Photoreactions on latex surfaces:
Excimer formation of 1-pyrenemethanol on polystyrene latex particles

K. Nakashima [a,*], N. Kido [a], A. Yekta [b], M.A. Winnik [b]

[a] *Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840, Japan*
[b] *Department of Chemistry and Erindale College, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6*

Abstract

Excimer formation from 1-pyrenemethanol (PyM) and several other pyrene derivatives is investigated in aqueous dispersions of polystyrene (PS) latex, as well as in homogeneous solutions. The efficiency of excimer formation is markedly enhanced on going from the homogeneous aqueous solutions to the particle surface in the presence of the PS latex. This is attributed to adsorption of the probes onto the latex surfaces. The peak height ratio between the excimer and monomer fluorescence bands (I_E/I_M) of PyM is measured as a function of the surface density of the probe. The ratio takes a maximum when the surface density is about 0.3 molecules nm^{-2}. Analysis of various spectral and kinetic data suggest that the probes are inhomogeneously distributed on the latex surface and that a significant portion of the probes self-associate into ground state dimeric forms. © 1997 Elsevier Science S.A.

Keywords: Polystyrene latex; 1-Pyrenemethanol; Fluorescence; Excimer; Lifetime; Adsorption isotherm

1. Introduction

Over the past decade considerable attention has been devoted to the study of photoreactions on solid surfaces. The solid materials so far extensively investigated are silica, clays, porous vycor glasses, alumina and titanium oxides. Some aspects of surface effects on photoreactions are nicely reviewed in recent literature [1,2].

Latex particles represent a type of organic solid material which can be employed as a micro-substrate for photoreactions. The surface consists of organic polymers embedded sparsely with functional groups such as sulfate, carboxyl, or amino groups. This structure is, in some sense, similar to that of silica which has been more extensively studied. In silica, the surface consists of a siloxane (-Si-O-Si-) matrix embedded with silanol (-Si-OH) groups, which act as binding sites for various reacting species. However, compared to silica, latices have several advantages: (a) many kinds of functional groups can be introduced onto the latex surfaces, whereas only the silanol group is available on native silica; (b) concentration of the functional groups on latex surfaces can be easily controlled by modern synthesis techniques; (c) different types of polymers such as polystyrene (PS) and poly-acrylates, with varying degrees of hydrophobicity can be employed as the support material; (d) the particle shape is highly uniform (spherical); (e) the particles size can be controlled within a narrow distribution.

We have investigated several photoreactions on the surface of PS and poly(butyl methacrylate) (PBMA) latices. For example, direct energy transfer from rhodamine dyes to malachite green [3,4] and electron transfer quenching reaction of the fluorescence of 1-pyrenemethanol (PyM) by methylviologen [5]. We find that on going from a homogeneous aqueous solution to the latex dispersion the efficiencies of the photoreactions are dramatically enhanced. In this paper, we report our studies of the excimer formation of PyM and other pyrene derivatives on the surface of PS latex.

Excimer formation relates to an important class of photoreactions [6]. It has attracted much attention because: (a) a group of important organic compounds undergo excimer formation, e.g. photodimerization of aromatic olefins proceeds via excimer formation [7]; (b) the reaction can be used to probe the microstructure of heterogeneous systems such as micelles, vesicles and solid surfaces [1,2,6]; (c) the reaction can be employed to elucidate the kinetics of diffusion-controlled reactions in the restricted space of polymeric systems [8].

The present study reveals that in the latex dispersion the excimer formation reaction is about 10^2 times more efficient

* Corresponding author. Fax: +81 952 28 8548; e-mail: nakashik@cc.saga-u.ac.jp

than in homogeneous solutions. We utilize measurements of fluorescence excitation spectra and decay curves to show that effective adsorption and ground-state dimer formation significantly enhance the reaction efficiency.

2. Experimental

1-pyrenebutyric acid (PyA), 1-pyrenebutyltrimethylammonium bromide (PyB), and 1-pyrenemethanol (PyM) were obtained from Molecular Probes, Inc., and were used as received. Structural formulae of these compounds are shown in Fig. 1. All solvents employed were spectrograde, and used without further purification.

The PS latex was synthesized by standard emulsion polymerization in the presence of sodium dodecyl sulfate. The details of the latex synthesis are described elsewhere [3]. The latex was purified by successive dialysis until the conductivity of the serum was reduced to that of deionized water. The diameter of the particles as determined by an Otsuka DLS-7000 dynamic light scattering spectrophotometer is 182 nm, with a narrow size distribution.

Stock solutions of the pyrene derivatives in water (20 μM) were prepared first. Aliquots of the PS dispersion and the probe stock solution were mixed in a 10 ml volumetric flask, followed by sonication for 5 min. The samples were stored in the dark for 1 day prior to any measurements. Spectroscopic measurements were carried out under aerated conditions, unless otherwise mentioned.

Adsorption isotherms of the pyrene derivatives onto the latex surface were measured by ultracentrifugation. First, aliquots of the latex dispersion containing known amounts of the probe were placed in ultracentrifuge tubes, and centrifuged (Hitachi 55 P-72) for 30 min at 40 000 rpm ($10^5 g$). Next, the concentration of the probe in the supernatant was determined by UV absorption or fluorescence measurements. The quantity of the probe adsorbed was calculated from the difference of the total concentration in the dispersion and the equilibrium concentration in the serum.

Fluorescence spectra were recorded on a Hitachi F-4000 spectrofluorometer with a cell-holder in the front-face con-

figuration. Spectra were corrected by using a standard tungsten lamp with a known color temperature. Absorption spectra were measured with a Jasco Ubest-50 spectrophotometer. Fluorescence lifetime (τ) measurements were carried out with a Horiba NAES 1100 time-resolved spectrofluorometer which employs a time-correlated single photon counting technique.

3. Results and discussion

Fig. 2 shows the fluorescence spectra of PyM and PyB in PS latex dispersions together with the spectra in homogeneous aqueous solutions. We note two types of emission from the pyrene derivatives in the latex dispersion. One is a fine-structured monomer emission ranging from 370 nm to 450 nm. The second is a broad excimer emission from 450 nm to 580 nm. Because of limited solubility of the pyrene derivatives in water, one cannot observe any excimer fluorescence from the aqueous solutions of the probes. For homogeneous solutions of pyrene derivatives in low viscosity solvents, a concentration of more than ca. 1 mM is normally necessary to observe excimer emission. In contrast, in the presence of the PS latex dispersions, we find significant excimer fluorescence of PyM and PyB at the level of 10 μM concentration. The results indicate that in the latex dispersions the excimers are formed some 10^2 times more effectively than in homogeneous solutions. This feature can be explained by the effective adsorption of the probes onto the latex surface [5].

It is well known that the peak height ratio between excimer and monomer fluorescence bands (i.e. I_E/I_M) can be used as a measure of the efficiency of excimer formation [6]. As in the case of molecular pyrene itself [9–11], it is known that

CH₂OH structure

1-Pyrenemethanol (PyM)

$(CH_2)_4N^+(CH_3)_3Br^-$ structure

1-Pyrenebutyltrimethylammonium bromide (PyB)

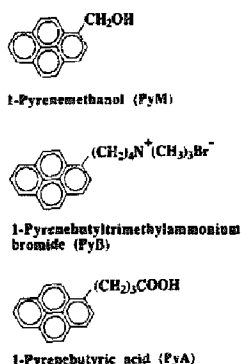$(CH_2)_3COOH$ structure

1-Pyrenebutyric acid (PyA)
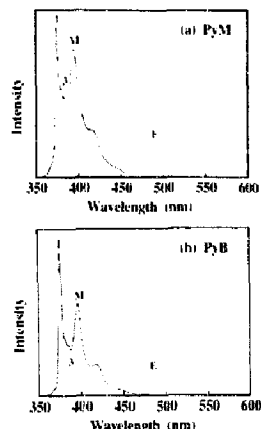
Fig. 1. Structural formulae of PyM, PyB, and PyA.

Fig. 2. Fluorescence spectra of (a) PyM and (b) PyB in pure water (——) and aqueous PS latex dispersions (···). [PyM] = 10 μM, [PyB] = 5.0 μM, [PS] = 0.50 g l⁻¹. Samples deaerated by nitrogen purging for 15 min. Excitation wavelength 325 nm. Excitation and emission band passes 5.0 nm and 1.5 nm, respectively. Spectra normalized at the band 3. See text for the band notations.

the peak height ratio between the band 1 and the band 3 of PyM (i.e. I_1/I_3) is a good measure of polarity of the probe environment, which has a high value for high polarity environments [5,12].

In Fig. 3, we show the fluorescence spectra of PyA in the PS latex dispersion. It is interesting that the excimer formation is strongly pH dependent. We note significant excimer fluorescence at pH 3, whereas none is detected at pH 8. If we assume that the pK_a of PyA is close to that of butyric acid (i.e. $pK_a = 4.6$), then nearly 97% of PyA have an unionized acid groups at pH 3, while almost all are ionized at pH 8. At pH 3, the hydrophobic interaction between the probe and PS matrix dominates and leads to a high degree of adsorption onto the latex surface, whereas at pH 8, repulsive interactions between the ionized form of the probe and the charged latex (sulfate groups) cause a shift in the partitioning of PyA toward the aqueous phase.

For a deeper understanding of the excimer formation phenomena on the latex surface, we need information about the adsorption behavior of the probes. Fig. 4 shows the adsorption isotherms of PyM and PyA for the PS latex surface. The horizontal axis represents the total concentration of the solubilized probe. The vertical axis represents the quantity of adsorbed probe, calculated as the difference between the total
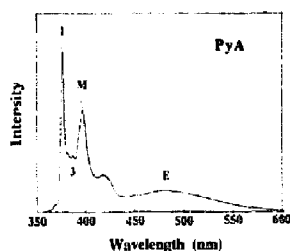

Fig. 3. Fluorescence spectra of PyA in PS latex dispersions at pH 3 (——) and pH 8 (···). [PyA] = 10 μM, [PS] = 0.50 g l^{-1}. Spectral settings as in Fig. 2.
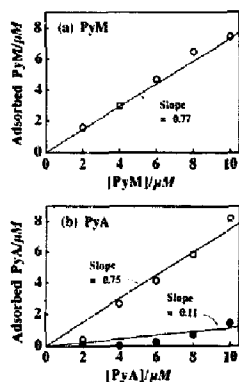

Fig. 4. Adsorption isotherms of pyrene derivatives onto PS latex particles at 20°C. (a) PyM; (b) PyA at pH 3 (O) and pH 8 (●). [PS] = 0.50 g l^{-1}. [PyM] and [PyA], respectively, the total probe concentration in the dispersion.

concentration put in the dispersion and the measured equilibrium value in the supernatant. Accordingly, the slope of the line gives the fraction of the total probe residing on the latex particles. In Fig. 4(a) we note that for a 0.5 g l^{-1} dispersion, about 80% of PyM are surface adsorbed, a value not sensitive to the pH. Consequently the effective local probe concentration much exceeds the μM bulk value, and surface excimer formation becomes possible. The same reasoning explains the pH dependence of excimer formation for PyA. Fig. 4(b) (empty circles) shows that at pH 3, about 75% of the probe is adsorbed (2.5% ionized, assuming $pK_a = 4.6$). On the other hand, when the pH is increased to 8 (filled circles), only 11% are adsorbed, leading to a reduction of PyA surface concentration and the disappearance of excimer emission (cf. Fig. 3).

To further study the partitioning effect, we measured the dependence of I_E/I_M of PyM on the latex concentration, for two fixed PyM concentrations at 5 μM and 10 μM, respectively. Fig. 5 shows the two profiles are similar (more excimer at higher load of probe) so that we focus the discussion on Fig. 5(a) only. We note that the I_E/I_M profile shows a maximum at a latex concentration of about 0.3 g l^{-1} (point B). Such behavior is also reported by Kaufman and Avnir [13] for the pyrene probing of sol–gel–xerogel transition in silica. In that work the maxima of I_E/I_M profile was related to the changes of surface irregularity and porosity.

To discuss the subject of the system of this report on a more quantitative level, we introduce the following equations

$$I_M = I_M^W + I_M^L \tag{1}$$

$$I_E = I_E^W + I_E^L \tag{2}$$

where I_M^W, I_M^L (I_E^W, I_E^L) denote the monomer (excimer) fluorescence intensities arising from the aqueous and latex surface, respectively. Dividing Eq. (2) by Eq. (1) and considering that $I_E^W \approx 0$, we obtain

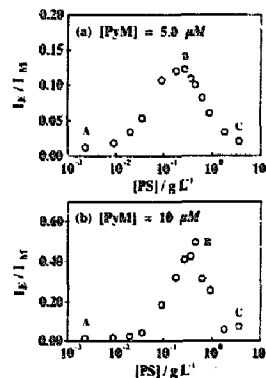$$I_E/I_M = I_E^L/(I_M^W + I_M^L) \tag{3}$$

Fig. 5. Dependence of I_E/I_M of PyM on the PS latex concentration: (a) [PyM] = 5.0 μM; (b) [PyM] = 10 μM.

When the PS concentration is low (point A, Fig. 5(a)), the value of I_E/I_M is small since most of the probe is partitioned into the aqueous phase. As the PS concentration is increased, the value of I_E/I_M increases because more of the probe partitions toward the latex. I_E/I_M reaches a maximum at the PS concentration of 0.27 g l^{-1} (point B). Considering that here 77% of the probe is surface adsorbed (cf. Fig. 4(a)), we calculate a mean surface density of 0.28 probe nm^{-2}, which corresponds to a mean nearest neighbor distance of 1.9 nm. It is believed that excimer formation requires the distance between the two reacting pyrene molecules to be ca. 0.5 nm [14,15]. Two independent excimer formation mechanisms can be envisioned. In the most common case, observed in homogeneous fluid media, dynamic diffusion after excitation brings the two probes to within the required distance. In the less prevalent case, also referred to as the static mechanism, the two pyrenes are preassociated (within 0.5 nm) prior to excitation, and the excimer is formed immediately upon excitation. For the case of probes on the latex surface, the spectral and partitioning data presented so far cannot distinguish the dominant mode of excimer formation. However, in the next section we shall present spectral and kinetic data which show that the dominant mode of excimer formation on the latex surface occurs via a static mechanism. Consequently, at point B of Fig. 5, the PyM probes must be highly associated on the latex surfaces. As we continue to increase the particle concentration, the value of I_E/I_M gradually decreases (region B–C), a feature which can be attributed to the dissociation of ground state dimer (lowering of the probe surface density). A similar situation is encountered for the dissociation of ground state aggregates for rhodamine dyes on PS latices [3,16] and rhodamine 6G on the surface of vesicles [17].

More corroborative evidence for the partitioning of PyM between water and latex can be obtained if we plot I_1/I_3 against the PS concentration (Fig. 6). At lower PS concentrations, the value of I_1/I_3 is 1.71, close to that of the probe
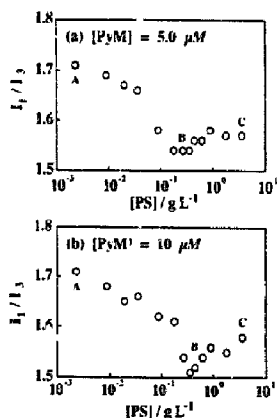
in pure water [5]. Under these conditions almost all PyM exist in the aqueous phase. As the PS concentration is increased, the I_1/I_3 value decreases gradually, reaching a minimum at point B. Because the PS surface has a lower polarity than that of water [5], we have evidence of more partitioning for the latex surface, an interpretation consistent with that offered for the change of I_E/I_M in Fig. 5. We also note here a slight increase in I_1/I_3 for the higher PS concentrations. At present, we cannot make any conclusive remarks for this effect. A possible explanation is that near point B the probes are in the most highly clustered state, reducing the overall polarity of the environment. Kaufman and Avnir [13] proposed a similar mechanism to account for the decrease of I_1/I_3 (also a measure of local polarity) in silica systems.

In this section we present evidence as to the mechanism of excimer formation on the surface of PS latex. The two types of mechanisms considered are (a) dynamic or (b) static in nature. Such studies are important to the understanding of the mechanistic details of substrate supported photoreactions. For example, it is reported that the products of photodimerization of acenaphthylene on silica surfaces are strongly dependent on the surface mobility of the reactants [18,19]. The dynamic process means that the excimer is formed by diffusive encounters of an excited monomer with a ground-state monomer [6,20,21]. The static process refers to the situation when the excimer originates by the direct excitation of the ground-state dimer [6,20,21]. We can distinguish between the two cases by examining fluorescence excitation spectra and/or fluorescence decay kinetics [6,20,21]. In Fig. 7, we compare the fluorescence excitation spectra of PyM in a methanolic solution (1 mM) and a 0.42 g l^{-1} PS latex dispersion (10 μM). The solid lines represent the spectra obtained by monitoring the monomer fluorescence (abbreviated as M-spectra) and the dotted lines show the spectra obtained by monitoring the excimer fluorescence (E-
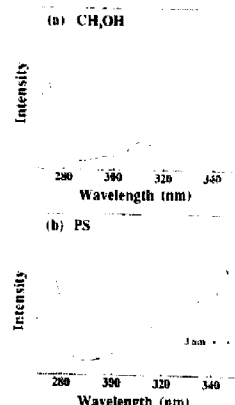

Fig. 6. Dependence of I_1/I_3 of PyM on PS latex concentration: (a) [PyM] = 5.0 μM; (b) [PyM] = 10 μM.

Fig. 7. Fluorescence excitation spectra of PyM monitored at 395 nm (——) and 500 nm (···). (a) Methanolic solution, [PyM] = 1.0 mM; (b) PS latex dispersion, [PyM] = 9.9 μM, [PS] = 0.42 g l^{-1}. Samples deaerated by nitrogen purging for 15 min. Excitation and emission band passes 1.5 nm and 5.0 nm, respectively.
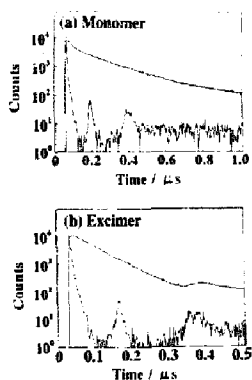
Fig. 8. Fluorescence decay curves of PyM in a PS latex dispersion. [PyM] = 10 μM, [PS] = 0.10 g l^{-1}. (a) Monitored by monomer emission at 395 nm; (b) Monitored by excimer emission at 500 nm. Samples deaerated by nitrogen purging for 15 min. Samples excited at 325 nm, band pass 14 nm. Emissions collected through a Hoya U-360 band pass filter and a Toshiba Y-49 cut-off filter, respectively.

spectra). In the methanolic solution (Fig. 7(a)), there is no difference in the band position of the M- and E-spectra. This indicates that in the methanolic solution excimers form by a dynamic process, as previously reported in earlier literature [6,20,21]. In the latex dispersion (Fig. 7(b)), however, we observe a significant shift (3 nm) of the band location on going from M- to E-spectra. The spectra indicate that the dominant mode of excimer formation is by the static process.

We measured the fluorescence decay curves of PyM by monitoring monomer and excimer emissions (Fig. 8). In the PS latex dispersion, the excimer decay curve fits a two-exponential profile, with no obvious growing-in term on this time scale. The averaged lifetime is $\langle \tau \rangle = \Sigma A_i \tau_i^2 / \Sigma A_i \tau_i = 93.1$ ns, with A_i and τ_i ($i = 1, 2$) defined, respectively, as the pre-exponential factor and lifetime of the ith component. From Fig. 8(b) it is clear that the excimer emission shows a very fast rise in the short-time region following excitation. It is well known that for the case of the dynamic mechanism, one generally observes a slow rise of the emission intensity indicating the time elapsed for diffusion related encounters [6,20]. Indeed this is observed for the case of excimer emission of PyM in methanol (data not shown). The fast rise of the excimer signal provides us with further evidence for the static mechanism.

The decay curve for the monomer emission fits a three-exponential function, with an averaged lifetime ($\langle \tau \rangle$) of 185 ns ($\chi^2 = 1.08$). Note that the decay shows a sharp decrease of intensity in the short-time region following excitation. This may be related to energy transfer from monomers to the excimer-forming sites (dimers), as reported by Ohmori et al. for pyrene in Langmuir–Blodgett films of poly(vinyl octal) [22] For a detailed discussion of the decay profiles one needs to employ the Förster or fractal models, as demonstrated by Ohmori et al. [22], or our own previous work

[3]. Presently we will not delve into the quantitative aspects of the decay kinetics because they will not add to the general conclusions reached here.

4. Conclusions

Adsorption to the particle surface and excimer formation for PyM, PyA, and PyB is investigated in aqueous solutions, in the presence and absence of PS latex. The efficiency of excimer formation of PyM and PyB is markedly enhanced on going from pure water to the aqueous latex dispersion. This is attributed to adsorption of the probes onto the latex surfaces, followed by partial association into ground state dimers. PyA shows a pH-dependent behavior for adsorption and excimer formation. Excimers are formed at pH 3 but not at pH 8, where the anionic form of PyA is repelled into the aqueous phase. Analysis of various spectral and kinetic data indicate that on the surface of the latex PyM self-associates into ground state dimers or higher aggregate forms. Further work is necessary before one can conjecture the presence of nanoscale grooves on the latex surface, serving as potential sites of aggregation.

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