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Room temperature phosphorescence of 6-bromo-2-naphthol adsorbed on latex substrates

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Abstract

Room temperature phosphorescence (RTP) of 6-bromo-2-naphthol (BNL) is investigated in an aqueous dispersion of polystyrene latex and on the dried latex particles as well as in an aqueous solution. RTP of BNL is markedly enhanced on going from the aqueous solution to the latex substrates under deaerated conditions. This is attributed to effective adsorption of the phosphorophor onto the latex surfaces, resulting in suppression of non-radiative deactivation of the phosphorescent state. © 1997 Elsevier Science S.A.

Keywords: Room temperature phosphorescence; 6-Bromo-2-naphthol; Polystyrene latex

1. Introduction

Many studies have been carried out on room temperature phosphorescence (RTP), because: (a) phosphorescence spectroscopy is a useful tool for elucidating photochemical and photophysical processes in the triplet states of molecules [1], (b) RTP affords some kinetic parameters of molecular dynamics (e.g. exit rate of solutes from micelles [2]), and (c) RTP measurement is a selective and conventional analytical method for a wide range of organic and inorganic compounds [3–5]. Since it is usually difficult to observe RTP in homogeneous solutions [6], various microheterogeneous systems (MHS) have been employed as substrates for enhancing RTP. The MHS so far employed include micelles [7], cyclodextrins [8], cellulose [9], silica [10], and their combined systems [11]. The main roles of MHS are: (i) to hinder the motions of phosphorophors to suppress intramolecular non-radiative deactivation in the triplet states, and (ii) to protect phosphorophors from intermolecular quenching by molecular oxygen and other quenchers.

The surface of latex particles is a member of MHS which has a unique structure consisting of a continuous hydrophobic domain embedded sparsely with ionic functional groups. The surface of typical polystyrene (PS) latices, for example, consists of a continuous PS area embedded with sulfate groups. Thus the latex surface has a continuous adsorption domain for hydrophobic species and various discrete adsorption sites for cationic species. Such a feature is not found in other solid surfaces. Therefore, it is expected that the latex particles can be employed as new micro-substrates for photoprocesses including RTP.

We have investigated several photoreactions on the surfaces of PS and poly(butyl methacrylate) latex particles in aqueous dispersions: energy transfer [12], electron transfer [13], and excimer formation [14]. In this study, we investigated the RTP of 6-bromo-2-naphthol (BNL) and two other similar compounds in an aqueous dispersion of PS latex and on the dried latex particles as well as in an aqueous solution, because RTP is a useful tool for monitoring triplet-state photoreactions. The RTP of BNL is dramatically enhanced on going from the aqueous solution to the latex dispersion and also to the dried latex particles. To our knowledge, this is the first report on successful observation of RTP in latex systems.

2. Experimental

BNL (Tokyo Kasei Kogyo Co., Ltd.) was sublimed in vacuo. 2-Naphthol (Wako Pure Chemical Industries, Ltd.) and 1-bromo-2-naphthoic acid (Tokyo Kasei Kogyo Co., Ltd.) were used as received. The PS latex was synthesized by standard emulsion polymerization in the presence of sodium dodecyl sulfate [12], and purified by successive dialysis.

An aliquot of a phosphorophor stock (1 mM methanolic solution) was transferred to a 10 ml volumetric flask, fol-

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lowed by gentle evaporation of the solvent. Then, 1 ml of the PS latex stock (11.4 g l^{-1} aqueous dispersion) was added to the volumetric flask. The mixture of the phosphorophor and latex was sonicated for 5 min after diluting to 10 ml with water. A part of the latex dispersions containing the phosphorophor was dried under vacuum at room temperature for preparing the samples of dried latex particles.

Adsorption isotherms of the phosphorophors onto the latex surface were measured by ultracentrifugation. Aliquots of the latex dispersion containing known amounts of the phosphorophor were placed in ultracentrifuge tubes, and then centrifuged with a Beckman Avanti 30 ultracentrifuge for 60 min at 26 000 rpm (57 430g). Concentration of the phosphorophor in the supernatant after centrifugation was determined by UV absorption measurements. The amount of the phosphorophor adsorbed was calculated from the total concentration in the dispersion and the equilibrium concentration in the serum.

Phosphorescence and fluorescence spectra were recorded on a Hitachi F-4000 spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube. As the latex samples were not transparent, a cell holder in the front-face configuration was employed. A sharp cut-off filter (Toshiba L-39) was set between the sample and the emission monochromator to remove the interference of excitation light with emission spectra. The samples were deaerated, if necessary, by nitrogen purging for 15 min (for aqueous solutions and latex dispersions) or by continuous flow of nitrogen gas stream (for dried latex particles). The emission spectra were corrected for the spectral response of the spectrofluorometer by using a standard tungsten lamp with a known color temperature.

3. Results and discussion

In Fig. 1 we show emission spectra of BNL in PS latex dispersions at room temperature. The spectra of BNL in aqueous solutions are also shown in Fig. 2 for comparison. The emission ranging from 360 to 460 nm can be assigned to the fluorescence and that ranging from 460 to 700 nm to the phosphorescence [15]. The assignment for the phosphorescence is supported by the fact that the corresponding emission is completely quenched by oxygen in the aerated samples. Since we put a L-39 sharp cut-off filter between the sample and the emission monochromator to prevent the interference by the excitation light, the fluorescence in Figs. 1 and 2 is reduced to some extent in intensity compared to the phosphorescence. We realize from Figs. 1 and 2 that RTP is dramatically enhanced on going from the aqueous solution to the latex dispersion. This is ascribed to effective adsorption of BNL onto the latex surface, resulting in suppression of non-radiative decay of the lowest triplet state. The marked enhancement of RTP in the latex dispersion suggests the usefulness of this material as a novel substrate for enhancing RTP.

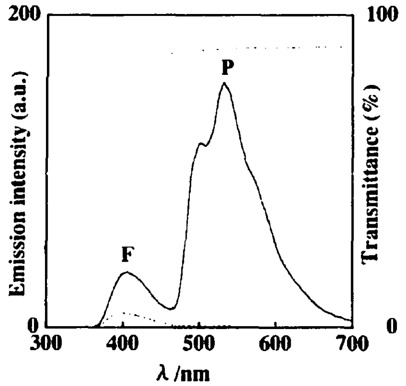

Fig. 1. Emission spectra of BNL in an aqueous PS latex dispersion at room temperature. The symbols F and P denote fluorescence and phosphorescence emissions, respectively. ——, spectra under deaerated conditions; - - -, spectra under aerated conditions; · · ·, a transmittance curve of the Toshiba L-39 sharp cut-off filter. The samples are excited at 287 nm. Concentrations: [BNL] = 0.1 mM, [PS] = 1.14 g l^{-1}.

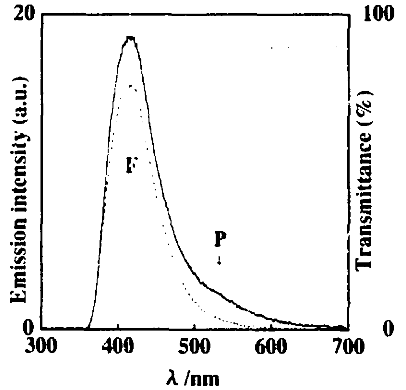

Fig. 2. Emission spectra of BNL in an aqueous solution at room temperature. Concentration: [BNL] = 0.1 mM. See Fig. 1 for notations and experimental conditions.

Recently, Hamai reported that by employing α-cyclodextrin, RTP of BNL was observable even in aerated conditions [15]. Therefore, it is worthwhile examining if we can observe the RTP of BNL in an aerated PS latex dispersion. In the latex dispersion, however, we were not successful in detecting RTP under aerated condition as seen from Fig. 1. It is of note that the fluorescence as well as phosphorescence is heavily quenched by oxygen in the latex dispersion (compare Figs. 1 and 2). This suggests that oxygen molecules are highly solubilized around the surface of PS latex particles. As the solubility of oxygen is generally increased with decreasing polarity of the solvent, it is inferred that oxygen molecules are also effectively adsorbed onto a hydrophobic area of the latex surface in the aerated dispersion. The high local concentration of oxygen on the latex surface may be the cause of the disappearance of RTP in the aerated latex sample, in contrast to the case of α-cyclodextrin solutions.

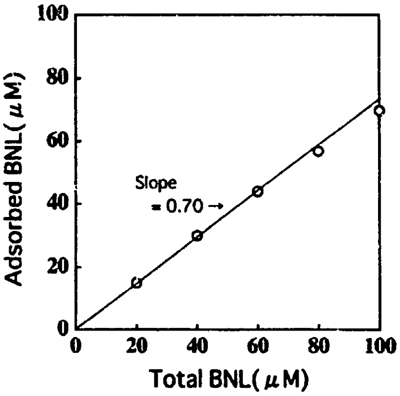

Fig. 3. Adsorption isotherm of BNL onto PS latex particles at 22°C. [PS] = 1.14 g l^{-1}.

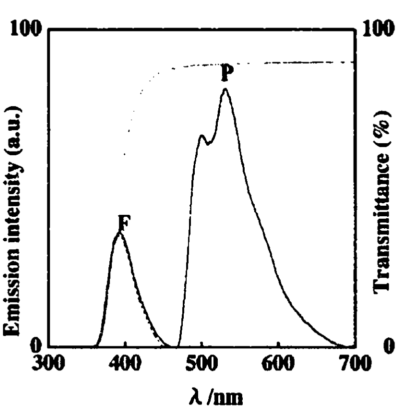

Fig. 4. Emission spectra of BNL on dried PS latex particles at room temperature. See Fig. 1 for notations and experimental conditions.

It is important to estimate the amount of BNL molecules adsorbed onto the latex surfaces. We measured the adsorption isotherm at 22°C (Fig. 3). The horizontal axis of Fig. 3 indicates the total concentration of BNL, and the vertical axis indicates the concentration of adsorbed BNL expressed as the difference between the total and supernatant concentrations. Therefore, the slope of the line in Fig. 3 corresponds to the fraction of BNL on the latex surface. As we can see, the slope is 0.70, indicating that 70% of BNL is adsorbed onto the latex surface.

Fig. 4 shows RTP of BNL on the surface of dried PS latex particles. As in the latex dispersion, we note remarkable enhancement of RTP of BNL on the dried latex particles. This suggests that the dried latex particles can also be employed as substrates for stabilizing RTP. It is of interest that the fluorescence spectra of BNL show blue shifts on going from aqueous solution (λ_{max} = 415 nm) to the latex dispersion (λ_{max} = 405 nm) and to the dried latex particles (λ_{max} = 393 nm). This indicates that the polarity sensed by BNL decreases in this order, because the fluorescence of BNL is originated from π–π^* transition which is generally known to show a blue shift in non-polar media.

Table 1
I_P/I_F values of BNL, 2-naphthol and 1-bromo-2-naphthoic acid in aqueous solutions and on PS latex substrates

Medium	I_P/I_F [a]		
	BNL [b]	NL [c]/$AgNO_3$ [d]	BNA [e]
Aqueous solution	0.05	0	0
PS latex dispersion	3.4	0	0
PS latex dried particle	1.3	0	0

[a] Measured under deaerated conditions. See text for details of calculation of the I_P/I_F values.
[b] [BNL] = 0.1 mM.
[c] NL, 2-naphthol; [NL] = 0.1 mM.
[d] [$AgNO_3$] = 0.1 mM.
[e] BNA, 1-bromo-2-naphthoic acid; [BNA] = 0.1 mM.

We extended our investigation to other similar luminophors, 2-naphthol and 1-bromo-2-naphthoic acid. For 2-naphthol, we employed silver cation as a perturber for inducing external heavy atom effect [1,3,7]. The results are summarized in Table 1, where a peak height ratio between phosphorescence and fluorescence (I_P/I_F) is introduced as a measure of yield of RTP. The I_P/I_F values are corrected for the transmittance curve of the L-39 cut-off filter.

As can be seen from Table 1, neither 2-naphthol nor 1-bromo-2-naphthoic acid do not emit RTP in the latex substrates. The absence of RTP of 1-bromo-2-naphthoic acid is attributed to the fact that this luminophor is not effectively adsorbed onto the latex surfaces, as confirmed by the measurement of adsorption isotherm (data not shown). The ionizable nature of 1-bromo-2-naphthoic acid might be the cause of inefficient adsorption of this luminophor onto the latex surfaces. On the other hand, the absence of RTP of 2-naphthol appears to be ascribed to another reason because this compound is efficiently adsorbed onto the latex particles. It seems that 2-naphthol (luminophor) and silver cation (RTP enhancer) are adsorbed onto different regions of the latex surface, i.e. 2-naphthol is adsorbed to the PS domain due to hydrophobic interaction whereas silver cation to the sulfate group due to electrostatic attractive interaction. Such different behaviors of adsorption might result in no observation of RTP of 2-naphthol.

4. Concluding remarks

In the present study, we have found that BNL emits strong RTP both in an aqueous PS latex dispersion and on the dried latex particles. These findings will open the use of the latex systems as novel substrates for stabilizing the triplet states of various photochemical reactants. In order to establish the usefulness of the latex systems, we have to examine a wide range of compounds under a variety of conditions. Such investigation is now in progress.

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