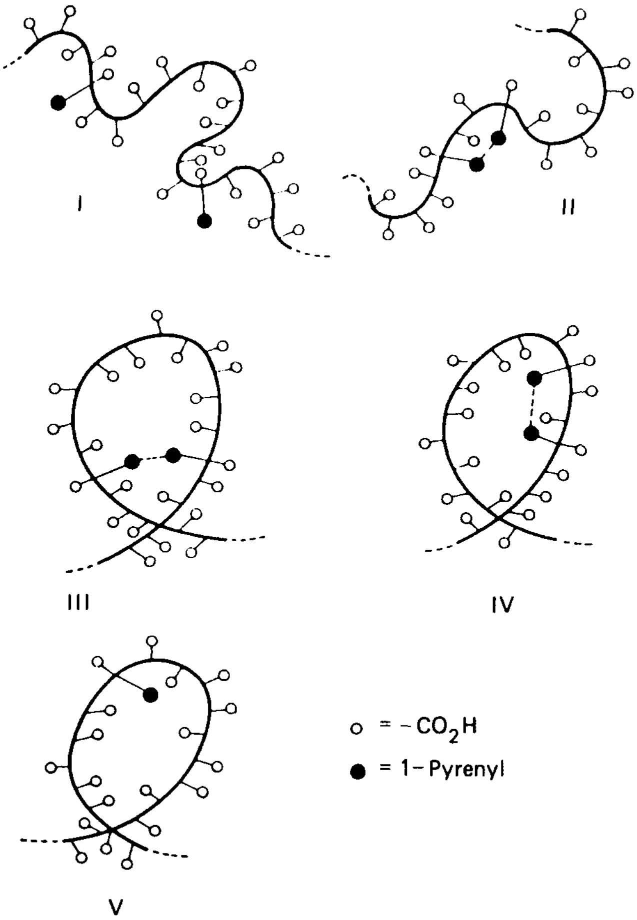


Figure 4 Schematic representation of the proposed microstructure of P(H)

The emission spectrum of P(H), concentration of polymer *ca.* $10^{-4}\,\mathrm{mol\,l^{-1}}$, in water or methanol gave emission due to pyrene monomer and excimer (*Figure 3*). The ratio of intensities of monomer (0,0) emission and excimer emission, that is, I_M/I_E value, and the wavelength at the maximum of excimer emission (λ_D) in these spectra are given in *Table 1*. A significant amount of excimer emission was observed in both solvents. The emission spectra in methanol and water were also measured at three different concentrations of P(H) in order to determine the contribution of interpolymer interactions to the excimer emission. The I_M/I_E values for these spectra are given in *Table 2*. The I_M/I_E value in methanol increased when concentration of polymer was reduced from 10^{-3} to $10^{-4}\,\mathrm{mol\,l^{-1}}$ and again showed a small increase when concentration was reduced to $10^{-5}\,\mathrm{mol\,l^{-1}}$. The magnitude of the change in I_M/I_E values suggested that interpolymer interactions were not a significant factor in excimer emission from solutions of P(H) under these conditions. There was a significant increase in the I_M/I_E value for the spectra measured in water when the concentration of P(H) was reduced from 10^{-3} to $10^{-5}\,\mathrm{mol\,l^{-1}}$. This could be attributed to the increased ionization of P(H) with dilution and thus a change in polymer conformation from a coiled to an expanded form. The emission spectra of P(H) measured in a buffer solution (pH = 4.63) supported the above conjecture as I_M/I_E values in these spectra also showed only a moderate increase with dilution (*Table 2*). There was a large increase in the I_M/I_E value for the emission spectrum of P(H) in water when an equivalent amount of sodium hydroxide was added to this solution

Table 1 Effects of medium on the absorption and emission spectrum of pyrene in P(H)[a]

	Emission		Absorption	
Solvent	I_M/I_E[b]	λ_D[c] (nm)	P[d]	λ[e] (nm)
Water (pH = 5.3)	1.8	480	1.6	345
Methanol	1.5	476	2.6	342
Water/NaOH[g]	4.9	486	1.7	344
NMP	10.3	–[f]	2.1	345
Buffer solution[h]	1.4	482	1.5	345

[a] $[P(H)] = 5 \times 10^{-4}$ mol l^{-1}

[b] This is the ratio of the intensities of monomer (0.0) and excimer emission

[c] Maximum of excimer emission

[d] This is the peak-to-valley ratio for the (0,0) transition in the ^1L_a band

[e] (0,0) transition in ^1L_a band

[f] No detectable maximum was observed in the long wavelength region

[g] $[NaOH] = 5 \times 10^{-4}$ mol l^{-1}

[h] Sodium acetate–acetic acid buffer, pH = 4.63

Table 2 Effect of polymer concentration on I_M/I_E value of pyrene in P(H)

Concentration of polymer (mol l^{-1})	I_M/I_E[a]			
	Water[b]	Methanol	Water/NaOH[c]	Buffer solution[d]
10^{-3}	1.4	1.1	4.8	1.4
10^{-4}	1.8	1.5	4.7	1.6
10^{-5}	3.7	1.6	4.7	1.8

[a] See footnote *b*, *Table 1*

[b] Deionized water

[c] $[NaOH] = [P(H)]$

[d] Sodium acetate–acetic acid buffer, pH = 4.63

(*Figure 3* and *Table 1*); the ionized form of P(H) obtained in this manner was designated P(−). This could be attributed to the polymer chain expansion caused by increased charge density on polymer chain due to conversion of P(H) to P(−). Interpolymer interactions were also reduced in solutions of P(−) as no increase in I_M/I_E values was observed when concentration of P(−) was changed from 10^{-3} to 10^{-5} mol l^{-1}.

When the emission spectrum of P(H) was measured in NMP as solvent the excimer emission was found to be significantly reduced (*Figure 3*). No detectable maximum was observed in the long wavelength emission in this spectrum and I_M/I_E value given in *Table 1* was calculated from the intensity of emission at 480 nm. The low efficiency of excimer formation in solutions of P(H) in NMP could be due to chain expansion of P(H) caused by this solvent and/or some excited state interactions between the pyrene groups and NMP. The absorption spectrum of P(H) in NMP did not give evidence of any ground state interactions between the pyrene groups in P(H) and NMP.

The absorption spectra of P(H) obtained in different media also provided evidence for the changes in conformation of P(H) brought about by different environments. Herkstroeter and coworkers[8] have shown that increased interactions of pyrene groups cause broadening of the absorption spectrum of pyrene which can be measured from the peak-to-valley ratio (*P*) of the absorption bands. The wavelengths and *P* values for (0,0) transitions in ^1L_a band of the absorption spectrum of P(H) are given in *Table 1*. The *P* value was found to decrease in water compared to that measured in methanol or NMP and was found to be increased by the addition of sodium hydroxide to a solution of P(H) in water. Thus, hydrophobic interactions of pyrene groups in P(H) were favoured in aqueous solutions of P(H) and these interactions were reduced by chain expansion in P(−).

The effect of charge shielding by sodium chloride in the emission spectrum of P(−) was also observed. The I_M/I_E value was found to decrease by the addition of an increasing amount of sodium chloride indicating a reduced expansion of polymer chain in P(−) in the presence of salt.

The changes in I_M/I_E value for P(H) were followed as a function of pH in water and in 0.1 M sodium chloride solution. The observed behaviour is shown in *Figure 5*. The I_M/I_E value was found to increase with increasing pH due to polymer chain expansion [3a] and thus less efficient excimer formation between intrachain pyrene moieties in P(H). In water, the plot of I_M/I_E against pH could be divided into three distinct regions. A moderate increase in I_M/I_E was observed in the pH range 3–5.5 (region I) because hydrophobic interactions of pyrene groups prevented expansion of polymer chain. This region was followed by a region of sharp increase in I_M/I_E (pH 5.5–7.5, region II) which was indicative of polymer chain expansion caused by increased charge repulsion in this pH range. The increase in I_M/I_E was moderate in the pH range 7.5–10 (region III) due to increased difficulty in further ionization of polymer because of the increased charge density of the polymer chain. A significant amount of excimer emission even at high pH (10) values indicated contributions from the structures of type II (*Figure 4*). In the presence of salt the effect of hydrophobic interactions (region I) was found to end at a lower pH value (4.2) and in the region II (pH 4.2–7) the I_M/I_E values in the presence of salt were higher than those in water at the same pH value (*Figure 5*). This behaviour could be attributed to a more efficient ionization of P(H) due to charge shielding by the salt. The I_M/I_E values in region III in the presence of salt were lower than those in water indicating less polymer chain expansion in the presence of salt.

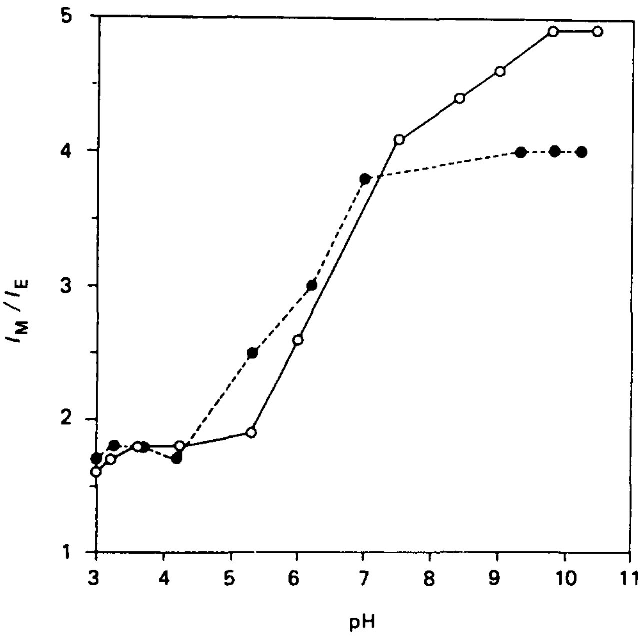


Figure 5 Effect of pH on I_M/I_E value of P(H) in water (○) and 0.1 M sodium chloride (●)

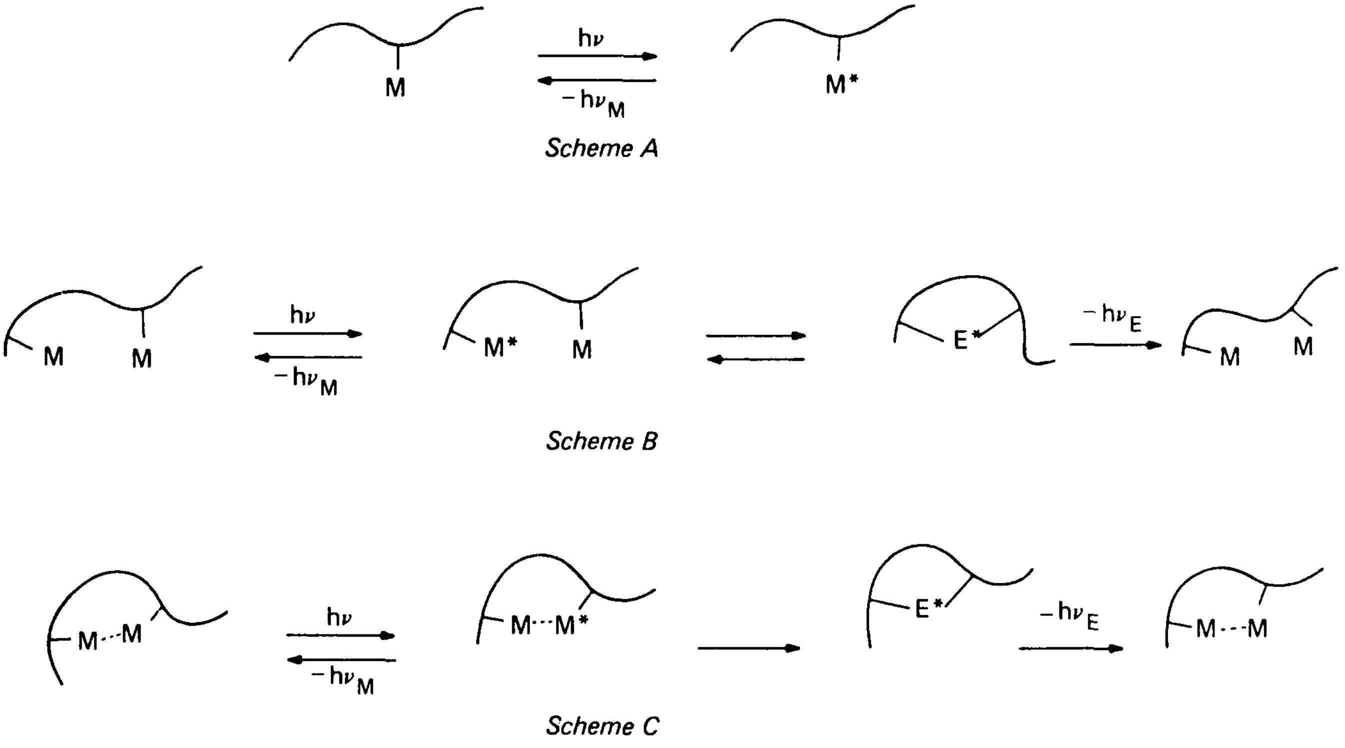
Fluorescence lifetime measurements. The determination of lifetimes for monomer and excimer emission from P(H) and P(−) in water was attempted using a single photon counting method. The monomer emission lifetime of M(−) was also determined under similar conditions for the purpose of comparison. The results are given in *Table 3*. The fluorescence lifetime for PBA in water has been reported in the range 123–146 ns[26]. The monomer emission from P(H) was found to show a non-exponential decay behaviour. The observed monomer emission decay curves showed contributions from short-lived and long-lived components but the decay curves could not be satisfactorily fitted to an equation containing two exponential components. However, the latter part of the decay curve could be fitted to a monoexponential decay and the lifetimes obtained from this curve fitting are given in *Table 3*. The decay curves for excimer emission also showed non-exponential behaviour and could not be fitted to an equation containing two exponentials.

The transient behaviour of monomer and excimer emission from pyrene groups in P(H) can be explained on the basis of polymer chain dynamics and microstructure of P(H) (*Figure 6*). The isolated pyrene groups in P(H) (*Figure 6*, *Scheme A*) could be expected to show a monoexponential decay behaviour for monomer emission[27] with a typical lifetime of 125–150 ns. The behaviour of intrachain pyrene groups in P(H) should depend on the polymer chain dynamics and the length of PAA blocks separating the pyrene groups. The kinetics of intramolecular excimer formation in solutions of polymers containing isolated pyrene groups have been discussed by Cuniberti and Perico[28] and Winnik[29]. The analysis of processes involved in intramolecular excimer formation under these conditions predicts that the response function of monomer emission consists of a sum of two exponential components and that of excimer emission consists of a difference of two exponential components[30]. Transient emission behaviour of intrachain pyrene groups in P(H) which were separated by PAA blocks in such a way that neighbouring pyrene groups could interact as a result of chain folding (*Figure 6*, *Scheme B*) would be expected to be analogous to that predicted for intramolecular excimer formation[31]. The formation of stable excimers could occur in P(H) due to the hydrophobic interactions of pyrene groups which were either closely spaced on the polymer main chain or were brought together by folding of the polymer (*Figure 6*, *Scheme C*). The response function for excimer emission shown by *Scheme C* could be expected to be a sum of a growth and a decay term[31]. If the excimer formation was very fast this growth term might not be observed and the excimer emission would be then observed to decay exponentially. Thus, the decay functions of monomer and excimer emission in P(H) could be expected to consist of at least three exponential terms each. The intramolecular excimer formation in the case of bichromophoric compounds containing the pyrene chromophore has also been postulated to show multiexponential decay behaviour on account of differences in the configurations of the excimer formed[32]. This factor could also contribute

Table 3 Decay parameters for monomer and excimer emission of pyrene in P(H) under different conditions[a]

Conditions for measurement	Monomer emission[b] τ (ns) M(−)[d]	Monomer emission[b] τ (ns) P(H)	Excimer emission[c] τ (ns) P(H)
Water	–	122±5[e]	58±3[e]
Water/NaOH	106±6	111±0[e]	49±2[e]
PEO-2270/water[f]	117±3	123±1[e]	83±0[e]
PVAm/water[f]	114±3	–	–
PVP-3240/water[f]	121±4	150±4[e]	94±3[e]

[a] $[P(H)] = 5 \times 10^{-4}$ mol l^{-1}
[b] Viewed at 370 nm
[c] Viewed at 540 nm
[d] $[M(-)] = 10^{-6}$ mol l^{-1}
[e] The decay curves also show a contribution from a short-lived component
[f] Concentration of complementary polymer $= 10^{-4}$ mol l^{-1}



Scheme A

Scheme B

Scheme C

Figure 6 Proposed schemes for transient behaviour of pyrene groups in P(H) (M = pyrene and E = excimer) to the transient decay behaviour of P(H) and therefore a very complex decay behaviour of monomer and excimer emission could be expected in this polymer.

The decay parameters obtained by a partial analysis of monomer and excimer decay curves for P(H) and P(–) vindicated the proposed microstructure of P(H) although a complete analysis of the decay curves was not possible in either case. An exponential fit of the latter part of monomer decay curves of P(H) and P(–) yielded decay parameters comparable to monomer lifetime of M(–) (*Table 3*) and were therefore representative of isolated pyrene groups in P(H) and P(–) (*Figure 6, Scheme A*). The decay parameters obtained by an exponential fit of the latter part of excimer decay curve were considered to be respresentative of stable excimers (*Figure 6, Scheme C*); these values compared well with those reported for excimer lifetime of pyrene groups bound to polymers[7] (*Table 3*).

The decay of monomer emission of PBA in NMP as solvent was found to show a non-exponential decay behaviour. The decay curves indicated that emission lifetime was decreased compared to that in water but the observed decay curves could not be fitted to an equation containing two exponential terms. The emission and absorption spectrum of PBA in NMP as solvent did not show any ground or excited state interactions between pyrene groups and NMP. The non-exponential decay of monomer emission and decreased lifetime suggested that some excited state interactions took place between excited pyrene groups and NMP. The weakly basic nitrogen in NMP can be expected to interact with excited pyrene groups analogous to the behaviour of amines[33]. Because of the excited state interactions between NMP and pyrene, the decay curves for monomer and excimer emission from P(H) in NMP were found to be very complicated.

Interactions of P(H) with complementary polymers

Based on the nature of secondary forces involved in interpolymer interactions[12a], three complementary polymers were selected for investigating the interpolymer interactions of P(H) (*Figure 1*). Poly(vinylamine hydrochloride) (PVAm) was selected as a polycation which could be expected to associate with P(H) mainly via Coulombic interactions. PVAm is the simplest polyamine containing pendant amino groups but this polymer has not been extensively investigated because the preparation of PVAm is a multistep procedure[18]. The investigations of the interactions of P(H) and PVAm were also considered to give an opportunity for studying the possible ground state, electron donor–acceptor (EDA), and excited-state interactions between pyrene and amino moieties in the two polymers[33,34]. The formation of hydrogen bonds between the carboxylic groups in PAA and the electronegative oxygens in PEO and PVP is considered to be the dominant secondary force in the association of PAA and PEO or PVP[35,36]. A stronger association of PAA and PVP than that of PAA and PEO is attributed to the contribution of hydrophobic and Coulombic interactions in the association of PVP and PAA[35]. In addition to the specific secondary forces, the association of polymers is also influenced by cooperative or 'polymer' effects[12a]. Thus, a minimum molecular weight of the complementary polymer which is dependent on the nature of secondary forces involved in interpolymer interactions[12a] is required before an effective association of the two polymers.

The investigations of interpolymer interactions between P(H) and complementary polymers were aimed towards finding the usefulness of the photophysical properties of pyrene for studying the effects of various secondary forces in the association of complementary polymers. The interactions of P(H) and monomer model compounds of the three complementary polymers, namely, M(+), NMP and M(O) (*Figure 1*), were studied in order to determine any specific interactions of the functional groups in complementary polymers. The compound M(O) was used as a monomer model for PEO in place of diethyl ether because of the volatile nature of diethyl ether. A comparison of the behaviour of monomer model compounds with that of the corresponding polymers was expected to provide information about the role of cooperative effects. Two samples of different molecular weight of the complementary polymers, where available, were used in order to further assess the role of cooperative forces on interpolymer association. Stoichiometric effects on interpolymer interactions were investigated by studying the interactions of complementary polymers and those of P(H) and monomer model compounds at different molar ratios of polymers.

Dilute solutions of polymers were required in the studies of interpolymer interactions of P(H) and complementary polymers in order to avoid the precipitation of interpolymer complexes. The concentration of P(H) chosen for studying interpolymer interactions was *ca.* 10^{-4} mol l^{-1} (corresponding to pyrene concentration of 10^{-6} mol l^{-1}) as good signal-to-noise ratios were obtained at this concentration of polymer.

Emission and absorption spectra. The effects of the addition of PVAm, PVP and PEO and the monomer model compounds on the absorption and emission spectra of P(H) are summarized in *Tables 4, 5* and *6*. These spectra were obtained under conditions expected to maximize the interactions of complementary polymers. An ionized form of P(H), that is, P(–) was used for studying the interactions of P(H) and PVAm. The interactions of PEO and P(H) were studied at a pH of 3 and those of PVP and P(H) were studied at a pH of 4.5 so that only a small fraction of the carboxylic groups in P(H) was in an ionized form. The use of a highly acidic solution for studying the interactions of P(H) and PVP was not necessary as these polymers showed strong interactions at pH 4.5 also.

The I_M/I_E and P values of P(H) in the presence of NMP or M(O) were not found to be significantly different even when a large excess of these compounds was used. There were no changes in the wavelengths of peaks observed in the emission and absorption spectra of P(H) in the presence of NMP or M(O) at molar ratios indicated in *Tables 5* and *6*. Thus, no association of P(H) with NMP or M(O) took place under these conditions. The I_M/I_E values of P(–) were reduced in the presence of an equimolar or an excess amount of M(+) (*Table 4*). The presence of M(+) also caused a broadening of the absorption spectrum of P(–) which was indicated by a reduction in P values (*Table 4*). The presence of M(+) could be expected to increase the interactions of pyrene groups in P(–) because of the increased ionic strength of the solution (salt effect). However, the observed changes in I_M/I_E values, in particular, at a P(–):M(+) molar ratio of 1:100, were greater than those observed in the presence of a similar

Table 4 Effect of poly(vinylamine hydrochloride) (PVAm) and a monomer model compound (M(+)) on the absorption and emission spectrum of pyrene in P(−)[a]

P(−):PVAm or M(+)[b]	P[c]		$I_{\mathrm{M}}/I_{\mathrm{E}}$[d]		λ_{D}[e] (nm)	
	P(−):PVAm	P(−):M(+)	P(−):PVAm	P(−):M(+)	P(−):PVAm	P(−):M(+)
10:1	1.8	1.7	4.2	4.7	486	486
1:1	1.3	1.6	1.9	4.5	475	486
1:10	1.2	1.4	1.3	4.0	456	485
1:100	–[f]	–[f]	1.3	2.8	445	486

[a] $[\mathrm{P}(-)] = 5 \times 10^{-4}\ \mathrm{mol\ l^{-1}}$

[b] Ratio of molar concentrations of the two compounds

[c] See footnote *c*, *Table 1*

[d] See footnote *b*, *Table 1*

[e] Maximum of long wavelength emission due to excimer/exciplex

[f] Vibrational transitions affected in these spectra

Table 5 Effect of poly(1-vinyl-2-pyrrolidinone) (PVP) and a monomer model compound (NMP) on the absorption and emission spectrum of pyrene in P(H)[a]

P(H):PVP or NMP[b]	P(H):PVP-3240		P(H):PVP-216		P(H):NMP	
	$I_{\mathrm{M}}/I_{\mathrm{E}}$[c]	P[d]	$I_{\mathrm{M}}/I_{\mathrm{E}}$[c]	P[d]	$I_{\mathrm{M}}/I_{\mathrm{E}}$[c]	P[d]
10:1	3.5	1.9	4.8	1.9	2.1	1.4
1:1	15.2	2.2	11.2	2.3	1.8	1.4
1:10	12.0	2.2	13.2	2.3	1.8	1.4
1:100	12.0	2.1	13.2	2.1	2.0	1.5

[a] $[\mathrm{P(H)}] = 5 \times 10^{-4}\ \mathrm{mol\ l^{-1}}$, pH = 4.5

[b] Ratio of molar concentration of the two compounds

[c] See footnote *b*, *Table 1*

[d] See footnote *c*, *Table 1*

Table 6 Effect of poly(ethylene oxide) (PEO) and a monomer model compound (M(O)) on the absorption and emission spectrum of pyrene in P(H)[a]

P(H):PEO or M(O)[b]	P(H):PEO-2270		P(H):PEO-114		P(H):M(O)	
	$I_{\mathrm{M}}/I_{\mathrm{E}}$[c]	P[d]	$I_{\mathrm{M}}/I_{\mathrm{E}}$[c]	P[d]	$I_{\mathrm{M}}/I_{\mathrm{E}}$[c]	P[d]
10:1	1.6	1.8	1.5	1.9	1.6	1.7
1:1	2.7	2.0	1.8	2.0	1.6	1.7
1:10	2.8	2.0	2.1	1.9	1.6	1.7
1:100	–[e]	–[e]	2.3	1.9	1.7	1.8

[a] $[\mathrm{P(H)}] = 5 \times 10^{-4}\ \mathrm{mol\ l^{-1}}$; pH = 3.0

[b] Ratio of molar concentration of the two compounds

[c] See footnote *b*, *Table 1*

[d] See footnote *c*, *Table 1*

[e] This solution was found to be turbid in appearance

amount of sodium chloride (cf. *Figure 5*). Therefore, the observed behaviour was considered to arise from a combination of the salt effect and association of P(−) and M(+). The association of P(−) and M(+) could be expected to be favoured by Coulombic and hydrophobic interactions; the binding of tetramethylammonium ions to PAA has been reported[37]. The broadening of the absorption spectrum of P(−) in the presence of M(+) implied ground state interactions between amino and pyrene groups. The increase in the intensity of the red emission could be caused by a contribution from the emission of exciplex formed between excited pyrene groups and amino groups. There was no significant change in the maximum of red emission in the presence of M(+) indicating that excimer and exciplex emitted in the same range. The observed effects in the emission and absorption spectrum of P(−) were directly related to the amount of M(+) present.

The formation of exciplex between pyrene and amines is a well-known phenomenon[33]. The formation of intramolecular exciplexes between pyrene and amino-group-containing polymers has been reported by Tazuke and coworkers[34]; the maximum of exciplex emission in those polymers was observed in the range 450–500 nm[38]. Emission spectra of some other polymers containing pyrene and amino groups have also been reported to show a 'red' structureless emission[7,8] but the observed behaviour in those cases was attributed to excimer formation.

The effects of PVAm on the absorption and emission spectra of P(−) were strikingly different from those of M(+) (*Table 4*). The $I_{\mathrm{M}}/I_{\mathrm{E}}$ value of P(−) was reduced in the presence of PVAm and this effect was observed even in the presence of an excess amount of P(−). When an equimolar or an excess amount of PVAm was present the $I_{\mathrm{M}}/I_{\mathrm{E}}$ values of P(−) were significantly reduced. The presence of PVAm also caused a broadening of the absorption spectrum of P(−) as reflected in lower P values. The maximum of the 'red' emission in the emission spectra of P(−) was found to show a hypsochromic shift in the presence of PVAm (*Figure 7*). All of these effects were enhanced by an increase in the amount of PVAm present. The observed behaviour could be attributed to ground and excited state interactions of pyrene and amino groups. Cooperative effects in PVAm:P(−) led to stronger interactions as observed in a greater broadening of absorption spectra and enhanced intensity of red (exciplex) emission compared to those of M(+):P(−).

Absorption and emission spectra of the solutions of M(−) (*ca.* 10^{-6} mol l^{-1}) in the presence of PVAm, PEO or PVP (10^{-4} mol l^{-1}) provided support for the hypothesis that the ground and excited state interactions observed in solutions of PVAm:P(−) and M(+):P(−) were caused by the interactions of amino and pyrene groups. No ground or excited state interactions were observed when spectra were obtained under alkaline conditions as determined from absorption spectra ($P = 2.2 \pm 0.1$), emission spectra (no 'red' structureless emission) and emission lifetime measurements (*Table 3*) of M(−) in the presence of these polymers. However, under acidic conditions (pH<7) spectra of M(−):PVAm indicated ground state as well as excited state interactions analogous to the behaviour of P(−):PVAm and P(−):M(+). These changes in the spectra were caused by association of M(−) and PVAm which was observed by the development of turbidity in these solutions.

The ground and excited state interactions of pyrene groups in P(H) were significantly reduced in the presence of PVP-3240 and PVP-216. The *P* and I_M/I_E values were significantly increased in the presence of PVP and these effects were observed even when an excess amount of P(H) was present (*Table 5*). In the presence of an equimolar or an excess amount of PVP no maximum was observed in the red region of the emission spectra and I_M/I_E values were calculated from the emission intensity at 480 nm. Both PVP samples exhibited strong association with P(H) in equimolar solutions of P(H) and PVP. The molecular weight of PVP-216 was higher than that required for effective association PAA and PVP[39]. At 1:1 mole ratio of P(H) and PVP the association between P(H) and PVP-3240 was stronger than that between P(H) and PVP-216 indicating the role of cooperative effects. The presence of an excess amount of PVP led to a decrease in I_M/I_E value for PVP-3240 and an increase in I_M/I_E value for PVP-216 but the observed changes were not significant in view of the dynamic nature of the association of polymers (see below).

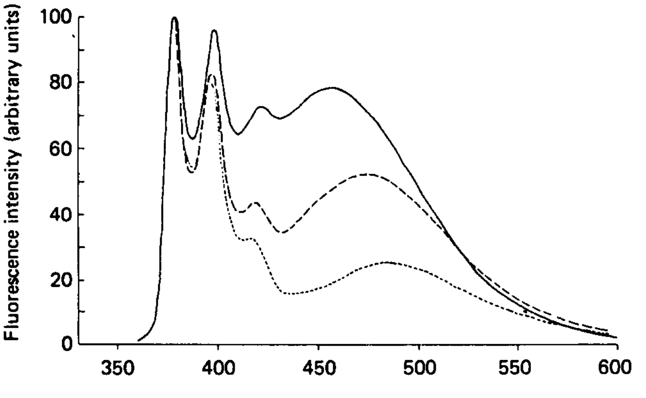


Figure 7 Emission spectra of P(−) in presence of PVAm: (a) P(−):PVAm = 10:1 (-----); (b) P(−):PVAm = 1:1 (– – –); (c) P(−):PVAm = 1:10 (———). [P(−)] = 10^{-4} mol l^{-1}

The solutions of P(H) and PEO-2270 or PEO-114 showed reduced ground and excited state interactions of pyrene groups in P(H) only when an equimolar or excess amount of PEO was present (*Table 6*). Furthermore, the association of P(H) and PEO was observed only under very acidic conditions (pH = 3) because no significant reduction in *P* or I_M/I_E values, compared to those for M(O), was noticed in solutions of P(H) and PEO at a pH of 4.5. The lower molecular weight sample of PEO, that is, PEO-114 also showed a significant effect on P and I_M/I_E values of P(H) although the molecular weight of this sample was lower than that reported for an effective association of PEO and PAA[35a,36]. The association of P(H) and PEO was enhanced in the presence of an excess amount of PEO as reflected by the reduction in I_M/I_E values (*Table 6*) and the fact that a solution of P(H) and PEO-2270 at a molar ratio of 1:100 was found to be turbid in appearance. The cooperative effects on association of P(H) and PEO were also shown in the I_M/I_E values of P(H) in the presence of PEO-2270 and PEO-114. The association of P(H) and PEO was found to be much weaker in comparison to that of P(H) and PVP as determined from I_M/I_E values and the pH effect on association of these polymers (see below also).

The changes in spectroscopic properties of P(H) with changes in the amount of complementary polymers (stoichiometric effects) could be attributed to the following factors—self-association of complementary polymers, changes in conformation and structure of the interpolymer complex due to increase in concentration of polymers, and association of interpolymer complexes and excess complementary polymer. The results of stoichiometric effects on the spectroscopic properties of P(H) showed that self-association of PVAm, PEO or PVP was not significant in the presence of P(H); interpolymer association, in general, was favoured by an increase in the amount of complementary polymer (*Tables 4*, *5* and *6*). Stoichiometric effects on the spectroscopic properties of P(−):PVAm indicated that association of interpolymer complex and excess PVAm took place in solutions of P(−) and PVAm (*Table 4*). In the case of P(H):PVP and P(H):PEO the stoichiometric effects could be due to combined effects of the changes in conformation and structure of interpolymer complexes (*Tables 5* and *6*). Tacticity and polydispersity could be expected to play an important role in the structures of interpolymer complexes formed from two complementary polymers. Therefore, we are unable to offer unequivocal explanations for all the stoichiometric effects observed in the association of P(H) and PVP or PEO. The spectroscopic properties of interpolymer complexes indicated that the complexes assumed a more compact conformation in the presence of sodium chloride (0.1–0.5 M). The interpolymer complexes precipitated when a large excess of sodium chloride (1 M) was added to solutions of complementary polymers at 1:1 molar ratio.

The effects of pH on I_M/I_E values of P(H) in the presence of complementary polymers and their monomer model compounds (at a molar ratio 1:1) were studied because the interactions of these compounds were expected to be affected by the degree of ionization of P(H). The results are shown in *Figures 8*, *9* and *10*. There was no significant effect of the presence of M(+), NMP or M(O) on the variation of I_M/I_E value with pH (cf. *Figure 5*), however, in the presence of complementary polymers the I_M/I_E values

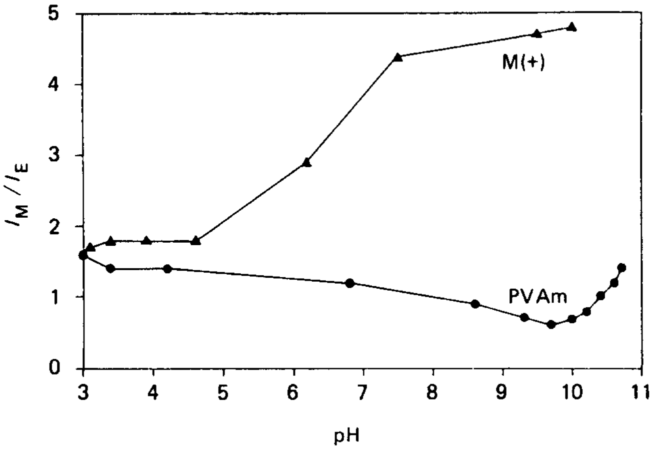


Figure 8 Effect of pH on the I_M/I_E value of P(H) in (a) P(H):PVAm = 1:1 (●) and (b) P(H):M(+) = 1:1 (▲). [P(H)] = 10^{-4} mol l^{-1}

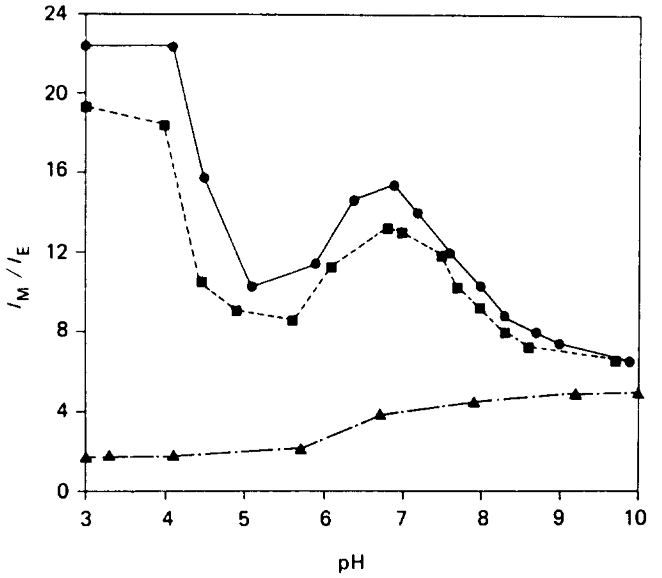


Figure 9 Effect of pH on the I_M/I_E value of P(H) in (a) P(H):PVP-3240 = 1:1 (●); (b) P(H):PVP-216 = 1:1 (■) and (c) P(H):NMP = 1:1 (▲). [P(H)] = 10^{-4} mol l^{-1}

changed with pH reflecting changes in the association of two polymers.

The association of P(−) and PVAm with an increasing pH was indicated by a large difference in the I_M/I_E value for M(+):P(−) and that for PVAm:P(−) after a pH of 4.5 (*Figure 8*). The interactions of PVAm and P(−) were strong even in the alkaline pH range and an increase in I_M/I_E value after pH 10 was indicative of some reduction in the association of PVAm and P(−). Thus, Coulombic interactions were favoured by ionization of P(H) (pH 4.5–9) and were reduced by a decreased charge density of PVAm (pH > 10). However, the low I_M/I_E values of PVAm:P(−) compared with those of M(+):P(−) in the alkaline region (pH > 10) reflected the importance of hydrophobic and electrostatic (ion-dipole) interactions in the association of PVAm and P(−).

The change in I_M/I_E values as a function of pH showed intriguing behaviour in the presence of PVP (*Figure 9*). The observed behaviour in the pH range 3–7 was thought to be due to the combined effects of pH change and the dynamic nature of the association process (see below). After a pH value of 7 the decrease in I_M/I_E value was thought to arise from a reduction in the efficiency of hydrogen bonding between P(H) and PVP. The higher I_M/I_E values for P(H):PVP than those for P(H):NMP in the alkaline region (pH > 7) indicated the importance of hydrophobic and electrostatic (ion–dipole) interactions in the association of P(H) and PVP. The I_M/I_E values for P(H):PVP-216 were lower than those for P(H):PVP-3240 over the entire pH range studied due to cooperative effects on the association of P(H) and PVP.

The change in I_M/I_E values of P(H) in the presence of PEO-114 or PEO-2270 indicated the weak nature of the secondary forces involved in the association of these polymers. The variation of I_M/I_E with pH was very similar to that in the presence of M(O) (*Figure 10*). However, the association of P(H) and PEO in the acidic region (pH < 4) was indicated by higher I_M/I_E values for P(H):PEO than those for P(H):M(O). In the pH range 6–8 the I_M/I_E values for P(H):PEO were lower than those for P(H):M(O); the presence of PEO probably caused P(H) to assume a more compact conformation in this pH range. At high pH values (> 9) the polymer P(H) assumed an expanded form even in the presence of PEO. PEO-114 was found to associate with P(H) even though the molecular weight of this polymer sample was lower than that reported for effective association of PEO and PAA[35a,36]. The emission spectra of P(H) were therefore found to be very sensitive to the environment of polymer.

The association of complementary polymers, namely, PEO:PAA and PVP:PAA has been shown to be an equilibrium process[6]. A variety of possibilities for the organization of two macromolecules in an interpolymer complex can be envisaged. Under the influence of environmental factors the interpolymer complexes formed in dilute solutions can be expected to undergo changes in structure due to equilibrium between association and dissociation processes. We were interested in determining the influence of these processes on the results obtained under kinetic conditions in this work. The changes in I_M/I_E values of P(H):PEO-2270, P(H):PVP-3240 and P(−):PVAm at a molar ratio of 1:1 were determined as a function of time and are shown in *Figure 11*. All measurements used for comparison in this work were completed in a maximum period of two hours from the time of mixing the two polymer solutions. Therefore, the changes in I_M/I_E values in this time interval are of particular significance.

The complex formed between P(−) and PVAm was found to undergo very little change over time. This could be attributed to the presence of P(−) in an expanded form and strong (Coulombic) interactions of P(−) and PVAm.

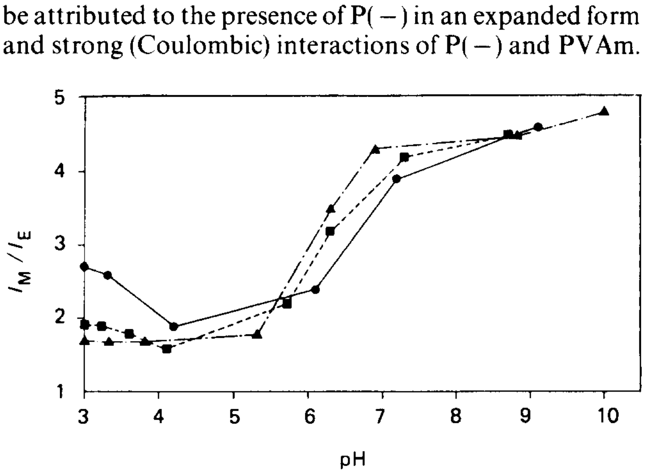


Figure 10 Effect of pH on I_M/I_E value of P(H) in (a) P(H):PEO-2270 = 1:1 (●); (b) P(H):PEO-114 = 1:1 (■) and (c) P(H):M(O) = 1:1 (▲). [P(H)] = 10^{-4} mol l^{-1}

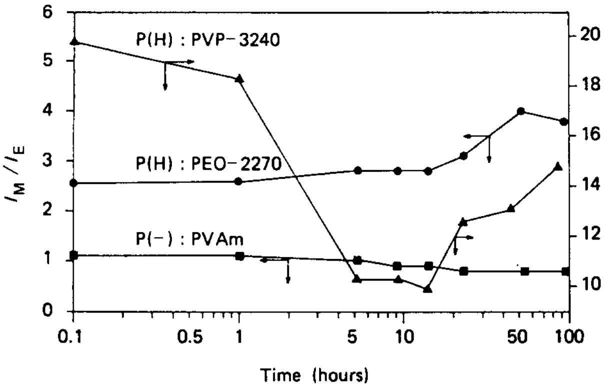


Figure 11 Change in I_M/I_E value of P(H) as a function of time in the presence of interacting polymers (a) P(H):PVP-3240 = 1:1 (▲); (b) P(H):PEO-2270 = 1:1 (●); (c) P(–):PVAm = 1:1 (■)

The complex formed between P(H) and PEO-2270 did not undergo significant changes over the first two hours but I_M/I_E values were found to increase slowly over longer periods of time. Under strongly acidic conditions used for P(H):PEO association P(H) could be expected to be in a compact form. In the presence of PEO-2270 the secondary forces for interpolymer association were required to overcome intrapolymer (hydrophobic) interactions of P(H) in its compact form. The slow increase in I_M/I_E for P(H):PEO-2270 reflected the weak nature of interpolymer interactions between P(H) and PEO.

The behaviour of P(H)-PVP-3270 was intriguing and I_M/I_E values in this case were found to undergo significant changes over time. The very low intensity of excimer emission in the emission spectra of P(H):PVP indicated that secondary forces between P(H) and PVP were very effective in overcoming intrapolymer interactions of P(H). Based on emission lifetime measurements excited state interactions between the pyrrolidinone moiety in PVP and pyrene groups were ruled out unlike the behaviour of P(H) in NMP solvent (see below). A definitive explanation of the observed changes in I_M/I_E values of P(H):PVP with time in terms of the structures of interpolymer complexes was not considered possible in view of the large number of factors involved in the association of these polymers including the microstructure of two polymers.

Emission lifetime measurements. Emission lifetime measurements on solutions containing complementary polymers (mole ratio 1:1) were performed in order to obtain further information about the association of these polymers. The results are given in *Table 3*. The decay curves for monomer and excimer emission from P(–):PVAm, P(H):PVP and P(H):PEO were non-exponential. The decay behaviour of P(–):PVAm was complicated due to the combined effects of excimer and exciplex emission in this case. The long-lived decay parameters for both monomer and excimer emission from P(H):PVP were higher than those for P(H) in water. Thus, excited state interactions between pyrrolidinone and pyrene groups were not possible unlike the behaviour of P(H) in NMP. The decay of monomer emission from P(H):PEO was similar to that for P(H) in water, however, the long-lived decay parameter for excimer emission was increased in comparison with that for P(H) in water. The increase in the decay parameter for excimer emission in P(H):PVP and P(H):PEO, which was thought to be representative of stable excimers in P(H) (*Figure 6*, *Scheme C*), could be due to a reduced mobility of pyrene groups in P(H) due to the association of complementary polymers.

Investigations of solutions containing three polymers

The emission spectra of P(H) in the presence of complementary polymers were found to be characteristic of the nature of the complementary polymer. The emission spectra of P(H):PEO-2270, P(H):PVP-3240 and P(–):PVAm at a molar ratio of 1:1 are shown in *Figure 12* and could be clearly distinguished from one another. Therefore, the emission spectra of P(H) were perfectly suited for studying the specific association and displacement reactions in solutions of complementary polymers. The results of these investigations are presented here. All measurements were performed in the presence of equivalent amounts of the polymers involved in order to avoid problems due to concentration effects.

The addition of P(H) to a solution of PEO-2270 and PVP-3270 or PVP-216 (pH = 3) led to association of P(H) and PVP as shown in equations (2) and (3).

$$\text{PEO-2270} + \text{PVP-216} + \text{P(H)} \rightarrow \text{PVP-216:P(H)}\ (I_M/I_E = 8.3) + \text{PEO-2270} \quad (2)$$

$$\text{PEO-2270} + \text{PVP-3240} + \text{P(H)} \rightarrow \text{PVP-3240:P(H)}\ (I_M/I_E = 10.4) + \text{PEO-2270} \quad (3)$$

The I_M/I_E values in the emission spectra of terpolymer solutions were higher than those observed in solutions of P(H):PEO. The I_M/I_E values were lower than those observed in solutions of P(H):PVP and could be caused by a compact form of the interpolymer complex due to the presence of PEO. When PVP-216 or PVP-3240 was added to a solution of P(H):PEO-2270 the displacement of PEO by PVP was noticed as shown in equations (4) and (5).

$$\text{P(H):PEO-2270}\ (I_M/I_E = 3.0) + \text{PVP-216} \rightarrow \text{PEO-2270} + \text{P(H):PVP-216}\ (I_M/I_E = 8.2) \quad (4)$$

$$\text{P(H):PEO-2270}\ (I_M/I_E = 3.0) + \text{PVP-3240} \rightarrow \text{PEO-2270} + \text{P(H):PVP-3240}\ (I_M/I_E = 10.9) \quad (5)$$

These results showed that association of P(H) and PVP was stronger than that of P(H) and PEO.

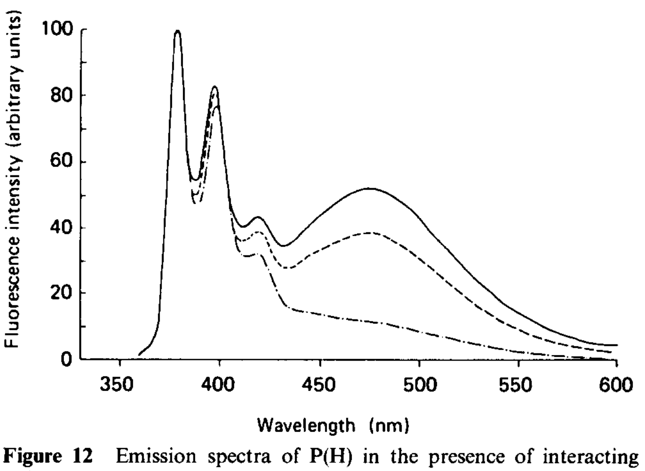


Figure 12 Emission spectra of P(H) in the presence of interacting polymers (a) P(H):PEO-2270 = 1:1 (– – –); (b) P(H):PVP-3340 = 1:1 (—·—·—); (c) P(–):PVAm = 1:1 (———). [P(H)] = 10^{-4} mol l^{-1}

Table 7 Emission spectra of solutions containing P(H), PVAm and PVP-216[a]

pH	I_M/I_E[b]	λ_D[c] (nm)
3.0	5.1	–[d]
4.0	4.2	–[d]
6.6	3.4	457
9.1	1.6	470
10.0	1.7	474

[a] $[P(H)] = 5 \times 10^{-4}$ mol l^{-1}; P(H):PVP:PVAm = 1:1:1
[b] Ratio of intensity of monomer (0,0) emission and emission at 480 nm
[c] Maximum of long wavelength emission
[d] No maximum was observed in long wavelength emission

Solutions of PVAm, P(H) and PVP-3240 were difficult to study as turbidity was observed in solutions of these polymers under acidic conditions. Such problems were not encountered in solutions of PVAm, P(H) and PVP-216 and results of emission spectroscopy on solutions of these polymers under different pH conditions are given in *Table 7*. The I_M/I_E values suggested that under acidic conditions association of P(H) and PVP-216 was favoured whereas alkaline conditions favoured the association of P(H) and PVAm.

The emission spectra of solutions containing P(H), PVP-216 and PVAm indicated that stable interpolymer complexes were formed between P(H) and PVP or P(H) and PVAm. The I_M/I_E values of a solution containing PVAm and P(H) (initial pH = 7) did not change significantly from an initial value of 1.1 after the addition of PVP-216. There was no significant change in I_M/I_E value if this solution was allowed to stand overnight indicating that PVP-216 did not displace PVAm under these conditions.

When PVAm was added to a solution of P(H) and PVP-216 (initial pH = 7) the I_M/I_E value decreased from 13.4 to 7.8 and further decreased to 5.2 upon allowing the solution to stand for 26 h. This could be due to association of PVAm with P(H):PVP-216 as well as some displacement of PVP-216 from P(H):PVP-216 by PVAm. A complete displacement of PVP-216 from P(H):PVP-216 did not take place as the observed I_M/I_E values were higher than those for P(H):PVAm. The association of PVAm and P(H):PVP-216 was also supported by a decrease in pH of solution containing PVAm and P(H):PVP-216; pH after 26 h was 4.9.

CONCLUSIONS

Photophysical properties of poly(acrylic acid) containing pyrene groups (P(H)) revealed the changes in conformation of P(H), from a compact form to an expanded form, upon the ionization of carboxylic groups in P(H). The presence of complementary polymers, PEO, PVP and PVAm, was found to affect the emission spectrum of P(H) in a characteristic manner. The emission spectra of P(H) were useful in studying the specific association and displacement of polymers in solutions containing P(H) and complementary polymers. The three complementary polymers could be ranked as follows in terms of the increasing strength of interpolymer interactions: PEO < PVP < PVAm. This order of the complementary polymers was related to the nature of secondary forces involved in the association of P(H) and the complementary polymers.

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