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Penetration of pyrene and its derivatives into polystyrene latex particles as studied by fluorescence spectroscopy

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Small hydrophobic pores (channels) in polystyrene latex particles were found by investigating the penetration of pyrene using fluorescence techniques.

Polystyrene latex (PSL) particles are solid nano- or microspheres with functional groups attached on the surfaces.[1] Latexes have many applications in coatings,[2] biomedical diagnostics[3] and drug delivery.[4] They are used also as model systems in colloid research because of their well-defined physicochemical characteristics.[5] Recently we used latex particles as microsubstrates for photoreactions and found that the efficiencies of the reactions are enhanced dramatically.[6,7] This effect is attributed to effective adsorption of the reactants on the particle surfaces. Although all the applications of latex are closely related to the composition and structure of the particle surfaces, some structural details, such as compactness of the polymer chains and penetration of chemicals into the particle, are still unclear.

One particular phenomenon we observed is that the efficiency of photoinduced electron transfer from pyrene (Py) to methylviologen (MV^{2+}) decreases with increase in the loading time (*i.e.* the time of storage after mixing of the reactants with PSL).[7] This result cannot be explained by considering that the reactants are adsorbed only on the surface of the particles. The decrease of the efficiency suggests that there are small channels or pores on the particle surface and Py molecules can go inside the particle to be protected from quenching.

In this work, we report the evidence for small pores in PSL by studying the penetrations of Py, pyrenemethanol (PyM) and 1-pyrenylbutyltrimethylammonium bromide (PBTAB) into PSL particles in aqueous dispersion. This finding will extend the application of PSL as a nano-scale substrate for coatings, drug delivery systems, ammunoassay and so on.

PyM and PBTAB were purchased from Molecular Probes, Inc. and used as supplied. Py was purified by vacuum sublimation. To avoid any aggregate or excimer of the probes, 0.60, 5.0 and 10.0 μM stock solutions were used to prepare samples in the penetration experiments for Py, PyM and PBTAB, respectively. The synthesis, purification and characterization methods of PSL were reported elsewhere.[7,8] The mean diameter of the latex particles used in this work is 212 nm as determined by dynamic light scattering measurements.[8]

Adsorption isotherms of the probes onto the latex particles were measured by ultra-centrifugation.[7,8] Fluorescence spectra were recorded on a Hitachi F-4000 spectrofluorometer. Steady-state fluorescence intensity is expressed in terms of peak heights. Fluorescence lifetime measurements were carried out with a Horiba NAES 1100 time-resolved spectrofluorometer. All Fluorescence measurements were carried out at room temperature with air-saturated samples.

It is well known that the microenvironment of a Py molecule can be measured by the I_1/I_3 ratio in the vibronic fine structure of its fluorescence spectrum.[9] Therefore, the location of a Py probe in a PSL aqueous dispersion can be determined by the I_1/I_3 ratio. Illustrated in Fig. 1 are the loading time effects on the relative fluorescence intensities (a) and I_1/I_3 ratios (b) of Py, PyM and PBTAB in PSL aqueous dispersions. The obvious decrease of I_1/I_3 ratio of Py indicates it was adsorbed from the environment with high polarity (aqueous phase, I_1/I_3 = 1.84)[9] to that with low polarity (polystyrene bulk, $I_1/I_3 \approx 1.05$). However, adsorption equilibrium is usually reached in minutes, the slow process of the decreasing I_1/I_3 ratio with loading time suggests that Py penetrates inside the particle. The homogeneous distribution of Py in poly(methyl methacrylate) latex particles after soaking in a methanolic solution of Py[10] also supports the penetration.

The remarkable increase of Py fluorescence intensity with loading time suggests that the quantum yield or lifetime was increased due to its microenvironmental change. Time-resolved fluorescence measurements suggest that the probes are located in two kinds of environments (Fig. 2). Environment 1 makes Py have a long lifetime (τ_1) and environment 2 makes it have a short lifetime (τ_2). The adsorption isotherm of Py onto PSL shows that more than 99.9% of Py exist in the adsorbed state

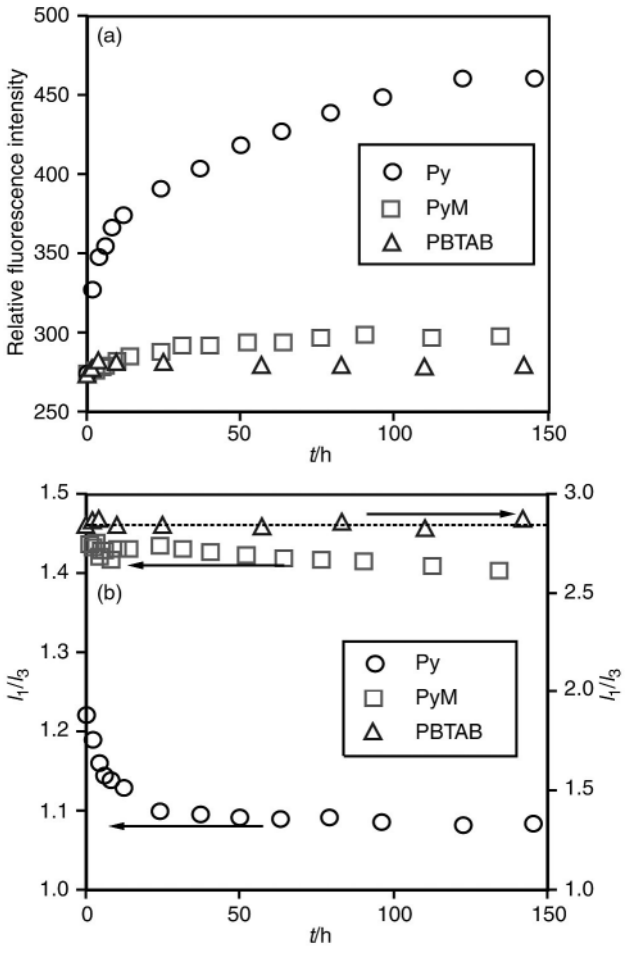

Fig. 1 Loading time effect on the relative fluorescence intensities (a), and I_1/I_3 ratios (b) of Py, PyM, and PBTAB in PSL dispersion at room temperature.

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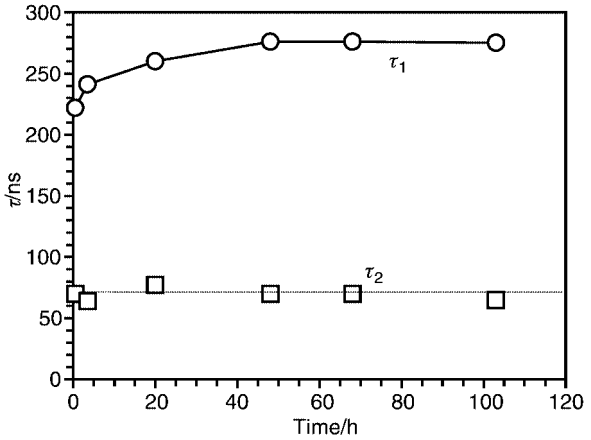

Fig. 2 Loading time effect on the fluorescence lifetimes of pyrene in PSL aqueous dispersion. [Py] = 0.40 μM, [PSL] = 0.40 g L^{-1}.

(data not shown). Therefore, the contribution from the species in aqueous phase is negligible. This means that both of the two environments locate in/on the particle.

The fluorescence lifetime of Py is mainly affected by the mobility of Py and O_2 concentration in the system. In aqueous phase, the fluorescence lifetime of Py decreases from 210 ns in O_2 free solution to 112 ns in air-saturated solution. It is expected in the PSL dispersion that the lifetime will decrease further when Py stays on the PSL surface due to adsorption of both Py and O_2.[11] Actually, we observed the decrease of fluorescence intensity within 2 min of the loading. On the other hand, when Py goes into the inner part of the particle, the lifetime increases due to the reduced mobility of Py. Thus, we ascribe environment 1 to pores or channels inside of PSL particle, and environment 2 to the adsorption sites at the liquid–solid interface.

Py molecules located in environment 2 seem to go gradually to environment 1. This is indicated by the change of fluorescence quantum yields of the two components (data not shown) and the increase of the total fluorescence intensity (Fig. 1a). The microenvironmental change with the loading time is concrete evidence for the penetration of Py.[9] In aqueous solution, the I_1/I_3 ratio of Py is 1.84. After Py was loaded onto PSL, the ratio decreased to 1.22 in 2 min. Then it decreased gradually to 1.08 in 5 d at rt (Fig. 1b). If we assume that the I_1/I_3 ratio of the adsorbed Py is 1.22 at the interface between PSL particle and water, we get some details about the particle surface structure and adsorption mechanism.

First, there are pores or channels in PSL particles through which Py penetrates into the inner part of the particle resulting in the decrease of I_1/I_3 ratio and increase of lifetime. Second, the pore or channel is small and hydrophobic. The hydrophobicity of the channel prevents water molecules and ionic species from penetrating but allows Py to go slowly into the inner part. It is known that a pyrene excimer can be easily formed in confined spaces such as polymer micelles,[12] and zeolites.[13] However, a Py aggregate or excimer was not detected even at high concentration. Thus the dimension of the pore should be slightly larger than the size of Py molecule. Thirdly, the number of the holes should be large because the uptake capacity of Py monomer can be as high as 2% (g/g).

As shown in Fig. 1, the I_1/I_3 ratio of PyM decreases slightly and that of PBTAB is almost constant during the loading. If PyM and PBTAB can go to the inside of the particle, their I_1/I_3 ratios should show obvious change because the I_1/I_3 ratios of PyM and PBTAB are also sensitive to the polarity of the environments.[14] Comparing with that of Py, we conclude that PBTAB does not go inside the particle and PyM goes slightly inside. Here the "passport" for entering into the particle seems to be mainly the polarity of the "passenger".

To confirm the existence of the pores in the latex particles, the control experiments were carried out using PSL and polystyrene cast films. The former was prepared by drying the latex dispersion, and the latter by casting from DCM solution. Both films were annealed at 150 °C for 20 min. The fluorescence intensities of Py from the films immersed in the aqueous solutions decreased and the I_1/I_3 ratio did not decrease below 1.2 as the loading time increased. These results are very different from that of the latex particles. Therefore, we conclude that there exist small hydrophobic pores in the PSL particles.

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