Photoinduced electron transfer from pyrene to methylviologen in polystyrene latex dispersions as studied by diffuse reflectance laser flash photolysis

K. Nakashima,*[a] T. Miyamoto[a] and S. Hashimoto[b]

[a] *Department of Chemistry, Faculty of Science and Engineering, Saga University, 1 Honjo-machi, Saga 840-8502, Japan. E-mail: nakashik@cc.saga-u.ac.jp*
[b] *Department of Chemistry, Gunma College of Technology, 580 Toriba-machi, Maebashi, Gunma 371-0845, Japan*

Received (in Cambridge, UK) 22nd September 1998, Accepted 15th Decemer 1998

Fluorescence and diffuse reflectance flash photolysis studies revealed that photoinduced electron transfer from pyrene to methylviologen was enhanced in polystyrene latex dispersions, and also that the back electron transfer was markedly suppressed in the dispersions, resulting in effective charge separation.

Latex particles represent a new 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 leads latex particles to have two types of adsorption sites on the surface: (1) the polymer matrix which affords continuous adsorption domains to non-polar and low polarity adsorbates, and (2) the functional group which gives discrete adsorption sites to ionic and highly polar species. Such a feature is not found in any other solid materials which are employed as adsorbents. Furthermore, latex particles have many other advantageous features as described in previous papers.[1,2]

We have investigated several photoreactions, such as electronic energy transfer[3,4] and electron transfer,[2,5] on the surface of polystyrene (PS) and poly(butyl methacrylate) latexes in aqueous dispersions, and demonstrated the usefulness of the latexes as micro-substrates for the photoreactions. Here, we report photoinduced electron transfer (PET) from pyrene (Py) to methylviologen (MV^{2+}) in PS latex dispersions.

The PS latex was synthesized by standard emulsion polymerization in the presence of sodium dodecyl sulfate. The latex was purified by repeated dialysis. The diameter of the latex particles was determined to be 85 nm with an Otsuka ELS-800 dynamic light scattering spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4000 spectrofluorometer. Transient absorption spectra were observed with a nanosecond diffuse reflectance laser photolysis system, the set-up of which was similar to that described previously.[6]

We measured fluorescence spectra of Py in the absence and presence of MV^{2+} [Fig. 1(a)]. It is well known that the fluorescence of Py is quenched by MV^{2+} through PET as follows:[7,8]

$$\mathrm{Py} + h\nu_a \rightarrow \mathrm{Py}^* \qquad (1)$$

$$\begin{array}{l}\mathrm{Py}^* + \mathrm{MV}^{2+} \xrightarrow{\mathrm{PET}} \mathrm{Py}^{\cdot +} + \mathrm{MV}^{\cdot +} \qquad (2)\\ \downarrow \text{Fluorescence}\\ \mathrm{Py} + h\nu_f\end{array}$$

Thus, we can observe the PET reaction by monitoring the fluorescence quenching of Py. As seen from Fig. 1(a), the fluorescence of Py is effectively quenched by MV^{2+} in the latex dispersion even when the MV^{2+} concentration is at a level of μM, which is several tens of times smaller than that needed for quenching in aqueous solutions. This means that PET in the latex dispersions takes place several tens of times more efficiently than in aqueous solutions. The marked enhancement of PET can be ascribed to the increase in local concentrations of the donor and acceptor on the latex surface, as confirmed by the adsorption isotherms (data not shown). The effective adsorption of the donor (Py) onto the latex surface is also evidenced by the vibronic fine structure of the fluorescence. The intensity ratio between the band I and III [the so-called I_1/I_3 value; Fig. 1(a)] is well known to be a measure of polarity around the probe.[9,10] The I_1/I_3 value obtained is 1.13 for the latex dispersion, which is much closer to the values for benzene (1.05)[10] and propan-1-ol (1.09)[10] than that for water (1.81). This means that most of the Py molecules are located on the latex particles.

There are generally two purposes for employing solid surfaces as substrates for PET: (A) to enhance PET by condensing and orienting the reactants, and (B) to suppress the back electron transfer to achieve effective charge separation.[11] We have shown in Fig. 1 the usefulness of the PS latex particles for realizing purpose (A). To examine (B), we intended to observe transient absorption spectra. As the latex dispersion is very turbid, a conventional (*i.e.* transmittance mode) flash photolysis technique is of no use for the system. Therefore, we employed the diffuse reflectance mode. The transient absorption spectra for the PS latex dispersion containing Py and MV^{2+} are shown in Fig. 2. The band at 408 nm is assigned to the $MV^{\cdot +}$ cation radical, and the band at 461 nm to the $Py^{\cdot +}$ cation radical [Fig. 2(a)]. We note from Fig. 2 that these radical bands remain for > 1 ms. If we consider that charge recombination between the products usually takes place on the time scale of picoseconds or nanoseconds in homogeneous solutions, we can see

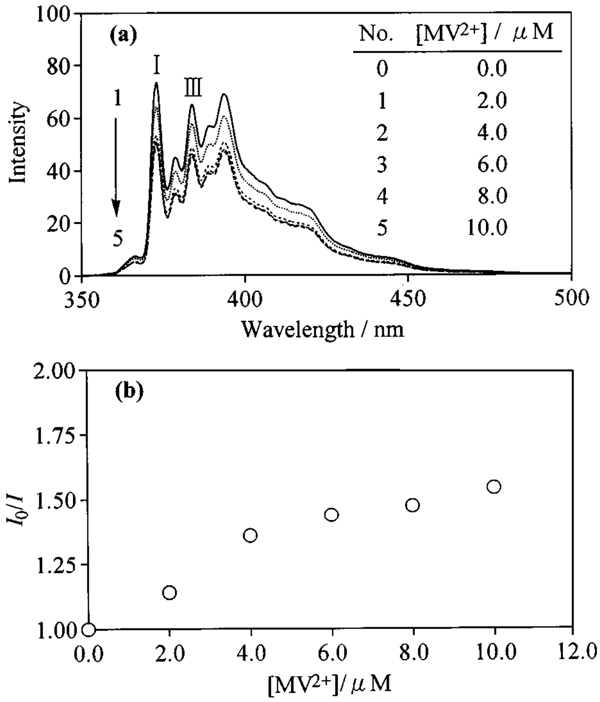

Fig. 1 Fluorescence spectra (a) and Stern–Volmer plot (b) for a Py/MV^{2+} pair in a PS latex dispersion. Concentrations: [Py] = 0.514 μM, [PS] = 1.00 g L^{-1}. The samples are excited at 334 nm. The spectra are corrected by subtracting background scattering of excitation light.

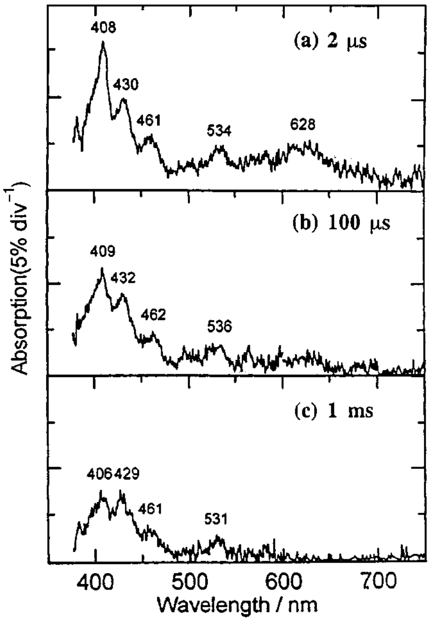

Fig. 2 Transient absorption spectra of a Py/MV^{2+} pair in a PS latex dispersion. Concentrations: [Py] = 250 μM, [MV^{2+}] = 300 μM, [PS] = 54.2 g L^{-1}.

that the back electron transfer is markedly suppressed in the latex dispersion. Thus, the present result demonstrates the usefulness of the latex system for performing effective charge separation.

In order to understand the remarkable effect of the latex system on suppression of charge recombination, we show in Fig. 3 a schematic diagram for behavior of the reactants and products of the PET reaction on the latex surface. Before the PET reaction, Py molecules are mostly adsorbed onto the continuous PS area by hydrophobic interaction, while MV^{2+} molecules are adsobed onto the sulfate groups by electrostatic attraction. After the PET reaction, both of the products will be fixed at the sulfate groups owing to electrostatic interaction. The fixation of the products seems to result in suppression of the back electron transfer.

(a) *Before* PET reaction (b) *After* PET reaction

Fig. 3 Schematic representation for the behavior of Py, MV^{2+} and their PET reaction products on a PS latex surface.

Recently, Hsiao and Webber investigated PET reactions from pyrene and anthracene derivatives to a viologen analogue using a PS latex dispersion.[12] They also observed a remarkable increase in the efficiency of charge separation for some donor–acceptor pairs, although the forward PET reactions were not improved by the use of the latex dispersion. They ascribed the remarkable increase in the yield of the charge separation to a 'compartmentalization effect' of the latex particles. It is likely that there are compartments (holes) on the latex surface which accommodate limited types of the products and/or reactants. The existence of such compartments is also suggested in our experiments for the present system and also for another system.[2] The Stern–Volmer plot [Fig. 1(b)] shows a downward curve, indicating that the fluorescence of Py is partly protected from quenching by MV^{2+} on the PS latex particles. We can attribute this protected quenching to the likelihood that some portion of Py molecules on the latex surface is incorporated into the holes in the latex particles (see ref. 2 for detailed discussion). In conclusion, it seems that both a 'fixation effect' and 'compartmentalization effect' play an important role in PET processes in latex systems.

Note and references

1 K. Nakashima, N. Kido, A. Yekta and M. A. Winnik, *J. Photochem. Photobiol. A: Chem.*, 1997, **110**, 207.
2 K. Nakashima, S. Tanida, T. Miyamoto and S. Hashimoto, *J. Photochem. Photobiol. A: Chem.*, 1998, **117**, 111.
3 K. Nakashima, J. Duhamel and M. A. Winnik, *J. Phys. Chem.*, 1993, **97**, 10702.
4 K. Nakashima, Y. S. Liu, P. Zhang, J. Duhamel, J. Feng and M. A. Winnik, *Langmuir*, 1993, **9**, 2825.
5 K. Nakashima and N. Kido, *Photochem. Photobiol.*, 1996, **64**, 296.
6 S. Hashimoto, N. Fukazawa, H. Fukumura and H. Masuhara, *Chem. Phys. Lett.*, 1994, **223**, 493.
7 R. D. Stramel, C. Nguyen, S. E. Webber and M. A. J. Rodgers, *J. Phys. Chem.*, 1988, **92**, 2934.
8 D. Fornasiero and F. Grieser, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 2955.
9 K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.*, 1977, **99**, 2039.
10 D. C. Dong and M. A. Winnik, *Photochem. Photobiol.*, 1982, **35**, 17.
11 K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, New York, 1987.
12 J.-S. Hsiao and S. E. Webber, *J. Phys. Chem.*, 1993, **97**, 8289; J.-S. Hsiao and S. E. Webber, *J. Phys. Chem.*, 1993, **97**, 8296.

Communication 8/07368F