Luminescence studies on sterically stabilized polymer colloid particles: pyrene excimer formation

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Detailed information about the conformation and dynamics of fluorescently labelled polymer chains free in solution and bound to colloidal sized particles can be obtained using luminescence techniques. Copolymers of pyrenealkyl methacrylate and 2-ethylhexyl methacrylate (EHMA) were used as stabilizers (St-Py) in the dispersion polymerization of vinyl acetate. In this way, poly(vinyl acetate) particles (0.3 μm) labelled in the stabilizer phase with pyrene (SLP) were prepared. Results from steady-state and time-resolved fluorescence studies on solutions of St-Py and dispersions of SLP are compared. In these systems, pyrene excimers are formed with a distribution of rate constants. We find that the mobility and dimensions of particle-bound stabilizer chains are less than the corresponding free stabilizer chains in solution, a consequence of the mechanism of particle synthesis. When the spacer separating pyrene from the stabilizer backbone is increased, excimer formation is facilitated, inferring an increase in stabilizer chain mobility relative to the systems with short spacer units. Studies on particles prepared with a mixture of labelled and unlabelled PEHMA showed that inter-chain interactions in the stabilizer phase are negligible.

(Keywords: luminescence; colloid particles; toners; pyrene; excimer)

INTRODUCTION

Non-aqueous dispersions (NAD) of colloidal polymer particles have important industrial applications in the coatings area, particularly in paints[1] and as toners for electrostatic imaging[2] technologies. Like many industrially important systems, their preparation remains more of an art than a science. It is not easy to carry out the kind of transformation or growth in understanding to allow new materials to be engineered from a basis of scientific understanding. It is accepted that the structure and composition of NAD particles is complex and varies from recipe to recipe; however, the situation is far from hopeless. It is probably true that a living cell is more complex in its structure and function than a colloidal polymer particle of the same size. Biochemists have demonstrated how new analytical techniques can provide remarkably detailed information about such systems[3]. We wish to follow their example in the area of synthetic polymer systems.

The utility of fluorescent techniques in biochemistry is well documented[3]. We have had some success in applying these methods to study the morphology of non-aqueous dispersions of polymer particles[4], particularly 0.3 μm diameter poly(vinyl acetate) (PVAc) particles[5] and 1–3 μm diameter poly(methyl methacrylate) (PMMA) particles[6], which form stable colloidal dispersions in aliphatic hydrocarbon media. These (insoluble) polymers comprise $>90\%$ of their respective particulate materials. Each is often referred to as the 'core' polymer. Colloidal stability is conferred by the presence of a second polymer, normally very soluble in the hydrocarbon solvent, which is somehow tightly bound to the particle and which covers its surface. If this stabilizer polymer were present exclusively as a thin spherical shell covering the core, the particle would be deemed to have a core–shell structure.

Perhaps the biggest success of our fluorescence experiments on these two materials has been to demonstrate that the core–shell model is a serious oversimplification. Extensive amounts of stabilizer polymer are trapped within the interior of the particle core. We have developed a microphase model[4], which envisions an interpenetrating network-type structure for the particle's interior. Chemical grafting (covalent bond formation) occurs between the two polymers during the synthesis step of the particle. An extensive interphase is formed between the individual phases of these otherwise incompatible polymers[5,7].

In those experiments, the *core* polymer was labelled with a fluorescent dye, naphthalene or phenanthrene, and we studied the ability of small molecules introduced into the solvent to quench their excited states. In this paper, we report that information of a quite different kind is available from the study of particles in which the *stabilizing* polymer is labelled with pyrene groups. The stabilizer chains are swollen with solvent. Chain flexibility leads to pyrene excimer formation[8]. While this in itself would be interesting, comparison of results from steady-state and transient decay experiments on labelled

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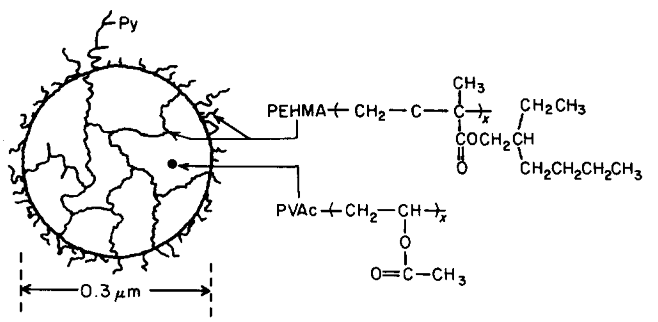
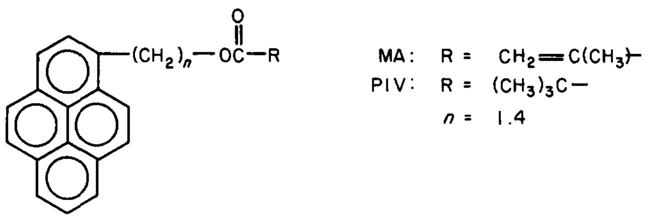


Figure 1 Representation of the molecular structure and morphology of fluorescently labelled, PEHMA stabilized, PVAc colloid particles

stabilizer chains bound to the particle and free stabilizer in isotropic solution indicates some peculiarities which are rich in information about the relative conformation and dynamics of the stabilizer chains incorporated into the particles. In another series of experiments, particles were prepared using a mixture of labelled and unlabelled PEHMA stabilizer chains. This procedure serves to dilute the labelled chains in the particle with unlabelled chains and allows us to assess the extent to which pyrenes on neighbouring chains contribute to excimer formation.



(Py)

The specific system we examined were PVAc particles stabilized with poly(2-ethylhexyl methacrylate) (PEHMA). Our representation of particle structure is illustrated in *Figure 1*. Copolymers of PEHMA were prepared with small quantities of two different pyrene (Py) containing methacrylates. In the structural formula above, Py_1MA refers to the methacrylate ester containing one CH_2 group. Some simple experiments intended to document the spectroscopy of the fluorescent group were carried out on solutions of the model compounds Py_1Piv and Py_4Piv, the pivalate esters containing one and four CH_2 groups, respectively.

MATERIAL AND METHODS

The preparation, purification and characterization of these particles has been described in detail[9]. Here we provide a brief overview of the method. Copolymers of EHMA and Py_1MA or Py_4MA, which serve as stabilizers, were prepared by standard free radical polymerization methods. Molecular weights are nominal M_n values obtained by gel permeation chromatography in ethyl acetate, relative to polystyrene standards. A tandem of fluorescence and refractive index detectors allowed us to establish that all pyrene groups were covalently linked to polymer. The number of pyrene groups per chain was determined either by u.v. absorption measurements in ethyl acetate or in combination with ^1H n.m.r. measurements in $CDCl_3$. The weight fraction of stabilizer in the particles was determined from n.m.r. spectra of isotropic solutions of particles in $CDCl_3$.

The reactivity ratios for copolymerization of EHMA and phenanthrylmethyl methacrylate are $r_1(EHMA) = 0.50 \pm 0.02$ and $r_2(PheMMA) = 3.7 \pm 1.0$ (ref. 9). Similar values for r_1 and r_2 would be expected for EHMA and $Py_{1,4}MA$ under the same polymerization conditions. The magnitude of the reactivity ratios and the low $Py_{1,4}MA$ concentrations present initially in the synthesis of the labelled stabilizers suggests that few adjacent pyrene pairs exist in the final copolymers.

Particles were synthesized by initiating free radical polymerization of a large excess of vinyl acetate in isooctane solution in the presence of ca. 10% by weight labelled PEHMA. PEHMA-*g*-PVAc graft copolymers are apparently formed *in situ* via hydrogen abstraction from the PEHMA copolymer during the PVAc polymerization and through this process become incorporated into the particles. PVAc is, of course, insoluble in isooctane. Particles are not formed in the absence of added PEHMA; rather, PVAc precipitates from solution as the polymerization progresses.

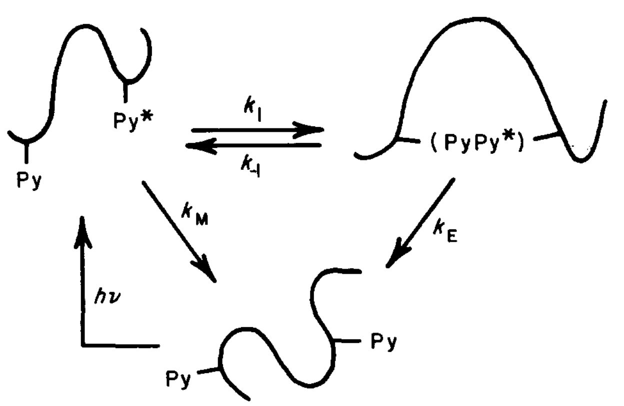
Ultra-violet spectra in ethyl acetate were run on a Cary 14 u.v. spectrometer. Steady-state fluorescence measurements were performed on a Perkin–Elmer Model MPF-44 instrument ($\lambda_{ex} = 345$ nm). Fluorescence decay profiles were obtained using the time-correlated single-photon counting method[10]. The excitation wavelength was selected using a Spex minimate monochromator (345 nm) and the emission (380–400 nm) collected by employing a combination of Schott KV-380 and Schott UG-11 filters. The data were analysed using the nonlinear least squares iterative reconvolution method[11].

KINETIC MODELS

In this paper we are careful to distinguish between bimolecular quenching phenomena and excimer formation[12]. Bimolecular fluorescence quenching is defined as any process in which the interaction of an electronically excited molecule, F*, with another species leads to dissipation of the excited state energy. Quenching leads to a decrease in the fluorescence intensity from F* and a shortening of the fluorescence lifetime. This is a phenomenological definition and includes all quenching mechanisms.

One quenching mechanism involves formation of excimers from the interaction of F* with its ground state counterpart, F. Excimers are defined as electronically excited, bound dimeric complexes and their formation is normally accompanied by the appearance of a new broad band in the fluorescence spectrum due to excimer emission. We emphasize this distinction because the results we report indicate the existence of two distinct processes in the interaction of pyrene in the excited singlet state with ground state pyrene. One type leads to classic pyrene excimer emission; the other leads only to quenching. The latter process is not unprecedented, but it is unusual[17].

The kinetics of excimer formation in isotropic solution between pyrene (Py) groups terminally attached to the ends of a polymer chain have been well studied[8,13]. For samples of low polydispersity and for chains of a reasonable length, the data are found to be well described by the simple two-state model in *Scheme 1*[12].



Scheme 1

In this scheme, Py and Py* represent ground state and locally excited state pyrene ('monomer'), respectively and (PyPy)* signifies a pyrene excimer. The rate constants k_1 and k_{-1} describe the processes of intramolecular excimer formation and excimer dissociation, and k_M and k_E represent the reciprocal lifetimes for pyrene monomer and pyrene excimer, respectively.

The above model predicts for the experimental monomer ($I_M(t)$) and excimer ($I_E(t)$) fluorescence decay profiles the following two decay laws:

$$I_M(t)=a_1\exp(-\lambda_1 t)+a_2\exp(-\lambda_2 t) \tag{1}$$

$$I_E(t)=a_3\exp(-\lambda_1 t)-a_4\exp(-\lambda_2 t) \tag{2}$$

where

$$\begin{gathered}\lambda_{1,2}=1/2\{X+Y\pm[(Y-X)^2+4k_1k_{-1}]^{1/2}\}\\ X=k_1+k_M \qquad \text{and} \qquad Y=k_{-1}+k_E\end{gathered} \tag{3}$$

The monomer fluorescence decays as a sum of two exponentials and the excimer emission decays according to a difference of two exponential terms. The decay constants λ_1 and λ_2 for both experiments should be equal and the ratio of pre-exponential factors in equation (2), a_3/a_4, should equal 1.0.

For samples at ambient temperatures, when $k_{-1} \ll k_1$, back reaction to form Py* from excimer can be ignored. Under these conditions, equation (1) simplifies to the law of single exponential decay:

$$I_M(t)=a_1\exp(-\lambda_1 t) \tag{4}$$

Furthermore, the individual rate constants can now be calculated from the experimental parameters λ_1 and λ_2 using the relations:

$$\lambda_1=k_1+k_M \tag{5}$$

$$\lambda_2=k_{-1}+k_E \tag{6}$$

provided that $k_M=1/\tau_M$ for a suitable model compound is known.

Steady-state measurements can provide a second, independent measure of the rate constant for excimer formation (k_1). According to the above model, the ratio of excimer to monomer fluorescence intensities I_E/I_M is:

$$I_E/I_M=\frac{k_{fE}}{k_{fM}}\left(\frac{k_1}{k_{-1}+k_E}\right) \tag{7}$$

where k_{fE} and k_{fM} are the radiative rate constants for monomer and excimer, respectively. In most pyrene–pyrene excimer-forming systems at 20 to 25°C, k_E is determined to be 10 times greater than k_1. Under these conditions, $k_{-1} \ll k_E$, the ratio I_E/I_M reflects directly the magnitude of k_1.

The rate constant of interest in this work is k_1. Previous investigations in our laboratory indicate that steady-state and transient decay measurements provide complementary estimates of its magnitude[8,13]. For monodisperse polymers end-labelled with pyrene groups in isotropic solution, it is found that both λ_1 (shorter decay time) and I_E/I_M increase as the length of polymer separating the labels is decreased. These findings are the result of an increase in k_1 with decreasing chain length. Furthermore, the rate of intramolecular excimer formation is limited by the rate of diffusion of the chain ends; one finds that k_1 increases with decreasing solution viscosity (η).

For polymers, and in particular stabilizers and colloids randomly labelled with pyrene, the situation is more complex[14]. In principle, all chromophore pairs are capable of interacting. Excimer may form from pyrene pairs that are closely spaced or far apart. For proximate labels, one expects large values for k_1 and short decay times while for well separated pyrenes, small values for k_1 and longer decay times are predicted. In the colloidal systems, excimer formation might also occur between pyrenes on different stabilizer chains. One expects the kinetics of excimer formation in these systems to be more complicated than those described in equation (1)–(7). In such a system there should be a distribution of rate constants for excimer formation[14].

Fluorescence decays from labelled stabilizers and colloids are non-exponential (see *Figures 4* and *5*). In this work they were fitted to a sum of exponential components (three) in order to parameterize the information. It was frequently convenient to calculate mean decay times, particularly for the locally excited pyrene monomer decay, $I_M(t)$. The mean decay time $\langle\tau\rangle$ is defined as:

$$\langle\tau\rangle=\frac{\int_0^\infty tI_M(t)\mathrm{d}t}{\int_0^\infty I_M(t)\mathrm{d}t} \tag{8}$$

Using a modified form of equation (5) and the experimentally determined mean decay times, estimates of the mean rate constant for excimer formation, $\langle k_1\rangle$, were calculated.

$$1/\langle\tau\rangle=\langle k_1\rangle+k_M \tag{9}$$

Steady-state data were analysed using equation (7), where k_1 is replaced by the mean rate constant $\langle k_1\rangle$.

Equation (9) presumes that excimer dissociation does not contribute to the shape of the $I_M(t)$ decay profile. At room temperature, this contribution is normally small, but it is difficult to ensure that it is completely

Table 1 Composition, size and molecular weights of pyrene-labelled, PEHMA-stabilized PVAc particles

Sample	Label in stabilizer[a] (mole%)	Stabilizer in colloid[b] (wt%)	Particle size[c] (nm)	Molecular weight[d] × 10^{-3} Stabilizer	Molecular weight[d] × 10^{-3} Colloid
$SLP_1(2)$	0.81	6.9	251	38	100 805
$SLP_1(7)$	2.80	8.5	231	35	79 2180
$SLP_4(3)$	1.57	6.2	292[e]	42	75
$SLP_1(2\%\text{-}7)$	2.80	8.2	228	35	105 885
$SLP_1(5\%\text{-}7)$	2.80	8.4	253	35	62 1880

[a] Calculated from u.v. spectra; represents an average of at least 4 analyses

[b] Calculated from 200 MHz ^{1}H n.m.r. spectra

[c] Obtained from light scattering analysis (Brookhaven Model BI-90)

[d] Molecular weights are obtained from the peak maxima of differential refractometer traces (similar to u.v.-v.i.s. traces) and are relative to polystyrene standards. The molecular weight of the unlabelled PEHMA employed in the synthesis of last 2 entries is 33 000. Note that bimodal distributions exist in the g.p.c. profiles of the colloidal materials, with the exception of $SLP_4(3)$, which showed a small high molecular weight shoulder

[e] Mean particle size from scanning electron microscopy is 185 nm

unimportant. At issue is the magnitude of the $4k_1k_{-1}$ term in equation (3) compared to that of the $(Y-X)^2$ term. The first term depends upon the magnitude of k_1 as well as on the magnitude of k_{-1}. For those pairs of pyrenes which are close in space and undergo rapid excimer formation, the $4k_1k_{-1}$ term is important, whereas for those pyrenes which undergo slower cyclization, it can be neglected. We have looked at this problem in some detail in the simpler system of end-labelled polymers described in *Scheme 1*. Short chains cyclize much more rapidly than long ones, and the data permit the magnitude of the feedback contribution to be determined. Basically, we find that feedback becomes important when k_1 is close to or exceeds $1 \times 10^7\ s^{-1}$. The net effect of feedback is that the values of k_1 calculated from equations (5) or (9) are too small. The deviations are small (10 to 30%) but increase as the values of k_1 calculated using equations (5) or (9) become very large. From our data and equation (9), we calculate values (*Table 4*) of k_1 on the order of $10^6\ s^{-1}$. Under these circumstances, we believe, the feedback term in equation (3) can safely be ignored, and the values of $\langle k_1 \rangle$ reported in *Table 4* are meaningful.

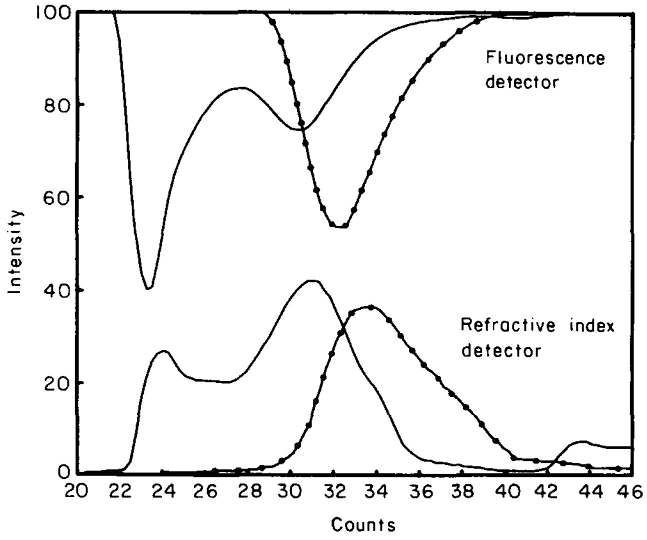


Figure 2 G.p.c. elution profiles from ethyl acetate solutions ($\approx 1\ mg\ ml^{-1}$) of $St_1(7)$ and $SLP_1(7)$. Excitation and emission wavelengths for the fluorescence detector were 280 nm and 325–390 nm (isolated with filters), respectively. -●-, Stabilizer; ———, colloid

RESULTS AND DISCUSSION

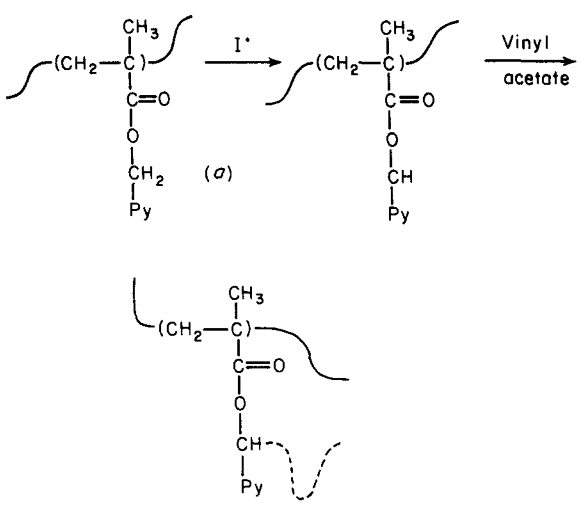
Particle characterization

U.v. analysis indicates that the stabilizer copolymers prepared with Py_1MA contain 1 or 3.5 mol% pyrene groups. On average, these polymers contain 2 or 7 pyrene groups per chain. We refer to these copolymers as $St\text{-}Py_1(2)$ and $St\text{-}Py_1(7)$, respectively. In our notation, $St\text{-}Py_4(3)$ (1.57 mol% Py_4MA) contains on average 3 pyrenylbutyl methacrylate moieties per stabilizer chain.

We refer to the particles produced from the pyrene-containing copolymers as 'stabilizer labelled' particles, $SLP_{1,4}(m)$, where m indicates the mean number of pyrenes per stabilizer chain and the subscript denotes the pyrene methacrylate derivative present. Colloidal particles were also prepared with a mixture of labelled PEHMA copolymer ($St\text{-}Py_1(7)$) and unlabelled PEHMA homopolymer. These materials contain 2 and 5% $St\text{-}Py_1(7)$ and are refered to as $SLP_1(2\%\text{-}7)$ and $SLP_1(5\%\text{-}7)$, respectively. The composition of the various materials we examined are summarized in *Table 1*.

M_n values from g.p.c. analysis were typically 50 000 for dissolved stabilizer samples. *Figure 2* shows bimodal g.p.c. chromatograms for a dissolved sample of $SLP_1(7)$. Note that the fluorescence profiles indicate the nature of the stabilizing moieties since PVAc is non-fluorescent. The fact that both peaks in the fluorescence response profile for the colloid sample are shifted to high molecular weight relative to the stabilizer curve indicates that each stabilizer chain becomes grafted to PVAc during particle synthesis. The appearance of an ultra-high molecular weight component (2 000 000) is indicative of a proportion of stabilizer chains that are highly grafted to PVAc chains. This high molecular weight component arises only when fluorescently labelled stabilizers are used to prepare particles. Colloid synthesized with unlabelled stabilizer yields unimodal g.p.c. chromatograms centred at 31 counts (near the low M_w peak in the colloid profiles in *Figure 2*).

A strong correlation between the mol% fluorophore methacrylate in the added stabilizer and the final particle size[9] and polymer molecular weight was observed. This suggests that the chromophore moieties in the stabilizer, which have activated benzylic hydrogens (*a*), play an important role during particle formation.



We believe the pyrene moieties to be the locus for growth of PVAc graft chains. However, since particles result even when an unlabelled stabilizer is employed, other sites for graft reactions having competitive rates must exist. Hence it is unreasonable to assume that all the pendant pyrenylmethyl substituents bear graft PVAc chains subsequent to particle formation.

Steady-state spectroscopy

Figure 3 shows the normalized u.v. spectra from ethyl acetate solutions of Py$_1$Piv and SLP$_1$(7). The model compound and the particle sample show the same characteristic absorption peaks. Notice, however, that the width of the peaks for SLP$_1$(7) are broader than those for Py$_1$Piv. Variations in spectral broadness in u.v. spectra of polymers containing pendant pyrene groups have been observed previously[15,16]. This phenomenon was attributed to ground state interactions between polymer-bound pyrene groups; the degree of chromophore aggregation was taken to reflect the local concentration of pyrene groups within the polymer coil.

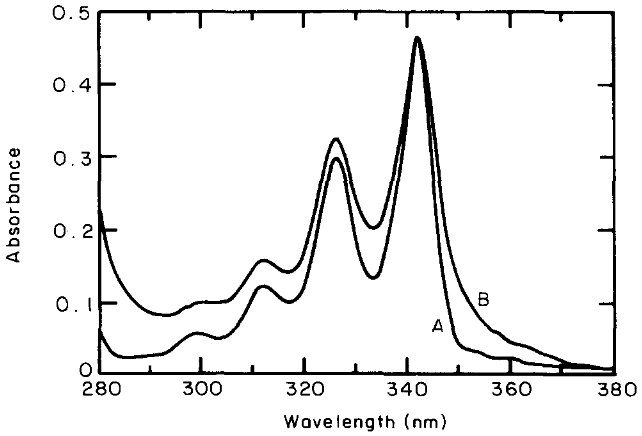


Figure 3 U.v. absorption spectra of Py$_1$Piv (1.22×10^{-5} M) and SLP$_1$(7) (0.83 mg ml^{-1}) in ethyl acetate solutions at 23°C

Table 2 Relative spectral broadness factors (*B*) for u.v. absorption peaks centred at 343 nm

Sample	*B*
Py$_1$Piv	1.00
St$_1$(2)	1.12
St$_1$(7)	1.30
SLP$_1$(2)	1.41
SLP$_1$(7)	1.64
SLP$_1$(2%-7)	1.75
SLP$_1$(5%-7)	1.89
Py$_4$Piv	1.00
St$_4$(3)	1.10

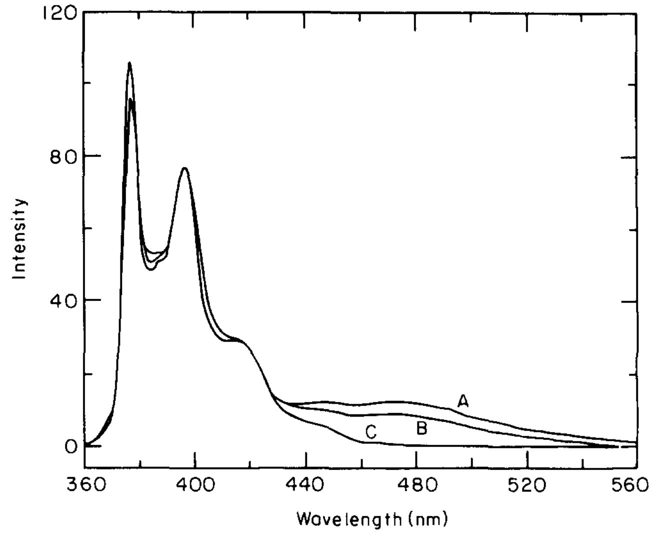


Figure 4 Steady-state fluorescence emission spectra of: A, Py$_4$Piv (4×10^{-6} M); B, St$_4$(3) stabilizer (0.75 mg ml^{-1}); C, SLP$_4$(3) colloid particles (1.62 mg ml^{-1}) in deoxygenated cyclohexane at 23°C, $\lambda_{ex} = 345$ nm

Listed in *Table 2* are relative peak broadness factors (*B*) for the absorption peaks centred at 343 nm for each of our stabilizer and colloid samples. *B* is defined as the ratio of the intensity at the peak maximum at 343 nm to the intensity at the first adjacent minimum (334 nm), to the corresponding ratio for the model compound. The value of *B* for St$_1$(2) is smaller than that for St$_1$(7). This is expected since St$_1$(2) has a lower pyrene loading and thus a lower local concentration of labels. Of interest is the fact that *B* for SLP$_1$(2) is greater than the value for the stabilizer St$_1$(7). In other words, in ethyl acetate (a good solvent) the pyrene groups bound to stabilizer chains in the dissolved SLP$_1$(2) sample (2 pyrenes per chain) are more concentrated locally than for isolated St$_1$(7) chains (7 pyrenes per chain) in ethyl acetate. *Table 2* also shows that broadness factors for the free stabilizers are considerably smaller than the respective colloid samples. This indicates that the local concentration of pyrene groups is greater in the particle-bound stabilizer chains.

Steady-state emission spectra of representative stabilizer and colloid samples, as well as Py$_1$Piv are presented in *Figure 4*. With the exception of the small variation in the $S_1 \rightarrow S_0$ transition 0,0 emission band at 375 nm, the fluorescence from the model compound and labelled polymers at short wavelengths is very similar. The broad structureless emission centred at 470 nm in the spectra of St$_4$(3) and SLP$_4$(3) is due to pyrene excimer. The fact that excimer emission is observed for these samples shows that pyrene groups can indeed associate when they are covalently attached to both free and particle-bound stabilizer.

The fluorescence excitation spectra for Py$_1$Piv [$\lambda_{em} = 393$ nm] and SLP$_1$(2) [$\lambda_{em} = 393$ and 500 nm] are compared in *Figure 5*. The excitation spectra measured for emission at 394 and 500 nm for SLP$_1$(2) superimpose and are similar in detail to the spectrum of Py$_1$Piv. The same is true for each of the colloid samples. Note, however, that the excitation spectrum for SLP$_1$(2) is broadened and shifted with respect to the spectrum for Py$_1$Piv. Moreover, even when the labelled stabilizer chains are diluted on the surface (SLP$_1$(2%-7)) the spectra at 394 and 500 nm superimpose and are practically identical to the SLP$_1$(2) spectra. This suggests that excimers are formed from diffusive encounters and not ground state pyrene aggregates.

According to equation (7), I_E/I_m is a measure of the excimer formation rate. One would anticipate that I_E/I_m values for the particle-bound stabilizer would be substantially larger than that for the simple stabilizer solutions because the u.v. absorption spectra and excitation spectra suggest that the pyrene groups are, on average, closer together when the stabilizer is bound to the particle. The experimental results do not support this prediction. From the data in *Table 4* we see that I_E/I_m values are significantly smaller in the polymer-bound stabilizers. For example, $I_E/I_m = 0.44$ for St$_1$(7); when this stabilizer is incorporated into a particle, the I_E/I_m value drops to 0.21. Normally one would conclude from such a result (equation (7)) that k_1 decreases as a consequence of anchoring.

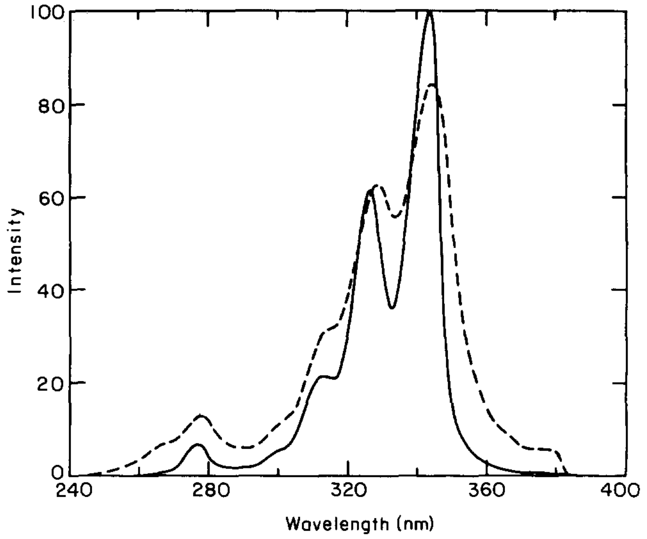


Figure 5 Steady-state fluorescence excitation spectra of deoxygenated cyclohexane samples of Py$_1$Piv (4×10^{-6} M, $\lambda_{em} = 393$ nm) and SLP$_1$(2) (x.xx mg ml^{-1} spectra collected at $\lambda_{em} = 393$ and 500 nm overlap)

Fluorescence decay measurements

Pyrene monomer fluorescence decay profiles from deoxygenated samples of St$_1$(7), SLP$_1$(7) and Py$_1$Piv in cyclohexane at 23°C are displayed in *Figure 6*. The fluorescence from Py$_1$Piv follows a single exponential decay law and is characterized by a decay time of 273.9 ns. The emissions from St$_1$(7) and SLP$_1$(7), however, are non-exponential. This fact indicates that the simple two-state model for excimer formation described above is not valid for the colloids and stabilizers we are examining. It also supports our model invoking a distribution of rate constants for excimer formation in the pyrene-labelled colloidal systems.

The characteristic decay times and pre-exponential factors obtained from analysis of the fluorescence decay profiles of stabilizers and colloids labelled with Py$_1$MA are listed in *Table 3*. The fact that each of the fluorescence decay times obtained for St$_1$(7) and SLP$_1$(7) are shorter than the decay time of the model compound Py$_1$Piv indicates that all pyrene labels in these samples are involved in quenching interactions. According to our model, which predicts a distribution of decay times and rate constants for excimer formation, we suggest that the

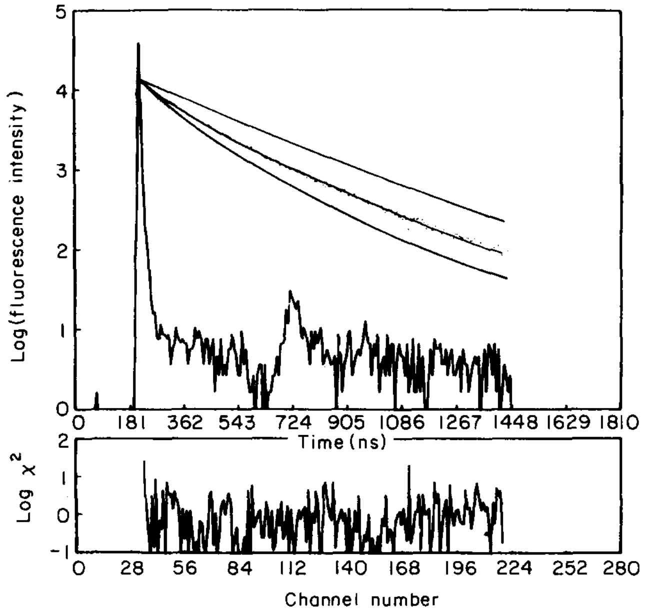


Figure 6 Fluorescence decay profiles, $I_M(t)$ of: A, Py$_1$Piv (2.2×10^{-6} M); B, St$_1$(7) stabilizer (1.5 mg ml^{-1}); C, SLP$_1$(7) colloid particles (12.4 mg ml^{-1}) in deoxygenated cyclohexane at 23°C. $\lambda_{ex} = 345$ nm

Table 3 Monomer decay times and coefficients for excimer formation from fluorescence decay profiles of model compounds and pyrene-labelled polymers. Deoxygenated samples in cyclohexane at 23°C were investigated. $\lambda_{ex} = 343$ nm

Sample	τ_1	τ_2	τ_3	A_1	A_2	A_3	$A_2/(A_2+A_3)$
Py$_1$Piv	–	–	273.9	–	–	–	–
St$_1$(2)	–	140.2	273.9	–	0.26	1.0	0.21
SLP$_1$(2)	11.6	146.0	273.9	0.31	0.53	1.0	0.35
St$_1$(7)	32.9	134.3	269.8	0.29	1.10	1.0	0.52
SLP$_1$(7)	28.9	128.9	240.5	0.67	1.42	1.0	0.59
SLP$_1$(2%-7)	10.2	100.3	240.4	1.74	1.34	1.0	0.57
SLP$_1$(5%-7)	10.9	102.9	238.0	1.00	1.17	1.0	0.54
Py$_4$Piv	–	–	240.6	–	–	–	–
St$_4$(3)	53.0	171.5	238.5	0.51	1.94	1.0	0.66
SLP$_4$(3)	46.4	151.0	223.3	0.66	1.90	1.0	0.66

Table 4 Ratios of excimer to monomer fluorescence intensity (I_E/I_M), mean decay times $\langle\tau\rangle$ and mean rate constants for excimer formation for pyrene-labelled stabilizers and colloids

Sample	I_E/I_M	$\langle\tau\rangle$	$10^{-5}k_1$
$St_1(2)$	0.07	258.4	2.2
$SLP_1(2)$	0.04	243.4	4.6
$St_1(7)$	0.44	217.7	9.4
$SLP_1(7)$	0.21	185.1	18
$SLP_1(2\%\text{-}7)$	0.20	182.0	18
$SLP_1(5\%\text{-}7)$	0.20	187.3	17
$St_4(3)$	0.29	192.8	10
$SLP_4(3)$	0.19	174.9	16

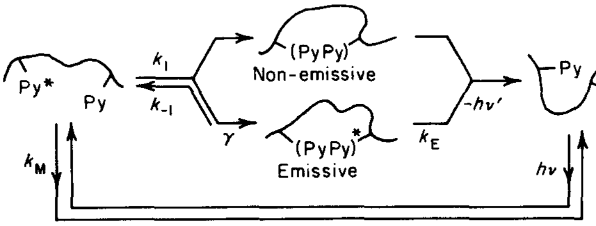
shortest decay times in *Table 3* are due to excimer formation between proximate pyrene–pyrene pairs and the longest decay times are due to interactions between well separated pyrenes. The concurrent increase in the ratio $A_2/(A_2+A_3)$ and decrease in the individual decay times suggests that the proportion of proximate pyrene pairs increases upon anchoring $St_1(7)$ to particles. These results are in agreement with the u.v. data presented above.

Pyrene excimer fluorescence decay profiles could not be fitted adequately to equation (2) or to a decay law having the sum of two exponential decaying components and a rising component. In spite of this, for each sample we observe a rough agreement between the parameters for the decay components in the excimer profiles and the parameters in *Table 3* for the long-lived components in the pyrene monomer decays. The rise times for excimer emission (λ_2) are estimated to be on the order of 5 ns. These results are further evidence for the formation of excimers from diffusive encounters.

Listed in *Table 4* are the excimer to monomer fluorescence intensity ratios (I_E/I_M), for all the stabilizer and colloid samples. Also presented are the mean decay times for pyrene fluorescence (calculated using equation (8)) and the rate constants for excimer formation (calculated using equation (9)). As shown in *Table 4*, two opposing effects occur upon anchoring the stabilizers to particles: the apparent value of $\langle k_1\rangle$ inferred from I_E/I_M decreases and the rate constant $\langle k_1\rangle$ from transient measurements increases. In other words, the pyrenes attached to particle-bound stabilizer are quenched to a greater degree than to free stabilizer, yet less pyrene excimer emission is observed. This result is unusual since reduced excimer emission normally implies less pyrene–pyrene quenching[17]. A model consistent with these conflicting results is shown in *Scheme 2*.

Quenching vs. excimer formation

In *Scheme 2*, quenching is described by the mean rate constant $\langle k_1\rangle$ and leads to one of two species: (1) non-emissive; and (2) emissive pyrene–pyrene complexes. The latter complex is, of course, commonly referred to as pyrene excimer and is characterized by a planar sandwich geometry. Pyrene–pyrene quenching leading to a non-emissive complex[17] would be accomplished in an unspecified geometry, perhaps a distribution of geometries other than the planar sandwich. The factor γ is defined as the fraction of quenched pyrene groups that form emissive excimer.



Scheme 2

Based on this model, the reason that more quenching is observed in the transient decay experiments and less quenching inferred in the steady-state studies upon stabilizer anchoring is because the transient decay technique monitors all quenching events (i.e. the formation of both emissive and non-emissive species) while analysis of the excimer band in steady-state spectra only provides information about the formation of emissive excimers[18].

For transient experiments, *Scheme 2* predicts for $I_M(t)$ a non-exponential decay law, where $\langle\tau_1\rangle^{-1}=\langle k_1\rangle+k_M$. For the steady-state technique, however, the excimer to monomer intensity ratio is of the following form:

$$\frac{I_E}{I_M}=\frac{k_{fE}}{k_{fM}}\frac{\gamma\langle k_1\rangle}{k_E}(k_E>k_{-1}) \tag{10}$$

The magnitude of I_E/I_M for pyrene-labelled stabilizer (St) relative to that for the corresponding colloidal material (SLP) can be expressed as:

$$\frac{I_E/I_M(\mathrm{St})}{I_E/I_M(\mathrm{SLP})}=\frac{\gamma(\mathrm{St})\langle k_1(\mathrm{St})\rangle}{\gamma(\mathrm{SLP})\langle k_1(\mathrm{SLP})\rangle} \tag{11}$$

For linear polymers in solution, there is substantial evidence that I_E/I_M increases in proportion to $\langle k_1\rangle$ and no indication of quenching events that do not lead to formation of an emissive excimer. Hence we assign a value of unity to γ(St) in equation (11).

From equation (11) and the data in *Table 4*, γ factors for $SLP_1(2)$ and $SLP_1(7)$ were both calculated to be 0.28. We attribute these small γ factors to the relatively small number of segments in the stabilizer phase that can undergo unrestricted motions; the pyrene labels have sufficient motional freedom to interact but not enough to achieve the planar excimer geometry during the lifetime of the excited state.

The colloidal sample $SLP_4(3)$ was prepared in order to test the model in *Scheme 2*, reasoning that in this case the pyrene moiety being attached to the polymer chain through a longer 'leash' $-(CH_2)_4-$ might be able more easily to attain the excimer geometry. This would lead to more excimer emission (an increase in γ) in the colloid relative to free stabilizer compared with the systems discussed above ($-CH_2-$).

The results from steady-state and fluorescence decay measurements for $SLP_4(3)$ are shown as the last few entries in *Tables 3* and *4*. The trends observed are the same as those found for $SLP_1(2)$ and $SLP_1(7)$; a decrease in I_E/I_M and an increase in $\langle k_1\rangle$ upon attaching the stabilizer to particles. The magnitude of the changes, however, is smaller than those observed for the polymers labelled with Py_1MA. It is interesting to note that the values of $\langle k_1\rangle$ for $St_4(3)$ and $SLP_4(3)$ in *Table 4* are similar to those for $St_1(7)$ and $SLP_1(7)$ in spite of the fact that the mol % of pyrene groups in the former systems is less than half that in the latter.

The γ factor for $SLP_4(3)$ was calculated and found to be equal to 0.43. This value is significantly larger than the value calculated for the Py_1MA-labelled particles. As expected, the fraction of quenched pyrenes that form excimer, and thus the mobility of the pyrene groups, does indeed increase when the spacer between the PEHMA backbone and the Py chromophore is increased by three methylene units. This is probably due to a combination of effects; (1) the greater conformational freedom of Py due to the extended leash; and (2) less grafting through the benzylic hydrogens, as indicated by g.p.c. and particle size analysis. In spite of the lower degree of grafting to stabilizer, γ is not equal to unity for $SLP_4(3)$. Even in these particles, the conformational mobility of polymer segments in the stabilizer layer is restricted.

Interpenetration of stabilizer chains

Interpenetration of stabilizer chains, both on the particle surface and those trapped in the particle interior, should lead to excimer formation between Py groups on different chains. This effect can be measured by preparing particles in which labelled stabilizer is mixed with a large excess of unlabelled stabilizer in the particle synthesis. In this way, the labelled chains tend to be diluted so that quenching and excimer formation occur only from pyrenes attached to the same polymer chain.

We prepared the particles $SLP_1(2\%\text{-}7)$ and $SLP_1(5\%\text{-}7)$ to examine the extent of interstabilizer chain interactions. These particles contain the PEHMA stabilizer containing 7 pyrene groups per chain. Chemical analysis indicates that only 2 and 5% of the stabilizer chains in these particles are the labelled PEHMA chains. The results of our measurements are included in the data of *Tables 2, 3* and *4*. Surprisingly, we find no effect on I_E/I_M, $\langle \tau \rangle$, $\langle k_1 \rangle$ or γ due to diluting the pyrene groups with unlabelled stabilizer. One has to conclude that for each of the pyrene-labelled NADs, interpenetration of stabilizer chains, if it occurs at all, does not lead to intermolecular fluorescence quenching or excimer formation.

In view of this result, the fact that $\langle k_1 \rangle$ decreases (see *Table 4*) upon anchoring the labelled stabilizer to particles suggests that the mean distance[8] between pyrene groups decreases and that the stabilizer chains become compressed to some extent. The validity of this interpretation remains to be proven, the data are only suggestive. However, other work[5,7] on phenanthrene-labelled PVAc particles indicates a substantial interphase containing a mixture of PVAc and PEHMA chains (e.g. through grafting). Because PVAc is a non-solvent for PEHMA, one would expect the PEHMA in the interphase to be strongly coiled.

CONCLUSION

Steady-state and time-resolved luminescent behaviour of pyrene-labelled poly(2-ethylhexyl methacrylate) stabilizer dissolved in cyclohexane solution and irreversibly bound to PVAc particles were compared. Anchoring the stabilizer to particles leads to shorter distances between the pyrene moieties. This effect manifests itself in a shorter mean decay time of the excited label as shown by transient fluorescence decay measurements and implies that the pyrene groups are quenched to greater degree. On the other hand, steady-state fluorescence spectra show reduced excimer intensites for the anchored stabilizer; this is consistent with less quenching in the anchored stabilizer chains. To explain these apparently contradictory results we propose a new model for the deactivation of excited pyrene species in our colloidal systems. The model accounts for the quenching of pyrene fluorescence by two competitive pathways: (1) emissive complex (excimer) formation; and (2) non-emissive complex formation. The latter process would account for the lower excimer intensities for the particles. Consideration of both steady-state and transient fluorescence data allows the fraction of quenched pyrenes that lead to excimer emission (γ) to be estimated.

The magnitude of γ for particles labelled with pyrenylmethyl and pyrenylbutyl methacrylate was found to be 0.28 and 0.43, respectively. These results suggest that the particle-bound pyrene groups are indeed close enough to interact (i.e. quench) but are sufficiently limited in their motion to restrict the number of pyrenes which can achieve the sandwich-like geometry necessary for excimer emission.

Fluorescence studies on particles containing a mixture of labelled and unlabelled PEHMA in the stabilizer layer indicate that neither fluorescence quenching nor excimer formation occurs between neighbouring stabilizer chains.

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18 In simple systems containing pyrene, changes in monomer intensity in steady-state spectra reveal information about non-radiative quenching[12]. This requires that fluorescence spectra be normalized by the absorbance of the samples. Since our colloidal samples are opaque, this procedure was not attempted